DOE/PC/92110--T13

QUARTERLY TECHNICAL PROGRESS REPORT 13
APRIL-JUNE, 1996

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

Prepared for
Arun C. Bose (Technical Project Officer)
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA 15236

RECEIVED
NOV 26 1996
OSTI

By
Robert L. McCormick (Principal Investigator)
Gokhan O. Alptekin (Graduate Assistant)
Department of Chemical Engineering and Petroleum Refining
and
Colorado Institute for Fuels and High-Altitude Engine Research

Colorado School of Mines
Golden, Colorado 80403-1887

DOE Contract No. DE-AC22-92PC92110
Contract Date: October 1, 1992
Anticipated Completion Date: March 31, 1997
Government Award For Current Fiscal Year: $125,496

Final
July 30, 1996

MASTER

TABLE OF CONTENTS

DISCLAIMER

LIST OF FIGURES AND TABLES

EXECUTIVE SUMMARY

This document is the thirteenth quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane" and covers the period April-June, 1996. Activities included analysis of all previously acquired data for methane, methanol, and formaldehyde oxidation over vanadyl pyrophosphate and testing of supported, promoted, and iron phosphate catalysts. Some experiments have been conducted with a small percentage of butane in the feed gas to help retain the catalyst in a reduced state and these results are reported. Iron phosphate, and iron phosphate supported on silica have also been tested in a preliminary way.

The specific objectives of this project are:

- To determine optimum conditions for methanol and formaldehyde production from methane using VPO catalysts. In particular to determine the effect of lean conditions (excess oxygen), oxygen deficient conditions (used in most other methane oxidation studies), and the potential of using the catalyst as a stoichiometric oxidant or oxygen carrier.
- To utilize promoters and catalyst supports to improve oxygenate 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.

INTRODUCTION

This document is the thirteenth quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane" and covers the period April-June 1996. The basic premise of this project is that vanadyl pyrophosphate (VPO), a catalyst used commercially in the selective oxidation of butane to maleic anhydride, can be developed as a catalyst for selective methane oxidation. Data supporting this idea include published reports indicating moderate to high selectivity in oxidation of ethane (Michalakos, et al., 1993), propane (Ai, 1986), and pentane (Busca and Centi, 1989), as well as butane (Centi, et al., 1988). Methane oxidation is a much more difficult reaction to catalyze than that of other alkanes and it is expected that considerable modification of vanadyl pyrophosphate will be required for this application. It is well known that VPO can be modified extensively with a large number of different promoters and in particular that promoters can enhance selectivity and lower the temperature required for butane conversion (Hutchings, 1991).

Additionally, it has been shown that strong Lewis acid sites on the surface of VPO are responsible for initial alkane activation (Busca, et al., 1986a). This Lewis acidity is thought to be caused by lattice defects or strain initiated by disorder in stacking of the layers of VPO (Busca, et al, 1986b; Horowitz, et al, 1988). One approach we have taken is directed at increasing the strength of these strong Lewis acid sites by enhanced strain or disorder in the layer stacking. Surface acidity was measured by FTIR of chemisorbed bases. By increasing Lewis acid site strength it is hoped that the temperature required for methane activation can be lowered resulting in improved selectivity. Other approaches include modification of VPO with promoters or by dispersion on supports. The effect of including reductants, such as butane, or oxidants, such as hydrogen peroxide, in the feed gas will also be examined. In this report we describe a compilation of our kinetic results for oxidation of methane, methanol, and formaldehyde over vanadyl pyrophosphate. We also describe preliminary results for methane oxidation over silica supported vanadyl pyrophosphate, Fe-promoted vanadyl pyrophosphate, iron phosphate, and silica supported iron phosphate. The iron phosphates have been reported to have good activity for methane conversion and are in many ways similar to the vanadium phosphates (Wang and Otsuka, 1995).

PROJECT DESCRIPTION

Objectives

The specific objectives of this project are:

- To determine optimum conditions for methanol and formaldehyde production from methane using VPO catalysts. In particular to determine the effect of lean

conditions (excess oxygen), oxygen deficient conditions (used in most other methane oxidation studies), and the potential of using the catalyst as a stoichiometric oxidant or oxygen carrier.
- To utilize promoters and catalyst supports to improve oxygenate 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.

Project Overview

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 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 surface area measurement, elemental analysis, x-ray powder diffraction, FTIR, as well as pulsed and continuous reactivity/selectivity studies.

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. Much of this task was accomplished during the first project year at Amax Research and Development but the work had to be repeated to restart the project at the Colorado School of Mines. Work on this task has been completed.

Task 2: Process and Catalyst Variable Study. Tests will be 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. Several important aspects of this task have been completed and were reported in the topical report describing results acquired on this project at Amax Research and Development. Results to date are summarized in this report, some additional data analysis is required to complete this task. Vanadyl pyrophosphate has not been found to be a selective catalyst for methane oxidation.

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. To date we have tested catalysts promoted with the first row transition metals and observed increased selectivity to HCHO for Fe, Cr, and Cu. Attempts at putting vanadyl pyrophosphate on a support are underway.

Task 4: Advanced Catalyst Testing. Advanced catalysts using the best ideas developed in previous tasks and from the literature will be prepared. Our first advanced catalysts are iron phosphates, based on a recent literature report (Wang and Otsuka, 1995). Both catalyst exhibit high selectivity to HCHO. We have also tested other catalysts with 1.5% butane in the feed gas as a reductant. This results in the formation of very low yields of HCHO (versus a yield of zero without butane).

PROJECT STATUS

Oxidation Over Vanadyl Pyrophosphate

Compilation of Data. During the course of this project we have acquired accurate measurements of reaction rates and selectivities for oxidation of methane and other C1 hydrocarbons over vanadyl pyrophosphate. To date we have examined oxidation of methane, methanol, and formaldehyde at a range of hydrocarbon/oxygen ratios, temperatures, and space velocities under differential reactor conditions. Our results suggest the following sequences of reactions:

$$CH_4 \xrightarrow{1} CO \xrightarrow{2} CO_2$$

$$CH_3OH \xrightarrow{3} CH_3OCH_3 \xrightarrow{4} HCHO \xrightarrow{5} CO \xrightarrow{2} CO_2$$

$$CH_3OH \xrightarrow{6} HCHO \xrightarrow{5} CO \xrightarrow{2} CO_2$$

A significant finding is that while vanadyl pyrophosphate is active for methane conversion, the only product observed at high selectivity is carbon monoxide. Catalytic reactivity studies suggest that methanol and formaldehyde are converted at roughly 250 times the rate of methane conversion and so are not observed in methane oxidation even if formed as intermediates. We have just begun to perform a kinetic analysis of our data to carefully quantify these reaction rates. The first step in that analysis has been to compile the data and identify gaps that can be filled by a small number of additional experiments.

Oxidation experiments were conducted over the temperature ranges, CH_4/O_2 ratios, and space velocities listed in Table 1. We wish to used these data to evaluate the rate constants, and then the activation energies, of the six reactions in the scheme above. We also wish to determine if the assumption of first order reaction is reasonable for all hydrocarbon reactants and if the assumption of zero order with respect to oxygen is reasonable. For reaction 1, the conversion of methane to CO, the available data allow determination of activation energy and allow us to test our assumptions about reaction order. For determination of activation energy some of the data are plotted in Figure 1, an Arrhenius plot based on the assumption that the reaction is first order in methane. The plot indicates the $E_a=20.3\pm2.6$ for $CH_4/O_2=1.54$ and 26.3 ± 1.2 kcal/gmol for $CH_4/O_2=8.32$. These values are probably independent of methane oxygen ratio and the average activation energy is 23.3 kcal/gmol. Testing of reaction order assumptions will be performed in the coming quarter.

Table 1. C1 hydrocarbon oxidation experiments with vanadyl pyrophosphate.

Reactants	Temperatures, °C	C1/O_2 Ratio	GHSV, hr^{-1}
Methane/Oxygen	310-410	1.54	4650
	310-440	8.32	4660
	340-480	10	1400
	340-500	25	1400
Methanol/Oxygen	150-405	0.26	13221
	200-355	0.35	4407
	150-305	0.35	6869
	150-305	0.51	6828
	150-305	0.70	6915
	300	3	12000
	250-350	10	12000
Formaldehyde/Oxygen	202-425	0.2	13221
	155-365	0.2	6828

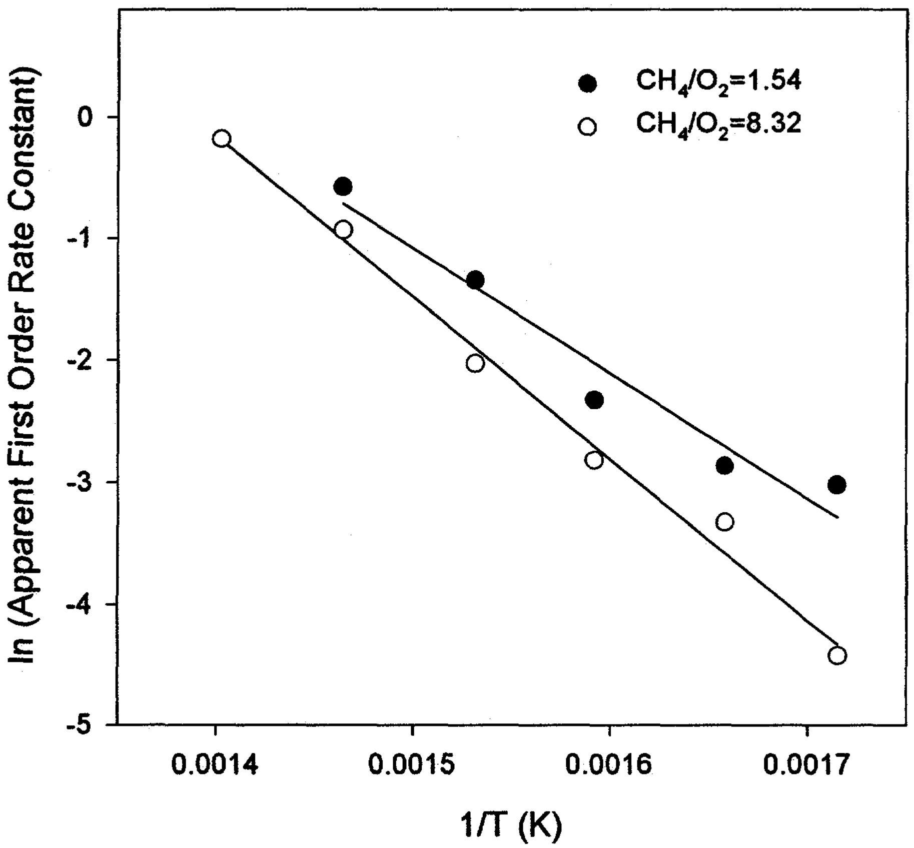

Figure 1. Arrhenius plot for methane oxidation over vanadyl pyrophosphate.

For reaction 2, oxidation of CO to CO_2, the rate constant could be determined from methane oxidation data by variation of space velocity at constant conditions (Froment and Bischoff, 1990). However, the methane oxidation data set does not contain adequate space velocities for determination of relevant parameters for this reaction. It may be possible to estimate the activation energy from the methanol oxidation data because three GHSV's were run at essentially the same $C1/O_2$ ratio. Obviously a fourth data point would be desirable.

For reaction 3, acid catalyzed condensation of methanol to dimethyl ether, the data set is not adequate for determining activation energy because most of the data points are complicated by parallel reaction 6, oxidation of methanol to formaldehyde. Insufficient data on the effect of methanol concentration is available to estimate the reaction order. This reaction in particular seems unlikely to be first order (unless the rate limiting, elementary step is first order). Adequate data are also not available for evaluation of DME oxidation to formaldehyde (note that no dimethoxy methane or methyl formate were observed in our GC traces).

For reaction 5, oxidation of formaldehyde to CO, an activation energy can easily be estimated. This is also true for reaction 6, oxidation of methanol to formaldehyde assuming that dimethyl ether formation is not significant at the higher temperatures where formaldehyde formation occurs. This hypothesis might be tested by poisoning the surface acid sites of the catalyst and measuring methanol oxidation rates. We could also examine this hypothesis by obtaining data under conditions where only the methanol to DME reaction occurs, then obtaining DME oxidation data, and finally modeling the entire reaction network to obtain direct methanol oxidation rate constants. For both reactions data at higher $C1/O_2$ ratios is also needed.

Identification of Data Needs. Based on the analysis presented above, the following additional experiments are needed to completely characterized the macrokinetics of C1 hydrocarbon oxidation over vanadyl pyrophosphate:

- Methane oxidation at two more space velocities, four or more temperatures each, a CH_4/O_2 ratio of 8 to 10.
- Methanol condensation to DME under conditions where this is the only reaction (<200°), two more temperatures, two more methanol concentrations.
- Oxidation of DME to formaldehyde at 4 or more temperatures, one space velocity, and one DME/O_2 ratio (preferably 2 or higher).
- Formaldehyde oxidation to CO at higher $HCHO/O_2$ ratio, preferably above 5, and 4 or more temperatures.
- Methanol oxidation to formaldehyde at higher CH_3OH/O_2 ratio and model kinetics including parallel reaction to DME using data from lower temperature methanol conversion and DME oxidation studies.

Effect of Butane in Feed Gas. As noted, vanadyl pyrophosphate is utilized industrially for selective oxidation of butane. Butane is a much more reactive molecule than methane and may be capable of retaining the catalyst in a more reduced state than the methane/oxygen feed used in our experiments. This catalyst reduction could be critical for activity and selectivity in oxidation reactions. To examine this hypothesis we have performed methane oxidation experiments with 1.5% butane in the feed gas. The presence of butane presents some complications in the data analysis as it is uncertain whether butane or methane was the source of the reaction products. We do have analyses for both butane and methane in the products and so can calculate butane, methane, and total carbon conversions. We are not analyzing the products for maleic anhydride which might be formed from butane and at the highest temperatures (and butane conversions) our carbon balances begin to fall.

Figure 2 reports the effect of temperature on methane conversion for this system and Figure 3 presents an Arrhenius plot. At the highest methane to oxygen ratio the methane conversion may be limited by oxygen consumption by butane. Analysis of activation energies yields a suspiciously low value of 4.3 kcal/gmol for this case. When more oxygen is present the results are similar to what was observed without butane and the activation energy is 27.4±7 kcal/gmol.

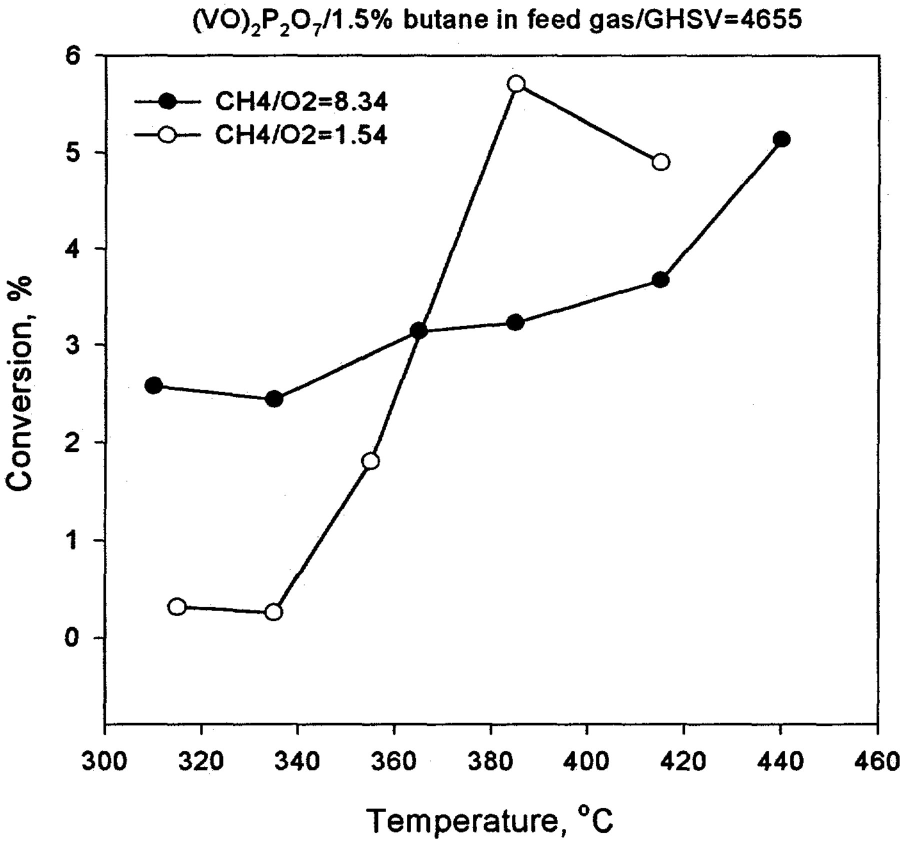

Figure 2. Methane conversion as a function of temperature for oxidation in the presence of butane over vanadyl pyrophosphate.

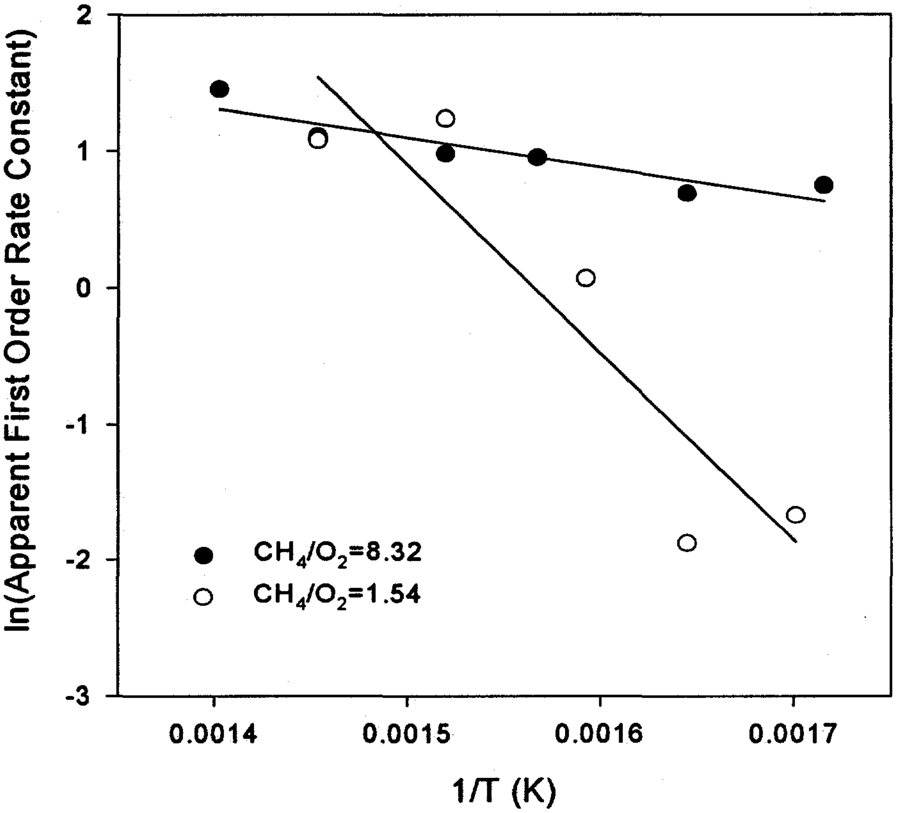

Figure 3. Arrhenius plot based on the data of Figure 2 and assuming the reaction is first order in methane, zero order in oxygen and butane.

The presence of butane makes calculation of selectivities particularly imprecise. In Figure 4 selectivities based on C1 products are reported as a function of total carbon conversion. Although formaldehyde selectivities are very low, they are greater than zero and so higher than observed in the absence of butane. Perhaps the addition of modifiers to this catalyst which enhance its reducibility would improve selectivity.

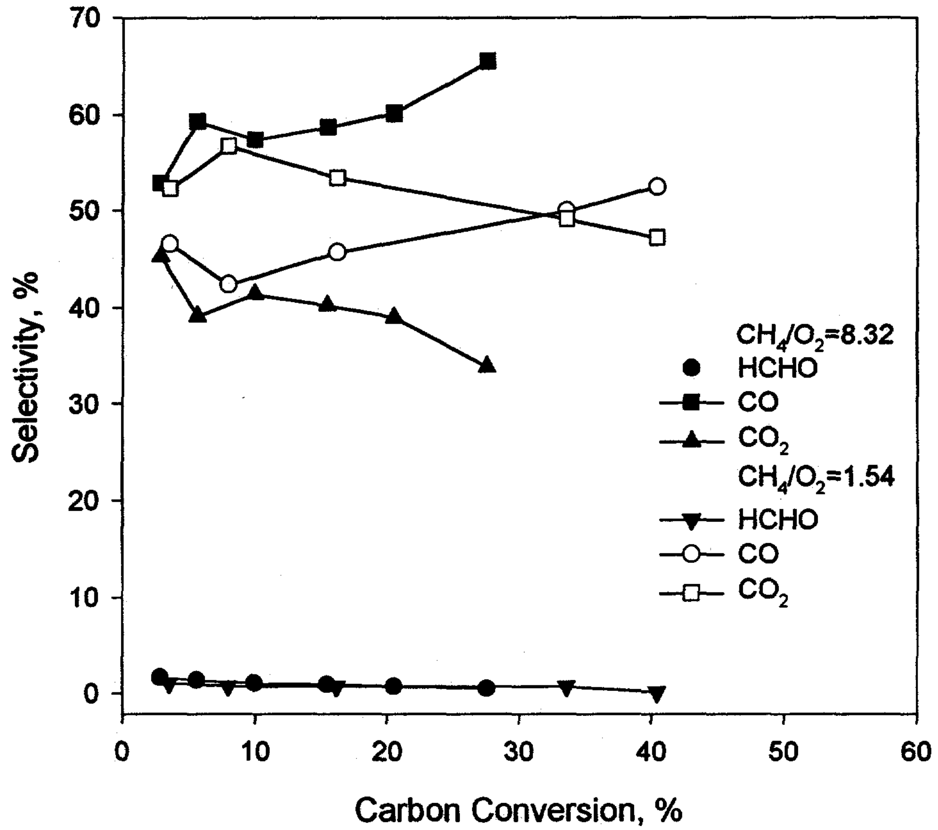

Figure 4. Selectivity as a function of total carbon conversion for methane oxidation in the presence of butane.

Oxidation Over Silica Supported Vanadyl Pyrophosphate

Recently Miyake and Doi (1995) have presented the results of a study of the preparation of vanadyl pyrophosphate. They show that the most active and selective preparations involve careful reduction of V_2O_5 to V_4O_9 followed by slow reaction with anhydrous phosphoric acid to form the catalyst precursor $VOHPO_4$-$0.5H_2O$. Their work suggests an approach for synthesis of vanadyl pyrophosphate on a support. The starting point for this synthesis is supported V_2O_5 prepared by conventional impregnation and calcining. This supported vanadia is then carefully reduced, using the isobutyl alcohol as described by Miyake and Doi, to produce silica supported V_4O_9. After filtration from the reaction mixture and resuspension in fresh solvent, anhydrous phosphoric acid dissolved in isobutyl alcohol is added dropwise to produce the precursor dispersed on the support. A catalyst based on this approach has been prepared. It was activated in air and x-ray diffraction results indicate that vanadyl pyrophosphate was not formed (the precursor was probably converted to $VOPO_4$). This material yielded only CO and CO_2 in preliminary methane oxidation experiments. We plan to activate another sample of this catalyst in butane/air in an attempt to produce the desired phase, vanadyl pyrophosphate.

A second approach to silica supported vanadyl pyrophosphate is currently being investigated. In this approach the hot precursor synthesis solution, obtained by refluxing V_2O_5 in isobutyl and benzyl alcohols for several hours followed by addition of anhydrous phosphoric acid, is used to impregnate the silica support in the usual manner for making supported catalyst. Activation of this material in butane/air appears to have produced vanadyl pyrophosphate. Scanning electron microscopy with EDX elemental analysis will be used to determine if the vanadyl pyrophosphate is actually on the support or merely mixed with the support particles.

Oxidation Over Fe-promoted Vanadyl Pyrophosphate

We previously reported results of methane oxidation experiments over this catalyst and observed traces of formaldehyde which, at that time, we could not quantify (McCormick, 1995). Here we have reinvestigated this material using our much improved reaction product analytical methods. The catalyst was prepared by addition of Fe^{III} nitrate nonahydrate to the initial benzyl/isobutyl alcohol and V_2O_5 suspension. The target molar Fe/V ratio was 0.075. X-ray powder diffraction revealed a pattern identical to that for vanadyl pyrophosphate.

Figure 5 reports conversion as a function of temperature for two CH_4/O_2 ratios. Conversions are somewhat lower at the lower oxygen content suggesting some dependence of the reaction kinetics on oxygen partial pressure. An Arrhenius plot of these data are shown in Figure 6. The calculated activation energies are 27.1 ± 5.3 at $CH_4/O_2=1.54$ and 22.8 ± 1.4 kcal/gmol at $CH_4/O_2=8.32$. These do not appear to be statistically different and the average value of 25.0 kcal/gmol is perhaps more accurate. Note, however, that this calculation of activation energy assumes the reaction to be first order in methane and zero order in oxygen. Selectivity as a function of conversion is shown in Figure 7. Formaldehyde selectivities are quite high at very low conversion but fall rapidly. Note that over unpromoted vanadyl pyrophosphate no formaldehyde is observed suggesting that Fe promotion has in some fundamental way altered the reaction pathway on this material. The results for the iron promoted catalyst suggest the reaction sequence:

$$CH_4 \longrightarrow HCHO \longrightarrow CO \longrightarrow CO_2$$

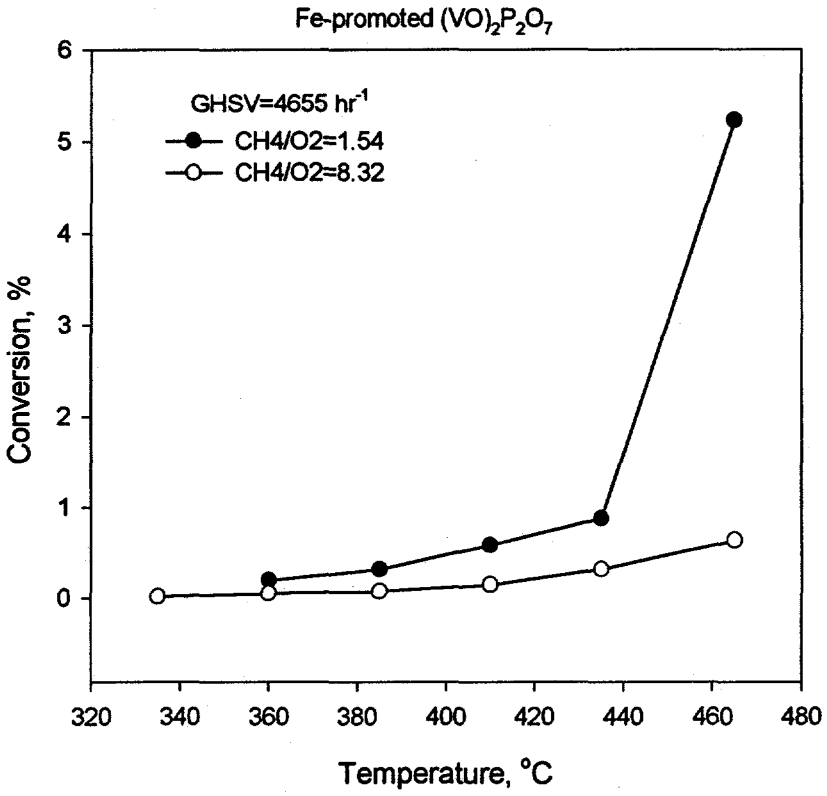

Figure 5. Conversion as a function of temperature for methane oxidation over Fe promoted vanadyl pyrophosphate.

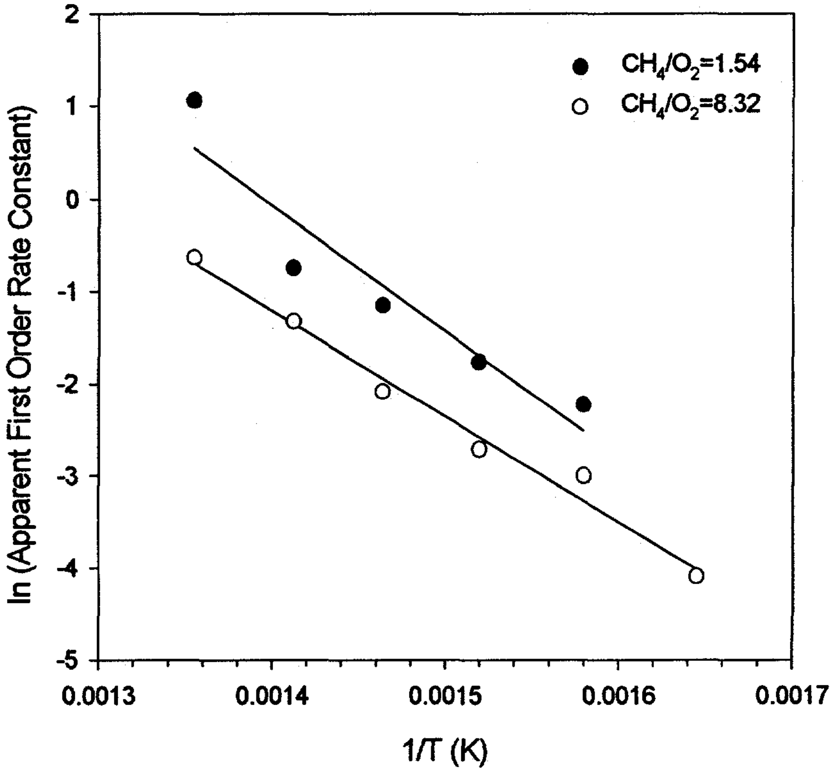

Figure 6. Arrhenius plot for data of Figure 5, methane oxidation over Fe promoted vanadyl pyrophosphate.

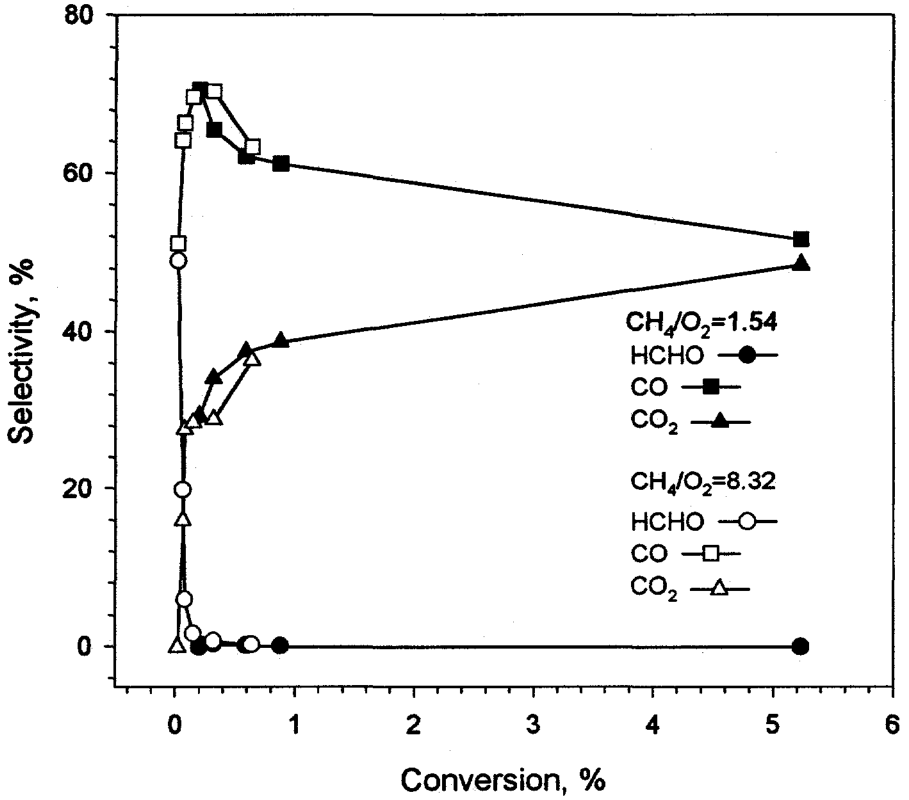

Figure 7. Selectivity as a function of conversion for methane oxidation over Fe promoted vanadyl pyrophosphate.

Iron Phosphates

Catalyst Preparation/Characterization. $FePO_4$ was prepared using the method described by Wang and Otsuka (1995). A stoichiometric, aqueous solution of $Fe(NO_3)_3$ and $NH_4H_2PO_4$ was prepared and dried at 363 K for 12 hr. The precipitate obtained was calcined at 823 K for 5 hr in air. Wang and Otsuka report the surface area of this material to be 8.5 m^2/g.

Silica supported $FePO_4$ was prepared from a precipitated, acid washed silica by incipient wetness impregnation with a solution of $Fe(NO_3)_3$ and $NH_4H_2PO_4$ with a target iron loading of 5wt%. This material was dried and calcined at 900 K/18 hr.

Methane Oxidation Over Unsupported Catalyst. This catalyst was tested using the methods out lined previously (McCormick and Alptekin, 1996) and identical to those employed for all other catalysts examined in recent months under this program. Figure 8 shows the effect of temperature on conversion for two CH_4/O_2 ratios and space velocities. Methane/oygen ratio has no apparent effect on methane oxidation rate. Conversion is also not affected by modest changes in the GHSV. An Arrhenius plot for these data, assuming first order in methane and zero order in oxygen, is shown in Figure 9. For CH_4/O_2=2.15, E_a=21.9±1.8 and for CH_4/O_2=8.32,

E_a= 16.7±3.7 kcal/gmol. It seems likely that the activation energy is unaffected by CH_4/O_2 and the best estimate of E_a is the average value of 19.3 kcal/gmol.

Figure 10 shows how selectivity changes with conversion for methane oxidation over this catalyst. The figure shows a very surprising result, selectivity to CO_2 is very high at low conversion and falls as conversion increases. Selectivity to both HCHO and CO actually increases with increasing conversion up to 35% selectivity at 1 percent conversion. This pattern is very different from what is observed with vanadyl pyrophosphate or other catalysts reported in the literature such as V_2O_5 or MoO_3 on silica (Parkyns, et al., 1993; Hall, et al., 1995). It is difficult to propose a reaction network based on this limited data set and more data will be obtained on this interesting catalyst in future months.

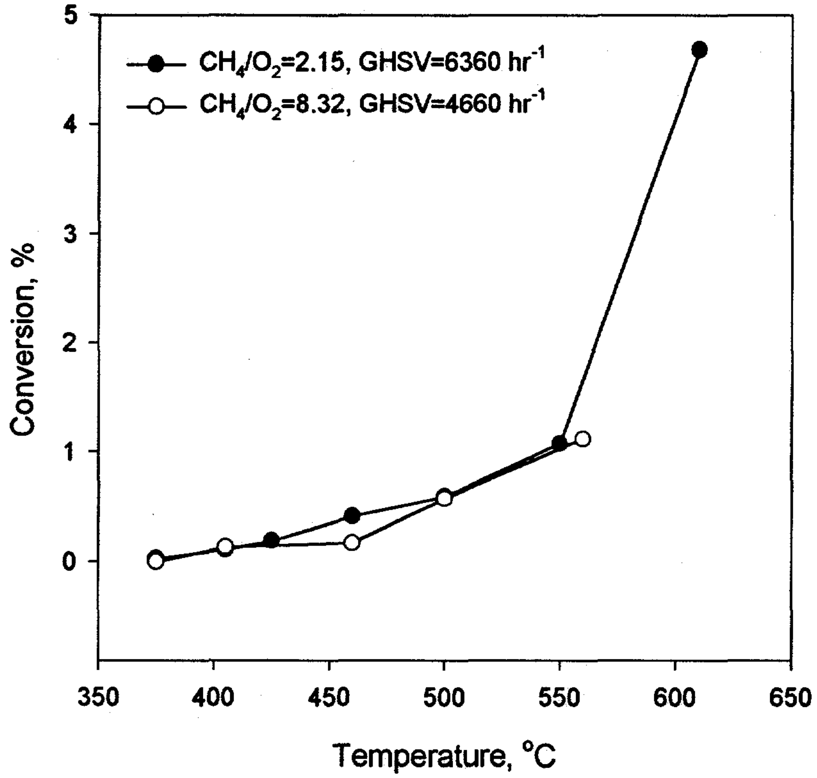

Figure 8. Conversion as a function of temperature for methane oxidation over $FePO_4$.

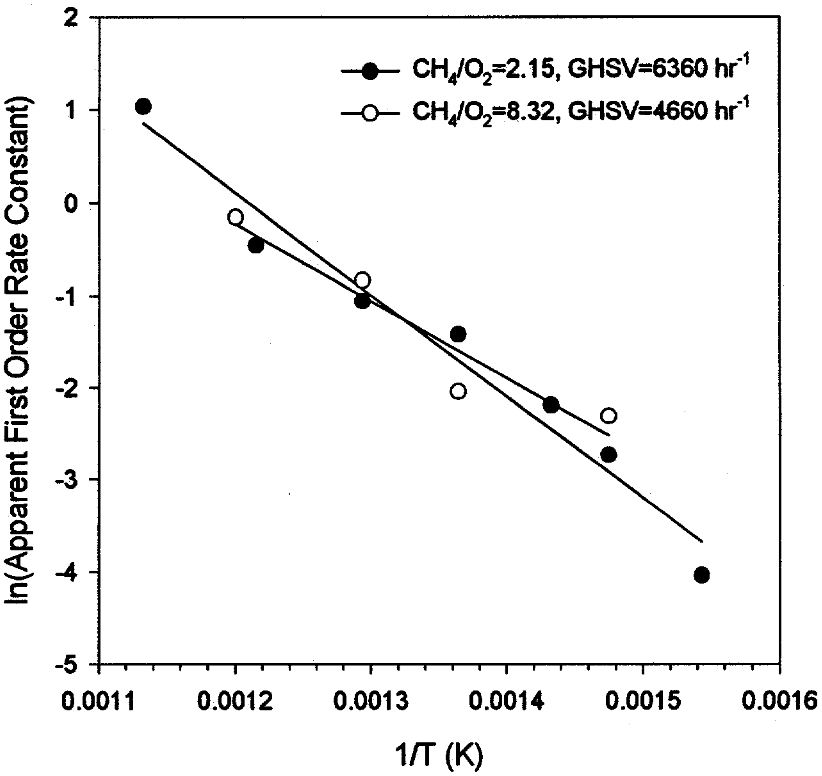

Figure 9. Arrhenius plot for methane oxidation over $FePO_4$ (data of Figure 8).

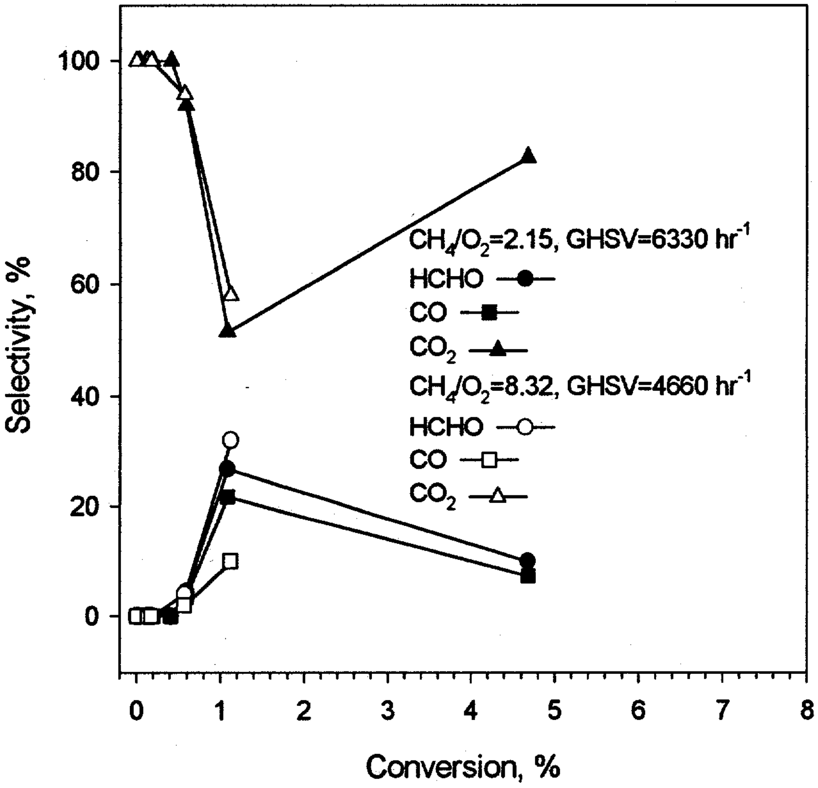

Figure 10. Selectivity as a function of methane conversion for oxidation over $FePO_4$.

Methane Oxidation Over Silica Supported Catalyst. Testing methods were identical to those used previously. Conversion as a function of temperature for two CH_4/O_2 ratios is reported in Figure 11. As for the unsupported catalyst, CH_4/O_2 ratio has no effect on methane oxidation rate. An Arrhenius plot of these data, assuming first order in methane and zero order in oxygen, is reported in Figure 12. The activation energies of 33.8±2.5 at CH_4/O_2=1.54 and 27.9±4.7 kcal/gmol at CH_4/O_2=8.32 are not different and the average value is 30.9 kcal/gmol. This value is significantly higher than the 19.3 kcal/gmol observed for the unsupported catalyst and is similar to the value of 32.5 kcal/gmol that we have observed for methane oxidation over just the silica support (McCormick and Alptekin, 1996). Oxidation over silica requires temperatures 75 to 100 K higher, however. The meaning of this increase in activation energy upon supporting $FePO_4$ on silica is unclear at this time but will hopefully be clarified through additional experiments and catalyst characterization.

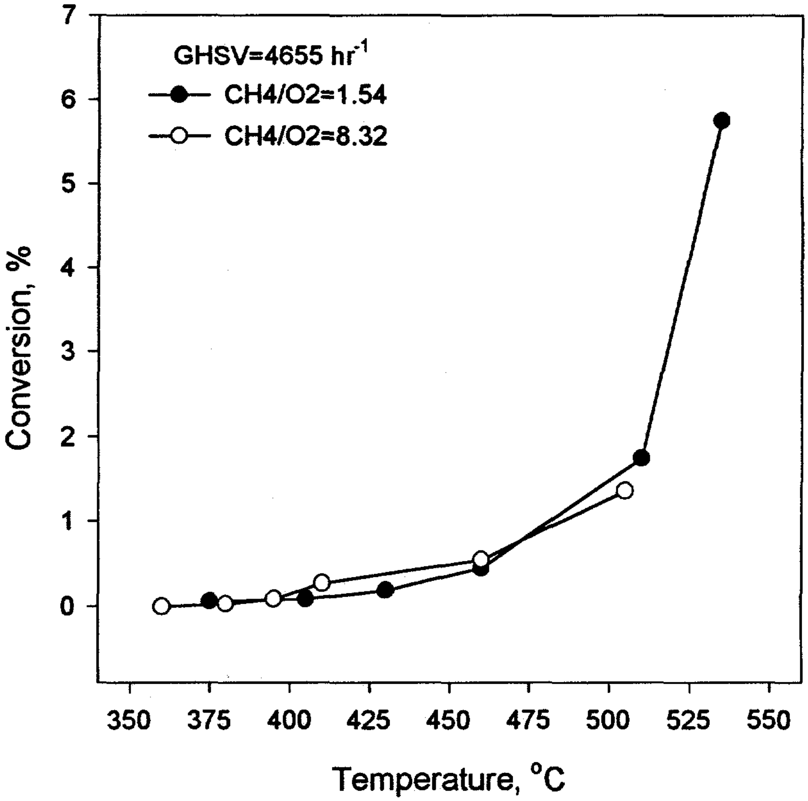

Figure 11. Conversion as a function of temperature for methane oxidation over silica supported $FePO_4$.

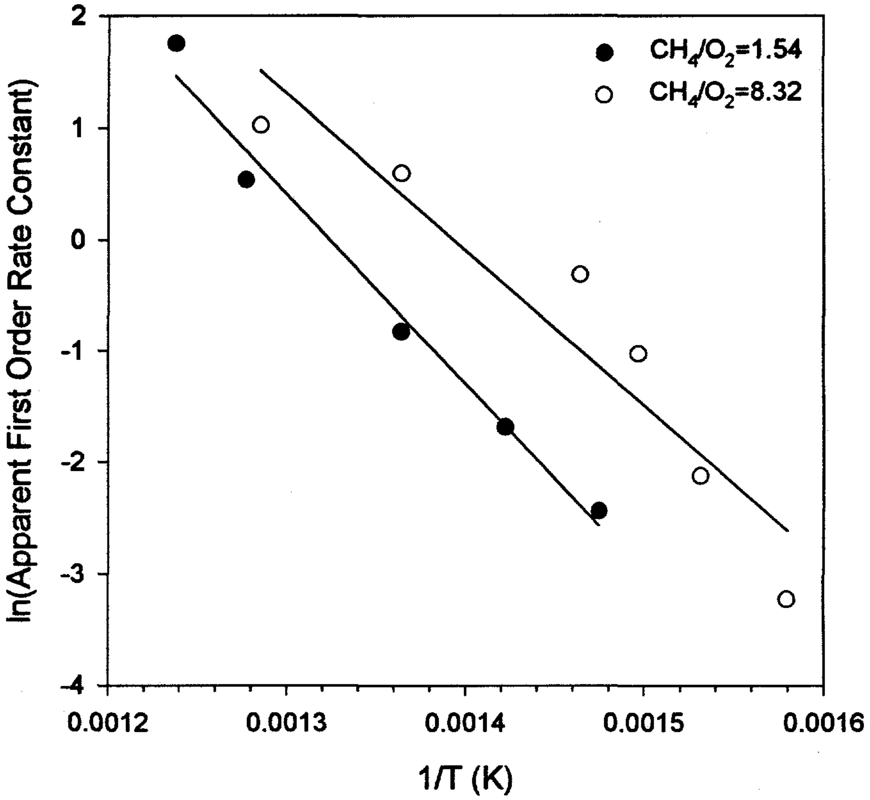

Figure 12. Arrhenius plot of data from Figure 11, methane oxidation over silica supported $FePO_4$.

Figure 13 reports selectivity as a function of conversion for this catalyst. The unusual pattern observed for unsupported $FePO_4$ is not observed here. Formaldehyde selectivities decrease with increasing conversion as is observed over most catalysts. However, the HCHO selecitivity over this catalyst is exceptionally high. For example, at 2% conversion and CH_4/O_2=8.32 the HCHO selectivity is slightly greater than 30%. Figure 14 shows the effect of GHSV on selectivity and conversion at various CH_4/O_2 ratios (which is reasonable given the lack of a dependence on this ratio demonstrated in Figure 11). These data and Figure 13 indicate the following reaction path:

$$CH_4 \longrightarrow HCHO \longrightarrow CO \longrightarrow CO_2$$

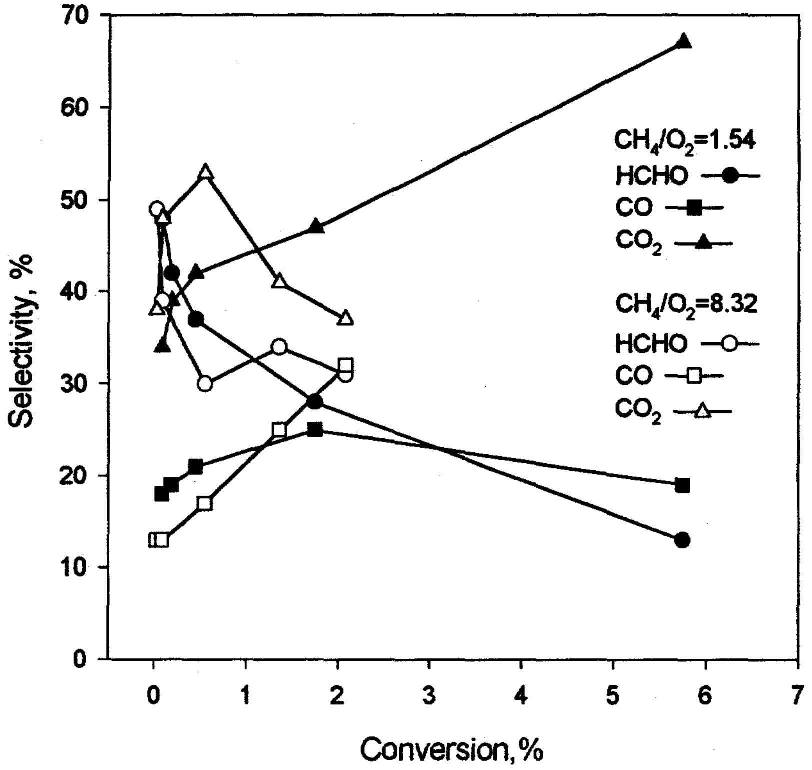

Figure 13. Selectivity as a function of conversion for methane oxidation over silica supported $FePO_4$.

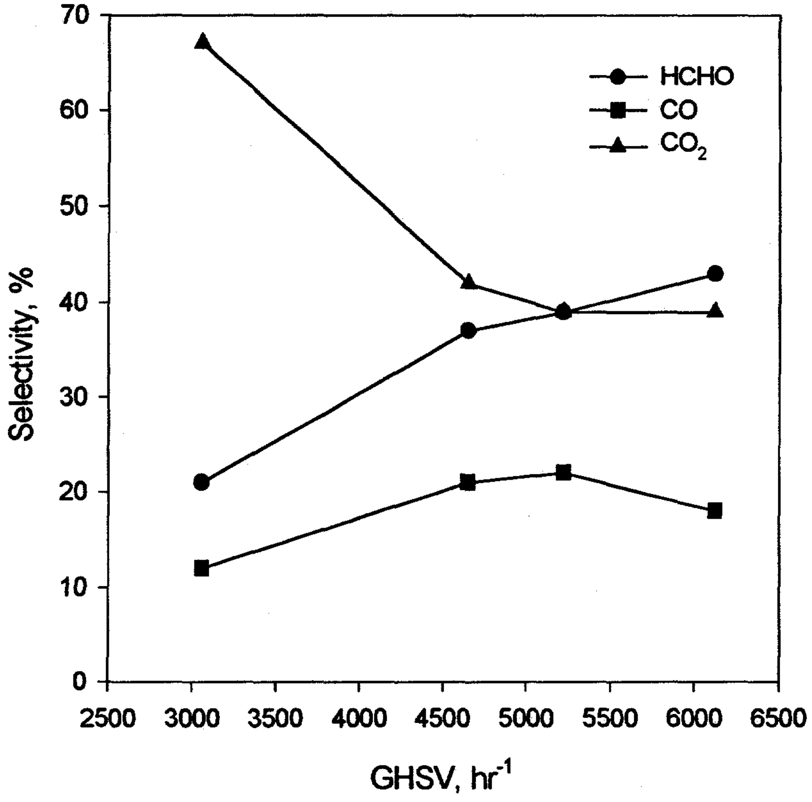

Figure 14. Selectivity as a function of space velocity for methane oxidation over silica supported $FePO_4$.

PLANNED ACTIVITIES

Data for Vanadyl Pyrophosphate Macrokinetic Model

Based on the discussion above, several more experiments will be conducted to completely specify kinetic parameters of this reaction network. This will include oxidation of dimethyl ether as well as other oxidation experiments.

Reexamination of Cu, Cr, and Co Promoted Catalysts

Methane oxidation results for vanadyl pyrophosphate promoted with the first row transition metals was reported last year. Several of these catalysts produced measurable but very poorly quantified amounts of formaldehyde. We plan to revisit this suite of catalysts using our new analytical approach. Estimated completion date: August 1996.

Detailed Studies of Iron Phosphate Catalysts

Given the very interesting results reported above for methane oxidation over these catalysts, the focus of our work on advanced catalysts will be detailed studies on iron phosphate materials.

Continued Studies of Silica Supported VPO

Efforts in this area will continue as noted in this report.

Butane Oxidation

Vanadyl pyrophosphate catalysts are used commercially for the conversion of butane to maleic anhydride by partial oxidation. We plan to perform a limited number of butane oxidation experiments to 1) verify that we have catalytic materials with similar properties to those reported for commercial catalysts and 2) to determine if any of the catalyst modifications we have performed have any effect on activity or selectivity for this well known reaction. Estimated completion data: December 1996.

Publication of Results

Preparation of manuscripts for publication continues with plans for submission of one or two papers by the end of September and others in October. Those currently in preparation are:

- Detailed study of kinetics of methane, methanol, formaldehyde, dimethyl ether, and perhaps CO conversion over vanadyl pyrophosphate.
- A research note on the effect of first row transition metal promoters on activity and selectivity of vanadyl pyrophosphate in methane oxidation.

- A paper describing our methods for modification of the surface acidity of vanadyl pyrophosphate.

It is expected that our work with iron phosphates as well as a study of methanol chemisorption of several oxides and phosphates can also be published in the relatively near future.

REFERENCES

Ai, M. J. Catal. 101 389 (1986).

Busca, G., Centi, G., Trifiro, F., Lorenzelli, V. J. Phys. Chem. 90 1337 (1986a).

Busca, G., Cavani, F., Centi, G., Trifiro, F. J. Catal. 99 400 (1986b).

Busca, G., Centi, G. J. Am. Chem. Soc. 111 46 (1989).

Centi, G., Trifiro, F., Ebner, J.R., Franchetti, V.M. Chem. Rev. 88 55 (1988).

Froment, G.F., Bischoff, K.B. "Chemical Reactor Analysis and Design", 2nd Edition, John Wiley and Sons, New York, 1990, pp. 45.

Hall, T.J., Hargreaves, J.S.J., Hutchings, G.J., Joyner, R.W., Taylor, S. Fuel Proc. Technol. 42 151 (1995).

Horowitz, H.S., Blackstone, C.M., Sleight, A.W., Teufer, G. Appl. Catal. 38 193 (1988).

Hutchings, G.J. Appl. Catal. 72 1 (1991).

McCormick, R.L. "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane" Quarterly Technical Progress Report No. 10, DE-AC22-92PC92110-10, 1995.

McCormick, R.L., Alptekin, G.O. "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane" Quarterly Technical Progress Report No. 12, DE-AC22-92PC92110-12, 1996.

Michalakos, P.M., Kung, M.C., Jahan, I., Kung, H.H. J. Catal. 140 226 (1993).

Miyake, T., Doi, T. Appl. Catal. A: General 131 43 (1995).

Parkyns, N.D., Warburton, C.I., Wilson, J.D. Catalysis Today 18 385 (1993).

Wang, Y., Otsuka, K. J. Catal. 155 256 (1995).