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

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EXECUTIVE SUMMARY

This document is the fifteenth 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 October-December, 1996. Vanadium phosphate, vanadyl pyrophosphate specifically, is used commercially to oxidize butane to maleic anhydride and is one of the few examples of an active and selective oxidation catalyst for alkanes. In this project we are examining this catalyst for the methane oxidation reaction. Initial process variable and kinetic studies indicated that vanadyl pyrophosphate is a reasonably active catalyst below 500°C but produces CO as the primary product, no formaldehyde or methanol were observed.

A number of approaches for modification of the phosphate catalyst to improve selectivity have been tried during this project. During this quarter we have obtained surface areas of catalysts prepared with modified surface acidity. The results confirm the enhanced activity of two of the modified preparations in methanol conversion (a test reaction for surface acid sites). In previous work we noted no improvement in methane oxidation selectivity for these catalysts. Surface areas, surface analysis by XPS, and bulk analysis by ICP-AA have been obtained for vanadyl pyrophosphate promoted by Cr, Cu, and Fe. These data indicate that roughly one tenth of the surface metal atoms are promoter. A similar analysis was obtained for the bulk. Preliminary examination of binding energies suggests a slightly more reduced surface for the Cr and Fe promoted catalysts which exhibit a significant selectivity to formaldehyde in methane oxidation. A more detailed kinetic model has also been developed to aid in comparing the promoted catalysts and is discussed. Plans for the coming months are outlined.

INTRODUCTION

This document is the fifteenth 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 October-December 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).

Preliminary results have shown that CO is the primary product of methane oxidation over this catalyst at temperatures below 500°C. Several approaches have been or are being taken to improve catalyst selectivity. These include:

- Modification of the surface acidity of vanadyl pyrophosphate through production of structural defects and exchange of surface hydroxyl groups.
- Promotion of the catalyst by addition of first row transition metals, especially Fe.
- Attempts to prepare vanadyl pyrophosphate on a silica support.
- Examination of iron phosphate and silica supported iron phosphates for the methane oxidation reaction.

Modification of acidity was not successful at improving methane oxidation selectivity. Attempts at supporting vanadyl pyrophosphate have also not been successful. Promotion with Cr and Fe produced significant yields of formaldehyde. Iron phosphate ($FePO_4$) and silica supported iron phosphate have much higher formaldehyde selectivities and methanol was observed as a trace product. In addition to these attempts at preparing more selective catalysts we have also been developing a simple macrokinetic model to aid in data analysis and interpretation.

This report describes the results of additional characterization of all catalysts used so far as well as additional analysis of the kinetic data. A description of activities planned for the remainder of the project is also provided.

PROJECT DESCRIPTION

Objectives

The original objectives of this project are:

- To determine optimum conditions for methanol and formaldehyde production from methane using VPO catalysts.
- 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 is to utilize promoters and supports to improve the activity and selectivity of the unmodified VPO catalyst.

The project is divided into four tasks:

Task 1: Laboratory Setup. Work on this task has been completed.

Task 2: Process and Catalyst Variable Study. Vanadyl pyrophosphate has not been found to be a selective catalyst for methane oxidation. Results have been summarized in previous reports

Task 3: The Effect of Promoters and Supports. To date we have tested catalysts promoted with the first row transition metals and observed increased selectivity to HCHO for Fe and Cr. Attempts at putting vanadyl pyrophosphate on a support are underway.

Task 4: Advanced Catalyst Testing. Our first advanced catalysts are iron phosphates, based on a recent literature report (Wang and Otsuka, 1995) and our own observation of the promoting effect of Fe.

Thus, Tasks 3 and 4 are on going. From a technical standpoint the catalyst development approaches we have followed are outlined below.

Modification of Surface Acidity. 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. By increasing Lewis acid site strength it is hoped that the temperature required for methane activation can be lowered resulting in improved selectivity. Bronsted acid sites have also been removed by exchange of protons with potassium under nearly anhydrous conditions. The degree of disorder of these materials was measured by XRD line broadening. Surface acidity of these materials was measured by FTIR of chemisorbed bases and by activity in methanol coupling to dimethyl ether. Activity and selectivity in methane oxidation were also measured. XRD indicates that modifications were successful at introducing disorder in the layer stacking. The methanol conversion results suggest that these catalysts do have more acid sites. IR suggests that sites on one of the catalysts may be of higher strength but the results are not conclusive. The potassium exchanged catalyst was poorly active in the methanol conversion reaction. The catalysts with enhanced acidity as gauged by methanol conversion were more active for methane conversion but not more selective than unmodified vanadyl pyrophosphate. While not a high priority, we may measure the number of acid sites in these materials by ammonia chemisorption in a TGA apparatus to confirm our ideas.

Supported Vanadyl Pyrophosphate. Because of the complex procedure required to prepare $(VO)_2P_2O_7$, it is very difficult to place on a support and no examples are available in the academic or patent literature. We have tried several approaches but none has yielded the desired phase on the support. This avenue of investigation may not be pursued further unless we come up with a new idea that has a high probability of success.

Promotion by First Row Transition Metals. Vanadyl pyrophosphate samples promoted with Mn, Cr, Fe, Co, Cu, and Zn have been prepared by addition of promoter salts to a suspension of the activated catalyst. Promotion with Fe and Cr have produced significant changes in catalyst activity and selectivity with measurable yields of formaldehyde at low conversions. Surface and bulk analysis of these materials indicates incorporation of the promoter on both the surface and bulk at a promoter:V ratio of roughly 1:10. Catalyst characterization studies to date have not revealed any fundamental cause of the promotion effect. These include x-ray diffraction, infrared spectroscopy, and XPS binding energies. Future work may focus on additional kinetics and characterization of the Fe promoted material.

Iron Phosphate Based Catalysts. Crystalline $FePO_4$ was tested in methane oxidation because of the interesting results noted for Fe promotion of vanadium phosphate and because of literature reports suggesting that it was an active and selective catalyst. Preliminary experiments reported previously indicated 30% selectivity to formaldehyde at 1% conversion, a much higher yield that observed of the vanadium phosphates. This result will be expanded upon and confirmed in the coming months. $FePO_4$ is also easily prepared on a silica support. This material exhibited a formaldehyde selectivity near 40% at 1% conversion. The activation energy for methane oxidation was much higher over this material than over vanadium phosphate or unsupported iron phosphate and was similar to values observed for methane oxidation over silica itself. The iron phosphate system appears to be much more interesting for the methane oxidation reaction than vanadium phosphate. There are several stable crystalline phases of iron phosphate and a great deal of practical research remains to be done on this system. Our focus for the remainder of the project is expected to be iron phosphates.

PROJECT STATUS

During the final quarter of calendar 1996 we focused primarily on measurement of catalyst surface areas and on obtaining surface (XPS) and bulk (ICP-AA) analysis of the promoted materials. Development of kinetic models for data interpretation also continues.

Surface Acidity Effects in Light of Total Surface Area

During this quarter we have obtained surface areas of the catalyst with modified surface acidity discussed in earlier reports. We attempted to modify the surface acid sites, with the goal of producing stronger Lewis sites, by altering the preparation method to introduce additional defects and disorder in the structure. A method where tetraethyl orthosilicate is included in the preparation had been shown in the literature (Horowitz, et al., 1988) to produce increased disorder. We hypothesized that by increasing the size of one of the organic molecules in the synthesis mixture we could increase disorder because the organic species are trapped between the layers of the inorganic crystals. To accomplish this we modified the preparation by substituting naphthalene methanol for benzyl alcohol. Surface areas are listed in Table 1 along with other important properties. The x-ray diffraction full width at half maximum is a measure of disorder in the layer stacking. Increased disorder is apparently accompanied by decrease in surface area. The ratio of Bronsted to Lewis acid sites (based on IR of chemisorbed pyridine) also increases.

Figure 1 shows catalyst activity for methanol coupling as a function of temperature. The measure of activity is the observed reaction rate on either a catalyst mass or surface area basis. In both cases the TEOS modified material is the most active catalyst. However, on a surface area basis the naphthalene methanol modified catalyst is more active than the unmodified material, a switch in relative activity from the mass basis comparison. These results may be of interest to others studying the surface acidity of vanadyl pyrophosphate and we therefore intend to prepare a publication. Additional data required includes a measure of the number of surface acid sites using TGA measurement of ammonia adsorption and analysis of the materials for P:V ratio. Note that surface acidity modification appeared to have little or no affect on selectivity for methane oxidation.

Table 1. Properties of catalysts with modified surface acidity.

Catalyst	*Surface Area, m^2/g*	*XRD FWHM (020)*	*Bronsted/Lewis Ratio (1540/1447)*	*Methanol Conversion E_a, kcal/mole*
Unmodified	33.1	1.5	2.1	16
TEOS	20.0	1.7	2.3	20
Naphthalene Methanol	14.7	1.6	2.8	15
Potassium Exchange	29.2	--	≈0	10

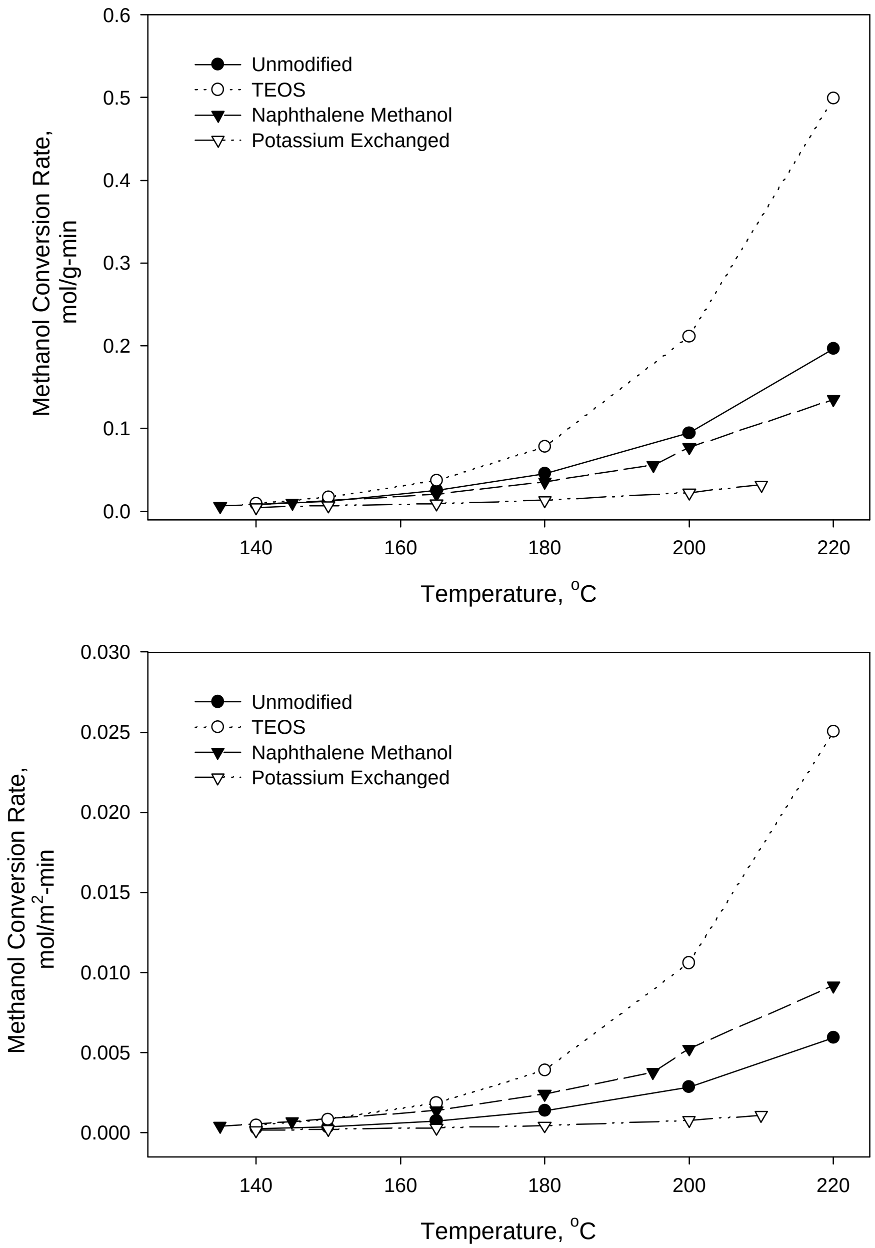

Figure 1. Activity of surface acidity modified materials for methanol conversion on a mass (top) and surface area (bottom) basis.

Detailed Characterization of Promoted Catalysts

Surface areas are listed in Table 2 and are nearly identical for all four catalysts. Results of surface analysis by XPS, also in Table 2, indicate that roughly one tenth of the surface metal atoms are promoter. Bulk analysis yields similar results indicating that the method of introducing promoters modifies both the surface and bulk composition. Surface P:V ratios are well above 1.0 as has been reported for commercial butane oxidation catalysts. Bulk P:V ratios are slightly below 1.0 which suggests that the target synthesis stoichiometry of P:V=1.04 may not have been obtained because of water in the presumably anhydrous phosphoric acid. Table 3 reports binding energies observed for vanadium, phosphorus, and the promoter elements.

Table 2. Characterization results for vanadyl pyrophosphate and promoted catalysts.

Catalyst	*Surface Area (m^2/g)*	*Surface Promoter:V*	*Bulk Promoter :V*	*Surface P:V Ratio*	*Bulk P:V Ratio*
VPO	32.1	--	--	1.23	0.97
Cr-VPO	33.8	0.13	0.08	1.58	0.99
Cu-VPO	30.4	0.07	0.10	1.47	0.99
Fe-VPO	32.6	0.09	0.11	1.16	0.92

X-ray photoelectron spectroscopy (XPS) has been used to determine the oxidation states of vanadium and the promoter elements. Although the oxidation state of vanadium on the surface of different compounds have been investigated in detail, only a few XPS measurements have been reported on the vanadium phosphorous oxides. The reported binding energies in the vanadyl pyrophosphate phase (P/V = 1.0 - 1.2) goes from 516.6 to 517.9 eV. Such a variation in the binding energy can be explained either by the presence of a surface and/or bulk impurity phases, or errors caused by the sample charging. Most authors took the C 1s binding energy as a reference with values between 284.5 and 285 eV. The carbon residues on the surface may be coming either from the preparation method (in the organic preparation methods an alcohol is used as the reducing medium) or from the activation process. Depending on the nature of its source C 1s binding energy can yield a broad signal. A better criterion to differentiate between the vanadium oxidation states is reported by Cornaglia and Lombardo (1995). The difference in the binding energy between O 1s and V $2p_{3/2}$ signals ($\Delta_{\text{O 1s - V 2p}}$) is used to assign the surface states. This binding energy difference is 14.5 ± 0.1 eV for the V^{IV} containing phase for P/V = 1.0, and varies 14.9 to 15.2 for P/V = 1.07 to 1.2. Binding energy difference for the β-VOPO4 is reported between 13.0 to 13.9.

V^{IV} compounds show a O 1s BE of 532.2 ± 0.1 eV. The full width at half maximum (FWHM) of the oxygen signal shows small variations between 2.8 and 3.1 eV. The pure $(VO)_2P_2O_7$ phase reported in the literature yields O 1s binding energies 531.1 to 532.8 eV with a narrow signal (FWHM 2.4 eV). The pure V^V phases with and without phosphorous exhibit much narrower O 1s signals (1.7-2.0 eV), shifted downwards to 531.2 (β-VOPO4) and 530.0 eV (V_2O_5). The vanadyl hydrogen phosphate hemihydrate, the precursor of vanadyl pyrophosphate, shows a V $2p_{3/2}$ BE of 517.5 eV which would correspond to V^{IV} in this oxide matrix. However, the V 2p signal of vanadyl pyrophosphate appears at 517.9 eV. This displacement towards higher BE may be due to either a different vanadium environment or to the coexistence of V^{IV} and V^V on the surface.

XPS data of promoted and unpromoted VPO catalysts are given in Table 3. Since the resolution of the V $2p_{1/2}$ is poorer than that of the V $2p_{3/2}$ due to overlapping with the oxygen signal the latter BEs are given. According to the criteria given above, the shift in the Δ value towards lower BE values with the addition of the promoter elements can be explained in terms of a change in the vanadium oxidation state. In the case of Cr and Fe promoted VPO catalysts, V^{V} compounds as well as V^{IV} exists on the surface. However, the different behavior in the catalytic activity of these promoted VPO catalysts, is not necessarily due to the change in the oxidation state of vanadium. Formation of different catalytic sites can also be the reason for formaldehyde formation.

Table 3. XPS Data for Promoted and Unpromoted VPO catalysts.

Catalyst	*V $2p_{3/2}$*	*O 1s*	*P 2p*	$D_{O\ 1s\ -\ V\ 2p}$	*Promoter Metal Peak* (*)
$(VO)_2P_2O_7$	516.5 (1.9)(**)	532.0 (2.2)	134.1 (1.9)	15.1	-
Cu-VPO	517.3 (2.0)	530.0 (2.2)	133.8 (1.9)	14.3	935.4 (4.5)
Cr-VPO	517.5 (1.8)	531.4 (1.6)	134.0 (1.8)	13.9	578.3 (2.7)
Fe-VPO	517.4 (2.4)	531.3 (1.8)	134.0 (1.8)	13.9	714.2 (5.3)

(*) Cu 2p, Cr $2p_{3/2}$, Fe $2p_{3/2}$
(**) Full length at half widths (shown in brackets).

The available data are limited to define completely the oxidation states of the promoter elements. But for the case of Fe, the obtained BE energy values yields very little possibility of presence of FeO or Fe_2O_3 on the surface. The difference between the Fe 2p doublets for Fe_2O_3 is given as 13.6 eV but is 12.6 eV for our catalyst. The BE value for Fe $2p_{3/2}$ is 709.5 eV for FeO, 710.8 eV for Fe_2O_3 and 711.5 eV for $FeCl_3$. In our case BE value is much greater, which can be explained as incorporation of this element with phosphorous. For Cu the same phenomena is valid as in the case of Fe. Cu $2p_{3/2}$ for CuO is 933.6 eV and for Cu_2O 932.5 eV. The shift in this signal can be explained in terms of electronegativity of phosphorous atoms in the neighborhood. In the case of Cr, its oxide yields a signal for Cr $2p_{3/2}$ in the range of 576.5 and 579.5 eV. For Cr_2O_3 this takes a value of 576.9 eV. For Cr-VPO catalyst, there may be chromium oxide on the surface.

Expanded Kinetic Analysis

Heterogeneous partial oxidation reactions of methane to formaldehyde can occur via two different reaction paths depending on the nature of the catalyst used. A parallel reaction path to the formation of CO and CO_2 is shown below:

$$\begin{tikzcd}
CH_4 \arrow[rr, "k_1"] \arrow[dr, "k_2"'] & & HCHO \arrow[dl, "k_3"] \\
& CO,\ CO_2 &
\end{tikzcd}$$

Hutchings and Higgins (1996) defined three different factors to establish a basis for comparison of catalyst activity, assuming each reaction in the given scheme as pseudo first-order. These three factors are: (a) the rate constant for methane conversion corrected for surface area $(k_1+k_2)/SA$ which is a measure of specific activity; (b) primary selectivity S_o (selectivity extrapolated to zero methane conversion); and (c) the relative rates of oxidation of methane and formaldehyde $k_3/(k_1+k_2)$, the latter two factors being a measure of the selectivity of the catalyst. A selective and active catalyst requires a high value of specific activity $(k_1+k_2)/SA$ and primary selectivity S_o and a low value of $k_3/(k_1+k_2)$. The given criteria will be useful for the catalysts in which the reaction follows a parallel path. MoO_3/SiO_2 (Spencer and Pereira, 1987), $FePO_4$ and $FePO_4/SiO_2$ (McCormick and Alptekin, 1996) catalysts yields a similar pattern.

The behavior of Fe and Cr promoted VPO and of V_2O_5/SiO_2 (Spencer and Pereira, 1989) catalysts follows a sequential reaction path as shown below:

$$CH_4 \xrightarrow{k_1} HCHO \xrightarrow{k_2} CO,\ CO_2$$

(Assume for simplicity $A \xrightarrow{k_1} B \xrightarrow{k_2} C$)

Similar criteria can be developed for reaction in series. An active and selective catalyst requires a high S_o and k_1/SA value, and a low k_2/k_1 ratio. However to test the catalyst performance rate constant for the formaldehyde oxidation reaction have to be known. The rate constant k_2 can be estimated analytically if the moles of formaldehyde produced by the reaction are known as outlined below.

Assuming differential operation conditions and a pseudo first-order methane dependence;

$$-r_A = \frac{dc_A}{dt} = k_1 C_A \qquad [1]$$

$$-r_B = \frac{dc_B}{dt} = k_1 C_A - k_2 C_B \qquad [2]$$

Solution of equation [1] yields;

$$C_A = C_{Ao}\, e^{-k_1 t}$$

Combining equations [1] and [2];

$$\frac{dc_B}{dt} = k_1\, C_{Ao}\, e^{-k_1 t} - k_2 C_B$$

$$\frac{dc_B}{dt} + k_2 C = k_1\, C_{Ao}\, e^{-k_1 t}$$

Left hand side is the integrating factor;

$$\frac{d(C_B\, e^{-k_2 t})}{dt} = k_1 C_{Ao}\, e^{(k_2 - k_1)t}$$

$$C_B = k_1\, C_{Ao} \left(\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \right)$$

Selectivity S can be defined for purposes of modeling as:

$$S = \frac{C_B}{C_{Ao}}$$

or,

$$S = k_1 \left(\frac{e^{-k_1 t} - e^{-k_2 t}}{k_2 - k_1} \right)$$

For the partial oxidation reactions of methane $k_2 >> k_1$. So the second term in the numerator can be neglected. Numerical solution will yield a k_2 value as;

$$k_2 = k_1 + \frac{k_1\, C_{Ao}\, e^{-k_1 t}}{S}$$

For comparison of the performance of Fe and Cr promoted VPO catalysts the criteria given above was applied and the results are tabulated in Table 4. According to the tabulated values of k_2/k_1 (which we desire to be low) and k_1/SA (which we desire to be high), Fe promoted VPO catalysts seems to be a slightly more active and selective catalyst than the Cr promoted VPO because the rate of product oxidation is lower.

Table 4. Catalytic Performance of Fe and Cr Promoted VPO Catalysts.

Catalyst	k_1	k_2	S_o (%)	k_1/SA	k_2/k_1
Fe-VPO			<90		
$T = 335\ ^{o}C$	$2.41\ 10^{-6}$	$2.87\ 10^{-5}$		$7.41\ 10^{-8}$	11.9
$T = 385\ ^{o}C$	$9.29\ 10^{-6}$	$2.25\ 10^{-4}$		$2.85\ 10^{-7}$	24.2
$T = 410\ ^{o}C$	$1.81\ 10^{-5}$	$7.64\ 10^{-4}$		$5.56\ 10^{-7}$	42.2
Cr-VPO			<90		
$T = 335\ ^{o}C$	$1.09\ 10^{-6}$	$2.95\ 10^{-5}$		$3.23\ 10^{-8}$	27.0
$T = 385\ ^{o}C$	$4.72\ 10^{-6}$	$2.49\ 10^{-4}$		$1.40\ 10^{-7}$	52.8
$T = 410\ ^{o}C$	$1.89\ 10^{-5}$	$1.17\ 10^{-3}$		$5.60\ 10^{-7}$	61.9

PLANNED ACTIVITIES

Detailed Studies of Iron Phosphate Catalysts

Given the very interesting results reported previously for methane oxidation over these catalysts, the focus of our work on advanced catalysts will be detailed studies on iron phosphate materials. Note that a report in the literature has appeared on methane conversion over iron phosphate (Wang and Otsuka, 1995).

Publication of Results

Preparation of manuscripts for publication continues with plans for submission of one or two papers soon. Those currently in preparation are:

- A paper describing results of methane partial oxidation over unpromoted and first row transition metal promoted vanadyl pyrophosphate should be submitted to *Journal of Catalysis* in a matter of weeks.
- Detailed study of kinetics of methane, methanol, formaldehyde, dimethyl ether, and perhaps CO conversion over vanadyl pyrophosphate. A draft of this paper is currently being updated and should be submitted during this quarter.
- A paper describing our methods for modification of the surface acidity of vanadyl pyrophosphate is being prepared. Some additional data may be required before publication

It is expected that our ongoing work with iron promoted vanadyl pyrophosphate, iron phosphates, as well as a study of methanol chemisorption on 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).

Cornaglia, L.M., Lombardo, E.A. Appl. Catal. A General 127 125 (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).

Hutchings, G.J., Higgins, R. J. Catal. 162 153 (1996).

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).

Spencer, N.D., Pereira, C.J. AIChE Journal 33 1808 (1987).

Spencer, N.D., Pereira, C.J. J. Catal. 116 399 (1989).

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