LOW TEMPERATURE VOC COMBUSTION OVER MANGANESE, COBALT AND ZINC
ALPO₄ MOLECULAR SIEVES

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Summary

A functional fixed bed continuous flow catalytic reactor was constructed for conducting experiments on the catalytic destruction of VOCs using cobalt and manganese containing aluminophosphate catalysts (MeAPOs). The reactor was also interfaced to a Gas Chromatograph in order to facilitate on line product analysis. As preliminary catalytic experiments, a cobalt exchanged form of large pore zeolite Y was used as a reference catalyst for the oxidation of methylene chloride (CH_2Cl_2). At 350°C , the catalyst was effective in partial conversion of this feed stream of VOC to CO_2 . Optimization of reaction conditions are currently underway in order to obtain higher conversion levels. The effect of variations in reaction conditions such as reactant flow rate, reaction temperature and catalyst compositions are currently being investigated. In the next phase of this project, the Co-exchanged Y zeolite will be substituted by the MeAPOs catalysts and the reactivities of the latter will be assessed.

The potential of the MeAPOs to function as oxidation catalysts was evaluated in the liquid phase conversion of phenol to hydroquinone and catechol. The percentage conversion and product yield were significant and varied depending on the metal type and content of the molecular sieve framework. Conversion levels were also dependent on molecular sieve pore dimensions as the medium pore MeAPO-11 was more active than the larger pore MeAPO-5 or MeAPO-36. Findings from this research were presented at ACS National Meeting, New Orleans, March, 1996 and the 15th ACS Mid Atlantic Regional Meeting, Villanova University, Pennsylvania 1996. The full paper was published in *Applied Catalysis A: General* 143 (1996) 101-110.

1.0 Introduction

The objective of this project is to prepare manganese and cobalt containing AlPO_4 large pore molecular sieves of structure type -36 and evaluate their ability to function as successful oxidation catalysts for the removal of low levels of VOC's from gas streams. This report highlights our progress for the period March 1, 1996 to August 31, 1996.

2.0 Work done

2.1 Construction of catalytic reactor

A fixed bed upflow continuous flow reactor was constructed consisting of the following components. A Pyrex reactor tube of dimensions 30 cm long x 1 cm I. D. diameter, containing Kovar metal (1/4 inch) to glass seals at both ends and a porous frit at the center. A Thermolyne Tube Furnace equipped with temperature control features for use in heating the reactor tube. A stainless steel thermocouple inserted inside the catalyst bed for monitoring the temperature of the latter. A 200 mL Dreshnel type bottle with metal to glass seals attached to the inlet and outlet for containing liquid VOCs. A constant temperature bath used for equilibrating the content of the

Dreshnel bottle. All components are connected through 1/4 inch or 1/8 inch stainless steel tubing. A schematic diagram of the reactor is shown in Figure 1.

The reactor is interfaced to a Shamadzu 14A Gas Chromatograph via a heated transfer line (1/6" stainless steel tube) which is in turn attached to a heated Valco six port sampling valve. The GC column is currently a 6 ft x 1/8 inch Stainless Steel containing 3% OV1 on Chromosorb as stationary phase. The GC is equipped with both a Flame Ionization Detector (FID) and a Thermal Conductivity Detector (TCD). Chromatograms are recorded on a Shimadzu CR501 Integrator.

2.2 Experimental Procedure

Preparation of Metal Substituted Aluminophosphate (MeAPOs) catalysts:

Procedures for the synthesis of MeAPOs were summarized in Semi Annual Report 1. (September 1, 1995 to February 28, 1996).

Preparation of cobalt exchanged zeolite Y

Recent research have shown that cobalt exchanged zeolite Y is very active for the decomposition of chlorinated VOCs such as CH_2Cl_2 and carbon tetrachloride (CCl_4). We therefore attempted to reproduce some of these results which we intend to use as reference in subsequent experiments with our subject metal substituted aluminophosphate catalysts. Zeolite Y was obtained from Union Carbide with trade name LZV-62. In order to convert it to a Co exchanged form, the zeolite (10 g) was mixed with 250 mL of 1M cobalt nitrate in a 500 mL round bottom flask. The stirred flask was heated at 60°C-70°C overnight after which the solid product was filtered and washed with deionized water. This procedure was repeated twice after which the solid was dried and calcined at 500 °C for 12 hr.

Catalytic experiments

A 1.0 g sample of Co-exchanged zeolite Y powder was placed on the glass frit inside the reactor tube. The catalyst was kept in place by a small plug of glass wool. The reactor tube was heated to the desired reaction temperature. Air from a cylinder was bubbled at a set flow rate (typically 40 mL/min) through CH_2Cl_2 contained in the Dreshel bottle equilibrated at 25°C. As the air/ CH_2Cl_2 mixture passed through the catalyst bed, 250 μL samples of the reactor effluent were injected into the GC at regular intervals (using the sampling valve). For preliminary experiments, the GC conditions were as follows: Injector port temperature 150°C, Detector temperature 200°C, Column temperature program: initial temperature 50°C for 2 min, rate 10°C/min, final temperature 160°C for 2 min. Qualitative analysis of the reaction products was performed by capturing a sample of the reactor effluent into a Hamilton 2 mL Gastight Syringe. The content of the syringe was then injected into a Hewlett Packard 5890 GC/MSD which was set at the following conditions: Injector temperature 150°C, Column temperature 35°C. Column type: 30M length capillary column coated with a methysilicone stationary phase.

3.0 Results and Discussion

Figure 2a shows chromatograms resulting from repeated injections of the reactor effluent (250 μ l) in the absence of catalyst (empty reactor tube at 350°C). This experiment was done to 1) monitor the degree of precision from repeated injections and 2) monitor the feed rate of CH_2Cl_2 passing through the reactor bed. The corresponding area counts listed in Table 1 shows excellent precision in repeated injections and that the flow rate of CH_2Cl_2 was constant over the 15 minutes during which it was monitored. Similar results were observed over the temperature range monitored up to 400°C.

Figure 2b shows a typical chromatogram of a sample of reactor effluent after passing through Co-exchanged zeolite Y in the reactor tube. More than one peaks can be observed in this case compared with Figure 2a in which a single peak was obtained from each injection. Mass spectral analysis of the effluent gas showed that the small peak was carbon dioxide and the large peak was unreacted CH_2Cl_2 (Figure 3a and 3b) and therefore demonstrated that CH_2Cl_2 conversion at low levels was successful in the presence of this catalyst. This was also determined semi-quantitatively from the reduction in area counts of its peak in the chromatograms (Table 2). A trend of increasing in conversion was noticeable as the reaction temperature was increased from 300°C to 400°C.

4.0 Presentations and Publications

- Catalytic Hydroxylation of Phenol Over MeAPO-11 Molecular Sieves; Presented at the Symposium on Selective Hydrocarbon Oxidation, 211 ACS National Meeting, New Orleans, March, 1996.
- Catalytic Hydroxylation of Phenol Over MeAPO-11 Molecular Sieves; presented at the 5th ACS Mid Atlantic Regional Meeting, Villanova University, Pennsylvania, May 1996.
- Metal Substituted Aluminophosphate Molecular Sieves as Phenol Hydroxylation Catalysts, Applied Catalysis A: General 143 (1996)101-110.

Copies of the above articles are attached.

5.0 Summary and Future work

A functional catalytic reactor was constructed for conducting experiments on the catalytic destruction of VOCs using MeAPOs. So far, the reactor was successfully used to demonstrate the conversion of CH_2Cl_2 to CO_2 using co-exchanged zeolite Y catalyst. Optimization of reaction conditions such as reactant flow rate and reaction temperature are currently underway. The concentration of CH_2Cl_2 in the Air/VOC feed will be calculated from its vapour pressure. The same applies to other VOCs to be investigated, such as carbon tetrachloride (CCl_4). Gas chromatography will also be employed in the quantitative analysis of reactants and products using

Figure 1. Schematic Diagram of Catalytic Reactor

appropriate calibration standards. In the next phase of this project, the Co-exchanged Y zeolite will be substituted by the MeAPOs catalysts and the reactivities of the latter will be assessed.

Table 1: GC Area counts for methylene chloride from reactor effluents at various reaction temperatures.

Injection #	Area counts at 300°C/no catalyst	Area counts at 300°C/with catalyst	Area counts at 350°C/with catalyst	Area counts at 400°C/with catalyst
1	1904094	1951040	1882400	1798649
2	1896834	1928032	1853143	1793410
3	1902751	1920641	1848283	1827358
4	1894918	1925002	1852851	1827285

(a)

(b)

Figure 2: Chromatograms of a) repeated injections of CH_2Cl_2 effluent from reactor in the absence of catalyst and b) reaction products in the presence of Co-Y zeolite catalyst. (For both a and b the reactor temperature was 350°C.)

Figure 3: GC/MS analysis of reactor effluent at 350°C showing a) chromatogram, b) mass spectrum of small peak with characteristic fragmentation pattern of CO_2 and c), mass spectrum of large peak with characteristic fragmentation pattern of CH_2Cl_2 .