NMR Studies of Structural Changes of Borosilicate Zeolites in the Process of Dehydration

Son-jong Hwang1*, C.Y. Chen2, and Stacey I. Zones2

1The Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125, USA.
2Chevron Texaco Energy Technology Co., Richmond, CA 94820, USA.

Introduction

Borosilicate zeolites have recently been studied in many aspects because they are useful in substitution of framework metal ions (to Al or Ga) and in catalyzing chemical reactions that uses relatively weak acid strength. Framework boron sites in zeolites are responsible for the weak acidity and they undergo drastic structural changes as the hydration level of the material changes. For example, the active O-B-O (H+) Si sites readily convert their coordinates to lower symmetry (trigonal geometry) upon dehydration. One and two dimensional $^1$H and $^{11}$B NMR methods have been used for investigating such geometrical changes at a number of different hydrated situations. A new trigonal site has been identified using high resolution techniques such as 2D MQMAS and 1D MAS spectra of at a higher field (830 MHz at NHMFL). $^1$H-$^1$B HETCOR NMR spectra showed improved picture of correlation between boron and hydroxyl protons, so that characterization of the weak acid site was better

$^1$H and $^{11}$B MAS NMR of B-beta

$^1$H and $^{11}$B MAS NMR of B-beta at a various level of hydration: (a) calcined and vacuum dried at 500°C, no history of exposition to moisture during and after evacuation; (b) calcined, sat for a year in closed vial; (c) after evacuation of (b) at room temperature; (d) after vacuum dry of (b) at 120°C; (e) after vacuum dry of (b) at 450°C.

$^1$H-$^1$B Correlation

1H and $^{11}$B NMR methods were effective in investigation of structural changes taking place around boron centers in the course of hydration/dehydration of B-zeolites.

Experimental

Borosilicate zeolites have recently been studied in many aspects because they are useful in substitution of framework metal ions (to Al or Ga) and in catalyzing chemical reactions that uses relatively weak acid strength. Framework boron sites in zeolites are responsible for the weak acidity and they undergo drastic structural changes as the hydration level of the material changes. For example, the active O-B-O (H+) Si sites readily convert their coordinates to lower symmetry (trigonal geometry) upon dehydration. One and two dimensional $^1$H and $^{11}$B NMR methods have been used for investigating such geometrical changes at a number of different hydrated situations. A new trigonal site has been identified using high resolution techniques such as 2D MQMAS and 1D MAS spectra of at a higher field (830 MHz at NHMFL). $^1$H-$^1$B HETCOR NMR spectra showed improved picture of correlation between boron and hydroxyl protons, so that characterization of the weak acid site was better

$^1$H and $^{11}$B MAS NMR of B-beta

$^1$H and $^{11}$B NMR methods were effective in investigation of structural changes taking place around boron centers in the course of hydration/dehydration of B-zeolites.

The spectroscopic evidence was found for the presence of B[3]* sites (see Fig. 3) that are formed as a result of replacing B-O-Si bond with B-OH. The formation of B[3]* is considered to be the first step of the boron extraction process out of the zeolite framework.

The B[3]* sites could be generated in large quantity when B-zeolites are stored in ambient atmosphere. The entities were found to be present even after dehydration treatments at temperatures greater than 500°C.

$^{11}$B NMR peaks that could be related to the formation of species like B[3]* or B[4]** were also observed (see Fig. 1 and 3).

$^{11}$B NMR Analysis of B-beta

$^1$H-$^1$B Correlation

$^1$H and $^{11}$B NMR methods were effective in investigation of structural changes taking place around boron centers in the course of hydration/dehydration of B-zeolites.

The spectroscopic evidence was found for the presence of B[3]* sites (see Fig. 3) that are formed as a result of replacing B-O-Si bond with B-OH. The formation of B[3]* is considered to be the first step of the boron extraction process out of the zeolite framework.

The B[3]* sites could be generated in large quantity when B-zeolites are stored in ambient atmosphere. The entities were found to be present even after dehydration treatments at temperatures greater than 500°C.

$^{11}$B NMR peaks that could be related to the formation of species like B[3]* or B[4]** were also observed (see Fig. 1 and 3).

$^{11}$B NMR peaks that were responsible for B-OH hydroxyl protons in B[3]* and the silanol group around B[3] (see the reaction scheme) were distinctively assigned (3.3 and 2.3 ppm, respectively) using $^{11}$H-$^{11}$B CPMAS and HETCOR NMR methods (see Fig 4). The 2.3 ppm peak could be attributed to the Brønsted acid proton.

Results and Discussion

1. $^1$H and $^{11}$B NMR methods were effective in investigation of structural changes taking place around boron centers in the course of hydration/dehydration of B-zeolites.

2. The spectroscopic evidence was found for the presence of B[3]* sites (see Fig. 3) that are formed as a result of replacing B-O-Si bond with B-OH. The formation of B[3]* is considered to be the first step of the boron extraction process out of the zeolite framework.

3. The B[3]* sites could be generated in large quantity when B-zeolites are stored in ambient atmosphere. The entities were found to be present even after dehydration treatments at temperatures greater than 500°C.

4. $^{11}$B NMR peaks that could be related to the formation of species like B[3]* or B[4]** were also observed (see Fig. 1 and 3).

5. $^{11}$B NMR peaks that were responsible for B-OH hydroxyl protons in B[3]* and the silanol group around B[3] (see the reaction scheme) were distinctively assigned (3.3 and 2.3 ppm, respectively) using $^{11}$H-$^{11}$B CPMAS and HETCOR NMR methods (see Fig 4). The 2.3 ppm peak could be attributed to the Brønsted acid proton.

Acknowledgements

We thank the ChevronTexaco Research Company for supporting this work. Acquiring of NMR spectra at 19.7 T was possible by help from Dr. Hyungtaik Kwek and Dr. Z. Gan at the NHMFL in Florida. Their support is greatly acknowledged. Helpful discussion from Professor Mark E. Davis at California Institute of Technology is also thanked. The NMR facility at Caltech was supported by the National Science Foundation under grant no. 9724240.

*Correspondence should be directed to Sonjong Hwang (sonjong@cheme.caltech.edu), 626-395-2323, http://www.che.caltech.edu/nmr