Mildly Acidic Aluminosilicate Catalysts for Ethanol Dehydration

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Dehydration of (bio)alcohols is an important catalytic reaction in the biofuel sector.[1] Among the most studied catalyst for (bio)ethanol dehydration to (bio)ethylene is HZSM-5 zeolite. However this catalyst suffers from rapid deactivation due to extensive coking caused by high acid strength. Therefore many studies are devoted to the modification of HZSM-5 zeolite in order to improve its coking resistance.[2-4] Amorphous silica-alumina materials are envisaged as an alternative but they are usually not competitive due to low acidity and activity in comparison to zeolites.[5]

Herein we present synthesis, characterization, and catalytic application of highly homogeneous amorphous aluminosilicates with medium strength acid sites. These catalysts were prepared by non-hydrolytic sol-gel (NHSG) [6,7], an unconventional synthetic method. The dispersion of aluminum is very homogeneous (XPS, ToF-SIMS) within the mesoporous silicate matrix (N_2 physisorption). Catalysts are amorphous and possess high amount of medium strength acid sites (NH_3-TPD). Decisively, this NHSG preparation technique also allows for the direct and homogeneous incorporation of organic groups using organosilane precursors. Both aliphatic and aromatic as well as terminal and bridging groups were used (IR and SS NMR spectroscopy) with the intention to increase the hydrophobicity of the surface (H_2O physisorption) and thereby boosting the performance and stability of the catalysts during the dehydration reaction.

Catalysts prepared by NHSG showed activity significantly higher than commercial amorphous silica-alumina, thanks to high homogeneity of Al dispersion, but lower than HZSM-5, owing to their mild acidity (Figure 1, left). As a result, neither oligomerization of ethylene nor coking was observed with our materials unlike with HZSM-5. Catalysts were stable during 15 h TOS maintaining high selectivity to ethylene and did not exhibit any loss of surface area and number of acid sites in contrary to HZSM-5 (Figure 1, right).

The key parameter influencing the activity of catalysts was identified as number of Al atoms in the surface layer, which could be increased on purpose by delayed addition

of Al precursor into the sol-gel reaction mixture. Other factors such as the number and nature of incorporated organic groups played only minor role in tuning the catalytic activity, selectivity, and stability.

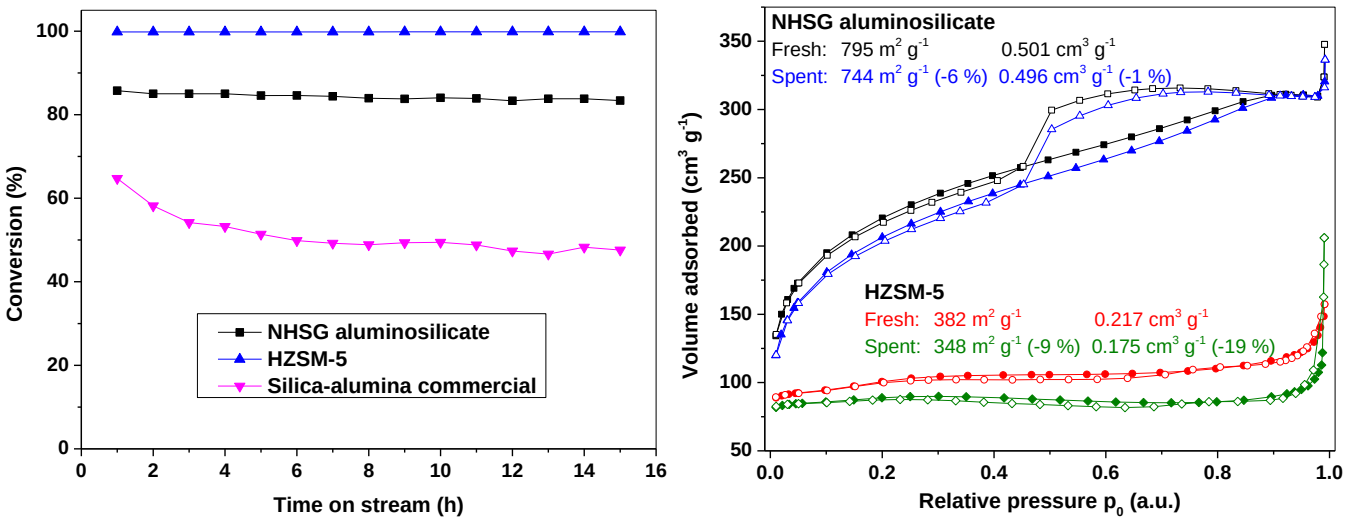

Figure 1: Conversion of tested catalysts with TOS = 15 h (left). N_2 physisorption isotherms of fresh and spent catalysts (right).

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