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QUARTERLY TECHNICAL PROGRESS REPORT 3
APRIL - JUNE, 1993

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

Prepared for
U. S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania 15236

By
Robert L. McCormick
Mahesh C. Jha
Robert D. Streuber
Amax Research & Development Center
Golden, Colorado 80403-7499

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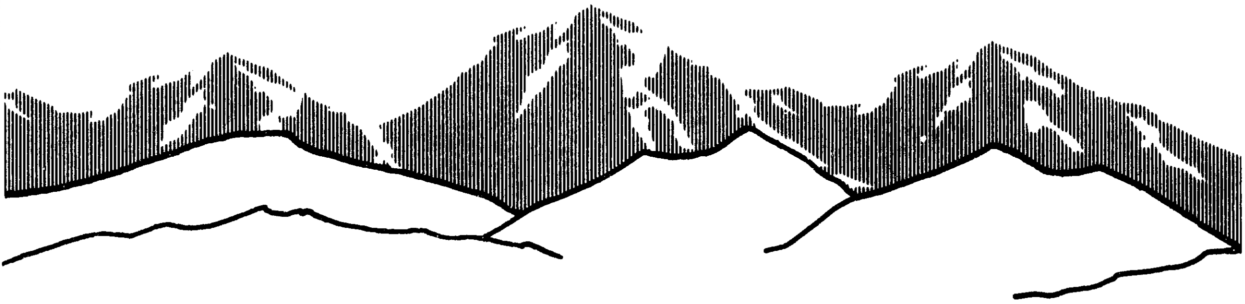

AMAX Research & Development Center
5950 McIntyre Street • Golden, Colorado 80403-7499

AMAX

QUARTERLY TECHNICAL PROGRESS REPORT 3
APRIL - JUNE, 1993

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

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

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

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LEGAL NOTICE

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EXECUTIVE SUMMARY

This document is the third 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, we have continued to develop methods for catalyst activation by investigating activation in wet gas environments. This procedure leads to the formation of highly crystalline $(VO)_2P_2O_7$, while activation under identical conditions, but with no moisture, leads to a poorly crystalline sample. Published data indicate that the highly crystalline form is representative of commercial butane oxidation catalysts.

The main focus of our work during this quarter has been in the area of catalyst testing in the microreactor system. We have tested a VPO catalyst using 3 percent methane in air and a stainless steel reactor under conditions similar to those reported last quarter for V_2O_5. The catalyst was initially a poorly crystalline sample of $(VO)_2P_2O_7$, but post reaction characterization demonstrated that this material had transformed into β-$VOPO_4$. This may have been caused by less than optimum preparation and activation procedures or inability of the 3 percent methane/air mixture to maintain the catalyst in a reduced state. Tests with this catalyst show that the VPO catalyst is significantly more active than V_2O_5 and produces primarily CO as compared to CO_2 for V_2O_5. This is somewhat surprising given the large excess of oxygen present under these conditions and suggests that modification of the VPO catalyst with promoters or a support might lead to the formation of selective products.

In order to confirm that our microreactor system was providing reliable data, we tested a V_2O_5/SiO_2 catalyst at atmospheric pressure and temperatures from 500 to 600°C using 90 to 95 percent CH_4/O_2. Several studies of methane oxidation using this catalyst have been published with reasonably good agreement between different research groups. We were not able to reproduce the literature data using steel reactors. However, when the steel reactor was lined with quartz and the post-catalyst reactor volume was minimized by packing with quartz chips, we obtained results which agree closely with those previously published.

Using the same quartz reactor and test conditions, we also tested a highly crystalline (wet activated) VPO catalyst. No partial oxidation products were observed, but the VPO catalyst was 3 to 4 times more active than V_2O_5/SiO_2 and active at 50°C lower temperature. This was true even though the VPO had a surface area only one tenth that of the silica supported catalyst. The primary reaction product was CO. A used catalyst removed from the reactor after testing at 500°C exhibited an X-ray diffraction pattern identical to that of the starting catalyst. This demonstrates that the wet activated VPO is stable in the 90 to 95 percent methane gas environment up to 500°C. Some mechanical degradation of the used catalyst pellets was observed and is being addressed by higher pelletization pressures and the use of 2 percent bentonite as a pelletization agent.

While methanol formation has not yet been observed over VPO, the high activity and stability of the catalyst are encouraging. Future tests under different process conditions in a quartz lined reactor and using supported or promoted catalysts will hopefully lead to the formation of selective products.

INTRODUCTION

The United States has vast natural gas reserves which could contribute significantly to our energy security if economical technologies for conversion to liquid fuels and chemicals were developed. Many of these reserves are small scale or in remote locations and of little value unless they can be transported to consumers. For natural gas, transportation is economically performed via pipeline, but this route is usually unavailable in remote locations. Another option is to convert the gas to liquid hydrocarbons such as methanol which can easily and economically be transported by truck. Therefore, the conversion of natural gas to liquid hydrocarbons has the potential to decrease our dependence upon oil imports by opening new markets for natural gas and increasing its use in the transportation and chemical sectors of the economy.

AMAX has a strong interest in developing new markets for natural gas because natural gas production/sales is one of the company's core businesses. Amax Oil and Gas Inc., headquartered in Houston, Texas, controls an estimated one trillion standard cubic feet (Tcf) of gas in the lower 48 United States. A new technology for methanol production from methane, the primary constituent of natural gas, could lead to increased production from these reserves.

Under Contract No. DE-AC22-92PC92110, 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.

The project was initiated in October of 1992 and has a 30-month duration. This document is the third quarterly technical progress report and presents results in the areas of catalyst activation and activity testing. The first quarterly report (McCormick and Jha, 1993a) discussed details of equipment setup and catalyst preparation. The second quarterly report (McCormick and Jha, 1993b) discussed catalyst preparation and activation as well as preliminary activity testing results.

PROJECT DESCRIPTION

OBJECTIVES

The specific objectives of this project are to:

- Develop an economical catalyst for partial oxidation of methane to methanol.
- Determine optimum conditions for methanol production from methane using VPO catalysts.
- Utilize promoters and catalyst supports to improve methanol yield relative to the base case catalysts.
- Provide a preliminary understanding of how these promoters and supports actually affect 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 (Hodnett, 1985) and propane (Ai, 1986) 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 percent methane, with the balance being 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 was set up and tested. Gas analytical procedures were developed. Blank reactor runs were conducted. This task was completed at the end of December 1992.

- Task 2. Process and Catalyst Variable Study

  Tests are being conducted to determine the optimum conditions of temperature, pressure, CH_4/O_2 ratio, H_2O/CH_4 ratio, space velocity, and catalyst P:V ratio for high activity and selectivity in methanol production. This task is ongoing.

- 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 is slated to begin in October 1993.

- 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

Work in the areas of catalyst activation and catalyst activity testing has been performed. These results are discussed in detail below.

CATALYST ACTIVATION

There is much experimental evidence that activation of the precursor to form the active catalyst is a critical step in catalyst preparation (Hodnett, 1985; Buchanan et al., 1985; Arnold and Sundaresan, 1988). This activation is typically carried out by first heating the precursor at 3°C/minute in air to 380°C and holding for 2 or more hours. A reaction gas environment (1 percent butane in air for maleic anhydride catalysts) is then introduced and the catalyst is heated at 3°C/minute to temperatures as high as 500°C. Activation to a fully equilibrated catalyst may take as long as 10 days, but a good indication of a catalyst's activity and selectivity can be obtained with times as short as 16 hours (Cornaglia et al., 1991). A large number of variations on this basic theme are reported in the patent and academic literature. For example, activation in hydrogen and nitrogen has been performed successfully. The heating rate can affect activation results. Steam has been shown to accelerate activation (Arnold and Sundaresan, 1988).

Optimal activation conditions for methane oxidation catalysts have not been determined. We are testing several different procedures and evaluating the results using X-ray diffraction. A good activation procedure should generate the X-ray diffraction pattern of $(VO_2)P_2O_7$ or the patented B-phase which is very similar to $(VO_2)P_2O_7$ (Schneider, 1975).

Methods Employed

VPO catalyst synthesis involves contacting V_2O_5 with aqueous acid or an organic alcohol under reflux conditions. During this stage, a portion of the vanadium is reduced to the +4 oxidation state. The slurry is then cooled and phosphoric acid is added. This mixture is then refluxed for an additional length of time wherein the remaining vanadium becomes reduced and the catalyst precursor $VO(HPO_4)\cdot 0.5H_2O$ is formed. The precursor is recovered by filtration or evaporation of the liquid. A very large number of variations on this basic method are described in the patent and scientific literature. We have only attempted a few of them, and a detailed description of the methods employed was provided in the second quarterly report (McCormick and Jha, 1993b).

Activation was carried out in a temperature programmable tube furnace under various flowing gas environments and for varying lengths of time as described below. Small porcelain boats were filled with precursor and inserted into the furnace cold. Initially 1 to 2 grams of sample was activated, but in later experiments, we utilized much smaller quantities in order to activate several samples at one time. Partial data on catalyst activation were presented last quarter and the full data set is presented here for completeness.

Activation Method 1

Activation was performed by heating directly to 500°C and holding for 24 or 48 hours under a 3 percent methane/air mixture.

Activation Method 2

The precursor was heated to 500°C at 5°C/minute under the 3 percent methane/air mixture and held for 24 hours.

Activation Method 3a

The sample was heated to 500°C at 5°C/minute under nitrogen and held for 24 hours.

Activation Method 3b

The sample was heated to 500°C at 3°C/minute under nitrogen and held for 16 hours.

Activation Method 4a

The sample was heated to 400°C at 5°C/minute in air and held at that temperature for 8 hours.

Activation Method 4b

The sample was heated to 400°C at 3°C/minute in air and held at that temperature for 24 hours.

Activation Method 4c

The sample was heated to 500°C at 3°C/minute in air and held 16 hours.

Activation Method 5a

The sample was heated in air at 3°C/minute to 380°C and held for 2 hours. The gas was switched to nitrogen and the sample was heated at 3°C/minute to 480°C and held for 16 hours.

Activation Method 5b

The sample was heated in air at 3°C/minute to 380°C and held for 2 hours. The gas was switched to nitrogen and the sample was heated at 3°C/minute to 500°C and held for 24 hours.

Activation Method 6

The sample was heated in air at 3°C/minute to 380°C and held for 2 hours. The gas was switched to 3 percent CH_4/air and the sample was heated at 3°C/minute to 480°C and held for 16 hours.

Activation Method 7

The sample was heated in nitrogen to 400°C at 3°C/minute and held 24 hours. The temperature was then increased at 3°C/minute to 500°C and held for 24 hours.

Activation Method 8

The sample was heated in air to 380°C at 3°C/minute and held 4 hours. The gas was then switched to nitrogen which was passed through a bubbler where it was saturated with moisture. The temperature was increased to 500°C at 3°C/minute and held for 16 hours.

Activation Method 9

The sample was heated in air to 400°C at 3°C/minute and held for 8 hours. The temperature was then raised to 500°C at 3°C/minute and held for an additional 8 hours.

Activated samples were characterized by X-ray powder diffraction, determination of P and V content, and measurement of BET surface area. XRD results suggest that the best results are obtained by holding at a temperature of 400°C or lower in any gas environment before going to higher temperatures. Non-oxidizing gas environments such as nitrogen are preferred for the higher temperature treatments. In dry gas environments, XRD patterns contain all of the peaks of $(VO)_2P_2O_7$, but intensities are highly skewed, suggesting that the solid state transformation is incomplete. Activation in wet gas leads to a highly crystalline sample of $(VO)_2P_2O_7$. This is shown in Figure 1 where a catalyst precursor made using preparation procedure D was activated using methods 5b and 8. Preparation methods were described in our last quarterly report. The sample activated in wet gas (activation method 8) exhibits a well developed diffraction pattern which closely agrees with literature data for $(VO)_2P_2O_7$.

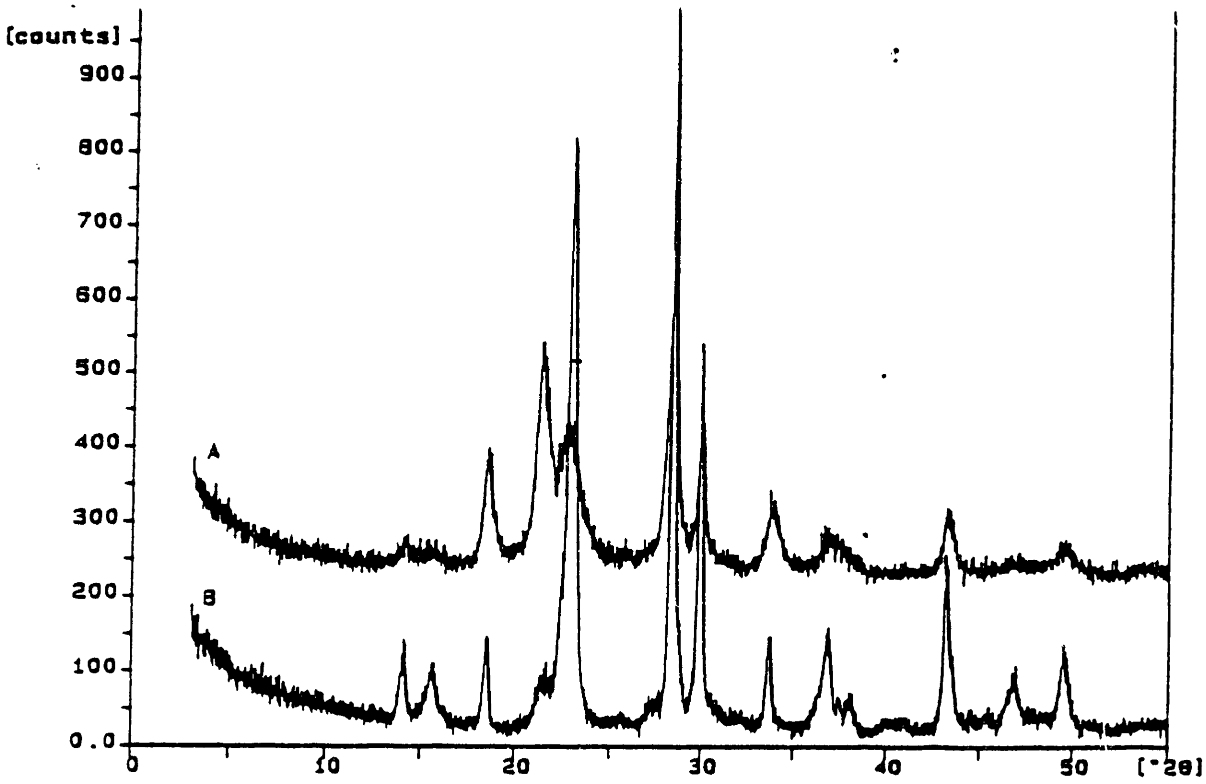

Figure 1. X-ray diffraction patterns of precursor D activated by a) activation method 5b and b) activation method 8.

Table 1 lists P:V ratios and surface areas for precursors and activated samples. Replicate P:V determinations on one sample produced the values 1.05, 1.01, 1.00, 1.03, 1.00, 1.04, and 1.02 for an average of 1.02 with standard deviation of 0.020. Given this level of analytical variability, it seems that the changes observed in the P:V ratio upon activation are significant in some cases.

Surface areas of the activated catalysts are generally in the range of 15 to 20 m^2/g. However, activation method 3 yielded catalysts with a higher surface area (27 m^2/g for preparation D and 71 m^2/g for preparation E). The much higher surface area of the sample from preparation E might have been caused by its significantly higher P:V ratio.

Table 1. P:V Ratios and Surface Areas for Activated Catalysts

Preparation Method	Activation Method	Precursor P:V	Activated P:V	Surface Area, m^2/g
B	1	0.91	0.96	19
B	2	0.91	0.92	20
C	1	0.94	0.99	20
D	2	1.02	0.97	19
D	3a	1.02	0.99	27
D	4a	1.02	1.01	23
D	4b	1.02	1.02	10
D	4c	1.02	1.01	22
D	5a	1.02	1.02	16
D	5b	1.02	1.00	15
D	6	1.02	1.02	15
D	7	1.02	0.99	21
D	8	1.02	0.97	18
D	9	1.02	1.02	19
E	2	1.11	1.07	8
E	3b	1.11	1.06	71
E	4c	1.11	1.06	16
E	8	1.11	1.04	16

CATALYST TESTING

Catalyst testing is performed in a microreactor system which has been described in previous reports. Stainless steel tubes of 3/8-inch diameter or quartz tubes of 6 mm inside diameter were used as the reactor vessel. The quartz tubes were cemented inside 1/2-inch stainless steel tubes. The catalyst precursor powder was pressed into a tablet using a hydraulic press and a pressure of 20,000 psi. These tablets were broken up and screened to 0.84 by 1.41 mm before activation. A bed height of 1 to 5 cm was employed which required a catalyst mass of 0.4 to 2.0 grams, depending upon which catalyst was being used. Fore and aft zones of the reactor were packed with quartz chips of the same particle size as the catalyst.

Tests Using 3 Percent Methane/Air

Last quarter we reported the results of a run using V_2O_5 as the catalyst. This catalyst produced only CO and CO_2, with CO_2 as the predominant product. This quarter we performed a similar run with the VPO catalyst produced by preparation method D and activated by activation method 9. This is probably not the optimum activation method, and other methods will be investigated in future runs.

The results of this run are listed in Table 2. Nominal temperatures are reported but actual bed temperatures were usually within 10°C of this value. Carbon balances were always between 95 and 105 percent. When compared to

V_2O_5, substantially higher conversions were obtained with the VPO catalyst. This can be seen in Figure 2 where methane conversion is plotted as a function of gas hourly space velocity (GHSV) for the runs at 260 psig. GHSV is the feed gas volumetric flow rate at STP divided by the reactor volume and is inversely proportional to residence time. Also shown in Figure 2 are the selectivities to CO as numbers above each data point. The fact that the VPO catalyst produces CO rather than CO_2 as the dominant product is significant in that literature reports suggest that CO forms from methanol and formaldehyde while CO_2 forms directly from methane via a different pathway (Amiridis et al., 1991). This suggests that changing the reaction conditions or modifying the catalyst with promoters or a support might lead to the production of selective products.

Table 2. Results of Methane Oxidation Run Using $(VO)_2P_2O_7$ (Preparation D, Activation 9) and 3 Percent CH_4/Air at 1 atm
(Experiment 1546-25)

Test	Nominal Temperature, °C	Pressure, psig	Air/CH_4 Flow, sccm	Steam Flow, sccm	% CH_4 Feed	% Conversion	% Selectivities	
							CO	CO_2
1	425	20	100	0	3.1	0	--	--
2	425	125	100	0	3.1	2	100	0
3	425	125	50	0	3.1	4	99	1
4	425	260	50	0	3.1	7	99	1
5	450	260	50	0	3.1	12	95	5
6	450	130	50	0	3.1	5	98	2
7	450	260	100	0	3.1	4	99	1
8	475	260	100	0	3.1	9	98	2
9	475	260	50	0	3.1	11	95	5
10	475	260	150	0	3.1	6	98	2

2.00 g catalyst (1546-24).
5.0 cm bed depth.
0.7747 cm diameter.

The VPO catalyst from this run was removed from the reactor and characterized. It was noted that the catalyst had changed in color from a dull green to a yellow-green during testing. This fact suggests that the $(VO)_2P_2O_7$ had transformed into ß-$VOPO_4$, a more oxidized phase, and this was confirmed by XRD. Diffraction patterns of the fresh and used catalyst are shown in Figure 3. The fresh catalyst is poorly crystalline $(VO)_2P_2O_7$. The used catalyst shows none of the peaks for this compound and all of the peaks of ß-$VOPO_4$. Non-optimum preparation and activation procedures are known to produce catalysts which are susceptible to oxidation. However, what seems more likely is that the reactivity of methane is much less than the reactivity of butane so that the reducing power of the feed gas mixture used in our tests was inadequate for maintaining the catalyst in a reduced

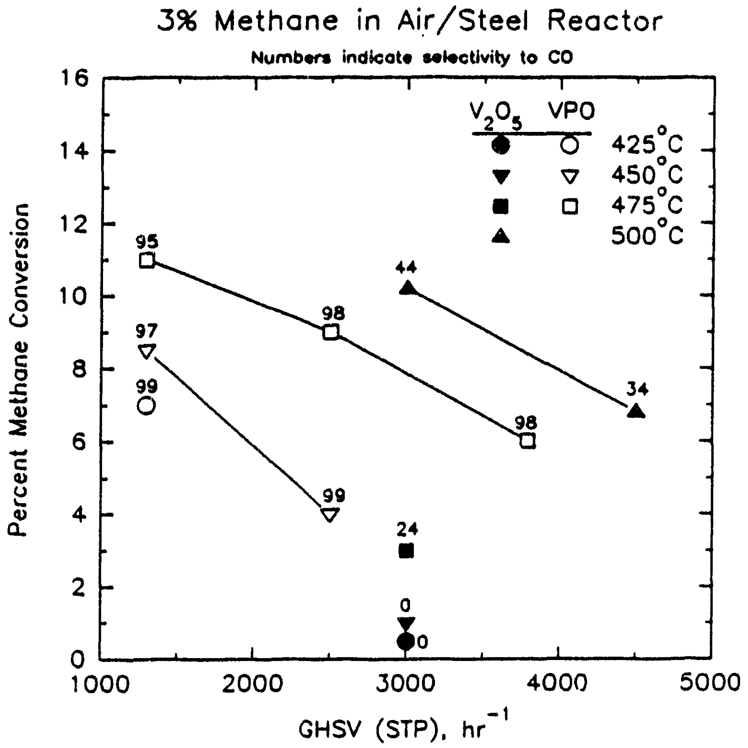

Figure 2. Percent methane conversion as a function of GHSV (STP) at various temperatures for runs conducted at 260 psig using V_2O_5 and a VPO catalyst.

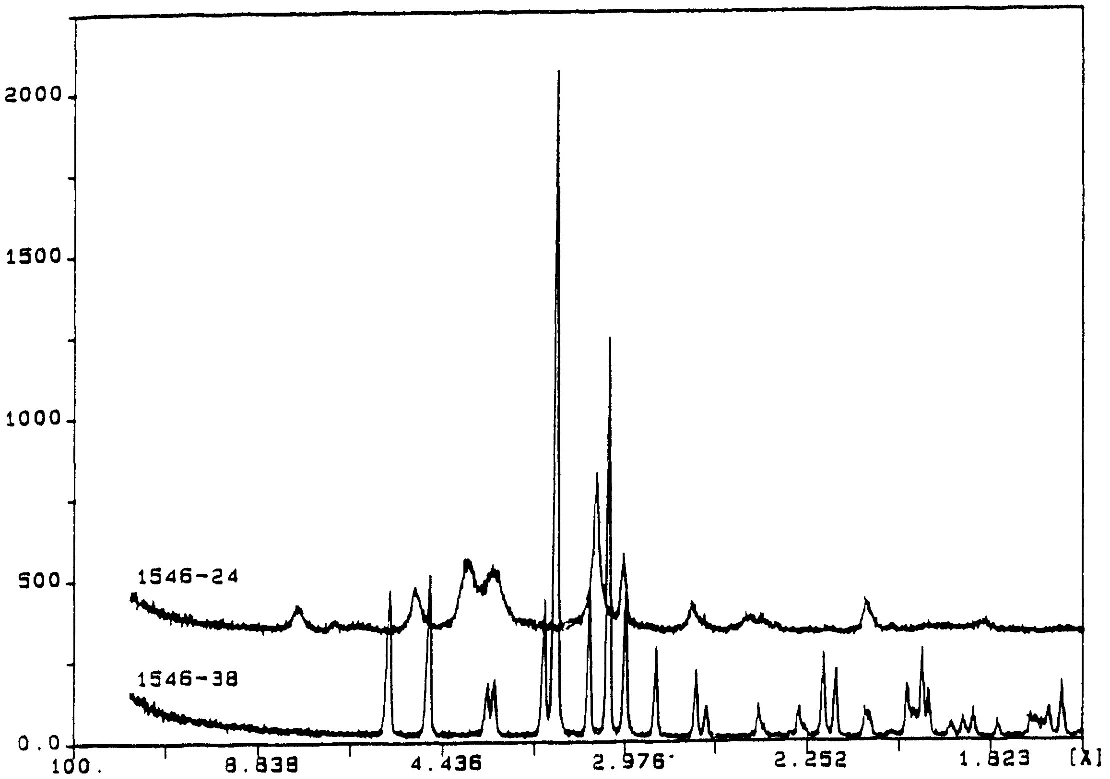

Figure 3. X-ray powder diffraction patterns for fresh (1546-24) and used (1546-38) VPO catalyst from the 3 percent methane run.

state. This might be addressed by the addition of promoters or by using higher concentrations of methane.

Tests Using 90 to 95 Percent Methane/Oxygen

In an attempt to stabilize the VPO catalyst with a more reducing gas environment, we elected to perform tests under conventional methane oxidation conditions using 90 to 95 percent methane in oxygen. While working with these conditions, it also seemed prudent to attempt to reproduce some literature data to confirm the reliability of our system. We attempted to reproduce the data reported by Spencer and Pereira (1989) and by Koranne and coworkers (1992) for methane oxidation at atmospheric pressure and high CH_4/O_2 ratios. Operating conditions were:

- 500 to 600°C.
- 5 to 10 percent O_2 in CH_4.
- 1 atm total pressure.
- V_2O_5/SiO_2 catalyst (1 weight percent V).

We found that to reproduce their results, the use of a quartz or quartz lined reactor was critical. Also, the volume of the post-reactor hot zone must be reduced as much as possible. Quartz is thought to reduce the contribution of gas phase free radical reactions. Using this type of the reactor, the results shown in Table 3 were obtained. Modifications to our analytical system improved carbon balances to 98 - 102 percent. Formaldehyde, CO, and CO_2 were the only products observed in measurable quantities. Trace quantities of methanol were observed under some conditions. Our results are in good agreement with the data reported in the literature as shown in Figure 4 where formaldehyde selectivity is plotted versus conversion. These tests confirm the reliability of our experimental system. However, the selectivities reported above using a stainless steel reactor may have been seriously skewed by gas phase reactions and should be regarded with suspicion.

Using the same quartz reactor and test conditions, a test was performed with a VPO catalyst activated in a wet environment to produce highly crystalline $(VO)_2P_2O_7$. Results are listed in Table 4. Carbon oxides are the only products observed under these conditions and CO is by far the predominant product. GC malfunction prevented determination of accurate selectivities for tests 1 - 10. The VPO catalyst was much more active than V_2O_5/SiO_2, as shown in Figure 5 where conversion is plotted as a function of temperature for both catalysts under otherwise identical conditions. It should be noted that the surface area of the silica supported catalyst is 160 m^2/g, while that of the VPO catalyst is only 18 m^2/g, which reinforces the conclusion that the VPO catalyst has a very high activity.

Table 3. Results of Methane Oxidation Run Using V_2O_5/SiO_2 and 90 to 95 Percent CH_4/O_2 at 1 atm
(Experiment 1546-57)

Test	Nominal Temperature, °C	CH_4/O_2 Flow, sccm	% CH_4 Feed	% Conversion	% Selectivities		
					CO	CO_2	HCHO
1	500	40	93.3	1.7	67	31	2
2	510	40	93.4	0.8	66	31	3
3	526	40	93.3	1.5	63	33	5
4	551	40	93.2	2.9	48	30	22
7	575	60	93.6	6.1	27	46	27
8	575	80	94.2	4.6	23	35	41
9	550	60	93.9	3.1	29	54	17
10	575	100	94.3	4.3	19	31	50
11	575	60	86.6	5.7	22	53	26
12	575	80	89.1	4.1	24	45	31
13	575	120	89.5	3.6	22	42	36
15	575	180	89.6	3.3	19	49	32

0.4 g catalyst.
1.0 cm bed depth.
0.6 cm diameter.

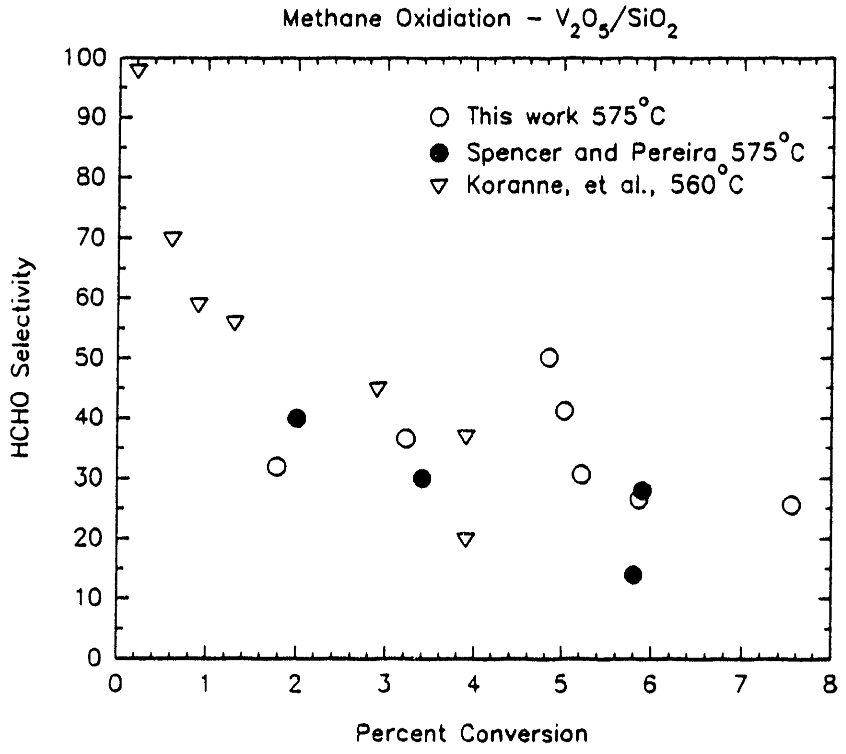

Figure 4. Formaldehyde selectivity as a function of conversion for tests conducted using V_2O_5/SiO_2 at atmospheric pressure.

Table 4. Results of Methane Oxidation Run Using $(VO)_2P_2O_7$ (Preparation D, Activation 8, 1546-34) and 90 to 95 Percent CH_4/O_2 at 1 atm (Experiment 1546-64)

Test	Nominal Temperature, °C	CH_4/O_2 Flow, sccm	% CH_4 Feed	% Conversion	% Selectivities CO		
					CO	CO_2	HCHO
1	460	40	92.5	1.2	--	--	0
2	475	40	92.5	2.1	--	--	0
5	502	80	88.1	2.3	--	--	0
6	475	80	88.0	0.3	--	--	0
7	500	100	88.3	2.6	--	--	0
8	504	120	88.4	3.0	--	--	0
9	504	80	88.1	2.0	--	--	0
10	450	80	90.3	0.9	--	--	0
11	450	120	91.2	3.1	92	8	0
12	450	160	91.3	3.5	94	6	0
13	475	160	91.4	4.1	96	4	0
14	425	80	90.9	2.1	95	5	0
16	450	80	87.6	1.8	97	3	0
18	450	40	92.3	2.3	95	5	0
19	475	40	92.5	2.2	95	5	0
20	500	40	92.3	3.8	94	6	0
21	525	40	92.2	5.7	91	9	0
22	550	40	92.2	7.0	87	13	0
23	525	120	92.9	2.6	96	4	0

0.6 g catalyst (1546-34).
1 0 cm bed depth.
0.6 cm diameter.

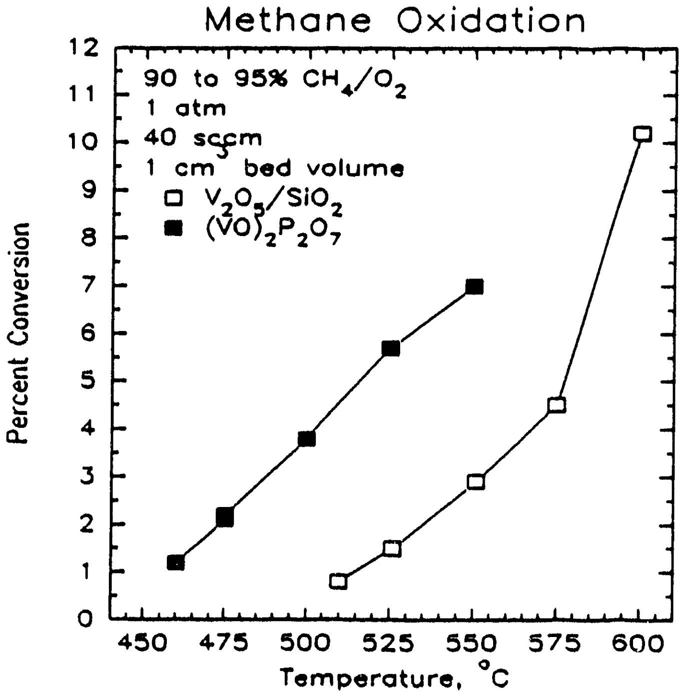

Figure 5. Conversion versus temperature for V_2O_5/SiO_2 and VPO (1546-34) catalysts (1 atm, 90 - 95 percent CH_4/O_2, 40 sccm).

Figure 6 shows XRD results for the fresh VPO catalyst and a sample removed from the reactor after testing at temperatures up to 500°C. The patterns are very nearly identical and both correspond to $(VO)_2P_2O_7$. We can conclude that the catalyst is stable under these conditions up to 500°C. A catalyst used at higher temperatures will be submitted for XRD analysis in the coming weeks.

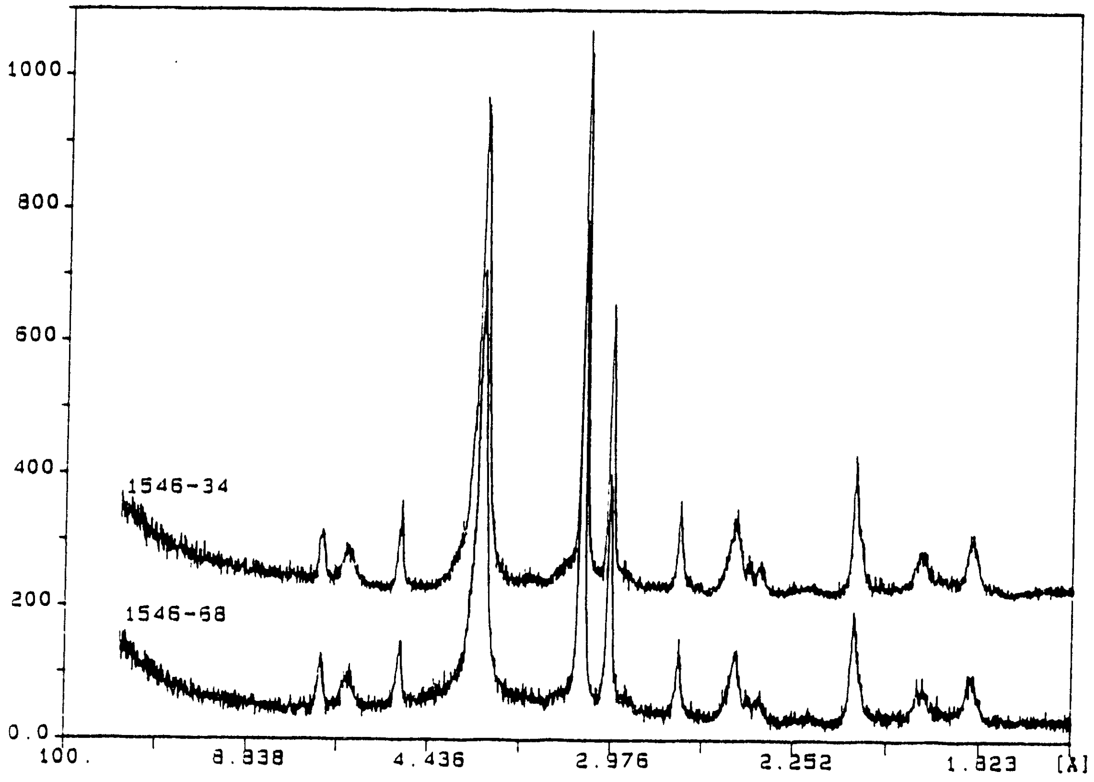

Figure 6. X-ray diffraction patterns of fresh (1546-34) and used (1546-68) VPO catalysts after testing up to 500°C.

Mechanical degradation of the catalyst pellets used at up to 500°C was observed in that the used catalyst consisted primarily of fines. This problem is being addressed by the use of higher pelletization pressures (up to 40,000 psi) and the use of 2 percent bentonite as a pelletization agent. Preliminary results indicate that this produces a much stronger catalyst pellet and that the presence of bentonite has little or no effect on activity or selectivity.

PLANNED ACTIVITIES

During the coming quarter we will continue to focus our activities on the area of catalyst reactivity testing. We will expand our data set to include the effect of steam in the feed gas and the effect of pressure. Data at elevated pressures have been reported in the literature for methane oxidation over V_2O_5/SiO_2, and we will attempt to reproduce these results. VPO catalysts prepared and activated by different methods will be examined. By the end of the fourth quarter we expect to have a good baseline data set for the activity and selectivity of VPO catalysts in the reactions of interest. This will allow the selection of standard reaction conditions for testing of promoted and supported catalysts in Task 3. Also a paper is being prepared for the contractor's review conference in September.

SUMMARY

During this quarter we have continued to develop methods for catalyst activation by investigating activation in wet gas environments. This procedure leads to the formation of highly crystalline $(VO)_2P_2O_7$, while activation under identical conditions, but with no moisture, leads to a poorly crystalline sample. Published data indicate that the highly crystalline form is representative of commercial butane oxidation catalysts.

The main focus of our work during this quarter has been in the area of catalyst testing in the microreactor system. We have tested a VPO catalyst using 3 percent methane in air and a stainless steel reactor under conditions similar to those reported last quarter for V_2O_5. The catalyst was initially a poorly crystalline sample of $(VO)_2P_2O_7$, but post reaction characterization demonstrated that this material had transformed into β-$VOPO_4$. This may have been caused by less than optimum preparation and activation procedures or inability of the 3 percent methane/air mixture to maintain the catalyst in a reduced state. Tests with this catalyst show that the VPO catalyst is significantly more active than V_2O_5 and produces primarily CO as compared to CO_2 for V_2O_5. This is somewhat surprising given the large excess of oxygen present under these conditions and suggests that modification of the VPO catalyst with promoters or a support might lead to the formation of selective products.

In order to confirm that our microreactor system was providing reliable data, we tested a V_2O_5/SiO_2 catalyst at atmospheric pressure and temperatures from 500 to 600°C using 90 to 95 percent CH_4/O_2. Several studies of methane oxidation using this catalyst have been published with reasonably good agreement between different research groups. We were not able to reproduce the literature data using steel reactors. However, when the steel reactor was lined with quartz and the post-catalyst reactor volume was minimized by packing with quartz chips, we obtained results which agree closely with those previously published.

Using the same quartz-lined reactor and test conditions, we also tested a highly crystalline (wet activated) VPO catalyst. No partial oxidation products were observed, but the VPO catalyst was 3 to 4 times more active than V_2O_5/SiO_2 and active at 50°C lower temperature. This was true even though the VPO had a surface area only one tenth that of the silica supported catalyst. The primary reaction product was CO. A used catalyst removed from the reactor after testing at 500°C exhibited an X-ray diffraction pattern identical to that of the starting catalyst. This demonstrates that the wet activated VPO is stable in the 90 to 95 percent methane gas environment up to 500°C.

While methanol formation has not yet been observed over VPO, the high activity and stability of the catalyst are encouraging. Future tests under different process conditions in a quartz-lined reactor and using supported or promoted catalysts will hopefully lead to the formation of selective products.

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