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Hydrogenation of acetophenone using a 10% Ni supported on zeolite Y catalyst: kinetics and reaction mechanism

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Abstract

The kinetics of hydrogenation of acetophenone was studied using a 10% Ni supported on zeolite Y catalyst in a temperature range 353–393 K. The effect of H_2 pressure, initial concentration of acetophenone and catalyst loading on the concentration-time profiles was studied. Water formed during the course of hydrogenation showed a strong inhibiting influence on the rate of reaction. A rate equation has been proposed based on L–H type rate mechanism assuming that the reaction between the non-competitively adsorbed hydrogen and the adsorbed organic substrate as rate limiting step. A semi-batch reactor model was developed to predict the concentration-time, H_2 consumption-time profiles at different sets of initial conditions. The model predictions were found to agree with experimental data very well at all temperatures. This model incorporates the inhibition of hydrogenation rate due to water. The inhibiting effect of water is also explained based on quantum chemical calculations.

Keywords: Hydrogenation; Kinetics; Acetophenone; Ni catalyst

1. Introduction

The catalytic hydrogenation of organic compounds containing a carbonyl group is important in the synthesis of fine chemicals, pharmaceuticals, dyes and agrochemicals. An important class of this reaction is the hydrogenation of acetophenone using supported metal catalysts. The products formed during the course of hydrogenation such as phenyl ethanol (PE), and cyclohexyl ethanol (CHE) are industrially important. For example, CHE finds application in the manufacture of polyvinylcyclohexane which is a high-temperature resistant polymer while PE finds application in the manufacture of perfumery products and pharmaceuticals. The reaction is usually carried out commercially in the liquid phase using supported metal catalysts or Raney Ni doped with Cr or Co catalysts in mechanically agitated reactors [1]. The kinetic modelling of such complex reactions is very often difficult due to the several complexities such as interphase and intraparticle mass transfer resistance, mixing of fluid phases and complex hydrodynamics of the reactors. There are only a few reports that discuss in detail the kinetic modelling of multistep catalytic hydrogenation reactions [2–4] and almost no reports are available which deal with a detailed kinetic analysis of hydrogenation of acetophenone using

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supported Ni catalysts in batch slurry reactors. The activity, selectivity and stability of Ni supported on zeolite Y catalyst has already been investigated by Rajashekharam et al. [5]. These authors have also proposed a reaction mechanism in which the support zeolite Y plays a major role during hydrogenation based on the extensive characterisation data on the catalyst.

Usually, during hydrogenation of oxygen containing functional groups of organic compounds, water forms as an unavoidable side product, and hence, the role of water on the overall rate of reaction needs to be understood. The literature reports that discuss in detail the role of water during such hydrogenation reactions are scanty. For example, Santacesria et al. [6] observed that water formed during the hydrogenation of anthraquinones using supported Pd catalysts was responsible for the substantial decrease in activity which leads the authors to propose a rate model incorporating the reversible deactivation of catalyst. Considering the industrial significance of multiphase catalytic hydrogenation reactors in general, it was thought important to study the kinetics of hydrogenation of acetophenone using a 10% Ni supported on zeolite Y (10% Ni/HY) catalyst in detail incorporating the influence of the products formed on the overall kinetics during the course of hydrogenation, and to develop a semi-batch slurry reactor model to predict the concentration-time profiles for different sets of initial conditions. The effect of acetophenone concentration, partial pressure of hydrogen, catalyst loading, agitation speed, water concentration on the concentration-time profiles and H_2 consumption-time profiles was investigated in a temperature range 353–393 K. The role of water on the initial rate was analysed and incorporated in the rate equation.

2. Experimental

2.1. Materials

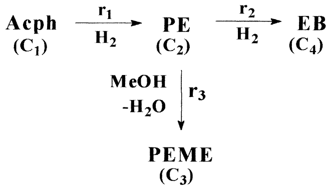
Acetophenone was obtained from Aldrich, USA, while the solvent, methanol was from SD Fine Chemicals, India, and was freshly distilled prior to use. H_2 and N_2 gases were obtained from Indian Oxygen, India, and were used directly. Ethyl benzene and Phenyl ethanol required as GC standards were obtained from Aldrich, USA. The catalyst used was 10% Ni/HY and these catalysts were prepared by a known method described by Roberts [7]. The catalyst was activated by reduction under H_2 flow (5×10^{-5} m^3/min) at 773 K for 10 h. The catalyst was then passivated under N_2 flow (3×10^{-5} m^3/min) for 2 h before using for hydrogenation experiments. The detailed specifications of the catalyst used for kinetic study are: Ni content (w/w): 10%, support: HY, surface area: 5×10^5 m^2/kg, particle size (d_p): 1×10^{-5} m, particle density (β_p): 2.5×10^3 kg/m^3, porosity (ε): 0.58, and tortousity (τ): 3.5.

2.2. Experiments for kinetic study

All hydrogenation experiments were carried out in a 3×10^{-4} m^3, capacity stirred pressure reactor which has provisions for automatic temperature control, variable stirrer speeds and sampling of gases and liquids. The details of the reactor set up were the same as described in our earlier paper [8]. In a typical hydrogenation experiment, known amounts of acetophenone, catalyst and solvent methanol were charged into the reactor. The reactor was first purged with N_2 and then with H_2 at room temperature. The contents were heated to a desired temperature and then H_2 gas was introduced to the required pressure level. The reaction was started by switching the stirrer on. The progress of the reaction was followed by recording the H_2 pressure drop in the reservoir vessel and concentration of liquid phase components as a function of time. The analysis of liquid samples was carried out using a HP 5840 Gas Chromatography containing a 5 m long SS column packed with 10% OV-17 on ChromosorbW. The conditions of gas chromatographic analysis are as follows: FID temperature: 523 K; injection temperature: 473 K; column temperature: 423 K; N_2 carrier gas: 4×10^{-5} m^3/min. The products were confirmed using a Shimadzu GC-MS-QP 2000A instrument. The range of conditions studied was concentration of acetophenone: 0.4–2 kmol/m^3, H_2 pressure: 0.5–7 MPa, catalyst loading: 10–40 kg/m^3, and concentration of water: 0–3 kmol/m^3.

3. Results and discussion

The hydrogenation experiments using 10% Ni supported on zeolite Y catalyst were carried out in order



Scheme 1.

to understand: (a) overall kinetics of this reaction; (b) to investigate the role of water, a side product formed during the course of hydrogenation; and (c) to develop a semi-batch reactor model incorporating the influence of water on the overall kinetics of the reaction. For this purpose, experimental data were obtained for a wide range of operating conditions to observe both initial rate of hydrogenation as well as integral concentration-time profiles. The products formed during the hydrogenation of acetopheone were found to be Phenyl ethyl alcohol (PEA), Styrene(Sty), Ethyl benzene(EB) and Phenyl ethyl methyl ether(PEME) (when methanol was used as a solvent) as identified GC and GC/MS analysis. Typical concentration profile is shown in Fig. 6 for 373 K. Scheme 1 is considered based on the observed product distribution.

The initial experiments on the hydrogenation of acetophenone showed that the material balance of the reactants consumed (H_2, and acetophenone) and the products formed (PEA, EB and PEME) agreed to the extent of 95–97% as per the above stoichiometry. Reproducibility of the rate measurements were found to be within 2–5% error indicated by a few repeated experiments.

3.1. Analysis of initial rate data

The effect of initial concentration of acetophenone, H_2 pressure, catalyst loading, agitation speed and water concentration on the initial rate data of hydrogenation of acetophenone was studied at 353, 373, and 393 K. For calculating the initial rate data, the hydrogen consumption-time profiles observed under different conditions were used. The effect of concentration of acetophenone on the initial rate of hydrogenation is shown in Fig. 1 at different temperatures. These results indicate a first order tending to zero order dependence with respect to acetophenone concentration. The data presented in Fig. 1 mainly represent the

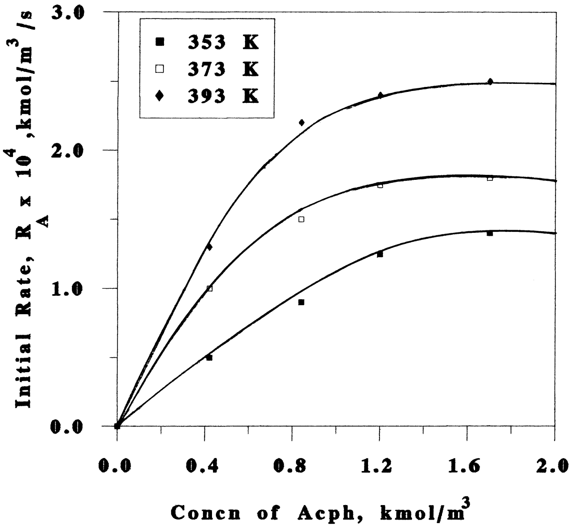


Fig. 1. Effect of acetophenone concentration on initial rates. Reaction conditions: catalyst loading: 10 kg/m^3; P_{H_2}: 2.14 Mpa; agitation speed: 18 Hz; reaction volume: 1×10^{-4} m^3; solvent: MeOH.

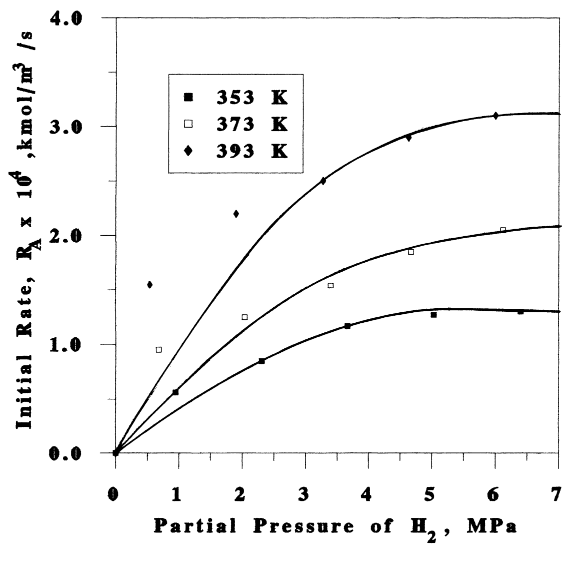


Fig. 2. Effect of partial pressure of hydrogen on initial rates. Reaction conditions: concentration of acetophenone: 0.84 kmol/m^3; catalyst loading: 10 kg/m^3; agitation speed: 18 Hz; reaction volume: 1×10^{-4} m^3; solvent: MeOH.

conversion of acetophenone to PEA and hence the trend observed cannot be generalised for all the hydrogenation steps. Fig. 2 shows the effect of H_2 pressure on the initial rate which indicates nearly a zero order

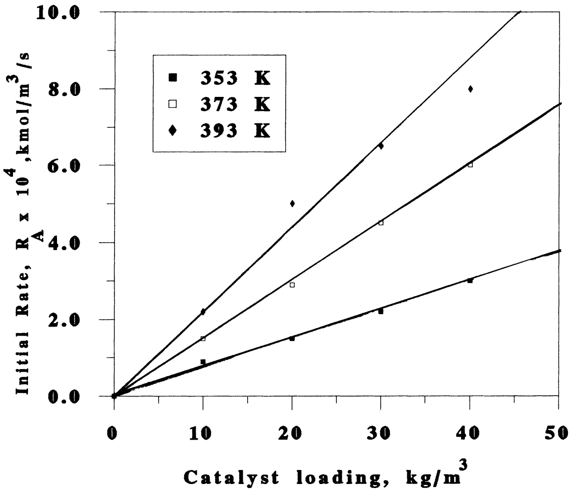


Fig. 3. Effect of catalyst loading on initial rates. Reaction conditions: concentration of acetophenone: 0.84 kmol/m^3; P_{H_2}: 2.14 Mpa; agitation speed: 18 Hz; reaction volume: 1×10^{-4} m^3; solvent: MeOH.

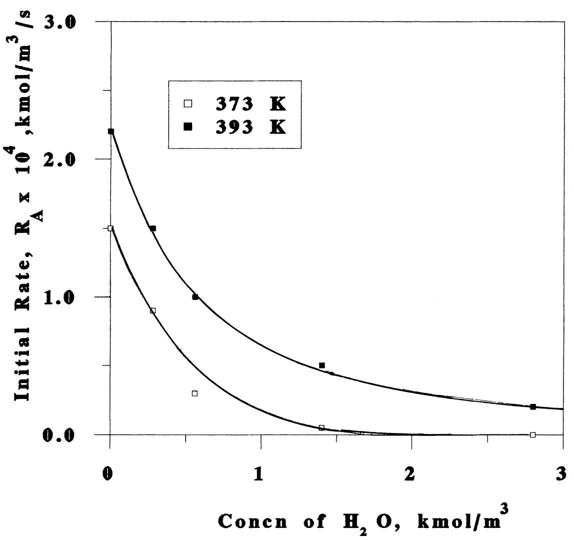


Fig. 4. Effect of water on initial rates. Reaction conditions: concentration of acetophenone: 0.84 kmol/m^3, P_{H_2}: 2.14 Mpa; catalyst loading: 10 kg/m^3; agitation speed: 18 Hz; reaction volume: 1×10^{-4} m^3, solvent: MeOH.

dependence, excepting for a very low partial pressures of hydrogen. The effect of catalyst loading on the initial rate (see Fig. 3), indicates a linear dependence. The initial rate was found to be independent of agitation speed indicating the absence of external mass transfer resistances (gas–liquid and liquid–solid). The effect of water concentration on the initial rate of hydrogenation at 393 K is shown in Fig. 4. These results clearly indicate a strong inhibition of rate in the presence of water. The other products formed, namely, PEA, EB and PEME showed no influence on the initial rate.

For the purpose of kinetic study it is important to ensure that the rate data obtained are under the kinetic regime. The initial rate data were analysed to check the significance of gas–liquid, liquid–solid and intraparticle mass transfer effects following the quantitative criteria proposed by Ramachandran and Chaudhari [9]. In these criteria, α_1, α_2, $\phi_{\rm exp}$ which are defined as the ratios of the observed rate to the maximum rates of gas–liquid, liquid–solid and intraparticle mass transfer steps, respectively, were calculated as $\alpha_1=(R_A/k_la_BA^*)$, $\alpha_2=(R_A/k_sa_pA^*)$ and $\phi_{\rm exp}=[(d_p/6)(\rho_pR_A/wD_eA^*)^{0.5}]$, respectively. In order to calculate these values, a knowledge of the gas–liquid mass transfer coefficient, k_la_B, liquid–solid mass transfer coefficient, k_s, effective diffusivity, D_e, external surface area of the catalyst particle, a_p, saturation solubility, A^* and the overall rate of hydrogenation, R_A are required. The value of k_la_B of 0.2 s^{-1} was used as determined by Chaudhari et al. [10] for the same equipment and the k_s value was evaluated from the correlation of Sano et al. [11]. These correlations are given in appendix A. The effective diffusivity value was calculated from the following expression $D_e=(D_{\varepsilon/\tau})$, where D represents the molecular diffusivity calculated from Wilke and Chang [12] equation, ε and τ represent the porosity and the tortousity of the catalyst particle, respectively. The values of τ, the tortousity factor, were chosen as 3.5. (An average value observed for similar catalyst supports [13]) The calculated values of effective diffusivity at different temperatures along with other parameters are shown in Table 1.

The external surface area of the catalyst particle was calculated from the following equality, assuming spherical catalyst particles:

$$a_p = 6w/\rho_pd_p. \tag{1}$$

The saturation solubility, A^*, was calculated as $A^* = P_{H_2} \times H_A$, where P_{H_2} represents the partial pressure of hydrogen, MPa and H_A, represents Henry's constant for solubility, kmol/m^3/atm. The partial pres-

Table 1
Values of different parameters used in evaluating the role of external and internal mass transfer resistance at different temperatures

No.	T (K)	Gas–liquid mass transfer coefficient (k_la_B, s^{-1})	Liquid–solid mass transfer coefficient ($k_sa_p\times10^2$ m/s)	Molecular diffusivity ($D\times10^9$ m^2/s)	Porosity (ε)	Tortuosity (τ)	Effective diffusivity ($D_e\times10^9$ m^2/s)
1	353	0.2	1.35	9.17	0.58	3.5	1.52
2	373	0.2	1.51	9.69	0.58	3.5	1.61
3	393	0.2	1.75	10.21	0.58	3.5	1.69

sure of hydrogen was calculated by subtracting the vapour pressure of the solvent (methanol) at the respective temperature from the total pressure indicated from the pressure gauge of the reactor. The vapour pressure of methanol at different temperatures was calculated using the following correlation:

$$\log P = \left[\left(\frac{0.2185\times A}{T}\right)\times B\right], \qquad (2)$$

where P is the vapour pressure in torr, T is the temperature in K, A and B are two constants given as A=8978.8 and B=8.639821 for methanol as mentioned earlier in literature [14]. The values of Henry's constant determined from experimental solubility data for acetophenone, methanol and the mixtures are shown in Table 2. As one can see that the addition of acetophenone to methanol solutions significantly decreases the solubility of hydrogen in the mixture. Hence, this correction factor needs to be considered while calculating the H_2 solubility values used in kinetic and mass transfer analysis.

After performing the above calculations, the values of α_1, α_2, and ϕ_{exp} were found to be less than 9.5×10^{-2}, 5.8×10^{-3} and 0.17, respectively, indicating that the rate data obtained are in kinetic regime and can be reliably used to evaluate the intrinsic kinetic parameters.

3.2. Quantum chemical calculations of interaction energies

The initial data analysis on the effect of water concentration indicates a strong inhibiting effect as shown in Fig. 4. This might be due to water blocking the active sites on the zeolite Y support responsible for the activation of the C=O bond and the Ni sites on which the hydrogen is adsorbed [5]. In order to check the former, it is necessary to know the different interaction energies of water and acetophenone with the support zeolite Y. The interaction energy of water molecule and acetophenone molecule with the zeolite Y dimer cluster were calculated using a quantum chemical programme MOPAC 6.0 on a Silicon Graphics Indigo 2 work station. The zeolite Y dimer was fixed in the crystallographically determined position [15]. The acetopheone and water molecules were built using Builder Software supplied by Biosym Technologies, and they were optimised to get the minimum energy configuration [16]. The interaction energies of acetophenone and water molecules with the zeolite Y were determined by using the minimum distance obtained from solid docking. Typical photographs showing zeolite Y dimer, the minimum distance used to calculate the interaction energies between acetophenone–zeolite Y and water–zeolite Y dimer are

Table 2
Experimentally determined Henry's Constant values ($H_A\times10^3$ kmol/m^3/atm) at different temperatures for mixtures of acetophenone and methanol

No.	T (K)	Pure MeOH	Pure Acph	Henry constant $\times10^3$ kmol/m^3/atm		
				5% Acph+95% MeOH	10% Acph+90% MeOH	20% Acph+80% MeOH
1	353	5.0	2.02	4.7	4.3	3.8
2	373	5.5	2.47	5.01	4.7	4.2
3	393	5.8	2.72	5.2	5.1	4.52

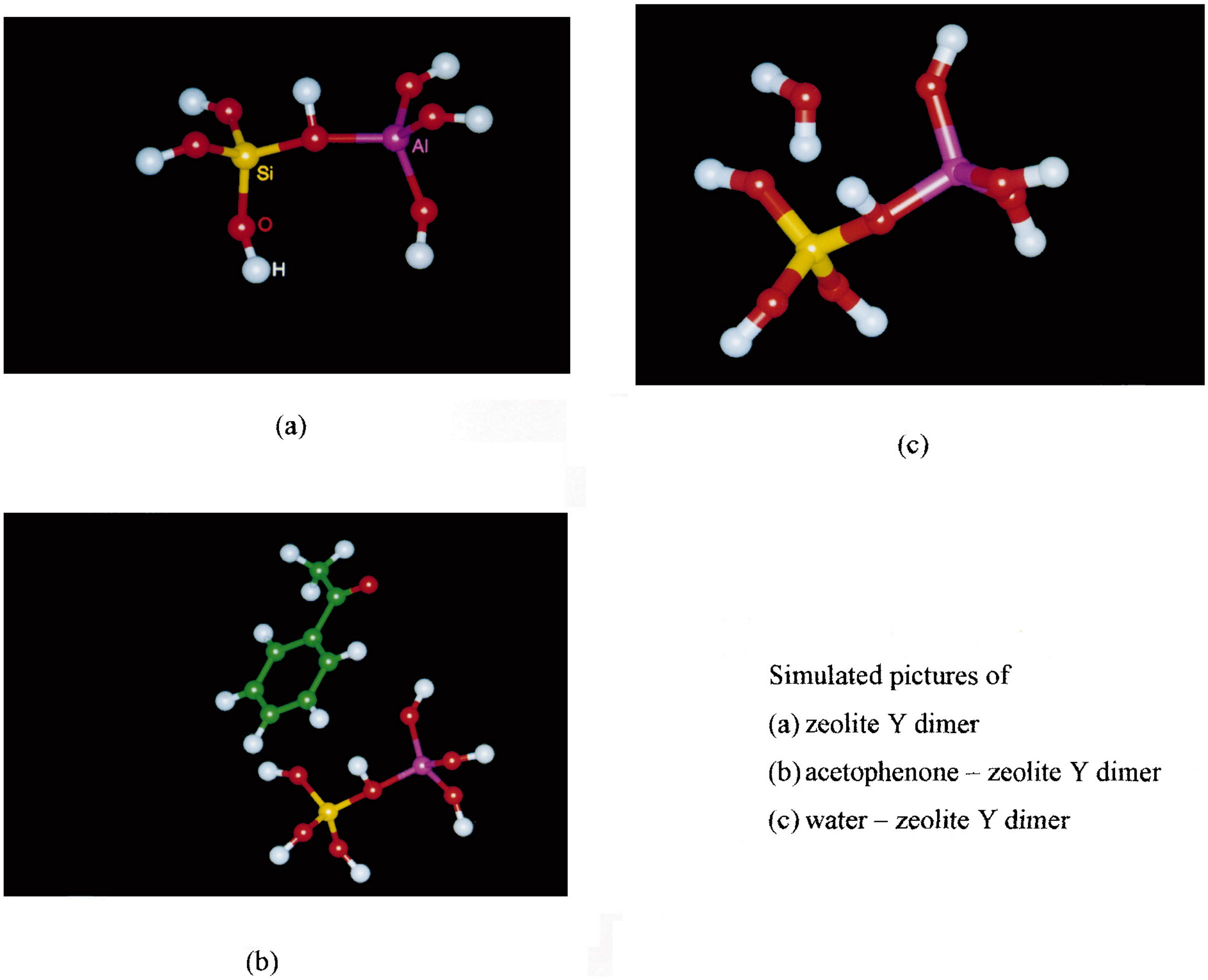


Fig. 5. Photographs of: (a) zeolite Y dimer; (b) acetophenone–zeolite Y dimer; (c) water–zeolite Y dimer.

shown in Fig. 5. The following equation reported by Himei et al. [17] was used to calculate the interaction energy or the adsorption energy:

$$E_{\text{adsorption}} = E_{\text{host}} + E_{\text{guest}} - [E_{\text{host}} + E_{\text{guest}}], \tag{3}$$

where the host represents the zeolite Y dimer and the guest represents water or acetophenone molecule, respectively. The results are shown in Table 3. These calculations were performed assuming that the following equality exists.

$$1\,\text{ev} = 1.60218 \times 10^{-19} \times 6.023 \times 10^{23} = 96.5\,\text{kJ/mol}, \tag{4}$$

where 1.60218×10^{-19} is the charge of an electron and 6.023×10^{23} is the avagadro number. The results indicate that the adsorption energy of water molecule is

Table 3
Calculated values of interaction energies

Guest	E_{host} (ev)	E_{guest} (ev)	$E_{\text{host+guest}}$ (ev)	$E_{\text{adsorption}}$ (ev)	$E_{\text{adsorption}}$ (kJ/mol)
Acetophenone	−2498.08	−1457.48	−3955.31	0.25	24.13
Water	−2498.08	−351.40	−2849.02	0.46	44.40

much higher than that of acetophenone, which explains the strong inhibiting influence of water on hydrogenation. Due to a high interaction energy, the protonic sites of the zeolite will be blocked by the water molecule and thereby leaving the acetophenone molecule inactivated. Also, during the course of hydrogenation, water is formed as a side product which might in turn influence the overall kinetics. Hence, this important effect needs to be incorporated in the rate model derived.

The fact that water has a strong inhibiting influence on the initial rate indicates that the Ni sites are also modified due to the presence of water. It has been reported for supported Pd catalysts during hydrogenation of anthraquinones that the Pd surface interacts with water leading to a significant inhibition [6]. However, these authors have explained the result as a reversible deactivation phenomenon and developed a semi-batch reactor model to predict the concentration-time profiles incorporating the water effect. Based on this information, we conclude that with Ni surfaces interactions of the type shown in Scheme 2 are possible. This suggests that a different type of Ni species that may not be active for the adsorption of hydrogen is a prerequisite for the hydrogenation to proceed (Scheme 2). This influence of water on the adsorption of H_2 on Ni sites has a significant effect by reducing the number of active Ni sites that are available.

3.3. Kinetic model

The kinetic modelling of complex multistep reactions has earlier been investigated [2–4,18]. It is now well established that for a complex multistep reaction network the initial rate approach to explain the overall kinetics of the reaction may not be adequate, and hence, integral concentration-time profiles at different sets of initial conditions need to be considered. One of the important goal of this paper is to analyse the role of water quantitatively and to incorporate its influence in the overall kinetics. Based on the general trends of the initial rate data, the following points need to be considered in deriving the rate expressions: (1) the hydrogenation of acetophenone using a 10% Ni/HY catalyst can be described by a L–H type of rate mechanism; (2) the catalyst acts bifunctionally; (3) water has a strong inhibiting effect on the overall kinetics of the reaction. Thus, assuming a reaction between adsorbed hydrogen (non-dissociative) and adsorbed reactants/products on two different sites as rate limiting, the following form of rate equations can be derived:

$$r_i = \frac{wk_iA^*C_j}{(1+K_AA^*)(1+\sum K_jC_j)}, \tag{5}$$

where i=1, 2 and j=1, 2, 3 and 5, where 5 represents water. For the reaction occurring on the support leading to the formation of the ether derivative, the rate expression can be given as

$$r_3 = \frac{wk_3C_2}{(1+\sum K_jC_j)}. \tag{6}$$

The overall rate of hydrogenation is given by

$$R_A = \frac{wA^*\sum k_iC_i}{(1+K_AA^*)(1+\sum K_jC_j)}. \tag{7}$$

The material balance of liquid phase reactant/products in a semi-batch slurry reactor in the absence of external and intraparticle mass transfer resistances can be represented as

$$-\frac{\mathrm{d}C_1}{\mathrm{d}t} = \frac{wk_iA^*C_1}{(1+K_AA^*)(1+\sum K_jC_j)}, \tag{8}$$

$$-\frac{\mathrm{d}C_2}{\mathrm{d}t} = \frac{wk_iA^*C_1}{(1+K_AA^*)(1+\sum K_jC_j)} - \left[\frac{wA^*k_2C_2}{(1+K_AA^*)(1+\sum K_jC_j)} + \frac{wk_3C_2}{(1+\sum K_jC_j)}\right], \tag{9}$$

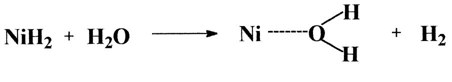
$$\frac{\mathrm{d}C_3}{\mathrm{d}t} = \frac{wk_3C_2}{(1+\sum K_jC_j)}, \tag{10}$$

$$\frac{\mathrm{d}C_4}{\mathrm{d}t} = \frac{wk_2A^*C_2}{(1+K_AA^*)(1+\sum K_jC_j)}, \tag{11}$$

The initial conditions are

$$t=0,\ C_1=C_{10},\ C_2=C_3=C_4=C_5=0, \tag{12}$$

where C_{10} is the initial concentration of acetophenone and C_2, C_3, C_4 and C_5, are the concentrations of PEA, PEME, EB and water, respectively, in kmol/m^3. Eqs. (8)–(12) were solved using an optimisation



Scheme 2.

Table 4
Rate and equilibrium parameters along with $\phi_{\min}$ values

No.	T (K)	Rate constants $\times 10^5$ (m^3/kg)(m^3/kmol/s)			Equillibrium constants (m^3/kmol)				$\phi_{\min}\times 10^4$
		k_1	k_2	k_3	K_A	K_1	K_2	K_3	
1	353	9.56	2.35	0.1	0.35	0.31	0.42	1.04	1.09
2	373	19.85	5.48	0.31	0.73	0.52	0.64	2.32	1.78
3	393	50.12	15.72	0.86	1.82	1.06	1.01	4.45	1.46

routine based on Marquardt's algorithm combined with a Runge–Kutta method. The experimental data were simulated for each temperature separately for different sets of initial conditions and the best common set of rate and equilibrium parameters were determined. The rate and equilibrium parameters were determined by minimising the objective function:

$$\phi_{\min} = \sum_{i=1}^{5}\sum_{i=1}^{n}(Y_{i_{\exp}} - Y_{i_{\mathrm{mod}}})^2, \tag{13}$$

where $Y_{i_{\exp}}$ is the measured concentration of component i, $Y_{i_{\mathrm{mod}}}$ is the calculated concentration of component i and n is the number of samples. The rate parameters estimated and $\phi_{\min}$ values are given in Table 4.

A comparison of experimental and predicted concentration-time profiles are shown in Fig. 6. Also, the H_2 consumption vs time data for different partial pressures of hydrogen at 393 K is shown in Fig. 7. These results indicate that the rate model given in Eqs. (5)–(7) represents the kinetics of hydrogenation of acetophenone satisfactorily for different sets of initial conditions. This model also incorporates the rate inhibition due to water. Fig. 8 shows a typical concentration-time profile, where in the initial concentration of water was 0.56 kmol/m^3. The concentration-time profile for the recycle experiment is shown in Fig. 9. It should be noted that in this case, the initial concentrations are different from those given in Eq. (13) and that the actual concentrations of the reactant and different products formed during the course of the first hydrogenation experiment (using a fresh catalyst) have been used as initial concentrations at the start of the recycle experiment. To study

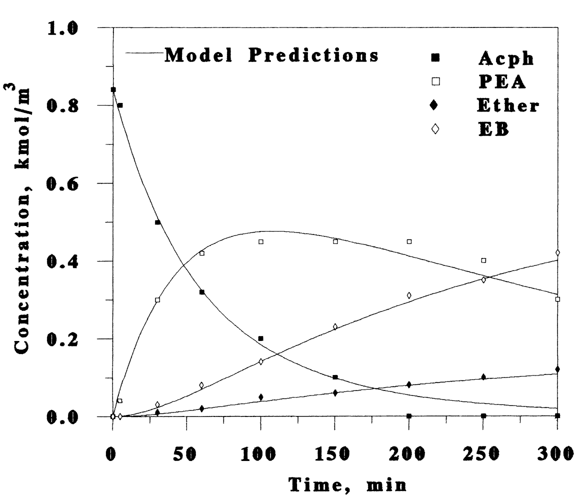


Fig. 6. Concentration-time profile at 373 K. Reaction conditions: concentration of acetophenone: 0.84 kmol/m^3; P_{H_2}: 6.48 Mpa; catalyst loading: 10 kg/m^3; agitation speed: 18 Hz; reaction volume: 1×10^{-4} m^3; solvent: MeOH.

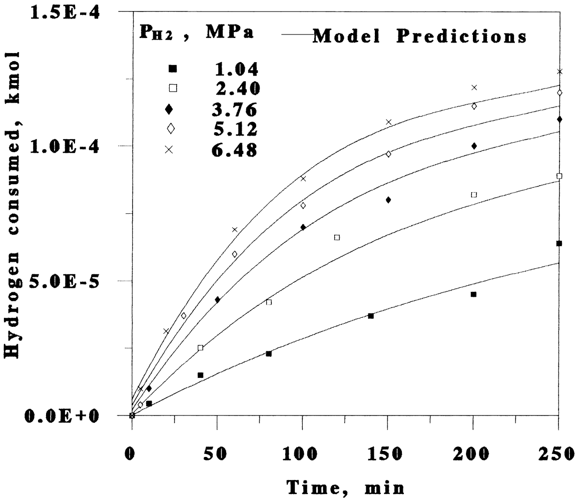


Fig. 7. H_2 consumption vs time plot at different partial pressures of hydrogen at 393 K. Reaction conditions: concentration of acetophenone: 0.84 kmol/m^3; catalyst loading: 10 kg/m^3; agitation speed: 18 Hz, reaction volume: 1×10^{-4} m^3; solvent: MeOH.

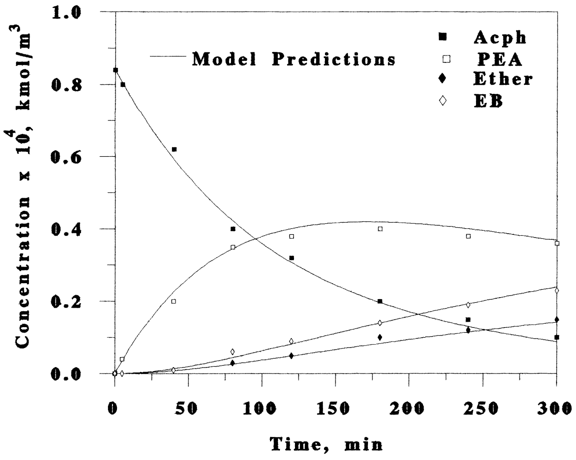


Fig. 8. Concentration-time profile at 393 K with water concentration=0.56 kmol/m^3. Reaction conditions: concentration of acetophenone: 0.84 kmol/m^3; P_{H_2}: 2.14 Mpa; catalyst loading: 10 kg/m^3; agitation speed: 18 Hz; reaction volume: 1×10^{-4} m^3; solvent: MeOH.

the catalyst recycle effect after the first reaction with the fresh catalyst, the contents in the reactor were cooled to room temperature. The unreacted H_2 was discharged from the reactor and contents flushed with N_2 2–3 times. Fresh amount of acetophenone added through the dip tube of the reactor and the hydrogenation experiments was carried out as before. In all the concentration-time profiles as shown (see Figs. 6, 7 and 9), the experimental water concentration was obtained by assuming that the following stoichiometry exists

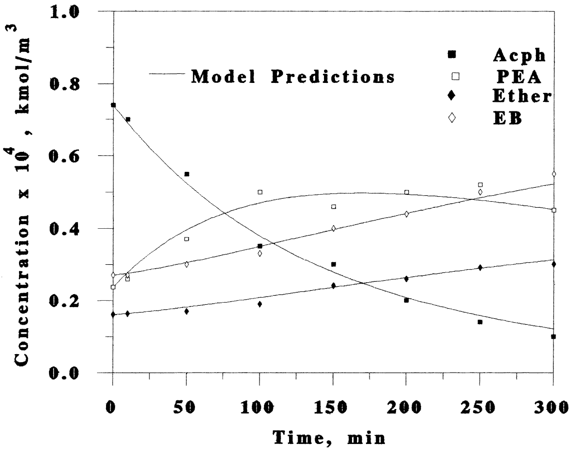


Fig. 9. Concentration-time profile at 393 K for recycled catalyst. Reaction conditions: concentration of acetophenone: 0.84 kmol/m^3; P_{H_2}: 2.14 Mpa; catalyst loading: 10 kg/m^3; agitation speed: 18 Hz; reaction volume: 1×10^{-4} m^3; solvent: MeOH.

$$\mathrm{PE} \underset{\text{Catalyst}}{\overset{\text{MeOH}}{\longrightarrow}} \mathrm{PEME} + \mathrm{H_2O}$$

$$\mathrm{PE} \underset{\text{Catalyst}}{\overset{\mathrm{H_2}}{\longrightarrow}} \mathrm{EB} + \mathrm{H_2O}$$

A reasonably good agreement between the predicted and experimental data was observed in most conditions. Thus, the rate model given in Eqs. (5)–(7) best represents the kinetics of hydrogenation of acetophenone over a wide range of initial conditions and also accounts for the inhibiting influence of the water concentration. The activation energy values were found to be in the range 40–60 kJ/mol and the heats of adsorption of different liquid phase components are in the range 30–50 kJ/mol. The heat of adsorption of hydrogen was found to be around 50 kJ/mol. Thus, the activation energies are typically in the range of values reported earlier by Rajashekharam and Chaudhari [8] for the hydrogenation of p-isobutyl acetophenone using a similar catalyst. Another interesting point to be looked at is the ratio of the adsorption equilibrium constant obtained for water to that of other liquid phase components, i.e., K_5/K_2 and K_5/K_3. This ratio of K_5/K_2 and K_5/K_3 is always >1 indicating the strong adsorption of water on the catalyst surface. Thus, this paper presents a study on kinetics of hydrogenation of acetophenone using a 10% Ni/HY catalyst in a slurry reactor incorporating some complex effects, such as inhibition of reaction rates due to the strong adsorption of a side product, i.e., water, during the reaction.

4. Conclusions

The kinetics of hydrogenation of acetophenone was studied using a 10% Ni/HY catalyst in a temperature range 353–393 K in a slurry reactor. The rate expressions were derived assuming L–H type of rate mechanism in which the non-competitively adsorbed non-dissociative hydrogen reacts with the adsorbed liquid phase reactant/product as rate limiting was found to best represent the rate data. Quantum chemical calculations on the interaction energies indicated that water interacts strongly with the active sites responsible for activation of the C=O bond and also modifies the Ni sites responsible for hydrogenation leading to inhibition of hydrogenation rates. This inhibiting influence of the water has been incorporated in the rate model. A semi-batch reactor model has been proposed and the predictions were found to be in excellent agreement with the experimental data.

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Appendix

The gas–liquid mass transfer, $k_L a_b$, was evaluated from the correlation proposed by Chaudhari et al. [10] for a stirred tank reactor:

$$k_1 a_b = 1.48 \cdot 10^{-3} N^{2.18} (V_g/V_L) 1.88 \times (d_I/d_T)^{2.16} (h_1/h_2)^{1.16}, \qquad (A.1)$$

where N is the agitation speed, Hz; V_g volume of gas in reactor, m^3; V_L is the volume of liquid in the reactor, m^3; d_I is the impeller diameter, m; d_T is the tank diameter, m; h_1 is the height of first impeller from the bottom, m; and h_2 is the height of the liquid, m.

For calculation of k_s, the correlation proposed by Sano et al. [11] was used.

$$\frac{k_s d_p}{D F_C} = 2 + 0.4 \left[\frac{e d_p^4 \rho_L^3}{\mu_L^3}\right]^{0.25} \left[\frac{\mu_L}{\rho_L D}\right]^{0.333}, \qquad (A.2)$$

where F_c is the shape factor assumed to be unity for spherical particle and e, the energy supplied to the liquid, was calculated by the procedure described by Calderbank [19].

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