Heterogeneous Catalysis

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A Nanoarchitecture Based on Silver and Copper Oxide with an Exceptional Response in the Chlorine-Promoted Epoxidation of Ethylene

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Abstract: *The selective oxidation of ethylene to ethylene epoxide is highly challenging as a result of competing reaction pathways leading to the deep oxidation of both ethylene and ethylene oxide. Herein we present a novel catalyst based on silver and copper oxide with an excellent response in the selective oxidation pathway towards ethylene epoxide. The catalyst is composed of different silver nanostructures dispersed on a tubular copper oxide matrix. This type of hybrid nanoarchitecture seems to facilitate the accommodation of chlorine promoters, leading to high yields at low reaction temperatures. The stability after the addition of chlorine promoters implies a substantial improvement over the industrial practice: a single pretreatment step at ambient pressure suffices in contrast with the common practice of continuously feeding organochlorinated precursors during the reaction.*

Ethylene oxide (EO) is a bulk chemical intermediate of paramount importance in the chemical industry for the production of multiple oxygenated end-products.[1] The main goal in EO production processes is to increase the selectivity and the EO concentration at the outlet of the reactor. However, maintaining a high selectivity at moderate to high conversion rates remains challenging in view of the susceptibility of ethylene and EO to be completely oxidized to CO_2 in the presence of oxygen.[2]

The reference industrial catalysts for this reaction consist of large silver nanoparticles (100–200 nm) supported (circa 15 % wt.) on low-surface-area alumina. Over the years, these catalysts have been highly optimized by promotion with alkali metals (mainly cesium)[3] and also with other metals, such as rhenium, molybdenum, tungsten, and chromium.[4,5] To minimize the formation of CO_2, chlorine-containing compounds, such as 1,2-dichloroethane (DCE), hydrochloric acid, and ethyl chloride, are also used as promoters.[6,7] These chlorinated compounds are added continuously to the reactor feed and have a strong influence on the final EO selectivity. Furthermore, it is also customary to add ethane to the reactor feed (around 10 % of the total volume) to facilitate the adsorption/desorption equilibrium of Cl on the Ag surface. Otherwise irreversible poisoning of the Ag active sites by Cl occurs.[3,7]

Due to the industrial importance of this reaction, many efforts have been devoted to the design of a catalyst that could outperform the silver–alumina system. Barteau et al. showed both theoretically[8] and experimentally[3,9] that copper–silver bimetallic catalysts increase the performance of conventional Ag catalysts, achieving higher selectivity towards EO. Other reports aiming at a rational design of catalytic surfaces suggest that the presence of Cu on the surface of the catalyst could critically affect the epoxidation mechanism.[8,10–12] Cu tends to oxidize at the reaction temperatures forming CuO surfaces alongside the Ag particles and, depending on the catalyst surface structure, this combination of silver and copper oxide can increase the selectivity towards EO.[11,13] Another important fact regarding the specific role of Cu is that both Cu and CuO can interact with Cl, in a similar way to how Ag does, with the already mentioned benefits regarding EO selectivity.[14–16]

Considering the above premises, herein we present a novel structure for a Ag/CuO catalyst with a high content of both metals. This material can be prepared by a facile co-precipitation method (see the Experimental Section in Supporting Information), followed by a careful thermal treatment. Unlike other structures that are prepared by similar methods (for example the $Ag_2Cu_2O_3$ material reported by Tejada-Rosales et al.[17] that is inactive for ethylene epoxidation), we have obtained Ag/CuO nanoarchitectures with highly accessible Ag nanoparticles and where the Ag and CuO are intimately linked, leading to an increase in the activity and the selectivity to EO.

A first examination of the morphology of the catalyst by using scanning electron microscopy (SEM) revealed a tubular configuration with a high aspect ratio with lengths of up to 1 μm and variable widths between 30–200 nm (see Figure S1 in Supporting Information). Energy-dispersive X-ray spectroscopy (EDX) analysis at different spots showed a homogeneous overall chemical composition with Ag:Cu atomic ratios of 0.97

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(57 % wt. Ag in the solid), in agreement with the equimolar ratio of the initial solution (see the Experimental Section and Figure S1 in the Supporting Information). X-ray diffraction (XRD) and HR-TEM analysis confirmed the presence of two crystallographic phases assigned to metallic Ag ($Fm\bar{3}m$ cubic) and CuO ($C2/c$ monoclinic), respectively (Figures S2, S4, S5). To gain further insight into the distribution of the Ag nanostructures in relation to the CuO phases, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were acquired, including a tomographic analysis carried out by taking up to 140 STEM images at varying angles from −70 to 70° and reconstructing a three-dimensional model of a single Ag/CuO tube. Different morphologies ranging from small nanoclusters to anisotropic rods accounted for the heterogeneous variety of shapes displayed in this Ag/CuO catalyst (Figure 1 a; Figures S3–S5). The energy-dispersive (EDX) mapping analysis of the different layers of material compositions suggested a core–shell distribution with an irregular Ag core (outlined in red in Figure 1 b,c) in conjunction with multiple clusters of Ag nanoparticles of a few nanometers in size (Figure 1 b, AgNPs shown in blue). A CuO outer shell (highlighted in yellow/orange in Figure 1 c; see also Figure S6 and the Movie in the Supporting Information) surrounds these Ag nanostructures but interestingly, does not completely covering them. In summary, from the above observations, and especially from the 3D tomographic reconstruction, a picture emerges of a complex hybrid nanostructure in which metallic Ag and CuO are segregated but intertwined, with a high amount of shared interface area that facilitates interaction, and where a representative fraction of the Ag remains accessible to gas-phase reactants.

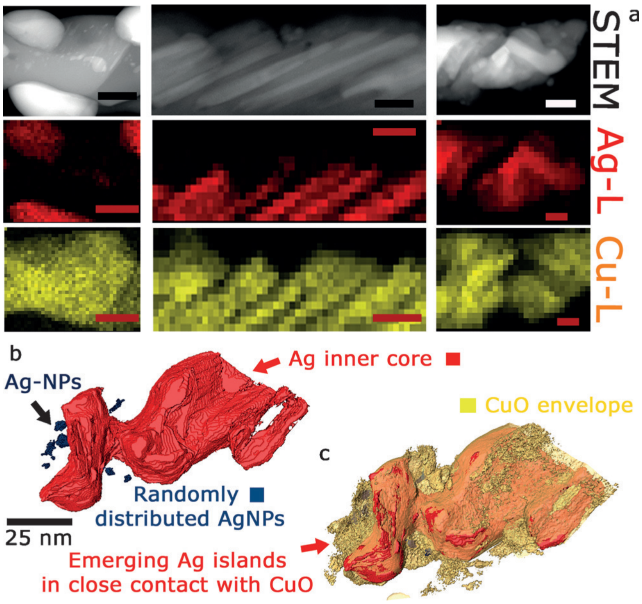

Figure 1. Morphochemical analysis of the Ag/CuO catalyst: a) Selection of representative HAADF-STEM images and the corresponding EDX mapping analyses to determine the chemical distribution of Ag (red) and Cu (yellow) on the catalyst; b) Snapshot of the Ag fraction in a HAADF-STEM 3D tomography reconstruction of a Ag/CuO nanotube: the red figure corresponds to the bulk Ag inner core while the blue dotted images are randomly distributed individual Ag NPs; c) Equivalent side-view reconstruction now including the CuO envelope (yellow color) covering the Ag core. The presence of Ag/CuO intertwined areas with Ag islands emerging on the surface can be detected. All scale bars = 25 nm.

The evaluation of the catalytic activity of the Ag/CuO hybrid catalyst for ethylene epoxidation was first carried out in the absence of promoters and compared with a reference silver-based catalyst (20 % wt. Ag) supported on α-alumina and prepared by a conventional wetness impregnation method (Figure S7). The performance of this catalyst is similar to other unpromoted Ag/Al_2O_3 catalysts in the literature (see for instance Ref. [9]). The results obtained during reaction under identical experimental conditions of both solids (that is, the Ag/Al_2O_3 reference catalyst and the Ag/CuO system) are summarized in Table S1. It can be observed that the Ag/CuO nanostructure greatly outperforms the reference Ag/Al_2O_3 catalyst. At 225 °C, the conversion obtained with the Ag/CuO catalyst is more than 20 times higher, but the reaction rate, referred to the mass of Ag, is more than 40 times higher. Furthermore, with the Ag/CuO catalyst, selectivity values are generally over 10 points higher at equivalent conversions and 21 % yields can be achieved at only 225 °C. Furthermore, the Ag/CuO structure starts to be active at a much lower temperature and 100 °C is sufficient to obtain measurable conversions, instead of the 175 °C typically reported for this reaction.[18]

As can be inferred from the preceding discussion, we credit the enhanced performance of the Ag/CuO catalyst to the strong interplay between both phases, with a high degree of entanglement shown through electron microscopy images. The presence of Cu can withdraw electrons from nearby Ag atoms rendering the Ag more electropositive, thereby increasing the electrophilicity of adsorbed oxygen species that favor the direct formation of EO.[19]

Perhaps the most compelling evidence regarding the singular nature of the Ag/CuO catalyst compared to standard epoxidation catalysts can be obtained from the different behavior against poisoning by chlorine-containing compounds. To study this, we challenged both Ag/CuO and Ag/Al_2O_3 reference catalysts by co-feeding of a Cl precursor (1,2-dichloroethane, DCE) during the ethylene epoxidation reaction in the absence of ethane (ethane is generally added in industrial practice to counterbalance the poisoning effect of Cl).[3,20] Their behavior was remarkably different, as shown in Figure 2, where the evolution of the rates of formation of EO and CO_2 during the ethylene epoxidation reaction at 200 °C is shown.

As expected, in the absence of ethane in the feed, the Ag/Al_2O_3 catalyst is quickly poisoned. After 30 min, the reaction rate is one tenth of the initial, and becomes negligible after 2 h on stream (Figure 2 b). In contrast, for the Ag/CuO catalyst the EO formation rate initially increases, reaching a maximum after about 25 min of poisoning and smoothly decreasing thereafter (Figure 2 a). Interestingly, for the Ag/CuO catalyst the effects of Cl pretreatment are permanent, and depend solely on the total amount of DCE fed to the reactor. If at any time during pretreatment the DCE feed is stopped, the catalyst remains thereafter "frozen" in that state, with constant conversion and selectivity (Figure S8), independent of the amount of Cl previously dosed. Moreover, the catalyst main-

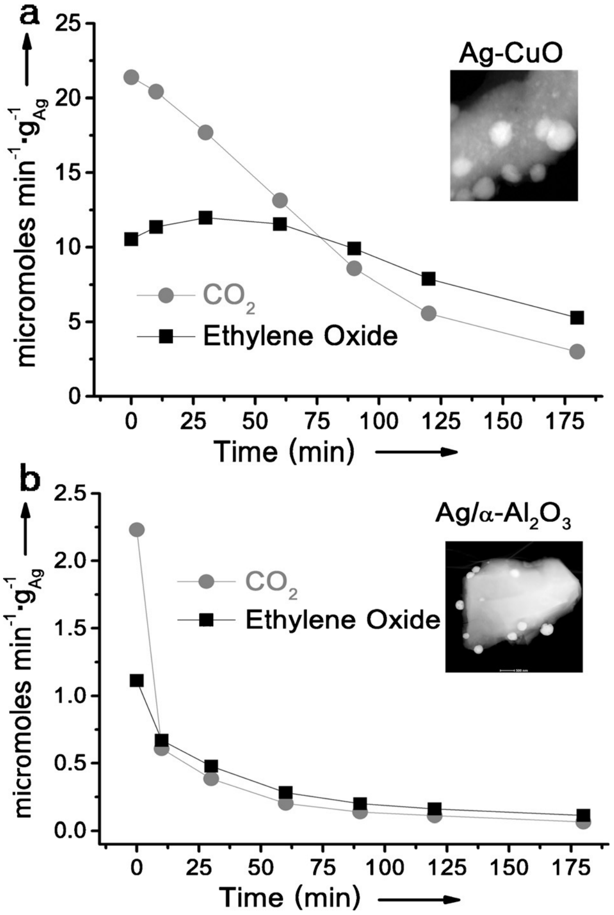

Figure 2. Evolution of the reaction rates of CO_2 and EO during pretreatment with 1.2-dichloroethane (4 ppm) of the a) Ag/CuO catalyst or the b) Ag/Al_2O_3 catalyst. Temperature = 200 °C. The inlet flow contains 6 % ethylene, 12 % oxygen, and 88 % helium. Insets: STEM-HAADF images of the catalysts (see also the Supporting Information).

tains a stable performance for at least 40 h of operation at 200 °C, indicating that the Cl species irreversibly remain on the surface during reaction (Figure S9). This could be expected, since it has been reported that temperatures above 400 °C are needed to remove the Cl from Ag[21] and Cu surfaces.[15] Therefore, the presence of copper oxide seems to be playing a determinant role in the stabilization of chlorine atoms. This distinct behavior means that chlorine promotion could be carried out only during the preparation of the catalysts, without the need to add DCE during reaction, with the economic and environmental advantages that this implies.

X-ray photoelectron spectroscopy (XPS) was used to confirm the presence of Cl on the catalyst surface and to evaluate the extent of penetration of Cl species into the Ag/CuO catalyst (Figure S10 and S11). Increasing the pretreatment time led to a deeper penetration of Cl species and after 1200 seconds of etching, Cl was only found for the catalyst pretreated for 3 h.

The effect of Cl addition during ethylene epoxidation has been intensely studied. A widely supported idea proposes that Cl promotion decreases the energy barrier from the oxometallacycle intermediate (OMC) to EO relative to the nonselective pathway.[22,23] Moreover, Cl species block oxygen vacancies on the Ag surface, thus preventing the formation of OMC, which is considered primarily responsible for the nonselective reaction[2,23] and favors the selective direct epoxidation route. Recently, Rocha et al.[24] demonstrated by in situ XPS analysis that Cl has a direct effect on oxygen atoms on the Ag surface, increasing the electrophilic nature of the oxygen adsorbed on Ag. In accordance with the direct epoxidation mechanism,[25] an overall increase of the EO selectivity was detected. The interaction of Cl with Ag depends on the degree of coverage, ranging from an initial chemisorption at low coverage to the consolidation of segregated AgCl phases at higher coverage levels.[21] The interaction with Cu or CuO is analogous but requires a lower number of intermediates to accommodate Cl atoms and forms CuCl or $CuCl_2$ regardless of the amount of Cl added.[15] Furthermore, the diffusion rates of the Cl atoms into Ag films are substantially lower than in Cu films.[14] In summary, Cl promotion appears to increase the electrophilicity of absorbed oxygen by electrostatic effects and is likely to be enhanced in the presence of Cu since copper chlorination occurs more readily than silver chlorination.

Considering our experimental observations, the reported studies of Cl promotion on Ag catalysts, and the interactions of Ag and CuO with Cl, we suggest a chlorination mechanism for our catalyst, schematized in Figure 3 a. Two different outcomes are possible, depending on the Cl amount dosed, which in turn depends on the Cl concentration and contact time. For low DCE amounts, Cl-containing species will interact preferably with the CuO, forming CuO/Cl derivatives and acting as a chlorine sponge. Thanks to the Ag/CuO intertwined structure of our catalyst, these Cl atoms will increase the electrophilicity of the oxygen adsorbed on neighboring Ag surfaces while avoiding most of the poisoning effect. This is consistent with the observations in Figure 2 a, where, at lower pretreatment times ($<$ 60 min), the rate of formation of EO slightly increases as a consequence of the increase in the selectivity to EO that offsets the decrease in conversion. On the other hand, for higher doses of Cl precursors (contact times greater than 60 min, see Figure 2 a), Cl interaction with Ag nanoparticles becomes more important, ultimately leading to poisoning of the catalyst. In this scenario, the selectivity continues to increase as Cl withdraws electrons from the adsorbed oxygen, but now Cl also blocks the vacancies available on Ag, reducing the EO produced.

The performance of the Ag/CuO catalyst with a pretreatment of 4 ppm of Cl for 180 min is compared in Figure 3 b with some of the best reported results[3,20,26,27] measured under similar experimental conditions (ethylene concentration (6–15 %), C_2H_4/O_2 ratios varying from 1 to 2, with and without promoters, at 1 bar of total pressure). In general, the selectivity to EO with the Ag/CuO catalyst presented in this work is higher and the temperatures required to reach a certain conversion are considerably lower (circa 75 °C lower), even when comparing with Cs or Cs + Cl promoted catalysts[20] or when using lower oxygen concentrations (Figure S12). Only the recent results reported by Li et al.[28] who prepared $Ag/\alpha\text{-}Al_2O_3$ by an impregnation–bioreduction process with *Cinnamomum camphora* extract match the performance of the Ag/CuO catalyst, although it is important to

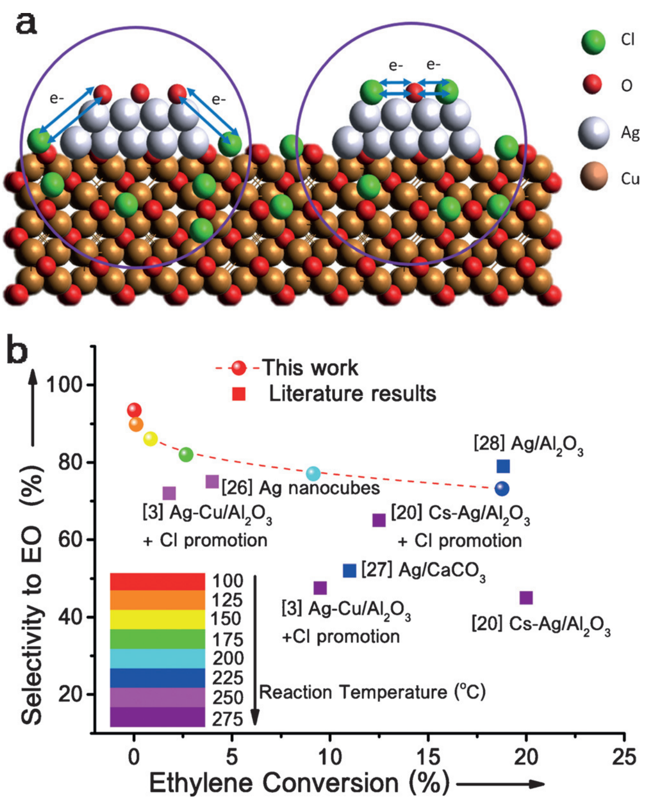

Figure 3. a) Representation of the proposed Cl promotion mechanism; the Cl atoms are readily adsorbed or substituted on both CuO and Ag surfaces and promote the generation of more electrophilic oxygen species in the vicinity; b) Overview of the best reported catalytic performances for ethylene epoxidation expressed in terms of selectivity to EO formation against total ethylene conversion. The Ag/CuO catalyst pretreated with 4 ppm of 1,2-dichloroethane for 180 min (circle symbols) is selected for comparison. Results for previously reported systems are shown as square symbols. The different colors of circles and squares indicate different reaction temperatures (see inset legend). Numbers in square brackets indicate the reference in which the indicated system is reported.

note that they were obtained under reaction at 20 bars of total pressure and at lower space velocity.

The fact that results comparable or better than the best reported in the open literature have been obtained with a simple and robust catalyst strongly suggests that Ag/CuO catalysts may be a key platform for increasing the performance of the ethylene epoxidation reaction in the near future. The high stability of the Cl promotion allows us to tune the catalytic performance simply by controlling the total dose of DCE supplied in the pretreatment step. This allows a simpler and more economical operation compared to standard practice with conventional catalysts, since the feeding of both ethane and chlorine-containing compounds during operation can be avoided.

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