Ethanol dehydration over hybrid aluminosilicate catalysts prepared by non-hydrolytic sol-gel

Ales Styskalik[1], Lucie Leonova[1], Jiri Pinkas[1], Damien P. Debecker[2]

[1] Masaryk University, Department of Chemistry, Brno, Czech Republic, [2] Université Catholique de Louvain (UCLouvain), Institute of Condensed Matter and Nanosciences (IMCN), Louvain-La-Neuve, Belgium, (corresponding author: styskalik@chemi.muni.cz)

ABSTRACT:

The dehydration of (bio)ethanol to ethylene is an essential catalytic reaction in the perspective of the development of bio-based industry.[1] Traditional catalysts employed in this reaction are fully inorganic: alumina, silica-alumina, and HZSM-5.[2] Each of these systems come with their limitations: only moderate activity in the case of Al_2O_3 and silica-alumina, and rapid deactivation by coking in the case of zeolite catalysts. Recently, we have shown, that non-hydrolytic sol-gel (NHSG) provides highly homogeneous and porous aluminosilicate materials exhibiting superior activity and long-term stability in ethanol dehydration.[3] The ethylene selectivity was improved by one-pot incorporation of organic groups.[4]

In this follow-up study, the best performing NHSG-prepared aluminosilicate catalysts (fully inorganic) were post-synthetically modified by grafting with trimethysilyl groups. In such a way, the Brønsted acid sites (≡Si–O(H)···Al≡) were transformed into Lewis acid sites (≡Si–OSiMe$_3$ and Al≡). The number of reacted ≡Si–OH moieties and thus the trimethylsilyl groups loading and Brønsted/Lewis ratio was controlled via a temperature-vacuum pretreatment of aluminosilicate samples.

Structure, porosity, acidity, and hydrophobicity of NHSG-prepared catalysts were closely followed by MAS NMR studies, N_2 physisorption, IR-pyridine analyses, and water adsorption. Moreover, aluminosilicates were tested in a gas-phase fixed-bed catalytic reactor in ethanol dehydration. Lewis acid Al sites were found to exhibit a high ethylene selectivity even at relatively low temperatures (200–300 °C). These tailored NHSG-prepared aluminosilicate catalysts exhibited high ethylene productivities, markedly outperforming commercial silica-alumina.

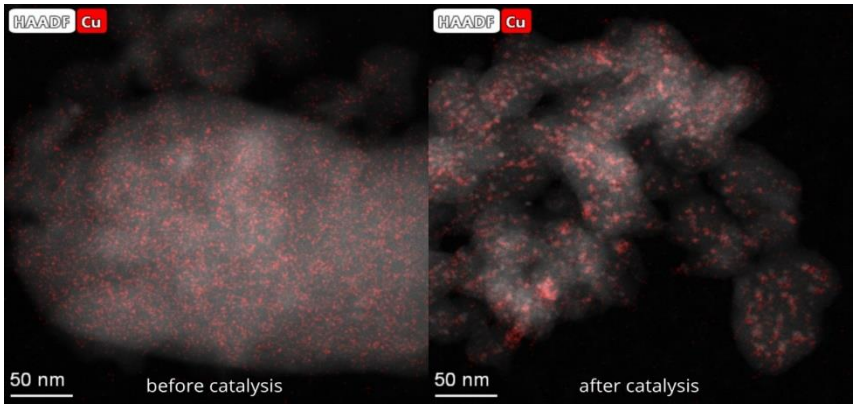

Figure 1: Sintering of Cu nanoparticles (red color) prepared by strong electrostatic impregnation during catalysis (STEM-EDS).

References

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