

The partial hydrogenation of benzene to cyclohexene over Ru–Cu catalyst supported on ZnO

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ARTICLE INFO

Article history:

Received 8 December 2010

Received in revised form 14 March 2011

Accepted 27 March 2011

Available online 6 April 2011

Keywords:

Benzene

Cyclohexene

Hydrogenation

Ru

ZnO

ABSTRACT

The selective hydrogenation of benzene to cyclohexene was studied over Ru–Cu/ZnO catalysts, which were prepared by deposition–precipitation, impregnation and co-precipitation methods. The influence of NaOH on the catalytic performance of catalysts prepared by these methods was discussed in detail. It was demonstrated that NaOH significantly enhanced the selectivity to cyclohexene over Ru–Cu/ZnO catalyst prepared by deposition–precipitation method. The properties of the catalysts were characterized by transmission electron spectroscopy (TEM), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption–desorption techniques. The effects of ratio of Ru to Cu, concentration of NaOH and other reaction conditions including reaction temperature, hydrogen pressure, and reaction time on the reaction were studied. Using the preferable catalyst, the yield of cyclohexene reached a maximum of 49.4% with benzene conversion of 72.3% and selectivity to cyclohexene of 68.3%.

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1. Introduction

Cyclohexene has a very active C=C bond, which is widely used in chemical industry as a key raw material in the synthesis of adipic acid, nylon 6, nylon 66, and other fine chemicals [1,2]. The production of cyclohexene involved dehydration of cyclohexanol, dehydrohalogenation of halogenated cyclohexane, or dehydrogenation of cyclohexane [3–5]. The processes for producing cyclohexene require complicated multiple steps in above methods, and the efficiencies are usually poor, thus leading to high production cost.

In recent years, environmental and economic considerations result in strong interest to redesign commercially important processes, and the partial hydrogenation of benzene to cyclohexene has attracted great scientific and industrial interest. The route of selective hydrogenation of benzene to cyclohexene is superior in terms of inexpensive starting feedstock, energy-saving, lower amounts of undesirable by-products. There have been many publications on this topic [6–37]. Solvents play a crucial role in determining the selectivity to cyclohexene. Cyclohexene cannot be produced in organic phase because cyclohexene is further converted to cyclohexane easily in organic phase. In aqueous solution, cyclohexene can be selectively produced and the selectivity is closely related to the hydrophilicity of catalysts. In aqueous envi-

ronment, the hydrophilicity of the catalysts is strongly influenced by the presence of hydrogen, as the adsorption enthalpy of water on Ru particles in the presence of hydrogen is half of the value when no hydrogen is present [6]. In addition, the low solubility of hydrogen in water lowers the hydrogen availability on the catalyst surface. These facts are unfavorable for hydrogenation of cyclohexene to cyclohexene.

It was found that the method for preparing the catalyst and the promoter has great impacts on the yield of cyclohexene. Mizukami et al. [38] and Niwa et al. [39] prepared a supported Ru catalyst doped with a small amount of Cu by the sol–gel method, and obtained a cyclohexene yield of 31% at a benzene conversion of 83%. Deng and co-workers [40,41] reported that RuB catalysts prepared by the chemical reduction method were more selective to cyclohexene than Ru catalysts reduced by H₂, giving a cyclohexene yield of 33%. The additives also have great impacts on the yield of cyclohexene such as TiCl₃ [11,42], ZnSO₄·7H₂O [8–10,12,13,15,18,20,21,23], metal hydroxides [24,37,43] and alcohols [16,36,44]. US patent reported that considerable amounts of cyclohexene were formed in the catalytic hydrogenation of benzene in the presence of an alcohol. The benzene conversion was about 10% and selectivity to cyclohexene was less than 20% in the presence of C1–C4 alcohol and Ru catalyst [44]. The cyclohexene yield of 34.4% was achieved over RuCoB/γ-Al₂O₃ catalyst with PEG-6000 as an additive [16]. It was also reported that cycloolefins can be prepared by partial hydrogenation of the corresponding aromatics in the presence of water, an alkaline agent and a catalyst comprising a reduced cation of a Group VIII element [43]. Ronchin and Toniolo [6] found that

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the selectivity to cyclohexene can be enhanced by treating unreduced Ru catalyst with NaOH. A few publications have reported the improvement of the yield of cyclohexene by conducting the hydrogenation in the aqueous solution of NaOH [24,37,43], but the reasons for the enhancement of the yield were not clear.

In the present work, the selectivity hydrogenation of benzene to cyclohexene was studied over the Ru–Cu/ZnO catalysts prepared by deposition–precipitation, impregnation and coprecipitation methods. Preparation procedures were found to be quite important in determining the catalytic activity and selectivity. The effect of NaOH on the catalytic performance of Ru–Cu/ZnO prepared by different methods was different. The addition of NaOH significantly improved the selectivity to cyclohexene over the catalyst prepared by deposition–precipitation method, while the effect of NaOH was very limited over the catalyst prepared by impregnation method. The catalyst was characterized by powder X-ray diffraction (XRD), transmission electron spectroscopy (TEM), scanning electron microscopy (SEM), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption–desorption method. The maximum yield of cyclohexene could reach 49.4% over Ru–Cu/ZnO prepared by deposition–precipitation method at optimized condition.

2. Experimental

2.1. Materials

Zn(NO₃)₂·6H₂O, RuCl₃·3H₂O, Cu(NO₃)₂·3H₂O, NaOH, dichloromethane, cyclohexene, cyclohexane and benzene were analytical grade and purchased from Beijing Chemical Reagent Company. H₂ (99.99%) was provided by Beijing Analytical Instrument Company.

2.2. Catalyst preparation

The ZnO was prepared as following: the aqueous solution of NaOH (0.05 M) was dropped to the aqueous solution of Zn(NO₃)₂ (0.025 M) until the molar ratio of NaOH to Zn(NO₃)₂ reached 2.4. After aging for 1 h, the obtained precipitation was collected on a ceramic filter and washed thoroughly with distilled water. The sample was dried overnight at 100 °C and then calcined for 3 h in a muffle furnace from room temperature to 350 °C with a increasing rate of 2 °C/min to decompose the Zn(OH)₂ to ZnO.

Ru–Cu/ZnO catalysts prepared by deposition–precipitation were denoted as Ru–Cu/ZnO (DP). Typically, 0.5 g of ZnO was dispersed in 11 mL of aqueous solution of NaOH (0.05 M) with stirring for 30 min. 10 mL of aqueous solution containing 0.0389 g of RuCl₃·3H₂O and 0.0036 g of Cu(NO₃)₂·3H₂O was dropped into the above aqueous solution and stirred for 2 h, and then aged for overnight. The calculated loading of Ru was 2.91 wt% and the molar ratio of Ru to Cu was 10. The ICP analysis of catalyst Ru–Cu/ZnO (DP) with a molar ratio of Ru/Cu 10:1 indicated that the content of Ru was 1.96 wt% in the catalyst and the molar ratio of Ru/Cu was 10.96/1. The obtained precipitation was collected on a ceramic filter and washed thoroughly with distilled water. The sample was then dried in vacuum at 60 °C overnight. The as-prepared Ru–Cu/ZnO (DP) samples were reduced in H₂ (99.99%) at 180 °C for 3 h.

Ru–Cu/ZnO catalysts prepared by impregnation were denoted as Ru–Cu/ZnO (IP). Typically, 0.0389 g of RuCl₃·3H₂O and 0.0036 g of Cu(NO₃)₂·3H₂O were dissolved in 10 mL of distilled water. 0.5 g of ZnO support was added to this solution and the resulting slurry was vigorously stirred for 12 h at room temperature. Then the water was removed under vacuum at 70 °C. The loading of Ru was 2.91 wt% and the molar ratio of Ru to Cu was 10. The as-prepared Ru–Cu/ZnO samples were reduced in H₂ (99.99%) at 180 °C for 3 h.

Ru–Cu/ZnO catalysts prepared by coprecipitation were denoted as Ru–Cu/ZnO (CP). Typically, 0.129 g of RuCl₃·3H₂O, 0.019 g of Cu(NO₃)₂·3H₂O and 0.914 g of Zn(NO₃)₂·3H₂O were dissolved in 18 mL of distilled water. 18 mL of aqueous solution of NaOH (0.5 M) was dropped into the above aqueous solution with stirring for 12 h and then aging for 12 h at room temperature. The solid materials were separated, washed, and dried in the same manner as described above for the Ru–Cu/ZnO (DP) samples. The content of Ru was 20 wt% and the molar ratio of Ru to Cu was 10. The as-prepared Ru–Cu/ZnO samples were reduced in H₂ (99.99%) at 180 °C for 3 h.

2.3. Activity test

For the reaction in liquid solvents, the hydrogenation was carried out in a Teflon-lined stainless-steel reactor of 6 mL in capacity with a magnetic stirrer [45]. The stir was realized through an outside controller and a magnetic stirrer which was put inside the reactor. The reactor was connected to a hydrogen cylinder of the reaction pressure, so that hydrogen of fixed pressure could be supplied continuously. The pressure was determined by a pressure transducer (FOXBORO/ICT, Model 93), which could be accurate to ±0.025 MPa. In a typical experiment, 0.35 mL of benzene and 50 mg of catalyst and 2 mL of aqueous sodium hydroxide solution were loaded into the reactor. The reactor was sealed and purged with hydrogen to remove the air. Then the reactor was placed in an air bath, which was controlled by a PID temperature controller (model SX/A-1, Beijing Tianchen Electronic Company), and the temperature fluctuation of the air bath was ±0.1 °C. Hydrogen was introduced into the reactor after desired temperature was reached and the stirrer was started. After reaction the reactor was placed in ice water and the hydrogen was released. The liquid products were extracted from the aqueous solution of NaOH by dichloromethane. The quantitative analysis of the reaction mixture was conducted using a GC (Agilent 6820) equipped with a flame ionization detector (FID) and a PEG-20M capillary column (0.25 mm in diameter, 30 m in length). Identification of the products and reactant was done using a GC–MS (SHIMADZU-QP2010) as well as by comparing the retention time of the standards in GC trace. Conversion of benzene (C), selectivity (S) and yield (Y) of cyclohexene were calculated according to the following equations:

$$C = \frac{\text{mole of reacted benzene}}{\text{mole of initial benzene}} \cdot 100\%$$

$$S = \frac{\text{mole of cyclohexene formed}}{\text{mole of reacted benzene}} \cdot 100\%$$

$$Y = \frac{\text{mole of cyclohexene formed}}{\text{mole of initial benzene}} \cdot 100\%$$

2.4. Catalyst characterization

The catalysts were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption–desorption method. The SEM examination was conducted on a Hitachi-s4300 electron microscope operated at 15 kV. The samples were spray-coated with a thin layer of platinum before observation. The TEM observation was carried out on JEM 2011 at an accelerating voltage of 200 kV. The samples were dispersed in ethanol and dropped on a carbon film supported on copper grid for TEM analysis. The nitrogen adsorption–desorption isotherms were measured at 77 K on ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer. The sample was degassed at 250 °C for 12 h under vacuum before the measurement. X-ray powder diffraction (XRD) was performed on a X'PERT SW X-ray diffractometer operated at 30 kV and 100 mA with CuK α radiation. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer

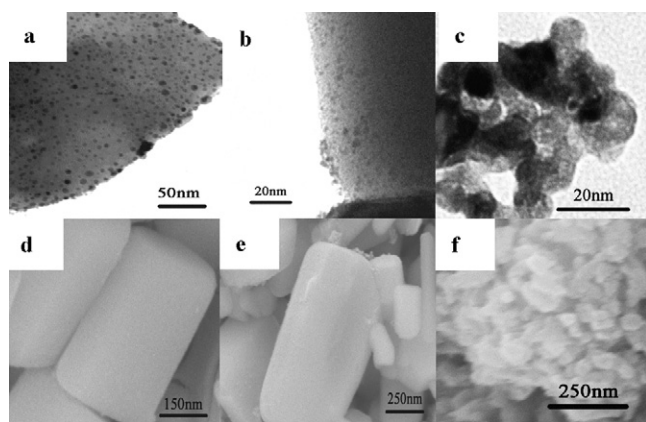


Fig. 1. TEM images of catalyst (a) Ru–Cu/ZnO (DP), (b) Ru–Cu/ZnO (IP), and (c) Ru–Cu/ZnO (CP) and SEM images of catalyst (d) Ru–Cu/ZnO (DP), (e) Ru–Cu/ZnO (IP), and (f) Ru–Cu/ZnO (CP).

from VG Scientific using 300 W MgK α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. The loading content of Ru/Cu in the catalysts was determined by ICP-AES (VISTAMPX).

3. Results and discussions

3.1. The effect of NaOH on different catalysts

Table 1 shows the catalytic performance of Ru–Cu/ZnO (IP), Ru–Cu/ZnO (DP) and Ru–Cu/ZnO (CP) in the hydrogenation of benzene and the effect of NaOH on the reaction. In the absence of NaOH, the catalyst Ru–Cu/ZnO (DP) exhibited high activity than Ru–Cu/ZnO (IP) and Ru–Cu/ZnO (CP). Obviously, the Ru–Cu/ZnO (DP) was much more efficient, indicating that catalyst Ru–Cu/ZnO (DP) prepared with deposition–precipitation method has better performance for the hydrogenation of benzene to produce cyclohexene. The TEM images of Ru–Cu/ZnO (DP), Ru–Cu/ZnO (IP) and Ru–Cu/ZnO (CP) are given in Fig. 1. The metallic particles were uniformly dispersed on the surface of ZnO for Ru–Cu/ZnO (DP), while the metallic particles on Ru–Cu/ZnO (IP) were not uniform. The TEM image of the Ru–Cu/ZnO (CP) showed the character of sample prepared by coprecipitation. It can be known from the SEM images of Ru–Cu/ZnO (DP) and Ru–Cu/ZnO (IP) in Fig. 1 that the support was partly destroyed when using the impregnation method.

The presence of NaOH greatly improved the selectivity and yield of cyclohexene for the catalyst Ru–Cu/ZnO (DP). In the presence of NaOH the selectivity to cyclohexene could be as high as 87.9% and the yield could reached 34.8%, while the yield of cyclohexene was only 6.8% when there was no NaOH. A reasonable explanation for this can be the enhancement of the surface hydrophilicity due to the presence of NaOH. Ronchin and Toniolo [6] found that the initial benzene hydrogenation rate, selectivity and maximum yield of cyclohexene increased when the unreduced Ru based catalyst

Table 2
Textural properties of Ru–Cu/ZnO (DP), Ru–Cu/ZnO (IP) and Ru–Cu/ZnO (CP).

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
Ru–Cu/ZnO (DP)	9.1	0.049	12.1
Ru–Cu/ZnO (IP)	8.4	0.036	7.6
Ru–Cu/ZnO (CP)	8.9	0.044	11.4

was treated with NaOH. They reported that the NaOH depressed the rate of cyclohexene hydrogenation. Thus, the base played an important role on determining the catalytic activity and selectivity, which was attributed to the influence of the interaction of the metallic Ru surface with the NaOH during the catalyst preparation. In this work, when conducting the hydrogenation of benzene in the aqueous solution of NaOH, the existence of NaOH also enhanced the hydrophilicity of the Ru catalysts by chemisorbed hydroxide anion. Some of the active centers available for cyclohexene hydrogenation were blocked by hydroxide anion chemisorption. The data in Table 1 also show that adding NaOH could not improve the yield of cyclohexene considerably for the catalyst Ru–Cu/ZnO (IP). We can get some information about the morphologies and structures of the catalysts from the procedures to prepare catalysts and the characterization results by different methods. TEM images in Fig. 1 showed that the metallic particles were on the surface of ZnO for Ru–Cu/ZnO (DP), while some of the metallic particles were in the pores of ZnO for Ru–Cu/ZnO (IP). The XPS spectra of Ru–Cu/ZnO (DP) and Ru–Cu/ZnO (IP) were shown in Figs. 2 and 3, respectively. By XPS characterization, the content of Ru and Cu on the surface of the catalyst can be roughly estimated. Cu content on the surface of Ru–Cu/ZnO (DP) was about 1.9% while Cu cannot be detected on the surface of Ru–Cu/ZnO (IP). Ru content on the surface of catalyst Ru–Cu/ZnO (DP) and Ru–Cu/ZnO (IP) was about 4.5% and 1.7%, respectively, indicating that Ru/Cu mainly existed on the surface of the catalyst when using deposition–precipitation method. Perhaps due to the metallic particles on the surface were more easily accessible to the NaOH in aqueous solution, the selective hydrogenation of benzene over Ru–Cu/ZnO (DP) was more sensitive to the addition of NaOH in the reaction system. To validate the aforementioned argument, the selective hydrogenation of benzene was conducted over Ru–Cu/ZnO (CP). The Ru–Cu/ZnO (CP) was prepared by coprecipitation where most of the metallic particles were covered by ZnO and it was difficult for them to approach NaOH. The results in Table 1 showed that the effect of NaOH on benzene hydrogenation over this catalyst was negligible and the yield of cyclohexene was very low in the presence or absence of NaOH.

Furthermore, the difference in BET surface area, pore size and pore volume between deposition-precipitated and impregnated samples could provide some useful information (Table 2). The pore volume and pore size of Ru–Cu/ZnO (DP) were larger than that of Ru–Cu/ZnO (IP), respectively, indicating that part of the pores of Ru–Cu/ZnO (IP) are blocked by some metallic particles. Therefore, the catalyst prepared by deposition–precipitation was better than that by impregnation and coprecipitation methods. Therefore, the Ru–Cu/ZnO (DP) catalyst was selected for the further study.

Table 1
The results of benzene hydrogenation over different catalysts with and without NaOH.

Catalyst	NaOH (M)	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
Ru–Cu/ZnO (IP)	0	30	23.6	20.7	4.9
	0.3	110	30.3	24.1	7.3
Ru–Cu/ZnO (DP)	0	3	37.2	18.3	6.8
	0.3	50	39.6	87.9	34.8
Ru–Cu/ZnO (CP)	0	320	47.6	1.2	0.6
	0.3	420	47.8	1.4	0.7

Reaction conditions: benzene, 0.35 mL; reaction temperature, 150 °C; H₂ pressure, 4.0 MPa; Ru–Cu/ZnO catalyst, 50 mg; water, 2.0 mL.

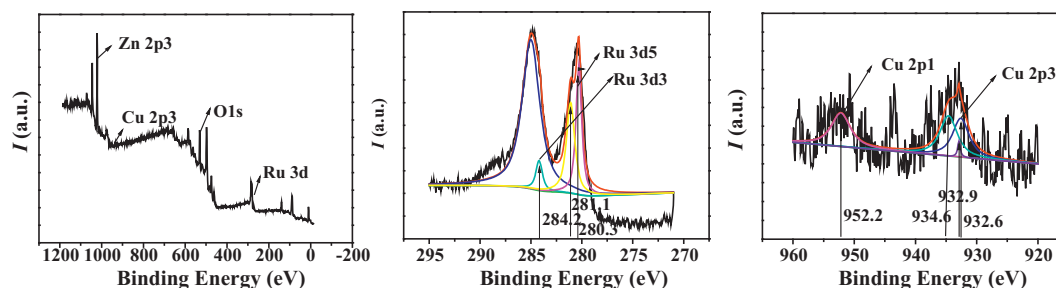


Fig. 2. XPS spectra of catalyst Ru–Cu/ZnO (DP).

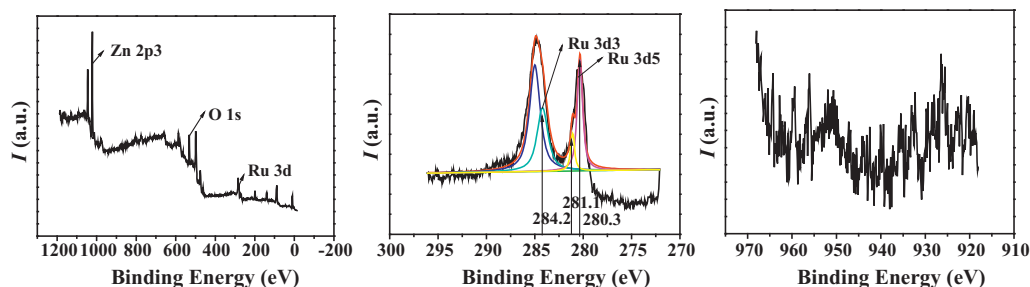


Fig. 3. XPS spectra of catalyst Ru–Cu/ZnO (IP).

3.2. The effect of molar ratio of Ru to Cu on the catalytic performance

The effect of molar ratio of Ru to Cu on the hydrogenation of benzene was investigated using the Ru–Cu/ZnO (DP) catalyst in the presence of NaOH. Table 3 shows the results. The reaction time required for reaching similar conversion increased with the increasing content of Cu in the catalyst, indicating that the addition of Cu decreased the catalytic activity. The selectivity to cyclohexene first increased and then decreased with the variation of Ru/Cu molar ratio. There was a maximum in the selectivity when the molar ratio of Ru/Cu was 10:1. The reaction conditions will be optimized using Ru–Cu/ZnO (DP) catalyst with a molar ratio of Ru/Cu 10:1.

3.3. Optimization of the reaction conditions

3.3.1. The effect of NaOH amount

Table 4 shows the hydrogenation of benzene over Ru–Cu/ZnO (DP) in NaOH aqueous solutions of different concentrations. The yield of cyclohexene was only 6.8% when no NaOH was added. The reaction proceeded so fast that only 3 min was needed for reaching 37.2% conversion of benzene. On the other hand, introducing NaOH in the hydrogenation process substantially decreased the activity. The reaction time required to reach similar conversion at different NaOH concentrations increased with increasing concentration of NaOH. The selectivity to cyclohexene could be increased at suitable NaOH concentration. Addition of 0.1 M NaOH in the reac-

Table 3
The results with different Ru/Cu molar ratios of Ru–Cu/ZnO (DP).

Ru/Cu molar ratio	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
1:0	20	32.3	46.3	15.0
12:1	36	37.0	62.7	23.2
10:1	50	39.6	87.9	34.8
10:2	72	35.6	59.6	21.2
10:3	88	35.6	43.2	15.4
0:1	400	22.4	23.8	5.3

Reaction conditions: benzene, 0.35 mL; reaction temperature, 150 °C; H₂ pressure, 4.0 MPa; Ru–Cu/ZnO (DP) catalyst, 50 mg; NaOH, 0.3 M; water, 2.0 mL.

tion readily led to a cyclohexene selectivity of 65.9% at a benzene conversion of 33.3% with a reaction time of 38 min. The selectivity to cyclohexene could be as high as 87.9% and cyclohexene yield reached 34.8% when using 0.3 M NaOH in the hydrogenation process, clearly verifying the positive effect for the production of cyclohexene. However, adding more NaOH resulted in lower cyclohexene selectivity. Some researchers reported that the yield of cyclohexene could be improved by adding NaOH [24,37], but the reason for NaOH to promote the selectivity to cyclohexene is still not clear. It can be known from Table 4 that the addition of NaOH retarded the hydrogenation of cyclohexene to cyclohexane, which are supported by the comparison experiments. The hydrogenation of cyclohexene was conducted over Ru–Cu/ZnO (DP) with and without NaOH. The results (Table 4, Entries 11 and 12) indicated that the hydrogenation of cyclohexene was depressed in the presence of NaOH. The promotion of aqueous solution of NaOH on the production of cyclohexene results mainly from two factors. One is the contribution of water, which has been discussed by some researchers. When there is a stagnant water film on the catalyst, the hydrogenation of cyclohexene to cyclohexane is slow because

Table 4
The results of benzene hydrogenation at different NaOH concentrations.

Entry	NaOH (M)	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
1	0	3	37.2	18.3	6.8
2	0.05	5	43.0	18.5	8.0
3	0.075	20	38.1	46.6	17.8
4	0.1	38	33.3	65.9	21.9
5	0.2	43	43.2	64.7	28.0
6	0.3	50	39.6	87.9	34.8
7	0.35	62	40.0	63.2	25.3
8	0.6	120	36.0	61.0	21.9
9	0.8	170	33.3	65.9	21.9
10	1.2	720	30.0	38.1	11.4
11 ^a	0	20	76.1	–	–
12 ^a	0.3	20	4.6	–	–

Reaction conditions: benzene, 0.35 mL; reaction temperature, 150 °C; H₂ pressure, 4.0 MPa; Ru–Cu/ZnO (DP) catalyst, 50 mg; water, 2.0 mL.

^a Cyclohexene hydrogenation under the same conditions as benzene. Cyclohexane was the sole product.

Table 5The results of benzene hydrogenation at different H₂ pressures.

Pressure of H ₂ (MPa)	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
2	240	37.3	68.3	25.5
3	100	40.0	74.6	29.8
4	50	39.6	87.9	34.8
5	95	30.7	48.7	15.0
6	145	29.6	44.1	13.1
7	220	29.6	30.8	9.1

Reaction conditions: benzene, 0.35 mL; reaction temperature, 150 °C; Ru–Cu/ZnO (DP) catalyst, 50 mg; NaOH, 0.3 M; water, 2.0 mL.

benzene is more soluble than cyclohexene in water [27]. Moreover, water competes with cyclohexene to adsorb on Ru surface, thus, disfavoring its hydrogenation to cyclohexane [46]. The other is the role of NaOH, which has been discussed in this work.

3.3.2. The effect of H₂ pressure

The influence of the hydrogen pressure on the reaction was studied at 150 °C between 2 MPa and 7 MPa. The results of benzene hydrogenation at different hydrogen pressures are presented in Table 5. The yield of cyclohexene at 4 MPa was greater than those at other pressures, and the benzene hydrogenation rate was the highest. The results indicated that there was an optimum pressure at which rate of benzene conversion and yield of cyclohexene was the highest. The appearance of the maximum can be ascribed to the postulation that the rates of all the individual hydrogenation steps are different functions of the hydrogen pressure. Odenbrand and Lundin [47] found that the cyclohexene yield increased with the increasing pressure from 0.9 MPa to 3.5 MPa and then dropped at higher pressure. Hu and Chen [24] found that the optimum pressure for the initial rate of conversion of benzene was about 3 MPa, while the highest yield of cyclohexene was obtained at 4.32 MPa. They interpreted the result based on a slow adsorption theory and the existence of a stagnant water film on the surface of the catalyst. By postulating that the reactants competitively adsorb on the same active sites of the catalyst, the hydrogenation rate of benzene would increase gradually with an increase in the hydrogen pressure to the maximum point, which corresponds to the optimal surface coverage of benzene and hydrogen. At higher hydrogen pressure, the rate would decrease because of the high surface coverage of hydrogen. As a matter of fact, the results in Table 5 demonstrate that benzene hydrogenation rate at 4 MPa was also greater than that at the higher pressures. Considering that the hydrogenation of benzene proceeds via the consecutive hydrogenation mechanism, cyclohexene can be readily hydrogenated to cyclohexane when there is an excessive amount of hydrogen on the surface of the catalyst. So the yield of cyclohexene decreased as the pressure of hydrogen exceeded a certain value.

3.3.3. The effect of reaction temperature

The effect of reaction temperature on benzene conversion and on cyclohexene yield was investigated in the temperature range of 100–180 °C over Ru–Cu/ZnO (DP) catalyst. Table 6 shows that the yield of cyclohexene increased with increasing temperature from 10.1% at 100 °C to 34.8% at 150 °C, and then the yield decreased with further increasing temperature. Struijk et al. [46] proposed that the higher reaction temperature promotes desorption of cyclohexene, and the surface coverage of hydrogen at higher temperature is lower, both of which disfavor the further hydrogenation of cyclohexene to cyclohexane. But this explanation cannot explain the reduction of yield of cyclohexene at higher temperatures. Fan and coworkers [8] suggested that increasing the reaction temperature could also enhance the solubility of cyclohexene in the stagnant water film surrounding the catalyst, which could increase the

Table 6

The results of benzene hydrogenation at different temperatures.

Temperature (°C)	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
100	240	35.3	28.8	10.1
120	180	37.3	32.8	12.2
140	110	42.2	45.1	19.0
145	80	40.7	60.2	24.5
150	50	39.6	87.9	34.8
155	40	43.0	58.3	25.1
160	35	41.5	46.3	19.2
180	30	40.9	47.5	19.4

Reaction conditions: benzene, 0.35 mL; H₂ pressure, 4.0 MPa; Ru–Cu/ZnO (DP) catalyst, 50 mg; NaOH, 0.3 M; water, 2.0 mL.

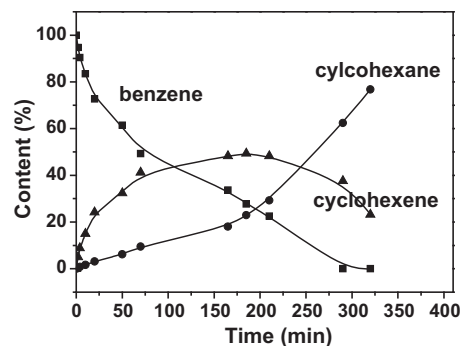


Fig. 4. The reaction course of benzene hydrogenation. Reaction conditions: benzene, 0.35 mL; reaction temperature, 150 °C; H₂ pressure, 4.0 MPa; Ru–Cu/ZnO (DP) catalyst, 50 mg; NaOH, 0.3 M; water, 2.0 mL.

surface coverage of cyclohexene and so the cyclohexene hydrogenation rate. Such an effect counteracts with the aforementioned positive effects. At above 150 °C it becomes the dominant factor, leading to the decrease of cyclohexene yield.

3.3.4. The effect of reaction time

Selective hydrogenation of benzene over Ru–Cu/ZnO (DP) catalyst at different reaction times was carried out with the addition of 0.3 M NaOH. Fig. 4 shows variation of the contents of benzene, cyclohexene and cyclohexane during the hydrogenation process. The conversion of benzene increased and the content of cyclohexene decreased monotonously with reaction time. The content of cyclohexene was much higher than that of cyclohexane at the beginning of the reaction. The yield of cyclohexene reached a maximum of 49.4% at benzene conversion of 72.3% and selectivity to cyclohexene of 68.3% with a reaction time of 185 min. The cyclohexene yield then declined gradually, exhibiting the characteristic behavior of a consecutive reaction.

3.4. Recycling of catalyst

The recycling of Ru–Cu/ZnO (DP) and Ru–Cu/ZnO (IP) for the hydrogenation of benzene was studied at 150 °C and H₂ pressure of 4.0 MPa, and the results are given in Table 7. It can be known from data in the table that Ru–Cu/ZnO (DP) was more stable than Ru–Cu/ZnO (IP). The deactivation of Ru–Cu/ZnO (DP) after three runs was not significant, while the activity and yield of Ru–Cu/ZnO (IP) decreased sharply. The morphological properties of the used Ru–Cu/ZnO (DP) and Ru–Cu/ZnO (IP) catalysts were studied by TEM and SEM. The TEM images of Ru–Cu/ZnO (DP) and Ru–Cu/ZnO (IP) after recycling three times are presented in Fig. 5a and b. The obvious agglomeration and desquamation of metallic particles could be observed for Ru–Cu/ZnO (IP), while the change was not obvious for Ru–Cu/ZnO (DP).

Table 7
Reuse of Ru–Cu/ZnO (DP) and Ru–Cu/ZnO (IP) for benzene hydrogenation.

Catalyst	Runs	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
Ru–Cu/ZnO (DP)	1	50	39.6	87.9	34.8
	2	50	36.8	82.6	30.4
	3	50	33.2	81.7	27.1
Ru–Cu/ZnO (IP)	1	110	30.3	24.1	7.3
	2	110	19.6	34.1	6.7
	3	110	9.8	36.3	3.6

Reaction conditions: benzene, 0.35 mL; reaction temperature, 150 °C; H₂ pressure, 4.0 MPa; Ru–Cu/ZnO catalyst, 50 mg; NaOH, 0.3 M; water, 2.0 mL.

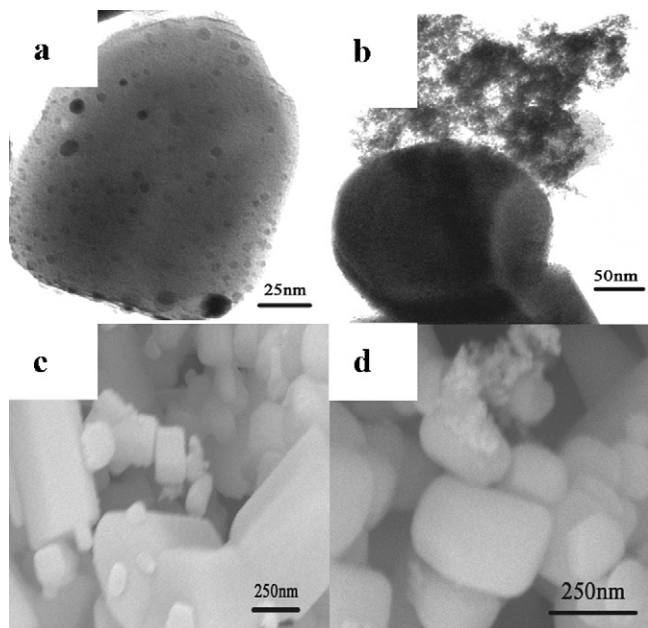


Fig. 5. TEM images of the catalysts after recycling (a) Ru–Cu/ZnO (DP) and (b) Ru–Cu/ZnO (IP), and SEM images of catalysts after recycling (c) Ru–Cu/ZnO (DP) and (d) Ru–Cu/ZnO (IP).

From the XRD patterns in Fig. 6, it can be known that there was no obvious peak of Ru for the Ru–Cu/ZnO (IP) and Ru–Cu/ZnO (DP) before the reaction, perhaps because the high dispersion and small particle of Ru–Cu on the ZnO. The dispersion and particle size of Ru–Cu/ZnO (DP) after reaction almost did not change, so there were no obvious peaks of Ru in XRD pattern. Although obvious aggregation and desquamation of metals occurred on catalyst Ru–Cu/ZnO (IP), no peaks of Ru are detected in Fig. 6d, perhaps because the metals desquamated existed in amorphous structure.

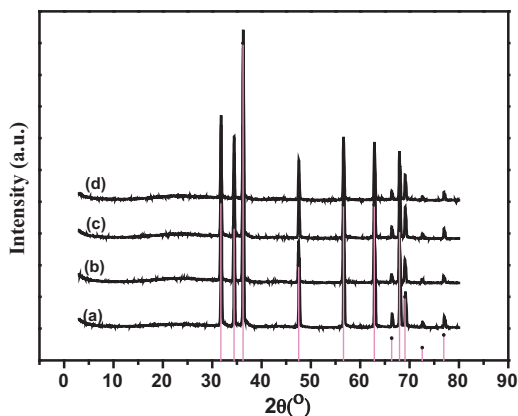


Fig. 6. The XRD pattern of catalyst (a) Ru–Cu/ZnO (IP) (fresh), (b) Ru–Cu/ZnO (IP) (after recycle), (c) Ru–Cu/ZnO (DP) (fresh) and (d) Ru–Cu/ZnO (DP) (after recycle).

4. Conclusions

The Ru–Cu/ZnO catalysts prepared by deposition–precipitation method exhibited better selectivity towards cyclohexene and stability than the Ru–Cu/ZnO catalyst prepared by impregnation method. The presence of NaOH greatly enhanced the selectivity and yield of cyclohexene for the hydrogenation of benzene over the former catalyst. The existence of NaOH depressed the hydrogenation of cyclohexene. At the optimized reaction conditions, the maximum yield of cyclohexene can reach 49.4% over Ru–Cu/ZnO catalyst prepared by deposition–precipitation method.

Acknowledgements

The authors are grateful to National Natural Science Foundation of China (20932002) and Chinese Academy of Sciences (KJCX2.YW.H16 and KJCX2.YW.H30.02) for financial supports.

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