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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 eighth quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". Activities during this quarter focused on fine tuning of catalyst characterization and synthesis techniques. Improvements in catalyst activity test methods were also implemented but more remains to be done.

Specific accomplishments include:

- Improved characterization of vanadyl pyrophosphate (VPO) and Si promoted VPO by FTIR and FTIR of chemisorbed bases.
- Several minor improvements in catalyst preparation technique resulting in enhanced catalyst yield, better control of catalyst composition, and generation of less waste.
- Preliminary pulsed reaction data on methane oxidation were also acquired.

The results reported in the last quarterly indicated that Si promotion produces structural disorder perpendicular to the layer planes in VPO. Strong Lewis acid sites are thought to be the active sites or initiating sites for alkane oxidation over this catalyst. The Si promoted catalyst exhibits a pyridine acidity similar to that of conventional vanadyl pyrophosphate as revealed by FTIR of adsorbed pyridine. FTIR of a weaker base, acetonitrile, suggests that the Si promoted catalyst contains significantly stronger acid sites than unpromoted VPO.

Preliminary activity measurements for methane conversion (without oxygen) in a pulsed reactor over VPO indicate that the primary reaction product is CO. Carbon dioxide is also formed but selectivity to CO_2 decreases with number of pulses. These results suggest that selectivity to partially oxidized products improves with catalyst reduction and suggest that some surface modification will be required to obtain oxidized hydrocarbon products. Note that catalyst activation (conversion from the precursor to VPO) has been carried out using air. For butane oxidation catalysts VPO is activated in a 1% butane/air mixture which produces a slightly reduced catalyst.

During next quarter the project will become fully operational as graduate students finish classes and begin to focus full time on research. Planned activities include:

- Improvements in activity testing to allow a detailed engineering kinetic study methane oxidation over VPO, including pulsed reaction studies.
- Testing of catalysts activated in butane/air.
- Synthesis and characterization of several new catalysts using various approaches designed to enhance Lewis acidity and modify other surface properties.

INTRODUCTION

This document is the eighth 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

This quarter we have continued to characterize vanadyl pyrophosphate and the Si promoted samples discussed in the last quarterly report. X-ray diffraction data for catalyst precursors and air activated catalysts were reported in Quarterly Report No. 7. Improvements in temperature control during activation have resulted in more completely activated catalysts. This is shown in Figure 1 where for both catalysts the (200) reflection is clearly much more symmetrical than for preparations reported before which indicates that they are more completely converted to VPO.

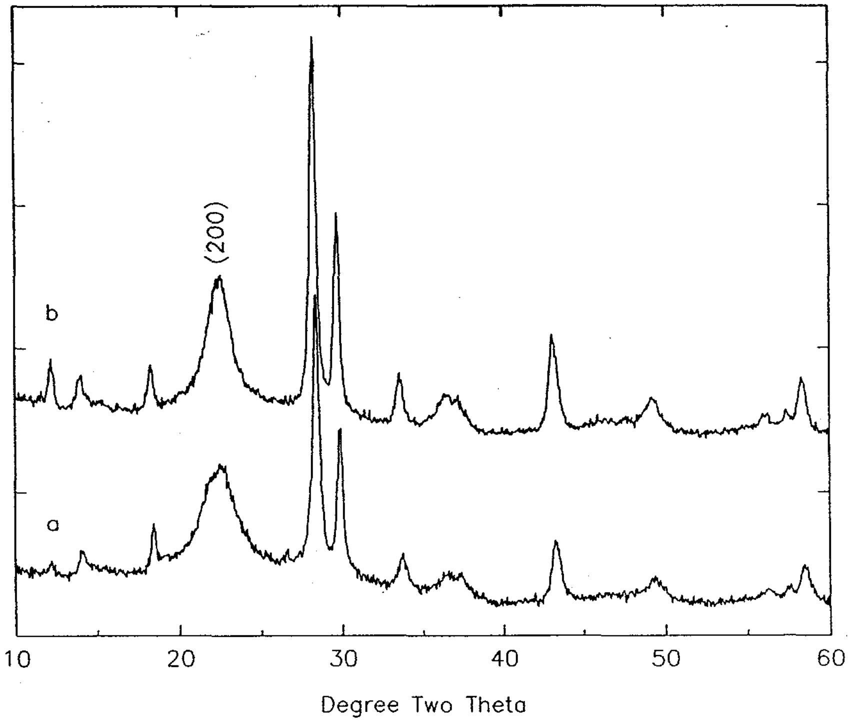

Figure 1. X-ray diffraction patterns of vanadyl pyrophosphate (a) and TEOS promoted vanadyl pyrophosphate (b).

We previously also reported infrared spectra for these catalysts. However, we have improved our infrared technique significantly and better spectra are shown in Figure 2. The current results indicate very little if any difference between these two samples in the region of P-O and V-O bond vibrations.

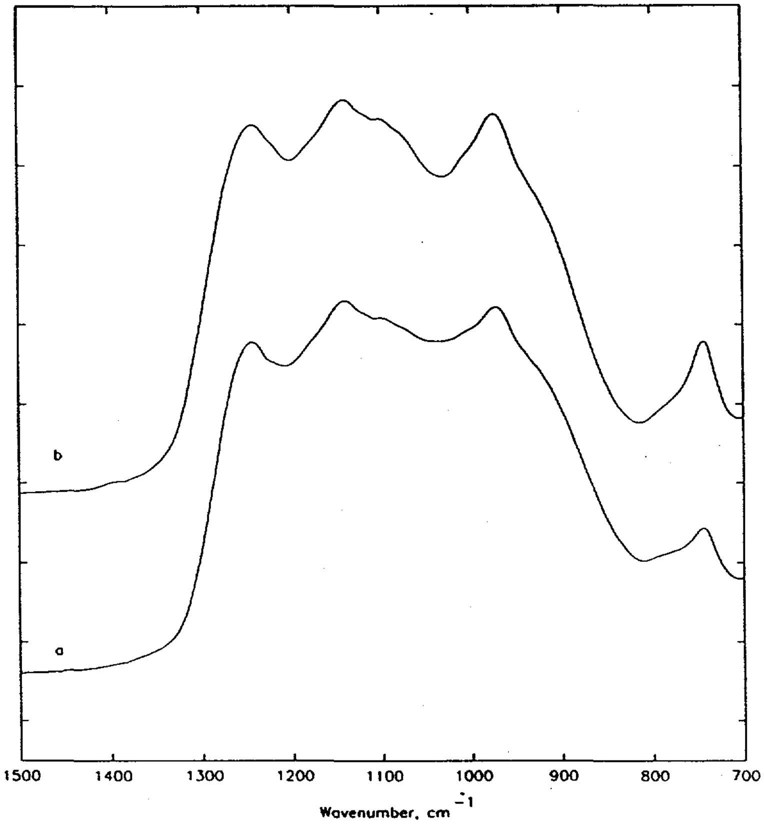

Figure 2. Infrared (DRIFTS) spectra of vanadyl pyrophosphate (a) and TEOS modified vanadyl pyrophosphate (b).

Figure 3 shows spectra of pyridine chemisorbed on vanadyl pyrophosphate (VPO) and the same material modified through addition of tetra-ethyl orthosilicate (TEOS). Addition of TEOS has been shown to disrupt the VPO layered structure resulting in exposure of more active surface and a more active butane oxidation catalyst (Horowitz, et al., 1988). It is of interest to determine the effect of this additive on VPO acidity. Pyridine IR results indicate similar levels of acid strength. At this time it appears that the pyridine used in these experiments was not thoroughly dried so no conclusions regarding Bronsted/Lewis ratios can be drawn. Drying of pyridine with molecular sieves is expected to eliminate this problem.

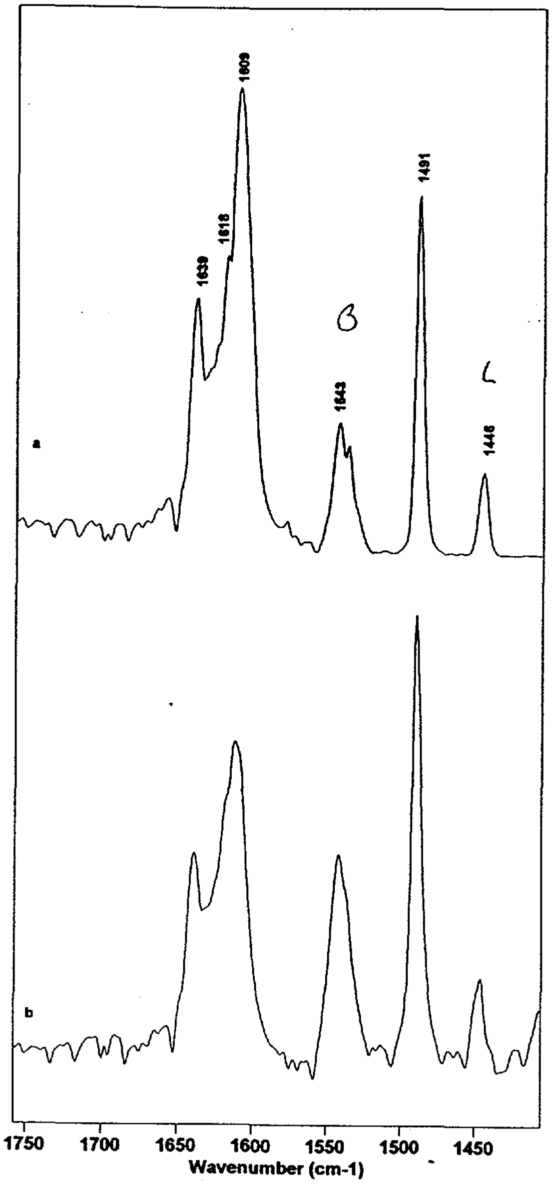

Figure 3. Pyridine chemisorbed on vanadyl pyrophosphate + TEOS (a) and unmodified vanadyl pyrophosphate (b).

Busca and coworkers (1986a) have shown that acetonitrile, a weaker base, can reveal the presence of strong acid sites on the surface of VPO. Figure 4 shows spectra of acetonitrile chemisorbed on the two catalysts under consideration. While these data must be regarded as preliminary, they do indicate considerably stronger acid sites on the Si promoted catalyst. In the unpromoted catalyst the peak at 2325 is assigned to bonding of the acid site to nitrogen. The shift of this peak relative to its value in the liquid phase (2254 cm^{-1}) is a qualitative measure of acid site strength (the force constant might be regarded as a quantitative measure). It can be seen that in the promoted catalyst this peak is at 2338 cm^{-1}, considerably higher than on the unpromoted catalyst. The significance of the shoulder at 2359 cm^{-1} is not understood at this time.

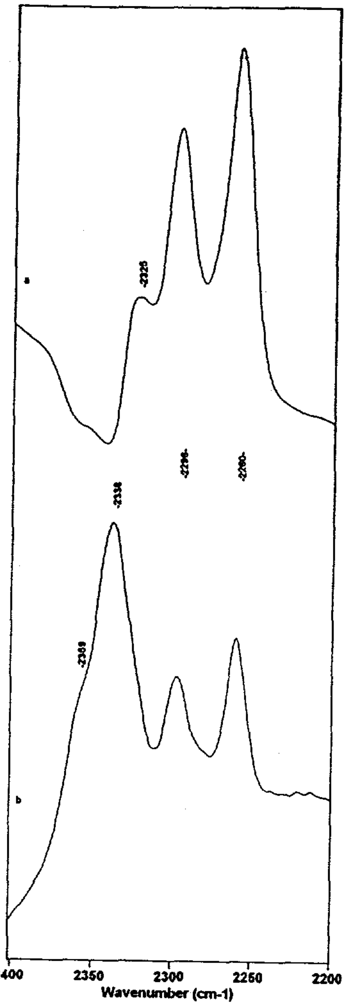

Figure 4. Infrared spectra of acetonitrile chemisorbed on the surface of vanadyl pyrophosphate (a), and Si promoted vanadyl pyrophosphate (b).

Catalyst Testing

A preliminary study of methane oxidation over a non-optimal sample of vanadyl pyrophosphate was conducted. Pulses of pure methane were passed over a sample of vanadyl pyrophosphate which had been accidentally prepared using a low P:V ratio and which had been activated in air. The only reaction products observed were CO and CO_2. CO selectivity was constant with pulse number while CO_2 selectivity decreased as the catalyst became more reduced. More detailed studies on better catalysts are expected in the near future.

PLANNED ACTIVITIES

During the next quarter the most important activities will be:

- To characterize the surface acid sites of vanadyl pyrophosphate and several novel preparations by FTIR of adsorbed pyridine and acetonitrile. We are on the verge of obtaining high quality data from this experiment.
- To obtain pulsed and continuous reactivity data on the activity of vanadyl pyrophosphate and novel catalysts in methane and methanol oxidation.

SUMMARY

Specific accomplishments include:

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