Ru Nanoparticles Entrapped in Ordered Mesoporous Carbons: An Efficient and Reusable Catalyst for Liquid-Phase Hydrogenation

Yue Ding · Xiaohong Li · Huiyan Pan · Peng Wu

Abstract Ru nanoparticles entrapped in ordered mesoporous carbons (CMK-3) served as an efficient and reusable catalyst for liquid-phase hydrogenation of benzaldehyde and its derivatives under our tested conditions (medium hydrogen pressure, room temperature, water as solvent). The Ru nanoparticles can be well stabilized by CMK-3 ordered mesoporous carbons so that the Ru leaching was below the detection limit of ICP-AES. Therefore, the Ru/CMK-3 catalyst can be used for at least five times without distinct loss in activity or selectivity for the hydrogenation of benzaldehyde. It is worthy of note that the Ru/CMK-3 catalyst was more efficient than the commercial Ru/C and homemade Ru/AC catalyst for the liquid-phase hydrogenation of benzaldehyde. The Ru/CMK-3 catalyst can also catalyze the liquid-phase hydrogenation of nitrobenzene and its derivatives with high conversions and excellent selectivities under optimal conditions.

1 Introduction

Catalytic processes play an important role in the chemical manufacturing processes around the world, and the roles of catalysis involve accelerating reaction and controlling the selectivity of the chemical reactions. Carbon materials have been used for a long time in heterogeneous catalysis, because they can act directly as catalysts or as supports due to that, they have superior physical and chemical properties, such as electric conductivity, thermal conductivity, chemical stability, and adsorption characteristics [1, 2].

Many carbon materials, such as fullerene [3], carbon nanofibers [4, 5], carbon nanotubes [6, 7], and mesoporous carbon [8] have been used as supports for heterogeneous hydrogenation reactions. They were proved remarkable supports for the studied reactions. For instance, Pt based on SiO_2–C_{60}, which was modified by Si–H, was proved high selective for cinnamyl alcohol (up to 89 % selectivity) [3]. The gas phase catalytic hydrodechlorination (HDC) of chlorobenzene was studied over Pd catalyst supported on activated carbon (Pd/AC), on graphite (Pd/graphite), and on graphitic carbon nanofiber (Pd/GNF), respectively. The HDC of chlorobenzene yielded benzene as the predominant product (with secondary hydrogenation to cyclohexane), where initial HDC activity increased in the order Pd/graphite < Pd/AC ≈ Pd/GNF [4].

Recently, ordered mesoporous carbon materials (OMCs) have attracted much attention due to periodic mesopores, uniform pore size, high surface areas, adequate pore volume and high thermal, chemical and mechanical stabilities [9, 10]. Among the OMCs, CMK-3 OMCs with p6 mm symmetry and CMK-8 OMCs with Ia3d symmetry are widely known and applied [11–15]. In our previous studies, we investigated the application of CMK-3 and CMK-8 OMCs supported Pt catalysts for the chiral hydrogenation of α-ketoesters after chirally modified with cinchona alkaloids or for the liquid-phase hydrogenation of benzaldehyde and its derivatives [12–14]. To the best of our knowledge, the results with Pt/OMCs catalysts are the

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better ones among those obtained with Pt catalysts supported on carbon materials for the chiral hydrogenation of α-ketoesters. We also found that there was tiny difference in the liquid-phase hydrogenation of benzaldehyde and its derivatives between the two kinds of OMCs with different symmetries [14].

In the catalytic processes, Ru-based catalysts have been widely studied [15–20]. Ordered mesoporous ruthenium containing carbon (Ru-OMC) catalyst with semi-embedded uniform Ru particle distribution was effective and reusable for hydrogenation of benzene under optimal conditions [15]. Ru nanoparticles embedded into FDU-15 mesopolymer, which was synthesized from organic–organic self-assembly of resols (phenol/formaldehyde) with triblock copolymers, was proved effective, robust and remarkably reusable for hydrogenation of arenes, olefins and carbonyl compounds in water under mild conditions [16]. Ru catalyst supported on Y zeolite demonstrated a reasonable activity for hydrogenation of cinnamaldehyde and afforded about 30 % selectivity to cinnamyl alcohol, while Ru/MCM-41 was not selective for the hydrogenation of the C=O bond with about only 5 % selectivity [17]. Ru catalysts prepared using a thermal reduction method and supported on different carbon substrates, including mesoporous silica SBA-15, surface-carbon coated SBA-15, templated mesoporous carbon, activated carbon, and carbon black, displayed high activity and stability in hydrogenation of benzene and toluene [18].

Encouraged by these achievements, we functionalized the CMK-3 OMCs by loading Ru nanoparticles, to study the catalytic performance of the resultant Ru/CMK-3 catalyst in selective hydrogenation of either carbonyl or nitryl compounds. The 5.0 wt% Ru/CMK-3 catalyst, prepared by a facile impregnation method and reduced under a hydrogen flow, exhibited superior activity for the liquid-phase hydrogenation of a series of benzaldehyde derivatives and nitrobenzene derivatives with different substituents at the phenyl ring under optimal conditions.

2 Experimental

2.1 Materials

Benzaldehyde was of analytical grade and used as received. Ruthenium chloride hydrate ($RuCl_3 \cdot 3H_2O$) (Ru ≥ 37 %) was purchased from Shanghai Experiment Reagent Co. Benzaldehyde derivatives were purchased from Alfa Aesar and used as received. Nitrobenzene and its derivatives were purchased from Aladdin and used as received. A commercial 5 wt% Ru/C catalyst was also purchased from Alfa Aesar as a reference catalyst.

2.2 Catalyst Preparation and Characterization

The procedures for preparing CMK-3 supported Ru catalysts were graphically illustrated in Scheme 1. The 5 wt% Ru/CMK-3 catalyst was prepared mainly according to Ref. [16]. The CMK-3 was impregnated with an aqueous solution containing $RuCl_3$ and stirred for 12 h. The excess water was removed using a rotary evaporator and then the catalyst precursor was dried in an oven at 353 K overnight. Subsequently, the catalyst precursor was reduced under a hydrogen flow at 623 K for 2 h and then stored naturally in a self-sealed plastic bag. The 5 wt% Ru catalyst supported on activated carbon (5 wt% Ru/AC) was also prepared using the same method for comparison.

The X-ray diffraction (XRD) patterns of samples were collected on a Bruker D8 Advance instrument using Cu-Kα radiation. The nitrogen adsorption–desorption isotherms were measured at 77 K on a Quantachrome Autosorb-3B system, after the samples were evacuated at 473 K for 10 h. The BET specific surface area was calculated using adsorption data in the relative pressure range from 0.05 to 0.35. The pore size distribution curves were calculated from the analysis of the adsorption branch of the isotherm using the BJH algorithm. The SEM images were taken on a Hitachi S-4800 electromicroscope. The TEM images were taken on an FEI Tecnai G2-TF30 electromicroscope with an acceleration voltage of 300 kV. Before taking TEM images, the samples were ground thoroughly and dispersed in ethanol. The surface electronic state of Ru was examined using X-ray photoelectron spectroscopy (XPS) measurement with a Thermo Fisher Scientific ESCALAB 250 spectrometer with Al-Kα radiation (1,486.6 eV) as incident beam. The Ru/CMK-3 catalyst after reduced but stored naturally was directly adopted for XPS analysis. The leached amount of Ru atoms into solution during the recycling experiment was detected with a Thermo Elemental IRIS Intrepid II XSP inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The thermogravimetric (TG) analysis of the Ru/CMK-3 catalyst was conducted from r.t. to 1,023 K under air atmosphere with Mettler Toledo TGA/SDTA851^e apparatus.

2.3 Catalytic Tests

For a typical reaction, 0.05 g 5 wt% Ru catalyst supported on different carbon materials, such as Ru/CMK-3, commercial Ru/C and homemade Ru/AC, was pretreated under a hydrogen flow at 623 K for 1 h before use. The catalyst was then mixed with 20 mL solvent containing substrate (3 mmol benzaldehydes or 8.1 mmol nitro benzenes) and transferred to a 100 mL autoclave. The hydrogenation reaction began at a designated temperature after 4.0 MPa hydrogen was introduced into the autoclave. The reaction was stopped after an allotted period and the products were analyzed by GC-FID

Scheme 1 Schematic illustration for preparation of the Ru/CMK-3 catalyst
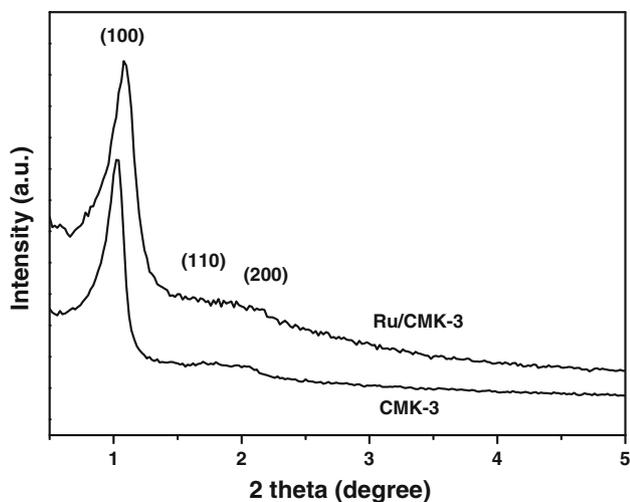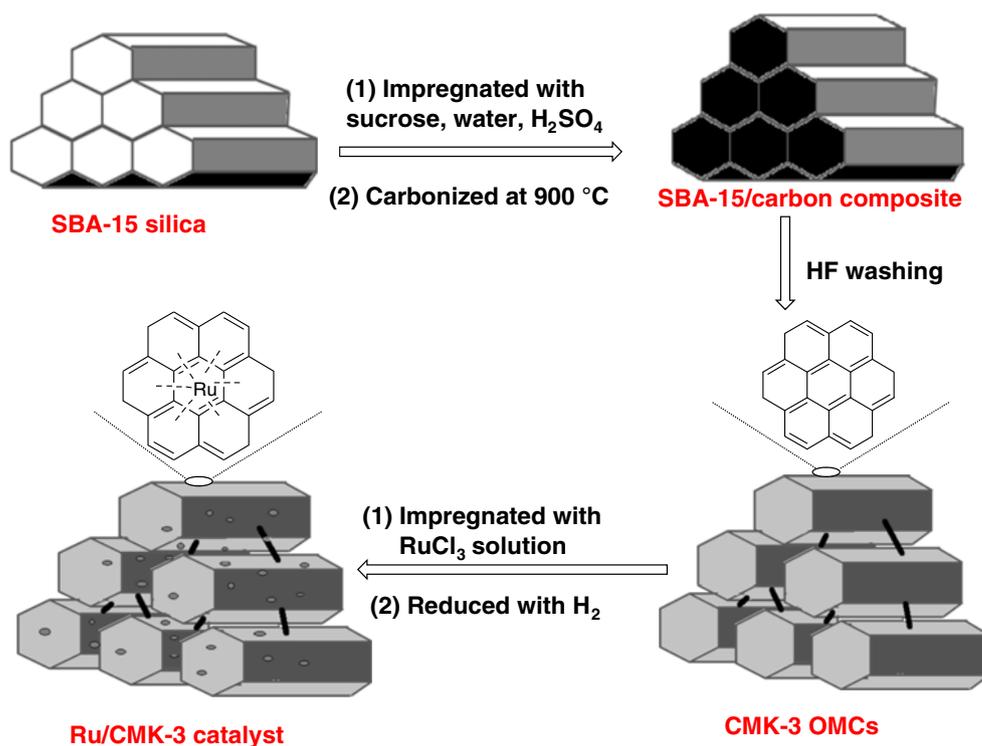
Fig. 1 Low-angle XRD patterns of CMK-3 and the Ru/CMK-3 catalyst
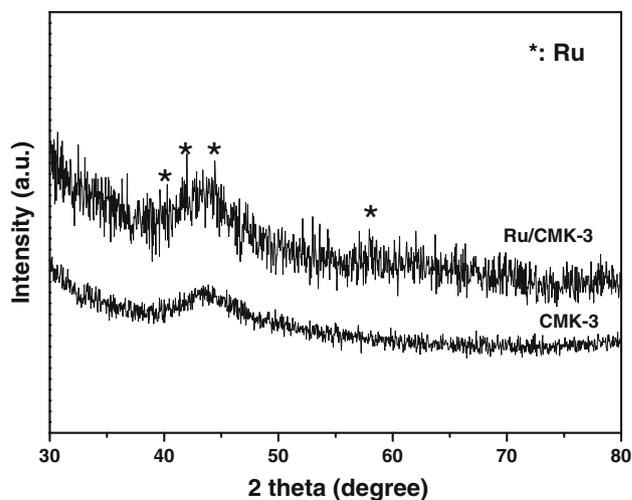
Fig. 2 Wide-angle XRD patterns of CMK-3 and the Ru/CMK-3 catalyst

(GC-2014, Shimadzu Co.) equipped with a capillary column (DM-WAX, 30 m × 0.25 mm × 0.25 μm).

3 Results and Discussion

3.1 Catalyst Preparation and Characterization

Figure 1 shows the low-angle XRD patterns of CMK-3 and the Ru/CMK-3 catalyst. Similar to CMK-3, the Ru/CMK-3

catalyst exhibited an intense diffraction peak together with two weak peaks indexed as (100), (110) and (200) planes of hexagonal structure (p6mm). Figure 2 shows the wide-angle XRD patterns of CMK-3 and the resultant Ru/CMK-3 catalyst. The characteristic peaks assignable to Ru particles were very weak [21], demonstrating that the Ru particles were well dispersed.

The well-ordered mesoporous structure of CMK-3 support could be further confirmed by N_2 sorption isotherm of the Ru/CMK-3 catalyst (Fig. 3). The Ru/CMK-3 catalyst

displayed a typical hysteresis loop in the relative pressure range from 0.4 to 0.9 and showed a narrow BJH pore size distribution centered at 3.7 nm. As listed in Table 1, the specific surface area of CMK-3 was 1,325 m² g⁻¹, while the specific surface area for the Ru/CMK-3 catalyst was 999 m² g⁻¹. The Ru/CMK-3 catalyst also had adequate pore volume higher than 1.0 cm³ g⁻¹. These physical features of Ru/CMK-3 catalyst would certainly be helpful to mass transfer.

The morphology of the Ru/CMK-3 catalyst was characterized using SEM and TEM. As revealed in SEM images (Fig. 4), the ordered mesoporous structure of CMK-3
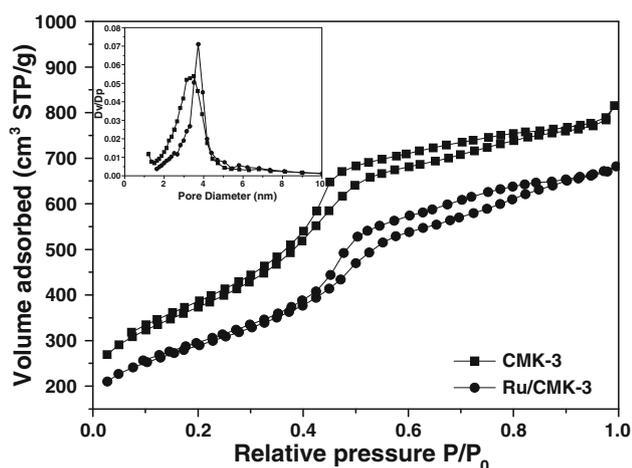
Fig. 3 N₂ adsorption–desorption isotherms and pore size distributions (*inset*) of CMK-3 and the Ru/CMK-3 catalyst

Table 1 Relevant parameters of CMK-3 and Ru/CMK-3 catalyst

Sample	S_{BET} (m² g⁻¹)	Vp (cm³ g⁻¹)	D (nm)
CMK-3[a]	1,325	1.26	3.5
Ru/CMK-3	999	1.06	3.7

[a] The data were quoted from Ref. [13]

(Fig. 4a) was reserved in the Ru/CMK-3 catalyst (Fig. 4b), and the Ru particles cannot be observed on the outer surface of CMK-3 mesopores.

Figure 5 displays the TEM images of the Ru/CMK-3 catalyst. The Ru/CMK-3 catalyst retained the typical p6mm meso-structure and the Ru nanoparticles were uniformly dispersed. Although we made every endeavor to obtain a TEM image with the structure of OMCs and the Ru nanoparticles at the same time, the contrast between black OMCs support and black Ru nanoparticles was too small, so that the image quality was not high. The Ru particle size for Ru/CMK-3 catalyst varied from 3.0 to 6.0 nm and centered at 3.8–4.2 nm, thus the mean particle size was around 4.3 nm with 32 % dispersion. The average Ru particle size is a little larger than the mean pore size of CMK-3 OMCs, suggesting that there were some Ru nanoparticles located outside the mesopores.

The Ru content of the resultant Ru/CMK-3 catalyst was also measured using TG analysis. Under air atmosphere, the CMK-3 support can be completely burnt up at elevated temperature and finally, the residue of RuO₂ was left over. According to the TG results, the Ru content immobilized on CMK-3 support was about 5.03 wt%, consistent with the nominal Ru loading.

3.2 Hydrogenation of Benzaldehyde and Its Derivatives

3.2.1 Hydrogenation of Benzaldehyde

In our previous researches, the Pt/CMK-3 catalyst has already been proved effective for liquid-phase hydrogenation of benzaldehyde under the tested conditions [14]. Considering that Ru is also an active component for hydrogenation of C=C and C=O double bonds, we attempted to load Ru nanoparticles onto CMK-3 to investigate their performance in the liquid-phase hydrogenation of benzaldehyde and its derivatives. As a mixture of water and ethanol with a volume ratio of 9:1 has been proved a
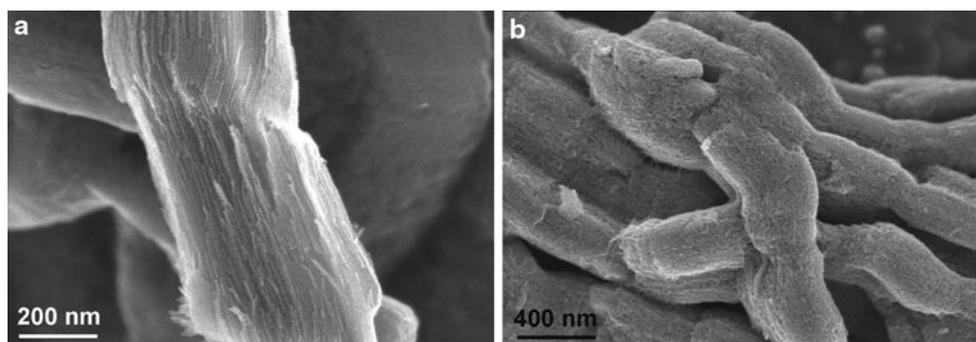
Fig. 4 SEM images of CMK-3 (**a**) and the Ru/CMK-3 catalyst (**b**)

Fig. 5 TEM images of the Ru/
CMK-3 catalyst
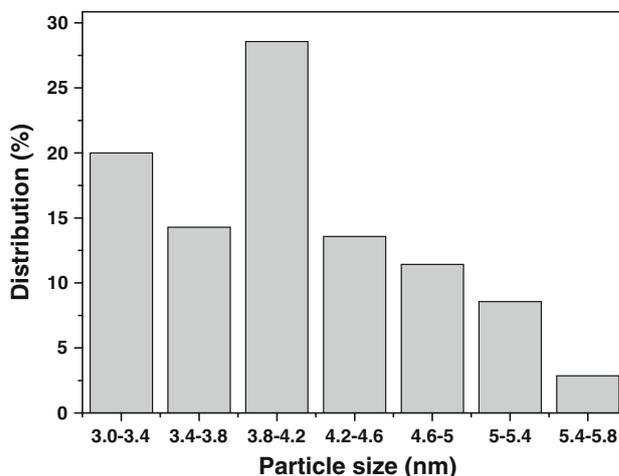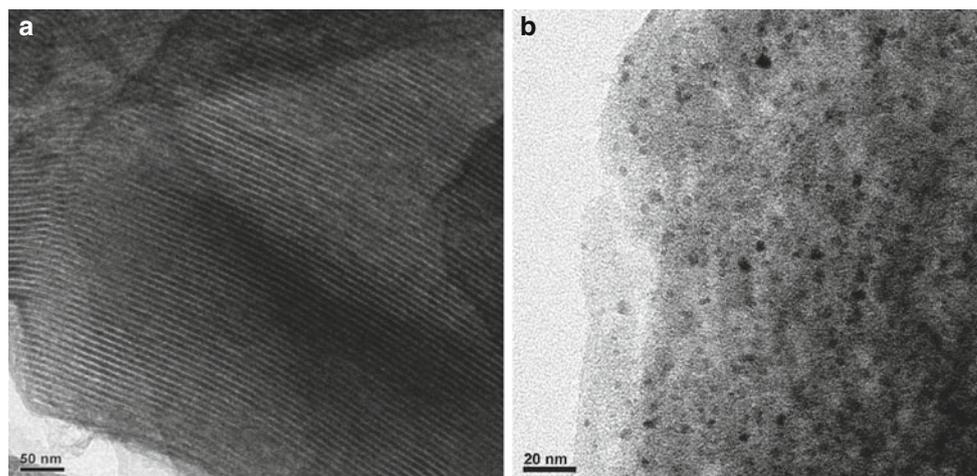
better solvent for the hydrogenation of benzaldehyde with the Pt/CMK-3 catalyst [14], we still applied the water/ethanol mixture as solvent in this case.

We firstly studied the kinetic profile of benzaldehyde hydrogenation with the Ru/CMK-3 catalyst in the water/ethanol mixture at room temperature. As displayed in Fig. 6, the conversion increased steadily with reaction time and completed after about 1 h. Based on the conversion obtained within 15 min, the TOF (defined as the moles of consumed reactant per mole of Ru active sites per hour) of 653.4 h^{-1} with the Ru/CMK-3 catalyst was achieved. This value was much higher than that with the Ru/FDU-15 mesopolymer catalyst, which afforded about 300.8 h^{-1} TOF calculated from the reported data for the same reaction under the similar conditions [16]. To exclude homogeneous catalysis, the hydrogenation of benzaldehyde with the Ru/CMK-3 catalyst was stopped after 30 min and the catalyst was filtered out. Then, the hydrogenation was prolonged without the solid catalyst for additional 30 min. As a result, no further conversion of benzaldehyde took place, indicating that the hydrogenation with the Ru/CMK-3 catalyst is really a heterogeneous process.
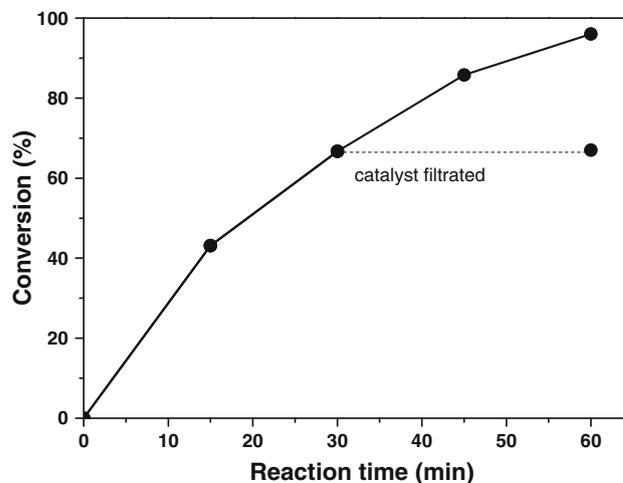
Fig. 6 Kinetic profiles of benzaldehyde hydrogenation with the Ru/CMK-3 catalyst. Reaction conditions: 0.05 g 5.0 wt% Ru/CMK-3 catalyst; 3 mmol benzaldehyde; 18 mL water and 2 mL ethanol; room temperature; 4 MPa H_2 pressure; 1,200 rpm

For comparison, homemade Ru/AC and commercial Ru/C catalyst were also applied for the liquid-phase hydrogenation of benzaldehyde under the same conditions. The

commercial Ru/C catalyst gave 46.6 % conversion within 30 min, while the homemade Ru/AC catalyst only showed 19.0 % conversion under the same conditions. While for the Ru/CMK-3 catalyst, two-thirds of benzaldehyde was converted to the corresponding benzyl alcohol within 30 min, much more active than the other two Ru catalysts. It suggests that the ordered mesoporous structure of CMK-3 is beneficial to mass transportation. As for the selectivity to benzyl alcohol obtained with Ru catalysts supported on different carbon materials, nearly 100 % selectivity was furnished with three Ru catalysts in that no by-product was detected by GC. Nevertheless, when compared with the Pt/CMK-3 catalyst, the Ru/CMK-3 catalyst is relatively inferior, only about one-sixth of substrate being converted within the same time [14].

3.2.2 Hydrogenation of Benzaldehyde Derivatives

Besides the simplest aromatic aldehyde, we also expanded the hydrogenation with the Ru/CMK-3 catalyst to a series of benzaldehyde derivatives with substituents at the phenyl ring. As listed in Table 2, for the hydrogenation of benzaldehyde derivatives with an electron-donating group such as methoxy, the *meta*-substituted isomer was less active, only obtaining 10.0 % conversion with a TOF of 37.9 h^{-1} after 1 h (Table 2, entry 3). Compared with the *para*-

Table 2 Hydrogenation of benzaldehyde derivatives with different substituents at the phenyl ring with the Ru/CMK-3 catalyst

Entry	R group	Time (h)	Conversion (%)[a]	Selectivity (%)[a]	TOF (h^{-1})
1	2-MeO	0.25	62.5	>99.0	947.5
2	2-MeO	0.5	96.9	95.9	–
3	3-MeO	1	10.0	>99.0	37.9
4	4-MeO	1	86.2	94.7	326.7
5	4-*tert*-butyl	1	78.9	97.8	299.0
6	2-Cl	0.5	67.3	95.2	510.2
7	2-Cl	1	96.7	>99.0	–
8	3-Cl	1	93.1	94.1	352.9
9	4-Cl	1	87.3	94.7	330.9
10	2-F	0.25	48.7	97.5	738.3
11	3-F	0.25	54.3	90.9	823.2
12	4-F	0.25	32.6	>99.0	494.2

Reaction conditions: 0.05 g 5.0 wt% Ru catalyst; 3 mmol substrates; 18 mL water and 2 mL ethanol; room temperature; 4 MPa H$_2$ pressure; 1,200 rpm

[a] Determined by GC

substituted methoxy-benzaldehyde, the *ortho*-substituted isomer was more active. Over 62 % of 2-MeO-benzaldehyde was converted to the corresponding alcohol after 15 min and the conversion was nearly complete after 30 min, giving a highest TOF of 947.5 h^{-1} (Table 2, entries 1 and 2). For 4-MeO-benzaldehyde hydrogenation, 86.2 % conversion was achieved within 1 h (Table 2, entry 4). A slightly lower conversion of 78.9 % within 1 h for hydrogenation of 4-*tert*-butyl-benzaldehyde was acquired with the Ru/CMK-3 catalyst, demonstrating there is somewhat steric effect during the liquid-phase hydrogenation with the Ru/CMK-3 catalyst.

With regards of the hydrogenation of benzaldehyde derivatives substituted with comparatively electron-withdrawing group such as Cl- or F-, the *para*-substituted isomers got the lowest conversions. As a result, 87.3 % conversion within 1 h for 4-Cl-substituted benzaldehyde was achieved (Table 2, entry 9). While 2-Cl- and 3-Cl-substituted isomers were more active than their *para*-substituted isomer (Table 2, entries 6–8). For F-substituted benzaldehydes, the 4-F-benzaldehyde gave the lowest conversion of 32.6 % within 15 min (Table 2, entry 12), whereas for 2-F- and 3-F-isomers, 16–22 % higher conversions were achieved under the same conditions (Table 2, entries 10 and 11).

It seems that there is the distinct electronic effect on the hydrogenation of benzaldehyde derivatives with the Ru/CMK-3 catalyst. For the electron-donating group substituted benzaldehydes, the *meta*-substituted isomer is the most inactive; while for benzaldehyde derivatives substituted with relatively electron-withdrawing group, the *meta*-substituted isomers were more active. As for the phenomena that 2-Cl- and 2-F-substituted benzaldehydes were more active than their *para*-substituted isomers, we cannot give a reasonable explanation currently.

With respect to the selectivity to the corresponding benzyl alcohols, the Ru/CMK-3 catalyst furnished good to excellent. Moreover, for some substituted benzaldehydes, the selectivities were much better with the Ru/CMK-3 catalyst than those with the Pt/CMK-3 one [14]. The side reactions in this case are coupling between substrates and dehalogenation. Sometimes, addition of ethanol to benzaldehydes also inevitably occurred.

3.2.3 Reusability of the Ru/CMK-3 Catalyst

The reusability of the Ru/CMK-3 catalyst is also an important matter to consider. In order to avoid too much weight loss of the Ru/CMK-3 catalyst in water during the recycling experiment taking into account that CMK-3 is hydrophobic and cannot be socked well in water, neat ethanol was chosen as solvent instead of the mixture of water and ethanol for the hydrogenation of benzaldehyde.

Figure 7 shows the conversions and selectivities to the corresponding benzyl alcohol against the run numbers. The Ru/CMK-3 catalyst can be used at least five times although trace decrease in activity in the fourth run was noticed. In order to make clear the reason for the activity decrease of the Ru/CMK-3 catalyst, we detected the Ru leaching using ICP-AES technique. According to the ICP analyses of the filtrates after the first and the fifth run, no typical Ru signals were detected, indicating the Ru leaching was below the detection limit and can be neglected. Moreover, we checked the catalyst weight after the recycling experiment. About 7.5 % catalyst weight was totally lost during five runs. Additionally, the used Ru/CMK-3 catalyst was also characterized using TEM and no distinct Ru particles aggregation or Ru particle size growth was observed. Hence, the decrease in activity of the Ru/CMK-3 catalyst can be attributed to gradual washing out of catalyst powder from the catalyst system.

3.2.4 Further Discussion

The interaction of substrate with noble metal particles, such as Ru, plays a decisive role in activation of carbonyl double bond. To understand the interaction, the chemical composition of the catalyst surface and the surface electronic state of the Ru/CMK-3 catalyst was also evaluated by XPS. According to the XP spectrum of the Ru/CMK-3 catalyst (Fig. 8), there were two Ru species on the surface, metallic Ru species (the peaks of $3d_{5/2} = 280.6$ eV, $3d_{3/2} = 284.5$ eV) and $Ru^{\delta+}$ species (the peaks of $3d_{5/2} = 281.3$ eV, $3d_{3/2} = 286.5$ eV). As shown in Fig. 7, the $Ru^{\delta+}$ species dominated on the Ru/CMK-3 catalyst surface with nearly 78.1 %. Besides partly originated from re-oxidation when

exposed to air, as mentioned in Ref. [22], the $Ru^{\delta+}$ species should be mainly derived from interaction of Ru nanoparticles with CMK-3 OMCs. This suggests that the
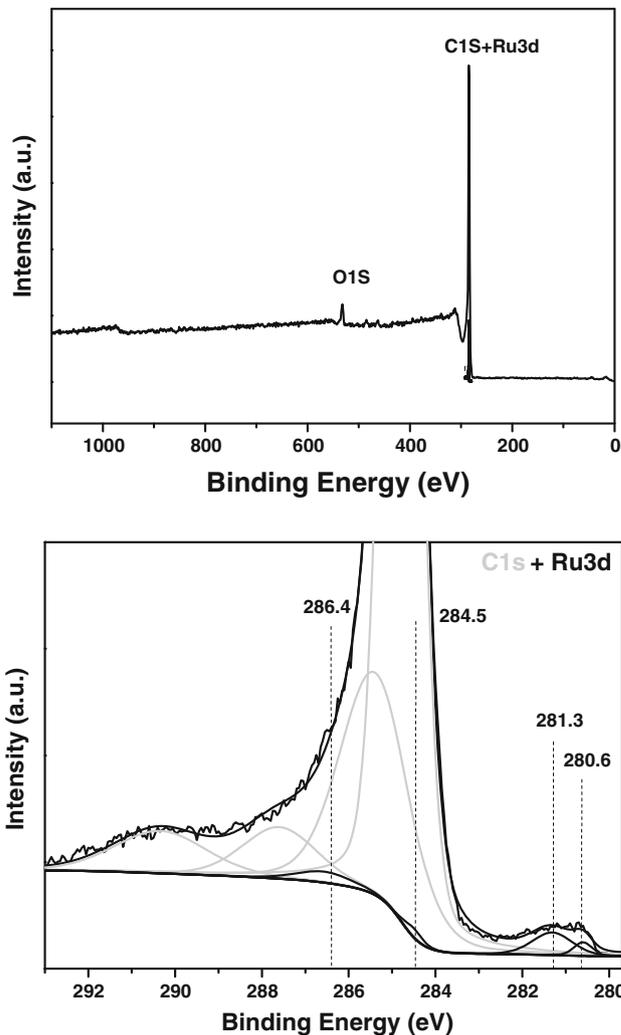
Fig. 8 XP spectrum of C1s region and Ru3d region of the Ru/CMK-3 catalyst

Fig. 7 Reusability of the Ru/CMK-3 catalyst in the hydrogenation of benzaldehyde in ethanol. Reaction conditions: 0.05 g 5.0 wt% Ru/CMK-3 catalyst added in the first run; 3 mmol benzaldehyde; 20 mL ethanol; room temperature; 4 MPa H_2 pressure; 1,200 rpm; 0.5 h
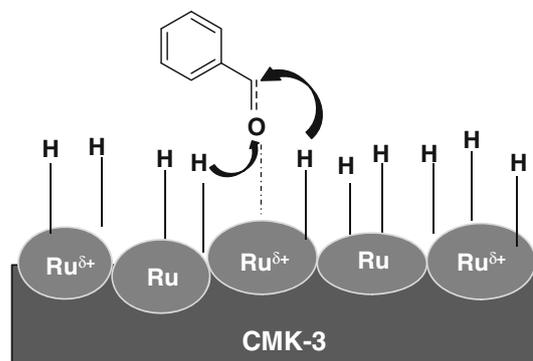
Scheme 2 Proposed adsorption/activation and hydrogenation model for benzaldehyde hydrogenation with Ru/CMK-3 catalyst

Ru/CMK-3 catalyst could easily activate the reactant, benzaldehyde, via adsorption of carbonyl oxygen atom bonding to the $Ru^{\delta+}$ species (Scheme 2). Then, hydrogenation occurred when adjacent hydrogen atoms adsorbed on the Ru/CMK-3 catalyst surface attacked carbonyl carbon or oxygen atom.

3.3 Hydrogenation of Nitrobenzene and Its Derivatives

3.3.1 Optimization of Reaction Conditions for Nitrobenzene Hydrogenation

As good results for the hydrogenation of benzaldehyde and its derivatives were obtained, we were motivated to explore the hydrogenation with the Ru/CMK-3 catalyst to another series of unsaturated compounds, nitrobenzene and its derivatives. Selective hydrogenation of nitro aromatic compounds is also an important industrial process to obtain immediate for the synthesis of many fine chemicals, such as dyes, herbicides, pesticides, pharmaceuticals and cosmetic products.

With respect to hydrogenation of nitrobenzene and its derivatives, we did not have any findings at hand. Consequently, the effect of reaction temperature was firstly investigated for the hydrogenation of nitrobenzene. The mixture solvent containing 18 mL water and 2 mL ethanol was applied for the hydrogenation of nitrobenzene initially. The hydrogenation of nitrobenzene with the Ru/CMK-3 catalyst at room temperature hardly took place. Only 2.0 % conversion was obtained after 3 h although the selectivity was nearly 100 %. To accelerate the reaction, the temperature was raised to 313 K and 21.7 % of nitrobenzene was converted to aniline after 3 h with higher than 99 % selectivity. Compared with the results obtained at room temperature, the conversion was increased by almost one order of magnitude at 313 K for the hydrogenation of nitrobenzene with the Ru/CMK-3 catalyst. Nevertheless, the conversion was rather low. When the reaction temperature was further increased to 323 K, the hydrogenation of nitrobenzene was finished after 3 h with 97.7 % selectivity. The side reaction was hydrogenation of phenyl ring with the Ru/CMK-3 catalyst at a higher temperature. Considering that the conversion was greatly increased although the selectivity was slightly decreased, the reaction was carried out at 323 K in the following studies by compromise.

Besides the reaction temperature, the kinetic behavior for the hydrogenation of nitrobenzene with the Ru/CMK-3 catalyst is also a matter of concern. Figure 9 exhibits the plots of conversion and selectivity VS time for nitrobenzene hydrogenation with the Ru/CMK-3 catalyst at 323 K. The reaction went very slowly at first and suddenly accelerated after 1.5 h, indicating that there was an
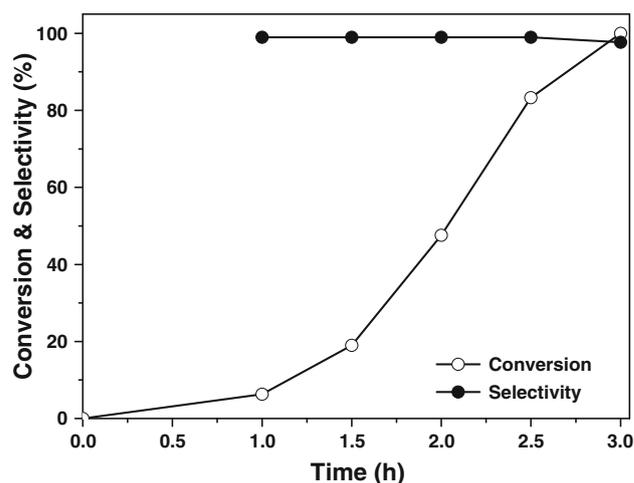
Fig. 9 Conversion and selectivity versus time plots for nitrobenzene hydrogenation with the Ru/CMK-3 catalyst. Reaction conditions: 0.05 g 5.0 wt% Ru catalyst; 8.1 mmol nitrobenzene; 18 mL water and 2 mL ethanol; 4.0 MPa H_2, 2.5 h; 323 K; 1,200 rpm

induction period for nitrobenzene hydrogenation with the Ru/CMK-3 catalyst. About 83 % conversion was afforded after 2.5 h. The whole reaction was nearly complete after 3 h. It is quite different from that for benzaldehyde hydrogenation with the same catalyst. The selectivities were excellent with trace by-product from the hydrogenation of benzene ring.

3.3.2 Hydrogenation of Nitrobenzene Derivatives

Based on the findings obtained for hydrogenation of nitrobenzene, we extended the substrate to the nitrobenzene derivatives with the Ru/CMK-3 catalyst. Table 3 lists the conversions of nitrobenzene derivatives with different substituents at the phenyl ring with the Ru/CMK-3 catalyst. Considering that, some substrates had very low solubility in the mixture of water and ethanol, neat ethanol was used as an alternative solvent to improve the mass transfer and to increase hydrogen solubility in some cases as well [23].

Compared with nitrobenzene without any substituent, the conversions of nitrobenzene derivatives with electron-withdrawing group, such as Cl- were mediocre (14.6–69.2 %) even if the reaction accelerated when conducted in ethanol (Table 3, entries 1–6). While for the hydrogenation of nitrobenzene derivatives with electron-donating groups such as methoxy and methyl at the *ortho*-position, the conversions were higher. The highest conversion of 100 % was obtained for *ortho*-methoxynitrobenzene, the TOF reaching 409.4 h^{-1} (Table 3, entry 7). The 2-CH_3-nitorbenzene gave a conversion of 93.8 % under the same conditions (Table 3, entry 10). However, for the nitrobenzene derivatives with methoxy or methyl substituents at the *para*- or *meta*-position, the conversions

Table 3 Hydrogenation of nitrobenzene derivatives with different substituents at the phenyl ring with the Ru/CMK-3 catalyst

R ⬡ NO$_2$ →(Ru Catalyst / Solvent, H$_2$, 323 K)→ R ⬡ NH$_2$
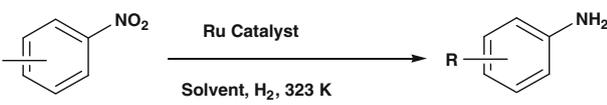
Entry	R group	Solvent	Conversion (%)[a]	TOF (h^{-1})
1	2-Cl	18 mL W + 2 mL E	21.6	88.4
2	2-Cl	20 mL E	32.9	134.7
3	3-Cl	18 mL W + 2 mL E	26.1	106.8
4	3-Cl	20 mL E	69.2	283.3
5	4-Cl	18 mL W + 2 mL E	14.6	59.8
6	4-Cl	20 mL E	35.2	144.1
7	2-MeO	18 mL W + 2 mL E	100	409.4
8	4-MeO	18 mL W + 2 mL E	37.6	153.9
9	4-MeO	20 mL E	100	409.4
10	2-CH$_3$	18 mL W + 2 mL E	93.8	384.0
11	3-CH$_3$	18 mL W + 2 mL E	24.1	98.6
12	3-CH$_3$	20 mL E	45.6	186.7
13	4-CH$_3$	18 mL W + 2 mL E	43.2	176.8
14	4-CH$_3$	20 mL E	65.6	268.5

Reaction conditions: 0.05 g 5.0 wt% Ru catalyst; 8.1 mmol substrates; 4.0 MPa H$_2$, 2.5 h; 323 K; 1,200 rpm

W water, *E* ethanol

[a] Determined by GC

were rather low (24.0–43.2 %) (Table 3, entries 8, 11 and 13). Although the reactions performed in ethanol went much fast and the conversions were increased by about 20 %, the conversions were not so high for 3-CH$_3$- and 4-CH$_3$-nitrobenzenes (Table 3, entries 12 and 14). As for 4-MeO-nitrobenzene, the hydrogenation was finished within 2.5 h in ethanol (Table 3, entry 9).

It is obvious that the electronic effect influences the results, as the 3-Cl-nitrobenzene was most active compared with the other two isomers (Table 3, entries 3, 4), while for the methyl-substituted isomers, the 3-methyl-nitrobenzene was the most inactive isomer (Table 3, entries 11, 12). It is worthy of note that the hydrogenation of nitrobenzene and its derivatives on the Ru/CMK-3 catalyst got excellent selectivities without dechlorination or any other side reaction, except for trace by-product from the hydrogenation of benzene ring [24]. It is well known that somewhat positive charges with Ru particles would increase the catalytic activity for this reaction [25].

4 Conclusion

The 5 wt% Ru/CMK-3 catalyst was prepared via a facile impregnation method using an aqueous solution containing RuCl$_3$ as Ru precursor. The Ru nanoparticles entrapped in OMCs worked well for the liquid-phase hydrogenation of benzaldehyde and its derivatives under the tested conditions (medium hydrogen pressure, water as solvent, at room temperature). The Ru/CMK-3 catalyst showed good performance as well in the liquid-phase hydrogenation of nitrobenzene and its derivatives under optimal conditions, especially for those with an electron-donating group at *ortho*- or *para*-position. Notably, the Ru/CMK-3 catalyst was more efficient than the commercial Ru/C catalyst and the homemade Ru catalyst supported on activated carbon under the same conditions for the liquid-phase hydrogenation of benzaldehyde. The Ru nanoparticles could be well stabilized by the ordered mesoporous carbons so that the Ru/CMK-3 catalyst could also be easily recovered and reused for several times.

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