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Catalytic conversion of glycerol into solketal with Ga-silicate nanoparticles prepared by aerosol process

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PURPOSE OF THE ABSTRACT

During the last decade, considerable attention has been devoted to the development of biofuels, above all biodiesel, as a promising alternative to fossil fuels. The transesterification reaction to produce biodiesel yields as by-product an amount of glycerol that represents approximately 10 wt % of the total biodiesel manufacture.[1] With the increasing biodiesel production, glycerol is now considered as a waste and its efficient and sustainable valorization have become a challenge for the scientific community. A promising route is represented by the condensation of glycerol with acetone to produce solketal, an added-value product with several applications such as surfactant, flavoring agent, safe solvent or in blend with biodiesel to improve its properties.[2] A sustainable way to perform this reaction envisages the use of heterogeneous catalysts displaying Brønsted and Lewis acidities. Porous silicates presenting a metal inserted as single site in the framework can be active and selective catalysts for this reaction. In particular, it has been already reported that Ga-MCM-41 nanoparticles are one of the most efficient catalysts in the conversion of glycerol into solketal.[3]

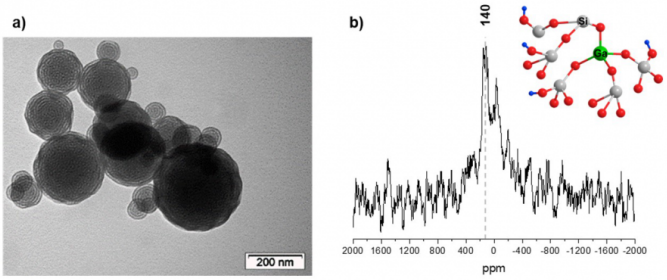
As reviewed recently,[4] aerosol processes have already been applied for the production of several metallosilicate materials exhibiting excellent catalytic performance in various chemical reactions.[5,6] In these preparation procedures, a precursors solution containing a texturing agent is sprayed and processed (dried) under mild temperature to rapidly trigger the inorganic polycondensation reactions, yielding materials with spherical shape, high homogeneity and tunable texture. The advantages of this process include: a limited number of steps, a limited waste generation and low environmental impact. Moreover, the catalyst preparation process can be scaled up easily and can be run in a continuous mode, making it industrially attractive.

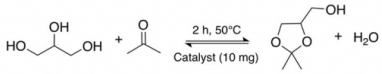
Here, the aerosol assisted sol-gel process was used as a powerful tool to synthesize silica-based solids with Ga inserted as single-site in the structure. The influence of different parameters on both morphological properties and catalytic activity were studied. Three different materials bearing a Si/Ga ratio of 34, 74 and 148 were synthesized and extensively characterized via N2 physisorption, XRD, TEM, ICP-OES spectroscopy, XPS and 29Si solid state NMR. All materials displayed promising features for catalytic applications such as high surface area (~ 400 m2/g), controlled mesoporosity and narrow particles size distribution. To investigate the coordination number/geometry of the metal center inserted as single site within the silica matrix, a deep structural investigation of the materials was performed via solid state NMR of 71Ga under magic angle spinning (MAS) or static conditions. The understanding and the quantification of the different species is of fundamental importance since it allows to strongly correlate the final properties of the solids with the metal coordination. The challenging study of quadrupolar 71Ga allowed to observe a signal with a maximum at around 140 ppm that can be assigned to a predominant contribution of tetrahedral gallium present as single site in the silica framework (see Figure 1).[7]

These aerosol-made mesoporous Ga-silicates showed excellent catalytic performance in the conversion of glycerol into solketal and in particular Ga-74 displayed the best turnover number and a very high selectivity (see Table 1). In order to further prove the stability of the solid under the selected reaction conditions, hot filtration tests

were performed, demonstrating the absence of leaching of active sites. Moreover, Ga-74 was successfully used in multiple catalytic cycles thus proving its stability under the selected reaction conditions.

FIGURES





Entry	Material	Si/Ga	Yield (%)	Sel. (%)	TON	Prod.
1	Ga-37	38	**30**	85	721	40
2	Ga-74	79	**28**	85	1353	37
3	Ga-148	160	**10**	79	974	15
4	Ga_2O_3	-	**0**	-	0	0

Si/Ga ratios determined by ICP-OES analysis; TON = $n_{solketal}/n_{Ga}$; Productivity = $m_{solketal}/m_{catalyst}$; Glycerol: Acetone = 1: 4 (mol)

FIGURE 1

Figure 1. a) TEM micrograph and b) solid state 71Ga MAS NMR spectrum of Ga-37 material

no legend

FIGURE 2

Table 1. Catalytic activity of Ga-silicates in the conversion of glycerol to solketal

no legend

KEYWORDS

glycerol valorization | spray drying | mesoporous materials | gallium

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