AIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

A3
A2

DOE/PC/92110--T5

QUARTERLY TECHNICAL PROGRESS REPORT 5
OCTOBER - DECEMBER, 1993

DEVELOPMENT OF VANADIUM-PHOSPHATE CATALYSTS FOR METHANOL
PRODUCTION BY SELECTIVE OXIDATION OF METHANE

Prepared for
Gary Stiegel (Technical Project Officer)
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236

By
Robert L. McCormick (Principal Investigator)
Mahesh C. Jha (Program Manager)
Robert D. Streuber (Intern)
Cyprus Amax Research and Development Center
Golden, CO 80403-7499

DOE Contract No. DE-AC22-92PC92110
Contract Date: October 1, 1992
Anticipated Completion Date: March 31, 1995
Government Award For Current Fiscal Year: \$210,000

January 28, 1994

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

RECEIVED
USDOE/ETIC
94 APR -4 PM 2:01
ACQUISITION & RECORDS

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

EXECUTIVE SUMMARY	1
INTRODUCTION	3
PROJECT DESCRIPTION	3
Objectives	3
Project Overview	3
PROJECT STATUS	5
Catalyst Testing	5
Tests for Transport Limitations	5
Methanol Oxidation Runs	5
Characterization of Used Catalysts	6
Preparation of Silica Supported Catalysts	7
Preparation of Promoted Catalysts	8
PLANNED ACTIVITIES	11
SUMMARY	11

LIST OF TABLES AND FIGURES

Table 1. Results of tests for external transport limitations.	5
Table 2. Results of methanol oxidation over $(VO)_2P_2O_7$.	6
Table 3. Characterization of silica supported catalysts.	8
Table 4. Characterization of promoted catalysts.	8
Figure 1. X-ray diffraction data for catalyst used in methanol oxidation tests.	7
Figure 2. X-ray diffraction data for silica supported catalyst precursors: a) small pore silica, 1.2 wt% V, b) small pore silica, 4.5 wt% V, c) large pore silica, 4.3 wt% V.	9
Figure 3. X-ray diffraction data for a) unpromoted catalyst precursor, b) Mo promoted catalyst precursor, c) Co promoted catalyst precursor, d) K promoted catalyst precursor.	10

EXECUTIVE SUMMARY

This document is the fifth quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". During this quarter several runs directed at revealing the presence of transport limitations, if present, were conducted. Also, methanol oxidation over vanadyl pyrophosphate was studied in a series of tests that investigated the effects of pressure, temperature, and methanol:oxygen ratio. Work on the preparation of a silica supported catalyst continued and several promoted catalysts were prepared.

To test for transport limitations external to the catalyst particle feed gas flow rate was varied while maintaining a constant residence time. These experiments revealed the possibility of transport limitations at flow rates below 100 sccm at 575°C. Future experiments will be conducted at flow rates well above this value. We also plan to vary catalyst particle size in future runs to test for pore diffusion limitations.

Methanol oxidation was investigated over the temperature range of 250-350°C, the pressure range of 1-10 atm, and methanol:oxygen ratios from 0.3 to 15. The main product observed under all conditions was dimethyl ether (DME). At the highest temperatures and 1 atm pressure some formaldehyde was produced. At high temperatures and pressures some methyl formate was produced. In many runs small amounts of methane were also observed. The observation of methane seems unusual and some future work will be directed at studying this further. Under all conditions selectivity to CO₂ was very low. Carbon monoxide was formed at the higher temperatures but in general selectivity to carbon oxides was quite low. Characterization of the catalyst used in these runs revealed no changes to the catalyst during testing. This is not surprising given the relatively low temperatures employed.

Attempts to prepare a silica supported vanadyl pyrophosphate have continued. To date several samples with different loading using both small and large pore silica have been prepared. The preparation involved impregnating the support with the reduced vanadate/phosphoric acid non-aqueous solution which results from the standard catalyst preparation. X-ray diffraction indicated that the desired precursor VO(HPO₄)-0.5H₂O is the only crystalline phase present. Activation of these materials will be performed in the next quarter.

Catalysts promoted with Co, Mo, and K have been prepared. The method of preparation was to add a small amount of the nitrate of these elements to the refluxing V₂O₅ solution before addition of phosphoric acid and precipitation. The target promoter to V ratio was 0.05 (molar) in all cases. X-ray diffraction indicated

that the Co promoted precursor was nearly identical to the unpromoted precursor. Addition of Mo produced a very poorly crystalline precursor which did, however, exhibit all of the diffraction lines of the desired compound. Potassium promotion lead to the formation of other phases in addition to the desired precursor. These samples will be characterized in more detail in the coming quarter. Additionally, activation of these samples will be performed.

At the end of the quarter all equipment for catalyst synthesis, characterization, and testing was transferred to the Colorado School of Mines. Work on the planned experiments will begin as soon as the contract is transferred to Mines, hopefully in February.

INTRODUCTION

This document is the fifth quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". During this quarter several runs directed at revealing the presence of transport limitations were conducted. Also, methanol oxidation over vanadyl pyrophosphate was studied in a series of tests that investigated the effects of pressure, temperature, and methanol:oxygen ratio. Work on the preparation of a silica supported catalyst continued and several promoted catalysts were prepared.

These results are discussed in detail below and plans for the coming quarter are outlined.

PROJECT DESCRIPTION

Objectives

The specific objectives of this project are:

- *To develop an economical catalyst for partial oxidation of methane to methanol.
- *To determine optimum conditions for methanol production from methane using VPO catalysts.
- *To utilize promoters and catalyst supports to improve methanol yield relative to the base case catalysts.
- *To provide a preliminary understanding of how these promoters and supports actually effect catalyst properties.
- *Use the information obtained to prepare advanced catalysts which will be tested for activity, selectivity, and stability.
- *Develop a simplified methanol production process flowsheet based on these advanced catalysts.

Project Overview

Under the project entitled "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane", Amax R&D is performing

laboratory scale development of a promising, practical catalyst for the selective oxidation of methane to methanol. The primary component of this catalyst is vanadium-phosphate (VPO) which has shown good activity and selectivity in the partial oxidation of n-butane and propane but has not been studied in detail for methane oxidation.

The goal of the project is to develop a catalyst which allows methane oxidation to methanol to be conducted at high conversion and selectivity. Ideally, a low CH_4/O_2 ratio will be employed with air as the source of oxygen. Initially some tests are being conducted under more conventional conditions of 90 to 95% methane, balance oxygen. Temperatures below 600 C and pressures up to 20 atm are to be investigated. The use of steam in the feed gas will also be investigated. The catalyst development strategy will be to utilize promoters and supports to improve the activity and selectivity of the unmodified VPO catalyst. Catalysts will be characterized by nitrogen adsorption/desorption, elemental analysis, x-ray powder diffraction, and FTIR.

The project is divided into four tasks:

Task 1: Laboratory Setup. Equipment for catalyst preparation and reactivity testing will be set up and tested. Gas analytical procedures will be developed. Blank reactor runs will be conducted. This task was completed at the end of December, 1992.

Task 2: Process and Catalyst Variable Study. Tests will be conducted to determine the optimum conditions of temperature, pressure, CH_4/O_2 ratio, $\text{H}_2\text{O}/\text{CH}_4$ ratio, space velocity, and catalyst P:V ratio for high activity and selectivity in methanol production. This task is essentially complete although a few more tests in this area may be conducted.

Task 3: The Effect of Promoters and Supports. Several promoters and supports will be tested. The measured response will be activity and selectivity in the methane oxidation reaction to methanol. Catalyst characterization will provide a fundamental understanding of these effects. This task has begun and work on preparing supported and promoted catalysts is described in this report.

Task 4: Advanced Catalyst Testing. Advanced catalysts which are both promoted and supported will be prepared. These catalysts will be tested in runs of relatively long duration (200 hours) to determine long-term activity, selectivity, and stability in methane oxidation to methanol. This task is slated to begin in August, 1994.

PROJECT STATUS

Catalyst Testing

Catalyst testing is performed in a quartz-lined microreactor system which has been described in previous reports.

Tests for Transport Limitations

Table 1 shows the results of several tests in which flowrate and bed volume were varied simultaneously. Our goal was to maintain constant bed residence time while varying gas velocity. Target conditions were not always obtained but the results indicate little significant difference in conversion for the different flow rates. We conclude that external transport limitations are not important for gas flow rates above 200 sccm. Future tests will employ varying catalyst particle size to test for pore diffusion limitations.

Table 1. Results of tests for external transport limitations.

<u>Flow</u> <u>Rate, sccm</u>	<u>Bed</u> <u>Volume, cc</u>	<u>V/F, sec</u>	<u>Percent</u> <u>Conversion</u>
208	0.868	0.25	6.4
315	1.736	0.33	6.6
450	2.604	0.35	6.7

Conditions: 575 °C, 1 atm, 2wt% V₂O₅/SiO₂

Methanol Oxidation Runs

Methanol oxidation was investigated because if the VPO catalyst does rapidly convert methanol, any methanol produced from methane will be rapidly consumed. The results of the tests in this series are shown in Table 2. The vanadium phosphate is a highly active catalyst for methanol conversion. Oxygen balances are generally good however the carbon balance was low for one or two of these runs. The primary product of methanol conversion over VPO is dimethyl ether (DME). Smaller amounts of formaldehyde, methane, and methyl formate (MF) were also observed. Formaldehyde formation is favored at the highest temperatures while DME is favored at lower temperatures.

The selectivity of the VPO catalyst is remarkable in that under most conditions carbon oxides are very minor products. DME is formed by dehydration of two methanol molecules producing one DME and one water. Formaldehyde and methyl formate are oxidation products of methanol and DME, respectively. The data in Table 2 indicate that for the formation of oxidation products higher temperatures,

pressures, and methanol/oxygen ratios are required. We plan to expand this data set with one or two more points at higher temperature. This may not be possible at elevated pressure because of reactor runaway.

Table 2. Results of methanol oxidation over $(VO)_2P_2O_7$.

Temperature °C	Pressure atm	Feed CH ₃ OH:O ₂	Percent Conversion	Percent Selectivity						Percent Balance	
				CO	CO ₂	DME	HCHO	MF	CH ₄	Carbon	Oxygen
250	1	0.3	27	0	0	93	0	0	7	100	98
350	1	0.3	85	11	0	39	48	0	2	81	97
300	1	3.1	31	2	0	77	19	0	2	102	98
250	1	9.9	10	0	0	93	0	0	7	100	99
350	1	10.8	45	1	0	80	17	0	2	96	90
250	5	1.4	7	7	0	83	30	0	0	99	99
250	5	3.1	12	1	5	94	0	0	0	100	97
300	5	2.3	31	6	1	92	0	0	1	100	94
350	5	2.7	85	28	1	73	0	0	0	98	73
300	5	15.3	18	2	1	94	0	2	1	101	102
250	10	1.1	8	0	4	95	0	0	1	100	99
300	7	2.1	20	12	1	86	0	0	1	102	93
250	10	13.9	7	2	2	90	5	0	1	99	98
350	10	8.7	44	10	1	86	1	2	0	95	88

Feed Flow Rate: 200 sccm

Catalyst Mass: 0.8 g

Feed Composition: 70 mole percent He/balance reactants

These results have important implications for development of methane conversion catalysts. They suggest that if methane activation and conversion could be obtained at temperatures below 400°C then high selectivities to DME might be observed. To date we have observed only very low activity for methane oxidation below 400°C. However, higher activities may be obtained by using longer residence time and lower methane:oxygen ratios than were employed in earlier tests. Also, to suppress secondary conversion of methanol it might be possible to destroy the active sites for dehydration by addition of basic ions such as alkali or alkaline earth metals. These ideas will be explored in future work.

Characterization of Used Catalysts

An x-ray diffraction pattern for the used catalyst from the methanol oxidation tests is shown in Figure 1. This pattern closely matches that of the fresh catalyst and corresponds to $(VO)_2P_2O_7$. The fact that the catalyst apparently did not decompose is not surprising considering that the highest temperature in this run was 350°C. Results of analysis for phosphorus have not yet been completed.

Figure 1. X-ray diffraction data for catalyst used in methanol oxidation tests.

Preparation of Silica Supported Catalysts

Efforts at preparing silica supported catalysts have continued and have focused primarily on impregnation of the support using the isobutyl/benzyl alcohol solution obtained during catalyst synthesis. The ratio of reactants to solvent has been reduced relative to the value used to prepared bulk catalyst. This allows preparation of supported catalysts with reasonable loadings, in the range of 1 to 10 weight percent vanadium. Results for three such preparations (in precursor form) are shown in Table 3. The supports employed are a small pore, acid

washed, precipitated silica obtained commercially and a large pore silica prepared by precipitation in the presence of a polymer from water glass. Loadings and P:V ratios for these supported precursors are in the desired range. Future characterization will include measurement of surface area and pore size distribution.

Table 3. Characterization of silica supported catalysts.

<u>Support</u>	<u>wt% V</u>	<u>Molar P:V</u>
Small pore	4.5	1.2
Small pore	1.2	1.3
Large pore	4.3	1.2

Figure 2 shows x-ray diffraction data for these three preparations. Both of the small pore samples exhibit only the peaks of the desired precursor $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$. The large pore sample shows additional peaks at 2.83 and 2.00 Å. X-ray diffraction data for the large pore support itself have not yet been obtained so it is unknown if these peaks are caused by an undesired VPO compound or are present in the support. These results are very encouraging and suggest that a supported VPO catalyst can be relatively easily prepared. The results of catalyst activation as well as surface area and pore structure characterization will be completed in the next quarter. We also plan to begin using other support materials and to test these catalysts in the microreactor system.

Preparation of Promoted Catalysts

To date catalysts promoted with Mo, Co, and K have been prepared. The procedure for promotion is to add precursor material to the refluxing V_2O_5 /solvent solution before addition of phosphoric acid. Table 4 lists the precursors, promoter:V ratios, and P:V ratios for these catalysts in precursor form.

Table 4. Characterization of promoted catalysts.
Values in parenthesis are target values, others are based on analysis.

<u>Promoter</u>	<u>Precursor</u>	<u>Molar Promoter:V</u>	<u>Molar P:V</u>
Mo	Ammonium Molybdate	0.01	1.03
Co	Cobalt Nitrate	0.04	0.99
K	Potassium Nitrate	(0.05)	(1.20)

Figure 3 shows x-ray diffraction data for these materials in precursor form along with an unpromoted precursor for comparison. All samples appear to contain the desired precursor $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$. In particular promotion with Co leads to a change of peak intensities but not to new peaks. Promotion with Mo or K

Figure 2. X-ray diffraction data for silica supported catalyst precursors: a) small pore silica, 1.2 wt% V, b) small pore silica, 4.5 wt% V, c) large pore silica, 4.3 wt% V.

Figure 3. X-ray diffraction patterns for a) unpromoted catalyst precursor, b) Mo promoted catalyst precursor, c) Co promoted catalyst precursor, d) K promoted catalyst precursor.

decreases the crystallinity of the sample and leads to the formation of several new peaks. Efforts in the coming months will be directed at identifying any other compounds that might be present based on their x-ray diffraction peaks. We also plan to activate these samples and test them in the microreactor system. Several other promoters are to be tested including Ce, Cr, Fe, Li, Ti, and Zn.

PLANNED ACTIVITIES

Planned activities focus on catalyst testing in the microreactor, more detailed characterization of promoted and supported catalysts, and synthesis of additional promoted and supported catalysts.

Future microreactor tests will employ varying catalyst particle size to test for pore diffusion limitations. Methanol oxidation tests will be conducted at slightly higher temperatures. Methane oxidation at temperatures below 400°C with higher feed oxygen content and longer residence time will be attempted. The effect of basic promoters on methanol oxidation over the VPO catalyst will be examined. The used methanol oxidation catalyst will be fully characterized.

More characterization results for the silica supported catalysts will be obtained. Specifically we will acquire x-ray diffraction data for the large pore silica to determine if any crystalline material is present. The measurement of surface area and pore size distribution for the silica supports and supported catalysts should provide some indication of the extent to which the active phase is actually within the pore structure of the support. We also plan to activate the supported materials and fully characterize these activated samples. Catalysts supported on other materials such as MgO, AlPO₄, and TiO₂ will be prepared. Testing of these materials in the microreactor system will begin as soon as possible.

More promoted catalysts will be prepared. These materials will be fully characterized in both precursor and activated forms. Testing of these materials in the microreactor will begin as soon as possible.

SUMMARY

The effort during this quarter has focused on testing of the VPO catalyst in methanol oxidation and on preparation of promoted and supported VPO catalysts. Additionally we have moved the project to the Colorado School of Mines in anticipation of contract transfer.

The VPO catalyst is highly active for conversion of methanol to dimethyl ether. Smaller amounts of formaldehyde and methyl formate were also observed.

Preliminary characterization results suggest that we have successfully prepared a silica supported VPO catalyst precursor. Activation of this sample will presumably lead to the desired catalytic phase, $(VO)_2P_2O_7$, on the silica support.

Catalysts promoted with Mo, Co, and K have been prepared. X-ray diffraction indicates that all of these materials contain the desired precursor phase although other materials may be present.

DATE

FILMED

6/22/94

END