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Development of Heterogeneous Ni-Ni Complex/HPA-RNi Catalyst for Hydrogenation of Benzene

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Raney nickel (RNi) was modified by $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ heteropoly acid (HPA) to give supported HPA-RNi through exchange of ammonium ion. A homo binuclear Ni-Ni complex was synthesized to form Ni-Ni complex/HPA-RNi heterogeneous catalyst, which was used for liquid phase benzene hydrogenation. The complex and the catalyst are well characterized and the heterogeneous catalyst thus prepared was found to be highly active at lower hydrogen pressures of 2.8-3.5 MPa and at moderate temperatures of 393-473 K. The catalyst was 100 % selective towards the formation of cyclohexane. The reaction rates of benzene reduction were considerably higher (1.4-5.0 times) compared to standard hydrogenation catalysts and comparable to those of noble metal catalysts reported in the literature. The catalyst was found to be thermally and chemically stable at higher temperatures and have shown that the hydrogenation of 100 h did not affect the nature of the catalyst.

Keywords: Benzene, Complex catalyst, Mo-heteropoly acid, Hydrogenation, Raney nickel support.

INTRODUCTION

Hydrogenation of aromatic hydrocarbons to their corresponding cyclic compounds is of current interest in the industrialized world because of the stricter environment legislation established in the year 2000 [1]. A high aromatic content in diesel fuel and kerosene has been recognized to contribute to the formation of particulate matter in exhaust gases causing serious air pollution [2]. The major applications of aromatics hydrogenation are in the production of aromatic-free fuels and solvents. The hydrogenation of aromatics can be carried out in gas as well as liquid phases, but the industrial hydrogenations are usually carried out in liquid phase, hence the preparation of active catalysts for liquid phase hydrogenations are of industrially important.

The hydrogenation of benzene is of an industrially important reaction because its reaction products, cyclohexane and cyclohexene are the raw materials for manufacturing nylon-6, nylon-66, cyclohexylamine, adipic acid and many other fine chemicals [3]. Catalysts based on group VIII metals, such as Ni [4], Fe [5], Pt [6], Pd [7], Ru [8] and Co [9] have been used for the hydrogenation of benzene. Among them, Ni and Pt-based catalysts have been extensively studied and are already used in commercial processes. The Ru-based catalysts are often used for partial hydrogenation of benzene to cyclohexene [8]. Some new catalytic materials, such as amorphous metal alloys and ionic liquid like copolymer stabilized nano catalysts in

ionic liquids [10], have also been used for hydrogenation of benzene. The most common (industrial) hydrogenation catalyst has been Raney-nickel, in which nickel is expected to play a major role in the hydrogenation [2,3,11]. Noble metals have also known to be good hydrogenating catalysts giving high conversions at low temperatures and pressures [7,12-16]. The use of heteropoly acids as hydrogenating catalysts has also been reported in the literature, which seem to perform better [11,17,18] than Raney nickel. Hydrogenation of benzene has been done either in liquid or gas phase and in this study the focus is on the liquid phase hydrogenation.

In this work, we have prepared a heterogeneous complex catalyst with Ni-Ni complex/HPA-RNi by exchanging ammonium group of the heteropoly acid. This catalyst was shown to be given higher rates for the liquid phase hydrogenation of benzene and highly specific towards the formation of cyclohexane compared to Raney nickel and heteropoly acid catalysts individually.

EXPERIMENTAL

Preparation of Ni-NiL·2H₂O [L = (CH₃C₆H₂(CH)₂ON₂C₃H₆Cl)₂] macrocyclic complex: 2,6-Diformyl-4-methylphenol (dialdehyde) was prepared according to the procedure given in literature [18,19]. The NMR spectrum of the dialdehyde showed singlets at 11.42 (phenolic), 10.2 (aldehydic), 7.74 (aromatic) and 2.36 ppm (methyl) and was consistent with that of the assigned structure and matched with that given in

literature [18,19]. In order to prepare the macrocyclic ligands, the 2,6-diformyl-4-methylphenol was reacted with 1,3-diaminopropane which gives two identical N_2O_2 sites. The 2,6-diformyl-4-methyl phenol (3.5 g, 0.021 mol) and nickel chloride hexahydrate (5.05 g, 0.021 mol) were taken in 250 mL of isopropanol. To this mixture, 2.34 g (0.0032 mol) of 1,3-diaminopropane was added and stirred with reflux at 353 K for 18 h. The solution was cooled and filtered to separate the solids. The solids obtained were heated with reflux in methanol (200 mL), at 343 K for 3 h with stirring. The green precipitate obtained was collected by filtration and dried.

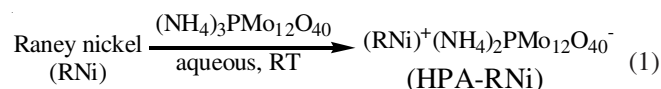
Preparation of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ heteropoly acid (HPA):

An ammonium salt of molybdenum heteropoly acid was prepared according to the procedure reported in literature [19]. Aqueous solution of ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (4.24g, 0.0034 mol) was prepared by dissolving it in 40 mL of water at 373 K. Similarly an aqueous solution of diammonium hydrogen orthophosphate, $(\text{NH}_4)_2\text{HPO}_4$ (0.27 g, 0.002 mol) was prepared in 20 mL of water. Then they were mixed and its pH was adjusted to 1.0 by addition of nitric acid. The yellow precipitate obtained was the ammonium salt of molybdenum heteropoly acid, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ (denoted by HPA). This suspension was directly used for the preparation of the heterogeneous catalyst.

Preparation of $\text{RNi-NH}_4\text{PMo}_{12}\text{O}_{40}$ -Ni-Ni complex catalyst: Leng *et al.* [20,21] has been shown that the ammonium groups of the HPA could be exchanged by organic cations. The following three step method of preparing the heterogeneous catalyst was based on the replacement of the ammonium ions of HPA as given below.

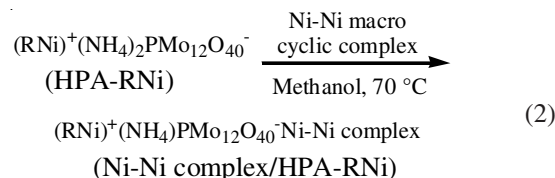
Step-I: Preparation of Raney nickel support: The Raney nickel has been used as support and is prepared by the following procedure given in literature [22]. The 50-50 wt % Ni-Al alloy (100 g) was slowly added in small quantities to 665 mL of a 20 % aqueous NaOH solution without stirring. Once the alloy was added the solution was maintained at boiling point for 2 h and then the solid was washed with a boiling 3 % NaOH solution. A subsequent leaching for another 2 h in a new 20 % NaOH solution was performed. After it has been washed in NaOH solution of decreasing concentrations (10, 6 and 3 %), it was stored in a 3 % alkali solution.

Step-II: Modification of the Raney nickel support with HPA: The aqueous solutions of ammonium heptamolybdate and diammonium hydrogen orthophosphate prepared as above were added to 30 g of the Raney nickel support. The pH of the resulting mixture was then adjusted to 1 by the addition of nitric acid and left for 1 h at room temperature to allow the deposition of HPA on to the Raney nickel support. The deposition was confirmed by an increase in the weight (6.67 % = $100 \times 2/30$) of the solid (30 g) after the filtration and drying and is denoted by HPA-RNi. The replacement of the ammonium groups of HPA would give the bonding with Raney nickel (denoted by RNi) as follows:



Step-III: Preparation of the final catalyst: The Ni-Ni complex (0.5 g) was dissolved in methanol (250 mL) and this

solution was added to 30 g of HPA modified Raney nickel, (HPA-RNi). This was then kept under reflux conditions at 70 °C for 8 h. The black solid material was filtered and dried was the final catalyst having 1.67 % of the complex. This final catalyst is denoted by Ni-Ni/HPA-RNi. The bonding of the Ni-Ni complex would similarly occur by the replacement of another ammonium group of the bonded HPA as follows:



RESULTS AND DISCUSSION

FTIR analysis of the Ni-Ni complex/HPA-RNi catalyst:

The FTIR analysis was carried out on a Bruker Vector 22 instrument in the 4000-400 cm^{-1} wave number range (Fig. 1). The bands corresponding to the C=O and C=N functional groups at 1641 and 1551 cm^{-1} , respectively indicate the presence of Ni-Ni complex on the surface of the support [23]. The deposition of molybdenum heteropoly acid on the surface of the support was shown by the bands at 1410, 1020 and 970 cm^{-1} which represent the stretching vibrations of NH_4^+ ion, P-O and Mo-O, respectively [19,24].

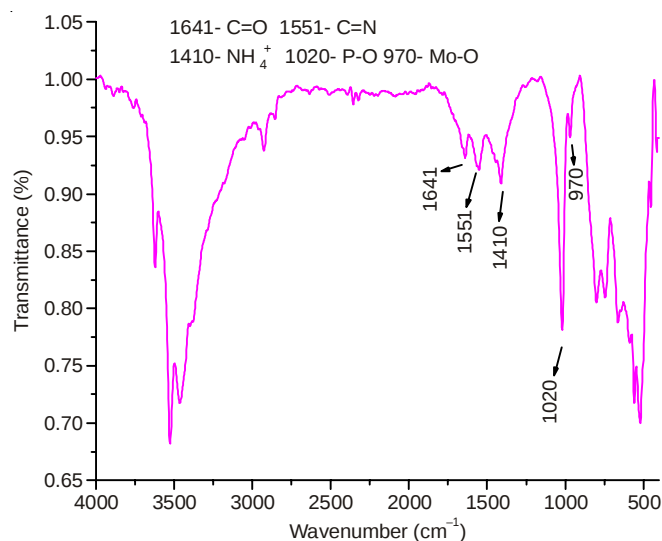


Fig. 1. FTIR Spectra of final heterogeneous catalyst, Ni-Ni complex/HPA-RNi

CHN analysis of Ni-Ni macro cyclic complex: The CHN analysis of the Ni-Ni complex was carried out on a CE-440 elemental analyzer (Leeman Labs Inc., USA). About 3-5 mg of the powdered sample is taken and first homogenized at 80 °C. Helium gas was used as a carrier and O_2 as oxidant and the sample was heated up to 950 °C. The percentage of carbon, hydrogen and nitrogen present in the complex were determined experimentally as: C, 45.231; H, 4.720; N, 8.895 %. The theoretical values (carbon, hydrogen and nitrogen in the complex) are calculated from the molecular structure of the complex $(\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_2\text{Ni}_2)\text{Cl}_2\cdot 2\text{H}_2\text{O}$, as C-45.933; H-4.785; N-8.931 % and experimental values are in good agreement with the theoretical values indicating that the assumed complex was formed.

X-ray diffraction analysis of catalyst: X-ray diffraction measurements of the catalyst were carried out on a Sietronics XRD diffractometer equipped with Cu-K α ($\lambda = 1.54$ nm) radiation. The voltage and current applied to the X-ray tube were 40 kV and 20 mA, respectively and the sampling step was set at 0.05° with scanning speed as $3^\circ/\text{min}$ ($2\theta = 10$ to 80°). The XRD pattern of the final catalyst, Ni-Ni/HPA-RNi is shown in Fig. 2. The diffraction peaks in the range of $2\theta = 40$ -50, 50-55, 75-80 correspond to the Raney nickel [25,26], $2\theta = 10$ -20 and 25-30 correspond to the deposition of molybdenum heteropoly acid (HPA) [19,27]. The absence of the diffraction peaks corresponding to Ni-Ni complex (at $2\theta = 40$ -45 and 70 -75, taken for pure complex) is due to the overlapping of the Ni-Ni peaks with those of Raney nickel peaks (at $2\theta = 40$ -50, 50-55 and 75-80, taken for pure Raney nickel) [28].

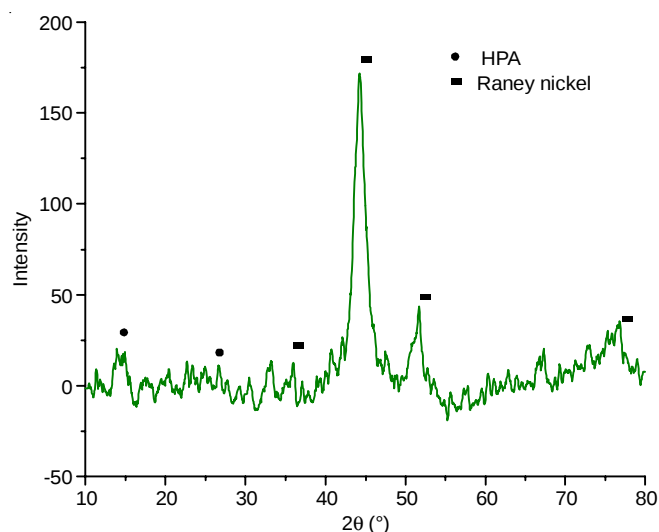


Fig. 2. XRD pattern of Ni-Ni complex/HPA-RNi catalyst

Scanning electron microscope (SEM) and EDX analysis:

The energy-dispersive X-ray spectrometry (SEM-EDX) analysis of the Ni-Ni complex has been taken on a JEOL JSM-840A and the presence of the nickel in the macro cyclic complex has been confirmed. The powder sample is gold coated under vacuum to make it conducting for electrons. The percentage of nickel in the macrocyclic complex obtained is 21.08 % corresponding to the theoretical value of 18.72 % based on the molecular structure of the complex ($\text{C}_{24}\text{H}_{26}\text{N}_4\text{O}_2\text{Ni}_2$) $\text{Cl}_2 \cdot 2\text{H}_2\text{O}$. The SEM micrographs (all at 200 nm) of the Raney nickel, HPA modified Raney nickel and final heterogeneous catalyst are shown in Figs. 3a-3c, respectively. The deposition of molybdenum heteropoly acid on Raney nickel support is confirmed by the presence of extra material as shown in the Fig. 3b, whose surface morphology is different from that of pure Raney nickel support (Fig. 3a). The SEM micrograph of the heterogeneous catalyst (*i.e.* RNi-NH $_4$ PMo $_{12}$ O $_{40}$ -Ni-Ni complex) shows (Fig. 3c) that the complex was present on the support in the form of tiny crystallites and the HPA in the form of white spots. To find out the reason for the formation of crystals on the surface of the support, we impregnated the Ni-Ni macrocyclic complex (0.5 g) directly on Raney nickel support (30 g) without any modification (denoted by Ni-Ni complex/R-Ni) and its SEM micrograph is shown in Fig. 3d. From this Fig. (3d) it is clearly

shown that the macro cyclic complex is responsible for the formation of crystallites on the surface of the support. The shape of the crystallites of Ni-Ni complex in Ni-Ni/HPA-RNi (Fig. 3c) is different from those of the Ni-Ni complex on Ni-Ni complex/R-Ni (Fig. 3d). This indicates that there is an interaction between the deposited molybdenum heteropoly acid and the Ni-Ni complex, which produces a new crystalline complex on the surface of the Raney nickel.

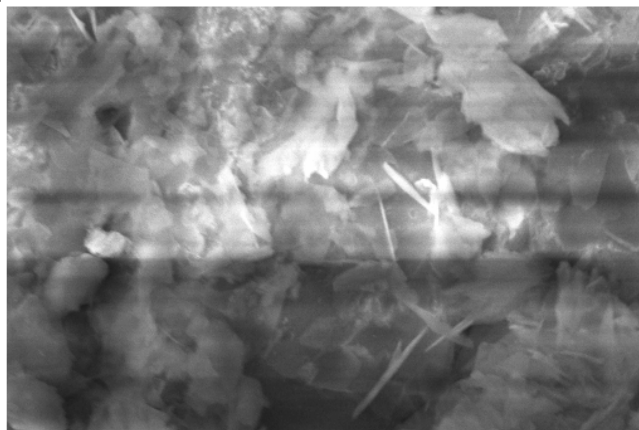


Fig. 3a. SEM micrograph of Raney nickel, RNi

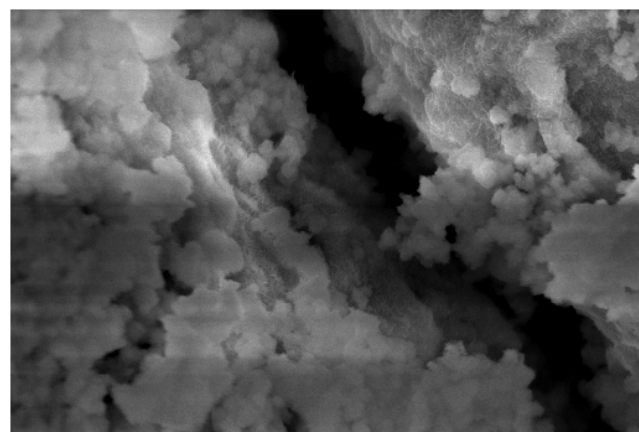


Fig. 3b. SEM micrograph of HPA modified Raney nickel, HPA-RNi

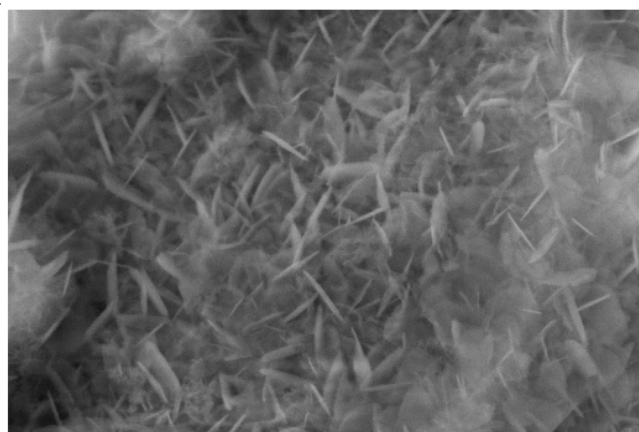


Fig. 3c. SEM micrograph of final heterogeneous catalyst, Ni-Ni complex/HPA-RNi

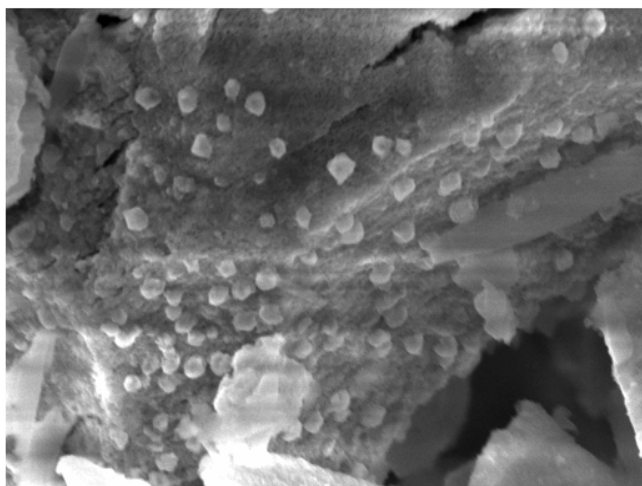


Fig. 3d. SEM micrograph of Ni-Ni complex supported Raney nickel, Ni-Ni complex/RNi

Hydrogenation of benzene: A high pressure (approx. 7.0 MPa) batch reactor made of stainless steel (330 mL volume) was used for conducting the hydrogenation reactions. Liquid phase benzene hydrogenation was initially carried out at 363 K and 2.8 MPa of hydrogen pressure and found that in 8 h of reaction time there was no conversion of benzene, a 25 % conversion is obtained at a temperature of 393 K and 2.8 MPa pressure. However, the conversion increases to 84 % at 423 K and 2.8 MPa and to 98 % at 473 K and 2.8 MPa. *i.e.* the rate of the reaction increases by about 4 times with an increase in temperature from 393 to 473 K.

Reaction at constant hydrogen pressure: The reaction was carried out at a constant pressure of 2.8 MPa and at four different temperatures (393, 423, 443 and 473 K). The variation of benzene concentration with time and temperature is shown in Fig. 4. The amount of conversion increases with increase in temperature. For an increase in temperature from 393 to 423 K, the rise in conversion is from 25 to 84 %, whereas for a temperature change of 443 to 473 K, the increase in conversion is only about 6 %. This indicates that the catalyst is more sensitive at low temperatures. The maximum conversion obtained is 98 % at 473 K and 2.8 MPa hydrogen pressure indicating that the reaction is irreversible. Experiments in this temperature range suggest that the reaction is zero order in terms of benzene concentration at constant hydrogen pressure. The reaction rate at 423 K and 2.8 MPa is nearly 1.50 times the rate with RuCoB/ γ -Al₂O₃ catalyst at 423 K and 5.0 MPa pressure [12] and nearly 5 times with the Ru-Y zeolite catalyst at 333 K and 3.0 MPa hydrogen pressure [14].

Reaction at constant temperature: In order to determine the exponent *m* for H₂ pressure dependency in eqn. 1, we carried out the hydrogenation at constant temperature of 423 K and four different hydrogen pressures {2.07, 2.41, 2.8 and 3.45 MPa}. By determining the value of 'n' at each pressure, the order of reaction in terms of H₂ pressure (*m*) is calculated according to the procedure mentioned above from eqn. 5. The dependency of the reaction rate on hydrogen pressure varies in the range of 0.9 to 1.30 depending upon the benzene concentration (*C_A*). The reaction orders (*m*) of 0.5 to 1.0 in terms of hydrogen pressure have been reported in literature [1].

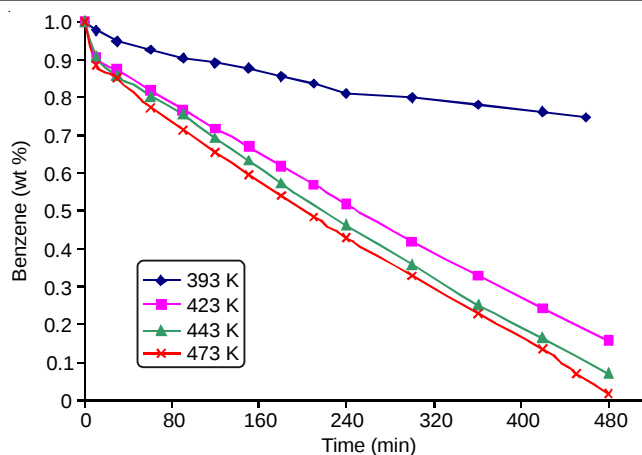
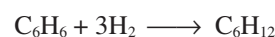


Fig. 4. Variation of benzene concentration with time at different temperatures in benzene hydrogenation with Ni-Ni/HPA-RNi catalyst

Procedure for data analysis: The hydrogenation of benzene over a nickel catalyst can be taken as irreversible in the temperature range of 333–473 K [29,30]. Benzene hydrogenation to cyclohexane can be represented as:



Then, the rate of the reaction can be calculated as:

$$-r_A = -\frac{1}{W} \times \frac{dN_A}{dt} = k C_A^n P_{\text{H}_2}^m \quad \text{mol/g.s}$$

where *n* and *m* are unknown parameters. The experimental studies reported up till now have shown that *n* is nearly zero and *m* is in the range of 0.5 to 1.0. In eqn. 1, *k* is the rate

constant having the units of $\frac{\text{mol}^{(1-n)} \cdot \text{lit}^n}{\text{g.s} \cdot (\text{pressure})^m}$, *C_A* is the concentration of benzene in mol/L and *P_{H2}* is the hydrogen pressure in bars. Since the reaction is carried out at constant hydrogen pressure (*P_{H2}*), eqn. 3 becomes,

$$-r_A = \frac{1}{W} \times \frac{dN_A}{dt} = k' C_A^n \quad (4)$$

where *k'* is an apparent rate constant given by

$$k' = k P_{\text{H}_2}^m \quad (5)$$

By differential method of analysis, the concentration dependence of the reaction rate is obtained from eqn. 4, by plotting log (–*r_A*) versus log (*C_A*) according to the following equation.

$$\log (-r_A) = \log (k') + n \log (C_A) \quad (6)$$

i.e. slope of log (–*r_A*) vs. log (*C_A*) plot gives the concentration dependence of rate (*n*).

From eqn. (3):

$$-r_A = k C_A^n P_{\text{H}_2}^m \quad (7)$$

On taking logarithm:

$$\log (-r_A) = \log (k) + n \log (C_A) + m \log (P_{\text{H}_2}) \quad (8)$$

$$\log \left(\frac{-r_A}{C_A^n} \right) = \log k + m \log (P_{\text{H}_2}) \quad (9)$$

Therefore, a plot of log (–*r_A*/*C_Aⁿ*) vs. log (*P_{H2}*) at a particular concentration of benzene (*C_A*) gives a straight line having a slope of *m* and intercept of log *k*.

Calculation of activation energy: From the above, the reaction is of zero order in terms of benzene concentration and first order in terms of hydrogen pressure. Thus, rate constants of the reaction at 393, 423, 443 and 473 K, and 2.8 MPa of pressure were calculated. Using these rate constants, activation energy of the reaction is determined according to the procedure described below.

Arrhenius relation (given in eqn. 8) was used for the calculation of activation energy of the reaction.

$$k = k_0 \times e^{\frac{-E_a}{RT}} \quad (10)$$

where k_0 is the Arrhenius constant, E_a is the activation energy of the reaction and R is the gas constant.

On taking logarithm:

$$\log(k) = \log(k_0) - \frac{E_a}{RT} \quad (11)$$

i.e. slope of the graph of $\log(k)$ vs. $1/T$ gives the activation energy and intercept gives the Arrhenius constant.

From the slope of the plot (Fig. 5), activation energy (E_a) of the reaction is determined as 35.64 KJ/mol, which is in good agreement with the values (37.7 KJ/mol [15], 35.4 KJ/mol [30]) reported in the literature. This implies that the increase in the rate constant is mostly because of the increase in the value of k_0 in eqn. 10.

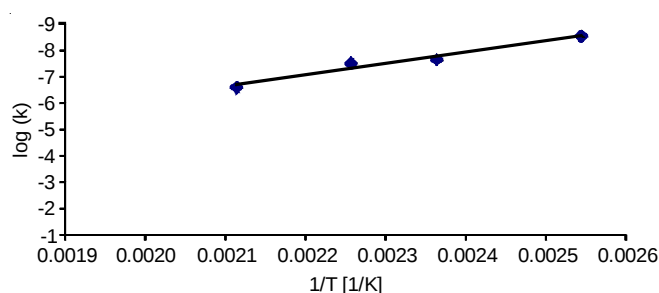


Fig. 5. Arrhenius plot for liquid phase benzene hydrogenation

Study of the stability of the catalyst: In order to find out whether there is any leaching of the complex from the support that can result in the deactivation of the catalyst; we carried out the reaction at 423 K and 2.8 MPa hydrogen pressure with the spent catalyst, which was used for about 100 h. The variation in the conversion of benzene with time in the first run and last run (12th run) are given in Table-1. From Table-1 it is clear that after using the catalyst for 100 h, it can still give the same conversion as that obtained with the fresh catalyst and from this we can conclude that there was no leaching of the catalytically active species. This was also confirmed by SEM analysis that there was no change in the surface morphology of the catalyst after 100 h of usage.

Conclusion

In the present work, a Ni-Ni macrocyclic complex supported on molybdenum heteropoly acid modified Raney Ni has been used as a catalyst for the hydrogenation of benzene. The predicted structure of the complex is confirmed by the close match between the experimentally obtained C, H, N values (%) and theoretically calculated C, H, N values (%) of the complex. It was also confirmed by the single crystal X-ray

TABLE-1
COMPARISON OF CONVERSION OF BENZENE (X_A) USING FRESH AND SPENT CATALYST (USED FOR 100 h) AT $T = 423$ K AND $P = 2.8$ MPa WITH Ni-Ni COMPLEX HPA-RNi CATALYST IN BENZENE HYDROGENATION

Time (min)	Conversion (X_A , %)	
	With fresh catalyst	Spent catalyst (after 100 h of usage)
10	0.0675	0.1045
30	0.1367	0.1616
60	0.1963	0.2331
90	0.2429	0.2883
120	0.2859	0.3347
150	0.3398	0.4272
180	0.3844	0.5277
240	0.4772	0.6367
300	0.5834	0.6869
360	0.6824	0.7421
420	0.7767	0.7732
480	0.8595	0.8429

analysis and various bond lengths and bond angles are reported. The SEM micrograph of the final heterogeneous catalyst has shown the presence of the complex in the form of well grown tiny crystallites on the surface of the support (HPA-RNi). The catalytic activity of the as prepared catalyst was checked by carrying out the liquid phase hydrogenation of benzene, in the temperature range of 393–473 K and in the pressure range of 2.8 to 3.5 MPa. The experiments were carried out in a semi batch reactor with continuous supply of hydrogen over 8 h of reaction time. The catalyst is highly active for the hydrogenation and very specific to cyclohexane formation. Maximum amount of conversion obtained is 98 % at a temperature of 473 K and 2.8 MPa and at 423 K and 3.45 MPa hydrogen pressure. The order of the reaction is nearly zero in terms of benzene concentration and in the range of 0.9 to 1.3 in terms of hydrogen pressure. Activation energy of the reaction is found to be 35.64 KJ/mol, which is equal to that reported in literature. We have also showed that the catalyst is highly stable by carrying out the hydrogenation of benzene with the spent catalyst used for about 100 h.

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