

Propene epoxidation on heterogeneous copper catalysts

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Introduction

Heterogeneous catalyzed alkene epoxidation is an academically interesting and technically important reaction. In particular, propene epoxide is a very valuable material currently made by indirect homogeneous chemical routes, that are inefficient in terms of atom economy, energy requirement and far from environmentally benign. Therefore the direct epoxidation of propene with molecular oxygen would represent a great innovation from an industrial point of view. Although Ag catalysts are successfully used in the epoxidation of ethene, they are very inefficient in propene oxidation, while very high selectivity was observed on Au/TiO₂ catalysts, but only a low alkene conversion[1]. Recently the epoxidation of propene and styrene on pure Cu (111) facets and on Cu/SiO₂ has been reported [2,3]. Here our results on the epoxidation of propene on supported Cu heterogeneous catalysts (Cu/SiO₂-Al₂O₃ and Cu/SiO₂) synthesized by chemisorption-hydrolysis method have been reported.

Experimental

The Cu catalysts (by chemisorption-hydrolysis method) were prepared by adding the support (SiO₂ or SiO₂-Al₂O₃) to a solution containing [Cu(NH₃)₄]²⁺ and slowly diluting the slurry with water. The solid was separated, dried overnight at 100 °C, and calcined in air at 350 °C for 4 h (Cu loading between 1-15 wt %). The reaction was carried out in fixed-bed reactor with 0.100 g of catalysts at atmospheric pressure with a gas flow of He, C₃H₆ and O₂, between 180-300 °C. The catalysts was pretreated under H₂, or alternatively only under He for non reductive pretreatment. The products were analyzed by quadripole mass Thermo Fischer Scientific VGQ

Results/Discussion

In agreement with the single crystal studies[2] we observed a significant activity only on pre-reduced catalysts with high metallic surface area, while unreduced catalysts show an activity considerably lower than the reduced ones. This is particularly evident on Cu/SiO₂-Al₂O₃

catalysts (Fig.1, left). Previous work from our group already showed that only unreducible Cu(I) is formed on the catalyst surface for 1-5 wt % of Cu. After this loading a CuO phase reducible to well formed Cu(0) crystallites begins to form on the surface [4]. However, the best activity is showed by pre-reduced Cu/SiO₂ catalysts, in particular by Cu/SiO₂ B catalysts. On SiO₂ only reducible Cu is formed (in very small nanoparticles) either at low Cu content or high, as shown by EXAFS-XANES analysis. The FT-IR spectra of adsorbed CO on Cu/SiO₂ B showed the presence of many bands under 2100 cm⁻¹ that can be attributed to a well formed Cu crystallite exposing (111) and (110) facets on the surface of reduced catalysts. In particular there is a good formation of formed nanoparticles with (111) facets on the catalyst with high Cu content (15 wt %), whereas on catalyst with 9 wt % of Cu they are only hint. As a matter of fact 15 wt % Cu/SiO₂ B achieves high partial pressure of PO due to well formed very small metal particles (Fig. 1, right). In the literature only low loading (1-5%) catalysts are reported to be active, but the chemisorption-hydrolysis method allows to obtaining very small copper particles also with higher loading (up to 15%) and this peculiarity should be allow to increase productivity of copper catalysts. Finally, by comparison SiO₂ support with similar surface area, the most active catalyst appears to be that one whose support has larger pore diameter.

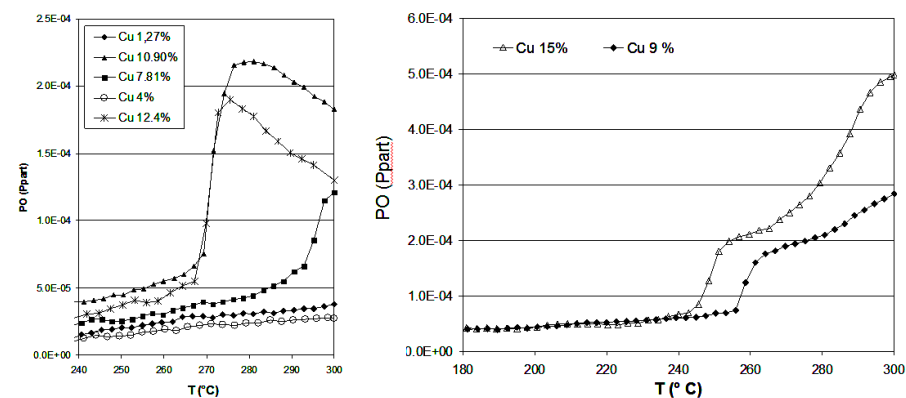


Figure 1. Left, Cu/SiO₂-Al₂O₃ series; 1-12% wt Cu; right, Cu/SiO₂ B 9% vs Cu/SiO₂ B 15%

References.

1. Hayashi, T. Tanaka, K., Haruta, M. *J. Catal.*, 1998, 178, 576
2. Lambert, R.M. et al., *J. Am. Chem.Soc.*, 2005 127, 6069; *Surface Sc.*, 2005, 578, L85; *J. Catal.*, 2005, 236, 401-404
3. Hui Chu, Lüjuan Yang, Qinghong Zhang, Ye Wang, *J. Catal.*, 2006, 241, 225-228
4. A. Gervasini, M. Manzoli, G. Martra, A. Ponti, N. Ravasio, L. Sordelli and F. Zaccheria, *J. Phys. Chem. B*, 2006, 110, 7851