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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

By

Robert L. McCormick (Principal Investigator)
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

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EXECUTIVE SUMMARY

This document is the eleventh quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". Activities focused on testing of additional modified and promoted catalysts and characterization of these materials. Methanol oxidation studies were performed as a method of acid site characterization. Improvements to our product gas analysis system continued to be developed. These results are reported.

Specific accomplishments include:

- Obtaining and interpreting infrared spectra of modified catalysts prepared to enhance surface acidity.
- Testing of these catalysts in methanol oxidation as a method of acid site characterization and to determine catalytic activity for conversion of this desired product. Catalysts were quite active for methanol conversion to dimethyl ether. Two of the modified catalysts prepared in this work exhibited the highest activity for this reaction, presumably because of their higher surface areas.
- Determination that acidity modifications had no effect on activity for methane conversion.

INTRODUCTION

This document is the eleventh 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 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). 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

No new catalysts were prepared this quarter. Catalyst characterization activities did continue, however, especially in the area of vibrational spectroscopy. Infrared spectra of catalyst precursors prepared by the standard method, with addition of TEOS, and with naphthalene methanol as one of the solvents are shown in Figure 1 for the 1800-1400 cm^{-1} region. The methods for preparing these catalysts have been described in some detail in our previous reports. All samples exhibit the strong peak at 1645 cm^{-1} typical of the in-plane deformation of coordinated water. This is in agreement with the chemical formula of the precursors, $VOHPO_4 \cdot 0.5H_2O$. The conventionally prepared and TEOS catalysts (isobutyl and benzyl alcohol solvents) exhibit bands at 1453 and 1496 from residual benzyl alcohol phenyl ring vibrations. In the preparation where naphthalene methanol was substituted for benzyl alcohol these bands are not present. Instead a number of weak bands can be seen between 1600 and 1500 cm^{-1} and a relatively strong band is observed at 1684 cm^{-1}. These vibrational bands may be characteristic of residual naphthalene structures. If so, then we would expect the layer stacking to be more disordered in this material because of the larger size of the trapped organic molecules.

Figure 2 shows IR spectra of the V-O and P-O stretching region for the same materials as Figure 1. There appears to little if any significant difference between the samples based on these spectra.

Figure 3 shows IR spectra of the activated catalysts prepared from these precursors. Only minor and probably insignificant differences are observed for the conventional preparations and the TEOS modified material. The catalyst prepared in naphthalene methanol exhibits broader peaks which may be caused by insufficient drying of the sample or which may indicate an increasing degree of disorder and heterogeneity in bond lengths and strengths.

We may conclude from these IR spectra that the use of naphthalene methanol was successful in that it appears to have been trapped between the layers, as planned. None of the modifications have resulted in major changes to the vibrational modes of this material and the data indicate that $(VO)_2P_2O_7$ was obtained as the activated catalyst in all cases.

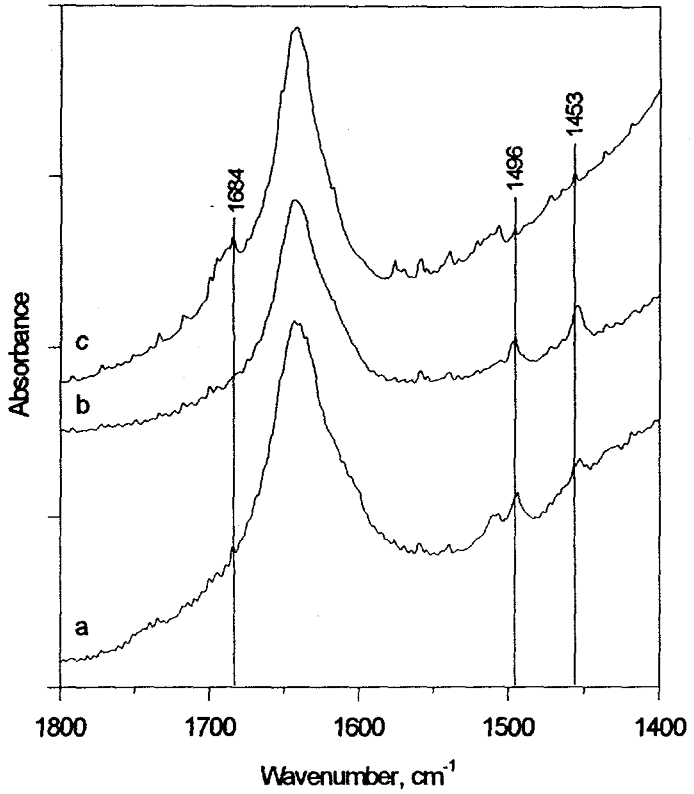

Figure 1. Infrared spectra (transmission, KBr pellets) of catalyst precursors: a)conventional organic preparation, b)TEOS modification, c)naphthalene methanol as a solvent.

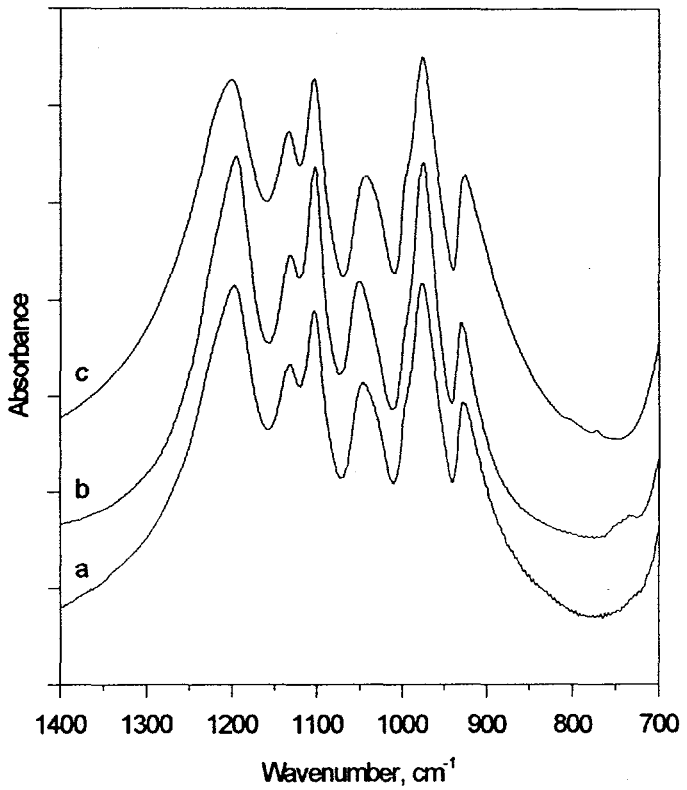

Figure 2. Infrared spectra (transmission, KBr pellets) of catalyst precursors: a)conventional organic preparation, b)TEOS modification, c)naphthalene methanol solvent.

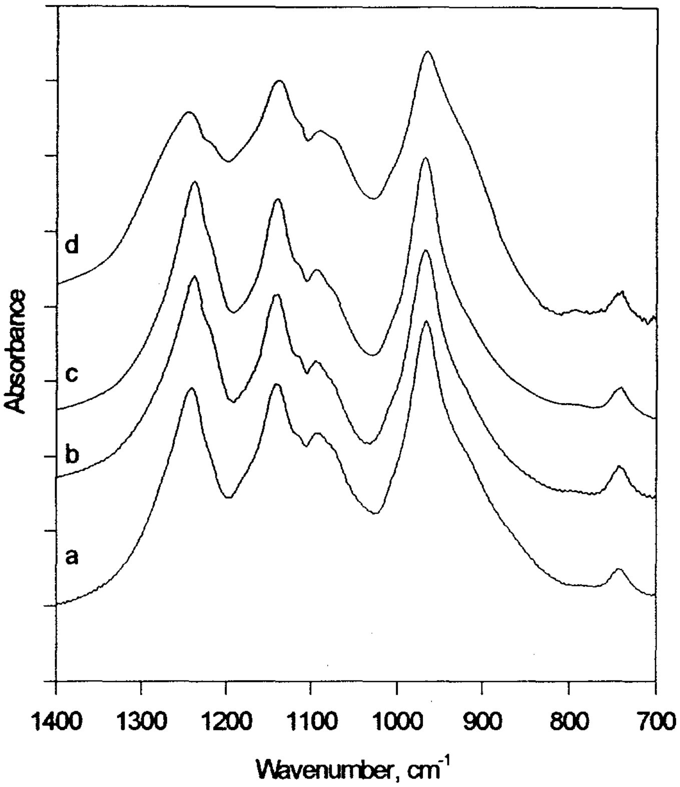

Figure 3. Infrared spectra (transmission, KBr pellets) of activated catalysts: a)conventional organic preparation-air activated, b)conventional organic preparation-butane/air activated, c)TEOS modification-butane/air activated, d)naphthalene methanol as a solvent-butane/air activated.

Catalyst Testing

Catalyst testing was performed in a quartz microreactor as described in previous reports. All tests were performed under flow conditions and using a catalyst particle size that had been demonstrated to be free from internal and external mass transfer limitations. Testing this quarter focused on determining if catalyst modifications had resulted in enhanced activity for methane activation and on methanol oxidation. Methanol is the desired product and catalysts which are not particularly active for further oxidation of methanol are thus desired. Also, methanol dehydration to dimethyl ether is a useful reaction for characterization of acid sites.

Methane oxidation experiments were performed to determine if the catalyst modifications attempted in this work resulted in enhanced activity for activation of the methane C-H bond. These experiments were conducted at very low conversions (differential reactor) and with a large excess of methane relative to oxygen (CH_4:O_2 molar ratio of 25:1). Oxygen conversions were always less than 50%. Gas hourly space velocities ranged from 1400 to 2400 hr^{-1}. Under these conditions the only reaction product observed was carbon monoxide. By measuring methane conversion at several temperatures over these catalysts and making the assumptions of a differential reactor and first order reaction kinetics for methane, the catalysts can be compared on the basis of these pseudo-first order rate constants.

Results of blank methane and methanol oxidation tests are shown in Table 1. At atmospheric pressure no methane conversion was observed at temperatures as high as 600°C. A somewhat surprising result is the lack of significant methanol conversion at atmospheric pressure and temperatures up to 550°C. In vanadium phosphate catalyst development we are endeavoring to convert methane at temperatures of 500°C and below. These blank reactor results suggest that gas phase reactions are not important at atmospheric pressure in this temperature range. Non-catalytic methanol oxidation produced primarily carbon oxides although formaldehyde and methane were also observed.

Table 1. Results of Non-Catalytic Oxidation of Methane and Methanol in Quartz Lined Reactor.

(GHSV=8000@NTP))

Temperature,	Feed Composition (balance He)			Pressure,	Percent	Percent Selectivity				
°C	%O_2	%CH_4	%CH_3OH	atm	Conversion	CO	CO_2	HCHO	CH_3OH	CH_4
550	10	20	0	1	0	0	0	0	0	–
600	10	20	0	1	0	0	0	0	0	–
525	10	0	20	1	0.2	14.1	53.9	31.9	0	0
550	10	0	20	1	0.2	22.2	12.8	0	0	64.8

Table 2 reports conversion and pseudo-first order rate constants for methane conversion at various temperatures. These rate constants are compared in Figure 4 where it is apparent that there is little significant difference between the conventional VPO catalysts, regardless of activation gas. The naphthalene methanol catalyst has a similar level of activity although only two data points are available. The catalyst modified through addition of TEOS has lower activity. These rate constants are based on reaction rates per gram of catalyst. For the air and butane activated conventional VPO catalysts, we have measured the number of surface acid sites per gram by acetonitrile chemisorption (8.4×10^{-5} and 1.4×10^{-4} mole of acid sites/g, respectively). Using these values, and assuming that all acid sites titrated by acetonitrile are active for methane conversion, we can use the mass basis rate constants to calculate rate constants on a per active site basis. These are in effect acid site turnover frequencies with units of 1/time-atm.

On this basis, the butane activated material which has many more acetonitrile chemisorption sites is found to be considerably less active as shown in the bar chart of Figure 5. It is tempting to conclude that butane activation has resulted in acid sites of lower strength or of lower activity. However other measures of acid site strength reported in previous sections do not support this conclusion and it seems likely that only a subset of the acid sites titratable by acetonitrile actually activate methane. Butane activation does not appear to increase the number of these sites even though it does dramatically increase the total number of acid sites. These data suggest that none of the catalyst modifications attempted have been successful at increasing the strength of the acid sites, at least within the context of methane conversion.

Table 2. Pseudo-first order rate constants, k (mol/min/g/atm) and percent conversion, X for methane oxidation, $CH_4:O_2=25:1$.

	Unmodified/ Air Activated		Unmodified/ Butane Activated		TEOS Modified		Naphthalene Methanol Solvent	
Temperature, °C	k	X	k	X	k	X	k	X
375	0.002997	0.07812	0.00055	0.042088	0.001137	0.078273	0	0
400	0.009213	0.240171	0.007153	0.547138	0.001622	0.111697	0.010538	0.276159
425	0.017573	0.45812	0.020358	1.557239	0.002835	0.181435	0.014025	0.36755
450	--	--	--	--	0.005925	0.407927	--	--
475	--	--	0.036314	2.777778	0.009591	0.639656	--	--

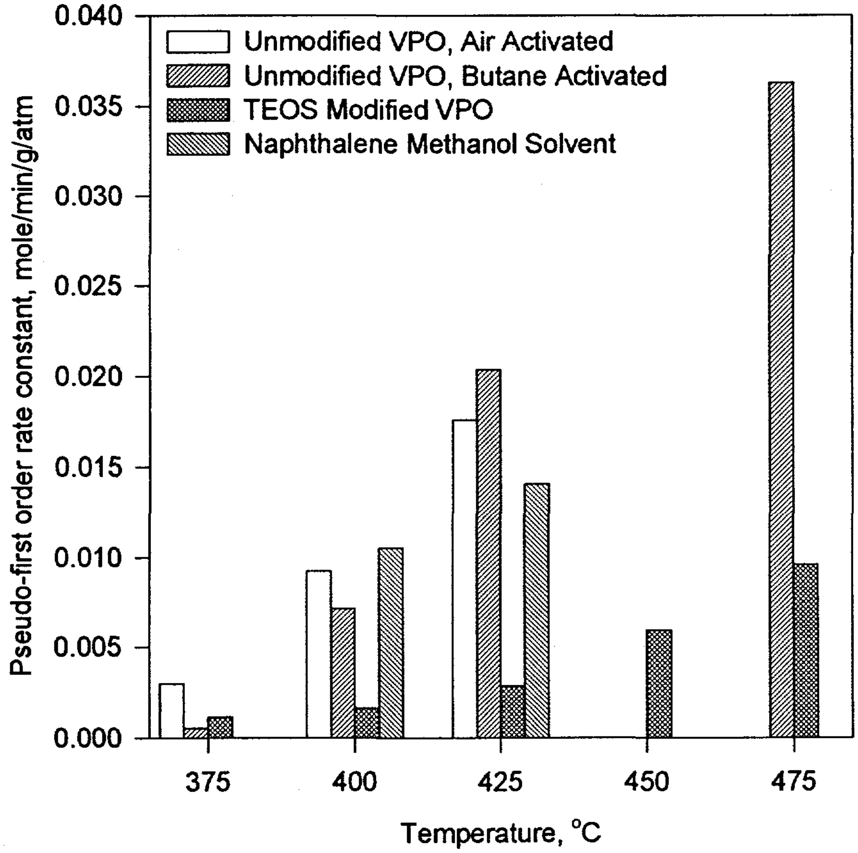

Figure 4. Pseudo-first order rate constants for methane conversion.

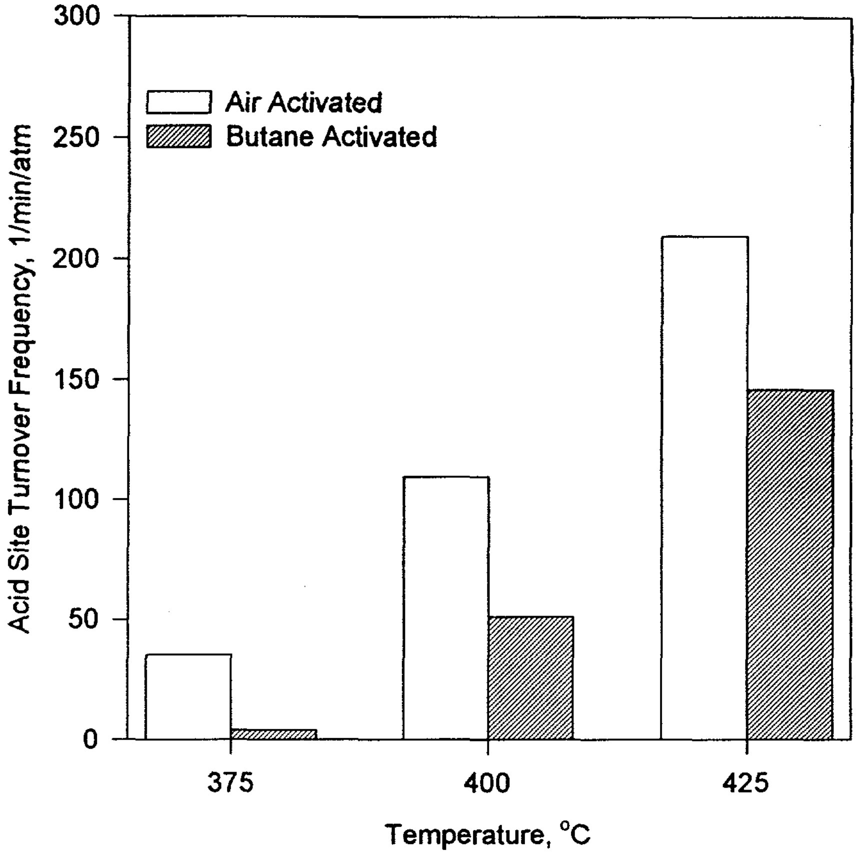

Figure 5. First order rate constants on per acid site basis (acid site turnover frequency) for unmodified VPO preparations.

In order to provide an additional measure of catalyst acidity, and to test the catalysts for activity in conversion of the desired product methanol, a series of methanol conversion experiments was conducted. The reactor was the same reactor used in methane oxidation studies. The results in terms of conversion and selectivity dimethyl ether, the product formed from acid catalyzed dehydration, are shown in Table 3. Other than dimethyl ether the products included CO and formaldehyde but these experiments were performed with our old analytical setup and formaldehyde is not easily quantified. These data were fit to the Arrhenius equation to allow calculation of pseudo-first order rate constants at 250, 275, and 300°C. These values of rate constant are used as our measure of activity in acid catalyzed reactions and are reported in Figure 6. Activity differences between the materials are small but the naphthalene methanol modification appears to be the most active followed by the TEOS modification. We speculate that these catalysts have a somewhat higher surface area, as reported by Horowitz and coworkers (1988) for the TEOS modification, and that this leads to higher observed activity because there are more acid sites per gram of catalysts. Note that Figure 6 compares catalysts on a per catalyst mass basis.

Table 3. Conversions and dimethyl ether selectivities for methanol dehydration over various catalysts.

Catalyst	Temperature, °C	% Conversion	% Selectivity
Air Activated VPO	250	21	86
	249	27	94
	250	29	94
	275	32	82
	273	28	83
	298	47	87
	298	48	82
	298	52	81
Butane Activated VPO	273	36	--
	273	33	--
	289	42	--
	287	45	--
	306	55	96
	307	50	98
	333	68	84
	332	67	84
TEOS Modified VPO	256	16	88
	252	20	85
	275	38	92
	301	51	95
	296	43	95
Naphthalene Methanol	252	24	82
Modified	249	14	83
	278	25	90
	277	23	90
	277	23	90
	304	51	86
	300	44	88
	299	40	88

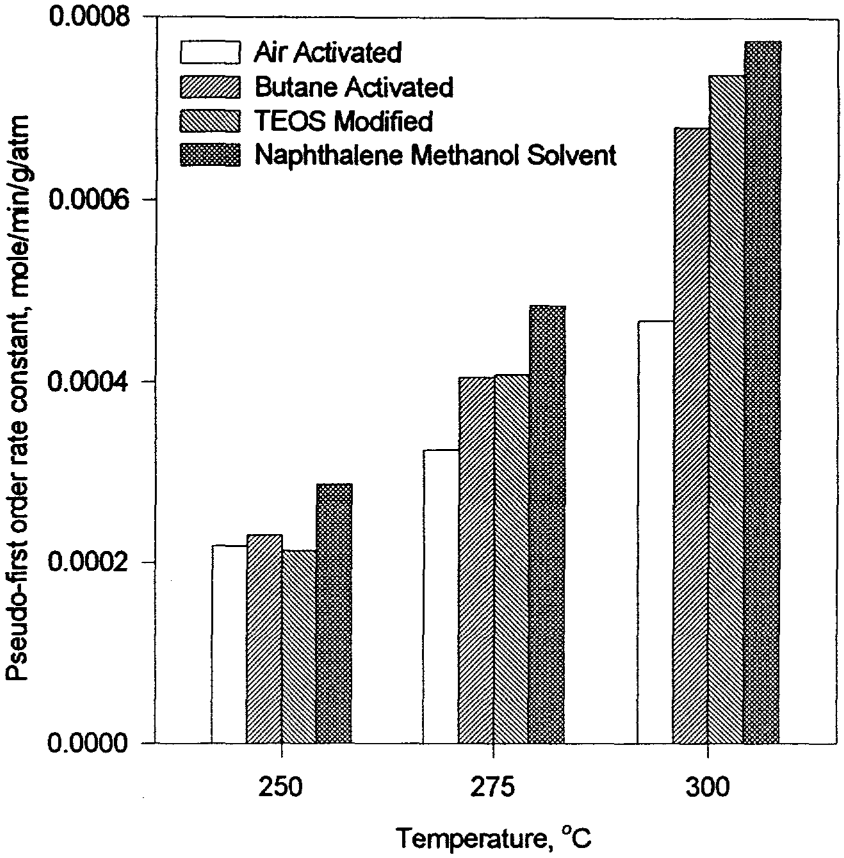

Figure 6. Relative activities of various catalysts for methanol dehydration in terms of pseudo-first order rate constant.

PLANNED ACTIVITIES

During the next quarter the most important activities will be:

- Complete characterization of the transition metal promoted catalysts by FTIR of KBr pellets and perhaps IR of chemisorbed bases or other molecules.
- Complete characterization of the VPO samples prepared with structural modifiers/disrupters via TGA measurements. TGA instrument has been down for several months and we expect to be addressing this problem soon.
- Examine the possibility of retaining the catalyst in a more active and selective reduced state by including a small percentage of butane in the methane feed.
- Begin to characterize and test VPO supported on silica, titania, and silica-alumina (these materials have been prepared).
- Implement a new GC method and install a new TC detector to allow much more accurate quantification of oxidation products.

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<950> ABSTRACT

Activities during this report period focused on testing of additional modified and promoted catalysts and characterization of these materials. Methanol oxidation studies were performed as a method of acid site characterization. Improvements to the product gas analysis system continued to be developed. These results are reported. Specific accomplishments include: (1) Obtaining and interpreting infrared spectra of modified catalysts prepared to enhance surface acidity. (2) Testing of these catalysts in methanol oxidation as a method of acid site characterization and to determine catalytic activity for conversion of this desired product. Catalysts were quite active for methanol conversion to dimethyl ether. Two of the modified catalysts prepared in this work exhibited the highest activity for this reaction, presumably because of their higher surface areas. (3) Determination that acidity modifications had no effect on activity for methane conversion.