



Ru catalyst supported on bentonite for partial hydrogenation of benzene to cyclohexene

Weitao Wang, Huizhen Liu, Tianbin Wu, Peng Zhang, Guodong Ding, Shuguang Liang, Tao Jiang*, Buxing Han*

Beijing National Laboratory for Molecular Sciences (BNLMS), Centre for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:

Received 28 September 2011
Received in revised form 7 December 2011
Accepted 8 December 2011
Available online 17 December 2011

Keywords:

Benzene
Cyclohexene
Hydrogenation
Ru
Bentonite

ABSTRACT

A ruthenium catalyst supported on the cheap bentonite with high activity has been prepared by impregnation-hydrothermal method and characterized by TEM, XRD, and XPS. The catalytic performance for selective hydrogenation of benzene to cyclohexene was investigated. The effect of additives NaOH and ZnSO₄ on the catalytic performances was studied. It was demonstrated that both NaOH and ZnSO₄ could significantly enhance the selectivity to cyclohexene over Ru/bentonite catalyst. The influences of reaction temperature, pressure, amounts of catalyst and additives, and reaction time on the selective hydrogenation of benzene were studied in detail.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Cyclohexene with the active C=C bond is commonly used as the chemical intermediates for the synthesis of adipic acid, nylon 6, nylon 66 and other fine chemicals. Conventionally, the production of cyclohexene involved dehydrogenation of cyclohexanol, dehydrohalogenation of cyclohexane halide and dehydrogenation of cyclohexane. But the efficiencies are usually poor for these processes. Alternatively, cyclohexene can be produced by partial hydrogenation of benzene [1–6]. The great interest in this new route is intrigued for the merits of that (1) it is a green route to produce cyclohexene compared to the traditional methods since it consumes less hydrogen and needs less steps; (2) both the product cyclohexene and cyclohexane are useful chemical materials, which lowers the production cost. Therefore, the route for selective hydrogenation of benzene to cyclohexene is superior over other routes in terms of inexpensive starting feedstock, energy-saving, lower amounts of undesirable products [7].

Since the 1970s, the research interests are increased year by year. Among the literatures, the heterogeneous catalysts are widely employed due to the easy separation after reaction. For design of the heterogeneous catalysts, ruthenium metal is recorded as the most active [4]. The catalyst supports are often single or binary hydrophilic oxides. Ruthenium on the SiO₂-based

support, such as SBA-15, gave the higher yield of cyclohexene [8,9]. A colloidal ruthenium catalyst stabilized by silica was prepared through microemulsion processing for selective hydrogenation of benzene to cyclohexene. Much higher activity and selectivity was obtained compared with its supported counterparts [10]. Figoli and coworkers studied the effect of the support Al₂O₃ and SiO₂ on the selective hydrogenation of benzene over ruthenium catalysts [11]. They found that more electron-deficient Ru species are present on Al₂O₃ than on SiO₂. The electronic state of Ru affects the selectivity to cyclohexene. The properties of Ru/Al₂O₃ catalysts were studied using different techniques by the same authors. Differences were found in the Ru species (Ru⁰, ruthenium oxides and ruthenium oxychloride), metal dispersion and chlorine content in the catalysts as well as in their catalytic activity and selectivity according to the preparation procedure used [12]. The colloidal RuB/Al₂O₃·xH₂O catalyst exhibited high activity and selectivity over the RuB/γ-Al₂O₃ catalyst in selective hydrogenation of benzene to cyclohexene. The higher selectivity was attributed to the existence of more structural water and surface hydroxyl groups on the RuB/Al₂O₃·xH₂O catalyst [13]. In addition, the cordierite monolithic catalysts showed potential application in fix-bed reactor for this reaction, which gave much higher selectivity than particulate catalyst [5,14,15].

Clays, as one of the SiO₂-based material, are considered to be a good support not only because of containing SiO₂ but also including several metal oxides since the metal oxides, even the binary metal oxides, are also good supports for the partial hydrogenation of benzene to cyclohexene. Bentonite is a layered clay

* Corresponding authors. Tel.: +86 10 62562821; fax: +86 10 62562821.
E-mail addresses: jiangt@iccas.ac.cn (T. Jiang), hanbx@iccas.ac.cn (B. Han).

mineral in the aluminosilicate smectite family. Water is thus able to enter into the interlayer to facilitate swelling and expanding the layers. Its porosity can be further improved by exchanging with the polymeric metal or organic cations [16]. The tunable surface and structural properties make bentonite widely used in catalysis such as hydrogenation and selective hydrogenation [17–20]. Furthermore, bentonite is widespread, easily available, low-cost and environmentally friendly. However, the bentonite supported ruthenium catalysts for the partial hydrogenation of benzene to cyclohexene are rarely documented to the best of our knowledge. Ruthenium over bentonite support is expected to have high activity considering the interlayer structure of bentonite giving the high dispersion of ruthenium [21]. It is no doubt that exploration of highly efficient, economical and simple catalysts for the selective hydrogenation of benzene is of great importance, but is challenging.

In the present work, the partial hydrogenation of benzene to cyclohexene was studied over the Ru/bentonite catalysts prepared by an impregnation-hydrothermal method. The catalyst was characterized by powder X-ray diffraction (XRD), transmission electron spectroscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The catalyst showed the high activity for hydrogenation of benzene. Both the addition of ZnSO₄ and NaOH to the reaction system can improve the selectivity to cyclohexene. Meanwhile, the influences of reaction temperature, pressure, concentration of the additives, and reaction time were studied.

2. Experimental

2.1. Materials

RuCl₃·3H₂O, ZnSO₄·7H₂O, NaOH, dichloromethane, cyclohexane and benzene were analytical grade and purchased from Beijing Chemical Reagent Company. Cyclohexene (99%) was from Alfa Aesar. Bentonite was obtained from Shanghai Fourth Chemical Reagent Factory. H₂ (99.99%) was provided by Beijing Analytical Instrument Company.

2.2. Catalyst preparation

The Ru catalyst supported on bentonite was prepared by an impregnation-hydrothermal method, which was designated as Ru/BEN (IP-HY). Typically, a desired amount of commercial bentonite (500 mg) without any treatment was added to the RuCl₃·3H₂O aqueous solution (0.038 g of RuCl₃·3H₂O, 30 mL of H₂O) under stirring for 30 min, and then the slurry was transferred to a stainless steel autoclave and sealed. Afterward, the autoclave underwent 120 °C for 10 h. 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/BEN (IP-HY) samples were reduced in H₂ (99.99%) at 300 °C for an hour. The nominal Ru loading of the catalyst was 3.0 wt.%.

2.3. Activity test

The reactor and the procedures used for the hydrogenation were similar to those described previously [22]. Typically, the hydrogenation was carried out in a Teflon-lined stainless-steel reactor of 6 mL in capacity with a magnetic stirrer. The reactor was connected to a hydrogen cylinder of the reaction pressure, so that hydrogen of fixed pressure could be supplied continuously. In the experiment, a desired amount of catalyst, benzene and ZnSO₄ aqueous solution was introduced. Then the reactor was sealed and purged with hydrogen to remove the air. After checking for leaks, the reactor was then placed in an air bath at the desired temperature 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 with desired pressure was fed into the reactor after desired temperature was reached. The hydrogenation reaction began by starting the agitation. The reaction was monitored with the consuming of the hydrogen. The total uptake of hydrogen which is related to the conversion was used to estimate the conversion of benzene. When desired conversion was reached, the reaction was stopped by quickly cooling down the reactor in ice water and the reaction time was recorded. After reaction the hydrogen was released slowly. The liquid products were extracted with dichloromethane. The products were analyzed using a gas chromatograph (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:

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

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

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

2.4. Characterization

The catalysts were characterized by transmission electron microscopy (TEM), powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) techniques. The TEM observations were carried out on JEOL JEM 1011 instrument with 100 kV. XRD was performed on a X'PERT SW X-ray diffractometer operated at 30 kV and 100 mA with Cu K α radiation. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg K 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. FT-IR spectra were recorded on Bruker Tensor 27 spectrometer with a resolution of 1 cm⁻¹ and 32 scans. The thickness of the liquid film was 0.015 mm.

3. Results and discussions

3.1. Characterization

The TEM image of Ru/BEN (IP-HY) catalyst is shown in Fig. 1. It can be seen that the ruthenium are well dispersed on the bentonite. The XRD patterns of the catalyst and support are shown in Fig. 2. There is no Ru or RuO₂ peaks appeared in the pattern of Ru/BEN (IP-HY) compared with that of bentonite. Only the intensity of the peaks was attenuated after the Ru was loaded on the bentonite, indicating that the Ru was highly dispersed on the bentonite support [8], which was consistent with the result of TEM image. Moreover, based on the XRD analysis, the basal spacing of the pristine bentonite was 0.97 nm, while the spacing of Ru/bentonite was enlarged to $d_{001} = 1.43$ nm due to the intercalation of Ru nanoparticles in the interlayers of bentonite [19,21].

The electronic state of the Ru element in the catalyst was analyzed by XPS. As shown in Fig. 3, in spite of the interference of the adventitious carbon, the XPS spectrum can be resolved fairly well with two spin-orbit-split doublets from two chemically different Ru entities and the C 1s peak. The peaks at 280.9 eV (Ru 3d5/2) and 284.5 eV (Ru 3d3/2) can be assigned to metallic Ru, while the peaks at 281.6 eV and 286.6 eV showed the presence of Ru oxide which

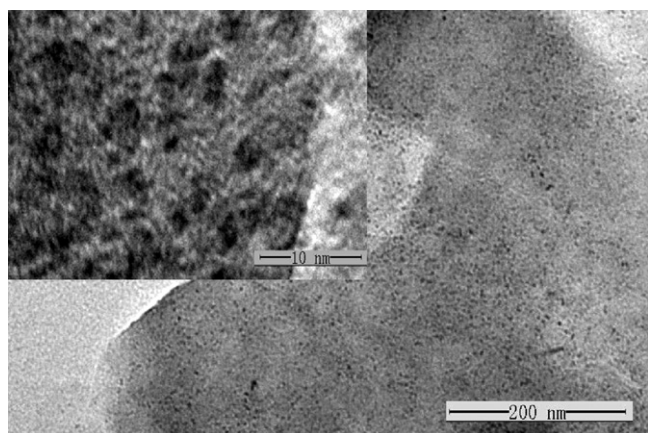


Fig. 1. TEM image of Ru/BEN (IP-HY) catalyst.

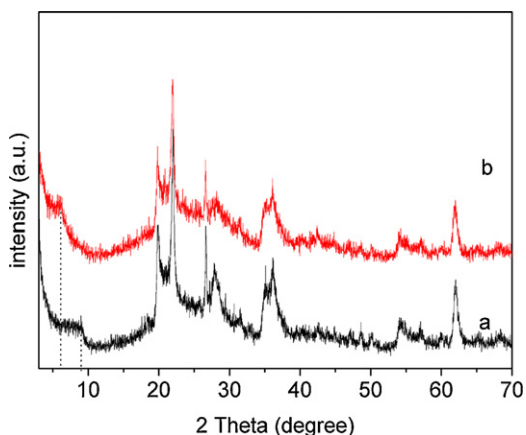


Fig. 2. Wide-angle XRD patterns of (a) bentonite and (b) Ru/BEN (IP-HY) catalyst.

indicated that the presence of a passivated Ru nanoparticles upon exposure to air [23].

3.2. Catalytic performance in selective hydrogenation of benzene

3.2.1. The effect of amount of the catalysts

The influence of catalyst amount on the reduction of benzene was carried out in the range of 2.5–20 mg, while the amount of the benzene, hydrogen pressure and the temperature were kept constant. As shown in Table 1, the selectivity of cyclohexene increased from 32.2% to 51.0% with a decrease in catalyst loading from 20

Table 1

The results of benzene hydrogenation over different amounts of Ru/BEN (IP-HY).

Entry	Catalyst (mg)	Selectivity (%)	Conversion (%)	Yield (%)	Time (min)
1	20	32.2	49.3	15.9	26
2	15	35.4	37.5	13.3	33
3	10	41.6	39.3	16.3	41
4	5.0	51.0	46.9	23.9	65
5	2.5	51.4	44.0	22.6	120

Reaction conditions: benzene, 1.0 mL; reaction temperature, 150 °C; H₂ pressure, 4.0 MPa; ZnSO₄ solution, 0.4 mol/L, 2.0 mL.

to 5.0 mg. Although the entries 4 and 5 had the similar selectivity, the conversion of entry 4 was larger than that of entry 5, which indicated that the yield of entry 4 was larger than that of entry 5. Therefore, with the decreased amount of the catalysts, the selectivity first increased and then decreased as well as the yield with the threshold of catalyst was 5.0 mg. It is worth noting that the molar ratio of substrate to ruthenium was more than 7500 in entry 4, which corresponded to the TOF of 1648 h⁻¹ (TON = mol of cyclohexene product/mol of Ru, TOF = TON/time). The TOF is higher than that of the nanoscale ruthenium catalysts in ionic liquids for the partial hydrogenation of benzene to cyclohexene [24] and the colloidal ruthenium catalyst stabilized by silica [10]. The high activity of the Ru/bentonite was ascribed to the high dispersion, and mainly due to the Ru particles in the interlayers of bentonite [21]. In addition, it can be found in Table 1 that the time of 26 min at a conversion of 49.3% with 20 mg catalyst increased to 120 min at a conversion of 44.0% with 2.5 mg catalyst, which indicated that at the high catalyst load the high reaction rate was obtained, and vice versa. And the similar behavior of the cyclohexene selectivity was found from 32.2% to 51.4% with the decrease of the catalyst load. Due to the ZnSO₄ concentration was kept constant, the decrease of the catalyst load led to the increase of the ruthenium coverage by ZnSO₄ resulting in the increased selectivity but the decreased reaction rate, which was consistent with the literature [25].

3.2.2. The effect of additives on the hydrogenation of benzene

Addition of ZnSO₄ aqueous solution to the reaction slurry has shown to increase the selectivity of hydrogenation of benzene to cyclohexene. Table 2 illustrates the influence of aqueous ZnSO₄ solution on the yield and selectivity of cyclohexene. The selectivity was only 0.7% without water and the ZnSO₄. When only water was added in the hydrogenation process, the reaction proceeded so fast that the conversion reached 58.1% after 17 min, and the selectivity of cyclohexene was increased to 10.5%, indicating that addition of water can greatly enhance the selectivity to cyclohexene. Due to the hydrophilicity of the catalyst, the water can stay on its surface to form a stagnant water film, which results in that the

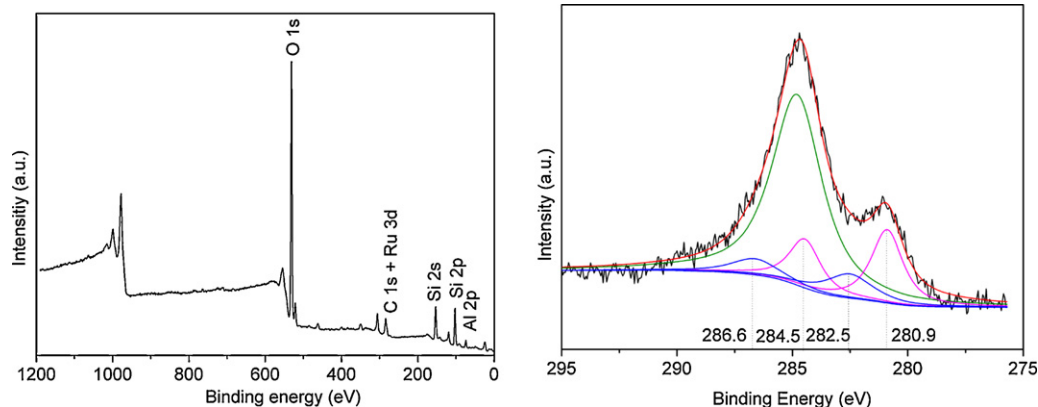


Fig. 3. XPS spectra of Ru/BEN (IP-HY) catalyst.

Table 2
The results of benzene hydrogenation under different ZnSO₄ concentration.

Concentration (mol/L)	Selectivity (%)	Conversion (%)	Yield (%)	Time (min)
Without additives	0.7	40.1	0.3	165
0	10.5	58.1	6.1	17
0.01	13.4	58.9	7.9	17
0.05	39.3	58.2	22.9	33
0.1	43.9	58.5	25.7	47
0.2	44.7	59.6	26.6	65
0.4	44.9	59.7	26.8	66
0.6	44.8	57.3	25.7	58

Reaction conditions: Ru/BEN (IP-HY) catalyst, 5.0 mg; benzene, 1.0 mL; ZnSO₄ solution, 1.0 mL; reaction temperature, 150 °C; H₂ pressure 4.0 MPa.

formation rate of cyclohexene is higher than that of hydrogenation of cyclohexene, and subsequently improve the selectivity because benzene is more soluble than cyclohexene in water [25]. Because of the different solubility of benzene and cyclohexene, the step mechanism is predominant since the hydrogenation of benzene is two consecutive reactions and a parallel one [26]. Furthermore, water competes with cyclohexene to adsorb on the surface, which inhibits the re-adsorption of cyclohexene and thus the hydrogenation of cyclohexene is suppressed [26].

When the concentration of ZnSO₄ was higher than 0.05 mol/L, the selectivity and yield of cyclohexene can be dramatically increased. It is noted that with the increasing concentration of ZnSO₄, the selectivity and yield of cyclohexene greatly enhanced with the maximum of 44.9% and 26.8%, respectively, being observed at the ZnSO₄ concentration of 0.4 mol/L. However, the hydrogenation rate was decreased with the increase of the ZnSO₄ concentration. As a matter of fact, various salts as additives have been studied such as zinc, iron, cobalt, nickel, cadmium, gallium, and indium etc. [4]. Among them, the strong acid salts of zinc, in which zinc sulphate was widely used, were particularly effective [2,27]. The zinc sulphate can be chemisorbed by the ruthenium catalyst to enhance the hydrophilicity and light poison the catalyst to increase the selectivity of cyclohexene [27].

The NaOH as the additive for the partial hydrogenation of benzene has been studied with metal oxides as the support of catalysts. Chen and Hu found that NaOH aqueous solution was prerequisite for ZnO based binary oxides [28–30]. Liu et al. studied the effects of NaOH on the ZnO supported ruthenium catalyst [31]. In this work, the effect of NaOH on the performance of hydrogenation of Ru/BEN (IP-HY) catalyst was investigated, as shown in Table 3. It is interesting that the NaOH can greatly improve the selectivity and gave a yield of cyclohexene (entry 3) similar to that in the presence of ZnSO₄, which was rarely reported with the SiO₂ based support. In the presence of NaOH, the rate of hydrogenation decreased with the increasing amount of NaOH when the amount of catalyst was kept constant (entries 1 and 2, 3 and 4, 5 and 6). Ronchin and Toniolo found that the rate of cyclohexene hydrogenation was depressed whenever the unreduced catalyst was treated with NaOH [26]. It can be proposed that the NaOH and water synergistically enhance the selectivity. NaOH improves the hydrophilicity of Ru catalyst while water and hydroxide anion combine to compete with

Table 3
The results of benzene hydrogenation in NaOH solution.

Entry	Catalyst (mg)	Solvent (mL)	Concentration (mol/L)	Selectivity (%)	Conversion (%)	Yield (%)	Time (min)
1	20	2.0	0.4	51.4	43.1	22.1	38
2	20	1.0	0.4	30.0	55.0	16.5	31
3	10	1.0	0.4	45.5	56.6	25.8	105
4	10	1.0	0.1	25.9	63.9	16.5	32
5	5	1.0	0.4	59.3	37.3	22.1	418
6	5	1.0	0.1	39.3	54.8	21.5	86

Reaction conditions: Ru/BEN (IP-HY) catalyst; benzene, 1.0 mL; NaOH solution; reaction temperature, 150 °C; H₂ pressure, 4.0 MPa.

Table 4
Hydrogenation of cyclohexene with additives.

Entry	Additives	Concentration (mol/L)	Time (min)	Conversion (%)
1	H ₂ O	–	65	11.9
2	ZnSO ₄	0.4	65	1.1
3	NaOH	0.4	69	0.4

Reaction conditions: Ru/BEN (IP-HY) catalyst, 5.0 mg; cyclohexene, 1.0 mL; water, 1.0 mL; reaction temperature, 150 °C; H₂ pressure 4.0 MPa.

cyclohexene to adsorb on the catalyst surface and result in the disfavor of hydrogenation of cyclohexene to cyclohexane.

To investigate the promotion effects of salt additives on the selective hydrogenation of benzene, cyclohexene hydrogenation to cyclohexane was studied under the same conditions as the hydrogenation of benzene. As shown in Table 4, by adding ZnSO₄ and NaOH the hydrogenation of cyclohexene can be greatly suppressed. It appeared that NaOH suppressed the hydrogenation of cyclohexene more strongly than ZnSO₄. Actually, the additives suppressed the hydrogenation of benzene to cyclohexene as well as hydrogenation of cyclohexene to cyclohexane. However, the hydrogenation of cyclohexene to cyclohexane was more suppressed, therefore giving the high selectivity [32].

The FT-IR was employed to study the effects of ZnSO₄ and NaOH. Aqueous solution of ZnSO₄ (0.4 mol/L) or NaOH (0.4 mol/L) were mixed separately with cyclohexene in the volume ratio of 1:1 and then stirred for an hour. Then the organic phase was used to record the FT-IR spectra. Compared with the pure cyclohexene, the interaction between the additives and cyclohexene were not observed from the FT-IR spectra of cyclohexene treated with ZnSO₄ or NaOH aqueous solution, which implied that the interaction between the cyclohexene and the additives was weak in this condition. Similar experiments were also conducted to investigate the interaction between benzene and ZnSO₄ or NaOH and the same results were obtained. Actually, Li et al. have theoretically proved that the formation of M(H₂O)_n(cyclohexene)_m²⁺ and M(H₂O)_n(benzene)_m²⁺ complexes from Zn²⁺ in water is energetically unfavorable [33]. Therefore the additives may not enhance the selectivity to cyclohexene through their interactions with cyclohexene or benzene, and probably through their interactions with the catalyst. Struijk et al. have proved that the additives covered the ruthenium not only to afford hydrophilicity of the catalyst but also to temper the intrinsic activity of the catalyst to lower the adsorption enthalpy of benzene and of cyclohexene [27]. Furthermore, water afforded the stagnant water film around the catalyst which brought the difference in solubility of benzene and cyclohexene. All of these effects combined together resulted in the enhanced selectivity.

3.2.3. The effect of reaction temperature

The effects of temperature on cyclohexene yield and benzene conversion were investigated in the temperature range from 120 to 175 °C over the Ru/BEN (IP-HY) catalyst. As shown in Table 5, the yields of cyclohexene increased firstly, and slightly decreased at the temperatures higher than 160 °C when the temperature

Table 5
The results of benzene hydrogenation under different temperatures.

Temperature (°C)	Selectivity (%)	Conversion (%)	Yield (%)	Time (min)
170	45.5	56.6	25.8	66
165	46.9	54.1	25.4	66
160	45.9	59.2	27.2	66
155	44.3	59.9	26.5	66
150	44.9	59.7	26.8	66
145	44.5	59.2	26.3	66
140	41.2	60.3	24.8	66
130	41.3	52.7	21.8	66
120	29.6	53.4	15.8	114

Reaction conditions: Ru/BEN (IP-HY) catalyst, 5.0 mg; benzene, 1.0 mL; H₂ pressure, 4.0 MPa; ZnSO₄ solution, 0.4 mol/L, 1.0 mL.

Table 6
The results of benzene hydrogenation under different pressures.

Pressure (MPa)	Selectivity (%)	Conversion (%)	Yield (%)	Time (min)
8	43.7	59.5	26.0	39
7	45.2	61.5	27.8	66
6	46.6	58.8	27.4	47
5	46.0	58.0	26.7	60
4	44.9	59.7	26.8	66
3	39.8	58.4	23.2	91
2	11.4	50.7	5.8	283

Reaction conditions: Ru/BEN (IP-HY) catalyst, 5.0 mg; benzene, 1.0 mL; ZnSO₄ solution, 0.4 mol/L, 1.0 mL; reaction temperature, 150 °C.

was increased. With the increasing temperature, the desorption of cyclohexene is promoted and the hydrogen coverage on the surface of catalyst is lower, which reduces the further hydrogenation of cyclohexene [25]. However, the solubility of cyclohexene and benzene are increased in the stagnant water film around the catalysts when elevating the reaction temperature [34], which lead to the enhancement of the cyclohexene hydrogenation. The counteracting of the opposite effects gives the maximum yield of cyclohexene.

3.2.4. The effect of the pressure

The influences of the hydrogen pressure on benzene conversion and on cyclohexene yield were studied by a series of experiments under the varying pressure from 2 MPa to 8 MPa. The relationship between the yield and hydrogen pressure is presented in Table 6. The yield of cyclohexene increased with elevating pressure from 2 MPa to 7 MPa, and then decreased slightly when the pressure increased to 8 MPa. The result indicates that there is an optimum pressure which gives the highest yield of cyclohexene. At low pressures, the step mechanism is predominant [10]. Furthermore, the hydrogenation of cyclohexene to cyclohexane is less dependent on the pressure than the hydrogenation of benzene to cyclohexene [35], which gave the high yield of cyclohexene. In addition, the hydrogen coverage is increased with the increasing hydrogen of pressure, which leads to the gradual increase of the hydrogenation rate. However, at high pressures, the rate decreases for that the adsorption of benzene is the relatively slow step in the reactants due to the excessive coverage of hydrogen on the surface [28]. The hydrogenation of cyclohexene to cyclohexane becomes easier at high pressures [10,36]. As a result, the yield of cyclohexene declined after a certain high hydrogen pressure was reached, corresponding to 7 MPa in the pressure range studied.

3.2.5. The effect of reaction time

The course of hydrogenation of benzene over Ru/BEN (IP-HY) catalyst in ZnSO₄ solution is presented in Fig. 4. With the increasing of the conversion, the selectivity decreased while the yield of cyclohexene first increased then declined gradually. In the reaction time range of 66–85 min, the yield of cyclohexene was almost constant,

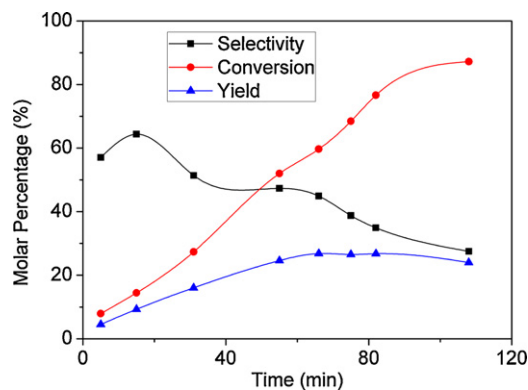


Fig. 4. The reaction course of benzene hydrogenation. Reaction conditions: Ru/BEN (IP-HY) catalyst, 5.0 mg; benzene, 1.0 mL; ZnSO₄ solution, 1.0 mL, 0.4 mol/L; reaction temperature, 150 °C; H₂ pressure, 4.0 MPa.

which indicated the formation and hydrogenation of cyclohexene temporarily reached balance.

4. Conclusions

The Ru/BEN (IP-HY) catalyst prepared by impregnation-hydrothermal method exhibited high activity for benzene hydrogenation with good selectivity to cyclohexene. The presence of an additive is essential for getting good cyclohexene yields. Both ZnSO₄ and NaOH can suppress the hydrogenation of cyclohexene and improve the selectivity and yield of cyclohexene. Water played an important role in this system to enhance the selectivity. This catalyst is easily prepared, cheap and environmentally friendly.

Acknowledgements

The authors are grateful to National Natural Science Foundation of China (20932002), Ministry of Science and Technology of China (2011CB808600) and Chinese Academy of Sciences (KJCX2.YW.H30.02) for financial supports.

References

- [1] S. Liu, Z. Liu, Z. Wang, Y. Wu, P. Yuan, J. Chem. Eng. 139 (2008) 157–164.
- [2] H. Nagahara, M. Ono, M. Konishi, Y. Fukuoaka, Appl. Surf. Sci. 121–122 (1997) 448–451.
- [3] S. Hu, Y. Chen, J. Chin. Inst. Chem. Eng. 29 (1998) 387–396.
- [4] P. Kluson, L. Cerveny, Appl. Catal. A: Gen. 128 (1995) 13–31.
- [5] Y. Zhao, J. Zhou, J. Zhang, S. Wang, J. Mol. Catal. A: Chem. 309 (2009) 35–39.
- [6] H. Sun, W. Guo, X. Zhou, Z. Chen, Z. Liu, S. Liu, Chin. J. Catal. 32 (2011) 1–16.
- [7] P.T. Suryawanshi, V.V. Mahajani, J. Chem. Technol. Biotechnol. 69 (1997) 154–160.
- [8] J. Liu, L. Zhu, Y. Pei, J. Zhuang, H. Li, H.X. Li, M. Qiao, K.N. Fan, Appl. Catal. A: Gen. 353 (2009) 282–287.
- [9] J. Bu, J.L. Liu, X.Y. Chen, J.H. Zhuang, S.R. Yan, M.H. Qiao, H.Y. He, K.N. Fan, Catal. Commun. 9 (2008) 2612–2615.
- [10] J. Ning, J. Xu, J. Liu, F. Lu, Catal. Lett. 109 (2006) 175–180.
- [11] V. Mazzieri, N. Figoli, F. Pascual, P. L'Argentière, Catal. Lett. 102 (2005) 79–82.
- [12] V. Mazzieri, F. Coloma-Pascual, A. Arcoya, P.C. L'Argentière, N.S. Figoli, Appl. Surf. Sci. 210 (2003) 222–230.
- [13] J. Wang, P. Guo, S. Yan, M. Qiao, H. Li, K. Fan, J. Mol. Catal. A: Chem. 222 (2004) 229–234.
- [14] Y. Zhao, J. Zhou, J. Zhang, S. Wang, Catal. Lett. 131 (2009) 597–605.
- [15] Y. Zhao, J. Zhou, J. Zhang, D. Li, S. Wang, Ind. Eng. Chem. Res. 47 (2008) 4641–4647.
- [16] C.H. Zhou, Appl. Clay Sci. 53 (2011) 87–96.
- [17] R. Zhang, F. Li, N. Zhang, Q. Shi, Appl. Catal. A: Gen. 239 (2003) 17–23.
- [18] M. Mazzei, W. Marconi, M. Riocci, J. Mol. Catal. 9 (1980) 381–387.
- [19] D. Divakar, D. Manikandan, G. Kalidoss, T. Sivakumar, Catal. Lett. 125 (2008) 277–282.
- [20] D. Divakar, D. Manikandan, T. Sivakumar, J. Chem. Technol. Biotechnol. 83 (2008) 1472–1478.
- [21] S. Miao, Z. Liu, B. Han, J. Huang, Z. Sun, J. Zhang, T. Jiang, Angew. Chem. Int. Ed. 45 (2006) 266–269.
- [22] H. Liu, T. Jiang, B. Han, S. Liang, Y. Zhou, Science 326 (2009) 1250–1252.

- [23] H. Dai, X. Kang, P. Wang, *Int. J. Hydrogen Energy* 35 (2010) 10317–10323.
- [24] E.T. Silveira, A.P. Umpierre, L.M. Rossi, G. Machado, J. Morais, G.V. Soares, I.J.R. Baumvol, S.R. Teixeira, P.F.P. Fichtner, J. Dupont, *Chem. Eur. J.* 10 (2004) 3734–3740.
- [25] J. Struijk, M. d'Angremond, W. Regt, J. Scholten, *Appl. Catal. A: Gen.* 83 (1992) 263–295.
- [26] L. Ronchin, L. Toniolo, *Appl. Catal. A: Gen.* 208 (2001) 77–89.
- [27] J. Struijk, R. Moene, T. Van der Kamp, J. Scholten, *Appl. Catal. A: Gen.* 89 (1992) 77–102.
- [28] S. Hu, Y. Chen, *Ind. Eng. Chem. Res.* 36 (1997) 5153–5159.
- [29] S. Hu, Y. Chen, *J. Chem. Technol. Biotechnol.* 76 (2001) 954–958.
- [30] S. Hu, Y. Chen, *Ind. Eng. Chem. Res.* 40 (2001) 3127–3132.
- [31] H. Liu, S. Liang, W. Wang, T. Jiang, B. Han, *J. Mol. Catal. A: Chem.* 341 (2011) 35–41.
- [32] P. Yuan, B. Wang, Y. Ma, H. He, Z. Cheng, W. Yuan, *J. Mol. Catal. A: Chem.* 309 (2009) 124–130.
- [33] Z. Li, J. Liu, M. Qiao, K. Fan, *Mol. Phys.* 107 (2009) 1271–1282.
- [34] J. Wang, Y. Wang, S. Xie, M. Qiao, H. Li, K. Fan, *Appl. Catal. A: Gen.* 272 (2004) 29–36.
- [35] C.U.J. Odenbrand, S.T. Lundin, *J. Chem. Technol. Biotechnol.* 30 (1980) 677–687.
- [36] H. Liu, T. Jiang, B. Han, S. Liang, W. Wang, T. Wu, G. Yang, *Green Chem.* 13 (2011) 1106–1109.