Mixed metal alkoxides as ascatalyst precursors

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MIXED METAL ALKOXIDES
AS
CATALYST PRECURSORS

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To Mam and Dad

DECLARATION

The work described in this thesis was carried out in the University of Durham between September 1983 and September 1986. It has not been submitted, either completely or in part, for another degree in this or any other University and is the original work of the author except where acknowledged by reference.

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CONTENTS

Mixed Metal Alkoxides as Catalyst Precursors

Kay Young, B.Sc.

Abstract

This thesis describes research carried out to explore the use of mixed metal alkoxides as precursors of materials with catalytic activity in synthesis-gas chemistry. The alkoxide derived catalyst materials are compared against catalysts prepared by traditional co-precipitation methods.

A discussion of the project objectives introduces the work and Chapter 1 includes a chronological survey of the literature up to the present day. A brief discussion of the commercial uses of alkoxides is given.

Chapter 2 describes the general methods of synthesis and the properties of simple and bimetallic alkoxides;

$M(OR)_x$ and $M[M'(OR)_n]_x$ respectively.

A more detailed treatment of the alkoxides of the first row transition elements is given, with emphasis on the properties and characteristics responsible for their possible potential as catalyst precursors.

Chapter 3 deals with the catalytic aspects of ammonia and methanol synthesis. The preparation of industrial, heterogeneous catalysts has traditionally been carried out by co-precipitation of, for example, basic carbonates. The catalytic materials obtained may display catalytic activities which vary markedly (and not always controllably) with the precipitation, ageing, calcination and/or reduction conditions employed.

A discussion of the reaction mechanisms involved in ammonia and methanol syntheses is included.

Several mixed metal alkoxides have been prepared from metals known to have catalytic activity in synthesis-gas chemistry (i.e. Mn, Fe, Co, Cu, Zn and Al). These metal alkoxides (e.g. $Cu[Al(OPr^i)_4]_2$) have been characterised and found to compare well with literature data. Analyses, Infra-red and Mass-spectra are reported.

After conversion to catalytic materials the alkoxide derived compounds were examined for surface properties (oxide phases present, copper surface area, crystallite size, pore size distributions and pore volumes). The alkoxide materials compared quite well with the precipitated analogues and there was a difference in the properties of materials derived from different alkoxy groups. These studies were limited to the copper-aluminium alkoxides.

The formation of a nickel (II) chloride, HMPA adduct is reported.

Abbreviations

OEt	$-OCH_2CH_3$
OMe	$-OCH_3$
OPr^i	$-OCH(CH_3)_2$
HMPA	Hexamethylphosphoramide
THF	Tetrahydrofuran

Discussion of Spectroscopy

I.R. Infra Red: cm^{-1} wavenumber; s- strong absorption; m- medium; w- weak.

Mass Spectrometry E.I. - Electron Impact; C.I. - Chemical Ionization; M - molecular ion; m/e - mass ion.

CHAPTER 1

CHAPTER 1

1.1 INTRODUCTION

The aim of this project was to explore the use of mixed metal alkoxides as precursors of materials with catalytic activity in synthesis-gas chemistry.

Traditionally, catalysts contain two or three different metals or metal oxides which need to be suitably dispersed on another oxide (or support) for optimum activity. These materials are normally prepared by co-precipitation reactions (e.g. of basic carbonates) followed by a series of ageing steps which ensure dispersion of the catalyst components. However the products may be quite heterogeneous with catalytic activity varying markedly (and not always controllably) with the precipitation, ageing, calcination and reduction conditions employed[1].

It was believed, on the basis of previous work[1-4], that mixed metal alkoxides, in which the metals M are selected from those known to have catalytic activity in synthesis-gas chemistry, could be used as better precursors from which to prepare well dispersed catalytically active materials.

$$M^{I}M^{II}(OR)_x$$
$$M^{I}M^{II}M^{III}(OR)_y$$

e.g. M = Cr, Ni, Cu, Zn, Al.

The project incorporated several areas of study:

Section One

The initial phase of this study was concerned with the synthesis and characterization of bi- or tri-metallic alkoxides,

$M^{I}_{x}M^{II}_{y}M^{III}_{z}(OR)_{n}$, by halogen-free routes. Particular attention was paid to the influence of the alkyl group, R, on such factors as crystallinity and degree of coordinative unsaturation of the metal atoms.

Section Two

This stage involved the conversion of the mixed metal alkoxides into catalytically active materials. The methods included calcination and reduction, the surface chemistry of the products being monitored by conventional techniques.

These two sections, together, required the use of a variety of techniques including;

a) synthetic chemistry
b) spectroscopic analysis
c) surface area and pore size distribution measurements
d) X-ray powder diffraction studies.

Extensive studies of certain mixed metal alkoxide systems had already been carried out[2]. These had shown how the metal environment could be controlled by the ratio of the metals used and by the choice of alkoxide residue, supporting the premise that the structure and surface properties of materials derived from alkoxy species might be expected to reflect these controllable parameters. These earlier studies had established the route by which metal alkoxides might be prepared. Simple alkoxides and oxy-alkoxides (μ-oxo-alkoxides) have already found use as catalysts[2-4] particularly as homogeneous catalysts for polymerizations[3]. In this work alkoxide chemistry was applied to the field of heterogeneous catalysis.

1.2 BACKGROUND AND ALKOXIDE HISTORY

In the present work it is the alkoxides of the elements of the first transition series with aluminium, sodium and potassium which are of primary importance. However the alkoxides of many elements have found use in a wide variety of industrial applications and this section provides a brief introduction to the development of alkoxide chemistry since the early nineteenth century and describes the commercial importance of these interesting compounds.

Metal alkoxides constitute an important class of compounds characterized by the metal-oxygen-carbon bond system. The strongly electronegative oxygen atom induces considerable polarity in the $\overset{\delta+}{M}-\overset{\delta-}{O}$ bond but this is partially offset by the electrophilic nature of metals which undergo covalency expansion by coordination with donor atoms.

The properties of the **M-O-C** system are also affected by the electronic behaviour of the alkyl (or aryl) group, the configuration of which gives rise to stereochemical effects.

Thus metal alkoxides offer great scope for producing materials with varied chemical and physical properties and it is surprising that, for many years, only the alkoxides of magnesium and aluminium were of commercial importance.

A rapid increase in the industrial value of metal alkoxides took place towards the end of the 1950's. This was especially true of the titanium alkoxides, where, between 1954 and 1955, output in the United States of America quadrupled. This was due, in part, to the discovery that titanium butoxide could be used in the production of heat-resistant paints. Further work, in 1950, indicated that titanium alcoholates conferred water repellency on textile fabrics, leather, wood and other materials.

Since the end of the 1950's the growth in interest in the metal alkoxides has been phenomenal and this is reflected in the number and range of commercial products incorporating alkoxides or their derivatives. Metal alkoxides are now used for a great variety of purposes; as catalysts (Ziegler polymerizations, tranesterifications and condensations); in coatings for plastics, textiles, glass and metals; as additives for adhesives and paints and as cross-linking agents (or hardeners) for epoxy, silicon, urea, melamine and terephthalate resins[6]. Some zirconium compounds are used as crosslinkers for natural materials such as skin with anti-perspirants.

The development of alkoxides and their chemistry is described in the following chronological survey.

PERIOD	**YEAR**	**COMMENT**
1831-1840	1837	Sodium ethoxide:- first metal alkoxide described by J. Leibig[7].
1841-1850	1846	Preparation of silicon tetra-iso-amyloxide[8]. $SiCl_4 + 4ROH \longrightarrow Si(OR)_4 + 4HCl$
	1846	Boron methoxide, ethoxide and amyloxide prepared in a similar manner[9]. $BCl_3 + 3ROH \longrightarrow B(OR)_3 + 3HCl$
1851-1860		
1861-1870	1863	Preparation of ethylorthocarbonate $C(OCH_2CH_3)_4$ in poor yield by the reaction of chloropicrin with sodium ethoxide[10,11].

PERIOD	YEAR	COMMENT
1861-1870	1863 1865	Studies of silicon alkoxides derived from primary alcohols[12,14].
	1864	Synthesis of thallous ethoxide by reaction of thallium metal with ethanol in air[13].
	1867	Preparation of boron triethoxide by digesting boric oxide with ethanol at 120°C in a copper vessel for 24 hours[15].
1871-1880	1874	Further studies on silicon alkoxides derived from primary alcohols[16].
	1875	Doubtful claim for the synthesis of solid titanium tetraethoxide by the reaction of the metal chloride with sodium ethoxide in excess ethanol. Also claim for titanium mono-chloride triethoxide by direct reaction of the tetrachloride with ethanol[17].
	1876	Erroneous claim that zirconium tetrachloride did not form the ethoxide when treated with ethanol[18].
1881-1890	1881	First preparation of aluminium triethoxide from the metal using iodine as the catalyst[19].
	1884	Unsuccessful attempt to prepare pure iron triethoxide by the reaction of the trichloride with sodium ethoxide[20]
	1887	Second erroneous claim for the product of reaction between zirconium tetrachloride and ethanol[21].

PERIOD	YEAR	COMMENT
1881-1890	1887	Preparation of selenyl-diethoxide[22], $SeCl_2 + 2NaOEt \longrightarrow Se(OEt)_2 + 2NaCl$
	1887	Independent report claiming the synthesis of selenyl diethoxide by reaction between: Ag_2SeO_3 and C_2H_5I[23].
1891-1900	1893	Alternative method for the preparation of normal and isomeric alkoxides of aluminium using amalgamated aluminium with excess ethanol[24].
	1897	Use of tin tetrachloride as a catalyst for the synthesis of aluminium alkoxides[25].
	1899	Observation that reaction of aluminium with tertiary alcohols is very slow even in the presence of a catalyst[26].
	1899	Failure to prepare ethylorthocarbonate by reaction of carbon tetrachloride with ethanol[27].
1901-1910	1901	Further work reported on the primary alkoxides of silicon[28].
	1901	Preparation of boron phenoxide by heating the trichloride with phenol in a sealed tube[29].
	1902	The action of alcohol on thallous found to yield alkoxides of thallium[30].

PERIOD	YEAR	COMMENT
1901-1910	1902	Ethanol adduct of lanthanum trichloride prepared[31].
	1903	Methanol and ethanol adducts of neodymium and praseodymium nitrates reported[32].
	1903	Paper published reporting the use of the acid, oxide and acetate of boron to prepare alkoxides[33].
	1903	Crystalline alcoholate of thorium tetrachloride reported[34].
	1905	Synthesis of ethyl sulphite by the reaction of thionyl chloride with alcohols[35].
	1906	Observation made that aluminium ethoxide catalyses the reduction of aldehydes and ketones to the corresponding esters[36].
1911-1920	1913	Attempt made to synthesise pure iron triethoxide[37].
	1913	Electrolysis of tungsten hexachloride in the presence of excess ethanol found to yield a mixed chloride-alkoxide[38,39].
	1913	Preparation of ethyl-orthovanadate using the trichloride or pentoxide. Mixed chloride-ethoxides were also obtained[40].
1921-1930	1922	Use of alkoxides in the preparation of finely divided alumina to be used to

PERIOD	YEAR	COMMENT
1921-1930	1922(cont)	catalyse dehydration and decarboxylation reactions[41].
	1923	Description of two allotropic forms of aluminium triethoxide (α and β) and their interconversion[42].
	1924	Successful synthesis of pure, liquid titanium tetraethoxide. This ethoxide was shown to be convertable to the solid methoxide by reaction with excess methanol[43].
	1925	Aldehydes shown to be reduced to primary alcohols by the use of aluminium ethoxide[44,45].
	1925	Germanium tetrachloride shown not to behave in a similar manner to silicon tetrachloride to produce alkoxides[46].
	1926	Alkoxides derived from primary or secondary alcohols shown to reduce aldehydes and ketones to corresponding alcohols[47].
	1928	Further exploitation of the method for producing boron alkoxides from the acid, oxide or acetate[48].
	1928	Preparation of selenyl di-methoxide, -ethoxide and -isopropoxide by treatment of the dichloride with sodium or silver alkoxides[49].
	1928	Synthesis of magnesium diethoxide by the reaction of amalgamated metal with ethanol

PERIOD	YEAR	COMMENT
1921-1930	1928(cont)	or, alternatively, using the metal and alcohol withsmall amounts of iodine as catalyst[50].
	1929	Use of alcohol exchange reactions to obtain new alkoxy derivatives of aluminium[51].
	1929	Successful synthesis of pure iron triethoxide reported[52].
	1929	Synthesis of mixed chloride-alkoxides of tantalum[53].
	1929	Preparation of beryllium diethoxide by direct metal-alcohol reaction[54].
	1929 1930	Ⓡ Major work by Meerwein and Bersin describing the synthesis of many new alkoxides and establishing the chemistry of double or mixed alkoxides[55,56].
	1930	Structure of thallous ethoxide shown to be tetrameric based on molecular weight determinations[57]. Oxygen bridges (from the ethoxy groups) proposed.
	1930	Preparation of dialkylthallium alkoxides reported[58,59].
1931-1940	1931	Synthesis of tin tetraethoxide-ethanolate reported[60].

PERIOD	YEAR	COMMENT
1931-1940	1932	Observation of the partial solvolysis of aluminium trichloride when treated with alcohol in the presence of ether[61].
	1932	Successful synthesis of germanium tetra-alkoxides[62].
	1932	Preparation of trialkylarsenites; highly volatile, distillable liquids[63].
	1933	Boron alkoxide derivatives prepared, again, using the method of treating the acid, oxide or acetate of boron[64].
	1933	Variations in the degree of complexity reported for aluminium alkoxides. Various structures proposed for the suggested oligomers[65].
	1934	Preparation of dialkylthallium alkoxides using thallium bromide and thallium trialkoxides[66].
	1934	Measurements made of the electrical conductivities of the methoxides and ethoxides of lithium, sodium and potassium[67].
	1935	Alcohol exchange reactions used as a route to prepare new alkoxide derivatives of aluminium[68].
	1935	Tetrameric structures proposed for aluminium trialkoxides[69].

PERIOD	YEAR	COMMENT
1931-1940	1936 1940	Several papers published describing the Meerwein-Ponndorf-Verley reductions[70,71,72].
	1936	Formation of the alcohol adduct of titanium dichloride diethoxide from the reaction between the tetrachloride and ethanol[73]. (see reference 17)
	1936	Ethyl sulphites shown to volatile, monomeric liquids by cryoscopic/ebullioscopic molecular weight determinations[74].
	1936	The thermal decompositions of several metal alkoxides studied;[75]. $Fe(OEt)_3$, $Co(OEt)_2$, $Ni(OEt)_2$, $Cu(OEt)_2$, $Sn(OEt)_4$, $Sb(OEt)_5$, $Te(OEt)_4$.
	1937	Reaction of thiocarbonyl tetrachloride with sodium alkoxides shown to give good yields of alkylorthocarbonates[76].
	1937	Preparation of dialkylselenites by reaction of alcohols with selenium oxide **reported**[77].
	1937	Dialkyl sulphites shown to be good alkylating agents; converting carboxylic acids to their esters[78].
	1937	Preparation of the ethoxides of chromium, manganese and cobalt[79].
	1938	First successful synthesis of aluminium tri-tert-butoxide[80].

PERIOD	YEAR	COMMENT
1931-1940	1938	Alcohol exchange reactions used to synthesise further alkoxy derivatives of aluminium[81].
	1938 1939	Other workers report using the acid, oxide or acetate to prepare alkoxides of boron for further investigations[82].
	1939	Alcoholysis reactions of lower alkoxy derivatives of boron used in the synthesis of higher alkoxides[83].
	1939 1940	Preparation of titanium tetra-alkoxides by treatment of the chloride with excess alcohol in the presence of ammonia-patented[84,85].
1941-1950	1941	Electron diffraction study indicated the planar structure of boron tri-methoxide[86].
	1942 1943	Further investigations into the nature and syntheses of boron alkoxides[87,88].
	1943	Several papers published reporting the action of acidic alkoxides (aluminium ethoxide) in producing simple esters from α-aldehydes. Mildly basic alkoxides e.g. $Mg(OEt)_2$, $Mg[Al(OEt)_4]_2$ and $Ca(OEt)_2$ tended to produce trimeric glycol esters[89,90].
	1944 1946	(see also references 87, 88) [91,93]

PERIOD	YEAR	COMMENT
1941-1950	1947	Covalent character of aluminium ethoxide indicated by conductivity measurements on the melt[94].
	1947	(see also references 89, 90)[95].
	1947) 1949	Meerwein-Ponndorf-Verley reaction (see also reference 92)[96,97,92].
	1949	Ammonia method of alkoxide synthesis failed to give titanium- tetra-tert-butoxide. However the addition of pyridine resulted in the formation of the pure alkoxide[98].
	1950	Reaction between zirconium tetrachloride and ethanol shown to yield alkoxide and not hydroxide as previously reported[99].
1951-1960	1956	Derivatives of uranium alkoxides reported[100].
	1960	Ⓡ Major work describing the chemical and physical properties of metal alkoxides[101].
1961-1970	1964	Paper describing the thermal decomposition of aluminium alkoxides and the alumina catalysed decomposition of ethers[102].
	1965	Thermal decomposition of methyl copper in methanol to produce copper methoxides[103].
		Synthesis of copper (II) methoxide and ethoxide chlorides. Products studied by physical methods[104].
	1965	Preparation of crystalline alkali and alkaline earth -aluminiumalkoxides described along with their properties[105].

PERIOD	YEAR		COMMENT
1961-1970	1966		Organometallic derivatives of β-diketones reviewed. A structural discussion[106].
	1967	Ⓡ	Major review of the alkoxides and aryloxides of metals and metalloids[107].
	1968		Preparation of double alkoxides of lanthanum and praseodymium[108].
	1969		Description of the preparation and properties of alkoxides and double alkoxides of zinc[109].
	1969		Preparation and properties of the alkoxides gallium[110].
1971-1980	1971	Ⓡ	Major work on the chemistry of double alkoxides of several elements. A description of structural studies on these compounds[111].
	1972		Double isopropoxides of aluminium, gallium and indium. Their synthesis via reaction between metal chloride and potassium-aluminium tetraisopropoxide and structural studies are described[112].
	1972		Volatile double alkoxides of hafnium. Synthesis and spectra reported[113].
	1972		Description of copper (I) tert-butoxide as a new and useful metallation reagent[114].
	1972		Alkoxides and double alkoxides of holmium[115].
	1973		Double isopropoxides of lanthanons with aluminium. Methods for the preparation of double isopropoxides of several lanthanons including yttrium and scandium[116].

PERIOD	YEAR	COMMENT
1971-1980	1973	Double isopropoxides of lanthanons with gallium by the use of anhydrous chlorides[117].
	1974	The synthesis, reactions and thermal decompositions of copper (I) alkoxides are described. These compounds are useful reagents for the formation of ethers from organic halides[118].
	1975	Alkoxides derived from allyl alcohols described and the spectroscopic properties of these new compounds discussed[119].
	1975	Double alkoxides of niobium and tantalum with aluminium and gallium. Discussion with some IR and NMR reported[120].
	1975	Double ethoxides of alkaline earth metals aluminium synthesised by reaction of aluminium ethoxide with the alkaline earth metal in alcohol[121]. These are soluble in ethanol and benzene.
	1975 Ⓡ	Crystal structures, NMR spectra, ESR spectra and magnetochemistry reported for a number metal and mixed metal alkoxides[122].
	1976	Double ethoxides of niobium with alkaline earth metals[123].
	1976	Double isopropoxides of hafnium with with alkaline earth metals[124].
	1976	Synthesis and characterization of double isopropoxides of niobium and tantalum with alkaline earth metals. Mercury (II) chloride used as a catalyst[125].

PERIOD	YEAR	COMMENT
1971-1980	1976	Ⓡ Major review of alkoxide derivatives of alkali and alkaline earth metals with covalent characteristics[126].
	1976	Synthesis of alkoxides of indium using anhydrous metal halides and sodium isopropoxides. Alcoholysis reactions used to convert the isopropoxides to other derivatives[127].
	1976	Conductometric and potentiometric titrations of aluminium trichloride (and alkoxides) with alkali metal alkoxides used to obtain mixed chloro-alkoxides and mixed metal compounds[128].
	1976	Synthesis of the double alkoxides of rubidium and caesium with aluminium, zirconium, tantalum, hafnium and niobium. Structures based on NMR information are suggested[129].
	1977	Ⓡ Synthesis of double isopropoxides of various metals with tetraisopropoxyaluminate as the coordinating ligand. A structural discussion[130].
	1978	Ⓡ Preparation and characterization of double isopropoxides of aluminium with alkaline earth metals. These compounds are volatile and can be isolated by vacuum distillation. General formula:$M[Al(OPr^i)_4]_2$. Proton and ^{13}C NMR spectra indicate interchange of bridging and terminal isopropoxy groups[131].

PERIOD	YEAR	COMMENT
1971-1980	1978	Volatile double isopropoxide of tin with aluminium reported[132].
	1979	® Description of the synthesis of double isopropoxide of later transition metals with aluminium. Double isopropoxides of the first row transition metals are coloured liquids, soluble in organic solvents and distillable under reduced pressure[133].
	1979	Structural and physical investigation of aluminium-triisopropoxide. Crystal structure and NMR data reported[134].
	1980	Review of alkoxide and related derivatives of the lanthanides[135].
1981-1990	1981	The reaction between copper(II) chloride and lithium alkoxides has been used to synthesise alkoxide and alkoxy derivatives of copper. Characterizations are based on infra-red and electronic reflectance spectra and magnetic susceptibility measurements[136].
	1983	Study of tetra-, penta- and hexa-coordinated aluminium using NMR and X-ray diffraction studies of complexes of ethylenediamine with aluminium triisopropoxide and fluoro-analogues[137]
	1983	Synthesis of alkoxy-chloro titanium(III) and vanadium(III) compounds. Reaction occurs between the anhydrous metal chlorides and trialkyl orthoformates[138].
	1983	® Major review published covering the chemistry and physical properties of the alkoxides and double alkoxides of the transition metals[139].

PERIOD	YEAR	COMMENT
1981-1990	1984	Magnetic and spectroscopic studies of bimetallic isopropoxides of transition metal alkoxides (3d) with aluminium[140].
	1984	Novel bimetallic alkoxides and derivatives of chromium tetra-alkoxy aluminates. Synthetic routes and physico-chemical studies are reported[141].
	1984	The synthesis, spectroscopic and magnetic studies of new alkoxy and allied bimetallic derivatives of nickel (II) with aluminium[142].
	1984	New method of synthesis of lanthanide alkoxides and an investigation into their catalytic activity in the Meerwein-Ponndorf-Oppenauer reactions[143].
	1985	Synthesis of cerium alkoxides from ceric ammonium nitrate[144].
	1986	New synthetic route to titanium (III) alkoxides by reduction of titanium (IV) tetraalkoxides with organosilicon compounds containing hydrogen. Solid state properties are reported (CP/MAS, ^{13}C NMR, X-ray and IR)[145].
	1987	NMR studies of β-diketone and β-ketoester derivatives of zirconium diisopropoxide bis(tetraisopropoxyaluminate)[146]. i.e. $ZrAl_2(OPr^i)_{10-x}L_x$ where L= acetylacetone, benzoylacetone, methylacetoacetone, ethylacetoacetone.
	1987	Bimetallic alkoxides of cadmium and aluminium. New derivatives synthesised by alcohol exchange reactions. Discussion of physical properties[147].

PERIOD	YEAR	COMMENT
1981-1990	1987	Synthesis, reactivity, magnetic and spectra studies on bimetallic alkoxides of iron(III) with zirconium. The alcohol exchange reactions have been investigated and the structures elucidated by various spectroscopic techniques[148].
	1987	Bimetallic alkoxides of cadmium (II) with aluminium prepared by alcohol exchange reactions. These derivative characterized by elemental analyses, IR, PMR and molecular weight measurements. Tentative structures proposed[149].
	1988	Chloride and alkoxide alkoxometallates and termetallic alkoxides of copper(II) reported[150].
	1988	Chloride and alkoxide isopropoxymetallates of cobalt (II) containing $Al(OPr^i)_4^-$ and $[Zr_2(OPr^i)_9]^-$ units reported. Preparation and physico-chemical studies included[151].
	1988	Preparation of new bimetallic alkoxides of zinc and aluminium by alcohol exchange reactions[152].

Ⓡ = review or major work.

1.3 COMMERCIAL USES OF METAL ALKOXIDES

As stated previously, the commercial uses of metal alkoxides and their derivatives are many and varied. The properties and reactions of the industrially important alkoxides are described in detail later but here a general survey is presented to indicate the scope of application.

The chemical reactivity, volatility and solubility in organic solvents of the alkoxides ensures their importance in industrial processes. However the metal alkoxides are strongly caustic and are rapidly decomposed by the humidity of air or moisture of the skin, necessitating careful handling and storage. The heat of the hydrolysis reaction

$$M(OR)_x + xH_2O \longrightarrow M(OH)_x + xROH$$

is capable of igniting alkali metals (especially potassium). Hence the alkoxides must be stored under cool, dry conditions, preferably under an inert atmosphere. The health hazards are dependent on the toxicity of the metal and on the oxides and alcohols formed on hydrolysis or decomposition.

Alkoxides are generally used in one or other of the following areas,

i) catalysis
ii) metal oxide preparation
iii) glasses and ceramics
iv) surface coatings and surface coating additives
    cross-linking agents
    water repellents.

i) CATALYSIS

The alkoxides are mainly used as catalysts or intermediates in a variety of reactions.

The catalytic behaviour of aluminium alkoxides was realised many years ago when it was observed that the ethoxide reduced aldehydes and ketones to the corresponding esters[36].

Metal alkoxides have also been used as catalysts in Ziegler-Natta polymerizations[153], transesterifications[154,155] and condensations or polyester formations[156-8].

Sodium alkoxides are used to catalyse the Tischenko condensation of aldehydes[159] and the transesterification of carboxylic esters. Sodium methoxide and ethoxide are, respectively, white and yellow-white, strongly hygroscopic powders, soluble in alcohol but insoluble in hydrocarbons and most other organic solvents.

Magnesium methoxide (a white powder sparingly soluble in methanol, ethanol and cyclohexane but insoluble in ethers and hydrocarbons) is used in a multitude of reactions;

i) the formation of acrylic and methacrylic acid amides from fatty acid amides[160]
ii) the formation of cyclic ketones[161]
iii) the formation of dimer aldehydes[162]
iv) the polymerization of epoxy compounds[163]

The ethoxide (similar in appearance to the methoxide) finds use as a catalyst in the Tischenko and other reactions[164-6], condensation of esters[167], alkylation and polymerization reactions[163].

The aluminium alkoxides are also used extensively as catalysts in, for example, the Meerwein-Ponndorf reaction[168].

The titanium alkoxides (isopropoxide and n-butoxide) are volatile liquids, generally used as catalysts for alkene polymerizations and for condensation reactions.

The commercially used zirconium n-propoxide and n-butoxide are also liquids but hydrolyse more slowly than their titanium counterparts and are used in condensation catalysts.

Other alkoxides used industrially as catalysts are those of vanadium and antimony. The vanadium derivatives are liquids and tend to darken in colour and decompose on heating, they are used mostly in alkene polymerizations.

More recently a new class of catalyst precursor has been identified and investigated. These are the μ-oxo alkoxides:

$$(RO)_n M-O-M'-O-M(OR)_n$$

They have been proposed as the active species in ring-opening polymerizations e.g. of oxiranes, thiiranes and other heterocyclic monomers. These species are soluble in organic media yet possess important properties of metal oxides in heterogeneous systems[169].

ii) METAL OXIDES

Alkoxides, through their ease of hydrolysis, provide a valuable route to high purity, high surface area, metal oxides[170].
The metal alkoxides are purified by vacuum distillation and the oxides are obtained by hydrolysis or Chemical Vapour Deposition. The alkoxides used are those whose metal oxides have catalytic activity in industrial processes.

These two areas form the background to this project, that is, the catalytic activity of the alkoxides themselves and their usefulness as precursors to impurity-free metal oxides.

iii) GLASSES AND CERAMICS

It has been shown[171] that the sol-gel route to ceramic materials, using alkoxide precursors, is ideally suited to the preparation of small quantities of high purity materials.

The term "sol-gel processing" refers to the fabrication of inorganic oxides using either metal alkoxide precursors or colloidal dispersions of hydrous oxides[172]. Different alkoxides are blended to the required composition and then hydrolysed to produce the precursor which sinters in low temperature ranges (300-600°C) to give uniform glasses. High purity spinels, MAl_2O_4, are obtained from the liquid double alkoxides[173].

$$M\left[Al(OR)_4\right]_x$$

This is an area which is receiving a great deal of attention, at present, as the market for high-tech ceramics expands.

iv) CROSS-LINKING AGENTS

Under the 'cross-linkers' heading are some of the specialised surface coatings, paint driers, water repellents and adhesives.

Titanium alkoxides were amongst the first to find use in surface coatings. As discussed previously titanium-n-butoxide was used in making heat resistant paints. The titanium alkoxides were also used as water repellents, adhesive agents (especially with foils) in the manufacture of non-corrodable, high temperature lacquers and for the cross-linking and hardening of epoxy, silicon, melamine and terephthalate resins. Zirconium alkoxides are useful as cross-linkers of isocyanate resins as are vanadium alkoxides.

The alkoxide derivatives of antimony are used in fire-proof coatings.

It is believed that the titanium and zirconium alkoxides react rapidly with hydroxy groups in paints and other surface coating formulations (especially printing inks), thus forming a vast cross-linked network yielding a structured paint.

Typical surface coatings dry as a result of an "auto-oxidation" reaction, and subsequent polymerization occurs by reaction of atmospheric oxygen with the coating after application. The mechanism is still not fully understood but it appearsthat oxygen reacts with active methylene groups or double bonds in the surface coating medium. This is usually an oil or resin derivative of an unsaturated fatty acid. Peroxides, of limited stability, are formed which initiate a free radical mechanism on breakdown and cause polymerization. This reaction, uncatalysed, is too slow to be of practicable value hence driers are added to increase the rate of coating hardening. Improved drying properties are claimed for alkoxy-aluminium compounds which do not dry by this conventional oxidative mechanism but rather by a cross-linking reaction. These are known as coordination driers and are favoured as replacements to lead driers due to their relative non-toxicity[174,175].

This is by no means a comprehensive study of the commercial uses of alkoxides but merely gives an idea of the range of applications. Areas such as surface coatings and ceramics are expanding rapidly and the understanding of alkoxide chemistry is improving.

CHAPTER 2

2.1 INTRODUCTION TO CHAPTER 2

This chapter provides a summary of the methods of synthesis of simple and mixed metal alkoxides and describes their physical and chemical properties. These areas have been covered in depth by other workers and several comprehensive reviews are available[2,101,139].

The concluding section of this chapter deals more specifically with the alkoxides (and also the μ-oxo-alkoxides) of the transition metals particularly relevant to this study.

2.2 METHODS OF SYNTHESIS OF ALKOXIDES

As a rule the method employed for the synthesis of alkoxy derivatives $M(OR)_x$ depends on the reactivity of the metal M and also, to some extent, on the nature of the alkoxy group.

For example, highly reactive metals (electropositive elements), like those of Groups I and II, displace hydrogen from the alcohol, directly, thus forming the alkoxide.

$$M + nROH \longrightarrow M(OR)_n + \frac{n}{2}H_2$$

For elements like silicon and phosphorous the reaction of the anhydrous halide with alcohol will lead to the alkoxy derivative.

2.3 SYNTHESIS OF SIMPLE METAL ALKOXIDES

There are several routes to the production of simple metal alkoxides (where 'metal' refers to the central element) and it is important to note that all the methods require conditions which are strictly anhydrous as the alkoxides are highly sensitive to moisture.

In summary the methods include;

1) synthesis from the metal and alcohol directly,
2) synthesis from metal halide and alcohol,
3) synthesis from metal hydroxide and alcohol,
4) synthesis from metal oxide and alcohol,
5) alcohol exchange reactions,
6) transesterification reactions,
7) synthesis from the metal dialkylamide and alcohol

and 8) various other 'miscellaneous' methods.

2.3(1) SYNTHESIS FROM THE METAL AND ALCOHOL

This is the simplest method of alkoxide synthesis and involves the direct reaction of a metal with an alcohol with the evolution of hydrogen gas.

$$M + xROH \longrightarrow M(OR)_x + \frac{x}{2} H_2$$

Where the metal **M** is one from Group I this reaction tends to be highly exothermic. The rate of the reaction depends both on the metal and on the alcohol. The rate increases with increasing electropositivity of the metal and decreases with the length and branching of the alcohol. As the branching of the alkyl chain increases the acidity of the hydroxyl hydrogen decreases, due to the +I inductive effect (electron releasing effect), producing a parallel decrease in reaction rate. Reactions with tertiary alcohols can take more than several hours to go towards completion.

Pure alkoxides of the alkali metals can be prepared by dissolving the metal in alcohol at reflux temperature under an inert atmosphere. The reaction is occasionally carried out in ether, benzene or xylene.

e.g. $Na + CH_3CH_2OH \longrightarrow Na(OCH_2CH_3) + \frac{1}{2} H_2$

Sodium[176] and potassium alkoxides have been synthesized by the treatment of the molten or amalgamated metal with small chain alcohols. Some industrial processes use the metal amalgam or hydride in place of the free metal[6].

Other metals, like the alkaline earths or aluminium, are almost always covered in an oxide film. Etching or cleaning of the metal surface is required, or the formation of chloride or iodide intermediates may be involved. The role of catalysts, such as iodine or mercury (II) chloride, is not fully understood but, in the case of the mercury (II) chloride catalyst, the formation of a surface amalgam would be expected.

The elements of Group II are less reactive than those of Group I and do not react directly with an alcohol but require the presence of a catalyst. Hence beryllium will react with ethanol, to form beryllium diethoxide, using catalytic amounts of mercuric chloride, iodine or beryllium dichloride. With methanol, however, products of variable composition are formed having the general formula;

$$[nBe(OCH_3)_2.n'Be(OCH_3)X]_x \qquad X = \text{halogen}$$ [177].

The use of catalytic amounts of mercuric chloride is widely applicable for the synthesis of alkoxides from the metal and alcohol. There is an observable gradation in reactivity of the Group II elements towards the formation of alkoxides from the metal and alcohol. For example, magnesium requires the use of a catalyst (as does beryllium) but the lower members of the Group can form alkoxides directly by reaction of the metal with refluxing alcohol. This variation in reactivity is observed in other groups of elements and also across the Periodic Table as would be expected.

2.3(1) cont.

As early as 1881 the triethoxide of aluminium was prepared by the reaction of the metal with ethanol using an iodine catalyst[19],

$$Al + 3CH_3CH_2OH \xrightarrow{I_2} Al(OCH_2CH_3)_3 + \frac{3}{2} H_2$$

and also by the use of amalgamated aluminium.

Pure trialkoxides have been prepared by the slow addition of alcohol to metallic aluminium suspended in either molten aluminium triethoxide or refluxing solvent[178].

Aluminium triisopropoxide can be very easily prepared by the reaction of cleaned metal with isopropanol using a small amount of aluminium triisopropoxide as the catalyst[179].

An unusual reaction is that of thallium which, if in the fresh metallic state, will not react with alcohol even under forcing conditions. However if the metal is exposed to the air the reaction to give the alkoxide rapidly takes place. It appears that thallium reacts with oxygen to form thallous oxide which then goes on to form the alkoxide (in this case, the ethoxide);

$$\text{i)}\ 2Tl + \tfrac{1}{2}O_2 \longrightarrow Tl_2O$$

$$\text{ii)}\ Tl_2O + 2CH_3CH_2OH \longrightarrow 2Tl(OCH_2CH_3) + H_2O$$

In large scale industrial processes the use of mercury (II) chloride as the catalyst presents problems, with the production of mercury in considerable quantities requiring strict monitoring.

2.3(2) SYNTHESIS FROM THE METAL HALIDE AND ALCOHOL

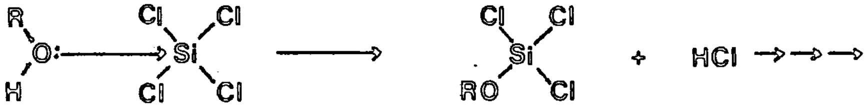
There are several variations of the method for producing alkoxides

$$MX_n + nROH \longrightarrow M(OR)_n + nHX$$

from the metal halide and an alcohol. This reaction appears to occur completely only for halides of electronegative elements where the hydrogen halide produced is continuously removed[181].

e.g. $SiCl_4 + 4CH_3CH_2OH \longrightarrow Si(OCH_2CH_3)_4 + 4\ HCl$

A stepwise mechanism has been proposed where the first step is the solvation of the halide;



The hydrogen halide produced can be removed by refluxing or by passing an inert gas through the reaction mixture. With more electropositive elements, or metals, the ease of this reaction decreases. The metal halides tend to form alcoholates (alcohol adducts) or undergo only partial substitution, e.g. germanium[182];

$$GeCl_4 + nCH_3CH_2OH \longrightarrow GeCl_{4-n}(OCH_2CH_3)_n + nHCl .$$

Germanium does, however, form the phenoxide after refluxing the tetrachloride with phenol in benzene for several days. This behaviour, shown by other elements, must be influenced by many complex factors including size of central metal atom, size and nature of the alkoxy group, relative strengths of the M-O and M-Cl bonds and the polarization of these bonds, amongst others.

The reaction of silicon tetrachloride with tertiary alcohols appears to yield orthosilicic acid and the alkyl chloride[2].

2.3(2) cont.

$$SiCl_4 + {}^{t}C_4H_9OH \longrightarrow Si(OH)_4 + 4H^{t}C_4H_9Cl$$

This has been explained by the excess tertiary butanol reacting with the hydrogen chloride to give water and alkyl chloride or alkene, hydrogen chloride and water.

$$\begin{tikzcd}
 & {}^{t}C_4H_9Cl + H_2O \\
{}^{t}C_4H_9OH + HCl \arrow[ur] \arrow[dr] & \\
 & C_4H_8 + HCl + H_2O
\end{tikzcd}$$

The water produced hydrolyses the tetrachloride or chloride alkoxide. This can be prevented by the addition of a base to the tertiary alcohol before reaction with the the silicon tetrachloride. The base (e.g. pyridine) takes up the hydrogen chloride by-product. This reaction can be represented by the following scheme;

$$\begin{aligned} SiCl_4 + 4{}^{t}C_4H_9OH \xrightarrow{C_5H_5N} & SiCl(OC_4H_9{}^{t})_3 \\ & + 3C_5H_5N.HCl \\ & + {}^{t}C_4H_9OH \end{aligned}$$

Steric hindrance prevents the fourth tertiary alcohol attacking the tetrachloride but a primary alkoxy group will replace the remaining chlorine;

$$SiCl(OC_4H_9{}^{t})_3 + CH_3CH_2OH \longrightarrow Si(OEt)(OBu^{t})_3 + HCl$$

Hence, except for a few metal halides which undergo complete reaction with alcohol, most elements give only partial or incomplete solvolysis reaction products or alcohol adducts. The successful preparation of pure, halide-free alkoxides can be achieved by the use of a base, for example, pyridine, ammonia, trialkylamines or sodium alkoxides.

The role of the base can described as follows:

2.3(2) cont.

$$\underline{B} + ROH \longrightarrow (\underline{B}H)^+ + (OR)^-$$

$$(OR)^- + M\text{-}Cl \longrightarrow M\text{-}OR + Cl^-$$

$$(\underline{B}H)^+ + Cl^- \longrightarrow [(\underline{B}H)^+Cl^-]$$

$[\ \underline{B} = \text{BASE}]$

This method has been applied to the synthesis of a large number of alkoxides[183,184].

e.g. $TiCl_4 + 4\ ROH + 4\ NH_3 \longrightarrow Ti(OR)_4 + 4\ NH_4Cl$

Strictly anhydrous conditions must be employed for the successful synthesis of alkoxides by this method. Benzene has been reported to be a good solvent for this reaction where the base is ammonia. The solubility of ammonium chloride is reduced and it is precipitated in crystalline form and can easily be removed by filtration.

Using ammonia has failed to produce pure tertiary butoxides. However addition of pyridine to the alcohol before reaction appears to inhibit any side reactions, with hydrogen chloride, which would lead to the production of water[185]. This method gives high yields of pure tertiary butoxides and is widely applicable.

In some instances, however, the metal halide would appear to act as a stronger base than ammonia resulting in only partial replacement of the chloride groups by alkoxy groups, e.g. thorium.

The use of sodium alkoxides in alcohol has proved successful. The sodium alkoxide acts as a very strong base and allows complete reaction. This method has been applied to the synthesis of alkoxides of tin and thorium[186].

2.3(2) cont.

$$ThCl_4 + 4\ NaOR \longrightarrow Th(OR)_4 + 4\ NaCl$$

$$\begin{tikzcd}
2SnCl_4 + 9\ NaOR \arrow[r] & NaSn_2(OR)_9 + 8\ NaCl \arrow[d, "HCl"] \\
 & 2Sn(OR)_4 + NaCl + ROH
\end{tikzcd}$$

The ammonia or sodium alkoxide methods are not applicable for the preparation of insoluble methoxides. The use of lithium methoxide, which is soluble in methanol, makes separation of the product alkoxide much easier. This method has been applied to the alkoxides of several metals but was not found to be suitable for zinc.

2.3(3) and (4) SYNTHESIS FROM THE METAL HYDROXIDE, OR OXIDE, AND ALCOHOL

Hydroxides and oxides of several elements will react with alcohols to form alkoxides and water.

$$M(OH)_n + n\ ROH \rightleftharpoons M(OR)_n + n\ H_2O$$

$$M_xO_y + 2y\ ROH \rightleftharpoons xM(OR)_{\frac{2y}{x}} + y\ H_2O$$

The continuous removal of water is essential to obtain good yields of the alkoxide products. This can be done by using various organic solvents which form azeotropes with water (benzene, toluene, xylene) and which can be fractionated out or separated using Dean-Stark apparatus. Although the method has fairly wide applicability there are limitations due to the boiling points of the alcohol and solvent and the acidity and steric properties of the alcohol.

An example of this method is the industrial production of boron esters by the dehydration of mixtures of boric acid and alcohols.

2.3(3) &(4) cont.

$$B_2O_3 + 6\ ROH \longrightarrow 2B(OR)_3 + 3\ H_2O$$

$$B(OH)_3 + 3ROH \longrightarrow B(OR)_3 + 3\ H_2O$$

2.3(5) SYNTHESIS BY ALCOHOL EXCHANGE REACTIONS

Alkoxides react with all hydroxy compounds, to some extent, to give products where some or all of their alkoxy groups have been exchanged. The following equilibrium represents the reaction;

$$M(OR)_n + xR'OH \rightleftharpoons M(OR)_{n-x}(OR')_x + xR'OH$$

and has been applied to the synthesis of many alkoxides.

The ease of alcoholysis is governed by several factors;

a) alkoxy group

An alkoxide derivative of tertiary alcohols will exchange alkoxy groups most readily with primary alcohols and fairly readily with secondary alcohols. Hence ease of alkoxy group exchange increases from tertiary to secondary to primary alcohols. The alcoholysis reaction from a more branched alkoxide to straight chain group is easier if the product alkoxide is more highly associated than the reactant alkoxide.

b) steric effects

The mechanism of the alcoholysis reaction has been proposed as an S_N2 type, susceptible to steric factors.

A mixture of titanium tetraethoxide and ethanol gave only one ethoxy proton signal in the ^1H n.m.r. spectrum indicating rapid exchange of ethoxy groups. However titanium tetrabutoxide in tert-butanol shows different methyl signals due to the slow rate of alcohol exchange[101,187].

c) fractionation

Alcoholysis reactions can be driven to completion by fractionation of the alcohol produced if this is more volatile than the reactant alcohol.

Hence, $Al(OPr^i)_3 + 3Bu^nOH \longrightarrow Al(OBu^n) + 3Pr^iOH$
although refluxing the isopropoxide with tertiary butanol yields only the dimeric product of part exchange $[Al(OPr^i)(OBu^t)_2]_2$.

In these alcoholysis reactions it would be necessary to incorporate an excess of the higher boiling reactant alcohol in order to drive the reaction towards completion. However this can be circumvented if a solvent is used which has a higher boiling point than either the reactant or product alcohol. Benzene is a good solvent for several reasons; it forms an azeotrope with isopropanol, it requires only a stoichiometric amount of the reactant alcohol, the reflux temperature can be lowered, thus minimizing occurrence of side reactions and, finally, one can use different stoichiometric amounts of reactants, enabling the preparation of mixed alkoxy alkoxides. It is also possible to follow the reaction quantitatively.

d) solubility

The insoluble methoxides can easily be obtained by reaction of the ethoxide or isopropoxide with methanol. The methoxide product can be filtered and dried. Methoxides are not, generally, used as starting materials for the synthesis of other alkoxides due to their insolubility and the lengthy reflux periods required.

Thus alcohol exchange reactions are useful methods by which to obtain a wide variety of alkoxide and mixed alkoxy compounds.

2.3(6) TRANSESTERIFICATION REACTIONS FOR ALKOXIDE SYNTHESIS

The previously described methods, although very useful and widely applicable for the synthesis of alkoxides, have several inherent problems. The method of using base (e.g. ammonia) can lead to hydrolysis of the product. Alcoholysis is highly susceptible to steric factors leading, often, to the formation of mixed alkoxy species.

Treatment of a metal alkoxide with an ester leads to the formation of a new alkoxide and a volatile ester is produced. The method requires the product ester to be more volatile than the reagent ester.

$$M(OR)_n + xCH_3COOR' \longrightarrow M(OR)_{n-x}(OR')_x + xCH_3COOR$$

Transesterification reactions have several advantages over alcoholysis routes:

i) tert-butoxides can be readily prepared due to the ease of fractionation of the volatile product ester.

ii) the esters are generally more stable to self condensation or oxidation than the corresponding alcohols, minimising the risk of side reactions.

iii) this route is less susceptible to steric factors than alcoholysis methods, hence making tertiary alkoxides more readily accessible.

As with the alcoholysis reactions the use of an inert, high boiling solvent negates the requirement for excess reactant ester and stoichiometric amounts can be utilised to obtain mixed alkoxy derivatives. The method is widely applicable.

2.3(7) SYNTHESIS FROM THE METAL DIALKYLAMIDE AND ALCOHOL

This route involves the reaction of a metal dialkylamide with alcohol. Metal alkoxide and volatile dialkylamine, which can easily be removed by fractionation, are produced in the reaction.

$$M(NR_2)_x + xROH \longrightarrow M(OR)_x + R_2NH$$

This method is useful where the metal has greater affinity for oxygen than for nitrogen but there are drawbacks. The metal dialkylamide is difficult to synthesise and is highly susceptible to hydrolysis so requiring extremely cautious handling.

2.3(8) MISCELLANEOUS METHODS

There are several other methods for synthesising metal alkoxides but these are of limited applicability. They include oxidation, reduction, the use of metal alkyls and alkyl metal hydrides.

2.4 SYNTHESIS OF DOUBLE METAL ALKOXIDES

The formation of double metal alkoxides can be considered to be due partially to an acid-base neutralisation reaction and partially to the tendency of the metal to form coordination complexes in order to achieve it's maximum coordination number.

The various methods are summarised below. Again there are several texts dealing with the syntheses of double metal alkoxides which provide the reader with a more detailed treatment[111,122,130,139]. (see also experimental section)

SYNTHESIS ROUTES

1) reaction of alkali alkoxide with another metal alkoxide

e.g. $$MOR + M'(OR)_3 \longrightarrow M[M'(OR)_4]$$

M'= Al, Ga; M= Na, K.

2) reaction of alkaline earth metals with metal alkoxides

e.g. $$M(OPr^i)_2 + 2M'(OPr^i)_3 \longrightarrow M[M'(OPr^i)_4]_2$$

M= Mg, Ca, Sr, Ba; M'= Al, Ga.

2.4 (2) cont.

The use of mercury (II) chloride as a catalyst is required for these reactions.

3) reaction of aluminium (gallium) alkoxides with other metal alkoxides

e.g. $3Al(OPr^i)_3 + Ga(OPr^i)_3 \longrightarrow Ga[Al(OPr^i)_4]_3$

4) reaction of metal halides with potassium-aluminium alkoxides

e.g. $MX_n + nK[Al(OPr^i)_4] \longrightarrow M[Al(OPr^i)_4]_n + nKX$

(where X is usually Cl)

5) reactions of two metal halides with potassium isopropoxide

This method has been used for the synthesis of double alkoxides of lanthanons with aluminium.

6) alcoholysis reactions

As with the simple metal alkoxides the double metal alkoxides undergo alcohol exchange reactions.

e.g. $M[Al(OPr^i)_4]_x + nROH \longrightarrow M[Al(OPr^i)_{4-n}(OR)_n]_x + nPr^iOH$

The use of metal halides reacting with potassium-aluminium alkoxides formed the majority of the synthetic work carried out for this project.

2.5 GENERAL CHARACTERISTICS OF ALKOXIDES AND TRENDS THEREIN

Metal alkoxides (or aryloxides) are compounds in which a metal is attached to one or more alkyl (or aryl) groups by an oxygen atom.

Simple metal alkoxides and double metal alkoxides have the general formulae $M(OR)_x$ and $M^I M^{II}(OR)_y$ respectively. Mixed alkoxy alkoxides, halide alkoxides, alkyl alkoxides and μ-oxo-alkoxides are also known and documented. The μ-oxo-alkoxides are important to this treatise and will be discussed further.

The alkoxides, or alcoholates or alky/aryl orthoesters as they are also known, can be considered as derivatives either of alcohols where the acidic hydrogen is replaced by the metal M;

$$ROH \longrightarrow ROM$$

or of metal hydroxides in which the hydrogen atoms are replaced by alkyl or aryl groups; $M(OH)_x \longrightarrow M(OR)_x$.

The physical properties of the metal alkoxides depend, in a striking manner, on the size and shape of the alkyl or aryl group and its substituents; and on the valency, atomic radius, stereochemistry and coordination of the metal.

There is a gradual change from insoluble, non-volatile, ionic alkoxides of the alkali metals to the volatile, covalent alkoxides of the non-metals.

non-metals (Si, P, S)------- covalent, volatile monomers

↓ ↓ decrease in volatility

Groups I and II ------------ electrovalent, non-volatile
Lanthanons polymeric solids

An alkoxide which is insoluble in non-polar solvents may not be ionic but a giant covalent polymer. This section attempts to describe, in general terms, the impact of various factors on the physical properties of the simple metal alkoxides.

Alkoxy derivatives of metals possess at least one $\overset{\delta+}{M}-\overset{\delta-}{O}-C$ system. The degree of this polarization is dependent, to some extent, on the relative electronegativities of the metal M and oxygen which in turn determines the physical characteristics.

Atomic Electronegativities

H 2.20																
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33		Mo 2.16			Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05		I 2.66
Cs 0.79	Ba 0.89	La 1.10			W 2.36			Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 2.04	Pb 2.33	Bi 2.02		
		Ce 1.12	Pr 1.13 (III)	Nd 1.14 (III)		Sm 1.17 (III)		Gd 1.20 (III)		Dy 1.22 (III)	Ho 1.23 (III)	Er 1.24	Tm 1.25 (III)		Lu 1.27 (III)	
					U 1.38 (III)	Np 1.36 (III)	Pu 1.28 (III)									

It can be seen from the table below that the alkoxides of the more electropositive elements, like the alkalis and alkaline earths, exhibit properties associated with electrovalent compounds, e.g., low volatility and insolubility in organic (non-polar) solvents.

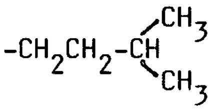
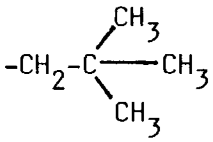
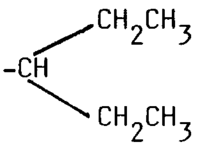
This is in marked contrast to the alkoxides of the more electronegative elements like tungsten and tantalum. The alkoxides of non-metallic elements like sulphur, phosphorus and silicon exhibit strong covalent characteristics, being soluble in organic solvents, volatile and, usually, monomeric.

Hence, taken in isolation, the electronegativity factor would seem to indicate that alkoxides of metallic elements would show largely ionic character.

ethoxide	colour	physical form	Mpt°C	Bpt°C/mmHg
Li	white	solid	20|24	not distillable
Na	white	solid	260(dec)	not distillable
K	white	solid	250(dec)	not distillable
Mg	white	solid	270(dec)	not distillable
Ca	white	solid	270(dec)	" "
Sr	white	solid	300(dec)	" "
Al	white	solid	140	189/3.0
Ga	white	solid	145	180-190/0.4
Tl	colourless	liquid	9.5	not distillable
Nb	pale yellow	liquid	6.0	156/0.05
Ta	colourless	liquid	22.0	147/0.05
W	red-black	liquid	/	120/0.05

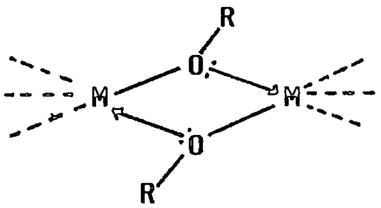
However most alkoxides show a fair degree of volatility and solubility in organic solvents. This offsetting of the polarity of the M-O⇀C system is explained by the +I inductive, or electron releasing effect, of the alkyl or aryl group and the tendency of the metal to expand it's coordination sphere.

For alkoxides of the same element the covalent character of the M-O bond increases with increasing +I inductive effects. Generally increasing the chain branching of the alkyl group affects the degree of association which, in turn, affects the volatility.

R in $[Al(OR)_3)]_n$	$[Al(OR)_3]_n$ Bpt°C/mmHg	Degree of association n
$-CH_2CH_2CH_2CH_2CH_3$	255/1.0	4.0
	195/ 0.1	4.1
	180/0.8	2.07
	165/1.0	2.08

As can be seen, the size and shape of the alkyl group play a prominent role in determining the properties of the alkoxides. For a series of monomeric alkoxides, where the alkoxy group is derived from a homologous series of alcohols, the volatility decreases with increased chain length. Where the alkoxides are derived from an isomeric series then increased branching may lead to an increase in volatility as the degree of association decreases.

The reduction in polarity of the M-O-C bond is also partially affected by the tendency of the metal to expand its coordination through dative covalent bonding leading to the formation of oligomers.



For oligomeric alkoxides the intermolecular forces are greatly affected by the M-O-M bridges. If these bridges are strong then the volatility is decreased due to increased size and the accompanying intermolecular forces. If these bridges are weak then the volatility is determined by the energy required to break these links. In the limit, steric forces can completely hinder intermolecular bonding and a volatile monomer results.

Finally the size of the central metal atom affects the molecular association and so volatility of alkoxide derivatives. For an analogous series of alkoxides within a Periodic Group molecular complexity increases and volatility decreases with increase in atomic size.

ALKOXIDE	$Ti(OEt)_4$	$Zr(OEt)_4$	$Hf(OEt)_4$	$Th(OEt)_4$
COVALENT RADII	1.32	1.45	1.44	1.55
Bpt^{o}C/mmHg	103/0.1	190/0.1	178/0.1	300/0.05
Degree of association	2.4	3.6	3.6	6.0

Simplistically, a large metal atom requires a larger and more highly branched alkoxy species to give effective shielding or screening than does a smaller atom.

The properties of the alkoxides are dependent on numerous interrelated factors. The ratio of metal atoms to alkoxide residues, or vice versa (the number of OR groups per metal atom) and how closely that number approaches the maximum coordination number possible for the metal atom, will be very important, as this will influence whether monomers $M(OR)_x$, oligomers $[M(OR)_x]_{2,3 \text{ or } 4}$ or extended lattices $[M(OR)_x]_n$ are likely, whatever the polarity of the M-O bond. The polarity of the M-O bond is affected by the nature of the metal and the electron donating effect of the alkyl or aryl group. All these factors must be taken into account when studying the reactions and properties of the alkoxides.

2.6 REACTIONS OF ALKOXIDES

This section illustrates, in short, some typical reactions of the alkoxides.

1) HYDROLYSIS REACTIONS

Metal alkoxides are rapidly hydrolysed leading to the formation of hydroxides or hydrated oxides;

$$2Al(OR)_3 + 6H_2O \longrightarrow Al_2O_3.3H_2O + 6ROH$$
$$\text{or } 2\ Al(OH)_3$$

When restricted amounts of water are added partial hydrolysis occurs sometimes yielding products of definite composition known as oxide alkoxides (or μ-oxo-alkoxides).

$$2Al(OR)_3 + H_2O \longrightarrow Al_2O(OR)_4 + 2ROH$$

$$2Al(OR)_3 + 2H_2O \longrightarrow Al_2O_2(OR)_2 + 4ROH \text{ or } Al_2(OH)_2(OR)_4$$

2) ALCOHOL EXCHANGE REACTIONS

Although alcohol exchange reactions have been exploited for the preparation of alkoxides the mechanism is not yet fully understood. Metal alkoxides react with primary, secondary and tertiary alcohols and phenols to set up the following equilibrium:

$$M(OR)_n + xR'OH \longrightarrow M(OR)_{n-x}(OR')_x + xROH$$

3) REACTIONS WITH HYDROGEN HALIDES, HALOGENS AND ACYL HALIDES

Metal halides are generally used as the starting materials for the synthesis of metal alkoxides. However the alkoxides can be converted to metal halides or mixed alkoxy-halides by reaction with halogen, hydrogen halide or acyl halide.

i) $xHX + M(OR)_n \longrightarrow M(OR)_{n-x}(X)_x + xROH$

ii) $X_2 + M(OCH_2R)_n \longrightarrow MX_2(OCH_2R)_{n-2} + 2RCH_2O$

$$\downarrow$$

$$RCH_2OH + RCHO$$

iii) $xR'COX + M(OR)_n \longrightarrow M(OR)_{n-x}X_x + R'COOR$

4) REACTIONS WITH ORGANIC ESTERS AND SILYL ESTERS

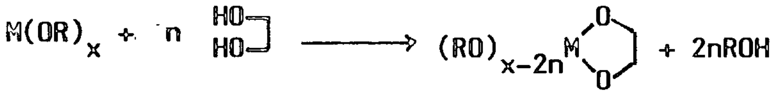
Metal alkoxides react with organic esters to form new alkoxy derivatives.

i) $M(OR)_n + xCH_3COOR' \longrightarrow M(OR)_{n-x}(OR')_x + xCH_3COOR$

ii) $M(OR)_n + xR'_3SiOH \longrightarrow M(OSiR'_3)_{n-x}(OR)_n + xROH$

5) REACTIONS WITH GLYCOLS

Glycols are di-hydroxy alcohols and react with metal alkoxides to form glycolates or mixed alkoxide glycolates. Glycolates tend to form highly polymeric derivatives compared to the analogous alkoxide derivatives and are more resistant to hydrolysis owing to the presence of a large organic chain.



Mixed glycolates can be obtained by reactions of monoalkoxide monoglycolates with different glycols in equimolar ratios.

6) REACTIONS WITH ORGANIC ACIDS AND ANHYDRIDES

Metal alkoxides react with organic acids and anhydrides to form metal acylates with the formation of alcohol or ester.

i) $M(OR)_n + nR'COOH \longrightarrow M(OOCR')_n + nROH$

ii) $M(OR)_n + n(R'CO)_2O \longrightarrow M(OOCR')_n + nRCOOR'$

7) REACTIONS WITH β-DIKETONES AND β-KETOESTERS

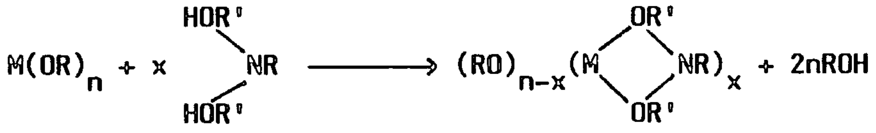
i) $M(OR)_n + xR'COCH_2COR'' \longrightarrow M(OR)_{n-x}(R'COCHCOR'')_x + xROH$

ii) $M(OR)_n + xR'COCH_2COOR'' \longrightarrow M(OR)_{n-x}(R'COCHCOOR'')_x + xROH$

8) REACTIONS WITH β-KETOAMINES AND SCHIFF BASES

i) $M(OR)_n + x(HO)R'C{=}NR \longrightarrow (RO)_{n-x}M(O(R')C{=}NR)_x + xROH$

ii)



9) REACTIONS WITH OXIMES AND HYDROXYLAMINES

i) $M(OR)_n + xR'_2C{=}NOH \longrightarrow M(OR)_{n-x}(ON{=}CR'_2)_x + xROH$

ii) $M(OR)_n + xR'_2C{=}NNOH \longrightarrow M(OR)_{n-x}(ON{=}CR'_2)_x + xROH$

10) REACTIONS WITH THIOLS

$$M(OR)_n + nR'SH \longrightarrow M(SR')_n + nROH$$

11) TISCHTSCHENKO AND MEERWEIN-PONNDORF-VERLEY REACTIONS

The presence of strongly basic alkoxides causes aldol-type condensations with aldehydes whereas acidic alkoxides ($Al(OR)_3$) cause the formation of simple esters.

This brief resumé of the reactions of alkoxides illustrates the typical chemical properties of the alkoxides. Generally the alkoxides are very reactive compounds. The polarization of the M-O-C bond makes the metal atom prone to nucleophilic attack.

2.7 TRANSITION METAL ALKOXIDES

Although heterogeneous catalysts, some of which are considered in this study, are of the greatest practical use in todays chemical industry, it is known that homogeneous catalysts offer several advantages in addition to high selectivity.

The homogeneous catalyst, typically a molecular species in solution, is uniform, often presenting only one type of active site which is not subject to physical surface effects. These catalysts and their modes of action have, effectively, greater reproducibility.

Homogeneous catalysts can readily be modified by the variation of a number of factors;

i) metal; type, coordination and oxidation state
ii) ligand; type, ligand:metal ratio, steric and electronic factors
iii) cations and anions
iv) solvent.

The homogeneous catalyst is potentially cheaper than a heterogeneous analogue because, theoretically, all the metal atoms are available for reaction rather than an unknown surface fraction. The study of homogeneous catalysis is also easier and it is possible to isolate key intermediates.

Certain organometallics (AlR_3 and ZnR_2) are catalytically active towards the polymerization of oxiranes. The active sites in these reactions are polynuclear, involving several metal atoms linked byoxygen bridges. The actual component of the active site is ill defined due to poor control of formation in the reaction medium.

Following these observations it was reported [188-191] that a series of well defined molecular compounds containing oxygen-linked metal atoms had been synthesised such that the compositions were reproducible.

The general formula of these compounds is

$$(RO)_n\text{-}M\text{-}O\text{-}M^1\text{-}O\text{-}M\text{-}(OR)_n$$

where M^1 = divalent metal e.g. Cr^{II}, Mn^{II}, Fe^{II},
M = usually Al^{III} or Ti^{IV} for example
R = alkyl group (usually propyl or butyl)

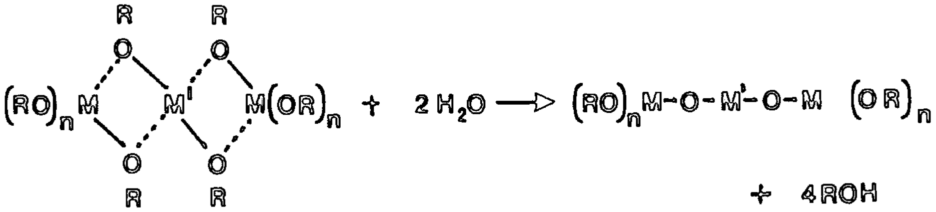
Several studies have been carried on this series of compounds which are highly soluble in organic solvents and are catalytically active[192-195].

These μ-oxo-alkoxides can be synthesised by two routes[188,189];

1) thermal condensation between a metal alkoxide and a metal acetate.

$$2(RO)_{n+1}M + M'(OAc)_2 \longrightarrow (RO)_nM\text{-}O\text{-}M'\text{-}O\text{-}M(OR)_n$$

2) carefully controlled hydrolysis of a bimetallic alkoxide



That these materials are highly soluble in organic solvents is due to their forming a core of μ-oxo bridged metals (i.e. intra- and inter- oxygen-metal bonds) surrounded by an organic sphere of alkoxy groups. Such oxygen bridging has been identified in simple and double metal alkoxides. The degree of association depends on the metal, the alkoxy group and the solvent.

The strength of the metal-oxygen bond increases with increasing electron donating power of the alkoxy groups; this is opposed by steric effects which increase with increasing size of the alkoxy group. Hence a bulky alkoxy group would favour low association whereas a methoxy group, for example, would lead to much more extensive association, even polymerization. The degree of association also depends upon the nature and possible coordination of the central metal atom. Again there is the opposing effect that bulky alkoxy groups would hinder the metal from attaining the maximum coordination possible.

It has proved possible, therefore, to control the size and shape of these coordinate aggregates by modifying the metal, solvent and alkoxy group. These modifications have allowed systematic variations of the bulk chemical activity. For the purpose of oxirane polymerizations the less associated μ-oxo-alkoxides obviously present more active and available sites to the monomer.

These polynuclear aggregates can be compared to small fragments of inorganic mixed oxides, especially those of the transition metals well known for their catalytic activity in heterogeneous systems. The μ-oxo-alkoxides represent an interesting model in-between heterogeneous and homogeneous catalysts. The presence of different oxygen-bridged metals show interesting synergistic effects, electronic distributions and magnetic exchanges. These electronic distributions and the steric environment of the catalytic centres can be controlled by the nature of the alkyl group and other factors determining size and shape (coordination geometry) of the aggregates. These properties of the μ-oxo-alkoxides and their close resemblance to mixed metal alkoxides provide the foundation for this preliminary study of bimetallic alkoxides as heterogeneous catalyst precursors.

The μ-oxo-alkoxides resemble, formally, the composition of the spinels. This is also true of the bimetallic alkoxides. Several industrial catalysts are derived from a spinel-type structure, for example, the ammonia synthesis catalyst derives from magnetite. After reduction of the precursor the iron particles are retained in an inverse spinel arrangement, thus giving a highly porous material.

The structures and general properties of transition metal (3d) alkoxides and double alkoxides are discussed here.

STRUCTURE AND PROPERTIES OF TRANSITION METAL ALKOXIDES

Interest in transition metal alkoxides has been a recent phenomena and has resulted in several publications since 1978.

A survey of the literature reveals two major points:

1) simple metal alkoxides of the transition metals are generally polymeric, involatile and insoluble.
2) mixed metal alkoxides are usually volatile, soluble and monomeric in organic solvents.

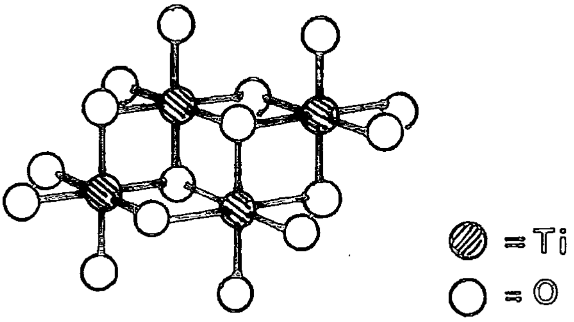
A review published in 1983[139] summarized the then known facts concerning the synthesis methods, structure and properties of the 3d, 4d and 5d transition element alkoxides.

2.7(1) SIMPLE ALKOXIDES OF THE '3d' TRANSITION ELEMENTS

Various titanium alkoxides and chloroalkoxides have been synthesised. The 'organic titanates' of Ti^{IV} have been known for many years and are commercially useful. They are prepared by the reaction of titanium tetrachloride with alcohol and dry ammonia;

$$TiCl_4 + 4ROH + 4NH_3 \longrightarrow Ti(OR)_4 + 4\ NH_4Cl$$

They are liquids or sublimable solids and titanium attains octahedral coordination by polymerization unless bulky groups are present[196].



They are susceptible to hydrolysis unless chelated with ligands such as β-diketonates (L-L), e.g. $[Ti(OR)_2(L\text{-}L)_2]$.

These compounds are water soluble and are useful as thixotropes in 'non drip' paints due to their crosslinking with cellulose ether colloids.

Alkoxy species of Ti^{III} have also been prepared using the chlorides. Mixed chloride-alkoxides have been prepared[138], using the anhydrous metal chloride and trialkylorthoformates, and characterised. They exhibit polymeric nature, IR spectra indicating the presence of alkoxy bridges, although anomalous M-Cl bands could point to chloride bridges. The magnetic susceptibility measurements indicate a value lower than expected for a spin-only μ_{eff}. This is indicative of some metal-metal interaction. All the chloro-alkoxytitanates are insoluble and decompose at around 300°C, although they are significantly more air stable than the titanium trichlorides. Similar vanadium compounds have been prepared and found to have comparable properties.

More recently pure titanium trialkoxides have been prepared by the reduction of titanium tetra-alkoxides with organosilicon compounds. The overall stoichiometry can be represented as follows;

$$Ti(OR)_4 + HSi(OR)_3 \longrightarrow Ti(OR)_3 + Si(OR)_4 + \tfrac{1}{2}H_2$$

The titanium trialkoxides have been variously described as tetrameric and soluble, or as insoluble polymers. These workers[197] found their compounds to be polymeric, diamagnetic, insoluble and to decompose on heating. On the basis of spectral and magnetic data, structures based on oxygen bridges have been tentatively proposed.

Chromium (III) chlorides are notoriously insoluble in pure water without the presence of a reducing agent. The reducing agent produces Chromium (II) ions in solution and solubilization occurs due to electron transfer across a chloride bridge from $Cr^{II}(aq)$ to $Cr^{III}(s)$ thus promoting hydration[198,199].

Chromium (III) chloride proved difficult to convert into alkoxide derivatives because of this insolubility. The use of a tetrahydrofuran adduct $CrCl_3.3THF$ eventually allowed the synthesis of simple chromium alkoxides from methanol, ethanol and n-butanol[139]. With secondary or tertiary alcohols only hydrolysed products were obtained. Tertiary butoxides were obtained from the treatment of the THF adduct with stoichiometric amounts of lithium tert-butoxide ($LiOBu^t$). The isopropoxide [$Cr(OPr^i)_3$] is a green insoluble solid whereas the butoxide [$Cr(OBu^t)_3$] is a distillable liquid.

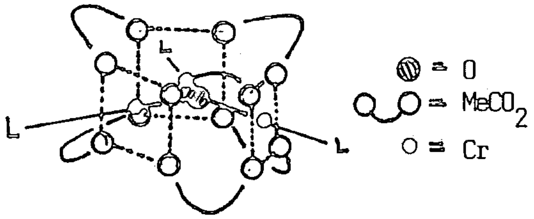
Primary and secondary alkoxides have been shown to have chromium in an octahedral environment using spectral and magnetic techniques. Although the primary alkoxide are stable to alcohol exchange reactions they do interchange with chelating agents such as β-diketones and carboxylic acids. This stability is ascribed to steric effects and the stability of octahedral Cr^{III} (i.e. three singly occupied t_{2g} levels).

e.g. $Cr(OR)_2(X)$ or $Cr(OR)(X)_2$; X = β-dk or RCOO.

As expected the the dialkoxides are insoluble and polymeric but the presence of long chain acid or β-diketone groups in the monoalkoxide derivatives contributes to the increased solubility in organic solvents.

These, possibly dimeric, species appear to show octahedral geometry around Cr^{III}. Oxygen-bridged octahedral chromium compounds are well known[198], the oxygen provides a π-bridge for the pairing of metal d-electrons, e.g. for carboxylates, as shown by magnetic measurements.

Trinuclear structure of $[Cr_3O(O_2CMe)_6L_3]^+$



Alkoxides of chromium (II), where the alkoxy group is derived from an aliphatic alcohol, are insoluble coordination polymers which are highly sensitive to oxygen. Bulky or branched alcohols form less associated alkoxides which are correspondingly more soluble in organic solvents and which form adducts with donor ligands..

Manganese (II) is resistant to oxidation and reduction due to the stability of its half filled d-shell. Compounds of manganese exhibit both octahedral and tetrahedral geometry. Manganese (II) alkoxides are air sensitive and range from amorphous, gelatinous coordination polymers to monomeric crystalline species. Several mixed carbonyl-alkoxy compounds have been investigated and shown to be trimeric (and unsymmetrical) or tetrameric (symmetrical).

Iron(II) aryloxides and alkoxides have been prepared as 2,2'-bipyridine complexes[139].

e.g. $Fe(C_6H_4X)L_n$; $Fe(OR)_2L_n$

X= H, Me, Ph, Cl, CN, NO_2

R= Me, Et, ^iPr, H_2CPh-

Reactions with acetic acid or acetates have yielded mixed acetate-alkoxides.

Up until 1983 alkoxy compounds of cobalt(II) had received very little attention. Various blue-coloured alcoholates have been formed from cobalt(II) chloride. Cobalt (II) alkoxides have been obtained from the treatment of anhydrous chloride with lithium alkoxides.

$$CoCl_2 + 2LiOR \longrightarrow Co(OR)_2 + 2LiCl$$

These purple coloured compounds are insoluble in organic solvents and are non-volatile. Where -OR is a primary alkoxy group no alcohol exchange reactions take place. Cobalt diisopropoxide will exchange with primary alcohols but not with other secondary or tertiary groups. Their visible spectra indicate an octahedral geometry for cobalt.

As with cobalt several alcoholate complexes of nickel halides, e.g., $NiCl_2.xROH$ are known[107,139,200]. Solutions of nickel(II) chloride (from which such complexes are obtained) are relatively simple to prepare but nickel (II) chloride is insoluble in secondary or tertiary alcohols so these derivatives are formed by alcohol exchange reactions. From visible electronic spectra the mono-alcoholates have a pseudo-octahedral geometry. Treatment of the chloride with lithium alkoxides LiOR, where -OR is derived from a primary alcohol, yields nickel(II) dialkoxides but the use of pyridine is required to aid solution of nickel(II) chloride for the preparation of secondary or tertiary alkoxides.

Primary nickel(II) alkoxides are non-volatile, green coloured solids. Their electronic spectra and magnetic moments indicate octahedral metal coordination. Secondary and tertiary nickel alkoxides are blue/violet compounds, unstable to heat (decomposing at around 90-100^{o}C). The tertiary alkoxides, in particular are very sensitive to hydrolysis undergoing a colour change from purple to green on exposure to moisture. Electronic spectra are indicative of a tetrahedral environment in the case of tertiary alkoxides.

Bulky groups are known to inhibit formation of planar nickel complexes and to favour tetrahedral geometry[198].

Although the nickel alkoxides (especially the methoxides) do not undergo alcoholysis reactions very easily they do react with β-diketones and carboxylic acids. They form coloured solids soluble in benzene but not soluble in alcohols. Bis-β-diketonates (e..g. $[Ni(acac)_2]_3$) are trimeric whereas the monoalkoxide-β-diketonates can be trimeric where the alkoxy group is isopropoxy or tert-butoxy and tetrameric where methoxy or ethoxy groups are involved.

In both carboxylates and β-diketonates the mono-substituted derivative is resistant to alcoholysis where methoxy groups form the alkoxy ligand. Isopropoxide β-diketonate or carboxylate will exchange with primary alcohols (CH_3OH, C_2H_5OH) but not with secondary or tertiary alcohols. In these nickel is shown to have a distorted octahedral environment[196].

In 1965 two reports on the production of alkoxide derivatives of copper (II) and copper (I) were published.

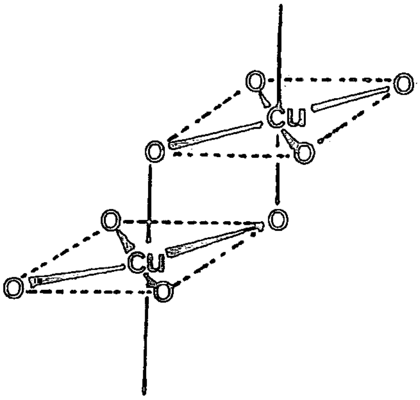
One describes the thermal decomposition of methyl copper in methanol to yield copper (I) methoxide. Copper (II) methoxide can be produced by the treatment of copper (II) bromide with sodium methoxide in methanol. The copper (II) derivative is a blue solid which can be recrystallised from liquid ammonia to give a blue crystalline material almost insoluble in organic solvents. On heating to 188°C under vacuum this compound undergoes violent homolytic fission to give copper metal, methanol and formaldehyde as decomposition products. Copper (I) methoxide decomposes at room temperature to give the same products[103].

The second paper [104] describes the preparation of a series of copper (II) alkoxides and chloro-alkoxides by treatment of copper(II) halides with lithium alkoxides.

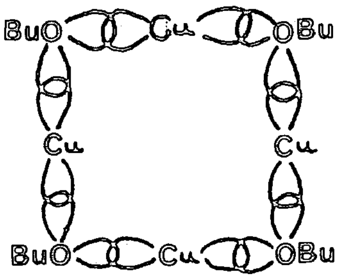
The products $Cu(OMe)_2$, $Cu(OMe)Cl$, $Cu(OEt)Cl$, and $Cu(OEt)_2$ are all non-volatile and insoluble in alcohols, ethers and hydrocarbons although the diethoxide is soluble in ketones and hydrolyses in aqueous solution.

On the basis of magnetic susceptibility measurements and spectra a variety of structures have been proposed. The data correspond with those for compounds known to contain oxygen bridges (e.g. in carboxylates) and the geometry around copper is thought to be distorted octahedral (known in copper complexes i.e. 4+2 coordination).

For chloride-alkoxides, IR spectra indicate that only alkoxy groups form bridges whereas in the dialkoxides bridging and terminal groups are present. A further possibility is that of a 3-d polymer with long Cu-O or Cu-Cl bonds between layers.



Unlike copper (I) methoxide, copper (I) butoxide ($CuOBu^t$) is soluble in organic solvents and can be isolated by sublimation at 170°C under reduced nitrogen pressure[114]. The product is a pale yellow solid which is diamagnetic and described as having tetrameric, square planar structure $[CuOBu^t]_4$ [201].



X-ray crystal structure shows a planar ring containing four copper and four oxygen atoms. These tetrameric units persist in the vapour phase. This compound is an excellent metallation agent[114].

$$\mathrm{PhC{\equiv}CH} + {}^{t}\mathrm{BuOCu} \longrightarrow \underset{97\%}{\mathrm{PhC{\equiv}CCu}} + {}^{t}\mathrm{BuOH}$$

Copper (I) alkoxides react with aryl halides to form alkyl-aryl ethers under mild conditions and thus provide useful reagents for their synthesis[118].

Unlike alkoxides of some other transition metals copper (II) alkoxides appear to undergo facile alcoholysis reactions. Various factors are suggested to explain these different alcohol exchange tendencies. These are; i) thermodynamic vs kinetic stability

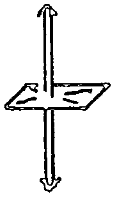
ii) role of crystal field stability in different plausible geometries.

Alcohol exchange in copper (II) alkoxides appears to be governed primarily by steric factors. Primary alkoxides give quantitative exchange with primary, secondary and tertiary alcohols. Secondary and tertiary alkoxides undergo facile interchange with primary alcohols but not with secondary or tertiary.

Magnetic susceptibility measurements show that compounds such as; $Cu(OMe)_2$, $Cu(OEt)_2$, $Cu(OPr^i)_2$, $Cu(OBu^s)_2$ and $Cu(OBu^t)_2$ are paramagnetic with distorted octahedral geometry around the copper, this is supported by visible electronic spectra [136].

As with the copper (I) carboxylates described, the lower than spin only values for magnetic moment measurements indicate some interaction between copper centres. For the carboxylates attempts have been made to specify the interaction as being through orbitals of σ-symmetry (dx^2-y^2) of the two metal atoms or through the π-orbitals of the bridging carboxylate groups.

Various reports of tetragonal or octahedral distortion for the copper (II) alkoxides could be explained by a structure of the type below[136,139].



2.7(2) MIXED METAL ALKOXIDES OF THE 3d TRANSITION METALS

As the previous section has illustrated, simple alkoxides are characterized by their insolubility, involatility and polymeric nature.

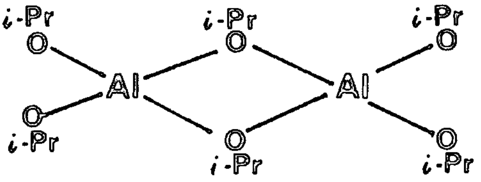
In the early 1920's Meerwein and Bersin[51] reported the synthesis of a series of 'alkoxo' salts by the titration of a basic alkoxide (e.g. NaOR) with a less basic, or amphoteric alkoxide (e.g. $Al(OR)_3$).

$$NaOR + Al(OR)_3 \longrightarrow Na^+[Al(OR)_4]^-$$

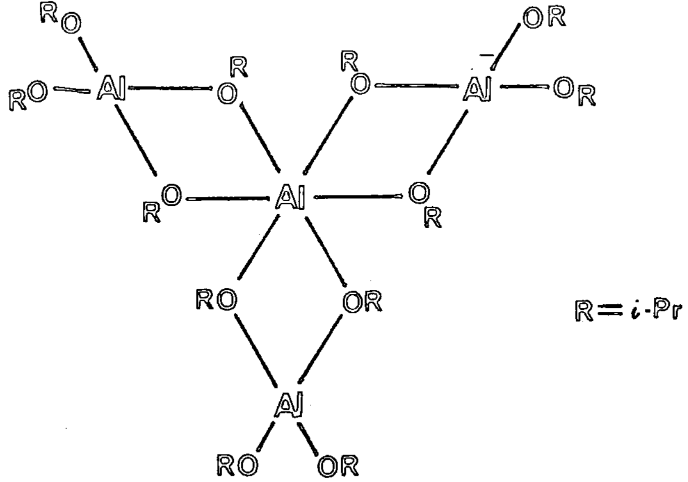
Their acid-base theory of mixed metal alkoxide formation proved difficult to correlate with the formation of stable double alkoxides from metals of similar basicity e.g. gallium and aluminium.

$$Ga[Al(OR)_4]_3$$

The preferred concept today is that of a coordination model where the tetraalkoxyaluminate (usually the isopropoxide) acts as a bidentate ligand. A bridge structure involving two tetraisopropoxyaluminate 'ligands' was suggested as long ago as 1953[202] for dimeric aluminium triisopropoxide in the vapour phase (cf Al_2Cl_6).



When freshly distilled the aluminium triisopropoxide is trimeric but 'ages' after a period of time to become tetrameric. This was ascribed[101] to the tendency of aluminium to attain it's maximum coordination number to give the structure below:-



This structure is suppor ted by n.m.r spectra and X-ray crystallographic studies[134].

The bimetallic transition metal alkoxides have the general formula;

$$M[Al(OR)_4]_n$$

n= 2 when M= e.g. Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}.
n= 3 when M= e.g. Cr^{III}, Fe^{III}.

They exhibit characteristics of covalent compounds, being monomeric, volatile, soluble in common organic solvents and, for the transition metals, are coloured. The geometry is affected by the alkoxy group and the alkoxy:metal ratio and by the nature of the metal itself.

The bimetallic alkoxides are synthesised in general by the reaction of the anhydrous chloride with a potassium-aluminium alkoxide in alcohol or hydrocarbon solvent.

$$MCl_x + xK[Al(OR)_4] \longrightarrow M[Al(OR)_4]_x + xKCl$$

Chromium (III) triisopropoxide undergoes facile alcoholysis with primary alcohols but not with secondary or tertiary alcohols.
Studies of the alcoholysis reactions of chromium-aluminium isopropoxide ($Cr[Al(OPr^i)_4]_3$) show quantitative exchange with primary alcohols[139-41]

(e.g. CH_3OH, CH_3CH_2OH, $n\text{-}C_4H_9OH$ and CF_3CH_2OH).

The properties of the compound vary with the degree of exchange;

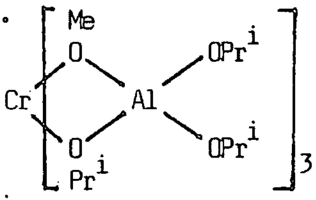
$Cr[Al(OMe)_4]_3$ is involatile, insoluble and a polymeric green solid,

$Cr[Al(OEt)_4]_3$) are both volatile green liquids or solids,
$Cr[Al(OBu^n)_4]_3$)

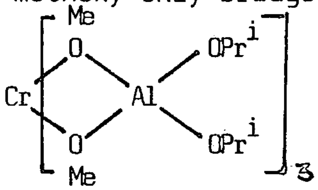
$Cr[Al(OMe)(OPr^i)_3]_3$ is volatile, monomeric and soluble in benzene,

$Cr[Al(OMe)_2(OPr^i)_2]_3$ is soluble only in hot benzene and sublimes to give poor yields of the product.

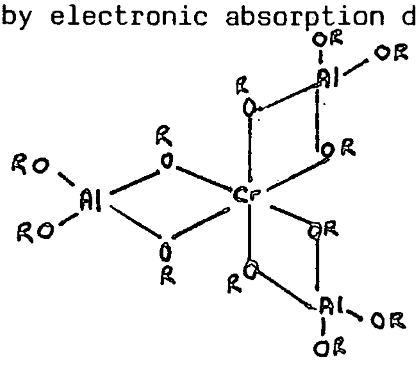
The presence of the small methoxy group leads to extended association and polymerization.



Here the terminal isopropoxy groups are susceptible to attack by methoxy groups but the methoxy group may then exchange with bridging isopropoxy to form methoxy-only bridged species.



In all cases the chromium appears to have octahedral coordination as indicated by electronic absorption data and magnetic susceptibility measurements.



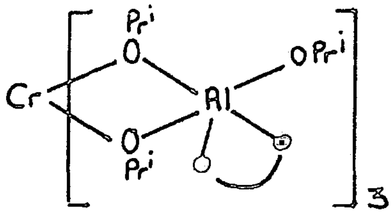
Exchange with acetylacetonate has revealed a similar series of derivatives with varying properties;

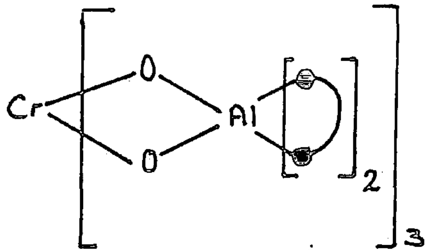
i.e. $Cr[Al(OPr^i)_3(acac)]_3$)
$Cr[Al(OPr^i)_2(acac)_2]_3$) distillable and monomeric,

$Cr[Al(acac)_4]_3$ shown to be a mixture of $Cr(acac)_3$ and $Al(acac)_3$ (spectra and separation by fractional crystallisation)

Again chromium has octahedral geometry whereas aluminium takes up five or six coordination ((a) and (b) respectively)

a)

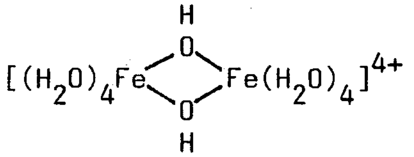




Manganese (II) forms isopropoxides with aluminium $Mn[Al(OPr^i)_4]_2$ although this metal does not appear to have been studied as extensively as others in the '3d' series (see later- experimental section). Magnetic susceptibility measurements and electronic spectra indicate octahedral geometry.

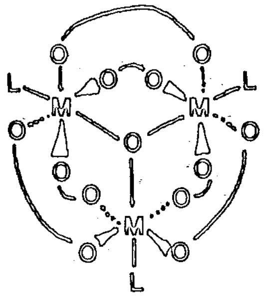
Iron (III) forms a compound of formula $Fe[Al(OPr^i)_4]_3$. The magnetic moment should be 5.9BM (spin only) for three unpaired electrons. However the value is lower than this for the alkoxide and decreases with decreasing temperature indicating antiferromagnetism.

Species such as



$$[(H_2O)_4Fe\begin{smallmatrix}\overset{H}{O}\\ \underset{H}{O}\end{smallmatrix}Fe(H_2O)_4]^{4+}$$

also show reduced values for μ_{eff} due to weakly coupled spins on the two metals. As in the case of chromium(III), oxygen-bridged species permit pairing or interaction of the d-electrons via the bridge. It is found that linear Cr-O-Cr compounds have even lower μ_{eff} values, evidently because the linear bridge permits pairing of the d-electrons via $d\pi$-$p\pi$ bonds more readily than the bent $Cr\nearrow\overset{H}{O}\searrow Cr$ (N.B. oxygen centred complexes found in so called 'basic' carboxylates)[196,198].



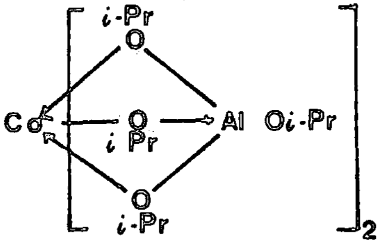
$[M_3O(CO_2R)_6L_3]^+$

4

Iron (III) is electronically similar to manganese (II) but, due to the additional positive charge, iron(III) is able to polarize ligands thus inducing intense charge transfer bands obscuring bands in electronic spectra (e.g. $Fe(acac)_3$ - deep red). Nonetheless it is likely that iron (III) will attain six coordination in these alkoxide species.

Cobalt- aluminium isopropoxide ($Co[Al(OPr^i)_4]_2$) is a purple liquid. There is a small stability difference between octahedral (pink-violet) and tetrahedral (blue) cobalt(II) complexes and an equilibrium exists between the two geometries. Ligand polarizability is an important factor in determining stereochemistry. More polarizable ligands favour the tetrahedral form since fewer ligands would be required to neutralise the metal's positive charge.

The spectra and magnetic susceptibility data indicate a distorted octahedral environment around the cobalt (II) and a tridentate $Al(OPr^i)_4^-$ ligand has been proposed.



Cobalt (II) acetylacetonate is known to achieve octahedral geometry by the formation of tetramers.

Nickel (II) can take up a variety of geometries (octahedral, tetrahedral, square planar, trigonal bipyramidal). Nickel (II) alkoxides provide a good model for illustrating the effect of the alkoxy group on the stereochemistry.

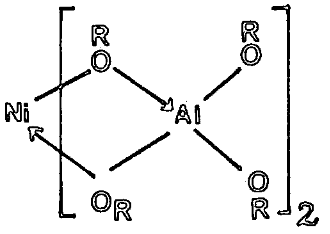
$Ni[Al(OMe)_4]_2$ is a yellow-green solid which is insoluble and involatile. Electronic spectra are characteristic of octahedral species.

$Ni[Al(OEt)_4]_2$ is a purple-green compound which is insoluble in benzene but is soluble in ethanol giving a pink-purple coloured solution. In ethanol this compound exhibits characteristics of octahedral geometry although there are indications of tetrahedral species being present.

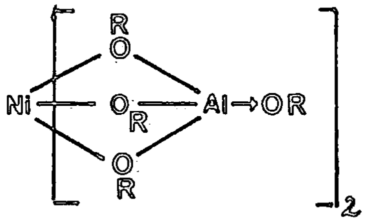
$Ni[Al(OPr^i)_4]_2$ is a pink liquid which is soluble in benzene and isopropanol in which it exhibits both tetrahedral and octahedral geometry. The addition of a strong donor molecule (e.g. pyridine) produces more chracteristics of octahedral stereochemistry (colour changes from pink to yellow green).

Magnetic susceptibilty measurements give values, for the isopropoxide, between those for octahedral and tetrahedral geometries (oct. = 2.9-3.4BM, tet. = 4.2 BM) and corresponding to those found for distorted octahedral-tetrahedral (3.0-3.5BM) i.e. around 3.34BM.

Nickel would tend to attain octahedral geometry therefore it is possible that the tetraisopropoxyaluminate ligand acts as either bidentate or tridentate



TET



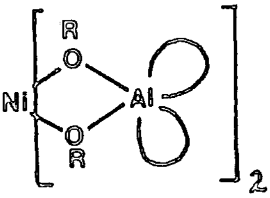
OCT

Alcoholysis reactions of $Ni[Al(OPr^i)_4]_2$ have been carried out with a variety of alcohols and acetylacetonate. With tert-butanol partial replacement of the isopropoxy groups occurs, forming e.g.

$Ni[Al(OBu^t)_3(OPr^i)]_2$ which is monomeric and stable. With acetyl acetonate;-

$$Ni[Al(OPr^i)_4]_2 + 4\ acac \longrightarrow Ni[Al(OPr^i)_2(acac)_2]_2$$
$$Ni[Al(OPr^i)_4]_2 + 8\ acac \longrightarrow Ni(acac)_2 + 2Al(acac)_3$$

For $Ni[Al(OPr^i)_2(acac)_2]_2$



its electronic spectra show mainly tetrahedral geometry although some octahedral characteristics are apparent. Ligand field parameters indicate considerable covalent character of the metal-ligand bond[142].

Copper (II) aluminium isopropoxide is reported as being a green-blue liquid[139]. Magnetic susceptibilities indicate octahedral geometry in solution. Antiferromagnetic characteristics are shown perhaps due to some metal-metal interaction. In copper (II) carboxylate μ_{eff} is also lower than the expected spin-only value and this compound is known to have a dimeric structure with the two copper centres held together by four acetate bridges to give distorted octahedral ('elongated octahedron') coordination around copper. This situation seems similar to that of copper (II) aluminium isopropoxide.

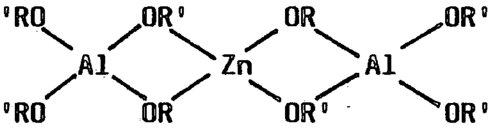
Zinc alkoxides ($Zn(OMe)_2$, $Zn(OPr^i)_2$) have been synthesised by the treatment of zinc chloride with lithium alkoxides[109]. Alcohol exchange reactions have been used to yield ethoxides, n-butoxides and tert-butoxides. They are all involatile solids, insoluble in organic solvents. Double alkoxides of zinc with aluminium show properties dependent upon the alkoxy group.

$Zn[Al(OMe)_4]_2$ is a non-volatile, insoluble white solid although it will dissolve in the polar solvent DMSO. $Zn[Al(OEt)_4]_2$ is also a non-volatile, insoluble white solid. $Zn[Al(OPr^i)_4]_2$ is, however, initially a liquid which, on standing, becomes a waxy solid.

Alcoholysis reactions of the isopropoxide are rapid, quantitative and exothermic with primary alcohols and less branched alcohols but tertiary alcohols exchange only slowly and with increasing difficulty as the isopropoxy groups are replaced by the tertiary alcohol.

e.g. $Zn[Al(OPr^i)(OBu^t)_3]_2$

Secondary butoxides and mixed tertiary butoxides-isopropoxides exhibit complex ^1H NMR signals due to intermediate rates of exchange between bridging and terminal alkoxy groups. On the basis of ^1H NMR, molecular weights and elemental analyses, including IR, the following structure has been proposed[152];

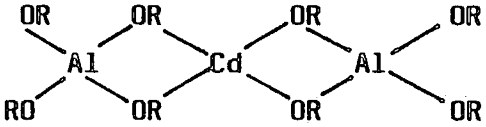


$R=R' = Me, Et, Pr^n, Pr^i, Bu^i, Bu^s.$
$R=Pr^i, \quad R'= Bu^t.$

With acetylacetone, zinc can achieve both five and six coordination by trimerizing to $[Zn(acac)_2]_3$.

It is possible that $Zn[Al(OPr^i)_4]_2$, when changing from a liquid to a waxy solid also undergoes similar association (cf $Al(OPr^i)_3$).

Cadmium, below zinc in the Periodic Table, has a very similar chemistry and forms analogous alkoxy derivatives. On the basis of IR, NMR, molecular weight and analytical data the following structure for several compounds of formula $Cd[Al(OR)_4]_2$ has been proposed.



Reports of other mixed alkoxides have been published over the last few years. Some of these are of interest to this project and are summmarized below.

Analogues of the iron (III)- aluminium (III) alkoxides have been prepared where the aluminium is replaced with zirconium, conforming to the general formula $[Fe(Zr_2(OR)_9)_3]$ where R= Me, Et, Bu^n and Bu^s[148].

Generally the isopropoxy derivative is prepared first then converted to other species by alcohol exchange reactions. In benzene the isopropoxy derivative is soluble and monomeric. However if this compound is mixed with isopropanol it is found to disproportionate to give $Zr(OPr^i)_4.Pr^iOH$.

$[Fe(Zr_2(OPr^i)_9)_3]$ exchanges alkoxy groups quantitatively with methanol and ethanol to give insoluble or low solubility products. With straight chain or secondary butanols mixed derivatives are obtained,

e.g. $[Fe(Zr_2(OPr^i)_6(OR)_3)_3]$ and $[Fe(Zr_2(OPr^i)_2(OR)_7)_3]$.

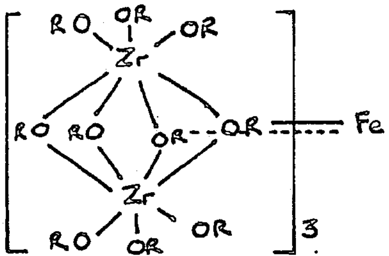
Complete replacement with these alcohols can be attained by azeotropic distillation of isopropanol although tertiary butanols still give mixed derivatives.

Iron (III) appears, from electronic and esr spectra and magnetic measurements, to be octahedrally sited. Theoretically iron(III) has two spin states; 1) low spin μ_{eff} = 1.73BM

2) high spin μ_{eff} = 5.92BM (octahedral and tetrahedral)

The present complex has the value μ_{eff} = 5.02-5.14BM indicating high spin arrangement but some antiferromagnetic interaction. It is also possible that some equilibrium exists between the low spin and high spin states. No conclusive evidence appears to have been provided to date.

The $Zr_2(OPr^i)_9^-$ appears to behave as a bidentate ligand to give the following structure;



A mono-zirconium di-iron entity $[Fe_2Zr(OPr^i)_{10}]$ or $[(Zr(OPr^i)_2)((Fe(OPr^i)_4)_2)]$ has also been prepared which is monomeric, volatile and soluble. Iron (III) would appear to occupy a tetrahedral position (cf. $Fe^{III} \Longleftrightarrow Al^{III}$). A low μ_{eff} indicates long range coupling Fe-Fe of the paramagnetic iron separated by the diamagnetic zirconium.

In the compound $[(Zr(OPr^i)_2)((Al(OPr^i)_4)_2)]$, tetrahedral aluminium has been confirmed by ^1H, ^{13}C and ^{27}Al NMR.

Similarly chloride and alkoxide isopropoxy metallates of cobalt (II) have been reported[151], which, potentially, provide useful starting materials for the preparation of termetallic alkoxides of transition metals.

e.g. $[ClCo[Al(OPr^i)_4]]$ dark blue solid,
$[ClCo[Zr_2(OPr^i)_9]]$ dark blue crystalline solid,
$[ClCo[Zr_2(OMe)_9]]$ blue solid,
$[ClCo[Zr_2(OPr^i)_6(OBu^s)_3]]$ blue crystalline solid,
$[ClCo[Zr_2(OPr^i)_4(OBu^s)_5]]$
$[ClCo[Zr_2(OBu^s)_9]]$ blue solids,
$[ClCo[Zr_2(OPr^i)_3(OBu^t)_6]]$
$[RO.Co[Zr_2(OPr^i)_9]]$ violet crystals.

Most of these are soluble and magnetic measurements indicate that cobalt displays either trigonal bipyramidal or tetrahedral geometry.

Again antiferromagnetic interactions appear to be involved indicating some possible coupling between the two cobalt (II) centres.

Recently a report was published describing the synthesis of chloride and alkoxide alkoxometallates of copper (II)[150].

The preparation of species like $[ClCu[Zr_2(OPr^i)_9]]$ by the treatment of copper (II) chloride with $K[Zr_2(OPr^i)_9]$, in benzene, pointed the way to the synthesis of other, novel, bimetallic and trimetallic alkoxides.

e.g. $$[ClCu[Zr_2(OPr^i)_9] + K[Al(OPr^i)_4] \longrightarrow \left[\{Al(OPr^i)_4\}Cu\{Zr_2(OPr^i)_9\}\right] + KCl$$

These compounds are highly sensitive to moisture. They are coloured solids or viscous liquids and are soluble in hydrocarbons (except for the methoxy derivatives). They can be volatilized under reduced pressure.

IR spectra, visible spectra and magnetic moments are reported for these species and provide evidence that these compounds are predominantly monomeric (except methoxy derivatives). There appears to be some inter-metal coupling and varying coordination around copper of trigonal bipyramidal and octahedral types.

SUMMARY

As discussed,the bimetallic alkoxides possess characteristics more in common with the μ-oxo-alkoxides than with the simple metal alkoxides. The bimetallic alkoxides are, usually, monomeric, volatile and soluble in organic solvents. The tendency of the central metal atom is to attain maximum coordination although this may be counteracted by the effect of bulky alkoxy groups. Hence methoxy groups tend to allow extensive polymerization whereas propoxides or butoxides are monomeric. The M-O bonds are characteristically covalent . The structures of these alkoxides are interesting although a great deal more investigative work is required to verify some of the proposed configurations.

Several of the compounds described here were synthesised during the course of this project although some modifications were made to the reported methods due to the requirements of the catalyst processes.

CHAPTER 3

CHAPTER 3

AMMONIA AND METHANOL SYNTHESIS OVER SUPPORTED METAL CATALYSTS

3.1 INTRODUCTION

This project was concerned with evaluating the efficacy of catalysts derived from mixed metal alkoxides. Although such alkoxides were proposed as precursors to a variety of heterogeneous catalysts, we were interested, specifically, in those involved in the ammonia-methanol synthesis loop.

The possibilities for using a catalytic process to produce ammonia was first indicated in 1884 when Ramsay and Young showed that the reaction of nitrogen and hydrogen over an iron catalyst resulted in an equilibrium mixture containing nitrogen, hydrogen and ammonia.[206]. Much of todays manufacturing technology stems from the Haber-Bosch commercial process introduced by BASF in 1913. The high-pressure technology developed for the ammonia process was applied to the production of methanol. In 1923 Mittasch, Pier and Winkler discovered that zinc oxide-chromium oxide catalysts were highly selective for the direct synthesis of methanol from fairly impure synthesis-gas.

With the availability of synthesis-gas of much greater purity, catalysts based on copper-zinc oxide-alumina were introduced and in 1966 the high-pressure process was replaced by the I.C.I low pressure method.[203].

Hydrogen is required for the production of both ammonia and methanol[203,204,208],

$$N_2 + 3H_2 \longrightarrow 2NH_3 \qquad \Delta H = -46\ kJmol^{-1}$$

$$CO + 2H_2 \longrightarrow CH_3OH \qquad \Delta H = -92\ kJmol^{-1}$$

and the preferred source of hydrogen for industrial processes is synthesis-gas.

Synthesis-gas is the term applied to a mixture of hydrogen and carbon oxides. Synthesis gas can be obtained from hydrocarbon sources by a variety of methods. In the I.C.I. process the steam reforming of natural gas or light hydrocarbons provides relatively pure synthesis-gas[203-6].

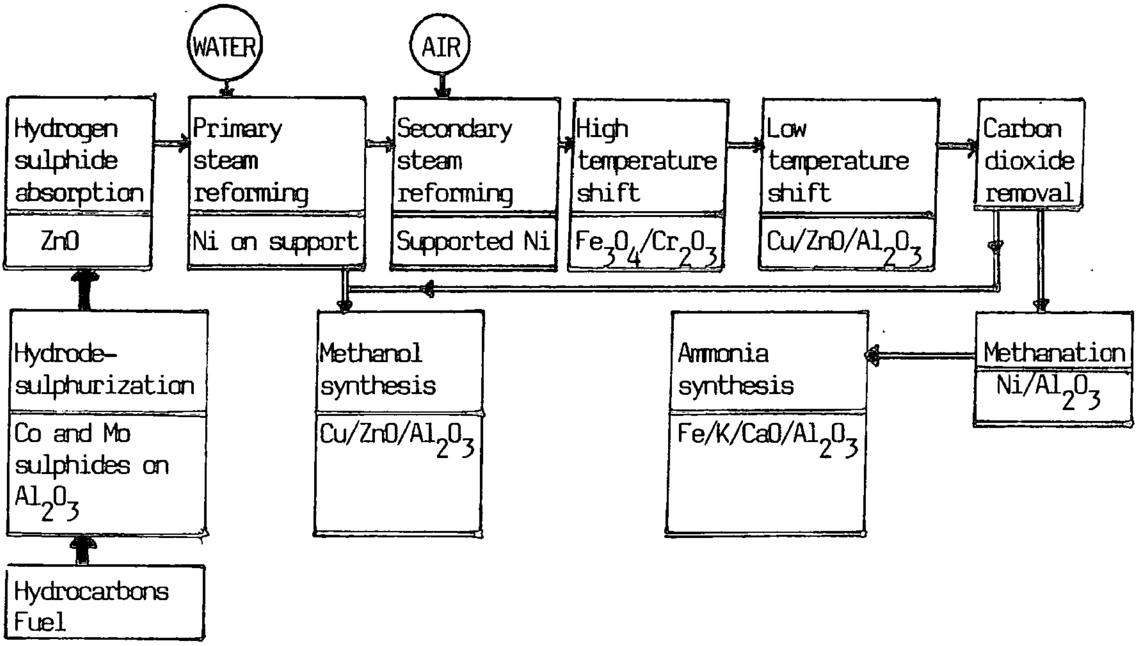
The primary reforming reaction is highly endothermic;

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad \Delta H = +206.1\ kJmol^{-1}$$

and the equilibrium only becomes favourable at temperatures above 700°C (operating conditions are 750-850°C and 20-30 bar). The exothermic water-gas shift reaction is also brought to equilibrium;

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H = -41.1\ kJmol^{-1}$$

so the product gas contains a mixture of carbon monoxide, carbon dioxide, hydrogen and methane. Supported nickel catalysts in the form of Raschig rings are used for this process. The ammonia process produces excess carbon dioxide which can be fed to the methanol synthesis loop and methanol synthesis can produce excess hydrogen which can be fed back to the ammonia loop. Hence ammonia and methanol syntheses can be integrated into one plant. Such is the case at I.C.I. where the overall process consists of a series of catalytic steps as shown below[203].



From the previous diagram it can be seen that many different types of heterogeneous catalyst are involved in the production of ammonia and methanol.

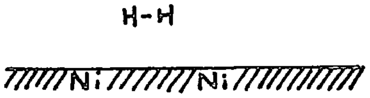
Catalysis is the key to the expanding, modern chemical and petroleum industries of today. In future the application of catalysis for fuel synthesis from coal and oil shale seems to offer enormous potential. Catalytic processes for chemical manufacture must increasingly involve synthesis transformations. Further developments in catalysis are dependent upon our gaining a much better understanding of the mode of action of heterogeneous catalysts.

The catalytic pathway is a series of reactions;

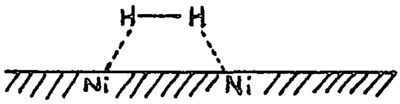
1) adsorption of reacting gases on the the catalyst surface (activated adsorption),
2) surface reaction,
3) desorption of the products.

Different types of adsorption occur, both physical and chemical[204].

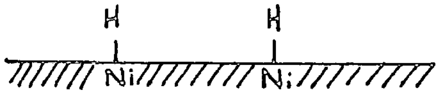
Physical adsorption allows the reactant molecules to come close to the surface at low potential energy. This is an unreactive state.



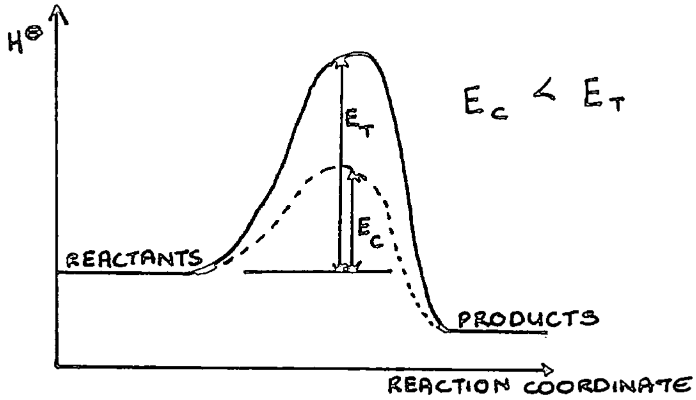
There exists then a transition state- crossing from physisorption to chemisorption. In this example, each hydrogen is equally bound to the other and to the nickel atoms.



The H-H bond is then broken and dissociative chemisorption occurs. The energy required to break the hydrogen molecule bond by these steps is less than direct dissociation of the hydrogen molecule. The adsorption is always exothermic - the amount of heat liberated being the minimum required to break the chemisorption bond.



The activation energy for the catalytic reaction is much less than that for the thermal reaction thus increasing the overall rate of reaction.



It appears that certain atoms, such as those on the corners and edges of a solid surface show a variation in adsorptive characteristics. Accordingly chemisorption and reaction would occur predominantly on active centres identified as certain types or faces of a crystal lattice. Orientation of reactant molecules and the catalyst crystalline lattice are geometric factors. The actual spacings of the metal atoms on the surface will clearly be important in making one face of a metal crystal catalytically active and another not, depending on how closely the actual atom spacings approximate to the bond distances in the reactant molecules. It is found, in practice, that only a small fraction of the total metal surface is catalytically active.

3.2 METHODS OF HETEROGENEOUS CATALYST PREPARATION[203-205]

Some catalysts are comparatively simple compounds or unsupported metals. Most industrial catalysts, however, are high area solids whose methods of manufacture are complex, time consuming and costly. Precise details are proprietary so only a general summary can be provided here.

3.2(1) UNSUPPORTED METALS

Examples are platinum alloy gauze, silver and Raney nickel. Platinum alloy gauze is woven from wires of a few thousandths of an inch in diameter. Silver is used in the form of small granules or whiskers. Raney nickel, which can be considered in this category, is prepared by leaching aluminium from a nickel-aluminium alloy thus yielding a high surface area material.

3.2(2) DECOMPOSITION OR FUSION

Not a widely used method,although the ammonia synthesis catalyst is prepared in this way. Decomposition of salts or hydrates is carried out at high temperature (1600°C) in an electric furnace leaving the metal or oxide. This is cooled and ground then pre-reduced to increase the porosity or surface area.

3.2(3) IMPREGNATION

In this case an active component is placed on asupport (usually alumina) which may be inert or active. After firing of the 'green' support,to improve strength,the formulation steps involved are;

i) evacuation of support,
ii) impregnation of the support by salt solution of active component,
iii) drying,
iv) calcination and activation.

A peripheral layer ('shell') or complete impregnation can be achieved. The nickel-based methane steam reforming catalyst is one example of a catalyst prepared by this method.

3.2(4) CRYSTALLISATION

Zeolites are silicates or aluminates with an open framework, ? regular structure and apertures of molecular dimensions. Solutions of the silicates and aluminates are mixed with additives at a specific pH. The gel which is formed is aged then heated to yield the crystalline product. This crystallinity is critical to the performance of the zeolite. The Mobil company have used zeolites to convert methanol to gasoline.

3.2(5) GEL FORMATION OR PRECIPITATION

Precusors to catalysts in this category are prepared by rapidly mixing concentrated solutions of metal salts (usually nitrates, hydroxides or carbonates as sulphates or chlorides can act as poisons). With multi-component systems homogeneous mixtures result from simultaneous precipitation. This can be achieved by careful pH control. The catalyst particle size is also affected by pH, and neutral solutions produce the smallest particles.

Overall surface areas are in the range 75-150m^2g^{-1} compared to surface areas up to 100m^2g^{-1} for impregnated catalysts. Precipitated catalysts usually exhibit high activity. The copper based low-temperature shift and the copper-zinc oxide-alumina synthesis catalysts are good examples.

Great care must be taken throughout catalyst preparations to ensure reproducibility of characteristics such as surface area, pore size, crystal structure and surface hydration and oxidation.

3.3 CATALYST PROPERTIES [204,205]

Several properties are considered when designing or selecting a catalyst for a specific process;

i) selectivity,
ii) activity,
iii) stability
iv) physical suitability
v) regenerability,
vi) cost.

Selectivity and activity (related to surface area) are the most important characteristics.

3.3(1) CATALYST SELECTIVITY

Selectivity is the efficiency of the catalyst in catalysing a desired reaction.

$$\text{selectivity} \propto \frac{\text{amount of product}}{\text{amount of reactants converted}}$$

Low selectivity represents a waste of reactants. Selectivity often exceeds 90% in commercial processes.

3.3(2) CATALYST ACTIVITY

Activity is the ability of the catalyst to transform reactants into products. Specific activity relates to a particular property of the catalyst e.g. activity per unit surface area. Several units are used;

g (product) per g (catalyst) per hour
g (product) per m^3(catalyst) per hour
mole (product) per mole (catalyst) per hour.

Catalysts often have additives which are used to enhance activity e.g. promoters and co-catalysts.

3.3(3) CATALYST STABILITY

It is important that the catalyst retains a level of activity and stability over a useful lifetime. Activity can be lost by several degradation processes.

i) sintering: aggregation of crystallites leading to decreased surface area and, hence, activity.

ii) poisoning: halogens and sulphur compounds are examples of poisons. Species with lone pairs bond strongly to the catalyst surface inhibiting reactant molecules access to active sites.

3.3(3) cont.

iii) fouling: this is caused by substances physically blocking active sites. Deposition of coke is the most common cause with the added problem of sulphur or nitrogen residues.

iv) mechanical: loss of strength and breakdown of the catalyst can cause an excessive pressure drop across the catalyst bed. Attrition results in the presence of unwanted amounts of fines (fine particles, dust).

3.3(4) REGENERABILITY

Where economically viable regeneration is carried out-usually to recoup precious metals. Common regeneration methods include oxidation, reduction, exposure to high temperatures (to desorb and decompose poisons) and chemical treatments.

Sintered catalyst are difficult to regenerate unless the active phase can be converted to a readily dispersible form (e.g. chlorides of precious metals) and then reactivated.

Poisons can be permanent or temporary. Hydrogen sulphide is a powerful but reversible poison for nickel steam reforming catalysts. Other poisons are irreversibly adsorbed or cause structural change. A pertinent example here is the sintering effect of chlorides on copper catalysts.

Coke fouling can be removed by combustion, the resultant heat being used elsewhere in the synthesis process.

3.3(5) PHYSICAL SUITABILITY

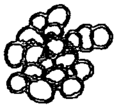
In addition to porosity, which affects diffusion and thus activity, catalysts also require mechanical strength.

3.3(5) cont.

The overall activity is dependent on both chemical and mechanical factors. The limit of activity is proportional to the total surface area available to the reactants which, in turn, depends on the diffusion of the reactants.

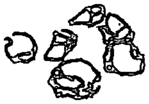
High surface areas are provided by small crystallite sizes but a catalyst bed consisting of fine particles would require enormous pressures to force the reactant gases through. Hence catalyst materials are formed into pellets.

The shape of the pellet can affect mechanical strength, surface area and pressure drop characteristics. Good gas flow is essential to prevent thermal 'hotspots' which can cause sintering. Pellet size can influence the lifetime expected of the catalyst (typical catalyst sizes range from 3-20mm in diameter). Some common catalyst shapes are shown below.[204]



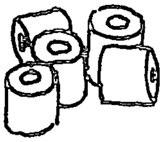
spheres

e.g. methanation



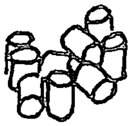
irregular granules

e.g. ammonia synthesis



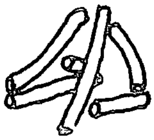
rings

e.g. steam reforming



pellets

e.g. low and high temperature shift



extrudate

e.g. hydrodesulphurization

3.3(6) COST AND ECONOMICS

Calculations on the economic viability of a plant are based on product value, raw material costs, the gradual decrease in plant capital outlay and the catalyst.

3.3(6) cont.

Catalysts are value commodities and, in absolute terms, are very expensive. However modern catalysts are efficient and effective, producing many times their own weight in product.

3.4 CATALYST CHARACTERIZATION [203,204,205,207]

Improvements are continually being sought in catalyst formulation and design. This aim, however, has inherent problems due to the difficulties associated with the characterization of the physical and chemical properties of working catalysts.

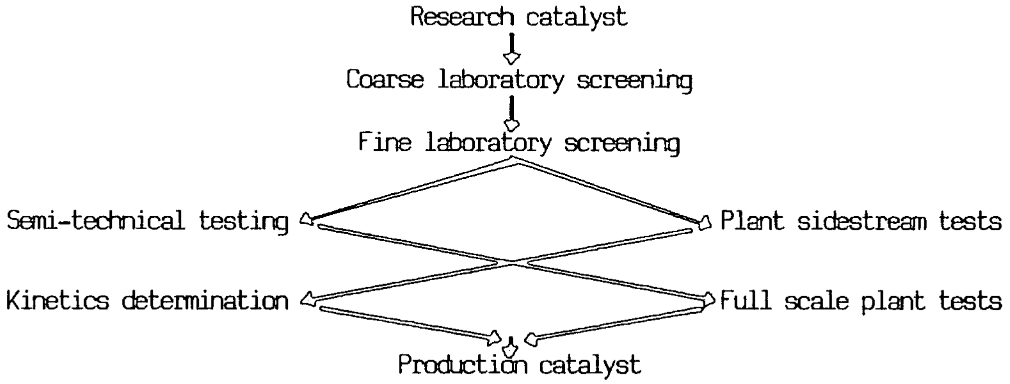
Catalysts are designed to maximise surface area of the active phase, usually by dispersion of the active phase on a high surface area support (alumina or silica). Surface areas range from 10-1000m^2g^{-1} with the dispersed active particles located on the internal (pores) and external surfaces of the support. Particle sizes range from 1-50nm typically. Variations in catalyst preparation procedures may simultaneously alter several properties making it difficult to correlate any particular property with observed activity changes.

A knowledge is required of the identity of the active surfaces and sites on a molecular level and the effect of promoters on these sites. Inter-reactions within multi-component systems cause further problems with analysis.

Catalyst kinetics provide useful information, but most important to future catalyst development is an understanding of the structure and mode of action of the reactive sites.

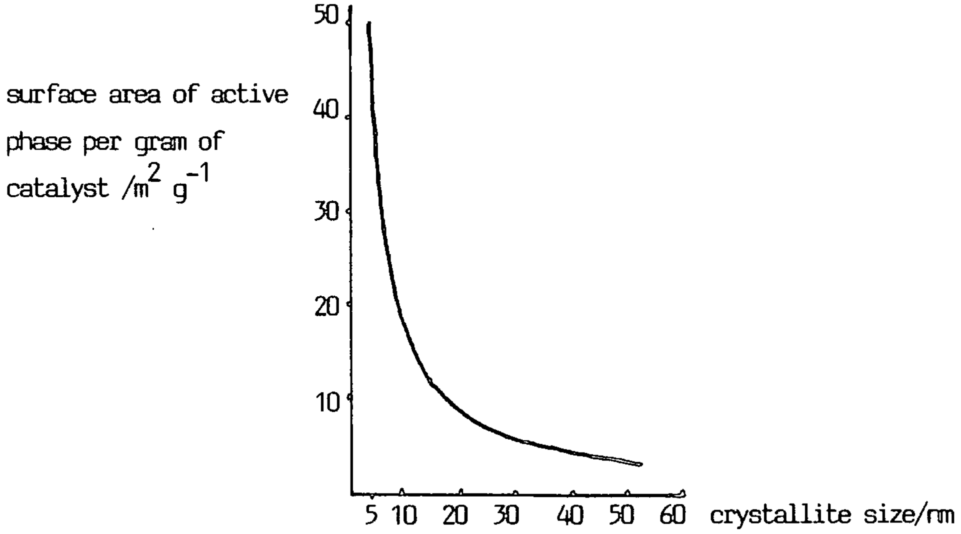
A vast range of techniques is available for studying bulk and surface chemical properties in addition to physical characteristics.

The flow diagram below illustrates the steps involved in catalyst development and testing. Activity testing is continuous to optimize catalyst performance.[204]



Chemical analysis determines the catalyst formulation and the levels of any poisons. X-ray diffraction is used to detect which crystalline phases are present and line broadening indicates mean crystallite size, thus enabling surface areas to be calculated. This technique is not accurate for particle sizes below 3-4nm. Line shape analysis gives some measure of crystallite size distribution.

By making arbitrary assumptions about the crystallite shape and surface area it is relatively easy to derive relationships between size, number and total surface area of the crystallites. Maximum activity requires maximum available surface area, hence minimum crystallite size.



The tables below outline the analytical methods available:

1) Bulk chemical properties

TECHNIQUE	PROPERTIES DETERMINED
Elemental analysis	Bulk chemical composition
X-ray diffraction	Crystalline phases and sizes
Electron microscopy	Particle shapes and sizes
X-ray fluorescence	Particle compositions
Electron diffraction	Particle crystal structures
Micro-probe analysis	Variation in pellet composition
Radiography	Distribution of radioactive label
NMR	Chemical environment of element
Mössbauer spectroscopy	" " "
IR, Visible, UV spectroscopy	Types of chemical bond present
EXAFS	" " " "
Thermal analysis (DTA, TGA)	Phase and weight changes
TPD	Size and range of reduction stages
Combined GC and mass spectroscopy	Analysis of volatile components

2) Surface chemical properties

TECHNIQUE	PROPERTIES DETERMINED
Photoelectron spectroscopy	Chemical identity of surface layers
Auger spectroscopy	" " " "
SIMS	" " " "
TPD and flash desorption	Chemical identity of adsorbed surface species
Physisorption of gases (e.g. N_2)	Total surface area
Chemisorption or surface reaction of gases	Surface area of metal components
Chemisorption of basic or acid gases	Surface area of acid or base sites
IR, visible, UV	Types of chemical bond present
HREELS	" " " "
EXAFS	Atomic structure of surfaces and adsorbates
Work function determination	Surface ionization
NMR	Chemical environment of element
Electron microscopy	Chemical identity of surface layers
Isotopic labelling	Origin of adsorbed species

The presence of very fine particles is not a thermodynamically stable state. Aggregation of crystallites occurs to reduce high surface energy and hence surface area. The rate of this sintering can be controlled by operating conditions, selection of suitable support, method of catalyst manufacture and the relative amounts of components.

Sintering involves the transfer of material from small to larger crystallites and this can occur through the gas phase or via the surface, due to particle or atomic migration. Impurities can form mobile complexes under operating conditions such as high temperatures or the presence of water.

Commercial catalysts can be roughly divided into three categories according to surface area;

low - up to $10m^2g^{-1}$
high - $10\text{-}100m^2g^{-1}$
very high - in excess of $200m^2g^{-1}$

Surface areas are best measured by selective adsorption using gases which chemisorb onto only one catalyst component. Gases commonly used are CO and NO which are useful for measuring iron, copper, chromium and nickel surfaces. Estimation of surface areas involves measuring the amount of gas required to form a monolayer on the catalyst surface at or about the boiling point of the gas. Knowledge of the molecular area enables total area to be calculated.

Related techniques make use of surface reactions e.g.,

$$Cu + N_2O \longrightarrow CuO + N_2$$

The pore structure of the catalyst is also important. The pores allow diffusion of the reactant gases into the catalyst.

Real catalysts have a range of pore sizes and it is important to know not only the mean pore size but also the pore size distribution. The distribution of pore sizes can be obtained by mercury porosimetry whereby mercury is forced, under high pressure, into the pores. The porosity is expressed in cm^3g^{-1} of catalyst and can be calculated from a knowledge of the true density of the catalyst material (measured in a helium atmosphere which fills all the pores) and apparent density (measured in mercury which does not access all the pores). Knowing pore volume and surface area allows mean pore sizes to be calculated.

In recent years a great deal of emphasis has been placed on the development and application of physical techniques to the study of catalysts and catalytic processes at a molecular level.

The aim is to obtain a detailed atomic picture of the structure of the active catalysts (metal environment e.t.c.) and to establish a relationship with the elementary chemical reactions responsible for the overall catalytic transformation.

Many of the methods developed can only be applied to 'clean' environments, that is, on model systems. This provides useful information but is not always representative of the catalyst under operating conditions. New developments in physical methods are taking place rapidly, including some which are able to function under the exacting conditions found in industrial processes[205,206].

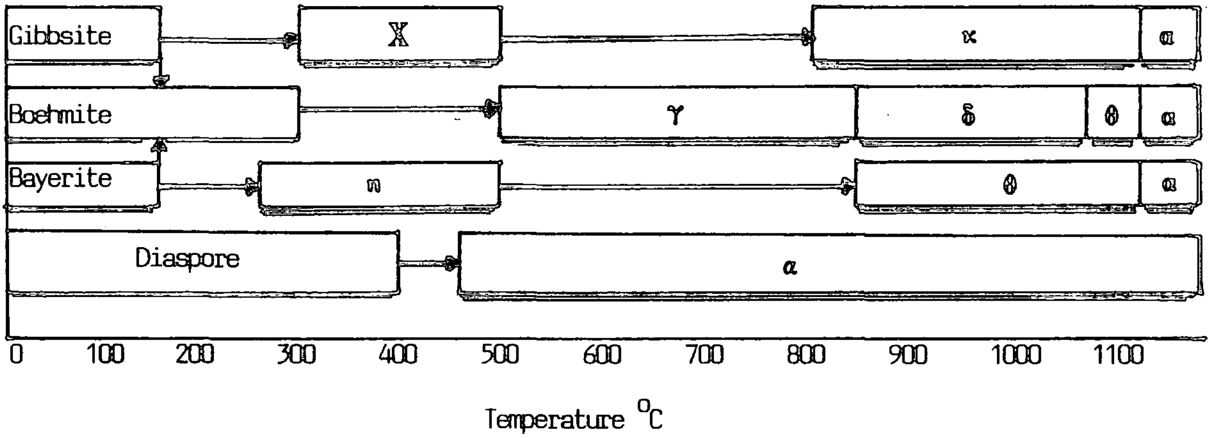
3.5 THE CATALYST SUPPORT

The support is a vital component of the catalyst. Supported catalysts exhibit decreased sintering due to steric and energetic interactions between dispersed phase and support. In effect the support stabilizes the crystallites of the active phase.

Active metal crystallites are supported onrefractory oxides. The oxides are usually alumina, titania or silica. Other oxides which also find use in the support role are those of zinc, magnesium or calcium.

Alumina is the most widely used support material. Although, stoichiometrically, there is only one oxide of aluminium (Al_2O_3) there exist several polymorphs and hydrated species.

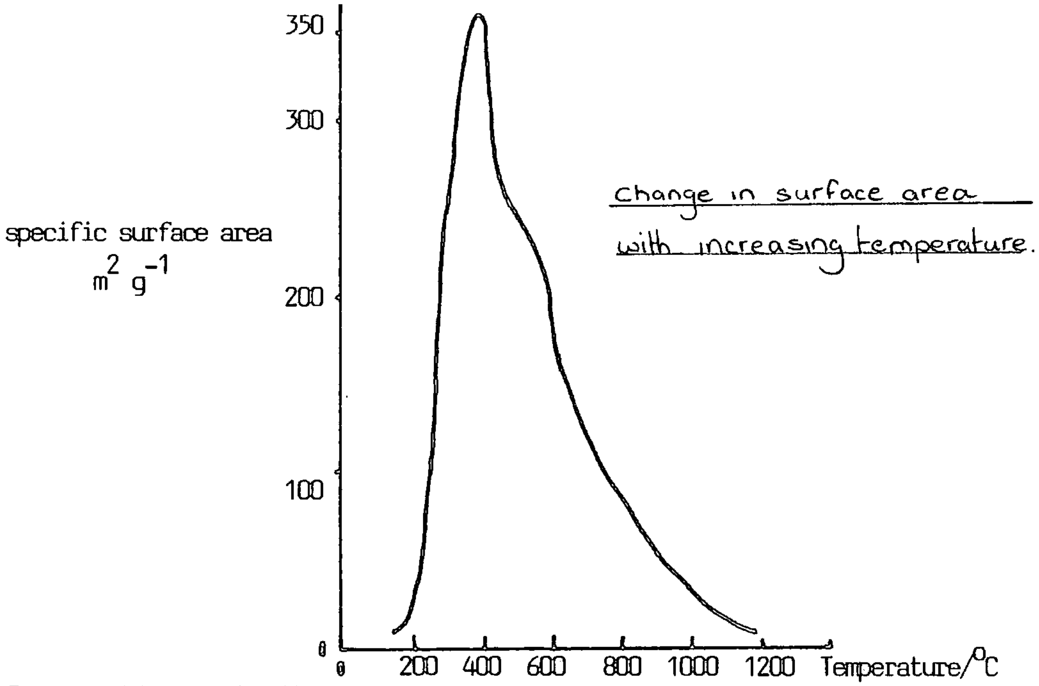
There are several hydrated forms of alumina corresponding to stoichiometries AlO.OH and $Al(OH)_3$. Dehydration of any hydrous oxide at around 450°C leads to γ-alumina; further heating of γ-alumina or any other oxide hydrate at temperatures in excess of 1000°C produces α-alumina. There are several other transition phases, as shown below, but α- and γ- alumina are the most important in the field of catalyst supports.



Decomposition sequence of aluminium hydroxides.

Properties of α- and γ-alumina	
α-Al_2O_3	γ-Al_2O_3
HEXAGONAL CLOSE PACKED	DEFECT SPINEL $M^{II}M_2^{III}O_4$
CHEMICALLY INERT	READILY TAKES UP WATER
VERY HARD	DISSOLVES IN ACIDS
SUPPORT FOR IMPREGNATED CATALYSTS	CATALYTICALLY ACTIVE FOR
OPERATING UNDER ARDUOUS CONDITIONS	DEHYDRATION/HYDRATION REACTIONS
Low surface areas 15m^2g^{-1}	High surface areas

Aluminas used as catalyst supports are prepared by heating a hydrated oxide to various temperatures to totally or partially dehydrate the surface. The activity of the alumina is affected by this treatment, or any subsequent exposure to moisture.



Preparations of alkoxides of aluminium can be used to yield an extremely pure gel. Alkoxides have already been mentioned as dehydrating agents.

3.6 AMMONIA AND METHANOL SYNTHESIS CATALYSTS [203,204]

3.6(1) INTRODUCTION

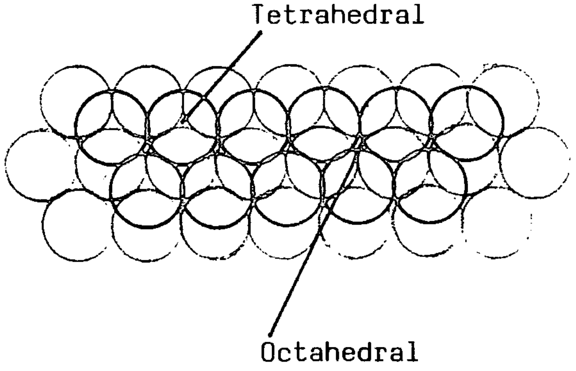
To describe in any depth all the catalysts used in the production of ammonia and methanol would be inappropriate in this treatment. Hence this discussion is limited to the major factors pertaining to the ammonia and methanol synthesis catalysts. The emphasis of this section reflects the progress made towards producing a copper-zinc-aluminium alkoxide catalyst precursor during the course of this project.

3.6(2) AMMONIA SYNTHESIS CATALYST[203,204,208]

The reaction of hydrogen and nitrogen to form ammonia on an industrial scale is always carried out over a catalytic surface based on metallic iron (derived from magnetite) which has been promoted with other oxides.

The original catalyst (Mittasch in 1913) required the fusion of magnetite, alumina and potash in the correct proportions. The melt was then shallow cooled and the product fragmented. Today modern catalysts may use oxides of calcium, magnesium, silicon, titanium or vanadium, in addition to potassium, as promoters. These oxides are able to form a solid solution in the magnetite lattice.

Magnetite has an inverse spinel structure (i.e. $[Fe^{III}(Fe^{II}Fe^{III})O_4]$) with all the iron (II) ions sitting in octahedral positions and the iron (III) ions being divided equally between octahedral and tetrahedral sites within the cubic close packed arrangement of oxide ions.



During reduction of the catalyst (activation) the oxygen is removed leaving the iron as a pseudomorph of the original magnetite. This is an extremely porous, high surface area, high activity form of metallic iron.

The promoters can be classified as structural or electronic.

Structural promoters (e.g. alumina) preserve the porous nature of the catalyst and promote growth of small iron crystallites.

The presence of alkali metals (e.g. potassium) is essential to the high activity of the catalyst although the exact mode of action is the subject of some debate. Various mechanisms have been proposed including an acid-base type reaction and promotion of electron release from iron to adsorbing nitrogen molecules. It may be of interest to note here that the electrical conductivity of magnetite (Fe_3O_4) is 10^6x that of haematite (Fe_2O_3) which is thought to be due to rapid valence oscillation between iron sites.

More recent work seems to point to the dissociative adsorption (chemisorption) of iron being sensitive to the crystal face of the iron crystallite as the important factor in the activity of these catalysts. The iron (111) face is more reactive than any other crystal face. It has been observed that alumina induces reorganization of iron (110) faces to iron (111) with a corresponding increase in activity. The iron (111) face has a high concentration of open iron atoms surrounded by seven near neighbours (so called C_7 sites). The presence of potassium is noted, but it's effect is not fully explained although it appears to be involved in promoting other crystal faces to the same level of activity as the iron (111) face.

Surface areas of supported catalysts are in the region of 15-20m^2g^{-1} comparing well with 1m^2g^{-1} for unpromoted iron. Loss of activity generally occurs through sintering or poisoning. Low concentration poisoning by water, carbon monoxide or carbon dioxide is reversible but sulphur, chlorine, arsenic or phosphorus cause irreparable damage.

3.6(3) AMMONIA SYNTHESIS REACTION MECHANISM

Exchange reactions with deuterium have indicated the following reaction sequence,

$$H_2 \longrightarrow 2H\ (ad) \qquad \text{rapid}$$

$$N_2 \longrightarrow N_2\ (ad)(\gamma) \longrightarrow N_2(ad)(\alpha) \longrightarrow 2N(ad) \quad \text{rate determining}$$

$$N\ (ad) + H\ (ad) \longrightarrow NH\ (ad)$$

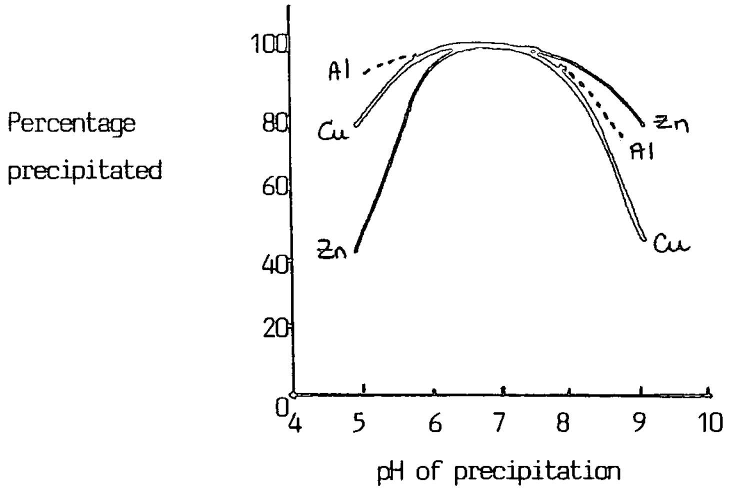
$$NH\ (ad) + H\ (ad) \longrightarrow NH_2\ (ad)$$

$$NH_2\ (ad) + H\ (ad) \longrightarrow NH_3\ (ad) \longrightarrow NH_3$$

Molecular nitrogen can be adsorbed in two states; a weakly held physisorbed state (γ) and an α-state which is the precursor to dissociation. This α-state has a π-bonded sideways-on arrangement to the crystal face. The conversion from molecular nitrogen to atomic nitrogen is the slow, rate-determining step. The promotional effect of potassium appears to be in influencing this rate-determining step by lowering the activation energy for the dissociation. This is possibly due to charge transfer from the potassium to the iron surface allowing strong π-back bonding from the iron to the nitrogen molecule although is speculative. It has also been shown[209] in carbon monoxide adsorption studies of silica supported iron that the presence of 0.5% K_2O increases the availability of sites for linear bonding and that the addition of 2.5% Al_2O_3 has a stabilizing effect on the surface area of exposed iron. This subject continues to be an area of investigation.

3.6(4) METHANOL SYNTHESIS CATALYST[203,204]

Modern copper-zinc oxide-alumina catalysts are prepared by the careful precipitation of mixed carbonates at controlled pH levels. Control of pH is essential since acid conditions would produce a precipitate rich in aluminium but deficient in zinc, whereas alkaline conditions would lead to a low copper content. Optimum particle size is also dependent on maintaining a pH value around 7.



Variation with pH of the composition of Cu-ZnO-Al_2O_3-catalysts prepared by precipitation

A period of ageing aids the formation of malachite containing in solid solution [$(Cu,Zn)CO_3(OH)_2$]. This multi-component mixture forms a catalyst with higher activity and stability than a binary system.

After calcination and pellet formation the catalyst has a surface area of around 60-100m^2g^{-1}. Reduction at 150°C using 5% H_2 in N_2 givesa copper surface area of around 30m^2g^{-1} (cf experimental results later).

3.6(5) METHANOL SYNTHESIS REACTION MECHANISM

The mechanism of methanol synthesis by catalytic routes and the function of the catalyst have been the subjects of intense study over recent years [203-4, 209-11, 213-16].

The available literature appears to provide conflicting or confusing evidence for various theories relating to the mechanism of methanol synthesis and the water-gas shift reaction. This arises from the number of variables contributing to the overall process. Many investigations have been undertaken on 'model' systems which, although providing useful information, may not be representative of the commercial process and the conditions under which it operates.

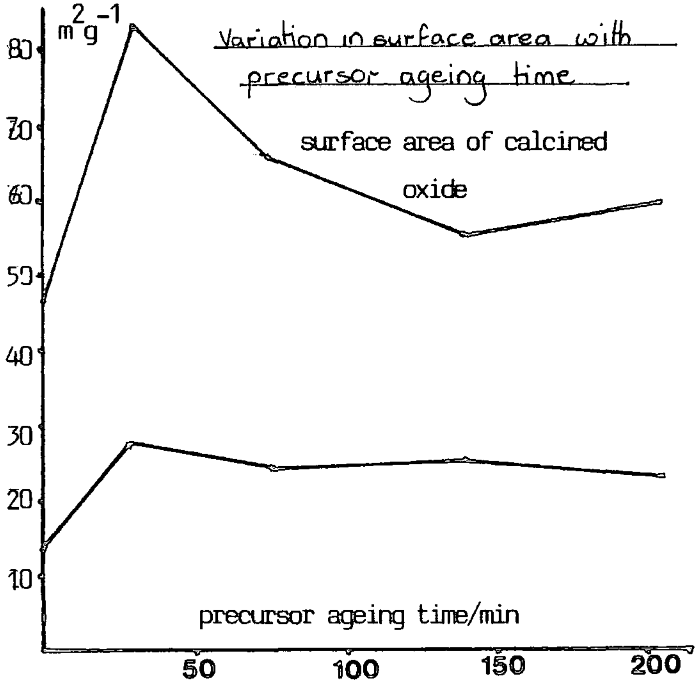
The activity of the catalyst is dependent on several interacting factors including;

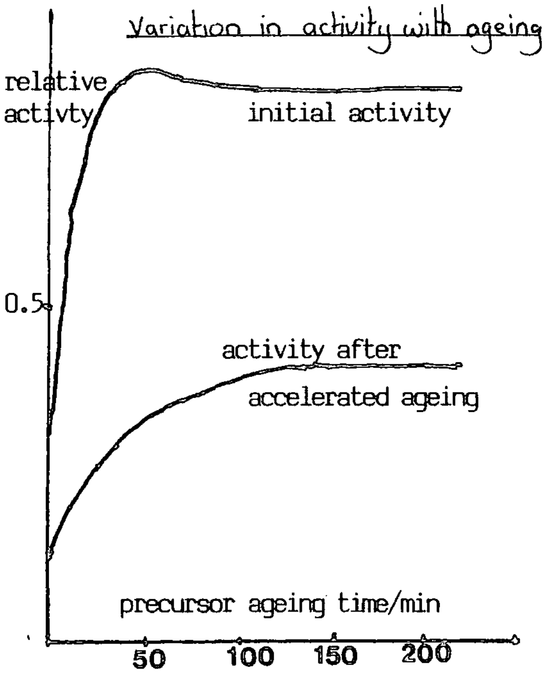
- i) ageing of the catalyst precursor,
- ii) nature of the support,
- iii) presence of alkali promoters,
- iv) method of catalyst formulation,
- v) nature of the feedstock,
- and vi) conditions of temperature and pressure.

Whether the catalyst is prepared by co-precipitation or impregnation (or other methods) affects the response of the catalyst to other factors even when the catalysts so formed have the same apparent composition (i.e. ratio of components).

Ageing effects have been studied for copper-zinc oxide catalysts prepared by co-precipitation methods[217].

Using a variety of analytical techniques, it was found that time spent 'ageing' the precursor prior to calcination resulted in quite marked differences in copper and total surface areas. This ageing period allowed the formation of small crystallites of malachite which resulted in the reduced catalyst having higher activity than one derived from an 'unaged' precursor. The activities of these copper-zinc oxide catalysts did not, however, compare favourably with the standard copper-zinc oxide-alumina co-precipitation catalyst.





The temperature of calcination has also been shown to have an effect on the activity of a copper-chromite ($Cu-Cr_2O_3$) catalyst towards methanol synthesis from a 33% CO: 67% H_2 feed gas[218].

X-ray photoelectron studies have illustrated that the activity can be related to the amount of surface stable Cu^+ and that the fraction of Cu^+ relative to Cu^o varies as a function of the calcination temperature.

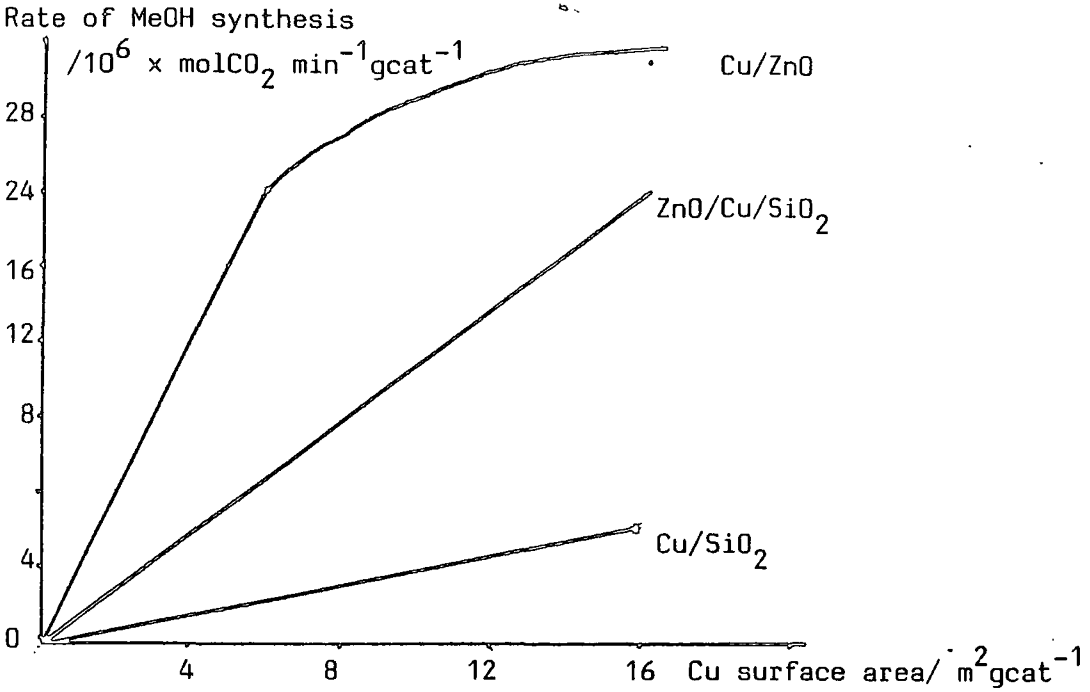
Calcination Temp /^{o}C	Formation of MeOH mol/m^2 catalyst	$Cu^+/(Cu^+ + Cu^o)$
300	0.017	0.17
350	0.020	0.21
400	0.010	0.05
500	0.007	0.04

These workers have proposed that $Cu^+-Cr_2O_3$ is active for methanol synthesis and that direct evidence is provided for a monovalent copper species, stable to hydrogen reduction at 270^{o}C, which is the active site for carbon monoxide associative adsorption.

Precipitated catalysts tend not to show the marked support effects demonstrated by catalysts prepared by other methods. Recently work aimed at exploring the role of supports and the nature of active centres in copper-zinc oxide methanol synthesis catalysts has been carried out and reported[219].

A series of catalysts prepared by impregnation methods (Cu/SiO_2, ZnO/SiO_2, $ZnO/Cu/SiO_2$ and $Cu/ZnO/SiO_2$) and a copper-zinc oxide catalyst prepared by co-precipitation were tested for methanol synthesis activity from a $CO/CO_2/H_2$ feed gas.

From the results it is implied that there is a strong support effect.

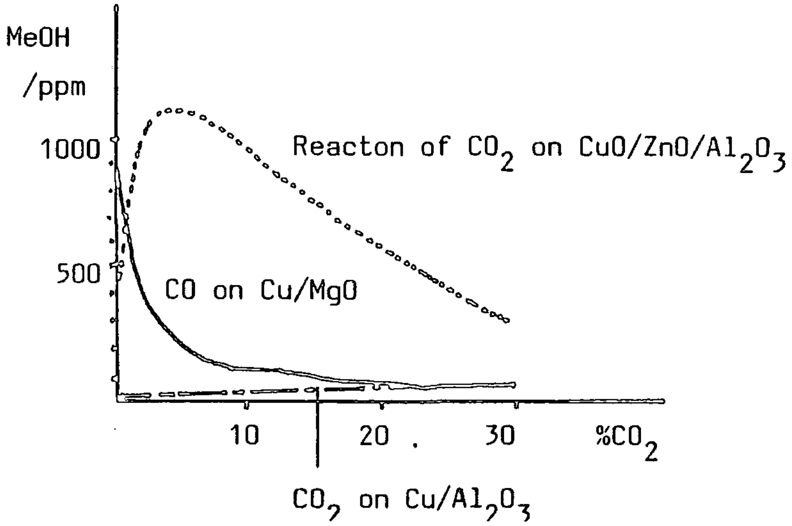


The SiO_2 supported catalysts display lower activities than ZnO supported copper catalysts. It is also reported that a physical mixture of these two materials has a synergistic effect on activity towards methanol synthesis.

Temperature programmed desorption studies indicate decomposition of the copper formate to yield hydrogen and carbon dioxide simultaneously, from separated beds of Cu/SiO_2 and ZnO/SiO_2. A physical mixture of these two catalysts resulted in hydrogen desorption at higher temperatures. The inferred conclusion is that there is an interaction between atomic hydrogen and zinc oxide.

Other workers have also reported support effects.[220]

Support effects appear to be more marked with a CO/H_2 feedstock than with CO_2/H_2 or $CO/CO_2/H_2$ mixtures. A series of catalysts prepared by impregnation methods was tested for activity towards methanol synthesis with varying ratios of CO/CO_2 in the feedstock gas.



To summarize the results the copper supported on alumina proved to be more active towards CO_2/H_2 whereas copper supported on magnesium or cerium oxide are more active towards CO/H_2.
The copper-zirconia catalyst reflects the action of the standard copper-zinc oxide-alumina precipitated catalyst which has an optimum activity for carbon dioxide concentration of approximately 6%.

Hence it would appear that basic supports favour a carbon monoxide feedstock whereas the presence of carbon dioxide is preferred alumina or zirconia supported copper catalysts. It can be presumed that with basic supports,carbon monoxide is the precursor to methanol. With the other catalysts methanol must derive either directly or indirectly from carbon dioxide. However it must be noted that with these latter catalysts carbon monoxide is also found in the products and it possible that carbon monoxide features as a precursor to methanol.

The results lead to the conclusion that there are two routes to methanol from carbon monoxide and carbon dioxide and that with these impregnated catalysts the support plays an important part with respect to the active sites.

$$CO_2 + 2H_2 \longrightarrow CH_3OH + O(s)$$

$$CO_2 \longrightarrow CO + O(s) \xrightarrow{H_2} MeOH$$

A more detailed study of carbon-dioxide/hydrogen transformation over copper-alumina and copper-zirconia catalysts indicated that methanol was a primary product and that carbon monoxide was formed in a second successive step from methanol.

A recent paper[221] has compared the actions of palladium catalysts with those of copper catalysts noting some important differences. For copper catalysts two types of mechanism have been proposed for methanol synthesis from carbon monoxide/hydrogen mixtures.

TYPE A: This mechanism occurs solely on unsupported metal surfaces or silica supported metals. Adsorbed carbon monoxide is hydrogenated by the addition of hydrogen atoms while the C-O bond remains intact.

TYPE B: In the presence of a base support or promoter carbon monoxide (or a partially hydrogenated species e.g HCO) reacts with an oxygen atom, on the catalyst surface, to give a formate intermediate.

$$CO + O(a) \longrightarrow (O\text{-}C\text{-}O)\ (a) \xrightarrow{4H} CH_3OH + O\ (a)$$

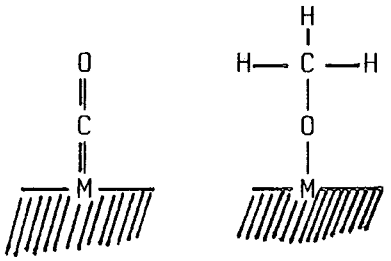
Similar mechanisms have been proposed for palladium catalysts although, unlike copper catalysts, the presence of carbon dioxide in the feedstock decreases the activity. Hence with palladium carbon monoxide is the main source of carbon for methanol synthesis.

It is also reported that the metal surface of working copper catalysts is covered with 0.1-0.4 monolayers of adsorbed oxygen. Palladium catalysts, on the other hand, have a much lower oxygen coverage but a higher concentration of adsorbed carbon monoxide (for $CO_2/CO/H_2$).

For copper catalysts with carbon dioxide free feedstock gases (i.e. CO/H_2) the Type A mechanism is much slower than the Type B mechanism or synthesis from carbon dioxide.

This has been explained in terms of a 'reversal' of the bonded species in the Type A mechanism.

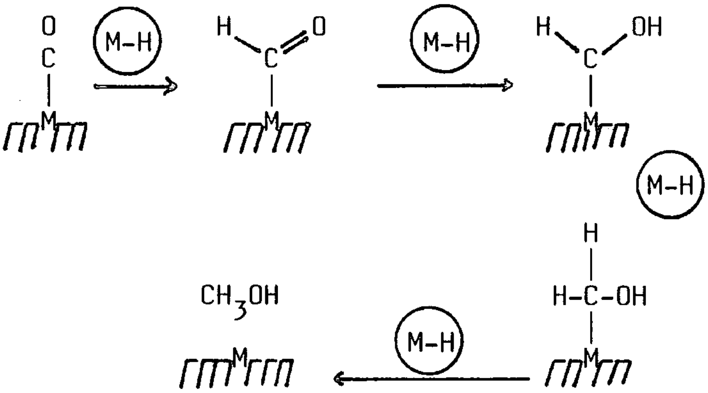
i.e. CO initially bonded to copper through the C atom but the proposed methoxy intermediate is bonded through the oxygen atom;



Palladium does not appear to exhibit this obvious difference in rate between the two mechanisms.

Other mechanisms have been proposed[222], the important factor being that the carbon monoxide is associatively adsorbed to prevent formation of hydrocarbons.

For example;



Here the adsorbed CO undergoes a sequence of hydrogenation steps involving intermediates bonded to the surface through the carbon atom (now thought to be bonded through the oxygen atom)

A second mechanism involves insertion of CO into surface hydroxyl to form a formate on the surface followed by subsequent hydrogenation and dehydration (methanol synthesis from $CO_2/CO/H_2$) now known to go through carbon dioxide-formate).

Common to both copper and palladium catalysts is that the presence of a basic support, or promoter, enhances activity for methanol synthesis from CO/H_2 mixtures. As with synthesis from CO_2, it appears that the key to a fast Type B mechanism is a fast rate of hydrogenolysis of the surface formate. It is uncertain, from experimental studies, whether hydrogenation occurs via hydrogen spillover from metal crystallites to the adsorbed formate (on the oxide support or alkali promoter) or by interaction between formate and hydrogen at the metal-base boundary.

Investigations of the working $Cu/ZnO/Al_2O_3$, prepared by co-precipitation methods, indicate a less ambiguous picture when the feedstock contains the optimum $CO/CO_2/H_2$ mixture. ^{14}C labelling techniques have shown that the methanol product derives from CO_2 rather than from CO and that the critical steps occur on the surface of specific crystal planes of the copper crystallites. About 30% of the copper surface area is covered with adsorbed oxygen under working conditions. The active sites are not fixed but consist of copper metal atoms next to an oxide surface (Cu^0/Cu^I). The adsorbed hydrogen exists mostly on Cu^0 sites with carbon dioxide mostly on oxide sites. The role of ZnO is not clear- it may stabilize Cu^+ ions, act as a physical 'spacer' between copper crystallites or allow formation of intermediate formate groups on its surface. Temperature programmed desorption and reaction spectroscopy techniques have shown that formate intermediates are present on the ZnO surface. Zinc oxide alone does not show good activity towards methanol synthesis under normal operating conditions but this activity increases with increasing temperature[223]. Formate species appear to be present on the ZnO component of standard $Cu/ZnO/Al_2O_3$ catalysts with more weakly bonded formate on the copper surface. Several workers[211] have proposed that the ZnO component, under synthesis conditions, carries adsorbed hydrogen and that no synergy, related to the rate determining step, exists between copper and zinc oxide.

Surface formate is produced by hydrogenation of adsorbed CO_2 with the rate determining step being the hydrogenolysis of the formate intermediate. The main reducing agent appears to CO with some hydrogen taking up adsorbed oxygen.

$$H_2 \longrightarrow 2H\ (ads)$$

$$CO_2 \longrightarrow CO_2 (ads)$$

$$CO_2\ (ads) + H\ (ads) \longrightarrow HCOO\ (ads)$$

Rate determining step: $2H\ (ads) + HCOO\ (ads) \longrightarrow CH_3O\ (ads) + O\ (ads)$

$$H\ (ads) + CH_3O\ (ads) \longrightarrow CH_3OH$$

$$H_2O + CO \longrightarrow CO_2 + H_2 \qquad H_2O \longrightarrow H_2 + O\ (ads)$$

water gas shift

$$O\ (ads) + CO \longrightarrow CO_2$$

Promotion by adsorbed oxygen appears to be vital to several of these reaction steps. The reverse water gas shift reaction has been shown to go through a sequence of steps not involving formate[225].

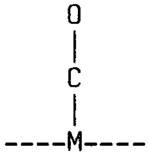
The mechanism of methanol synthesis using carbon dioxide-free feedstock is less well understood. It has already been stated that two basic mechanisms have been proposed. One involves the presence of a support and a formate intermediate. The other mechanism is thought to occur on unsupported metals or silica supported catalysts. There is agreement that activity towards methanol synthesis is related to the amount of copper (Cu^0) surface area regardless of the nature of the support. It is proposed that the support plays a minor role in the rate determining step of the reaction mechanism. However coverage of surface oxygen does vary with the type of support present (about 30% of a working catalyst is covered).

Reaction sites consist of Cu^{0} next to Cu^{I}. These sites are dynamic and move across the surface. Since methanol is formed from carbon monoxide only at low oxygen concentrations the oxygen must be on the oxide surface. Hence the presence of a support would lead to faster reaction rates. In this instance formate may be involved as the intermediate by reaction of CO with residual surface oxygen. This may also occur, to some extent, on the surface of unsupported metals. With unsupported copper (and other metals) the carbon monoxide adsorbs on the surface through the carbon atom. It is then hydrogenated to give methoxy species. As has already been stated this would involve 'flipping' the adsorbed species over to allow bonding through the oxygen atom.

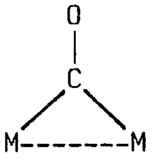
Carbon monoxide is a very versatile ligand and normally coordinates to metals through the carbon atom (σ-donation). Carbon monoxide can also bond simultaneously through the oxygen atom thus acting as either a 2- or 4-electron source. Carbon monoxide can also act as a receiver of electrons (π-back bonding).

There are several modes of carbonyl-metal bonding

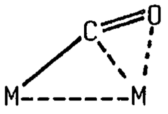
i) terminal



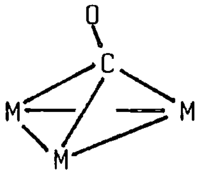
ii) doubly bridging



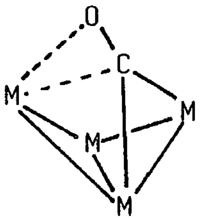
iii) doubly bridging (unsymmetrical)



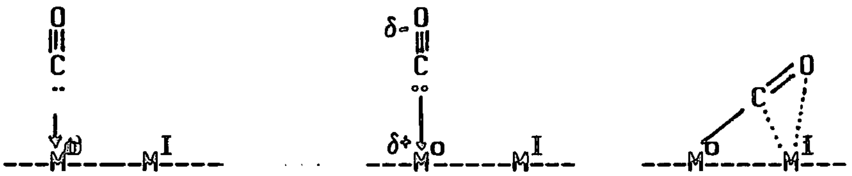
iv) triply bridging



v) triply bridging (coordinating)



When coordinating to a metal atom the M-C bond is shorter than those found in metal alkyls. The C-O bond in carbonyl complexes is longer than in free CO. The 'lone pair' electrons on carbon are donated to a suitable vacant metal orbital (σ-donation). The electron flow C-M for a metal ion of charge less than +2 would lead to an unacceptable build up of electron density. Hence the metal reduces this electron density by donating electrons back to the ligand carbonyl (through π^*-antibonding orbitals, i.e. $d\pi$-$p\pi^*$). This back bonding in CO orbitals tends to make the carbonyl more negative and hence more basic. This effect is reduced, to some extent by the σ-donation back to the metal atom through the carbon atom. The σ-donation to the metal is less effective than the π-back donation and so the carbonyl ligand possesses increased electron density on the oxygen atom. This bonding arrangement is supported by theoretical and spectroscopic studies[226]. (Note see also ref[223] evidence of a carbonyl or formyl bridged Zn; IR indicates a very low C-O stretching frequency of 1520cm^{-1})
It would seem possible that the Type A mechanism involves some kind of bridging carbonyl rather than expecting the carbon monoxide to 'flip' on the copper atom on which it is adsorbed. It has been shown that the active sites involve Cu^{0}/Cu^{I} neighbouring sites hence the following mechanism could be envisaged taking into account the negative charge carried by the carbonyl 'ligand';



This could then be followed by hydrogenation to give a methoxy species on the Cu^{+} site. It is possible that this kind of interaction also occurs with the presence of a basic oxide such as ZnO where the Zn^{2+} takes the role of the M^{I}. This could account for the observation that the presence of ZnO (or other basic oxide) results in a marked increase in reaction rate to produce methanol, i.e. the oxide provides more 'falling over' sites in addition to the formation of formate species. Palladium also displays Type A mechanism characteristics. However the rate of this reaction is not markedly slower than the supported catalyst route. Since palladium has a higher carbon monoxide and lower oxygen coverage than copper it would be expected that on the introduction of a support the reaction rate would increase dramatically. There must be, however, some relationship between the strength of adsorption of carbon monoxide on the metal surface and the overall rate of reaction ie rate of production (desorption) of methanol. The adsorption energy for carbon monoxide on palladium ranges from 90-230 kJ mol^{-1} whereas that for copper is only 55 kJ mol^{-1}.

There is a great deal of work to be carried out in order to gain a better understanding of the mechanisms involved in the synthesis reactions catalysed by these materials. Recent developments have concentrated on improving present catalyst formulations and energy efficiency. Novel catalysts with high activity to methanol synthesis have been developed though none are commercially viable prospects.

e.g.

i) Raney copper, prepared by leaching Cu/Zn/Al alloys to produce a catalyst containing 98% Cu, has activity comparable to that of a standard $Cu/ZnO/Al_2O_3$ co-precipitated catalyst. This would seem to support the evidence that Cu is the catalytically active phase.

ii) Intermetallic thorium-copper compounds have high activity to methanol synthesis.

iii) Supported palladium.

iv) Liquid phase copper catalysts have been developed.

v) Rhodium carbonyl clusters supported on basic oxides are selective for methanol synthesis. Varying the the support yields other products;
La_2O_3, TiO_2 and ZrO_2 = ethanol,
Al_2O_3 or SiO_2 = hydrocarbons.

Summary and Conclusions

The many varying factors which affect the activity and selectivity of the catalyst material make the study of catalysis both fascinating and, to some degree, frustrating. The obvious influence of the catalyst precursor and its treatment prior to activation have relevance to this study of the use of metal alkoxides as the catalyst precursors.

The one overriding influence on the catalyst activity is that of copper surface area (in the case of methanol synthesis) irrespective of other variables. The nature of the feedstock, the support and reaction conditions are all important and must be taken into consideration when investigating any catalytic material or process.

In this project the number of variables was restricted to the nature of the precursor and its treatment.

CHAPTER 4

CHAPTER 4

PREPARATION OF ALKOXIDES

4.1 INTRODUCTION

This chapter describes the syntheses of alkoxides of aluminium, sodium, potassium and the mixed metal alkoxides of aluminium with potassium and a selection of the first row transition metals. The methods used for their preparations are described in the literature[133] although only several proved to be reproducible syntheses during the course of this project.

4.2 DISCUSSION

The initial part of this project was concerned mainly with the preparation of metal alkoxides by known routes. The sensitive nature of the alkoxides required the use of careful handling techniques and manipulations. For the purposes of the catalyst investigations large samples were required (50-100g) which introduced some problems, mainly related to the adequate storage of these compounds.

The synthesis of aluminium triisopropoxide proved an ideal starting point for gaining knowledge of the methods of alkoxide synthesis and also experience in handling these materials. After several attempts the best method for the synthesis of aluminium triisopropoxide involved the reaction of grease-free aluminium powder with isopropanol in the presence of a catalyst. The initial catalyst tried was mercury (II) chloride which, although successful, introduced problems with chloride contamination of the final product. This was reduced to a minimum by repeated washings and filtrations. This product was then used as the catalyst in further preparations. With the necessity for large samples of product the use of a commercial source of this starting material proved to be more appropriate.

The preparation of mixed metal alkoxides involves the reaction of anhydrous metal halides with alkali metal-aluminium isopropoxide.

$$MCl_x + xKAl(OPr^i)_4 \longrightarrow M[Al(OPr^i)_4]_x + xKCl$$

Sodium isopropoxide was easily prepared by reacting the metal in an excess of the alcohol and then removing the solvent under reduced pressure. However this compound was difficult to use in subsequent reaction steps because of its low solubility and tendency to discolour. The preparation of potassium was also facile and the product proved easier to handle. The formation of the potassium-aluminium isopropoxide was achieved by dissolving the potassium alkoxide and the aluminium alkoxide in the reactant alcohol (isopropanol) and then mixing the two together. An exothermic reaction occurs to give a clear solution of the mixed metal alkoxide. This was isolated by removing the excess solvent under reduced pressure. After the initial few trials, to ensure reproducibility, the potassium-aluminium isopropoxide was prepared in situ for the synthesis of the mixed transition metal -aluminium alkoxides.

The preparation of manganese, iron(III), cobalt, zinc and copper mixed metal alkoxides (with aluminium) proved relatively simple to achieve. However the synthesis of nickel-aluminium isopropoxide ($Ni[Al(OPr^i)_4]_2$ was not achieved. It is reported as being a pale pink, viscous liquid[133]. After having persevered with the reported route for some time other methods were attempted, some of which are listed here. The problem appeared to be the insolubility of the nickel (II) chloride in the secondary alcohol and various attempts were made to solubilize the chloride.

i) attempted syntheses by reported route,
ii) attempted syntheses by the use of different solvents (other than isopropanol),
iii) attempt to form soluble adduct with pyridine in isopropanol,
iv) use of bromide rather than chloride
v) attempts to extract $NiCl_2$ into the solvent by Soxhlet extraction method,

vi) attempted synthesis through nickel (II) acetylacetonate,
vii) use of THF as solvent,
viii) use of HMPA as adduct

In several of these attempted syntheses there did appear to be some reaction however, on analysis, the products had high chloride contents and low aluminium levels. The reaction of nickel (II) chloride with HMPA (hexamethylphosphoramide) yielded interesting blue crystals. On analysis the ratio of Ni:Cl:P indicated a compound of formula $NiCl_2$. 1.5HMPA. A more likely formula would be $NiCl_2$.2HMPA with nickel in a tetrahedrally coordinated environment.

Although several attempts were made to prepare the simple alkoxides of the first row transition metals, with varying degrees of success, it was decided to concentrate on the bimetallic alkoxides since these were of more immediate use in the assessment of alkoxides as catalyst precursors.

The copper-aluminium alkoxides were the most readily prepared by the reaction of the soluble chloride (in isopropanol) with potassium-aluminium isopropoxide followed by alcohol exchange reactions.

Copper-aluminium isopropoxide is a viscous, green liquid whereas the ethoxide and methoxide are both blue solids. Attempts were made to distil the isopropoxide under reduced pressure but even at low temperatures (60-70 ^{o}C) the liquid decomposed. A fine blue powder was produced in the vacuum line and a brown solid in the flask. It appeared that the isopropoxide had undergone a reduction to produce either copper metal or copper (I) oxide.

Copper-zinc-aluminium alkoxides were 'prepared' by mixing the copper-aluminium and zinc-aluminium alkoxides together (isopropoxides) and then precipitating the methoxide or ethoxide by the slow addition of the requisite alcohol.

Attempts were made to extend the characterization to ^{1}H NMR but the resultant spectra were very poor with only broad bands observable. With the copper-aluminium isopropoxide there was an interesting colour change observed on cooling the liquid down to liquid nitrogen temperature (-196 ^{o}C). A range of shades from green through to blue was obtained which would seem to indicate some rearrangement of the copper environment. The blue colour was typical of that seen in octahedral copper complexes.

Generally the metal-aluminium alkoxides which were prepared had properties indicative of covalent character. They were all coloured liquids and were soluble in organic solvents.

The copper-aluminium alkoxides were used in the second stage of the project- to assess the efficacy of alkoxides as precursors of materials with catalytic activity in methanol. Copper-zinc-aluminium alkoxides were also tested in addition to iron (III)-aluminium alkoxides. These latter materials did not undergo extensive testing due to time constraints but preliminary observations showed that the Cu/Zn/Al species possessed slightly superior qualities than the bimetallic alkoxides.

Some work was carried out with diols in the alcohol exchange reactions but the resultant materials were difficult to isolate and this route was not followed although it would have been of interest to characterise these compounds more fully. One useful property which they possessed was resistance to hydrolysis.

All manipulations and reactions with these alkoxy compounds were carried out with attention paid to the exclusion of moisture.

4.3 EXPERIMENTAL SECTION

4.3 (1) Preparation of aluminium triisopropoxide

Grease-free aluminiumpowder (4.698g, 174.13mmoles) and mercuric chloride powder (0.250g, 0.92mmoles) were placed into a dry, nitrogen purged flask fitted with reflux condenser and drying tube. Dry isopropanol (50.0ml, 653.4mmoles) was added and the mixture heated to reflux over a water bath. After one hour the flask was removed from the heat and the reflux continued overnight. On completion the product, a grey black semi-solid, was slurried with isopropanol (30ml) and filtered on a nitrogen purged sinter. The filtrate, a clear liquid, was collected and chilled (-30^{o}C) affording a white, crystalline material (2A).

The residue from this filtration was slurried with toluene (30ml) and filtered. The filtrate was collected and chilled (-30^{o}C) again yielding a white solid (2B).

The small amount of solid remaining from this second filtration was washed with pentane leaving only a residual amount of grey powder identified as unreacted aluminium. The washings, after concentration under vacuum, yielded a white crystalline solid (2C).

In each case the white solids were collected by filtration and dried under vacuum. Characterised as follows:

Analysis Found (2A) Al, 13.35; C,52.79; H, 10.95% (Cl, 1.82%)
(2B) Al, 11.39; C,53.49; H, 9.33% (Cl. 0.34%)
(2C) Al, 12.52; C,53.08; H, 10.76% (Cl, 0.16%).
$AlO_3C_9H_{21}$ requires Al, 13.23; C, 52.99; H, 10.29%.

Infra-Red (Nujol) (cm^{-1}): 2960(s) (C-H); 2920-2850 (s) (Nujol); 2620(w); 1460 (m) (Nujol); 1385 (ms) 1375 (ms) (gem-dimethyl groups); 1360(ms) (Nujol); 1185 (s); 1175 (s) 1130 (s)

IR cont. 1120 (s) (C-O); 1070 (s) (terminal C-O); 950 (s) (bridging C-O); 860 (w) 835(s) (Al-O(C)-Al bridging); 700(ms) 680(s) 610 (m) 560 (m) 550-530 (w) 485 (m) 460 (w) 430 (w) (Al-O).

Mpt/^{o}C 126-131 (literature: 137^{o}C for the tetramer $[Al(OPr^{i})_3]_4$]).

4.3 (2) Preparation of halide-free aluminium triisopropoxide

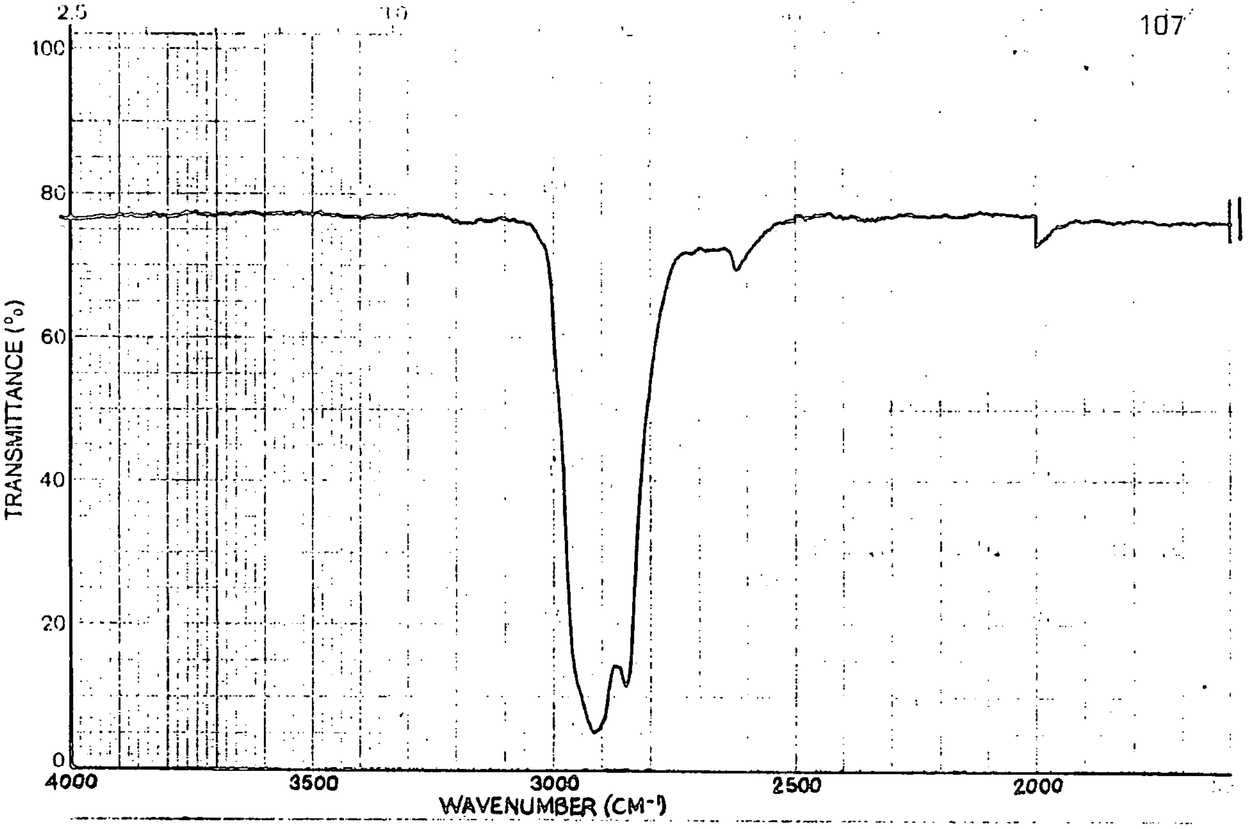
Grease-free aluminium powder (0.500g, 18.53mmoles) was placed into a dry, nitrogen-purged flask. Dry isopropanol (4.25ml, 55.56mmoles) was added plus an excess (30ml) as solvent and the mixture was heated to reflux (80-90^{o}C) with stirring over a period of 1-2 hours. At reflux temperature a few crystals of previously prepared aluminium triisopropoxide (2C) were added whilst maintaining a positive nitrogen pressure. This addition initiated the reaction which continued under reflux for six hours. The product, a black liquid, was filtered and washed with toluene* to give a clear filtrate leaving a finely divided black residue. The filtrate was concentrated under reduced pressure and cooled overnight (5^{o}C) affording large white crystals of aluminium triisopropoxide. The black residue was characterised as being alumina and unreacted aluminium. Product characterized as follows:

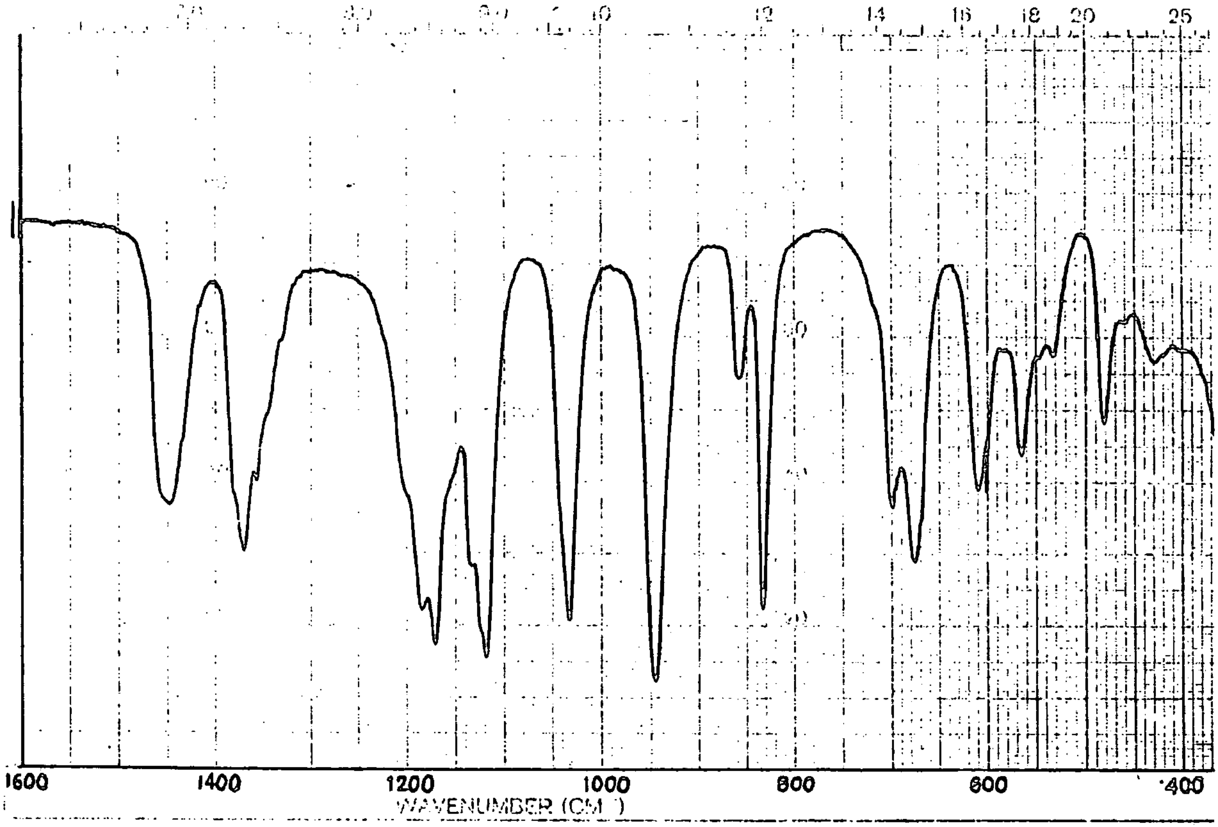
*Later preparations used pentane in washings.

Analysis Found: Al, 12.72; C, 52.33; H, 10.40% (Cl absent)

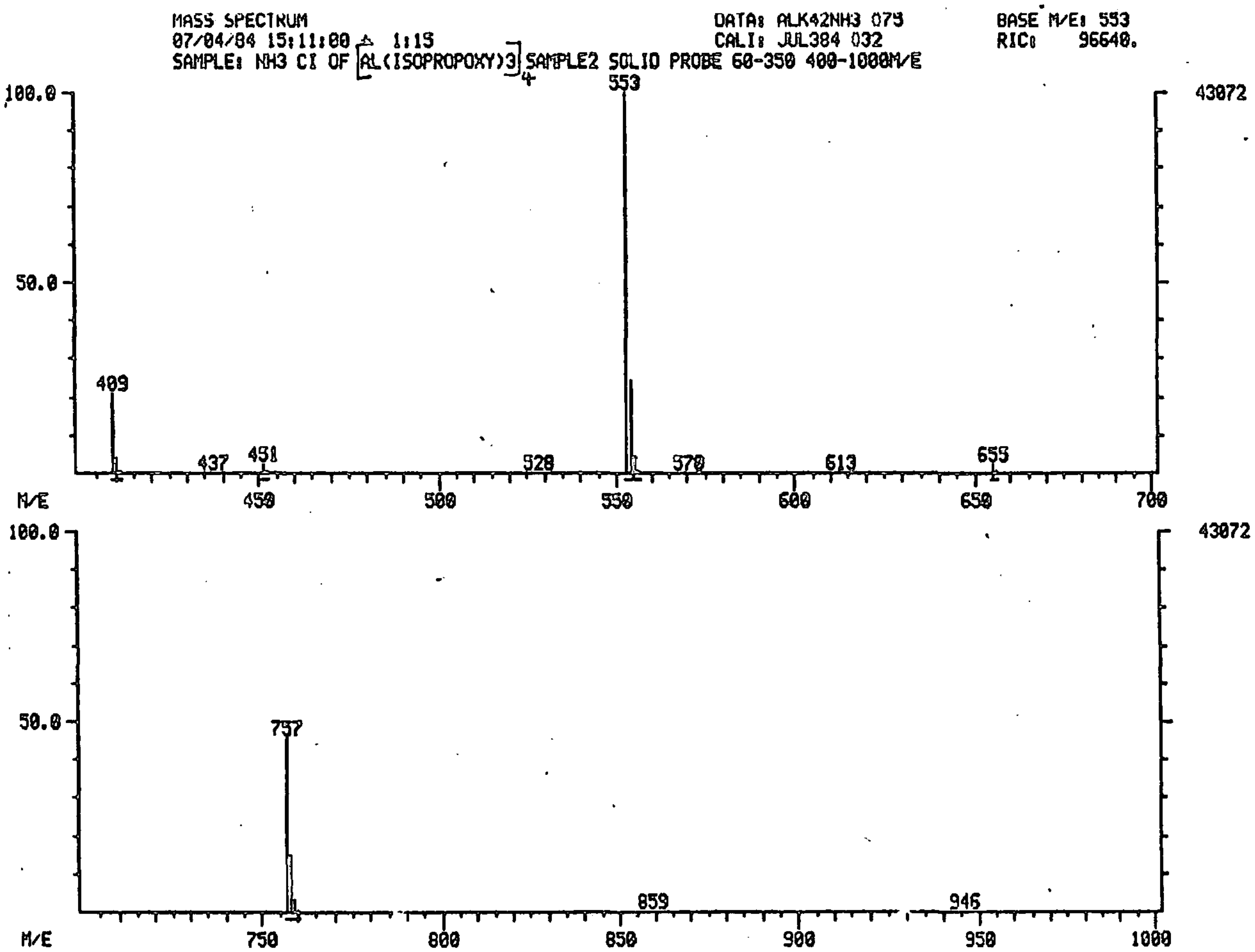
$AlO_3C_9H_{21}$ requires: Al, 13.23; C, 52.99; H, 10.29%

Infra Red (Nujol) (cm^{-1})


2.5
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
3500
3000
2500
2000
WAVENUMBER (CM⁻¹)


10
12
14
16
18
20
25
1600
1400
1200
1000
800
600
400
WAVENUMBER (CM⁻¹)

Mass Spectrum (E.I. and C.I.) A highest mass peak was observed at m/e 757 corresponding to the species $[Al_4(OPr^i)_{11}]^+$. Other major peaks are observed at m/e 553, m/e 451 and m/e 409 corresponding to the species $[Al_4O_2(OPr^i)_7]^+$, $[Al_3O(OPr^i)_6]^+$ and $[Al_2(OPr^i)_6]^+$ respectively. There is evidence of loss of $(-OCH(CH_3)_2)$, $CH_3CH{=}CH_2$ and CH_3CHO.



4.3 (3) Preparation of sodium-aluminium isopropoxide [Na[Al(OPr^i)$_4$]]

Sodium isopropoxide (NaOPr^i) was prepared by the addition of sodium metal (0.872g, 37.93mmoles) to isopropanol in excess. The resultant liquid was filtered to remove impurities and the solid product obtained by removal of solvent under reduced pressure.

Freshly prepared sodium isopropoxide (3.11g, 37.93mmoles) was dissolved in dry toluene (50ml) with the addition of a small amount of dry isopropanol (5ml) to yield a clear solution. Aluminium triisopropoxide (prepared by method 4.3(2)) (7.74g, 37.94mmoles) was dissolved in dry toluene (20ml) with the aid of heat. This solution was introduced, by syringe, into the solution of sodium isopropoxide with vigorous stirring. This mixture was stirred for one hour at room temperature affording a cream coloured semi-solid. The solvents were removed by distillation followed by heating (160^{o}C) under reduced pressure. The product, a light, off-white solid, was isolated and stored under nitrogen. Characterized as follows:

Analysis Found: Al, 9.43; Na, 6.81; C, 52.50; H, 10.98%.
$NaAlO_4C_{12}H_{28}$ requires: Al, 9.44; Na, 8.04; C, 50.53; H,9.79%.

Infra Red (Nujol) (cm^{-1}): 3000-2760 (s) (Nujol); 2620 (w) (C-H); 1375(s) (gem-dimethyl C-H); 1165 (m) 1140(m) (C-O); 1000 (s) (C-O terminal, solvate); 845 (m) 710 (m) 660 (w) 480 (w) (Al-O).

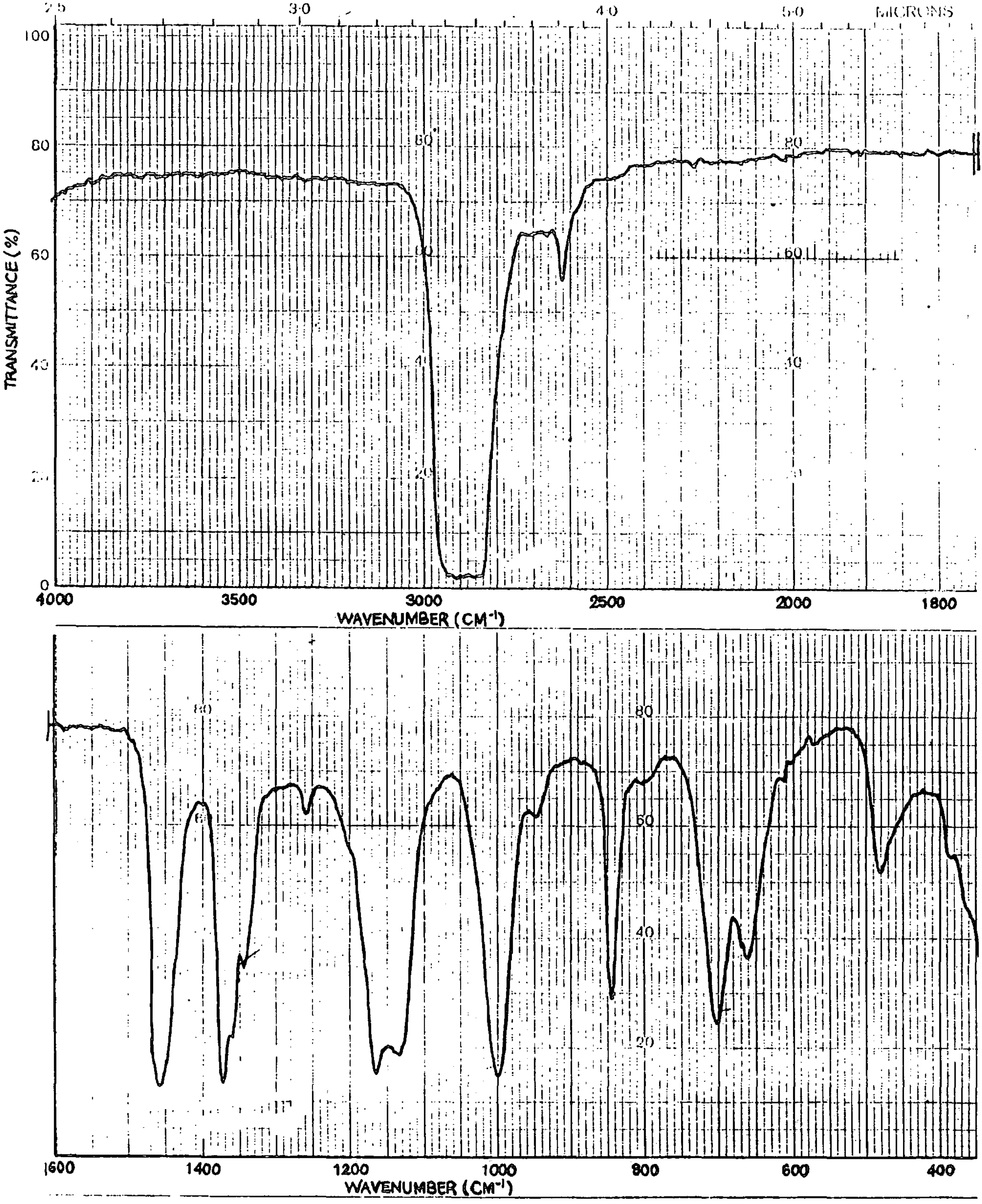
4.3 (4) Preparation of potassium-aluminium isopropoxide [K[Al(OPr^i)$_4$]]

Potassium-aluminium isopropoxide was prepared by the method described in 4.3(3). In this case the reaction of potassium is very vigorous and caution must be exercised. The product, a white solid, was characterized as follows:

Analysis Found: K, 10.33; Al, 9.84; C, 53.49; H, 9.33%

$KAlO_4C_{12}H_{28}$ requires: K, 12.94; Al, 8.94; C, 47.67; H, 9.27%.

Infra Red (Nujol) (cm^{-1})



4.3 (5) Preparation of manganese-aluminium isopropoxide $[Mn[Al(OPr^i)_4]_2]$

Potassium-aluminium isopropoxide was prepared from potassium metal (2.83g, 72.4mmoles) dissolved in isopropanol (90ml) reacted with a solution of aluminium triisopropoxide (14.79g, 72.5mmoles) in isopropanol by the method described in 4.3(3).

Anhydrous manganese (II) chloride (4.50g, 35.8mmoles) was dissolved in isopropanol with heating to yield a clear pink coloured solution. The alcoholic solution was added to the potassium-aluminium isopropoxide with vigorous stirring. The reaction mixture was heated at reflux temperature for six-seven hours. The resultant product, a dark red-brown liquid, was filtered to remove the white solid which proved to be potassium chloride. The product was concentrated under reduced pressure and then slurried with cold pentane. The precipitated potassium chloride was filtered off and the process repeated. The final product, after removal of excess solvent, proved to be a viscous brown liquid which was stored under nitrogen. Characterization as follows:

Analysis Found: Mn, 6.27 (8.27); Al, 9.27 (11.57); K, 3.34 (3.98); C, 38.56 (37.08); H, 8.60%(8.05); Cl^- absent in both cases.

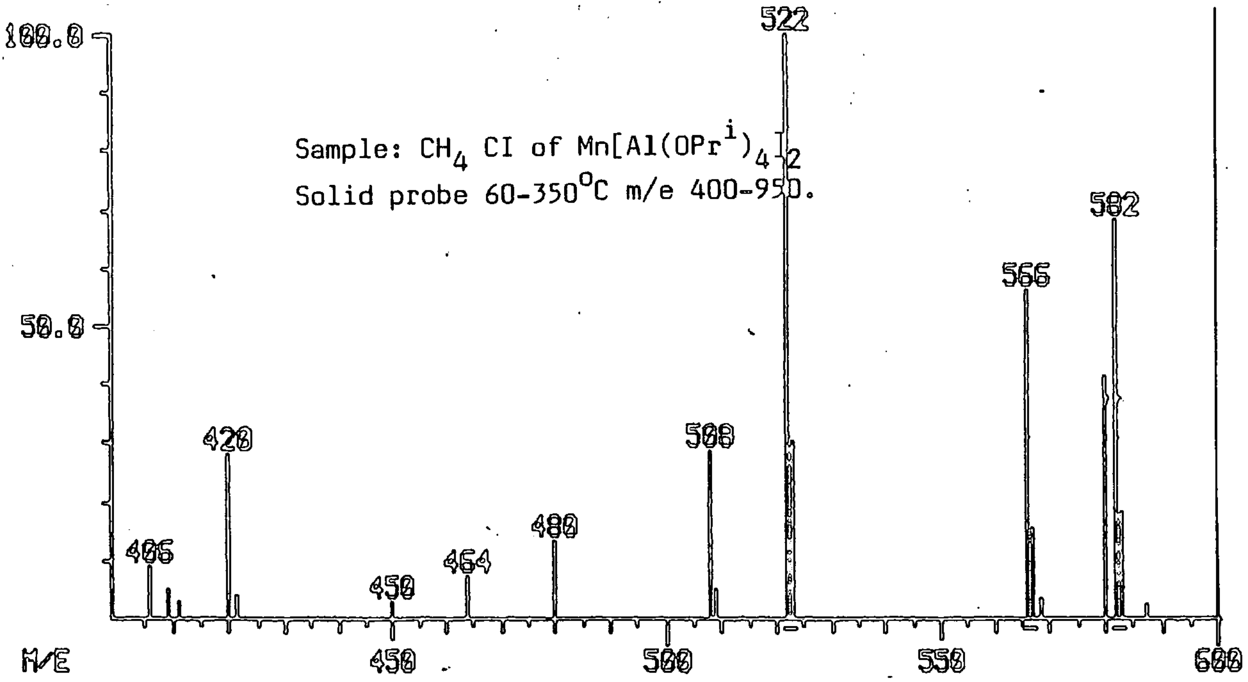
$MnAl_2O_8C_{24}H_{56}$ requires: Mn,9.4; Al, 9.3; C, 49.6; H, 9.7%.

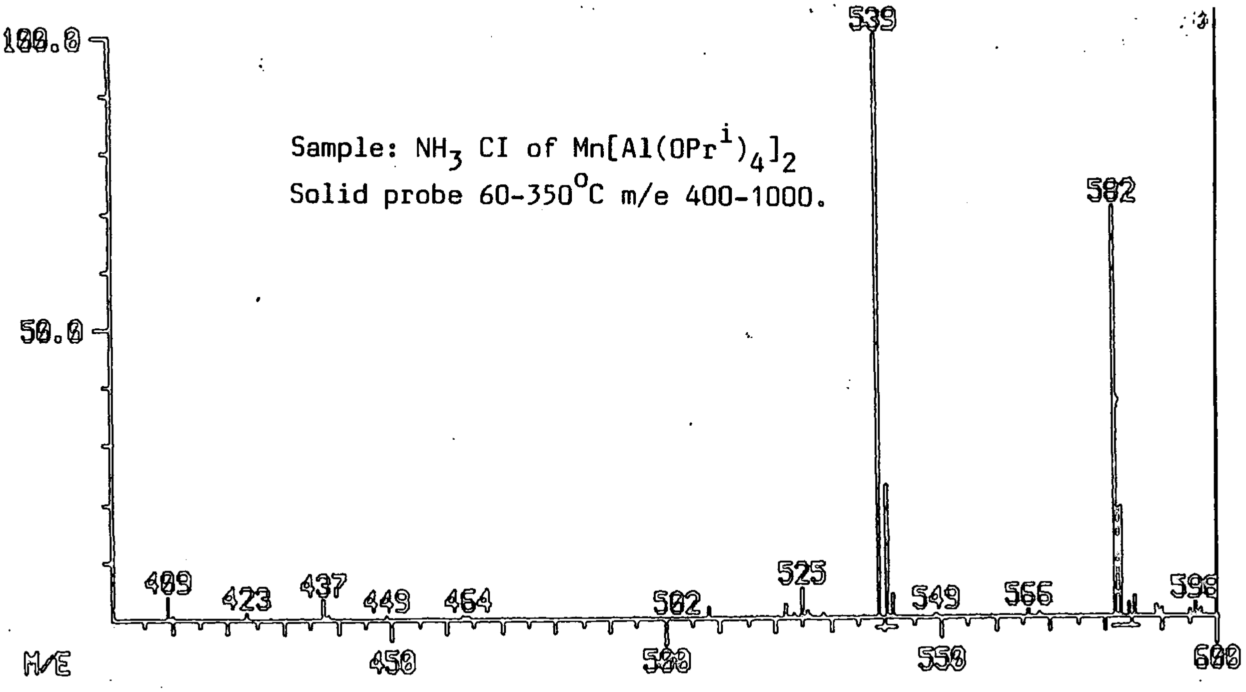
High carbon and potassium levels due to contamination of the product by potassium and potassium-aluminium isopropoxide. Taking this into consideration the metal ratios are correct for the formula.

Infra Red (Nujol) (cm^{-1}) 3550-3100 (s. broad) (O-H); 2620(s); 1455 (m) (CH_3);1365 (s) (Nujol/ gem-dimethyl); 1165 (s) 1135 (s) (C-O); 1030 (s) (terminal C-O); 995 (s) 950 (m) (bridging C-O); 845 (s); 695-675 (s) (Al-O); 460-(m) (M-O).

Mass Spectra $Mn[Al(OPr^i)_4]_2$ molecular weight = 581

Electron Impact M/e 41-950. Gives M-15 at m/e 566 and $M+M_n$ ion at m/e 636 plus lower fragment ions. CH_4 Chemical Ionization m/e400-950. Gives M +1 ion at m/e 582 and M-isopropoxy ion at m/e 522. NH_3 Chemical Ionization m/e 400-950 gives M +1 ion at m/e 582 and other fragment ions. Also M-42 ion at m/e 539.





4.3 (6) Preparation of manganese-aluminium methoxide $[Mn[Al(OMe)_4]_2]$

Anhydrous manganese (II) chloride (5.15g, 40.87mmoles), potassium metal (3.20g, 82.05mmoles) and aluminium triisopropoxide (16.78g, 82.25mmoles) were used in the preparation of manganese-aluminium isopropoxide by the method described in 4.3(5).

To a portion of this product dissolved in isopropanol small aliquots of methanol (5ml) were added with rapid stirring. The precipitated solid was filtered off and dried under vacuum. Characterized as follows:

Analysis Found: Mn, 11.43; Al, 15.67; K, 5.67; Cl, trace;
C, 22.66; H, 6.2%.
$MnAl_2O_8C_8H_{24}$ requires: Mn, 15.4; Al, 15.1; C, 26.9;
H,6.8%.

The presence of potassium and the relatively high aluminium to manganese ratio indicates the presence of unreacted potassium-aluminium isopropxide (converted to the methoxide). On correction for this factor the correct ratio is obtained.

Infra Red (Nujol) (cm^{-1}) 3000-2760 (Nujol); 1370 (Nujol); 1185(w.sh); 1165 (C-O); 1090 (C-O terminal); 1000 (w) 955 (w) (C-O, bridging) 845 (m); 720-500 (m, broad) (Al-O).

Attempts to prepare the ethoxide by this route were not successful.

4.3 (7) Preparation of cobalt-aluminium isopropoxide $[Co[Al(OPr^i)_4]_2]$

Anhydrous cobalt (II) chloride (0.50g, 8.48mmoles) was dissolved in isopropanol (20ml) to give a clear blue liquid. Addition of this to a solution of potassium-aluminium isopropoxide (0.66g, 16.92mmoles K; 3.45g, 16.91mmoles $Al(OPr^i)_3$) in isopropanol yielded a purple precipitate which after refluxing for six-seven hours afforded a clear purple liquid and a white precipitate. This white solid was removed by filtration and the filtrate was concentrated under reduced pressure to yield a viscous, purple liquid. Characterization as follows:

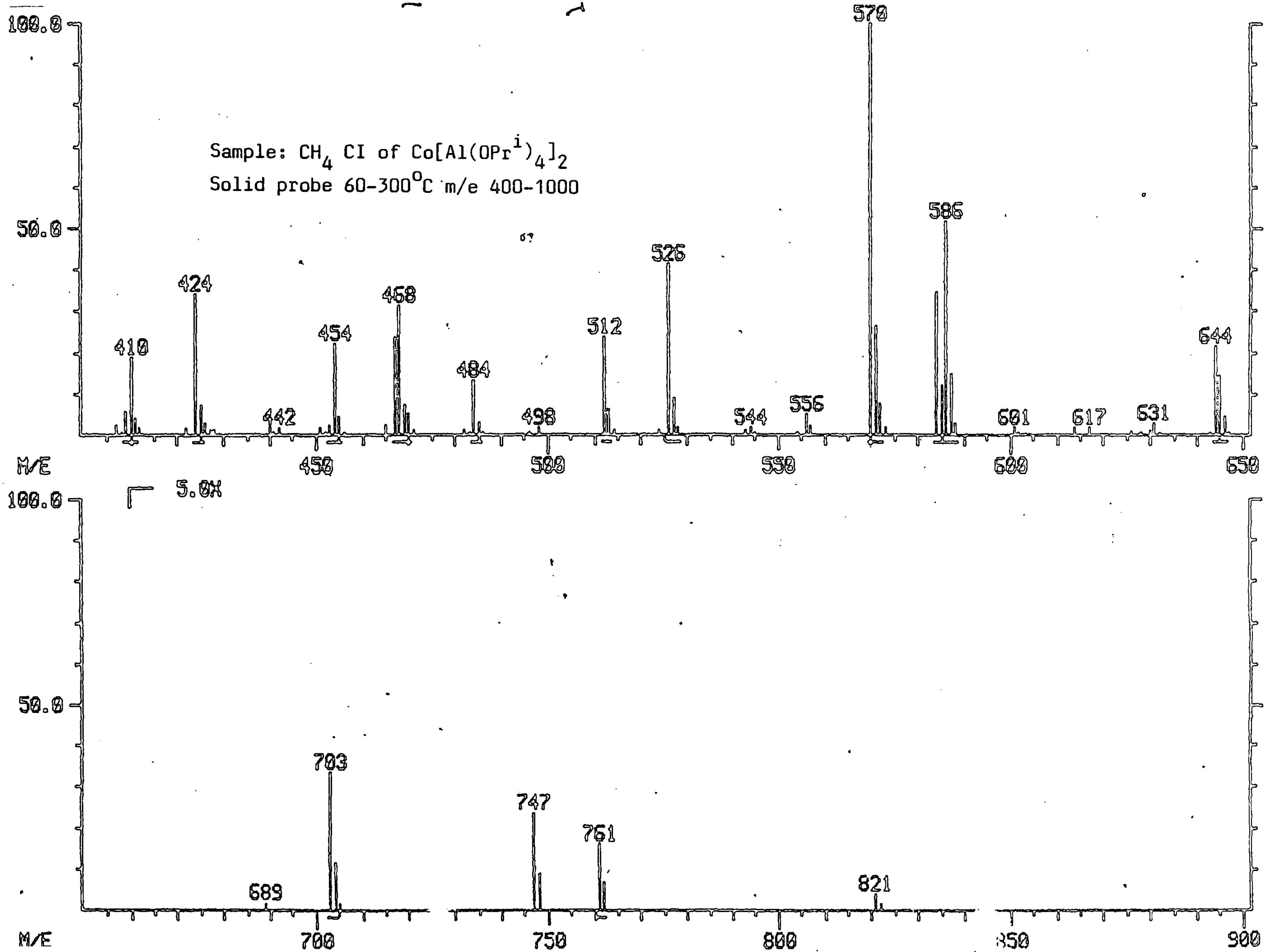
Analysis Found: Co, 14.1; Al, 9.87; C, 41.27; H,9.45% (K, 0.80, Cl^- absent).
$CoAl_2O_8C_{24}H_{56}$ requires: Co, 10.1; Al, 9.2; C, 49.2; H, 9.64%.

The small amount of potassium present indicates some impurities, possibly unreacted $K[Al(OPr^i)_4]$.

Infra Red (Nujol) (cm^{-1}) 3000-2760 (s) 1450 (s) 1370 (s)(Nujol); 1365-1360 (m) (gem-dimethyl); 1165 (s) 1130(s) ($-OPr^i$ and bridged C-O); 1030 (s) (terminal C-O); 1000(s); 970 (s) (bridged C-O); 830 (m); 690 (m) (Al-O); 595 (w); 530 (w); 445-400(w) (Co-O).

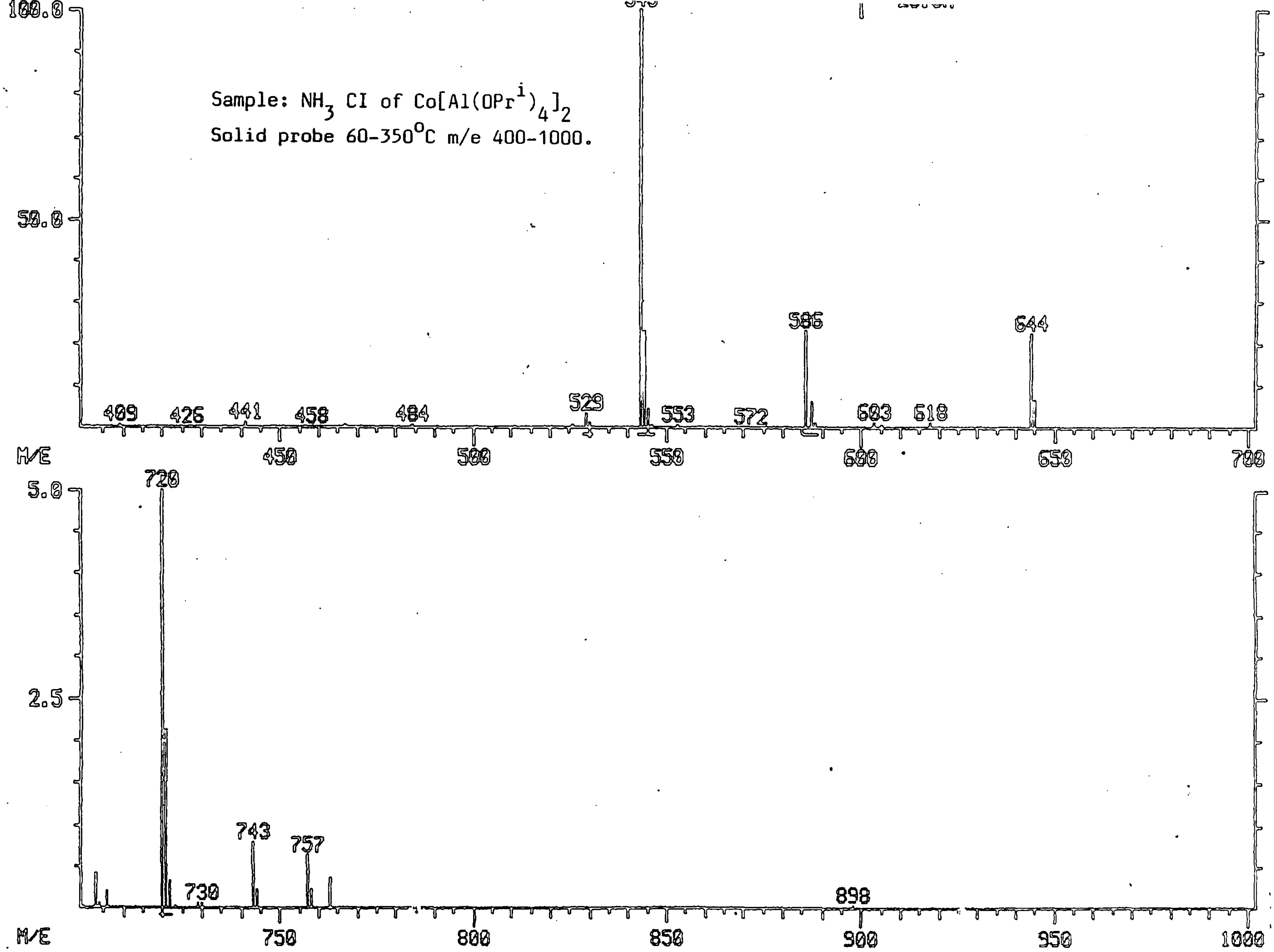
Mass Spectra $Co[Al(OPr^i)_4]_2$ Mol. Wt = 585.

Electron Impact m/e 41-950. Appears to give M-15 ion at m/e 570 and M+Co ion at m/e 644. CH_4 Chemical Ionization m/e 400-950 gives M+1 ion at m/e 586 plus aseries of M+59 ions at m/e 644, 703, 762 and 821. NH_3 Chemical Ionization m/e 400-950 gives minor M+1 ion atm/e 586 plus M+59 ion at 644. Also M-42 ion at m/e 543.



Sample: CH$_4$ CI of Co[Al(OPr^i)$_4$]$_2$

Solid probe 60-300°C m/e 400-1000



Sample: NH$_3$ CI of Co[Al(OPr^i)$_4$]$_2$
Solid probe 60-350°C m/e 400-1000.

4.3 (8) Preparation of copper-aluminium isopropoxide $[Cu[Al(OPr^i)_4]_2]$

Anhydrous copper (II) chloride (1.20g, 8.93mmoles) was dissolved in isopropanol (20ml) to give a clear, green solution. A fresh sample of potassium-aluminium isopropoxide was prepared by the method described in 4.3(4) (0.698g, 17.9mmoles, dissolved in isopropanol added to a solution of aluminium triisopropoxide, 3.65g, 17.9mmoles, in toluene*).

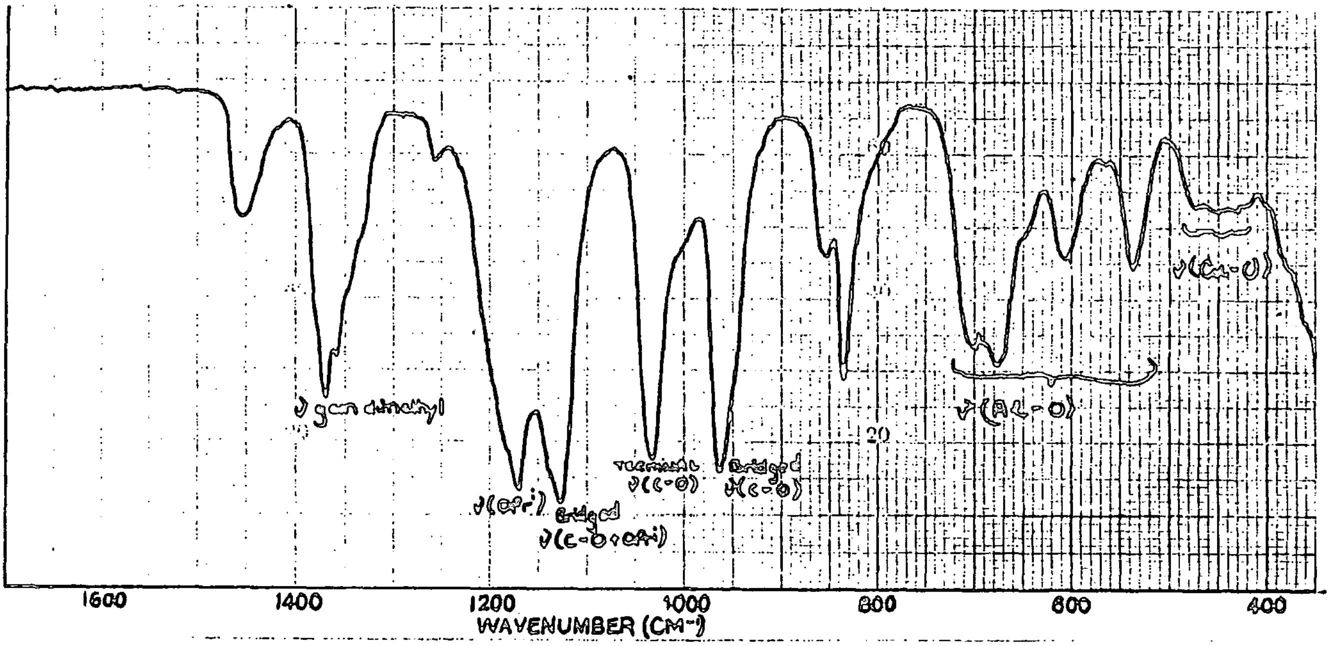
* Other preparations used pentane or isopropanol as solvent for ease of removal from product.

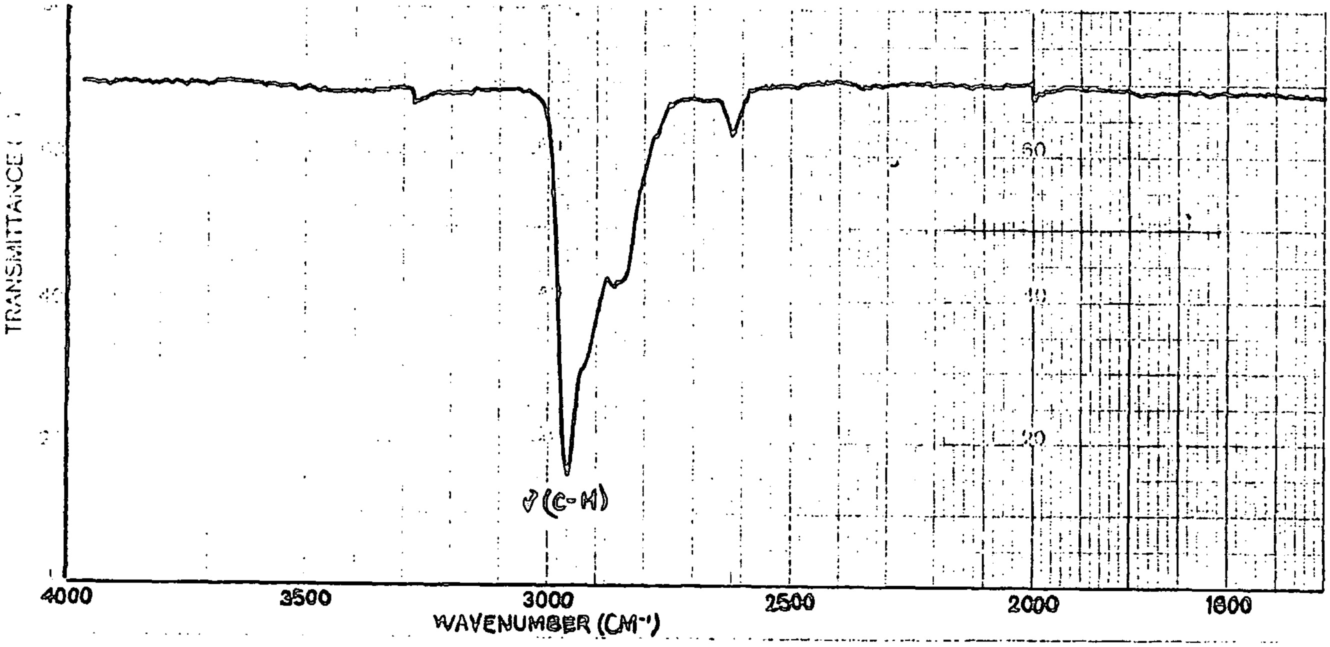
The solution of copper (II) chloride in isopropanol was added to the solution of potassium-aluminium isopropoxide with vigorous stirring. An exothermic reaction occurred affording a bright green precipitate. After a lengthy period of reflux a white solid was precipitated from a clear green liquid (reflux periods varied from four to eight hours). The white solid (potassium chloride) was removed by filtration and the filtrate, a clear, green liquid, collected. The liquid product was concentrated under reduced pressure to yield a viscous, dark green liquid. Initial analyses indicated a high chloride content which caused concern with respect to the known promotion of sintering by chloride in copper catalysts. To overcome this problem the product was slurried with pentane which caused the precipitation of potassium chloride (potassium chloride is slightly soluble in isopropanol). This procedure was repeated several times for each preparation and reduced the chloride content to less than 1ppm. The final product was characterized as follows:

Analysis Found: Cu, 9.65, 9.79; Al,10.20, 9.91; C, 46.9, 47.73;
H,9.83, 8.70%

$CuAl_2O_8C_{24}H_{56}$ requires Cu, 10.8; Al, 9.1; C,48.8; H, 9.6%

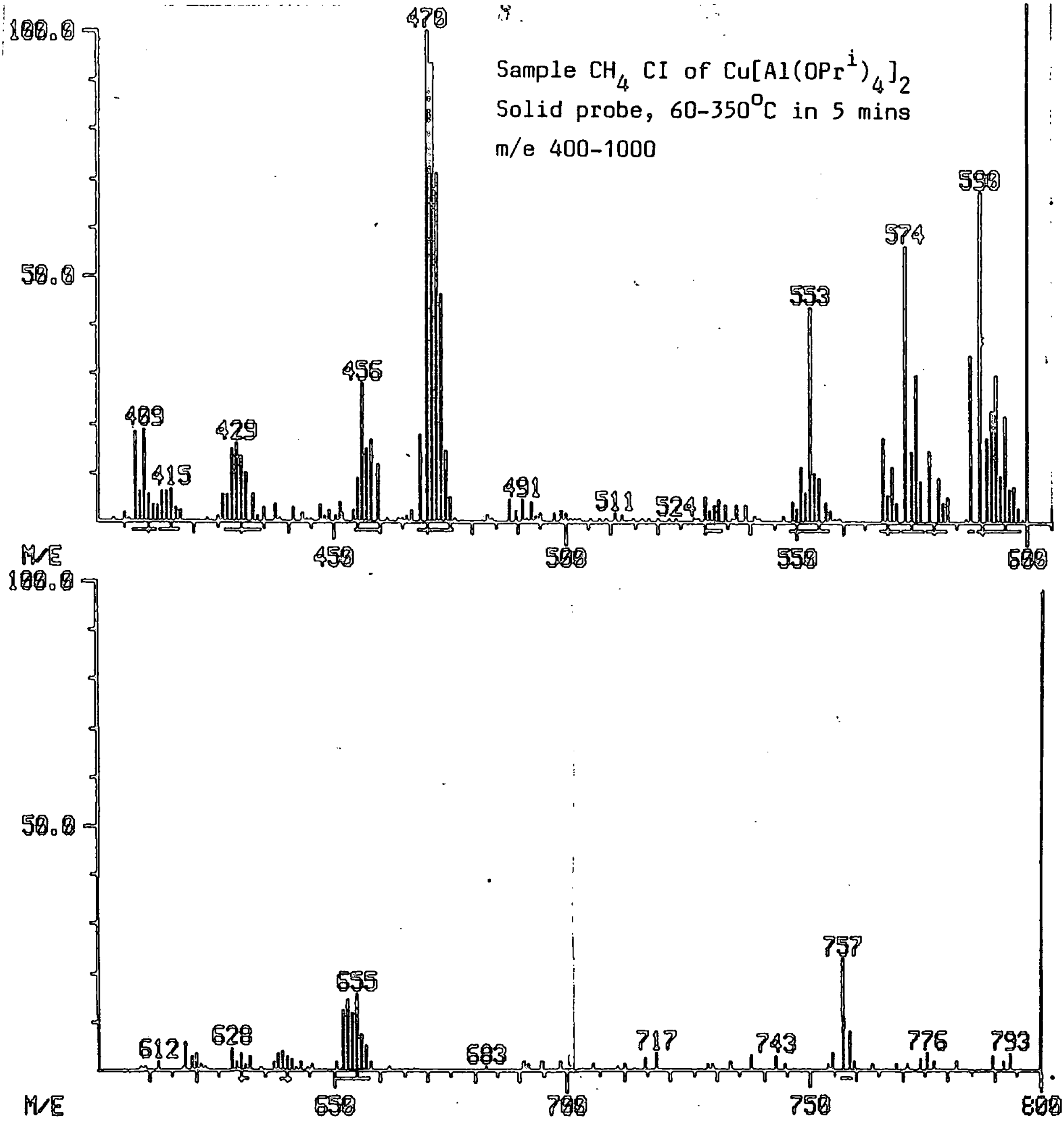
<u>Infra Red</u> (thin film, neat) (cm^{-1}) 2960 (s) (C-H), 2850 (m) (C-H); 2620 (w); 1450 (m); 1375-1365 (s) (gem-dimethyl); 1170 (s) (O-Pr^{i}); 1130 (s) (bridged C-O, OPr^{i}); 1040 (s) (C-O terminal); 965 (s) (C-O, bridged); 850 (m. sh); 835 (s); 700-675 (m. br.) (Al-O) ; 600 (m) (Al-O); 535 (m) (Al-O); 480-420 (w. br) (Cu-O).





<u>Mass Spectra</u> $Cu[Al(OPr^i)_4]_2$ mol. wt. = 589

Electron Impact m/e 41-950 gives M-15 ion at m/e 574. CH_4 Chemical Ionization m/e 400-950 gives M+1 ion at m/e 590 and a possible group of M+Cu 63/65 ions at m/e 652-656. NH_3 Chemical Ionization m/e 400-950 gives M+1 ion at m/e 590 and possible of M + Cu 63/65 ions at m/e 652-656 and also M-42 ion at m/e 547.


Sample CH_4 CI of $Cu[Al(OPr^i)_4]_2$
Solid probe, 60-350°C in 5 mins
m/e 400-1000

4.3 (9) Preparation of copper-aluminium ethoxide $Cu[Al(OEt)_4]_2$

A small sample of the previously prepared copper-aluminium isopropoxide was placed into a dry, nitrogen purged flask and dissolved in a small volume of pentane. With vigorous stirring an excess of dry ethanol was added. This caused the immediate precipitation of a blue solid. The solid product was filtered off and dried under reduced pressure. Characterization as follows:

Analysis Found: Cu, 13.43; Al, 11.36; C,36.35; H, 6.28%
$CuAl_2O_8C_{16}H_{40}$ requires Cu, 13.3; Al, 11.3; C, 40.2; H, 8.4%

Infra Red (Nujol) (cm^{-1}) Broad -OH band (weak); 1450 (s) (Nujol); 1370 (s) (Nujol); 1300 (w); 1260 (w); 1165 (m) (C-O); 1110 (s) (C-O); 1065 (s) (bridging C-O ?); 890 (w) (C-O); 800 (w) (Al-O); 650-400 (w. broad) (Al-O, Cu-O).

Mass Spectra $Cu[Al(OEt)_4]_2$ mol. wt. = 469

No real fragmentation pattern in either electron impact or chemical ionization modes.

4.3 (10) Preparation of copper-aluminium methoxide $Cu[Al(OMe)_4]_2$

Following the same method as for the precipitation of the ethoxide 4.3(9) copper-aluminium methoxide was prepared by the addition of excess methanol to copper-aluminium isopropoxide. An extremely fine purple-blue powder is the product. Characterization as follows:

Analysis Found: Cu, 14.82, Al, 12.6; C, 28.36; H, 6.26%
$CuAl_2O_8C_8H_{24}$ requires: Cu, 17.4; Al, 14.8; C, 26.3; H, 6.6%.

Infra Red (Nujol) (cm^{-1}) 3000-2760 (C-H) (Nujol); 1450 (s) 1370(s) (Nujol); 1260 (w); 1070 (s. broad) (C-O); 850-800 (w. broad) (bridging OMe ?); 530 (s. broad) (Al-O, Cu-O).

Mass Spectra $Cu[Al(OMe)_4]_2$ mol. wt. = 365

No real fragmentation pattern in either electron impact or chemical ionization modes.

4.3 (11) Preparation of zinc-aluminium isopropoxide $Zn[Al(OPr^i)_4]_2$

Anhydrous zinc chloride (2.11g, 15.5mmoles) was dissolved in isopropanol (50ml) with the aid of heat. This was added with vigorous stirring to a solution of potassium-aluminium isopropoxide (1.21g K, 30.94mmoles; 6.31g $Al(OPr^i)_3$, 30.93mmoles) dissolved in isopropanol. Immediately a white precipitate was produced. The contents of the flask were heated to reflux temperature and reflux maintained for a period of seven-eight hours. At the end of this period of time the mixture was filtered to remove the white solid which proved to potassium chloride. The filtrate was slurried with pentane to remove residual potassium chloride and then concentrated under pressure. A tacky, white solid was obtained from the, originally, clear liquid. This material proved quite difficult to handle and consequently only cursory analyses were obtained.

Analysis Found: Zn, 7.47; Al, 9.73; C, 41.8; H, 10.4%.
$ZnAl_2O_8C_{24}H_{56}$ requires: Zn, 11.06; Al, 9.1; C, 48.7; H, 9.5%.

4.3 (12) & (13) Preparation of copper-zinc-aluminium methoxide and ethoxide

Approximately equimolar amounts of copper-aluminium isopropoxide and zinc-aluminium isopropoxide were dissolved in isopropanol and mixed together. This mixture was stirred and heated for a period of two-four hours. At the end of this period an excess of the requisite alcohol was added whilst maintaining vigorous stirring. The precipitated solid was analysed for metal content. The values obtained are lower than required for direct comparison with theoretical results probably due to associated solvent. (these materials were prepared simply to provide a Cu-Zn-Al metal ratio comparable with that found in the standard precipitated catalyst)

Analysis.	Cu%	Zn%	Al%	Cu:Zn:Al
1)	4.53	3.89	9.28	(1.2):(1.0):(5.8)
2)	4.77	3.34	8.18	(1.5):(1.0):(5.9)
3)	6.53	4.24	8.62	(1.6):(1.0):(4.9)
4)	4.61	3.22	6.92	(1.5):(1.0):(5.2)
5)	5.52	5.57	8.85	(1.0):(1.0):(3.88)
6)	6.04	6.13	9.94	(1.0):(1.0):(3.9)
7)	6.80	7.14	11.92	(1.0):(1.0):(4.1)

$[Cu[Al(OR)_4]_2{:}Zn[Al(OR)_4]_2]$ requires Cu:Zn:Al = 1:1:4

4.3 (14) Preparation of iron(III)-aluminium isopropoxide

$Fe[Al(OPr^i)_4]_3$

Anhydrous iron (III) chloride was dissolved in isopropanol (1.14g, 7.03mmoles; 50ml) to give a clear orange-yellow solution.

This was added to a solution of potassium-aluminium isopropoxide (0.82g, 21.08mmoles K; 4.31g, 21.1mmoles $Al(OPr^i)_3$) dissolved in isopropanol. An immediate precipitate was formed which disappeared after a long period of reflux (seven-eight hours). At the end of this period a white solid was filtered off (potassium chloride) affording a clear orange liquid. This was slurried with pentane to remove residual potassium chloride. The excess solvent was removed under reduced pressure to yield a highly viscous, dark orange-brown liquid.

Analysis Found: Fe, 5.70; Al, 9.32; C, 48.1; H, 9.6%

$FeAl_3O_{12}C_{36}H_{84}$ requires: Fe, 6.6; Al, 9.58; C, 51.1, H, 10.0%.

(found ratio of metals = 1.0:3.39, Fe:Al)

4.3 (15) Preparation of HMPA adduct of nickel (II) chloride

A small amount of anhydrous nickel chloride (0.8g) was slurried in toluene at room temperature. An excess of HMPA (hexamethylphosphoric triamide $[(CH_3)_2N]_3PO$) was added whilst maintaining rapid stirring. This mixture was then warmed gently to give a clear blue solution. On chilling (-30°C) overnight there appeared a small quantity of blue crystals (the colour of the solution had paled significantly). These crystals were analysed as follows:

Analysis Found: P, 9.64%; Ni, 11.68; Cl, 14.35%

This gives Ni : HMPA : Cl
1.0 : 1.6 : 2.04 implying $NiCl_2$.1.5HMPA.

A more probable formula would be $NiCl_2$.2HMPA, requiring;
P, 6.35; Ni, 12.03; Cl, 14.5%.

These crystals were sent for crystallographic analysis but, to date, no data received.

CHAPTER 5

CHAPTER 5

SYNTHESIS AND CHARACTERIZATION OF CATALYSTS

5.1 INTRODUCTION

This chapter describes the conversion of the alkoxides into materials suitable for catalyst characterization. Calcination and reduction of the alkoxides produces a mixture of oxides and copper metal. The alkoxy compounds are compared against materials prepared by traditional precipitation methods. The standard ICI catalyst 51-2 (methanol synthesis) is used as the 'model' system. The techniques used in the characterization of the calcined and reduced materials include; thermogravimetric analysis under calcining and reducing atmospheres, X-ray powder diffraction, total surface area measurement by BET isotherm method, copper surface areas by N_2O reaction, pore size and pore size distribution, pore radii and mean crystallite size determinations.

5.2 DISCUSSION

The alkoxide derivatives used for this investigation were

i) $Cu[Al(OPr^i)_4]_2$,

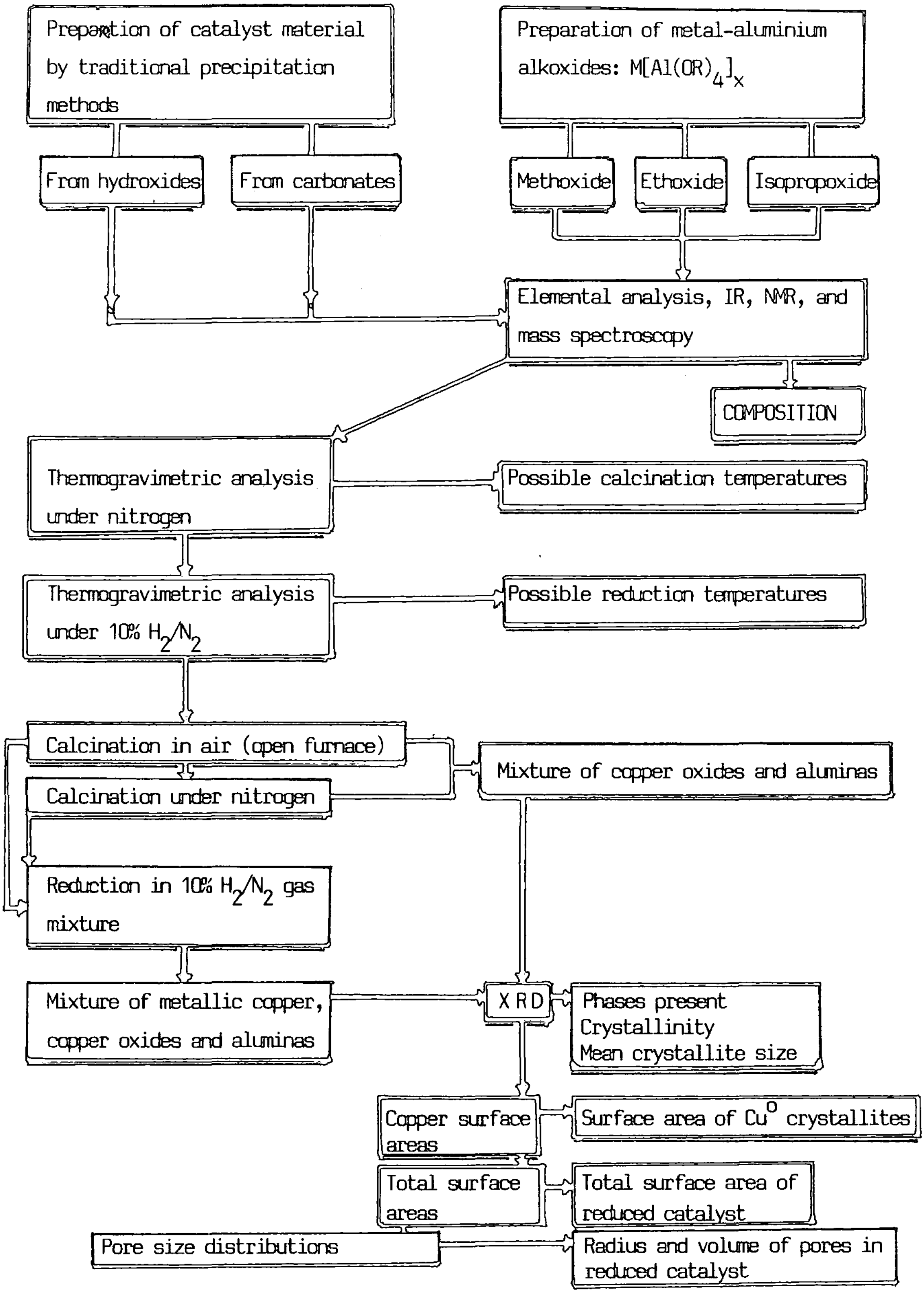
ii) $Cu[Al(OEt)_4]_2$,

and iii) $Cu[Al(OMe)_4]_2$.

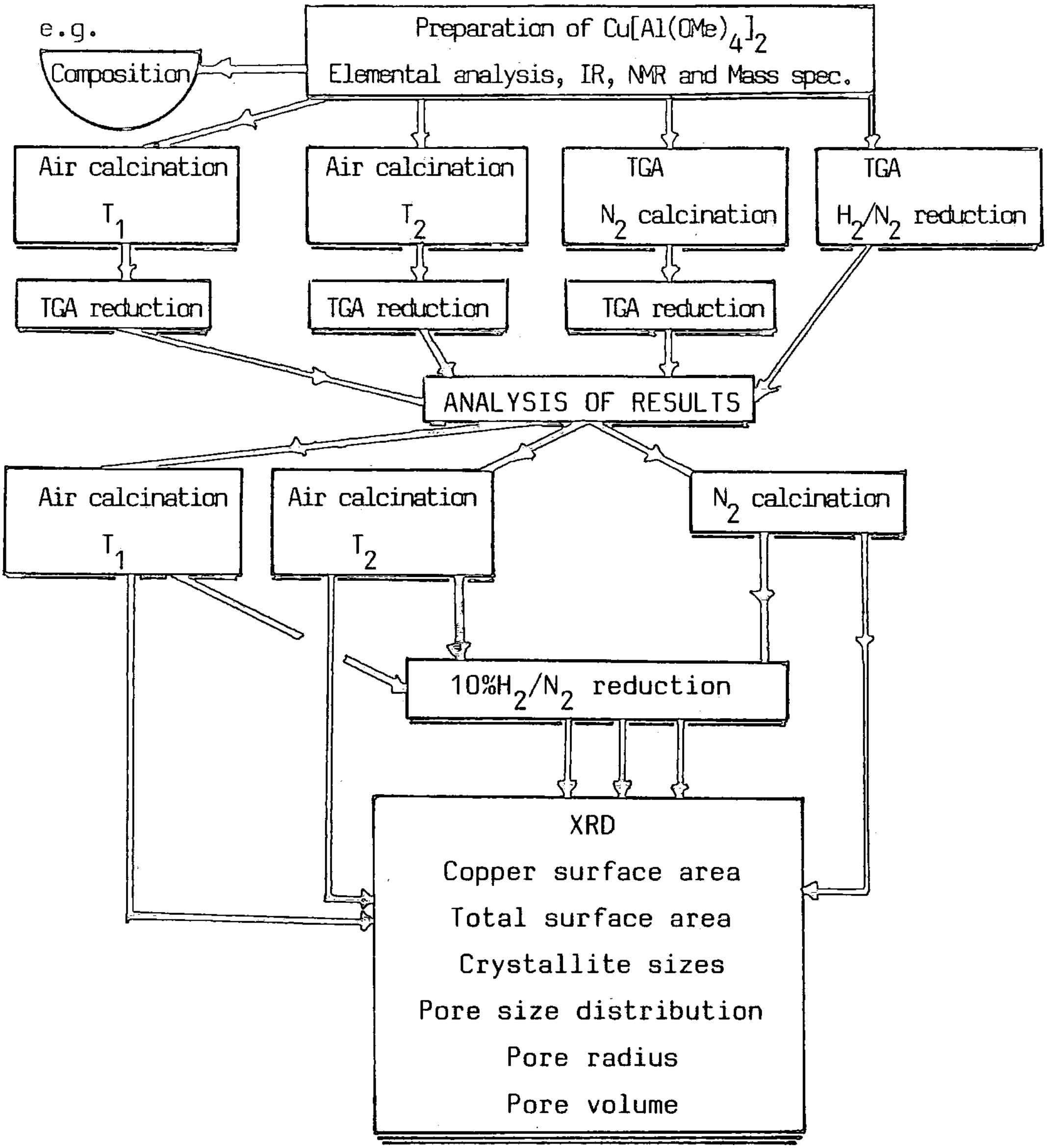
As a comparison two precipitated catalysts were prepared by ICI such that their composition contained the same copper:aluminium ratio as the alkoxides. The precipitated materials were derived from hydroxides and carbonates. These materials were calcined and reduced by standard procedures.

The diagrams on the following two pages illustrate the testing procedures followed. Each alkoxide or precipitate was calcined in air at two different temperatures and in nitrogen using thermogravimetric analysis. Each of these calcined materials was then reduced using the TGA. Each sample was reduced directly in addition to the

SUMMARY OF EXPERIMENTAL CATALYST WORK



INDIVIDUAL SAMPLE



Each individual sample was analysed by the same route. The results of these analyses are described in this chapter.

calcination-reduction steps. The thermogravimetric analysis results were used to optimise the calcination and reduction temperatures for each material.

1) air calcinations were carried out at two temperatures; 230°C and 340°C
2) nitrogen calcinations were performed at 300°C
3) reductions (using 10% H_2/N_2 at 8lit h^{-1}) were performed at two different temperatures
    i) alkoxides = 200-250°C
    ii) precipitates = 200-230°C

Thermogravimetric analyses were performed with the thermogravimetric analyzer inside a glove-bag. This allowed the atmosphere conditions to be controlled. Nitrogen and hydrogen/nitrogen atmospheres were introduced into the glove-bag and a steady flow rate maintained throughout the temperature rise. Obviously, with the high temperatures involved, this was not an ideal arrangement but, with the apparatus available, was the most suitable set-up and did, in fact, work remarkably well.

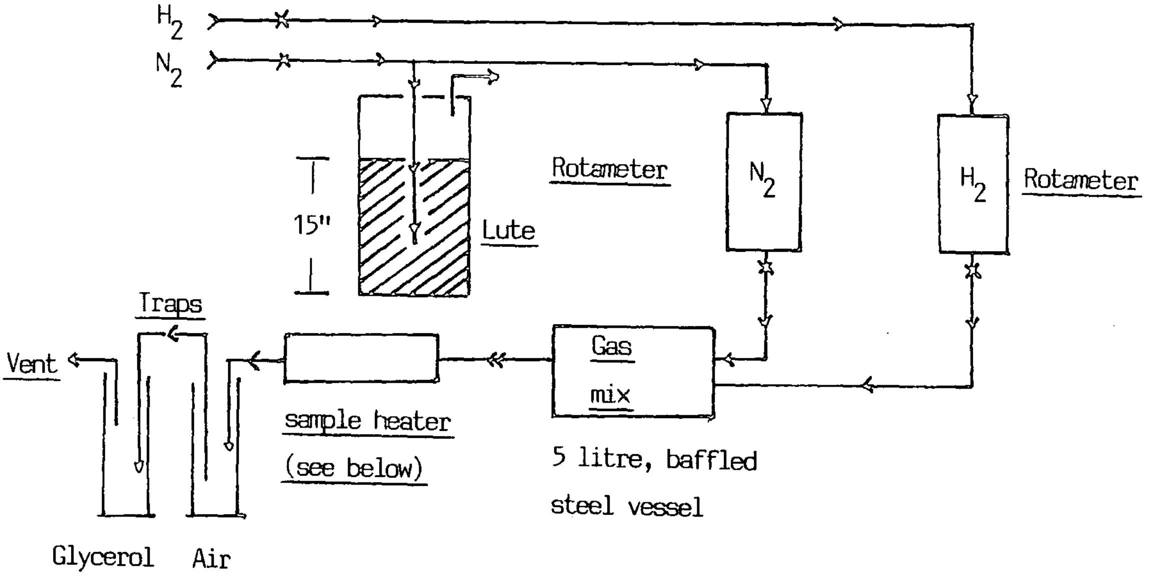
Having completed the themogravimetric analyses, larger samples were calcined and reduced. Air calcinations were carried out in an open furnace, calcinations under nitrogen and reductions were carried out in the apparatus illustrated on the following page. The samples were loaded, into the heating tube, inside a glove-box.

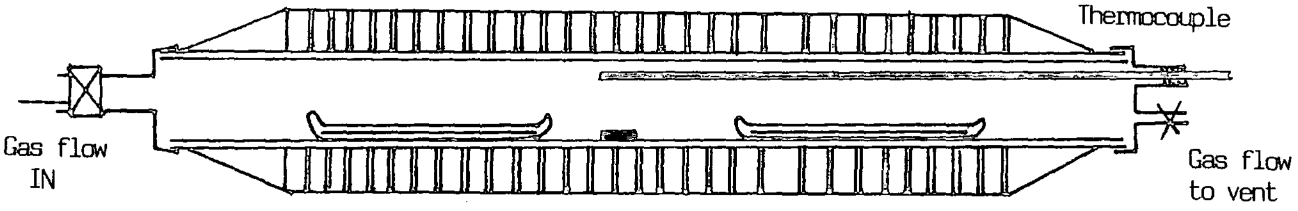
Calcined and reduced samples from this stage were then prepared for XRD analysis and also sent for copper surface area, total surface area and pore size determinations.

On calcination of the copper-aluminium isopropoxide ($Cu[Al(OPr^i)_4]_2$) a copper mirror was formed on the inside surface of the silica-glass heating tube. This did not occur with any of the other alkoxides

CALCINATION AND REDUCTION APPARATUS

The apparatus, shown below, was used for the calcination and reduction of the alkoxide and precipitated materials under controlled atmosphere and temperature conditions.





Silica glass tube and sample boats   Heating element (upto 360^{0}C)

(the silica glass tube and sample boats can be removed from the heating element for sample loading in a dry box) and it would appear that the isopropoxy formed a mobile copper species on thermal decomposition. The copper-aluminium isopropoxide is volatile and thermal decomposition of alkoxides can produce alkenes. It is possible that hydrogen, produced in this decomposition caused the reduction of the Cu(II). This is an area which would be worth detailed investigations. Workers on a similar project, using carboxylates, have also found the formation of copper mirrors with certain derivatives.

Samples for XRD analysis were prepared by grinding the calcined or reduced material to a very fine powder. This was then compacted into a die (20mm diam; 2mm depth) to produce a smooth surface. It was imperative that no movement of the sample surface occurred during analysis and the procedure to produce the optimum sample is tedious.

The results of the XRD analyses are given in the experimental section but a summary is shown here:

ALKOXIDES	PRECIPITATED CATALYSTS
CALCINED	
Copper (II) oxide (Copper (I) oxide) Highly crystalline-isopropoxide Amorphous-ethoxide	Identical copper(II) oxide peaks Reasonably crystalline Other phases present; e.g. malachite
With the isopropoxide under nitrogen calcination, peaks due to Cu^{o} are prominent	Greater amount of alumina indicated than for alkoxides
REDUCED	
Highly crystalline copper Presence of Cu^{I} indicated for methoxide and ethoxide	Crystalline copper Cu^{I} also indicated
Small amount of alumina	Alumina

On this basis the alkoxides compare quite well with the precipitated materials. There is some indication that the nature of the alkoxy group affects the properties of the calcined and reduced products.

For high activity, small crystallite sizes are required which, in turn, produce high surface areas. Typical industrial catalysts have crystallite sizes in the region of 5-50nm and precipitated catalysts, in particular, in the range 4-14nm. Analysis of line broadening in XRD patterns enabled the estimation of the mean crystallite sizes of several of the experimental samples to be carried out. It was noted that in some cases the copper (0) lines were lying on top of alumina lines thus distorting the values. The reported results can not really be considered accurate but provide a comparative assessment.

K1 (NaOH ppte; reduced) = 9.0nm
KCM (Methoxide;reduced) = 6.0nm
KBI (Isopropoxide;calcined) = 34.0nm
KCI (Isoprpoxide; reduced) = 50.0nm
KDE (Ethoxide; reduced) = 24.0nm

These results lie within the range found for commercial catalysts with the smallest crystallite being produced by the methoxide. It is interesting to note that the isopropoxide produced a large value for mean crystallite size even though the sample was only calcined and was not reduced. This would seem to confirm the idea that the isopropoxy group causes reduction of the copper (II). The large crystallite size may be due sintering caused by the formation of a mobile copper species.

These results are reinforced by the values obtained for copper surface areas. The reduced methoxide gives values of around $5.1m^2g^{-1}$ whereas the isopropoxide produces a copper surface area of $2.4m^2g^{-1}$.

The copyper surface area of the precipitated catalyst is the highest
of all the values obtained from the experimental materials at $6.5m^2g^{-1}$.

These results do not compare well with the copper surface area found typically in the standard 51-2 $Cu/ZnO/Al_2O_3$ catalyst. Surface areas for this material are in region of $30.0\ m^2g^{-1}$. However the effect of introducing a ZnO component into the alkoxide compounds is unknown (although preliminary thermogravimetric analyses were performed on mixed copper-zinc-aluminium alkoxides) but by making a direct comparison with the analogous precipitated catalyst (K1, K2) it can be seen that the alkoxide materials have similar metal surface areas and it is possible that a copper-zinc-aluminium alkoxide precursor would produce a high copper surace area due to the inclusion of a zinc species.

Surface areas of precipitated catalysts are usually in the region of $60\text{-}100m^2g^{-1}$, though some catalysts have surface areas higher than $200m^2g^{-1}$.

The precipitated materials exhibit high surface areas ($230\text{-}235m^2g^{-1}$ for the reduced materials; $150\text{-}160m^2g^{-1}$ for the calcined precursors) which are matched by the total surface areas of the ethoxides and isopropoxides ($104\text{-}217m^2g^{-1}$). The surface area of the methoxy derivative is, however, extremely low in comparison. So although the methoxides produce higher copper surface areas than the ethoxides or isopropoxides their total surface areas(which includes the alumina component) are much lower. It has been proposed that this is a result of the alkoxy group being very small and the alkoxide precursor consequently being highly polymerized. A more detailed study would be required to discover the effect of the alkoxy group, or other factor, on the total surface area of the product.

Pore volume measurements agree with the results obtained for surface areas in that the higher pore volumes are found in the precipitated materials and the lower volumes being produced by methoxides. An interesting point is that the ethoxides are microporous which explains their very high surface areas.

The results gained from these experiments imply that although the alkoxide-derived materials are not vastly superior to the precipitated analogues they do produce values comparative with those of the precipitated materials. On that basis alone it would be interesting to undertake further, more detailed studies of these alkoxide compounds.

While carrying out this project it soon became apparent that more questions were being asked than were being answered. Several areas of investigation present themselves;

i) a wider range of alkoxide derivatives subjected to this kind of study could, possibly, provide a better pattern of results from which to draw some conclusions as to the effect of the alkoxy group on the nature of the precursor.

ii) the inclusion of mixed alkoxy-alkoxides would widen this range and would allow some analysis of the effect of individual alkoxy groups on the final catalyst properties.

iii) better control of the conditions of treatment of the alkoxide precursor would allow a better and clearer understanding of the effect of each variable. For example, with some of the alkoxy compounds, the temperature of calcination had some effect on the phases present in the calcined material.

These are just a small number of the possible areas of investigation which have presented themselves as being justified. There were also a number of points raised during the synthesis of the alkoxides which would have been interesting to follow up had time permitted.

These points are discussed in the, brief, final chapter of this work.

5.3 EXPERIMENTAL SECTION

5.3 (1) Thermogravimetric Analyses

A series of thermogravimetric analyses was carried out on samples of copper-aluminium alkoxides, copper-zinc-aluminium alkoxides, iron-aluminium alkoxides and copper-aluminium catalyst precursors prepared by co-precipitation methods at I.C.I.. These studies were performed to determine the most appropriate calcination and reduction conditions for the alkoxide and precipitated materials. For the purpose of these investigations the thermogravimetric analyzer was placed inside a glove bag to provide both nitrogen and hydrogen/nitrogen atmospheres for calcinations and reductions. This was not an ideal arrangement with respect to the temperatures involved but was the most appropriate with the apparatus available to achieve the aims of the experiment.

The following is a summary of the thermogravimetric analyses carried out (note: several samples were calcined in air prior to reduction in thermogravimetric analyzer).

SAMPLE		DESCRIPTION	
1.		$[Al(OPr^i)_3]_4$	calcination under N_2
2.		$[Al(OPr^i)_3]_4$	reduction under 10% H_2/N_2
3.		$[Al(OEt)_3]_n$	calcination under N_2
4.		$[Al(OEt)_3]_n$	reduction under 10% H_2/N_2
5.		$Cu[Al(OMe)_4]_2$	calcination under N_2
6.		$Cu[Al(OMe)_4]_2$	reduction under 10%H_2/N_2
7.	(200°C) air calcined	$Cu[Al(OMe)_4]_2$	reduction under 10% H_2/N_2
8.	(320°C) air calcined	$Cu[Al(OMe)_4]_2$	reduction under 10% H_2/N_2
9.	(230°C) N_2 calcined	$Cu[Al(OMe)_4]_2$	reduction under 10% H_2/N_2
10-13 repeated steps 5-9 for second sample of $Cu[Al(OMe)_4]_2$			
14. repeated step 5 for third sample of $Cu[Al(OMe)_4]_2$			
15.		$Cu[Al(OEt)_4]_2$	calcination under N_2

SAMPLE	DESCRIPTION
16.	$Cu[Al(OEt)_4]_2$ calcination under N_2 (2nd sample)
17.	repeat
18.	$Cu[Al(OEt)_4]_2$ reduction under H_2/N_2
19. (200°C) air calcined	$Cu[Al(OEt)_4]_2$ reduction under 10%H_2/N_2
20. (340°C) air calcined	$Cu[Al(OEt)_4]_2$ reduction under 10%H_2/N_2
21. (230°C) N_2 calcined	$Cu[Al(OEt)_4]_2$ reduction under 10%H_2/N_2
22. (20°C) air exposed	$Cu[Al(OPr^i)_4]_2$ calcination under N_2
23. (20°C) air exposed	$Cu[Al(OPr^i)_4]_2$ reduction under 10% H_2/N_2
24. (200°C) air calcined	$Cu[Al(OPr^i)_4]_2$ reduction under 10% H_2/N_2
25 (340°C) air calcined	$Cu[Al(OPr^i)_4]_2$ reduction under 10% H_2/N_2
26. Cu:Al (1:2)	Na_2CO_3 ppte calcination
27. (300°C) calcined	Na_2CO_3 ppte reduction under 10% H_2/N_2
28.	Na_2CO_3 ppte calcined, cooled, reduced

29-31 steps 26-28 repeated for NaOH (Cu:Al, 1:2) precipitated precursor

32-36 steps 5-9 repeated for copper-zinc-aluminium ethoxide

33-37 steps 5-9 repeated for copper-zinc-aluminium methoxide

38-42 steps 5-9 repeated for iron-aluminium methoxide

RESULTS

i) calcination $[Al(OPr^i)_3]_4$

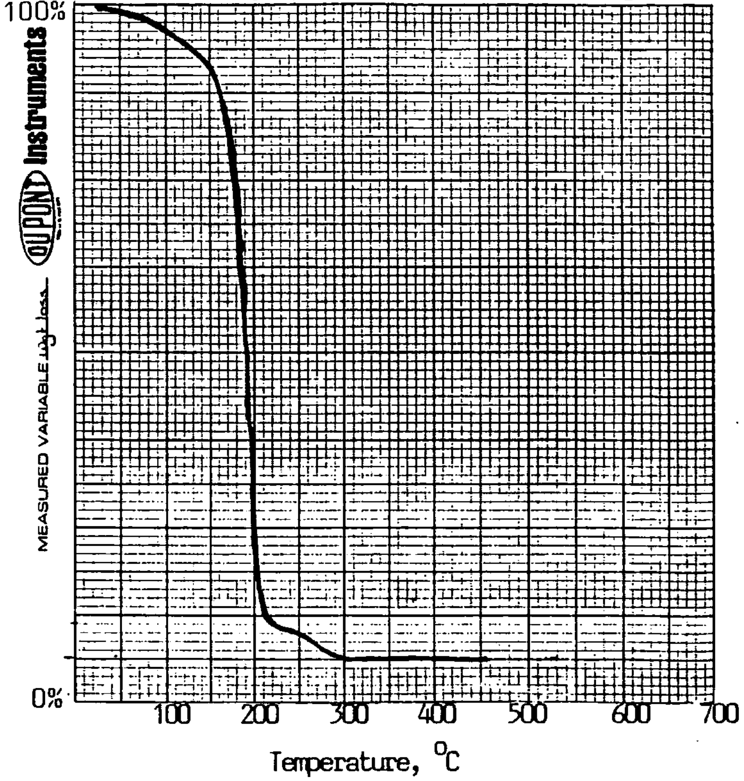
Theoretical weight loss for $[Al(OPr^i)_3]_4 \longrightarrow 2Al_2O_3 = 75\%$
Actual weight loss of 88.75% at 200°C with smaller weight loss of 5.0% over 200-300°C.

ii) reduction $[Al(OPr^i)_3]_4$

Theoretical weight loss for $[Al(OPr^i)_3]_4 \longrightarrow 4Al = 86.8\%$
Actual weight loss of 89.4% at 200°C.

It would appear that in both cases reduction has occurred. It is also noted that some loss of sample off the balance has occurred.

$[Al(OPr^i)_3]_4$ calcination under N_2



Total weight loss of 93.75%

iii) calcination $[Al(OEt)_3]$

Theoretical weight loss for $[Al(OCH_2CH_3)_3] \longrightarrow \frac{1}{2}Al_2O_3$ = 68.5%

Actual weight loss a) minor weight loss (8.75%) upto 130°C

b) major weight loss (67.5%) at 240°C

c) small weight loss (8.125%) at 350°C

Total weight loss of 76.25%.

iv) reduction $[Al(OEt)_3]$

Theoretical weight loss for $[Al(OCH_2CH_3)_3] \longrightarrow Al$ = 83.3%

Actual weight loss a) weight loss (22.5%) at 80-150°C

b) weight loss (23.75%) at 190-230°C

c) weight loss (22.5%) from 250-400°C

Total weight loss of 68.75%.

v) calcination $Cu[Al(OMe)_4]_2$

Sample of methoxide (A) heated to 850°C in nitrogen gives a total weight loss 50.625% over broad range 50-400°C. Theoretical conversion to CuO/Al_2O_3 requires total loss of 55.9%.

vi) reduction $Cu[Al(OMe)_4]_2$

Sample of methoxide (A) heated to 850°C in hydrogen flow gives a total weight loss of 49.4% over temperature range upto 300°C. Theoretical conversion to Cu/Al_2O_3 requires total weight loss of 54.7%.

vii) reduction of air and nitrogen calcined $Cu[Al(OMe)_4]_2$

Samples of this methoxide (A) were calcined in air and under a nitrogen atmosphere at two temperatures (only the lower temperature for nitrogen) The resultant material was then analysed using thermogravimetric analysis for the reduction temperature.

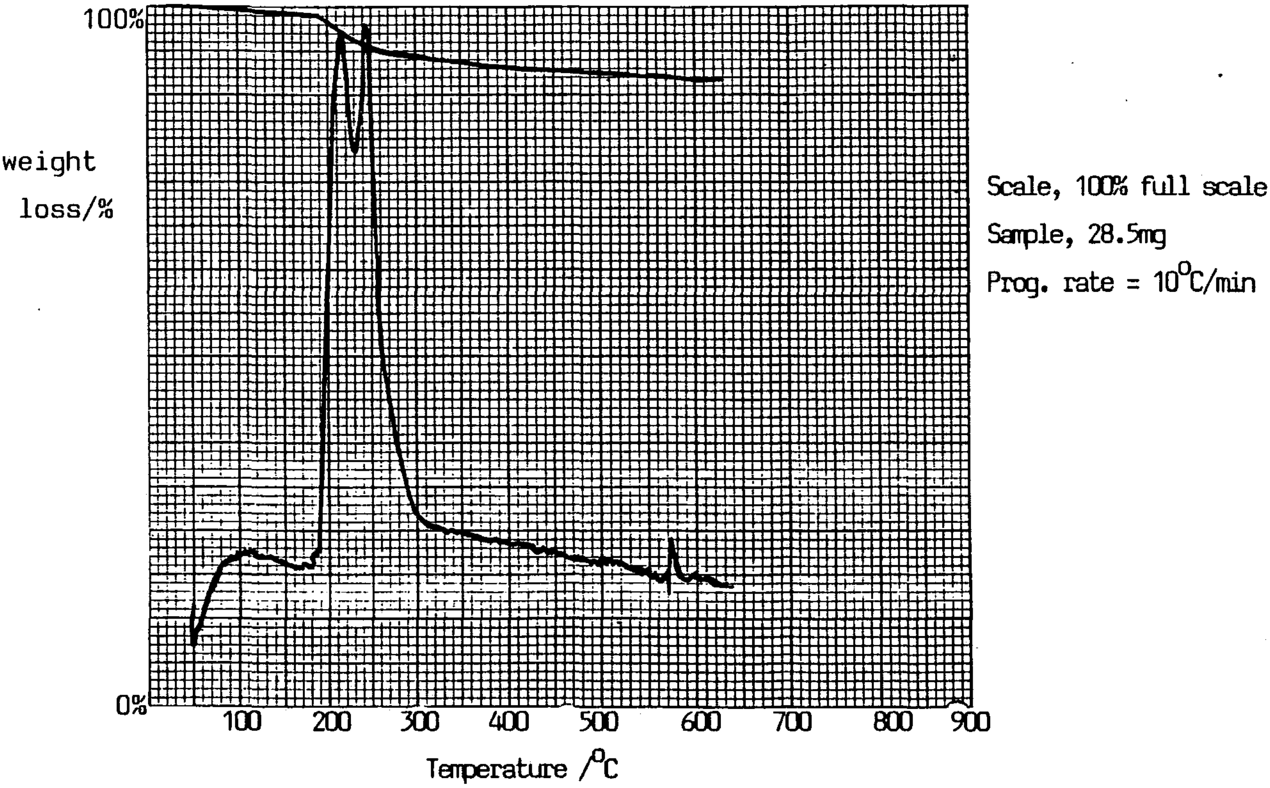
a) sample of copper-aluminium methoxide (A) calcined in air at 200°C for 3 hours: product (CuO/Al_2O_3) is a green black powder. Reduction weight loss is 9.4% at 240°C. Theoretically the weight loss for the conversion CuO/Al_2O_3 - Cu/Al_2O_3 is 8.84%.

b) sample of copper-aluminium methoxide (A) calcined in air at 320°C for 3 hours: product (CuO/Al_2O_3) is a dark black-brown solid. Reduction weight loss occurs in two steps (7.5%) at 250°C and (2.0%) at 120°C. This gives a total weight loss of 9.5% corresponding quite well with the expected value.

c) sample of copper-aluminium methoxide (A) calcined in nitrogen at 230°C for 3 hours: product is a black granular solid. Total weight loss of 8.75% occurs over a wide temperature range.

viii) steps v-vii were repeated for a second sample of the copper-aluminium methoxide (B). This second sample was prepared by an identical route as that for sample (A) but had a slightly different appearance (i.e. blue granular solid rather than blue powder).

a) copper-aluminium methoxide (B) calcined in air at 200-230°C for 3 hours: product is a black-green solid.
Reduction weight loss occurs in two steps, small weight loss (1.25%) upto 150°C and the major weight loss (6.25%) over the temperature range 200-260°C. Note two peaks at 215°C and 245°C. Total weight loss (9.38%) compares well with the theoretical.



b) copper-aluminium methoxide (B) calcined in air at 340°C for 3 hours. Small weight loss (1-2%) upto 150°C and major weight loss (6.25%) at 300°C. Total weight loss of 8.75%.

ix) calcination $Cu[Al(OEt)_4]_2$

Theoretical weight loss for $Cu[Al(OEt)_4]_2 \longrightarrow CuO/Al_2O_3$ = 61.9%
Actual weight loss of 61.5% over a wide temperature upto 350°C

x) reduction $Cu[Al(OEt)_4]_2$

Theoretical weight loss for $Cu[Al(OEt)_4]_2 \longrightarrow Cu/Al_2O_3$ = 65.3%
Actual weight loss occurs in several steps; (26.25%) over the temperature range 60-130°C, (15%) at 200°C and a further weight loss (10%) up to 400°C. Total = 51.25%

xi) steps v-vii were carried for the sample of copper-aluminium ethoxide.

a) sample of copper-aluminium ethoxide calcined in air at 200°C for 3 hours: product is a light green powder.
Reduction weight loss occurs in a series of steps illustrated by the appearance of several sharp peaks at 110°C, 215°C, 355°C and370°C. Total weight loss = 23.75%. This corresponds to a conversion from CuO/Al_2O_3 to (Cu:(1.25)Al: (0.375) Al_2O_3).

b) sample of copper-aluminium ethoxide calcined in air at 340°C for 3 hours: product is a dark green solid. Major reduction weight loss occurs in the temperature range 200-290°C, total weight loss = 16.25%. This corresponds to the conversion from CuO/Al_2O_3 to $Cu.Al.\frac{1}{2}Al_2O_3$.

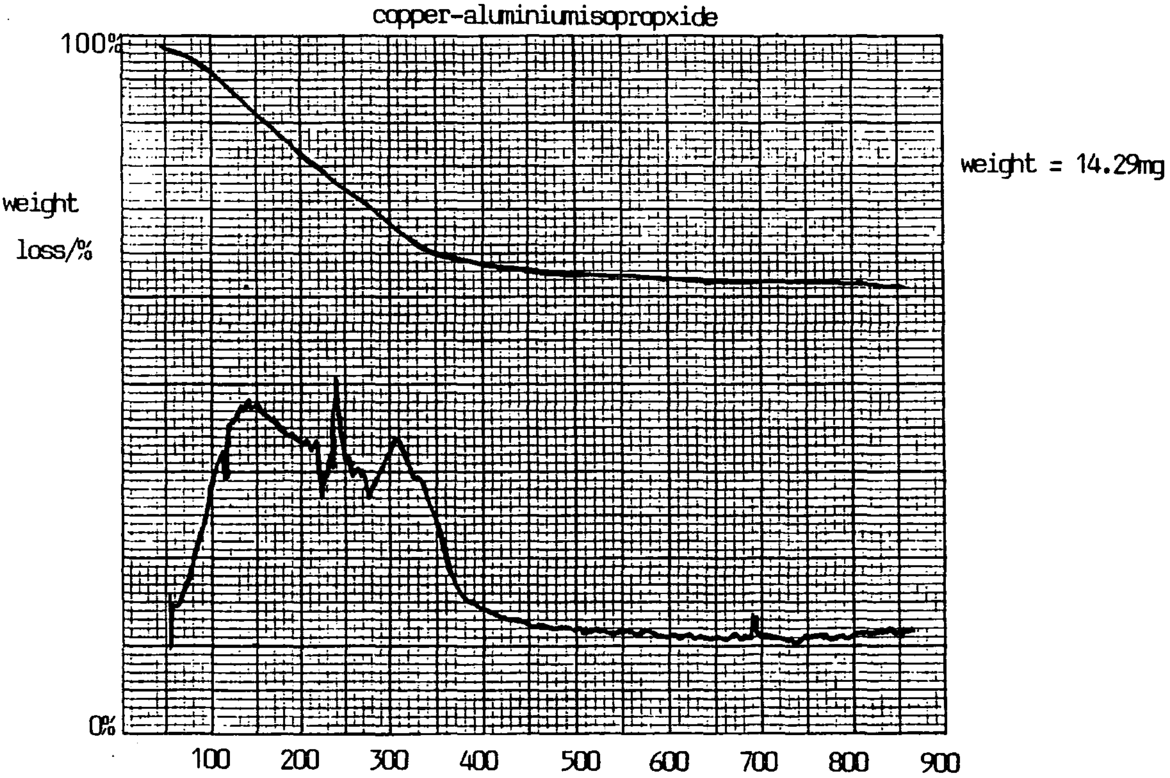
c) sample of copper-aluminium ethoxide calcined under nitrogen at 230°C for 3 hours: product is a brown solid with indications of the presence of copper metal or copper (I)oxide. Major weight loss occurs in the temperature range 200-300°C. Reduction weight loss = 16.25%. This would appear to correspond to the conversion from CuO/Al_2O_3 to $Cu.Al.\frac{1}{2}Al_2O_3$.

xii) calcination of $Cu[Al(OPr^i)_4]_2$

On exposure to air the copper-aluminium isopropoxide rapidly hydrolyses, changing from a green liquid to a blue powder. The handling of the isopropoxide caused difficulties and the nature of the starting materials in these thermogravimetric analyses is uncertain. Working back from the thermogravimetric traces and assuming the end material is CuO/Al_2O_3 the starting material corresponds to the composition $CuAl_2O_6.4H_2O$.

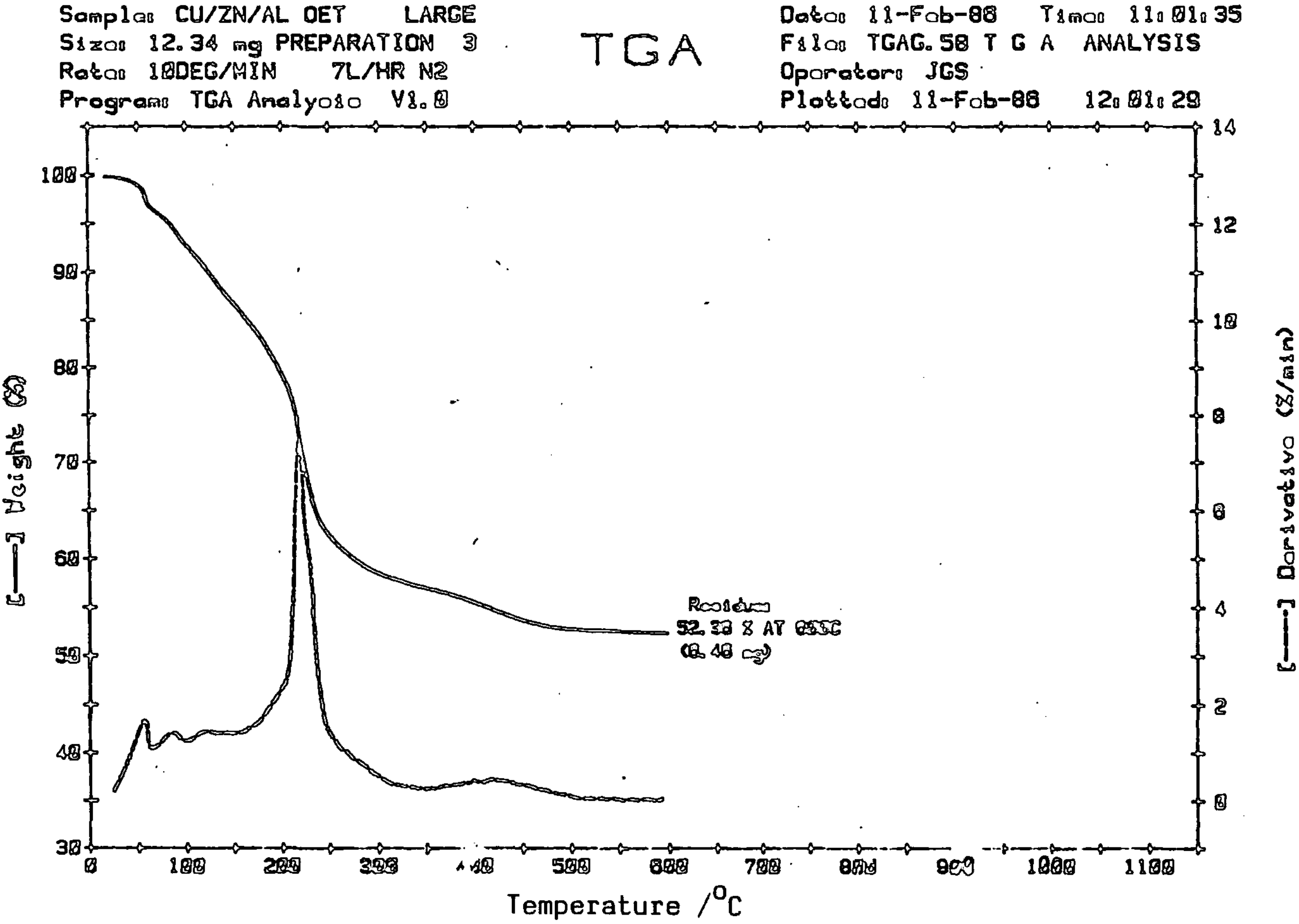
a) sample of copper-aluminiumisopropoxide calcined in air at 200^oC for 3 hours: product is a dark brown solid. Reduction weight loss (7.5%) at 260^oC compares quite well with the theoretical value of 8.84%.

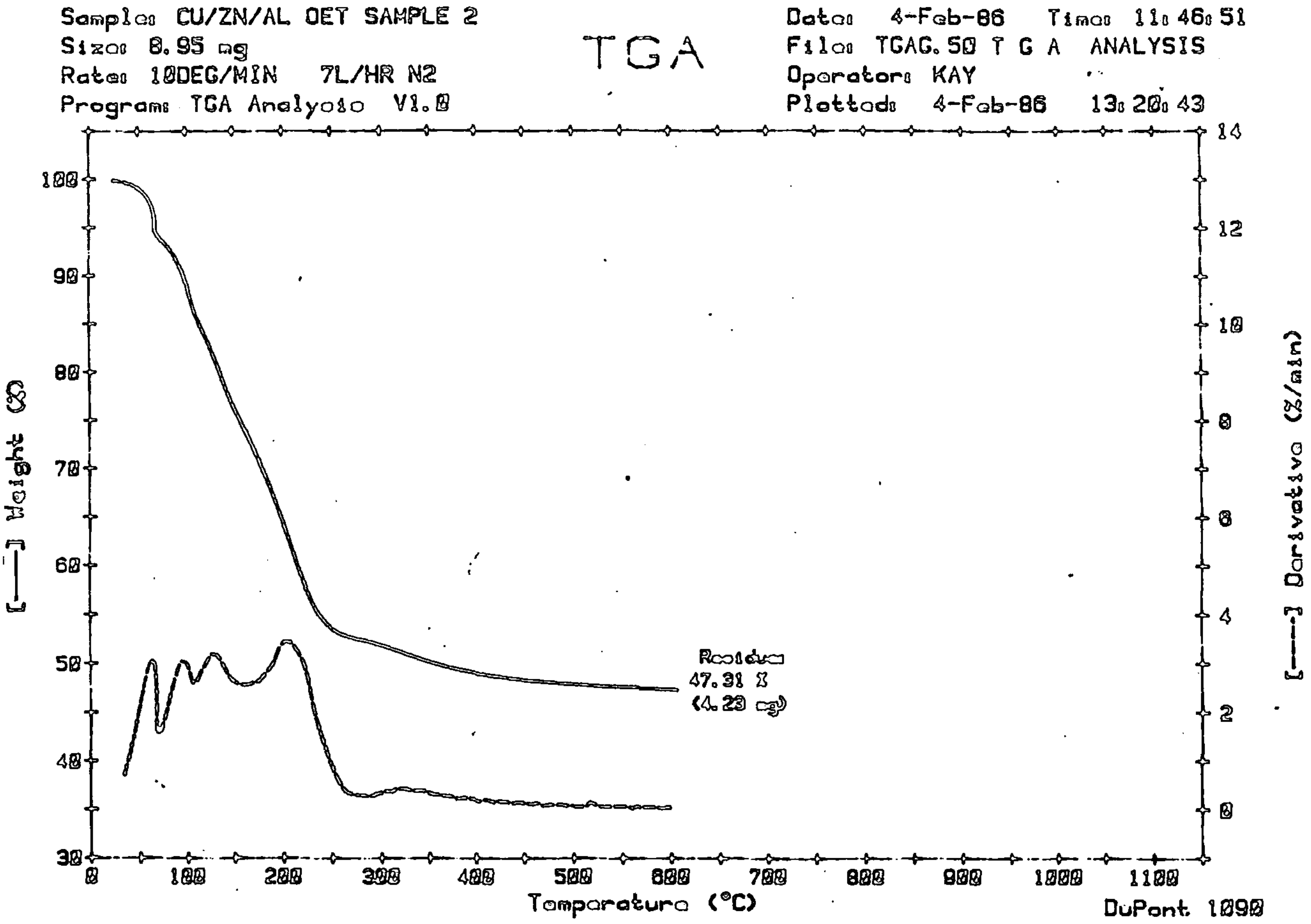
b) sample of copper-aluminium isopropoxide calcined in air for 3 hours at 340^oC: product is ashlike.
Reduction weight loss occurs mainly at 320^oC (8.75%).



xiii) Samples of the copper-zinc-aluminium methoxides and ethoxides were calcined and reduced using thermogravimetric analysis. Some of the resultant traces are shown below which are typical of the results obtained.

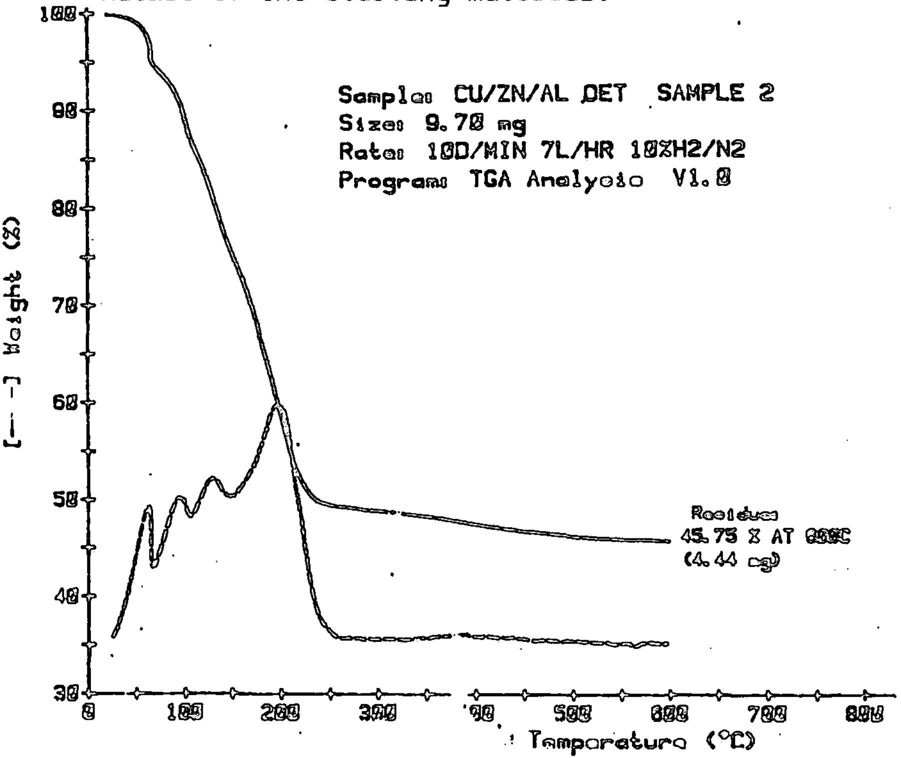
a) copper-zinc-aluminium ethoxide:calcination under nitrogen. Theoretical conversion to a mixture of $CuO/ZnO/Al_2O_3$ would require a weight loss of 61.8%. These traces indicate values somewhat lower than required indicating perhaps that the material is retaining part of the ethoxy group.



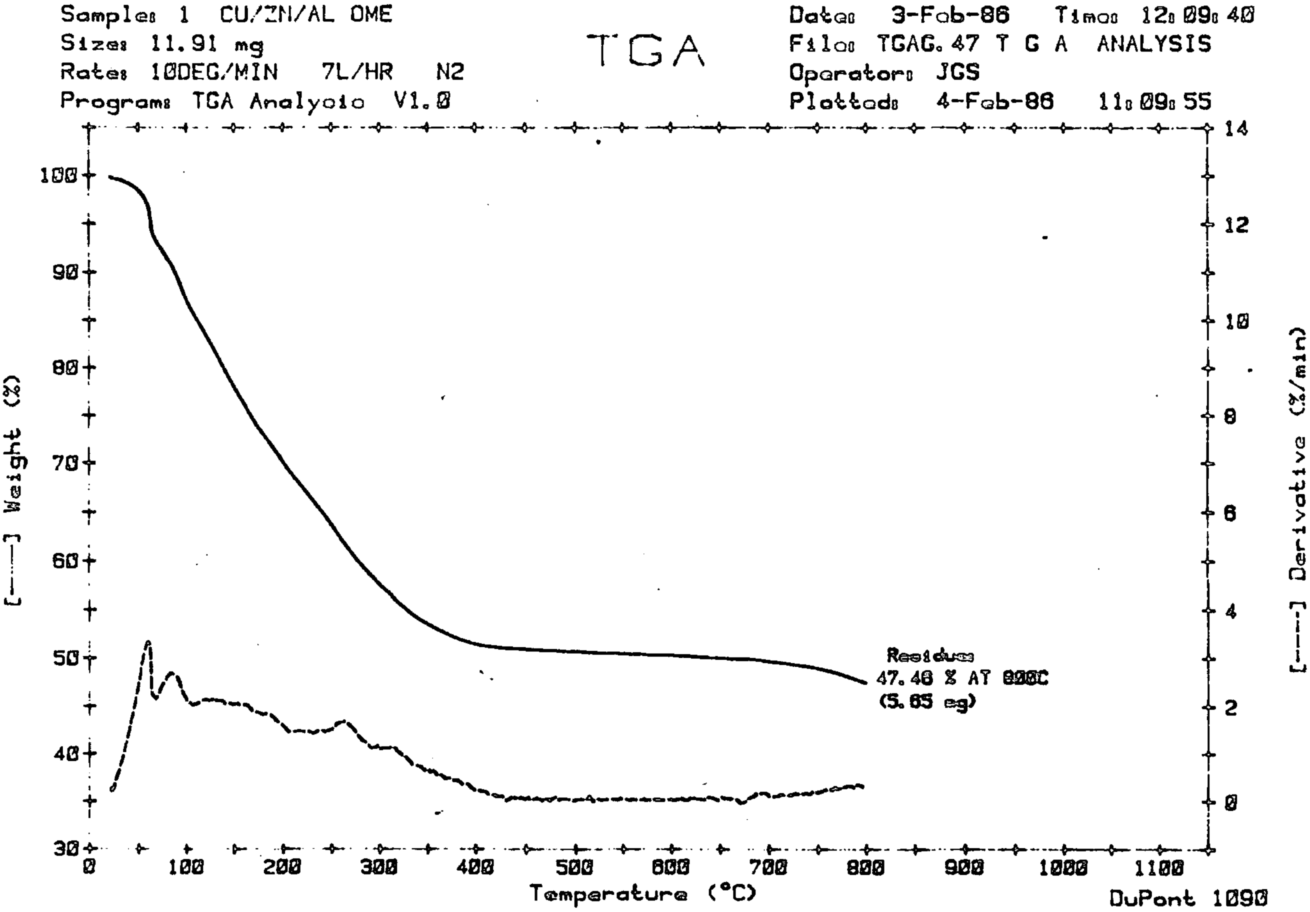


b) copper-zinc-aluminium ethoxide: reduction.

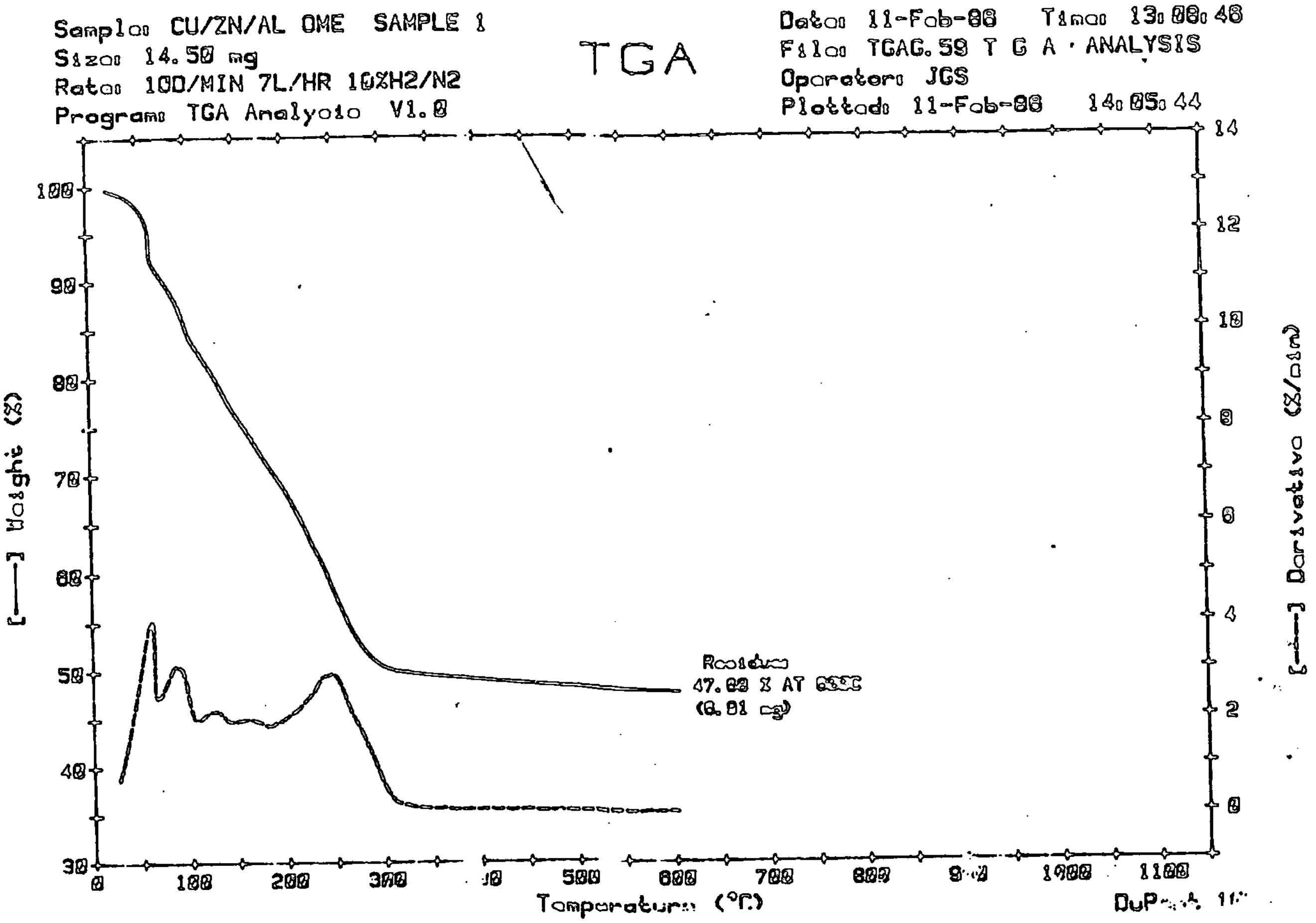
Theoretical conversion to a mixture of $Cu/ZnO/Al_2O_3$ requires a weight loss of 63.5%. As shown in the trace below the weight loss is only 54.25% implying incomplete reduction or unknown nature of the starting material.



c) copper-zinc-aluminium methoxide: calcination under nitrogen. Theoretical conversion to a mixture of $CuO/ZnO/Al_2O_3$ would require a weight loss of 50.2% (49.8% residues). The trace below matches the theoretical value quite well.

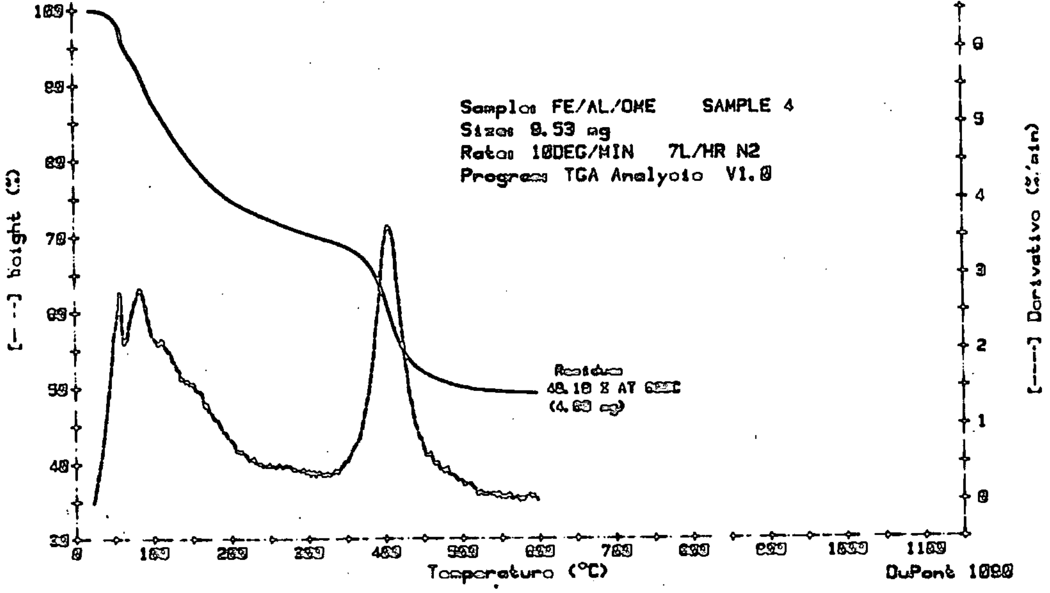


d) copper-zinc-aluminium methoxide: reduction.
Theoretical conversion to a mixture of $Cu/ZnO/Al_2O_3$ would require a weight loss of 52.4% (47.6% residues). This corresponds well with the experimental value.



xiv) calcination and reduction of iron-aluminium methoxide.

Samples of the iron-aluminium isopropoxide were converted to methoxide by alcoholysis reactions. Preliminary thermogravimetric analyses indicated that these materials undergo calcination to Fe_2O_3/ Al_2O_3 (54.2% weight loss, 45.8% residues)



xv) calcination and reduction of precipitated catalyst material. Samples of the prepared NaOH and Na_2CO_3 precipitated catalyst precursors (Cu:Al = 1:2) were tested using thermogravimetric analysis. They both indicated major weight losses in the temperature region up to 350°C corresponding to conversions to Cu/Al_2O_3 and CuO/Al_2O_3.

5.3 (2) Preparation of samples for characterization

Following the thermogravimetric investigations a selection of materials was prepared for analysis by XRD, surface area measurements, copper-surface areas, pore volume and pore size distributions. The results of the thermogravimetric analyses indicated the best temperatures at which to carry out larger scale calcinations and reductions;

1) calcination (N_2 atmosphere) = 300°C
2) reduction (H_2/N_2 atmosphere) = 200-250°C (alkoxides)
= 200-230°C (precipitates)

(note: the precipitated catalyst materials refer to precursors prepared by the precipitation of carbonates and hydroxides by a standard route such that the Cu:Al ratio matches that found in alkoxide precursors)

The following table summarizes the samples used in the subseqeugt investigations.

Sample Code	Description
K1	NaOH ppte; reduced
K2	Na_2CO_3 ppte; reduced
K3	NaOH ppte; fresh
K4	Na_2CO_3 ppte; fresh
K5	NaOH ppte; calcined
K6	Na_2CO_3 ppte; calcined

Sample Code		Description
KM	Cu-Al	Methoxide: fresh
KAM	Cu-Al	Methoxide; air calcined
KBM	Cu-Al	Methoxide; nitrogen calcined
KCM	Cu-Al	Methoxide; reduced (air calcined)
KDM	Cu-Al	Methoxide; reduced (N_2 calcined)
KE	Cu-Al	Ethoxide; fresh
KAE	Cu-Al	Ethoxide; air calcined
KBE	Cu-Al	Ethoxide; nitrogen calcined
KCE	Cu-Al	Ethoxide; reduced (air calcined)
KDE	Cu-Al	Ethoxide; reduced (N_2 calcined)
KI	Cu-Al	Isopropoxide; fresh
KAI	Cu-Al	Isopropoxide; air calcined
KBI	Cu-Al	Isopropoxide; N_2 calcined
KB2I	"	" "
KCI	Cu-Al	Isopropoxide; reduced(air calcined)
KDI	Cu-Al	Isopropoxide; reduced(N_2 calcined)

5.3 (3) XRD analysis

a) Sample preparation

Samples were prepared in a glove box by grinding the solid (calcined or reduced) to a very fine powder. The powder was then compacted into a mould (approx. 20mm diam. 2mm deep) to give a smooth surface. It was imperative that the sample surface did not 'move' during XRD analysis.

b) Results

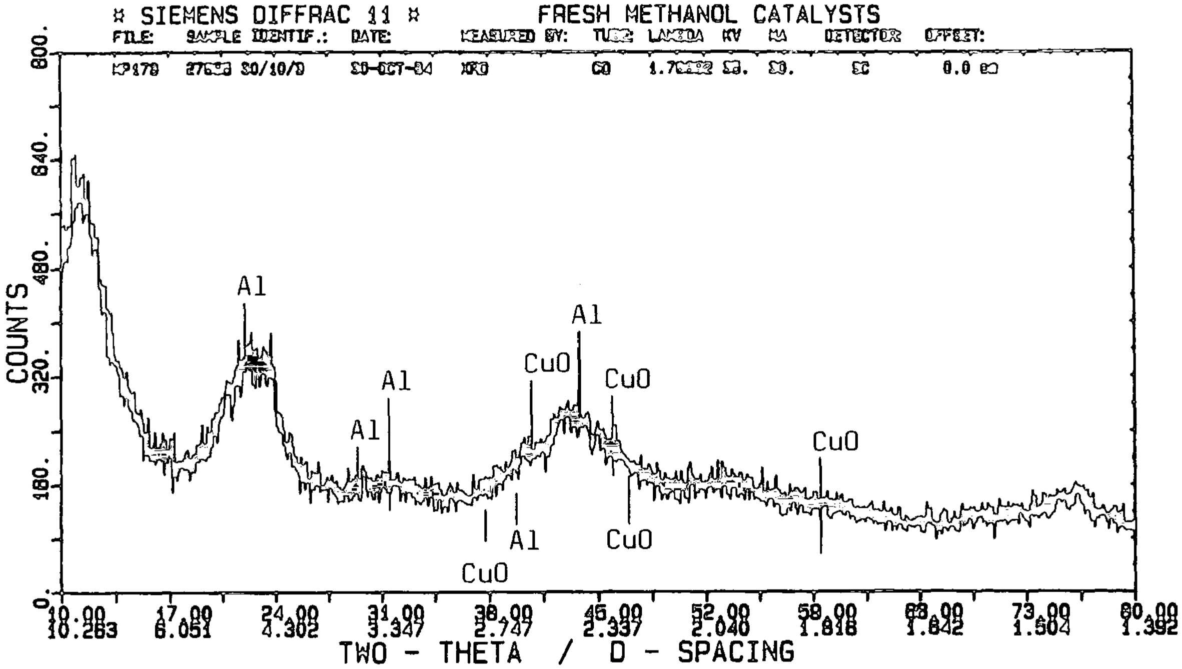
The diffraction patterns shown in the following pages were compared against a file of standards to obtain the best match.

Code	Copper (II) oxide	Copper (I) oxide	Metallic copper	Amorphous	Other
KAM(1)	*	trace	trace		alumina
KAM(2)	*	trace	trace		alumina
KCM	trace	trace	*	Cu-Xline	alumina
KDM	amorphous trace	amorphous trace	* amorphous	*	alumina
KAE(1)	amorphous trace			*	KCl
KAE(2)	*				$NaNO_3$
KCE	trace		*		alumina
KDE	trace		*		alumina
KAI(1)	*	*	*		KCl
KAI(2)	*	*	*		KCl
KCI	* trace		* V. Xline		alumina trace
KDI			* V. Xline		alumina trace
K4	copper present in various forms mainly as malachite (quite crystalline)				$Al(OH)_3$ alumina
K6	copper also present as malachite				"
K2		* trace	*		alumina
K3				*	
K5	*			*	alumina amorph.
K1	* trace		*		alumina

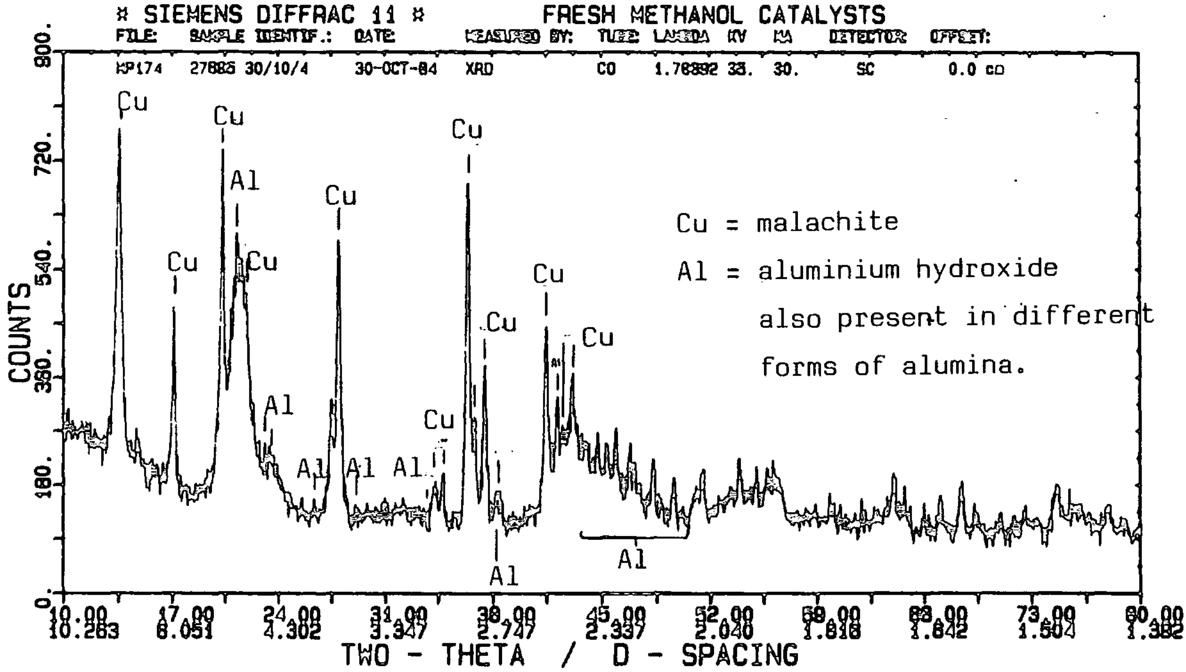
* = indicates presence of line

Xline = crystalline

i) Sample: K3 fresh NaOH ppte



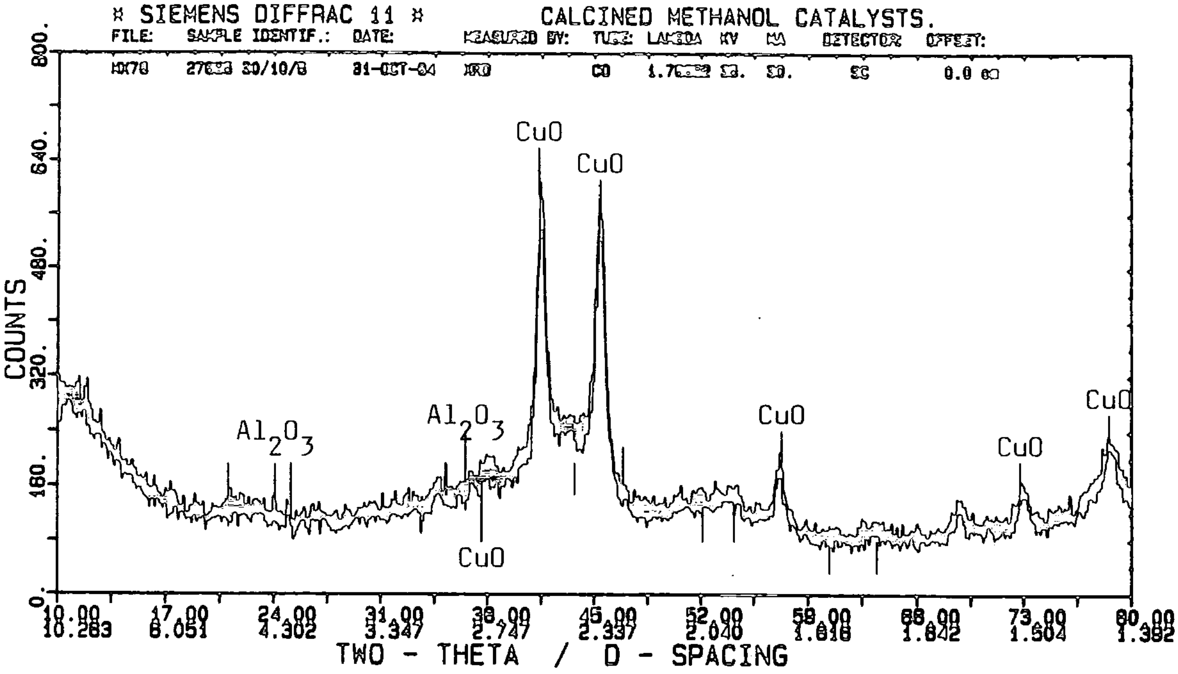
ii) Sample: K4 fresh Na_2CO_3 ppte



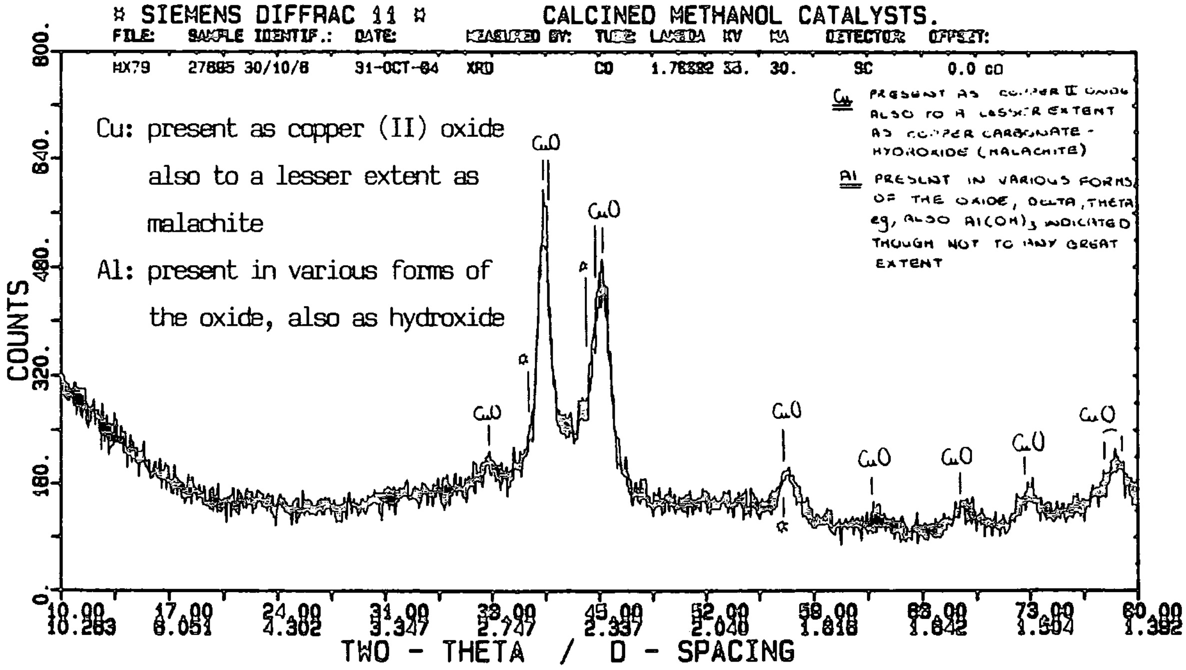
Cu = malachite

Al = aluminium hydroxide also present in different forms of alumina.

iii) Sample: K5 calcined NaOH ppte



iv) Sample: K6 calcined Na_2CO_3 ppte



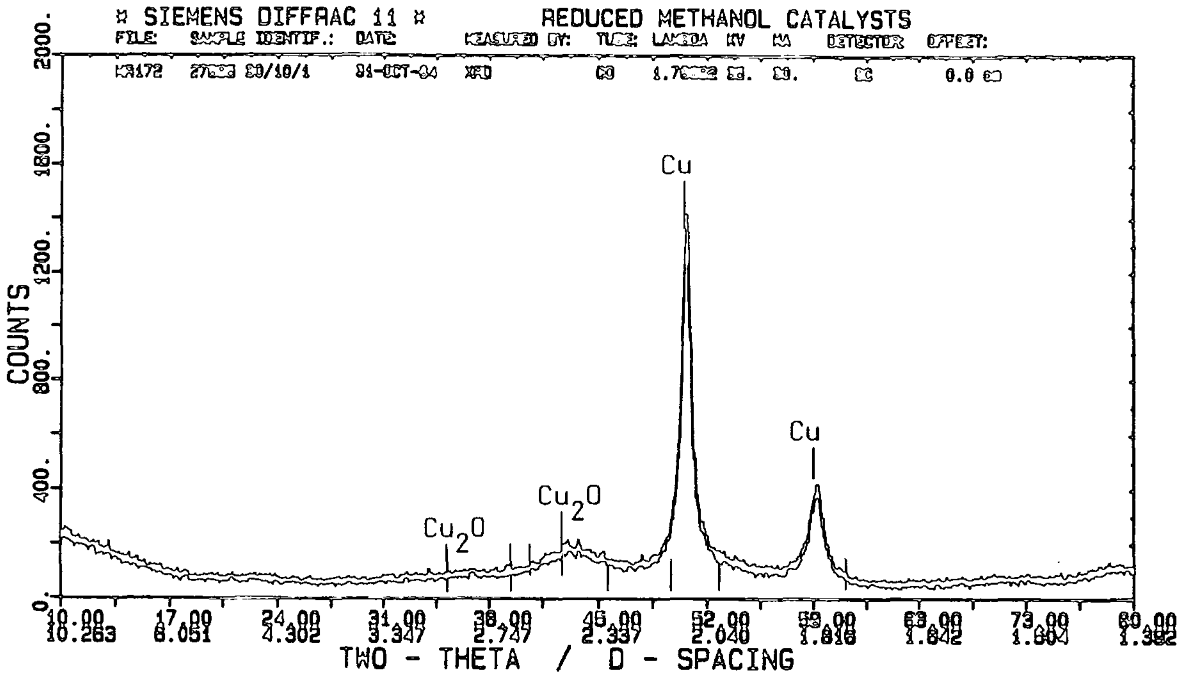
Cu: present as copper (II) oxide also to a lesser extent as malachite

Al: present in various forms of the oxide, also as hydroxide

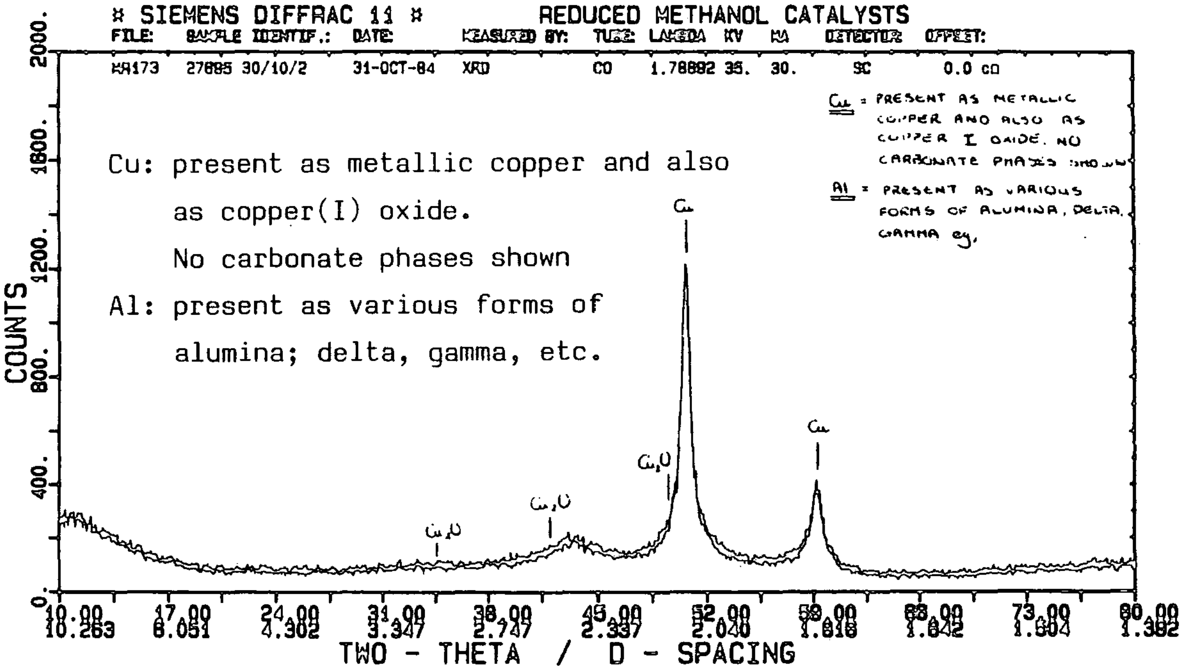
Cu PRESENT AS COPPER II OXIDE ALSO TO A LESSER EXTENT AS COPPER CARBONATE - HYDROXIDE (MALACHITE)

Al PRESENT IN VARIOUS FORMS OF THE OXIDE, DELTA, THETA eg, ALSO Al(OH)3 INDICATED THOUGH NOT TO ANY GREAT EXTENT

v) Sample: K1 reduced NaOH ppte



vi) Sample: K2 reduced Na_2CO_3 ppte



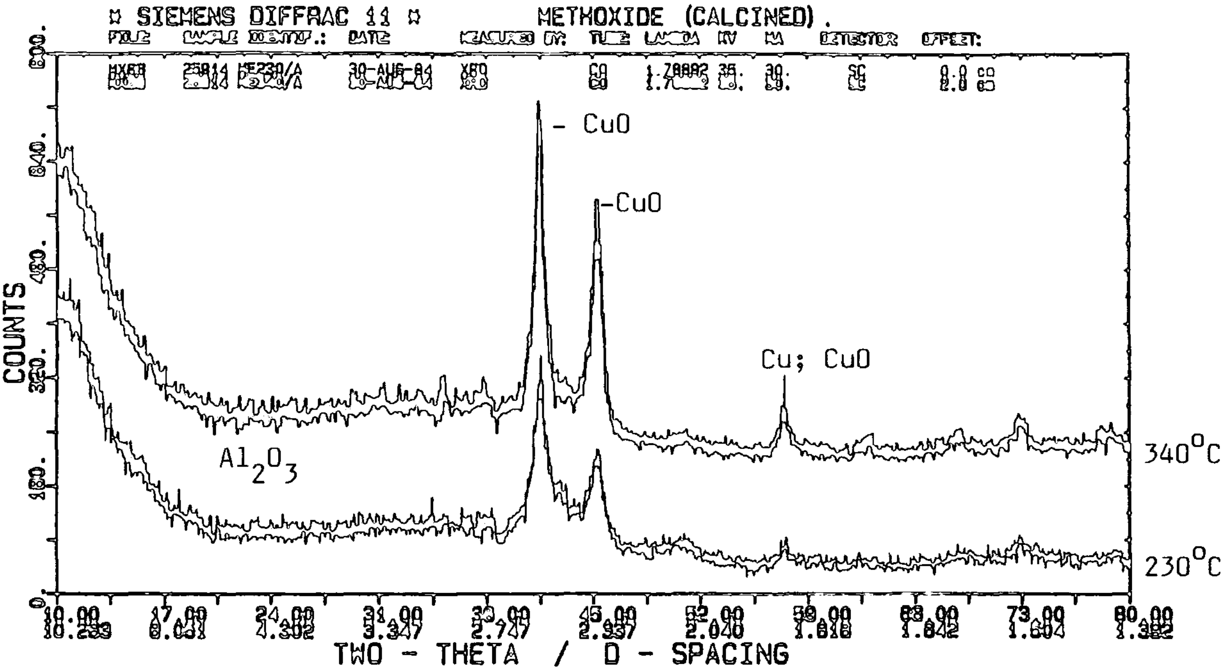
Cu: present as metallic copper and also as copper(I) oxide.
No carbonate phases shown

Al: present as various forms of alumina; delta, gamma, etc.

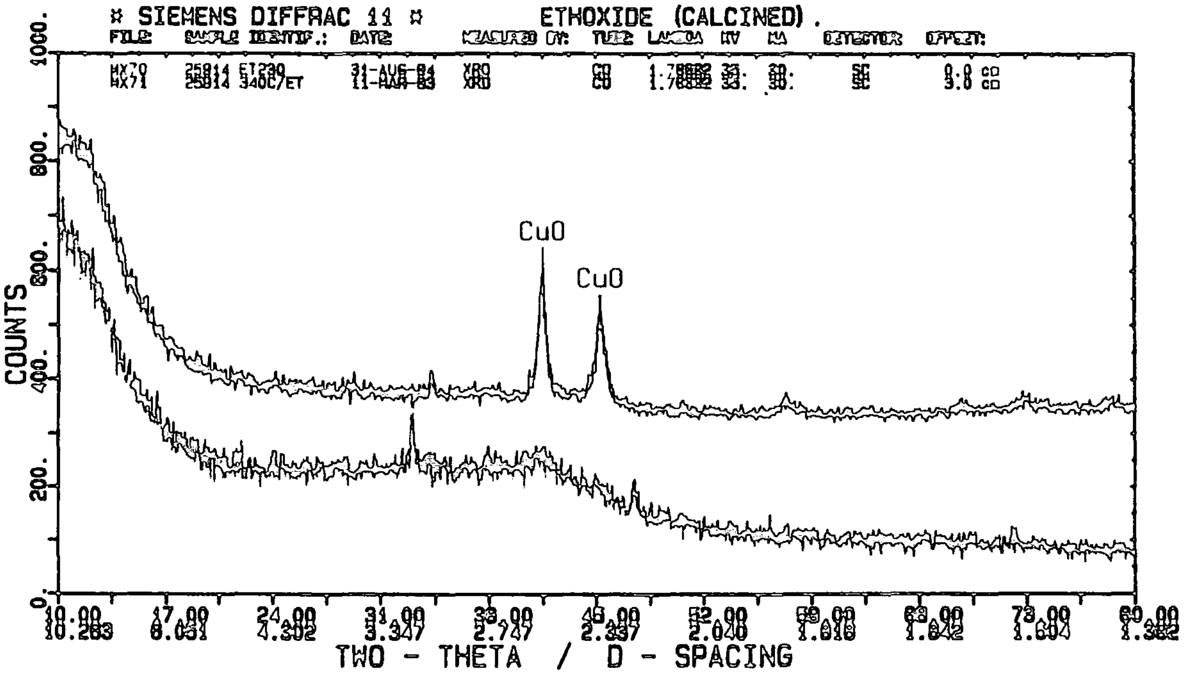
CU = PRESENT AS METALLIC COPPER AND ALSO AS COPPER I OXIDE. NO CARBONATE PHASES SHOWN

AL = PRESENT AS VARIOUS FORMS OF ALUMINA, DELTA, GAMMA eg.

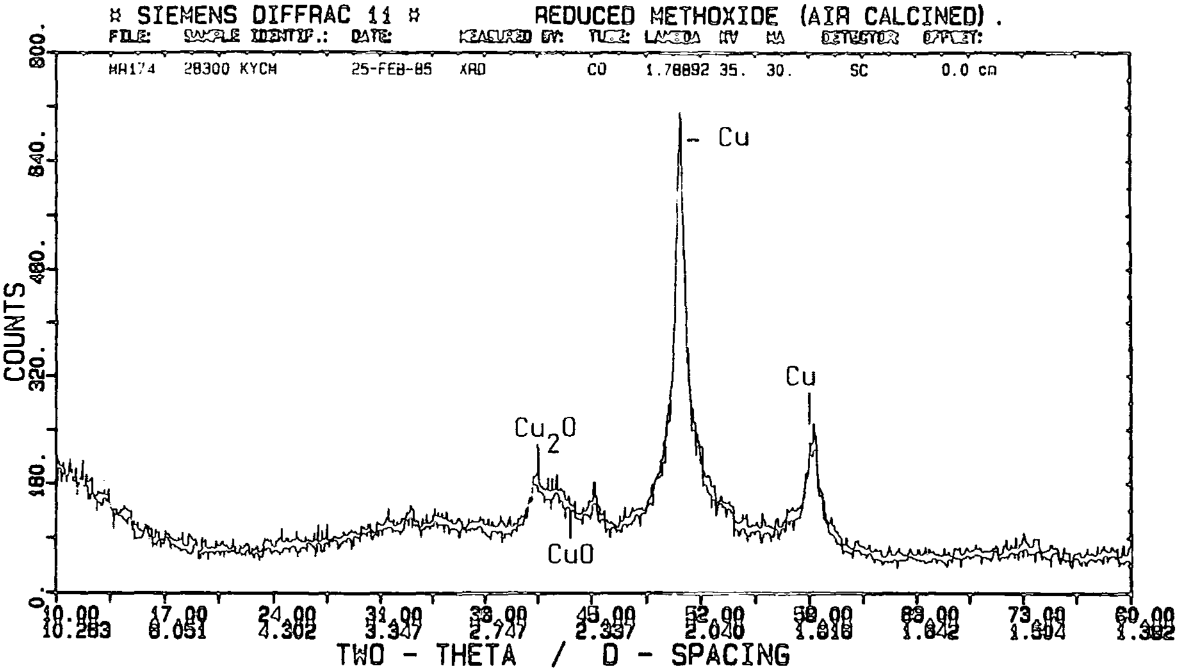
vii) Sample: KAM (1) and (2) methoxide air calcined at 230°C and 340°C



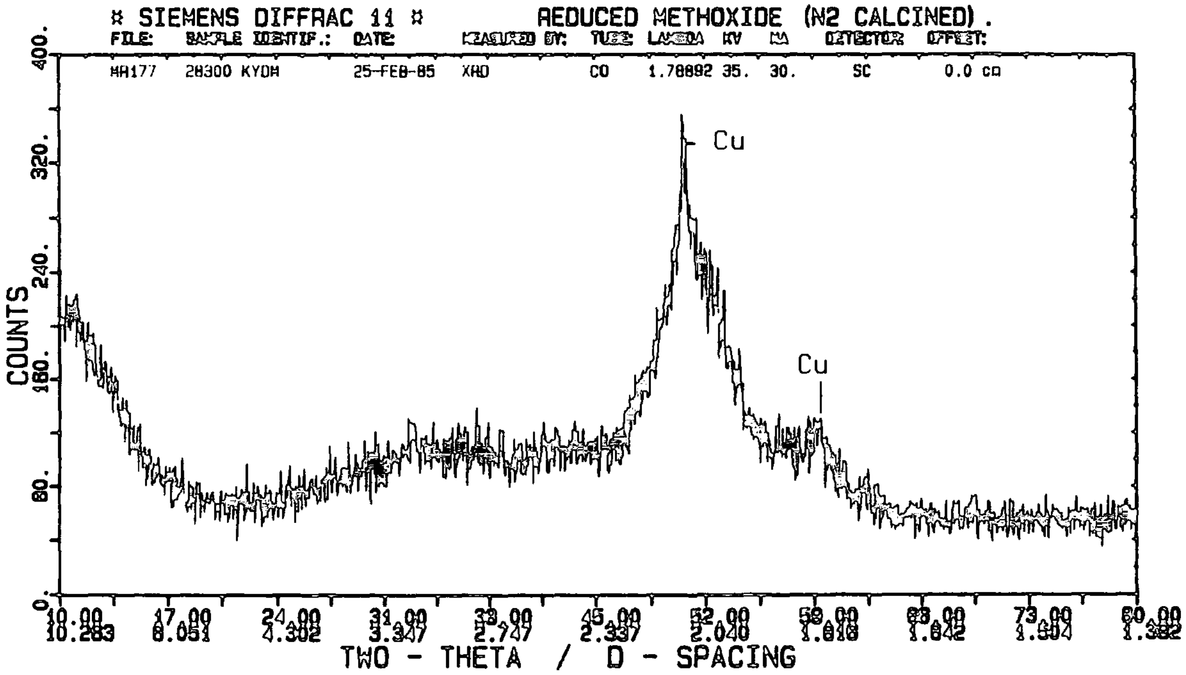
viii) Sample: KAE (1) and (2) ethoxide air calcined at 230°C and 340°C



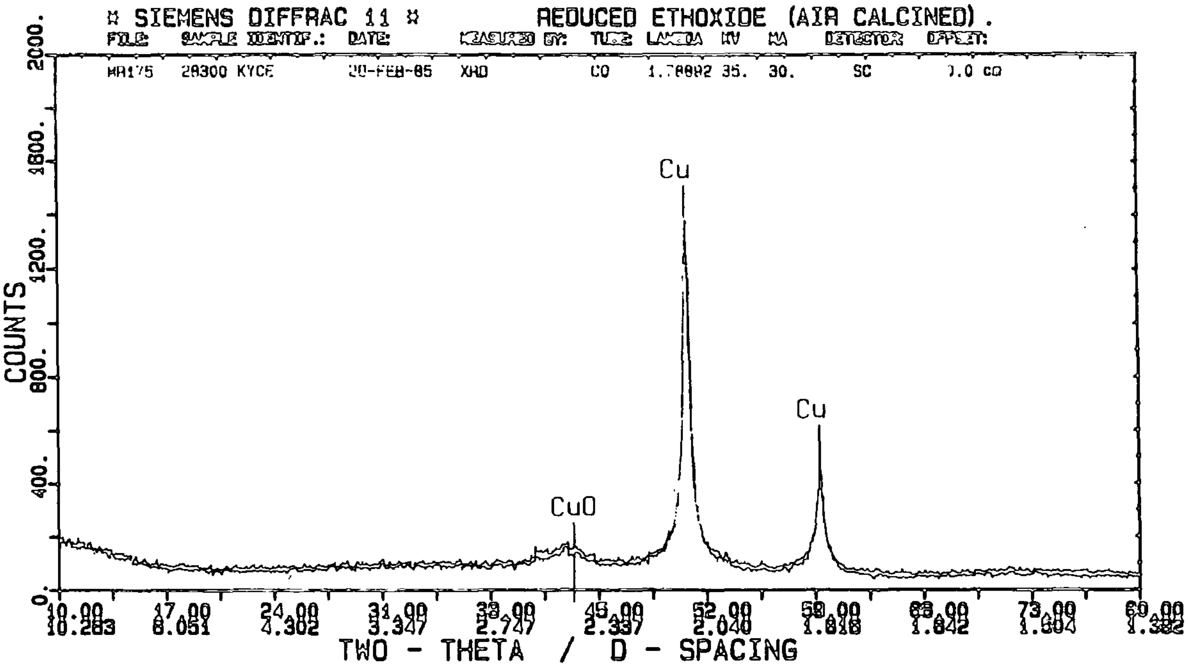
ix) Sample: KCM methoxide reduced (air calcined)



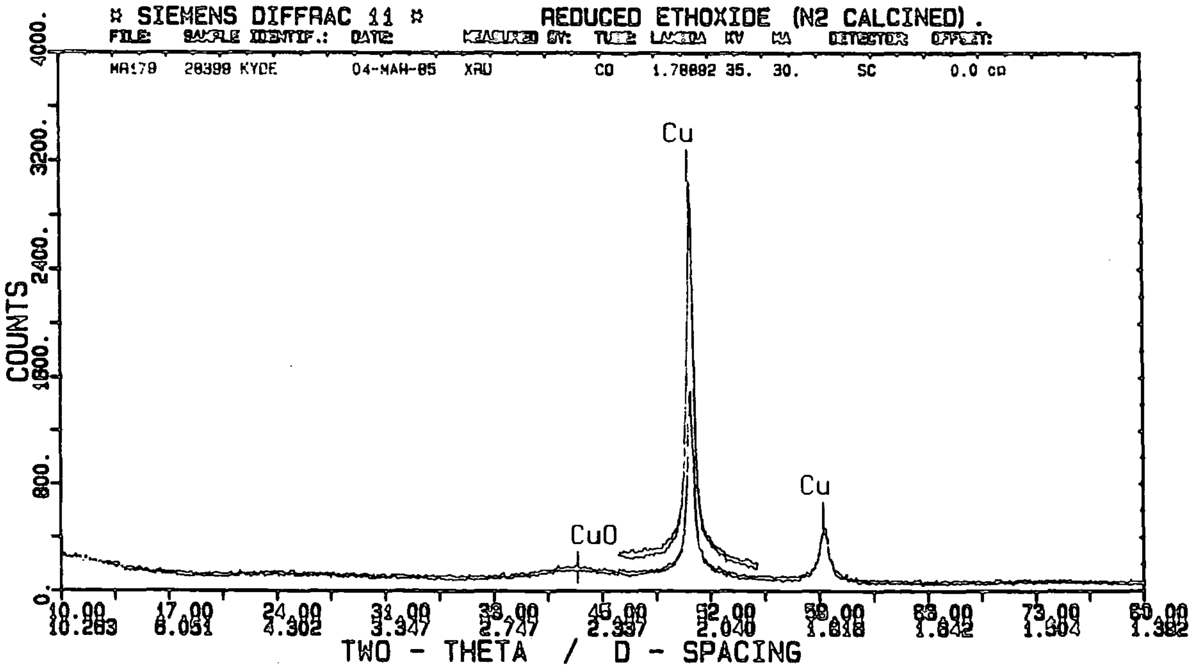
x) Sample: KDM methoxide reduced (nitrogen calcined)



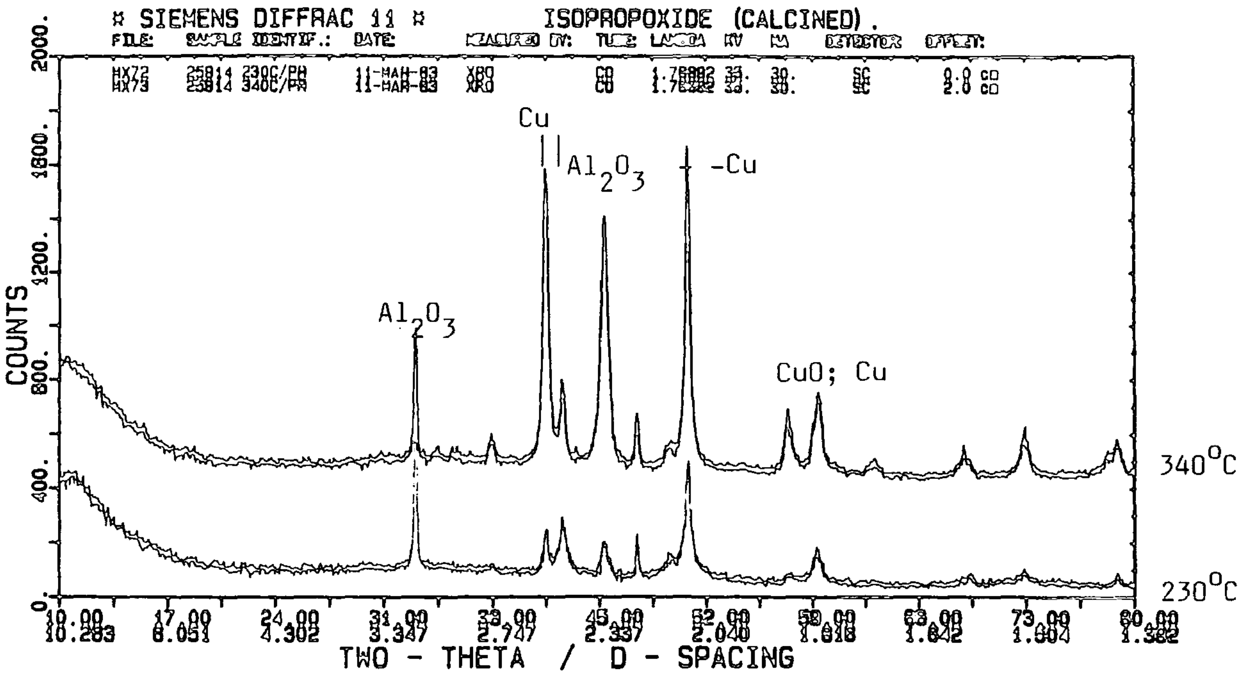
xi) Sample: KCE ethoxide reduced (air calcined)



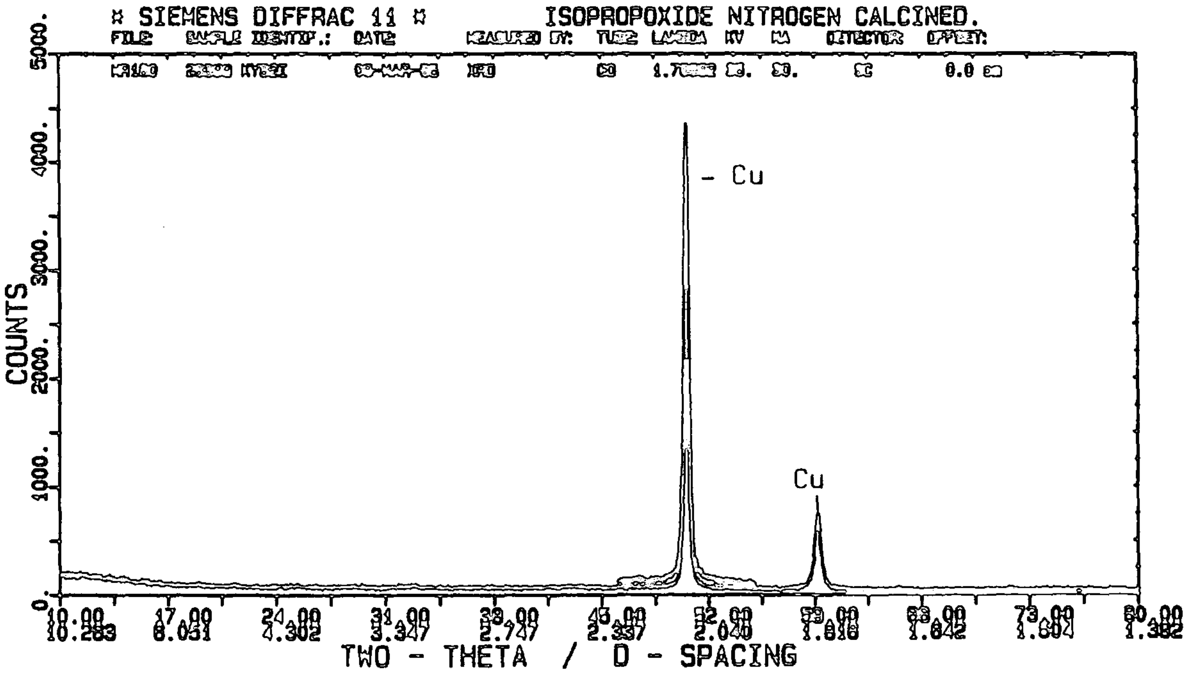
xii) Sample: KDE ethoxide reduced (nitrogen calcined)



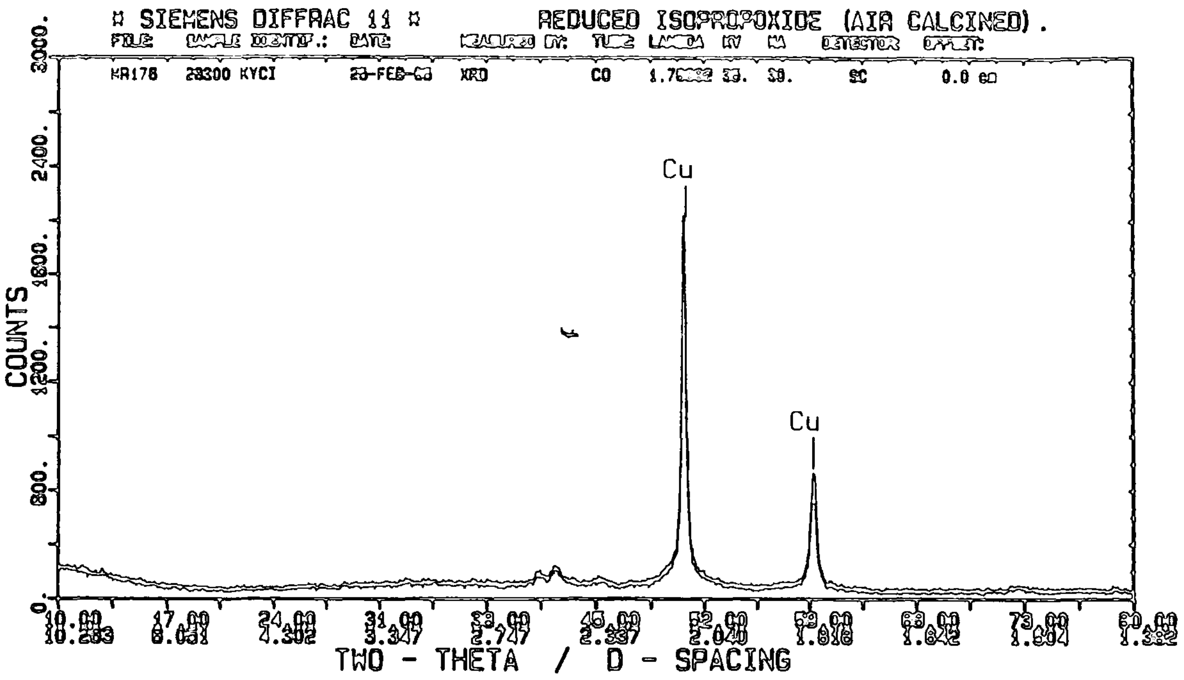
xiii) Sample: isopropoxide air calcined KAI



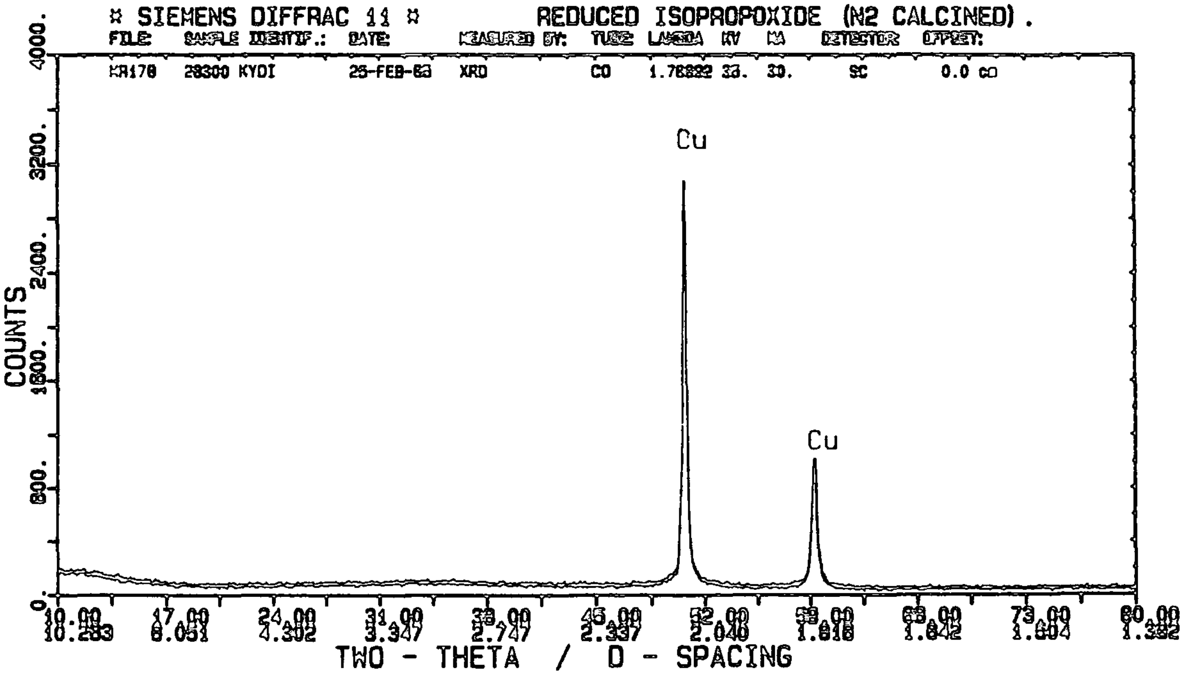
xiv) Sample: KBI isopropoxide nitrogen calcined



xv) Sample: KCI isopropoxide reduced (air calcined)



vvi) Sample: KDI isopropoxide reduced (nitrogen calcined)



5.3 (4) Mean crystallite sizes

From line broadening analysis mean crystallite sizes were determined for several of the samples. However it would appear that the copper diffraction lines are lying on top of broader alumina lines. This would have the effect of distorting the crystallite figures to lower values. Hence the figures are not reliable and can only be used in a comparative sense.

Sample	Mean Crystallite size / nm
K1	9.0
KCM	6.0
KDE	24.0
KBI	34.0
KCI	50.0

5.3 (5) Surface areas

Surface areas were measured by mercury porosimetry and nitrogen adsorption method (BET). The values obtained by these two methods should be in close agreement. However if there are pores below 3.75nm then there will be a variation in the results. The surface area determined by the BET method should be taken as the true total surface area of a sample. Values for 'surface area covered' correspond only to the area of pores down to 3.75nm radius. High surface area materials generally have the larger portion of their areas associated with pores below 3.75nm i.e. below the detection limit of the porosimeter.

Sample	BET surface area m^2/g	'surface area covered' m^2/g
K1	228.9	/
K2	234.1	/
K3	56.2	6.1
K4	102.2	128.0
K5	147.6	137.4
K6	160.1	131.0

Sample	BET surface area m^2/g	'surface area covered' m^2/g
KAM	24.4	/
KBM	64.2	/
KCM	36.7	/
KDM	48.4	/
KAE	217.3 (microporous)	/
KCE	192.1 (microporous)	/
KBI	113.5	/
KDI	104.6	/

5.3 (6) Cumulative pore volumes

Sample	Cumulative pore volume cm^3/g
K1	0.291
K2	0.548
K3	0.070
K4	0.323
K5	0.309
K6	0.460
KAM	0.075
KBM	0.155
KCM	0.110
KDM	0.129
KAE	0.061 (microporous)
KCE	0.076 (microporous)
KBI	0.097
KDI	0.101

5.3 (7) Copper surface areas

Sample	Copper surface area m^2/g	sample/ STD 51-2
STD 51-2	30.9	
K1	6.5	0.21
K2	1.0	0.03
KCM	5.1	0.17
KDM	2.8	0.09
KCE	2.1	0.07
KCI	2.4	0.08
KDI	4.3	0.14
(KDE & KBI less than 0.5)		

SUMMARY

SAMPLE	COPPER SURFACE AREA m^2/g	BET SURFACE AREA m^2/g	CUMULATIVE PORE VOLUME cm^3/g	MEAN X-lite size/nm
K1	6.5	228.9	0.291	9.0
K2	1.0	234.1	0.548	/
K3	/	56.2	0.070	/
K4	/	102.2	0.323	/
K5	/	147.6	0.309	/
K6	/	160.1	0.460	/
KAM	/	24.4	0.075	/
KBM	/	64.2	0.155	/
KCM	5.1	36.7	0.110	6.0
KDM	2.8	48.4	0.129	/
KAE	/	217.3 (microporous)	0.061 (microporous)	/
KCE	2.1	192.1 (microporous)	0.076 (microporous)	/
KBI	/	113.5	0.097	34.0
KCI	2.4	/	/	50.0
KDI	4.3	104.6	0.101	
				(KDE = 24.0)

CHAPTER 6

CHAPTER 6

SUMMARY DISCUSSION AND FUTURE WORK

The alkoxides are interesting compounds ranging from electrovalent, polymeric solids to covalent, monomeric liquids. The nature of the metal alkoxides is dependent to a large extent on the nature of the alkoxy group and the ratio of alkoxy groups to metals.

From the results obtained during the course of this project there would appear to be some correlation between the nature of the alkoxy precursor and the properties of the catalytically active product.

There are many aspects of this work which require further investigation and study to extend the findings of this preliminary research.

The method used to prepare the alkoxides is relatively straightforward if time consuming. Problems were encountered with nickel and it was not possible to repeat the reported synthesis[133]. The use of metal chlorides presented some problems with the possibility of chloride remaining in the catalytically active material. This problem was overcome, to a large extent, by repeated washings with pentane to remove residual potassium chloride. In most of the later syntheses, chloride could not be detected in the alkoxide sample.

A halide-free route would remove the problem totally and some thought has been given to the development of a new synthesis route. The acetates or acetylacetonates of the metals could provide one pathway to the metal alkoxides.

In relation to this problem, a useful study would be the determination of the levels of chloride in a catalyst sample and the effect of these various levels on the extent of sintering in copper catalysts.

The observed thermal decomposition of the bimetallic (and single metal) alkoxides provides another area for experimentation. A useful study would involve following the thermal decomposition of alkoxides by detection and analysis of the volatile species (GC-mass spec ?) produced. Ascertaining what species are produced in the vapour would have a bearing on the methods of treatment for converting the alkoxides into catalytically active materials. This type of study should focus on the decomposition of the copper-aluminium isopropoxide which affords a copper mirror when heated in a stream of nitrogen. The formation of a copper-formate is possible. The copper-aluminium isopropoxide is volatile and may undergo a decomposition to produce alkenes (there is evidence of propene formation in the mass spectra of aluminium triisopropoxide and cobalt-aluminium isopropoxide) or hydrogen.

Due to the number of tests required per sample this study was limited to three alkoxy derivatives of copper with aluminium. There is clearly some effect on the final properties of the catalyst material related to the nature of the alkoxide precursor. To gain a better idea of the effect of the alkoxide group it would be advantageous to extend the range of alkoxy derivatives. A suggestion would be to prepare alkoxides of straight chain alcohols and examine the effect of increase in chain length on such properties as metal surface area, total surface area and crystallite size. This range could then be extended further to include isomeric alkoxides (looking at chain branching effects) and also mixed alkoxy-alkoxides. This increased range of alkoxides would allow the identification of any pattern in properties. There would be the added possibility that it may prove feasible to tailor the alkoxide precursor to provide the required properties.

The final test for these experimental precursors would be to assess their activity towards methanol synthesis. This would require the use of continuous-flow micro-reactors.

A more extensive study of the surface properties of these compounds could be carried out. This could involve the use of surface techniques including ESCA, SIMS, electron microscopy in addition to the techniques already discussed here.

The problem with synthesising nickel alkoxides could be overcome if a reactive from of nickel could be prepared in situ, e.g. bis-pi-allyl nickel.

The use of alkoxides as catalyst precursors poses some problems because of their sensitive nature. The formation of alkoxy derivatives containing diols would lead to species with much greater resistance to hydrolysis and, therefore, facilitate handling.

The presence of formate intermediates on the surface of supported copper catalysts during methanol synthesis suggests that metal carboxylates may prove to be useful precursors to catalytically active materials. This topic is being investigated at Durham and forms the basis of a Ph.D research project.

The initial findings of this work are sufficiently encouraging to warrant further research into some of the questions raised. The continuing need to improve catalytic processes and catalysts will necessarily involve the study of experimental precursors, such as alkoxides, in addition to improving existing materials. This is particularly important to the petrochemicals industries since the supply of oil is finite and maintenance of the present chemical profile of todays society will rely increasingly on the production of synthetic materials from synthesis gas derived from other hydrocarbon sources.

APPENDIX 1

GENERAL TECHNIQUES

1. Nitrogen supply.

Nitrogen gas was supplied to the laboratory as boil off from a liquid nitrogen tank, having been passed through a deoxygenation plant. The gas was dried at the bench by passage through columns packed with Phosphorus Pentoxide and A4 molecular sieve.

2. Manipulation of air and moisture sensitive compounds.

All such compounds were manipulated inside a glove box purged with nitrogen gas, or using standard vacuum line techniques.

3. Chemical Analysis.

Carbon, hydrogen and nitrogen were determined on a Carlo Erba Strumentzione Elemental Analyser (model 1106). Metals were determined on a Perkin Elmer 5000 Atomic Absorption Spectrophotometer. Halogens were determined by oxygen flask combustion followed by potentiometric titration.

4. Infra Red Spectroscopy.

I.R. spectra in the range 4000-250 cm^{-1} were recorded on Perkin Elmer 457 or 577 grating spectrometers. Samples were mounted as nujol mulls or contact films between KBr plates.

5. Thermogravimetric Analysis.

T.G.A. was carried out using a Du Pont 951 thermogravimetric analyser coupled to a Du Pont 990 thermal analyser. Later samples were run on a Du Pont 1050 analyser. All analyses were carried out at I.C.I. Billingham.

6. X-Ray Powder Diffraction.

All measurements were made using a Siemens 11 Diffractometer. Fe filtered Co radiation [$\lambda(K\alpha)$= 1.78892 Å] was used to obtain diffraction patterns.

7. Surface Area Determination.

BET surface areas were determined by nitrogen absorption using isotherms generated gravimetrically. Copper metal areas were determined by the N_2O decomposition method. This work was kindly carried out by personnel at I.C.I. Billingham.

APPENDIX 2

RESEARCH COLLOQUIA, SEMINARS, LECTURES, MEETINGS AND CONFERENCES

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix, listing:

(a) all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(b) lectures organised by Durham University Chemical Society;

(c) all research conferences and meetings attended and papers presented by the author during the period when research for the thesis was carried out;

(d) details of the postgraduate induction course.

(a) LECTURES ORGANISED BY DURHAM UNIVERSITY 1983 - 1986

5.10.83	Prof. J.P. Maier (Basel, Switzerland) "Recent approaches to spectroscopic characterization of cations".
12.10.83	Dr. C.W. McLeland (Port Elizabeth, Australia), "Cyclization of aryl alcohols through the intermediacy of alkoxy radicals and aryl radical cations".
19.10.83	Dr. N.W. Alcock (Warwick), "Aryl tellurium (IV) compounds, patterns of primary and secondary bonding".

26.10.83	Dr. R.H. Friend (Cavendish, Cambridge). "Electronic properties of conjugated polymers".
30.11.83	Prof. I.M.G. Cowie (Stirling), "Molecular interpretation of non-relaxation processes in polymer glasses".
2.12.83	Dr. G.M. Brooke (Durham), "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoro-aryl and -hetero-aryl systems".
14.12.83	Prof. R.J. Donovan (Edinburgh), "Chemical and physical processes involving the ion-pair states of the halogen molecules".
10. 1.84	Prof. R. Hester (York) "Nanosecond Laser Spectroscopy of Reaction Intermediates".
18. 1.84	Prof. R.K. Harris (UEA) "Multi-nuclear solid state magnetic resonance".
8. 2.84	Dr. B.T. Heaton (Kent), "Multi-nuclear NMR studies".
15. 2.84	Dr. R.M. Paton (Edinburgh) "Heterocyclic Syntheses using Nitrile Sulphides".
7. 3.84	Dr. R.T. Walker (Birmingham), "Synthesis and Biological Properties of some 5-substituted Uracic Derivatives; yet another example of serendipity in Anti-viral Chemotherapy".
21. 3.84	Dr. P. Sherwood (Newcastle) "X-ray photoelectron spectroscopic studies of electrode and other surfaces".
21. 3.84	Dr. G. Beamson (Durham/Kratos) "EXAFS: General Principles and Applications.
23. 3.84	Dr. A. Ceulemans (Leuven) "The Development of Field-Type models of the Bonding in Molecular Clusters".
2. 4.84	Prof. K. O'Driscoll (Waterloo) "Chain Ending reactions in Free Radical Polymerisation".
3. 4.84	Prof. C.H. Rochester (Dundee). "Infrared Studies of adsorption at the Solid-Liquid Interface".

25. 4.84	Dr. R.M. Acheson (Biochemistry, Oxford) "Some Heterocyclic Detective Stories".
27. 4.84	Dr. T. Albright (Houston, U.S.A.) "Sigmatropic Rearrangements in Organometallic Chemistry".
14. 5.84	Prof. W.R. Dolbier (Florida, U.S.A.). "Cycloaddition Reactions of Fluorinated Allenes".
16. 5.84	Dr. P.J. Garratt (UCL) "Synthesis with Dilithiated Vicinal Diesters and Carboximides".
22. 5.84	Prof. F.C. de Schryver (Leuven) "The use of Luminescence in the study of micellar aggregates" and "Configurational and Conformational control in excited state complex formation".
23. 5.84	Prof. M. Tada (Waseda, Japan) "Photochemistry of Dicyanopyrazine Derivatives".
31. 5.84	Dr. A. Haaland (Oslo) "Electron Diffraction Studies of some organometallic compounds.
11. 6.84	Dr. J.B. Street (IBM, California) "Conducting Polymers derived from Pyrroles".
19. 9.84	Dr. C. Brown (IBM, California) "New Superbase reactions with organic compounds".
21. 9.84	Dr. H.W. Gibson (Signal UOP, Illinois) "Isomerization of Polyacetylene".
19.10.84	Dr. A. Germain (Languedoc, Montpellier) "Anodic Oxidation of Perfluoro Organic Compounds in Perfluoroalkane Sulphonic Acids".
24.10.84	Prof. R.K. Harris (Durham) "N.M.R. of Solid Polymers".
28.10.84	Dr. R. Snaith (Strathclyde) "Exploring Lithium Chemistry: Novel Structures, Bonding and Reagents".
7.11.84	Prof. W.W. Porterfield (Hampden-Sydney College, USA) "There is no Borane Chemistry (only Geometry)".
7.11.84	Dr. H.S. Munro (Durham) "New Information from ESCA Data".

21.11.84	Mr. N. Everall (Durham) "Picosecond Pulsed Laser Raman Spectroscopy".
27.11.84	Dr. W.J. Feast (Durham) "A Plain Man's Guide to Polymeric Organic Metals".
28.11.84	Dr. T.A. Stephenson (Edinburgh) "Some recent studies in Platinum Metal Chemistry".
12.12.84	Dr. K.B. Dillon (Durham) "31p N.M.R. Studies of some Anionic Phosphorus Complexes".
11. 1.85	Emeritus Prof. H. Suschitzky (Salford) "Fruitful Fissons of Benzofuroxanes and Isobenzimic azoles (umpolung of <u>o</u>-phenylenediamine)".
13. 2.85	Dr. G.W.J. Fleet (Oxford) "Synthesis of some Alkaloids from Carbohydrates".
19. 2.85	Dr. D.J. Mincher (Durham) "Stereoselective Synthesis of some novel Anthracyclinones related to the anti-cancer drug Adriamy and to the Steffimycin Antibiotics".
27. 2.85	Dr. R. Mulvey (Durham) "Some unusual Lithium Complexes".
6. 3.85	Dr. P.J. Kocienski (Leeds) "Some Synthetic Applications of Silicon-Mediated Annulation Reactions".
7. 3.85	Dr. P.J. Rodgers (I.C.I. plc. Agricultural Division, Billingham) "Industrial Polymers from Bacteria".
12. 3.85	Prof. K.J. Packer (B.P. Ltd./East Anglia) "N.M.R. Investigations of the Structure of Solid Polymers".
14. 3.85	Prof. A.R. Katritzky F.R.S. (Florida) "Some Adventures in Heterocyclic Chemistry".
20. 3.85	Dr. M. Poliakoff (Nottingham) "New Methods for detecting Organometallic Intermediates in Solution".
28. 3.85	Prof. H. Ringsdorf (Mainz) "Polymeric Liposomes as Models for Biomembranes and Cells?".

24. 4.85 Dr. M.C. Grossel (Bedford College, London)
"Hydroxypyridone dyes - Bleachable one-dimensional metals?".

25. 4.85 Major S.A. Shackelford (U.S. Air Force)
"In Situ Mechanistic Studies on Cendensed Phase Thermochemical Reaction Processes: Deuterium Isotope Effects in HMX Decomposition, Explosives and Combustion".

1. 5.85 Dr. D. Parker (I.C.I. plc. Petrochemical and Plastics Division, Wilton)
"Applications of Radioisotopes in Industrial Research".

7. 5.85 Prof. G.E. Coates (formerly of University of Wymoning, USA)
"Chemical Education in England and America: Successes and Deficiencies".

8. 5.85 Prof. D. Tuck (Windsor, Ontario)
"Lower Oxidation State Chemistry of Indium".

8. 5.85 Prof. G. Williams (U.C.W. Aberystwyth)
"Liquid Crystalline Polymers".

9. 5.85 Prof. R.K. Harris (Durham)
"Chemistry in a Spin: Nuclear Magnetic Resonance".

14. 5.85 Prof. J. Passmore (New Brunswick, U.S,A.)
"The Synthesis and Characterisation of some Novel Selenium-Iodine Cations, aided by Se N.M.R. Spectroscopy".

15. 5.85 Dr. J.E. Packer (Auckland, New Zealand)
"Studies of Free Radical Reactions in aqueous solution using Ionising Radiation".

17. 5.85 Prof. I.D. Brown (McMaster University, Canada)
"Bond Valence as a Model for Inorganic Chemistry".

21. 5.85 Dr. D.L.H. Williams (Durham)
"Chemistry in colour".

22. 5.85 Dr. M. Hudlicky (Blacksburg, USA)
"Preferential Elimination of Hydrogen Fluoride from Vicinal Bromofluorocompounds".

22. 5.85 Dr. S. Grimmett (Otago, New Zealand)
"Some Aspects of Nucleophilic Substitution in Imidazoles".

4. 6.85	Dr. P.S. Belton (Food Research Institute, Norwich) "Analytical Photoacoustic Spectroscopy".
13. 6.85	Dr. D. Woolins (Imperial College, London) "Metal -Sulphur - Nitrogen Complexes".
14. 6.85	Prof. Z. Rappoport (Hebrew University, Jerusalem) "The Rich Mechanistic World of Nucleophilic Cinylic Substitution".
19. 6.85	Dr. R.N. Mitchell (Dortmund) "Some Synthetic and NMR - Spectroscopic Studies of Organotin Compounds".
26. 6.85	Prof. G. Shaw (Bradford) "Synthetic Studies on Imidazole Nucleosides and the Antibiotic Coformycin".
12. 7.85	Dr. K. Laali (Hydrocarbon Research Institute, University of Southern Californa) "Recent Developments in Superacid Chemistry and Mechanistic Considerations in Electrophilic Aromatic Substitutions: A Progress Report".
13. 9.95	Dr. V.S. Parmar (University of Delhi), "Enzyme Assisted ERC Synthesis".
30.10.85	Dr. S.N. Whittleton (University of Durham), "An Investigation of a Reaction Window".
5.11.85	Prof. M.J. O'Donnell (Indiana-Purdue University), "New Methodology for the Synthesis of Amino acids".
20.11.85	Dr. J.A.H. MacBride (Sunderland Polytechnic). "A Heterocyclic Tour on a Distorted Tricycle-Biphenylene".
28.11.85	Prof. D.J. Waddington (University of York), "Resources for the Chemistry Teacher".
15. 1.86	Prof. N. Sheppard (University of East Anglia), "Vibrational and Spectroscopic Determinations of the Structures of Molecules Chemisorbed on Metal Surfaces".
29. 1.86	Dr. J.H. Clark (University of York), "Novel Fluoride Ion Reagents".
12. 2.86	Prof. O.S. Tee (Concordia University, Montreal), "Bromination of Phenols".

12. 2.86 Dr. J. Yarwood (University of Durham),
"The Structure of Water in Liquid Crystals".

19. 2.86 Prof. G. Procter (University of Salford),
"Approaches to the Synthesis of some Natural Products".

26. 2.86 Miss C. Till (University of Durham),
"ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics".

5. 3.86 Dr. D. Hathway (University of Durham),
"Herbicide Selectivity".

5. 3.86 Dr. M. Schroder (University of Edinburgh),
"Studies on Macrocycle Complexes".

12. 3.86 Dr. J.M. Brown (University of Oxford),
"Chelate Control in Homogeneous Catalysis".

14. 5.86 Dr. P.R.R. Langridge-Smith (University of Edinburgh),
"Naked Metal Clusters - Synthesis, Characterisation and Chemistry".

9. 6.86 Prof. R. Schmutzler (University of Braunschweig),
"Mixed Valence Diphosphorous Compounds".

23. 6.86 Prof. R.E. Wilde (Texas Technical University),
"Molecular Dynamic Processes from Vibrational Bandshapes".

(b) LECTURES ORGANISED BY DURHAM UNIVERSITY CHEMICAL SOCIETY DURING THE PERIOD 1983 - 1986

20.10.83 Prof. R.B. Cundall (Salford)
"Explosives".

3.11.83 Dr. G. Richards (Oxford)
"Quantum Pharmacology".

10.11.83 Prof. J.H. Ridd (U.C.L.)
"Ipso-Attack in Electrophilic Aromatic Substitution".

17.11.83 Dr. J. Harrison (Sterling Organic),
"Applied Chemistry and the Pharmaceutical Industry"
(Joint Lecture with the Society of Chemical Industry).

24.11.83	Prof. D.A. King (Liverpool) "Chemistry in 2-Dimensions".
1.12.83	Dr. J.D. Coyle (The Open University), "The Problem with Sunshine".
26. 1.84	Prof. T.L. Blundell (Birkbeck College, London). "Biological Recognition: Interactions of Macromolecular Surfaces".
2. 2.84	Prof. N.B.H. Jonathan (Southampton), "Photoelectron Spectroscopy - A Radical Approach".
16. 2.84	Prof. D. Phillips (The Royal Institution), "Luminescence and Photochemistry - a Light Entertainment".
23. 2.84	Prof. F.G.A. Stone F.R.S. (Bristol), "The Use of Carbene and Carbyne Groups to Synthesise Metal Clusters" (The Waddington Memorial Lecture).
1. 3.84	Prof. A.J. Leadbetter (Rutherford Appleton Labs.), "Liquid Crystals".
8. 3.84	Prof. D. Chapman (Royal Free Hospital School of Medicine, London) "Phospholipids and Biomembranes: Basic Science and Future Techniques".
28. 3.84	Prof. H. Schmidbaur (Munich, F.R.G.), "Ylides in Coordination Sphere of Metal: Synthetic, Structural and Theoretical Aspects" (R.S.C. Centenary lecture).
18.10.84	Dr. N. Logan (Nottingham), "N_2O_4 and Rocket Fuels".
23.10.84	Dr. W.J. Feast (Durham), "Syntheses of Conjugated Polymers. How and Why?".
8.11.84	Prof. B.J. Aylett (Queen Mary College, London), "Silicon - Dead Common or Refined?".
15.11.84	Prof. B.T. Golding (Newcastle-upon-Tyne), "The Vitamin B_{12} Mystery".
22.11.84	Prof. D.T. Clark (I.C.I. New Science Group), "Structure, Bonding, Reactivity and Synthesis as revealed by ESCA". (R.S.C. Tilden lecture).
29.11.84	Prof. C.J.M. Stirling (University College of North Wales)

6.12.84	Prof. R.D. Chambers (Durham), "The Unusual World of Fluorine".
24. 1.85	Dr. A.K. Covington (Newcastle-upon-Tyne), "Chemistry with Chips".
31. 1.85	Dr. M.L.H. Green (Oxford), "Naked Atoms and Negligee Ligands".
7. 2.85	Prof. A. Ledwith (Pilkington Bros.), "Glass as a High Technology Material" (Joint Lecture with the Society of Chemical Industry).
14. 2.85	Dr. J.A. Salthouse (Manchester), "Son et Lumiere".
21. 2.85	Prof. P.M. Maitlis, F.R.S. (Sheffield) "What Use is Rhodium?".
7. 3.85	Dr. P.W. Atkins (Oxford), "Magnetic Reactions".
17.10.85	Dr. C.J. Ludman (University of Durham) "Some Thermochemical aspects of Explosions". (A Demonstration Lecture).
24.10.85	Dr. J. Dewing (U.M.I.S.T.), "Zeolites - Small Holes, Big Opportunities".
31.10.85	Dr. P. L. Timms, (University of Bristol), "Some Chemistry of Fireworks" (A Demonstration Lecture).
7.11.85	Prof. G. Ertl, (University of Munich), "Heterogeneous Catalysis", (R.S.C. Centenary lecture).
14.11.85	Dr. S.G. Davies (University of Oxford), "Chirality Control and Molecular Recognition".
21.11.85	Prof. K.H. Jack, F.R.S. (University of Newcastle-upon-Tyne), "Chemistry of Si-Al-O-N Engineering Ceramics" (Joint Lecture with the Society of Chemical Industry).
28.11.85	Dr. B.A.J. Clark (Research Division, Kodak ltd.) "Chemistry and Principles of Colour Photography".

23. 1.85	Prof. Sir Jack Lewis, F.R.S. (University of Cambridge), "Some More Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls" (The Waddington Memorial Lecture).
30. 1.86	Dr. N.J. Phillips (University of Technology, Loughborough) "Laser Holography".
13. 2.86	Prof. R. Grigg (Queen's University, Belfast), "Thermal Generation of 1,3-Dipoles". (R.S.C. Tilden lecture).
20. 2.86	Dr. C.J.F. Barnard, (Johnson Matthey Group Research), "Platinum Anti-Cancer Drug Development - From Serendipity to Science".
27. 2.86	Prof. R.K. Harris, (University of Durham), "The Magic of Solid State NMR".
6. 3.86	Dr. B. Iddon (University of Salford), "The Magic of Chemistry" (A Demonstration lecture).

(c) RESEARCH CONFERENCES AND MEETINGS ATTENDED

September 1984, Royal Society of Chemistry Autumn Meeting University of Hull.

April 1984, Graduate Symposium, Durham University.

April 1985, Meeting of CASE and JRS workers on Methanol Synthesis Catalysts, I.C.I. Billingham.*

April 1985, Graduate Symposium, Durham University.

September 1985, Mechanism and Structure in Heterogeneous Catalysis (Proceedings of the Anglo-Dutch Conference) Noordwijkerhout.

April 1986, Graduate Symposium, Durham University.

May 1986, 2nd Meeting of CASE and JRS workers on Methanol Synthesis Catalysts, I.C.I. Billingham.*

* indicates oral presentation.

(d) FIRST YEAR INDUCTION COURSE, OCTOBER 1983

This course consisted of a series of one hour lectures on the services available in the Department.

1. Departmental organisation.
2. Safety Matters.
3. Electrical appliances and I.R. spectroscopy.
4. Chromatography and Microanalysis.
5. Atomic Absorptiometry and Inorganic Analysis.
6. Library facilities.
7. Mass Spectrometry.
8. Nuclear Magnetic Resonance Spectroscopy.
9. Glass Blowing techniques.

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