STUDIES OF ZEOLITES

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This research program encompasses the synthesis and characterization of zeolite materials, their modification and testing for specific catalytic applications, and the study of properties of adsorbates on intracrystalline surfaces of zeolites. The objectives are: (1) to investigate basic physical and chemical properties of zeolites by analysis of contributing structural, electronic, and dynamical factors; and (2) to develop bifunctional shape-selective catalysts for direct Fischer-Tropsch synthesis of low molecular weight chemical feedstock hydrocarbons.

Description of Research Effort

Materials development has been focussed on new approaches to formulating catalysts in which shape-selective zeolites support ultrafine particles of the Group VIII metals, Fe, Co, Ru, and Rh, alone or in combination. Such bifunctional catalysts are very promising candidates for the selective hydrogenation of CO to low molecular weight hydrocarbons. Simultaneously, we are attempting to refine methods of characterizing such composite materials.

The following novel approach has been successfully demonstrated: (a) aluminoferrisilicate [AFS] materials having the crystal structure of ZSM-5 type zeolite were synthesized; (b) electron paramagnetic resonance (EPR) and electronic photoacoustic spectroscopy (EPAS) techniques were used to show that the Fe^{3+} ions are incorporated in both framework and non-framework locations in the zeolite lattice; (c) non-framework Fe^{3+} ions were reacted so as to precipitate "inclusion compounds" of the type $[Fe\ M(CN)_5(L)]$ in the zeolite, where M = Fe, Co, Ru; (d) EPAS was used to identify the "inclusion compounds" and describe the chemistry of the modification reactions; (e) the "inclusion compounds" were reduced in hydrogen at>400°C; (f) ferromagnetic resonance (FMR) spectroscopy was used to establish the formation of metallic particles in the reduced zeolite. Catalytic testing of these materials will follow.

The chemistry of formation of metal particles from metal-ammine complexes in large pore zeolites is also being investigated using EPAS, EPR, and FMR techniques.

Nuclear magnetic resonance (NMR) spectroscopy is being applied to study various aspects of structure and dynamics. For example, high resolution solid state ^{13}C NMR has been used to show an unusual consequence of the packing of template bases in the pore structure of ZSM-5 type zeolite. Nuclear spin relaxation measurements are being used to determine the diffusion dynamics of methanol in the shape-selective ZSM-5 type zeolite.

Future Research

We will explore methods for low temperature reduction of Fe^{3+} ions in AFS zeolites so as to produce metal particles in the 10A diameter range. High resolution electron microscopy, X-ray absorption spectroscopy, and magnetization methods will be among the additional techniques which will be employed for more extensive characterization of these materials. The

synthesis of AFS zeolites with different crystal structures will be attempted in an effort to extend the concepts demonstrated for the ZSM-5 type structure.

Testing of new metal/zeolite materials for catalytic activity and selectivity in Fischer-Tropsch conversions will be initiated.

The application of NMR methods for strucutral and diffusion studies will be extended. ^{27}Al and ^{29}Si NMR will be exploited, and direct methods of diffusion constant measurement will be attempted.