

ZEOLITES; CHARACTERIZATION AND CATALYSES OF METHANOL CONVERSION

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Research Scope and Objectives

Our work is devoted to: a) understanding the mechanisms of the formation of crystalline zeolites from the gel phase, and b) characterizing the elementary reactions taking place on zeolites during conversion of methanol to selected hydrocarbons. Of special interest is the mechanism of the formation of the first carbon-carbon bond in these processes.

Description of Research Effort

ZSM-34 and Offretite are synthesized and characterized by standard physical probes such as thermogravimetry and FTIR, and by more recently developed techniques such as transient techniques in nuclear magnetic resonance. The process of calcination and decomposition of quaternary ammonium alkyl cations, used to template the zeolite cage, has been followed by DSC, TGA, and FTIR. Acidities of Lewis and Bronsted sites are followed by FTIR, monitoring the appearance of hydroxyl bands after pyridine absorption and desorption with temperature. Populations of charge compensating protons, after ammonium exchange and calcination, are monitored by proton NMR using spin counting. The proton spectra of the powdered solids is a convolution of contributions due to dipolar interactions, shielding anisotropies, and lifetime broadening. Recent results of selectively attacking the interactions responsible for these contributions vis pulse techniques in NMR have shown that there are three populations of protons in ammonium exchanged and calcined offretite, two localized pairs at 6 and 7 angstroms separation, and groups separated by more than 10 angstroms. ZSM-34 is found to be more selective for conversion of methanol to ethylene than offretite. This selectivity is correlated with high proton mobility, as inferred from NMR spectra, of protons on ZSM-34.

Future Research

The process of zeolite formation from the gel phase will be followed for offretite using ^{29}Si , ^{27}Al , and ^1H NMR. Of special interest is determining if silicon and aluminum transfer from the gel to the crystalline phases in a non-uniform manner, thus yielding crystals in which the Si/Al ratio varies within the crystals, thus yielding crystals in which Bronsted acidity does not have a fixed value, but is a variable within each crystal.

One possibility for the formation of the first carbon-carbon bond in methanol conversion is the formation of an aluminum alkyl. ^{13}C , ^{27}Al heteronuclear spin dynamics will be used as part of an effort to test this idea. The number of Lewis, Bronsted, and

surface hydroxyl sites will be quantified using ^{15}N NMR of pyridine adsorbed on the zeolite. These data will be correlated with reactivity and selectivity toward methanol conversion. The process of methanol conversion will be followed by NMR of ^{13}C during conversion at temperatures and pressures characteristic of the conversion process, i.e. 250°C and 2 atm, as well as by standard kinetic studies.