



Ruthenium containing hydrotalcite as a heterogeneous catalyst for hydrogenation of benzene to cyclohexane

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ABSTRACT

Ruthenium containing hydrotalcite (Ru-HT) was synthesized by partial substitution of Mg²⁺ or Al³⁺ cations by ruthenium metal in octahedral layers of hydrotalcite and used as a catalyst for hydrogenation of benzene to cyclohexane. Effect of catalyst amount, reaction temperature, partial pressure of hydrogen and volume of solvent on conversion of benzene was studied in detail. Higher conversion of benzene in lower reaction time was observed in lower volume of solvent. Complete conversion of benzene with 100% selectivity of cyclohexane was observed at 120 °C reaction temperature and 60 atm partial pressure of H₂ in 2 h reaction time. Presence of moisture in the reaction mixture showed negligible effect on catalytic activity of Ru-HT, however, activity decreased significantly on increasing the sulfur concentration. Catalyst was recycled upto four times without significant loss in its activity. No conversion of benzene was observed in case of pristine hydrotalcite (without ruthenium) as a catalyst.

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1. Introduction

Hydrogenation of benzene to cyclohexane is of significant importance in the petroleum industry and for environmental protection due to stringent environmental legislation established worldwide [1–6]. It is known that the presence of aromatics result into poor ignition quality and lower cetane number of diesel. It raises the smoke point of jet fuel and also increases the emission of particulate matters [2–4]. Thus, removal of aromatic compounds is valuable for enhancing the fuel quality as the cetane number of diesel fuel increases with decreasing aromatic content [2–4,7]. The hydrogenation of benzene is important in the petrochemical industries for the production of cyclohexane, which is one of the key intermediates in the synthesis of Nylon-6 and Nylon-66 [8]. Thus, the development of active catalysts for benzene hydrogenation could also be useful from commercial point of view.

For hydrogenation of benzene metal sulfides and noble metal supported catalysts are generally studied [2–4,9,10]. Although cat-

alytic activity of these metal sulfide catalysts is not sufficient to reach the required aromatic saturation but these catalysts have the advantage of high sulfur tolerance. Noble-metal supported catalysts, which can work at lower temperatures to avoid the thermodynamic constraints associated with the metal sulfides, are preferred for aromatic saturation. The activity of noble metals supported catalysts synthesized by impregnation and anchored/intercalation method are widely studied for hydrogenation reaction (Table 2) [3,11–19]. The main drawback of impregnated catalysts is leaching of active metal from the support [19]. Therefore, more efforts are directed on anchored/intercalation approach to avoid leaching problem. Recently, Ru(0)/NaY catalyzed hydrogenation of benzene was reported in solvent free conditions at 22 °C and 3 atm hydrogen pressure [20]. The cracking of aromatic hydrocarbons to low molecular weight compounds and undesired coke formation during hydrogenation reaction was also reported on the use of acidic supports. Therefore, emphasis has been made in the present study to develop a catalyst based on a basic support to avoid cracking reactions as well as leaching of metal during the hydrogenation reaction.

Hydrotalcite (HT) is a class of anionic clays in which some of the divalent cations (Mg²⁺) have been substituted with trivalent cations (Al³⁺) resulting into positively charged layers. This charge is balanced by anions intercalated in the interlayer space [21]. Various metal ions can be introduced into the brucite layer via isomorphic substitution of Mg²⁺ or Al³⁺ cations at the octahedral sites, which are supposed to be active sites for catalytic reactions. Vaccari et al. synthesized hydrotalcite having rhodium (Rh) and ruthenium

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(Ru) cations and used for partial oxidation of methane to syn-gas ($\text{CO} + \text{H}_2$) [22]. Ruthenium supported hydrotalcite have been efficiently demonstrated by several other researchers for the synthesis of various organic transformation reactions [23–28]. The novelty of the present study lies in the synthesis of a highly active catalyst via partial substitution of Mg^{2+} or Al^{3+} cations by ruthenium metal cations in octahedral layers of hydrotalcite (Ru-HT) for hydrogenation of benzene. The effect of reaction temperature, partial pressure of hydrogen, amount of catalyst, volume of solvent and reusability of catalyst was studied for the hydrogenation of benzene. The effect of moisture and sulfur content on the catalytic activity of Ru-HT for hydrogenation of benzene was also studied.

2. Experimental

2.1. Catalyst synthesis and characterization

Ruthenium grafted hydrotalcite (Ru-HT) was prepared using the procedure reported in the literature [24,28]. In a typical synthesis procedure, an aqueous solution (A) of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0432 mol), $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ (0.0144 mol) and $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (0.0005 mol) was prepared in 50 mL double distilled de-ionized water. The solution A was added dropwise into a second solution (B) containing NaOH (0.13 mol) and Na_2CO_3 (0.0747 mol) in 50 mL double distilled de-ionized water under vigorous stirring at room temperature. Following this, the content was transferred into a teflon coated stainless steel autoclave and aged at 70°C for 16 h. After that the precipitate formed was filtered and washed thoroughly with hot distilled water until filtrate was free from Cl^- ions and has pH 7. The washed precipitate was dried in an oven at 80°C for 14 h. For the comparison, hydrotalcite ($\text{Mg}-\text{Al}-\text{CO}_3$) having Mg/Al ratio of 3.5 (HT-3.5) was also synthesized without adding $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in solution A.

2.2. Hydrogenation of benzene

Hydrogenation of benzene was performed in 100 mL stainless steel Parr reactor (Parr Instrument Co., USA, Model 4843). In a typical experiment, desired concentration of benzene, catalyst, *n*-tridecane (0.1 g, as GC internal standard), and *n*-hexane as a solvent (50 mL) were charged into the reactor. Reactor was then brought to desired reaction temperature, which was considered as the zero time. Hydrogenation reaction was initiated by starting the stirrer at 600 rpm. Constant pressure of reactor was maintained by supplying the hydrogen during the reaction. For kinetic analysis, samples were withdrawn via sampling valve from the reactor at different time interval during the course of reaction. In each case, the change in concentration of reactant was determined by gas chromatography (GC, Shimadzu 17A, Japan) equipped with a flame ionization detector (FID), 5% diphenyl and 95% dimethyl siloxane universal capillary column (60 m length and 0.25 mm diameter). Furthermore, reaction mixture was analyzed by GC-MS (Shimadzu, GC-MS QP 2010, Japan) to confirm the products via mass fragmentation patterns. Initial rate of reaction was calculated by reported method in lower conversion range [29]. Few kinetic experiments were carried out by varying the agitation speed from 100 to 600 rpm initially to find out pure kinetic regime. Rate of reaction was observed to be independent of agitation speed after 400 rpm, which indicate negligible diffusional (mass transfer) resistance and hence reaction is in kinetic regime, therefore, all experiments were performed at 600 rpm. To ensure reproducibility of the results, repeated experiments were carried out under identical reaction conditions and data were found to be reproducible within $\pm 2\%$ variation.

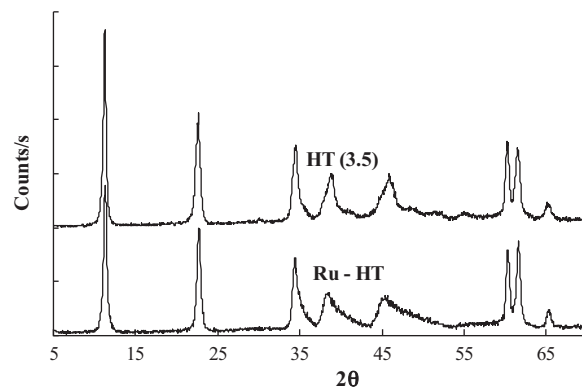


Fig. 1. P-XRD patterns of HT-3.5 and Ru-HT samples.

3. Results and discussion

The catalyst was characterized thoroughly by various instrumental techniques and detailed characterization is reported elsewhere [28]. Powder X-ray diffraction (P-XRD) pattern of Ru-HT sample showed all typical characteristic peaks of pure hydrotalcite containing carbonate anions ($d_{(003)} = 7.65 \text{ \AA}$) and revealed a good dispersion of aluminum and ruthenium in the brucite-like layers (Fig. 1). Any additional peak corresponding to another crystalline phase was not observed in the XRD of Ru-HT which confirmed that the characteristic original planes of hydrotalcite are retained after incorporation of ruthenium in the brucite-like sheet. However, an amorphous phase was reported in the literature for the higher Ru content hydrotalcite samples [22]. Crystallinity of hydrotalcite sample was observed to decrease for Ru-HT sample as compared to HT-3.5. Crystallite size of HT-3.5 and Ru-HT samples were calculated as 18.2 nm and 11.2 nm, respectively at (003) plane. Slight increase in the value of unit cell parameter (*a*) was also observed for Ru-HT (3.069 \AA) as compared to HT-3.5 (3.064 \AA) due to larger ionic radii of ruthenium (0.68 \AA) as compared to aluminum (0.53 \AA), however, value of *c* was observed to decrease from 23.38 \AA for Ru-HT to 23.41 \AA for HT-3.5 sample [28]. BET surface area of HT-3.5 and Ru-HT was found to be 76 and 80 m^2/g , respectively [28]. Pore volumes of HT-3.5 and Ru-HT were calculated as 0.42 and 0.36 cm^3/g , respectively and mean pore diameters of HT-3.5 and Ru-HT samples were found to be 22.8 and 18.2 nm, respectively. Percentage ruthenium content in Ru-HT was calculated by chemical analysis using Inductive Coupled Plasma (ICP) Spectrometer and found to be 1.0% (by wt). No significant difference was observed in the ICP analysis of Ru-HT related to the Mg/Al molar ratio and was found to be in accordance with the calculated compositions.

3.1. Effect of catalyst amount

Effect of the catalyst amount on conversion of benzene to cyclohexane was studied by varying the amount of catalyst from 0.02 to 0.25 g at 13 mmol benzene concentration at 120°C and 60 atm partial pressure of H_2 using *n*-hexane as a solvent. The corresponding results at varied amount of catalyst and reaction time are shown in Fig. 2a. It was observed that the 11% conversion of benzene was obtained using 0.04 g catalyst amount that increased to 52% at 0.05 g of catalyst amount after 2 h. Complete conversion of benzene was observed at 0.1 g catalyst amount in same reaction time. The conversion of benzene was not affected by further increase in the amount of catalyst to 0.25 g under the employed experimental conditions. However, higher conversion of benzene was observed in the lower reaction time at higher catalyst amount. 76% conversion of benzene was achieved within 15 min at 0.25 g cata-

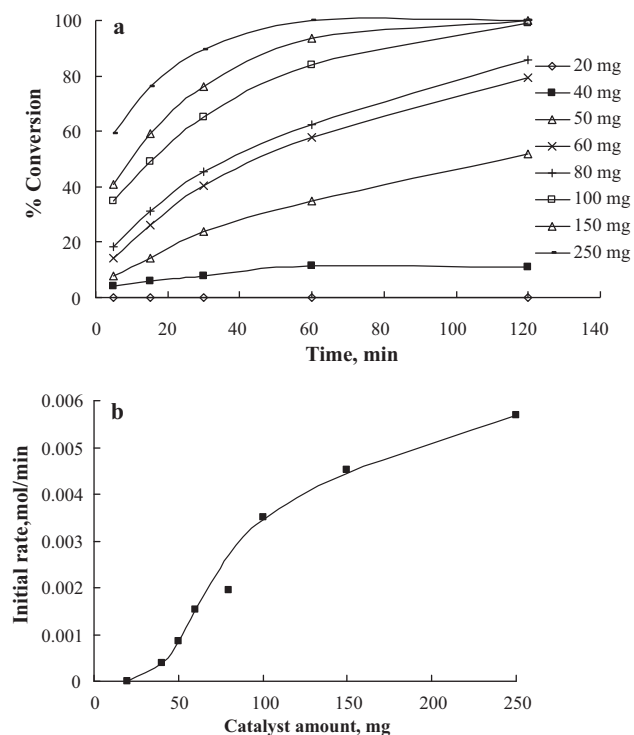


Fig. 2. (a) Effect of catalyst amount on the (a) conversion of benzene with respect to reaction time using Ru-HT catalyst and (b) initial rate of reaction.

lyst amount, which decreases to 44% at 0.1 g and only 8% at 0.04 g catalyst amount in similar reaction time (15 min).

The higher conversion of benzene at higher catalyst amount can be explained in terms of the number of active sites present on the surface of catalyst. The active sites for the hydrogenation of benzene are the ruthenium cations attached to the hydroxyl groups via isomorphic substitution of Mg or Al cations at the octahedral and are located at the surface and edges of the sheets. As the amount of catalyst increases, catalytically active sites also increase which results into higher conversion of benzene. Only one product of benzene hydrogenation, i.e., cyclohexane was formed under the studied experimental conditions. This may be due to a concerted hydrogenation mechanism wherein cyclohexene (C_6H_{10}) formed is directly converted to cyclohexane (C_6H_{12}) before it is desorbed from the catalyst surface. Effect of catalyst amount on initial rate of reaction is shown in Fig. 2b. Observed “S” shape of the initial rate curve suggested that the reaction is very slow at lower amount of catalyst. Initial rate of reaction was calculated as 87×10^{-5} mol/min at 0.05 g catalyst amount which increased to 345×10^{-5} mol/min at 0.1 g catalyst amount. At 0.25 g, the rate of reaction was found to be 568×10^{-5} mol/min. The further reaction parameters were optimized by taking 0.1 g of catalyst amount and 13 mmol of benzene concentration since after 0.1 g catalyst amount no significant effect on conversion of benzene was observed in 2 h.

To confirm the role of ruthenium present in the Ru-HT catalyst, one experiment for benzene hydrogenation was carried out using HT-3.5 (Mg–Al– CO_3) as a catalyst at $120^\circ C$ and 60 atm partial pressure of hydrogen. No conversion of benzene was observed even after 4 h reaction time, which indicates that the ruthenium present in the Ru-HT catalyst is only the active metal centre (or active sites) for hydrogenation of benzene in the present study.

3.2. Effect of reaction temperature

Catalytic activity for hydrogenation of benzene was observed to increase on increasing the reaction temperature upto $120^\circ C$

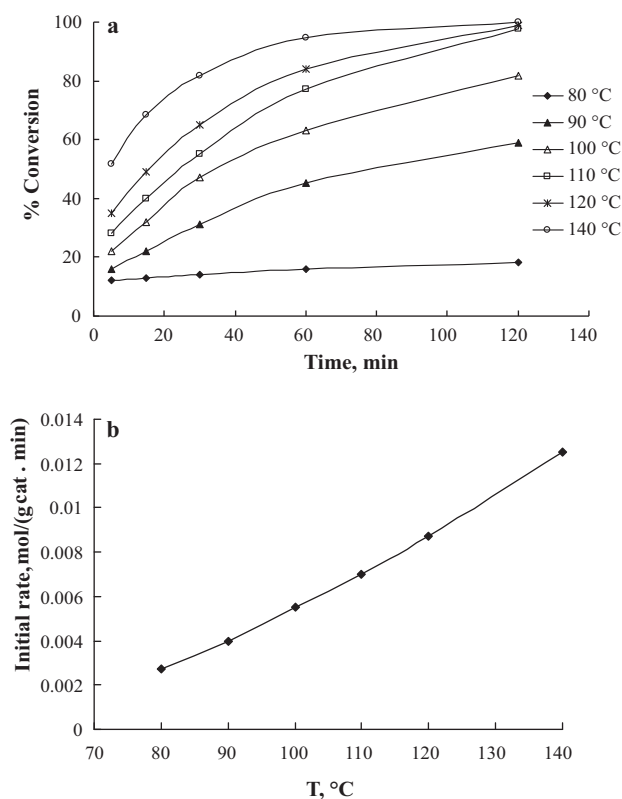


Fig. 3. Effect of reaction temperature on the (a) conversion of benzene at varied reaction time using Ru-HT as a catalyst and (b) initial rate of reaction.

(Fig. 3a). The complete conversion of benzene to cyclohexane was achieved at $120^\circ C$. On further increase in the reaction temperature to $140^\circ C$, the conversion of benzene reached to 82% in 30 min. Initial rate of reaction was found to increase almost linearly on increasing the reaction temperature (Fig. 3b). Initial rate of reaction was calculated as 275×10^{-5} mol/(g_{cat} min) at $80^\circ C$ that increased to 700×10^{-5} mol/(g_{cat} min) at $110^\circ C$. On further increasing the temperature to $140^\circ C$, the rate of reaction was found to be 125×10^{-4} mol/(g_{cat} min). Higher rate of reaction was observed in the present study as compared to the use of rhodium intercalated montmorillonite as a catalyst for hydrogenation of benzene [15]. The activation energy for hydrogenation of benzene was calculated using Arrhenius plot (plot of $\ln k$ vs $1/T$) in the temperature range of 80 – $110^\circ C$. The activation energy for the reaction was found to be 35.2 kJ/mol. From the literature it was observed that activation energy for liquid phase hydrogenation of benzene varies in a wide range depending on the experimental conditions and the catalyst used. However, in general activation energies for hydrogenation of benzene in liquid phase were reported in the range of 35–62 kJ/mol using Pt and Ni based catalysts [30–32]. Calculated activation energy in the present study also indicated that the reaction is far away from the diffusional (mass transfer) limitations and is in the pure kinetic regime.

3.3. Effect of partial pressure of hydrogen

The conversion of benzene to cyclohexane was observed to increase linearly on increasing the partial pressure of hydrogen (Fig. 4a). The complete conversion of benzene to cyclohexane was obtained at 60 atm partial pressure of H_2 . The higher hydrogen pressure favors low equilibrium concentrations of benzene which results into higher conversion of benzene in lower reaction time. Increase in the partial pressure of hydrogen increases

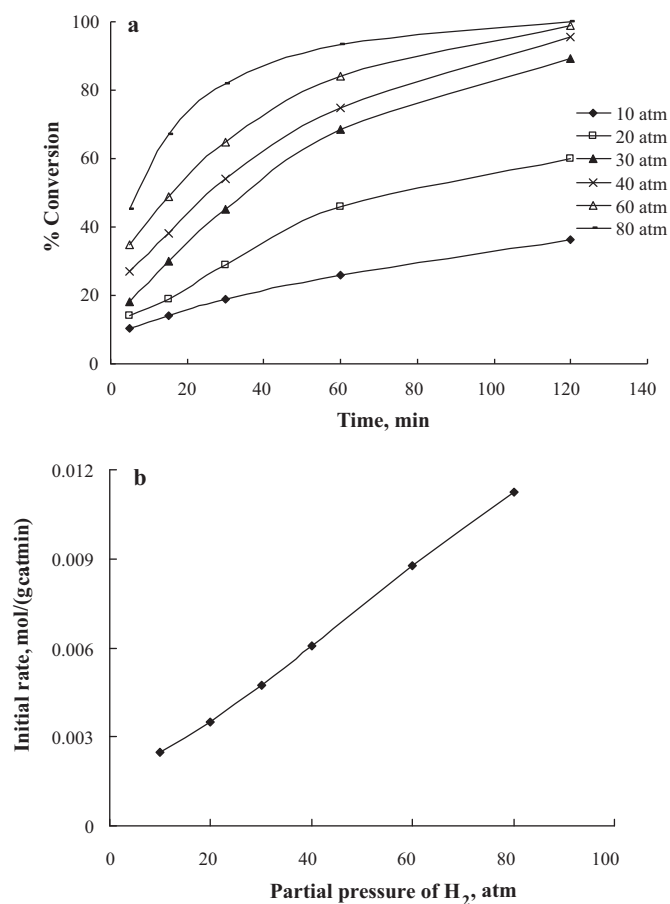


Fig. 4. Effect of partial pressure of hydrogen on the (a) conversion of benzene at varied reaction time using Ru-HT as a catalyst and (b) initial rate of reaction.

hydrogen dissociation on the metal (Ru) sites of the catalyst and, thus, increased the concentration of hydrogen available for benzene hydrogenation. Therefore, at higher partial pressure of hydrogen, the adsorption and desorption of hydrogen on the metal surface is higher, which increases the conversion of benzene. Initial rate of reaction was observed to increase almost linearly on increasing the partial pressure of hydrogen (Fig. 4b). Initial rate of reaction was calculated as 250×10^{-5} mol/(g_{cat} min) at 10 atm, which increased upto 0.0112 mol/(g_{cat} min) at 80 atm partial pressure of hydrogen.

3.4. Effect of solvent volume

The results illustrated in Fig. 5 showed that the concentration of solvent plays an important role in inhibiting the conversion of benzene. At 20 mL *n*-hexane volume, 97% conversion of benzene was observed in 1 h that decreased to 89% on increasing the volume of solvent to 40 mL. On further increase in the solvent volume to 60 mL, benzene conversion was observed to decrease significantly to 81%. This trend continued with further increase in the solvent volume. However, 100% conversion of benzene was observed in the studied solvent volumes (20–80 mL) on increasing the reaction time from 1 to 2 h. The lower conversion of benzene at higher volume of solvent could be due to the dilution effect.

3.5. Effect of moisture and sulfur content

To study the effect of moisture on the catalytic activity of Ru-HT for hydrogenation of benzene, the experiments were carried out by varying the water content (0.1, 0.5, 1 and 2 mL) in the 50 mL *n*-hexane (Table 1). No significant difference was observed even at

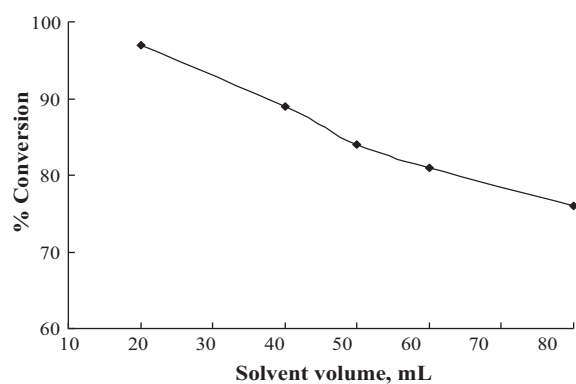


Fig. 5. Effect of solvent volume on the conversion of benzene using Ru-HT as a catalyst.

Table 1

Effect of moisture content on the catalytic activity of Ru-HT for hydrogenation of benzene.

Run	Water, mL	% Conversion of benzene	% Selectivity of cyclohexane
1	0.1	100	100
2	0.5	100	100
3	1.0	99	100
4	2.0	99	100

Reaction conditions: Benzene = 13 mmol; Ru-HT = 0.1 g; $T = 120^\circ\text{C}$; Partial pressure of hydrogen = 60 atm; Reaction time = 2 h.

2 mL water content on the conversion of benzene (99%) and selectivity for cyclohexane (100%), which indicates that the activity of Ru-HT as a catalyst was not affected by the presence of moisture in the reaction mixture. The formation of cyclohexene was not observed even at 2 mL water content in the reaction mixture.

The effect of sulfur on the catalytic activity of Ru-HT for benzene hydrogenation was studied by varying the sulfur (thiophene as a sulfur source) concentration from 1 to 20 ppm at 0.1 g Ru-HT catalyst, 13 mmol benzene concentration, 120°C and 60 atm pressure of hydrogen (Fig. 6). The conversion of benzene was observed to decrease drastically on increasing the concentration of sulfur in the reaction mixture. Complete conversion of benzene (100%) was observed in the absence of sulfur that decreased to 96% on addition of 1 ppm sulfur. As the concentration of sulfur increased to 3 ppm, conversion of benzene decreases to 45%. Decrease in the catalyst activity of Ru-HT in the presence of sulfur is mainly due to the strong adsorption of sulfur on the metal sites (M–S bond formation), which results into loss of active metal sites available for the hydrogenation reaction [33]. The adsorption of sulfur compound during the reaction was also confirmed by the FT-IR spectra of the Ru-HT (Fig. 7;

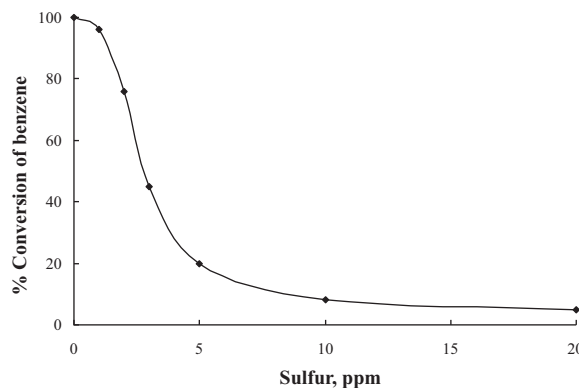


Fig. 6. Effect of sulfur concentration on the catalytic activity of Ru-HT for hydrogenation of benzene.

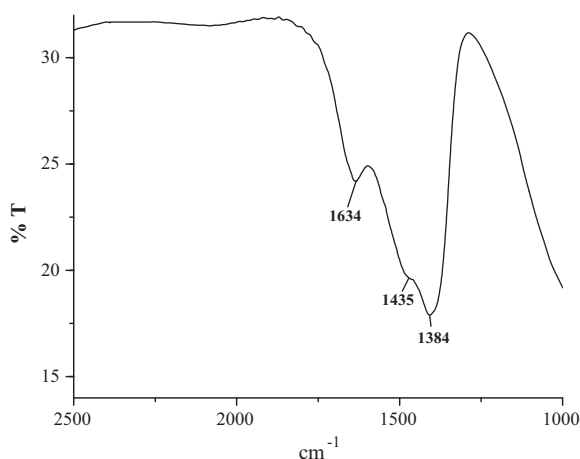


Fig. 7. FT-IR spectra of Ru-HT after thiophene adsorption.

after exposure to the 20 ppm sulfur solution). The peak appeared at 1435 cm^{-1} in the FT-IR spectra of the Ru-HT sample is attributed to the adsorbed thiophene to the metal surface. The bands at 1634 and 1384 cm^{-1} showed the presence of interlayer water molecules and carbonates anions, respectively [21].

3.6. Reusability of catalyst

For reusability experiments, the catalyst was filtered from the reaction mixture, washed with 50 mL *n*-hexane and dried at $80\text{ }^{\circ}\text{C}$ for 10 h. The regenerated catalyst was used for hydrogenation of benzene under similar reaction conditions as used for the fresh catalyst. No significant loss in the conversion of benzene and selectivity of cyclohexane was observed upto four cycles (Fig. 8), suggesting that the catalyst is reusable upto four cycles under employed reaction conditions. The ICP analysis of spent catalyst after fourth cycle showed $\sim 0.99\text{ wt.}\%$ ruthenium was present in the catalyst. The initial rate of reaction for liquid phase hydrogenation of benzene was observed to decrease slightly at the end of fourth cycle (Fig. 9).

One sample was synthesized by impregnation of ruthenium on hydrotalcite (HT) to compare its catalytic activity with Ru-HT sample for hydrogenation of benzene. The catalytic activity of Ru impregnated on HT also showed similar conversion and selectivity to Ru-HT catalyst. However, conversion of benzene was observed to decrease on reusability of the catalyst due to leaching of ruthenium from support.

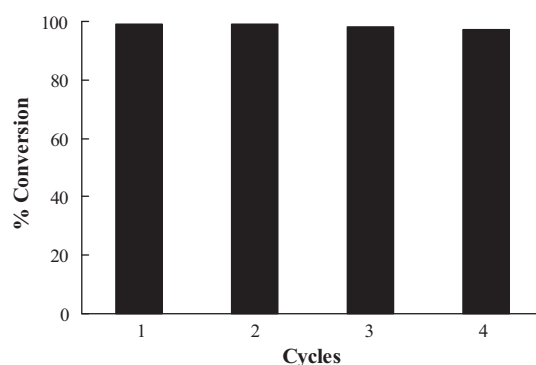


Fig. 8. Reusability of Ru-HT catalyst for hydrogenation of benzene.

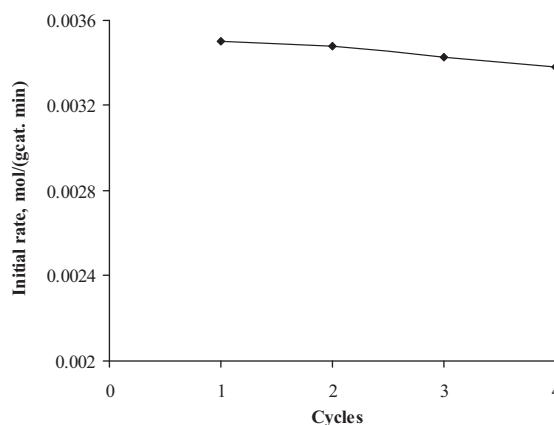


Fig. 9. Effect of catalyst reusability on initial rate of reaction.

20% leaching of ruthenium from impregnated catalyst was confirmed by ICP analysis after second reusability test. The catalytic activity of Ru-HT was also compared with other reported catalysts in the literature for hydrogenation of benzene to cyclohexane (Table 2) and found that Ru-HT as a reusable catalyst gave 100% selectivity to cyclohexane with complete conversion of benzene.

Table 2

Comparison of catalytic activity of Ru-HT with other catalysts for hydrogenation of benzene to cyclohexane.

Catalyst	Observation/Remarks	Ref.
Ru exchanged montmorillonite	Complete benzene conversion was achieved with 100% selectivity of cyclohexane at $100\text{ }^{\circ}\text{C}$ and 34.5 bar hydrogen pressure; sensitive to higher sulfur concentration	[13]
Ru(0) nanoclusters in intrazeolite (Y)	90% of benzene with turnover of 2420 mol benzene/mol Ru and a TOF value of 1040 mol benzene/(mol Ru h) was reported at $22\text{ }^{\circ}\text{C}$ and 40 psi g hydrogen pressure	[14]
Rh intercalated montmorillonite	Complete conversion of benzene with 100% cyclohexane selectivity at $180\text{ }^{\circ}\text{C}$ and 62 atm hydrogen pressure; sensitive to sulfur	[15]
Ru/Hectorite	71% benzene conversion was achieved with 100% selectivity of cyclohexane after 1.1 h at $50\text{ }^{\circ}\text{C}$ and 50 bar hydrogen pressure	[16]
RuO ₂ (<i>in situ</i> reduced to Ru ⁰)	100% conversion of benzene at $75\text{ }^{\circ}\text{C}$ and 4 atm hydrogen pressure; mixture of cyclohexane and cyclohexene as a product; sensitive to sulfur; poor reusability of catalyst	[17]
Ni/Carbon nanofibers [2–15% Ni (by wt)]	99.5% conversion of benzene was achieved after 7 h using 10% Ni (by wt) loaded CNFs at $180\text{ }^{\circ}\text{C}$	[5]
Ru(III) tetrahydro-Schiff base complexes encapsulated in zeolite Y	Ru[H ₄]salen-Zeolite Y gave 98.3% conversion of benzene in 2 h reaction time at $60\text{ }^{\circ}\text{C}$ and 30 atm hydrogen pressure; catalyst reused for three times	[18]

4. Conclusions

Ruthenium grafted hydrotalcite (Ru-HT) was found to be an efficient heterogeneous catalyst for hydrogenation of benzene. Complete conversion of benzene was achieved at 120 °C reaction temperature and 60 atm partial pressure of hydrogen with 100% selectivity for cyclohexane. No significant change in the conversion of benzene and selectivity of cyclohexane was observed on addition of water to the reaction system, however, conversion of benzene decreased significantly on increasing the concentration of sulfur in the reaction mixture. The catalyst studied in present study is suitable for the hydrogenation of sulfur free benzene. The catalyst was recycled upto four times without significant loss in its activity and selectivity for hydrogenation of benzene.

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References

- [1] S. Lu, C.A. Menning, Y. Zhu, J.G. Chen, *ChemPhysChem*. 10 (2009) 1763–1765.
- [2] M. Sanati, B. Harrysson, M. Faghihi, B. Gevert, S. Jaras, *Catalysis*, vol. 16, Royal Society of Chemistry, Cambridge, 2002, p. 1 (Chapter 1).
- [3] A. Stanislaus, B.H. Cooper, *Catal. Rev. Sci. Eng.* 36 (1994) 75–123.
- [4] K.B. Sidhpuria, P.A. Parikh, *Bull. Catal. Soc. India* 3 (2004) 67–71.
- [5] P. Liu, H. Xie, S. Tan, K. You, N. Wang, H. Luo, *React. Kinet. Catal. Lett.* 97 (2009) 101–108.
- [6] Wikipedia Benzene effect (<http://en.wikipedia.org/wiki/Benzene>).
- [7] A.C. Pulikottil, U. Manna, M. Santra, R.P. Verma, *Bull. Catal. Soc. India* 1 (2002) 9–17.
- [8] J.F.L. Page, *Applied Heterogeneous Catalysis: Design, Manufacture, Use of Solid Catalysts*, Technip, Paris, 1987, pp. 291.
- [9] B.H. Cooper, B.B.L. Donnis, *Appl. Catal. A: Gen.* 137 (1996) 203–223.
- [10] R.L. Augustine, *Heterogeneous Catalysis for the Synthetic Chemist*, Marcel Dekker, New York, 1996, p. 17 (Chapter 17).
- [11] K.B. Sidhpuria, P.A. Parikh, P. Bahadur, B. Tyagi, R.V. Jasra, *Catal. Today* 141 (2009) 12–18.
- [12] K.B. Sidhpuria, P.A. Parikh, P. Bahadur, R.V. Jasra, *Ind. Eng. Chem. Res.* 47 (2008) 4034–4042.
- [13] A.B. Boricha, H.M. Mody, H.C. Bajaj, R.V. Jasra, *Appl. Clay Sci.* 31 (2006) 120–125.
- [14] M. Zahmakiran, S. Ozkar, *Langmuir* 24 (2008) 7065–7067.
- [15] K.B. Sidhpuria, H.A. Patel, P.A. Parikh, P. Bahadur, H.C. Bajaj, R.V. Jasra, *Appl. Clay Sci.* 42 (2009) 386–390.
- [16] G. Süss-Fink, F. Khan, J. Boudon, V. Spassov, *J. Clust. Sci.* 20 (2009) 341–353.
- [17] L.M. Rossi, G. Machado, *J. Mol. Catal. A: Chem.* 298 (2009) 69–73.
- [18] P. Chen, B. Fan, M. Song, C. Jin, J. Ma, R. Li, *Catal. Commun.* 7 (2006) 969–973.
- [19] J. Panpranot, K. Phandinthong, P. Praserttham, M. Hasegawa, S. Fujita, M. Arai, *J. Mol. Catal. A: Chem.* 253 (2006) 20–24.
- [20] M. Zahmakiran, T. Kodaira, S. Ozkar, *Appl. Catal. B: Environ.* 96 (2010) 533–540.
- [21] F. Cavani, F. Trifiro, A. Vaccari, *Catal. Today* 11 (1991) 173–301.
- [22] (a) F. Basile, L. Basini, G. Fornasari, M. Gazzano, F. Trifiro, A. Vaccari, *Chem. Commun.* (1996) 2435–2436;
(b) F. Basile, G. Fornasari, M. Gazzano, A. Vaccari, *Appl. Clay Sci.* 16 (2000) 185–200.
- [23] K. Kaneda, Patent No. JP2005255599-A to Shionogi & Co. Ltd. (2005).
- [24] K. Kaneda, T. Yamashita, T. Matsushita, K. Ebitani, *J. Org. Chem.* 63 (1998) 1750–1751.
- [25] T. Matsushita, K. Ebitani, K. Kaneda, *Chem. Commun.* (1999) 265–266.
- [26] K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 126 (2004) 5662–5663.
- [27] H. Fukuhara, F. Matsunaga, Y. Nakashima, US Patent 4923837-A (1990) to Mitsui Petrochemical Ind. Ltd.
- [28] S.K. Sharma, P.A. Parikh, R.V. Jasra, *J. Mol. Catal. A: Chem.* 317 (2010) 27–33.
- [29] H.S. Fogler, *Elements of Chemical Reaction Engineering*, Third Ed., Prentice-Hall, Inc., USA, 2002.
- [30] J. Franco, S. Marzuka, J. Papa, J.T. de Herrera, *Recent Prog. Genie Proc.* 13 (1999) 123–130.
- [31] Y.D. Murzin, A.N. Sokolova, V.N. Kulkova, I.M. Temkin, *Kinet. Katal.* 30 (1989) 1352–1358.
- [32] S. Toppinen, T.K. Rantakyla, T. Salmi, J. Aittamaa, *Ind. Eng. Chem. Res.* 35 (1996) 1824–1833.
- [33] L.J. Simon, J.G. van Ommen, A. Jentys, J.A. Lercher, *J. Catal.* 201 (2001) 60–69.