CO oxidation on gold nanoparticles supported over titanium oxide nanotubes

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ARTICLE INFO

ABSTRACT

Titanium oxide nanotubes (TN) were synthesized and used as support for Au nanoparticles obtained by deposition–precipitation with urea. The activity of Au/TN catalysts prepared under different conditions was tested in the oxidation of CO. The results indicate that titanium oxide nanotubes (TN) can be used as support for gold nanoparticles obtained by deposition–precipitation, since adequate gold nanoparticle sizes (<5 nm.) for CO oxidation can be obtained.

Varying the preparation conditions of the catalysts it was found that the best catalyst performance is obtained by calcining the TN support at temperatures higher than 400 °C, temperature at which the trititanate phase obtained in the as-prepared material is completely transformed into TiO_2-anatase. Higher calcination temperatures lead to a significant decrease in the surface area of TN.

It was also observed that the activity of the Au/TN catalysts was negatively affected by long storage periods. This fact was evidenced by the significant increase in gold particle size, which is apparently due to the high mobility of gold nanoparticles on the support.

Increasing the gold loading from 3 to 9 wt% does not improve the CO oxidation activity because, at 9 wt% Au the particle sintering increases leading to particles greater than 5 nm, which are not effective for CO oxidation.

To obtain good catalytic activity it is necessary to pretreat the catalysts at least at 300 °C to assure the complete reduction of the gold precursor. The use of hydrogen or air in the catalyst pretreatment to obtain the reduction of the gold precursor did not affect the performance catalysts.

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1. Introduction

Titanium oxide nanotubes (TN) prepared by hydrothermal synthesis have attracted special attention since 1998, when Kasuga published his work describing them for the first time [1]; since then some researchers have published works related to their synthesis [2–19,28] or applications [20–27]. TN present three main advantages: high specific area (400 m²/g) [1], low cost, and feasibility to be produced in great quantities. These materials can be potentially used in the fields of photocatalysis [20,29,31], solar cells [21], adsorbents [22] and heterogeneous catalysis [23–28,30,32,33]. Specifically, TN have been used as catalytic support for different metal active phases (metallic, oxides or sulfides): platinum for cyclohexene hydrogenation–dehydrogenation [23], copper for NO reduction with NH_3 [24], cobalt and molybdenum for fuels hydrodesulfurization (HDS) [25–27], iridium and cobalt for water

splitting for hydrogen production [28], iron for photocatalytic oxidation of acetaldehyde [29], gold for water–gas shift reaction [30], photocatalytic mineralization of benzene [31] and CO oxidation [32,33].

Gold is a metal with no reactivity in bulk, but if it is divided into nanoparticles it displays high activity for several reactions; Haruta et al. showed that gold nanoparticles supported on oxides can perform the carbon monoxide (CO) oxidation [35]. This application is interesting for pollution control because of the capability of gold nanoparticles to oxidize CO at temperatures even lower than 0 °C. It has been shown that the reactivity of gold depends on both the nanoparticle size, which must be lower than 5 nm [36], and on the support used. Titanium oxide has demonstrated to be one of the best supports [36,37], despite its low specific area (45 m²/g) as in Degussa P-25 [38]. A way to improve the Au/TiO_2 catalysts would be the use of TiO_2 supports with high specific surface area. It appears interesting then to analyze the performance of Au nanoparticles supported on TiO_2 nanotubes in the CO oxidation reaction, and test their activity and stability when some of the preparation and catalyst activation conditions are varied.

An adequate way to support gold nanoparticles on TiO_2 with sizes below 5 nm is the deposition–precipitation method used by
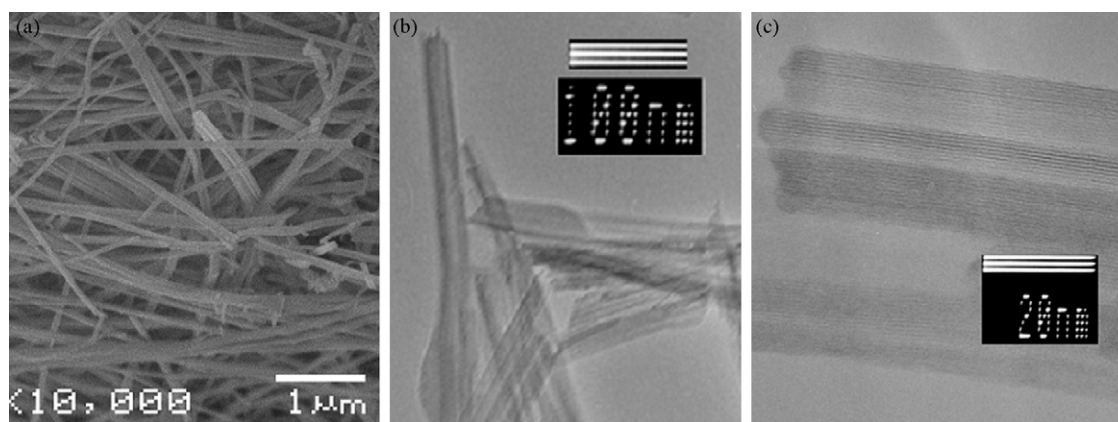
Fig. 1. (a) SEM image of as-prepared TN; (b) TEM image of as-prepared TN; and (c) magnified TEM image of a nanotube, where a central channel and wall details can be observed.

Zanella et al. [38–40], which uses urea to increase the solution pH instead of sodium hydroxide as proposed by Haruta et al. [35]. The aforementioned method allows the deposition of metal loadings close to 100% of the metal in solution.

In the present work we analyze the possibility to obtain highly active CO oxidation catalysts by the deposition of gold nanoparticles, smaller than 5 nm, over titanium oxide nanotubes (TN). In particular, attention will be focused on the changes produced in the CO oxidation activity when the calcination temperature of the support, the storing time of catalysts, the gold loading and thermal treatment conditions before reaction (temperature and gas type) are varied. To this end the supports and catalysts were characterized by N_2 fisisorption, X-ray diffraction and transmission electron microscopy (TEM). The catalysts were evaluated in the CO oxidation reaction using a temperature-programmed reaction system.

2. Experimental

2.1. Support preparation

Titanium oxide nanotubes (TN) were prepared as described elsewhere according to Kasuga's method [1]. In short, 2 g of TiO_2 (P-25, Degussa) were mixed with 134 mL of an aqueous solution of NaOH (10 M). The mixture was kept under stirring in a Teflon autoclave at 110 °C for 24 h. Then, the autoclave was quickly cooled to room temperature and opened to recover a white precipitate, which was thoroughly washed with distilled water and with an aqueous solution of HCl (0.1 M). The product was then filtered, dried in air at 120 °C for 12 h and later calcined in static air at 300–500 °C for 4 h.

2.2. Au/TN preparation

One gram of TN was suspended in 37 mL of an aqueous solution of $HAuCl_4 \cdot 3H_2O$ (0.0042 M) and urea (0.42 M) at room temperature in a vessel protected from light. Then the suspension was heated up to 80 °C and kept under stirring for 16 h to allow the deposition–precipitation of gold over the support surface, then the mixture was centrifuged to recover the solid. To eliminate residual ions, the solid was stirred in 50 mL of distilled water at 50 °C and centrifuged again at 50 °C, this process was repeated four times. The solid was then dried under vacuum at 80 °C for 2 h and stored away from light in a desiccator under vacuum at room temperature. The same procedure was applied to prepare a Au/TiO_2 catalyst but in this case the support employed was titania P-25 (Degussa). Catalysts with 3 and 9 wt% Au were prepared. The catalyst with high Au load was only used for the experiments performed to analyze the effect of gold load.

2.3. Characterizations

SEM images and EDX microanalysis were obtained using a JEOL JSM-5900 LV scanning electron microscope equipped with an Oxford-Isis energy dispersive X-ray analyzer. TEM images were obtained using a JEOL 2010 transmission electron microscope at 200 kV. For TEM analysis the samples were dispersed by ultrasonication in ethyl alcohol for 20 min and a drop of the supernatant liquid was placed onto a holey carbon film supported on a copper grid. The structure of the nanotubes was characterized by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with a Cu Kα source (λ = 1.5406 Å). Textural properties were determined by nitrogen physisorption, using a Micromeritics TriStar apparatus. The specific area was calculated from Brunauer–Emmett–Teller (BET) equation and the pore size distribution was analyzed with the Barrett–Joyner–Halenda (BJH) method. The catalytic experiments were performed in a In Situ Research RIG-150 catalyst characterization system, using a fixed bed quartz reactor with 42.5 mg of catalyst and gas flow of 100 mL/min. The gas mixture consisted of 98% of N_2, 1% of CO and 1% of O_2. The exit gases were analyzed with an online gas chromatograph (Agilent Technologies 6890N) equipped with FID detector and a HP Plot Q column. The temperature during the reaction tests was programmed from −5 to 300 °C with a linear ramp of 2 °C/min. Before the reaction the catalyst was pretreated for 2 h with air or hydrogen (80 mL/min) at temperatures between 200 and 400 °C.

3. Results and discussion

3.1. Nanotube synthesis

SEM observations of the as-prepared material showed the presence of bundles of filaments of different widths, 40–100 nm, and lengths of several hundreds of nanometers (Fig. 1a). The presence of nanotubes was made evident by the observation of the samples by TEM. Fig. 1b and c shows some details of the tubular structure of the filaments. The nanotube walls seem to be formed by several layers separated by ca. 0.7 nm, in good agreement with previous reports of 0.78 and 0.71 nm in the separation of the layers forming the nanotube wall [2,5]. The inner diameter of the observed TN ranged from 5 to 15 nm, and the outer diameter from 11 to 18 nm.

Since the TN are intended to be used as catalyst supports, it is important to know the textural and structural changes that they undergo with the calcination temperature. Fig. 2 shows the TEM images of TN calcined in static air at 300 and 500 °C. It is evident that as the calcination temperature is increased, the tubular structure of the TN, which was well defined for the as-prepared material,