

Supporting Information for

Epoxidation of alkenes through oxygen activation over a bifunctional CuO/Al₂O₃ catalyst

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Experimental Section

CuO/Al₂O₃ was prepared by the chemisorption-hydrolysis technique (CH). First the support (Al₂O₃, SSA = 140 m²/g; PV = 0.55 mL/g) was added to a basic solution of [Cu(NH₃)₄]²⁺. After 20 min under stirring the mixture was transferred in a flask held in an ice bath and slowly diluted with water. Finally the solid was filtered, dried overnight at 100 °C and calcined at 350 °C for 4 h in air. The copper loading, measured by ICP-AES, after acid digestion of the sample, was 7.6 wt%. CuO/SiO₂ was prepared with the same technique and the a copper loading was 8.5 wt%.

Catalyst pre-treatment consisted on dehydration at 270 °C (20 min in air and 20 min in vacuum).

The reactions were performed at 100 °C and under stirring (1250 rpm) in a 100 mL glass flask operating at atmospheric pressure, without the use of radical initiators. In particular the one-pot epoxidation was carried out by bubbling molecular oxygen (30-35 mL/min), in the presence of cumene as both solvent and reactant (20 ml), olefin 10 mmol (*trans*-stilbene = 1.8 g, *trans*- β -methylstyrene = 1.2 g, *cis*-cyclooctene = 1.1 g), and catalyst (250 mg). The reaction of oxidation of cumene was performed under the same conditions, but without adding the olefinic compound. Finally, the simple epoxidation of *trans*-stilbene was carried out in the presence of N₂ instead of O₂, the alkene (10 mmol) and by adding further amount of CHP (5 ml, 80 wt%). All the products were analysed by GC-MS and ¹H-NMR. The reactions condition were then improved by using 50 mg of the catalyst and 20 ml of cumene or 5 ml of cumene and 5 ml of toluene, with the same amount of the olefin.

For the recycle tests the catalyst was recovered, dried, weighted and dehydrated at 270 °C. Reactants were dosed on the base of the weight of the recovered catalyst, TOF were calculated on the basis of the total Cu content in the recovered catalyst.

Epoxidation of *trans*-stilbene using CHP

Figure S1 shows how the epoxidation reaction requires the co-presence of $\text{CuO}/\text{Al}_2\text{O}_3$ catalyst and CHP. Once the first 5 ml of CHP (80 wt%) are added to the reaction mixture ($t=0$ h) the conversion of stilbene increases up to 25% ($t=4$ h). After 4 h CHP is totally consumed (see $^1\text{H NMR}$) and in fact the conversion does not increase again until a new addition of 5 ml of CHP ($t=6$ h), where the reaction starts again with the same rate, then stabilises for the CHP consumption.

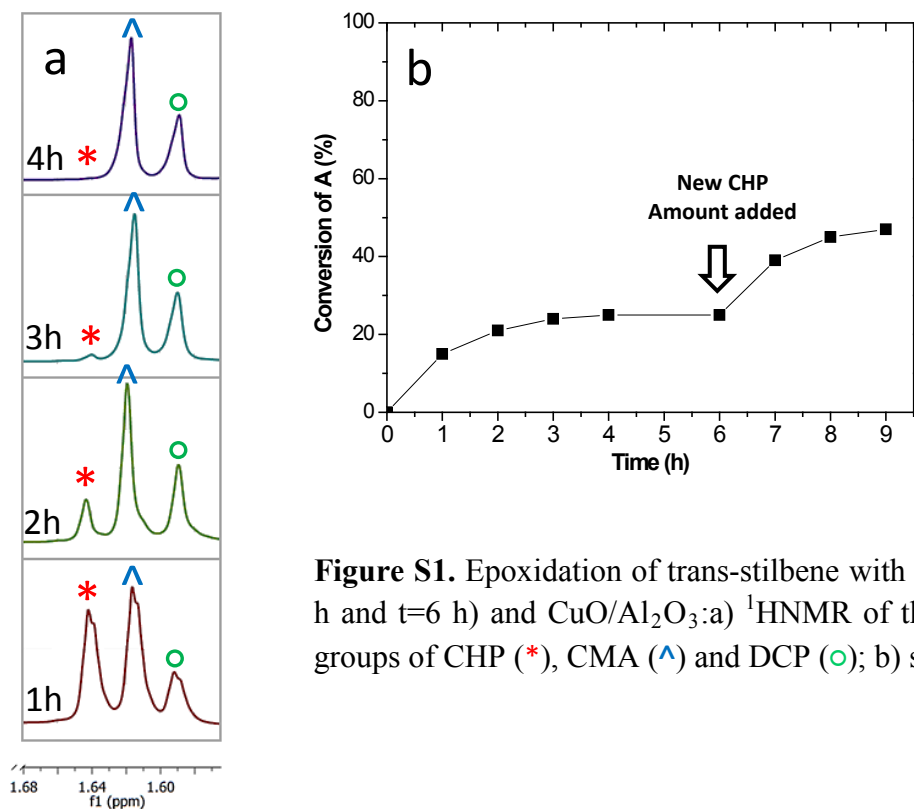


Figure S1. Epoxidation of *trans*-stilbene with CHP (two addition: $t=0$ h and $t=6$ h) and $\text{CuO}/\text{Al}_2\text{O}_3$; a) $^1\text{H NMR}$ of the region of the methyl groups of CHP (*), CMA (^) and DCP (o); b) stilbene conversion (■).

Recycling Tests

Figure S2 shows the reaction profiles of the recycle experiments. The catalyst can be successfully reused for at least three times, without a substantial decrease in *trans*-stilbene conversion and epoxide selectivity. The SAs (Specific Activity, $\text{mol}_{\text{conv}}/(\text{g}_{\text{Cu}}\cdot\text{h})$) were calculated after 4 h of reaction and show even a slight increase. The small amount of copper leached each reaction (4-7 wt% of the copper loading) and the partial aggregation of the copper phase (Figure S3 and Figure 3), highlighted by HRTEM, do not affect significantly the catalytic activity of the investigated material.

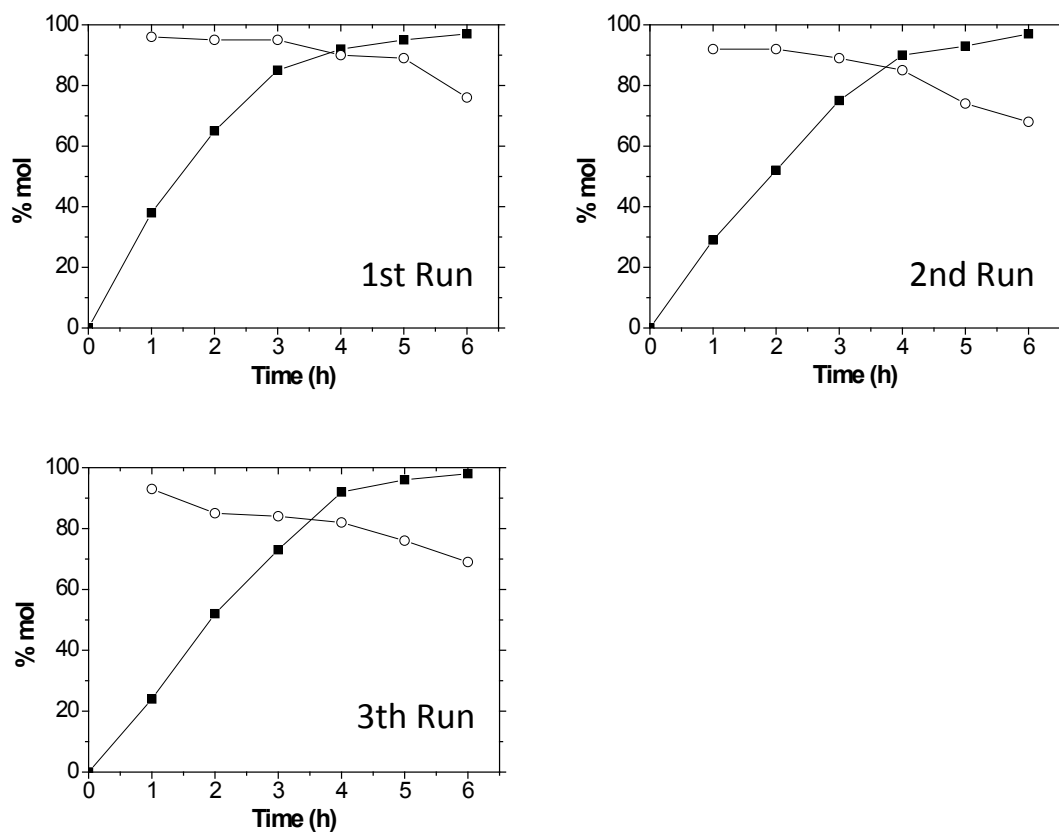


Figure S2. Recycling tests of CuO/Al₂O₃ catalysts: ■ = conversion of stilbene, ○ = selectivity to stilbene oxide.

Full histogram of recycled CuO/Al₂O₃

Figure S3 shows the full histogram of the CuO/Al₂O₃ after three catalytic runs. This figure reports also the fraction of the copper particles that underwent the low and partial aggregation.

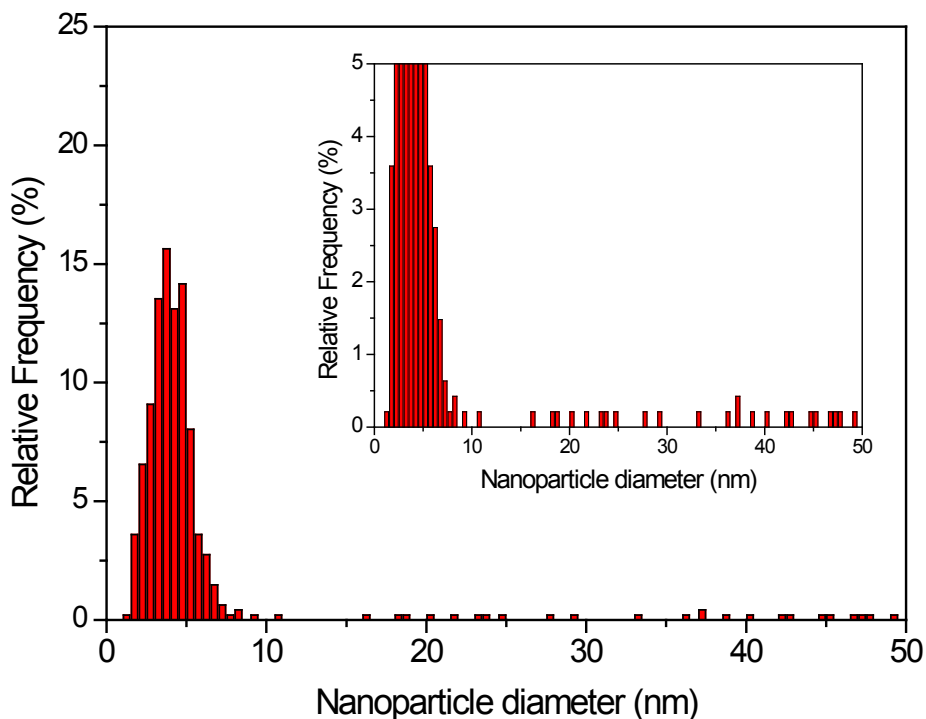


Figure S3. Histogram of the particle size distribution of CuO/Al₂O₃ recovered after three catalytic runs including particles with diameter > 10 nm. The inset reports the expansion that highlight the copper crystallites with an increased size.

Homogeneous reaction and Sheldon test

Figure S4 shows the comparison between CuO/Al₂O₃ (250 mg, 0.30 mmol) and homogenous Cu(acac)₂ (80 mg, 0.30 mmol). The epoxidation of stilbene occurs also using a homogeneous catalyst, but the reaction profiles is practically the same of that obtained with the heterogeneous CuO/Al₂O₃. However, in the case of CuO/Al₂O₃ we observed just a 4% of leached copper after 6 h of reaction, that alone cannot be accountable for the high activity of the system, that proceeds with the same rate of the homogenous one. The Sheldon Test (Figure S5) shows that, after the hot filtration of the catalyst, the mixture is still active, although the reaction rate decreases significantly, that is consistent with the removal of the active CuO/Al₂O₃.

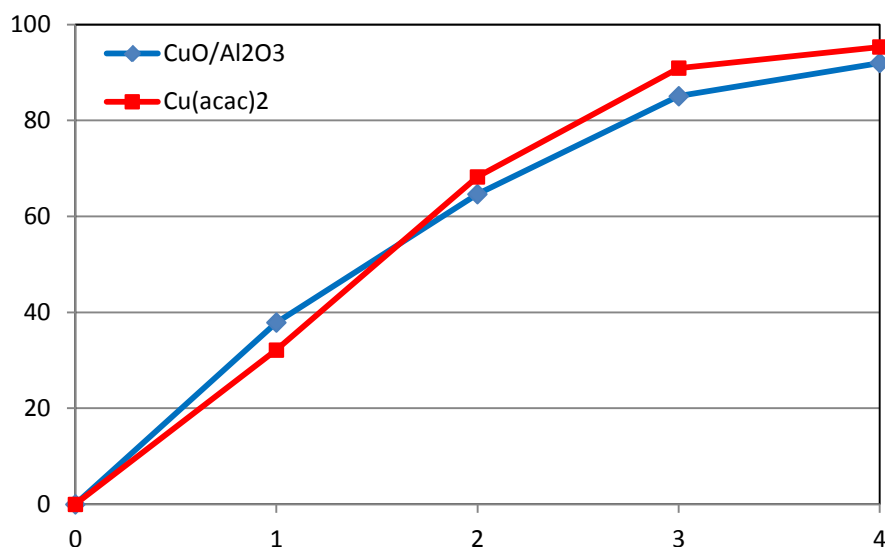


Figure S5. Comparison between CuO/Al₂O₃ heterogeneous catalyst (250 mg) and the homogeneous Cu(acac)₂ (80 mg). The homogenous reaction was carried out by using the same amount of copper contained into 250 mg of 7.6 wt% CuO/Al₂O₃.

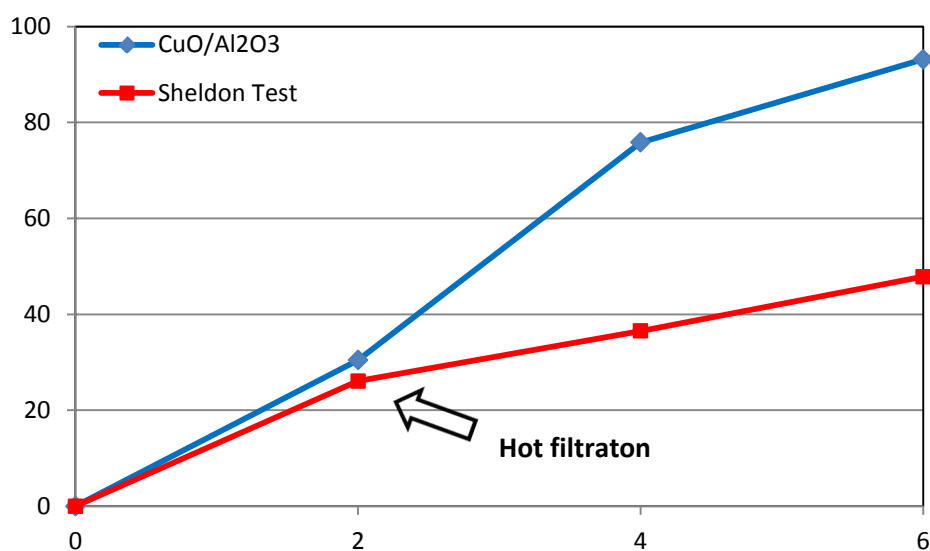
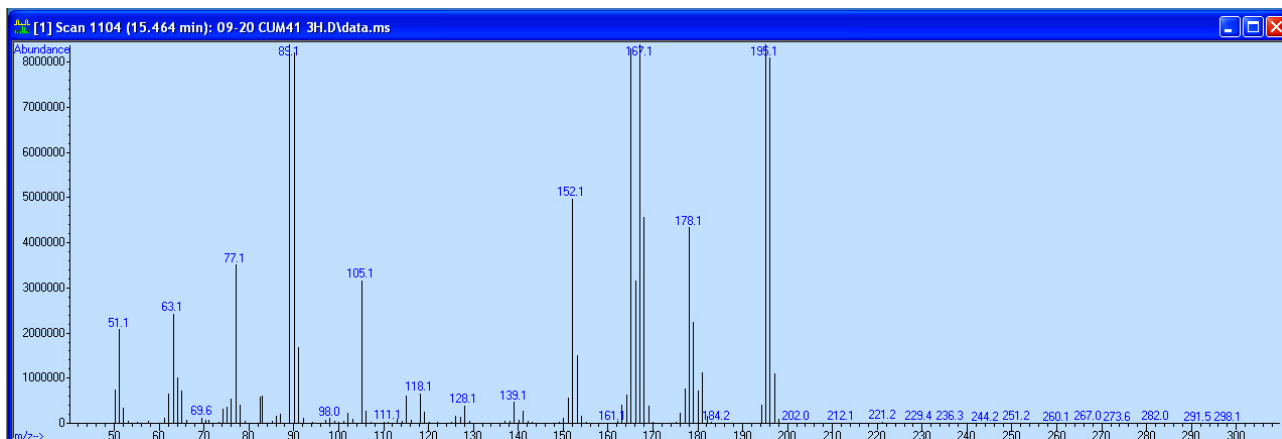


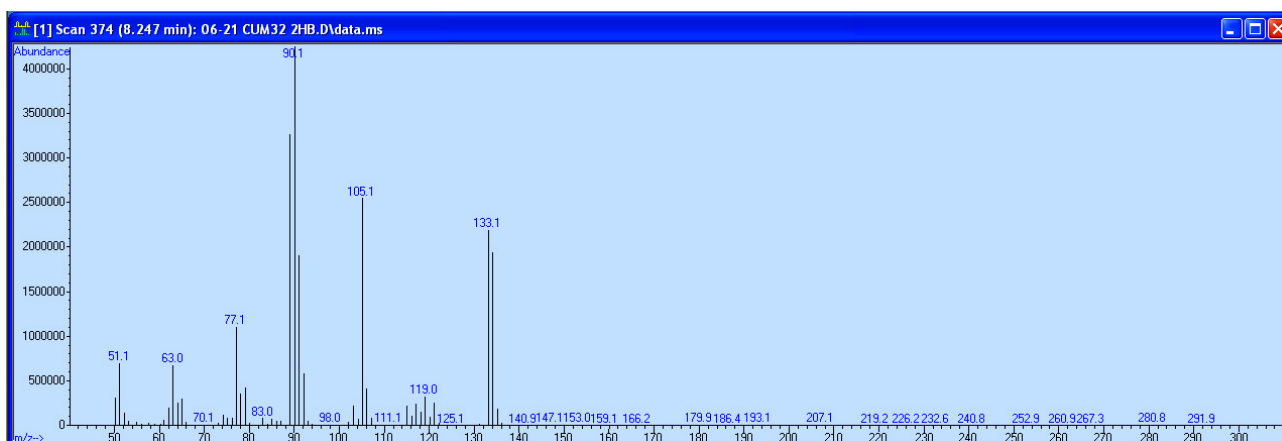
Figure S4. Comparison between CuO/Al₂O₃ (50 mg) and the Sheldon Test performed by the hot filtration of the suspension of 50 mg of CuO/Al₂O₃ in the reaction mixture after 2 h of react

Products characterization – Mass spectra

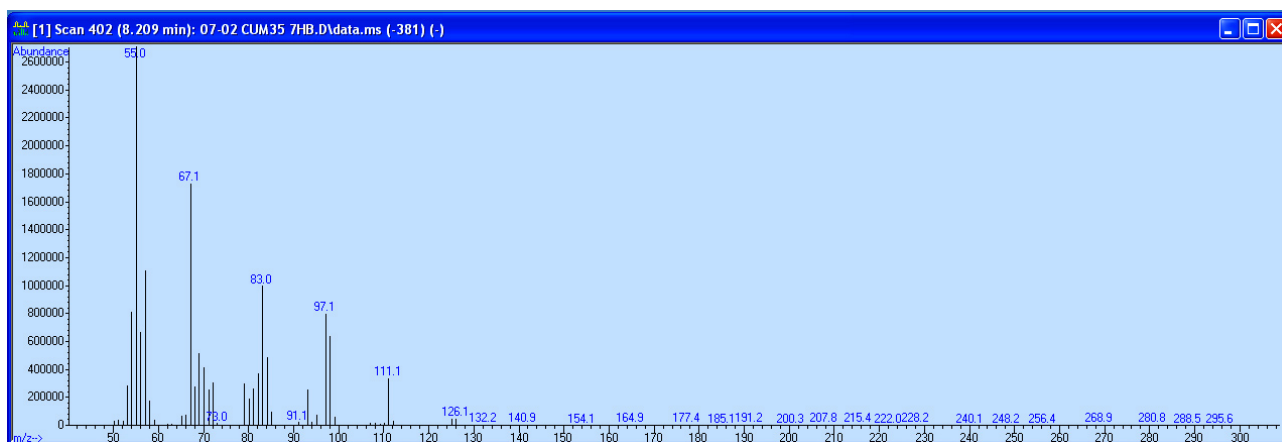
- Stilbene oxide



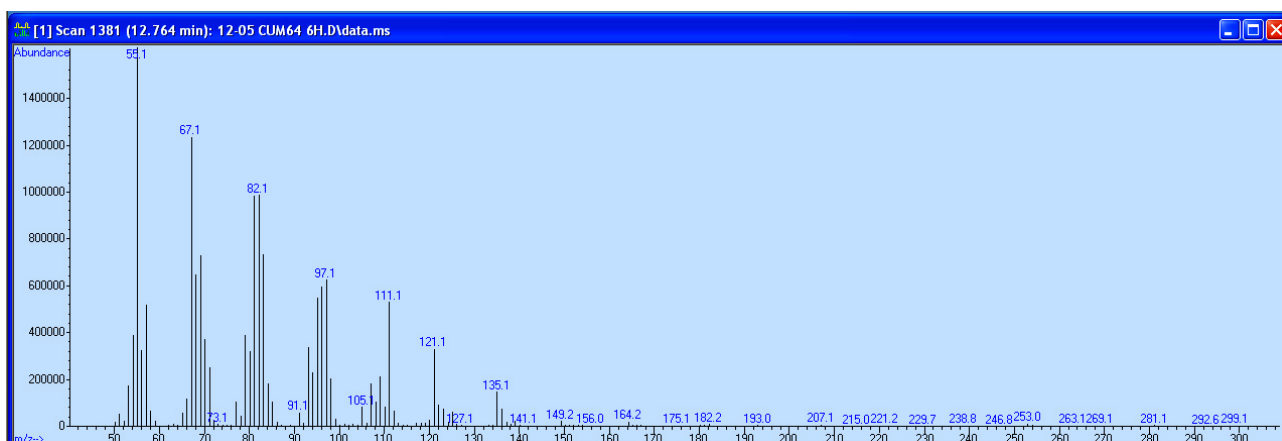
- β -methylstyrene oxide



- 1,2-Epoxyoctane



- 1,2-Epoxydodecane



- 1,2-Epoxydecane

