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CuO/SiO₂: a simple and efficient solid acid catalyst for epoxide ring opening^{†‡}

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A cheap, non toxic, easy to prepare and easy to use supported CuO material has shown to be a very effective catalyst for the alcoholysis of epoxides giving β -alkoxyalcohols in very good yield without generating any waste. The catalyst is heterogeneous in nature and can be reused without any reactivation treatment.

The search for new acids to substitute homogeneous ones and acids used in stoichiometric amounts is still far from a practical and simple solution. Over 15 million tons of sulfuric acid are still annually consumed for the production of important chemicals while the industry is continuously searching for highly active and stable solid acids to improve the environmental safety of the processes.¹ The use of zeolites, that proved to be so decisive in the petrochemistry area, has not found the same outcome in synthetic organic chemistry.² The use of conventional acids in these kind of transformations is still widespread, leading to large amounts of inorganic wastes and often imposing strict reaction conditions.

This is a serious issue, particularly for the production of speciality chemicals, which require high product purity and

Table 1 Styrene oxide alcoholysis promoted by CuO/SiO₂^a

Alcohol	t (h)	Conv. (%)	Sel. (%) ^b
MeOH	8.5	97	92
EtOH	2	99	90
2-Propanol	0.75	100	83
	0.75	100	82 ^c
2-Butanol	0.5	98	83
Isobutanol	0.5	100	81
1-Octanol	0.5	94	88
2-Octanol	0.5	100	87
Cyclohexanol	0.25	56	81
	0.5	100	78

^a Alcohol as solvent (5 mL), 60 °C, N₂. ^b Main byproduct being phenylacetaldehyde derived from the acid promoted epoxide isomerisation. ^c Reaction carried out under air.

versatile protocols.³ Thus, to find innovative and flexible systems is mandatory.

Epoxides represent a valuable instrument in organic synthesis due to their reactivity and versatility as intermediates, but their application is largely associated with the use of Lewis or Brønsted acids as catalysts for isomerisation or activation to nucleophilic attack.⁴

In particular β -alkoxyalcohols can be obtained through the alcoholysis of epoxides. However, the alcohol addition is promoted by traditional homogeneous systems as metal chlorides or tetrafluoroborates⁵ and different kinds of metal triflates.⁶

Some heterogeneous catalysts, relying on the use of traditional solid acids such as amberlyst-15⁷ and mesoporous aluminosilicate,⁸ supported iron complexes⁹ or Cu and Fe metal organic frameworks¹⁰ have been recently proposed.

Here we wish to report on the activity of supported copper oxide as an effective acid catalyst, able to promote the epoxides alcoholysis under very mild and no waste reaction conditions.

Results obtained in the opening of styrene epoxide by means of different alcohols (Table 1, Scheme 1) over a CuO on silica catalyst unravel the unexpected acidity of this material, where none of the partners shows acidic activity itself.

Thus, although the use of Cu(II) salts as Lewis Acids is known,¹¹ reports on CuO are lacking. On the other hand, the use of chromatographic silica ensures the inertness of the support used under these conditions (*vide infra*).

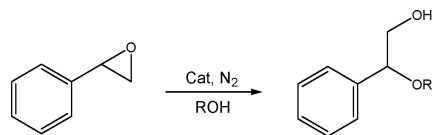
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[‡] The copper catalyst is prepared as already reported¹⁶ by using chromatographic silica as support (SSA = 580 m² g⁻¹, PV = 0.75 ml g⁻¹). The powder was added to a [Cu(NH₃)₂]²⁺ solution prepared by dropping aqueous NH₃ to a Cu(NO₃)₂·3H₂O solution until pH 9 had been reached. After 20 min under stirring, the slurry, held in an ice bath at 273 K, was diluted with water. The solid was separated by filtration, washed with water, dried overnight at 383 K, and calcined in air at 673 K for 4 h. TPR profiles were recorded with a modified version of the Micromeritics Pulse Chemisorb 2700 apparatus; catalysts (25 mg) were diluted with an equal amount of quartz, calcined at 500 °C under O₂ (40 mL min⁻¹) and then reduced at 8° per min with a 8% H₂/Ar mixture at 15 mL min⁻¹.

In a typical alcoholysis reaction a solution of the epoxide (0.8 mmol) in the alcohol (5 mL) is stirred with the solid catalyst (100 mg, 12 wt% Cu) at 60 °C under nitrogen and the reaction mixture analysed by GC and GC-MS chromatography (5%-phenyl-methyl polysiloxane column). The products were analysed by MS and NMR spectroscopy. For the recycling tests, the solution was separated from the catalyst after each run by simple decantation and a fresh reaction mixture was charged in the reactor without treating the catalyst.

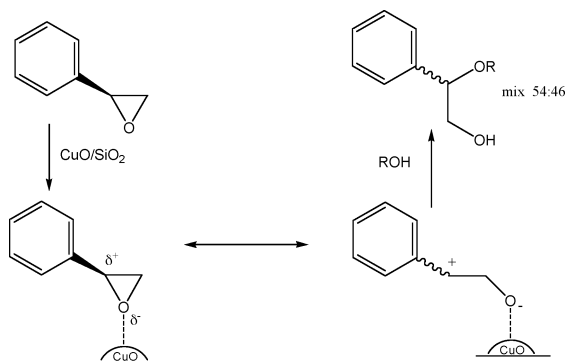
On the contrary, heterogeneous acidic catalysts usually rely on the use of materials showing well defined acidic features such as –OH groups in zeolites or clays, or metal ions in Lewis acids like Sn-beta.¹²



Scheme 1 Styrene oxide opening with alcohols.

The β -alcohoxyalcohol is obtained in all cases with complete regioselectivity, showing that electronic effects dominate over steric rules.

The almost complete regioselectivity observed in the ring opening strongly suggests that a prevalent S_N1 mechanism occurs, but this is furthermore evident from experiments carried out on (+)-*R*-styrene epoxide (Scheme 2). In this case the opening reaction leads to a racemic mixture, thus showing that a carbocation is formed as intermediate.



Scheme 2

More detailed studies, including comparison with the aminolysis reaction, are in progress in order to elucidate the species involved.

A remarkable activity can be claimed if compared with the other heterogeneous catalysts reported so far, while interesting differences can be highlighted by changing the alcohol. The activity observed when using bulky alcohols, both primary and secondary ones, is striking particularly if compared with the other systems, whose activity drops down when using alcohols others than methanol.^{7–10} As an example, activity in the addition of cyclohexanol (TOF = 10) is higher than that reported for SBA-15 functionalized with propylsulfonic acid (TOF = 6) and for Ti-MCM41 (TOF = 8).¹³

On the contrary the use of methanol and ethanol as nucleophiles results in a slower reaction with respect to the other alcohols. This behaviour could be due to competitive adsorption phenomena of the alcohol on the catalyst, widely studied at least on metallic copper surface,¹⁴ where methoxy and ethoxy species are highly stabilised. According to this hypothesis, the same reactions carried out with $\text{Cu}(\text{NO}_3)_2$ by using methanol or 2-propanol as nucleophiles do not show any significant difference in rate (Table 2, entries 6 and 8).

This evidence supports the true heterogeneous character of the catalyst, which is further proven by the hot filtration test

Table 2 Styrene oxide alcoholysis carried out with 2-propanol as nucleophile and different catalytic systems^a

Entry	Catalyst	t (h)	Conv. (%)	Sel. (%)
1	SiO_2 ^b	18	2	0
2	CuO	18	0	—
3	CuO/SiO_2 IW	18	33	—
4	CuO/SiO_2	0.75	100	83
5 ^c		0.75	33	88
6	$\text{Cu}(\text{NO}_3)_2$	0.75	100	86
7 ^c		0.75	33	97
8 ^d	$\text{Cu}(\text{NO}_3)_2$	0.75	100	100

^a $T = 60^\circ\text{C}$, $P = 1$ atm N_2 , magnetic stirring = 1400 rpm, 0.18 mmol Cu.

^b $\text{SiO}_2 = 100$ mg. ^c 0.02 mmol Cu. ^d Methanol used as nucleophile.

(Fig. 1), carried out by separating the catalyst from the reaction mixture at the same temperature.

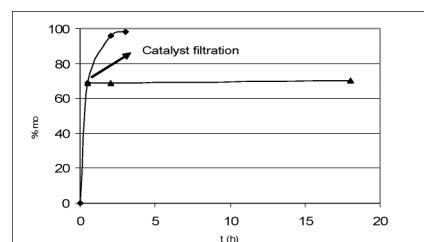


Fig. 1 Filtration test carried out in the alcoholysis of styrene oxide.

Moreover the catalytic system is reusable for at least five catalytic runs even without the need of any pretreatment or activation before the catalytic test (Fig. 2). Fig. 2 shows conversions and selectivities obtained by separating the reaction mixture after decantation and by charging a new reagent solution, in a semi-continuous way. The slight decrease observed in activity could therefore be due to a feeble poisoning of the catalyst surface, rather than to an actual deactivation.

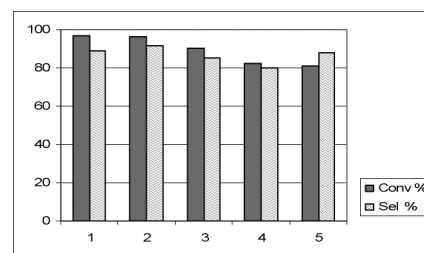


Fig. 2 Recycling test for styrene oxide alcoholysis with ethanol.

A significant modification of the catalyst during reaction can also be ruled out by comparing the TPR analysis of the fresh catalyst with the one performed on the five times used system.

Fig. 3 represents the superimposition of the two analyses and clearly shows in both cases the presence of a single peak with a maximum reduction temperature at 255 and 260 $^\circ\text{C}$ respectively. Such a reduction profile is diagnostic of the presence of highly dispersed CuO in a single and easily reducible state, significantly different from what observed for catalysts prepared by simple impregnation, in agreement with literature data.¹⁵ The absence of any other peak at higher temperatures allows us to rule out the occurrence of isolated ionic copper species.¹⁶ These data

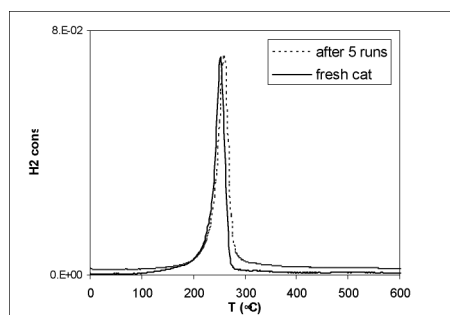


Fig. 3 TPR analysis.

unambiguously show that catalytic activity has to be ascribed to the presence of dispersed copper oxide on the catalyst surface.

Some other important points about the catalyst activity rise from the comparison with related materials. Silica used as the support does not show any activity in this reaction under the same conditions, showing that the presence of copper oxide is essential to generate acidity (Table 2, entry 1).

On the other hand, bulk copper oxide does not lead to any reaction (Table 2, entry 2) and poor activity was also observed with a catalyst prepared by Incipient Wetness (IW) technique with a comparable copper content (Table 2, entry 3). These data strongly support the hypothesis of a direct correlation between copper oxide dispersion and acidic activity and once again put in light the peculiar features of catalysts prepared with this technique. Thus, the preparation method used, that is the so-called chemisorption hydrolysis one, grants the formation of highly dispersed CuO, in turn generating dispersed metallic phase upon reduction, as shown by comparison with catalysts prepared by IW technique.¹⁷











Tests carried out with a much lower amount of catalyst show that the catalyst still performs like his homogeneous counterpart (Table 2 entry 5 vs. 7) but rising the TOF up to 18 (Table 2, entry 5).

As far as substrate scope is concerned, the reaction protocol can be successfully applied also to other epoxides (Table 3), even if poorly activated, showing to be competitive with respect to the other heterogeneous systems reported, especially when using bulky alcohols.

Opening of 1,2-epoxyoctane, for example, is reported to be promoted by [Fe(BTC)] with 1-propanol with 50% yield after 24 h.^{10b} The difference in activity is more evident by comparing the turnover numbers; namely TON = 1.67 in the case of [Fe(BTC)] in the *n*-propanolysis of epoxyoctane and TON = 3.84 in the case of the alcoholysis of the same substrate with the more hindered 2-propanol by using CuO/SiO₂. This particular behaviour puts CuO/SiO₂ in a favorable position, as it reveals its highest activity right when the other systems slow down.

From these results it is evident that the catalyst preparation method used represents a convenient tool in order to have a robust and reliable catalyst starting from homely materials. Activity observed under air further demonstrates the high versatility of this material. CuO/SiO₂ is in addition an economic, safe and non toxic catalyst, allowing one to carry out a no-waste reaction due to both its heterogeneous nature and high selectivity.

Table 3 Alcoholysis carried out over CuO/SiO₂ on different substrates^a

Epoxide	Product	Alcohol	t (h)	Conv. (%)	Sel. (%)
		2-PrOH	1	98	92 ^b
		EtOH	4	98	93 ^b
		2-PrOH	3	98	96
		EtOH	8	96	98
		2-PrOH	0.75	100	100
		2-PrOH	18	91	100
		2-PrOH	18	39	66

^a *T* = 60 °C, *P* = 1 atm N₂, magnetic stirring = 1400 rpm. ^b 6% of the other regioisomer was formed.

Moreover, the presence of a metallic phase obtained through reduction of CuO would give the chance to spread the synthetic scope of the material to polyfunctional transformations and to make a step forward with respect to common heterogeneous acidic systems.

Thus, this catalyst in its reduced form already showed outstanding properties for synthetic purposes, particularly in alcohol dehydrogenation and both C=O and C=C double bond reduction.¹⁸

Work is in progress in order to further investigate the features of the material and to widen its application as an acidic catalyst.

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