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Hydrogenation of Benzaldehyde over Palladium Intercalated Bentonite Catalysts: Kinetic Studies

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Abstract Bentonite, a 2:1 type swellable phyllosilicate clay mineral having exchangeable inorganic cations in the interlamellar space to nullify their charge deficiency was used to generate palladium nanoparticles. It was found that 1% w/w palladium nanoparticles were generated in the interlamellar space using adsorption excess technique. The synthesized catalysts were characterized by using XRD, TEM, BET surface area analysis, and AAS. The modified clay catalysts were tested for their catalytic activity towards the hydrogenation of benzaldehyde to benzyl alcohol in liquid phase using a high-pressure reactor at various temperatures and pressures. High selectivity (100%) towards the desired product of benzyl alcohol was achieved with conversion over 80% in all cases. These results showed different hydrogen dependency for the reaction at various temperatures. The kinetics of the reaction was studied using Langmuir Hinshelwood single site model. The rate constant was determined using pseudo first-order kinetics and activation energy for benzaldehyde hydrogenation was calculated at various temperatures using Arrhenius equation and was found to decrease with increase in temperature.

Keywords Palladium · Nanoparticles · Adsorption excess isotherm · Kinetic model · Benzaldehyde

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1 Introduction

Hydrogenation of benzaldehyde is of industrial importance as the product benzyl alcohol is used as intermediate in the synthesis of pharmaceuticals, flavor, fragrances, chemical intermediates and photographic chemicals [1, 2]. It is also used as raw material in the manufacture of various esters (such as benzyl formate, acetate, propionate, and butyrate) which are extensively used in the flavor and fragrance industries.

In general noble metals (Pd, Pt, Rh and Ru) and transition metals (Cu, Co and Ni) are selected and used as catalysts for hydrogenation because they have characteristic ability towards adsorption of hydrogen [3]. They can be used without any attack by the reactants. The precursors, supports and the techniques used in catalyst preparation such as ion exchange, grafting, impregnation and gas phase deposition also influence the catalyst properties and activity towards hydrogenation.

Nanoparticle of noble metal behaves different from their bulk counterpart as they possess more surface area. This has led many researchers around the world to synthesize and study the activity of nanoparticle-based catalysts towards various chemical transformations including hydrogenation. However, synthesis of nanoparticles still induces great interest as controlling the particle size and stabilization of nanoparticles is complicated. Various methodologies have been adopted for the synthesis and stabilization of nanoparticles which include using surfactants [4, 5], polymers [6], etc.

Swelling type smectite clays like bentonite, montmorillonite, hectorite, etc. behave as a wonderful host for the synthesis and stabilization of nanoparticles-based catalysts. Pillaring and intercalation are the two predominant methods for generating nanoparticles in the internal surface of

clay [7, 8]. Our previous work using micellar technique and adsorption excess technique to generate and stabilize nanoparticles for selective hydrogenation has produced positive results [9, 10].

In the AET, to generate noble metal of nano size, the binary solvent mixture was chosen in such a way that it satisfied the following conditions as described by Dekany et al. [11].

1. Both the solvents (alcohol and hydrocarbon) must be completely miscible with each other.
2. One of the components (alcohol) should be preferentially adsorbed in the interlamellar space of clay.
3. The metal precursor must be highly soluble in the other component (hydrocarbon).
4. The preferentially adsorbed component must be a good reducing agent of the precursor.

Based upon the above criteria, palladium nanoparticles were generated in the interlamellar space of bentonite using adsorption excess technique with ethanol and toluene as binary mixture for palladium acetate precursor.

In the present study, we report the intercalation of palladium nanoparticles in bentonite clay using adsorption excess technique. Characterization by various physicochemical techniques such as XRD, TEM, BET surface area, evaluation of catalytic activity towards hydrogenation of benzaldehyde and kinetic modeling studies using single site model of Langmuir Hinshelwood model.

Previous literatures show that benzaldehyde hydrogenation follows first-order rate law; however, the rate equation do not describe the benzaldehyde kinetics satisfactorily [12–14] and requires more extensive kinetic model for the reactions [15]. Neri et al. studied the effect of temperature using Langmuir Hinshelwood kinetics [16], they found that adsorption of reactant and desorption of product are in equilibrium and surface reaction is the rate controlling step. Vergunst et al. compared three different models and concluded that a single site model gives the best results [17]. Adsorption, surface reaction and desorption are all rate determining steps in single-site model.

2 Experimental

2.1 Catalyst Synthesis by Adsorption Excess Isotherm

Cetyltrimethylammonium bromide (CTABr) from Merck was exchanged for exchangeable Na^+ ions present in the interlamellar space of bentonite (Merck) with a cation exchange capacity of 94 meq/100 g of clay. The exchanged organo clay (CTA^+-Bent) was washed repeatedly several times with double distilled water and air-dried.

To 1 g of organo clay, ethanol:toluene (AR, Merck) binary mixture (total volume 20 mL) with varying mole fraction of ethanol was added each time. This was allowed to equilibrate for 24 h, centrifuged and the composition of the equilibrium mixture was determined by using Abbe's refractometer. The molar reduced surface excess amount ($n_1^{\sigma(n)}$) was calculated for ethanol via the relation: [18, 19]

$$n_1^{\sigma(n)} = n^{\mathrm{o}}\left(X_1^{\mathrm{o}} - X_1\right)/M \quad \mathrm{mol/g}$$

The adsorption excess isotherm was constructed as $n_1^{\sigma(n)}$ versus X_1, where X_1 is the mole fraction of ethanol. From the adsorption excess isotherm, the ratio of ethanol:toluene required for minimization of Pd reduction in the bulk was determined and Pd was then intercalated into the interlamellar region of bentonite as detailed below:

The required amount of ethanol–toluene binary mixture as calculated by adsorption excess isotherm was added to 2.5 g CTA^+-bentonite, equilibrated; and stirred for another 30 min till a homogeneous mixture was obtained. Later palladium acetate (1% Pd wt. content, >99%, Merck) dissolved in toluene was added to it drop wise and stirred. Complete reduction was visually noted as orange red solution of palladium acetate turned into deep black. This precipitate was filtered, washed and dried at 423 K and labeled as Pd-A.

2.2 Characterization of the Catalysts

The BET surface area of bentonite, CTA^+ bentonite, Pd intercalated bentonite were determined by using Micromeritics Pulse Chemisorb 2700 system using nitrogen as the probe molecule. The samples were pre-heated in vacuum at 473 K for 3 h and were analyzed at 77 K. The range of relative pressure P/P_{o} in which the analysis was carried out was between 0.02 and 0.2.

The amount of palladium intercalated into the clay was determined by using Perkin Elmer 2380 Atomic Absorption spectrophotometer after digesting the catalyst in aqua regia.

The basal spacing of bentonite and change in basal spacing after exchange of CTA^+ were determined by using PANalytical X'Pert Pro X-ray diffractometer with Cu $K\alpha$ source with a wavelength of 1.54 Å operating at 20 mA and 50 kV.

Transmission electron micrographs were taken to find out the particle size of the metal particles. JEOL JEM-2010F field emission microscope with an operating voltage of 200 kV was used. The sample was well dispersed in isopropyl alcohol and sonicated, a drop of it was taken on the copper grid and TEM pictures were taken.

2.3 Catalytic Reaction

Hydrogenation of benzaldehyde was carried out in a high-pressure reactor of 150 mL capacity (Tecnomic Autoclave Engineers, Mumbai) with an inbuilt stirrer, pressure gauge,

safety valve, valves for gas inlet and outlet, a thermocouple for temperature sensing. The whole setup was mounted over a furnace whose temperature was controlled. Benzaldehyde (>99% Merck) was used as reactant and ethanol (AR grade SRL) was used as solvent. The catalyst, 0.5 g, was taken and 25 mL of ethanol was added and was pretreated by bubbling hydrogen for 2 h 373 K, then the temperature was decreased to room temperature. Then, 5 mL of the reactant (0.049 mole benzaldehyde) was added to it along with 50 mL of the solvent taking the total volume to 80 mL. The autoclave was charged with hydrogen (2.5 or 5 bar) and maintained at different temperatures (323, 348 and 373 K). The reaction was carried out for 5 h and samples withdrawn for every hour were analyzed using GC (Shimadzu 17A) with OV-1 column and FID detector.

3 Results and Discussions

3.1 Adsorption Excess Isotherm

Adsorption excess isotherm of CTA^+-bentonite with ethanol–toluene binary mixture was constructed and the amount of ethanol completely adsorbed was determined from the plot (Fig. 1). The molar reduced surface excess amount ${n_1}^{\sigma(n)}$ is related to the actual amount present in the interlamellar space by Ostwald-de-Izaguirre equation [20]. The experimental values were fitted in the empirical equation to determine the surface excess. The adsorption excess isotherm belonged to the III type of Schay–Nagy classification [21]. From the isotherm, the mole fraction of ethanol completely adsorbed by bentonite was found to be 0.132 which corresponds to an ethanol:toluene ratio of 1.6:18.4 mL. The error on duplication was found to be <2%.

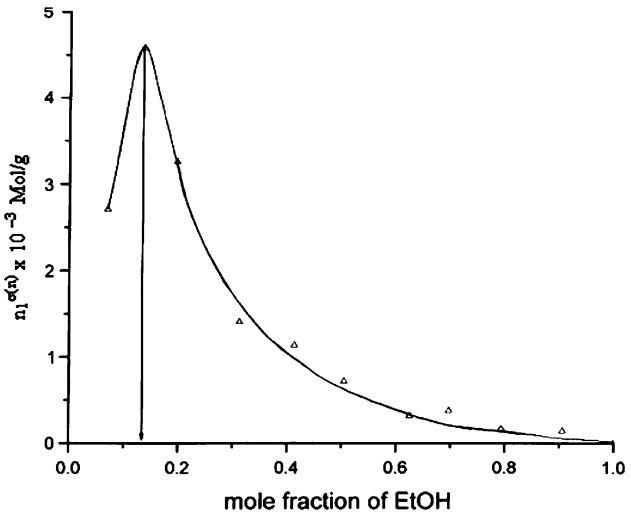


Fig. 1 Adsorption excess isotherm of CTA^+ bentonite

Table 1 BET surface area analysis

Material	Surface area, m^2/g
Bentonite	28
CTA^+ bentonite	6
1% Pd-A	21

3.2 BET Studies

The surface area of CTA^+-bentonite and Pd intercalated bentonite are shown in Table 1. The decrease in the surface area was observed for CTA^+-bentonite. This is because nitrogen molecule cannot access the internal surface of CTA^+-bentonite [18].

3.3 AAS Studies

Exact palladium content in bentonite was determined by AAS by digesting the samples in aqua regia. The metal loading found out by AAS was 0.89% for Pd–A.

3.4 XRD Studies

X-ray diffraction studies were carried out for bentonite and CTA^+-bentonite to determine whether there was any increase in basal spacing. XRD patterns of bentonite and CTA^+-bentonite are shown in Fig. 2. The XRD patterns show that

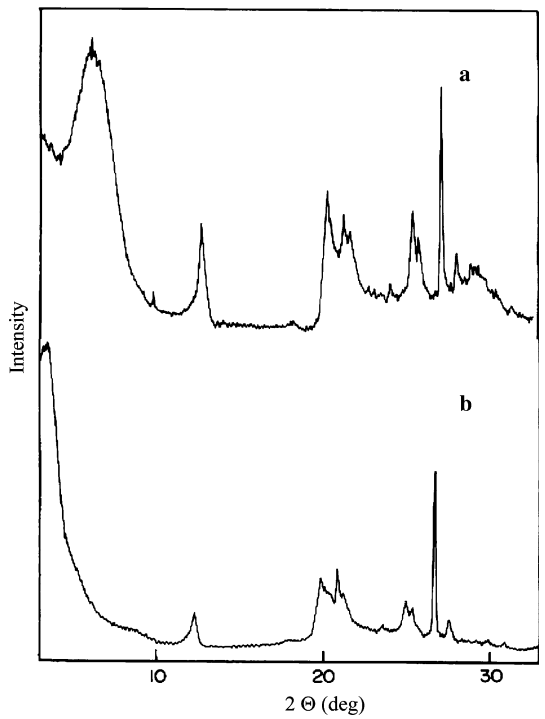


Fig. 2 X-ray diffraction pattern of (**a**) raw bentonite and (**b**) CTA^+ bentonite

the (001) peak of CTA^+-bentonite was shifted from $2\theta = 5.8^\circ$ to $2\theta = 1.2^\circ$ which confirm the increase in d spacing of CTA^+ bentonite. The d-spacing in raw bentonite was found to be 15.2 Å and that of CTA^+ exchanged bentonite was 73.5 Å. Since the metal loading was very low no characteristic peak for Pd (111) was obtained at $2\theta = 40^\circ$. However, no change in (001) peak was observed indicating that the basal spacing remained unchanged after intercalation.

3.5 TEM Studies

TEM micrographs were taken to determine the particle size of palladium present in the interlamellar space of bentonite (Fig. 3) (the particle size distribution is as shown in Fig. 3a). The average particle size was found to be 6.5 nm for Pd-A. The picture also confirms that the palladium particles were well dispersed and in the nano range.

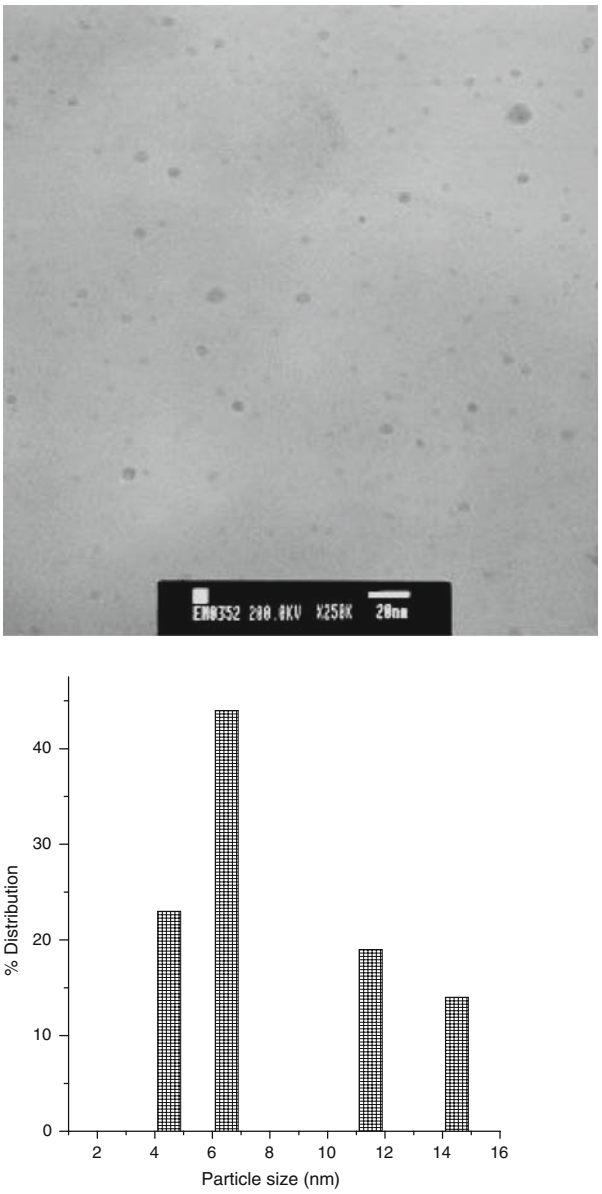
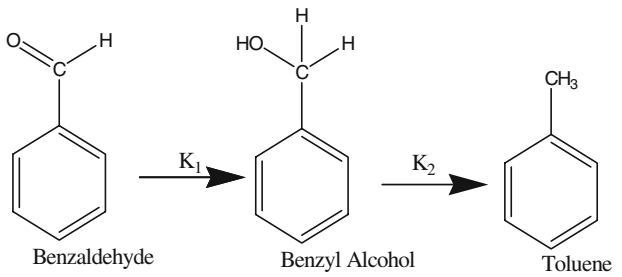


Fig. 3 Transmission electron micrograph of 0.89% Pd-A. (**a**) Particle size distribution of Pd nanoparticles in Pd-A

3.6 Benzaldehyde Hydrogenation

Catalytic activity was evaluated using high-pressure reactor with ethanol as solvent. The scheme of benzaldehyde hydrogenation is shown in Scheme 1. No reaction was found to proceed in the absence of catalyst or hydrogen. Hydrogenation of benzaldehyde was carried out over the catalysts at different temperatures (323, 348 and 373 K), hydrogen pressures and weights of catalyst to optimize the conditions at which the catalysts were the most active and selective towards benzyl alcohol. The effect of temperature on conversion of benzaldehyde was shown in Fig. 4. From the figure we infer that conversion increases with temperature which may be due to the fact that more number of active sites gets activated at high temperature. The effect of time on stream on the selectivity towards benzyl alcohol over 0.5 g of the catalysts at 373 K and 5 bar pressure is shown in Figs. 5 and 6. It shows selectivity towards benzyl



Scheme 1 Benzaldehyde reaction scheme

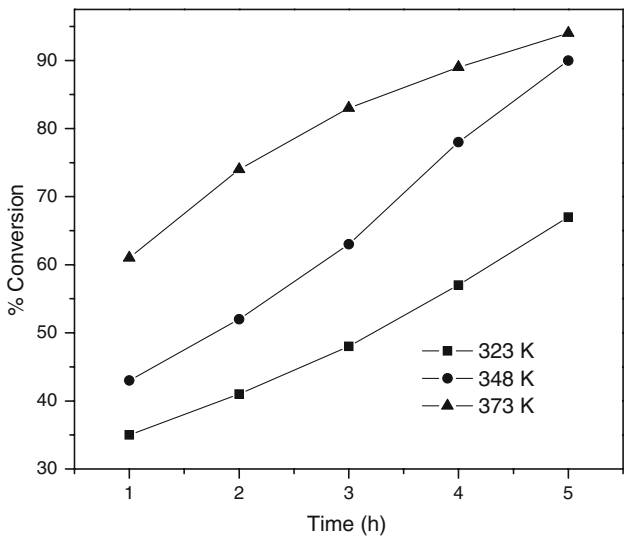


Fig. 4 Effect of time on stream on conversion at different temperature (Cat. wt. 0.5 g, P: 5 bar)

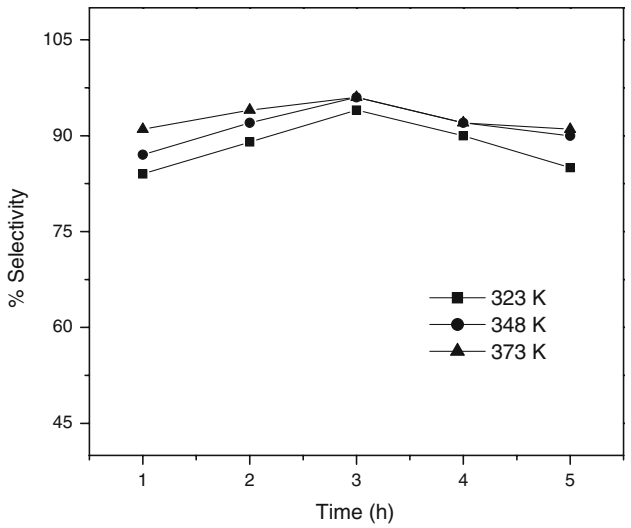


Fig. 5 Effect of time on stream on selectivity at different temperatures (Cat. wt. 0.5 g, P: 5 bar)

alcohol around 94%. The selectivity was found to decrease with temperature. As the weight of the catalyst was increased, conversion also increased as the number of active site increases. The effect of pressure on conversion and selectivity was studied at 2.5 and 5 bar hydrogen pressures. It was noticed that the conversion increased while there was a marginal decrease in the selectivity.

3.7 Kinetic Modeling

Benzaldehyde hydrogenation reactions followed the Langmuir Hinselwood kinetics. According to this kinetics one of the reactants is adsorbed on the surface of the catalyst and the reaction was found to proceed via first-order kinetics.

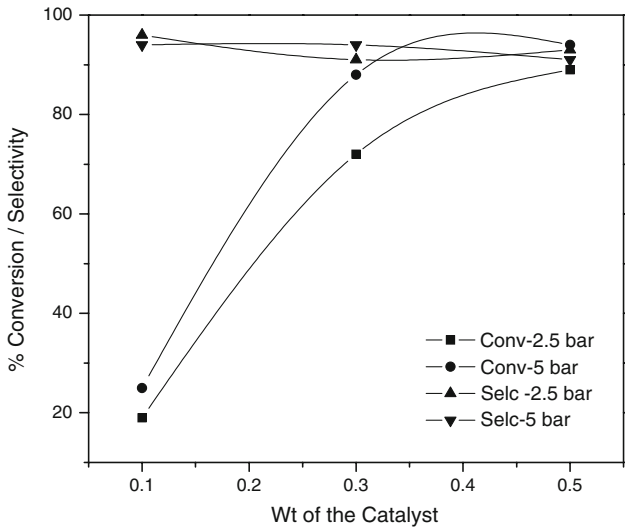


Fig. 6 Effect of pressure on selectivity and conversion for different weight loading of the catalyst (Temp: 373 K)

Based on the assumption that adsorption and desorption steps are in quasi equilibrium and surface reaction is the rate determining step, single site model was proposed. In single site model, hydrogenation of C=O takes place on a single site. The following are the assumptions made for the kinetic study.

Assumptions:

1. Hydrogenation of C=O occurs through one site (single site model).
2. Surface reaction is rate determining step. Adsorption and desorption are considered to be in quasi equilibrium.
3. Spherical catalyst particle of uniform size.
4. Reaction is irreversible.

Rate of hydrogenation,

$$r_1 = K_1\,\theta_{\mathrm{Bad}}$$

$$r_2 = K_2\,\theta_{\mathrm{Bad}}$$

$$r_{\mathrm{ads}} = K_{\mathrm{ads}}\,C_{\mathrm{Bad}}\,\theta^* \tag{1}$$

$$r_{\mathrm{des}} = K_{\mathrm{des}}\,\theta \tag{2}$$

At equilibrium, $r_{\mathrm{ads}} = r_{\mathrm{des}}$

$$K_{\mathrm{ads}}\,C_{\mathrm{Bad}}\,\theta^* = K_{\mathrm{des}}\,\theta$$

$$\frac{K_{\mathrm{ads}}}{K_{\mathrm{des}}} = K_{\mathrm{Bad}} = \frac{\theta_{\mathrm{Bad}}}{C_{\mathrm{Bad}}\theta^*}$$

$$\theta_{\mathrm{Bad}} = K_{\mathrm{Bad}}\,C_{\mathrm{Bad}}\,\theta^*$$

$$r_1 = K_1\,K_{\mathrm{Bad}}\,C_{\mathrm{Bad}}\,\theta^* \tag{3}$$

$$r_2 = K_2\,K_{\mathrm{Bad}}\,C_{\mathrm{Bad}}\,\theta^* \tag{4}$$

Site balance

$$\theta^* + \theta_{\mathrm{Bad}} + \theta_{\mathrm{Bal}} + \theta_{\mathrm{Tol}} = 1 \tag{5}$$

$$\theta^* + K_{\mathrm{Bad}}C_{\mathrm{Bad}}\,\theta^* + K_{\mathrm{Bal}}C_{\mathrm{Bal}}\,\theta^* + K_{\mathrm{Tol}}C_{\mathrm{Tol}}\,\theta^* = 1$$

$$\theta^* = \frac{1}{1 + k_{\mathrm{Bad}}C_{\mathrm{Bad}} + K_{\mathrm{Bal}}C_{\mathrm{Bal}} + K_{\mathrm{Tol}}C_{\mathrm{Tol}}} \tag{6}$$

Substituting the value of (1) and 5 in Eqs. 3 and 4 we get

$$r_1 = \frac{K_1K_{\mathrm{Bad}}C_{\mathrm{Bad}}}{1 + K_{\mathrm{Bad}}C_{\mathrm{Bad}} + K_{\mathrm{Bal}}C_{\mathrm{Bal}} + K_{\mathrm{Tol}}C_{\mathrm{Tol}}} \tag{7}$$

$$r_2 = \frac{K_2K_{\mathrm{Bal}}C_{\mathrm{Bal}}}{1 + K_{\mathrm{Bad}}C_{\mathrm{Bad}} + K_{\mathrm{Bal}}C_{\mathrm{Bal}} + K_{\mathrm{Tol}}C_{\mathrm{Tol}}} \tag{8}$$

The above equations represent the rate of change of concentration with respect to time. The rate constant values at different temperatures for benzaldehyde hydrogenation is shown in Table 2. The concentration of benzaldehyde decreases with respect to time, the formation of benzyl alcohol increases with time. The activation energy for the hydrogenation reaction was calculated by substituting the rate constant value in Arrhenius equation.

Table 2 Rate constant and activation energy values for benzaldehyde hydrogenation reaction at various temperatures

Temperature, K	Rate constant, $K \times 10^{-3}$	Activation energy, kJ/mol
323	2.3	16.3
348	5.6	15.00
373	8.1	14.93

$$\ln k = \frac{-Ea}{RT}$$

The activation energy for benzaldehyde hydrogenation reaction calculated at 323,348 and 373 K was found to increase with increase in temperature; the activation energy at various temperatures is given in Table 2.

4 Conclusion

By using the swelling and ion exchange property of bentonite, palladium nanoparticles were intercalated by constructing adsorption excess isotherm. By using adsorption excess isotherm one can minimize the reduction of the metal in the bulk. XRD study reveals that the basal spacing of the clay mineral increased by the ion exchange with cationic surfactant and TEM analysis show that the metal particles were in nanometer range and were well dispersed. By suitable selection of binary mixture, adsorption excess method can be fruitfully applied for generation of transition/noble metal nanoparticles in various other clay minerals. The activity of the intercalated catalysts are found to be good and selective towards the desired product namely benzyl alcohol. Kinetic study for the hydrogenation of benzaldehyde was carried out using Langmuir-Hinshelwood mechanism and was found to follow pseudo first-order kinetics with respect to benzaldehyde.

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