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RESEARCH AND DEVELOPMENT STUDY
RELATED TO THE SYNTHESIS OF
FORMALDEHYDE FROM CO₂ AND H₂

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SYNTHESIS OF FORMALDEHYDE

Introduction

This report summarizes the activities of the General American Research Division during August through October, 1967 on Contract NAS2-3889, Synthesis of Formaldehyde. The activities during this quarter were concerned with (1) oxidation of methane to formaldehyde by air using a gaseous nitric oxide catalyst in conjunction with various solid, heated reaction beds in a single pass reactor (2) preliminary testing of a recycle system using nitric oxide catalyst, and (3) oxidation of methane to formaldehyde with ozonized air or oxygen in the heated potassium tetraborate reaction bed.

Reaction beds filled with silica-alumina, alumina, porcelain, and silicon carbide coated with metal salts, were tested in conjunction with gaseous NO catalyst. None of these surpassed potassium tetraborate deposited on either hard porcelain or alumina in its ability to produce formaldehyde while holding the concentrations of carbon oxides at low levels.

Since a recycle system will probably necessitate a build-up of carbon oxides, experiments were performed where the nitrogen of the air in feed gas was replaced by carbon dioxide. It was established that the presence of even high concentrations (55%) of carbon dioxide in the system does not inhibit the formation of formaldehyde.

An analysis of total nitrogen oxides ($\text{NO} + \text{NO}_2$) in the feed and in the product was made using a colorimetric method based on Griess-Ilosvay reaction. It indicated that there was no significant loss of NO_x during the methane oxidation in single pass reactors.

A recycle system capable of recirculating gas at a rate of up to 9 l/min was built and tested with gaseous NO catalyst. Operating this system at 650 - 678°C, at a recycled gas velocity of 5000 cc/min, and with a feed consisting of methane-air mixtures added to the system at a rate of 180 cc/min. (i.e., recycle ratio of approximately 28), the highest formaldehyde yield achieved was 17.7%. The formaldehyde yield, however, drops with time apparently because a steady composition of the recycling gas cannot be maintained using an air-methane feed; the use of air results in a sharp drop in oxygen concentrations.

In spite of numerous attempts, high formaldehyde yields claimed by Guttehoffnungshutte in German patents using ozone and BaO_2 could not be repeated. However, as noted in the monthly reports, a proprietary catalyst bed gave up to 0.9 - 1.1% yield of formaldehyde in single pass reactors using ozonized oxygen.

As a preliminary to a recycle system, experiments were performed to ozonize oxygen-methane mixtures. When passed through an ozonator, the presence of methane in higher concentrations decreases the O_3 production sharply; however, mixtures containing up to 4% CH_4 in oxygen produce sufficient amounts of ozone to be recirculated in a recycle system.

Work Performed

1. Oxidation of Methane Using Nitric Oxide Catalyst.

The use of nitric oxide as a homogeneous gas phase catalyst for the partial oxidation of methane to formaldehyde was investigated in single pass reactors having a heated reaction bed packed with various solid materials. Among the materials investigated, none surpassed hard porcelain Berl saddles coated with potassium tetraborate in the formation of formaldehyde; besides, the use of nearly all other materials resulted in much higher production of CO and CO₂ than with potassium tetraborate under the same operating conditions. Analysis of the nitric oxides (NO + NO₂) in the intake and in the product indicated that there was no significant loss of nitric oxides during the reaction in single pass reactors. Experiments were performed both with methane-air and methane-oxygen mixtures; however, the methane-oxygen mixtures are much more difficult to operate with because of the ever present danger of ignition or even explosion inside of the reaction tube. Since recycling systems will probably necessitate a build-up of carbon oxides, tests were made with gas mixtures where the nitrogen of the air was replaced by carbon dioxide. It was found that the presence of carbon dioxide does not inhibit the formation of formaldehyde.

1.1 Single Pass Reactor Using NO Catalyst.

Investigation of the partial oxidation of methane by air using a gaseous nitric oxide catalyst was continued in a single pass reactor. The experiments were performed in a 23 mm I.D. Vycor reaction tube containing a 4" long heated reaction zone which was filled with approximately 40 cc of

various solid materials. Nitric oxide was premixed with the cold air stream in amounts necessary to produce 0.2% NO in the reaction mixture. Methane was then mixed with this NO containing air to give a mixture of 30% CH₄, 70% air, and 0.2% NO before entering the reaction tube.

Numerous experiments indicated that a more controlled operation was achieved with a diluent in the reaction gas. Better temperature control, lower conversion to carbon oxides, and much less chance of ignition or explosion have been experienced with air-methane mixtures as compared with oxygen-methane mixtures. Since a recycling system will probably cause a build-up of carbon oxides in the recirculating gas, tests were made to determine to what extent the yield of formaldehyde would be influenced if nitrogen were replaced by carbon dioxide. Therefore, single pass experiments were performed using a feed gas consisting of a mixture containing 30% CH₄, 14.7% O₂, 55.3% CO₂, and 0.2% NO. This mixture has the same concentrations of oxygen and methane as that of 30% CH₄ in air, except the nitrogen is replaced by carbon dioxide. Experiments using potassium tetraborate beds have indicated that replacement of nitrogen with carbon dioxide did not change the formaldehyde yield. As an example, a run obtained with methane-oxygen-carbon dioxide mixture at 610°C and space velocity of 5250 hr⁻¹ produced a 2.2% yield of formaldehyde, while an air-30% methane feed under the same conditions gave a 2.1 % yield. From these tests it appears that the presence of CO₂ in the system does not inhibit the formation of formaldehyde.

To determine whether there is any loss of NO during the partial oxidation of methane, total nitrogen oxides (NO + NO₂) were measured in the intake and in the product of an operating, single pass system using air-methane feed. The analysis for NO_x was made by a modified ASTM procedure D1607-60 which is based on Griess-Ilosvay reaction and indicates the sum of NO and NO₂ present in the system. A known volume of the nitrogen oxides, NO_x, containing gas is taken and the NO is converted to NO₂ by oxygen in the presence of an absorbing solution of sulfanilic acid and a N(1-naphthyl) ethylenediamine dihydrochloride dye in 14% acetic acid. The intensity of color due to the presence of NO₂ is measured by a colorimeter at 550 m μ and the NO_x concentration read from a calibration curve.

Analysis of a feed gas mixture to which 0.2% NO was added dynamically showed the presence of 0.21% NO_x. This feed was passed through a potassium tetraborate bed at 705°C; the product contained CH₂O, H₂O, CO, and CO₂ besides unreacted CH₄ and air. This product was found to contain 0.21% NO_x indicating that there was no measurable loss of NO_x during the methane oxidation in a single pass reactor.

1.2 Recycle System Using NO Catalyst

A recycling system capable of recirculating gas at a velocity of up to 9 l/min has been assembled and tested. The reactor of the recycling system is the same Vycor glass 23 mm I.D. tube containing a 4" long heated zone filled with approximately 40 cc of porcelain Berl saddles coated with potassium tetraborate. The entire gas mixture is recirculated by a Neptune diaphragm pump. From the reactor, the product gas passed through one or two

condensers immersed in dry-ice-acetone cooling bath where the formaldehyde and water are condensed as solids. Then the gas, freed from CH_2O and H_2O , goes to the pump and is recycled to the intake of the reactor. Fresh gas, consisting of CH_4 , air, and NO is added to the system at the intake end of the reactor. A portion of the recycling gas is vented primarily to remove nitrogen, at a rate which is somewhat lower than the feed rate but sufficient to maintain a stable internal pressure.

Runs were made with potassium tetraborate beds (40 cc vol.) maintained at $650^\circ - 678^\circ\text{C}$. The gas was recirculated at a rate of 5000 cc/min. and a fresh feed was added to the system at a rate of 180 cc/min; thus, the recycle ratio was approximately 28. Sufficient gas was vented (approximately 160 - 170 cc/min) to maintain the recycling system at 2.5 - 3 inches water pressure above atmospheric. Nitric oxide was added to the feed gas at a rate sufficient to maintain its concentration in the feed gas at 0.2%.

When the feed gas composition was 30% CH_4 and 70% air, formaldehyde yields reaching up to 17.7% of the methane in feed were obtained during the first hour of operation. However, the yields decreased continuously in subsequent hourly checks during a continuous 5 hour long operation. Gas analysis indicated that the composition of the recirculating gas changes with time and the oxygen concentration drops sharply from 15 - 17% at the start to 5 - 6% after the first hour.

To improve the formaldehyde yield, the methane to air ratio in the feed gas was varied lowering the CH_4 concentration in feed to 16.6% and increasing the air accordingly. At 650°C , the formaldehyde yield during the first hour

remained 16 - 17% of methane input; however, after one hour the yield decreases to an average of approximately 13%, which corresponds to approximately 0.47% per pass.

A reduction of the recycling gas velocity to 3000 cc/min. which, correspondingly, changed the recycle ratio to 17, gave a 17% yield of formaldehyde during the first hour but later decreased to an average of 11%, i.e., 0.65% per pass. The concentration of oxygen dropped, but it could be maintained eventually at 7 - 9% for several hours.

Calculations indicate that at high recycle ratios the oxygen concentration cannot be maintained at desirable levels (approaching 15%) with air-methane mixtures alone. Experiments are underway in which additional oxygen is being added to the feed gas to maintain the oxygen concentrations in the recycled gas stream at the desired level.

2. Oxidation of Methane Using Ozonized Oxygen

Oxidation of methane to formaldehyde using ozone is attractive because excess ozone is decomposed in the heated reaction bed. The product gas contains only unreacted CH_4 , O_2 , or air and products of methane oxidation, namely, CH_2O , H_2O , CO , and CO_2 . Separation of the product is simplified by comparison to systems utilizing a NO catalyst which does not decompose and which may have to be removed in a separate process. Therefore, additional tests were conducted to achieve the formaldehyde yields claimed by Guttehoffnungshutte in German patents. However, the yields obtained with barium peroxide were meager, reaching up to 0.3% of the methane input. Somewhat better results were obtained with proprietary reactor beds where the form-

aldehyde yield reached 0.9% of methane input; this yield is approximately comparable to those reported previously with potassium tetraborate beds.

The feasibility of producing ozone by passing oxygen-methane or air-methane mixtures through an ozonator was investigated. Unfortunately, the presence of methane in concentrations above 5% reduces the ozone production very sharply; however, when 4% methane in oxygen mixtures were used, the concentration of ozone in the product was essentially the same as in oxygen alone, that is, about 1.2% by volume of total gas. Interestingly, small amounts of formaldehyde accounting for 0.04 - 0.08% of methane were formed when oxygen-methane mixtures were passed through an ozonator.

2.1 Single Pass Reactor Using Ozonized Oxygen

Renewed efforts were made to achieve good formaldehyde yields claimed by Guttehoffnungshutte in German patents using a barium peroxide reactor bed. Extensive previous investigations, using BaO_2 made in the U.S.A., gave meager formaldehyde yields. A barium peroxide sample was obtained from Remy and Company, Hamburg, Germany and a reactor bed was prepared from this material to compare its activity to BaO_2 made in U.S.A.

First, finely ground BaO_2 powder was deposited on moistened procelain Berl saddles. This material was tested at temperatures ranging up to $430^{\circ}C$ and space velocities of 3600 hr^{-1} using oxygen-methane mixtures containing 0.4 volume % O_3 . The highest formaldehyde yield obtained was 0.29% of the methane input.

Next, materials were prepared by blending 98.5 wt % BaO_2 , 1 wt % Na_2O_2 , and 0.5 wt % Ag_2O and depositing on silica wool; this was tested with oxygen-methane mixtures containing up to 0.55% O_3 . No formaldehyde was obtained in the temperature range of $40^\circ - 430^\circ\text{C}$.

Technical barium oxide from U. S. sources was deposited on porcelain Berl saddles and tested in the temperature range $150^\circ - 540^\circ\text{C}$. With oxygen-methane mixtures containing 0.47% O_3 , the formaldehyde yield was 0.13 - 0.15% based on methane. Air-methane mixtures containing 30% CH_4 and 0.28% O_3 gave formaldehyde yields up to 0.23% of methane at 540°C .

A proprietary material reported previously, was tested with a mixture containing 20% CH_4 , 17% O_2 , 63% N_2 , and ozone concentrations of 0.35%. At a space velocity of $12,000 \text{ hr}^{-1}$ and reaction temperature of 705°C , a formaldehyde yield of 0.9% based on methane input was achieved in a single pass reactor; however, the CO concentration in the product was high, equivalent to a yield of 2.5% of the methane feed.

In spite of numerous attempts and variations in the experimental conditions and in the preparation of the reactor bed material, high formaldehyde yields using barium peroxide claimed by German patents could not be repeated. In fact, the proprietary material gave formaldehyde yields of 0.9 - 1.1% based on methane, which are 3 - 4 times higher than yields obtained with BaO_2 under similar conditions and the same O_3 concentrations in the gas intake.

2.2 Feasibility of Production of Ozone in Methane-Oxygen Mixtures

To avoid excessive bleed-off and still maintain an adequate ozone concentration, a recycle system with ozonized oxygen or air will probably necessitate passing all or at least a large part of the methane-oxygen mixture through an ozonator. To determine the feasibility of producing ozone directly in methane-oxygen mixtures, gas streams of various compositions were passed through a small, air cooled ozonator and the percent of O_3 produced determined by iodometric titration.

The ozonator used in these tests consists of two concentric glass tubes (the outside tube is 1-3/8" O.D., the inside, 13/16" O.D.); the outer surface of the outside tube is surrounded by a 5-3/8" long strip of aluminum foil and the entire inner surface of the smaller tube is aluminized with finely divided aluminum particles deposited on the surface. The aluminized surfaces were connected to the output of a 15,000 V transformer whose voltage is regulated by varying the voltage of the primary. Ozone is produced by passing oxygen or air between the two glass tubes. Generally, there is no ozone produced until the voltage of the primary reaches approximately 80 - 85 v, corresponding to the voltage applied to the ozonator of approximately 11,000 volts. It was found that the uncooled ozonator generates enough heat to increase its temperature quite rapidly, resulting in arcing and stoppage of O_3 production. However, by cooling the center core of the ozonator with an air stream prechilled in a dry-ice-acetone bath the temperature of the ozonator can be maintained in the $-10^{\circ}C$ to $10^{\circ}C$ region quite easily; a stable electrical current and constant O_3 production is then readily obtained.

Gases were passed through the ozonator kept at an average temperature of 0°C with the primary kept at 90 V (resulting in approximately 12,000 V applied to the ozonator). The percent of O₃ produced under various flow conditions and with different gases were as follows:

<u>Gas</u>	<u>Flow, ml/min</u>	<u>% O₃</u>
Oxygen	500	1.2
Oxygen	1000	0.6 - 0.7
Air	500	0.75
Air	1000	0.33
98% O ₂ + 2% CH ₄	500	1.14
96% O ₂ + 4% CH ₄	500	1.16
80% Air - 20% CH ₄	500	0.10
40% O ₂ - 60% CH ₄	500	0.01 - 0.06

These results indicate that the presence of methane decreases the ozone production very sharply; however, mixtures containing up to 4% CH₄ in oxygen produce sufficient amounts of ozone to be recirculated in a recycle system.

Small amounts of formaldehyde, reaching yields of 0.04 - 0.08% based on methane input, were produced in the ozonator with the 40% O₂ - 60% CH₄ mixtures. In one test, the product was analyzed for carbon oxides; there were no detectable amounts of CO₂ but the CO concentration was approximately 0.2% of the product gas.

A mixture of 95% O₂ - 5% CH₄ was passed through the ozonator at a rate of 500 cc/min. The product gas was then passed directly through a reactor containing 40 cc of porcelain Berl saddles coated with potassium tetraborate

maintained at 650°C. The formaldehyde yield obtained was 0.8% of the methane. Therefore, it appears possible that oxygen-methane mixtures containing a low percent of CH₄ can be recycled directly through an ozonator and reactor.

Future Activities

The recycling system with the NO gaseous catalyst will be tested further with variations in the flow, recycling ratio, feed composition, bleed-off rate, and reaction temperature to obtain the optimum conditions for the production of formaldehyde without excessive formation of carbon monoxide and carbon dioxide. Also, a closed recycling system operating with a recirculating gas of constant composition (approximately 30% CH₄, 15% O₂, remainder N₂, CO, CO₂) which is maintained by adding suitable amounts of oxygen and methane will be investigated.

A recycling system with ozone will be investigated. One variation of system operation will be to add ozonized oxygen and maintain a suitable bleed-off; the other, to recirculate the entire gas mixture through the ozonator. As has been shown, this method of recycling is feasible with gas mixtures containing low methane concentrations. This would result in small total amounts of formaldehyde produced; however, it has an advantage in that it requires no bleed-off and can possibly be operated as a completely closed system.