Specific role of polymorphs of supporting titania in catalytic CO oxidation on gold

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ABSTRACT

Dependence of catalytic activity in CO oxidation on the structure of gold nanoparticles supported on various TiO_2 polymorphs has been investigated. Pure brookite, brookite–anatase (45:55) and anatase–rutile (85:15) mixtures were compared as supports of Au/TiO_2. Au nanoparticles were deposited on different TiO_2 supports by adsorption of Au colloids of about 6 and 15 nm mean diameter and by deposition precipitation (DP) with urea providing Au particles smaller than 5 nm in size. Sol derived gold particles were more stable against sintering on brookite than on anatase containing supports. Taking into account the particle sizes of gold and titania for all types of gold deposition methods, the Au–anatase perimeter seems to be significantly more active in CO oxidation than the Au–brookite perimeter. The difference in activity should be originated from the different electronic, physical and surface properties of anatase and brookite.

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1. Introduction

It has been a wide scale of research for TiO_2 as support for Au nanoparticles catalysing CO oxidation. The different polymorphs of a compound have a large variation in their properties. TiO_2 has three different crystal structures, namely anatase, rutile (both tetragonal) and brookite (orthorhombic), which have different photocatalytic properties because of the variation in the energy of band gaps [1–3]. The band gaps of anatase, brookite and rutile are 3.05, 3.26 and 2.98 eV respectively. In addition, the potential of the bottom of the conduction band of anatase, rutile and brookite are at −0.45, −0.46 and −0.37 vs NHE, respectively. Variation in the photocatalytic properties of these allotropic forms of TiO_2 were explained successfully based on the above points. It is also known that brookite and anatase transform to the rutile phase at 800 °C and 915 °C respectively. The surface enthalpy follows the order rutile $(2.2 \pm 0.2 \, J\,m^{-2})$ > brookite $(1.0 \pm 0.2 \, J\,m^{-2})$ > anatase $(0.4 \pm 0.2 \, J\,m^{-2})$ [4]. These variations in the properties of the allotropic forms are expected to influence the catalytic activity, when they are used as supporting material for gold.

Meanwhile, gold, that was considered earlier as a highly inactive metal as a catalyst was found to be active when present in nanometer sized particles [5,6]. Various supports have been used for gold nanoparticles of the same size and used for promoting the catalytic CO oxidation. Among TiO_2, Al_2O_3, CeO_2, ZnO, SiO_2, ZrO_2, and Co_3O_4 as supports TiO_2, Co_3O_4 and Al_2O_3 were found to be the most active [7–9]. Comotti et al. [8] reported the CO oxidation activity of samples prepared by colloidal deposition method, where pre-synthesized gold nanoparticles of uniform size were deposited on different supports, the activity followed the sequence of TiO_2 > Al_2O_3 > ZnO > ZrO_2. These results show that the support plays a significant role in deciding the CO oxidation activity of the catalyst. The different morphology of given oxide may also affect the activity as was reported for TiO_2 promoted Au/SiO_2 catalysts. The highly dispersed, mainly amorphous TiO_2 formed a perimeter with gold which was more active than the perimeter of Au with crystalline anatase [10–12].

There are other factors which have been reported to influence the catalytic activity. They are size of the gold particles, oxidation state (cationic sites) of gold species [13,14], and the preparation method [15–19]. In addition, low-coordinated step and corner atoms [20–23], metal–support interface area [6,24–26], and the charge transfer from the support to the metal [27,28] are also reported to influence the activity.

Most of the CO oxidation studies were carried out using anatase and rutile phases of TiO_2 as support for Au. Systematic compar-

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ison on the effect of different titania polymorphs was reported only in several papers [29–32]. The results indicated that anatase is a better support than rutile and the thermal stability of rutile supported catalysts is less compared to that of anatase. Studies using brookite as support for gold were not carried out extensively so far. Yan et al. [31,32] recently reported the brookite phase to be more active towards CO oxidation than anatase and rutile forms of TiO_2. The brookite as support was described to prevent more efficiently the sintering of the gold nanoparticles than the anatase and rutile forms of TiO_2. However, the report by Yan et al. is based on the results from the deposition–precipitation method, where the support considerably influences the particle size and shape of the particles of Au. Among the various methods of preparation of supported gold nanoparticles described, deposition precipitation methods are reported to yield the most active catalysts [33–35]. However, for comparing the effect of the various supports on the metal and subsequently the catalytic activity, deposition–precipitation method may not be reliable. With the different sizes and shapes of gold on different supports, the variation in the activity of the different catalysts cannot be attributed specifically to the interaction between the support and gold. This led us to prepare catalysts by sol deposition method where same size and shaped gold particles were prepared separately and then deposited on the different support. Furthermore, this method leads to uniform weight loading of gold on the various supports.

The issue on which the literature is silent is: how does the brookite–metal interaction differ from that of anatase or rutile–metal interaction concerning the CO oxidation activity? In order to obtain appropriate answer to this question, brookite has been prepared by two different methods and compared with anatase and rutile containing Degussa P25 type TiO_2 as supports of gold in catalytic CO oxidation. Gold was deposited with similar loadings by sol adsorption method and deposition–precipitation by urea (DPU).

2. Experimental

2.1. Preparation of TiO_2 from $TiCl_3$

TiO_2 was prepared using $TiCl_3$ (Loba Chemie) according to the procedure adopted by Lee et al. [36] as follows. Urea (0.5 M) was dissolved in 1000 ml of an aqueous solution containing titanium trichloride ($TiCl_3$, 0.015 M). The resulting solution was refluxed at 100 °C for 7 h while stirring leading to the formation of cream coloured precipitate. The precipitate was separated by centrifuging and washing repeatedly (four times with de-ionized water and once with anhydrous ethanol). The precipitated powders were then dried at 100 °C for 2 h in an oven. TiO_2 prepared by this method is being denoted as BA.

2.2. Preparation of TiO_2 from $TiCl_4$

Additionally, TiO_2 was also prepared by following the previously reported method [37]. 0.15 M $TiCl_4$ (99% purity, Merck) was added to 250 ml of 3 M HCl in a 500 ml sealed bottle and heated to 100 °C for 48 h. The obtained precipitate contained brookite and rutile TiO_2. The brookite phase was separated by peptization. The precipitate was dispersed in 3 M nitric acid and the resulting suspension was centrifuged. The solid phase obtained was dispersed in water and then centrifuged. The centrifugate was freeze dried to obtain pure brookite which was dried at 100 °C for 4 h. The TiO_2 prepared this way was denoted as B.

2.3. Preparation of Au/TiO_2 by sol method

40 ml of 5 mM aqueous $HAuCl_4$ solution (Sigma–Aldrich) was made up to 600 ml using bidistilled water. Another solution was made by mixing 32 ml 1% sodium citrate, 8 ml of 1% tannic acid and 120 ml of water. pH of the solution was adjusted to 8 using 4% sodium carbonate solution. The two solutions were heated separately to 60 °C under stirring, then mixed and maintained at 60 °C for 30 min under stirring. The solution turned deep red due to the formation of gold sol. Three sols were prepared denoted as SAu_{15}, SAu_6 and SAu_5.

Gold sols were adsorbed on the two types brookite containing TiO_2 prepared (BA, B) and on the commercial Degussa P25 TiO_2 composed of anatase and in smaller amount rutile (denoted as AR) by addition of poly (diallyldimethylammonium chloride) (PDDA). This polycation adsorbing on the support surface increased the attraction between the support and the colloid Au particles stabilised by negatively charged citrate-tannic acid shell [11]. The amount of PDDA solution (0.08 wt%) required for complete adsorption was different, 23, 35 and 20 ml/g support for AR, BA and B type TiO_2, respectively. The dispersion obtained was stirred magnetically for 90 min. The solution became colourless and the TiO_2 attained a purple colour due to the adsorption of gold nanoparticles. The resulting precipitate was washed with water and dried at 60 °C for 24 h. Using this method gold sols were loaded on to the three different types of TiO_2, BA, B and AR providing samples SAu_{15}/AR, SAu_{15}/BA, SAu_{15}/B and SAu_6/AR, SAu_6/BA and SAu_5/B. Based on calculations, the gold loading on these catalysts was 2 wt%.

2.4. Preparation of Au/TiO_2 by DPU method

Gold was deposited onto all three types of TiO_2 supports also by deposition precipitation with urea [38]. In a typical preparation 1 g of TiO_2 was suspended in 96 ml bidistilled water and 4 ml of 25 mM $HAuCl_4$ solution and 2.5 mg urea was added. The suspension was heated up to 80 °C during about 3 h and kept at this temperature for 2–4 h under stirring, while the pH raised up to 7.0–7.5. The sample was filtered, washed and dried at 60 °C overnight. The pH raise was significantly slower in case of B titania, than in case of AR and BA. That is why the preparation with B type titania was repeated. Similarly slow increase of pH was observed as in the first preparation. The samples produced are denoted as DPUAu/AR, DPUAu/BA, DPUAu/B_1 and DPUAu/B_2.

2.5. Sample characterisation

Crystalline phase composition of the prepared TiO_2 was analyzed by X-ray diffraction (XRD) (Rigaku D/max 2400 instrument, Ni-filtered Cu Kα radiation, λ = 1.5418 Å). The crystallite sizes of the different phases were calculated from the line broadening of the most intense reflections using the Scherrer equation. The surface of the supports was measured by BET technique. Gold loading on TiO_2 was confirmed partly by X-ray fluorescence spectroscopy and ICP-OES analysis (Model: Perkin Elmer Optima 5300 DV).

The size of gold and TiO_2 particles was studied by a Philips CM20 transmission electron microscope (TEM) operating at 200 kV equipped with energy dispersive spectrometer (EDS) for electron probe microanalysis. The aqueous suspensions of the samples were dropped on carbon-coated grid and after evaporating water the electron micrographs of the particles were taken. The gold particle size distribution was obtained by measuring the diameter of about 200–300 metal particles.

Oxidation states and relative surface concentrations of Au were determined by X-ray photoelectron spectroscopy (XPS) performed by a KRATOS XSAM 800 XPS machine equipped with an atmospheric reaction chamber. Spectra were taken on the "as prepared"