

Structural Changes of Zeolites in Hot Liquid Water

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Introduction

The development of processes for the production of fuels and chemicals from alternative resources is one of the great challenges of our society. Biomass is a particularly interesting resource because it is sustainable and CO₂-neutral. A major difference between biomass and fossil feedstocks is the high oxygen content in the former, which results in a rather low vapor pressure for many of its constituents. Therefore, liquid phase processes will probably play a major role in future biorefineries. Water is a likely solvent of choice because it readily dissolves considerable amounts of polar oxygenates from biomass. The availability of heterogeneous catalysts with sufficient stability for aqueous phase biomass conversion was identified as one of the key challenges for the development of economical processes for biofuel production [1]. Many heterogeneous catalysts that are commonly used in traditional refineries have a limited hydrothermal stability. Modifications of zeolites by steaming have been investigated in numerous publications [2]. However, relatively little is known about how the structure of zeolites is affected in liquid phase.

Materials and Methods

Zeolite Y was obtained from Zeolyst. For the stability studies, 1 g of the zeolite was suspended in 20 ml of the aqueous medium (pure water, 1 M acetic acid, 1 M glucose). The mixture was placed in pressure reactors and heated for 4 h under constant agitation. After cooling, the mixture was filtrated (0.2 µm Nylon filter) and the modified zeolite was washed with distilled water. ²⁷Al MAS NMR measurements were performed on a Bruker DSC 400 spectrometer with magic angle spinning at 12 kHz. The Resonance frequency for ²⁷Al was 104.2 MHz. A p/12 pulse was used for excitation and the recycling delay was 250 msec. ²⁹Si NMR measurements were performed on a Bruker DSX 300 spectrometer at a resonance frequency of 59.6 MHz for ²⁹Si. The samples were and spun at 5 kHz. The micropore volume was determined by physisorption of argon using the DFT method for analysis.

Results and Discussion

A Si/Al ratio of 13.6 was determined from the ²⁹Si MAS NMR spectrum of untreated zeolite Y (Figure 1). The ²⁷Al MAS NMR spectrum of the same sample contained a resonance at -1 ppm indicating that 9% of the Al nuclei were present in octahedral coordination (Figure 2a). These nuclei are located in extraframework positions. A micropore volume of 0.31 cm³g⁻¹ was determined, while the total pore volume was 0.49 cm³g⁻¹. Treatment with pure condensed water at 100 °C had a mild effect on the structure of zeolite Y. The micropore volume remained almost unchanged (0.32 cm³g⁻¹) but the ²⁷Al MAS NMR spectrum indicated that the concentration of extraframework aluminum (EFAI) increased to 21% (Figure 2b). The resonance corresponding to octahedrally coordinated Al was symmetric and narrow indicating a symmetric coordination sphere of the Al nuclei. Omega et al. assigned similar resonances to

Al species that are still partially connected to the zeolite framework [3]. The modifications of the zeolite were much stronger after treatment at 200 °C. A decrease of the micropore volume to 0.14 cm³g⁻¹ indicated significant modifications of the pore structure. Note that the total pore volume only decreased slightly to 0.45 cm³g⁻¹. Interestingly, hardly any octahedrally coordinated Al was present (Figure 2c). This shows that the Al nuclei, which are removed from the framework positions, are completely removed from the sample. In the ²⁹Si MAS NMR spectrum, a new peak was observed at -113 ppm (Figure 1). Note that this position is upfield from the resonance at -109 ppm (Si nuclei with four next-nearest Al neighbors). Typically, an upfield shift indicates a higher degree of condensation (fewer protons or Al nuclei as next-nearest neighbors). XRD analysis showed that no additional crystalline phase formed. Therefore, the formation of an amorphous silica alumina phase is suggested as a possible explanation for these observations. Initial experiments were performed with solutions of biomass molecules. In agreement with literature, the EFAI content increased in the presence of acetic acid (a primary component in pyrolysis oils), whereas glucose enhances leaching of EFAI species.

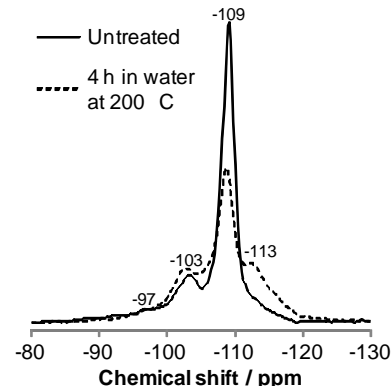


Figure 1. ²⁹Si MAS NMR spectra of zeolite Y before and after treatment in hot water

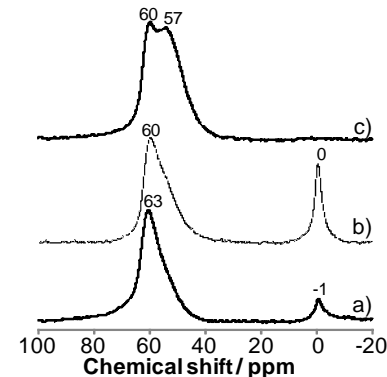


Figure 2. ²⁷Al MAS NMR spectra of zeolite Y: a) untreated, b) after treatment at 100 °C, c) after treatment at 200 °C

Significance

The development of heterogeneous catalysts with sufficient stability for biomass conversion is one of the great challenges for developing biorefinery technology. The present work aims to elucidate degradation mechanism of zeolites under typical conditions for biomass conversion so that synthesis strategies for materials with increased stability can be developed.

References

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