

# Ethanol dehydration over aluminosilicate catalysts prepared by non-hydrolytic sol-gel and aerosol-assisted sol-gel

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**Introduction.** The dehydration of (bio)ethanol to ethylene is an essential catalytic reaction in the perspective of the development of bio-based industry.<sup>1</sup> Traditional catalysts employed in this reaction are fully inorganic: alumina, silica-alumina, and HZSM-5.<sup>2</sup> Each of these systems come with their limitations: only moderate activity in the case of Al<sub>2</sub>O<sub>3</sub> 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.<sup>3</sup> Moreover, hybrid organic-inorganic materials based on metallosilicates (including aluminosilicates) exhibit better catalytic performance in various reactions when their surface is more hydrophobic.<sup>4</sup> Herein, a thorough and complex study was performed to evaluate the influence of acidity and hydrophobicity on catalytic performance of aluminosilicate materials in ethanol dehydration with the aim to further improve the catalytic performance of aluminosilicates prepared NHSG.

**Experimental/methodology.** In this study, the aluminosilicate catalysts were prepared by non-hydrolytic sol-gel (NHSG) either by acetamide elimination or alkylhalide elimination.<sup>5</sup> The non-aqueous condensations provided well-dispersed aluminum atoms (Si/Al = 16) in the porous silica structure. The introduction of organic groups into the structure was approached by two various synthetic strategies – either post-synthetic modification<sup>6</sup> or one-pot synthesis.<sup>7</sup> Structure, porosity, acidity, and hydrophobicity of NHSG-prepared catalysts, and the stability of organic groups were closely followed by MAS NMR studies, N<sub>2</sub> physisorption, IR-pyridine analyses, water adsorption, and TG/DSC, respectively. Finally, aluminosilicates were tested as heterogeneous catalysts in ethanol dehydration to ethylene.

**Results and discussion.** In the two-step synthesis the fully inorganic matrix was post-synthetically modified by grafting trimethylsilyl groups.<sup>6</sup> While porosity and structure of aluminosilicates after trimethylsilyl groups grafting were very similar to the parent material, the water sorption measurements showed that trimethylsilylated aluminosilicates adsorb 2.5–3 times less water ( $p/p_0 = 0.3$ ) in comparison to the parent aluminosilicate catalyst. The truly hydrophobic surface of these catalysts did influence the course of ethanol dehydration: The turn-over frequency scaled up with the number of trimethylsilyl groups grafted on the catalyst surface.<sup>6</sup>

In the one-pot synthesis, the methylsilyl groups were introduced and the water sorption measurements revealed that the hydrophilicity of both methylated samples and non-methylated samples were virtually identical.<sup>7</sup> The total number of acid sites did not change upon methylsilyl groups introduction. However, some Brønsted acid sites converted into Lewis acid sites upon methylation. In this case, acidity modulation played a pivotal role in ethanol dehydration. Ethanol conversion increased with the number of acid sites while higher Lewis acid sites content provided an increased selectivity to ethylene.<sup>7</sup>

In conclusion, this study discloses the differences between the one-pot and two-step organic groups introduction into the NHSG-prepared aluminosilicate catalysts. Moreover, it compares the impact of organic groups incorporated by diverse strategies on structure, acidity, and hydrophobicity of aluminosilicate catalysts and put it into the context of ethanol dehydration.

## References

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