Acidity studies of zeolite β dealuminated in solid-state with AHFS

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Abstract

An acidity study of solid-state dealuminated zeolite β was performed to define types, amount and strength of acid sites.

Introduction

Solid-state dealumination with ammonium hexafluorosilicate (AHFS) is a remarkable technique capable of remove Al from zeolite framework and maintain, theoretically,intact zeolite structure and crystallinity by filling the remaining spaces with Si atoms. This process involves the formation of byproducts (including extra-framework Al – EFAL - species) that can be removed from zeolitic porous by washing procedure, leaving the active sites unblocked.[1]

Results and Discussion

Solid-state dealumination of NH_4-β (Zeolyst) was performed with AHFS (Aldrich) using different methods resulting in the following samples: BM3 (10% Al removal; dealumination reaction at 150 °C; presence of washing procedure); BM6 (70% Al removal; reaction at 190 °C; presence of washing procedure); and BM7 (70% Al removal; reaction at 190 °C; no washing procedure). All samples were calcined at 550 °C/ 8 h.

Adsorption of gaseous pyridine was performed in all materials to verify the types of acid sites by infrared spectroscopy. All samples presented both Brønsted and Lewis acid sites. However, BM7 showed a very small band of Lewis acid sites (at 1452 cm^{-1}) resulting in the highest value of Bronsted/Lewis ratio (12.8, when compared to 1.1, 1.6 and 1.7 for Hβ, BM3 and BM6, respectively). The absence of washing procedure might have caused the blockage of internal channels and porous in BM7 by several EFAL species created with dealumination. Thus, pyridine was not able to access those internal Lewis sites, but solely those in the pore entrance.

Liquid adsorption of pyridine was also performed and the amount of base adsorbed was plotted in Figures 1 and 2 for Hβ and BM6, respectively. In this preliminary study, only BM6 was chosen to this experiment because it presented an outstanding catalytic activity in previous work.[2]

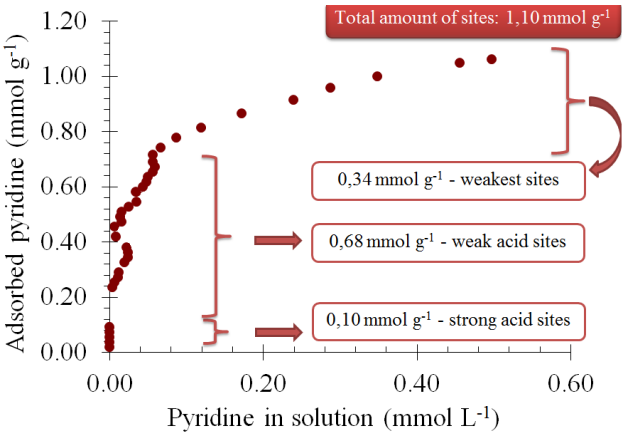

Figure 1. Amount of pyridine adsorbed on Hβ versus concentration of pyridine in solution.

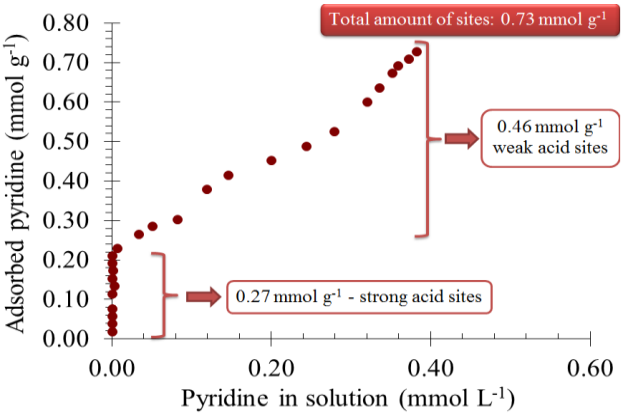

Figure 2. Amount of pyridine adsorbed on BM6 versus concentration of pyridine in solution.

Conclusions

Liquid adsorption of pyridine showed a decrease of the total amount of acid sites and an increase of quantity of strong acid sites after dealumination processes. Dealumination also seemed to create homogeneous weak acid sites since no significant changes were found in the slope of the adsorption curve.

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