Highly Dispersed Metal Atoms in Zeolites

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I. Research Scope and Objectives

The purpose of our research project is to synthesize and characterize highly dispersed metal atoms and clusters in the pores of zeolite catalysts. These catalysts are characterized before, during and after reaction with CO/H_2 mixtures with several spectroscopic techniques including Mossbauer spectroscopy, surface analysis, extended X-ray absorption fine structure, electron paramagnetic resonance, magnetic susceptibility, electron microscopy and X-ray powder diffraction methods. The emphasis of these spectroscopic methods is to characterize the catalysts during reaction. The equipment has for the most part been modified for in-situ studies of these catalysts. By exploiting the unusual reaction medium provided by the zeolites a systematic study of the interrelationships between molecular structure and catalytic activity will be made. Our studies should contribute to a better understanding of the nature, distribution and role of active sites in zeolites and ultimately permit one to obtain selective catalysts.

II. Description of Research Effort

The preparation of highly dispersed zero-valent metal species in zeolite catalysts is becoming an increasingly important area of research as nonrenewable energy supplies are diminished. Our research deals with the use of iron-containing zeolites prepared by thermal, photochemical and metal atom vaporization procedures. The main goals of the research proposed here are to prepare and characterize new iron-containing zeolite catalysts and to test their selectivity, activity and stability in reaction with mixtures of CO and M_2.

We have just published a review[1] concerning the reduction of iron species in zeolite molecular sieves. Mossbauer spectroscopy has been of primary importance in the characterization of such materials. It is very difficult to prepare highly reduced and highly dispersed iron (O) species in zeolites. We have studied photoactivated $Fe(CO)_5$ zeolite catalysts, bimetallic iron-containing catalysts and organometallic (ferrocene) supported catalysts. These materials have been characterized with in-situ Mossbauer spectroscopic methods. Reduction with hydrogen at high temperature is necessary in order to prepare zero valent iron zeolite catalysts.

These materials have been studied as Fischer-Tropsch catalysts.[2] Transient pulse kinetic experiments with products being identified by mass spectrometry have been carried out. The kinetic experiments indicate that the surface species are dynamic and that bulk iron carbide species form on the surface of the zeolite particles. The product distribution is markedly influenced by the presence of other metals in addition to the iron. The development of carbide phases can be independently tracked by x-ray powder diffraction and Mossbauer spectroscopy. The number and type of active sites can be determined with the transient pulse experiments.

III. Future Research

The direction of our future research is to prepare highly dispersed zero-valent iron atoms or small clusters in zeolites. Other metals and bimetallic systems are also of interest. Much of our current effort will involve use of the metal atom vaporization method. Metal atom vaporization technique have an advantage over several other preparation procedures due to the high probability of the generation of atoms or small atom clusters. Our primary synthetic route will be the metal atom vaporization method.

New characterization procedures are presently being developed. Most of our work is now involved with the installation of a combined X-ray photoelectron spectroscopy, ion scattering, spectroscopy secondary ion mass spectrometry, Auger electron spectroscopy (XPS, ISS, SIMS, AES) system. A cell for gas and heat treatment of catalysts on a side chamber of the surface analysis instrument is also being organized. In addition, a treatment chamber for photolysis of these catalysts has also been added.

Once these new catalysts are prepared and characterized, they will be studied as Fischer-Tropsch and methanation catalysts. The transient pulse method and in-situ Mossbauer experiments will be used to further understand the mechanism of reaction of these materials.

IV. References

1. Suib, S. L.; McMahon, K. C.; Psaras, D. in Intrazeolite Chemistry, ACS Symposium Series, No. 218, (G. D. Stucky and F. G. Dwyer, eds.), 301-317, 1983.

2. Suib, S. L.; McMahon, K. C.; Tau, L. M.; Bennett, C. O., J. Phys. Chem., submitted.