Low Temperature Chemoselective Hydrogenation of Aldehydes over a Magnetic Pd Catalyst

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Received: 20 February 2019; Accepted: 24 April 2019; Published: 29 April 2019

Abstract: Chemoselective hydrogenation of aldehydes with heterogeneous catalysts under mild conditions is of great importance but remains a major challenge. Herein, an efficient strategy was developed for low temperature chemoselective hydrogenation of aldehydes with broad substrate scope over a magnetic material supported palladium catalyst ($\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$). Aldehydes bearing various reducible functional groups readily underwent hydrogenation to give the corresponding primary alcohols with moderate to excellent yield at room temperature in aqueous solutions. The Hammett equation revealed that the hydrogenation of aromatic aldehydes proceeded via an anionic intermediate. Additionally, when the temperature increased to 70 °C, toluene was obtained by the deoxygenation of benzaldehyde in excellent yield. Furthermore, the $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ could be recycled up to six times without loss of activity and metal leaching.

Keywords: selective hydrogenation; aldehydes; Pd catalysts; mild conditions

1. Introduction

Catalytic hydrogenation reactions are one of the most important processes, which are key routes for the production of numerous bulk products and intermediates in the chemical industry [1]. In particular, the chemoselective reduction of aldehydes in the presence of reducible functional groups under mild conditions has been recognized as a major challenge [2–5]. Hence, there has been a growing focus on the purity of the hydrogenation of aldehydes in recent years.

The catalytic hydrogenation of aldehydes can be performed either using hydrogen or other hydrogen donors such as organic silanes [6–8] and alcohols [9]. Transfer hydrogenation of carbonyl compounds by organic silanes can be performed under very mild conditions in the presence of homogeneous catalysts, but the use of organic silanes was neither cheap nor green due to the high cost of the organic silanes and the lower atom efficiency [7]. Alcohols especially *iso*-propanol had also been reported to be used for the transfer hydrogenation of carbonyl compounds [9]. However, these catalysts were usually not recyclable and required harsh reaction conditions [10,11]. Nonetheless, molecular hydrogen is a lower cost, much more atom-economic and cleaner reducing agent compared to the silanes. Therefore, the reduction of aldehydes with H_2 represented one of the most efficient and atom-economical transformations.

Both heterogeneous and homogeneous catalysts had been used for the reduction of aldehydes with molecular hydrogen. Generally, reactions with homogeneous catalysts could be performed under

relative mild conditions, as the homogeneous catalysts moved freely in the reaction solution [12–14]. Of particular note was that several kinds of homogeneous base metal catalysts had been discovered to be active for the hydrogenation of aldehydes under mild conditions. For example, Beller and co-workers demonstrated that manganese complexes could promote the aromatic carbonyl compounds into the corresponding alcohols under mild conditions (60 °C and 10 bar H₂ pressure) [14]. However, this method required the use of additional additives such as *t*-BuONa, which is sensitive to the air and moisture. More importantly, it was difficult to recycle and reuse the homogeneous catalysts [15,16].

To overcome the associated drawbacks of homogeneous catalysts [17–20], great effort has been devoted to the design of heterogeneous catalysts for the reduction of carbonyl groups at low temperature. Several kinds of metal catalysts have been reported to be active for the hydrogenation of carbonyl compounds into alcohols at low temperatures or hydrogen pressure. For example, Sekar and co-workers reported palladium nanoparticles (Pd-BNP) stabilized by a binaphthyl-backbone can be efficiently used for the chemoselective reduction of aldehydes in the presence of hydrogen at room temperature in water [17]. To further recycle the heterogeneous catalyst easily, a graphene-modified Ru catalyst was also reported to be active for the reduction of carbonyl groups into hydroxyl groups at a low temperature of 20 °C and 40 bar H₂ [18]. Acknowledging these important achievements, however, the range of chemoselective heterogeneous hydrogenation of aldehydes using molecular hydrogen in the presence of reducible functional groups was still quite limited [20], which restricted their application. For example, the Pd-BNP [17] could not reduce aliphaticaldehydes and heteroaromatic aldehydes, while graphene-modified Ru [18] could not selectively reduce aldehydes from ketone. Indeed, to the best of our knowledge, there are no heterogeneous catalysts that can selectively hydrogenation of aldehydes bearing various reducible functional groups including halogen, ketone, ester, carbon-carbon double bond, amine, nitro, or cyano group at low temperature yet. Furthermore, the subsequent hydrogenolysis of the hydroxyl group into the saturated groups is an even greater challenge [21], which is also very useful in the synthesis of value-added chemicals and liquid fuels. Therefore, it is important to continually develop efficient methods for the hydrogenation of aldehydes into corresponding alcohols or alkane under mild conditions with abroad substrate scope. In the present study, we tackle these problems with a new robust magnetic supported Pd catalyst.

In our previous work, we had successfully prepared a magnetic material supported Pd catalyst (abbreviated as γ -Fe₂O₃@HAP-Pd) and found that the as-prepared γ -Fe₂O₃@HAP-Pd catalyst was active for the oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid [22–24]. As palladium catalysts have also been widely used as the catalysts to activate molecular H₂ for reductive chemical reaction [25,26], it is expected that the γ -Fe₂O₃@HAP-Pd is active for the reduction aldehydes under mild conditions.

2. Experimental Section

2.1. Materials

All other chemicals were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). All solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), and used directly.

2.2. Catalyst Synthesis and Characterization

The γ -Fe₂O₃@HAP-Pd catalyst was prepared and characterized as reported in our previous work [22]. The synthetic route maybe summarized as follows (Scheme 1), Fe²⁺ and Fe³⁺ ions in alkaline solution were co-precipitated under nitrogen to produce Fe₃O₄nanoparticles. These were then coated with HAP, formed fromCa²⁺ and PO₄³⁻ at pH 11, and the product calcined at 300 °C for 3 h to produce γ -Fe₂O₃@HAP. The brown powdery-Fe₂O₃@HAP-Pd²⁺ was prepared by cation exchange of Ca²⁺ in γ -Fe₂O₃@HAP with Pd²⁺, and the Pd²⁺ reduced by NaBH₄inethanol to generate the γ -Fe₂O₃@HAP-Pd(0) catalyst. After addition of NaBH₄, the color of the catalyst changed immediately from brown to dark grey, confirming that the Pd²⁺ in γ -Fe₂O₃@HAP-Pd²⁺ had been successfully

reduced to Pd(0) nanoparticles. The content of Pd was determined as 2 wt% by ICP- OES analysis, while the particle size distribution of Pd nanoparticles was determined as 2.8 nm by TEM [22].

Scheme 1. Schematic illustration of the preparation of the γ -Fe₂O₃@HAP-Pd(0) catalyst.

2.3. General procedure of the Reduction of Carbonyl Compounds

The catalytic reduction of benzaldehyde was used as a model reaction. Typically, the reaction was performed in a stainless steel 40 mL Parr batch reactor. Typically, benzaldehyde (1 mmol), γ -Fe₂O₃@HAP-Pd (20 mg), and H₂O (10 mL) were charged into the reactor. The reactor was purged with H₂ by 5 times to completely remove the air in the reactor and the reaction solution, then charged with 2.5 bar H₂ at room temperature. The reactor with H₂ was heated to 70 °C within 4 min, commencing the catalytic reaction. The reaction was maintained at 70 °C for 12 h, while the reaction mixture was mechanically stirred at 1000 rpm. The reaction was stopped by cooling the reactor to room temperature and depressurized. The reaction mixture was extracted by ethyl acetate and analyzed by gas chromatography (GC) using ethylbenzene as the internal standard.

2.4. Analytical methods

Quantities of the products was analyzed by a GC (7890F) instrument with a crosslinked capillary HP-5 column (30 m × 0.32 mm × 0.4 mm) equipped with a flame ionization detector. The temperature of the column was initially kept at 80 °C for 3 min, and then increased at a rate of 20 °C min⁻¹ to 220 °C. Products were identified by comparison of the retention time of the unknown compounds with those of standard compounds and quantified based on the internal standard method. The products were confirmed by GC-MS (Agilent 7890A GC/5973 MS, HP-5 column). Some products with reducible functional groups were separated and further confirmed by ¹H NMR (Bruker AVANCE III, 400 MHz).

Aldehyde conversion and Alcohol selectivity were defined as follows:

Aldehyde conversion = moles of converted aldehyde / moles of starting aldehyde × 100%

Alcohol yield = moles of generated alcohol / moles of starting aldehyde × 100%

Alcohol selectivity = alcohol yield / aldehyde conversion × 100%

3. Results and Discussion

3.1. Effect of the Reaction Solvents on the Hydrogenation of Benzaldehyde

Generally speaking, the reaction solvent played a key role in the chemical reaction, as different solvents had different properties such as the polarity, dielectric constant, and steric hindrance [27]. Therefore, the hydrogenation of benzaldehyde was initially carried out in various solvents catalyzed by γ -Fe₂O₃@HAP-Pd to study the solvent effect. As listed in Table 1, it was noted the conversion of benzaldehyde over the γ -Fe₂O₃@HAP-Pd catalyst was greatly affected by the reaction solvents, while the selectivity was all above 90%. The lowest benzaldehyde conversion was observed in hexane with the weakest polarity (Table 1, Entry 1). The conversion of benzaldehyde increased from 34.2% in tetrahydrofuran (THF) to 56.9% in *iso*-propanol, further greatly increasing to 95.6% in ethanol (Table 1, Entries 3–4). The possible reason should be that the γ -Fe₂O₃@HAP-Pd catalyst can well dispersed in polar solvents instead of nonpolar solvents, as the surface of the γ -Fe₂O₃@HAP-Pd catalyst was

a layer inorganic HAP, which was hydrophilic. Hence, the higher polarity of the solvents led to the higher conversion of benzaldehyde. Interestingly, the best result was attained in water with the highest benzaldehyde conversion of 98.7% (Table 1, Entry 5), although benzaldehyde was less soluble in water than in ethanol. We presumed that a stronger hydrogen bonding between water and benzaldehyde should benefit the hydrogenation reactions [28,29]. It was noted that benzyl alcohol was attained in an almost quantitative yield at room temperature and atmospheric H₂ pressure after reacted for 4 h (Table 1, Entry 6), which was capable with the Pd-BNP (Table 1, Entry 7) [17].

Table 1. Results of the hydrogenation of benzyl aldehyde in different solvents ^a.

Entry	Catalyst	Solvent	Con. of Benzyl Aldehyde(%)	Sel. of Benzyl Alcohol(%)
1	γ -Fe ₂ O ₃ @HAP-Pd	Hexane	17.2	90.1
2	γ -Fe ₂ O ₃ @HAP-Pd	THF	34.2	90.9
3	γ -Fe ₂ O ₃ @HAP-Pd	<i>i</i> -PrOH	56.9	99.0
4	γ -Fe ₂ O ₃ @HAP-Pd	EtOH	95.6	96.5
5	γ -Fe ₂ O ₃ @HAP-Pd	H ₂ O	98.7	96.4
6 ^b	γ -Fe ₂ O ₃ @HAP-Pd	H ₂ O	100	>99
7 ^c	Pd-BNP	H ₂ O	90 ^d	

^aReaction condition: benzyl aldehyde (1 mmol), 10 mg γ -Fe₂O₃@HAP-Pd catalyst (2 wt.% by ICP-OES analysis); S/C= 530, solvent (10 mL), H₂(10 bar), 25 °C, 1h.

^bS/C= 530, H₂(1 bar), 25 °C, 4h.

^cfrom ref 15, S/C=100, H₂ (1 bar), 25 °C, 6h.

^dIsolated yield.

3.2. Effect of the Hydrogen Pressure on the Hydrogenation of Benzaldehyde

The effect of hydrogen pressure on the reduction of benzaldehyde was also studied. As shown in Figure 1, the conversion of benzaldehyde increased with the increasing of the hydrogen pressure. As the hydrogen pressure increasing from 1 bar to 10 bar, the conversion of benzaldehyde increased from 36.8% to 100% after reacted for 1 h at room temperature. The increasing hydrogen pressure might result in the increasing hydrogen concentration in the reaction solution, which accelerated the reaction. However, it seemed that the selectivity of benzyl alcohol was insensitive to the hydrogen pressure, which remained >95% under different hydrogen pressures. Considered the reaction efficiency, we chose 10 bar as the optimized hydrogen pressure.

Figure 1. Results of the reduction of benzaldehyde at different hydrogen pressure. Reaction conditions: benzaldehyde (1 mmol), 2 wt.% γ -Fe₂O₃@HAP-Pd catalyst (10 mg), H₂O (10 mL), 25 °C, 1 h.

3.3. Substrate Scope of the Reduction of Aldehydes to Alcohols

After achieving the best reaction conditions, the scope of the hydrogenation of various aldehydes was investigated and the results were summarized in Table 2. To our delight, aldehydes bearing various

kinds of labile groups on the aromatic ring were well tolerated and gave the corresponding alcohols with moderate to excellent yields in 1–21 h at room temperature. It was interestingly to note that the reaction rate was accelerated in presence of electron-withdrawing groups such as $-\text{CF}_3$, $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{NO}_2$, and $-\text{CN}$ (Entries 1–6, Table 2). 4-(Trifluoromethyl) benzaldehyde, 4-fluorobenzaldehyde, and 4-chlorobenzaldehyde were converted to the corresponding alcohol smoothly in 4 h with nearly quantitative yields; however, debromination occurred when 4-bromobenzaldehyde used as substrate (Entry 4, Table 2). Interestingly, our catalyst could selectively reduce aldehydes, while other carbonyl compounds such like ester or ketone groups were well preserved (Entries 7–8, Table 2). Lower reaction rates were observed for substrates with electron-donating substituted groups than those with electron-withdrawing substituents (Entries 10–14 Table 2 vs. Entries 1–8 Table 2). Longer reaction times (5–21 h) were needed to get good to excellent yields of corresponding alcohols. These results suggested that the electron state of other functional groups controls the activation state of the intermediate in this reaction. The reaction rate increasing with the electron-withdrawing groups indicated that electron went towards the aromatic ring in intermediates [30]. Moreover, all fused-ring aromatic aldehyde (2-naphthaldehyde), the heterocyclic aldehyde (4-pyridinecarboxaldehyde), aliphatic aldehydes (heptanal), and α,β -unsaturated aldehydes (cinnamaldehyde), which were reported unreactive by Sekar [17], could be reduced to corresponding alcohols with good to excellent selectivity by our method (Entries 15–19, Table 2). This means that our method had a broad scope for aldehydes.

It was worth noting that our method provided an economical and environmentally-friendly protocol for the hydrogenation of aldehydes into alcohols, because of the use of cheap and green solvent of water, and the mild reaction conditions. Our method could selectively hydrogenation of aldehydes bearing all kinds of reducible functional groups such as ketone, halogen, nitro, amine, or cyano groups with moderate to excellent yield, which expanded the scope of substrates for this kind of reaction and could be very useful in organic synthesis.

To get more insights into the catalytic reduction of aldehydes over the $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ catalyst, the reaction rates were studied in detail using the Hammett equation as an empirical rule. The results were shown in Figure 2. The hydrogenation rate of the substituted benzaldehyde showed a reasonable linear Hammett correlation and a Hammett value of 1.59 was obtained, indicating that the reduction of the aldehyde group to a hydroxy group was substituent-sensitive and proceeded via an anionic intermediate [30,31]. According to the results of Hammett equation, We predicted the reaction mechanism as follows: (1) hydrogen molecular cleaved by heterolysis in the presence of catalyst and afford a H^- and a H^+ ; (2) the H^- reacted with aldehydes and gave the anionic intermediate PhCH_2O^- ; (3) PhCH_2O^- reacted with proton and give the product PhCH_2OH .

Figure 2. Correlation study for catalytic reduction of various aromatic aldehydes to the corresponding aromatic alcohols. Reaction conditions: substrate (1 mmol), $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ (10 mg) catalyst, 25 °C, H_2 (10 bar), H_2O (10 mL).

Table 2. Substrate scope of the reduction of aldehydes to alcohols over $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ catalyst^a.

$\text{R-CHO} \xrightarrow[\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}]{10 \text{ bar H}_2, \text{H}_2\text{O, r.t.}} \text{R-CH}_2\text{OH}$					
Entry	Substrate	Product	Time (h)	Conv. (%)	Yield (%)
1			1.5	100	99.1
2			1.5	100	99.3
3			2	100	99.8
4			2.5	67.9	58.9(55.3 ^b)
5			1.5	100	99.7(96.1 ^b)
6			4	79.3	79.3(75.3 ^b)
7			6	96.5	82.6(80.5 ^b)
8			8	93.1	88.7
9			1	100	95.1
10			21	100	100
11			11	100	99.3
12			6	100	99.8
13			8	100	100
14			5	100	99.0
15			2	100	71.6(68.4 ^b)
16			2	97.5	97.5(94.8 ^b)
17			7.5	100	99.6
18			21	46.2	46.2(45.1 ^b)

^a Reaction conditions: substrate (1 mmol), $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ (10 mg) catalyst, 25 °C, H₂ (10 bar), H₂O (10 mL).^b Isolated yield.

3.4. Effect of the Temperature on the Deoxygenation of Benzaldehyde

We also tried to use this catalyst for the deoxygenation of benzaldehyde into the saturated compounds, which was also very useful in the synthesis of value-added chemicals and liquid fuels. As the hydrogenolysis of hydroxyl group was much more difficult than the reduction of the carbonyl groups into alcohols, we performed the reduction of benzaldehyde at 2.5 bar and elevated temperatures, and the results were shown in Figure 3. We could find that the reaction rate was greatly affected by the reaction temperature. As the reaction temperature increased, the yield of toluene increased, while the yield of benzyl alcohol decreased. When the reaction temperature below 70 °C, the yield of toluene was very low in 12 h, while the temperature exceeded 70 °C, the yield of toluene could reach to 95% in a shorter time (Table S3). These results showed that higher reaction temperature benefited the hydrogenolysis of hydroxyl group, indicating the activation energy of the hydrogenolysis

of hydroxyl group is higher than the hydrogenation of the aldehyde group. At the reaction temperature of 130 °C, toluene could be produced with an excellent yield of 97.9% in a short time of 1 h over the γ -Fe₂O₃@HAP-Pd catalyst, which was comparable with the reported homogeneous catalyst of Ru–pincer complexes that promoted the deoxygenation of carbonyl groups at 130 °C and 2 bar H₂ [21].

Figure 3. Results of the reduction of benzaldehyde at different temperatures. Reaction conditions: Benzaldehyde (1 mmol), 2 wt.% γ -Fe₂O₃@HAP-Pd catalyst (10 mg), H₂O (10 mL), 2.5 bar H₂, 1 h.

3.5. Time Course of the Product Distributions

There were two pathways for the deoxygenation of aromatic aldehyde (Scheme 2): (A) hydrogenation/hydrogenolysis, and (B) direct hydrogenolysis of the C–O bond. According to the results in Figure 4, benzaldehyde was almost completely consumed in 1 h with 68.8% toluene and 41.2% benzyl alcohol generated. As the reaction time was prolonged to 12 h, the yield of benzyl alcohol gradually decreased from 41.2% to 0.4%, meanwhile the yield of toluene gradually increased from 68.8% to 99.6%. Actually, as the reaction time increased, the yield of toluene of all the reactions at different reaction temperatures increased, while the yield of benzyl alcohol decreased (Table S3 and Figure 4), which means that obtaining toluene as the final product of the successive pathway was just a question of time. Thus, we could conclude that the deoxygenation of carbonyl groups over the γ -Fe₂O₃@HAP-Pd catalysts followed Pathway A in Scheme 2.

Scheme 2. Reaction pathways for the deoxygenation of the aromatic aldehydes.

Figure 4. Time course of the deoxygenation of benzylaldehyde into toluene. Reaction conditions: benzylaldehyde (1 mmol), 2 wt.% $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ catalyst (10 mg), H_2O (10 mL), 2.5 bar H_2 , 70 °C.

3.6. Recycling of the $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ Catalyst

Finally, the stability of the $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ was also studied, and the recycling experiments were conducted (Figure 5). The hydrogenation of benzaldehyde was used as the model reaction, which was performed at room temperature and 10 bar H_2 pressure. After reaction, the $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ catalyst was separated with an external magnet. The resulting solid was washed with water and ethanol, dried in a vacuum oven and reused for the next time. The $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ was successfully recovered and reused six times without significant loss of catalytic activity (95.1% yield initially, 94.1% yield after the sixth run). Additionally, the stability of the catalyst was assessed by carrying out two twin experiments in which one of them the solid catalyst was separated with an external magnet at 20 min reaction time, when conversion was about 60%, and allowing the reaction to continue in the absence of catalyst (Figure 6). It can be seen that the experiment with catalyst reacted completely (blue line), while the other process without catalyst was very minor (red line), indicating that the catalyst was stable. The reaction of small amount of aldehyde could be the result of the physical loss of catalytic material during separating. Furthermore, ICP-OES also showed the Pd content remain 2 wt.% after the catalyst was reused six times, indicating that the catalyst was stable.

Figure 5. The results of the recycling experiments of the $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ catalyst. Reaction conditions: Benzaldehyde (1 mmol), $\gamma\text{-Fe}_2\text{O}_3\text{@HAP-Pd}$ catalyst (10 mg), H_2O (10 mL), 10 bar H_2 , 25 °C and 1 h.

Figure 6. Plots For the hydrogenation of benzaldehyde into benzyl alcohol catalyzed by γ -Fe₂O₃@HAP-Pd. Reaction conditions: Benzaldehyde (1 mmol), γ -Fe₂O₃@HAP-Pd catalyst (10 mg), H₂O (10 mL), 10 bar H₂, 25 °C, and 1 h.

4. Conclusions

In conclusion, the magnetic material supported palladium catalyst (γ -Fe₂O₃@HAP-Pd) exhibited excellent activity and selectivity for the room-temperature hydrogenation of aldehydes under 10 bar H₂ pressure. Aldehydes bearing various reducible functional groups such as ketone, halogen, nitro, or cyano groups could be reduced into corresponding alcohols with good to excellent selectivity. The deoxygenation of carbonyl compounds was successfully attained by further increasing the reaction temperature to 70 °C. The hydrogenation rate of the substituted benzaldehyde showed a reasonable linear Hammett correlation and a Hammett value of 1.59 was obtained, revealing that the hydrogenation of aromatic aldehyde was substituent-sensitive and proceeded via an anionic intermediate. Furthermore, the γ -Fe₂O₃@HAP-Pd catalyst was shown to be recyclable up to six times without any observable decrease in efficiency.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2076-3417/9/9/1792/s1>.

Acknowledgments: The project was supported by Natural Science Foundation of China (grant no. 21606066), Anhui Provincial Natural Science Foundation (grant no. 1708085QB46), the General Project in Education Department of Anhui Province (grant no. KJ2015B1105907), Talent Research Fund Project of Hefei University (grant no. 16-17RC13).

Conflicts of Interest: The authors declare no conflict of interest.

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