

# Partial hydrogenation of benzene to cyclohexene over $Ru/\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocatalyst via w/o microemulsion using boric acid and ethanolamine additives

S. U. Nandanwar<sup>1</sup> · A. A. Dabbawala<sup>2</sup> · M. Chakraborty<sup>1</sup> · H. C. Bajaj<sup>2</sup> · S. Mukhopadhyay<sup>3</sup> · K. T. Shenoy<sup>3</sup>

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**Abstract** Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocatalyst was synthesized by water-in-oil reverse microemulsion technique and characterized by TEM, SEM–EDX, XRD, N<sub>2</sub> adsorption–desorption, and H<sub>2</sub> chemisorption. The surface area and active sites (S<sub>M</sub>) of 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was obtained around 217.6 m<sup>2</sup>/g and 45.70 m<sup>2</sup>/g<sub>cat</sub>, respectively. The catalyst performance of Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was assessed in the selective hydrogenation benzene to cyclohexene in the presence of boric acid (BA) and ethanolamine (EA) additives. The effect of such specific additives alone and in combination on the activity and selectivity of benzene hydrogenation was systematically investigated. Ru catalyst displayed pre-eminent performance at 0.5 mmol ratio of BA to EA exhibiting the highest selectivity (40 %) and yield (16 %) of the intermediate product, cyclohexene at 40 % of benzene conversion.

**Keywords** Ruthenium nanocatalyst  $\cdot$  Ethanolamine (EA)  $\cdot$  Selective hydrogenation  $\cdot$  Cyclohexene  $\cdot$  Intermediate

S. U. Nandanwar sunandanwar@gmail.com

M. Chakraborty mch@ched.svnit.ac.in

- <sup>1</sup> Department of Chemical Engineering, S.V. National Institute of Technology, Surat 395 007, Gujarat, India
- <sup>2</sup> Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSMCRI-CSIR), Bhavnagar 364 021, Gujarat, India
- <sup>3</sup> Chemical Engineering Division, Bhabha Atomic Research Center (BARC), Mumbai 400 085, Maharashtra, India

## Introduction

Benzene hydrogenation has significant importance in the petrochemical industry due to stern environmental regulations established worldwide for the presence of aromatics in fuels [1–5]. Hydrogenation of benzene produces two products cyclohexene and cyclohexane. Cyclohexene is the intermediate product. Conventionally, benzene is difficult to hydrogenate due to the resonance stabilization energy and occurs under drastic temperature/pressure over a metal-supported heterogeneous catalyst [6]. The two types of strategies can be realized for the benzene hydrogenation: (1) to develop efficient catalyst systems to hydrogenate benzene under mild conditions [7–9], and (2) to enhance the selectivity of cyclohexene, i.e. selective hydrogenation of benzene to cyclohexene [10–29]. Generally, cyclohexene can be produced by different processes like cyclohexanol dehydrogenation, dehydrogenation of cyclohexane and dehydrohalogenation of cyclohexane halide but suffer from the lower efficiency and complicity to recover the product [18, 30].

Among the reported catalysts in the literature for benzene hydrogenation [10–31], a ruthenium-based catalyst has been indicated as being more effective than other metal catalysts, while the addition of a second transition metal, metal salt, NaOH, or ionic liquids are necessary to enhance cyclohexene selectivity [18-27]. Liu et al. [16] developed a novel Ru/ZnO–ZrOx(OH)y catalyst and reported 56 % yield and 76 % selectivity of cyclohexene. Schwab et al. [25] carried out hydrogenation of benzene using a  $Ru/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of ionic liquids, [B3MPyr][DCA] and achieved 11 % yield with 60 % selectivity. Zanutelo et al. [26] reported that the catalytic performance of a Ru/C system was influenced by functional groups (e.g. carbonyl, carboxylic group) present on the activated carbon surface. Zhou et al. [27] reported that Ru-B/ZrO<sub>2</sub>-T produced 47 % yield and 56 % selectivity of cyclohexene. Spinace and Vaz [28] reported that 14 % and 60 % yields of cyclohexene and conversion of benzene were obtained, respectively, at 423 K and 5 MPa of hydrogen pressure using a Ru/SiO<sub>2</sub> catalyst. A waterorganic mixture such as ethylene glycol/water and glycerol/water, which consist mainly of hydrated organic molecules, can enhance the hydrophilicity around the ruthenium particles favoring cyclohexene desorption. Schwab et al. [29] reported 70 % selectivity of cyclohexene using a Ru/La<sub>2</sub>O<sub>3</sub> catalyst in the presence of a small amount of sodium dicyanamide (NaDCA). The Ru-B/TNS catalyst enhances the catalytic performance toward the selective hydrogenation of benzene to cyclohexene, yielding 50.7 % cyclohexene without any additives [33]. Recently, Wu et al. [34] reported that the addition of a small amount of ZnO in a NaOH solution effectively enhanced the selectivity to cyclohexene and the yield of cyclohexene could reach 41.5 % over a Ru/TiO2 catalyst.

A great deal of progress has been made in the recent past by developing inorganic salts, additional transitional metal and expensive ionic liquid free catalyst systems for selective benzene hydrogenation. The present work describes noncorrosive, inexpensive and efficient catalyst system for selective hydrogenation of benzene. In this context,  $Ru/\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocatalyst, synthesized by water-in-oil (w/o)

microemulsion, was used in presence of BA and EA as task-specific additives. Effect BA to EA molar ratio and different other organic additives on selective hydrogenation of benzene in presence of BA were also studied.

# Materials and methods

# Materials

Ruthenium trichloride (RuCl<sub>3</sub>.*n*H<sub>2</sub>O, Ru content  $\geq$ 37 %), cyclohexane and acetone were purchased from Finar Chemicals, India. Benzene was purchased from Qualigens Fine chemicals, India. Sodium borohydride (NaBH<sub>4</sub>, 95 %), boric acid (BA), ethanolamine (EA) and polyoxyethylene octyl phenyl ether (Triton X-100) were purchased from S.D. Fine Chemicals, India. The support,  $\gamma$ -alumina powder, Al<sub>2</sub>O<sub>3</sub> of 98 % purity and 100 mesh size was purchased from National Chemicals, India. All chemicals were used without further purification. Distilled water (Millipore, Elix, India) was used throughout the experiments.

# Synthesis of supported Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst

Ru nanoparticles were synthesized by w/o reverse microemulsion technique comprising cyclohexane, Triton X-100 as surfactant, aqueous solution of salt, RuCl<sub>3</sub> and reducing agent, NaBH<sub>4</sub>, as reported [35]. A 1–5 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocatalyst was synthesized by transferring the Ru nanoparticles onto the support to maintain the homogeneous distribution. The concentrated colloidal Ru nanoparticles (accumulated after repeated experimentation) were re-dispersed in methanol, and a known quantity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support was added under vigorous stirring. The mixture was mechanically stirred (6500 rpm using Ultraturax) for 24 h. After evaporating the methanol, the mixture was washed with acetone and water to remove the organic and inorganic impurities, and dried at 100 °C for 6 h. Ruthenium nanoparticles supported on  $\gamma$ -alumina (dark brown colour powder) were calcined at 300 °C for 8 h in an oven.

# **Catalytic reaction**

Partial hydrogenation of benzene was carried out in a 100 mL stainless steel autoclave (model E 01055A; Autoclave Engineers, USA) equipped with a controlling unit. The high-speed magnetic stirrer was adjusted to 1500 rpm. In a typical experiment, 5 mL benzene (56.33 mmol), 15 mL solvent, aqueous and synthesized catalyst, and 100 mg Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were charged into the reactor. Before starting the reaction, the autoclave was flushed with nitrogen three times, followed by flushing with hydrogen twice at room temperature, after which the autoclave was brought to the reaction temperature and pressurized with hydrogen at the desired pressure. After reaching the suitable temperature and pressure, the reaction was started. After 30 min reaction time, the stirring was stopped and autoclave was cooled in an ice bath. The catalyst was recovered by filtration, and the liquid was

separated into two layers in aqueous and oil. The product was analysed by GC (Shimadzu 17A, Japan) with a flame ionization detector (FID). A 5 % diphenyl and 95 % dimethyl siloxane universal capillary column (60 m length and 0.32 mm diameter) was used to analyze the reactant and product. The product was analyzed by GC (Shimadzu 17A, Japan) with FID. The initial column temperature was increased from 40 to 200 °C at the rate of 10 °C/min. N<sub>2</sub> gas was used as a carrier gas. Conversion of benzene ( $C_{\text{Benzene}}$ ), selectivity of cyclohexene ( $S_{\text{Cyclohexene}}$ ) and yield of cyclohexene ( $Y_{\text{Cyclohexene}}$ ) were calculated by the following equation:

$$\% C_{\text{Benzene}} = \frac{\text{Mole of reacted benzene}}{\text{Mole of initial benzene}} \times 100$$
(1)

$$\% S_{\text{Cyclohexene}} = \frac{\text{Mole of cyclohexene formed}}{\text{Mole of reacted benzene}} \times 100$$
(2)

$$\% Y_{\text{Cyclohexene}} = \frac{\text{Mole of cyclohexene formed}}{\text{Mole of initial benzene}} \times 100$$
(3)

### Characterization

The surface morphology and size of the Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was analyzed by using transmission electron microscopy (TEM) (JEOL, JEM 2100) and scanning electron microscopy (SEM–EDX) (LEO SUPRA 35VP). Powder X-ray diffraction (P-XRD) measurement of supported Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was carried out using a Philips X'Pert-MPD diffractometer employing Ni-filtered Cu  $K\alpha$  radiation with 40 kV and 30 mA at a scanning rate of 5°/min. N<sub>2</sub> adsorption–desorption were measured at liquid nitrogen temperature by a Micromeritics ASAP 2010. The specific active metal surface area was determined by hydrogen chemisorption using an Autochem 2920 Chemisorption analyzer (Micromeritics, USA).

## **Results and discussion**

#### Characterization of Ru/y-Al<sub>2</sub>O<sub>3</sub> nanocatalyst

A TEM image of the 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst is shown in Fig. 1. It was observed that monodispersed and spherical-shaped ruthenium nanoparticles, which were obtained by the water-in-oil microemulsion method, were highly dispersed on the support,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The average size of the ruthenium nanoparticles was in the range of 10–20 nm. SEM–EDX was performed in order to study the morphology and elemental distribution of the synthesized 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocatalyst (Fig. 2). Figure 2a represents the view of the sample at 12.93 KX magnification (Ru nanoparticles were not clearly visible and might be the white spots), and tiny ruthenium nanoparticles cover the whole surface of the support,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. EDX indicated the presence of ruthenium, aluminium and oxygen on the surface of the



Fig. 1 TEM image of 3 wt% Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst

catalyst, no other peak was observed, which indicates that the purity of catalyst was very high (Fig. 2b).

Powder X-ray diffraction (P-XRD) of pure  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst are represented in Fig. 3. The highest peak of alumina was observed at  $2\theta = 67.5$  (Fig. 3a). The smaller peaks of ruthenium were observed due to low content of Ru mainly present on the surface of the support (Fig. 3b). The diffraction peaks at  $2\theta = 44.7^{\circ}$  can be attributed to metallic ruthenium which represented (101) planes of the crystal structure of ruthenium metal. The size of the ruthenium nanoparticles was calculated by the Debey Scherrer formula; it was close to the average diameter (16.7 nm) observed by TEM analysis. A new peak appeared at  $2\theta = 28^{\circ}$  and was assigned to RuO<sub>2</sub> due to the oxidation of air at the time of drying of the catalyst [11].

The nitrogen adsorption–desorption of 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst curve is shown in Fig. 4. It can be concluded from the hysteresis curves that the shape of the pores of this catalyst was capillary cubic with both sides open and the pore size distribution ranged from 4 to 57 nm. The relative pressure (*P*/*P*<sub>0</sub>) at the separate region in the adsorption curve and desorption curves was 0.4. BET surface area of the 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was 217.6 m<sup>2</sup>/g. It was found to be higher when associated with 1–2 wt% Ru loading (not shown). The metal surface area (*S*<sub>M</sub>) and ruthenium dispersion of the catalyst was determined by hydrogen chemisorption, as presented in Table 1. It was observed that 4 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst has maximum active sites (1 % more than 3 wt% Ru loading), but metal clusters were observed due to agglomeration of the particles [36]. Prior to that, 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has



Fig. 2 (a) SEM analysis and (b) EDX analysis of 3 wt% Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst

similar active sites ( $S_M = 45.70 \text{ m}^2/\text{g}_{cat}$ ) for the reaction. Therefore, the 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> prepared catalyst was selected for partial hydrogen of benzene to cyclohexene.

## Effect of amount of boric acid and ethanolamine

The selective hydrogenation of benzene to cyclohexene is a complex process and, usually, Zn salts are added to enhance cyclohexene selectivity. It is also reported



Fig. 3 Powder-XRD of (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (b) 3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst



Fig. 4 Nitrogen adsorption-desorption isotherm for 3 wt% Ru/y-Al<sub>2</sub>O<sub>3</sub> catalyst

that the addition of various organic additives to Zn salts such as ethanolamine, diethanolamine, PEG-6000 and 1,3-propanediol, i.e. combination of both, augmented cyclohexene selectivity more than their counterparts [11]. Such organic additives and inorganic salts are dissolved in the aqueous phase to increase the hydrophilicity of the catalyst and reduce the solubility of cyclohexene, which precludes further cyclohexene hydrogenation. Moreover, the interaction between N or O atoms of organic additives with ruthenium assists the desorption of

Sr. No.	Ru (wt%)	Supported metal surface area per g of catalyst ( $S_M$ , m <sup>2</sup> /g <sub>cat</sub> )
1	1	22.53887
2	2	35.68495
3	3	45.69873
4	4	46.17428
5	5	10.14869

Table 1 Hydrogen chemisorption of Ru/γ-Al<sub>2</sub>O<sub>3</sub> catalyst

cyclohexene, crucial for enhancing the selectivity toward cyclohexene. On the other hand, boron-modified Ru/Al<sub>2</sub>O<sub>3</sub> catalyst, especially the colloidal RuB/Al<sub>2</sub>O<sub>3</sub>·xH<sub>2</sub>O catalyst, displayed high activity and cyclohexene selectivity in the hydrogenation of benzene due to the existence of structural water and surface hydroxyl groups on the RuB/Al<sub>2</sub>O<sub>3</sub>·xH<sub>2</sub>O catalyst [37]. Encouraged by the above results and to replace Znbased inorganic salts, we selected specific additives, boric acid B(OH)<sub>3</sub> (BA) and ethanolamine (EA).

The influence of such specific additives alone and in combination on the activity and selectivity of benzene hydrogenation was systematically investigated using the most commonly used Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (with 3 wt% of Ru) in aqueous. Addition of BA, a mild acidic in nature, considerably increased the conversion of benzene although obvious selectivity to cyclohexene was not realized (Table 2). In the absence of any additives, the hydrogenation of benzene catalyzed by Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> showed 38 % conversion without the formation of cyclohexene in water due to a faster rate of conversion to cyclohexane. When a small amount of BA, 0.74 mmol, was introduced into the system, benzene conversion increased from 38 to 49 % (entry 2), but 0.8 % selectivity of cyclohexene was observed. The opposite trend was observed in the case of EA, with the addition of 1.47 mmol of EA resulting in a decrease in the conversion of benzene from 38 to 34 % (entry 3), and increased the selectivity of cyclohexene up to 16 %. From the individual results of BA and EA, it can be concluded that the catalytic activity was influenced by BA while EA affected

Entry	BA (mmol)	EA (mmol)	BA/EA mmol ratio	% C <sub>Benzene</sub>	$\% S_{cyclohexene}$	% Y <sub>cyclohexene</sub>
1	0	0	0	38	0	0
2	0.74	0	_	49	0.8	0.7
3	0	1.47	_	34	16	5.4
4	0.147	1.47	0.1	41	25	10.2
5	0.74	1.47	0.5	45	27	12.1
6	1.47	1.47	1.0	48	23	11.0

 Table 2
 Effect of amount of boric acid (BA) and ethanolamine (EA) on selective hydrogenation of benzene to cyclohexene

Reaction conditions: temp. = 150 °C, H<sub>2</sub> pressure = 5.0 MPa

the cyclohexene selectivity. The surprising result was observed when both BA to EA were added into the system (entries 4-6). The mmol ratio of BA to EA was varied from 0.1 to 1. The conversion of benzene increased constantly (41-48 %) with an increased mmol ratio of BA to EA from 0.1 to 1.0, whereas the selectivity and yield of cyclohexene increased from 0.1 to 0.5. The selectivity and yield of cyclohexene attained up to 27 and 12 %, respectively, at 0.5 mmol ratio of BA to EA (entry 5). Therefore, further reaction optimizations were carried out at 0.5 mmol ratio of BA to EA. The selectivity and yield of cyclohexene were increased with an increase in the amount of BA and EA at 0.5 mmol ratio. The highest cyclohexene selectivity (40 %) and yield of cyclohexene (16 %) were achieved at 1.44 mmol of BA and 2.88 mmol of EA with a concentration mmol ratio of 0.5 at 40 % conversion of benzene (Table 3, entry 3). The question remains as to why the BA and EA combined at 0.5 mmol ratio causes such an enhancement in the selectivity and yield of cyclohexene. The exact reason is not yet clear, but the authors think that BA enhanced the activity of the catalyst resulted in a higher rate of reaction and proportionally the EA increased the hydrophilicity of the catalyst that controlled the rate of reaction.

## Effect of organic additives

The influence of organic additives on the Ru-based catalyst for hydrogenation of benzene by keeping BA concentration constant is shown in Table 4. In the absence of any organic additives, the conversion of benzene up to 49 and 0.5 % selectivity was observed (entry 1). EA imparted pre-eminent cyclohexene selectivity (27 %) and yield (12 %) at 45 % conversion of benzene in the presence of boric acid at BA/ EA = 0.5 (entry 2). But some amine groups did not show promising results (entries 3–6). The alcoholic additives were not very effective (entries 7–9) for selective hydrogenation of benzene. In all cases, no cyclohexene was formed. From the above results, it can be concluded that the presence of both free amine ( $-NH_2$ ) and free hydroxy (-OH) groups in organic additives having substituted amine or hydroxy groups alone.

The pre-adsorption of additives on the surface of ruthenium could enhance the selectivity to cyclohexene. It has been proposed that the formation of a hydrogen bond (-3 to -5 kJ/mol) between cyclohexene and a modifier molecule weakened

Entry	BA (mmol)	EA (mmol)	% C <sub>Benzene</sub>	% S <sub>Cyclohexene</sub>	% Y <sub>Cyclohexene</sub>
1	0.37	0.72	49	12	5.9
2	0.74	1.44	45	27	12.1
3	1.44	2.88	40	40	16
4	2.16	4.32	25	36	9

Table 3 Effect of BA/EA-0.5 molar ratio amount on selective hydrogenation of benzene

Reaction conditions: temp. = 150 °C; H<sub>2</sub> pressure = 5.0 MPa

Entry	Organic additive	% C <sub>Benzene</sub>	$\% S_{\rm Cyclohexene}$	% Y <sub>Cyclohexene</sub>
1	_	49	0.5	0.3
2	Ethanolamine	45	27	12.1
3	Diethanolamine	63	12	7.6
4	Triethanolamine	71	5	3.7
5	Dimethyl ethanolamine	69	3	2.4
6	Diethyl ethanolamine	70	2	1.5
7	Diethylamine	73	0	0
8	Triethylamine	73	0	0
9	Ethanol	74	0	0

 Table 4
 Effect of different organic additives on selective hydrogenation of benzene in the presence of boric acid

Reaction conditions: boric acid = 0.74 mmol; organic additive = 1.44 mmol; temp. = 150  $^\circ\text{C};~\text{H}_2$  pressure = 5.0 MPa

the overlap of the  $\pi$ -electrons of the C=C double bond in the cyclohexene molecule with the d orbital of ruthenium, so that it caused the hydrogen-bonded cyclohexene to desorb rapidly on the surface of the ruthenium and improved the selectivity to cyclohexene [38, 39]. The additive EA is completely soluble in water and has a high boiling point, and this additive forms a strong interaction with the ruthenium metal



Fig. 5 Effect of temperature on selective hydrogenation of benzene to cyclohexene at BA/EA mmol ratio = 0.5, H<sub>2</sub> pressure = 5 MPa

catalyst. The metal components and the EA interact creating a water layer around the active metal centers, which might be an important reason for the enhancing of the selectivity toward cyclohexene. Due to the interaction between EA and ruthenium, the electron transfer from N or O to d orbital of ruthenium probably occurs and makes ruthenium become an electron-riched center, in which the desorption of cyclohexene becomes easy [11].

#### Effect of temperature

The temperature of the reaction was varied from 110 to 160 °C at constant hydrogen pressure (5.0 MPa) (Fig. 5) keeping the BA/EA mmol ratio at 0.5 (1.44 mmol BA and 2.88 mmol EA). With the increase of reaction temperature from 110 to 150 °C, there was an increase of the selectivity of cyclohexene from 7 to 40 %, but it was dropped to 18 % at 160 °C. Wang et al. [18] suggested that the solubility of benzene and cyclohexene increased in a stagnant water film around the catalyst with raising the reaction temperature, which resulted in the enhancement of the rate of cyclohexene hydrogenation. Also, Struijk et al. [40] suggested that the higher reaction temperature (>150 °C) facilitated the desorption of cyclohexene and hydrogen from the catalyst surface. The best performance for the hydrogenation of benzene to cyclohexene was optimized at 150 °C.



Fig. 6 Effect of pressure on selective hydrogenation of benzene to cyclohexene at BA/EA mmol ratio = 0.5; temp. = 150  $^{\circ}\mathrm{C}$ 

#### Effect of pressure

The effects of hydrogen pressure on the conversion of benzene and selectivity of cyclohexene were studied between 1 and 6 MPa at 150 °C and mmol ratio BA/ EA = 0.5 (1.44 mmol BA and 2.88 mmol EA) (Fig. 6). The selectivity of cyclohexene was increased with an increase in the hydrogen pressure, whereas the benzene conversion was increased gradually with the increase in the hydrogen pressure. The selectivity of cyclohexene at 5 MPa was highest (40 %) compared with the other hydrogen pressures, but, above 5 MPa, the selectivity of cyclohexene decreased. This could be attributed to a decrease in the adsorption of benzene on the catalyst surface due to the excessive coverage of hydrogen on the surface [40]. Moreover, the hydrogenation of cyclohexene to cyclohexane is facilitated at high pressures [16, 42]. As a result, the yield of cyclohexene decreases at high hydrogen pressure, corresponding to 6 MPa in the pressure range studied. The results indicate that 5 MPa is an optimum pressure which gives the highest selectivity of cyclohexene.

# Conclusions

From present work, it was observed that fine-tuning with both and BA and ethanolamine (EA) would improve the yield and selectivity of the intermediate product. Though the obtained result showed a lower yield (16 %) and selectivity (40 %) compared to other reported data, our noncorrosive, inexpensive and efficient catalyst system has proven to be an effective green catalytic process for selective hydrogenation of benzene to cyclohexene.

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