Hollow silica nanospheres as efficient catalysts for the acid-catalyzed upgrading of glycerol

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Introduction

Over the past decades, the synthesis of mesoporous silica-based materials bearing a metal cation inserted in the silica matrix was widely explored. These solids display a series of key features for catalytic applications as high specific surface area, tunable particle size, porosity and targeted architectures. Moreover, the eventual diffusion limitations can be decreased adjusting pore size and/or morphology. In the broad series of porous silicates, highly interesting structures are represented by hollow silica nanospheres and nanotubes. Very recently, the insertion of Sn and Hf as single site in the silica network of nanotubes allowed obtaining excellent catalytic performances for the conversion of glycerol into high added-value products.[1, 2] Glycerol, obtained as by-product of the biodiesel manufacturing, is a feedstock of high interest due to its large availability in the market.[3] It is also an attractive platform chemical that allow producing various molecules economically interesting. In particular, the catalytic production of cyclic acetals - such as solketal - via an acetalization reaction is one of the most relevant valorization pathways displaying a high atom economy (88% with only water as by-product) and a potential low E-factor.

In this work, a micelle templated sol-gel approach was employed to design both silica nanotubes and nanospheres embedding gallium as single site in their silica framework. Nanotubes (Ga-NT) and nanospheres (Ga-NS) were tested for the conversion of glycerol to solketal. In this context, a positive influence of the nanosphere structure was clearly evidenced. Furthermore, Ga-doped silica nanospheres were reused in multiple cycles thus proving the stability of the material under selected reaction conditions.

Materials and Methods

Ga-NS and Ga-NT were synthesized via micelle-templated sol-gel procedure, using TEOS as a silica precursor and $Ga(acac)_3$ as a metal precursor (theoretical Si/Sn ratio = 74). Pluronic F127 was used as a structure-directing agent. The solids were characterized by N_2 physisorption (Micromeritics ASAP 2420), TEM (Philips Tecnai 10 microscope operating at 80 kV), ICP-OES spectroscopy (Optima 8000 Spectrometer). ^{71}Ga solid-state NMR experiments were done on a Jeol ECZ-R 600 MHz spectrometer operating at 14.1 T using a 3.2 mm CP-MAS probe.

Results and Discussion

In this work the synthesis of hollow silica nanospheres bearing Ga inserted in the silica structure is reported for the first time. The solids were fully characterized via various techniques including TEM, N_2 physisorption, XPS (Table 1). ^{71}Ga solid state NMR was employed to investigate the isomorphic substitution of Si with Ga in the SiO_2 architecture.

Table 1. Textural properties of Ga-NS and Ga-NT

Sample	S_{BET} / m².g^{-1}	D_{BJH} / nm	V_p / mL.g^{-1}
Ga-NS	470	27	2.0
Ga-NT	600	22	2.3

The solids were tested as catalysts in the conversion of glycerol into solketal. The influence of different parameters including the effect of the calcination temperature (figure 1 left) was studied. As can be clearly observed in figure 1, the best catalytic performances were obtained with the material calcined at 550 °C, this behavior was ascribed to the ideal combination between the insertion of gallium in tetrahedral coordination (^{71}Ga NMR) and high specific surface area (N_2 physisorption). Moreover, the catalytic activity of the Ga-NS was compared with the one of the corresponding silica-based nanotubes displaying Ga inserted as single site (Ga-NT). Ga-NS displayed better catalytic performances than the parent Ga-NT and of other solids previously reported in literature. In addition, the absence of leaching of active species in solution was proved via hot-filtration experiments and the best catalyst resulted active in consecutive catalytic runs (figure 1 right).

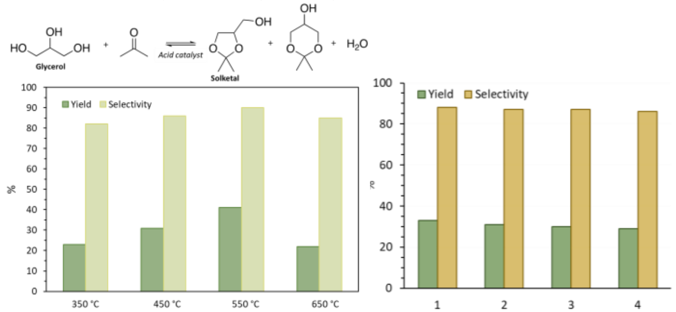

Figure 1. Yield of solketal influenced by the calcination temperature on Ga-NS (left). Recycle experiments performed on Ga-NS; conditions: 1 h, 50 °C, glycerol: acetone = 1: 4 (right).

Significance

Th synthesis of hollow silica nanospheres and silica nanotubes bearing Ga inserted in the silica structure are herein reported for the first time. The best catalyst (Ga-NS) displayed excellent catalytic performances in the conversion of glycerol in solketal exceeding the activity of other solids reported in the literature.

References

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