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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". During this quarter the project was initiated, after transfer via a novation agreement, at the Colorado School of Mines. Project initiation activities have included:

- Set up of catalyst synthesis apparatus.
- Training on x-ray diffraction and FTIR apparatus.
- Set up of catalyst testing reactor.
- Set up of reactor product analytical systems.
- Set up and method development for measuring catalyst acidity via FTIR.

At the end of this quarter significant progress had been made towards completion of these initiation activities. Several catalyst syntheses have been performed and the catalysts characterized by x-ray diffraction and FTIR. The catalyst testing reactor system is operational. Reactor product analysis system is nearing completion. Initiation of this system was delayed by the unavailability of a Valco valve which has just recently arrived. Set up of the in-situ FTIR cell for catalyst acidity studies has begun.

In this report the results of several catalyst syntheses are reported along with characterization results. In particular, impregnation of vanadyl pyrophosphate with potassium nitrate dramatically reduced the number of surface hydroxyl groups. Such groups may be important in the non-selective, total oxidation of hydrocarbons. Also, preliminary experimental results on FTIR spectra of adsorbed pyridine are presented. It is shown that pyridine adsorbed on the catalyst surface can be easily observed by the diffuse reflectance IR technique. We plan to apply this technique to measurement of the acid site strength of surfaces modified with promoters.

INTRODUCTION

This document is the sixth quarterly technical progress report under Contract No. DE-AC22-92PC92110 "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane". This report covers the first quarter after the program was initiated at the Colorado School of Mines following transfer via a novation agreement. The status of project initiation activities as well as characterization results for several catalysts are reported.

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.
- To utilize promoters and catalyst supports to improve methanol 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

Under the project entitled "Development of Vanadium-Phosphate Catalysts for Methanol Production by Selective Oxidation of Methane", the Colorado School of Mines is performing laboratory scale development of a promising, practical catalyst for the selective oxidation of methane to methanol. The primary component of this catalyst is vanadium-phosphate (VPO) which has shown good activity and selectivity in the partial oxidation of n-butane and propane but has not been studied in detail for methane oxidation.

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 use of steam in the feed gas will also 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, and FTIR.

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.

Task 2: Process and Catalyst Variable Study. Tests will be conducted to determine the optimum conditions of temperature, pressure, CH_4/O_2 ratio, $\text{H}_2\text{O}/\text{CH}_4$ ratio, space velocity, and catalyst P:V ratio for high activity and selectivity in methanol production. This task is essentially complete although a few more tests in this area may be conducted.

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.

Task 4: Advanced Catalyst Testing. Advanced catalysts which are both promoted and supported 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 Testing

The catalyst testing reactor is a microfixed bed system typically used in catalyst screening studies. The reactor system has been described in earlier reports and is now fully operational. The analytical system consists of a HP 5890 gas chromatograph, equipped with a TCD, and originally configured for a different project. To configure this system for the current project we have converted from packed to megabore columns, added gas sampling and column switching valves, and added an electronic interface for valve control. All parts for reconfiguration of this GC have finally arrived and it should become operational during the next quarter.

Catalyst Characterization

Figure 1 shows FTIR spectra for vanadyl pyrophosphate and vanadyl pyrophosphate modified by impregnation of potassium nitrate. It is noteworthy that the intensity of the hydroxyl groups is significantly reduced in the potassium modified sample suggesting that acidic hydroxyls have exchanged a proton for a potassium ion.

Figure 2 shows FTIR spectra of vanadyl pyrophosphate and of pyridine adsorbed on the surface of vanadyl pyrophosphate. The important pyridine bands at 1448, 1490, and 1542 cm^{-1} are evident.

These preliminary results indicate that the acidic properties of vanadyl pyrophosphate can be studied by infrared spectroscopy. More detailed experiments are currently underway.

PLANNED ACTIVITIES

Over the next several months the following activities are planned:

- Examine the activity of catalysts activated in butane/air mixtures. This is the preferred procedure for butane oxidation catalysts. We will also conduct a limited amount of butane oxidation experiments to demonstrate that the catalysts we are preparing are the same in terms of activity and selectivity as those reported in the literature.
- The project could benefit from the capability to acquire good quality kinetic data along with the catalyst screening data which we currently acquire. To this end a modified reactor will be fabricated and tests will be conducted to demonstrate that data are free of transport limitations and to quantitatively evaluate reaction rates over candidate catalysts. Reactor and kinetic models will be developed.
- Modification of the catalyst Bronsted acidity by exchange of the acidic protons for potassium. This modification will be followed through observation of the -OH region of the infrared spectra. Removal of the Bronsted acid sites should reduce catalyst activity for dehydrogenation (undesirable when converting methane to methanol) and reduce activity for methanol coupling to dimethyl ether.
- Doping of vanadium phosphate with small amounts of Si or other transition metals is thought to introduce strain into the structure and perhaps lead to stronger acid sites. These dopants may also have other effects. The patent literature provides some clues on dopants and procedures which lowered the required reaction temperature for butane oxidation by 100°C. We plan to investigate a wide variety of dopants looking at their effect on catalyst acidity and crystallinity as well as activity for methane oxidation.
- Catalyst supports can have a large influence on catalyst activity and selectivity through strong interaction with the supported catalysts. Some researchers have even claimed that the silica support using in most methane oxidation studies is

actually the active catalyst and that the "supported" transition metal oxides are merely promoters. We plan to investigate the use of several supports for this reaction using the catalyst preparation procedure described in this report.

- The surface of vanadyl pyrophosphate is thought to consist of pendant pyrophosphate groups sticking out from the surface and providing a 3-dimensional "cleft" around the vanadium/oxygen surface sites (strong Lewis acid sites). It may be possible to alter these pendant groups through reaction with organo-phosphorus compounds and thereby change the shape and energy of the surface sites. Furthermore, the inclusion of such compounds has been used in Ti and Zr pyrophosphates to control the layer spacing in the crystal. These approaches will be attempted in the coming months.

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In this report the results of several catalyst syntheses are reported along with characterization results for several previously prepared catalysts. Preliminary experimental results on FTIR spectra of adsorbed pyridine are also presented.

Figure 1. FTIR (DRIFTS) spectra of vanadyl pyrophosphate a) unmodified, and b) modified by impregnation with potassium nitrate to remove acidic hydroxyl groups.

Figure 2. FTIR (DRIFTS) spectra of vanadyl pyrophosphate a) without, and b) with adsorbed pyridine indicating that pyridine can be observed on this surface using this technique.