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 stems from the presence of microporosity, the high surface area and the tunable Bronsted acid sites (BAS) Si–OH–Al. 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 K. The dehydroxilation mechanism is believed to proceed via a dehydration path of the acid sites. However, M. J. Nash 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. Nash 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 [AlO₂]⁺ are formed by the dehydrogenation channel. 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 unsuitable 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.

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 H-Mordenite activated at 480 °C for the fresh sample and 725 °C are similar but the products distributions are different. The sample activated at 480 °C using 0.1 M solution of NH₃ is fixed at 436 °C by about 40%. In addition, we observed that the dehydroxilated sample after the sample 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

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Actual wt loss (mg)</th>
<th>Theoretical wt loss if only H₂ (mg)</th>
<th>Theoretical wt loss if only H₂O (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOR H₂O: Al₂O₃: 10SiO₂</td>
<td>0.5426</td>
<td>0.2317</td>
<td>2.086</td>
</tr>
<tr>
<td>ZSM5 H₂O: Al₂O₃: 50SiO₂</td>
<td>0.038</td>
<td>0.01</td>
<td>0.093</td>
</tr>
<tr>
<td>Zeolite Y H₂O: Al₂O₃: 5SiO₂</td>
<td>0.2429</td>
<td>0.0964</td>
<td>0.867</td>
</tr>
</tbody>
</table>

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

Scheme 1: proposed dehydrogenation path

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Si₄O₁₂⁻Si₄O₁₂⁻H⁻⁺ \[→\] Si₄O₁₂⁻Si₄O₁₂⁻H⁺ + H₂
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1) Si₄O₁₂⁻Si₄O₁₂⁻H⁺ + H₂O → Si₄O₁₂⁻Si₄O₁₂⁻H⁺ + H₂ + H₂O
2) Si₄O₁₂⁻Si₄O₁₂⁻H⁺ + H₂O → Si₄O₁₂⁻Si₄O₁₂⁻H⁺ + H₂ + H₂O
3) Si₄O₁₂⁻Si₄O₁₂⁻H⁺ + H₂O → Si₄O₁₂⁻Si₄O₁₂⁻H⁺ + H₂ + H₂O

Scheme 1: proposed dehydrogenation path