TITLE: **Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane**

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OBJECTIVE:

The United States has vast natural gas reserves which could contribute significantly to our energy security if economical technologies for conversion to liquid fuels and chemicals were developed. Many of these reserves are small scale or in remote locations and of little value unless they can be transported to consumers. Transportation is economically performed via pipeline, but this route is usually unavailable in remote locations. Another option is to convert the methane in the gas to liquid hydrocarbons, such as methanol, which can easily and economically be transported by truck. Therefore, the conversion of methane to liquid hydrocarbons has the potential to decrease our dependence upon oil imports by opening new markets for natural gas and increasing its use in the transportation and chemical sectors of the economy. In this project, we are attempting to develop, and exploring for new catalysts capable of direct oxidation of methane to methanol.

The specific objectives of this work are:

- To determine the activity and selectivity of vanadium phosphate catalysts in methane oxidation.
- To utilize promoters and catalyst supports to improve oxygenate yield relative to the base case catalysts.
- To provide a preliminary understanding of the catalytic mechanism and how promoters and supports actually effect catalytic properties.
- Use the information obtained to prepare advanced catalysts which will be tested for activity, selectivity, and stability.

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- Develop a simplified methanol production process flowsheet based on these advanced catalysts.

The basic premise of this project is that $(VO)_2P_2O_7$ (vanadyl pyrophosphate or VPO), a catalyst used commercially in the selective oxidation of butane to maleic anhydride, can be developed as a catalyst for selective methane oxidation. Supporting this idea are published reports indicating moderate to high selectivity in oxidation of ethane,[1] propane,[2] and pentane,[3] as well as butane[4] to various oxygenates. Thus, VPO appears to have a unique catalytic functionality for selective activation of alkanes. Methane oxidation is a much more difficult reaction to catalyze and it is expected that considerable modification of VPO will be required for this application. It is well known that VPO can be modified extensively with different promoters and in particular that promoters can enhance selectivity and lower the temperature required for butane conversion.[5] A key problem in methane selective oxidation is that, at the high temperatures typically required for methane activation, the selective reaction products are rapidly converted to carbon oxides.

Background on Vanadyl Pyrophosphate

Vanadyl pyrophosphate is prepared from V_2O_5 and phosphoric acid. The most active and selective catalysts are obtained using organic solvents such as a mixture of *iso*-butyl and benzyl alcohols and anhydrous phosphoric acid.[4,6] Excess phosphorus is generally employed in the reaction mixture. The catalyst precursor obtained from reaction of these materials under reflux is $VO(HPO_4)\cdot 0.5H_2O$ which has a layered structure. The use of organic solvents and excess phosphorus is thought to lead to a desirable crystalline face exposure and to the development of disorder in the layer stacking through entrapment of benzyl alcohol molecules between the layers.[7,8] This procedure may also introduce anion vacancies.[9]

The catalyst precursor is then converted to vanadyl pyrophosphate by heating under a variety of gas environments. The precursor undergoes a topotactic transformation such that structural disorder in the precursor is preserved in the active phase.[10] Strong Lewis acid sites on the surface of VPO

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[1] Michalakos, P.M., Kung, M.C., Jahan, I., Kung, H.H. J. Catal. 140 226 (1993).
[2] Ai, M. J. Catal. 101 389 (1986).
[3] Busca, G., Centi, G. J. Am. Chem. Soc. 111 46 (1989).
[4] Centi, G., Trifiro, F., Ebner, J.R., Franchetti, V.M. Chem. Rev. 88 55 (1988).
[5] Hutchings, G.J. Appl. Catal. 72 1 (1991).
[6] Cavani, F. and Trifiro, F. Chemtech April, pp. 18 (1994).
[7] Busca, G., Cavani, F., Centi, G., Trifiro, F. J. Catal. 99 400 (1986).
[8] Horowitz, H.S., Blackstone, C.M., Sleight, A.W., Teufer, G. Appl. Catal. 38 193 (1988).
[9] Cornaglia, L.M., Caspani, C., Lombardo, E.A. Appl. Catal. 74 15 (1991).
[10] Johnson, J.W., Johnston, D.C., Jacobson, A.J., Brody, J.F. J. Am. Chem. Soc. 106 8123 (1984).

are responsible for initial alkane activation.[11] It has been proposed that this Lewis acidity is caused by lattice defects or strain initiated by the disorder in stacking of the layered structure.[7,11] However, equilibrated catalysts (used for at least 200 hours) exhibit a lower degree of structural disorder but a higher level of strong Lewis acidity compared to freshly activated catalysts[12] indicating that the source of the strong Lewis acidity is not well understood. One hypothesis is that anion vacancies are introduced through the use of organic solvents and excess phosphorus. These vacancies are the source of both disorder in the stacking plane and the strong Lewis acidity. After many hours on stream the disorder in the layer stacking is eliminated but the anion vacancies remain. After the activation process some carbon is present on or in the catalyst which may also contribute to structural disorder or to the active site structure.[3,13] The P:V ratio of the active catalyst is typically about 1.05, assuming some excess phosphorus was present, regardless of the starting P:V ratio.[8] Most or all of the excess phosphorus is found on the surface where the P:V ratio has been found to be closer to 2. This observation lead to a model of the VPO surface consisting of pendant pyrophosphate groups.[14]

Catalyst Development Approach

One approach to catalyst development that we are taking is directed at increasing the strength of the strong Lewis acid sites by enhanced strain or disorder in the layer stacking. Presumably this will also alter the nature of the anion vacancies more directly responsible for Lewis acidity. 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 activity and selectivity. A second approach involves addition of promoters to alter the metal-oxygen bond strength and the oxidation activity of the catalyst. These approaches, and others, are being investigated through a combination of catalyst activity measurements and characterization of catalyst surface and bulk properties.

In this paper we describe baseline methane oxidation activity and catalyst characterization results for conventionally prepared VPO, a catalyst prepared under conditions known to enhance disorder in the layers, and a Zn promoted catalyst. These results provide a general idea of the type of work being performed under this contract. Results of other approaches including modification of the VPO surface through various ion exchange and doping

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

[12] Cornaglia, L.M., Lombardo, E.A., Anderson, J.A., Garcia Fierro, J.L. Appl. Catal. 100 37 (1993).

[13] Pepera, M.A., Callahan, J.L., Desmond, M.J., Milberger, E.C., Blum, P.R., Bremer, N.J. J. Am. Chem. Soc. 107 4883 (1985).

[14] Ebner, J.R., Thompson, M.R. Catal. Today 16 51 (1993).

procedures and preparation of VPO on various supports will be presented at the Contractors Review Conference.

ACCOMPLISHMENTS & CONCLUSIONS:

Over the past year our main accomplishment has been to set up a new laboratory and bring equipment for catalyst synthesis, catalyst characterization, and activity studies on line. Additionally, we have begun to employ these facilities to examine vanadyl pyrophosphate and novel modifications of this material. Specific equipment brought on line includes:

- Apparatus for catalyst synthesis, drying, and activation.
- Diffuse reflectance infrared cell for studies of surface acidity and surface reactions via spectroscopy of chemisorbed molecules.
- Catalytic microreactor and gas chromatograph analytical system.

These facilities have been used to examine the surface acidity and oxidation activity of several catalysts. Activity for oxidation of methane and methanol has been examined for VPO prepared using the *iso*-butyl/benzyl alcohol method. A modified catalyst prepared in the presence of tetraethyl orthosilicate (TEOS) has been studied in methane oxidation. Addition of TEOS has been shown to disrupt the VPO layered structure resulting in exposure of more active surface and producing a more active butane oxidation catalyst.[8] A Zn promoted catalyst has also been prepared and characterized. Zn is added to many commercial butane oxidation catalysts and is thought to increase the rate of butane oxidation, possibly by enhancing the rate of oxygen incorporation into the catalyst.[15]

An interesting observation in this work has been the formation of small amounts of methanol and formaldehyde from methane at atmospheric pressure and temperatures from 350 to 450°C. The observation of more than a trace of methanol at these relatively mild conditions appears to be somewhat surprising based on previous literature reports.[16]

Catalyst Preparation

$(VO)_2P_2O_7$. 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,

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[15] Takita, Y., Tanaka, K., Ichimaru, S., Ishihara, T., Inoue, T., Arai, H. J. Catal. 130 347 (1991).
[16] Brown, M.J., Parkyns, N.D. Catal. Today 8 305 (1991).

washed in water, and dried at 150°C overnight. A light blue precipitate recovered.

$(VO)_2P_2O_7$-TEOS Modified. After Horowitz and coworkers,[8] V_2O_5, (15.0 g), *ortho*-phosphoric acid (anhydrous, 19.4 g), and tetraethyl orthosilicate (9.2 ml) were added to a solution of 90 ml *iso*-butyl alcohol and 60 ml of benzyl alcohol. This solution was heated under reflux for 6 hours. A light blue precipitate was then filtered from the solution, washed with water, and dried overnight at 150°C.

9%Zn-$(VO)_2P_2O_7$. V_2O_5(15.24 g) and $ZnCl_2$(1.0 g) were suspended in a mixture of *iso*-butyl alcohol(90 ml) and benzyl alcohol(60 ml). The suspension was stirred under reflux for 3 hours and then overnight at room temperature giving an almost black suspension. *Ortho*-phosphoric acid(20.8 g) was added and the suspension stirred under reflux for 1hour giving a light blue suspension. Benzyl alcohol(*ca.* 50 ml) was added to the cooled suspension which was then filtered, washed with *iso*-butyl alcohol, ethanol, acetone and air dried. A portion of the solid was then dried in a stream of air at 140°C giving a blue-gray solid.

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. The resultant pellets were crushed in a mortar and pestle and sieved to 1.4 x 0.7 mm.

Catalyst Characterization

X-Ray powder spectra were recorded using a Rigaku controlled powder camera using a 2 theta step size of 0.05°. Infrared spectra were recorded on a Bio-Rad FTS-40 spectrometer in the FT mode using an MCT detector with 2 cm^{-1} resolution. Typically 1032 scans were recorded from KBr discs or, for adsorption studies, using a heatable diffuse reflectance cell.

For infrared studies of adsorbed acetonitrile, a portion of the activated catalyst was ground in a steel Wiggle-Bug mill for 60 s. This material was then transferred to the heatable cell of a Harrick diffuse reflectance attachment and enclosed in a dome containing KBr windows. The sample was typically conditioned in a flow of He by heating to 400°C, holding the temperature for 30 min., and then cooling to 27°C and holding that temperature for 30 min. The He flow was then saturated with the required anhydrous base for 10 min. after which time the sample was purged with He for a further 10 min. The sample was then heated to various temperatures for 10 min. and spectra recorded.

Figure 1 shows x-ray diffraction data for the region of the (001) reflection in the catalyst precursors ($VO(HPO_4)\cdot 0.5H_2O$). The (001) reflection serves as an indication of the order and spacing of the layers in this layered structure.[7] It is evident that precursor preparation in the presence of TEOS has resulted in broadening of this peak indicating increased disorder (FWHM=0.9 for TEOS versus 0.55 for regular VPO). A very slight broadening may also be evident for the Zn promoted precursor. Figure 2 presents similar data for catalysts prepared from these precursors by activation in air. Here, the (200) reflection indicates degree of disorder in the layer stacking. Both the catalyst prepared with TEOS and the catalyst promoted with Zn exhibit broadening of this peak (FWHM=1.60 and 1.50, respectively versus 1.35 for regular VPO) indicating enhanced disorder relative to unmodified vanadyl pyrophosphate.

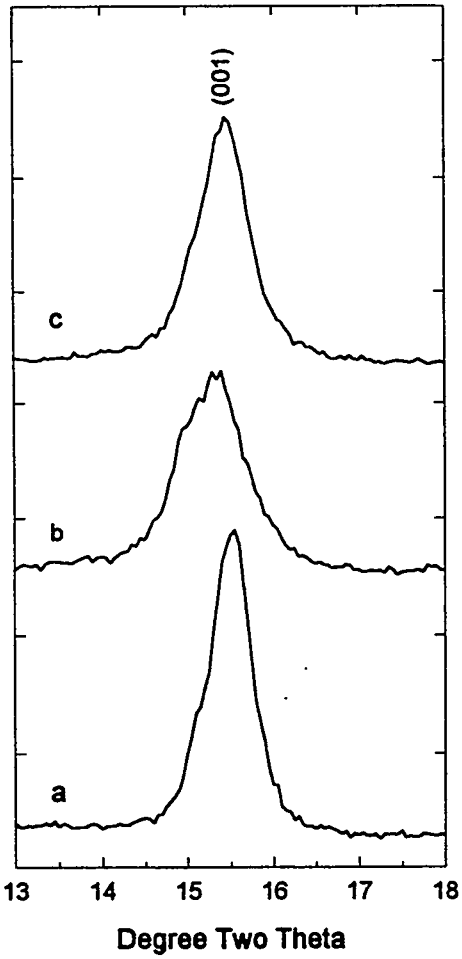

Figure 1. X-ray diffraction results for catalyst precursors, (001) reflection for a)$VO(HPO_4)$-$0.5H_2O$, b)TEOS modified, c) Zn promoted.

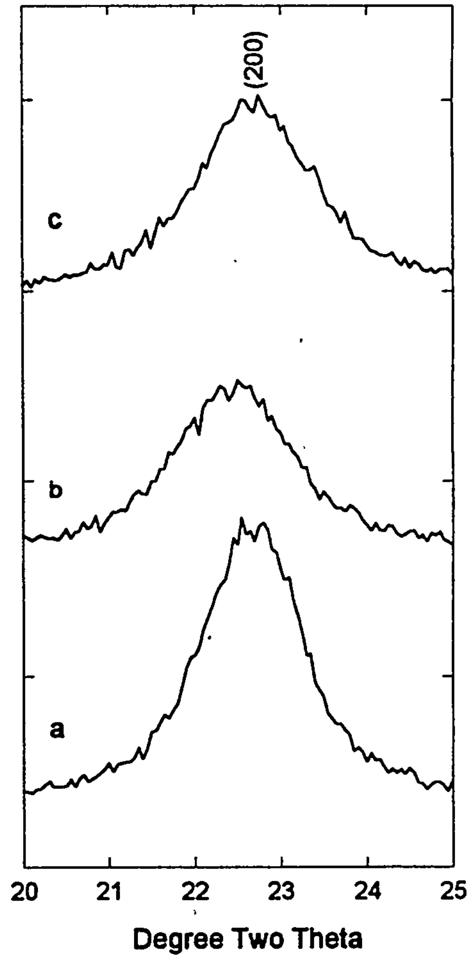

Figure 2. X-ray diffraction results for air activated catalysts, (200) reflection for a)vanadyl pyrophosphate, b)TEOS modified catalyst, c) Zn promoted catalyst.

We have hypothesized that enhanced disorder in the catalyst layer stacking will lead to enhanced Lewis acidity. Surface acidity has been investigated via infrared spectra of chemisorbed acetonitrile. This weak base has a high specificity for the very strong Lewis sites which have been linked to activity in butane oxidation.[11] Spectra of acetonitrile on these catalysts are shown in Figure 3. The doublet at roughly 2325 and 2300 cm^{-1} is caused by acetonitrile adsorbed on very strong Lewis acid sites.[17] The peak at 2260 cm^{-1} and much of the intensity at 2300 results from hydrogen bonded or liquid acetonitrile. Spectrum (a) was taken after heating to 120°C to remove this non-chemisorbed material and this procedure resulted in improved peak resolution. The band at 2327 is clearly an indication of very strong Lewis acid sites and they appear to

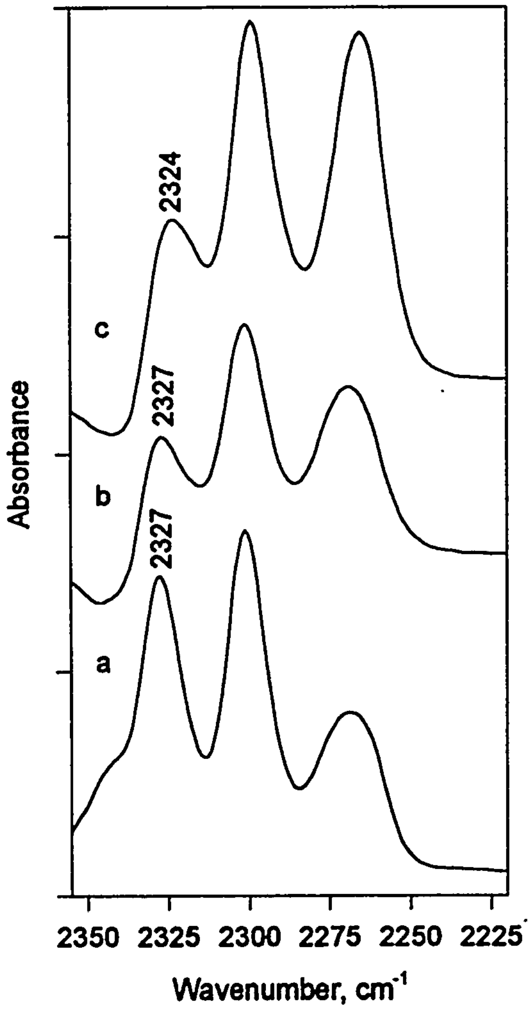

Figure 3. DRIFTS results for acetonitrile chemisorbed on air activated a)vanadyl pyrophosphate, b)TEOS modified catalyst, c)Zn promoted catalyst.

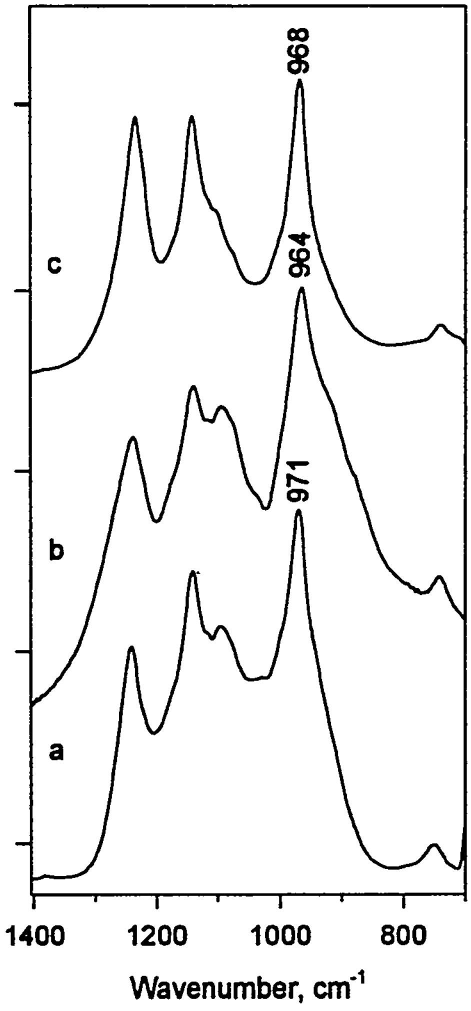

Figure 4. Transmission IR results for air activated a)vanadyl pyrophosphate, b)TEOS modified catalyst, c)Zn promoted catalyst.

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[17] Knozinger, H., Krietenbrink, H. JCS Faraday 1 71 2421 (1975).

be similar on all three catalysts. This method of surface characterization will be refined to allow some distinction of differing acid site strengths to be made. Also, the use of other weak bases (including pyridine) will provide other measures of acid strength as well as Bronsted to Lewis site ratios. The number of acid sites will be measured thermogravimetrically in future work.

Figure 4 presents infrared spectra of the air activated catalysts. The V=O stretch for the unmodified catalyst is observed at 971 cm^{-1}. For the TEOS modified and Zn promoted catalysts this band is at 964 and 968 cm^{-1}, respectively. Takita and coworkers[18] have shown that promoters which lead to a reduction in the wavenumber of the V=O stretch also produce catalysts with enhanced butane oxidation activity. The V=O stretch has shifted significantly for the TEOS modified catalysts suggesting that higher activity is to be expected.

Oxidation Activity Studies

Reactivity studies conducted to date include blank (empty) reactor studies of methane and methanol oxidation, methane and methanol oxidation over air activated VPO, and methane oxidation over butane activated VPO and TEOS modified VPO. Experiments have been conducted in 7.75 mm (3/8") stainless steel or in 4 mm i.d. quartz tube reactors. At temperatures below 500°C no significant difference in activity or selectivity was observed for the two reactor materials. At higher temperatures lower selectivities are obtained in steel presumably because of wall catalyzed oxidation of CO, methanol, and formaldehyde. Carbon balances were better than ±5% for all data reported and better than ±2% for most runs. Catalytic methane oxidation tests employed a GHSV of 1400, and this is within the range used for butane oxidation over VPO catalysts.[4]

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. Oxidation of methane and methanol did occur at higher pressures. Methane oxidation results are generally in agreement with those reported in the literature.[16] Non-catalytic methanol oxidation produced primarily carbon oxides although formaldehyde and methane were also observed.

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[18] Takita, Y., Tanaka, K., Ichimaru, S., Mizihara, Y., Abe, Y., Ishihara, T. Appl. Catal. A: General 103 281 (1993).

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
400	10	20	0	6.8	0	0	0	0	0	--
450	10	20	0	6.8	0	0	0	0	0	--
450	10	20	0	15.3	0	0	0	0	0	--
500	10	20	0	5.1	0.06	0	100	0	0	--
500	10	20	0	6.8	0.11	78.1	21.8	0	0	--
500	10	20	0	10.2	0.81	5.3	16.6	0	78.0	--
500	10	20	0	15.3	31.1	63.4	23.3	0.89	12.3	--
525	10	20	0	6.8	45.8	55.6	18.2	0	26.2	--
525	10	20	0	10.2	56.4	65.3	16.1	0.25	18.3	--
550	10	20	0	1	0	0	0	0	0	--
550	10	20	0	5.1	1.3	21.2	37.8	0	40.9	--
550	10	20	0	6.8	49.5	61.7	24.3	0	13.9	--
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
525	10	0	20	5.1	96.5	49.0	50.3	0	0	0.7
550	10	0	20	1	0.2	22.2	12.8	0	0	64.8
550	10	0	20	5.1	80.3	84.2	10.4	0.86	0	4.4

Figure 5 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 6 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. Recall that TEOS/VPO exhibited a V=O stretch shifted 7 cm^{-1} relative to the unmodified catalyst. This weakening of the V=O bond had indeed resulted in a more active catalyst.

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.* Examination of the literature on catalytic methane partial oxidation (in particular the reviews of Brown and Parkyns[16] and of Pitchai and Klier[19]) suggests that to obtain methanol, previous researchers had to operate at lower oxygen content, higher temperature, and higher pressure or use nitrous oxide rather than dioxygen. Under similar conditions to those employed here methanol is rarely observed, even in trace quantities.[16,20]

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[19] Pitchai, R., Klier, K. Catal. Rev.-Sci. Eng. 28 13 (1988).

[20] Spencer, N.D. and Pereira, C.J. J. Catal. 116 399 (1989).

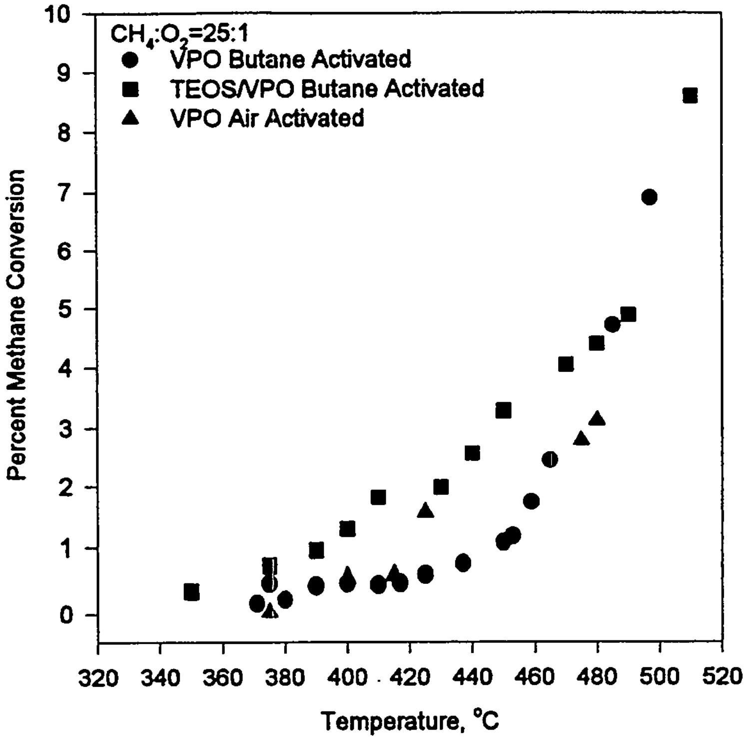

Figure 5. Methane conversion as a function of temperature, GHSV=1400.

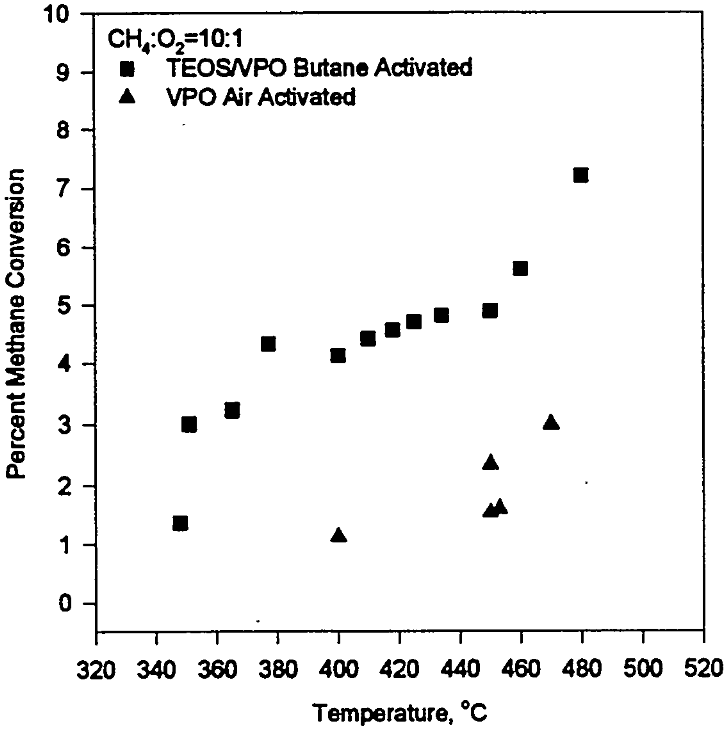

Figure 6. Methane conversion as a function of temperature, GHSV=1400.

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 7. 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. 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.

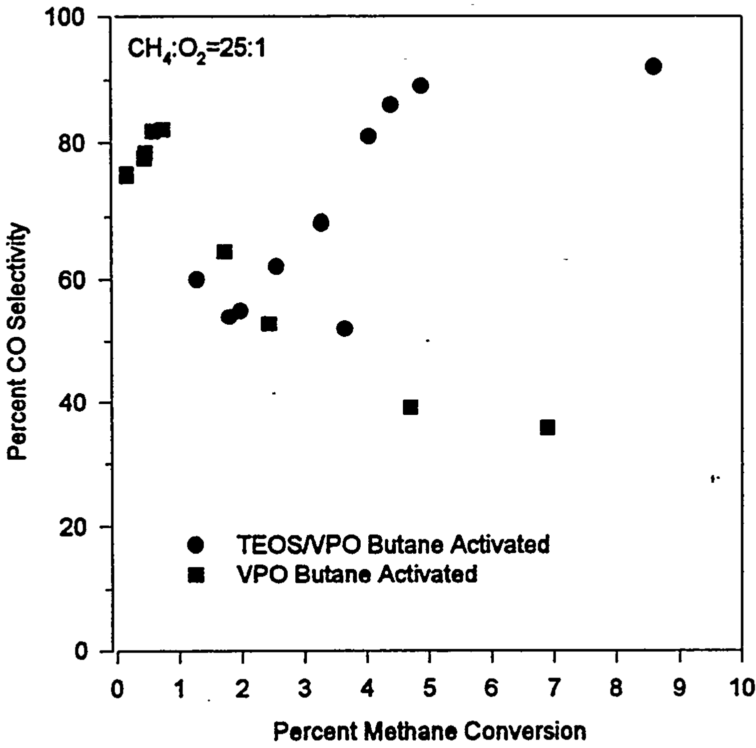

Figure 7. Carbon monoxide selectivity versus methane conversion for two catalysts. GHSV=1400.

Finally, a series of methanol oxidation tests was conducted over air activated VPO. The results are shown in Table 2. Vanadyl pyrophosphate is a highly active catalyst for methanol conversion to dimethyl ether (DME). DME formation is believed to be catalyzed exclusively by Bronsted acid sites and not by Lewis acid sites.[21] Smaller amounts of formaldehyde, methane, and methyl formate (MF) were also observed. Formaldehyde and methyl formate are oxidation products of methanol and DME, respectively. The selectivity of the catalyst in methanol conversion is remarkable in that under most conditions carbon oxides are very minor products. The data in Table 2 indicate that for the formation of oxidation products higher temperatures or pressures are required. Attempts to

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[21] Klier, K., Herman, R.G. Coal Liquefaction and Gas Conversion Contractors' Review Conference, Pittsburgh, September 7-8, (1994).

perform methanol oxidation at higher temperatures using this reactor configuration resulted in reactor runaway. This indicates that at temperatures above about 350°C methanol oxidation is facile with carbon oxides as the most likely products.

Table 2. Results of methanol oxidation over air activated vanadyl pyrophosphate.

(Feed containing 70% He, GHSV=12,000@NTP)

Temperature, °C	Methanol/ Oxygen	Pressure atm	Percent Conversion	Percent Selectivity					
				CO	CO_2	DME	HCHO	MF	CH_4
250	0.3	1	27	0	0	93	0	0	7
300	3.1	1	31	2	0	77	19	0	2
250	9.9	1	10	0	0	93	0	0	7
350	10.8	1	45	1	0	80	17	0	2
250	1.4	5	7	7	0	63	30	0	0
250	3.1	5	12	1	5	94	0	0	0
300	2.3	5	31	6	1	92	0	0	1
350	2.7	5	65	26	1	73	0	0	0
300	15.3	5	18	2	1	94	0	2	1
250	1.1	10	6	0	4	95	0	0	1
300	2.1	7	20	12	1	86	0	0	1
250	13.9	10	7	2	2	90	5	0	1
350	8.7	10	44	10	1	86	1	2	0

The activity/selectivity results reported above indicate that VPO is an active catalysts for methane oxidation. The catalyst is unusual in that methanol is observed as a minor reaction product at atmospheric pressure and at relatively high oxygen partial pressure compared to previous studies. The desired reaction product, methanol, is also easily converted over this catalyst. A catalyst development approach suggested by these results is to modify the surface so that methanol conversion is inhibited. Because DME is the main product from methanol at lower temperatures, removal of the surface Bronsted acid sites by ion exchange with an alkali metal is an obvious approach.

PLANS:

Future plans for the project involve improvements in experimental techniques and synthesis of more novel catalysts followed by testing for activity and selectivity in methane oxidation. Improvements to experimental methods include:

- Surface site characterization using infrared spectroscopy. Improved procedures for obtaining spectra of acetonitrile and pyridine are being developed. Additional surface probe molecules will also be investigated.
- Measurement of acid site density. A thermogravimetric method for measurement of the number of acid sites will be developed.
- Catalyst activity testing. Improved reactors and analytical methods are tested on a regular basis and this will continue. In particular, quantitative analysis of formaldehyde and methanol observed in products has not been obtained although peaks for these materials are easily seen in the GC trace.

A number of new catalysts based on the approaches outlined above as well as catalysts based on other approaches will be prepared and tested. In particular, a number of preparations involving intercalation or pillaring of the vanadyl pyrophosphate layered structure are planned. Modification of the oxidation functionality by several different promoters will be investigated. Direct modification of the vanadyl pyrophosphate surface through ion exchange and reaction also appears to be a promising approach. For example, ion exchange of acidic or basic hydroxyl groups appears feasible and may dramatically effect activity and selectivity.[22] The results reported above strongly suggest attempting to remove surface Bronsted sites by ion exchange. Finally, in preliminary work we have developed practical procedures for preparing supported vanadyl pyrophosphate. Catalyst supports provide enhanced surface area and can interact strongly an with oxide or phosphate active phase. Catalysts based on each of these approaches will be characterized and tested in the microreactor system.

As time and funds allow, other experiments will also be performed. These include butane oxidation tests to verify that we are using *bona fide* vanadyl pyrophosphate and because some of the novel catalysts may be interesting for this application. Also, pulsed reactor testing could be performed to provide information on the performance of the catalyst in the absence of gas-phase oxygen. If activity and selectivity are adequate, a process using the catalyst as an oxygen carrier might be developed.

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[22] Centi, G., Golinelli, G., Busca, G. J. Phys. Chem. 94 6813 (1990).