

Catalytic transfer hydrogenolysis of 2-phenyl-2-propanol over palladium supported on activated carbon

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Abstract

Transfer hydrogenolysis of 2-phenyl-2-propanol to isopropylene using formic acid as hydrogen donor was performed over the supported palladium, platinum and ruthenium catalysts. The hydrogen-donating abilities of various hydrogen donors and the effect of the pH value in a reaction medium were studied. It was found that Pd/C is an effective catalyst and formic acid is much better than formate salts and other agents of donating-hydrogen for the catalytic transfer hydrogenolysis of 2-phenyl-2-propanol. The protons in a reaction medium have a promotive effect on the catalytic hydrogenolysis of 2-phenyl-2-propanol. At the reaction condition of using formic acid as hydrogen donor and the Pd/C catalyst at 80 °C for 4 h, the conversion of 2-phenyl-2-propanol and selectivity to isopropylbenzene reaches 95.2 and 98.4%, respectively.

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1. Introduction

Catalytic transfer hydrogenolysis (CTH) is an important synthetic technique in organic chemistry [1–3]. As neither hydrogen containment nor a pressure vessel is required, the mild reaction conditions offer considerable advantages over the conventional method of catalytic hydrogenolysis. CTH is available for a wide variety of functional groups including halo, nitro and benzyl groups [4–7], in which formic acid or formate salts was used often as hydrogen donors. Generally, metal (VIII group elements) such as palladium, ruthenium and Raney nickel [8–10] were employed as the catalysts for the transfer hydrogenolysis.

Oxygen-containing benzyl (*O*-benzyl) groups are among the most useful protecting groups in synthetic organic chemistry, because of their ease of formation, their relative stability, and an efficiency of cleavage under mild conditions [11], in which 2-phenyl-2-propanol (ArPrOH) is often used as one of the model compounds including oxygen-containing benzyl groups, and is widely used in the perfumeries. As a model reaction, the transfer hydrogenolysis of 2-phenyl-2-propanol has been studied by our group, because that 2-phenyl-2-propanol includes not only the

most useful protecting groups of *O*-benzyl group, but also is a very important intermedium to manufacture the propylene oxide (PO) by isopropylbenzene hydroperoxide oxidizing propylene [12,13]. When propylene is epoxidized to PO by isopropylbenzene hydroperoxide as an oxidant, 2-phenyl-2-propanol was obtained as a side-product, and should be hydrogenolyzed to isopropylbenzene that is the raw material to produce isopropylbenzene hydroperoxide, which forms a cycle of oxidizing isopropylbenzene to isopropylbenzene hydroperoxide, and then being reduced to isopropylbenzene.

For the transfer hydrogenolysis or hydrogenation, it is necessary to select an efficient catalyst and suitable hydrogen donors. In this paper, CTH of 2-phenyl-2-propanol was used as a model reaction, the preparation of the Pd/C catalyst, the effects of various hydrogen donors and the pH value in reaction medium on the hydrogen-donating ability were studied. Furthermore, the mechanism for the catalytic transfer hydrogenolysis of 2-phenyl-2-propanol over Pd/C by formic acid was discussed.

2. Experimental

H₂PdCl₄, H₂PtCl₆ and RuCl₃·*n*H₂O (AR) aqueous solution were used as the precursors of the catalyst active components. Commercial γ-Al₂O₃, activated carbon and MCM-41 molecu-

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lar sieve (TEOS as silica precursor) that was prepared according to the reference [14] were used as the carriers of catalysts. Their BET surface areas are 215, 1080 and 1023 m²/g, respectively.

The supported catalysts were prepared as follows. The activated carbon was added into 0.01 M aqueous solution of the active metal precursors under stirring at 60 °C, and the pH value of the slurry solution was adjusted to 6–7 by the aqueous solution of NaHCO₃. After 2 h, the solid sample was filtered and dried at room temperature. Pd/Al₂O₃ and Pd/MCM-41 were prepared by an impregnation method and calcined at 550 °C for 5 h in air. The catalysts should be treated with H₂ at 120 °C for 1 h before they were used.

The active metal loading on the catalysts was about 3.8% (wt.) that was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), which was done on an IRIS 1000 (Thermo Elemental, USA) instrument.

The XRD patterns of the catalysts were determined on a Rigaku D-MAX RB X-ray diffractometer at 40 kV and 40 mA, and the radiation source was Cu K α .

The catalytic transfer hydrogenolysis of 2-phenyl-2-propanol was operated as follows. 2-Phenyl-2-propanol (1.5 mmol), hydrogen donor (3 mmol), catalyst (0.2 g) and ethanol solvent (10 ml EtOH and 2 ml H₂O) were put into a flask equipped with a water-cooled condenser and a magnetic stirrer. The flask was placed in an oil bath and maintained at 80 °C and atmosphere. After the reaction with reflux was carried out for 4 h, the hydrogenolysis products were withdrawn and analyzed by the gas chromatograph of Perkin-Elmer Autosystem XL with the FID detector and fused silica capillary column (methyl 5% phenyl silicone, 25 m \times \varnothing 0.32 mm).

The hydrogenolysis products obtained with HCOOH as hydrogen donor over the Pd/C catalyst were analyzed qualitatively by GC-Mass (HP 5890 II gas chromatograph and Micro-mass GCT CA 055) and GC-IR (HP 5890 II gas chromatograph and a BIO-RAD FTS-40 IR spectrometer).

The initial pH value of the reaction mixtures was measured by the pH meter (Leici PHS-3C, Shanghai).

3. Results and discussion

3.1. Performance of the catalyst

Using HCOOH as hydrogen donor, the catalytic transfer hydrogenolysis of 2-phenyl-2-propanol over the Pd/C, Pt/C and Ru/C catalyst was studied. As shown in Table 1, the catalytic activity of Pd/C is far superior to the Pt/C and Ru/C catalysts. Over the Pd/C catalyst reduced, the conversion of ArPrOH and the selectivity to cumene reaches 95.2 and 98.4%, respectively. Palladium is widely used for the cleavage of the benzylic–O bonds, because it has a high activity for hydrogenolysis with a low activity for the saturating aromatic rings. However, platinum and ruthenium catalysts are usually effective catalyst to saturate aromatic rings with minimal hydrogenolysis [11]. Therefore, for the catalytic transfer hydrogenolysis of 2-phenyl-2-propanol, the performance of Pt/C or Ru/C catalyst is very low.

Table 1

Performance of catalyst for CTH of 2-phenyl-2-propanol by HCOOH as H-donor at 80 °C for 4 h^a

Catalyst	Conversion of ArPrOH (%)	Selectivity to <i>i</i> -PrAr (%)	Yield of <i>i</i> -PrAr (%)
Pd/C	95.2	98.4	93.7
Pd/C ^b	92.6	97.1	89.9
Pt/C	53.4	1.2	0.6
Ru/C	37.1	–	–
Pd/ γ -Al ₂ O ₃	35.8	11.1	4.0
Pd/MCM-41	33.1	3.9	1.3

ArPrOH: 2-phenyl-2-propanol; *i*-PrAr: isopropylbenzene.

^a 1.5 mmol ArPrOH, 3 mmol HCOOH, 0.2 g catalyst, 10 ml EtOH and 2 ml H₂O.

^b Untreated.

3.2. Effect of the support

Effects of the support on the catalytic performance of the supported palladium catalysts are shown in Table 1. The results show that Pd/C reduced or unreduced behaves a high activity for the transfer hydrogenolysis of ArPrOH. When MCM-41 or γ -Al₂O₃ is used as the support, the catalytic performance of the Pd catalyst is remarkably lower than that of Pd/C. For the γ -Al₂O₃ support, its comparable stronger surface acidity would promote the dehydration of 2-phenyl-2-propanol to α -methyl styrene to reduce the selectivity to isopropylbenzene, and its low surface area would reduce its activity. Pd/MCM-41 has a larger surface area like Pd/C, but its performance is very low and is similar to that of Pd/ γ -Al₂O₃. This implies that the performance of the Pd catalyst is independent of the support's surface area, and depends on the properties of the Pd sites on the support.

Fig. 1 shows the XRD patterns of the palladium catalysts untreated. For Pd/ γ -Al₂O₃ and Pd/MCM-41, their XRD patterns display the diffraction peaks of PdO that is formed during calcination in air. It is interesting there are the diffraction peaks of metallic Pd⁰ in the XRD spectrum of the Pd/C catalyst untreated, which is the reason of the Pd/C catalyst untreated having a great catalytic activity (Table 1, entry 2). In the preparation of Pd/C, after H₂PdCl₄ in aqueous solution adsorbs on the surface of

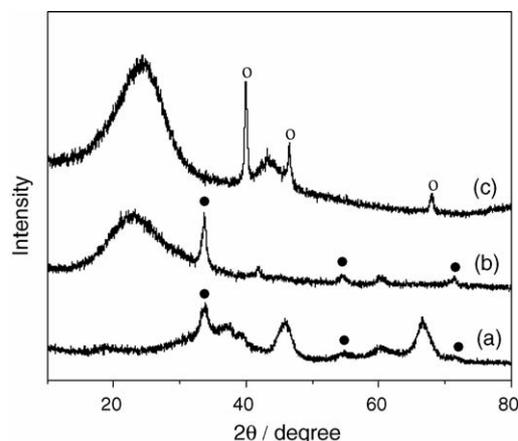
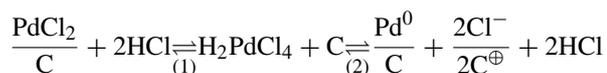


Fig. 1. XRD patterns of the catalysts untreated of Pd/Al₂O₃ (a), Pd/MCM-41 (b) and Pd/C (c). \circ , Pd⁰; \bullet , PdO.

carbon, two competitive reactions may occur, that is, H_2PdCl_4 ($\text{PdCl}_2 + 2\text{HCl}$) is reduced to form metallic Pd particles (process 2) and reacts with the C=C fragments of carbon matrix to form the π -complexes of PdCl_2 (process 1) [15,16]:



Therefore, the Pd^{2+} cations can be reduced during an adsorption of H_2PdCl_4 in aqueous solutions on the surface of activated carbon. It is due to the high reducing potential and the conductivity of activated carbon [17]. Furthermore, Simonov et al. [15] have reported an adsorption of H_2PdCl_4 on carbon from a dilute solution can produce greater amount of deposited Pd^0 than from a concentrated solution. As the H_2PdCl_4 aqueous solution used in this paper is dilute (0.01 M), there will be a relatively smaller quantity of Pd^{2+} and a mass of Pd^0 adsorbed on the carbon surface. However, there are no diffraction peaks of PdCl_2 in the XRD patterns of the Pd/C catalyst. It is probably because that the adsorption of PdCl_2 is present either as particles of less than 3 nm size, or in molecularly dispersed form [15]. At one time, the complex features of the activated carbon surface are very important for the Pd/C catalyst, such as, the residual acid properties on the surface of carbon can help to increase the reaction rates [11].

3.3. Effect of hydrogen donor

Using the Pd/C catalyst, the effect of hydrogen donor on the transfer hydrogenolysis of 2-phenyl-2-propanol is shown in Table 2. The results show that the kind of hydrogen donor has a great influence on the transfer hydrogenolysis of 2-phenyl-2-propanol. Among HCOOH , 2-propanol, HCOOK , HCOONH_4 , $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, HCOONa and CH_3COOH , formic acid is most efficient hydrogen donor, in which the conversion of 2-phenyl-2-propanol and selectivity to isopropylbenzene reaches 95.2 and 98.4%, respectively.

When CH_3COOH is used as hydrogen donor, the conversion of 2-phenyl-2-propanol is 27.8% and selectivity to isopropylbenzene was $\sim 0\%$. It is attributed to the reaction of acetic acid with 2-phenyl-2-propanol to form the correspond-

ing ester. For formate salts as hydrogen donor, its hydrogen-donating ability is in the inverse proportion of an initial pH value of the reaction solution, that is, the higher the pH value of the reaction solution, the poorer hydrogen-donating ability of formate salt is. The fact of HCOOK and HCOONH_4 (not CH_3COOH) having the hydrogen-donating ability indicates that H of HCOO^- plays the role of hydrogen resource for the transfer hydrogenolysis.

3.4. Effect of water content

In order to investigate an influence of the water content in solvent on the hydrogenolysis of 2-phenyl-2-propanol with formic acid, the mixture solvent of water/ethanol was used. The results in Fig. 2 show that the conversion of 2-phenyl-2-propanol and selectivity to isopropylbenzene increase with an increase of the amount of water, and they reach the maximums as 2 ml water is used. This is because that increasing the water amount in solvent makes the HCOOH concentration in the medium decrease and the ionizability of HCOOH increase. However, water is one of products in the hydrogenolysis reaction, and more water added in a reaction system would restrain the hydrogenolysis of 2-phenyl-2-propanol.

3.5. Effect of the pH value in a reaction medium

The studies above mentioned show that, formic acid is more efficient hydrogen donor than formate salts for the transfer hydrogenolysis of 2-phenyl-2-propanol. This situation is different from the transfer hydrogenolysis of aryl chlorides or benzyl acetate catalyzed by palladium, in which formate salts as hydrogen donors are superior to formic acid [18–20].

It has been reported that the hydrogenolysis of benzyl ester is much easier than that of benzyl alcohol in the traditional catalytic hydrogenolysis by molecular hydrogen [21]. When HCOOH is used as a hydrogen donor, whether the hydrogenolysis of 2-phenyl-2-propanol can be promoted by forming an intermediate of ester of 2-phenyl-2-propanol and HCOOH ? The analysis for the products obtained with HCOOH as hydrogen donor (Table 2, entry 4) by GC-Mass and GC-IR shows there a few formate of 2-phenyl-2-propanol in the products. If sodium formate was added

Table 2
Effect of hydrogen donor on the transfer hydrogenolysis of 2-phenyl-2-propanol over the 3.8 wt.% Pd/C catalyst at 80 °C for 4 h^a

Hydrogen donor	pH ^b	Conversion of ArPrOH (%)	Selectivity to <i>i</i> -PrAr (%)
2-Propanol		6.4	65.8
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$		0.4	~ 100
CH_3COOH		27.8	0
HCOOH	2.93	95.2	98.4
HCOOK	5.83	1.9	51.8
HCOONH_4	6.97	1.4	100
HCOONa	8.02	–	–

ArPrOH: 2-phenyl-2-propanol; *i*-PrAr: isopropylbenzene.

^a ArPrOH (1.5 mmol), hydrogen donor (3 mmol), Pd/C (0.2 g), EtOH (10 ml), H_2O (2 ml).

^b The initial pH value of the reaction mixture.

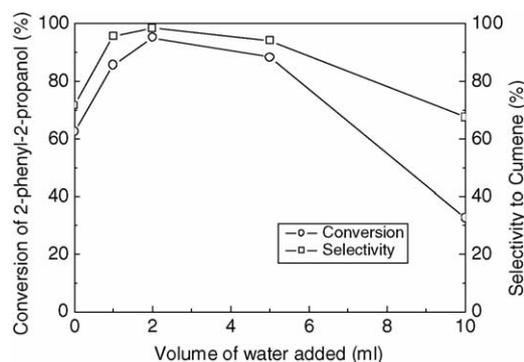


Fig. 2. Effect of water content in ethanol solvent on the transfer hydrogenolysis with formic acid over Pd/C catalyst at 80 °C for 4 h.

Table 3

Effect of pH value on the transfer hydrogenolysis of 2-phenyl-2-propanol with HCOONa over Pd/C catalyst at 80 °C for 4 h^a

Additive	pH ^b	Conversion of ArPrOH (%)	Selectivity to <i>i</i> -PrAr (%)
None	8.02	–	–
CH ₃ COOH ^c	7.52	1.4	27.6
0.15 mmol CH ₃ COOH	5.90	2.0	55.5
0.3 mmol CH ₃ COOH	4.81	17.9	95.0
1.8 mmol CH ₃ COOH	3.78	43.8	95.7
HBO ₃ ^c	7.21	1.7	33.3
HCOOH ^d	4.71	20.6	98.9

^a ArPrOH (1.5 mmol), hydrogen donor (3 mmol), Pd/C (0.2 g), EtOH (10 ml), H₂O (2 ml).

^b The initial pH value of the reaction mixture.

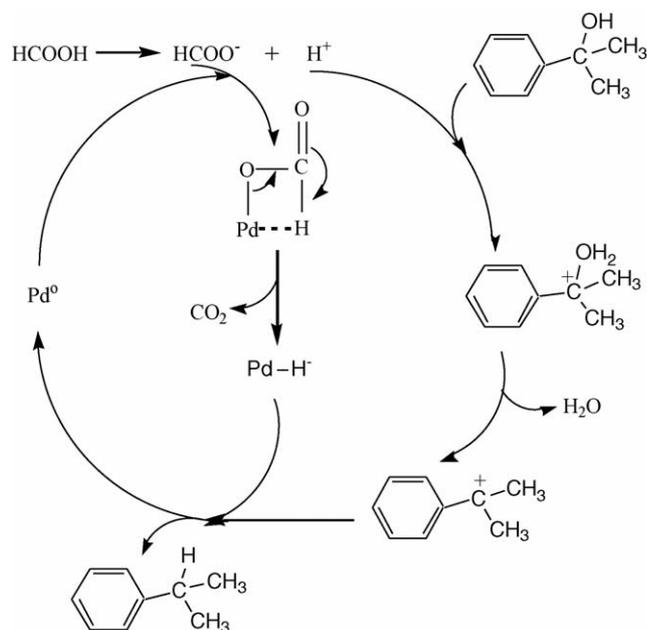
^c The pH value of HAc solution equals to that of HBO₃ solution.

^d The amount of HCOOH equals to that in Table 2.

in the hydrogenolysis system using formic acid as hydrogen donor (Table 2, entry 4), the rate of hydrogenolysis fell sharply (Table 3, entry 7). Differing from formic acid, boric acid is an inorganic acid and its acidity is weaker than formic acid, and does not react with 2-phenyl-2-propanol to form ester. Adding boric acid in the hydrogenolysis system using HCOONa as hydrogen donor reduces the pH value of the reaction solution from 8.02 to 7.21, and increases the rate of hydrogenolysis of 2-phenyl-2-propanol (Table 3, entry 6). This implies it is not necessary to promote the hydrogenolysis of 2-phenyl-2-propanol by a formation of an intermediate of ester, and the initial pH value of the reaction mixture is an important factor to affect the rate of hydrogenolysis.

To further demonstrate the role of the pH value of reaction medium, the effects of the pH value of reaction medium modified by acetic acid on the hydrogenolysis were investigated, and the results are shown in Table 3. With an increase of the amount of acetic acid, the pH value of medium decreases, and the rate of hydrogenolysis enhances. When 1.8 mmol HAc is added, the conversion of 2-phenyl-2-propanol and selectivity to isopropylbenzene reaches 43.8 and 95.7%, respectively. But the conversion of alcohol is much lower than that using formic acid as H-donor, even the amount of acetic acid added is much more than the stoichiometric molar weight to react with 2-phenyl-2-propanol (Table 3, entry 5), which attributes to its higher pH value (3.78) than that of medium including formic acid as hydrogen donor (pH 2.93).

The results mentioned above show that, the acidic medium is in favor of the transfer hydrogenolysis of 2-phenyl-2-propanol, which is perhaps induced by protons in a medium. The less the pH value of reaction medium, the higher the concentration of proton is. The protons are available to a formation of the leaving group, i.e. O⁺H₂ instead of OH [22], and a cleavage of the carbon–oxygen bond to give a carbonium ion. Then the carbonium ion reacts with hydrogen on the surface of catalyst to form isopropylbenzene (Scheme 1). On the contrary, if the reactants include basic groups, more acid molecules need to be added to protonize the basic groups. That is consistent with the catalytic hydrogenolysis by molecular hydrogen [23].



Scheme 1. Mechanism of transfer hydrogenolysis of 2-phenyl-2-propanol over Pd/C with formic acid.

3.6. Mechanism of the catalytic transfer hydrogenolysis of 2-phenyl-2-propanol

Based on the results and discussion above, the mechanism for the catalytic transfer hydrogenolysis of 2-phenyl-2-propanol over Pd/C by formic acid has been proposed as shown in Scheme 1. HCOOH is ionized to HCOO⁻ and H⁺ in a reaction medium. HCOO⁻ adsorbed on the palladium sites dissociates H⁻ adsorbed and CO₂, and H⁺ attacks the carbon–oxygen bond to form a carbonium ion. Then the carbonium ion reacts with H⁻ adsorbed on the sites of palladium to form isopropylbenzene.

From the mechanism proposed in Scheme 1, it can be seen that the amount of protons and formoxy ions is important for the transfer hydrogenolysis of 2-phenyl-2-propanol with formic acid over Pd/C. Formate salts would dissociate more formoxy ions than formic acid, but the performance of Pd/C with formate salts as H-donor is poorer than that with formic acid. Low pH value in a reaction medium is in favor of increasing the performance of catalyst. Based on the facts above, it can be concluded that the step of forming carbonium ion is more difficult than the step of HCOO⁻ adsorbed dissociating H⁻ adsorbed and CO₂, that is to say, the former is the controlling step for the catalytic transfer hydrogenolysis of 2-phenyl-2-propanol over Pd/C.

4. Conclusions

For the transfer hydrogenolysis of 2-phenyl-2-propanol by formic acid, Pd/C is an effective catalyst. As a hydrogen donor, formic acid is much better than formate salts and other agents of donating-hydrogen. With a decrease of the pH value of reaction medium, the catalytic performance of Pd/C increases for the transfer hydrogenolysis of 2-phenyl-2-propanol. The reason is there is a promotive effect of protons in a reaction medium on the catalytic hydrogenolysis of 2-phenyl-2-propanol.

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