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Epoxidation of alkenes through oxygen activation over a bifunctional CuO/Al$_2$O$_3$ catalyst†

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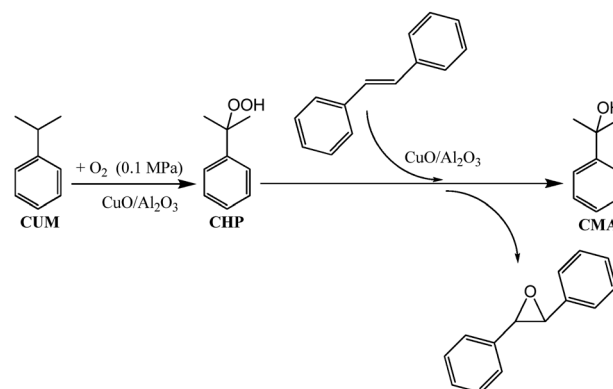
The epoxidation of alkenes was carried out over a CuO/Al$_2$O$_3$ catalyst using cumene as an oxygen carrier, through a one-pot reaction, giving high conversion and selectivity with different substrates. *Trans*-β-methylstyrene gave the corresponding epoxide in 95% yield after 3 h.

Epoxides are valuable and versatile synthetic intermediates used in the production of epoxide resins, plasticizers, cosmetics, pharmaceuticals and others, but actually their production routes overlook energy, atom efficiency and environmental concerns. Because of the importance of these chemicals, more affordable production routes are constantly pursued.[1]

Hydroperoxides are widely used for the industrial production of epoxides in a two steps process: first the organic hydroperoxide (or hydrogen peroxide) is produced by reaction with O$_2$, then the epoxide is formed from the olefin and the oxidizing compound.[2] In particular in the Sumitomo process[3] cumene (CUM) is used to produce cumyl hydroperoxide (CHP) by reaction with oxygen and then, in a second reaction step, CHP reacts with propene to give propylene oxide (PO) and cumyl alcohol as the co-product. The great advantage of this process is that cumyl alcohol is hydrogenated (the hydrogenolysis step) to give back cumene that could be reused in the process. In this view, a process in which the hydroperoxide is generated *in situ* and therefore immediately available for the epoxidation reaction, without problems of storage and transportation, would be very attractive.[4]

Here we wish to report our results of the one-pot epoxidation of alkenes over a bifunctional supported copper catalyst (CuO/Al$_2$O$_3$), mediated by the *in situ* formation of CHP, generated by reaction between cumene and O$_2$, without the use of any radical initiators (Scheme 1).

The catalytic oxidation of cumene with atmospheric oxygen, over supported copper catalysts in the presence of a radical initiator, which is usually required to start the reaction,[5] has been recently reported.[6] On the other hand, Xu *et al.* reported that copper oxide (CuO) with a high surface area is able to promote

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† Electronic supplementary information (ESI) available: Experimental, epoxidation with CHP, reuses, homogeneous reaction, Sheldon Test, full histogram of particles size distribution, products MS. See DOI: 10.1039/c3cc37843h

Scheme 1 One-pot epoxidation of *trans*-stilbene to give *trans*-stilbene oxide, in the presence of *in situ* formed CHP generated by reaction between cumene and O$_2$ over bifunctional CuO/Al$_2$O$_3$.

stilbene epoxidation in the presence of *tert*-butyl hydroperoxide with good conversion (88%) and selectivity (83%), but with a long reaction time (24 h).[7] Moreover CuO on Ag nanowires was recently reported to be active in the epoxidation of *trans*-stilbene, giving high yields in 24 h.[8] Heterogeneous copper catalysts were also found to be active in the direct gas phase epoxidation of propene, but with a different reaction mechanism, passing through the formation of the propylene oxametallacycle intermediate.[9]

Moreover, homogeneous copper catalysts are also able to catalyse the oxidation of alcohols to aldehydes and ketones by means of O$_2$.[10]
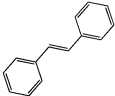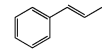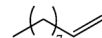
In this work a CuO/Al$_2$O$_3$ 7.6 wt% supported catalyst was prepared by chemisorption–hydrolysis, which is a method that ensures high dispersion and very small size of the crystallites even at high metal loading.[11]

Results reported in Table 1 clearly show that CuO/Al$_2$O$_3$ is extremely efficient in the one-pot epoxidation process, thus highlighting a unique activity. Using *trans*-stilbene as olefin within 3 h (entry 1) the conversion reached 85%, together with a high selectivity towards epoxide (95%), while after 6 h the conversion was 97% (entry 2). Looking at the cumene oxidation reaction, after 3 h the conversion was 42%. On the other hand, even after several hours

Table 1 One-pot epoxidation of alkenes with CuO/Al$_2$O$_3$ 7.6 wt%

Substrate	Entry	Time (h)	Conv. (%)	Sel. (%)
	1[a]	3	85	95
	2[a]	6	95	76
	3[b]	6	93	87
	4[c]	6	>99	85
	5[a]	3	100	95
	6[a]	6	76	95
	7[a]	6	72	87
	8[a]	6	29	94

Reaction conditions: $T = 100$ °C, O$_2$ = 30–35 ml min^{-1}, olefin = 10 mmol. [a] CuO/Al$_2$O$_3$ = 250 mg, CUM = 20 ml. [b] CuO/Al$_2$O$_3$ = 50 mg, CUM = 20 ml. [c] CuO/Al$_2$O$_3$ = 50 mg, CUM = 5 ml, toluene = 5 ml.

of reaction, bare Al$_2$O$_3$ was very poorly active and a different copper catalyst, namely CuO/SiO$_2$ 8.5 wt%, was totally inactive (Table 2). Moreover the reaction conditions were further improved. The amount of catalyst could be reduced from the initial 250 mg to 50 mg (entry 3), keeping high conversion and selectivity (93% and 87%), with a small decrease in reaction rate. At the same time the concentration of cumene could be reduced: finally, we performed the reaction with 50 mg CuO/Al$_2$O$_3$ and 5 ml of cumene, obtaining very high conversion and selectivity (>99% and 85%, entry 4) in the epoxidation reaction, while the cumene conversion reached 42%.

The great potentiality of the studied system relies on its versatility towards other olefins, not only stilbene: indeed, very good results were obtained with *trans*-β-methylstyrene, *cis*-cyclooctene, cyclododecene and 1-decene (entries 5–8).

The study of the two separate steps of the process (the cumene oxidation and the stilbene epoxidation respectively) gave the evidence that the catalyst plays a fundamental role in both reactions. Indeed, cumene oxidation is truly catalytic and requires the presence of CuO/Al$_2$O$_3$: bare Al$_2$O$_3$ gave only traces of oxidation products in 24 h (conversion less than 7%). Conversely when CuO/Al$_2$O$_3$ was used in 2 h the conversion reached 37% and the selectivity towards CHP was 42%. The major by-product in the first hours of reaction was cumyl alcohol (CMA), then dicumyl peroxide, acetophenone and α-methylstyrene were observed after long reaction time.
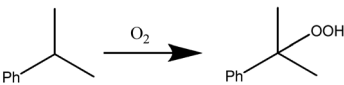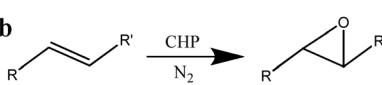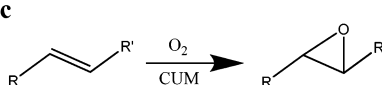
On the other hand, the epoxidation reaction requires the co-presence of both the catalyst and CHP, as it was demonstrated by carrying out the reaction using cumene as the solvent, under an inert atmosphere in order to avoid cumene oxidation, and by adding a small amount of CHP. After the first addition of hydroperoxide ($t = 0$ h, Fig. S1, ESI†) the conversion of stilbene increased as long as CHP was totally consumed ($t = 3$ h), and then stabilized. After the second addition of CHP ($t = 6$ h, Fig. S1, ESI†) the reaction started again with an initial rate comparable to the one registered after the first addition of CHP. As in the case of the cumene oxidation, Al$_2$O$_3$ was very poorly active in the epoxidation step and when this reaction was carried out in its presence or without any catalyst, after 6 h only traces of epoxide (<2%) were obtained and no CHP consumption was observed.

These results clearly show that the catalyst plays a fundamental role in the entire process, both in the oxidation of cumene and the epoxidation of stilbene. It is reported that the redox couple Cu(I) → Cu(II) could have a role in the formation of CHP from cumene, while Cu(II) species, especially Cu(II) organometallic complexes, are reported to be active in epoxidation reactions in the presence of hydroperoxides.[6] In particular an intermediate between a copper complex and CHP was isolated by Kunishita *et al.*[12] Moreover the copper–dioxygen interaction and the formation of hydroperoxo species from O$_2$ over copper complexes have been deeply elucidated by Solomon and co-workers and Mirica, Ottenwaelder and Stack[13] on homogeneous, biomimetic and heterogeneous catalysts.

Our results brought to light how the interaction between the copper phase and Al$_2$O$_3$ has a crucial role in the catalytic activity of the system. Thus, bare Al$_2$O$_3$ or a different copper catalyst such as CuO/SiO$_2$ was very poorly active, or totally inactive (Table 2). In particular, CuO/SiO$_2$ resulted to be surprisingly totally inactive in spite of the high dispersion of the copper phase (mean diameter of the crystallites = 3.0 nm[14]), which is comparable to that of the CuO/Al$_2$O$_3$ catalyst (see further for TEM details of the copper–alumina catalyst).

Al$_2$O$_3$ could have a direct effect on the reaction pathway, *i.e.* helping the abstraction of the benzylic hydrogen of cumene.[6] The ability of Cu/Al$_2$O$_3$ in abstracting an hydrogen atom during secondary alcohol dehydrogenation has already been reported.[15] However, the role of the support could also be an indirect one, that is to determine the nature of the copper phase on its surface. Work is currently in progress in order to elucidate the role of the copper phase and morphology and that of alumina in the reaction mechanisms.

Table 2 Activity of copper catalysts in the different reaction steps

Catalyst	t (h)	Conv. (%)	Catalyst	t (h)	Conv. (%)	Catalyst	t (h)	Conv. (%)
CuO/Al$_2$O$_3$	2	37	CuO/Al$_2$O$_3$	4	25[d]	CuO/Al$_2$O$_3$	6	97
Al$_2$O$_3$	24	7	Al$_2$O$_3$	4	2	Al$_2$O$_3$	24	13
CuO/SiO$_2$	24	<1	CuO/SiO$_2$	4	<1	CuO/SiO$_2$	24	<1

[a] cat. = 250 mg, CUM = 20 ml, O$_2$ = 30–35 ml min^{-1}, T = 100 °C. [b] cat. = 250 mg, CUM = 15 ml, CHP = 5 ml, *trans*-stilbene = 10 mmol, N$_2$, 100 °C. [c] cat. = 250 mg, CUM = 20 ml, *trans*-stilbene = 10 mmol, O$_2$ = 30–35 ml min^{-1}, 100 °C. [d] CHP was totally consumed, the reaction starts again after the addition of a new amount (5 ml) of CHP.
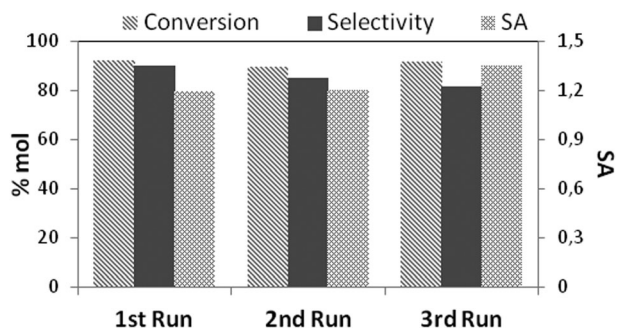
Fig. 1 Recycling tests of CuO/Al_2O_3 catalysts after 4 h of reaction. SA is the specific catalytic activity $(mol_{conv} (g_{Cu} h)^{-1})$.

A relevant role may be played by homogeneous species. Some leaching of Cu from the catalyst was observed, around 4%. The Sheldon test (Fig. S4, ESI†) showed that the solution is active in the reaction but with a reaction rate much lower than that observed without removing the solid catalyst. Moreover when the reaction was carried out in the presence of an equimolar amount of $Cu(acac)_2$ the reaction profile was identical to the one observed in the presence of CuO/Al_2O_3 (Fig. S5, ESI†). This unequivocally shows that the amount of Cu leached from the solid is not the only reason for the activity observed.

It should be outlined that some Cu leached out also from CuO/SiO_2 under the reaction conditions but it did not show any activity. Therefore we can suggest that only the CuO phase present on the surface of CuO/Al_2O_3 is able to promptly produce a very active species.

The CuO/Al_2O_3 catalyst shows good stability and reusability and it can be used at least 3 times, with only a slight decrease in its catalytic performances in terms of conversion of stilbene and selectivity towards the epoxide (Fig. 1 and Fig. S2, ESI†). As a matter of fact a small increase in the specific activity (SA) was observed. Similar behaviour has already been reported in the literature[16] and in our case could be related with the better availability and exposure of the copper particles on the support.

HRTEM analysis of the fresh catalyst shows the presence of uniform and very small copper particles well dispersed on the Al_2O_3 support. The related histogram of the particle size distribution (Fig. 2a) indicates copper particles with a mean diameter of 4.0 nm. On the other hand, the analysis of the recovered catalyst after the third catalytic run shows again the presence of small particles (around 4 nm, Fig. 2b). Although some bigger particles (20–50 nm) are also present (Fig. S3, ESI,† full histogram), this low aggregation did not significantly affect the catalytic efficiency of the system.
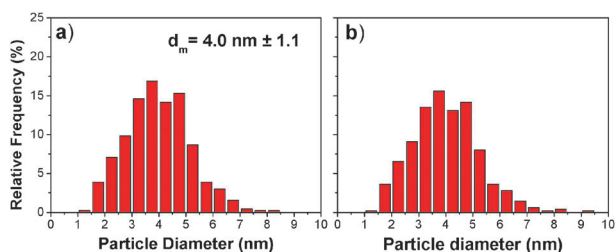
In summary, the data reported in the present communication indicate that CuO/Al_2O_3 is a very active catalyst for the one-pot epoxidation of olefins, thanks to the *in situ* generation of CHP by reaction of cumene and O_2, without the use of a radical initiator. The results show that the catalyst is essential for both reactions, namely cumene oxidation and olefin epoxidation, and suggest the existence of a synergy between the alumina support and the copper phase, which is crucial for the high catalytic activity observed. The real need to improve the existing epoxidation routes makes the process reported here extremely attractive. Therefore, its optimization, in particular regarding the catalyst stability and recyclability, could be of significant interest in order to improve the efficiency of the existing processes based on the use of hydroperoxides, and in particular CHP, for the synthesis of epoxides, such as PO and others.

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Fig. 2 Histograms of the particle size distributions of the fresh (a) and the recycled (b) $CuO–Al_2O_3$ system.