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Reaction kinetics of the liquid-phase hydrogenation of benzonitrile to benzylamine using Raney nickel catalyst

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Abstract

The liquid-phase catalytic hydrogenation of benzonitrile to benzylamine was carried out in 2-propanol using Raney nickel as a catalyst. The effects of hydrogen partial pressure (500–2000 kPa), reaction temperature (328–358 K), catalyst loading (2–8 g dm^{-3}), benzonitrile concentration (0.4–1.6 mol dm^{-3}) and additives (acetic acid, water and liquor ammonia) on the hydrogenation of benzonitrile and the yield of benzylamine have been studied. The speed of stirring >15 rps has no effect on the initial rate of reaction. Effect of various solvents (2-propanol, methanol and dimethylformamide) on the hydrogenation of benzonitrile has been investigated. The reaction was found to be first order with respect to the hydrogen partial pressure and benzonitrile concentration. The activation energy for the catalytic hydrogenation of benzonitrile was found to be 60.27 kJ mol^{-1}.

Keywords: Hydrogenation; Benzonitrile; Benzyslamine; Raney nickel

1. Introduction

Benzylamine is an important intermediate for the manufacture of various drugs—amosulalol, burnidipine, biotin, nialamide and sulbentine [1]. It is used as an intermediate in dyestuffs and synthetic resins and as an absorbent for carbon dioxide and as a cell-active penetration aid in the formulation of insecticides and also used as a corrosion inhibitor [2].

Several methods have been reported for the preparation of benzylamine. Kliger et al. carried out amination of benzyl alcohol in the presence of a Fe catalyst at 200 °C to give 77% yield of benzylamine [3]. Vasilev and Ionova reported 62% yield of benzylamine in the reaction of benzyl chloride with ammonia and disubstituted thiourea [4]. Electrolytic reduction of benzonitrile in ethanol and sulfuric acid solution using Ni-black deposited on graphite as a cathode to yield 63% benzylamine has been reported by Udapa et al. [5]. Vlassa used potassium-phthalimide, benzyl chloride and dimethyl formamide to obtain *N*-benzyl phthalamide which on hydrolysis in methanol gave benzylamine [6]. Yamada and Fujimoto reported electrocatalytic hydrogenation of benzonitrile in methanol and $NaClO_4$ solution to give 60% yield of benzylamine [7]. Aoki et al. obtained 44% yield of benzylamine by reacting benzyl chloride with hexamethylenetetramine in butanol at 65 °C [8] and Sugiyama claimed 80% yield by reacting benzyl chloride with aqueous ammonia in the presence of benzaldehyde [9] and 75.4% yield in the presence of 4-ethylbenzaldehyde [10]. Prasad et al. carried out reduction of benzonitrile using $NaBH_4$–I_2 to obtained 70–75% yield of benzylamine [11]. Grey and Pez carried out homogeneous hydrogenation of benzonitrile using bisphosphine as a catalyst at 90 °C for 18 h [12]. Plunkett et al. obtained 93.2% yield of benzylamine in the hydrogenation of benzonitrile in a continuous countercurrent reactor system using Raney nickel catalyst at 100 °C [13]. Dines et al. carried out hydrogenation of benzonitrile using palladium-loaded pyridyl catalyst at 100 °C and obtained 26% yield of benzylamine [14]. Takumasa et al. claimed 99.2% benzylamine from benzonitrile hydrogenation in the presence of Ni/silica catalyst using methanol as a solvent and ammonia as an additive at 120 °C [15]. Sempuku carried out hydrogenation of benzonitrile in

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Nomenclature

C_{A0}	initial concentration of benzonitrile ($mol\,dm^{-3}$)
C_B	concentration of hydrogen ($mol\,dm^{-3}$)
D	diffusivity of hydrogen in porous catalyst ($m^2\,s^{-1}$)
M	molecular weight of the solute
r_0	initial rate of the hydrogenation of benzonitrile ($mol\,dm^{-3}\,s^{-1}$)
r_p	radius of catalyst particle (m)
S_g	surface area of catalyst per unit mass of catalyst ($m^2\,g^{-1}$)
w	catalyst loading ($g\,dm^{-3}$)

Greek letters

Φ	Thiele modulus
η	effectiveness factor
θ	porosity of catalyst particle
ρ_p	density of catalyst particle ($g\,m^{-3}$)
τ_m	tortuosity factor

the presence of CO_2 using Pd/Al_2O_3 catalyst to obtain 94.3% benzylamine [16]. Suleimanov et al. hydrogenated benzonitrile in dioxane at 90 °C using Ni/kiselguhr and obtained 76.3% benzylamine [17]. Ryoichi et al. obtained 81% benzylamine in the hydrogenation of benzonitrile using Raney Co alloys and methanol at 130 °C [18].

However, information related to the preparation of benzylamine from benzonitrile is available mainly in the patent literature. There is lack of systematic investigation of effects of various operating parameters on the progress of the reaction and the yield of benzylamine. The present investigation was aimed at the same and evaluation of kinetics of the reaction using a commercial Raney nickel catalyst.

Nitriles are converted to the corresponding amines through the following reactions [19,20]:

$$\underset{\text{Benzonitrile}}{C_6H_5C\equiv N} \xrightarrow{H_2} \underset{\text{Aldimine}}{C_6H_5CH{=}NH} \xrightarrow{H_2} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} \tag{1}$$

$$C_6H_5CH{=}NH + C_6H_5CH_2NH_2 \rightleftarrows \underset{\alpha\text{-Aminodialkylamine}}{C_6H_5CH(NH_2)NHCH_2C_6H_5} \tag{2}$$

$$C_6H_5CH(NH_2)NHCH_2C_6H_5 \xrightarrow{H_2} \underset{\text{Dibenzylamine}}{(C_6H_5CH_2)_2NH} + NH_3 \tag{3}$$

$$C_6H_5CH(NH_2)NHCH_2C_6H_5 \rightleftarrows \underset{\text{Schiff base}}{C_6H_5CH{=}NCH_2C_6H_5} + NH_3 \tag{4}$$

$$C_6H_5CH{=}NCH_2C_6H_5 \xrightarrow{H_2} (C_6H_5CH_2)_2NH \tag{5}$$

Thus, dibenzylamine is a by-product in this reaction.

2. Materials

Methanol, 2-propanol, dimethylformamide, acetic acid, liquor ammonia (30% by volume), and benzonitrile used were of laboratory reagent grade and obtained from S.D. Fine Chemicals Ltd., Mumbai, India. Hydrogen (cylinder purity 99.98%) was obtained from Indian Oxygen Limited, Mumbai, India and used as such. Commercially prepared 5% Pd/C, 5% $Pd/BaSO_4$, 5% Pt/C, 5% $Pd/CaCO_3$, were obtained from Parekh Platinum Ltd., Mumbai, India, and Raney nickel was obtained from Monarch Chemicals, Mumbai, India.

3. Experimental set-up

The heterogeneous catalytic hydrogenation of benzonitrile was carried out in a Parr high-pressure reactor of capacity 100 mL. The reactor was equipped with an electrically heated jacket, a turbine agitator and a variable speed magnetic drive. The temperature and the speed of agitation were controlled by means of a Parr 4842 controller. The gas inlet, the gas release valve, the pressure gauge and the rupture-disk were located on top of the reaction vessel. The liquid sample line and the thermocouple were well immersed in the reaction mixture. The reactor was also provided with a cooling coil.

4. Experimental procedure

The reactor was first charged with appropriate quantities of the benzonitrile, the solvent and the catalyst. It was then purged with nitrogen, prior to the start of the experiment to ensure an inert atmosphere in the reactor. Hydrogen from the cylinder was introduced into the reactor and nitrogen was replaced with it. All the lines were closed. The reactor contents were heated to the desired temperature. The autoclave was then pressurized with hydrogen to get the desired partial pressure of hydrogen. Agitation was then started at the predetermined speed. The consumption of hydrogen due to reaction as well as due to small sampling led to decrease in the total pressure as indicated on the pressure gauge. So, more hydrogen was charged intermittently from the cylinder through manually operated control valve, thus maintaining a constant partial pressure of hydrogen. Samples were withdrawn periodically after sufficient flushing of the sample line with the reaction mixture.

5. Reactant and product analysis

The analysis of the liquid-phase samples for the quantitative estimation of reactants and the products formed during the course of hydrogenation was carried out using gas chromatography (GC) using a SS column, 2 m long and packed with 5% SE-30 on chromosorb WHP material. The conditions of analysis for the reaction mixture were as follows: FID

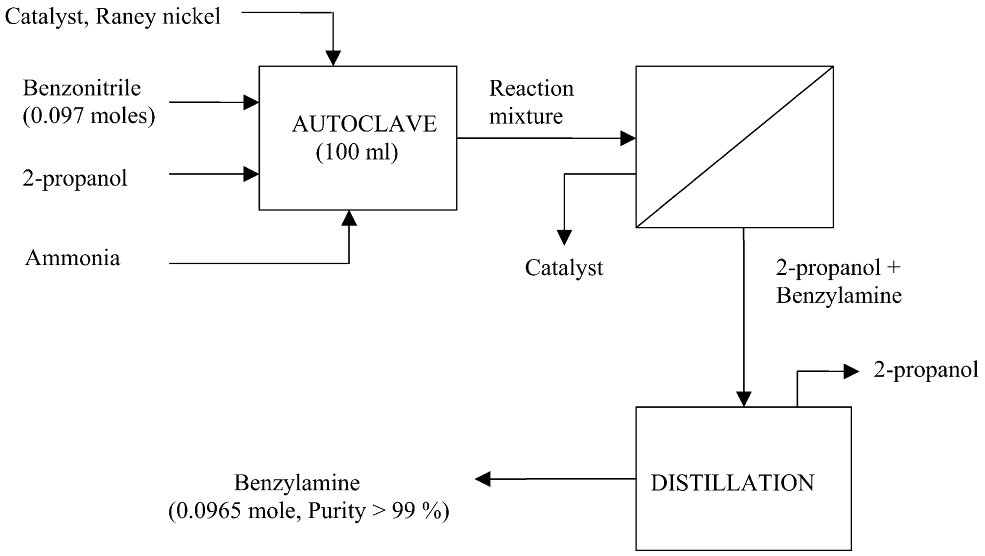

Fig. 1. Hydrogenation of benzonitrile to benzylamine and its recovery.

temperature: 573 K, injection temperature: 573 K, column temperature: 343 K, carrier gas (N_2): $1.9 \times 10^{-5}\,m^3\,min^{-1}$.

Initial experiments on catalytic hydrogenation of benzonitrile were carried out to establish the material balance of benzonitrile consumed and the product formed and the balance to the extent of 99% was established. After completion of the reaction, the catalyst was separated by filtration and washed with 2-propanol. The filtrate and the washings were mixed and distilled to separate 2-propanol and the product (Fig. 1). The product thus obtained had purity >99%. In a typical experiment, starting with 0.097 mol benzonitrile and complete conversion, the benzylamine recovered by this process was 0.0965 mol, amounting to >99% process recovery of the product.

For kinetic experiments, the data were obtained for benzonitrile consumed as a function of time for different sets of operating conditions and fitted by a linear regression procedure from which the initial rates of consumption of benzonitrile were calculated.

6. Results and discussion

Heterogeneous catalytic hydrogenation is a reaction involving gas–liquid–solid phase operation. Various steps occur in series when a gas–liquid–solid reaction occurs. The minimum speed of agitation used was higher than the minimum speed required for the suspension of the catalyst particles.

6.1. *Effect of additives*

Hydrogenation of nitriles to primary amines is usually accompanied by the formation of secondary amines. The selectivity to respective amines depends on the structure of the substrate, the nature and amount of the catalyst, basic or acidic additives, the reaction medium and the other reaction conditions. Among these factors the nature of the catalyst appears to be the most important in determining the selectivity [20].

The hydrogenation of benzonitrile was studied at different temperatures but in the absence of any additive. The yield of benzylamine increased with increase in the reaction temperature. The highest yield of benzylamine (54.52%) was obtained at 553 K in the absence of additives. In the hydrogenation of nitriles, use of additives such as alkaline (ammonia, sodium carbonate, sodium hydroxide) [21] and acidic (acetic acid, dry HCl, concentrated H_2SO_4) [22] substances as well as water [19] was made to improve the yield of amines. Initial experiments were performed to study the effect of additives (acetic acid, water and liquor ammonia) on the hydrogenation of benzonitrile.

The experiments indicated that the yield of benzylamine decreases and dibenzylamine increases with increasing the acetic acid concentration (Fig. 2). The reaction is reasonably fast with the addition of water and yield of benzylamine increases with increasing water concentration from 2 to 4% (by volume). Further increase in the water concentration decreases the yield of benzylamine. The maximum yield of benzylamine obtained with the addition of water was 75.25%.

The reaction was studied at different proportions of liquor ammonia (2–10%, by volume) and the quantity of liquor ammonia for 100% yield was found to be dependent on the catalyst concentration as well as on the reaction temperature. As the liquor ammonia proportion increases from 2 to 6% (by volume) in the reaction mixture, the yield of benzylamine increases from 75.6 to 99.2% and further increase in the liquor ammonia proportion (>6%, by volume) decreases the yield of benzylamine. For temperatures >358 K, higher proportion of liquor ammonia was needed (>6%) for higher yield (99%) of benzylamine. The secondary amines results from a series of

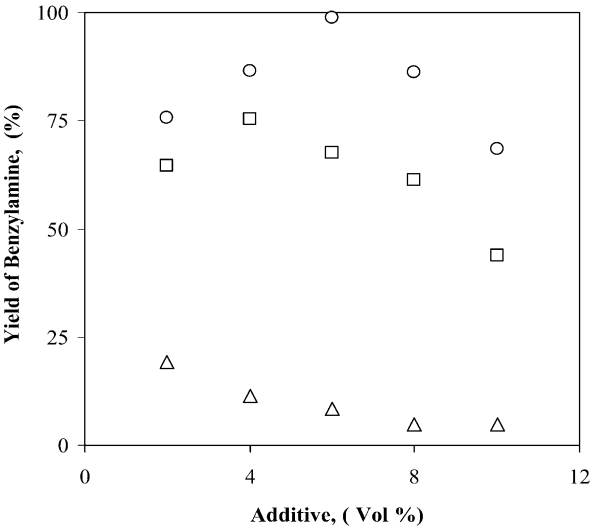

Fig. 2. Effect of additives on the yield of benzylamine: (◯) ammonia; water; (△) acetic acid; benzonitrile concentration: 0.78 mol dm^{-3}; catalyst loading: 4 gm dm^{-3}; reaction temperature: 358 K; hydrogen partial pressure: 1500 kPa; agitation speed: 27 rps; 2-propanol: 0.05 dm^3.

reactions (Eqs. (1)–(5)). The reason for increase in the yield of benzylamine with increase in liquor ammonia concentration is probably the addition of ammonia to the aldimine and thus may suppress the condensation reaction leading to dibenzylamine formation. Further, in the presence of ammonia, the intermediates α-aminodialkylamine and Schiff base may decompose to give 1 mol of aldimine and 1 mol of benzylamine by the reversal of the reaction in Eqs. (2) and (4), and may thus effectively increase the yield of benzylamine [20].

6.2. Mass-transfer consideration

In the hydrogenation reactions, gas–liquid, liquid–solid and intra-particle diffusion (pore diffusion) resistances are likely to be important for consumption of hydrogen.

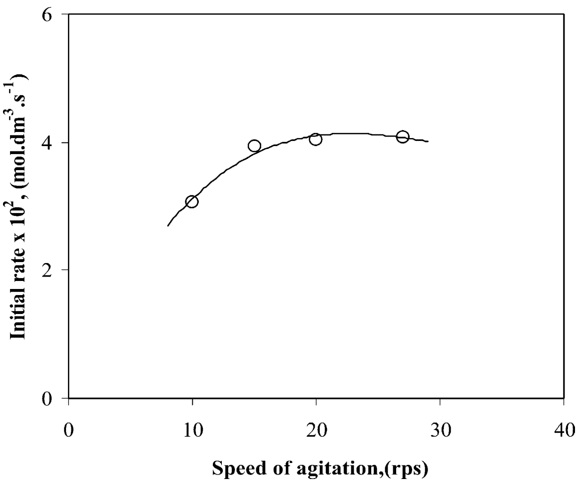

Fig. 3. Effect of speed of agitation on the initial rate of hydrogenation of benzonitrile: benzonitrile concentration: 0.78 mol dm^{-3}; catalyst loading: 4 gm dm^{-3}; reaction temperature: 358 K; hydrogen partial pressure: 1500 kPa.

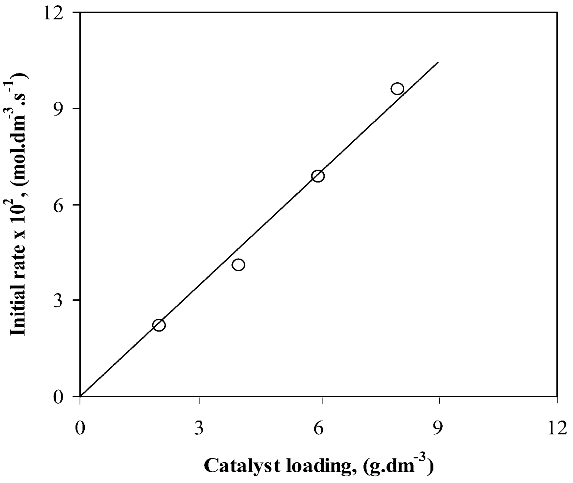

Fig. 4. Effect of catalyst loading on the initial rate of hydrogenation of benzonitrile: benzonitrile concentration: 0.78 mol dm^{-3}; agitation speed: 27 rps; reaction temperature: 358 K; hydrogen partial pressure: 1500 kPa.

A direct test of the importance of gas–liquid and liquid–solid transport was made by carrying out several experiments at different agitation speeds, with all other variable constant (Fig. 3). The initial rate of hydrogenation of benzonitrile was found to increase significantly when the speed increased from 10 to 15 rps but remained constant after 15 rps. It appears from these results that the resistance to gas–liquid/liquid–solid mass transfer is not significant above an agitation speed of about 15 rps. All of the experiments were conducted at agitation speed of 27 rps.

The effect of catalyst loading on the initial rate of catalytic hydrogenation of benzonitrile is shown in Fig. 4. The catalyst loading was varied between 2 and 8 g dm^{-3} for the catalytic hydrogenation of benzonitrile. The initial rate of reaction was found to increase linearly with the catalyst loading.

The intra-particle (pore diffusion) mass-transfer in any porous solid catalyzed reaction can be eliminated by using the small catalyst particle size ≤45 μm [23]. In the present study, the catalyst particle size was <45 μm and hence intra-particle mass transfer resistance was assumed to be insignificant.

To confirm the absence of pore diffusion, the values of effectiveness factor (η) was calculated using the following correlation [24]:

$$\eta = \frac{3}{\phi}\left[\frac{1}{\tanh(\phi)} - \frac{1}{\phi}\right] \tag{6}$$

The value of effectiveness factor is very close to zero when the pore-diffusion resistance is significant and when the effectiveness factor is very close to 1, pore-diffusion has an insignificant effect on the reaction. These values are all very close to 1 at all temperature and show that pore diffusion was insignificant in this study. Thiele modulus (Φ) was calculated

Table 1
Effect of various catalyst on the hydrogenation of benzonitrile

Catalyst	Liquor ammonia (vol.%)	Yield of benzylamine (%)
5% Pd/C	–	21.34
5% Pd/C	1	33.79
5% Pd/C	2	44.06
5% Pd/C	4	54.03
5% Pd/C	6	49.20
5% Pd/$BaSO_4$	–	24.28
5% Pd/$BaSO_4$	4	56.33
5% Pd/$CaCO_3$	–	14.64
5% Pd/$CaCO_3$	4	46.87
5% Pt/C	–	9.75
5% Pt/C	4	40.4
Raney nickel	–	35.57
Raney nickel	6	99.25

Initial benzonitrile concentration: 0.78 mol dm^{-3}; agitation speed: 27 rps; reaction temperature: 358 K; hydrogen partial pressure: 1500 kPa; 2-propanol: 0.05 dm^3.

by the following equation [24]:

$$\Phi = \frac{(r_p^2)(-r_0)}{DC_B} \tag{7}$$

Usually, the absence of pore-diffusion is assumed when values of $\Phi < 1$ are obtained, and very severe pore-diffusion controls for $\Phi > 10$ [25]. In this study, the values of Thiele modulus are <1 at all temperature, indicating the absence of pore-diffusion resistance.

Diffusivity of the solute in the porous catalyst was estimated from the following correlation [26]:

$$D = 19400\frac{\theta^2}{\tau_m S_g \rho_p}\sqrt{\frac{T}{M}} \tag{8}$$

6.3. *Effect of various catalysts*

Effect of several catalysts was investigated in the hydrogenation of benzonitrile in the present study (Table 1). From experiments it was observed that use of noble metal catalysts (5% Pd/C, 5% Pd/$BaSO_4$, 5% Pd/$CaCO_3$, 5% Pt/C) gave low yield of benzylamine after complete conversion of benzonitrile and addition of ammonia did not improve the yield of benzylamine significantly. Among the catalysts used, Raney nickel was found to be an effective and selective catalyst in hydrogenation of benzonitrile to benzylamine and hence in subsequent studies it was used as a catalyst.

6.4. *Effect of solvent*

Solvents are known to have a significant effect on the rate of catalytic hydrogenations. The effect of solvent is attributed to various factors, which include solubility of hydrogen, thermodynamic interaction of the solvent with the reactants and products, agglomeration of catalysts in some solvents, competitive adsorption of the solvent, etc. [27]. Methanol, 2-propanol and dimethylformamide were used as solvents. The rate of benzonitrile hydrogenation was the highest with 2-propanol as a solvent as compared to methanol and dimethylformamide (Table 2). Hence, it was used as a solvent in subsequent studies.

Table 2
Effect of various solvents on the hydrogenation of benzonitrile

Solvent	Initial rate × 10^2 (mol dm^{-3} s^{-1})
2-Propanol	4.08
Methanol	2.97
Dimethylformamide	2.07

Initial benzonitrile concentration: 0.78 mol dm^{-3}; agitation speed: 27 rps; catalyst loading (Raney nickel): 4 gm dm^{-3}; reaction temperature: 358 K; hydrogen partial pressure: 1500 kPa.

6.5. *Effect of hydrogen partial pressure*

The effect of hydrogen partial pressure on the initial rate was studied in the range of 500–2000 kPa (Fig. 5). Solubility of hydrogen in 2-propanol was estimated by a correlation given by Shaw [28]. The initial rate was found to increase linearly with the hydrogen partial pressure. The result indicates first order dependence of the initial rate of reaction on the hydrogen partial pressure.

6.6. *Effect of benzonitrile concentration*

Benzonitrile concentration was varied from 0.4 to 1.6 mol dm^{-3} for the catalytic hydrogenation of benzonitrile. Fig. 6 shows the effect of reactant concentration on the initial rate of catalytic hydrogenation. The initial rate was found to increase linearly with the benzonitrile concentration indicating first order dependence on the reactant concentration.

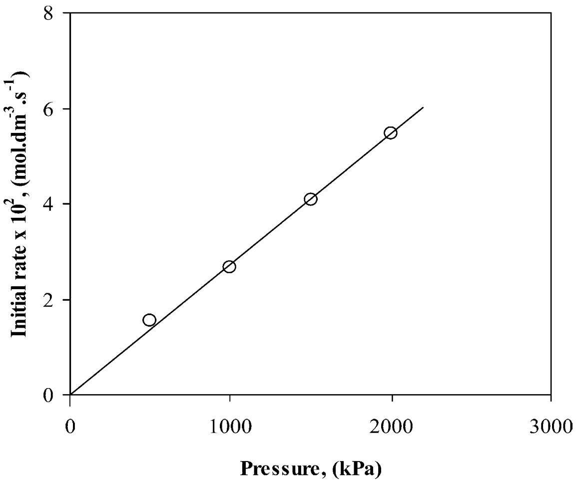

Fig. 5. Effect of hydrogen partial pressure on the initial rate of hydrogenation of benzonitrile: benzonitrile concentration: 0.78 mol dm^{-3}; agitation speed: 27 rps; catalyst loading: 4 gm dm^{-3}; reaction temperature: 358 K.

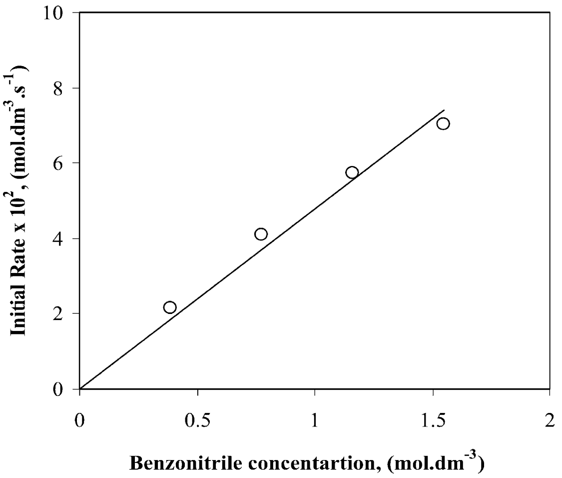

Fig. 6. Effect of benzonitrile concentration on the initial rate hydrogenation of benzonitrile: agitation speed: 27 rps; catalyst loading: 4 gm dm^{-3}; reaction temperature: 358 K; hydrogen partial pressure: 1500 kPa.

6.7. *Effect of temperature*

The reaction was carried out at different temperatures in the range of 328–358 K. The reaction temperature had a strong effect on the initial rate of the reaction and the initial rate was found to increase with increase in the reaction temperature.

The values of reaction rate constant ($k = r_0/wC_{A0}C_B$) at all temperatures (328–358 K) and constant benzonitrile concentration were calculated and Arrhenius plot (Fig. 7) for these values gave activation energy 60.27 kJ. mol^{-1} for hydrogenation of benzonitrile. Normally, a reaction controlled by mass transport (either gas–liquid or liquid–solid mass transport or pore diffusion) has activation energy less than about 25 kJ/mol [29]. Therefore, the high value of observed activation energy suggests that the influence of both gas–liquid and liquid–solid mass transport was negligible in this study.

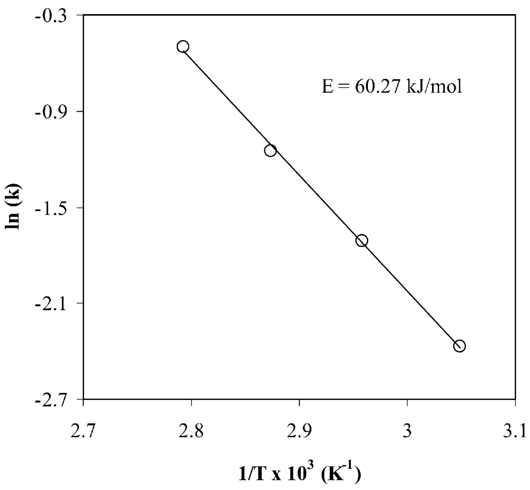

Fig. 7. Arrhenius plot for benzonitrile hydrogenation.

7. Conclusion

The kinetics of liquid phase hydrogenation of benzonitrile to benzylamine has been studied over a wide range of operating conditions. Liquor ammonia as an additive gave the highest yield (>99%) of benzylamine from benzonitrile. First order dependence of the initial rate with respect to each the hydrogen partial pressure and benzonitrile concentration was observed. The activation energy for the catalytic hydrogenation of benzonitrile to benzylamine was found to be 60.27 kJ mol^{-1}.

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