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

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EXECUTIVE SUMMARY

This document is the fourteenth 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 July-September, 1996. Activities included studies of the oxidation of dimethyl ether over vanadyl pyrophosphate and synthesis of all previously acquired kinetic data. This synthesis revealed the need for additional data on methane and methanol oxidation and these experiments were performed. A further series of methanol oxidation/dehydration experiments was conducted on samples with varying surface acidity that have been described in earlier reports. Oxidation of methane over Cr-promoted VPO was also reinvestigated.

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.

The kinetic studies performed to date allow us to satisfy the first objective above. However, unpromoted VPO yields only CO as the primary oxidation product. Studies of promoters have shown improvements in the formaldehyde selectivity but no methanol has been observed. The best promoters tested have been Fe and Cr (results for Cr are described in this report). We have also examined the use of iron phosphate for the methane conversion reaction. $FePO_4$ is a more selectivity catalyst than the promoted VPO materials. Support of this iron phosphate on silica results in further improvements in selectivity. Current work is directed at understanding the improved selectivity for promoted VPO and at obtaining a knowledge of the optimum conditions for methane conversion of iron phosphate.

INTRODUCTION

This document is the fourteenth 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 have also described preliminary results for methane oxidation over silica supported vanadyl pyrophosphate, Fe-promoted vanadyl pyrophosphate, iron phosphate, and silica supported iron phosphate in previous reports. 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). The focus of the project in the remaining quarters will be on iron phosphate catalysts.

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

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. As noted in quarterly report No. 13, to fully understand the reaction network data on the oxidation of dimethyl ether are needed. These have been acquired and results are reported below.

Oxidation of Dimethyl Ether. DME is obtained from Scott Specialty Gases as 5.31% certified DME-He mixture, which is fed to the system via helium mass flow controller (recalibrated for this mixture). DME-to-oxygen ratio is changed from 0.66 to 1.0 at a fixed gas hourly space velocity (GHSV) of 9050 hr^{-1}. DME oxidation results are shown in Figure 1. Methanol, formaldehyde, CO and CO_2 were the significant reaction products. Formation of some methyl formate, dimethoxymethane (DMM) and, interestingly, methane have also been observed.

Presence of methanol as a product indicates an acid catalyzed reversible reaction between DME and methanol. At very low DME conversions, methanol and carbon dioxide tends to be the only reaction products. Methanol selectivity decreases monotonically with increasing DME conversion. Carbon dioxide selectivity on the other hand increases sharply and reaches to a high saturation level, which suggests that DME is directly oxidized into carbon dioxide. Selectivity to formaldehyde tends to zero at zero DME conversion and increases with DME conversion up to a certain level, implying that formaldehyde is a secondary product. At much higher conversions, formaldehyde has further oxidized to give carbon oxides. Carbon monoxide selectivity also tends to zero at zero DME conversion. It increases until after significant amounts of formaldehyde is observed, which strongly suggests that there is no direct oxidation route from DME to carbon monoxide. Our results suggest the following sequences for reactions:

$$\begin{tikzcd}
CH_3OCH_3 \arrow[rr] \arrow[dr] \arrow[dd, shift right, leftarrow] \arrow[dd, shift left] & & CO_2 \\
& CH_4 \arrow[dr] & \\
CH_3OH \arrow[r] & HCHO \arrow[r] & CO \arrow[uu]
\end{tikzcd}$$

At high oxygen partial pressure, selectivity to formaldehyde and to the carbon oxides increases. Presence of methane in the reactor effluent even at low selectivity is important because this indicates the possibility of a direct oxidation route from methane to DME. Because no methane is observed when methanol is fed to the reactor, DME must be the methane precursor.

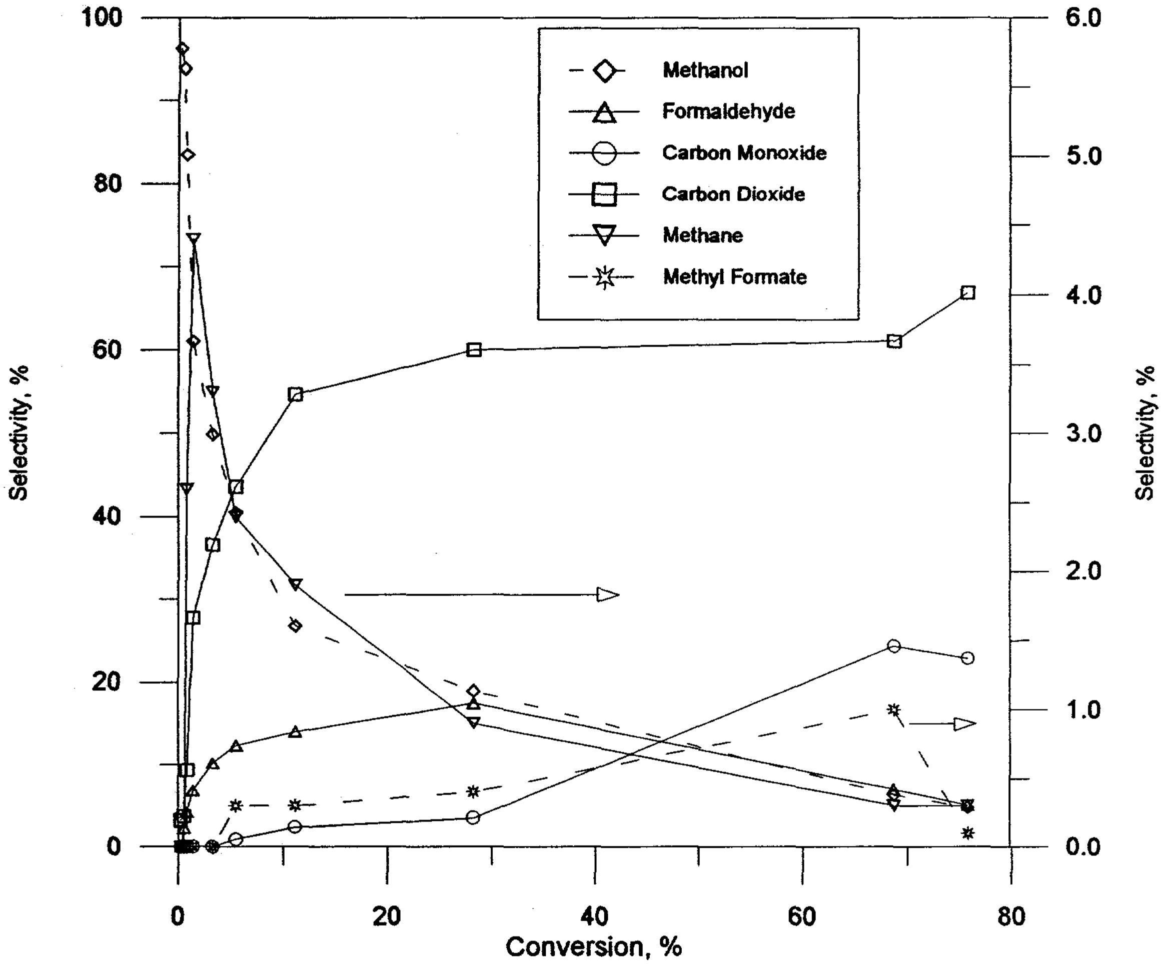

Figure 1. Selectivity versus conversion for DME oxidation over VPO.

Summary of Kinetic Studies. The large data set we have acquired on kinetics (macro- or global kinetics) for methane and other hydrocarbons over vanadyl pyrophosphate can be summarized with the kinetic parameters listed in Table 1. This is the first study to comprehensively examine conversion of methane and possible intermediates over this catalysts. Ultimately, the data should also yield parameters for CO oxidation as well. Reaction order for hydrocarbons tends to be 1 except for methane. The observation that the reaction order for methane is less than one may imply that adsorption (activation?) of methane is somehow rate controlling. Methane oxidation also exhibited a small dependence on oxygen partial pressure while other oxidation were zero order in oxygen. Comparison with literature indicates that activation energies and reaction orders compare reasonably well with those reported for other catalysts. However, the methane activation energy is near the lower end of the reported rage. Further analysis of this data and comparison with literature on methane oxidation and on oxidations over vanadyl pyrophosphate is being performed.

Table 1. Kinetic parameters for oxidation over vanadyl pyrophosphate.

Reaction	Activation Energy, kcal/mol	Hydrocarbon Order	Oxygen Order
Methane oxidation	24.4	0.75	0.1
Methanol oxidation	14.9	1.05	~0
DME oxidation	17.0	1.00	~0
Formaldehyde oxidation	16.6	0.95	~0

Oxidation Over Cr-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.

Methane oxidation over this catalyst was carried out at a fixed gas hourly space velocity (GHSV) of 9300 hr^{-1} and at two different methane-to-oxygen ratios of 1.5 and 8.3. The results are shown in Figure 2. At very low methane conversions, formaldehyde selectivity is very high. Formaldehyde selectivity drops below 5% above 0.5% conversion. Selectivity versus conversion behavior for the different methane-to-oxygen ratio runs is almost identical. However, at methane-to-oxygen ratio of 1.5 formaldehyde yields are higher than at a ratio 8.3. As formaldehyde disappears in the reactor effluent with increasing conversion, carbon monoxide selectivity peaks up. At conversions above 0.5 %, carbon dioxide becomes the principal product. As far as we know, this is the first report of the use of Cr-promoted VPO for methane conversion.

1.8 % n-Butane was mixed with the feed to reduce the catalyst and perhaps to increase activity. Although moles of formaldehyde produced per mole of methane fed increased significantly, formaldehyde selectivity did not change very much, because carbon monoxide and carbon dioxide production was increased as well.

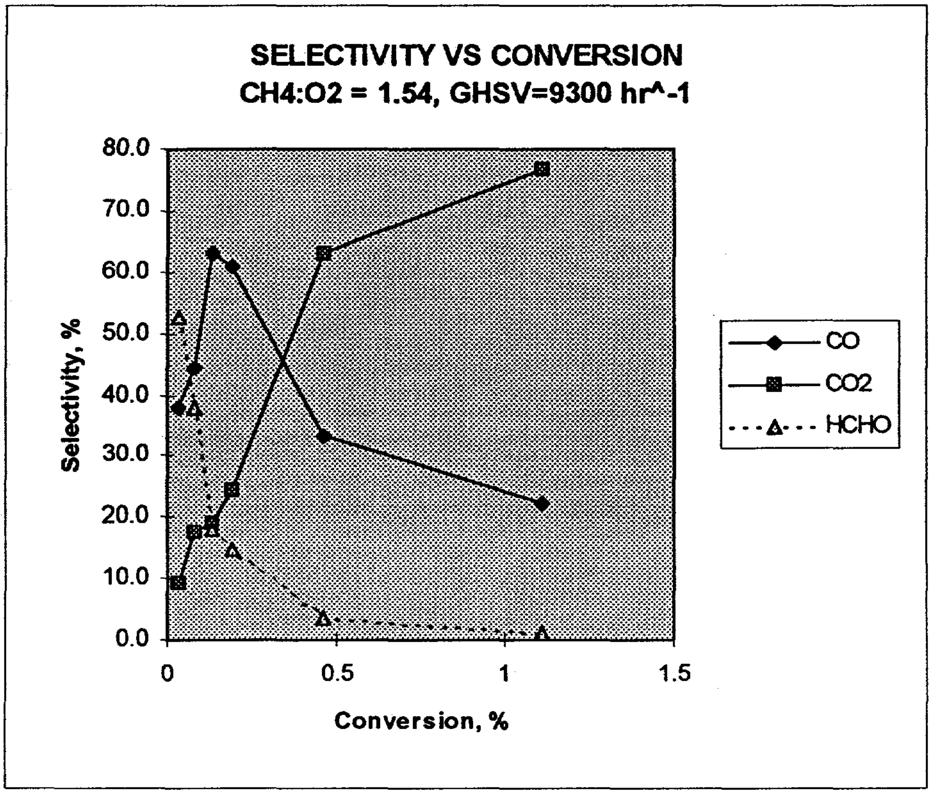

Figure 2. Selectivity as a function of conversion for methane oxidation over Cr-promoted VPO.

PLANNED ACTIVITIES

Detailed Studies of Iron Phosphate Catalysts

Given the very interesting results reported last quarter 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:

- Detailed study of kinetics of methane, methanol, formaldehyde, dimethyl ether, and perhaps CO conversion over vanadyl pyrophosphate. A draft of this paper was recently completed.
- 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.

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