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3 RESEARCH AND DEVELOPMENT STUDY

RELATED TO THE SYNTHESIS OF

FORMALDEHYDE FROM CO_2 AND H_2 4

GARD Project 1416

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SYNTHESIS OF FORMALDEHYDE

Introduction

This report summarizes the activities of the General American Research Division during November 1966 through January 1967 on Contract NAS2-3889, Synthesis of Formaldehyde. The activities during this quarter were concerned with (1) selection of solid catalysts and a correlation of their activities for the oxidation of methane to formaldehyde with their chemical and physical properties, (2) construction of an experimental system for methane oxidation to formaldehyde and the development of experimental procedures, and (3) testing solid catalysts and investigating the effects of variables such as temperature, feed gas composition, and space velocity on the yields of formaldehyde.

The best results were obtained using an etched silica tube as the catalyst with a maximum formaldehyde yield ranging up to 0.7% of the methane in the feed gas.

1. Selection of Solid Catalysts

The literature survey revealed a considerable number of metals and metal oxides which have been claimed as catalysts for the oxidation of methane to formaldehyde. Table 1 presents the solid catalysts arranged according to the frequency of their appearance in published reports. The reported reaction temperatures with these catalysts range from 330° to 1,000°C, usually being 500 - 600°C. Although elemental metal catalysts are claimed, it is improbable at these temperatures and in the presence of oxygen that elemental surfaces

were present, except in the cases of Au, Ag, and the Platinum Group metals.[1] Therefore, it appears that the real catalytic surfaces were oxides or oxide films.

Table 1. CATALYSTS FOR THE PRODUCTION OF CH_2O FROM CH_4

ARRANGED ACCORDING TO THE FREQUENCY OF APPEARANCE IN PUBLISHED REPORTS

No. of Claims	8	7	6	5	4	3	2	1
Metal	Cu				Ag	Mn	Cu, Fe, Ni, Pd, Pt	Rb, Ce, Co Au, Pb, Al
Oxide	Mo	Si	Cu	V, Fe	Cr, Mn, Ag		Al, Ni, W, Th	Ti, Zr, Ce, U, Co, P, B, Alkali metals

Attempts were made to correlate the activities of the solid catalysts used for the conversion of methane to formaldehyde with their chemical and physical properties. Some of the properties of oxides claimed most frequently as catalysts are given in Table 2. Although most of these metals are capable of forming several oxides, the literature shows little indication which oxides were used; therefore, data on the more common regular oxides are given.

None of the proposed solid catalysts exhibit an outstanding activity for the conversion of methane to formaldehyde. The catalytic activities of metal oxides listed in Table 2 do not indicate any general trends or

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1. G. C. Bond, "Catalysis by Metals," Academic Press, Inc., London, 1962.

Table 2. PROPERTIES OF METAL OXIDES CLAIMED AS CATALYSTS FOR THE PRODUCTION OF CH_2O FROM CH_4

Oxide	Mo	Si	Cu	V	Fe	Cr	Mn	Ag	Al	B	W
Electronegativity of Metal	1.8	1.8	1.9	1.6	1.8	1.6	1.5	1.9	2.0	2.0	1.7
% Ionic Character of Metal	55	55	59	47	55	47	43	59	63	63	51
% d Character of Metal	43		36	35	39.5	39	40	36			
Acidity of oxide*	AM	A-VW	AM	AM-A	AM-B	AM-B	A-S	AM-B	AM	A-VW	A
Semiconductivity of oxide	n		p insul.	n	n	p insul.	p (?)	insul.	insul.		
Reaction Temperature, °C	375-550	350-1,000	350-650	500-650	350	550	550-650	350-550	330	575	650

*Acidity: A-acid; B-base; AM-amphoteric; S-strong; W-weak; VW-very weak; M-medium

correlation with their chemical and physical properties. The reason for this behavior can be explained by the relatively high reaction temperatures used with all these catalysts. Since these oxides are general oxidation catalysts, a large portion of the formaldehyde formed is oxidized further to CO_2. Besides, at increasing reaction temperatures formaldehyde becomes unstable and decomposes appreciably. Therefore, the reported yields of formaldehyde depend both on the rates of formation and of destruction during the process. The production of formaldehyde depends not only on the activity of the catalyst but also on the effectiveness of the measures employed for the prevention of the destruction of formed formaldehyde, such as increased space velocity, immediate quenching, or absorption of the product. The result is that the true activity of a catalyst becomes masked by these other effects and definite activity patterns are not readily apparent.

From a practical viewpoint, the number of appearance in patent claims and publications can be considered as some indication of the suitability of a catalyst. Although the yields of formaldehyde from the oxidation of methane using various solid catalysts are of approximately the same order, it can be expected that catalysts which give somewhat better results would receive more attention and would be described more frequently in the literature. Therefore, the arrangement of solid catalysts in Table 1 can serve as a starting point in their evaluation.

2. Experimental System and Procedures

An experimental system for the production of formaldehyde from methane which is suitable for use with both solid and gaseous catalysts is shown schematically in Figure 1. The actual reactor consists of a Vycor glass tube, 18" long, having a 23 mm. inside diameter. A four-inch long reaction

zone is heated to the desired temperature by an electric heater surrounding the Vycor tube. A movable thermocouple permits measurement of the temperature at various levels of the reaction zone. When testing solid catalysts, a catalyst bed of known volume is located in the center of the reaction zone.

Metered streams of oxygen and methane are premixed and fed into the reaction zone. The oxygen concentration is monitored continuously by an oxygen analyzer and the absolute rate of total gas flow is determined from the gas composition and oxygen flow measurements obtained with a mass flowmeter.

The reaction product is passed through a gas washing bottle containing a known amount of water where the condensables such as formaldehyde, methanol, and water vapor are absorbed. The amount of formaldehyde formed is determined from the analysis of the resulting solution.

Sample ports permit sampling of the feed gases and of the product from which the condensables have been removed for an accurate gas-chromatographic analysis for CH_4, O_2, CO_2, CO, N_2, and H_2. Continuous non-dispersive infra-red analyzers monitor the concentrations of CO_2 and CO in the reaction product.

To faciliatate the screening of the solid catalysts, runs of two hour duration are performed and the concentration of formaldehyde in the condensate collected in the gas wash bottle is determined by a colorimetric method using either a Nessler's or a modified Schiff reagent.(2) Only runs producing formaldehyde yields of at least 1% (yield = formaldehyde produced/methane in the feed) are further considered and a complete analysis of the feed and of the product is then performed.

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2. J. F. Walker, "Formaldehyde", Third Edition, Reinhold Publishing Corp., New York, N.Y., 1964.

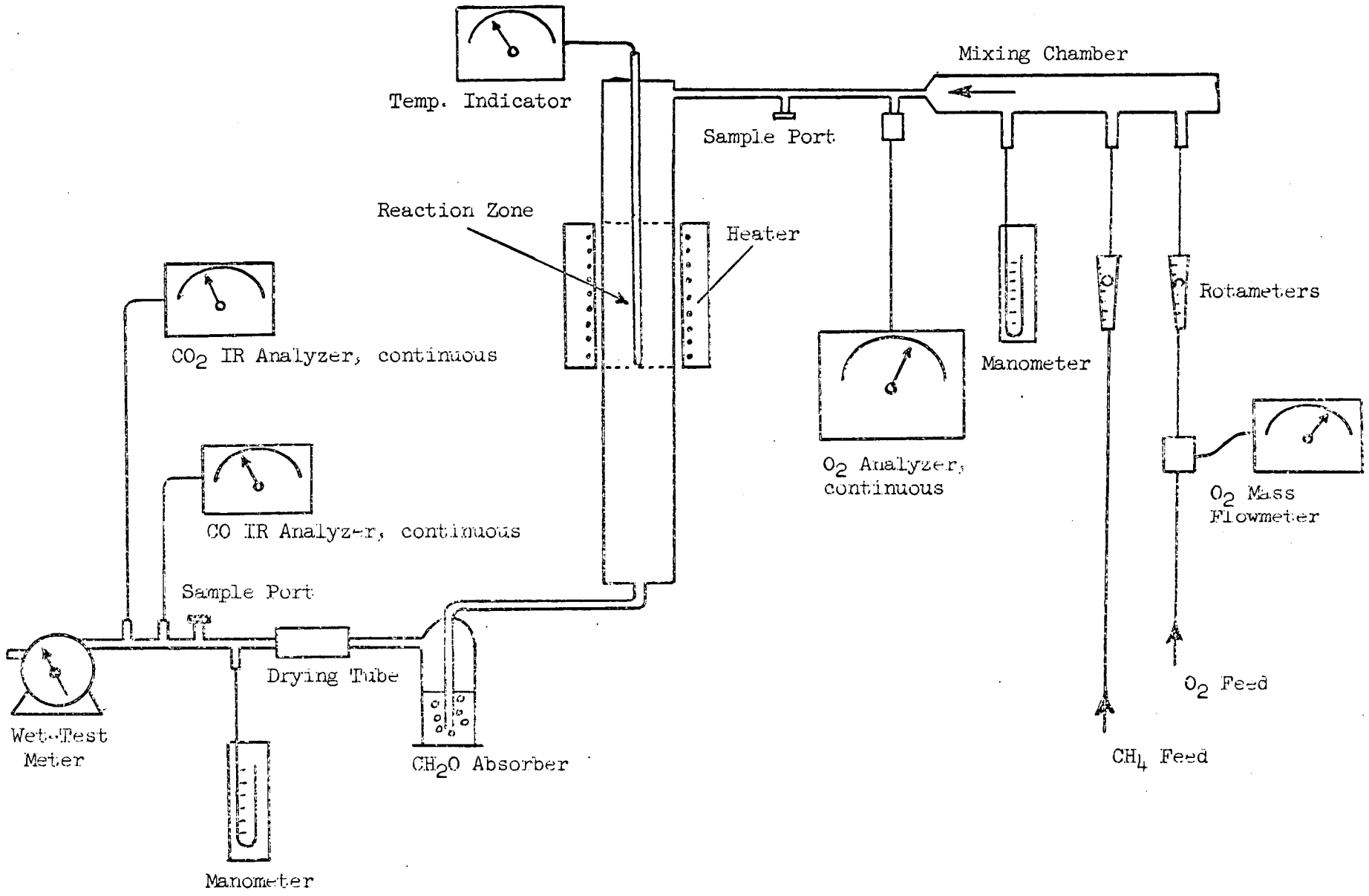

Figure 1. TESTING SYSTEM FOR THE PRODUCTION OF CH_2O FROM CH_4

A complete gas analysis both of the feed gas and of the reaction product is conveniently achieved by gas chromatographic techniques using a thermal conductivity detector. The feed gas and the non-condensable products are analyzed using a silica gel column heated to 90° - 110°C and a molecular sieve column at room temperature connected in series. This arrangement allows a separation of the peaks for H_2, CO_2, O_2, N_2, CO, and CH_4. The condensables (CH_2O, CH_3OH, and CHOOH) collected in water are analyzed using a Porapak N Column heated to 110° - 160°C.

3. Testing of Solid Catalysts

The suitability of solid catalysts for the production of formaldehyde from methane has been tested under various experimental conditions. The activity of each catalyst was tested at 800, 1,000, and 1,200°F using space velocities of 450 hr^{-1}, 900 hr^{-1}, and 1,200 hr^{-1}. Initially, the feed gas composition was varied from 95% O_2 and 5% CH_4 to 10% O_2 and 90% CH_4; however, most of the experiments were performed using a feed consisting of 47.5% O_2 and 52.5% CH_4.

Certain oxygen - methane mixtures were found to be explosive under the experimental conditions. The reported lower flammability limit of oxygen - methane mixtures is 5.4% CH_4; the upper, 59% CH_4.[3] However, the tendency to explode also appears to depend on the temperature, the composition, and the flow rate. The amount of energy input necessary to initiate an explosion is lowest for mixtures containing 25% of methane, but increases sharply with an increase in the methane concentration. Using a reaction tube of 23 mm inside diameter,

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3. R. E. Kirk and D. F. Othmer, "Encyclopedia of Chemical Technology," Vol. 5, p. 962, The Interscience Encyclopedia, Inc., New York, N.Y., 1950

mixtures containing at least 52.5% of methane do not explode even at flow rates as low as 100 cc/min. At 1,000°F, gas feed mixtures containing less than 52.5% of methane can be used at high flow rates, but tend to explode as the flow rate is lowered. Therefore, most of the experimental runs were performed with feed mixtures containing 52.5% or slightly more of methane.

A summary of the experimental results obtained with solid catalysts tested to date is given in Table 3. Although 70 separate tests have been performed, only the best result achieved with each catalyst is listed. The most effective catalyst was found to be the etched walls of a Vycor glass tube, producing up to a 0.78% yield of formaldehyde. Tungsten oxide was second giving up to 0.32% yields, while all other solid catalysts produced only very small yields of formaldehyde. With the exception of silica, all other catalysts initiate a complete oxidation of methane at temperatures of 1,000°F and 1,200°F. With Ni, Co, Zn, and Cr oxides, the complete oxidation already begins at 800°F to such an extent that it causes flashing (i.e. formation of an intermittent flame in the reactor) in the reaction tube and a runaway of temperature.

4. Future Activities

During the next quarter, experimental investigation of formaldehyde production from methane will be continued by:

a) Further screening of solid catalysts

b) Investigation of nitrogen oxide catalysts

c) Investigation of the use of ozone, as an additive to oxygen alone and in conjunction with solid catalysts.

Table 3. SUMMARY OF FORMALDEHYDE PRODUCTION

FROM METHANE USING SOLID CATALYSTS

No.	Catalyst		Highest Yield, * %	Remarks
	Active Ingredient	Description		
1.	Etched SiO_2	Etched wall of the Vycor reaction tube, 23 mm I.D., 4" long	.78	
2.	Etched SiO_2	Same as #1; tube filled with 6" O.D. etched Vycor tubes	< .002	
3.	Etched SiO_2	Same as #1; reaction zone filled with etched silica boiling chips	< .002	
4.	MoO_3	10% MoO_3 on high activity alumina, Harshaw Mo-1201 T 1/8	< .02	
5.	V_2O_3	10% V_2O_3 on high activity alumina, Harshaw V-0601 T 1/8	< .02	
6.	MnO_2	19% MnO_2 on activated alumina, Harshaw Mn-0201 T 1/8	< .002	
7.	NiO_2	15% Ni in oxide form on activated alumina, Harshaw Ni-0302 T 1/8	< .002	Flashing. Temp. control impossible.
8.	WO_3	10% WO_3 on activated alumina, Harshaw W-0101 T 1/8	.32	Flashing when 1100°F is reached.
9.	Co	39% Co on kieselguhr, Harshaw Co-0108 T 1/8	< .002	Stable temp. impossible.

*Yield = Moles of Formaldehyde Formed/ Moles of Methane in Feed.

No.	Catalyst		Highest Yield, %	Remarks
	Active Ingredient	Description		
10.	Zn oxide	24% Zn oxide on activated alumina, Harshaw Zn-0701 T 1/8	< .002	Temp. control very difficult.
11.	Cr oxide	Cr oxide (Cr^{vi-iv}) on activated alumina, CERLOX catalyst	< .02	Stable temperature cannot be maintained.
12.	Cr oxide, Ba oxide	Cr^{vi-iv} oxides, Ba oxide, Ba chromates on activated alumina, CERLOX 8615 catalyst	< .02	Stable temperature cannot be maintained.
13.	Ni - W	6% Ni, 19% W sulfided on alumina, Harshaw Ni-4303 E 1/12	< .02	

Laboratory investigation of methanol formation from CO_2 will be initiated during the next quarter. A listing of catalysts and processes found in the literature will be made from which promising candidates will be selected for the actual laboratory testing. Also, a reactor suitable for the investigation of reactions under pressure as required for the methanol synthesis from CO_2 will be built and tested.