# Supporting Information

## Experimental

High-Throughput Experimentation (HTE) was employed for the rapid and efficient synthesis of the gallia/silica composites and for their catalytic testing in the epoxidation of cyclooctene. The HTE samples were prepared using a Tecan Genesis RSP 100 liquid-handling robotic workstation coupled with a personal computer supplied with Gemini software for programming the workstation. Liquids were dispensed and transferred using two kinds of needles: fixed metal needles and disposable plastic needles suitable for handling viscous or contaminant liquids. The workstation was equipped with a reaction block from Stem/ProSense (RS-5000 Reacto Station, maximum working temperature of 150$^o$C), enabling heating and individual magnetic stirring of 50 samples in parallel reaction vessels. The used vessels were either in-house developed stainless-steel autoclaves (working volume: 11 ml), for the synthesis of the materials, or glass vials for the catalytic testing. The low-angle powder X-ray diffraction (XRD) patterns of the samples were recorded on a STOE STADI MP diffractometer operating in Debye-Scherrer geometry using CuK$\alpha_1$ radiation with a wavelength of 1.54056 Å selected by a curved Ge(111) monochromator. Measurements were carried out between 2$\theta$ values of 0.5 and 10° ($\Delta 2\theta = 0.01°$) using a 6° linear position sensitive detector. Dynamic Light Scattering (DLS) was measured on Brookhaven 90plus particle size analyzer. Transmission electron microscopy images were taken using a Philips CM 200 FEG with an operating voltage of at 200kV. Isothermal $N_2$ gas sorption experiments were performed in Micrometrics ASAP 2000 equipment after outgassing the samples at 400$^o$C under reduced pressure until constant weight.

Synthesis of Gallium Oxide nanoparticles (pre$Ga_2O_3$):

Gallium chloride (1.030 g, 5.85 mmol) was dissolved in a 2:3 mixture of ethylene glycol: water (15 ml) and the stirred solution was basified by dropwise addition of NaOH 1M until pH=10. After stirring for 2 h, the white solution was transferred into a Teflon-lined autoclave up to 80% volume occupancy and then treated at 120$^o$C for 4 h. After cooling to room temperature naturally, the product was separated from the solution by repeated centrifugation followed by washing with ethanol and water. The resulting white powder was dried and characterized by DLS and by wide and low-angle XRD.

General synthesis of mp$Ga_2O_3$ materials:

In all the series of gallia/silica composites, the molar ratio of the materials was: 1.00X : 0.12 CTAB : 8.0 $NH_3$(aq., 28%) : 114 $H_2O$, where X corresponds to the sum of the Ga and Si atoms. In a typical procedure, a templating solution containing cetyltrimethylammonium bromide (CTAB) was prepared by adding CTAB to a solution of $NH_4OH$ and deionized water followed by stirring at room temperature for 30 min in a closed polyethylene bottle to form a homogeneous solution. The pre$Ga_2O_3$ nanoparticles (700 mg) were suspended in ethanol (15.5 ml). The suspension was sonicated for 30 min and then kept under continuous stirring. Tetraethylorthosilicate (TEOS) was diluted with absolute ethanol shortly before its addition, to prevent eventual hydrolysis and condensation. The two precursor solutions and the suspension were placed in the liquid-handling robotic workstation while being stirred and the synthesis was performed in a completely automated way. The templating solution was added using the fixed metal needles. After the addition the temperature was increased to 45$^o$C. The pre$Ga_2O_3$ suspension and the TEOS solution were sequentially added to each sample, while stirring, using the disposable plastic needles by means of a tailored protocol: an aliquot of the solution and an aliquot of the suspension were aspirated almost simultaneously with two separated needles and rapidly dispensed into the autoclave with a very short delay between the dispensing of the two aliquots. This operation was repeated four times waiting 10 minutes between two successive additions. This protocol was developed to maximize the formation of a homogeneous reaction mixture, which is expected to lead to a final material with a homogeneous distribution of gallium and silicon. After closing the autoclaves, the prepared mixtures were stirred at 45$^o$C for 2 h and then put into an oven at 100$^o$C for 4 days under static conditions. The solid obtained was washed thoroughly with water and ethanol and dried at 100 °C for 2 h. The structure-directing agent was removed by calcination using the following temperature program: from room temperature to 500°C with a heating rate of 3°C·min$^{-1}$, 500°C for 10 h. Initially the oven was purged with $N_2$ and after the first 3 h the flow was gradually replaced with air to complete surfactant combustion.

Catalytic test:

A solution containing *cis*-cyclooctene (1 mmol), di-n-butyl ether (0.5 mmol) and ethyl acetate (1308 µl) was added to the each sample of the series of mp$Ga_2O_3$-x (20 mg of catalyst). Then, hydrogen peroxide (2 mmol, *i.e.* 114 µl of a 50wt.% aqueous solution) was added. Both solutions were dispensed using the HTE workstation. The reaction mixtures were stirred for 4 h at 1200 rpm and 80$^{o}$C in capped glass vials placed in the 50-wells reaction block. The rubber septa of the caps were pierced with a sharp needle to prevent the development of an overpressure in the reactors during the catalytic test. After the reaction, the samples were centrifuged and the cyclooctene conversions and yields were determined by gas chromatography (GC) on a Trace GC Ultra from Interscience (RTX-5 column, 5 m, 0.1 mm). The samples for GC analysis were prepared by adding 0.4 ml of each solution and 0.3 ml of decane. A short analysis time for each sample (2.40 min) was made possible by the rapid heating and cooling system of the column (Ultra Fast Module). The temperature profile during the analysis was as follows: 45 s at 70$^{o}$C, 70 to 250$^{o}$C at 180$^{o}$C·min$^{-1}$, 30 s at 250$^{o}$C. The conversions and yields were calculated by GC analysis using di-n-butyl ether as internal standard.

# Figures

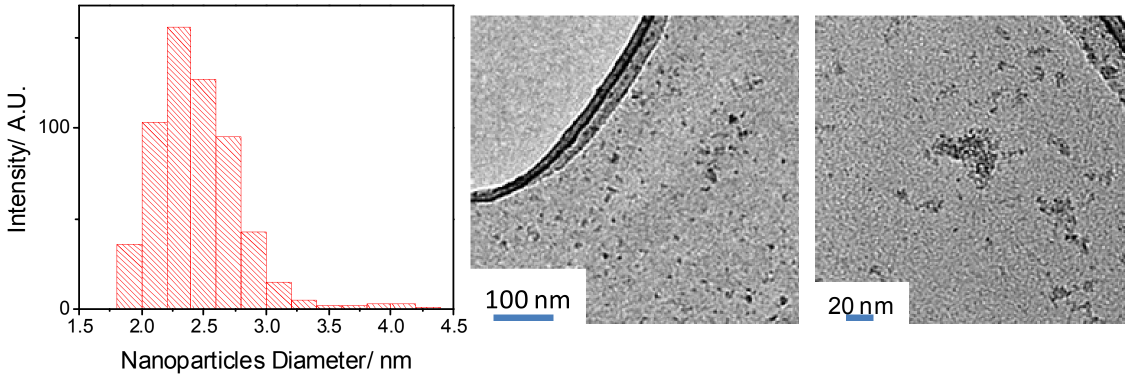

Figure S1. DLS particles size distribution (left) and TEM pictures (right) of pre$Ga_2O_3$.

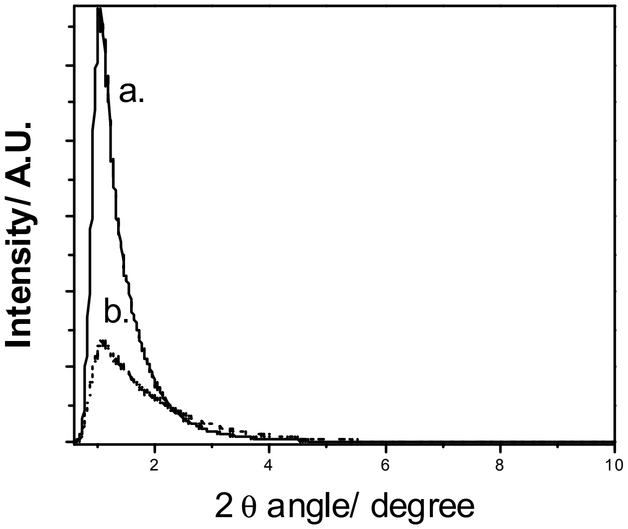

Figure S2. Low-angle XRD pattern of mp$Ga_2O_3$-90(a) and pre$Ga_2O_3$ nanoparticles (b).

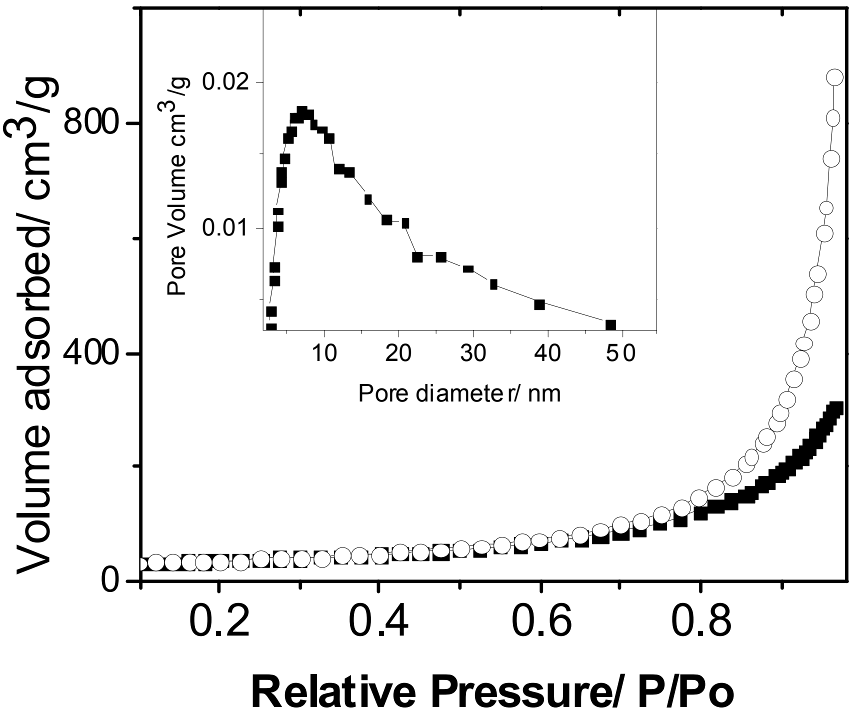

Figure S3. Isothermal $N_2$ adsorption/desorption plots of pre$Ga_2O_3$ nanoparticles. The insets show the broad pore size distribution.

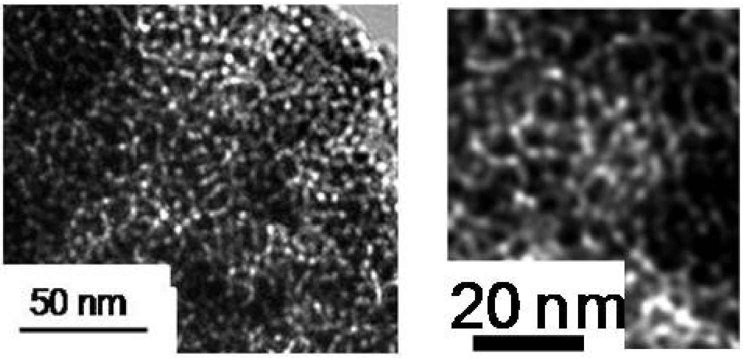

Figure S4. Selected TEM images of mp$Ga_2O_3$-50.

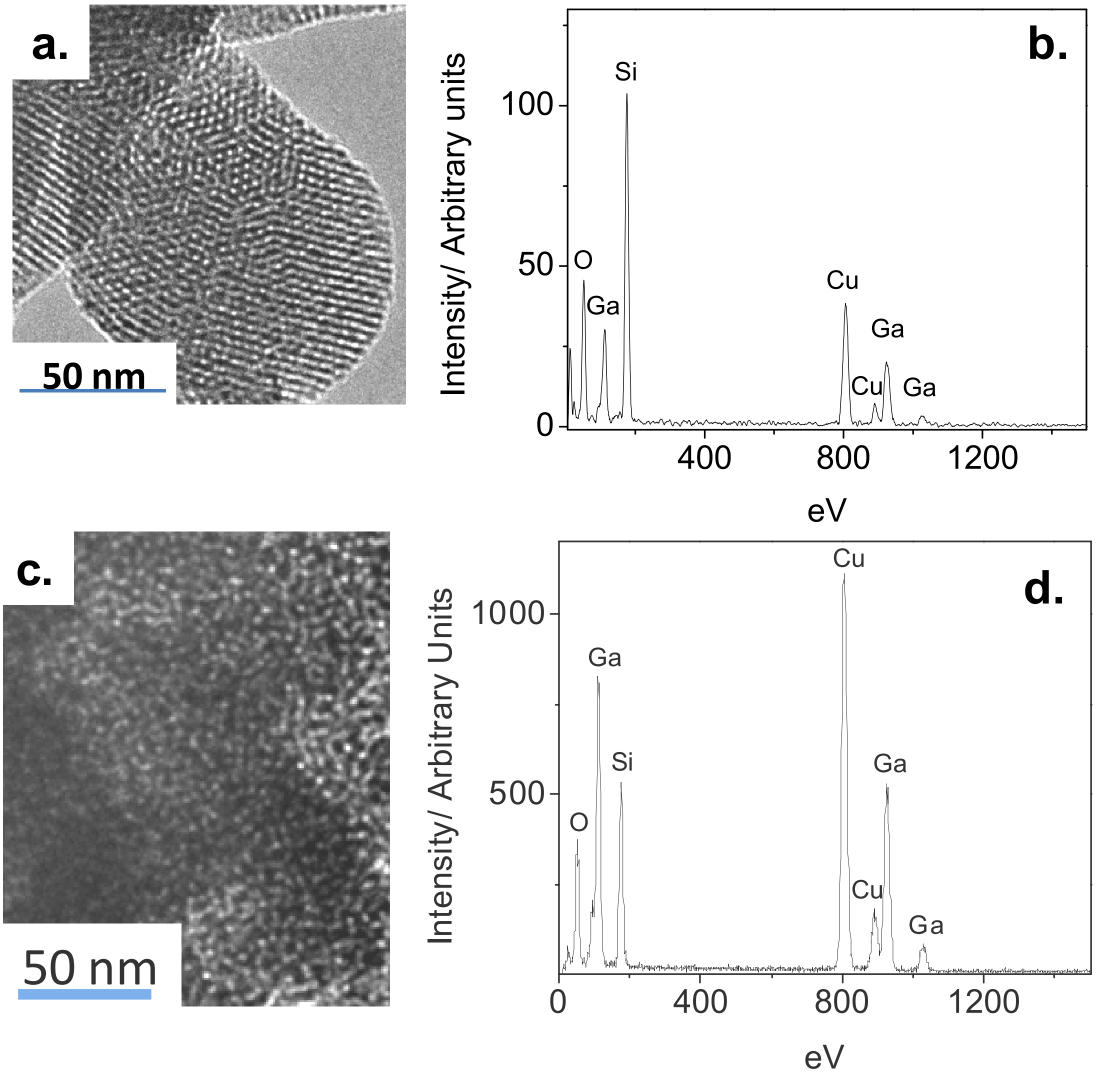

Figure S5. Energy Dispersive X-ray (EDX) spectroscopy measurements (figures b and d) performed on different regions of mp$Ga_2O_3$-10 (a) and mp$Ga_2O_3$-50 (c), proving the homogeneous distribution of gallia and silica in the materials. The presence of Cu is due to the chemical composition of the TEM grid.

Table S1. Epoxidation of cyclooctene for the library of mesoporous gallia/silica composites and gallium oxide nanoparticles.

| **Material** | **Cyclooctene Conversion [%]** | **Selectivity [%]** | **TON [$\mathrm{mol_{alkene\ converted}/mol_{Ga}}$]** |
|---|---|---|---|
| mp$Ga_2O_3$-10 | 10.5 | 79.4 | 4.92 |
| mp$Ga_2O_3$-20 | 9.5 | 93.5 | 2.23 |
| mp$Ga_2O_3$-30 | 10.7 | 91.3 | 1.66 |
| mp$Ga_2O_3$-40 | 12.2 | 89.6 | 1.14 |
| mp$Ga_2O_3$-50 | 13.7 | 85.0 | 1.28 |
| mp$Ga_2O_3$-60 | 14.8 | 86.9 | 1.16 |
| mp$Ga_2O_3$-70 | 20.7 | 90.7 | 1.38 |
| mp$Ga_2O_3$-80 | 27.2 | 92.1 | 1.60 |
| mp$Ga_2O_3$-90 | 30.8 | 95.2 | 1.60 |
| mp$Ga_2O_3$-100 | 25.8 | 95.6 | 1.21 |
| pre$Ga_2O_3$ | 11.2 | 85.0 | 0.35 |

Note: When considering the TON data, it should be kept in mind that these values are calculated on the basis of the total Ga content, while only a fraction of these atoms is expected to be able to act as catalytic sites for the epoxidation.[S1] Therefore, these TON are useful for comparison among the catalysts presented here or with related systems but are not suitable for comparison with heterogeneous catalysts of different nature.

---

[S1] Rinaldi R., Fujiwara F.Y., Hölderich W., Schuchardt U., *J. Catal.*, **2006**, *244*, 92-101.

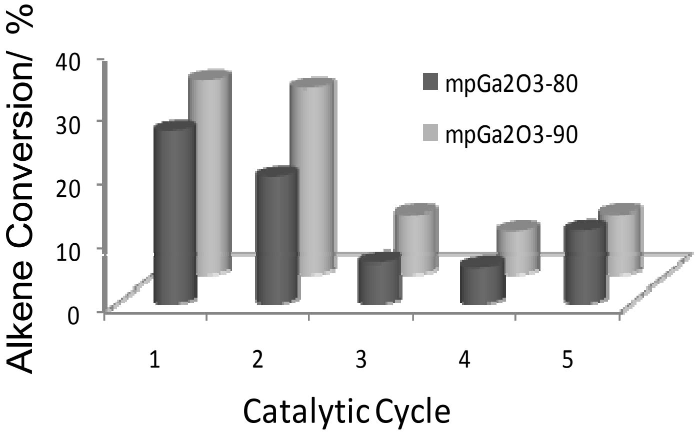

Figure S6. Catalytic epoxidation of cyclooctene after the first (1), second (2), third (3), fourth (4) and fifth (5) use.

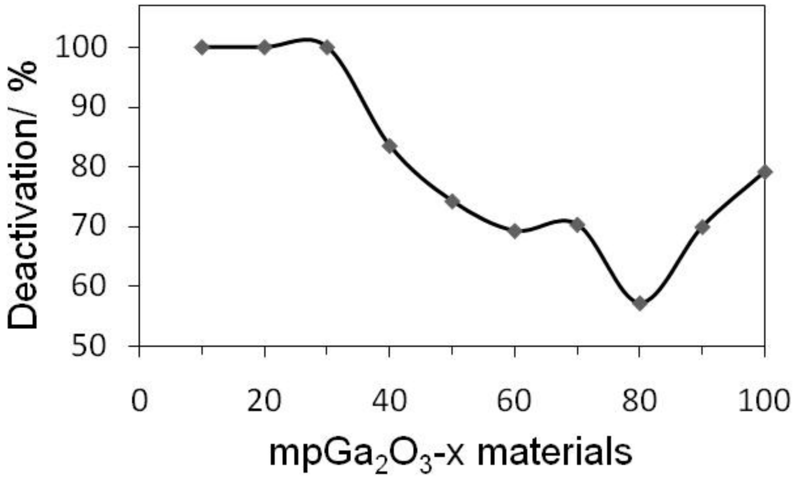

Figure S7. Deactivation of the series of mpG$_2$O$_3$-materials between the 1st and the 5th run in the epoxidation of cyclooctene (the materials were calcined at 300°C only before the last run).