

# Mono and Bifunctional Catalysts for Styrene Oxide Isomerization or Hydrogenation

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**Abstract** Styrene oxide can be effectively isomerized to phenyl-acetaldehyde (98%) over amorphous silica alumina catalysts under very mild liquid phase conditions. On the other hand, a copper catalyst prepared using a silica zirconia support gave up to 80% yield in the hydrogenation of styrene oxide to 2-phenyl-ethanol.

**Keywords** Solid acids · Bifunctional catalysts · Cu catalysts · Epoxides ring opening · Lewis acids · Hydrogenation

## 1 Introduction

In specialty chemicals synthesis, the need of low waste technologies has recently increased the interest in solid acids as substitutes for both mineral acids and homogeneous Brønsted and Lewis ones. On the other hand, epoxides are among the more versatile and important intermediates in pharmaceutical and agrochemical industries. Most useful transformations are isomerization to carbonyl compounds, hydrogenation and nucleophilic addition of nitrogen, oxygen and sulfur compounds.

The most commonly used Lewis acid to promote the acid catalyzed rearrangement of epoxides is  $\text{BF}_3$ , usually as the etherate, which is rather a reagent than a catalyst.

We already reported on the use of amorphous mesoporous mixed oxides and of Fe based catalysts [1] in the isomerization of epoxides. In particular, we found that low

loading  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  on silica can effectively substitute  $\text{ZnCl}_2$  in the isomerization of  $\alpha$ -pinene oxide to canpholenic aldehyde, an intermediate in the synthesis of santalol, a possible substitute for environmentally unfriendly musks, while the two isomers of limonene oxide gave two different products [2].

We also reported that copper deposited on this kind of solids is an effective catalyst in bifunctional transformations such as intra- [3] and inter-molecular [4] ether formation starting from a ketone and an alcohol.

Here we wish to report our results in the isomerization of styrene oxide to phenylacetaldehyde over amorphous mixed oxides and in its hydrogenation to 2 phenyl-ethanol over a bifunctional supported Cu catalyst.

Phenylacetaldehyde, used as semiochemical and in perfume compositions for hyacinth notes, can be obtained in high yield by vapor phase isomerization of styrene oxide over alkali treated silica alumina [5] or hydrotalcite derived basic solids [6]. It can also be obtained by oxidation of 2-phenylethanol but the product purity never exceeds 85% as the aldehyde readily polymerizes under reaction conditions. In the liquid phase Ti-silicalite TS-1 gives a 95% yield in 1 h at 70 °C, showing that this reaction requires only weak Lewis acid sites [7].

2-phenylethanol is also a valuable molecule for the Flavours and Fragrances industry and it can be produced on an industrial scale through Friedel–Crafts reaction of benzene and ethylene oxide in the presence of  $\text{AlCl}_3$  and through hydrogenation of styrene oxide over Raney Ni and NaOH. In particular, 99.3% selectivity can be achieved using Raney Nickel with 48% aqueous alkali at 20 atm of  $\text{H}_2$  and 40–50 °C [8].

Both methods raise concerns from the environmental point of view, therefore a catalyst based on a non toxic metal, not requiring basic additives should be an interesting

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one. However, though a number of patents are available, the published information is conspicuously absent. Platinum and palladium catalysts gave excellent results both in gas [9, 10] and in liquid phase [11, 12] but the use of bases as promoter or of superatmospheric pressure of H<sub>2</sub> is required, while a catalyst prepared by calcining a borosilicate with Cu(NO<sub>3</sub>)<sub>2</sub> was found to give 78.4% of PEA under gas phase conditions [13].

A preliminary investigation on the potential of supported copper catalyst in this reaction and on the influence of some experimental conditions may then be useful.

## 2 Experimental Section

All the mixed oxides used were kindly supplied by Grace Davison (Worms, Germany). Their textural properties are reported in Table 1.

Solids acids were pretreated at 270 °C for 20 min in air and for 20 min under reduced pressure at the same temperature.

Copper catalysts, with a 8–9% metal loading, were prepared as follows: the support (10 g) was added to a 0.7 M [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> solution prepared starting from Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (4 g) dissolved in 25 mL of water and adding NH<sub>4</sub>OH until pH 9 [14]. After 20 min under stirring, the slurry, held in an ice bath at 0 °C, was slowly diluted in order to allow hydrolysis of the copper complex and deposition of the finely dispersed product to occur. Under these conditions, no dissolution of silica was detected. The solid was separated by filtration, washed with 0.5 L of water, dried in oven overnight at 120 °C, and calcined in static in air at 350 °C for 4 h. In all cases the Cu content was ca. 8 wt% (Table 1). Other relevant surface and textural properties of the samples, BET specific surface area, pore volume and size are listed in Table 1. Before reaction, catalysts were treated for 20 min in air at 270 °C and for 20 min under rotary vacuum and thereafter reduced in static at the same temperature with 1 atm of pure H<sub>2</sub>.

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 O<sub>2</sub> (40 mL/min) and then reduced at 8 °C/min with a 8% H<sub>2</sub>/Ar mixture at 15 mL/min.

The X-ray characterization was performed at the XAFS beamline of the Elettra Synchrotron facility in Trieste (Italy) with a Si(311) double crystal monochromator. EXAFS and XANES spectra of Cu catalysts and of Cu reference systems (Cu foil for constant angle/energy calibration, Cu<sub>2</sub>O and CuO) were collected at the Cu K edge (8979 eV) in transmission mode during in situ calcination and reduction treatments (carried out inside an EXAFS-catalysis cell, designed to work in transmission mode over powder sample under controlled gas flow and temperature). At the end of each treatment spectra were recorded at both room and liquid nitrogen temperature. XANES spectra have been recorded with a sampling of 0.25 eV. EXAFS spectra have been recorded over a 900 eV range. The spectra were analysed with the IFEFFIT software package and the best fitting results are reported in Table 2 (coordination numbers, distance and Debye–Waller factors of Cu–Cu first neighbours shell) together with the estimated metal particle size.

**Catalytic tests** Styrene oxide (≥97%, 200 mg), obtained from Aldrich was dissolved in the solvent (8 mL) and the solution transferred under N<sub>2</sub> into a glass reaction vessel in which the catalyst had been previously activated. In the case of hydrogenation reactions N<sub>2</sub> was removed under vacuum and substituted with H<sub>2</sub>. Reactions were carried out under atmospheric pressure and magnetic stirring (1400 rpm).

Reaction mixtures were analyzed by GC–MS using a HP5 (5% phenyl)-methyl-polysiloxane capillary column, length 30 m (injection T = 60 °C).

**Recycling tests** were carried out as follows: 200 mg SiAl 0.6, 2 mL styrene oxide, 8 mL toluene, 90 °C, N<sub>2</sub>, 0.5 h. After each run the solution is withdrawn by means of a syringe, the catalyst washed with 2 mL toluene under

**Table 1** Textural features of different cogels used as acids and of the corresponding Cu catalysts

Catalyst	Co-oxide loading (wt%)	Acronym	BET (m <sup>2</sup> /g)	PV (mL/g)	APR (Å)
SiO <sub>2</sub>	–	Si	480	0.75	60
8% Cu/SiO <sub>2</sub>		Cu/Si	363	0.68	72
SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	0.6	SiAl 0.6	483	1.43	117
8% Cu/SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> 0.6		Cu/SiAl 0.6	430	0.86	80
SiO <sub>2</sub> –Al <sub>2</sub> O <sub>3</sub>	13	SiAl 13	400	0.77	33
8% Cu/SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> 13		Cu/SiAl 13	412	0.75	37
SiO <sub>2</sub> –ZrO <sub>2</sub>	1	SiZr 1	453	0.91	80
8% Cu/SiO <sub>2</sub> ZrO <sub>2</sub> 1		Cu/SiZr 1	382	0.75	79
SiO <sub>2</sub> –ZrO <sub>2</sub>	4.7	SiZr 4.7	304	1.62	106
8% Cu/SiO <sub>2</sub> ZrO <sub>2</sub> 4.7		Cu/SiZr 4.7	331	1.05	64

**Table 2** Curve fitting results of Cu K edge EXAFS data (at the end of in situ reduction, first Cu–Cu shell)

SAMPLE	CN	R (Å)	$\Delta\sigma$ (Å)	$\Delta E_0$ (eV)	$D^a$ (Å)
CuSi	7.6	2.560	0.074	−0.3	17
CuSiAl 0.6	9.8	2.547	0.068	0.1	30
CuSiZr 1	8.7	2.548	0.066	0.3	21
CuSiZr 4.7	8.8	2.549	0.076	0.4	22

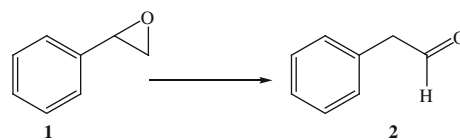
<sup>a</sup> Estimated Cu particle size diameter

stirring for 5 min, the solvent removed and a fresh solution of the substrate added.

### 3 Results and Discussion

Results obtained in the isomerization of styrene oxide to phenylacetaldehyde over a series of amorphous, commercial mixed cogels are summed up in Table 3. All the silica alumina catalysts showed high activity, in agreement with the well known Brønsted and Lewis acidity of these materials [15–19] but the most selective one was a silica with a very low content in alumina giving up to 98% phenylacetaldehyde under very mild experimental conditions, in agreement with the high dispersion of Al Lewis sites on the surface. These results are comparable to those obtained by the ANIC group by using a Ti containing zeolite under very similar experimental conditions [7] and ascribed to the presence of weak Lewis acid sites. The main difference is represented by the solvent, TS-1 requiring the use of polar solvents like alcohols and ketones (Scheme 1).

Productivity values reported in Table 3 show on the contrary that silica zirconia mixed oxides, even with a very low content of ZrO<sub>2</sub>, are poorly active in this reaction. This is consistent with the observation that zirconium doped mesoporous silica promotes the methanolysis of styrene to

**Scheme 1** Isomerization of styrene oxide

2-methoxy-2-phenylethanol but produces only very low amount of phenylacetaldehyde and the corresponding acetal [20]. However, the activity of SiZr materials was much higher than that of pure silica.

The silica alumina catalyst is also reusable up to four times without re-activation, as it is shown in Fig. 1. After four cycles a dramatic drop in activity was observed although selectivity kept constant.

The high selectivity observed toward formation of phenylacetaldehyde prompted us to use this kind of materials as support for a catalyst to be used in the hydrogenation of styrene oxide to 2-phenylethanol. All the 8% Cu (by weight) catalysts prepared by using the acidic materials as supports, were found to show a reduction profile very similar to that of Cu/SiO<sub>2</sub> but the one supported on SiAl 13 (Fig. 2).

This is in agreement with the fact that Cu on this catalyst is mainly ionic [21] therefore this material was not tested in the hydrogenation reaction.

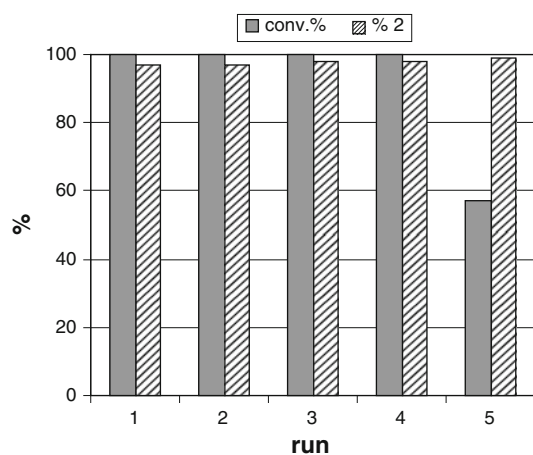
XANES spectra of the reduced catalysts show that only metallic Cu is present on the surface of all materials. Table 2 reports the curve fitting results of the Cu K edge EXAFS data that allow one to estimate the metal particle size on in situ reduced samples. Very small Cu particles, similar in size to those supported on pure silica are present on all the catalysts tested.

Results on the hydrogenation reaction (Scheme 2) are reported in Table 4. In this reaction, Cu/SiAl 0.6 gave very poor results, selectivity to phenethyl alcohol never exceeding 68%. Significant amounts of products with high MW,

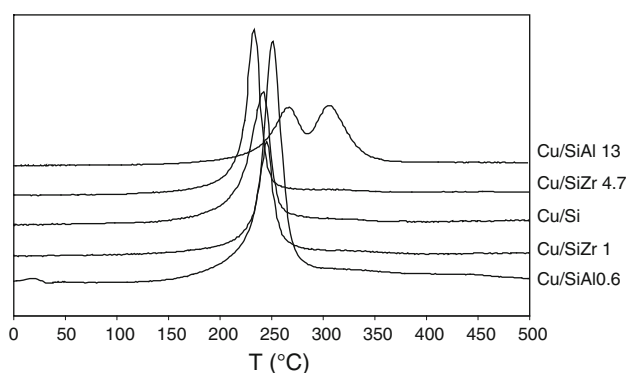
**Table 3** Isomerization of styrene oxide over different acidic catalysts

Entry	Catalyst	C/S <sup>a</sup> (wt)	t (h)	Conv. (%)	Sel to <b>2</b> (%)	Productivity (mmol prod/g <sub>cat</sub> h)
1	SiAl 13	1/10	0.5	100	92	153.3
2	SiAl 0.6	1/10	0.5	100	95	158.3
4	SiAl 0.6	1/20	0.5	100	98	326.7
4	SiAl 0.6	1/30	3.5	78	97	51.5
5	SiZr 4.7	1/10	6	100	72	10.0
6	SiZr 1	1/10	7	100	95	11.3
7	SiZr 1	1/1	0.5	100	65	11.8
8	SiO <sub>2</sub>	1/10	6	26	85	3.1

90 °C, 1 bar N<sub>2</sub>, toluene; <sup>a</sup> Catalyst to substrate ratio



**Fig. 1** Conversion and selectivity in recycling tests (see Sect. 2)



**Fig. 2** TPR profiles of copper supported catalysts prepared over different mixed oxides

in particular C–O coupling dimers such as 2,5-diphenyl-1,4-dioxane were formed, as already observed when the reaction was carried out in the presence of homogeneous cationic Rh complexes [22]. Parallel experiments carried out using phenylacetaldehyde as substrate under the same

experimental conditions, show that in fact the same product distribution was obtained over Cu/SiAl 0.6. A similar product distribution was found also with Cu/SiZr 4.7. This may be due to relevant penetration of the metal in the mesopores of these two materials, significantly reducing the average pore radius (Table 1). Work is in progress in order to elucidate relationships between C–C and C–O coupling activity and the presence of Cu in the bigger pores. Silica was also tested for the sake of comparison as the catalyst support, but in this case the reaction gave huge amounts of ethylbenzene, likely formed through dehydration of **3**. This catalyst has already shown very high activity in hydrogenation reactions often leading to deoxygenated products, particularly in the case of aromatic compounds [23]. Intermediate formation of 1-phenylethanol was ruled out as this alcohol, under the same experimental conditions and over both Cu/SiO<sub>2</sub> and Cu/SiZr catalysts gave small amount of styrene whereas the symmetric ether was found to be the main product.

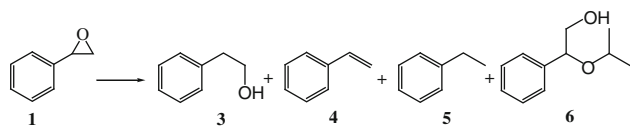
The best catalyst appeared to be Cu/SiZr 1. This catalyst at 90 °C in toluene gives 70% of the desired product, limited hydrogenolysis to ethylbenzene and limited formation of high MW byproducts. In order to increase the selectivity to 2-Ph-ethanol we examined four parameters: Cu loading, reaction T, catalyst activation T and solvent effect. Lowering the metal loading to 5% gave a catalyst with poor hydrogenation activity that for long reaction times converted **2** into high MW products but not into **3**. However it is interesting to note that adding Cu to SiZr 1 a catalyst more selective than the pure support in styrene epoxide isomerization was obtained (Table 4, entry 8 vs. Table 3, entry 7). Lowering reaction and activation T had both a negative effect on this reaction, whereas the only positive effect was found by changing the solvent.

In acetonitrile no reaction occurred, in agreement with the Lewis base character of this solvent. In 2-propanol

**Table 4** Hydrogenation of styrene oxide to phenetyl alcohol

Entry	Catalyst	Solvent	t (h)	<b>3</b> (%)	<b>2</b> (%)	<b>4</b> (%)	<b>5</b> (%)	Others (%)	<b>6</b> (%)
1	Cu/SiAl 0.6	Toluene	1.5	59	1	0	6.5	33.5	–
2	Cu/SiAl 0.6	Dioxane	2.5	68	2	0	2.2	27.4	–
3	Cu/Si	Toluene	3	32	14	6.8	43	4.5	–
4	Cu/SiZr 1	Toluene	4.25	70	1	0.2	13.8	14.4	–
5	Cu/SiZr 1	2-PrOH	3	20	0	0	4.2	16.3	58.7
6	Cu/SiZr 1	2-PrOH +diox.	2.5	64	3	0	6.9	8.4	18
7	Cu/SiZr 1	Dioxane	5	80	2	0	12.3	5.8	–
8	5% Cu/SiZr 1	Dioxane	0.5	–	89	1.6	0.2	8	–
9		Dioxane	4	8	33	0.98	1.0	57	–
10	Cu/SiZr 4.7	Toluene	0.5	10.8	35	0.6	1.2	52	–
11		Dioxane	3	14	66	1.4	7	11	–

8% Cu loading, 90 °C, 1 bar H<sub>2</sub>, C/S = 1 by weight, 1000 rpm



**Scheme 2** Products of the hydrogenation reaction

mainly the corresponding  $\beta$ -alkoxy alcohol was formed due to a nucleophilic addition mechanism at the more substituted C atom, while in dioxane a significant increase in selectivity was obtained and the product was formed in 80% yield.

#### 4 Conclusions

Commercial mixed oxides can be conveniently used for the opening of styrene oxide to phenylacetaldehyde with good selectivity and productivity. Copper catalysts supported on the same acidic materials show moderate selectivity in the hydrogenation of styrene oxide to phenethylalcohol. However, reaction conditions were very mild with respect to other reported systems, particularly as far as  $H_2$  pressure is concerned, and no basic additives were needed. Moreover, the study of different supports and different experimental conditions made available a number of informations that may be useful also in other transformations.

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#### References

1. Ravasio N, Zaccheria F, Gervasini A, Messi C (2008) *Catal Commun* 9:1125
2. Ravasio N, Zaccheria F, Guidotti M, Psaro R (2004) *Top Catal* 27:157
3. Ravasio N, Leo V, Babudri F, Gargano M (1997) *Tetrahedron Lett* 38:7103
4. Zaccheria F, Psaro R, Ravasio N (2009) *Tetrahedron Lett* 50:5221
5. Matsuzawa Y, Yamashita T, Ninagawa S (1972) JP 47042278 to Ajinomoto. CAN 78:135878
6. Kochkar H, Clacens JM, Figueras F (2002) *Catal Lett* 78:91
7. Neri C, Buonomo F (1985) US Patent 4,495,371 to ANIC SpA. CAN 101:23130
8. Hirako Y (1987) JP 62,286,939 to Daicel Chemical Industries. CAN 108:152560
9. Kirm I, Medina F, Rodriguez X, Cesteros Y, Salagre P, Sueiras JE (2005) *J Mol Catal A Chem* 239:215
10. Kirm I, Medina F, Sueiras JE, Salagre P, Cesteros Y (2007) *J Mol Catal A Chem* 261:98
11. Chaudari RV, Telkar MM, Rode CV (2000) US Patent 6,166,269 to CSIR, India. CAN 134:41976
12. Yadav VG, Chandalia SB (1998) *Org Proc Res Dev* 2:294
13. Hoelderich W, Goetz N, Hupfer L (1990) US patent 4,943,667 to BASF AG. CAN 112:55217
14. Boccuzzi F, Martra G, Coluccia S, Ravasio N (1999) *J Catal* 184:316
15. Chizallet C, Raybaud P (2010) *Chem Phys Chem* 11:105
16. Fihri A, Durand R, di Renzo F, Fajula F, Coq B, Roussel TM, Vuillemin B (2010) *Appl Catal B Environ* 98:224
17. Dragoi B, Gervasini A, Dumitriu E, Auroux A (2004) *Thermochim Acta* 420:127
18. Gervasini A, Fenyvesi J, Auroux A (1997) *Catal Lett* 43:219
19. Bevilacqua M, Montanari T, Finocchio E, Busca G (2006) *Catal Today* 116:1
20. Barreca D, Copley MP, Graham AE, Holmes JD, Morris MA, Seraglia R, Spalding TR, Tondello E (2006) *Appl Catal A General* 304:14
21. Gervasini A, Manzoli M, Martra G, Ponti A, Ravasio N, Sordelli L, Zaccheria F (2006) *J Phys Chem B* 110:7851
22. Fujitsu H, Shirahama S, Matsumura E, Takeshita K, Mochida I (1981) *J Org Chem* 46:2287
23. Zaccheria F, Ravasio N, Ercoli M, Allegrini P (2005) *Tetrahedron Lett* 46:7743