

Nanocrystalline and mesostructured Y_2O_3 as supports for gold catalysts

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The structure of yttrium oxide influences the CO oxidation activity of $\text{Au}/\text{Y}_2\text{O}_3$ catalysts; nanocrystalline Y_2O_3 stabilizes more active species of gold and increases the activity of the gold catalyst in comparison with mesostructured and precipitated Y_2O_3 .

Highly dispersed gold on metal oxide supports has been found to catalyze reactions including CO oxidation,¹ ethylene hydrogenation,² ethylene hydrochlorination,³ and propene epoxidation.⁴ Although it is accepted that factors such as gold particle size, synthesis method, pre-treatment conditions, and support influence the reactivity of the supported gold catalysts,⁵ the nature of the active sites and the relevance of the support properties to CO oxidation activity are still subjects of debate.

In a recent communication,⁶ our group demonstrated that the characteristics of the cerium oxide surface are extremely important in determining whether or not a CeO_2 -supported gold catalyst is active for CO oxidation. It was found that nanocrystalline (nanoparticles of about 4 nm in size with a fluorite structure) CeO_2 increases the activity of gold for CO oxidation by two orders of magnitude with respect to a precipitated CeO_2 support. In the present work, we report the synthesis of mesostructured nanoparticles of yttrium oxide. Also, gold has been deposited on a precipitated Y_2O_3 , which is considered to be an inadequate support for gold,⁵ on a nanocrystalline Y_2O_3 (~5 nm) precursor, and on a mesostructured Y_2O_3 . These catalysts were used for CO oxidation and the results show that it is not only the size of the gold particles and the chemical composition of the support that are determinant catalytic parameters; the structure and crystallite size of the support have also been found to influence the oxidation state of the supported gold, and consequentially the catalytic activity.

A colloidal dispersion of Y_2O_3 , containing particles with an average diameter size of about 5–6 nm, was supplied by Nyacol, Inc. The dispersion was purified and concentrated in order to obtain nanocrystalline Y_2O_3 . For the synthesis of mesostructured yttrium oxide, 6-aminocaproic acid (ACA) was mixed with 12 g of a colloidal dispersion of Y_2O_3 (14 wt%) with a molar ratio of ACA– Y_2O_3 of 0.30. This solution was added at room temperature to a mixture of nonionic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock copolymer (2 g) with the structural formula $(\text{EO})_{20}(\text{PO})_{70}(\text{EO})_{20}$ (Pluronic P123, BASF) and H_2O (10 g). The resultant dispersion was stirred for 30 min and then it was allowed to evaporate in air; the as-synthesized sample was calcined at 400 °C for 4 h to remove all the organic compounds.⁷ As a reference and to compare our materials, precipitated Y_2O_3 was obtained from Aldrich.

Gold was deposited on the three different yttrium oxide supports by the following procedure: a solution of HAuCl_4 (0.14 g) in deionized water was brought to pH 9 by the addition of 0.2 M NaOH (~6.0 g). The solution was added to a slurry containing Y_2O_3 (1.26 g) in H_2O (40 ml). The pH of the slurry was adjusted to 9 with 0.2 M NaOH (~1.0 g), and it was vigorously stirred for 18 h at room temperature. The solid was then isolated by filtration, thoroughly washed to remove chloride, and dried for 16 h at 100 °C. The gold content of 2.5 wt% Au was determined by chemical analysis. The gold catalysts were not calcined nor pre-treated with any gas prior to catalysis tests.

Transmission electron microscopy (TEM) characterizing the Y_2O_3 obtained from the colloidal dispersion (Fig. 1a) shows that the support is made up of regular nanoparticles of about 6 nm in diameter, confirming that the size of the colloids (5–6 nm) defines the size of the nanoparticles.⁷ The TEM images characterizing the mesostructured Y_2O_3 (Figs. 1b–c) show a structure with well defined hexagonal symmetry with pore diameters of about 6 nm, consistent with XRD results showing a main peak at 1.3° that indicates d_{100} (6.8 nm) of mesoporous structure and N_2 adsorption–desorption isotherm results (Table 1) indicating a pore diameter of 6.5 nm and a wall thickness of ~6 nm;⁸ suggesting that the hexagonal structure of the mesoporous walls are formed by self-assembly of individual nanoparticles in liquid crystal phase to form a monolayer of individual Y_2O_3 nanoparticles.⁷ To the

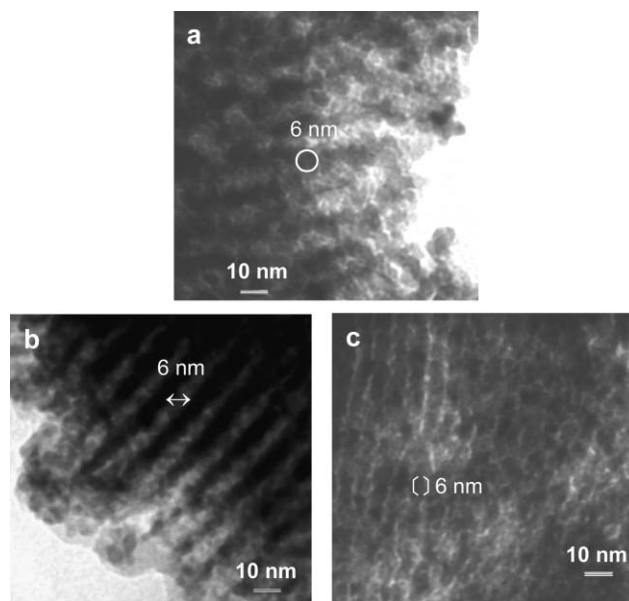


Fig. 1 TEM images of yttrium oxide supports: (a) nanocrystalline Y_2O_3 , and mesostructured Y_2O_3 showing the pore channels along the (b) [100] and (c) [001] directions.

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Table 1 Textural characterization of the Y₂O₃ supports^a

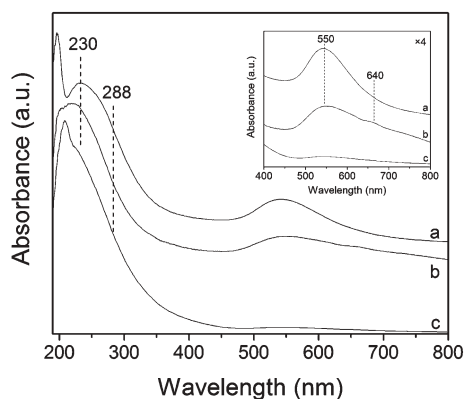
Sample	S _{BET} /m ² g ⁻¹	V/cm ³ g ⁻¹	D _{pore} /nm	D _{particle} /nm
Powder	44	0.0665	—	27.0
Nanocrystalline	70	0.2363	—	6.2
Mesostructured	90	0.3245	6.5	6.6

^a All supports were calcined at 400 °C in air for 4 h.

best of our knowledge, this is the first report of the synthesis of mesostructured Y₂O₃.

TEM images characterizing the Au/Y₂O₃ catalysts (using precipitated, nanocrystalline, and mesostructured Y₂O₃) show a narrow size distribution of gold particles with an average diameter size of 4 nm for all the catalysts (not shown); however, we cannot rule out the presence of small gold particles undetectable with TEM. Indeed, the UV–vis results indicate that the gold species supported on the three different supports are not the same. The catalyst prepared with nanocrystalline Y₂O₃ shows absorption bands at 230 and 288 nm (Fig. 2c), which are assigned to a positively charged gold species,⁹ either as isolated cations or as a part of gold clusters (most likely at the perimeter of the contact area between the Au clusters and the support). The catalyst prepared with mesostructured Y₂O₃ shows bands at 230, 288, 550, and 640 nm (Fig. 2b). The broad band at 550 nm is characteristic of metallic gold clusters, whereas the band at 640 nm corresponds to the d–d electron transitions of Au³⁺.⁹ Similarly, the catalyst prepared with precipitated Y₂O₃ shows bands at 230, 288, 550, and 640 nm, but the intensity of the bands at 550 and 640 nm indicates the presence of larger metallic gold clusters and less Au³⁺ in comparison with the mesostructured sample. Thus, the UV–vis results indicate that nanocrystalline Y₂O₃ assisted in the stabilization of active Au^{δ+} species and limited the formation of large metallic gold clusters.^{6,10} Mesostructured Y₂O₃ stabilized Au^{δ+} species too, but it also contains Au³⁺ and metallic gold clusters. In contrast, precipitated Y₂O₃ contains predominantly metallic gold clusters.

To confirm our assignments, we characterized the catalysts with infrared (IR) spectroscopy and CO adsorption experiments. Gold supported on nanocrystalline Y₂O₃ shows an IR band at 2153 cm⁻¹, which is assigned to CO adsorbed on a positively charged gold species,¹¹ whereas two bands at 2153 and 2094 cm⁻¹

**Fig. 2** UV–vis spectra characterizing 2.5 wt% Au/yttrium oxide catalysts prepared with different supports: a) precipitated Y₂O₃, b) mesostructured Y₂O₃, and c) nanocrystalline Y₂O₃.

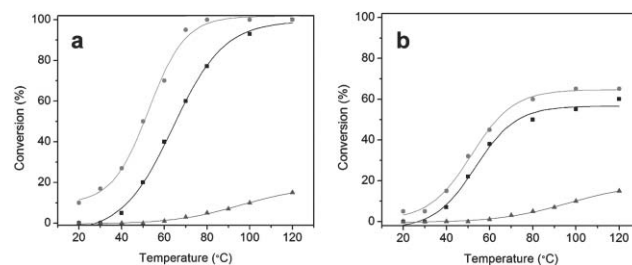
were observed for gold supported on mesostructured Y₂O₃. The new band at 2094 cm⁻¹ is assigned to CO adsorbed on Au⁰. When CO was adsorbed on the gold catalyst prepared with precipitated Y₂O₃, the spectrum shows an intense band at 2094 cm⁻¹ and a shoulder at 2153 cm⁻¹. The results are consistent with the UV–vis data indicating that nanocrystalline and mesostructured Y₂O₃ stabilize predominantly cationic gold.

The Au/Y₂O₃ catalysts were tested for CO oxidation and the results demonstrate a strong influence of the structure of the Y₂O₃ support on the CO oxidation activity. The gold catalyst synthesized with a conventional Y₂O₃ support prepared by precipitation shows a minimum activity at 80 °C (5% conversion), consistent with the conventional wisdom about Y₂O₃ being an inadequate support for gold catalysts. In contrast, when gold is deposited on nanocrystalline Y₂O₃ particles, the conversion of CO at the same temperature was 100% (Fig. 3a). Interestingly, the observed CO conversion of the gold catalyst prepared with the mesostructured Y₂O₃ support was just 75%. When the reaction was carried out at 50 °C, the specific rate per gram of Au of the catalyst prepared with nanocrystalline Y₂O₃ was found to be 2.1 × 10⁻⁴ mol_{CO} s⁻¹ g_{Au}⁻¹, which is comparable with those of other gold catalysts prepared on “active” supports at the same temperature and under similar reaction conditions.¹²

A plausible explanation for the enhanced reactivity of the catalysts prepared with nanocrystalline Y₂O₃ is associated with the stabilization of Au^{δ+} species at the cluster–support interface, caused in part by oxygen vacancies on the surface of the nanocrystalline support and by a synergistic effect associated with the nanosize of both the gold and the support.

To further investigate the reactivity of our catalysts, we carried out the selective oxidation of CO to CO₂ in a H₂-rich gas stream. This reaction is of special interest for fuel cell technologies when carried out at low temperatures (60–80 °C).¹³ The gold catalysts prepared with nanocrystalline and mesostructured Y₂O₃ show a decrease in CO conversion (as expected by the presence of H₂) and excellent selectivity for CO oxidation in the presence of H₂. The oxygen consumption demonstrated a 99.5% selectivity for the oxidation of CO at 80 °C, and only 0.5% of the oxygen reacted with H₂ to give H₂O. In contrast, the performance of the gold catalysts prepared with precipitated Y₂O₃ is poor, both in reactivity and selectivity.

In summary, we have shown that the structure–properties of the support influence the stabilization of active gold species, and therefore, determine the CO oxidation activity of the

**Fig. 3** CO oxidation in the absence (a) and in the presence (b) of H₂ on 2.5% Au/Y₂O₃ catalysts using three different types of yttrium oxide: (●) nanocrystalline, (■) mesostructured, and (▲) precipitated. Reaction conditions: the molar ratio of CO : O₂ : He : X (X = H₂ or N₂) was 0.8 : 0.4 : 40.4 : 58.4, with a contact time (W/F) of 27.6 g_{cat} h mol_{CO}⁻¹.

Y₂O₃-supported gold catalysts. Y₂O₃, an “inadequate” support for gold catalysts, was transformed into a highly active material for the oxidation of CO in the absence or in the presence of H₂. This is also the first report of the synthesis of mesostructured Y₂O₃.

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