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CATALYTIC OXIDATION BY TRANSITION METAL IONS IN  
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CHEMISTRY J H LUNSFORD 28 SEP 84 ARO-18005.4-CH

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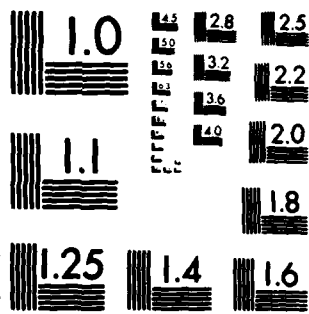
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 18005.4-CH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Catalytic Oxidation by Transition Metal Ions in Zeolites		5. TYPE OF REPORT & PERIOD COVERED Final, June 1, 1981 - May 31, 1984
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Jack H. Lunsford		8. CONTRACT OR GRANT NUMBER(s) DAAG 29-81-K-0096
PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Texas A&M University College Station, Texas 77843		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE September 28, 1984
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES 6
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

AD-A146 828

16. DISTRIBUTION STATEMENT (of this Report)  
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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  
NA

18. SUPPLEMENTARY NOTES  
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  
Zeolite, Oxidation Catalysis, Molybdenum Zeolite, Cobalt Zeolite, Oxygen Adduct, Cobalt-Oxygen Complexes, Epoxidation

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  
The regular cavities within zeolites form a unique environment for carrying out both stoichiometric and catalytic oxidation reactions. Transition metal ions such as molybdenum and cobalt may be introduced into zeolites, where they form complexes with oxidants and substrate ligands. Molybdenum-Y zeolites were effective catalysts for the epoxidation of propylene using tert-butyl hydroperoxide as the source of oxygen. They exhibited high selectivity to the epoxide, and initially were quite active. The activity,

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however, declined over several hours because of the buildup of polyoxypropylene within the zeolite cavities.

Addition of bipyridine and terpyridine to a CoY zeolite resulted in a five-coordinate  $[\text{Co}^{\text{II}}(\text{bpy})(\text{terpy})]^{2+}$  complex, which in the presence of  $\text{O}_2$  formed the  $[\text{Co}^{\text{III}}(\text{bpy})(\text{terpy})\text{O}_2^-]^{2+}$  complex. The latter was completely reversible upon evacuation of the  $\text{O}_2$  at  $25^\circ\text{C}$ , although the stability constant was considerably greater than is found with analogous homogeneous complexes. The superoxo complex in the zeolite was stable in the presence of excess oxygen at temperatures up to  $70^\circ\text{C}$ , which may make it suitable for activating  $\text{O}_2$  in certain catalytic cycles.

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CATALYTIC OXIDATION BY  
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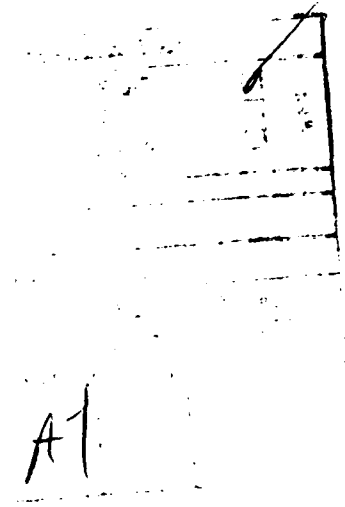
FINAL REPORT



SEPTEMBER 28, 1984

U. S. ARMY RESEARCH OFFICE

DAAG 29-81-K-0096



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## STATEMENT OF THE PROBLEM

The regular cavities within zeolites form a unique environment for carrying out both stoichiometric and catalytic oxidation reactions. Transition metal ions such as molybdenum and cobalt may be introduced into zeolites, where they form complexes with oxidants and substrate ligands. The objectives of the research were (a) to understand oxidation reactions in zeolites at a molecular level and (b) to evaluate the potential of zeolites as catalysts in selective oxidation reactions.

## SUMMARY OF RESULTS

Zeolites continue to be an interesting medium for carrying out oxidation reactions by transition metal ions. In the absence of an external ligand the oxide ions of the zeolite function as ligands, and the coordination numbers are typically three or four. The available coordination sites on the metal may serve to form complexes with substrate molecules as a pathway for oxidation. Such is believed to be the case in the epoxidation of olefins which is catalyzed by MoY zeolites.<sup>1,2</sup>

As an alternative, more strongly coordinating ligands, for example ethylenediamine (en), may be added to the zeolite. The metal ion will favor these ligands and coordinate with them rather than the oxide ions of the lattice. More conventional coordination complexes such as bis(ethylenediamine)cobalt(II) may be formed in the large cavities where the zeolite now functions as an anion and a solvent.<sup>3</sup> The  $\text{Co}^{\text{II}}(\text{en})_2$  complexes form reversible,

mononuclear oxygen adducts which are active for the conversion of pyrocatechol to orthoquinone.<sup>4</sup> A unique feature of the zeolite, relative to more conventional liquid solvents, is its ability to stabilize these oxygen adducts in the mononuclear state.

Research under this contract has focused on (a) the catalytic properties of molybdenum-exchanged zeolites in the epoxidation of propylene and (b) the synthesis of more robust cobalt complexes so that the ligand will not be attacked by the coordinated oxygen.

#### Synthesis, Characterization and Catalytic Properties of Mo-Zeolites:

Considerable effort has been devoted to the synthesis and characterization of MoY zeolites. Simple aqueous exchange of a hydrated ion is not possible, therefore more exotic schemes were developed. It was previously demonstrated that  $\text{MoCl}_5$  may be reacted with a  $\text{HY}_u$  (here  $Y_u$  denotes a steam-stabilized or "ultrastable" zeolite) to form a  $\text{MoY}_u$  zeolite and HCl which is removed from the system.<sup>1</sup> In this study,  $\text{MoY}_u$  zeolites have been prepared by reacting  $\text{HY}_u$  with  $\text{Mo}(\text{CO})_6$ . During the reaction the carbonyl ligands are lost,  $\text{H}^+$  in the zeolite is reduced to  $\text{H}_2$ , and Mo is oxidized. A third method of introducing the Mo into the zeolite involved an aqueous exchange of  $[\text{Mo}_2(\text{en})_4]^{4+}$  into a NaY zeolite. The complex is of particular interest because it contains multiple Mo-Mo bonds and represents the first example of such a complex being introduced into a zeolite.

These MoY zeolites were studied as catalysts for the epoxidation of propylene using tert-butyl hydroperoxide as the source of oxygen. The  $\text{MoY}_u$  catalysts derived from  $\text{MoCl}_5$  or  $\text{Mo}(\text{CO})_6$  exhibited a high initial activity which was up to 11 times as active as homogeneous catalysts derived from  $\text{Mo}(\text{CO})_6$ . Moreover, the selectivity to the epoxide was ca. 95%. The high

activity, however, was not maintained, and after a period of 200 min. at 70°C the remaining activity was largely the result of a small amount of Mo which had been leached out of the zeolite. Nevertheless, conversions of up to 85%, with tert-butyl hydroperoxide as the limiting reagent, were achieved before the activity of the zeolite was completely poisoned.

The decline in activity with time is attributed to the formation of polyoxypropylene within the zeolite cavities. Infrared spectra of catalysts exposed to propylene oxide confirm the formation of this polymer. Originally it was thought that acid sites in the zeolite promoted the polymerization and bases were added to the system in an attempt to neutralize the acidity. More recent results indicate that the Mo itself catalyzes the polymerization reaction.

An unusual phenomenon was observed in that the specific activity increased markedly as the loading was increased from 4 to 5% by weight Mo. The latter value corresponds to the maximum exchange capacity of the zeolite. X-ray photoelectron spectroscopy confirms that this Mo is not localized on the external surface of the zeolite crystallites. It seems likely that the more active Mo is located at new sites, perhaps site III, in the zeolite where coordination to the oxygen is different. Relative to the homogeneous system, the enhanced activity in the zeolite is attributed to electron withdrawal from the Mo. This in turn renders the peroxidic oxygens more electrophilic and more susceptible to attack by the olefin.

In contrast, the MoY zeolites prepared from the  $[\text{Mo}_2(\text{en})_4]^{4+}$  complex were relatively inactive and nonselective for epoxidation. Preliminary XPS evidence indicated that the multiple metal-metal bond did not remain intact during the pretreatment, although bridged oxo species may have been formed which were not very active for epoxidation.



Cobalt Complexes in Zeolite-Y: Previous work in our laboratory has shown that reversible oxygen complexes of the type  $[\text{Co}^{\text{III}}\text{L}_n\text{O}_2^-]^{2+}$  may be formed in zeolites with a number of different ligands including  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $n\text{-CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$  and en.<sup>3</sup> These ligands, however, were subject to attack by the coordinated oxygen. This is an interesting problem in itself, but we wished to study more robust complexes so that the oxygen would react with other substrate molecules. Likewise, with more inert ligands the system could be used in a reversible cycle to separate oxygen from air. Nitrogen heterocycles including bipyridine (bpy) and terpyridine (terpy) were examined with these applications in view.

Bipyridine forms the  $[\text{Co}^{\text{II}}(\text{bpy})_3]^{2+}$  complex which is significant from a fundamental standpoint since it exhibited a spin-crossover from the low-spin to the high-spin state as the temperature was increased from 77 to 140 K. This is the first example of such a phenomenon existing in a zeolite. It is also important to note that the cobalt was totally complexed when a stoichiometric amount of bpy had been added to the zeolite.

Addition of terpyridine to the zeolite resulted in the formation of the  $[\text{Co}^{\text{II}}(\text{terpy})_2]^{2+}$  complex, but in this case only about 15% of the cobalt ions reacted. When bpy and terpy were simultaneously introduced into the zeolite the five-coordinate  $[\text{Co}^{\text{II}}(\text{bpy})(\text{terpy})]^{2+}$  complex was formed which is capable of reversibly coordinating oxygen as  $[\text{Co}^{\text{III}}(\text{bpy})(\text{terpy})\text{O}_2^-]^{2+}$ . Each of these complexes may be followed by observing their characteristic EPR spectra. No spectrum of the oxygen adduct was detected after evacuation of the gas phase for 5 min. at 25°C, and the spectrum of the  $[\text{Co}^{\text{II}}(\text{bpy})(\text{terpy})]^{2+}$  complex reappeared. The superoxo complex was stable in the presence of excess oxygen at temperatures up to 70°C, which may make it suitable for certain catalytic reactions.

From an evaluation of  $P_{\frac{1}{2}}$ , the  $O_2$  pressure at half-oxygenation, a stability constant of  $K_{O_2} = 1.7 \text{ torr}^{-1}$  at 298 K was determined. This may be compared with  $K_{O_2}$  values of  $0.53 \text{ torr}^{-1}$  for human hemoglobin A at 298 K in  $H_2O$  and  $0.0030 \text{ torr}^{-1}$  for  $Co(salen)^{2+}$  (salen = 1.6-bis(2'-hydroxyphenyl)-2,5-diaza-1,5-hexadiene) at 293 K in DMSO. The unusually large stability constant in the zeolite may result, in part, from the fact that  $K_{O_2}$  is determined from the gas phase pressure, not the actual concentration of  $O_2$  in the solvent. In water, for example, the concentration of  $O_2$  is considerably less than the concentration of  $O_2$  in the gas phase at the same pressure, but in the zeolite the  $O_2$  concentration at 298 K is essentially that of the gas phase. Moreover, during the formation of the complex the solvent may have to be displaced from the coordination site on the metal ion, but in the zeolite the oxygen framework does not interfere with the formation of the oxygen adduct.

#### LIST OF PUBLICATIONS

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### SCIENTIFIC PERSONNEL

1. Dr. Mark B. Ward - received Ph.D. while employed on project.
2. Dr. Koichi Mizuno
3. Dr. Seiichiro Imamura

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