

High Temperature Decomposition and Reactivity of Bronsted Acid Sites in Zeolites

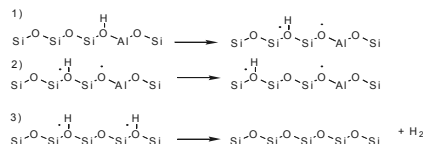
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Introduction

Zeolites are crystalline materials that have wide application in industry as solid acid catalyst. Their importance stem from the presence of microporosity, the high surface area and the tunable Bronsted acid sites (BAS) Si-OH-Al¹. The OH group in the BAS sites absorbs IR in the range of 3600-3660 cm⁻¹ in which its absorption intensity decreases until it disappears upon heating above 973 K². The dehydroxilation mechanism is believed to proceed via a dehydration path of the acid sites³. However, M. J. Nash⁴ et al recently reported that hydrogen is also formed during the dehydroxilation process. Moreover, the amount of hydrogen is related to the silica to alumina ratio. Using ZSM5 with silica to alumina ratios of 20 and 40, M. J. Nash⁴ et al showed that more hydrogen is produced in the first sample with some water but essentially hydrogen is produced from the second sample.

A new mechanism was proposed based on the new findings in which dehydrogenation by homolytic decomposition of BAS in addition to dehydration by heterolytic decomposition of BAS are the main paths to describe the dehydroxilation process (see scheme 1). Specifically hydrogen and [AlO₄]⁰ are formed by the dehydrogenation channel⁴. Which path is predominant depends on the silica to alumina ratio. At high silica to alumina ratio as in the case of ZSM5 homolytic decomposition pathway is the dominant one while at low ratio as in the case of zeolite Y dehydration mechanism is the dominant one.

We are pursuing several approaches to determine the structure of the sites formed upon dehydrogenation since the samples are ESR silent (which might indicate that the electrons are paired or delocalized within the surrounding oxygen atoms) and ²⁷Al NMR spectroscopy is unfeasible because an important fraction of the Al NMR signal becomes 'invisible' upon heating. In this report, we study the dehydroxilation process using Fourier transform infrared spectroscopy (FTIR) coupled with ²⁷Al NMR in order to investigate the extent of dehydroxilation and the fraction of tetrahedral versus trigonal (or other) aluminum atoms. Also the ability to reverse the decomposition of the BAS by adsorbing hydrogen on the thermally heated sample is investigated. Transient experiments using propane cracking as a reaction probe are conducted to study the contribution of redox chemistry on the product distribution of the cracking products.



Scheme 1: proposed dehydrogenation path

Materials and Methods

FTIR is employed to monitor in-situ the dehydroxilation process using different zeolite (H-MOR, H-ZSM5) samples with different silica to alumina ratio. The samples are heated under vacuum. To investigate the reversibility of the decomposed BAS, we exposed the zeolite samples to 3% of hydrogen in helium and the IR spectra are recorded. For propane transient experiments, we inject the propane through a GC pulse valve of 1 mL volume. The temperature of reaction is fixed at 436 °C. The sample activation temperature is changed using 480 °C for the fresh sample and 725 °C for dehydroxilated sample. The products are analyzed by mass spectrometry.

The zeolite samples in the H-form are prepared by ion exchanging the zeolite sample twice at 80 °C using 0.1 M solution of NH₃NO₃. The mordenite sample is obtained from Tricat Zeolites and the ZSM5 sample is prepared in our laboratory.

Results and Discussion

Preliminary results from our ongoing studies showed that the propane conversion for H-mordenite activated at 480 °C and 725 °C are similar but the products distributions are different. The sample activated at 480 °C produced more hydrogen than the sample activated at 725 °C by about 40%. In addition, we observed that the dehydroxilated sample after the propane reaction produced hydrogen when it was heated to 725 °C again which means that the sites are regeneratable. To confirm the dehydrogenation path, we monitored the weight loss upon heating the samples using thermal gravimetric analyzer (TGA) and we found out that weight loss can not be accounted for by only one of the proposed BAS decomposition paths (see table 1).

Table 1. TGA analysis of different zeolite samples

Zeolite	Actual wt loss (mg)	Theoretical wt loss if only H ₂ (mg)	Theoretical wt loss if only H ₂ O (mg)
MOR H ₂ O: Al ₂ O ₃ : 10SiO ₂	0.5426	0.2317	2.086
ZSM5 H ₂ O: Al ₂ O ₃ : 50SiO ₂	0.038	0.01	0.093
Zeolite Y H ₂ O: Al ₂ O ₃ : 5SiO ₂	0.2429	0.0964	0.867

Significance

This work will shed the light on the role of redox chemistry on the catalytic cracking mechanism which is important for fluid catalytic cracking (FCC) process.

References

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