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Oxidation Activity of Catalyst 3-7A Toward Formaldehyde, Hydrogen Cyanide, And Some Alkane Gases

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OXIDATION ACTIVITY OF CATALYST 3-7A TOWARD
FORMALDEHYDE, HYDROGEN CYANIDE, AND
SOME ALKANE GASES

A Thesis

Presented to

the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by

John Kawas

December 1982

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OXIDATION ACTIVITY OF CATALYST 3-7A TOWARD
FORMALDEHYDE, HYDROGEN CYANIDE AND
SOME ALKANE GASES

Recommended November 6, 1982
(Date)

Robert D. Ferris
Director of Thesis

Norman L. Holly

Wilhelm G. Lloyd

Approved December 3, 1982
(Date)

Elmer Gray
Dean of the Graduate College

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OXIDATION ACTIVITY OF CATALYST 3-7A TOWARD FORMALDEHYDE,
HYDROGEN CYANIDE, AND SOME ALKANE GASES

John Kawas

December 1982

61 pages

Directed by: Dr. R. D. Farina, Dr. N. L. Holy, and
Dr. W. G. Lloyd.

Department of Chemistry

Western Kentucky University

The activity of Catalyst 3-7A toward the oxidation of formaldehyde, hydrogen cyanide, methane, propane, and isobutane was examined at temperatures between 25°C and 400°C. The catalyst consists of palladium(II) and copper(II) salts impregnated on an alumina support. The oxidation measurements were made primarily with gas chromatographs, although formaldehyde and hydrogen cyanide were also examined using the colorimetric fushsin method and Liebig titrations, respectively. Catalyst 3-7A demonstrated appreciable activity toward the oxidation of all gases studied except formaldehyde where there was no evidence of oxidation. The latter result is quite unexpected since aldehydes are more easily oxidized than alkanes. It is suggested that the inactivity of Catalyst 3-7A toward formaldehyde is attributed to the lack of moisture which is required by the catalyst during oxidation.

All oxidation reactions are believed to occur via a Qacker-type process under pseudo-first order conditions with the palladium(II) concentration maintained constant via the presence of copper(II) which oxidizes metallic palladium,

the product in the oxidation reaction. The oxidation products in all the gases examined are believed to be carbon dioxide and water except for hydrogen cyanide where an additional product containing nitrogen should be formed but could not be detected with the gas chromatograph. Rate constants (reported in parenthesis) at 400°C for the following gases are hydrogen cyanide ($>26.2 \text{ sec}^{-1}$), methane ($6.5\text{-}6.6 \text{ sec}^{-1}$), propane ($>12.8 \text{ sec}^{-1}$), and isobutane ($>15.7 \text{ sec}^{-1}$). These results show that hydrogen cyanide is the most active gas to be oxidized by the catalyst excluding carbon monoxide which is the test gas used in our system and has been previously determined to demonstrate the greatest activity with the catalyst. The three alkane gases show an order of oxidation reactivity which lends some support for ruling out an anionic mechanism since tertiary C-H bonds were found to be more reactive than secondary C-H bonds which in turn were shown to be more reactive than primary C-H bonds. A comparison of Catalyst 3-7A with other catalysts reported in the literature which show similar oxidation behavior with gases could not be made due to lack of data regarding their experimental conditions.

INTRODUCTION

One of the major problems which has resulted from the Industrial Revolution is pollution of the atmosphere. Considerable attention has been directed toward air pollution because of the toxic or otherwise harmful pollutants which are eventually inhaled by the general population. The major atmospheric pollutants are reported to be carbon monoxide, sulfur oxides, nitrogen oxides, hydrocarbons, and particulate matter.⁽¹⁾ In 1968, it was estimated that the transportation industry was responsible for 42% of the total air pollutants in the American atmosphere with the internal combustion engine emitting 64% of the 91 million tons of carbon monoxide and 52% of the 29.1 million tons of hydrocarbons in the 1968 American atmosphere.⁽¹⁾

In the past few decades, considerable attention has been given to the catalytic oxidation of these pollutants. Gasoline powered vehicles are now manufactured with catalytic converters to reduce the emission of pollutants to the atmosphere. Although a variety of catalytic systems have been proposed to reduce pollutant emissions from cars and industrial processes, most of them have disadvantages such as high cost, short catalyst lifetimes, and poor efficiency at low temperatures.

A variety of transition metal catalysts have been developed for the oxidation of carbon monoxide and hydrocarbons in

automobile exhausts.⁽²⁻¹⁰⁾ For example, palladium, copper, nickel, manganese, chromium, platinum, rhodium, ruthenium, tin, and antimony are incorporated into catalysts either as the free metal, a metallic oxide, an ionic salt, or in combinations with other metals in their various forms. For instance, catalytic compounds can be impregnated on high surface area supports such as alumina or silica, or they can be mixed with binding materials and compressed to form pellets, needles, or various other shapes. A metal surface can be coated with a monolayer of the active catalyst to maximize surface area while conserving precious metals.

Of specific interest to our work are palladium and copper containing catalysts. Catalytic systems containing palladium and copper have been utilized not only for the oxidation of carbon monoxide and hydrocarbons,^(2,3) but also as dehalogenation catalysts for aromatic amino compounds,⁽¹¹⁾ dehydrogenation catalysts for cyclohexane and cyclohexanol,^(12,13) hydrogenation catalysts for alkynes and diolefins,⁽¹⁴⁻¹⁸⁾ as well as in the synthesis of vinyl acetate.⁽¹⁹⁻²¹⁾

The mechanism of palladium-copper catalyzed oxidations cannot be elucidated in this project since this was not one of our objectives and, hence, the appropriate kinetic studies were not performed. However, there are several mechanistic proposals discussed in the literature which may be applicable to our work. In homogeneous solution, the mechanism of the Wacker process is attractive since it involves palladium(II) chloride and copper(II) chloride oxidation of organic substances.⁽²²⁾ In heterogeneous gas phase reactions, the Eley-Rideal and

Langmuir-Hinshelwood mechanisms have been proposed to describe the oxidation of carbon monoxide on a platinum or palladium surface.⁽²³⁾

In solution, the oxidation of carbon monoxide to carbon dioxide (and olefins to carbonyl compounds) by palladium(II) chloride was first reported in 1894 by Phillips.^(24,25) Since the oxidation of palladium metal to palladium(II) by molecular oxygen is very slow, copper(II) chloride is added to the solution to oxidize the palladium metal and thereby increase the efficiency of the system.^(26,27) The product of the palladium metal oxidation, copper(I) chloride, is oxidized by oxygen under relatively mild conditions and serves to regenerate the copper(II) chloride.^(28,29) The net result is the oxidation of carbon monoxide to carbon dioxide by oxygen.

The use of this catalytic cycle in solution is not only applicable in the oxidation of carbon monoxide to carbon dioxide but also in the commercial production of acetaldehyde from ethylene (Wacker process),⁽²²⁾ the formation of acetals and ketones from alcohols,⁽³⁰⁾ and the formation of acetals and ketals from olefins.⁽³¹⁾

The oxidation of carbon monoxide on platinum and palladium surfaces has been extensively investigated.⁽²³⁾ Langmuir pioneered the kinetics of heterogeneous catalysis with the platinum oxidation of carbon monoxide. Since then, there have been two different mechanisms proposed--both involving chemisorption of one or more of the gaseous reactants on the metal surface.⁽²³⁾ On a palladium surface, oxygen is more strongly adsorbed than carbon monoxide as shown by their heats of

adsorption (55 kcal/mol for oxygen as opposed to 30 kcal/mol for carbon monoxide). The Eley-Rideal mechanism proposes the reaction occurs between an adsorbed oxygen atom and a gas phase carbon monoxide molecule, while the Langmuir-Hinshelwood mechanism postulates the reaction occurs between carbon monoxide and oxygen which are both chemisorbed on the palladium surface. Studies have shown that the latter mechanism occurs more slowly than the former mechanism, but the actual path of carbon dioxide formation is governed by other parameters such as temperature and the partial pressures of carbon monoxide and oxygen.⁽²³⁾

Catalyst 3-7A used in this study contains palladium(II) and copper(II) salts^(32,33) which are also utilized in the Wacker process, but our system is not in homogeneous solution. Instead, Catalyst 3-7A has these metal salts on an alumina support where oxidation occurs in the gas phase. Hence, the Eley-Rideal or Langmuir-Hinshelwood mechanism may be more applicable. Finally, Catalyst 3-7A has been reported to oxidize carbon monoxide to carbon dioxide and sulfur dioxide to sulfur trioxide.⁽³²⁻³⁵⁾ In view of these facts and the need for the removal of pollutant gases from the atmosphere, this study was made to determine if Catalyst 3-7A is capable of oxidizing other pollutant gases found in automobile exhausts or industrial stack gases.

EXPERIMENTAL

Two hundred grams of Catalyst 3-7A were obtained from D. R. Rowe of the Industrial and Engineering Technology Department of Western Kentucky University. Catalyst 3-7A contains palladium(II) and copper(II) salts on an activated alumina support and requires oxygen and water to perform continuous oxidation of the gaseous reactants, carbon monoxide and sulfur dioxide. (32,33)

A gas train (Figure 1) was constructed in order to evaluate the activity of Catalyst 3-7A on the oxidation of five gases at temperatures between ambient and 400°C. The gases tested were formaldehyde, hydrogen cyanide, methane, propane, and isobutane. Carbon monoxide was also re-examined and provided a calibration check on our catalyst assembly.

A. Materials

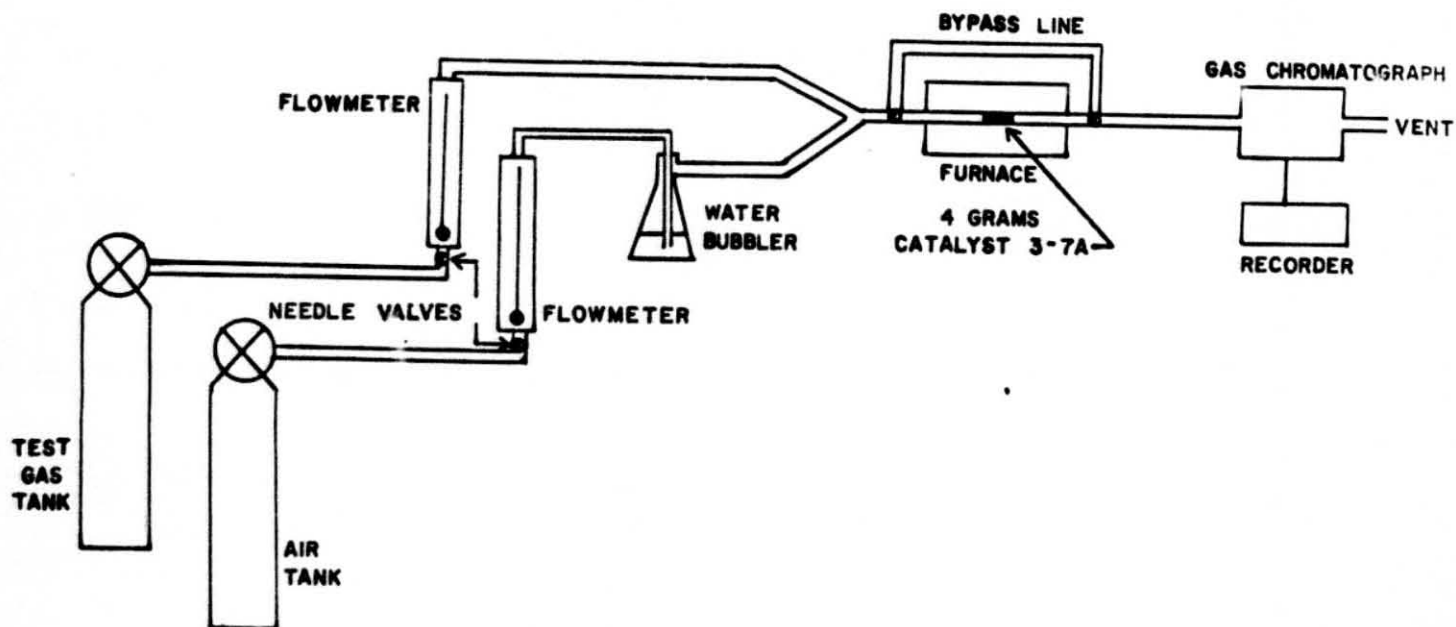
1. Gases

Compressed gas cylinders containing the gases used in this study were obtained primarily from Airco Industrial Gases. The contents of these tanks were as follows:

- a) breathing air (21% oxygen in nitrogen)
- b) 105 ppm carbon monoxide + 10% oxygen in nitrogen
- c) 0.989% methane in helium
- d) 0.970% propane in helium
- e) 1.01% isobutane in helium

A gas tank containing 1.06% hydrogen cyanide in helium was obtained from Matheson Gas Products.

FIGURE 1. Schematic Diagram of Gas Train Assembly



2. Chemicals

All reagents were used without further purification unless otherwise noted. Reagent grade potassium iodide, paraformaldehyde (95%), and standard Ottawa sand were obtained from MCB Manufacturing Chemists, Inc. The silver nitrate and sodium cyanide were Baker reagent grade. The neutral alumina, 1.000 N \pm 0.002 HCl standard, and the formaldehyde solution (37% w/w) were Fisher certified reagents. Eastman reagent grade bromothymol blue was used as the indicator.

B. Apparatus

1. Flowmeters

The flowmeters used in this work were obtained from Fisher & Porter Company. The Century Series 100 flowmeter was equipped with a flowtube (catalogue # 448-225) and a 1/8 inch stainless steel float. The Mark III series 10A1460-LK flowmeter was loaded with flowtube FP-1/8-13.3-G-6 and 1/8 inch floats composed of either stainless steel or black glass, depending on the desired flow rate. The flowmeters were calibrated either with a wet test meter or a soap bubble technique.

2. Furnace

A Lindberg Hevi-Duty sixteen inch horizontal tube furnace equipped with a Platinel #2 thermocouple was used in this study. A pyrometer controlled the temperature up to 1370°C in the furnace.

3. Gas Chromatographs

Two gas chromatographs were used in this study, and both were equipped to handle light gas analysis. This type of analysis involved a system of two columns mounted in series

with valve controls. The first column material consists of a nonpolar porous polymer in which oxygen, nitrogen, methane, and carbon monoxide gases are not strongly adsorbed. Consequently, these light gases have short retention times and cannot be resolved by the porous polymer column. Other gases such as carbon dioxide, water, and propane are adsorbed more strongly and hence have longer retention times. The second column material is a molecular sieve which is capable of resolving oxygen, nitrogen, methane, and carbon monoxide but is deactivated (clogged) by water and carbon dioxide. Consequently, these latter gases must bypass the molecular sieve during the operation of the gas chromatograph. Also, important in light gas analysis are two six-port valves which are used with the gas chromatograph. The first valve controls the amount of gas sample injected into the gas chromatograph by utilizing an in-line sample loop calibrated for 1.00 cc. Turning the valve to the standby position permits the sample loop to be purged with sample gas; but when the valve is placed in the sample position, the sample loop is then in series with the helium carrier gas of the chromatograph allowing the gas sample to be injected into the instrument. The second valve controls the column sequence within the gas chromatograph. Since water and carbon dioxide deactivate the molecular sieve, it is desirable to send these gas fractions through the porous polymer column only eluting them directly into the detector. This valve allows the molecular sieve to be placed either in series with the first column or to be bypassed completely.

The first gas chromatograph used in this study was a modified Carle Model 8500 Basic Gas Chromatograph equipped with thermistor detectors, an eighteen foot Porapak Q (50-80 mesh) column, an eight foot MS 5A (40-60 mesh) molecular sieve, and two manual valve controls. For the gas analysis, the helium carrier gas was maintained at 20 cc/min at 30 psi tank pressure with a column temperature of 64°C. The output from the chromatograph was connected to a Houston Instruments OmniScribe strip chart recorder.

The second gas chromatograph was a Carle Analytical Gas Chromatograph Series S Model AGC-111. In addition to the thermistor detectors and valve controls, this instrument was equipped with an eight foot 80% Porapak N + 20% Porapak Q (50-80 mesh) column and a six foot molecular sieve MS 5A (42-60 mesh) column. The helium carrier gas flow was 30 cc/min (44 psi) with a column temperature of 100°C. Although the instrumentation allowed an automatic valve switching program to be used, only the manual controls were used. A Hewlett-Packard Model 3390A Reporting Integrator allowed strip chart recording and digital integration of each gas chromatogram.

4. Gas Train Assembly

Figure 1 is a schematic diagram of the gas train assembly used in our work. The assembly consisted of compressed gas cylinders, one containing the various gases to be tested and the other air with each cylinder connected to a flowmeter. Also present in the assembly is a water bubbler, a furnace housing the catalyst, and the detection system. Unless

otherwise noted, all connections were made with 1/16 inch I.D. Tygon tubing. An 11 mm I.D. Vycor tube containing four grams of Catalyst 3-7A held in place with glass wool was placed horizontally in the furnace. Three-way Teflon stopcocks were positioned at both ends of the Vycor tube to allow a parallel gas flow to circumvent the catalyst bed in the furnace. This served not only as the bypass line but also allowed the gas stream to be calibrated with the detector system before the gas was passed over the catalyst. The gas train terminated at the detection system which was primarily a gas chromatograph.

C. Methods of Analysis

1. Carbon Monoxide

Four grams of Catalyst 3-7A were tested initially with a stream of carbon monoxide (105 ppm) gas flowing at 4-6 cc/sec and maintained at ambient temperature (25°C). Since the compressed gas cylinder contained 10% oxygen as well as carbon monoxide, it was fed directly to the water bubbler instead of being diluted with a humidified air stream as shown in Figure 1. The gas stream was then routed to the catalyst bed and the detection system. An ECOLYZER brand electrochemical carbon monoxide meter was used to monitor the concentration of carbon monoxide in the effluent gas stream. The instrument had previously been calibrated with a known amount of carbon monoxide gas to allow direct readings in ppm. Samples were collected by filling an evacuated gas sample bag with effluent gas from the gas train. The gas sample bag when attached to the carbon monoxide meter allows measurements of the carbon

monoxide concentrations. The gas chromatographic technique was not only successful in monitoring the oxidation of our reactant gas, carbon monoxide, but also in the identification of the oxidation product (carbon dioxide). Manual control of the column sequence was utilized with the Carle Model 8500 gas chromatograph. The normal standby positions of the chromatograph are purge and series for the sample valve and column valve, respectively. When the sample is to be collected and injected into the chromatograph, the sample valve is switched from purge to sample for thirty seconds, at which time the recorder is started. Since Porapak columns do not resolve the light gases (oxygen, nitrogen, carbon monoxide, and methane) they emerge as one composite peak and enter the molecular sieve. Before carbon dioxide and water emerge from the Porapak column (3.5 min), the column valve is switched from series to bypass. This traps and holds the gases on the molecular sieve while the contents of the Porapak column are eluted to the detector (carbon dioxide, 3.9 min). After carbon dioxide is eluted, the column valve is switched back to the series position to elute oxygen, nitrogen, and carbon monoxide (6.0 min) from the molecular sieve. The column valve is then switched back to bypass for thirty minutes to empty the water from the Porapak column.

This type of manual switching allows monitoring of both carbon monoxide and carbon dioxide on the chromatograph. Only qualitative identifications could be made because the detector response to 105 ppm of carbon monoxide or carbon dioxide is at the lowest level of detection on this particular instrument.

Samples were collected after the gas stream was passed over four grams of Catalyst 3-7A at ambient temperature and also while the gas stream circumvented the catalyst bed (bypass samples). The effluent gas from the catalyst run was also bubbled through an aqueous solution of barium hydroxide to qualitatively test for the presence of carbon dioxide.

In addition to testing the catalyst for oxidation of carbon monoxide, the effects of the alumina support on the oxidation process were also evaluated by substituting four grams of neutral alumina for Catalyst 3-7A. The four grams of neutral alumina were then replaced with four grams of standard Ottawa sand at 400°C to test for oxidation by thermal effects. These measurements with the alumina support and sand were made for each of the gases tested.

2. Formaldehyde

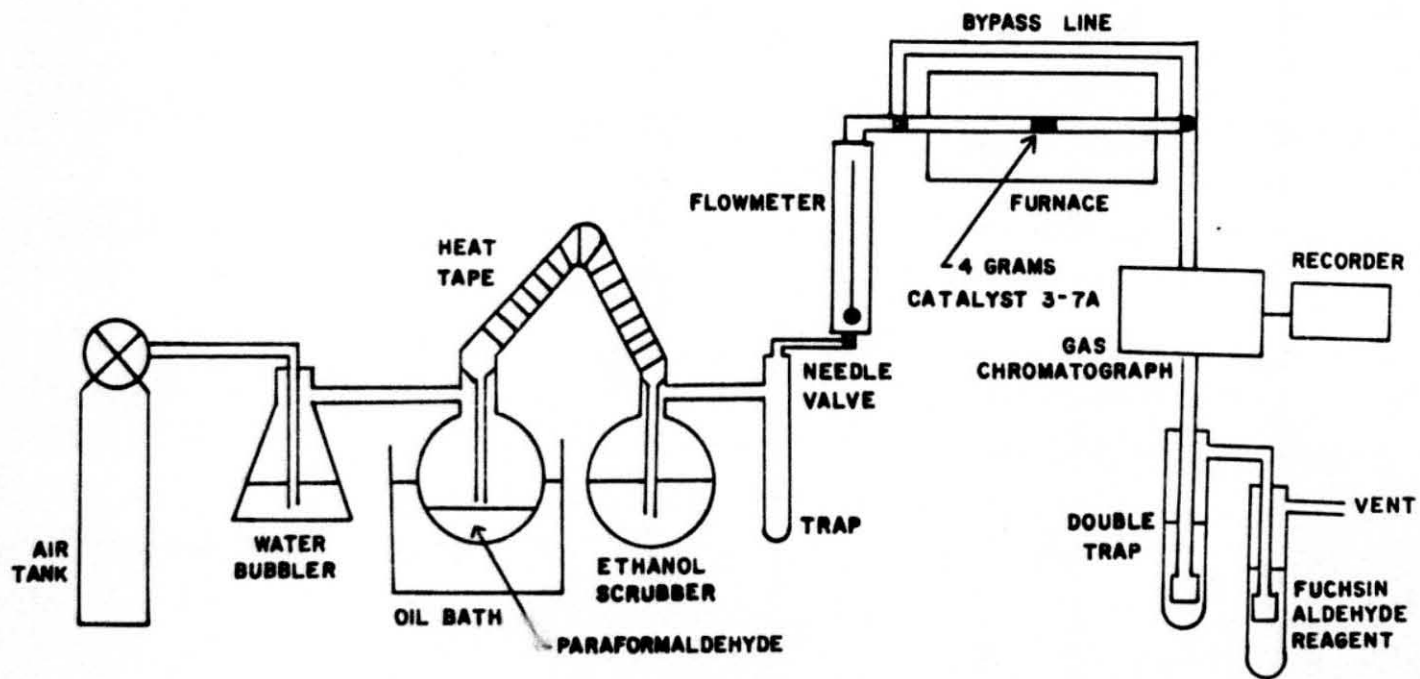
Originally it was thought that a sufficient amount of formaldehyde vapors could be generated for catalytic testing by bubbling an air stream through a formalin solution (37% w/w formaldehyde in aqueous solution).^(36,37) However, it was determined that this method did not generate sufficient amounts of formaldehyde in the gas stream. Moreover, the Porapak column of the chromatograph did not effectively resolve the formaldehyde peak from the water peak to permit a quantitative analysis. Due to these difficulties, a new source of formaldehyde and a new method of detection were required to evaluate the activity of Catalyst 3-7A towards the oxidation of formaldehyde. The method selected for use involved the generation

of anhydrous formaldehyde vapor by subliming paraformaldehyde in a 143°C oil bath.^(38,39) The resulting formaldehyde vapors were then carried through the gas train by a continuous humidified air purge of 4 cc/sec. Repolymerization of paraformaldehyde on the walls of the gas train was prevented by bubbling the gas stream through an ethanol scrubber. A Pyrex connector positioned between the paraformaldehyde sublimation flask and the ethanol scrubber was wrapped with electrical heating tape to prevent any repolymerization of the gas stream prior to being scrubbed with ethanol.

The gas train assembly used in the formaldehyde system is shown in Figure 2. The paraformaldehyde and ethanol flasks were both 125 ml Pyrex with standard taper 24/40 ground glass joints. An empty side arm test tube was placed after the ethanol scrubber to serve as a trap for collecting any entrained ethanol. The gas stream was then directed through a flowmeter and the catalyst bed before being terminated at the detection system. Formaldehyde was tested at ambient temperature and at 400°C by means of a colorimetric fuchsin aldehyde method^(40,41) in addition to being monitored by gas chromatography.

Fuchsin aldehyde reagent is commonly used in qualitative tests for the presence of aldehydes. With only slight modifications, this reagent can be used as a quantitative method for determining formaldehyde concentrations in a gas stream.^(40,41) The test solution consisted of a 0.1% basic fuchsin (histologic grade) solution in deionized water containing 1% sodium metabisulfite and 0.2 M hydrochloric acid. The solution was

FIGURE 2. Schematic Diagram of Formaldehyde
Gas Train Assembly



stoppered and protected from light while being decolorized overnight. The Fuchsin aldehyde reagent was stored in a refrigerator when not in use.

Calibration samples of 185, 370, 740 and 925 ppm formaldehyde were prepared by appropriate dilutions of a 37% formaldehyde solution. These samples were scanned in the visible region of the light spectrum on the Cary Model 14 Recording Spectrophotometer for the purpose of preparing a calibration plot and testing Beer's Law over this formaldehyde concentration range. The spectra were obtained using sample cells with a 0.1 mm path length.

Formaldehyde samples from each experimental run were collected for twenty five minutes by passing the gas stream through a double trap system containing the Fuchsin test solution. Each trap consisted of a fritted glass gas dispersion tube submerged in 50 ml of Fuchsin reagent. The samples were then diluted to 250 ml with deionized water and stored for six hours prior to being scanned on the Cary 14 to allow for full color development and stabilization.

3. Hydrogen Cyanide

Gas streams of 9039-9880 ppm hydrogen cyanide flowing at 8.8-9.2 cc/sec thru the gas train assembly (Figure 1) were evaluated for oxidation activity by Catalyst 3-7A from 25°C to 400°C. The effluent gas stream was monitored by gas chromatography and the hydrogen cyanide concentration was independently determined by Liebig titrations with silver nitrate. (42)

The gas chromatography (AGC-111) was operated in the bypass mode only since the Porapak column is the only one needed. Oxygen and nitrogen are eluted to the detector as one composite air peak in the chromatograms while the hydrogen cyanide is well separated from it. Initially, the air line in Figure 1 was clamped off, and the hydrogen cyanide-helium mixture was routed through the bypass line to the chromatograph. This allowed not only the identification of the retention time for hydrogen cyanide but also served as the standard for hydrogen cyanide concentration (10,600 ppm) from which the detector response could be calibrated to determine other concentrations of hydrogen cyanide.

Samples for Liebig titrations were collected by scrubbing the effluent gas stream in 50 ml of 2% sodium hydroxide solution for 180 seconds. Then 2.5 ml of 2% potassium iodide were added to the solution prior to the titration to provide a turbid endpoint with standard silver nitrate (0.017351 M). The silver nitrate solution had previously been standardized by titration with a sodium cyanide solution. The latter solution in turn was standardized by titration with a standard hydrochloric acid solution using bromothymol blue as an indicator.

4. Methane

Oxidation activity of Catalyst 3-7A toward methane was evaluated by gas chromatography at ambient and 400°C. The gas train assembly was the same as that used for the hydrogen cyanide experiment (Figure 1). Initially the air stream was removed for the purpose of obtaining a peak area calibration

of methane (9890 ppm). A humidified air stream was then allowed to mix with the methane-helium stream and was tested at 25°C and 400°C. Gas chromatographic samples were performed on bypass samples to serve as a standard for comparison runs over the catalyst.

Analysis of methane by gas chromatography requires use of the molecular sieve to resolve the methane from the oxygen and nitrogen. The AGC-111 was operated in the series configuration until the oxygen, nitrogen, and methane peaks were recorded with the integrator. The integrator was then shut off and the AGC-111 switched manually to bypass in order to elute carbon dioxide and water. Since the runs performed in this manner showed only a reduction in the methane peak, it was necessary to make additional runs in the bypass mode to identify the oxidation products.

The effluent gas streams of the 400°C catalyst runs were passed through a barium hydroxide solution in order to test for the presence of carbon dioxide. Moreover, the acidity of the reaction product was tested with the pH indicator, bromothymol blue.

5. Propane

Catalyst 3-7A was evaluated for oxidation activity toward a gas stream flowing at 7-9.2 cc/sec and containing 600-800 ppm propane. The gas train assembly is depicted in Figure 1. As in the case of hydrogen cyanide and methane, the gas chromatography was calibrated using a propane-helium gas mixture (9700 ppm propane). Humidified air streams were then mixed with the propane mixture and passed through the

bypass line. After establishing propane concentrations in the bypass line, the gas stream was passed over four grams of Catalyst 3-7A. The oxidation was monitored at 25°C, 250°C and 400°C by means of the AGC-111 gas chromatograph. The effluent gas stream was also tested with a solution of barium hydroxide for carbon dioxide as well as with bromothymol blue pH indicator.

6. Isobutane

The experimental procedure for the analysis of isobutane was identical to that of methane and propane. The gas chromatograph was calibrated using an isobutane-helium gas mixture (10,100 ppm isobutane). Bypass and catalyst runs were performed at 25°C, 250°C and 400°C using flowrates of 9.1 - 9.3 cc/sec. The resultant isobutane concentrations of the gas stream was in the 626-842 ppm range. The effluent gas stream was tested as before using barium hydroxide for carbon dioxide and bromothymol blue for the pH.

RESULTS AND DISCUSSION

Carbon Monoxide. Table 1 lists the data collected at 25°C on carbon monoxide using both the gas chromatograph and the carbon monoxide meter. Flow rates of 4.10, 5.30 and 5.50 cc/sec were directed through the bypass line and onto the carbon monoxide meter which indicated 104 ppm carbon monoxide. These serve as the calibration checks for the catalyst runs performed under the same conditions. When the gas stream was passed over four grams of Catalyst 3-7A with a contact time of 585 milliseconds, the carbon monoxide level decreased from 104 ppm to 0.4 ppm. A psuedo first order rate constant of 9.5 sec^{-1} was obtained under these conditions. The gas chromatograms indicated the qualitative absence of carbon monoxide (retention time = 6.0 minutes) and the presence of carbon dioxide (retention time = 3.9 minutes). At slightly faster flow rates (5.3 cc/sec) and correspondingly shorter contact times (453 milliseconds) the oxidation was still 99.6 - 99.8% complete with psuedo first order rate constants of $12.3 - 13.8 \text{ sec}^{-1}$. At 5.50 cc/sec the contact time was reduced further to 436 milliseconds, but the catalyst still succeeded in oxidizing 97.1% of the carbon monoxide. A rate constant of 8.1 sec^{-1} was obtained under these conditions. In addition, the effluent gas streams of the catalyst runs were bubbled through an aqueous solution of barium hydroxide where the formation of a white precipitate (barium carbonate)

TABLE 1
Catalyst 3-7A Oxidation Activity Toward Carbon Monoxide
T = 25°C

Gas Flow (cc/sec)	Contact Time (millisec)	GC*		CO Meter (ppm)	Sample	% Oxidation	k (sec ⁻¹)
		CO	CO ₂				
4.10	---	+	-	104	bypass	----	----
4.10	585	-	+	0.4	catalyst	99.6	9.5
4.10	585	-	+	0.4	catalyst	99.6	9.5
5.30	---	+	-	105	bypass	----	---
5.30	---	+	-	104	bypass	----	---
5.30	453	-	+	0.4	catalyst	99.6	12.3
5.30	453	-	+	0.2	catalyst	99.8	13.8
5.50	---	+	-	104	bypass	----	----
5.50	---	+	-	104	bypass	----	----
5.50	---	+	-	104	bypass	----	----
5.50	436	-	+	3.0	catalyst	97.1	8.1

*Retention times for carbon monoxide and carbon dioxide are 6.0 and 3.9 minutes respectively.
The + and - indicate the qualitative presence and absence of the given species.

indicated the presence of carbon dioxide. The pH of the gaseous solution was acidic when tested with bromothymol blue indicator.

Runs made with an alumina support and with sand at 400°C in lieu of the catalyst did not indicate any detectable oxidation. These results show that Catalyst 3-7A has considerable oxidation activity towards carbon monoxide at ambient temperature, and is in agreement with the work performed by Lloyd and co-workers. (32-35)

Formaldehyde. Catalyst 3-7A was evaluated for oxidation activity toward formaldehyde at 25°C and 400°C by means of the colorimetric Fuchsin method previously described. For calibration purposes, visible spectra of standard formaldehyde samples (185, 370, 740 and 925 ppm) were obtained as shown in Figure 3. The absorbances at 570 nm (the absorption maximum) were plotted against their corresponding formaldehyde concentration, as can be seen in Figure 4, and the linear plot shows that Beer's Law is applicable over this formaldehyde concentration range. Since the response of the Cary model 14 is sensitive to ± 0.001 absorbance units, the sensitivity of this method corresponds to ± 11 ppm formaldehyde concentration.

Formaldehyde vapors were generated by subliming paraformaldehyde in the apparatus depicted in Figure 2. The humidified air stream was maintained at 3.60-4.20 cc/sec, and colorimetric samples were collected for both bypass and catalyst runs. The efficiency of the double trap was excellent, as indicated by the absence of formaldehyde in the second trap.

FIGURE 3. Absorption Spectra of Formaldehyde
Calibration Solutions

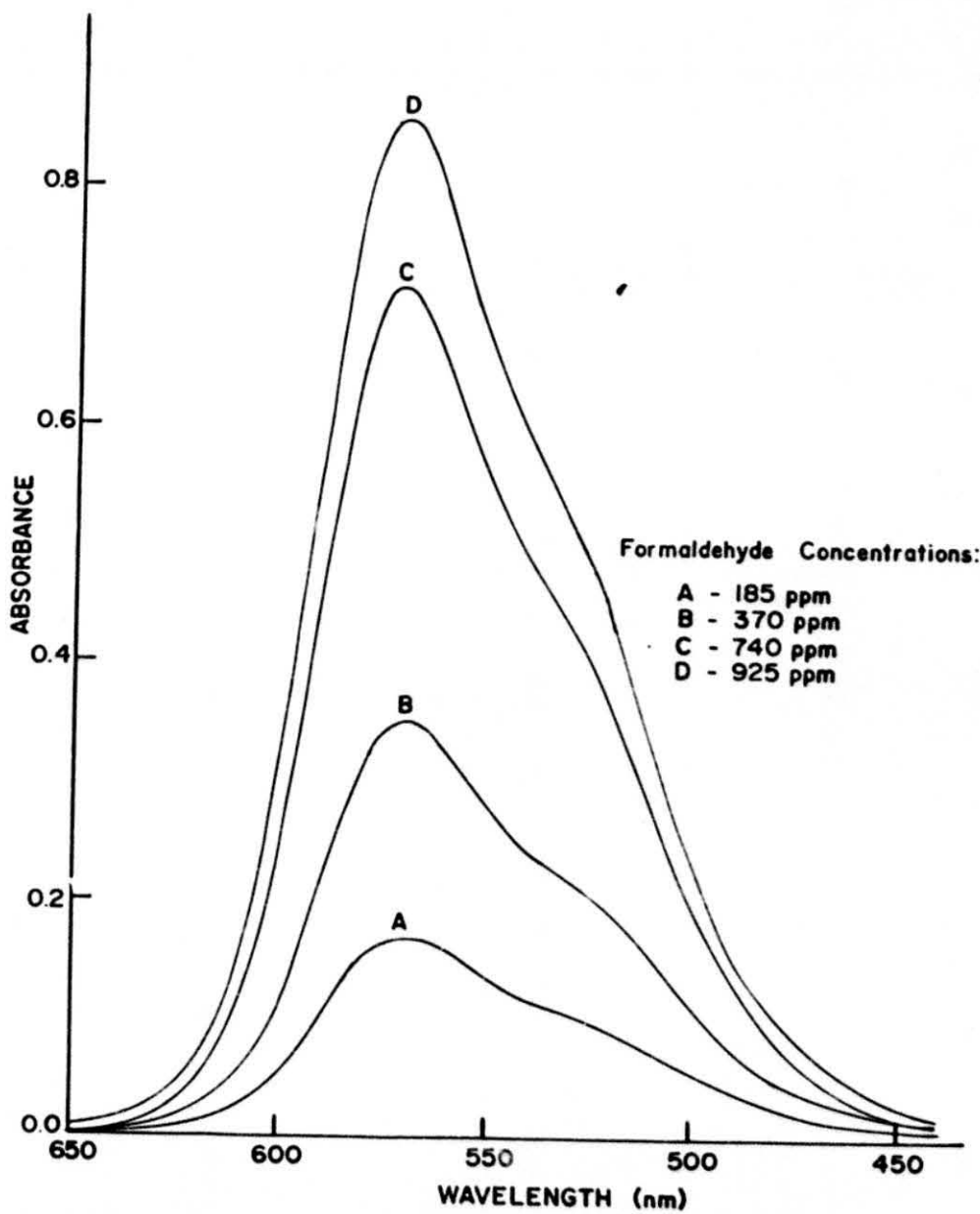


FIGURE 4. Plot of Absorbance vs Formaldehyde
Concentrations

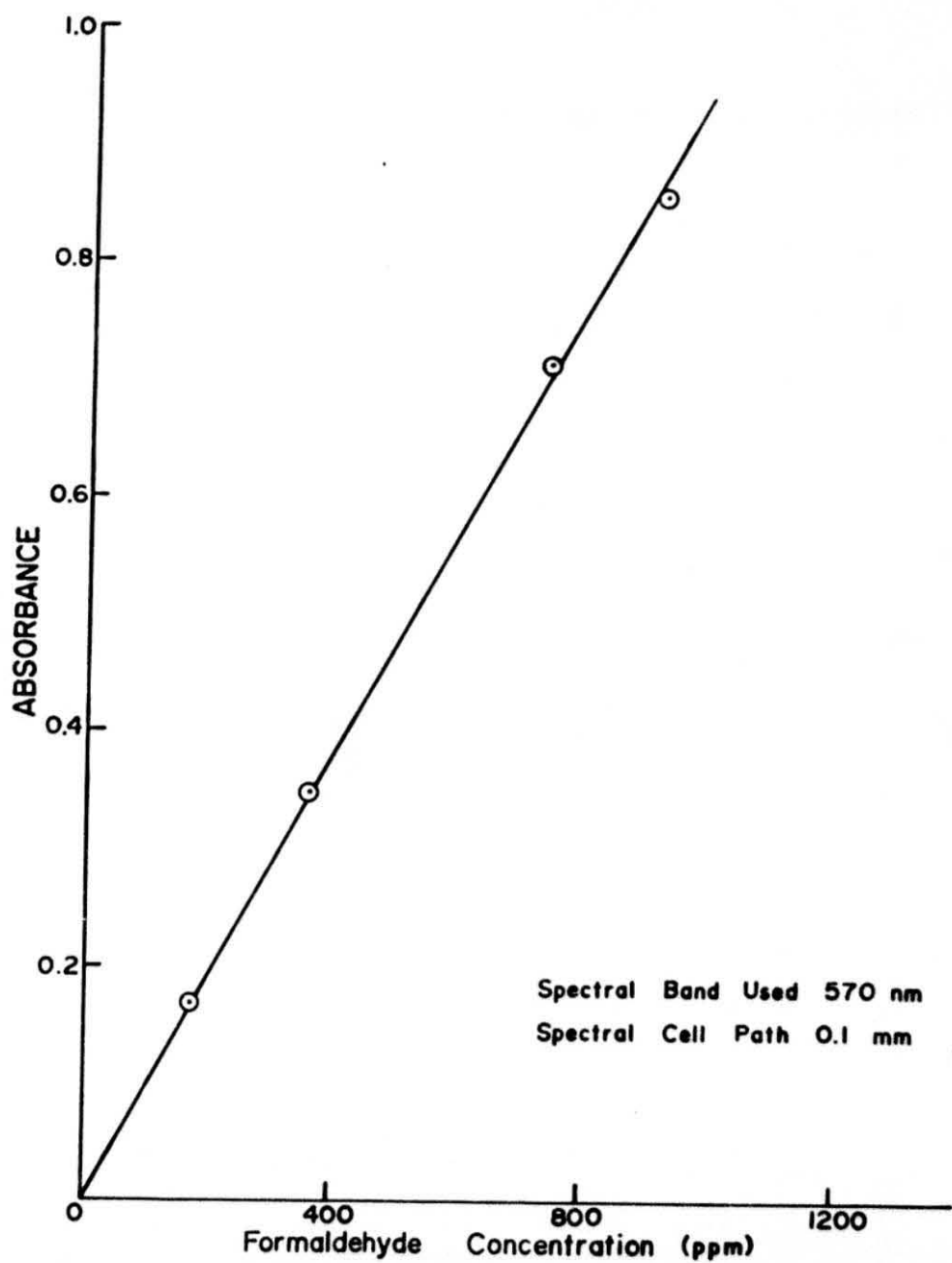


Table 2 contains the experimental data collected for the formaldehyde system. At ambient temperature, bypass samples contained 328-370 ppm formaldehyde in the gas stream as estimated from colorimetry. The gas stream was then passed through a four gram charge of Catalyst 3-7A at flow rates of 3.60-4.00 cc/sec. Colorimetric samples from the catalyst runs were shown to contain 370 ppm formaldehyde. Although the contact times are relatively long (600-667 millisecc) there was no apparent oxidation of formaldehyde at ambient temperature.

The temperature of the furnace was then elevated to 400°C and the formaldehyde vapor passed over the catalyst again. At 3.90 cc/sec, the gas stream through the bypass line contained 636 ppm formaldehyde. When passed over the catalyst, the colorimetric samples had absorbances identical to the bypass sample (636 ± 11 ppm) within experimental error. The last catalyst runs made on the formaldehyde system utilized flow rates of 4.00-4.10 cc/sec (contact times of 600 millisecc) with the formaldehyde concentration reduced to 106 ppm. The results were the same, i.e., no evidence of oxidation could be detected.

Colorimetric data suggest Catalyst 3-7A has no activity toward formaldehyde even at low formaldehyde concentrations (106 ppm) and high temperature. Gas chromatography confirms these results since no oxidation products could be detected. One possible experimental difficulty is the fact that the catalyst suffered discoloration at 400°C, and the chromatograms indicated only a trace of moisture. Therefore, the possibility

TABLE 2
Catalyst 3-7A Oxidation Activity Toward Formaldehyde

Ave Air Flow (cc/sec)	Contact Time (millisec)	Temp (C)	HCHO Conc* (ppm)	Sample	% Oxidation
4.00	---	25	328	bypass	---
3.80	---	25	328	bypass	---
4.20	---	25	370	bypass	---
3.60	667	25	370	catalyst	0
4.00	600	25	370	catalyst	0
3.90	---	400	636	bypass	---
4.00	600	400	636	catalyst	0
4.10	---	400	106	bypass	---
4.00	600	400	106	catalyst	0

*Colorimetric Fuchsin Aldehyde Method.

of catalytic poisoning cannot be ruled out and will be discussed later.

Hydrogen Cyanide. Gas streams containing hydrogen cyanide were passed over four grams of Catalyst 3-7A and the effluent gas monitored for oxidation by gas chromatography and Liebig titrations. After calibrating the detector with 10,600 ppm hydrogen cyanide, a 1.06% hydrogen cyanide gas sample in helium was mixed with a humidified air stream both at 25°C to form combined gas flow rates of 8.80-9.17 cc/sec. In the bypass mode, gas chromatography showed hydrogen cyanide concentrations in the gas stream to be 9283-9776 ppm while Liebig titrations with silver nitrate (0.017 M) showed 9847-9873 ppm hydrogen cyanide (Table 3). Since the two independent methods of analysis appear to be fairly consistent with each other, the gas stream was then allowed to flow over four grams of Catalyst 3-7A at ambient temperature with flow rates of 8.80-9.17 cc/sec. The catalyst showed low activity with less than 6% oxidation as verified by gas chromatography while the titration method showed less than 3% oxidation by the catalyst.

The temperature was then elevated to 100°C and then to 250°C with the respective chromatograms failing to detect any hydrogen cyanide at these temperatures, an indication that catalyst completely oxidized hydrogen cyanide gas under these conditions (8.83 cc/sec, 272 millisecc). The psuedo first order rate constant was calculated to be greater than 26 sec^{-1} with greater than 99.9% oxidation. At 400°C, the titration data shows 159-168 ppm hydrogen cyanide in the effluent gas stream

TABLE 3

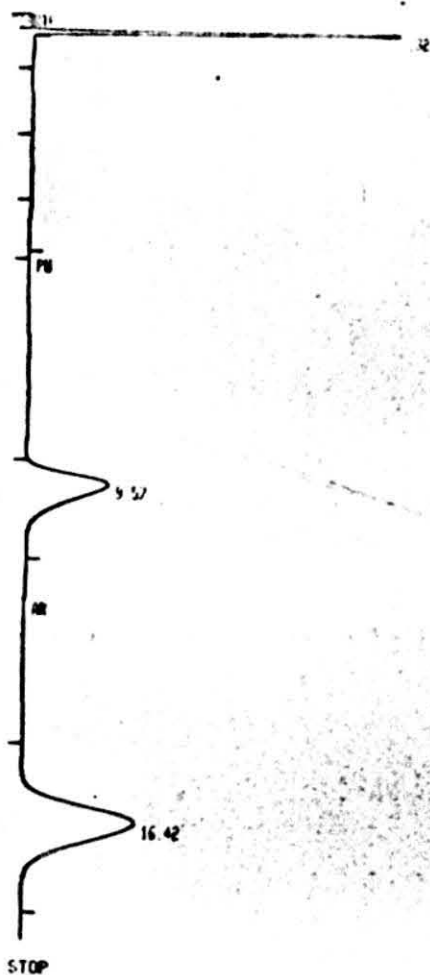
Catalyst 3-7A Oxidation Toward Hydrogen Cyanide

Total Gas Flow cc/sec	Contact Time (millisec)	Flow- Meter	GC*	Liebig	AgNO ₃ (ml)	Temp (°C)	Sample	GC	Liebig	GC	Liebig
8.23	---	10600	10600	10600	14.25	25	standard	---	----	---	----
8.83	---	9800	9776	9873	13.31	25	bypass	---	----	---	----
8.80	---	9877	9283	9847	13.20	25	bypass	---	----	---	----
8.80	273	9757	9212	9789	13.16	25	catalyst	5.6	1.1	0.2	<0.1
9.17	262	9039	8818	9522	12.80	25	catalyst	2.4	2.7	0.1	0.1
8.83	272	9880	<8	----	---	100	catalyst	>99.9	----	>26.2	----
8.83	272	9880	<8	----	---	250	catalyst	>99.9	----	>26.2	----
8.83	272	9880	<8	----	---	250	catalyst	>99.9	----	>26.2	----
8.83	272	9880	<8	159	0.20	400	catalyst	>99.9	98.5	>26.2	15.4
8.83	272	9880	<8	168	0.21	400	catalyst	>99.9	98.4	>26.2	15.2

which corresponds to a lower rate constant of about 15 sec^{-1} . Figures 5A and 5B depict chromatograms of the gas stream through the bypass line and over the catalyst, respectively at 400°C . The latter chromatogram (Figure 5B) shows the disappearance of the hydrogen cyanide peak (retention time = 16.4 min) and the appearance of an oxidation product peak (identified as carbon dioxide by its retention time of 1.08 min). It was noted that there was an increase in the water peak (retention time = 9.57 min). The effluent gas stream of the catalyst at 400°C was bubbled through a barium hydroxide solution to test for the presence of carbon dioxide. The appearance of a cloudy white precipitate (barium carbonate) suggested the presence of carbon dioxide. A similar test of the effluent gas stream from the bypass line indicated carbon dioxide was not present. If carbon dioxide is the oxidation product, it is suspected that the titration data at 400°C may not provide an accurate estimate of hydrogen cyanide in the gas stream. Interference from the precipitation of silver carbonate could be responsible for the discrepancy between the gas chromatography results and the results obtained from the Liebig titrations (premature endpoints due to turbidity of silver carbonate).

The gas chromatogram has a lower limit of detection of 100 area units corresponding to 8 ppm hydrogen cyanide and, hence, presents a more reliable method of hydrogen cyanide analysis. In either case, Catalyst 3-7A shows considerable activity toward the oxidation of hydrogen cyanide. One question which still remains is the fate of the nitrogen component of

FIGURE 5. Gas Chromatograms of Hydrogen Cyanide

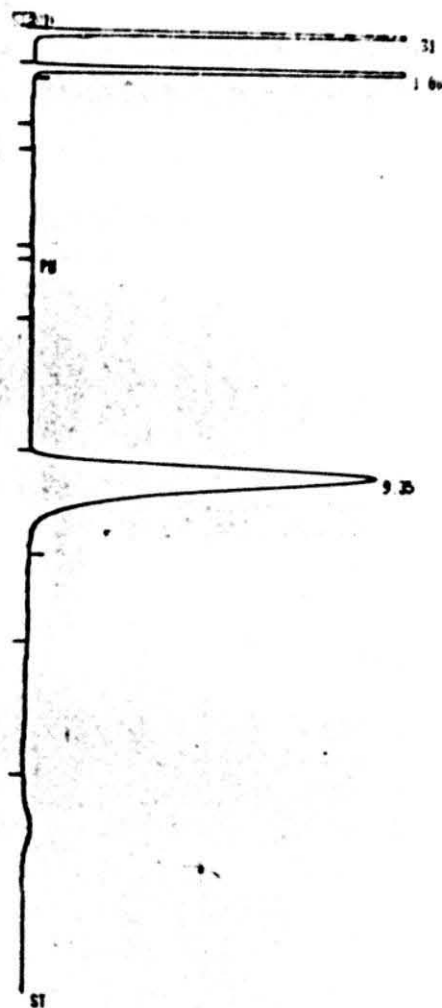


RUN # 119

SEP/02/81 23:17:25

AREA#	RT	AREA	TYPE	AR/MT	AREA#
0.32	42884	PB	0.043	18.174	
9.57	67586	BB	0.625	28.650	
16.42	125488	BB	0.846	53.176	

TOTAL AREA= 245378
 MUL FACTOR= 1.0000E+00



RUN # 112

SEP/02/81 16:41:06

AREA#	RT	AREA	TYPE	AR/MT	AREA#
0.31	654190	PB	0.038	62.315	
1.00	144570	PB	0.070	13.771	
9.35	251850	BB	0.562	23.914	

TOTAL AREA= 1049000
 MUL FACTOR= 1.0000E+00

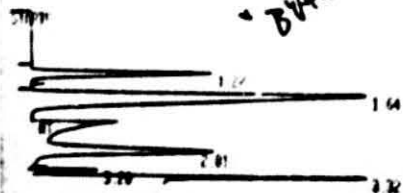
hydrogen cyanide. Chromatograms failed to show any peaks which could be attributed to an oxidation product containing nitrogen. Attempts to identify the oxidation products as oxides of nitrogen failed due to the insensitivity of the Porapak column or thermistor detectors in the gas chromatograph when nitrous oxide and nitric oxide were introduced as blanks.

Methane. Methane was analyzed for oxidation at ambient temperature and 400°C by means of gas chromatography. After calibrating the detector with 9890 ppm methane, the methane-helium gas stream was mixed with a humidified air stream and allowed to flow through the bypass line at 9.10 cc/sec and methane concentrations of 590-612 ppm (Table 4). The gas stream was then directed through a four-gram bed of Catalyst 3-7A using the same experimental conditions. Chromatographic analysis of the effluent gas stream failed to indicate a reduction of the methane peak (retention time 2.8 min) indicating no apparent oxidation of methane occurs at ambient temperature.

The temperature of the catalyst bed was then elevated to 400°C, and the total gas stream (6.84 cc/sec) was retested for oxidation. Chromatographic data indicates a 90.3-90.5% reduction of the methane peak at this elevated temperature. The concentration of methane in the gas stream is estimated to be 56-58 ppm with a contact time of 351 milliseconds, thus yielding a rate constant of 6.5-6.6 sec⁻¹.

Figures 6A and 6B are chromatograms of the bypass sample and a catalyst sample, respectively. Since the molecular sieve was used, oxygen, nitrogen, and methane are each separated

FIGURE 6A, B, C. Gas Chromatograms
of Methane

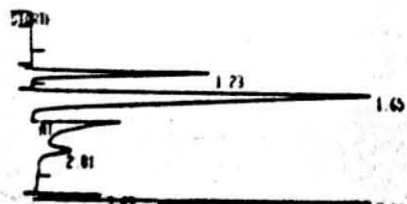


STOP

RUN 31 NUC/28/81 22:40:52

RT	AREA	TYPE	AR/HT	AREA%
1.22	2014700		0.091	19.832
1.64	1.217E+07	SPB	0.191	80.073
2.81	9312	BB	0.135	0.055
3.32	5229	PB	0.025	0.041

TOTAL AREA= 1.5292E+07
 MUL FACTOR= 1.0000E+00

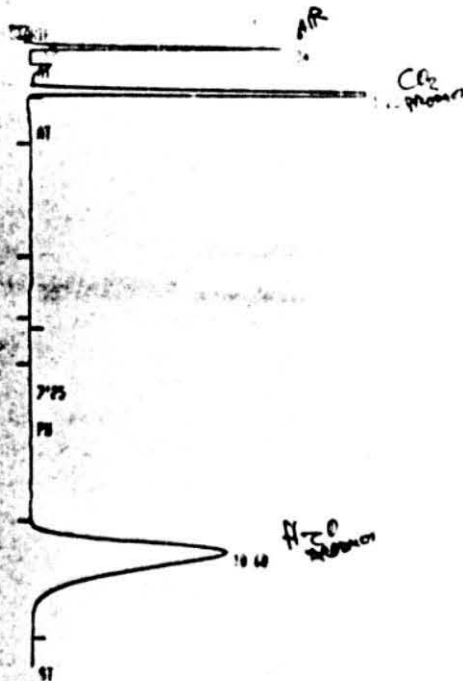


STOP

RUN 38 NUC/29/81 00:21:29

RT	AREA	TYPE	AR/HT	AREA%
1.23	2912500	PB	0.090	19.465
1.65	1.1015E+07	SPB	0.109	70.961
2.81	785	BB	0.008	0.005
3.69	376	D PB	0.018	0.003
10.63	238560	BB	0.026	0.025

TOTAL AREA= 1.4561E+07
 MUL FACTOR= 1.0000E+00



RUN 5

RT	AREA	TYPE	AR/HT	AREA%
0.25	483	PD	0.061	0.004
0.34	1.2079E+07	SPB	0.069	94.246
1.26	24692	BB	0.077	0.181
10.60	761090	PB	0.678	5.569

TOTAL AREA= 1.3664E+07
 MUL FACTOR= 1.0000E+00

into individual peaks. The peak between nitrogen and methane is the result of a change in the attenuation of the detector. Due to an increase in sensitivity, nitrogen tailing is apparent before the signal returns to the baseline. The peak at 3.3-3.8 minutes is a result of manually switching to the bypass mode since the flow rates through the different columns are not the same as in the catalyst. Figure 6C is a chromatogram of the oxidation products (carbon dioxide and water) obtained by operating the gas chromatograph in the bypass mode.

In addition to identifying carbon dioxide as an oxidation product by gas chromatography, the effluent gas stream was also bubbled through a solution of barium hydroxide. The formation of a cloudy white precipitate suggests the presence of carbon dioxide.

Tests using alumina support and sand in place of the catalyst did not indicate any detectable oxidation at 400°C.

Propane. Propane was tested for oxidation at flow rates of 7.02-9.15 cc/sec and concentrations of 626-788 ppm (Table 5). Calibration runs were performed on the propane-helium mixture (9700 ppm) in a manner as previously discussed. When the propane-helium gas stream was mixed with a humidified air stream, the resultant gas flow rates were 9.14-9.15 cc/sec through the bypass line with propane concentrations of 627-657 ppm in the gas stream as measured by the gas chromatograph. These concentrations were in good agreement with the flow meter estimates. After being passed over four grams of Catalyst 3-7A at a contact time of 263 millisecc, the chromatograms show no reduction of the propane concentration in the

TABLE 4

Catalyst 3-7A Oxidation Activity Toward Methane

Ave Gas Flow (cc/sec)			Contact Time (millisec)	Methane conc.(ppm)		Temp (°C)	Sample	% Oxidation	k (sec ⁻¹)
Methane	Air	Total		Flow meter	GC*				
0.55	---	0.55	---	9890	9890	25	Standard	----	---
0.55	8.55	9.10	---	598	612	25	bypass	----	---
0.55	8.55	9.10	---	598	590	25	bypass	----	---
0.55	8.55	9.10	264	598	591	25	catalyst	0	---
0.55	8.55	9.10	264	598	612	25	catalyst	0	---
0.39	6.45	6.84	351	564	56	400	catalyst	90.5	6.6
0.39	6.45	6.84	351	564	58	400	catalyst	90.3	6.5

*Methane retention time = 2.8 minutes.

TABLE 5

Catalyst 3-7A Oxidation Activity Toward Propane

Ave Gas Flow (cc/sec)			Contact Time (millisec)	Propane conc.(ppm)		Temp (°C)	Sample	% Oxidation	k (sec ⁻¹)
Propane	Air	Total		Flow meter	GC*				
0.59	---	0.59	---	9700	9700	25	standard	----	---
0.59	8.55	9.14	---	626	627	25	bypass	----	---
0.60	8.55	9.15	---	636	657	25	bypass	----	---
0.62	8.51	9.13	263	659	703	25	catalyst	0	---
0.62	8.51	9.13	263	659	670	25	catalyst	0	---
0.62	7.63	8.25	---	729	722	25	bypass	----	---
0.62	7.63	8.25	---	729	732	25	bypass	----	---
0.62	7.63	8.25	291	729	580	250	catalyst	20.4	0.8
0.62	7.63	8.25	291	729	595	250	catalyst	18.4	0.7
0.57	6.45	7.02	---	788	774	25	bypass	----	---
0.57	6.45	7.02	---	788	765	25	bypass	----	---
0.57	6.45	7.02	342	788	<10	400	catalyst	>98.7	>12.8
0.57	6.45	7.02	342	788	<10	400	catalyst	>98.7	>12.8

*Propane retention time = 6.5 minutes.

effluent gas at ambient temperature (25°C). The flow rates were then decreased to a total flow of 8.25 cc/sec through the bypass while increasing the propane concentration to 722-732 ppm. Using a slightly longer contact time of 291 millisecc, the chromatograph showed an 18.4-20.4 percent reduction of propane concentration at 250°C. This represents modest pseudo first order reaction rate constants of 0.7-0.8 sec⁻¹. The temperature was then elevated to 400°C and the flow rate reduced to 7.02 cc/sec. Bypass samples showed 765-774 ppm propane in the gas stream while catalyst samples were void of propane as shown in the gas chromatogram in Figure 7. Assuming the limit of detection for the gas chromatograph is 10 ppm propane, this represents an oxidation of over 98% with a rate constant greater than 12.8 sec⁻¹ for a contact time of 342 millisecc. Figure 7 depicts chromatograms for propane. Figure 7A is a chromatogram of the bypass sample while Figure 7B is for the catalyst run, both at 400°C. Note that the propane peak (retention time 6.5 min) disappears and the carbon dioxide peak appears. The effluent gas stream also gave a positive test for carbon dioxide when tested with a barium hydroxide solution. Tests with alumina and same at 400°C did not reveal any oxidation activity by the catalyst.

Isobutane. Table 6 lists the results of catalytic oxidation toward isobutane. Isobutane (10,100 ppm) was standardized on the gas chromatograph and the gas stream diluted with humidified air to obtain a flow rate of 9.14 cc/sec. Bypass samples contained 587-622 ppm isobutane from gas

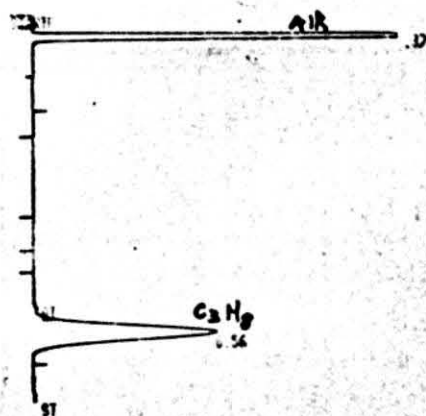
TABLE 6

Catalyst 3-7A Oxidation Activity Toward Isobutane

Ave Gas Flow (cc/sec)		Total	Contact Time (millisec)	Isobutane Flow meter	Conc. (ppm) GC*	Temp (°C)	Sample	%Oxidation	k (sec ⁻¹)
Isobutane	Air								
0.59	----	0.59	---	10100	10100	25	Standard	----	---
0.59	8.55	9.14	---	626	622	25	bypass	----	---
0.59	8.55	9.14	---	626	587	25	bypass	----	---
0.64	8.55	9.19	261	703	734	25	catalyst	0	---
0.78	8.55	9.33	257	842	841	25	catalyst	0	---
0.59	8.55	9.14	---	626	623	25	bypass	----	---
0.59	8.55	9.14	263	626	412	250	catalyst	34.2	1.6
0.59	8.55	9.14	263	626	483	250	catalyst	22.8	1.0
0.59	8.55	9.14	263	626	<10	400	catalyst	>98.4	>15.7
0.59	8.55	9.14	263	626	<10	400	catalyst	>98.4	>15.7

*Isobutane retention time = 16.3 min.

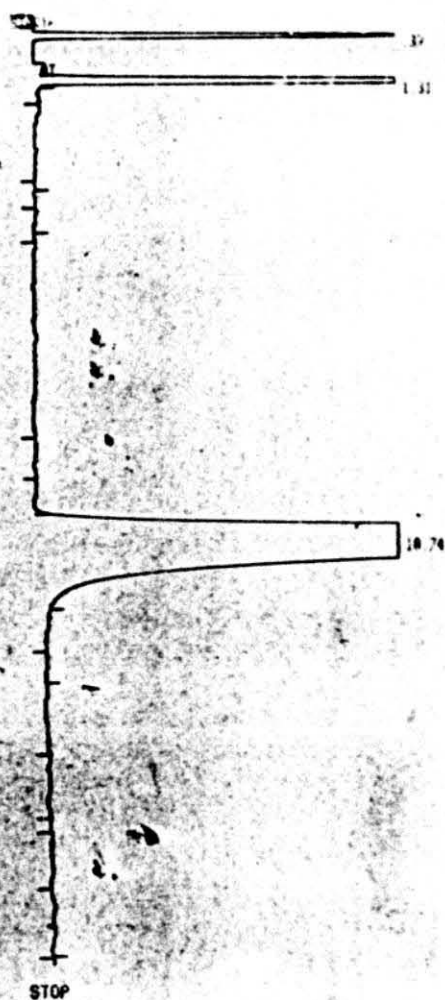
FIGURE 7. Gas Chromatograms of Propane



RUN # 41 AUG/29/81 01:55:27

AREA#	RT	AREA	TYPE	AR/HT	AREA#
0.37	1.4299E+07	SPB	0.078	99.864	
6.56	19540	BB	0.327	0.137	

TOTAL AREA= 1.4318E+07
 MUL FACTOR= 1.0000E+00



RUN # 45 AUG/29/81 03:08:15

AREA#	RT	AREA	TYPE	AR/HT	AREA#
0.37	1.380E+07	SEB	0.077	97.000	
1.31	41546	BB	0.050	0.200	
10.74	207100	BB	0.585	1.000	

TOTAL AREA= 1.4318E+07
 MUL FACTOR= 1.0000E+00

chromatograph measurements in fair agreement with the flow meter estimates. When the gas stream was passed over four grams of Catalyst 3-7A with contact times of 257-261 milliseconds there was no apparent oxidation at ambient temperature.

At 250°C, the catalyst appeared to partially oxidize isobutane in the gas stream showing between 22.8-34.2 percent oxidation. The effluent gas was estimated to contain 412-483 ppm isobutane leading to rate constants of 1.0-1.6 sec⁻¹ at a contact time of 263 millisecond.

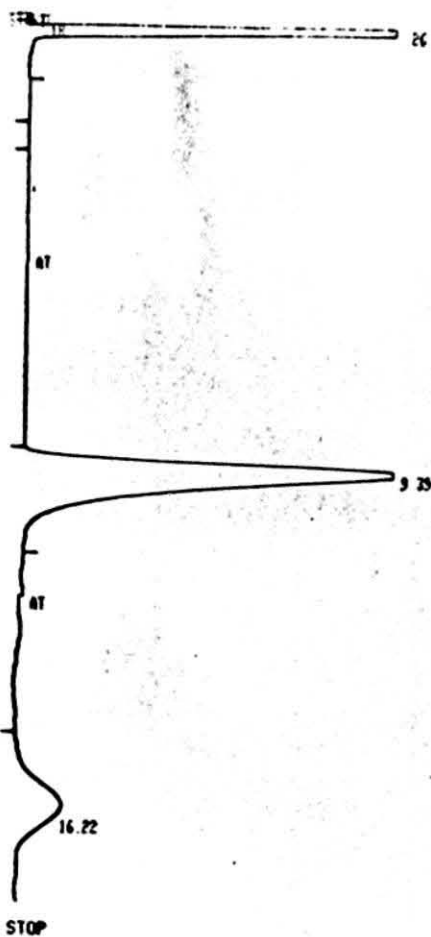
When the temperature was elevated further to 400°C, the gas chromatograph failed to detect any isobutane in the effluent gas stream (less than 10 ppm). For contact times of 263 milliseconds, the pseudo first order rate constant was calculated to be greater than 15.7 sec⁻¹ with oxidation activity in excess of 98%.

Figures 8A and 8B are chromatograms of bypass and catalyst runs at 400°C, respectively. The disappearance of the isobutane peak is accompanied by the appearance of the carbon dioxide peak together with an increase in the water peak. The effluent gas gave a positive test for carbon dioxide when bubbled through barium hydroxide solution.

Comparable flow rates and isobutane concentrations were used over four grams of alumina support and of sand at 400°C. In each case, there was no evidence of activity toward oxidation of isobutane.

Summary and Discussion. Figure 9 summarizes the oxidation behavior of the five gases at different temperatures. The oxidation products in all instances were believed to be carbon

FIGURE 8A, B. Gas Chromatograms of Isobutane

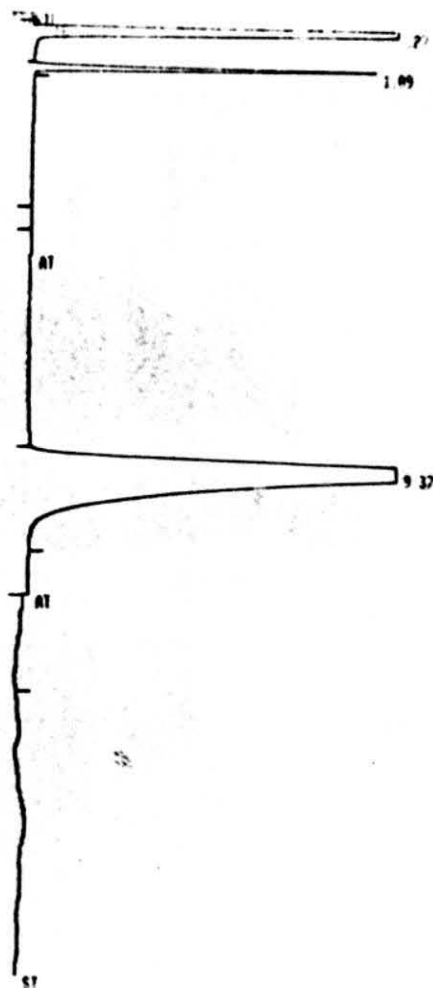


RUN 0132

SEP/03/01 04:25:27

AREA	RT	AREA TYPE	AR/MT	AREA
0.10	424	PB	0.057	0.003
0.25	1.2400E+07	SPB	0.069	97.550
9.39	294120	PB	0.500	2.314
16.22	16030	IM	1.004	0.133

TOTAL AREA= 1.2711E+07
 MUL FACTOR= 1.0000E+00



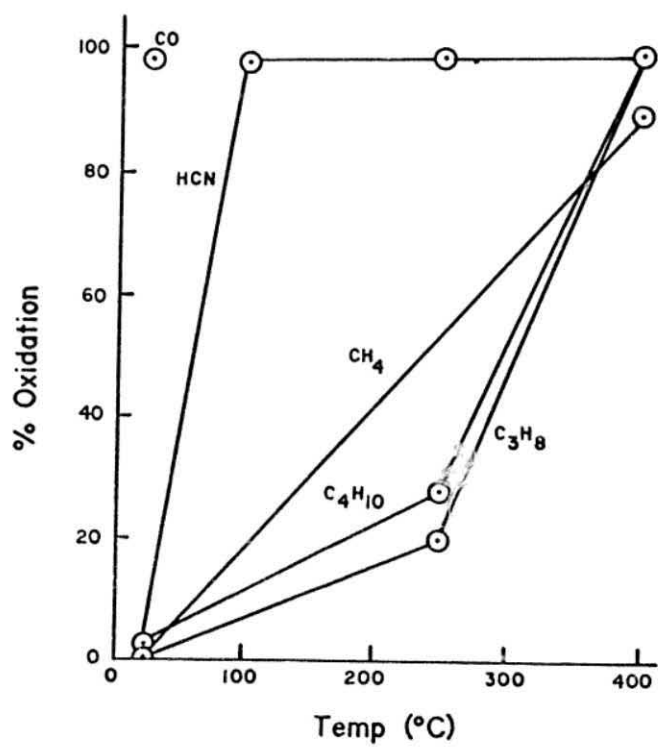
RUN 0133

SEP/03/01 05:02:40

AREA	RT	AREA TYPE	AR/MT	AREA
0.10	355	PB	0.045	0.003
0.27	1.0703E+07	SPB	0.064	95.900
1.09	63035	IM	0.071	0.595
9.37	30550	IM	0.500	3.440

TOTAL AREA= 1.0706E+07
 MUL FACTOR= 1.0000E+00

FIGURE 9. Summary of Oxidation Results



dioxide and water except in the oxidation of carbon monoxide where carbon dioxide is the only product and HCN where an additional product involving nitrogen could not be detected. Catalyst 3-7A has the greatest activity toward carbon monoxide, which was the only gas to be oxidized at ambient temperature. The second most active gas to be oxidized appears to be hydrogen cyanide, which is completely oxidized at temperatures above 100°C.

The three alkane gases show the expected order of oxidation reactivity over a range of temperatures as reflected by their rate constants at 400°C (Table 7). Studies have been performed on alumina supported palladium metal catalysts which examine the adsorption and retention of hydrocarbons.⁽⁴³⁾ It was shown that propane was retained by the catalyst in greater concentrations than either methane or ethane. The reason given is the case of the dissociatively adsorbed fragments which result from C-H cleavage. However, at temperatures above 200°C, cleavage of C-C bonds was also shown to be a factor. Our observed sequence of hydrocarbon reactivity (isobutane > propane > methane) appears to rule out an anionic mechanism since tertiary C-H bonds were found to be more reactive than secondary and primary C-H bonds in this type reaction.⁽⁴⁴⁾

There was no evidence for the oxidation of formaldehyde with Catalyst 3-7A as mentioned earlier, and results are subject to scrutiny since aldehydes are more easily oxidized than alkanes. It is possible that the experimental method may be inappropriate. Perhaps oxidation did occur and was

TABLE 7
SUMMARY OF KINETIC RESULTS
FOR VARIOUS GASES

Gas	Temp (°C)	% Oxidation	k (sec ⁻¹)
Carbon Monoxide	25	97.1 - 99.8	8.1 - 13.8
Hydrogen Cyanide	400	>99.9	>26.2
Methane	400	90.3 - 90.5	6.5 - 6.6
Propane	400	>98.7	>12.8
Isobutane	400	>98.4	>15.7

not detected. On the other hand, the catalyst could have been poisoned. Possible explanations for poisoning may be a surface phenomena between the formaldehyde and the catalyst or insufficient moisture for the catalyst to perform the oxidations. The surface of the catalyst could have been covered by repolymerized paraformaldehyde rendering the catalyst inactive or there could be a chelating effect between formaldehyde and the metal active sites on the catalyst. However, at 400°C there may be sufficient thermal energy to dissociate metal complex formations or sublime repolymerized paraformaldehyde, thus weakening these arguments. The most plausible explanation for the apparent inactivity of Catalyst 3-7A toward formaldehyde is the lack of moisture. The gas train assembly included an ethanol scrubber mounted out of the gas stream by the ethanol, thus resulting in only trace amounts of water being available for the catalyst. This is supported by the low concentration of water recorded on the gas chromatograph.

Although it is difficult to rationalize the inactivity toward formaldehyde, it is clear that Catalyst 3-7A is quite efficient at oxidizing the other gases. The oxidation activity of the catalyst is attributed to the palladium and copper salts on the alumina support since neither the alumina support nor high temperatures showed any oxidation activity toward these gases. Comparison of Catalyst 3-7A with other catalytic systems discussed in the literature is difficult since experimental conditions were not always reported. As can be seen

in Table 8, Catalyst 3-7A has activity toward the oxidation of carbon monoxide and hydrocarbons which is comparable to other catalysts. Several other catalysts achieve high conversions of carbon monoxide although they appear to require somewhat higher temperatures. The zeolite catalyst containing manganese and copper oxides has activities similar to Catalyst 3-7A at comparable temperatures although the zeolite catalyst requires a dessicant and reversal of the direction of gas flow every ten minutes since moisture deactivates this catalyst. For the oxidation of hydrocarbons, Catalyst 3-7A has similar activity at comparable temperatures. It is impossible to make direct comparisons since information such as amount of catalyst, and flow rates are not reported.

TABLE 8

Comparison of Catalyst 3-7A with Other Catalytic Systems

	Temp (°C)	% Conversion		Ref
		Carbon Monoxide	Hydro- Carbon	
SnO ₂ -Sb ₂ O ₃ -MnO-PdO	350	100	---	45
MnO ₂ -CuO	350	60	---	45
Fe ₂ O ₃ -Fe ₃ O ₄	350	40	---	45
CuO-Cr ₂ O ₃ on alumina	350-390	75-98	---	46
PdCl ₂ on carbon	---	98	---	47
Mn-Co oxides	---	<50	---	48
Mn-Co-NaOCl oxides	---	>99	---	48
MnO ₂ -CuO Zeolite with dessicant	20	98	---	49,50
Cs-Cr oxides on alumina	---	94	90	51
Ba-Cr oxides on alumina	---	96	99	51
Cs-Cr oxides on alumina with PbBr ₂	---	92	92	51
Ba-Cr oxides on alumina with PbBr ₂	---	83	93	51
Pt-Rh oxides on alumina	300	79-91	34-35	52
Pd-Cu-Ba oxides on alumina	370	90	---	53
Pd-Cu-Ba oxides on alumina	470	---	90	53
Cu-Pd-Cr oxides	---	91	96	54
Pd on alumina	450	98-99	95-91	55
Pd on alumina	---	36-41	49-50	56
Cr-oxide-Pd	300-350	---	93-100	57
MnO ₂ -Pb ₃ O ₄ -Cu	600	90	90	58
Cu-Fe oxides	>600	100	100	59
Mn ₂ O ₃ on alumina and silica	---	99	35	60
Pt on alumina and silica	230	100	---	61
Pt on alumina and silica	430	---	100	61
Catalyst 3-7A	400	100	90	--

RECOMMENDATIONS

Since our results in the evaluation of Catalyst 3-7A have shown considerable oxidation activity toward hydrogen cyanide, methane, propane, isobutane, and carbon monoxide, there is sufficient evidence to warrant further studies on this catalyst system. In order to optimize the utilization of this catalyst, it would be desirable to determine such parameters as maximum flow rates and substrate concentrations which can be used per given amount of catalyst before the efficiency of the oxidation is reduced. The catalyst should also be subjected to practical testing such as a catalytic converter in a car where typical automotive exhausts contain high concentrations of pollutants and a low concentration of oxygen. Catalyst 3-7A could be used in other ways such as in cigarette filters. Finally, the catalyst should be retested with formaldehyde to rule out the possibility of catalytic poisoning. Formaldehyde could be tested in the presence of carbon monoxide so that the oxidation of carbon monoxide could serve as the indicator instead of formaldehyde. In this way it may be determined if formaldehyde poisons the catalyst or if the catalyst is inactive toward formaldehyde.

The information on the following page was contained within a patent and during the writing of this thesis was believed to be vital security information. Certain portions of this patent are not complete at this time and may necessitate withholding publication of this thesis. On November 20, 1982, after the oral examination of Mr. Kawas it was decided to include this information to enhance the thesis. Therefore, the information contained on the following page has been included in the form of an Addendum.

Robert D. Farina

Dr. Robert D. Farina
Director of Thesis

ADDENDUM

Catalyst 3-7A consists of the following palladium(II) and copper(II) salts based on one gram of dry catalyst at 200°C:

Pd	3.05 mg as Pd(II)
Cu	22.70 mg as Cu(II)
Cl	9.62 mg as chloride
S	8.01 mg as sulfate

These transition metal salts are placed on a neutral alumina (80-200 mesh) support.

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