Surface modified Ga-silicates catalysts prepared via the aerosol process

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Background. The production of biodiesel as an alternative to fossil fuels yields approximately 10wt% of glycerol as by-product. A promising route for its valorization is represented by the condensation of glycerol with acetone into solketal. A sustainable way to perform this reaction envisages the use of heterogeneous catalysts displaying both Brønsted and Lewis acid sites. Porous silicates presenting a metal inserted as single site in the framework can be active and selective catalysts for this reaction.[1]

Aim. In this work, the role played by the hydrophobic/ hydrophilic balance of the catalyst surface will be investigated. A series of Ga-silicate catalysts with different degrees of methylation were synthesized via the aerosol process and tested in the acetalization of glycerol with acetone to produce solketal.

Methods. Methyl-functionalized Ga-silicates were synthesized via the aerosol process from a mixture of TEOS and methyltriethoxysilane using $Ga(NO_3)_3$ as Ga precursor. Three degrees of functionalization have been selected: 5, 10 and 15 mol%. Pluronic® P123 or F127 was used as templating agent.

Results. The aerosol process allowed to synthesize a series of methylated Ga-silicates. The solids were characterized by N_2 physisorption, XRD, TEM and ICP-OES spectroscopy. The successful incorporation of Ga as single site within the silica framework was assessed via ^{71}Ga Solid State NMR and XPS spectroscopy. These mesoporous Ga-silicates showed excellent catalytic performance in the conversion of glycerol into solketal under solventless conditions and the best catalyst displayed outstanding turnover number and selectivity. A positive influence of the methylation on the performances the catalysts was observed. Furthermore, it was observed that even a very low degree of methylation was effective to enhance the catalytic performance of the materials.

Conclusion. A series of methylated Ga-silicates was successfully synthesized and tested in the valorization of glycerol. The best catalyst displayed high turnover number, evidencing the positive influence of surface functionalization. (Figure 1)

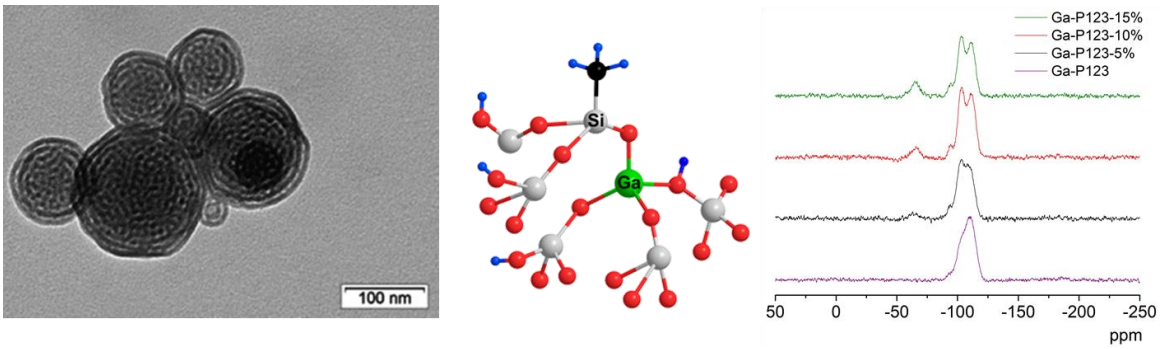

Figure 1: TEM micrograph of methylated Ga-silicate (left) and solid state magic angle spinning (MAS) ^{29}Si NMR spectra of the synthesized materials (right)

References A. Vivian, L. Fusaro, D. P. Debecker, C. Aprile, *ACS Sustain. Chem. Eng.* 6 (11) **2018**, 14095–14103.