Novel Mesoporous Gallia/Silica Composites as Catalysts for the Selective Epoxidation of Alkenes with Hydrogen Peroxide

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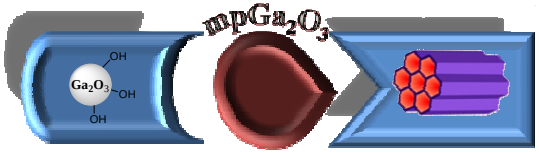
Introduction

Transition-metal-free oxides represent a recently discovered class of promising catalysts for the selective epoxidation of alkenes with the environmental benign hydrogen peroxide as oxidant [1]. Here, we present a new family of structured mesoporous solids consisting of gallium oxide nanoparticles ($mpGa_2O_3$) embedded in a silica matrix, and their application as epoxidation catalysts [2]. The results prove that these materials can successfully bridge the gap between Ga_2O_3 nanoparticles and MCM-41-like materials, coupling the benefits of particles in the nanoscale to their organisation in a mesoporous structure.



Experimental

Gallium oxide nanoparticles ($preGa_2O_3$) were synthesised via the hydrolytic condensation of $GaCl_3$ and characterised by TEM and DLS. A series of periodic mesoporous materials ($mpGa_2O_3$-x) was prepared by mixing different weight percentage of $preGa_2O_3$ (x, with 10%<x<100%) with tetraethylorthosilicate, in the presence of cetyltrimethylammonium bromide as structure directing agent. The reaction mixtures for the series of gallium oxide/silica composites with different Ga/Si ratio were prepared in less than 2 h and in a complete automated and reproducible way using a novel high-throughput approach. After the hydrothermal synthesis, the solids were calcined at 500°C and characterised by XRD, isothermal N_2 adsorption/desorption and TEM. The composites were tested as catalysts in the epoxidation of alkenes: 1 mmol of alkene, 2 mmol H_2O_2, 20 mg of catalyst, 1.3 ml ethyl acetate, 4h at 80 °C. Conversion and selectivity were determined by GC.

Results and Discussion

Characterisation by TEM and DLS indicates that the parent gallium oxide nanoparticles ($preGa_2O_3$) were successfully prepared with a very narrow particle size distribution from 1.5 to 3.0 nm. These nanoparticles were embedded and stabilised in a silica matrix by hydrothermal synthesis, using different ratios between gallium oxide and silica. The obtained series of mesoporous gallia/silica composites was characterised by TEM, XRD and isothermal N_2 adsorption/desorption, proving that the materials have a high surface area and narrow pore size distribution with a hexagonal ordering (MCM-41 like) for low Ga content, and a clear wormlike organization [3] for high loading of gallium oxide nanoparticles (Fig. 1).
The novel mesoporous gallia/silica composites were tested as catalysts in the epoxidation of cyclooctene with aqueous hydrogen peroxide. The materials with low relative amount of gallia display only moderate epoxidation activity, but starting from $mpGa_2O_3$-50 the alkene conversion increases with the concentration of the metal oxide reaching a maximum for $mpGa_2O_3$-90 (Fig. 1). High selectivity towards the epoxide product was achieved with all catalysts, reaching >95% with the most active materials. Remarkably, the epoxide yield over $mpGa_2O_3$-100 is much higher than that obtained with $preGa_2O_3$ nanoparticles, underlining the beneficial role of mesoscopic structuring on the catalytic properties of gallium oxides (Fig. 1). The scope of these novel catalysts was extended to the epoxidation of various alkenes.

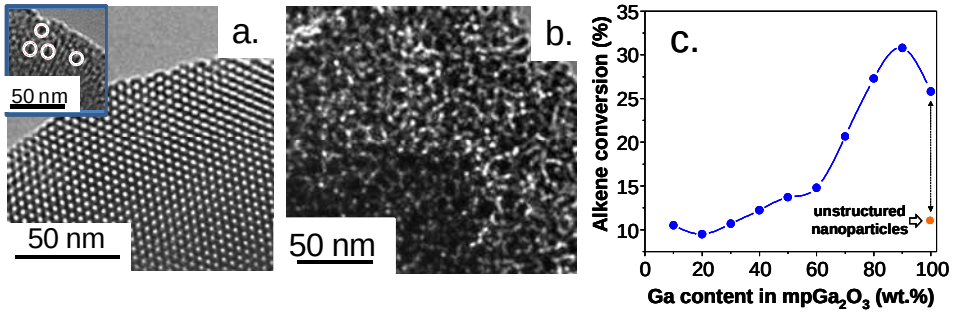


Figure 1. Selected TEM images of $mpGa_2O_3$-10 (a) $mpGa_2O_3$-90 (b) and catalytic epoxidation of cyclooctene (c) for the entire series of gallia/silica composites.

References.

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3. C. Aprile, L. Teruel, M. Alvaro, H. Garcia, *J. Am. Chem. Soc*, **131**, 1342 (2009).