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Chemoselective Transfer Hydrogenation of Aldehydes and Ketones with a Heterogeneous Iridium Catalyst in Water

Zhi Wang · Lei Huang · Longfei Geng · Rizhi Chen · Weihong Xing · Yong Wang · Jun Huang

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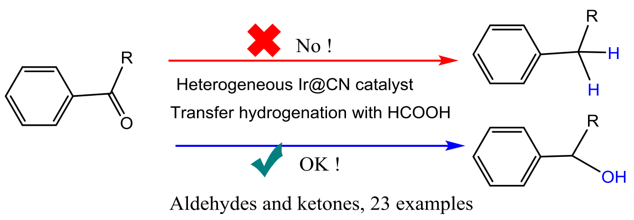
Abstract Ir nanocatalyst Ir@CN was prepared by pyrolysis of the $IrCl_3$ complex with 1,10-phenanthroline in the activated carbon. The iridium nanocatalyst Ir@CN was highly selective for the transfer hydrogenation of aldehydes and ketones including benzaldehyde derivatives, and the hydrogenative alkylation of C=O bonds was suppressed effectively. The iridium nanocatalyst Ir@CN is a heterogeneous catalyst and can be reused several times for the transfer hydrogenation of aldehydes and ketones.

Graphical Abstract Ir nanocatalyst Ir@CN was prepared and the Ir@CN was found to be highly selective for the transfer hydrogenation of ketones and aldehydes including benzaldehyde derivatives in water. The iridium nanocatalyst Ir@CN is a heterogeneous catalyst and can be reused several times.



Keywords Ir nanocatalyst · Transfer hydrogenation · Heterogeneous catalysts · Aldehydes · Ketones

1 Introduction

The reduction of carbonyl compounds to the corresponding alcohols is an important chemical transformation in both academic research and industry application. Historically, boron and aluminum hydride agents and their derivatives were used as reductives for the reduction of carbonyl compounds, and the method is still a reliable route for the reduction of carbonyl compounds today [1–5]. Transition metal catalyzed hydrogenation of carbonyl compounds was investigated widely due to the advantages of mild reaction conditions and high atom efficiency [6, 7]. However, the hydrogenation of acetophenone, benzaldehyde and the derivatives is highly problematic since the hydrogenative alkylation (by reaction) of carbonyl group (benzoyl group) to methylene group is ready to be occurred, and the corresponding alcohols were often obtained in low yields [8, 9]. In order to overcome the problem, homogeneous catalysts have been investigated extensively and some reliable catalyst systems were developed for the hydrogenation of aldehydes and ketones [10–14]. But the efficient heterogeneous catalysts were few and the selectivity was always bad for the hydrogenation of aldehydes and ketones, especially for the hydrogenation of acetophenone, benzaldehyde and the derivatives [15–18]. Transition metal catalytic transfer hydrogenation is an important and practical way for the reduction of carbonyl compounds [19–25], as the hydrogen donors are easy to handle (without flammable and explosive hydrogen gas and pressure vessels) and the mild reaction conditions are used [26, 27].

Electronic supplementary material The online version of this article (doi:10.1007/s10562-014-1473-4) contains supplementary material, which is available to authorized users.

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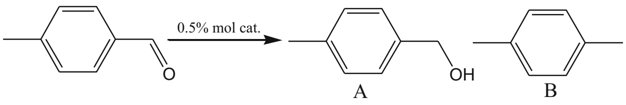
Table 1 The reduction of 4-methyl benzaldehyde with different catalysts



Entry	Catalyst	Conv (%)	Yield A (%)	Yield B (%)
1[a]	Pd/C	100	40	60
2[b]	Pd/C	19	18	1
3[a]	Ir/C	3	3	0
4[b]	Ir/C	47	43	4
5[a]	Ir@CN	4	4	0
6[b]	**Ir@CN**	**99**	**99**	**0**

Reaction conditions: 4-methyl benzaldehyde, 1 mmol, 0.5 mol % catalyst (Ir or Pd), water, 3.5 mL. The conversion and yield were determined by GC analysis ($C_{16}H_{34}$ used as internal standard)

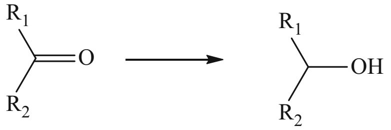
Bold Values indicate optimized (best) catalyst systems

[a] H_2 balloon as reductant, 100 °C, 10 h

[b] HCOOH, 3.5 mmol and NaOH, 2.0 mmol used; 100 °C, 18 h; Pd/C and Ir/C prepared by impregnation methods

Since the first report of the transfer hydrogenation of the carbonyl compounds in 1925 (Meerwein–Ponndorf–Verley reaction) [28], various catalyst systems have been developed for the reduction of carbonyl compounds. Some ruthenium [29], iridium [30], rhodium [31] and palladium complexes [32] were reported for the transfer hydrogenation of carbonyl compounds, but these systems were homogeneous and difficult to be recycled. Besides, some heterogeneous nanocatalysts (nickel [33, 34], platinum nanoparticles [35]) were developed for the transfer hydrogenation of the carbonyl compounds, but organic solvents were needed for the transformation, and the selectivity was not good enough [36–38]. Thus, the development of highly efficient and heterogeneous catalysts for the transfer hydrogenation of aldehydes and ketones (especially acetophenone, benzaldehyde and the derivatives) are highly desirable as benzyl alcohols are important intermediates for the synthesis of fragrances.

Recently, Fe and Co complexes with N contained ligands were pyrolysed as heterogeneous catalysts for the hydrogenation of nitro aromatics with high activity and high selectivity [39, 40]. The 1,10-phenanthroline can be linked with the activated carbon to form stable N-doped carbon materials, which were used as good catalyst supports. Here, iridium nanoparticles were supported on N-doped carbon materials as heterogeneous catalyst Ir@CN, which was highly efficient and highly selective for the transfer hydrogenation of carbonyl compounds to the corresponding alcohols. Various carbonyl compounds (aldehydes and ketones including acetophenone, benzaldehyde and the derivatives) were applicable for the transfer hydrogenation, and the corresponding alcohols were obtained in good to excellent yields (Scheme 1).



Scheme 1 Ir catalyzed the transfer hydrogenation of the carbonyl compounds

2 Experimental Section

2.1 The Preparation of Catalysts

$IrCl_3 \cdot 3H_2O$ (0.034 g) was dissolved in ethanol (30 mL) with stirring, then 1,10-phenanthroline monohydrate (0.062 g) was added into the solution at room temperature. After stirring for another 1 h, activated carbon (0.93 g) was added into the solution and the mixture was stirring for 10 h at 60 °C. After the mixture cooled to room temperature, the ethanol was removed by the rotary evaporation under vacuum. The black solid was dried in a drying oven at 60 °C under vacuum for 12 h, and then the solid was transferred into a quartz boat and placed in the tube furnace under N_2. The tube furnace was heated to 800 °C at the rate of 10 °C per minute, and kept at 800 °C for 2 h under N_2. After the tube furnace cooled to room temperature, the catalyst Ir@CN (containing Ir 2.01 wt%, detected by ICP) was obtained as black powders.

2.2 Typical Procedures for Transfer Hydrogenation of Carbonyl Compounds

The transfer hydrogenation reactions were carried out under argon atmosphere using standard Schlenk technique unless otherwise stated. Benzyl aldehyde (1 mmol), formic acid (3.5 eqiv.), and water (3.5 mL) were injected into a sealed tube with the catalyst (0.048 g Ir@CN) and sodium hydroxide (2 eqiv.) under Ar. Then the mixture was stirred under 100 °C (with an oil bath) for the given time. After cooled, the reaction mixture was diluted with 3 × 5 mL of ether, and then the catalyst Ir@CN was filtered. The conversions and yields were determined by GC using *n*-hexadecane as an internal standard.

3 Results and Discussion

3.1 Catalyst Characterization

The Ir@CN catalyst was characterized by N_2 adsorption, TEM, TGA and XPS. The N_2 adsorption–desorption isotherms of AC and Ir@CN were shown in Fig. 1. The isotherm of the Ir@CN catalyst was typical IV curve (Type H4) with nitrogen uptake under the relative pressure of

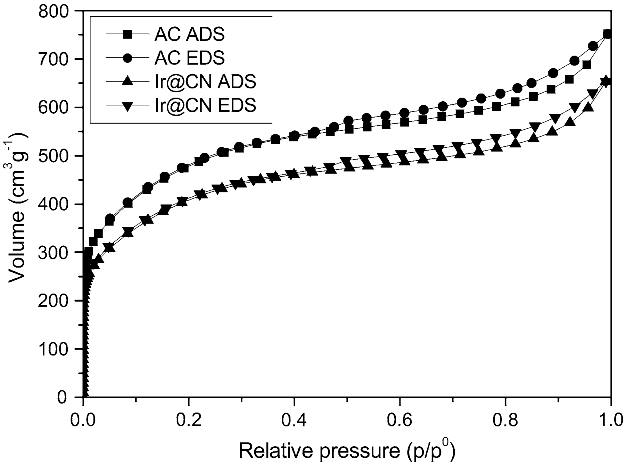


Fig. 1 N2 adsorption–desorption isotherms of the AC and Ir@CN

0.5–1.0, which was always associated with narrow slit-like pores. The BET surface areas of the AC and Ir@CN catalyst were 1,706.7 and 1,456.2 m^2/g respectively. The pore volume of the AC and Ir@CN catalyst were 1.15 and 0.85 cm^3/g respectively, which meaned that some CN material and Ir were filled into the pores of the AC. The high resolution TEM (HRTEM) images in Fig. 2 gave more details of Ir@CN catalyst and the recovered Ir@CN after 3 reaction cycles. The Ir nanoparticles were highly dispersed on the N hybrid carbon material, and the average particle size of Ir was about 2–4 nm (Fig. 2a). Moreover, the Ir nanoparticles in Ir@CN were quite stable, and the particle size of Ir did not change evidently after three times of the reaction (Fig. 2b). Since the catalyst Ir@CN was prepared through high temperature (800 °C), the Ir nanoparticles were kept at about 2–4 nm, which indicated that the Ir@CN was highly thermal stable, and the 1,10-phenanthroline structure was highly beneficial for the stability of the nanocatalyst Ir@CN. The TG curve of the precursor of Ir@CN was presented in Fig. 3. Only very small slight weight loss was observed at temperatures less than 550 °C due to the desorption of moisture and constitutional water.

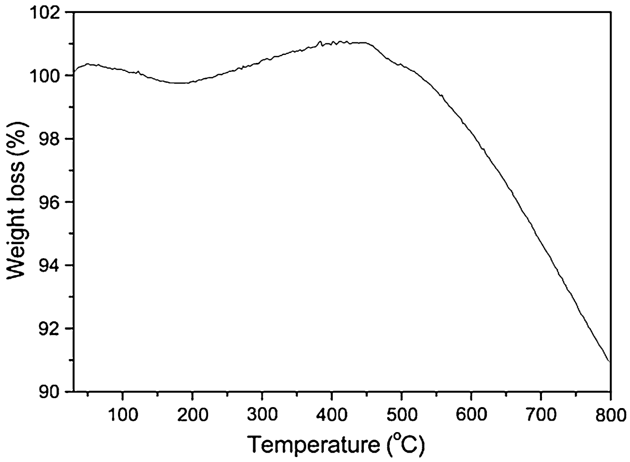


Fig. 3 The TG analysis of the precursor of Ir@CN

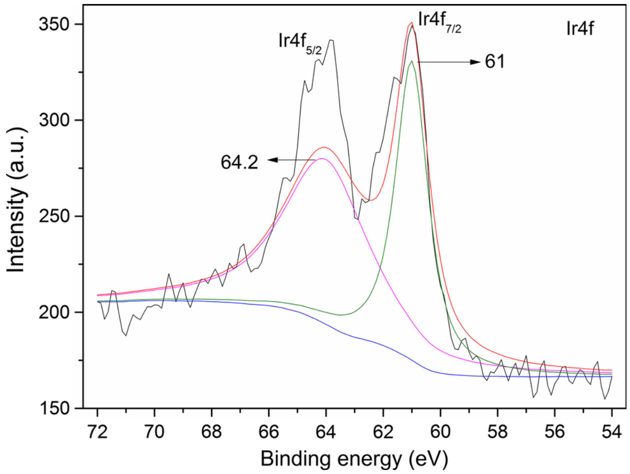


Fig. 4 Ir4f XPS spectra of 2 % Ir@CN catalyst

About 8 % weight loss was observed between 550–800 °C, which meaned the stable N hybrid C material (CN) was formed [39]. The XPS Ir4f and N1s spectra of the Ir@CN catalyst are shown in Figs. 4 and 5 respectively. According to the binding energies of Ir4f$_{7/2}$ at 61 eV and Ir4f$_{5/2}$ at

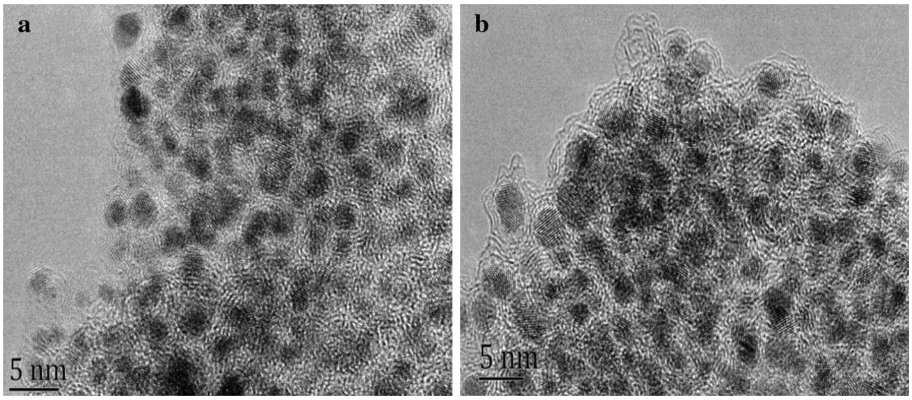


Fig. 2 TEM micrographs of **a** fresh Ir@CN; **b** recovered Ir@CN after 3 reaction cycles

64.2 eV, iridium species in the catalyst Ir@CN was reduced to metallic state Ir (0) after being treated at 800 °C [41, 42]. Moreover, the N1s binding energies of pyridine-type nitrogens were at 399.0 and 400.8 eV, which indicated that the phenanthroline structure was kept and coordinated with the Ir nanoparticles [39].

3.2 The Reduction of 4-Methyl Benzaldehyde with Different Catalysts

The reduction of 4-methyl benzaldehyde was chosen as a template reaction to test the Ir@CN catalyst. For comparison, Pd/C, Ir/C and Ir@CN were used for the transfer hydrogenation of 4-methyl benzaldehyde and hydrogenation of 4-methyl benzaldehyde with H_2 (Table 1). When H_2 was used as reductant (under 1 atm), Pd/C was highly active for the hydrogenation of 4-methyl benzaldehyde. 4-Methyl benzaldehyde was converted completely, but 4-methylbenzyl alcohol was obtained only in 40 % yield, and *p*-xylene (hydrogenative alkylation) was obtained in 60 % yield. (Table 1, entry 1). By contrast, Ir/C and Ir@CN were not active for the hydrogenation 4-methyl benzaldehyde with H_2, and the conversion of 4-methyl benzaldehyde was low with both Ir/C and Ir@CN (Table 1, entry 3, 5). Then, we tested the transfer hydrogenation of 4-methyl benzaldehyde with HCOOH/NaOH as a reducing agent using Pd/C, Ir/C and Ir@CN catalysts. Delightedly, Ir@CN was not only highly active but also highly selective for the transfer hydrogenation of 4-methyl benzaldehyde, and 4-methylbenzyl alcohol was obtained in 99 % yield (Table 1, entry 6). But the Pd/C and Ir/C were not active enough for the transfer hydrogenation of 4-methyl benzaldehyde, and 4-methylbenzyl alcohol was obtained in low yield (Table 1. entry 2, 4). The Ir nanoparticles in Ir@CN catalyst were stablized by the linked 1,10-phenanthroline structure, and showed high activity and selectivity for the transfer hydrogenation of 4-methyl benzaldehyde. But the Ir nanoparticles in Ir/C can not be retained without phenanthroline linked on the surface of the AC when the catalyst heated to 800 °C, thus the catalyst Ir/C was not active for the transformation. The optimization of the reaction conditions was provided in the supplementary material.

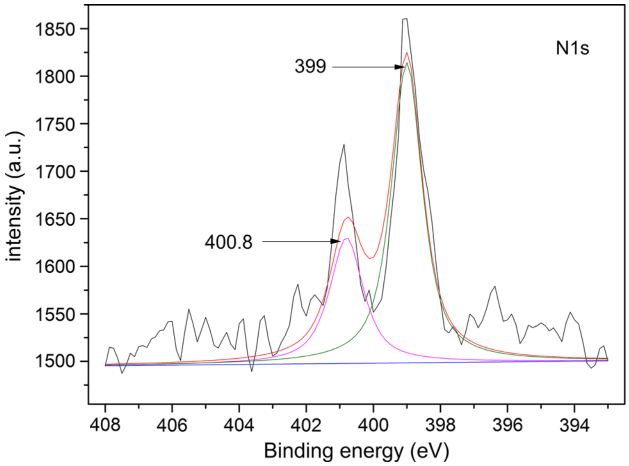


Fig. 5 N1s XPS spectra of 2 % Ir@CN catalyst

3.3 The Transfer Hydrogenation of Carbonyl Compounds with Ir@CN

Using the optimized reaction conditions, the Ir@CN catalyst was used for the transfer hydrogenation of carbonyl compounds to the corresponding alcohols. Various aldehydes and ketones were used for the transfer hydrogenation under the optimized conditions, the results are summarized in Table 2. A range of aromatic aldehydes can be transfer hydrogenated to the corresponding alcohols in good to excellent yields (Table 2, entry 1–11). The transfer hydrogenation of benzaldehyde gave benzyl alcohol in quantitative yield (Table 2, entry 1). When the benzaldehydes substituted with halides (F and Cl) were used, no dehalogenation was detected, and the corresponding benzyl alcohols were obtained in high yields (Table 2, entry 2, 3, 5 and 6). The transfer hydrogenation of bromobenzaldehyde afforded the corresponding benzyl alcohols in 90–95 yields, and small amount of benzyl alcohol generated by the side reaction dehalogenation (Table 2, entry 4 and 7). The transfer hydrogenation of benzaldehydes with methoxyl and methyl groups gave the corresponding benzyl alcohols in excellent yields (Table 2, entry 8–11). Moreover, 1-naphthaldehyde can be converted smoothly to 1-naphthalenemethanol in high yield (Table 2, entry 12). Furthermore the Ir@CN catalyst was highly active and selective for the transfer hydrogenation of heterocyclic aldehydes, and furfural alcohol and 2-pyridylmethanol were obtained in high yields respectively (Table 2, entry 13–14). Besides, aliphatic aldehydes were also applicable for the transfer hydrogenation, and cyclohexanecarboxaldehyde, 1-pentanal, 1-hexanal, 1-octanal and phenyl propyl aldehyde were converted to the corresponding alcohols in good to excellent yields (Table 2, entry 15–19). And then, unsaturated aldehydes 3-cyclohexene-1-carboxaldehyde and cinnamaldehyde were tested for the transfer hydrogenation with Ir@CN catalyst, and 3-cyclohexene-1-methanol and cinnamic alcohol were obtained in 90 and 65 % yields respectively (Table 2, entry 20, 21). In addition to aldehydes, ketones were also tested for the transfer hydrogenation with Ir@CN catalysts. Cyclohexanone was converted to cyclohexanol smoothly in high yield, but the transfer hydrogenation of acetophenone gave corresponding alcohol in moderate yield under harsher reaction conditions.

Table 2 The transfer hydrogenation aldehydes and ketones to alcohols

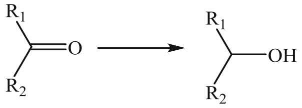
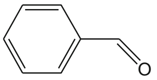
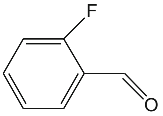
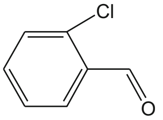
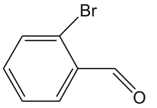
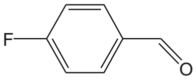
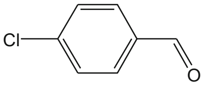
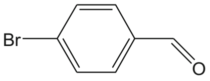
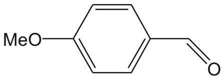
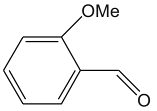
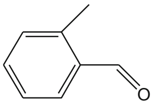
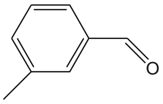
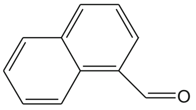
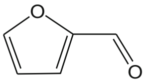
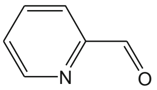
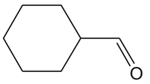
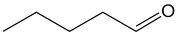
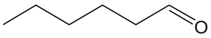
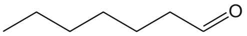
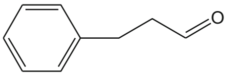
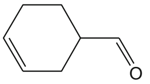
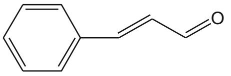
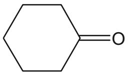
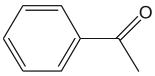


Table 2 continued

Entry	Substrate	Yield (%)
1		>99
2		99
3		>99
4		90
5		>99
6		>99
7		95
8		80[a]
9		>99
10		>99
11		>99
12		88 (98)
13		99
14		95
15		>99
16		>99
17		99
18		75 (95)
19		>99
20		90[b]
21		65[c]
22[d]		93
23[e]		65 (91)

Reaction conditions: substrate, 1.0 mmol; water, 3.5 mL; temperature, 100 °C; reaction time, 18 h; HCOOH, 3.5 mmol; NaOH, 2.0 mmol; Ir@CN catalyst, 48 mg, Ir (0.5 %); yields in parentheses with 24 h. Conversion and yield were determined by GC analysis ($C_{16}H_{34}$ used as internal standard)

[a] By-product was 4-methylanisole

[b] Yield of 3-cyclohexene-1-methanol, and the by-product was cyclohexane methanol

[c] Yield of cinnamic alcohol, major by-product was phenyl propyl alcohol

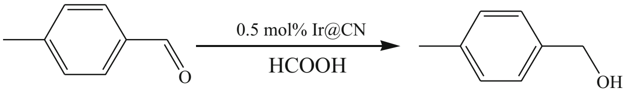
[d] Ir@CN catalyst, 10 mg, Ir (0.1 %)

[e] Ir@CN catalyst, 96 mg, Ir (1 %)

3.4 Catalyst Reusability

Finally, the recyclability of the Ir@CN catalyst was tested, and the results are listed in Table 3. The Ir@CN catalyst can be used at least four times without obvious loss of activity. The activity decreased slightly was due to the loss of the Ir@CN catalyst during the recovery of the catalyst (filtration and drying of the Ir@CN). Furthermore, no Ir was detected in the filtrate after filtration of the Ir@CN catalyst (by ICP), which meaned no Ir leached into the reaction solution, and the Ir@CN is a real heterogeneous catalyst for the transfer hydrogenation of aldehydes and ketones. With 1,10-phenanthroline structure tethered on the surface of the AC, Ir nanoparticles were homogeneously dispersed on the nitrogen-carbon surface in the Ir@CN catalyst, which afforded excellent activity and stability of the Ir@CN catalyst.

Table 3 Recycling of the catalyst



Recycled No.	Yield (%)
1	97
2	96
3	92
4	90

Reaction conditions: 4-methyl benzaldehyde, 1 mmol; water, 3.5 mL; temperature, 100 °C; time, 18 h; HCOOH, 3.5 mmol; NaOH, 2.0 mmol; Ir@CN catalyst, 48 mg, Ir (0.5 %); yield determined by GC analysis ($C_{16}H_{34}$ used as internal standard)

4 Conclusions

In summary, Ir nanocatalyst Ir@CN was developed and the Ir@CN catalyst was highly selective for the transfer hydrogenation of carbonyl compounds into the corresponding alcohols in water. The Ir@CN catalyst was applicable widely for the transfer hydrogenation of aldehydes and ketones including benzaldehyde derivatives, and the alcohols were obtained in good to excellent yields as the hydrogenative alkylation of C=O bonds was suppressed effectively. Moreover, the iridium nanocatalyst Ir@CN is highly stable, heterogeneous and reusable for the transfer hydrogenation of aldehydes and ketones.

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