Journal of Molecular Catalysis A: Chemical 335 (2011) 183–188

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Deactivation of Au/TiO_2 catalyst in the hydrogenation of *o*-chloronitrobenzene in the presence of CO_2

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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_2
Deactivation
o-Chloronitrobenzene
Hydrogenation
CO_2

ABSTRACT

The hydrogenation of *o*-chloronitrobenzene over Au/TiO_2 was investigated in supercritical carbon dioxide ($scCO_2$), ethanol, H_2O, and H_2O/CO_2 at 140 °C. The reaction rate followed the order of $H_2O > H_2O/CO_2 >$ ethanol $> scCO_2$. Au/TiO_2 was deactivated in the systems containing CO_2. Changes of Au/TiO_2 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_2 and H_2 were detected by *in situ* IR spectroscopy. The results of XPS and DR-UV/Vis reveal that the active species of Au^0 was oxidized in the presence of CO_2. The possible formation of CO and its influence on the activity of Au/TiO_2 were also discussed. Accordingly, the formation of carbonates, the oxidation of surface Au^0 by CO_2, and the CO formation are proposed to be the possible factors for the deactivation of Au/TiO_2.

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 ($scCO_2$) 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_2O_3 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 $scCO_2$ over Pd/C, Pt/C, Ni/Al_2O_3 and Ni/TiO_2, and found the selectivity to anilines in $scCO_2$ is higher than that in ethanol [13–16]. The interaction of compressed CO_2 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 $scCO_2$ 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 $scCO_2$ was superior to other organic solvents when supported gold catalysts was used to catalyze the alcohols oxidation. For the hydrogenation reactions, Chaterjee et al. *in situ* inlayed the gold nanoparticles into the pores of MCM-48 in $scCO_2$ and found special selectivity in the crotonaldehyde hydrogenation [19]; and the physically and chemically mixed TiO_2-supported Pd and Au catalysts presented dramatically improved reaction rate for the hydrogenation of citral in $scCO_2$ in our previous work [20]. In addition, a direct interaction between gold particles and CO_2 was suggested by the results that the optical absorption spectrum of

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doi:10.1016/j.molcata.2010.11.029

small gold particles in $scCO_2$ significantly changed with CO_2 pressure in the literature [21]. Therefore, it is significant to discuss the catalytic performance of Au catalyst in the presence of CO_2, it was expected to obtain some unexpected results by the variation of CO_2 pressure.

The present work was undertaken to study the hydrogenation of *o*-CNB over Au/TiO_2 in $scCO_2$ or H_2O/CO_2. The Au catalyst deactivated in the presence of 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_2-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 $HAuCl_4$ (0.0025 mol l^{-1}, Sinopharm Chemical Reagent Co. Ltd.) was added into beaker, and NaOH solution (5 mol l^{-1}) was added dropwise to $HAuCl_4$ 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 $NaBH_4$, 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 $AgNO_3$ solution to ensure there was no residual Cl^- on the catalyst. Then the solid material was dried in vacuum at 60 °C overnight. The gold particle sizes were adjusted by controlling the pH value of $HAuCl_4$ 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 $HAuCl_4$ was controlled with NaOH at 10 and 6.2 and the Au particle size was dispersed at 2–5 nm (denoted as Au/TiO_2 (I)) and 8–12 nm (denoted as Au/TiO_2 (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_2, deionized water and *o*-CNB were loaded in the reactor. After that the reactor was sealed, flushed three times with N_2 to remove the air, and heated to 140 °C for 15 min. Hydrogen (4 MPa) and then liquid 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 m × 0.25 mm × 0.25 μm), and was identified by gas chromatography/mass spectrometry (GC/121 MS, Agilent 5890). Hydrogenation reactions in ethanol, water, and H_2O/CO_2 were conducted in the same reactor using similar procedures. The extent of error for the conversion was in the range of ±2%.

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

2.3. Catalyst characterization

The particle sizes of Au on Au/TiO_2 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_2 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 ±0.2 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 rmp, and dried in vacuum at 60 °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 °C for 0.5 h under a gas flow of 90% He and 10% H_2 to get rid of the oxide on the gold surface. The temperature was raised to 140 °C and the chamber was purged with high purity helium for 5 min. A background spectrum was collected. Then, a flow of 90% H_2 + 10% 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_2 in different reaction media

The catalytic performances of Au/TiO_2 were evaluated for the hydrogenation of *o*-CNB in several media such as $scCO_2$, ethanol and water. As hydrogen is completely miscible with $scCO_2$ and this is beneficial to the hydrogenation reactions, the hydrogenation of *o*-CNB over Au/TiO_2 was performed in $scCO_2$ and compared with that in ethanol. The conversion of *o*-CNB in $scCO_2$ 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_2 catalyst. Over Ni/TiO_2, the conversion of *o*-CNB in $scCO_2$ is much higher than that in ethanol at 35 °C [14]. Moreover, the conversion of *o*-CNB in H_2O 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 H_2O 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 g l^{-1} at 20 °C [26]). The promoting effect of H_2O might be partially attributed to the H-bond interaction of interfacial H_2O molecules with hydrophobic reactant or transition state intermediates [27]. When CO_2 was introduced into the H_2O system, the conversion decreased with the increase of CO_2 pressure (entries 3–5 in Table 1). It seems that CO_2 molecule plays a negative effect on the catalytic activity of Au/TiO_2 in the present hydrogenation.

Table 1
Hydrogenation of *o*-CNB over Au/TiO_2 in different reaction media.

Entry	Medium	Conversion (%)	Selectivity (%)		No. of phases
			o-CAN	Others	
1	$scCO_2$ (12 MPa)	14.3	98.7	1.3	1
2	Ethanol (5 ml)	27.8	96.6	3.4	1
3	H_2O (5 ml)	83.7	92.7	7.4	2
4	H_2O (5 ml) + 6 MPa CO_2	76.9	94.1	5.9	2
5	H_2O (5 ml) + 8.3 MPa CO_2	71.1	88.7	11.3	2

Reaction conditions: *o*-CNB 0.2 g, Au/TiO_2 (I) 0.02 g, H_2 4.0 MPa, 140 °C, reaction time 1 h.

The selectivity to *o*-CAN in $scCO_2$ was better than those in other systems containing liquid H_2O and ethanol. The main byproducts were *o*-chloronitrisobenzene, *N*-chlorophenylhydroxylamine and aniline. The higher selectivity in $scCO_2$ might be related with the lower concentration of reacting species in the CO_2 gas phase than that in the liquid phase. A nearly 100% selectivity to CAN has been achieved over Au/TiO_2 in the gas phase hydrogenation of CNB at 180 °C [12].

3.2. *Influence of CO_2 pressure and reaction time*

To further study the effect of CO_2 on the catalytic feature of Au/TiO_2 in *o*-CNB hydrogenation, Au/TiO_2 catalysts with different particle sizes were investigated in $scCO_2$ and H_2O/CO_2. In $scCO_2$ (Fig. 1), the conversion of *o*-CNB and the selectivity to *o*-CAN did not change with CO_2 pressure. This trend is totally different to our previous results that the conversion of *o*-CNB increases with CO_2 pressure and reaches the maximum at 10 MPa when Pt/C was used as catalyst [16]. In H_2O/CO_2 (Fig. 2), the *o*-CNB conversion decreased with increasing CO_2 pressure. In both $scCO_2$ and H_2O/CO_2 reaction media, Au/TiO_2 catalysts with smaller gold particles were more active than that with the larger ones. Claus et al. reported that the TOF value increased with decreasing of particle size when supported gold catalysts were used for the selective hydrogenation of acrolein [28]. Keane et al. also reported that the hydrogenation of *m*-dinitrobenzene over supported Au/TiO_2 exhibited a particle size sensitivity where higher specific rates were obtained with smaller Au particles; the catalysts bearing the smaller Au particles (d_p = 3.4 nm) delivered an order of magnitude higher specific rate when compared with larger ones (d_p = 6.1 nm) [29].

The influence of reaction time was also investigated in present work (Fig. 3). For both Au/TiO_2 (I) and Au/TiO_2 (II), the selectivity to *o*-CAN remained at nearly 100% through the whole reaction process, but the *o*-CNB conversion increased with reaction time in the first 8 h and did not change anymore. This indicates that the Au/TiO_2 catalysts deactivated during the reaction.

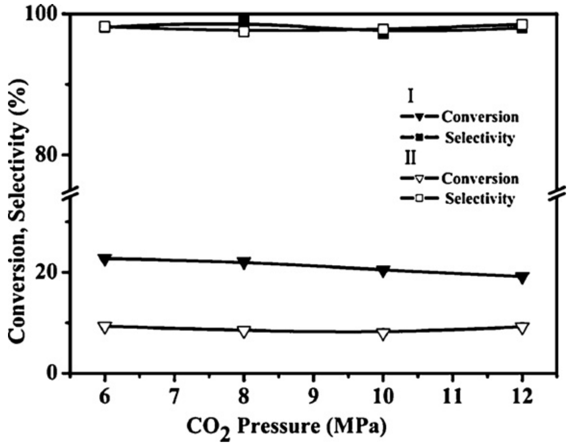

Fig. 1. Hydrogenation of *o*-CNB over Au/TiO_2 with different particle sizes in $scCO_2$. Reaction conditions: *o*-CNB 1.5 g, Au/TiO_2 0.15 g, H_2 4 MPa, 140 °C, 1 h. Au/TiO_2 (I), the Au particle sizes are in the range of 2–5 nm; Au/TiO_2 (II), the Au particle sizes are in the range of 8–12 nm.

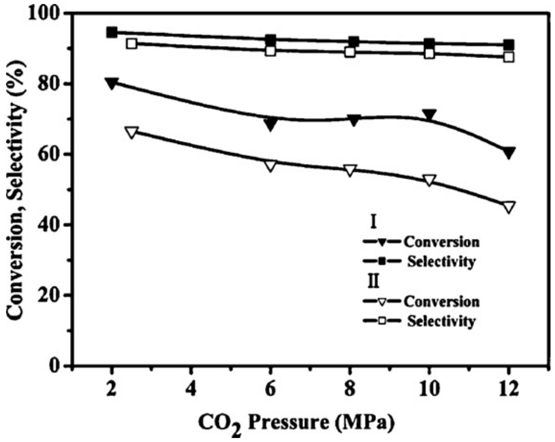

Fig. 2. Hydrogenation of *o*-CNB over Au/TiO_2 with different particle sizes in H_2O/CO_2. Reaction conditions: *o*-CNB 0.2 g, Au/TiO_2 0.02 g, H_2O 5 ml, H_2 4 MPa, 140 °C, 1 h.

3.3. *Possible factors resulting in the deactivation of Au/TiO_2*

Since deactivation of supported catalysts usually relates with agglomeration of metal particles, the change of the particle sizes before and after reaction in $scCO_2$ at 140 °C was examined with XRD and TEM. But no diffraction peaks corresponding to Au were found, which is mainly due to the highly dispersity of gold particles and the low loading of gold. TEM results (Fig. 4) demonstrate that there was no significant agglomeration of gold particles after reaction. It was reported that the calcination of Au/TiO_2 catalysts at 200 °C could

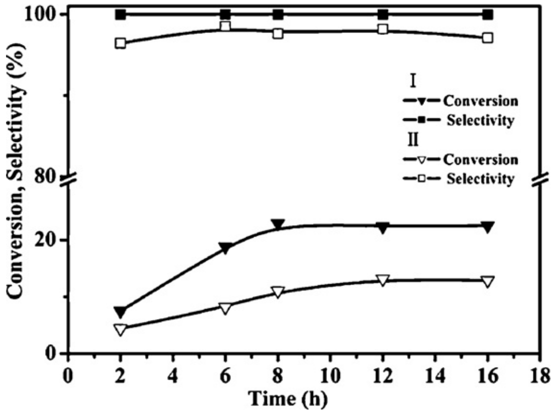

Fig. 3. Effect of reaction time in $scCO_2$. Reaction conditions: *o*-CNB 1.5 g, Au/TiO_2 0.04 g, H_2 4 MPa, CO_2 12 MPa, 140 °C.

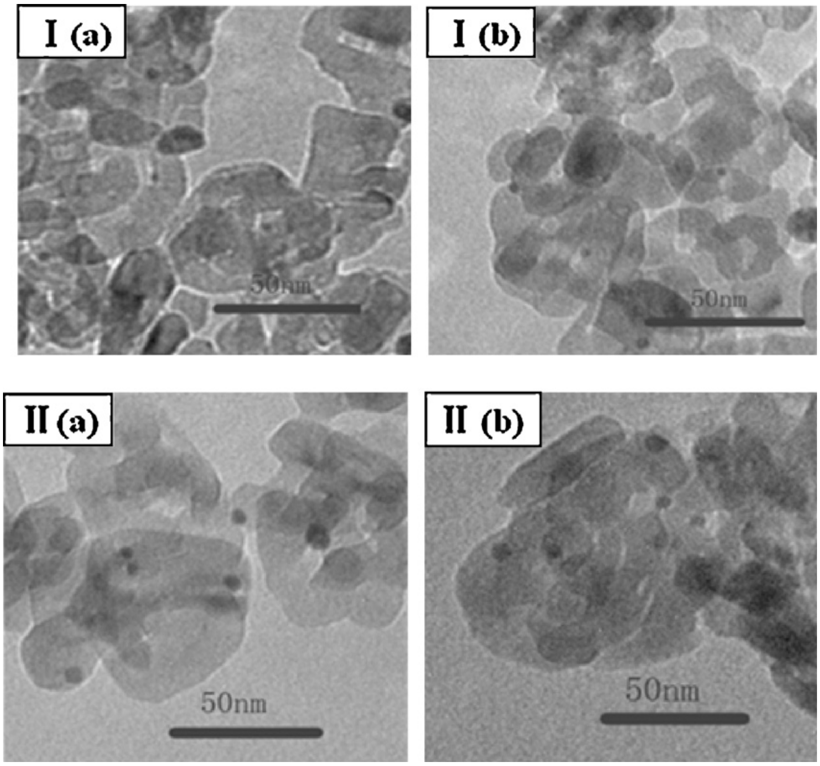

Fig. 4. TEM images of the fresh (a) and used (b) Au/TiO_2 catalysts in $scCO_2$.

not lead to the agglomeration of the Au particles [22]. Therefore, the agglomeration of Au particles was not the main factor causing the deactivation of catalysts.

Because carbonate formation is one of common factors that cause the deactivation of supported metal catalysts in the presence of CO or CO_2 [30,31], DRIFTS experiment was made to detect whether carbonate-like species were formed on Au/TiO_2 under the gas flow of CO_2 and H_2. Fig. 5 shows the IR difference spectra of Au/TiO_2 in the 1000–1800 cm^{-1} region with increasing time on stream. Carbonate-like species on gold are characterized by IR bands at 1277, 1315, 1343, 1534, 1566, and 1606 cm^{-1} [31]. Thus, among the bands at 1270–1655 cm^{-1} in Fig. 5, the peaks at 1270, 1353, 1534 and 1610 cm^{-1} might be attributed to carbonate-like species on gold. The intensity of the bands did not change with increasing contact time with CO_2 and H_2. Hence, carbonate-like species are formed on gold during the hydrogenation in the presence of CO_2 and this might be one of reasons that causing the deactivation of Au/TiO_2 in $scCO_2$.

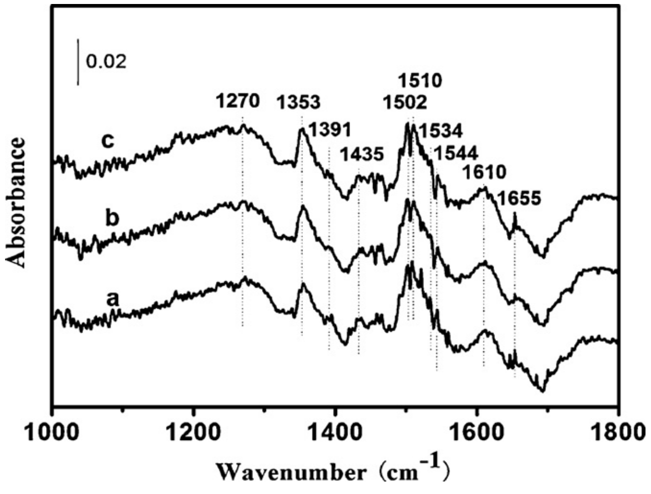

Fig. 5. IR difference spectra in the 1000–1800 cm^{-1} region recorded during 10% CO_2/90% H_2 treatment of Au/TiO_2 at 140 °C with increasing time on stream (min): (a) 5; (b) 15; (c) 30.

To further investigate the factors causing the deactivation of Au/TiO_2 catalyst, XPS was used to investigate the electronic state of gold on the surface of the fresh and used catalysts. The C 1s peak of contaminant carbon at 284.6 eV was used as a reference. Analysis of Cl 2p region shows that the amount of Cl on the activated catalyst is negligible. As shown in Fig. 6, the peaks with binding energy of Au $4f_{7/2}$ at 83.0 eV and Au $4f_{5/2}$ at 86.7 eV are characteristic of Au^0 [32], which indicates the complete reduction of gold catalyst on the fresh Au/TiO_2. It is worth to note that there is a shift of 1 eV to lower binding energy from standard values (84.0 and 87.7 eV) due to the strong metal–support interaction [32–34]. For the used Au/TiO_2 catalyst in $scCO_2$, new bands at 84.5 (Au $4f_{7/2}$) and 89.1 eV (Au $4f_{5/2}$) were found, which indicates that oxidized Au species are present. The band at 84.5 eV (Au $4f_{7/2}$) was possibly assigned to Au $4f_{7/2}$ of $Au^{\delta+}$, and the one at 89.1 eV assigned to Au $4f_{5/2}$ of Au^{3+} [30]. For the used catalyst in H_2O/CO_2, Au^{3+} and $Au^{\delta+}$ were also detected together with metallic gold species (Fig. 6(iii)). For the used catalyst in H_2O (Fig. 6(iv)), only two peaks corresponding to Au^0 were found, which is the same as the fresh catalyst. The results of UV/Vis measurement are shown in Fig. 7. The peak position of nanosized Au metal particles is between 500 and 600 nm; small clusters such as $(Au)_n^{\delta+}$ exhibit a band around 390 nm [35,36]. Fig. 7 shows that the absorption spectrum of the used Au/TiO_2 in H_2O is similar to that of the fresh catalyst; however, for the used Au/TiO_2 catalysts in $scCO_2$ or in H_2O/CO_2, new absorption bands appeared around 430 nm, indicating the presence of oxidized Au species. The above results suggest that the original Au^0 species was oxidized by CO_2 rather than by H_2O and reacting species. Mihaylov et al. reported the same phenomenon that the Au^0 species was oxidized by CO_2 during the catalytic oxidation of CO at room temperature [37–39].

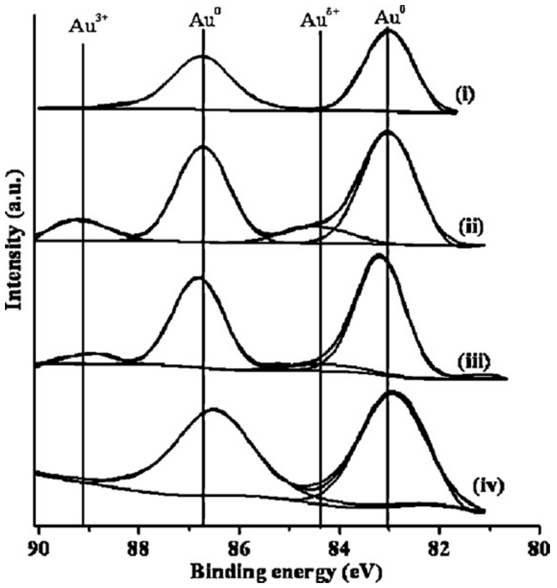

Fig. 6. Au 4f XPS spectra of Au/TiO_2 (I). Fresh (i), after reaction in $scCO_2$ (ii), in H_2O/CO_2 (iii), and in H_2O (iv). Reaction conditions: *o*-CNB 1.5 g, Au/TiO_2 0.15 g, H_2 4 MPa, 140 °C, 1 h.

Metallic gold Au^0 is the main active species for hydrogenation reactions. Therefore, the oxidation of Au^0 in the presence of CO_2 should be another reason for the deactivation of catalyst. The oxidized gold species could not be reduced into metallic state in the present hydrogenation temperature of 140 °C. It is consistent with the following temperature programmed reduction results: oxidized gold should be reduced at >170 °C for the 1 wt% Au/TiO_2 [40].

Moreover, to get a further insight of the influence of CO_2 on the gold catalysts, Au/TiO_2 was pretreated under different conditions before reaction (Table 2). The conversion of *o*-CNB over the catalyst pretreated in $scCO_2$ was slightly lower than that over the fresh catalyst (entries 1 and 2), but higher than that over the Au/TiO_2 treated under CO_2 and H_2 (entries 2 and 3). This suggests that the presence of H_2 would accelerate the deactivation of the catalyst.

XPS results (Fig. 8) show that both the Au/TiO_2 catalysts pretreated with $scCO_2$ or with $scCO_2$ and H_2 were partially oxidized. The ratio of $Au^{\delta+}$ was larger for the catalyst treated with $scCO_2$ than that with $scCO_2$ and H_2. This indicates that there might be other factors affecting the activity of Au/TiO_2.

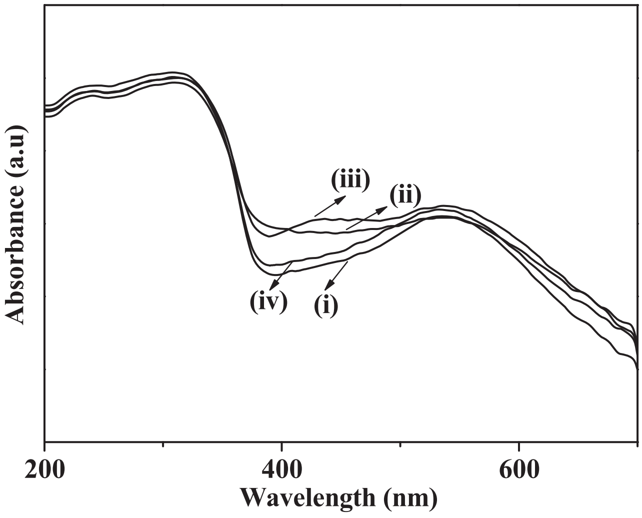

Fig. 7. Diffuse reflectance UV/Vis spectra of different Au/TiO_2 catalysts: fresh (i), after reaction in $scCO_2$ (ii), in H_2O/CO_2 (iii), and in H_2O (iv). Reaction conditions: *o*-CNB 1.5 g, Au/TiO_2 (I) 0.15 g, H_2 4 MPa, 140 °C, 1 h.

Table 2
Results for the hydrogenation of *o*-CNB over Au/TiO_2 pretreated under different conditions.

Entry	Conversion (%)	Selectivity (%)
1[a]	8.2	98.5
2[b]	6.1	99.0
3[c]	2.9	94.8
4[d]	1.5	96.5

Reaction conditions: *o*-CNB 1.5 g, Au/TiO_2 (II) 0.04 g, H_2 4 MPa, CO_2 12 MPa, 140 °C, reaction time 1 h.

[a] Fresh Au/TiO_2 (II) catalyst.

[b] Au/TiO_2 (II) was treated in 12 MPa CO_2 at 140 °C for 8 h.

[c] Au/TiO_2 (II) was treated in 12 MPa CO_2 and 4 MPa H_2 at 140 °C for 8 h.

[d] Charged CO (0.1 MPa) into the reaction system.

As CO could be generated from CO_2 during the hydrogenation process, and may block the active sites [41], we have made attempts to detect CO adsorbed on gold by DRIFTS measurement, but CO was not found under a gas flow of 90% H_2 and 10% CO_2 at 140 °C. In another DRIFTS study, CO was first introduced into the chamber and the CO adsorbed on Au/TiO_2 was detected; however, the adsorbed CO was removed from the catalyst surface by He purge. This indicates that the adsorption of CO on Au/TiO_2 is weak and reversible. In addition, CO could not be detected by GC analysis of the reactor effluent gas mixture using a TCD detector, due to the relatively high concentration of CO_2 and less amount of CO formed. However, when a trace amount of CO (0.1 MPa) was introduced into the reaction system, the *o*-CNB conversion decreased significantly (entry 4 in Table 2), implying that CO produced from CO_2 and H_2 might be another possible factor for the deactivation of Au/TiO_2. ICP analysis was also made to investigate the possibility of Au leaching during the reaction. The ratio of the leached to the original amount was 0.59%, implying the Au leaching is negligible even though the H_2O/CO_2 reaction system presents somewhat acidity (pH = 3) [42].

Thus, besides the molecular interactions of CO_2 with reacting species as proposed in previous work [13,14], compressed CO_2 plays the following roles in the present work: (1) increasing the solubility of H_2 in the liquid phase (positive); (2) forming carbonate-like species over Au/TiO_2 (negative); (3) oxidizing the active species of Au^0 (negative); and (4) acting as the source of CO (negative). The counterbalance of these positive and negative effects resulted in the constant conversion of *o*-CNB with increasing CO_2 pressure in $scCO_2$. For the reaction in H_2O/CO_2, besides the above factors, the amount of *o*-CNB dissolved into CO_2 may increase and the concentration of *o*-CNB in H_2O may decrease with

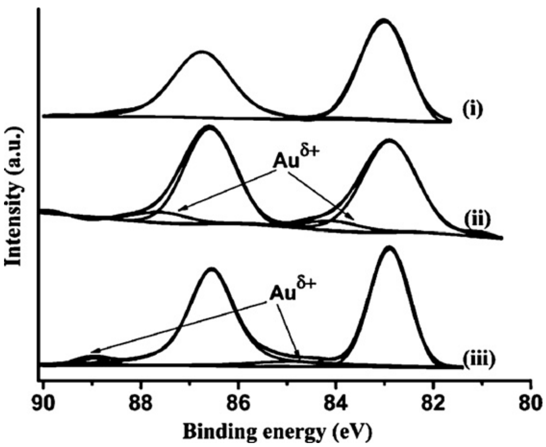

Fig. 8. Au 4f XPS spectra of Au/TiO_2 (II): (i) fresh, (ii) treated in 12 MPa CO_2 at 140 °C for 8 h, (iii) treated in 12 MPa CO_2 and 4 MPa H_2 at 140 °C for 8 h.

increasing CO_2 pressure. Hence, the conversion in H_2O/CO_2 linearly decreased.

4. Conclusion

The conversion of *o*-CNB during hydrogenation over Au/TiO_2 in $scCO_2$ changes little with CO_2 pressure. The Au/TiO_2 catalyst deactivates during the hydrogenation in $scCO_2$. Carbonate-like species are formed on gold and may cover some of active sites. The original Au^0 species was partially oxidized by CO_2 even in the presence of H_2. It seems likely that CO might be formed in the hydrogenation process and poisons some active sites. The above three factors, formation of carbonate-like species, the oxidation of surface metallic Au, and the generation of CO might be responsible for the deactivation of Au/TiO_2 during the hydrogenation of *o*-CNB in $scCO_2$.

Acknowledgments

The authors gratefully acknowledge the financial support from the One Hundred Talent Program, NSFC 20873139 and KJCX2, YW. H16.

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