DOE/ER/1

DOE/ER/13622--T2

DE92 040359

ANNUAL TECHNICAL PROGRESS REPORT FOR DOE.

Structure Sensitive Reactions Over Co, Fe and Mixed Metal
Clusters in Zeolites.

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Aug. 1, 1992

Received by OSTI

SEP 9 1992

A. Overview.

This annual technical progress report covers the last 3 years of our DOE research program. Three major areas of research will be discussed. Transient and steady state kinetic studies of structure sensitive reactions of cyclopropane ($c\text{-C}_3\text{H}_6$) and hydrogen over zeolites is the first area. Low level impurity Fe^{3+} ions in zeolites complicate interpretation of spectroscopic and catalytic studies of these systems. We focused our efforts on selectively substituting Fe^{3+} ions in the frameworks of various zeolites to understand their role in catalytic reactions such as with $c\text{-C}_3\text{H}_6$ and H_2 . These studies led to isomorphous substitution of other ions like B^{3+} and their use in isomerization of n-butenes to isobutylene. The third area of research involves the synthesis, characterization and catalysis of a new class of molecular sieve manganese oxide tunnel structure materials.

B. Transient and Steady State Kinetics of Cyclopropane Over Zeolites.

The primary focus of our DOE project was to study the role of metal clusters in zeolites in structure sensitive reactions of $c\text{-C}_3\text{H}_6$ and H_2 . Previous studies from our lab had shown the different size clusters of cobalt led to

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drastically different selectivities and turnover frequencies in such reactions as outlined in Scheme I:

The Co clusters had been studied with a battery of methods including chemisorption, transmission electron microscopy, spin echo nuclear magnetic resonance, ferromagnetic resonance, Rutherford backscattering, X-ray photoelectron spectroscopy and others. These studies were done with NaX zeolite due to its low acidity and to the ability to use microwave plasma decomposition of sorbed Co precursors in such large pore zeolites.

Steady state kinetic studies showed that turnover frequencies for isomerization to propylene were an order of magnitude lower than supported Co particles on silica, that hydrogenation occurred selectively when particle sizes grew to 10 Å size and that as Co particles migrated to the surface of the zeolite and sintered to 15 Å size that hydrogenolysis to a 1:1 mixture of methane to ethane occurred. Our proposed work involved the use of transient kinetic methods to investigate such reactions.

Transient kinetic studies have been done with a self

stirred flow reactor or continuously stirred tank reactor (CSTR) with a thin layer of catalyst with an on-line high resolution sector mass spectrometer detector. A gas sampling valve for selection of products to be stored and analyzed with off-line gas chromatography methods is also used. All experiments are done at 1 atm.

Initial studies with NaX zeolite¹ showed that some molecular H₂ could be encapsulated in the zeolite on exposure to H₂ at 1 atm and 37°C as shown in Fig. 1.

Fig. 1. TPD for H₂ Encapsulation in NaX (1.1 g), 15°C/min in Ar.

Fig. 2. Encapsulation for Exchanged NaX Zeolites.

Encapsulation is slow but complete after about 18 h. Note that the temperature maximum (T_M) increases as sorption time increases (20 min to 4 h to 18 h). This behavior is opposite to that found for chemisorption on metals and is due to encapsulation of H₂. Further studies with ion exchanged zeolites like Cs⁺, Ni²⁺ and Eu³⁺ (picked because their cation site locations in the zeolite were known from crystallographic studies) showed no encapsulation for the Eu³⁺ system. Eu³⁺ ions form Eu₄¹⁰⁺ complexes in the sodalite

cages of NaX and, therefore, the H_2 is trapped in sodalite cages.

Similar studies were done for NaA zeolite² and results of Figs. 3 and 4 show a similar encapsulation of H_2 .

however, in this case, 2 sites for encapsulation were observed, the lower T_M @ 90 $^{\circ}C$ being due to encapsulation in the supercages of NaA which are considerably smaller than in NaX and a higher T_M near 205 $^{\circ}C$ due to encapsulation in sodalite cages.

Cyclopropane, on the other hand, sorbs in NiNaX zeolite as shown by the temperature programmed desorption (TPD) data of Fig. 5; the T_M values decrease as time of sorption decrease (opposite to the encapsulation phenomena of Figs. 1-4). Isobars for sorption of $c\text{-C}_3\text{H}_6$ over different ion-exchanged zeolites are similar as shown in Fig. 6. These data suggest that cation size and charge have little effect and that most sorption must be controlled by interaction between $c\text{-C}_3\text{H}_6$ and the inner walls of NaX.

Fig. 5. Sorption of $c\text{-C}_3\text{H}_6$ in NiNaX at 40°C .

Fig. 6. Isobars for $c\text{-C}_3\text{H}_6$ Over Various Zeolites.

The data of Fig. 6 show that the equilibrium quantity adsorbed varies by more than two orders of magnitude as the temperature changes from 40°C to 240°C . This is quite different from chemisorption behavior, and argues against adsorption on specific sites such as cations. These data also suggest that the selectivity differences shown in Scheme I may be related to the composition of the reactant gases in the pores of the zeolite at various temperatures in addition to any structure sensitive effects.

TPD data for EuNaX (Fig. 7) show that the sorption of $c\text{-C}_3\text{H}_6$ is quite different than that of NaX (Fig. 5). In Fig. 7, the first peak is $c\text{-C}_3\text{H}_6$ and the second is C_3H_6 . The EuNaX acts as an isomerization catalyst due to Brönsted sites generated during dehydration of EuNaX.⁴ Na vapor has been used to poison these Brönsted sites and no ring opening of $c\text{-C}_3\text{H}_6$ occurs. Fourier transform infrared studies⁵ show a concomitant decrease of Brönsted acid sites and no change of Lewis sites. Lewis sites are, therefore, inactive.

Fig. 7. TPDs from Sorption of $c\text{-C}_3\text{H}_6$ Over EuNaX.

Fig. 8. Simulation of Sorption Response.

Enthalpies and entropies for sorption of $c\text{-C}_3\text{H}_6$ and C_3H_6 in Cs^+ and Ni^{2+} NaX zeolites have also been reported.⁶ The rates of intracrystalline mass transport and the equilibrium uptakes are strongly dependent on temperature. No reaction of $c\text{-C}_3\text{H}_6$ occurs except for NiNaX above 240°C where reduction of Ni^{2+} to Ni metal leads to hydrogenation and with further increase of temperature to 325°C to hydrogenolysis.⁷

Simulations of heat transfer effects⁸ show that temperature gradients are negligible if H_2 is used as a carrier gas as shown in Fig. 8. The $[\text{c-C}_3\text{H}_6]$ in H_2 has been limited to 0.005 mole fraction ($p = 3.8$ torr) here. Sorption of $c\text{-C}_3\text{H}_6$ does not occur with NaA due to the 4.2 Å pore size, however, sorption does occur with zeolite 5A.⁹ Further studies of entropies and enthalpies of sorption for $c\text{-C}_3\text{H}_6$ and C_3H_6 in all these systems have been done.¹⁰

These transient methods permit the use of a single sample of catalyst for characterization, sorption, and

reaction studies, including those in the transient regime or involving isotopes.¹¹ H₂ encapsulation at 1 atm involves the uptake of quantities on the order of 1 μ mol/g in NaX and these are successively reduced by the replacement of Na⁺ by Cs⁺, Ni²⁺ or Eu³⁺. Such methods are fast, have high sensitivity and have been discussed in the context of controlling selectivity in catalysis¹² and in their use in the area of zeolitic and layered materials.¹³

After unraveling the complexity of c-C₃H₆ reactions over zeolites and ion-exchanged zeolites, we have initiated similar studies with Co and Fe clusters in such systems. Some studies of metal clusters in zeolites have also been done in collaboration with W. M. H. Sachtler and coworkers.¹⁴ Transient and surface science methods have also been applied to the study of Rh/Al₂O₃ catalysts used to produce oxygenates from syn gas.¹⁵

C. Isomorphous Substitution in Zeolites.

Since Fe³⁺ ions are difficult to completely remove from zeolites, it is important to understand the potential role of Fe³⁺ impurity ions for clear interpretation of spectroscopic and catalytic studies of zeolites.¹⁶ Simulations of electron paramagnetic resonance data for Fe³⁺ ions substituted into ZSM-5 zeolites have shown that 3 major species can be identified; framework tetrahedral species, defect hydroxyl 4 coordinate species and octahedral iron oxide clusters¹⁷ as shown in Fig. 9. These three species were identified with a combination of EPR, FTIR,

Fig. 9. EPR Simulation of Fe^{3+} in ZSM-5 Zeolite.

———— Experimental.
 xxxxxxxx Theoretical.

luminescence, ion-exchange, X-ray powder diffraction and bulk analytical methods.

In addition, synthesis of ^{57}Fe labeled isomorphously substituted species in ZSM-5 show that at even at 0.40 weight % Fe^{3+} that three species exist as shown by methods mentioned above, Mössbauer and diffuse reflectance spectroscopy.¹⁸ The catalytic activity of these materials in olefin upgrading has also been studied in collaboration with researchers at Mobil.¹⁸ Methanation reactions have also been studied with these and similar catalysts.¹⁹

Isomorphous substitution of B^{3+} in gels of ZSM-5 with in situ characterization with luminescence methods have shown that the coordination environment of B^{3+} varies initially from trigonal to tetrahedral after nucleation.²⁰ Solid state magic angle nuclear magnetic resonance (MASNMR) data support these assignments of coordination environment.²⁰

These B^{3+} isomorphously substituted ZSM-5 and other zeolite systems have been studied as n-butene isomerization catalysts in collaboration with researchers at Texaco, Inc.

The reaction order for isobutylene (I) formation from n-butenes (B) is 1 and slow deactivation occurs via coke formation. A 2 step mechanism has been proposed; one step is the formation of I from B. The other step is the irreversible formation of polymeric species from B.

Catalytic data were simulated²¹ as shown in Fig. 10 and the data suggest that the order for polymer formation is closest to 3/2.

Fig. 10.

Simulation of Yield of I vs Total Conversion.

• Exp.; Δ 3/2 Order; o 1st Order; + 2nd Order in Polymer.

The use of luminescence to distinguish Brönsted and Lewis sites in such systems^{22,23} and to probe catalytic reactions²⁴ have been discussed. In addition, photogravimetric analysis methods have been developed to study stability in inorganic and catalytic materials.^{25,26}

D. New Catalytic Systems.

Characterization of Raney nickel catalysts treated with ultrasonic cavitation has been done. A small increase in surface area was observed for these deuteration catalysts due to cracking of the Raney nickel alloy during cavitation. Electron microscopy, X-ray photoelectron spectroscopy,

scanning Auger microscopy and BET methods were used to study these systems.²⁷

A final system that will be the focus of the attached renewal proposal is the synthesis, characterization and catalytic activity of a new family of molecular sieve manganese oxide materials. We have synthesized a 3 x 3 octahedral [MnO₆] tunnel structure analog of the mineral todorokite which has a 6.9 Å pore opening.²⁸ These materials have ion-exchange capacity, are thermally stable to 500°C, are crystalline, can sorb hydrocarbons, are unusual electrical conductors and possess acid sites.²⁹

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