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Nanocrystalline cerium oxide produced by supercritical antisolvent precipitation as a support for high-activity gold catalysts

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Abstract

Nanocrystalline CeO_2 was prepared by precipitation of a solution of the acetate using supercritical CO_2 as an antisolvent. It was demonstrated that gold supported on this material is very active for the oxidation of CO at ambient temperature, particularly in comparison with CeO_2 prepared in a conventional manner by thermal decomposition of the acetate. Comparing the catalytic performance for CO oxidation with the most active catalysts in the current literature confirms the high activity of these new materials. They are considerably more active than previous Au/CeO_2 catalysts. The catalyst activity was found to be dependent on the precipitation conditions, which in turn was found to influence the dispersion of gold on the support, as evidenced by detailed microscopy and spectroscopy characterization. The most active fresh catalyst exhibited highly dispersed gold and showed no evidence of the existence of Au nanocrystals using detailed STEM analysis. Following reaction with CO/O_2, subtle microstructural changes were apparent, although the morphology of the nanocrystalline CeO_2 support was unchanged; in particular, the Au, which was previously uniformly dispersed, showed signs of beginning to agglomerate into sub-5 nm particles. The stability and origin of the catalytic activity are discussed.

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1. Introduction

Oxidation is a key process that can be used to functionalize molecules using selective oxidation or to remove pollutants using total oxidation. Increasing attention is being given to green chemical reactions, which focuses interest on the design of chemical processes that are atom-efficient. This is particularly true in the fine chemicals industry, where many reactions are done with low atom efficiency [1]. Recently, there has been interest in using gold as a catalyst for oxidation by O_2 [2–4]. Gold dispersed on oxide supports exhibits excellent activity in various important catalytic redox reactions, including CO oxidation [5], which is particularly useful for the purification of hydrogen in fuel cells [6,7]. Supported gold catalysts also have been shown to be very active for the epoxidation of propene [8] and the selective oxidation of alcohols [9]. In recent studies, we have shown that gold can epoxidize alkenes under solvent-free conditions [10] and that supported gold-palladium alloy nanoparticles are highly effective for the direct formation of hydrogen peroxide [11] and oxidation of alcohols [12]. The nature of the supporting matrix for the gold and gold-palladium nanoparticles is of great importance [13–18], and nanocrystalline oxide supports (e.g., CeO_2 and Y_2O_3) have been shown to greatly increase the activity of gold catalysts for CO oxidation compared with supports comprising larger crystallites [16,17].

The extensive literature concerning the low-temperature oxidation of CO has recently been reviewed [19]. In the design of active catalysts for the low-temperature oxidation of CO, much emphasis has been placed on the method of catalyst preparation, as well as the nature of the support, and most investigators

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agree that high-activity catalysts can be observed with α-Fe_2O_3 [20–26] and TiO_2 [27–35]. Until recently, CeO_2 [16,17,36–38] was not favored as a support, although it was used as a support for very active supported gold low-temperature water-gas shift catalysts [39,40], and although CO oxidation can be considered mechanistically related to the water-gas shift reaction, these catalysts operate at significantly higher temperatures. Recent studies by Corma et al. [16] showed that very active catalysts can be achieved using a nanocrystalline form of CeO_2. However, detailed studies have concentrated on TiO_2 and Fe_2O_3 as supports, and it is now well established that the method of preparation is crucial to controlling the activity of the catalyst [32]. In general, impregnation of titania tends to produce large particles (>10 nm) that are inactive for CO oxidation. Consequently, Haruta et al. [5] devised the method of deposition precipitation, in which a preformed support is stirred in a solution of a gold compound, the pH value is varied by the addition of a base, and small gold nanocrystals are deposited on the surface of the support. This method of preparation has been widely adopted.

The recent interest in using CeO_2 as a support for Au for the CO oxidation reaction has prompted us to study the synthesis and properties of nanocrystalline CeO_2 prepared using a different methodology: precipitation using supercritical CO_2 ($scCO_2$) as an antisolvent. The use of $scCO_2$ as an antisolvent for the controlled precipitation of materials from conventional solvents has been widely applied to the production of a range of materials, including polymers, pharmaceutical chemicals, explosives, superconductors, and catalysts [41–46]. When a solution is brought into contact with $scCO_2$, the solvent power of the conventional solvent is reduced, and the solutes precipitate. Furthermore, the diffusivity of $scCO_2$ is about two orders of magnitude larger than that of conventional liquids. This rapid diffusion can produce supersaturation immediately before precipitation, leading to the formation of nanoparticle morphologies not usually accessible by standard catalyst preparation methods. Using this precipitation method, we have successfully prepared vanadium phosphate catalysts that exhibit enhanced activity compared with conventional materials for the selective oxidation of butane to maleic anhydride [46]. We consider using supercritical carbon dioxide as an antisolvent to facilitate precipitation as the basis of a new green preparation method in which the use of nitrates can be eliminated, thereby decreasing the environmental impact of catalyst preparation in the longer term. We now show that nanocrystalline CeO_2 prepared using this precipitation route can be a highly effective support for Au catalysts for the oxidation of carbon monoxide at ambient temperature.

2. Experimental

2.1. Preparation of CeO_2

Chemicals were purchased from Aldrich and used as received. The synthesis of the $scCeO_2$ was performed as described previously [46]. $scCO_2$ was pumped at pressures of 110–150 bar at a flow rate of 7 ml/min, and the entire system was held at a fixed temperature (40 or 60 °C). A solution of $Ce(acac)_3$ in methanol (13.33 mg/ml) was pumped through a fine capillary into the precipitation vessel at a flow rate around 0.1 ml in co-current mode with $scCO_2$. As the solution exited the capillary, the droplet and $scCO_2$ rapidly diffused into each other, causing the solute to precipitate rapidly. The precursor was recovered and calcined at 400 °C for 2 h. The $unCeO_2$ support was obtained by calcining the unprocessed $Ce(acac)_3$ at 400 °C for 2 h.

2.2. Preparation of gold catalysts

Gold was deposited on the supports by a deposition–precipitation procedure. A solution of H_4AuCl_4 (28 mg) was adjusted to pH 10 using 0.2 M NaOH and added into a slurry containing CeO_2 (200 mg) in water (10 ml), then stirred for 20 h. The solid was recovered by filtration, washed, and dried overnight at 100 °C.

2.3. Catalyst testing

Catalysts were tested for CO oxidation using a fixed-bed microreactor (3 mm i.d.), operated at atmospheric pressure. Typically, CO (0.5% in synthetic air) was fed at 22.5 ml/min and passed over the catalyst (15 mg). The temperature was maintained at 25 °C by immersing the bed in a water bath. The products were analyzed using online GC.

2.4. Catalyst characterization

Materials were characterized by powder XRD using an Enraf Nonius PSD120 diffractometer with a Cu$K\alpha$ source operated at 40 keV and 30 mA. Surface areas were determined by nitrogen adsorption at −196 °C using the BET method. Au loadings were determined using a Varian 55B AA spectrometer.

Samples of each catalyst were prepared for TEM characterization by dispersing the powder in ethanol. A drop of the suspension was then placed on a 300-mesh lacey carbon TEM grid and allowed to dry. Bright-field imaging experiments were carried out in a JEOL 2000 FX TEM operating at 200 kV. Annular dark-field (ADF) imaging and X-ray energy dispersive spectroscopy (XEDS) analyses were carried out at 300 kV using a VG HB 603 dedicated STEM fitted with a Nion Inc. spherical aberration corrector and an Oxford Instruments INCA 300 system for XEDS spectrum imaging.

XPS was done using a Kratos Axis Ultra DLD spectrometer using a monochromatic Al$K\alpha$ X-ray source (75 W) and an analyzer pass energy of 160 eV (survey scans) or 40 eV (detailed scans). Samples were mounted using double-sided adhesive tape, and binding energies are referenced to the C(1s) binding energy of adventitious carbon contamination taken to be 284.7 eV.

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