



## Deactivation of Au/TiO<sub>2</sub> catalyst in the hydrogenation of *o*-chloronitrobenzene in the presence of CO<sub>2</sub>

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### ARTICLE INFO

#### Article history:

Received 11 April 2010

Received in revised form 23 October 2010

Accepted 26 November 2010

Available online 10 December 2010

#### Keywords:

Au/TiO<sub>2</sub>

Deactivation

*o*-Chloronitrobenzene

Hydrogenation

CO<sub>2</sub>

### ABSTRACT

The hydrogenation of *o*-chloronitrobenzene over Au/TiO<sub>2</sub> was investigated in supercritical carbon dioxide (scCO<sub>2</sub>), ethanol, H<sub>2</sub>O, and H<sub>2</sub>O/CO<sub>2</sub> at 140 °C. The reaction rate followed the order of H<sub>2</sub>O > H<sub>2</sub>O/CO<sub>2</sub> > ethanol > scCO<sub>2</sub>. Au/TiO<sub>2</sub> was deactivated in the systems containing CO<sub>2</sub>. Changes of Au/TiO<sub>2</sub> catalysts were investigated by means of transmission electron microscopy (TEM), *in situ* infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and diffuse reflectance ultraviolet-visible spectra (DR-UV/Vis). Aggregation of Au particles was excluded from origins of deactivation by TEM. Carbonate-like species formed on gold in the presence of CO<sub>2</sub> and H<sub>2</sub> were detected by *in situ* IR spectroscopy. The results of XPS and DR-UV/Vis reveal that the active species of Au<sup>0</sup> was oxidized in the presence of CO<sub>2</sub>. The possible formation of CO and its influence on the activity of Au/TiO<sub>2</sub> were also discussed. Accordingly, the formation of carbonates, the oxidation of surface Au<sup>0</sup> by CO<sub>2</sub>, and the CO formation are proposed to be the possible factors for the deactivation of Au/TiO<sub>2</sub>.

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### 1. Introduction

Catalysis by gold is attracting increasing interest in the preceding few years because gold, when highly dispersed on various supports, is catalytically active for a number of reactions, including CO oxidation [1]; alcohol oxidation [2]; olefin epoxidation [3]; selective hydrogenation of unsaturated hydrocarbons, etc. Recently, Corma et al. reported that the supported gold catalysts were highly chemoselective for hydrogenation of aromatic nitrocompounds due to the cooperation between gold nanoparticles and support which lead to preferentially activation of the nitro group [4]. To dissolve the substrate, organic solvents such as methanol, ethanol, cyclohexane, ethyl acetate and toluene are often used in both the liquid and conventional gas phase hydrogenation [4–7]. But these organic solvent are volatile, toxic and associate with serious health hazards and environmental problems. To avoid the drawbacks of organic solvents, supercritical carbon dioxide (scCO<sub>2</sub>) was proposed to be a green alternative for its environmental benign nature such as non-flammability, relative inertness, complete miscibility with gas and easy separation from liquid/solid products after reaction [8–11].

Besides those environmental considerations, the use of solvent also has large effects on the reaction rate and selectivity. Keane et al. studied the gas-phase hydrogenation of

*p*-chloronitrobenzene (*p*-CNB) over Au/Al<sub>2</sub>O<sub>3</sub> in ethanol, propanol, butanol, and pentanol, and obtained the activity in the order of ethanol > propanol > butanol > pentanol. They attribute the lower hydrogenation rate in pentanol to a more facile polarization of pentanol relative to ethanol that results in a stronger interaction with the catalyst and inhibits *p*-CNB hydrogenation to a greater degree [12]. We have investigated the hydrogenation of nitrocompounds in scCO<sub>2</sub> over Pd/C, Pt/C, Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/TiO<sub>2</sub>, and found the selectivity to anilines in scCO<sub>2</sub> is higher than that in ethanol [13–16]. The interaction of compressed CO<sub>2</sub> with reacting species (i.e., nitrobenzene, nitrosobenzene, and *N*-phenylhydroxylamine) is one of the important factors for this improved selectivity. The reactivity of nitro group is decreased but that of nitroso group is increased and the transformation of *N*-phenylhydroxylamine to aniline is promoted [13,14].

The combination of supported gold catalyst and scCO<sub>2</sub> seems to be worthy of studying, but up to now there are limited reports about it. For the selective oxidation reactions, Wang et al. [17] and Baiker et al. [18] found scCO<sub>2</sub> was superior to other organic solvents when supported gold catalysts was used to catalyze the alcohols oxidation. For the hydrogenation reactions, Chatterjee et al. *in situ* inlayed the gold nanoparticles into the pores of MCM-48 in scCO<sub>2</sub> and found special selectivity in the crotonaldehyde hydrogenation [19]; and the physically and chemically mixed TiO<sub>2</sub>-supported Pd and Au catalysts presented dramatically improved reaction rate for the hydrogenation of citral in scCO<sub>2</sub> in our previous work [20]. In addition, a direct interaction between gold particles and CO<sub>2</sub> was suggested by the results that the optical absorption spectrum of

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small gold particles in  $\text{scCO}_2$  significantly changed with  $\text{CO}_2$  pressure in the literature [21]. Therefore, it is significant to discuss the catalytic performance of Au catalyst in the presence of  $\text{CO}_2$ , it was expected to obtain some unexpected results by the variation of  $\text{CO}_2$  pressure.

The present work was undertaken to study the hydrogenation of *o*-CNB over Au/TiO<sub>2</sub> in  $\text{scCO}_2$  or  $\text{H}_2\text{O}/\text{CO}_2$ . The Au catalyst deactivated in the presence of  $\text{CO}_2$ . Possible factors which may induce the deactivation were discussed in detail by using the transmission electron microscopy (TEM), *in situ* infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), and diffuse reflectance ultraviolet–visible spectra (DR-UV/Vis).

## 2. Experimental

### 2.1. Catalyst preparation

The anatase TiO<sub>2</sub>-supported (Nanjing Haitai Nano material Co.) gold catalysts with different particle sizes were prepared by deposition–precipitation as described in the literature [22]. The required amount of an aqueous solution of  $\text{HAuCl}_4$  ( $0.0025 \text{ mol l}^{-1}$ , Sinopharm Chemical Reagent Co. Ltd.) was added into beaker, and NaOH solution ( $5 \text{ mol l}^{-1}$ ) was added dropwise to  $\text{HAuCl}_4$  under vigorous stirring. After the desired pH value was reached, the required amount of anatase was added to this solution with keeping vigorous stirring and the resulted suspension was aged at room temperature for 2 h while stirring. A solution of  $\text{NaBH}_4$ , prepared in ice water, was added to the suspension, the color of the mixture turned to dark purple from yellow, indicating the reduction of auric ion. After aging for 8 h, the formed solid samples were washed with deionized water and ethanol, and separated by centrifugation at 10,000 rpm. The supernatant was detected with  $\text{AgNO}_3$  solution to ensure there was no residual  $\text{Cl}^-$  on the catalyst. Then the solid material was dried in vacuum at  $60^\circ\text{C}$  overnight. The gold particle sizes were adjusted by controlling the pH value of  $\text{HAuCl}_4$  with NaOH. The higher was the pH value, less fraction of gold deposited on the support, thus smaller the Au particles would be. In this process the pH value of  $\text{HAuCl}_4$  was controlled with NaOH at 10 and 6.2 and the Au particle size was dispersed at 2–5 nm (denoted as Au/TiO<sub>2</sub> (I)) and 8–12 nm (denoted as Au/TiO<sub>2</sub> (II)), respectively.

### 2.2. Hydrogenation of *o*-chloronitrobenzene

The hydrogenation of *o*-CNB was carried out in a 50 ml high-pressure stainless steel batch reactor. A certain amount of Au/TiO<sub>2</sub>, deionized water and *o*-CNB were loaded in the reactor. After that the reactor was sealed, flushed three times with  $\text{N}_2$  to remove the air, and heated to  $140^\circ\text{C}$  for 15 min. Hydrogen (4 MPa) and then liquid  $\text{CO}_2$  was introduced into the reactor to the desired pressure. The reaction mixture was stirred continuously with a magnetic stirrer during reaction. The stirring speed was 900 rpm to make sure the reaction was free from any significant mass transport limitations. After reaction the reactor was cooled in ice-water bath, depressurized carefully, and the liquid product was extracted with 10 ml diethyl ether. The reaction mixture was analyzed with a gas chromatograph (GC, Shimadzu GC-2010, FID, Rtx-5 capillary column,  $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ ), and was identified by gas chromatography/mass spectrometry (GC/121 MS, Agilent 5890). Hydrogenation reactions in ethanol, water, and  $\text{H}_2\text{O}/\text{CO}_2$  were conducted in the same reactor using similar procedures. The extent of error for the conversion was in the range of  $\pm 2\%$ .

The phase behavior was examined by the naked eye through the transparent sapphire windows attached to an  $85 \text{ cm}^3$  high-pressure reactor [13].

### 2.3. Catalyst characterization

The particle sizes of Au on Au/TiO<sub>2</sub> catalysts were examined by transmission electron microscopy (TEM, JEOL JEM-2000 EX). The TEM samples were prepared by dispersing the catalyst powder in ethanol under ultrasonic and then allowing a drop of the suspension to evaporate on copper grids covered with holey carbon film. An area containing about 50 particles was selected from the TEM pictures to calculate the Au particle size distribution.

Diffuse reflectance UV/Vis spectra were recorded with a Shimadzu UV-3100 PC spectrophotometer. X-ray photoelectron spectroscopy (XPS, VG Microtech 3000 Multilab) was used to examine the electronic properties of Au on the surface of the Au/TiO<sub>2</sub> catalysts. The C 1s peak at 284.6 eV arising from adventitious carbon was used as reference. This reference gives binding energy values with a precision of  $\pm 0.2 \text{ eV}$ . The surface composition of the samples was determined from the peak areas of the corresponding lines using a Shirley type background and empirical cross section factors for XPS. The freshly prepared catalysts were characterized directly. The used catalysts, prior to characterization, were washed thoroughly with diethyl ether 6 times, separated by centrifugation at 10,000 rpm, and dried in vacuum at  $60^\circ\text{C}$  overnight.

The metal loadings were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES; Thermo Scientific ICAP6000, USA) after the extraction of metal species from the support by aqua regia. To detect the carbonate-like species on gold, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out on a JASCO FT/IR-620 spectrometer equipped with a MCT detector. Prior to the measurement, the sample was heated to  $50^\circ\text{C}$  for 0.5 h under a gas flow of 90% He and 10%  $\text{H}_2$  to get rid of the oxide on the gold surface. The temperature was raised to  $140^\circ\text{C}$  and the chamber was purged with high purity helium for 5 min. A background spectrum was collected. Then, a flow of 90%  $\text{H}_2$  + 10%  $\text{CO}_2$  was introduced into the chamber and the spectra were collected in 5, 15, and 30 min, respectively.

## 3. Results and discussion

### 3.1. Catalytic performances of Au/TiO<sub>2</sub> in different reaction media

The catalytic performances of Au/TiO<sub>2</sub> were evaluated for the hydrogenation of *o*-CNB in several media such as  $\text{scCO}_2$ , ethanol and water. As hydrogen is completely miscible with  $\text{scCO}_2$  and this is beneficial to the hydrogenation reactions, the hydrogenation of *o*-CNB over Au/TiO<sub>2</sub> was performed in  $\text{scCO}_2$  and compared with that in ethanol. The conversion of *o*-CNB in  $\text{scCO}_2$  was about half of that in ethanol (entries 1 and 2 in Table 1), which is different from our previous results obtained with Ni/TiO<sub>2</sub> catalyst. Over Ni/TiO<sub>2</sub>, the conversion of *o*-CNB in  $\text{scCO}_2$  is much higher than that in ethanol at  $35^\circ\text{C}$  [14]. Moreover, the conversion of *o*-CNB in  $\text{H}_2\text{O}$  was about 3 times larger than that in ethanol. It was reported that the hydrogenation rate of *p*-nitrophenol in water–ethanol and water–dioxane increased with water content and became the highest in pure water [23]. The promoting effect of  $\text{H}_2\text{O}$  on the hydrogenation of nitroaromatics was also reported over supported Pt, Ni, Ag, and Cu catalysts [24,25]. *o*-CNB is soluble in ethanol and sparingly soluble in water ( $0.44 \text{ g l}^{-1}$  at  $20^\circ\text{C}$  [26]). The promoting effect of  $\text{H}_2\text{O}$  might be partially attributed to the H-bond interaction of interfacial  $\text{H}_2\text{O}$  molecules with hydrophobic reactant or transition state intermediates [27]. When  $\text{CO}_2$  was introduced into the  $\text{H}_2\text{O}$  system, the conversion decreased with the increase of  $\text{CO}_2$  pressure (entries 3–5 in Table 1). It seems that  $\text{CO}_2$  molecule plays a negative effect on the catalytic activity of Au/TiO<sub>2</sub> in the present hydrogenation.

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