Title:

Ethanol Dehydration Over Hydrophobic Aluminum and Niobium Silicates: Influence of Homogeneity of Metal Mixing on Catalytic Activity and Stability of Si−C Bonds

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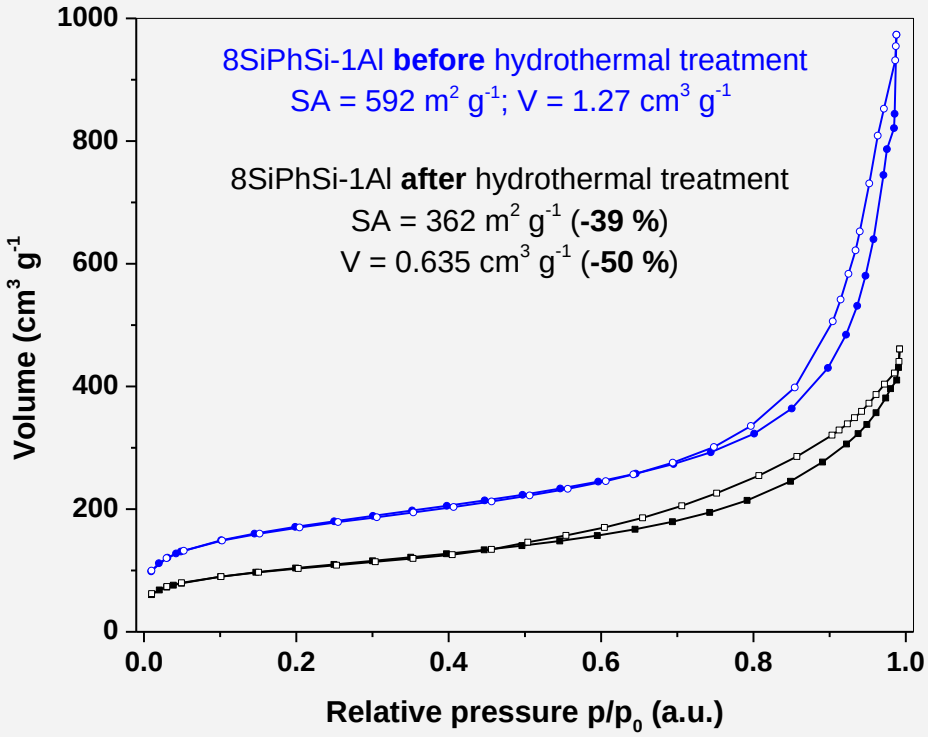
Abstract:

Hydrophobic silica materials have recently attracted considerable attention because of their superior properties, like for example hydrothermal stability.[1] Hydrophobic catalysts exhibited improved performance, when bulky organic molecules need to be transformed, while water should be repelled.[2-4] Most of those reports on the stability of hybrid materials are however conducted in batch reactors with hydrophobic silicas as catalyst supports, not as catalysts themselves. In gas phase phenylene silsesquioxane materials were shown to degrade at lower temperature, when the calcination proceeded in moist air atmosphere in comparison to dry atmosphere.[5] To the best of our knowledge, the gas phase stability and catalyst performance of hybrid metallosilicates, an important class of heterogeneous catalysts, have not been assessed yet.

Herein we report on the stability and catalytic activity of aluminum and niobium silicates hybridized with phenylene bridges in the gas phase dehydration of (bio)ethanol to (bio)ethylene. Highly porous hybrid metallosilicate catalysts were prepared by non-hydrolytic sol-gel technique.[6, 7] The introduction of organic groups took place during the polycondensation reactions, as verified by IR and MAS NMR. The homogeneity of active metal sites distribution was influenced by condensation route chosen, as studied by XPS and ToF-SIMS. Catalytic performance was evaluated in a fully-automated gas-phase fixed-bed micro-reactor. The (hydro)thermal stability was assessed by measuring weight loss (TGA), loss of surface area (see Figure), and extent of hydrolysis of Si−C bonds (IR, MS, GC). More homogeneous metal distribution provided samples with higher catalytic activity, however, the hydrothermal stability decreased abruptly. Hydrolysis of Si−C bonds was observed already at 200 °C. The hydrothermal stability was improved by applying precursors with Si−C(sp3) bonds. Based on the data acquired we conclude that the observed stability drop is due to the introduction of partial charges into the silica network by metals with low electronegativity thus making the metallosilicates prone to hydrolysis.



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