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An exceptionally active and selective Pt–Au/TiO₂ catalyst for hydrogenation of the nitro group in chloronitrobenzene[†]

Daiping He,*a Xiangdong Jiao, Ping Jiang, Jian Wanga and Bo-Qing Xub

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Adding a very small amount of Pt entities (0.01–0.03 wt%) onto the Au surface of a Au/TiO₂ catalyst is found to be an efficient approach to improve the catalytic activity of Au for the hydrogenation of *p*-chloronitrobenzene (*p*-CNB), without loss of selectivity towards *p*-chloroniline (*p*-CAN). The effect of catalyst amount, reaction temperature, H₂ pressure and reaction time on *p*-CNB hydrogenation was studied with 0.02wt%Pt–0.5wt%Au/TiO₂ (Pt_{0.0002}–Au_{0.005}/TiO₂). The selectivity to *p*-CAN could be up to 100% at complete conversion of *p*-CNB with reaction temperatures at or below 333 K. The catalyst also exhibited perfect stability. The catalyst structure was characterized by TEM and XRD, and the mechanism of the high activity of the catalyst was discussed.

1. Introduction

Chloroanilines are an important class of industrial intermediates for a variety of specific and fine chemicals, including pharmaceuticals, dyes, herbicides and pesticides.¹ p-CAN, a high production volume compound, can be synthesised via Fe promoted reduction of p-CNB in acid media (Bechamp reaction) or by selective hydrogenation using transition-metal catalysts. Industrial implementation of the Bechamp reaction is no longer viable due to the generation of significant amounts of toxic metal waste which requires costly and laborious separation and disposal.² Liquid phase catalytic hydrogenation has emerged as a cleaner alternative to the Bechamp process with higher associated product yields.3 However, the economic benefits are dependent on catalyst performance, where unwanted C-Cl bond hydrogenolysis is difficult to fully avoid. Reaction selectivity is critical as p-CNB hydrogenation can generate a range of intermediates and by-products as shown in Scheme 1, which presents the reaction pathways proposed for batch liquid phase hydrogenation.4

With a variety of catalysts (e.g., platinum, palladium, rhodium, nickel), the hydrogenation of *p*-CNB to the corre-

Tel: (+86)23-6536-2777



Scheme 1 The hydrogenation reaction pathways of *p*-CNB.

sponding *p*-CAN is always accompanied by some dechlorination reaction. Furthermore, hydrogen chloride (HCl) produced from the dechlorination contributes to the corrosion of the reactor. To achieve high selectivity towards *p*-CAN, great attempts have been made to tailor the hydrogenation selectivity of supported metal catalysts toward a specific hydrogenation of the nitro group in *p*-CNB, *e.g.*, by modifying the active metal with different promoters⁵ or a second metal component,⁶ by assembling metal-colloids onto suitable oxide nanoparticles⁷ or using amorphous structures⁸ and by using delicate approaches for catalyst preparation.⁹ However, the side reaction of hydrodechlorination still cannot be avoided completely.

Having started a couple of decades ago, catalysis by gold continues to show a fascinating future in the field of catalysis.¹⁰ Nanosized Au particles in interaction with a variety of support materials showed special selectivity in catalyzing a number of reactions including CO oxidation,¹¹ alcohol oxidation,¹² olefin epoxidation,¹³ vinyl chloride synthesis,¹⁴ selective hydrogenation of unsaturated hydrocarbons,¹⁵ aldehydes and ketones.¹⁶ For the reduction of nitro compounds with H₂, Au/TiO₂, Au/Fe₂O₃ and Au/SiO₂ catalysts were recently found to be very specific in

^aKey Lab of Advanced Materials, College of Chemistry, Chongqing Normal University, Chongqing, 401331, China. E-mail: hedaiping@126.com; Fax: (+86)23-6536-2777;

^bInnovative Catalysis Program, Key Lab of Organic Optoelectronics & Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing, 100084, China. E-mail: bqxu@mail.tsinghua.edu.cn; Fax: (+86)10-6279-2122; Tel: (+86)10-6277-2592

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reducing the nitro group in various compounds containing other functional groups.¹⁷ Our previous work also found that selective production of chloroanilines from chloronitrobenzenes without any dechlorination was feasible by catalytic hydrogenation over Au/ZrO₂.¹⁸ However, the hydrogenation activity of Au nanoparticles was often much lower than those of the platinum-group metals,¹⁹ most probably due to an "intrinsic" nobleness of Au for H₂ activation, that the dissociative adsorption of H₂ on Au is an activated process and is restricted to the edge and corner sites or at the interface perimeter around the Au nanoparticles in contact with oxide support.²⁰ Such low hydrogenation activity of the Au nanoparticles has been a major obstacle in view of practical applications.

In the present study, we report that adding a very small amount of Pt entities (0.01–0.03 wt%) onto the Au surface of a Au/TiO₂ catalyst is an efficient approach to improve the catalytic activity of Au for the hydrogenation of *p*-chloronitrobenzene, without changing the selectivity propensity of the Au nanoparticles for the reaction. Our results can provide the basis for the development of a clean, high efficient route for the production of *p*-CAN under mild conditions.

2. Results and discussion

Table 1 shows the catalytic results of p-CNB hydrogenation over a Pt-Au/TiO₂ catalyst at 323 K, 1.0 MPa H₂. Pt/TiO₂ and Au/TiO₂ catalysts were also included for comparison. Blank tests showed no reaction of p-CNB in the absence of the catalyst. The conversion of p-CNB over the 0.01 wt%Pt/TiO₂ (Pt_{0.0001}/TiO₂) was not detected at all. The 0.5 wt%Au/TiO₂ (Au_{0.005}/TiO₂) produced a low *p*-CNB conversion (only 0.9%) in 1 h. When the same $Au_{0.005}/TiO_2$ were loaded with a very small amount of Pt (only 0.01 wt%), however, a dramatically higher p-CNB conversion (99.2%) was achieved under the same reaction conditions, and the undesired hydrodechlorination reaction usually observed over other metal catalysts²¹ was not detected, which indicated that the C-Cl bond in the p-CNB molecule was kept intact during the reaction. In addition, the selectivity for p-CAN increased from 94.7% to 99.9%, most probably due to the intermediates²² (4, 4'-dichloroazoxybenzene and 4, 4'-dichloroazobenzene) produced in the reaction process being further hydrogenated to the desired product p-CAN, which

Table 1 Selective hydrogenation of *p*-CNB over Pt/TiO₂, Au/TiO₂ and Pt-Au/TiO₂ catalysts^{*a*}

	D (CNID	Sel. (%)		
Catalyst	React. time (min)	<i>p</i> -CNB Conv. (%)	p-CAN	AN	Others ^b
Pt _{0.0001} /TiO ₂	60	n.d.	n.d.	n.d.	n.d.
$Au_{0.005}/TiO_2$	60	0.9	94.7	n.d.	5.3
Pt _{0.0001} -Au _{0.005} /TiO ₂	60	99.2	99.9	n.d.	0.1
Pt _{0.0002} -Au _{0.005} /TiO ₂	45	100	100	n.d.	n.d.
Pt _{0.0003} -Au _{0.005} /TiO ₂	40	100	100	n.d.	n.d.
$Pt_{0.0004}$ -Au_{0.005}/TiO ₂	38	100	99.9	0.1	n.d.
$Pt_{0.0005} - Au_{0.005} / TiO_2$	37	100	99.5	0.5	n.d.

n.d.: not detected.^{*a*} Reaction conditions: 25.0 mg catalyst, 0.39 g *p*-CNB in 4.0 mL ethanol (solvent), 323 K, 1.0 MPa H₂, stirring speed: 900 rpm. ^{*b*} 4,4'-dichloroazoxybenzene and 4,4'-dichloroazobenzene.

was supported by the observed increase in the selectivity of the desired p-CAN with increasing p-CNB conversion. Increasing the amount of Pt up to 0.03 wt% in the Pt-Au_{0.005}/TiO₂ catalyst resulted in continued shortening of the reaction period for achieving a complete conversion of p-CNB. For instance, a reaction period of 40 min was found to be long enough to produce a p-CNB conversion of 100% over the Pt_{0.0003}-Au_{0.005}/TiO₂ catalyst. With the amount of Pt in the Pt–Au_{0.005}/TiO₂ increasing continuously, the reaction period for achieving a complete conversion of p-CNB was further reduced, but the selectivity of p-CAN began to decrease due to hydrodechlorination, and so the selectivity of aniline (AN) increased. For example, the selectivities for p-CAN and AN were 99.9% and 0.1% over Pt_{0.0004}-Au_{0.005}/TiO₂, respectively. Galvagno et al.²³ reported that the activity of bimetallic M-Pt is enhanced at low M/Pt ratios, whereas at high M content the platinum is poisoned. With the amount of Pt in the Pt-Au_{0.005}/TiO₂ increasing continuously, the Au/Pt ratio reduced, so that the activity of $Pt-Au_{0.005}/TiO_2$ was probably enhanced to result in hydrodechlorination. Therefore, the amount of Pt in the Pt-Au_{0.005}/TiO₂ may be restricted to 0.03 wt%.

The effect of the $Pt_{0.002}$ – $Au_{0.005}$ / TiO_2 catalyst amount expressed as weight percent of catalyst based on *p*-CNB was studied in the range of 0–9% (w/w) (Fig. 1). The conversion of *p*-CNB varied linearly with the increase in catalyst amount up to 6.4% and then levelled off. Therefore, it appears that up to a catalyst amount of 6.4% (w/w) the reaction is mainly controlled by either the rate of mass transfer from the bulk liquid to the catalyst surface or the intrinsic kinetics of the reaction. Since, for the size of the catalyst used and the conditions employed, the diffusion of hydrogen from the bulk liquid to the solid is estimated to be unimportant, the data appears to represent the true kinetics of the process at a catalyst amount of 6.4% (w/w), temperature of 323 K and 1.0 MPa H₂ for 97.5 mg mL⁻¹ of *p*-CNB.



Fig. 1 Effect of $Pt_{0.002}$ -Au_{0.005}/TiO₂ catalyst amount on hydrogenation of *p*-CNB. 0.39 g *p*-CNB in 4.0 mL ethanol (solvent), 323 K, 1.0 MPa H₂, 30 min, stirring speed: 900 rpm.

We investigated the influence of reaction temperature on the hydrogenation of *p*-CNB over the $Pt_{0.0002}$ -Au_{0.005}/TiO₂ catalyst under 1.0 MPa H₂. The results, summarized in Table 2, show that the increase in reaction temperature resulted in continuous increase in both *p*-CNB conversion and the selectivity to *p*-CAN without the formation of any decholorination product. The outstanding selectivity for *p*-CAN (100%) at complete

Table 2 Effect of reaction temperature on selective hydrogenation of
p-CNB over $Pt_{0.0002}$ -Au_{0.005}/TiO₂^a

		Sel. (%)		
temp. (K)	<i>p</i> -CNB Conv. (%)	p-CAN	AN	Others
303	10.1	93.9	n.d.	6.1 ^b
313	55.2	97.3	n.d.	2.7 ^b
323	100	100	n.d.	n.d.
333	100	100	n.d.	n.d.
343	100	99.7	0.2	0.1^{c}

n.d.: not detected.^{*a*} Other reaction conditions: 25.0 mg catalyst, 0.39 g *p*-CNB in 4.0 mL ethanol (solvent), 1.0 MPa H_2 , 1 h, stirring speed: 900 rpm.^{*b*} 4,4'-dichloroazoxybenzene and 4,4'-dichloroazobenzene.^{*c*} N-ethyl-*p*-chloroaniline.

conversion of *p*-CNB was obtained at 323–333 K. However, a hydrodechlorination process was observed with further increasing of the reaction temperature up to 343 K, and *N*-ethyl*p*-chloroaniline, a condensation product of *p*-CAN with the solvent (ethanol), was also detected. Therefore, the optimum reaction temperature may be restricted to 323–333 K.

H₂ pressure has a significant effect on the substrate reactivity and product selectivity (Table 3). The conversion of *p*-CNB and selectivity to *p*-CAN were seen to increase with the H₂ pressure. The conversion of *p*-CNB and selectivity to *p*-CAN were 63.2% and 97.9%, respectively, at 0.5 MPa H₂. The conversion increased to 100% and the selectivity reached 100% at 1.0 MPa H₂. The H₂ utilization rate in the reaction was *ca.* 89% by theoretical calculations according to the following formula: % utilization rate = $m/M \times 4/(25 \times 10^{-3} \times 10/22.4)$, where *m* is the mass of *p*-CNB; *M* the mole mass of *p*-CNB. It is interesting to note that the selectivity to *p*-CAN could be maintained even when the reaction was conducted at 4 MPa H₂. These data demonstrate that the undesired hydrodechlorination can be avoided over the Pt_{0.0002}-Au_{0.005}/TiO₂ catalyst even when very high H₂ pressure is used for the reaction.

The effect of the reaction time for the hydrogenation of *p*-CNB over $Pt_{0.0002}$ -Au_{0.005}/TiO₂ was studied at 323 K, 1.0 MPa H₂. As shown in Table 4, both *p*-CNB conversion and the selectivity for *p*-CAN increased along with the reaction time. When the reaction was continued for 45 min, we observed a complete conversion of *p*-CNB and 100% selectivity for *p*-CAN. It is known for the catalytic reaction of interest, that a high

Table 4 Effect of reaction time on selective hydrogenation of *p*-CAB over $Pt_{0.002}$ -Au_0.005/TiO₂^{*a*}

	CDUD	Sel. (%)			
React. time (min)	<i>p</i> -CNB Conv. (%)	p-CAN	AN	Others	
15	51.8	97.1	n.d.	2.9 ^b	
30	83.4	98.7	n.d.	1.3 ^b	
45	100	100	n.d.	n.d.	
60	100	100	n.d.	n.d.	
120	100	100	n.d.	n.d.	
180	100	100	n.d.	n.d.	
240	100	99.9	n.d.	0.1^{c}	

n.d.: not detected.^{*a*} Other reaction conditions: 25.0 mg catalyst, 0.39 g *p*-CNB in 4.0 mL ethanol (solvent), 323 K, 1.0 MPa H₂, stirring speed: 900 rpm. ^{*b*} 4,4'-dichloroazoxybenzene and 4,4'-dichloroazobenzene. ^{*c*} N-ethyl-*p*-chloroaniline.

selectivity is difficult to maintain once the substrate has been exhausted completely over most metal-supported catalysts, since in the absence of a substrate the catalytic hydrodechlorination reaction will occur at a much faster rate. To our surprise, the high selectivity could be maintained even when the reaction time was extended by several hours after *p*-CNB was exhausted.

To explore the stability of the $Pt_{0.002}$ - $Au_{0.005}$ / TiO_2 for *p*-CNB hydrogenation, the catalyst was separated from the reaction system after the *p*-CNB hydrogenation reaction had completed, it was washed with ethanol, dried under vacuum and then reused for the same reaction. After reusing it five times, the *p*-CNB conversion and *p*-CAN selectivity data obtained over this recovered catalyst were found similar to those over the fresh one (Table 5). The results suggest that the $Pt_{0.002}$ - $Au_{0.005}$ / TiO_2 catalyst is very stable and suitable for practical applications.

The X-ray diffraction (XRD) patterns of the TiO₂, Au_{0.005}/TiO₂ and Pt_{0.0002}-Au_{0.005}/TiO₂ catalysts are given in Fig. 2. Peak assignments for TiO₂ (Fig. 2a, $2\theta = 25.2$, 37.8, 48.1, 53.9 and 55.1°) are consistent with the (101), (004), (200), (105) and (211) planes associated with tetragonal anatase (JCPDS-ICDD 21-1272). Apart from the diffraction peaks of the anatase TiO₂, there were no peaks in the XRD patterns of the Au_{0.005}/TiO₂ (Fig. 2b) and the Pt_{0.0002}-Au_{0.005}/TiO₂ (Fig. 2c), *i.e.*, no new phases were detected. Moreover, neither the Au_{0.005}/TiO₂ nor the Pt_{0.0002}-Au_{0.005}/TiO₂ presented obvious change compared to the TiO₂ in the XRD spectra (Fig. 2). This result can presumably be ascribed to the combinations of low contents of doping Au

Table 5 Reusability of the $Pt_{0.0002}$ -Au_{0.005}/TiO₂ catalyst for the selective hydrogenation of *p*-CAB^{*a*}

over Pt _{0.0002} -Au	$I_{0.005}/\text{TiO}_2^{a}$	$O_2{}^a$			
TT	CNID	Sel. (%)			
(MPa)	<i>p</i> -CNB Conv. (%)	p-CAN	AN	Others ^b	
0.5	63.2	97.9	n.d.	2.1	
1.0	100	100	n.d.	n.d.	
2.0	100	100	n.d.	n.d.	
4.0	100	100	n.d.	n.d.	

Table 3 Effect of H₂ pressure on selective hydrogenation of p-CAB

n.d.: not detected.^{*a*} Other reaction conditions: 25.0 mg catalyst, 0.39 g *p*-CNB in 4.0 mL ethanol (solvent), 323 K, 1 h, stirring speed: 900 rpm. ^{*b*} 4,4'-dichloroazoxybenzene and 4,4'-dichloroazobenzene.

	CNID	Sel. (%)			
<i>p</i> -CNB Conv. (%	<i>p</i> -CNB Conv. (%)	p-CAN	AN	Others	
	100	100	n.d.	n.d.	
	96.5	99.9	n.d.	0.1^{b}	
	95.6	99.9	n.d.	0.1^{b}	
	95.1	99.9	n.d.	0.1^{b}	
	94.8	99.9	n.d.	0.1^{b}	

n.d.: not detected.^{*a*} Reaction conditions: 25.0 mg catalyst, 0.39 g *p*-CNB in 4.0 mL ethanol (solvent), 323 K, 1.0 MPa H₂, 45 min, stirring speed: 900 rpm. ^{*b*} 4,4'-dichloroazoxybenzene and 4,4'-dichloroazobenzene.



Fig. 2 XRD patterns of TiO_ (a), $Au_{0.005}/TiO_2$ (b) and $Pt_{0.002}-Au_{0.005}/TiO_2$ (c).

and Pt below the detection limits of the XRD, small grain size, and homogeneous distribution.

In order to obtain explicit details of Au and Pt particle size, Au_{0.005}/TiO₂ and Pt_{0.0002}-Au_{0.005}/TiO₂ were examined with transmission electron microscopy (TEM) in the dark field mode. As can be seen from the TEM images (Fig. 3a,b), small bright spots can be discerned from the background over $Au_{0.005}/TiO_2$ and Pt_{0.0002}-Au_{0.005}/TiO₂. A combined EDX analysis, using an electron beam of 0.8 nm in diameter, showed that the signal of Au could be detected only at the small bright spots (Fig. 3b1,b2). No Pt signals were observed in the EDX spectrum (Fig. 3b2). The crystal lattice spacing of a selected metal particle (Figure S1, ESI[†]) is rather uniform and consistent with that of Au single crystallites,²⁴ suggesting that the Pt and Au are probably not alloyed. These are probably due to the low content of Pt in the $Pt_{0.0002}$ -Au_{0.005}/TiO₂ (only 0.02 wt%). Therefore, we conclude that the small bright spots in Fig. 3b are the image of the Au or Au and Pt species. The Au or Au and Pt particles in the Pt_{0.0002}- $Au_{0.005}/TiO_2$ catalyst have an average diameter of 5 nm, with a size distribution from 3 to 6 nm (Fig. 3b), which is consistent with the absence of characteristic diffraction peaks of Au and Pt in the XRD pattern of Pt_{0.0002}-Au_{0.005}/TiO₂, suggesting that the Au and Pt species on TiO₂ are in a homogenous dispersion without any obvious aggregation.



Fig. 3 TEM images of $Au_{0.005}/TiO_2$ (a), $Pt_{0.0002}-Au_{0.005}/TiO_2$ (b) and EDX spectra of the selected area 1 (b1) and 2 (b2).

Gold particle size and distribution can have a direct impact on the hydrogenation activity where the presence of nanoscale Au particles (<10 nm) has been deemed essential for significant activity,²⁵ with a decrease in efficiency for larger Au particles. This interpretation cannot be applied in the present work, for these Au particles in the Pt_{0.0002}-Au_{0.005}/TiO₂ did not change obviously in size when Pt was added (Fig. 3a,b). The hydrogenation activity of the Au nanoparticles was often much lower than those of the platinum-group metals. Some observations show that the low hydrogenation activity of the Au nanoparticles is most probably due to an "intrinsic" nobleness of Au for H₂ activation, and that the dissociative adsorption of H₂ on Au is an activated process and is restricted to the edge and corner sites or to the interface perimeter around the Au nanoparticles that are in contact with the oxide support.²⁰ Therefore, the activity enhancement of Au nanoparticles by the deposition of Pt entities for the chemoselective hydrogenation of p-CNB could be explained by a synergic effect of Pt, Au and the TiO₂ support (Fig. 4). It seems reasonable that the Pt sites were responsible for the dissociative activation of H₂ molecules while Au sites, especially the perimeter interfaces around the Au particles in contact with the TiO₂ support for the adsorption-activation of the substrate molecules. The activated H atoms would then migrate by spilling over toward nearby Au sites, especially perimeter interfaces between TiO₂ and Au nanoparticles for a fast reaction with the adsorbed substrate. The dramatic enhancement of the Au activity by the Pt entities would suggest that the overall reaction rate was determined by the activation of H_2 or by the supply of H atoms. On the other hand, the well maintained selectivity propensity of the Au nanoparticles in the hydrogenation reactions, regardless of Pt in the $Pt_{0.0002}$ - $Au_{0.005}/TiO_2$ catalyst, would indicate that such chemoselective hydrogenation selectivity was governed by the adsorption mode of the substrate molecules on the Au sites, especially perimeter interfaces between the TiO₂ and Au nanoparticles.



Fig. 4 Pt promotion of the hydrogenation catalysis of Au nanoparticles.

3. Conclusions

In conclusion, adding a small amount of Pt entities (0.01-0.03 wt%) onto the Au surface of a Au/TiO₂ catalyst is an efficient approach to improve the catalytic activity of Au for the hydrogenation of *p*-chloronitrobenzene, while the C–Cl

bond in the p-CNB molecule remained intact. XRD, TEM and catalytic results implied that this unusually high reaction rate and selectivity might be due to the Pt sites acting to activate the H₂ molecules while the Au sites, especially perimeter interfaces around the Au particles in contact with the TiO₂ support serve to activate p-CNB by chemisorption. There was a remarkable effect of the Pt loading and reaction temperature on p-CAN selectivity. Excess amounts of Pt (>0.03 wt%) and high reaction temperatures will cause the occurrence of the undesired catalytic hydrodechlorination reaction of p-CNB. As for Pt_{0.0002}- $Au_{0.005}/TiO_2$, the selectivity for *p*-CAN could be up to 100% at complete conversion of p-CNB with reaction temperatures at or below 333 K. In addition, the catalyst was quite stable and could be used repetitively without significant deactivation. These facts allow us to view it as a prospective heterogeneous catalyst for selective production of p-CAN from p-CNB.

4. Experimental

4.1 Catalyst preparation

 TiO_2 with a BET surface area of 42 m² g⁻¹ and an average grain size of 35 nm was prepared by hydrothermal homogeneous precipitation according to the following procedure: 6 g urea was added into 50 mL of 16.5% (w/v) Ti(SO₄)₂ aqueous solution (Beijing Chem. Co.). After stirring for 30 min at room temperature, the mixture was transferred into an 80 mL teflonlined autoclave for hydrothermal reaction under 433 K for 20 h and cooled to room temperature naturally. The resultant precipitate was filtered and washed with distilled water until it was free from sulfate ions, then dried at 383 K overnight. Finally, the TiO_2 was obtained by calcination in flowing air at 873 K for 5 h. The Pt-Au/TiO₂ catalyst was prepared using HAuCl₄, H₂PtCl₆ for the precursors of gold and platinum by depositionprecipitation with urea. Typically, 2.0 g of TiO₂ was suspended in 50 mL aqueous solution of HAuCl₄ ($1.015 \times 10^{-3} \text{ mol } \text{L}^{-1}$), H_2PtCl_6 (4.1 × 10⁻⁵ mol L⁻¹) and urea (0.2 mol L⁻¹). The mixture was heated to 353 K and maintained at this temperature for 4 h under vigorous stirring and allowed to cool to room temperature overnight. The precipitate was isolated and washed thoroughly with distilled water by filtration until it was free from chloride ions. Finally, the sample was dried at 383 K for 12 h and calcined at 473 K for 5 h in flowing air (60 mL min⁻¹). The amount of gold and platinum in the catalyst was 0.49 wt% and 0.018 wt%, respectively, according to ICP-AES analysis.

4.2 Catalyst characterization

The gold and platinum contents in the $Pt_{0.002}$ - $Au_{0.005}$ /TiO₂ catalyst were analyzed by means of inductively coupled plasmaatomic emission spectroscopy (ICP-AES, Leeman Prodigy) after the sample was dissolved in aqua regia. X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max Ultima IV X-ray diffractometer with Cu K α radiation ($\lambda = 0.154056$ nm). The catalyst for XRD characterization was prepared by placing some sample on a glass slide. The transmission electron microscopy (TEM) measurement was performed on a JEOL JEM-2000EX microscope operated at an accelerating voltage of 120 kV. An energy-dispersive X-ray (EDX) spectroscopic detecting unit was used to collect the EDX spectra for elemental analysis. A sample for TEM examination was made by placing a drop of the catalyst powder dispersion in ethanol on a carbon-coated copper grid, followed by drying at room temperature.

4.3 Catalysis procedure

Catalytic tests were performed with magnetic stirring in a 25 mL stainless steel autoclave containing 0.39 g *p*-CNB in 4.0 mL ethanol (solvent). The catalyst (Pt–Au_{0.005}/TiO₂ powder, particle size 0.1 mm) used in each run of the reaction was 25.0 mg. The overall molar *p*-CNB/Au ratio in the reaction mixture was 3902. The reactor was flushed five times with 0.5 MPa H₂ before it was pressurized to the desired H₂ pressure and placed into an oil bath maintained at the reaction temperature. The reaction was stopped at a selected time by cooling the reactor in an ice–water bath. Analysis of the reaction products was done on an HP6890A GC instrument with a HP-5 capillary column with a FID detector, using benzene as an internal standard.

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