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Propene epoxidation over TiO_2-supported Au–Cu alloy catalysts prepared from thiol-capped nanoparticles

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ABSTRACT

Propene oxidation to propene oxide (PO) was performed with N_2O in the temperature range of 473–673 K using TiO_2-supported Au and Au–Cu alloy nanoparticles synthesized from pre-formed thiol-capped nanoparticles of controlled composition and size. Catalysts were activated by calcination at different temperatures in the range 573–873 K and characterized by HRTEM, XPS, and TPR. Among a series of catalysts with different Au/Cu ratio and metal loading, the Au_1Cu_3/TiO_2 with 1.2 wt% exhibited the best catalytic performance for epoxidation, both in terms of propene conversion rate and selectivity towards PO ($0.25\ \mathrm{mol\,PO\,g_M^{-1}\,h^{-1}}$ at 573 K). The highest TOF was obtained over a catalyst calcined at 673 K. At this calcination temperature, HRTEM revealed a large perimeter interface between the nanoparticles and the support, which was accompanied by an intense TPR hydrogen uptake at low temperature. At increasing calcination temperature, the surface of Au–Cu alloy nanoparticles was progressively decorated with oxidized Cu species, which were detrimental for epoxidation and favored allylic oxidation products. Isolation effects and control of the extent of Cu oxidation by Au in the alloy nanoparticles as well as the perimeter interface between Au–Cu alloy nanoparticles and TiO_2 are imagined to play pivotal roles in the epoxidation of propene.

1. Introduction

When dispersed as fine particles of less than ~10 nm in dimension over selected metal oxides, gold exhibits exceptionally high activity in a variety of reactions such as CO oxidation, hydrogenation of CO and CO_2, water gas shift, reduction of NO to N_2, hydrogenation of unsaturated substrates, oxidation of alcohols and aldehydes, hydrochlorination of ethyne, and epoxidation of propene, among others [1–6]. Current industrial methods used for the epoxidation of propene, the chlorohydrin and organic hydroperoxide processes, have important disadvantages in terms of environmental pollution and by-products. However, propene oxide is one of the most important feedstocks for the production of many useful chemicals, such as polyurethane, polyester resins, and surfactants [7], and a process based on the direct epoxidation of propene in the gas phase using only oxygen or any other oxidant, resulting in benign side products, is highly desirable. In this context, the high catalytic activity of gold supported on TiO_2 and titanium-containing materials (such as Ti-MCM-41 and TS-1) in the direct epoxidation of propene with O_2/H_2 mixtures has attracted considerable industrial and academic interest [8–16]. The mode of operation of Au–Ti–O catalysts for this reaction remains unclear, but the role of the support, the Au particle size, and the periphery between the support and the Au particles have been recognized [11,16,17]. In particular, only the anatase form of TiO_2 leads to the formation of propene oxide, whereas the rutile form and amorphous TiO_2 cause the complete oxidation of propene into CO_2 [18]. As regards the Au particle size, there is a strong particle size dependence and only small nanoparticles (1–5 nm) are selective towards the formation of propene oxide, whereas larger Au particles increase the selectivity to combustion [9,16,19,20]. However, the high reactivity of surface-activated oxygen species generated from O_2 often leads to consecutive oxidation and, consequently, to a loss of propene oxide selectivity. For this reason, recent attention has been given to the use of nitrous oxide as a mild oxidant in the propene epoxidation reaction [21–29]. Usually N_2O is activated at metal sites, leading to N_2 and atomically adsorbed oxygen with a mild electrophilic character, suitable for the transformation of the vinyl group of propene into an oxirane ring [21,26]. In addition, N_2O is a greenhouse warming gas which is produced abundantly in industrial processes (i.e. in the production of precursors of nylon and of nitric acid) and its use in propene epoxidation, with

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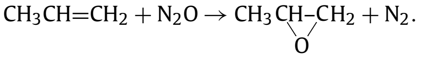
the only byproduct N_2, could offer an interesting solution to the environmental problems associated with this gas [28]:



$$CH_3CH{=}CH_2 + N_2O \rightarrow CH_3\underset{\diagdown O \diagup}{CH{-}CH_2} + N_2.$$

In addition to nanosized Au, it is well known that Cu-based catalysts are particularly effective for alkene epoxidation when allylic hydrogen atoms are present because Cu favors metallacycle formation instead of allylic hydrogen stripping [30,31], which is the main obstacle for epoxidation. Several examples have been reported in the literature concerning direct propene epoxidation with O_2 [32–35]. However, at sufficiently high oxygen coverage, nucleation and growth of copper oxide occurs, which inhibits epoxidation [30]. One way to control the extent of Cu oxidation under reaction conditions involves the use of alloys. It has been reported recently that Au–Cu/TiO_2 bimetallic catalysts prepared by impregnation methods perform better than Au/TiO_2 and Cu/TiO_2 for propene epoxidation [36]. However, precise control of particle size was not achieved due to the preparation route, and particles in the range 2–20 nm were encountered, which prevented accurate interpretation of the alloying effect, taking into account the dependence of propene oxide selectivity with particle size.

Several approaches have been used to prepare gold nanoparticles on metal oxide supports including incipient wetness impregnation, co-precipitation, deposition–precipitation, ion exchange, gas-phase grafting, co-sputtering, organic capping, and dendrimer and micelle encapsulation [1,2,9,37–45]. Impregnation and precipitation methods are very simple and scalable, but normally suffer from precise particle size control. In contrast, organic capping and encapsulation methods produce size-controlled gold nanoparticles whose particle size is established before deposition on the metal oxide support. Moreover, the coordinating ligands in the precursor solution and on the oxide surface prevent aggregation of the nanoparticles [12,41,46–48]. In this work, we have prepared a variety of well-defined Au and Au–Cu alloy nanoparticles with different composition and size supported on anatase from dodecanethiol-capped nanoparticles. These have been characterized by high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), and temperature programmed reduction (TPR), and tested in the direct epoxidation of propene by N_2O. We have attempted to study the role of alloy composition as well as the contact structure between TiO_2 and the alloy nanoparticles in the propene epoxidation reaction by studying the effect of calcination temperature, particle size, and surface composition.

2. Experimental

2.1. Preparation of Au–Cu/TiO_2 catalysts

Bimetallic Au–Cu nanoparticles with Au:Cu molar ratios of 3:1, 1:1, and 1:3 as well as monometallic Au nanoparticles encapsulated with dodecanethiol monolayer shells were synthesized following the two-phase method described for the synthesis of dodecanethiol-capped monometallic Au nanoparticles [49–51] and metal alloy clusters [52]. $AuCl_4^-$ and Cu^{2+} species were first transferred from aqueous $HAuCl_4$ and $Cu(NO_3)_2$ solutions (30 mM) to toluene solution using tetraoctylammonium bromide as a phase transfer reagent. Dodecanethiol was then added to the solution at a dodecanethiol:$(Au + Cu) = 3:2$ mole ratio, and an excess of aqueous $NaBH_4$ was slowly added to reduce the metal salts. Bimetallic particles of different sizes were obtained by changing the concentration of metal salt solutions from 30 to 15, 6, and 3 mM. The resulting dodecanethiol-capped metallic nanoparticles were subjected to solvent removal and cleaned using ethanol. The nanoparticles were then dissolved in toluene and impregnated onto commercial anatase (Sigma–Aldrich, 99.8+%, $S_{BET} = 10\ m^2\,g^{-1}$). The solvent was evaporated slowly overnight and the samples were calcined at 573, 673, 773, or 873 K for 2 h. No organic residues were detected by thermogravimetric analysis, infrared spectroscopy, and XPS after calcination at any of these temperatures. All samples attained a pale pink color typical of the presence of gold nanoparticles over TiO_2. Au and Cu contents were measured by wet methods by inductively coupled plasma.

2.2. Characterization of catalysts

High resolution transmission electron microscopy (HRTEM) was carried out using a JEOL JEM 2010F electron microscope equipped with a field emission source at an accelerating voltage of 300 kV. Electron energy-loss spectroscopy (EELS) was performed in STEM mode with a Gatan detector. In the case of thiol-capped solutions, the sol was directly dropped onto carbon-coated grids. For Au–Cu/TiO_2 catalysts, powders were suspended in methanol for about 1 min under ultrasonic treatment before they were deposited on holey carbon-coated grids. The microscope was calibrated at different magnifications before and after measurements using appropriate standards. The point-to-point resolution achieved was 0.19 nm and the resolution between lines was 0.14 nm. A minimum of 250 particles were measured in each sample for particle size determination. The size limit for the detection of nanoparticles on the support was about 1 nm. The average particle diameter was calculated from the mean diameter frequency distribution with the formula: $d = \sum n_i d_i / \sum n_i$, where n_i is the number of particles with particle diameter d_i in a certain range. For surface analysis, X-ray photoelectron spectroscopy (XPS) was performed with a Perkin–Elmer PHI-5500 instrument equipped with an Al X-ray source operated at 12.4 kV and a hemispherical electron analyzer. Temperature programmed reduction (TPR) experiments were performed with a Thermo Finnigan TPDRO 1100 apparatus equipped with a thermal conductivity detector and coupled to a Omnistar QMS 422 mass spectrometer. A 20 $mL\,min^{-1}$ gas flow of 5% H_2 in Ar was used as a reducing agent and the temperature was raised from 323 to 1073 K at a constant rate of 20 $K\,min^{-1}$.

2.3. Catalytic tests

Propene epoxidation was carried out in a fixed-bed reactor at atmospheric pressure. Experiments were carried out typically with 0.15 g of catalyst and a total flow rate between 30 and 90 $mL\,min^{-1}$. The gas mixture consisted of 10% propene and 10% N_2O balanced in Ar. The reaction was monitored at increasing temperature from 473 to 673 K. Reaction products were analyzed on-line with two gas chromatographs equipped with a molecular sieve and Porapak T columns using TCD and FID detectors. Transfer line and valves were maintained at 373 K in order to prevent condensation of products.

3. Results and discussion

3.1. Characterization of catalysts

Table 1 compiles the composition of catalysts investigated in this work. Two series of samples were prepared. In one of them, the total metal loading was maintained at ca. 1.2 wt% while the ratio Au:Cu was varied from 1:0 to 1:3 on a molar basis. In the other series, the nominal ratio Au:Cu was fixed at 1:3 and the total metal loading was varied from ca. 0.5 to 1.2 wt%. All these catalysts were characterized in detail by transmission electron microscopy techniques and XPS after calcination at different temperatures. The corresponding precursor nanoparticles were also studied by HRTEM. Details of particle size distribution of these samples are summarized in Table 2.