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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 ninth quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". Activities were focused on fine tuning of the microreactor system by elimination of transport effects and improvements in the analytical system. Process variable studies were conducted on vanadyl pyrophosphate and screening studies were conducted on several modified catalyts. One additional catalyst was prepared and characterization studies continued. These results are reported.

Specific accomplishments include:

- Determination that pore diffusion effects were insignificant under all conditions of interest and for all particle sizes. Poor gas-solid contacting was observed at larger particle diameters with $d_r/d_p<10$. Our experiments are conducted at $d_r/d_p \approx 20$.
- At convenient flow rates external transport resistance was determined to be significant for temperatures above 450°C. Operation at higher flow rates allowed extension of the kinetic regime to 475 or perhaps 500°C. All future experiments will be performed under kinetically controlled conditions.
- A process variable study/kinetic study over vanadyl pyrophosphate (VPO) indicated higher conversion at lower oxygen concentration. Methane to oxygen ratios of from 10:1 to 25:1 were found to produce the best results. Under all conditions the primary product was CO but as conversion increased the formation of CO_2 became more significant. Trace quantities of methanol and formaldehyde were observed suggesting that similar species are reaction intermediates.
- TEOS promoted and ZnO promoted vanadyl pyrophosphate were tested for activity and selectivity in methane oxidation. Both catalysts were more active than unmodified VPO. The TEOS catalyst produced only CO, even at relatively high conversion where unmodified VPO produced significant quantities of CO_2. The ZnO promoted catalyst was roughly as active as unpromoted VPO and produced only CO.
- An additional catalyst was prepared using naphthalene methanol in place of benzyl alcohol as one of the solvents. Benzyl alcohol is trapped between the layers of the precursor and influences the development of defect structures related to the presence of strong Lewis acid sites. The use of a larger molecule was investigated in an attempt to enhance acid site strength. Characterization results are reported.
- A suit of catalysts promoted by first row transition metals has been prepared. Precursor characterization results are reported.

INTRODUCTION

This document is the ninth quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". 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 promotes 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). The approach we are currently taking is directed at increasing the strength of these strong Lewis acid sites by enhanced strain or disorder in the layer stacking. Surface acidity is being 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 to be taken in future work include synthesis of other vanadium phosphates known to be active and selective butane oxidation catalysts and modification of the VPO surface through various ion exchange and doping procedures.

PROJECT DESCRIPTION

Objectives

The specific objectives of this project are:

- To develop an economical catalyst for partial oxidation of methane to methanol.
- To determine optimum conditions for methanol production from methane using VPO catalysts. 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.
- Develop a simplified methanol production process flowsheet based on these advanced catalysts.

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. Ideally, a low CH_4/O_2 ratio will be employed with air as the source of oxygen. Temperatures below 600°C and pressures up to 20 atm are to 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 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.

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. A number of other experiments will be conducted in coming months.

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 work has been initiated in this area and many more catalyst should be prepared in the next quarter.

Task 4: Advanced Catalyst Testing. Advanced catalysts using the best ideas developed in previous tasks 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.

PROJECT STATUS

Catalyst Preparation and Characterization

Vanadyl pyrophosphate was prepared by the following procedure. V_2O_5 (15.0 g) was suspended in a solution of 90 ml of *iso*-butyl alcohol and 60 ml of benzyl alcohol. The solution was stirred and heated under reflux for 3 hours. A black solution was formed. The solution was cooled to room temperature and left stirring overnight. Then *ortho*-phosphoric acid (anhydrous, 19.4 g) was added and the solution was heated under reflux for an additional 2 hours. A blue suspension formed. This suspension was filtered, washed in water, and dried at 150°C overnight. A light blue precipitate recovered. Conversion of the dried catalyst precursors to the active phase was performed in ceramic boats placed in a quartz tube furnace under a stream of air or 1.5% butane in air. The temperature was gradually increased from room temperature through 125°C (40 min.), 350°C (40 min.) and finally 400°C where it was held for 24 hours. Large amounts of maleic anhydride were deposited at the quartz tube outlet during activation in butane/air mixtures. Catalyst samples for kinetic studies were pelletized at 15,000 psi.

Preparation procedures of tetraethyl *ortho*-silicate (TEOS) modified and ZnO promoted VPO have been described in previous reports. An additional catalyst was prepared using a procedure identical to that detailed above except that naphthalene methanol was substituted for benzyl alcohol in the preparation reflux. This molecule is similar chemically to benzyl alcohol but of significantly larger size. As benzyl alcohol is thought to become trapped between the layers of the precursor structure and lead to defect and acid site formation, it was of interest to determine if the use of a larger organic molecule could enhance the number or strength of the acid sites formed.

X-ray diffraction results for these catalyst precursors, including the naphthalene methanol (NM) modified material, are shown in Figure 1. This precursor material was completely amorphous. As noted before, modification by TEOS results in reduced intensity for the (001) reflection indicative of disorder in the direction perpendicular to the layer plane. Figure 2 reports x-ray diffraction patterns of various activated catalysts. All four materials show only the presence of vanadyl pyrophosphate. In activated materials the (200) reflection can indicate degree of ordering in the direction perpendicular to the layers. There is little difference in materials activated in air or butane/air mixtures. Modification with TEOS or NM results in a significant lowering of relative intensity and broadening of this reflection, as shown in the inset. Figure 3 reports infrared spectra of these materials. These is little difference between them, particularly in the position of the V=O stretch at roughly 970 cm^{-1}. For the NM modified catalyst this peak has broadened but so have all the other peaks suggesting the presence of water in the sample.

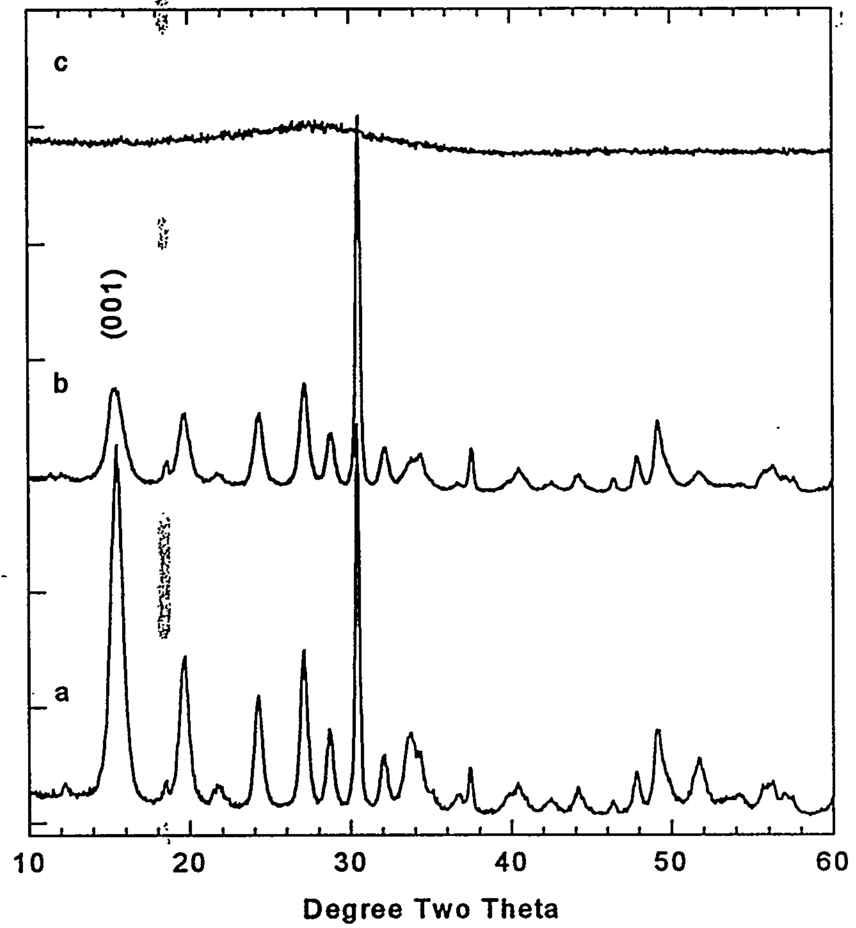

Figure 1. X-ray powder diffraction results for catalyst precursors: a) VOHPO$_4$-0.5H$_2$) prepared in benzyl/isobutyl alcohols, b) similar catalyst modified by addition of TEOS, c) similar catalyst with naphthalene methanol replacing benzyl alcohol.

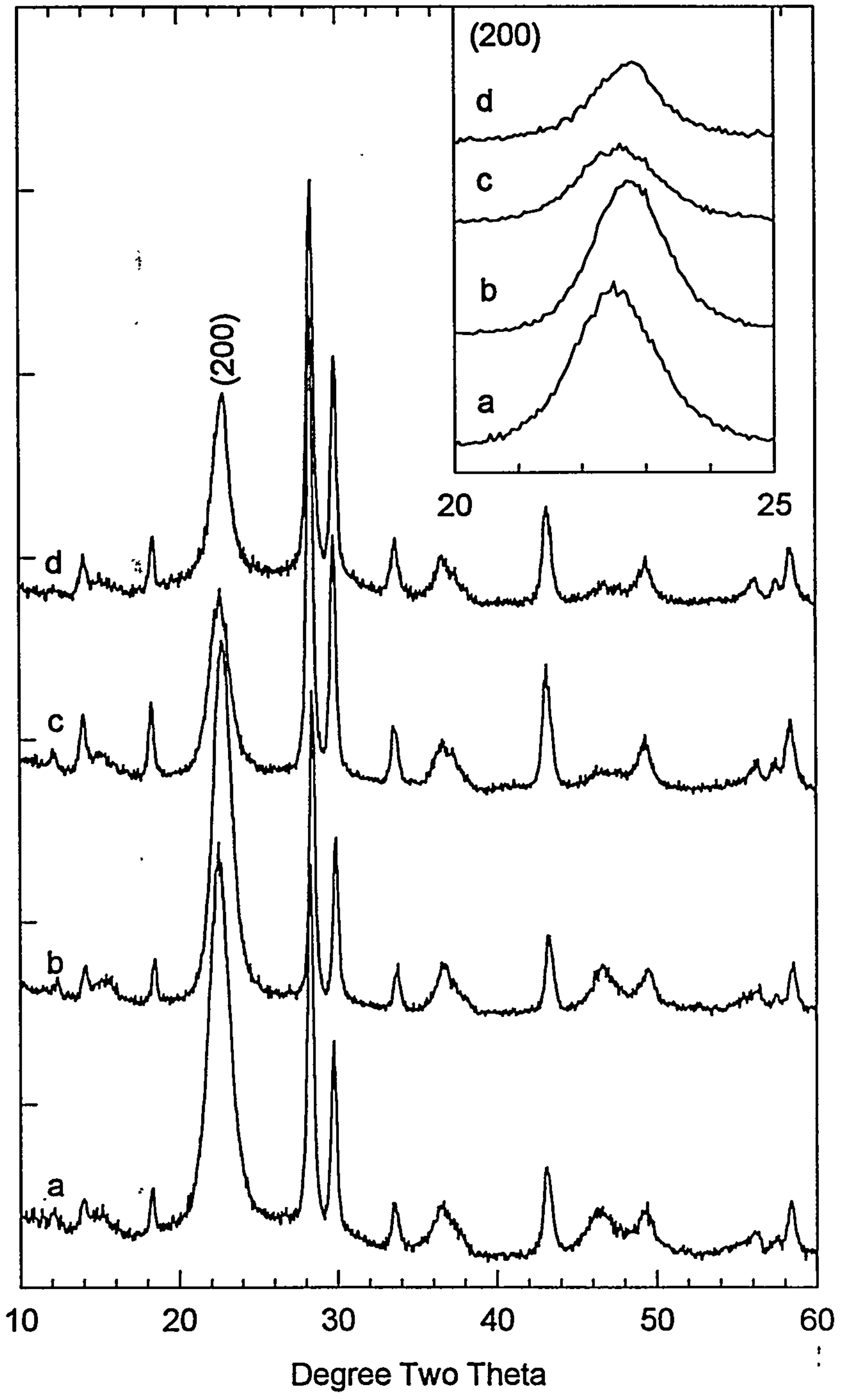

Figure 2. X-ray powder diffraction results for activated catalysts: a) $(VO)_2P_2O_7$ activated in air, b) similar catalyst activated in butane/air, c) TEOS modified catalyst activated in butane/air, d) naphthalene methanol preparation activated in butane/air.

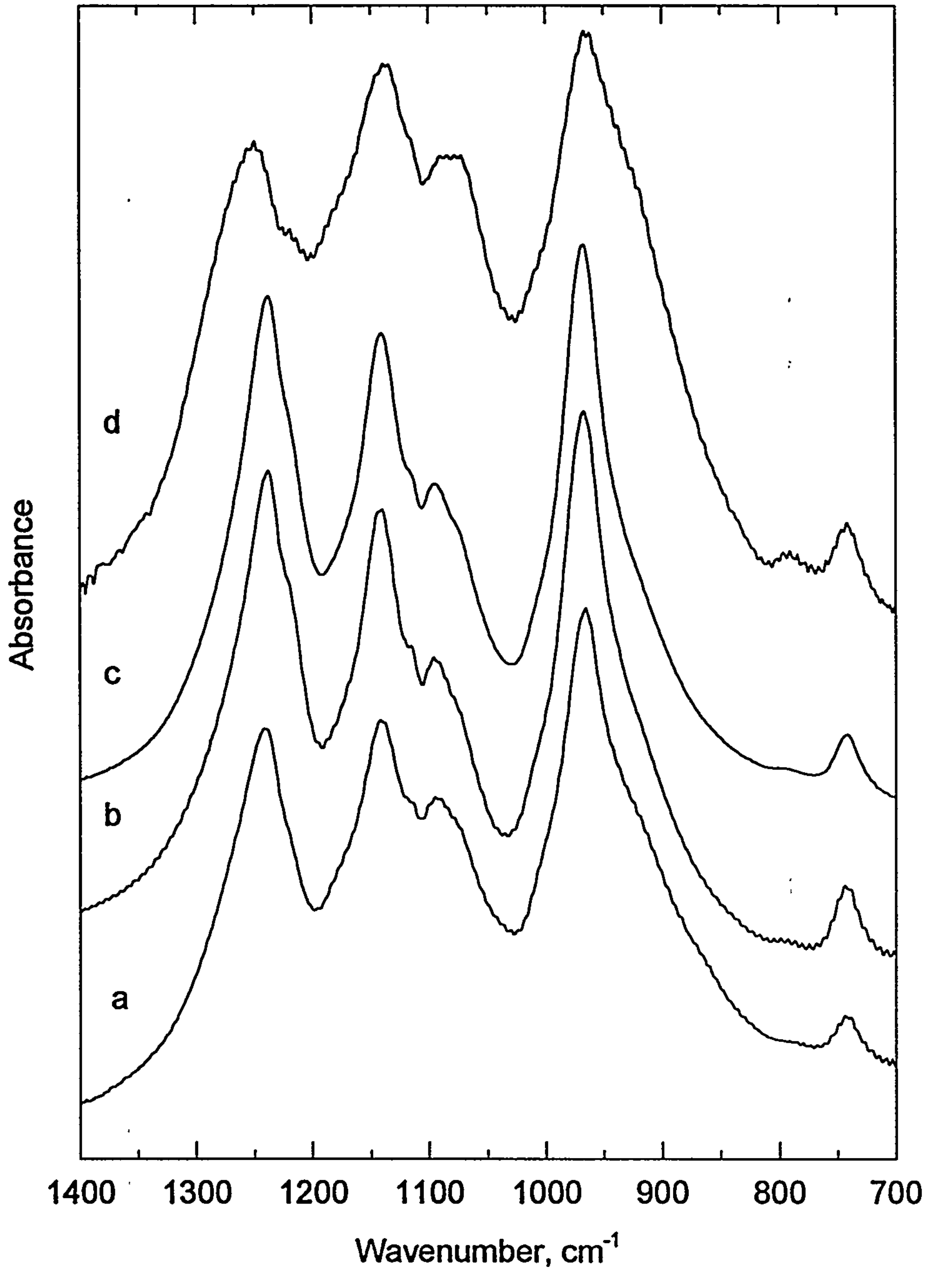

Figure 3. Infrared spectra of KBr pellets containing $(VO)_2P_2O_7$: a) air activated, b) butane/air activated, c) TEOS modified butane/air activated, d) naphthalene methanol preparation butane/air activated.

These catalysts have also been characterized by infrared spectra (diffuse reflectance) or chemisorbed based, in particular pyridine and acetonitrile. The purpose of these studies was to determine if preparation method modifications had resulted in increased surface acid site strength. Pyridine IR results are shown in Figure 4. All catalysts exhibited peaks characteristic of pyridine chemisorbed on both Bronsted (1640 and 1542 cm^{-1}) and Lewis (1612, 1578, 1490, and 1450 cm^{-1}) acid sites. The position of the ν(8a) vibration (1578 cm^{-1} in the liquid) is sometimes employed to measure the strength of the Lewis sites. For the four catalysts shown in Figure 4 the position of this band ranges from 1609 to 1612 indicating little significant difference in Lewis site strength as determined by pyridine adsorption. There do appear to be differences in the relative numbers of Bronsted and Lewis sites, however. Bronsted to Lewis site ratios were obtained from integrated areas of the 1542 and 1450 cm^{-1} bands. For the air activated catalyst this ratio is 14. For all of the other catalysts this ratio is about 4. Inspection of the spectra suggests that this difference is caused by the presence of substantially fewer Lewis sites for the air activated catalysts, a conclusion in agreement with the results of Busca and coworkers (1986a).

A more accurate measurement of acid site strength might be obtained through the use of a weaker base. We are using acetonitrile for this purposed. Results obtained to date are shown in Figure 5. The band at 2328 cm^{-1} indicates the presence of strong Lewis sites. The development of this experimental method is still ongoing. Spectrum d) in Figure 5 shows much improved resolution of the peak of interest by heating the in-situ cell to 150°C to desorb physisorbed and hydrogen bonded acetonitrile. Experiments along these lines will continue. We will also investigate the use of acetonitrile-d_3 which apparently yields a less ambiguous interpretation. Diffuse reflectance IR of adsorbed methanol may also provide useful information about acid sites and about potential adsorption sites for selective intermediates.

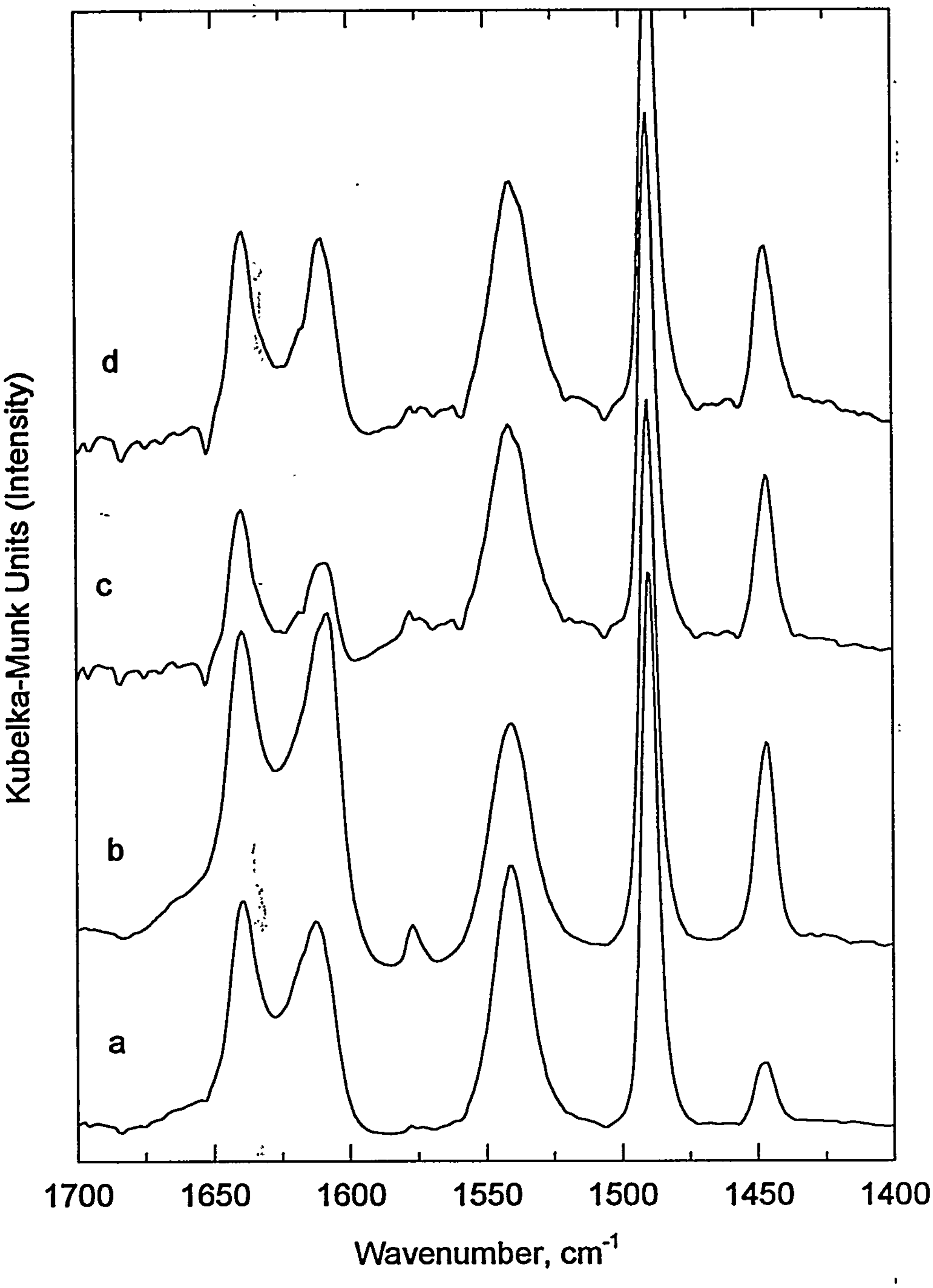

Figure 4. DRIFT spectra of chemisorbed pyridine on $(VO)_2P_2O_7$: a) air activated, b) butane/air activated, c) TEOS modified butane/air activated, d) naphthalene methanol preparation butane/air activated.

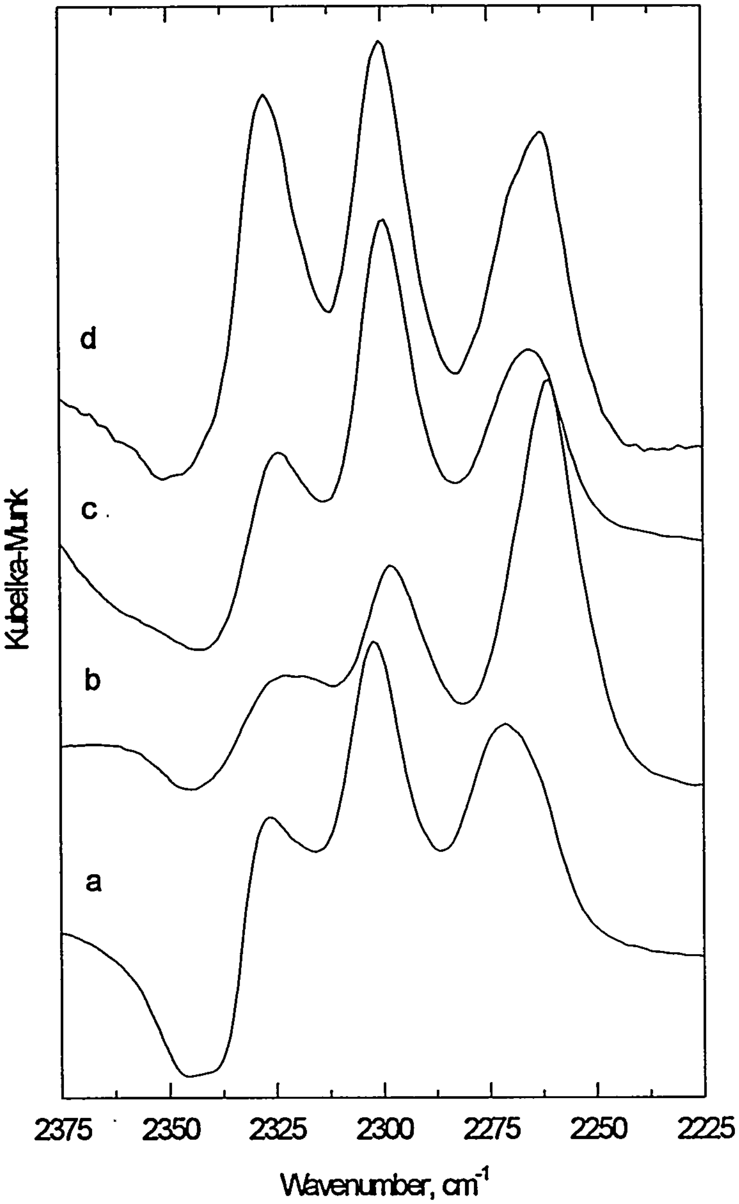

Figure 5. DRIFT spectra of chemisorbed acetonitrile on $(VO)_2P_2O_7$: a) air activated, b) butane/air activated, c) naphthalene methanol preparation butane/air activated, d) same as (b) but heated to 150°C.

We have also begun to investigate most of the first row transition metals as promoters of the VPO catalyst. Two methods of preparation have been employed. For the Zn promoted catalyst $ZnCl_2$ (1.0 g) was added to the initial reflux of an organic VPO preparation as described above (15.24 g V_2O_5). The preparation then continued as for unpromoted catalyst. For preparations containing Ti (1.0 g TiO_2), Cr (5.0 g Cr^{III} nitrate nonahydrate), Mn (2.16 g Mn^{II} acetate), Fe (5.05 g Fe^{III} nitrate nonahydrate), Co (3.12 g Co^{II} acetate tetrahydrate), and Cu (2.27 g Cu^{II} acetate); the noted metal salts were suspended in a benzyl/isobutyl alcohol mixture. These were added to 45 g of previously prepared precursor which had been resuspended under reflux in a benzyl/isobutyl alcohol mixture and cooled. This mixture was then stirred at 50°C overnight, filtered and washed with more solvent, and dried in a rotary vacuum drier for 8 hours at slightly greater than ambient temperature.

All promoter salts were soluble in the alcohol mixture except TiO_2. Available x-ray diffraction data for the precursors obtained is reported in Figure 6. All precursors show the peaks of $VOHPO_4$-$0.5H_2O$, the desired precursor. For the Ti promoted catalyst additional peaks marked with an asterisk are also present and indicate the presence of a separate TiO_2 phase. Future attempts at this preparation will utilize a different precursor such as $TiCl_3$.

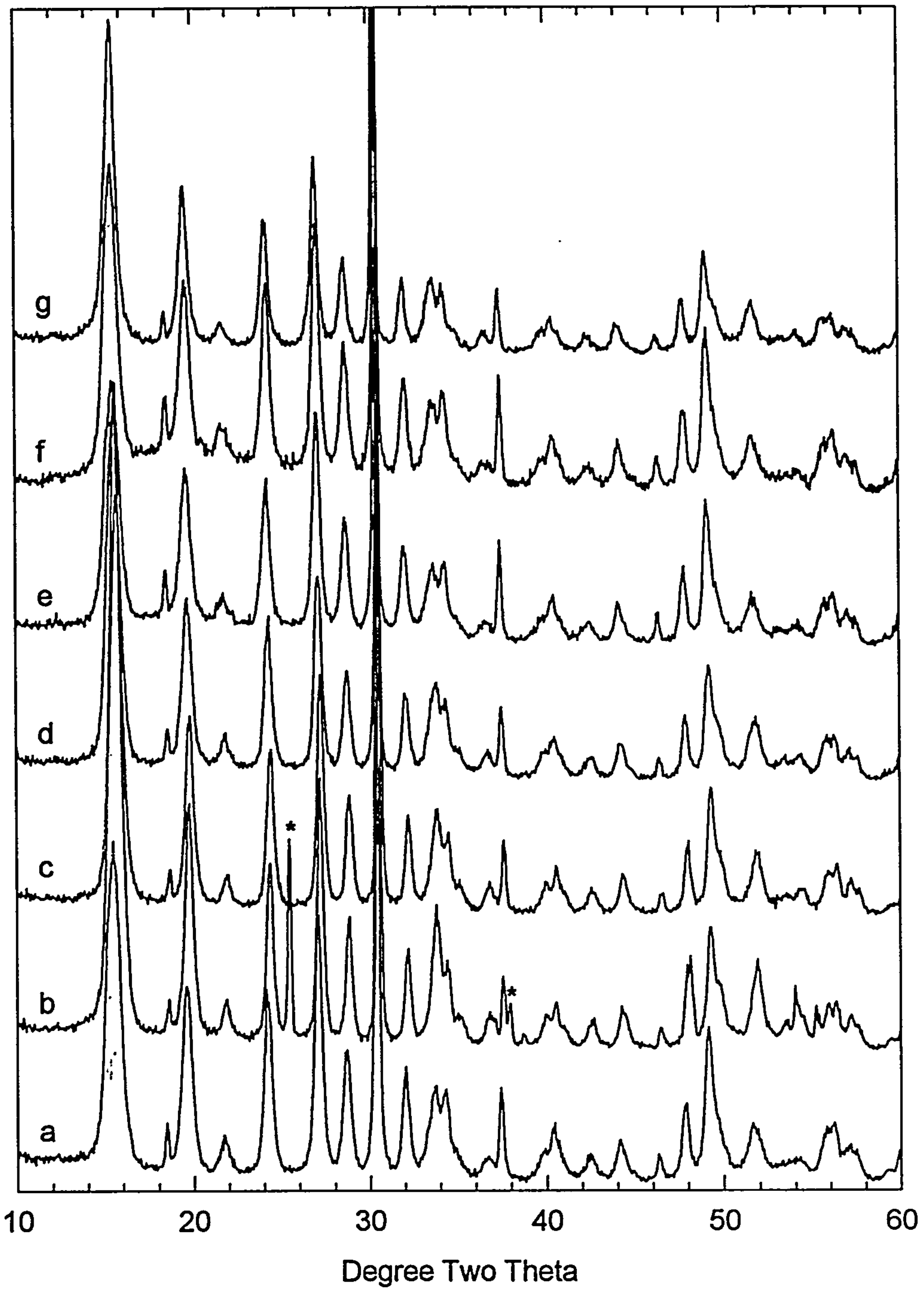

Figure 6. Transition metal promoted VPO precursors: a) unpromoted, b) Ti, c) Mn, d) Fe, e) Co, f) Cu, g) Zn.

Catalyst Testing

Tests for internal transport limitations were conducted by varying catalyst particle size while maintaining constant GHSV and feed gas composition. The experiments conducted using a ZnO promoted vanadyl pyrophosphate are listed in Table 1. The only reaction product observed was CO and carbon balances were always in excess of 97%. The results for two temperatures are shown in Figure 7. Conversions are low under these conditions however they appear to be constant for all but the largest particle diameter. We do not believe that pore diffusion limitations are becoming important for this particle size but rather that the reactor diameter/particle diameter ratio has become so small that gas-solid contacting is poor. The quartz reactor diameter was 14 mm in these experiments.

Table 1. Experiments conducted to test for internal transport limitations. (CH_4:O_2=10, 450 and 475°C)

Mean Diameter, mm	*1.696*	*1.122*	*0.711*	*0.504*	*0.315*	*0.181*
Mesh Range	10-14	14-20	20-28	28-40	40-70	70-100
Weight, g	0.506	0.501	0.503	0.507	0.500	0.502
Volume, cc	0.90	0.85	0.85	0.82	0.80	0.80
Flowrate, ml.min	33.0	30.8	30.8	29.7	29.1	29.1
GHSV, hr^{-1}	2200	2174	2174	2173	2183	2183

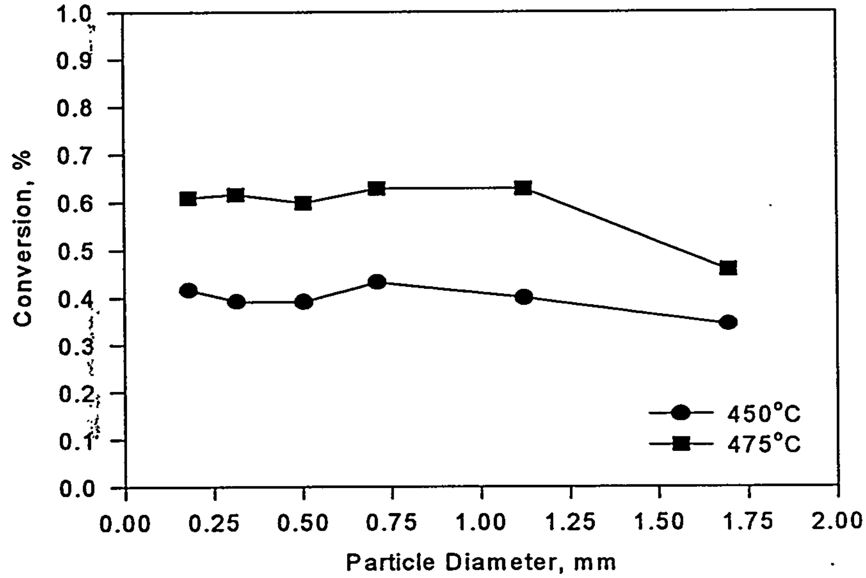

Figure 7. Conversion versus particle diameter data testing for pore diffusion limitations.

Tests for external transport limitations were conducted at GHSV of 2300 hr^{-1} with flow rates of 62 and 31 ml/min and bed volumes of 1.6 and 0.82 ml, respectively. The ZnO promoted VPO catalyst was employed with a CH_4:O_2 ratio of 10. Temperature was varied from 400 to 475°C. For conditions where external transport is significant lower gas flowrate should yield a lower conversion even though GHSV is the same. Results are shown in Figure 8. For temperatures of 450°C and greater transport limitations are evident in that higher conversion is observed at higher flow rate. While most of the data to be acquired in this study can be obtained below this temperature, experiments to find experimental conditions allowing kinetic regime data to be acquired above 450°C are underway.

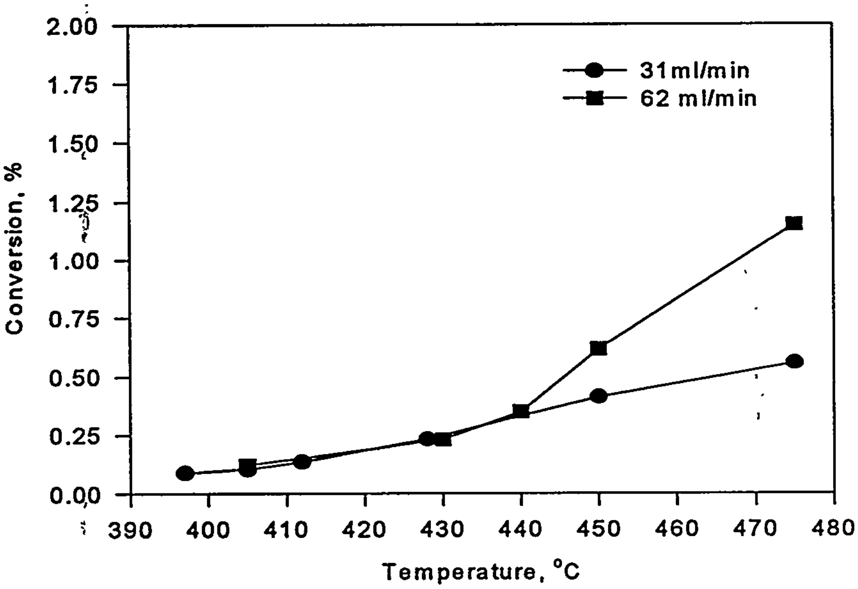

Figure 8. Conversion versus temperature at two flow rates and constant GHSV testing for external transport limitations.

Figure 9 reports methane conversion as a function of temperature for several catalyst preparations at a CH_4:O_2 ratio of 25:1. The TEOS modified catalyst is slightly more active at lower temperatures. Butane activation had little effect on catalyst activity relative to air activation. A similar plot is shown in Figure 10 for CH_4:O_2 ratio of 10:1. Higher conversions are observed than at 25:1 and the TEOS modified catalyst is much more active. Under similar conditions the Zn promoted/butane activated catalyst gave a conversion of 2.4% at 460°C, roughly the same as the air activated VPO.

These catalysts also exhibited significantly different selectivity behavior. Air activated VPO produced almost exclusively CO as the reaction product although traces of methanol and formaldehyde were observed. Butane activated VPO, on the other hand, produced CO, CO_2, and *low yields of formaldehyde and methanol.*

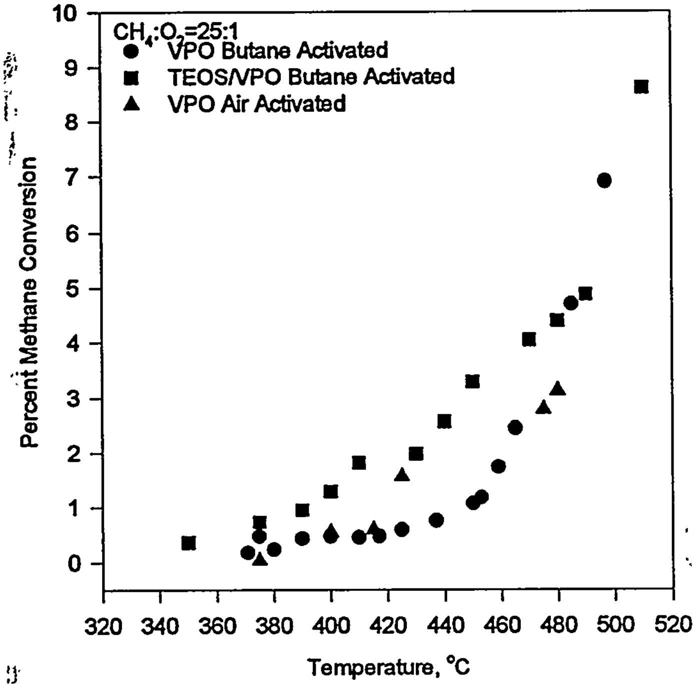

Figure 9. Methane conversion as a function of temperature, GHSV=1400.

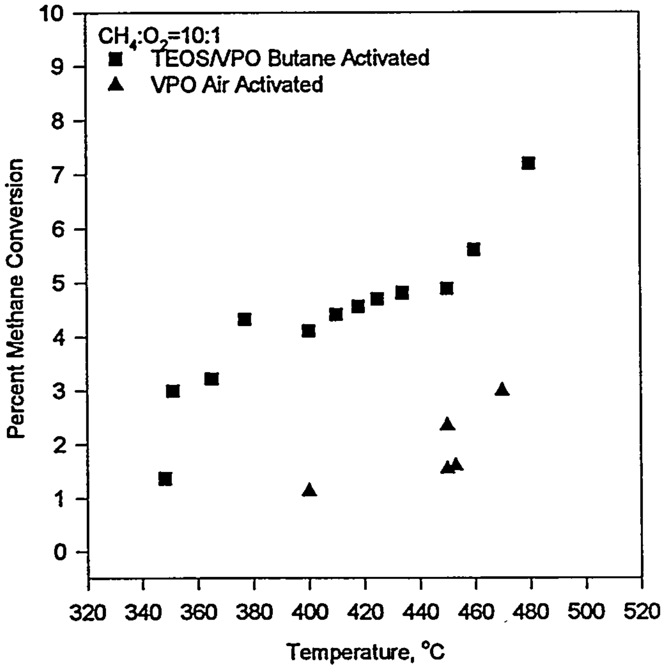

Figure 10. Methane conversion as a function of temperature, GHSV=1400.

The slightly more active TEOS modified catalyst produced only CO and CO_2 as reaction products. Additionally, the selectivity behavior was much different for this catalyst as shown in Figure 11. For TEOS/VPO, CO is by far the major product at relatively high conversions. For butane activated VPO, CO and CO_2 occur at roughly 40 and 60% selectivity, respectively. Co was the only product observed over Zn promoted VPO. Much more data will be required to fully understand important kinetic and mechanistic aspects of methane oxidation over these catalysts. Future plans include acquisition of data over a much broader range of conditions and improvements to the reactor design and analytical system.

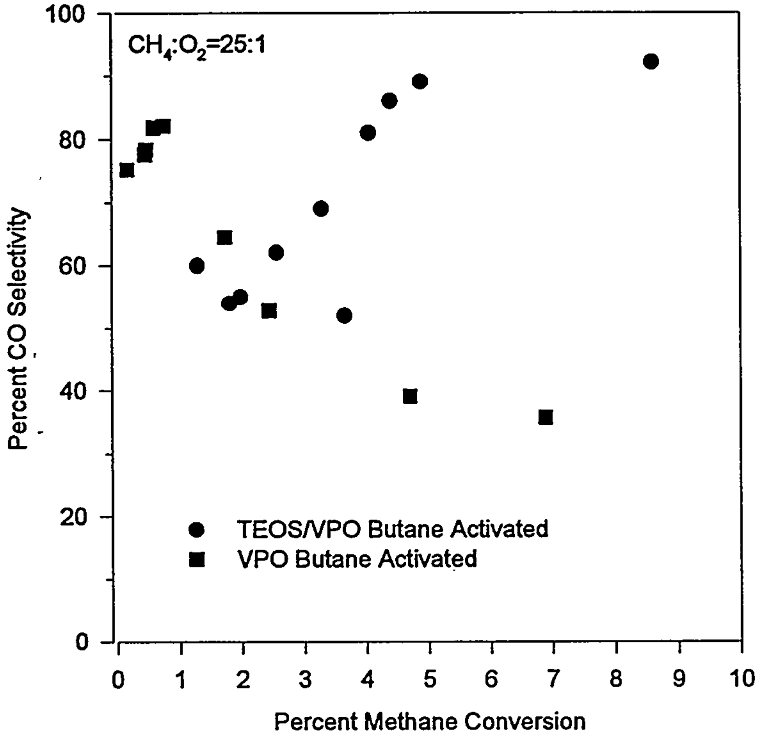

Figure 11. Carbon monoxide selectivity versus methane conversion for two catalysts, GHSV=1400.

PLANNED ACTIVITIES

During the next quarter the most important activities will be:

- Screen catalysts promoted with the first row transition metals Ti, Cr, Mn, Fe, Co, Cu, and Zn in methane and methanol oxidation and obtain relevant characterization by IR and XRD.
- Prepared VPO catalysts with surface modification by exchange of K, Ca, and F with acidic or basic hydroxyl groups. Screen these catalysts in methane and methanol oxidation and obtain relevant characterization results by IR and XRD.
- Develop IR of adsorbed methanol as a characterization technique and refine surface characterization using acetonitrile.

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