



Gold/titania composites: An X-ray absorption spectroscopy study on the influence of the reduction method



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ABSTRACT

The functionalization of titania based materials with noble metal cocatalysts such as gold or platinum is a well known procedure to improve the catalytic activity of these materials in for example the degradation of organic pollutants or CO conversion. Parameters such as cocatalyst load, noble metal particle size and oxidation state influence the efficiency of these materials. We have impregnated a mesoporous titania powder with a gold salt and used different synthesis routes to reduce the gold ions. A structural analysis was performed using electron microscopy and nitrogen sorption. An X-ray absorption near edge structure spectroscopy study, in both high and low resolution, was performed to investigate the influence of the different reduction methods on the oxidation state of the gold atoms. This technique can also provide information on the local environment of the gold atoms and their interaction with the titanium dioxide host. We found that varying the reduction method has a significant impact on the oxidation state of the gold cocatalysts. This lead to varying interactions with the titania support and charging of the gold nanoparticles.

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1. Introduction

Gold/titania composite materials gained more and more interest in recent years because they can be used in a wide range of applications including catalysis (e.g. water–gas shift reaction), photocatalysis (e.g. water purification, H₂ production), photovoltaics and photoelectrochemical solar cells [1–4]. Different synthetic approaches to obtain Au/TiO₂ composite materials have been described [5]: a) mixing of presynthesized Au nanoparticles with the TiO₂ material [6,7], b) adsorbing a gold salt onto a preformed titania powder followed by the reduction of the salt [8–10], c) blending premade gold nanoparticles with the titanium precursor during the synthesis of the titania material [11] and d) combining a gold salt with a titanium precursor, simultaneously forming metal nanoparticles and titanium dioxide [12,13].

During our research we focused on the analysis of Au/TiO₂ composite materials prepared according to route b in which a mesoporous titania powder is impregnated with an aqueous solution of HAuCl₄. In a subsequent step, the salt can be reduced using different reduction methods: chemical (citrate, NaBH₄) [8,14], thermal (H₂ atmosphere) [9,15] or by UV irradiation [10,16].

Several papers discuss the influence of the used synthesis method on the obtained materials and mention large differences in terms of gold particle size, specific surface area of the titania matrix and

(photo)catalytic activity depending on the production procedure [9,15, 17–20]. Yet, only few papers address the determination of the oxidation state of the gold atoms present in the composite material [21,22]. Positively charged gold ions have other properties than metallic gold particles and this can increase or decrease the activity of these materials depending on the application. A positive charge on gold particles increases the activity in the case of CO conversion due to a better adsorption of CO [21], but in the case of photocatalytic hydrogen production on a Pt/TiO₂ material, the ionized atoms have a smaller effect than the metallic atoms [23]. Therefore, it is important to investigate the oxidation states present in a synthesized material. In most cases, X-ray photoelectron spectroscopy (XPS) is used to determine the oxidation state of the gold atoms. However, shifting of the binding energies due to support interactions, particle size/shape and geometric effects makes correct analysis of the spectra complex, as it is very difficult to determine the exact cause of the observed shift [24,25].

To overcome these problems, we used X-ray absorption spectroscopy (XAS) as an alternative and improved method. XAS is an element-specific technique that allows for the determination of oxidation state as well as local chemical environment of the probed atoms by monitoring the amount of X-ray absorption as a function of excitation beam energy. In XAS, the oxidation state is directly related to the so-called absorption edge position, the energy at which the incident X-ray photons have sufficient energy to eject an electron of the absorbing atom into an unbound state, characterized by a sharp increase in X-ray absorbance. As such, a shift in absorption edge position relates to a shift in

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oxidation state of the absorbing atom. Additionally, XAS also provides information on the absorbing atom's local structure and is able to resolve mixtures of differently coordinated species of the absorbing atom by means of linear combination analysis [26]. X-ray adsorption near edge structure (XANES) spectroscopy is the part of XAS situated from approximately 20 eV before to 100 eV after the absorption edge. Information on the local structural environment of the gold atoms can help to better identify the gold species that are present and, in turn, to better understand the nature of their interaction with the titania matrix. This has already been demonstrated for the case of gold on ceria [27].

In this paper, we prepared different composite materials following a synthesis approach that involves adsorption and reduction of HAuCl_4 on mesoporous titania, using different reduction methods. In this way we can investigate the effect of the reduction method (NaBH_4 , H_2 , UV irradiation and microwave irradiation) on material parameters such as particle size, oxidation state and interaction with the titania support.

2. Materials and methods

2.1. Chemicals

Titanium(IV) isopropoxide ($\text{Ti}(\text{O}i\text{Pr})_4$, $\geq 97\%$), gold(III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, ACS reagent, $\geq 49\%$ Au basis), sodium hydroxide (NaOH, reagent grade, $\geq 98\%$) and sodium borohydride (NaBH_4 , $\geq 98\%$) are purchased from Sigma-Aldrich. N-cetyl-N,N,N-trimethylammonium bromide (CTAB, pro analysis) is acquired from Merck, hydrochloric acid (HCl, 36%) from Fiers and ethanol (EtOH, absolute PA) from Panreac. All chemicals are used as received.

2.2. Synthesis

2.2.1. Mesoporous titania

The synthesis of mesoporous titania is based on a recipe described by Beyers et al. [28,29]. Six mL of a clear, colorless ethanolic solution containing 0.59 g CTAB at 40 °C is mixed with a colorless solution of 5.7 mL EtOH, 3 mL $\text{Ti}(\text{O}i\text{Pr})_4$ and 1.2 mL HCl. Deionized water (2.06 mL) is added drop wise while vigorously stirring. The resulting clear mixture is stirred for 15 min and transferred to a Petri dish. This is placed in an oven at 60 °C for 3 days. The obtained yellow solid is subjected to a base treatment comprising 48 h refluxing in 50 mL 0.1 M NaOH solution. The resulting mixture is filtered and the obtained white powder is washed 3 times with deionized water and dried overnight at ambient conditions. To calcine the sample, it was heated to 450 °C at a heating rate of 2 °C min^{-1} , leaving it at this temperature for 2 h, under air.

2.2.2. Au/TiO₂ powders

The as-synthesized titania (1.5 g) was dispersed in a yellow, aqueous solution of HAuCl_4 (0.015 g) and the pH was adjusted to 10 with an aqueous NaOH solution. Additionally, water was added to obtain a total volume of 20 mL. The dispersion was stirred for 18 h in the dark, the latter to avoid reduction of the salt. The dispersion was filtered and a white powder and a colorless filtrate were obtained. The powder was dried in the dark under ambient conditions, and split into 5 equal portions. One part was kept as a reference while the other four portions were subjected to different reduction procedures: 1) illumination for 6 h with a UV black light (Vilber, 136 $\mu\text{W}/\text{cm}^2$, maximum intensity at 365 nm), 2) thermal reduction for 2 h at 200 °C under 5% H_2/Ar atmosphere, 3) microwave (MW) irradiation for 1 h at 120 °C, dispersed in 4 mL aqueous solution of NaOH (pH = 10). The powder was washed with water and dried at room temperature in the dark and finally 4) 0.2 mL of 0.1 M NaBH_4 was added to a dispersion of Au/TiO₂ in 15 mL deionized water and stirred for 3 h. Afterwards, the powder was washed with deionized water and dried at room temperature in the dark. All samples were stored in the dark at 25 °C and all characterization was performed within a week after synthesis.

2.3. Characterization

Nitrogen sorption experiments were carried out on a TriStar 3000 (Micromeritics) at -196 °C. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method [30]. Samples for high angular annular dark field scanning transmission electron microscopy (HAADF STEM) were prepared by dispersing the powder in deionized water and dipping the copper support TEM grid (200 mesh) in the dispersion. The HAADF STEM samples were air-dried and measured using a JEOL JEM-2200FS transmission electron microscope with post-sample Cs corrector and an accelerating voltage of 200 kV. The gold load of the samples was quantitatively determined using inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer Elan DRC).

XANES spectroscopy experiments were performed at BM26A, the XAS station of the Dutch–Belgian beamline (DUBBLE) at the European Synchrotron Radiation Facility (ESRF) located in Grenoble, France [31]. The beamline uses a 0.40 T bending magnet as a primary radiation source. The energy of the X-ray beam was tuned by a double-crystal Si(111) monochromator (energy resolution $\Delta E/E$ of $\sim 1.7 \times 10^{-4}$ at 9.659 keV) operating in a fixed-exit mode. The beam size at the sample position was approximately $3 \times 1 \text{ mm}^2$, limited by slit systems. Samples were fixed as powder between two 25 μm polyimide tapes (Goodfellow SARL). The X-ray absorption signal was monitored in emission mode using a Vortex-EM silicon drift detector. A XANES scan consisted of 139 energy steps, with an acquisition time of 1 s/step. High resolution XANES data were acquired at ID26 (ESRF, Grenoble, France) using a Si(311) monochromator (energy resolution $\Delta E/E$ of $\sim 0.3 \times 10^{-4}$). A wavelength dispersive spectrometer with an energy resolution lower than the core-hole lifetime (5.41 eV for the Au-L₂ edge [32]) was used to monitor the emitted radiation, resulting in significantly sharpened spectral features [33–35]. The spectrometer was tuned to 9.713 keV (Au-L_α fluorescence line) using the spherically bent Ge(600) wafer Bragg reflection. A beam size of $0.3 \times 1 \text{ mm}^2$ at the sample position was used. Samples were pressed to pellets (5 mg powder dispersed in cellulose) and moved through the beam after each scan to avoid beam induced changes. A XANES scan consisted of 1003 energy steps, with an acquisition time of 30 s/scan. 60 scans were averaged to obtain better counting statistics. At both beamlines experiments were performed at room temperature (298 K). Raw XANES data were normalized for incident beam flux using the primary ionization chamber signal, pre-edge subtracted using a linear function and post-edge normalized at an energy of $E_0 + 50$ eV. Additionally, the slow variations caused by the atomic absorption profile before and after the edge were subtracted to facilitate linear combination analysis spectra comparisons [26]. The obtained XANES profiles were compared to the transmission mode XANES profiles of a series of reference compounds (Au foil, AuCN, $\text{KAu}(\text{CN})_2$ and HAuCl_4) by means of linear combination fitting, resulting in the semi-quantitative chemical speciation of the gold in the sample [36,37].

3. Results and discussion

In-house synthesized mesoporous titania was impregnated with Au^{3+} ions by stirring the titania matrix in an aqueous HAuCl_4 solution overnight prior to the reduction of the salt. The pH of the titania/ HAuCl_4 dispersion was adjusted to 9–10 resulting in a negatively charged titania surface, facilitating the adsorption of the positively charged gold atoms [24]. Neither the impregnation step nor any of the four different reduction methods (UV, MW, H_2 and NaBH_4) changed the specific surface area of the materials, which was approximately 100 m^2/g for all samples (Table 1 and Figure S1 (Appendix)). The amount of gold deposited on the matrix was determined using ICP-MS to be approximately 0.3 wt.% (nominal concentration 0.5 wt.%) and did not differ much among the samples aside from the NaBH_4 reduced sample which has a smaller load of 0.23 wt.% (Table 1). Reduction using NaBH_4 involves the re-dispersion of the powder in excess water

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