Reductive amination of cyclohexanone in the presence of cyclohexanol over zeolites Hβ and HY

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ARTICLE INFO

ABSTRACT

Reductive amination of a mixture of cyclohexanone/cyclohexanol in varying proportions has been carried out in the gas phase over zeolites Hβ and HY. The products identified were cyclohexylamine, N-cyclohexylcyclohexanimine, 2-cyclohexen-1-ylcyclohexanone and 2-cyclohexylcyclohexanone. The product distribution during the experiments indicates that cyclohexanol does not undergo reductive amination over acid catalysts; it only forms a condensation product with cyclohexanone. The reaction rates were obtained from experimental data and fit to a kinetic model derived for this reaction. The fits show that this reaction follows a Langmuir–Hinshelwood pathway by the adsorption of both cyclohexanone and the NH_3 on the surface of the zeolite.

1. Introduction

A number of commercial processes are employed in amine synthesis. Amines are produced by alkylation of organic halides with ammonia, reductive amination of carbonyl compounds, hydrocyanation of alkenes followed by reduction, hydroamination of olefins, etc. [1–4]. Amongst these processes reductive amination being a single-step process, which employs inexpensive starting materials, is the most practical and convenient approach. The transformation of alcohols, ketones or aldehydes to the corresponding secondary or primary alkylamines occurs in a single reactor without isolation of the intermediary imines or hydroxyamines. Reductive amination is generally a heterogeneous process [5]. It involves the reaction of a carbonyl compound with ammonia and hydrogen over a catalyst, at temperatures ranging from 150 to 350 °C and pressures of 18 to 200 atm.

Cyclohexanone can be aminated in the gas phase over acidic metal catalysts [6–8]. As can be seen in Scheme 1, cyclohexanone (A) reacts with ammonia to form cyclohexylideneimine (B), which in turn is readily hydrogenated to cyclohexylamine (C) [9].

Cyclohexylamine can undergo condensation reaction with cyclohexanone to form N-cyclohexylcyclohexanimine (D). Apart from the aminated products during the reaction cyclohexanone can also form condensation products with cyclohexanone to form 2-cyclohexen-1-ylcyclohexanone (E) and with cyclohexanol to form 2-cyclohexylcyclohexanone (F). Cyclohexanol may also undergo dehydrogenation to cyclohexanone over a metal catalyst [10]. Amination of cyclohexanol/cyclohexanone mixture is important because this mixture is the product of cyclohexane oxidation [11,12]. Becker et al. have studied the gas phase reductive amination of cyclohexanol/cyclohexanone to cyclohexylamine and aniline over Cu- and Ni-containing catalysts [13]. Reductive amination of cyclohexanol has also been studied over acidic and Ni-containing metallosilicate catalysts [14]. Bronsted acid (H+) was found to be inactive for this reaction.

Shape selective zeolites, which catalyze alkylation of ammonia with alcohols, have attracted significant attention for long years [15–17]. This interest is due to their potential to replace the traditional silica-alumina catalysts over which bulky trialkylamines can be formed, with zeolites, which are able to produce mono- and dialkylamines selectively. Zeolites have also been applied to the amination of phenol to aniline [18–20]. Zeolite β and ZSM-5 displayed high activity for this reaction [19,20]. Zeolite β demonstrated higher activity than ZSM-5, which was attributed to its relatively weak acidity [20]. Zeolite Y containing UO_2^{2+} cations has been used as a catalyst for the amination of 1-octanol [21]. The amination of 1-octanol was tested on zeolites having MFI structure and

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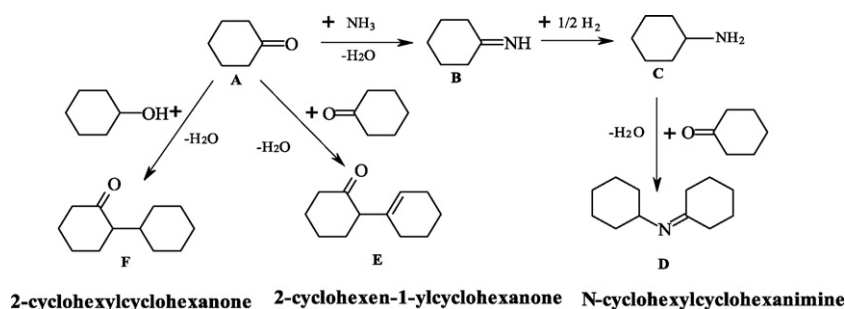
Scheme 1. Reaction pathways for the formation of products in the reductive amination of cyclohexanone/cyclohexanol mixture.

found to proceed through a nucleophilic substitution pathway [22]. However, the conversion achieved was not high. Although zeolites have been successfully employed for the amination of alcohols, the low pressure amination of cyclohexanol was found to result in dehydrogenation products only; amination products were not formed [23].

In order to overcome the limitations of the present generation of zeolite catalysts with respect to their activity during the reductive amination of cyclohexanol, it is necessary to understand the complex reaction sequences occurring during acid-catalyzed aminations in the molecular sieve pores. Cyclohexanone is an intermediate in the formation of cyclohexylamine from cyclohexanol [14]. The aim of this work is to systematically study the reductive amination of cyclohexanone/cyclohexanol mixtures over acidic zeolite catalysts under atmospheric pressure in order to identify the conditions under which the amination products C and D are formed. To fulfill this objective three different types of zeolites with strong, medium and weak acid active sites were employed in the current study. More specifically, in the research presented here, reductive amination of cyclohexanol/cyclohexanone mixtures over zeolites β, Y and ZSM-5 (Si/Al = 8, 25 and 30, respectively) were studied. The kinetics of reductive amination of a starting mixture of optimum proportion, shown later, over the aforementioned catalysts was also studied and the overall rate of its reductive amination is presented.

2. Experimental

Zeolites β, Y and ZSM-5 were used in the reductive amination of cyclohexanone/cyclohexanol. Proton forms of the zeolites Y (Si/Al = 25) and ZSM-5 (Si/Al = 30) were obtained from Conteka, The Netherlands. The sodium form of zeolite β (Si/Al = 8) was obtained from United Catalysts India Limited. It was converted to its proton form via an ion exchange process using an aqueous 1 M NH_4NO_3 solution at 353 K for 12 h, which was then followed by calcination in air at 823 K. BET surface area of the zeolite samples was measured on a Micromeritics Pulse Chemisorb 2700 instrument using N_2 as the adsorbate. Acidity of the zeolites was measured by stepwise temperature programmed desorption (STPD) of ammonia on the same instrument; the relative final strengths of acidity were established by bracketing the temperature of desorption. The measured properties of the zeolites used are given in Table 1.

Table 1
Physicochemical properties of zeolites.

Zeolite	BET surface area (m^2/g)	Acidity (mmol/g) NH_3		
		Weak (A)	Medium (B)	Strong (C)
Hβ	434	1.03	2.3	4.50
HY	730	1.51	1.70	0.99
HZSM-5	400	1.89	1.16	3.05

The reductive amination reactions were performed in a differential down-flow fixed bed Pyrex glass reactor (length 35 cm, diameter 1.5 cm) at atmospheric pressure. A known mass of the catalyst (0.25–1.0 g) of mesh size 14–20 was introduced into the reactor, the zone (∼5 cm) above the catalyst bed packed with quartz grains being served as the preheater. The reactor was placed in a tubular furnace with temperature control. A thermocouple placed close to the catalyst bed was used to measure the reaction temperature. The catalyst was activated under air flow (25 ml min^{-1}) at 723 K for 2 h before the start of the experiment. The reaction was carried out in the temperature range of 473–623 K. The liquid feed consisting of a mixture of cyclohexanone/cyclohexanol was charged into the reactor using a syringe pump (Braun Melsugun, Germany) at a constant predetermined rate together with NH_3 and H_2 gases whose flow rates were also constant during the reaction. The liquid products were collected at the bottom for 1 h using an ice-trap. Analyses of the products were done on a GC–MS apparatus (HP 5973 Mass selective detector, column: HP-1MS 15 m × 0.25 mm × 0.25 μm). The data were recorded after 1 h of steady-state operations. The products identified were cyclohexylamine (C), N-cyclohexylcyclohexanimine (D), 2-cyclohexen-1-ylcyclohexanone (E) and 2-cyclohexylcyclohexanone (F). The major products being N-cyclohexylcyclohexanimine (D) and 2-cyclohexen-1-ylcyclohexanone (E), their concentrations were measured together with those of the unreacted cyclohexanol and cyclohexanone. The total carbon balance was found to be >98%.

Reactions using pure cyclohexanol gave no reductive amination products. They only resulted in dehydrogenation products in low quantities, and thus conversions were calculated based on cyclohexanone concentration only. The conversion and selectivity were calculated based on the GC results.

3. Results and discussion

Initial experiments were performed using different cyclohexanone/cyclohexanol proportions in order to choose the cyclohexanone/cyclohexanol ratio that result in the optimum selectivity for the amination products for this reaction. All reactions were carried out over 0.5 g of zeolite HY. The results are shown in Table 2. The conversion of cyclohexanone increased when its concentration in the feed decreased. A feed containing only cyclohexanol did not yield any products under the current reaction conditions. When only cyclohexanone was used in the feed, its conversion was 40% and it increased to around 71% in a feed mixture containing 10 mol% cyclohexanone and 90 mol% cyclohexanol. The variation in the product selectivity was quite interesting. When cyclohexanone was in excess in the feed, 2-cyclohexen-1-ylcyclohexanone (E), was formed by the condensation of two cyclohexanone molecules; when cyclohexanol was in excess, 2-cyclohexylcyclohexanone (F) was formed by the condensation of one molecule of cyclohexanol and one molecule of cyclohexanone. Cyclohexylamine (C) was detected only when the

Table 2
Conversion of cyclohexanone (A) and the product distribution during the reductive amination reaction using different % of cyclohexanone in a cyclohexanone/cyclohexanol feed.

% A in feed	Conv. A (%)	Selectivity (%)			
		Cyclohexyl amine (C)	N-cyclohexyl cyclohexanimine(D)	2-Cyclohexen-1-ylcyclohexanone (E)	2-Cyclohexyl cyclohexanone (F)
100	40	–	59.2	40.8	–
90	46.2	–	69.4	30.6	–
80	55.5	–	95.2	4.8	–
70	57.9	–	90	–	10
50	59.6	13	63	–	24
40	62.3	15	54	–	31
10	71.4	19	35	–	46

Reaction conditions: HY = 0.5 g, feed:NH$_3$:H$_2$ = 1:15:15, feed rate = 2 ml h^{-1}, temperature = 523 K.

cyclohexanone concentration in the feed was 50% or less. Cyclohexylamine reacts with excess cyclohexanone during the reaction to form N-cyclohexylcyclohexanimine (D). The selectivities for the condensation products E and F were the lowest when the cyclohexanone concentration was 80%, which corresponds to a cyclohexanone/cyclohexanol molar ratio of 8:2. This molar ratio in the feed was used for further studies.

3.1. Effect of catalyst type

The variation in the cyclohexanone conversion and the product selectivity during the reductive amination in the absence of any catalyst (blank) and when zeolites Hβ, HY and HZSM-5 are employed were studied. Results are shown in Fig. 1. As can be seen in the figure, zeolites Hβ and HY resulted in a higher conversion than HZSM-5. Moreover, the selectivity for the reductive amination products was high on these two zeolites. The selectivity for D was 95% over HY compared to 90% over Hβ. It is interesting to note, however, that in the absence of any catalyst the condensation reaction producing E predominated. This indicates that the formation of product E is a facile reaction, which is hindered by the zeolites.

3.2. Effect of reaction temperature

The effect of temperature on this reductive amination reaction over each catalyst was studied in the temperature range of 473–673 K. Results are shown in Fig. 2. As can be seen, the conversion of cyclohexanone (closed triangular marks) increases with temperature over all three zeolite catalysts. It increased from 45 to 64% over Hβ, 51 to 69% over HY and 32 to 45% over HSM5. The selectivity for D reached a maximum in the temperature range of 523–573 K with a concomitant decrease in the selectivity for E. The select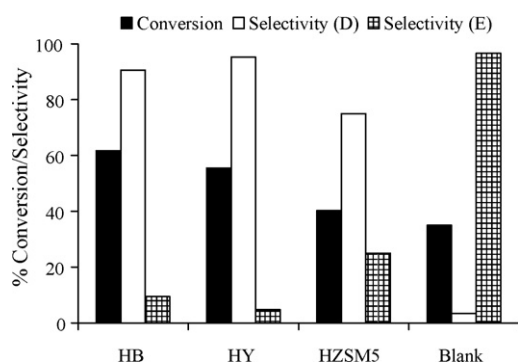ivity for D was >90% over zeolites Hβ and HY in this temperature range. Beyond this temperature range cyclohexene formation was observed. Since the variation in the conversion-selectivity pattern is similar over all three zeolites, only zeolite HY was used to optimize the other reaction conditions.

3.3. Effect of catalyst mass

The effect of zeolite catalyst HY mass was studied and the results are shown in Fig. 3. The catalyst mass was varied from 0.25 to 1.0 g. The reactions were performed at 523 K and cyclohexanone/cyclohexanol ratio of 8:2 (mol/mol) was employed. As can be seen in Fig. 3, the conversion increased steadily from 19.5 to 80% as catalyst mass increases from 0.25 to 1.0 g. The yield of D increased from 8.7 to almost 82% and yield of E decreased from 11 to 2.5% as catalyst mass increased from 0.25 to 1.0 g. This study clearly shows that HY facilitates the formation of D and suppresses that of E. The only products in measurable concentrations were D and E. It is worth mentioning again that in the absence of a catalyst the cyclohexanone conversion was 35% and the selectivity for E was 96%.

3.4. Effect of time on stream

The effects of time on stream on reductive amination at 523 K over all three catalysts employed in this research were studied. The results obtained after 1 h of steady-state operation over HY zeolite are shown in Fig. 4. As can be seen, the conversion decreased steadily from 56% after 60 min time on stream to 26% after 240 min.
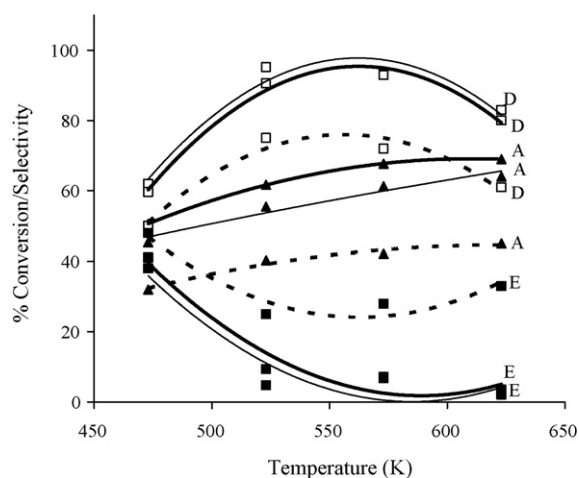

Fig. 1. Effect of catalyst type on reductive amination of cyclohexanol/cyclohexanone. Reaction conditions: feed = cyclohexanone/cyclohexanol 8:2 (mol/mol), temperature = 523 K. Catalyst mass = 0.5 g, feed:NH$_3$:H$_2$ = 1:15:15, feed rate = 2 ml h^{-1}. D = N-cyclohexylcyclohexanimine, E = 2-cyclohexen-1-ylcyclohexanone.

Fig. 2. Effect of temperature on reductive amination of cyclohexanol/cyclohexanone over different catalyst types. Hβ (—), HY (—) and HZSM-5 (---). Reaction conditions: feed = cyclohexanone/cyclohexanol 8:2 (mol/mol), temperature = 523 K. Catalyst mass = 0.5 g, feed:NH$_3$:H$_2$ = 1:15:15, feed rate = 2 ml h^{-1}. A (▲) = conversion of cyclohexanone, D (□) = N-cyclohexylcyclohexanimine, E (■) = 2-cyclohexen-1-ylcyclohexanone.
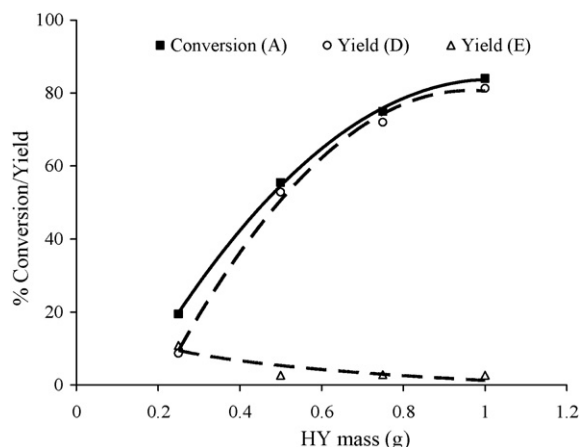
Fig. 3. Effect of catalyst mass on reductive amination of cyclohexanol/cyclohexanone. Reaction conditions: feed = cyclohexanone/cyclohexanol 8:2 (mol/mol), temperature = 523 K. Catalyst = HY, feed:NH_3:H_2 = 1:15:15, feed rate = 2 ml h^{-1}. A = cyclohexanone, D = N-cyclohexylcyclohexanimine, E = 2-cyclohexen-1-ylcyclohexanone.

The selectivity for D also decreased from 95 to 40% with a corresponding increase in that for E. This implies that the active sites on the zeolite HY were deactivated with time on stream. Similar trends were also observed over zeolites Hβ and HZSM-5.

3.5. Effect of NH_3

The effect of NH_3 on the reductive amination was studied by varying the NH_3 flow rate from 0 to 4 mol h^{-1}. The cyclohexanone/cyclohexanol feed rate was 2 ml h^{-1}; this corresponds to a cyclohexanone flow rate of 15 mmol h^{-1} and the feed to H_2 ratio was kept constant at 1:15 (mol/mol). 0.5 g of zeolite HY was used to catalyze this reaction. Results are shown in Fig. 5. The conversion of cyclohexanone increased with increase in NH_3 concentration. It reached a maximum of 55% when NH_3 concentration was 2.5 mol h^{-1}. Further increase in NH_3 concentration led to a decrease in the conversion. This may be due to zeolite acid sites neutralization by excess NH_3 molecules. The selectivity for D constantly increased with NH_3 concentration while the selectivity for E dropped. This is presumably due to NH_3 concentration rate-dependence of the reaction resulting in the formation of D.
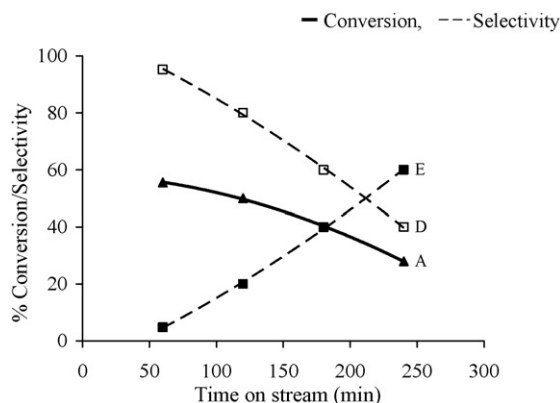

Fig. 4. Effect of time on stream in reductive amination of cyclohexanol/cyclohexanone over HY catalyst. Reaction conditions: feed = cyclohexanone/cyclohexanol 8:2 (mol/mol), temperature = 523 K. HY = 0.5 g, feed:NH_3:H_2 = 1:15:15, feed rate = 2 ml h^{-1}. A (▲) = cyclohexanone, D (□) = N-cyclohexylcyclohexanimine, E (■) = 2-cyclohexen-1-ylcyclohexanone.
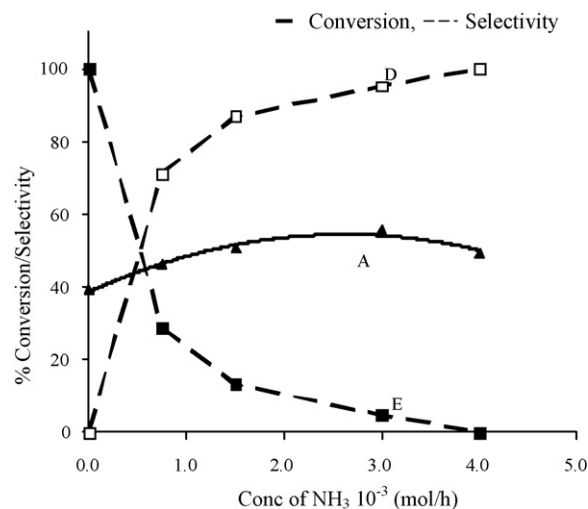

Fig. 5. Effect of NH_3 on reductive amination of cyclohexanol/cyclohexanone, over HY zeolite. Reaction conditions: feed = cyclohexanone/cyclohexanol 8:2 (mol/mol). Temperature = 523 K, HY catalyst mass = 0.5 g, feed:H_2 = 1:15, feed rate = 2 ml h^{-1}. A (▲) = cyclohexanone, D (□) = N-cyclohexylcyclohexanimine, E (■) = 2-cyclohexen-1-ylcyclohexanone.

3.6. Effect of H_2

The effect of H_2 on the reductive amination was studied by varying the H_2 flow rate from 0 to 4 mol h^{-1}. The cyclohexanone/cyclohexanol feed rate was 2 ml h^{-1} (15 mmol cyclohexanone h^{-1}), the feed to NH_3 ratio was kept constant at 1:15 (mol/mol), and 0.5 g of zeolite HY was employed. Results are shown in Fig. 6. The conversion of cyclohexanone increased marginally from 52 to 57% with increasing H_2 concentration from 1 to 4 mol h^{-1}. An increase in the H_2 flow rate above 1 mol h^{-1} did not produce any significant increase in the selectivity for D. The selectivity was always greater than 80%.

3.7. Effect of feed rate

The effect of the feed rate on the reductive amination was studied by varying the cyclohexanone/cyclohexanol feed rate from 1 to
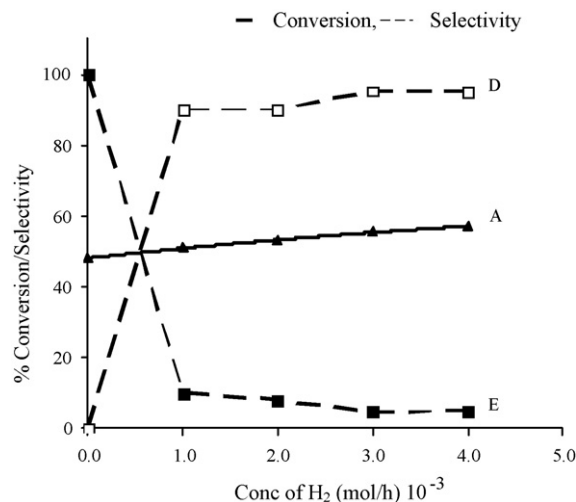

Fig. 6. Effect of H_2 flow rate on reductive amination of cyclohexanol/cyclohexanone, over HY zeolite. Reaction conditions: feed = cyclohexanone/cyclohexanol 8:2 (mol/mol). Temperature = 523 K, HY catalyst mass = 0.5 g, feed:NH_3 = 1:15, feed rate = 2 ml h^{-1}. A (▲) = cyclohexanone, D (□) = N-cyclohexylcyclohexanimine, E (■) = 2-cyclohexen-1-ylcyclohexanone.
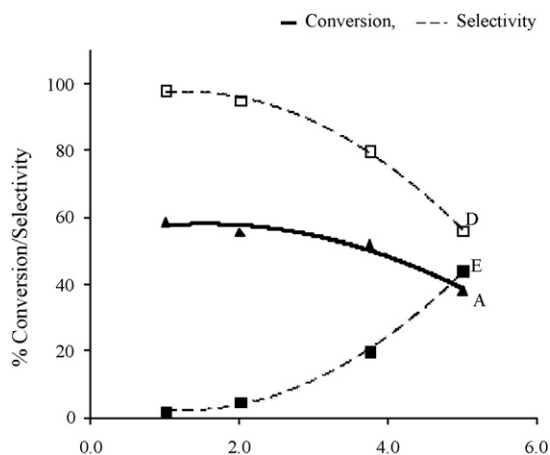
Fig. 7. Effect of feed rate on reductive amination of cyclohexanol/cyclohexanone, over HY zeolite. Reaction conditions: feed = cyclohexanone/cyclohexanol 8:2 (mol/mol). Temperature = 523 K. HY catalyst mass = 0.5 g, H_2:NH_3 = 1:1, feed rate = 2 ml h^{-1}. A (▲) = cyclohexanone, D (□) = N-cyclohexylcyclohexanimine, E (■) = 2-cyclohexen-1-ylcyclohexanone.

5 ml h^{-1} (7.5–37.5 mmol h^{-1} of cyclohexanone) with the NH_3:H_2 ratio kept constant at 2.25 mol h^{-1} each. 0.5 g of zeolite HY was used. Results are shown in Fig. 7. The feed rate had an important effect on the conversion as well as the selectivity levels in this reaction. Increase in the feed rate from 1 to 5 ml h^{-1} caused a 30% drop of cyclohexanone conversion (from 59 to 38%). Although NH_3 and H_2 were always kept in a substantial excess, a dramatic drop of the selectivity for D was observed (from 95 to 56%) accompanied by a concomitant rise in the selectivity for E (from 5 to 44%). This indicates that as the contact time of the feed with the catalyst decreases the conversion of cyclohexanone as well as the formation of D decreases whereas the formation of E increases. This again underlines the importance of the catalyst in the formation of D.

3.8. Kinetic studies

Kinetic studies of the amination reactions over zeolite catalysts have been reported before [24–27]. According to these reports the reaction is first order with respect to ammonia over Na-mordenite [24] as well as other H-zeolites [25]. Kogelbauer et al. employed a Langmuir–Hinshelwood model to describe the kinetics of amination of methanol over Na-mordenite and Na,K-erionite catalysts [26]. Ilao et al. [28] suggested that a reaction of adsorbed methanol and ammonia upon sequential adsorption and heating took place over zeolite chabazite but not in zeolite mordenite. Based on this a Langmuir–Hinshelwood mechanism was proposed for chabazite and an Eley-Rideal one for mordenite. Baiker et al. [9] have used the Langmuir model to describe the kinetics of Cu catalyzed amination of long-chain aliphatic alcohols. Becker et al. [13] have performed kinetic experiments for the amination of the cyclohexanone/cyclohexanol mixture, which are indicative of a pseudo-first order. They stated that up to 523 K, the rate-limiting step was the chemical reaction; at higher temperatures however, the mass transfer resistance predominated.

Becker et al. [13] have also stated that over supported Cu catalysts, mass transfer resistance strongly influences the selectivity of this reaction. They, moreover, stated that bulky products like N-cyclohexylcyclohexanimine, (D) are preferred when mass transfer limits the reaction rate. However this was not found to be the case over zeolites Hβ and HY. HZSM-5 was not chosen for kinetic studies as this catalyst was not found to be very active in this reaction. This may be because the smaller pore size in ZSM-5 may hinder the formation of the products of this reaction. To study the kinetics
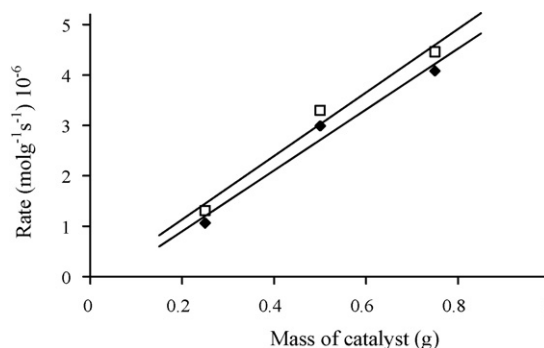

Fig. 8. Reductive amination of cyclohexanol/cyclohexanone: effect of catalyst mass on reaction rate. Hβ (□), HY (♦). Reaction conditions: feed = cyclohexanone/cyclohexanol 8:2 (mol/mol). Temperature = 523 K, feed:H_2:NH_3 = 1:15:15, feed rate = 4 ml h^{-1}.

a differential (low-conversion) reactor was employed. The reactor was fed with a cyclohexanone/cyclohexanol mixture (8:2 mol/mol) at the rate of 4 ml h^{-1} over 0.25 g of the catalyst. Conversion data after 1 h of steady-state operation at 573 K were collected, and the rate of the reaction in the differential reactor was calculated. The data were used in the following equation to calculate the reaction rate

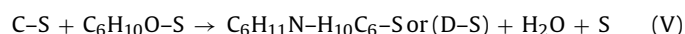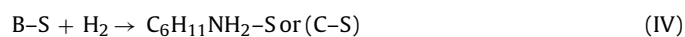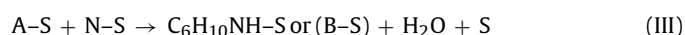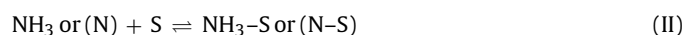$$r = -\frac{(X_{io} - X_i) \cdot F}{\text{Catalyst mass } (g)}$$

where $(X_{io} - X_i)$ is the conversion of cyclohexanone and F = molar flow rate of cyclohexanone.

Fig. 8 gives a plot of the reaction rate as a function of zeolite mass. The mass of zeolites was varied in the range of 0.25–0.75 g, a linear relationship exists between the mass and the rate of the reaction. This indicates that diffusion limitations are not dominant. It must also be noted that in the absence of catalyst 2-cyclohexen-1-ylcyclohexanone (E) is formed whose dimensions are very similar to D. Thus, in the analysis that follows we assume that the rate-determining step is the chemical reaction step. Very small variation in the conversion of cyclohexanone with H_2 concentration indicates that it plays only a minor role in this reaction, and thus the kinetics should depend primarily on adsorbed cyclohexanone and NH_3.

For the reductive amination reaction, where the rate-limiting step is the chemical reaction, the reaction rate can be described by the equation using the Langmuir–Hinshelwood (L–H) model and assumptions. The rate equation can be derived based on the following (additional to L–H ones) assumptions:

- Hydrogen is not adsorbed or very weakly adsorbed on the zeolite surface during the reaction.
- Due to the excess of cyclohexanone in the feed and the basic nature of cyclohexanone when compared to cyclohexanol, the adsorption of cyclohexanol on the acid sites of zeolites is negligible.

For the reductive amination reaction the following elementary steps are proposed:

$$C_6H_{10}O \text{ or } (A) + S \rightleftharpoons C_6H_{10}O–S \text{ or } (A–S) \tag{I}$$

$$NH_3 \text{ or } (N) + S \rightleftharpoons NH_3–S \text{ or } (N–S) \tag{II}$$

$$A–S + N–S \rightarrow C_6H_{10}NH–S \text{ or } (B–S) + H_2O + S \tag{III}$$

$$B–S + H_2 \rightarrow C_6H_{11}NH_2–S \text{ or } (C–S) \tag{IV}$$

$$C–S + C_6H_{10}O–S \rightarrow C_6H_{11}N–H_{10}C_6–S \text{ or } (D–S) + H_2O + S \tag{V}$$

$$D–S \rightleftharpoons D + S \tag{VI}$$

It is moreover assumed that $C_6H_{10}O$ and NH_3 react with the catalyst site S via very fast steps, always in equilibrium to form intermediates $C_6H_{10}O–S$ and $NH_3–S$, respectively. These intermediates react further according to reactions (III)–(V), to give adsorbed products $C_6H_{10}NH–S$ and $C_6H_{11}NH_2–S$, which subsequently react to give adsorbed $C_6H_{11}N–H_{10}C_6–S$. $C_6H_{11}N–H_{10}C_6–S$ is subsequently desorbed via a very fast step also always in equilibrium.

As mentioned earlier in this section, the amination of cyclohexanone, reaction (III), is considered the rate-limiting step. Adsorption/desorption reactions (I), (II) and (VI) are considered to be very fast and always in equilibrium.

$C_6H_{10}O–S$ is also consumed via its reaction with cyclohexanol for the production of $C_{12}H_{20}O$ (F). However, at the selected temperature and conditions of reaction no measurable amount of $C_{12}H_{20}O$ (F) was produced.

For reactions (I), (II) and (VI) which have been considered to be always in equilibrium:

$$C_{AS} = K_A C_A C_S \tag{1}$$

$$C_{NS} = K_N C_N C_S \tag{2}$$

$$C_{DS} = K_D C_D C_S \tag{3}$$

where C_i is the concentration of substance i, and K_j its equilibrium constant at 573 K. From a balance over the active catalyst sites C_{tot} and subsequent replacement of concentrations of intermediates from relations (1), (2) and (3)

$$C_{tot} = C_S + C_{AS} + C_{NS} + C_{DS} = C_S(1 + K_A C_A + K_N C_N + K_D C_D). \text{ Therefore,}$$

$$C_S = \frac{C_{tot}}{1 + K_A C_A + K_N C_N + K_D C_D} \tag{4}$$

As mentioned earlier, the amination of cyclohexanone, reaction (III), is considered the rate-limiting step. Thus the rate of A–S destruction is:

$$-\frac{dC_{AS}}{dt} = r_{III} + r_V \tag{5}$$

$$r_{III} = k_{III} C_{AS} C_{NS} \tag{6}$$

$$r_V = k_V C_{CS} C_{AS} \tag{7}$$

where r_j is the rate of elementary reaction j and k_j its rate coefficient. Time is depicted as t. The concentration of $C_6H_{11}NH_2$ was not measurable. Evidently reaction (5) is very fast but because the concentration of $C_6H_{11}NH_2$ is practically zero, the contribution of reaction (5) in the rate of destruction of A–S is negligible. In other words $r_{III} \gg r_V$ and $r_{III} + r_V \approx r_{III}$. The rate, r, of A–S destruction thus is:

$$r = k_{III} C_{AS} C_{NS} = k_{III} K_A K_N C_A C_N C_S^2 = \frac{k_{III} K_A K_N C_{tot}^2 C_A C_N}{(1 + K_A C_A + K_N C_N + K_D C_D)^2} \tag{8}$$

In the conditions of the experiments the concentration of NH_3 is 15 times higher than that of cyclohexanone. Therefore the change in NH_3 concentration can be considered negligible and the product $K_N C_N$ can be taken as constant. Its concentration in the numerator can also be incorporated in a overall constant as shown below. Moreover weak product adsorption is expected from a good catalyst surface so that the products can be easily desorbed. It is thus assumed that adsorption of D is much weaker than that of A, so that $K_D \ll K_A$, and thus the above relation can be reduced to:

$$r = \frac{k_t C_A}{(K + K_A C_A)^2} \tag{9}$$

where $k_t = k_{III} K_A K_N C_{tot}^2 C_N$ and $K = 1 + K_N C_N$, or by dividing numerator and denominator by K^2, the final rate equation becomes:
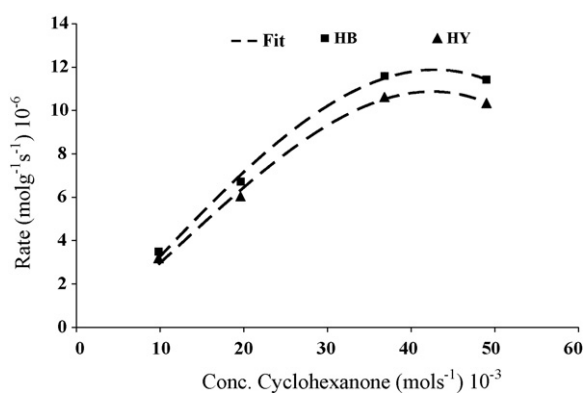
$$r = \frac{k_s C_A}{(1 + K_s C_A)^2} \tag{10}$$

Fig. 9. Reductive amination of cyclohexanol/cyclohexanone at 523 K. Fitting of data to Eq. (10) for catalysts Hβ and HY.

Table 3
Kinetic data for the reductive amination of cyclohexanone/cyclohexanol over zeolites Hβ and HY.

Catalyst	k_s (10^{-4} mol g^{-1} s^{-1})	K_s	Nonlinear regression, R^2
Hβ	1.48	0.87	0.921
HY	1.62	1.02	0.936

where $k_s = k_t/K^2$ and $K_S = K_A/K$.

The nonlinear curve fitting of the above kinetic equation was performed utilizing the Levenberg–Marquardt method. A plot of the reaction rate as a function of the concentration of cyclohexanone is shown in Fig. 9. As can be seen in Fig. 9 there is a very good correlation between the fit and the experimental results. The rate constants and the adsorption constants are given in Table 3. The rate constant over HY is greater than that over Hβ. The adsorption constants indicate that the adsorption of cyclohexanone is slightly stronger over HY than over Hβ.

4. Mechanism

According to Corbin et al. [29] during the amination of methanol, the most probable mechanism for the methylamine formation is an S_N2 attack of a protonated methanol by weakly adsorbed ammonia; i.e. the weak acid sites were found to be responsible for this step. Kotrla et al. [30] have reported a correlation between zeolite acidity and activity in the amination of acetone over zeolites. Zamlynny et al. [14] have proposed a mechanism for cyclohexanol amination over Ni catalysts where cyclohexanol is assumed to be dehydrogenated over Ni particles to cyclohexanone, which is further aminated over acid sites to imine-like species and hydrogenated, again over Ni^0, to cyclohexylamine. In the present study the reductive amination of cyclohexanone is found to follow a L–H mechanism where both cyclohexanone and NH_3 are adsorbed on adjacent Bronsted acid sites. The fact that both zeolites HY and Hβ are active for this reaction implies that the active sites are the weak and the moderate acid and not the strong acid sites. This is based on the assumption that since both these zeolites have a 12-membered pore opening, the difference in the pore structures do not contribute to a difference in their catalytic activity for this reaction. An S_N2 type attack of NH_3 leads to the formation of the imine. N-cyclohexylcyclohexanimine (D) is the dimerization products of cyclohexylamine with cyclohexanone. This reaction route has already been suggested by Hamada et al. [10]. The data collected via the present research support Scheme 1 as the probable reaction route. The variation in the selectivity for different products when the feed composition is varied can be explained based on this pathway.

5. Conclusions

The gas phase reductive amination of a mixture of cyclo-hexanone/cyclohexanol in varying proportions has been carried out over zeolites Hβ and HY. The product distribution during the experiments indicates that cyclohexanol does not undergo reductive amination over acid catalysts; it only forms a condensation product with cyclohexanone. The product distribution and cyclohexanone conversion were greatly influenced by the cyclohexanone/cyclohexanol ratio. The highest selectivity for reductive amination was seen when the cyclohexanone:cyclohexanol mole ratio was 8:2. The reaction rates were obtained from experimental data and fit to a kinetic model derived for this reaction based on the Langmuir–Hinshelwood pathway. This reaction proceeds by the adsorption of both cyclohexanone and the NH_3 on the surface of the zeolite. The adsorbed species interact to give the condensation and reductive amination products.

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