

Reaction kinetics of the selective liquid phase hydrogenation of styrene oxide to β -phenethyl alcohol

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Received 29 July 2002; received in revised form 15 November 2002; accepted 13 January 2003

Abstract

Liquid phase hydrogenation of styrene oxide using 1% Pd/C and NaOH as a promoter was found to give selectively β -phenethyl alcohol (PEA) under very mild conditions (313–333 K; 0.68–5.5 MPa). The kinetics of this system was investigated by collecting initial rate data in a batch slurry reactor. Rate of hydrogenation was found to decrease beyond a certain concentration of both hydrogen (>3 MPa) and styrene oxide (>0.5 kmol/m³). A Langmuir–Hinshelwood type rate equation has been proposed based on the initial rate data in the kinetic regime. The model predictions agree very well with the experimentally observed concentration–time data indicating the applicability of the proposed rate model.

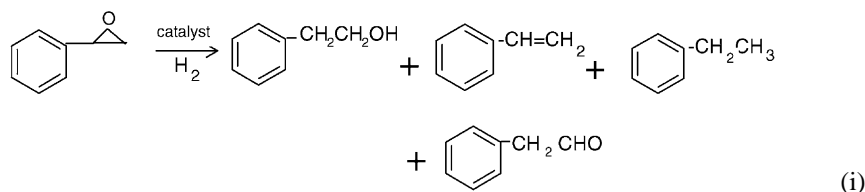
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Keywords: β -Phenethyl alcohol; Styrene oxide; Selective catalytic hydrogenation; Pd/C; L–H kinetics; Substrate inhibition; Rate equation

1. Introduction

Environmentally clean processes for fine chemicals and pharmaceuticals production by catalysis have been the focus of research in recent years. Generation of large amount of inorganic salts due to the use of stoichiometric reagents and multi-step syntheses are major drawbacks of the conventional processes for fine chemicals. Synthesis of β -phenethyl alcohol (PEA) is one such example [1–6]. PEA is extensively used in

perfumery and deodorant formulations and also for the preparation of important chemical intermediates such as phenylacetaldehyde, phenylacetic acid, and benzoic acid [1]. Catalytic hydrogenation of styrene oxide to PEA is an environmental friendly process and several homogeneous as well as heterogeneous catalysts have been reported in the literature; however, hydrogenation of styrene oxide is usually accompanied with formation of several side products such as phenylacetaldehyde, ethylbenzene and styrene as shown below [7,8].



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Even the presence of 1% ethylbenzene destroys the aroma of the PEA, making it unsuitable for perfumery formulations. Mitsui et al. [9] have compared the

product distribution pattern for hydrogenation of styrene oxide using different catalysts: Pd/C, PtO₂, Pt black and Raney Ni. In their work, maximum selectivity to PEA obtained was 92% with 5% Pd/C catalyst and formation of ethylbenzene was observed to be ≈10%. Similar comparative study was also done by Kondo et al. [10] on Pd, Co and Ni catalysts, in which selectivity to PEA was found to be dependent on H₂ pressure. In the literature published so far, studies have been mainly aimed at the product distribution and selectivity issues using different solvent and catalyst systems for the liquid phase hydrogenation of styrene oxide [7,11–14]. Therefore, an important objective of our work was to develop an intrinsic kinetic rate equation using the experimental initial rate data obtained from a batch slurry reactor. The effects of catalyst loading, hydrogen partial pressure, concentration of styrene oxide and PEA and agitation speed on the rate of hydrogenation were investigated

at different temperatures. Finally, a batch slurry reactor model was also developed and the predicted concentration–time profiles were compared with those obtained experimentally under a wide range of conditions.

2. Experimental

2.1. Materials and catalyst preparation

Styrene oxide was procured from Aldrich, USA. Sodium hydroxide and methanol were procured from M/s Loba Chemie, Bombay, and the latter was distilled for use as a solvent in all the experiments. Hydrogen gas of >99.9% purity was supplied by Indian Oxygen Ltd., Bombay.

One percent Pd on carbon catalyst was prepared by impregnation method using water as the impregnation

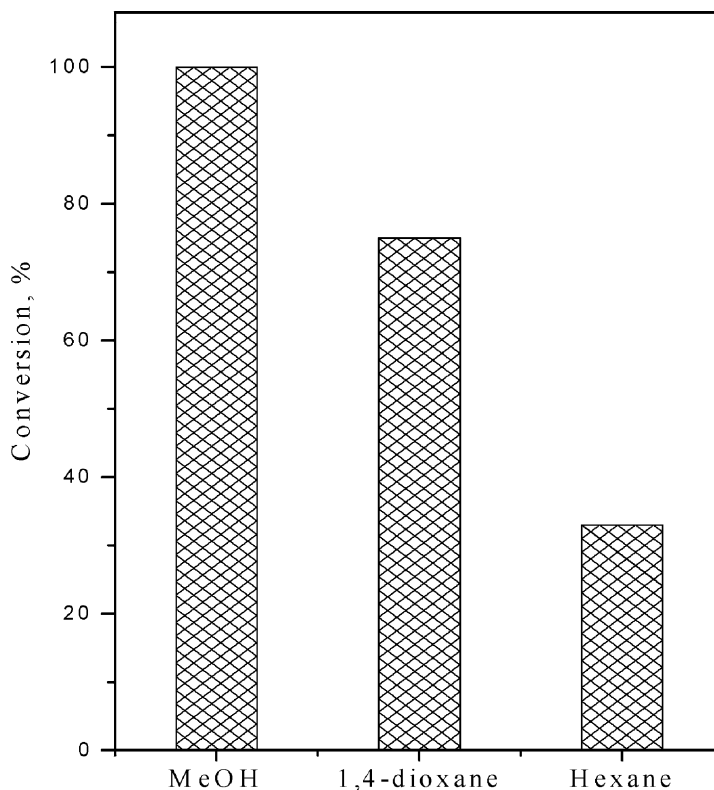


Fig. 1. Effect of solvent on conversion of styrene oxide. Reaction conditions: temperature, 313 K; pressure, 2.04 MPa; catalyst concentration, 0.375 kg/m³; initial concentration of styrene oxide, 0.416 kmol/m³; concentration of NaOH, 0.013 kg/m³; agitation speed, 15 Hz; liquid volume, 1 × 10⁻⁴ m³.

solvent and was reduced in situ by chemical reagent without prior calcination [15]. In a typical procedure, 0.16 g of PdCl₂ was completely dissolved in aqueous hydrochloric acid (26% v/v) under stirring at 80 °C. After cooling the solution to room temperature, it was further diluted by adding distilled water (70 ml). To this solution (pH adjusted to 4.5), activated carbon (10 g) was added with constant stirring at 80 °C. The reducing agent, 0.7N sodium formate solution was added dropwise to the PdCl₂ solution. The suspension was maintained at 80 °C for further 40 min. Then it was allowed to cool and kept overnight for thorough settling of fine particles. The filtered catalyst was dried at 90 °C to give 1% Pd/C. It was ensured that all Pd was in the reduced form by XRD and XPS analysis and the BET surface area was determined by nitrogen physisorption (770 m²/g). The crystallite size of the catalyst determined by XRD was found to be 30 nm.

2.2. Hydrogenation experiments

Catalytic hydrogenation of styrene oxide reactions was carried out in a 3×10^{-4} m³ capacity SS-316 stirred reactor (Parr Instruments Co., USA) provided with automatic temperature control, variable stirrer speeds, gas inlet–outlet and sampling of liquid phase. The reactor was also equipped with safety rupture disc (gold faced), high temperature cut-off and a transducer for pressure recording. A reservoir for H₂ gas was used along with a constant pressure regulator for supply of hydrogen at a constant pressure to the reactor. The hydrogen consumption was measured from the pressure drop observed in the hydrogen reservoir. This arrangement ensured the kinetic measurements at a constant pressure condition. A schematic of the experimental set-up used is given elsewhere [14].

In a typical hydrogenation experiment, desired amount of styrene oxide was charged to a reactor

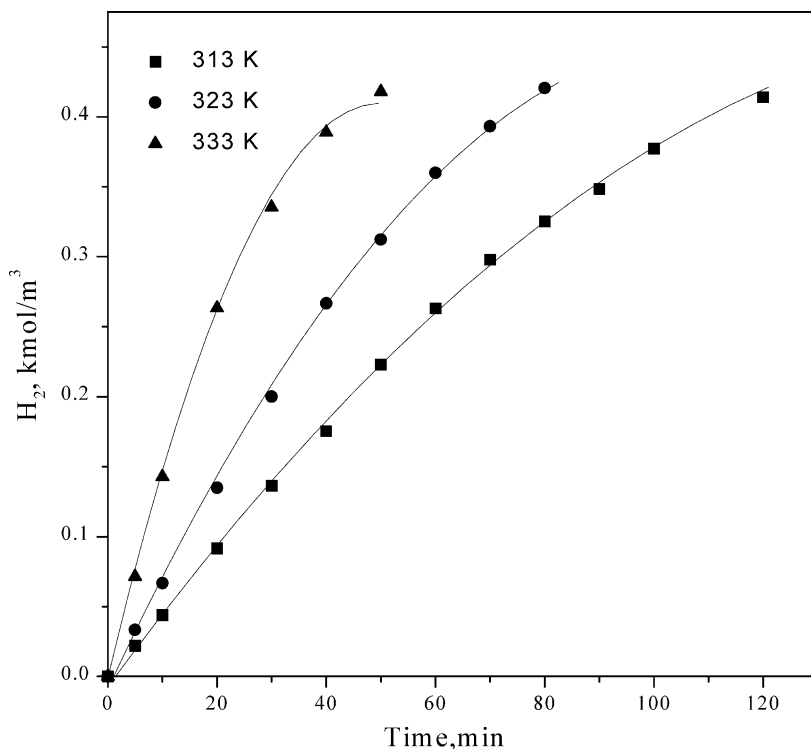


Fig. 2. Hydrogen consumption vs. time profiles. Reaction conditions: solvent, methanol; pressure, 2.04 MPa; catalyst concentration, 0.375 kg/m³; initial concentration of styrene oxide, 0.416 kmol/m³; concentration of NaOH, 0.013 kg/m³; agitation speed, 15 Hz; liquid volume, 1×10^{-4} m³.

along with the catalyst, solvent and a promoter. The contents were first flushed with nitrogen and then with hydrogen at room temperature. After the desired temperature was attained the system was pressurized with hydrogen at required pressure. The reaction was started by switching the stirrer on. The progress of the reaction was monitored by observing the pressure drop in the reservoir as a function of time. After the reaction was over as indicated by a constant hydrogen pressure in the reservoir, the reactor was cooled to room temperature and excess hydrogen was vented out safely and the contents were removed for subsequent analysis. In some experiments, concentration–time data were collected by intermediate sampling of the liquid phase. Liquid samples were analyzed using a HP 5840 gas chromatograph fitted with a packed column of 10% OV-17. The conditions of GC analysis were: FID detector temperature, 573 K; injector temperature, 523 K; and column temperature, 413 K (isothermal). Nitrogen was used as a carrier gas with the flow rate of $3 \times 10^{-5} \text{ m}^3/\text{min}$.

3. Results and discussion

3.1. Preliminary studies

From our earlier work on screening of catalysts, supports and solvents, NaOH promoted 1% Pd/C system in methanol was found to give complete conversion of styrene oxide and selectivity to PEA; hence, all the kinetic studies were carried out using the same catalyst system [13]. Neither deoxygenated (e.g. ethylbenzene) nor any isomerization products (e.g. α -phenethyl alcohol) were formed with the present catalyst system. The formation of such products was reported in earlier work for other epoxy compounds, in which mostly the gas phase hydrogenation experiments were conducted in the temperature range of 293–453 K [16]. The absence of any deoxygenated product in this work suggests that metal–styrene oxide interaction is weak, particularly for the Pd catalyst. This is also supported by the solvent effects as shown in Fig. 1. It is well known that a polar solvent enhances

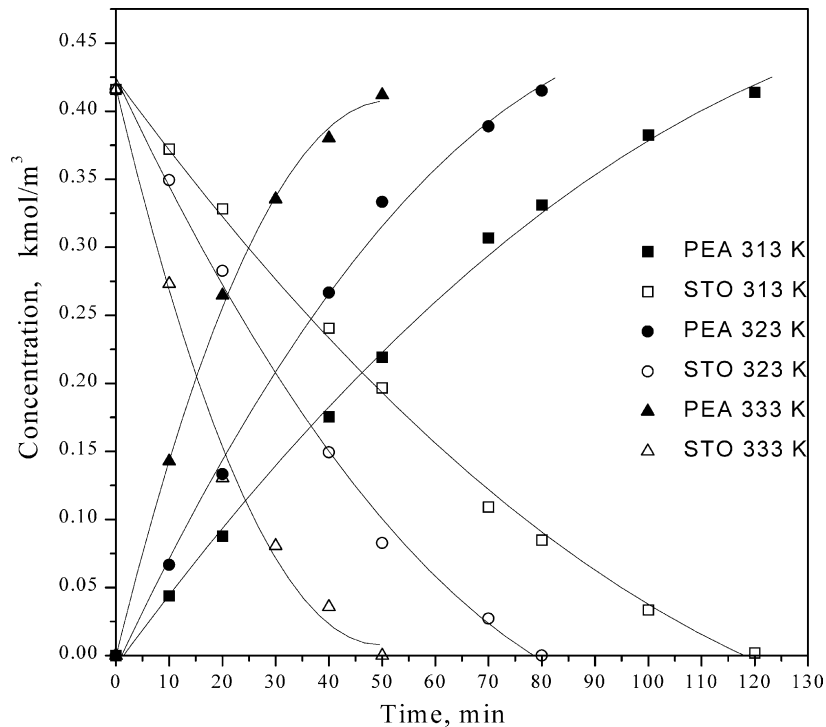


Fig. 3. Liquid concentration vs. time profiles. Reaction conditions as mentioned in Fig. 2.

adsorption of the non-polar reactant while a non-polar solvent enhances the adsorption of a polar reactant [17]. In the present case, if styrene oxide adsorption was through epoxide oxygen (a polar atom), higher conversions were expected in non-polar solvents such as dioxane and *n*-hexane. However, it was found that poor conversions were obtained for non-polar solvents, such as dioxane and *n*-hexane, while complete conversion was achieved for methanol which indicates the absence of any metal–epoxide interaction. Isomerization products were neither observed because of addition of alkali, which neutralizes the acid sites responsible for the isomerization, a reaction reported to be parallel with hydrogenation of epoxy compounds [18].

3.2. Kinetic studies

A few repeated experiments on selective hydrogenation of styrene oxide to PEA using 1% Pd/C with

Table 1

Range of operating conditions

Conditions	Range
Temperature	313–333 K
Hydrogen pressure	0.687–5.51 MPa
Concentration of styrene oxide	0.416–2.5 kmol/m ³
Concentration of catalyst	0.375–1.5 kg/m ³
Concentration of promoter	0.013–0.026 kg/m ³
Agitation speed	6.3–16.3 Hz
Volume	1 × 10 ⁻⁴ m ³

NaOH as a promoter showed that the material balance according to the stoichiometric reaction (i) was >98% in all experiments. Moles of styrene oxide consumed and the product (PEA) formed was as per the stoichiometric consumption of hydrogen and, hence, for the kinetic runs, absorption of H₂ in the reservoir with time was observed under different operating conditions. A range of operating conditions for the kinetic runs are given in Table 1. No hydrogenation was found to

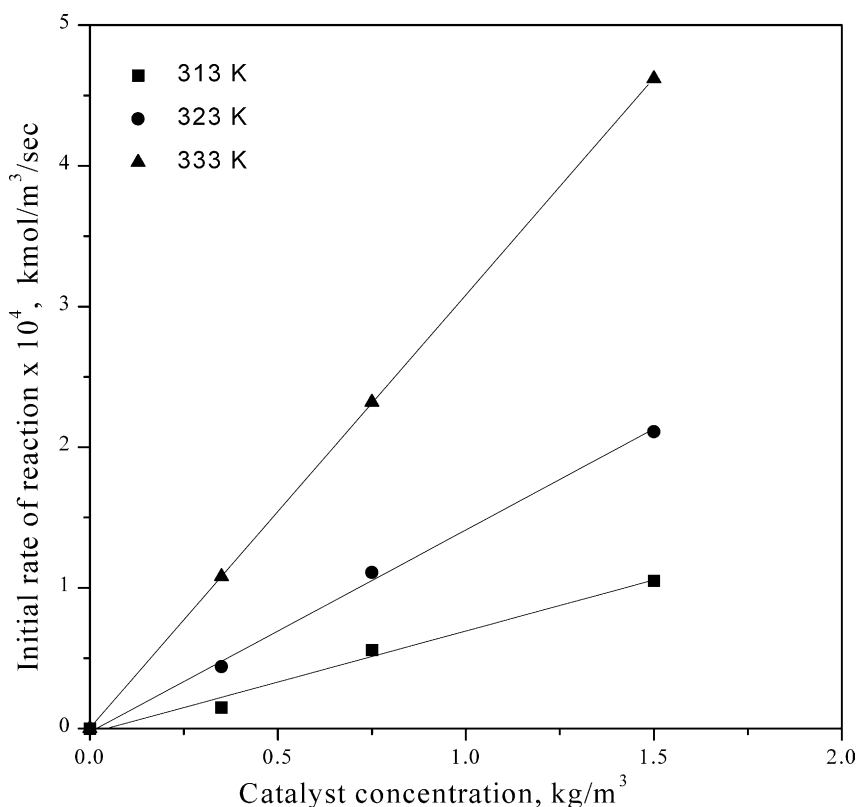


Fig. 4. Effect of catalyst concentration on initial rate of hydrogenation. Reaction conditions: solvent, methanol; pressure, 2.04 MPa; initial concentration of styrene oxide, 0.416 kmol/m³; concentration of NaOH, 0.013 kg/m³; agitation speed, 15 Hz; liquid volume, 1 × 10⁻⁴ m³.

occur in the absence of a catalyst, indicated the absence of any homogeneous reaction. Reproducibility of the rate measurements was found to be within 2–5% error as indicated by a few repeated experiments.

The analysis of initial rate data provides a first approximation in understanding the dependency of the reaction rate on individual operating parameters and also in the evaluation of mass transfer effects. A typical hydrogen consumption–time profile is shown in Fig. 2. A second-order polynomial was fitted to the curve and the slope at 0 time was taken as the initial rate of hydrogenation. Liquid samples were also drawn from time to time and were analyzed on a GC for concentrations of styrene oxide and products during the course of hydrogenation reaction. Typical concentration–time profiles for all the three temperatures are given in Fig. 3, which closely agreed with H₂ consumption data as per the stoichiometry. Fig. 4 shows the influence of

catalyst loading (ranging from 0.375 to 15 kg/m³) on the initial rate of reaction in the temperature range of 313–333 K and hydrogen pressure of 2.408 MPa for hydrogenation of styrene oxide. The hydrogenation rate was found to be linearly dependent on the catalyst loading for all the temperatures, indicating the absence of gas–liquid mass transfer resistance. In order to further check the significance of gas–liquid mass transfer resistance, a few experiments were also carried out at different agitation speeds (6.66–16.66 Hz) with the lowest as well as the highest catalyst loading in the temperature range of 313–333 K. As can be seen from Fig. 5, the initial rates were independent of agitation speed irrespective of catalyst loadings. This observation further supports our conclusion of the absence of external mass transfer effects that were absent under the experimental conditions of the present work.

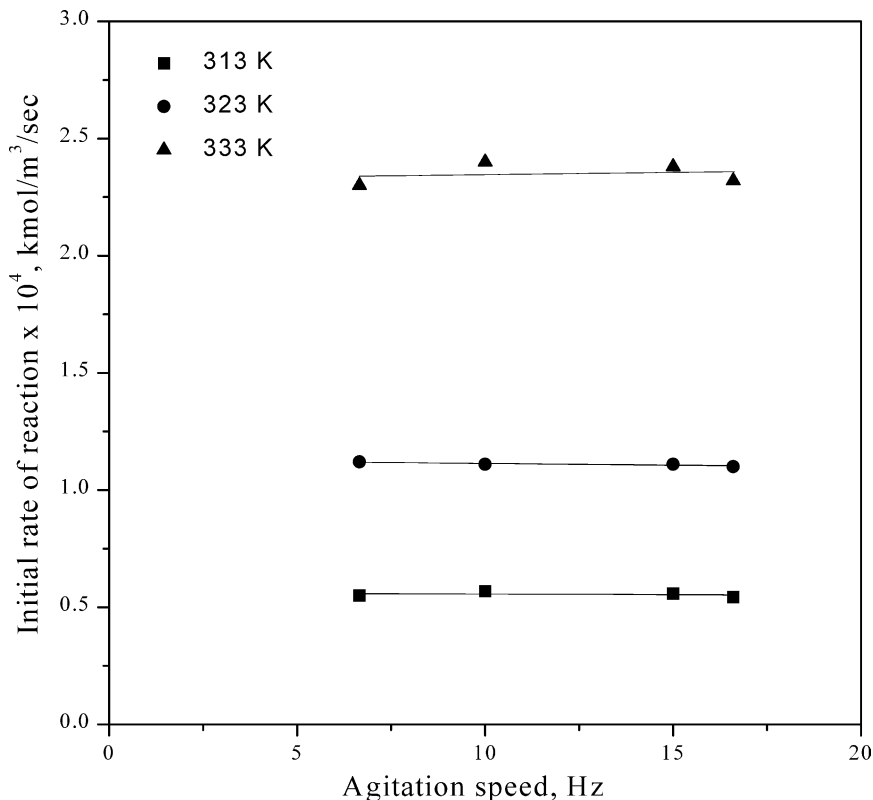


Fig. 5. Effect of agitation speed on initial rate of hydrogenation. Reaction conditions: solvent, methanol; pressure, 2.04 MPa; catalyst concentration, 0.375 kg/m³; initial concentration of styrene oxide, 0.416 kmol/m³; concentration of NaOH, 0.013 kg/m³; liquid volume, 1 × 10⁻⁴ m³.

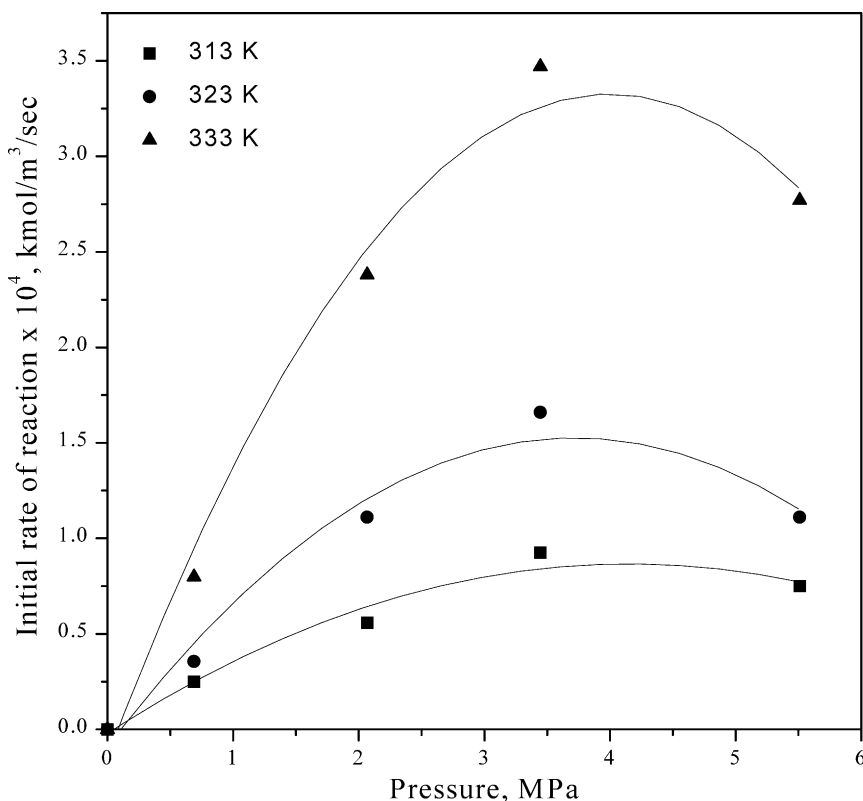


Fig. 6. Effect of H_2 pressure on initial rate of hydrogenation. Reaction conditions as mentioned in Fig. 2.

Effect of hydrogen pressure on the initial rate of reaction, for different temperatures, using 1% Pd/C as a catalyst and NaOH as the promoter is shown in Fig. 6. It was found that initially the rate of reaction increased with increase in the pressure to a maximum (3.44 MPa) and then decreased with further increase in H_2 pressure, indicating the possibility of inhibition by hydrogen at higher pressure. Similar type of inhibition effect was also observed for higher substrate (styrene oxide) concentration ($>1.2 \times 10^{-4} \text{ kmol/m}^3$) and the results are shown in Fig. 7. Inhibition of hydrogenation for higher concentrations of both H_2 and styrene oxide was more pronounced at temperature $>313 \text{ K}$. This behavior could be explained by competitive adsorption of H_2 and styrene oxide on a single type of active sites. Substrate-inhibited kinetics in case of citral hydrogenation using Pt catalyst and H_2 -inhibited kinetics for partial hydrogenation of benzene using Ru catalyst have been also explained based on competi-

tive adsorption models [17,19–21]. A liquid substrate inhibited kinetics behavior can also be explained by the strong adsorption of styrene oxide on the catalyst surface which can be possibly tackled by conducting the reaction at higher temperature than maximum used in this work ($>313 \text{ K}$). An alternative way is the use of higher catalyst concentration, which can overcome the problem of inhibition by both the substrates. The effect of concentration of product (PEA) was studied at 313 and 333 K. In these experiments, PEA was added along with the substrate at the start of the reaction. The results are presented in Fig. 8, from which it is clear that the reaction has zero order dependence on the concentration of the product. Such a trend is consistent with the fact that the two substrates were found to exhibit competitive adsorption behavior.

This being a gas–liquid–solid catalytic reaction system, it is important to ensure that the mass transfer limitations are eliminated or accounted for when

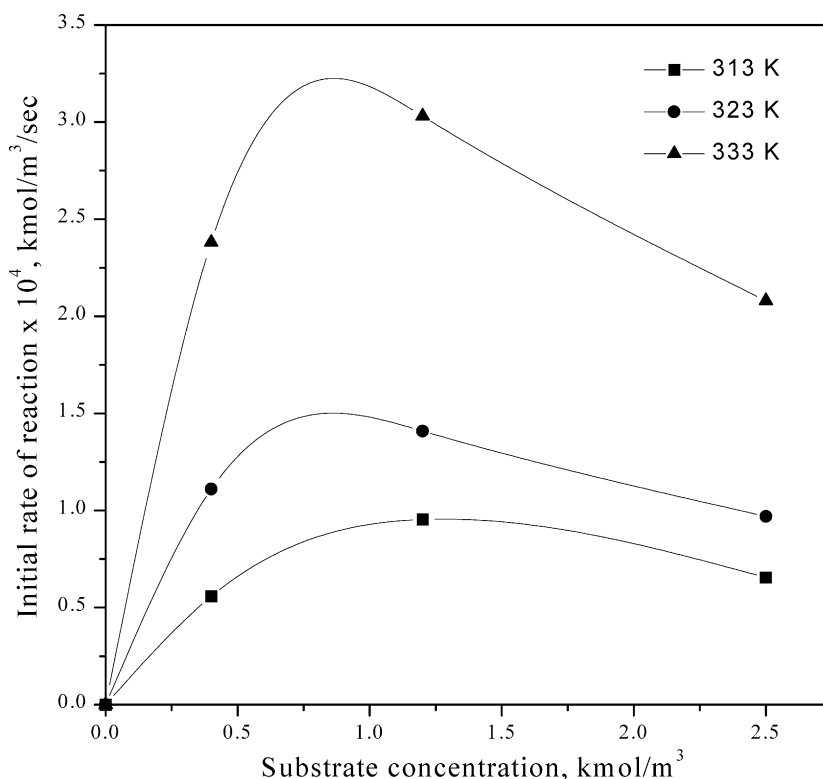


Fig. 7. Effect of substrate concentration on initial rate of hydrogenation. Reaction conditions: solvent, methanol; pressure, 2.04 MPa; catalyst concentration, 0.375 kg/m³; concentration of NaOH, 0.013 kg/m³; agitation speed, 15 Hz; liquid volume, 1 × 10⁻⁴ m³.

determining the intrinsic kinetics of the reaction. As discussed above, the initial rate of reaction showed linear dependence on the catalyst loading and also was independent of agitation speed, indicating the absence of external gas–liquid mass transfer effects under the conditions of present work [22]. The intra-particle and liquid–solid mass transfer resistance also can be neglected, since very fine catalyst powder was used and the reaction rate was low compared to the effective diffusion rate under the experimental conditions. Based on the observed reaction trends with respect to the effect of pressure and concentration of styrene oxide on the initial rate of reaction and by assuming the conventional Langmuir–Hinshelwood type mechanism, several forms of rate equations are proposed as presented in Table 2.

A non-linear least square regression analysis based on Marquardt's method was used to obtain the kinetic parameters for all the equations given in Table 2.

The sum of ϕ_{\min} , representing the sums of squares of the difference between the observed and the predicted rates and the values of rate parameters are also given in Table 2. It was found that the value of ϕ_{\min} for Model 4 was minimum for all the temperatures. However, discrimination between the models cannot be solely based upon ϕ_{\min} only. Therefore, these models were examined further for their suitability under integral conditions by comparing the simulated and experimental concentrations versus time. For this purpose, the experimental data on liquid phase concentration of styrene oxide and β -phenethyl alcohol as a function of time were also obtained. The variation of the concentration of styrene oxide and β -phenethyl alcohol can be expressed by the following mass balance equations, for conditions of constant H₂ pressure in the reactor:

$$-\frac{dB_1}{dt} = \frac{wkA^*B_1}{(1 + K_A A^*)^{1.5}(1 + K_B B_1)^{1.5}} = R_i \quad (1)$$

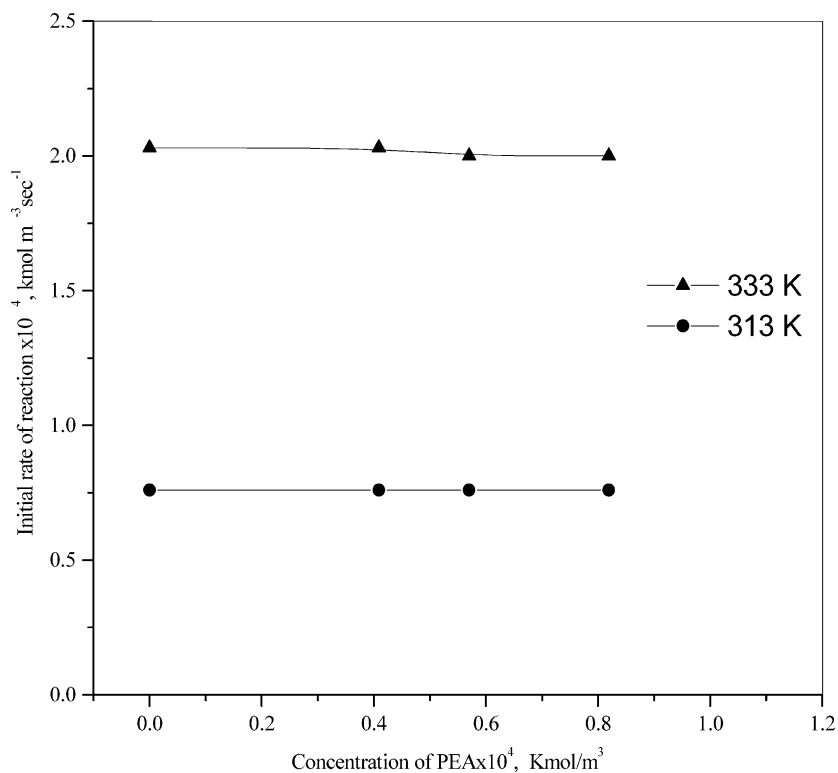


Fig. 8. Effect of PEA concentration on initial rate of hydrogenation. Reaction conditions as mentioned in Fig. 2.

Table 2
Comparison of various models for hydrogenation of styrene oxide

Model no.	Model	Temperature (K)	k (m ³ /kg s)	K_A (m ³ /kmol)	K_B (m ³ /kmol)	$\phi_{\min} \times 10^9$
(1)	$\frac{wkA^*B_1}{(1 + K_A A^* + K_B B_1^2)}$	313	0.0276	29.71	3.33	6.34
		323	0.0314	27.71	3.85	3.32
		333	0.1313	51.99	7.85	3.93
(2)	$\frac{wkA^*B_1}{(1 + K_A A^*)(1 + K_B B_1)}$	313	0.0612	17.65	9.34	3.09
		323	0.0989	16.40	10.32	4.72
		333	5.509	20.27	23.9	4.96
(3)	$\frac{wkA^*B_1}{(1 + K_A A^*)^{1.5}(1 + K_B B_1)}$	313	0.0570	7.618	10.34	3.28
		323	0.0985	7.119	12.16	4.18
		333	0.5211	7.712	28.17	5.99
(4)	$\frac{wkA^*B_1}{(1 + K_A A^*)^{1.5}(1 + K_B B_1)^{1.5}}$	313	0.0271	8.193	1.82	2.29
		323	0.0423	7.559	1.95	3.06
		333	0.126	8.378	2.40	2.92

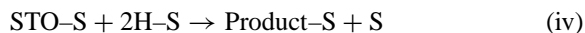
w , concentration of catalyst (kg/m³); k , rate constant; A^* , dissolved concentration of hydrogen (kmol/m³); B_1 , concentration of styrene oxide (kmol/m³); K_A and K_B , equilibrium adsorption constants for hydrogen and styrene oxide (m³/kmol).

$$\frac{dP_1}{dt} = \frac{wkA^*B_1}{(1 + K_A A^*)^{1.5}(1 + K_B B_1)^{1.5}} \quad (2)$$

The initial conditions are at $t = 0$, $B_1 = B_{Li}$, and $P_1 = 0$ ($P_1 =$ concentration of PEA, kmol/m^3) and R_i is the initial rate of the reaction (Model 4, in Table 2).

Eqs. (1) and (2) were solved numerically by using the Runge–Kutta method to obtain the concentrations of styrene oxide and β -phenyl ethyl alcohol as a function of time. The intrinsic rate parameters, given in Table 2, were used for Model 4 in Eqs. (1) and (2). The predictions for all the models were compared with the experimental concentration–time data and the results are presented in Fig. 9, from which it is clear that the prediction results of Model 4 match very well the experimental data. The kinetic model can be shown by

the following sequence of elementary steps:



Styrene oxide (STO) is assumed to be adsorbed on the active site ‘S’ of the catalyst surface by π -bonding and the adsorption of hydrogen is dissociative [13,23]. It is further assumed that the surface reaction (iv) is irreversible and rate-determining, whereas, the adsorption steps: (ii) of hydrogen, and (iii) of styrene oxide, are rapid enough for the quasi-equilibrium hypothesis

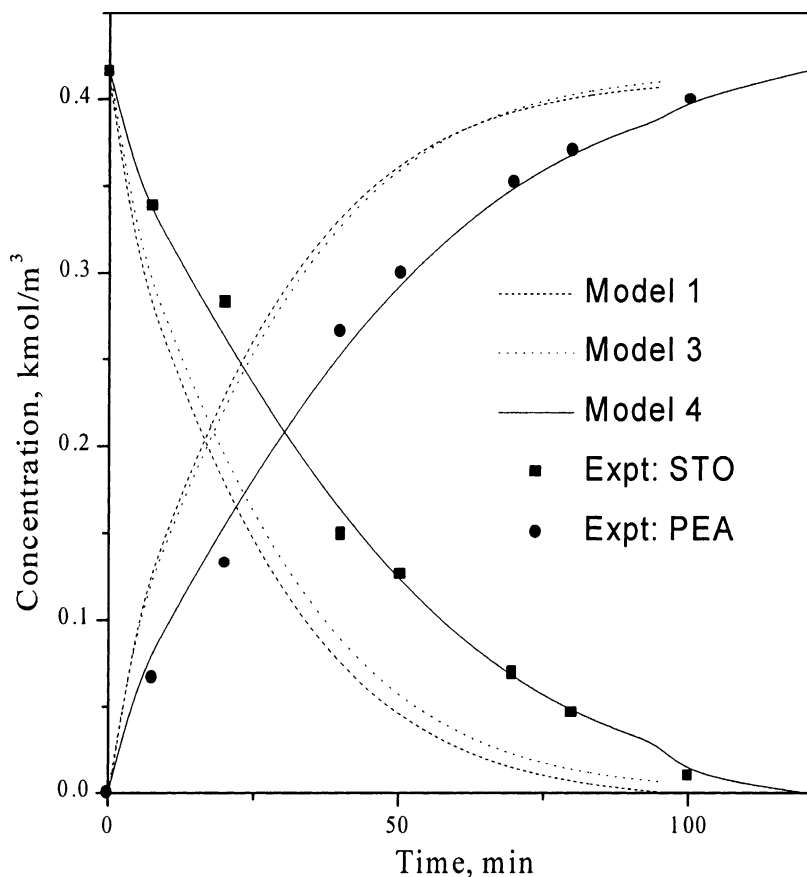


Fig. 9. Comparison between experimental and predicted concentration–time profiles for various rate equations. Reaction conditions: temperature, 323 K; solvent, methanol; pressure, 2.04 MPa; catalyst concentration, 0.375 kg/m^3 ; initial concentration of styrene oxide, 0.416 kmol/m^3 ; concentration of NaOH, 0.013 kg/m^3 ; agitation speed, 15 Hz; liquid volume, $1 \times 10^{-4} \text{ m}^3$.

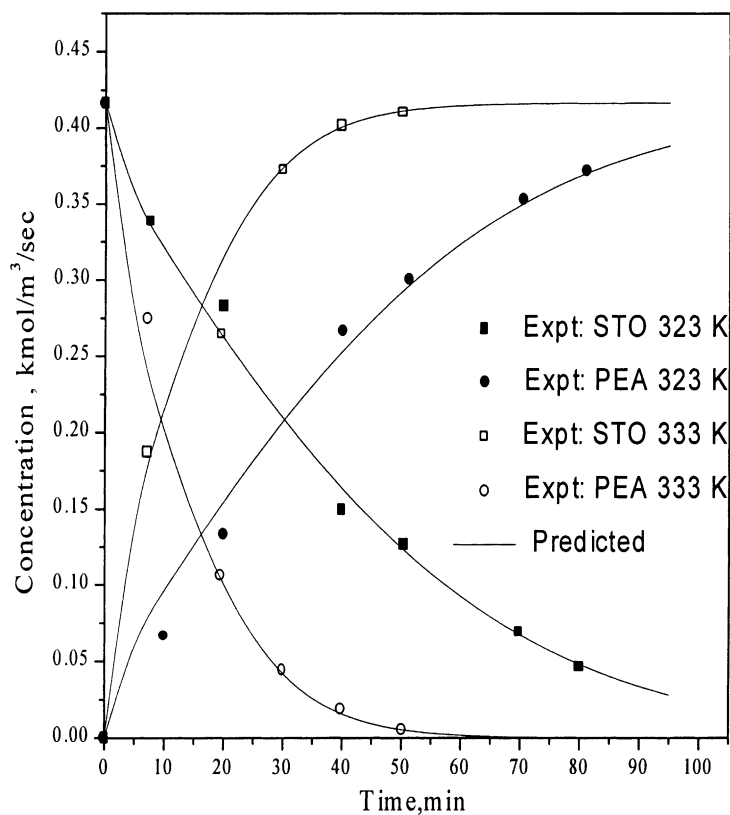


Fig. 10. Comparison between experimental and predicted concentration–time profiles for Model 4, at various temperatures. Reaction conditions as mentioned in Fig. 2.

to be applied. The desorption of β -phenethyl alcohol step (v) is assumed to be irreversible and very fast, which is quite reasonable because the product concentration showed a zero order kinetics.

Further comparison between the predictions of Model 4 and the experimental concentration–time data at different temperatures is shown in Fig. 10, which also indicates good agreement confirming the validity of the proposed kinetic model. The activation energy evaluated from the present data was found to be 55 kJ/mol.

4. Conclusions

Kinetics of liquid phase hydrogenation of styrene oxide was studied in the presence of 1% Pd/C catalyst and NaOH as a promoter. This catalyst system was found to give only β -phenethyl alcohol (PEA) without

formation of any deoxygenated side products. A systematic study on the effect of major reaction parameters such as H_2 pressure, substrate concentration and temperature on the catalyst activity and selectivity was carried out. Negative order rate dependence on both hydrogen and styrene oxide was observed, indicated competitive adsorption of both the substrates. Based on the trends observed, several L–H type rate equations were proposed and the selected rate model was verified under integral reactor conditions. The model predictions and the experimental results were found to be in good agreement over a wide range of conditions and, hence, can be useful for the design purpose.

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