



Kinetic Study for Chemoselective Hydrogenation of Benzoic Acid to Benzyl Alcohol in a Batch Slurry Reactor using Ru-Sn/Al₂O₃ Catalyst

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Chemoselective hydrogenation of benzoic acid was carried out using Ru-Sn/Al₂O₃ catalyst at temperature and hydrogen pressure range of 473-513 K and 3.8-8.8 MPa, respectively. The Sn/Ru ratio in Ru-Sn/Al₂O₃ catalyst was 5. The initial rates for multiphasic hydrogenation reaction were observed to be first order with respect to catalyst loading, hydrogen partial pressure and benzoic acid. The initial rate data obtained were fitted to different rate equations based on Langmuir-Hinshelwood (L-H) type model and a rate model was obtained which predicted the rate of reaction with an error less than $\pm 5\%$. Rate model suggests two different type of active site on Ru-Sn/Al₂O₃ catalyst for hydrogenation of benzoic acid. The activation energy for hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al₂O₃ was found to be 81.64 kJ/mol.

Keywords: Benzoic acid, Hydrogenation, Chemo-selectivity, Kinetics, Benzoic acid, Ru-Sn/Al₂O₃ catalyst.

INTRODUCTION

Hydrogenation of aromatic carboxylic acids is multifaceted as it contains two functional groups, which can be hydrogenated to give different compounds [1]. It is difficult to hydrogenate carboxylic group of aromatic carboxylic acid as compared to aromatic ring [2]. Hydrogenation of benzoic acid with Pd/C catalysts gives cyclohexane carboxylic acid and with Ru/C catalyst gives cyclohexane carboxylic acid and cyclohexyl methanol [3]. Binary solvent system of 1:1; 1,4-dioxane-water was found to increase the selectivity of Ru/C catalyst for hydrogenation of aromatic ring of benzoic acid instead of carboxylic group [4]. In literature, there are various examples for chemo-selective hydrogenation like hydrogenation of oleic acid using supported Ru-Sn catalyst to give unsaturated alcohol [5] and Ru-Co catalyst for selective hydrogenation of succinic acid to γ -butyrolactone [6]. Hydrogenation of cinnamic acid using Ru-Sn/Al₂O₃ catalyst gave small amount (15%) of cinnamyl alcohol as inhibition of C=C double bond hydrogenation is tough [7]. A supported Ru-Pt-Sn catalyst is observed to suppress hydrogenolysis reaction occurring during hydrogenation of 1,4-cyclohexane dicarboxylic acid to 1,4-cyclohexane dimethanol

[8]. Pt/SnO₂ catalyst selectively hydrogenates carboxylic group of benzoic acid to give benzyl alcohol [9]. Ru-Sn/Al₂O₃ catalyst was also found to be selective for hydrogenation of benzoic acid to benzyl alcohol and also reduce hydrogenolysis products [3].

In Ru-Sn catalyst, the role of Sn is to activate -COOH group and role of Ru is to activate hydrogen for hydrogenation of carboxylic acids to respective alcohol [10]. Electron deficient platinum sites in Pt/TiO₂ catalysts were found to interact more with aromatic ring of benzoic acid and electron rich platinum sites were found to help dissociated hydrogen of carboxylic group to participate in benzoic acid hydrogenation indicating involvement of different sites for hydrogenation [11]. Kinetic study for hydrogenation of lauric acid to lauryl alcohol using Ru-Fe/TiO₂ catalyst also supported presence of two active sites for hydrogenation reaction [12]. The kinetic study for hydrogenation of benzoic acid over Ru-Sn/Al₂O₃ catalyst is carried out to understand (i) effect of reaction parameters on hydrogenation of benzoic acid using Ru-Sn/Al₂O₃ catalyst; (ii) rate model based on Langmuir-Hinshelwood (L-H) type model; (iii) an insight regarding the number of catalytically active sites involved in hydrogenation of benzoic acid, which contains -COOH group

and aromatic ring; and (iv) activation energy for hydrogenation of benzoic acid to benzyl alcohol.

EXPERIMENTAL

The chemicals *viz.* benzoic acid, 1,4-dioxane, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) were procured from S.D. Fine Chemicals Ltd. (India). Catalyst support alumina was procured from Aldrich Chemicals (USA). Hydrogen and nitrogen gas of purity greater than 99.9% were obtained from Indian Oxygen Ltd. Bombay, India.

Catalyst preparation: A homogeneous solution of 1.29 g $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 7.23 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was prepared in 50 mL water. To this solution, 10 g of required support was added and the suspension was stirred vigorously for 5 min. After stirring for 5 min the slurry was transferred into 100 mL round bottom flask and surplus water was removed using rotary evaporator. The dried impregnated catalyst was dried overnight in oven at 363 K. This dried catalyst was then calcined at 773 K for 12 h in a calcination furnace. After calcination, the catalyst was reduced at 573 K in a tubular quartz reactor placed in a furnace under constant flow of hydrogen gas (5 mL/min) for 12 h. After the reduction period, the quartz reactor was cooled under nitrogen flow to room temperature. The reduced catalyst was transferred into a 50 mL container and stored in the desiccator under nitrogen.

The catalyst was characterized with the help of scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The XPS measurement for $\text{Ru-Sn/Al}_2\text{O}_3$ catalyst was recorded using a VG Microtech ESCA 3000 instrument.

Reactor set-up for high pressure reactions: The reactions were carried in a 250 mL volume high pressure–high temperature reactor supplied by Parr Instruments Co. USA. The reactor has adjustable speed overhead stirrer. The reaction temperature is maintained by means of an external electrically heated jacket and internal cooling coils. A gas inlet/outlet and a sampling facility for liquid contents are available with the reactor. The reactions can be carried out safely as the reactor has a high pressure–high temperature cut-off facility in addition to a rupture disc. The autoclave was designed to operate at a temperature up to 623 K and 250 bar pressure of hydrogen gas.

The reactor was coupled with a hydrogen reservoir kept at a pressure higher than that of the reactor, through a constant pressure regulator. The gas consumed during the progress of the reaction was calculated from the pressure drop in the reservoir at various time intervals.

Experimental procedure for high pressure reactions: A known quantity of benzoic acid, $\text{Ru-Sn/Al}_2\text{O}_3$ catalyst and 1,4-dioxane solvent were charged into a clean and dry reactor. The reactor and reaction mixture was flushed with nitrogen, followed by hydrogen. As the desired temperature was attained, the autoclave was pressurized with hydrogen and the reaction was started by adjusting the agitation speed to 1200 rpm. The drop in the hydrogen pressure in the reservoir vessel was monitored to get hydrogen consumed during hydrogenation. The liquid samples were withdrawn at specific time intervals from reactor and analyzed for benzoic acid and benzyl alcohol concentrations.

GC-MS analysis: The hydrogenation products formed during the reaction were identified using GC-MS (Agilent GC 6890 with 5973 mass selective detector instrument). For quantitative analysis, the sample from the reaction mixture was filtered to remove catalyst and analyzed by gas chromatography. For separation and detection of reactants/products, a HP INNOWax, polyethylene glycol capillary column along with flame ionization detector was used on an Agilent 6890 gas chromatograph.

RESULTS AND DISCUSSION

SEM studies: From the SEM image shown in Fig. 1 it is observed that the shape of $\text{Ru-Sn/Al}_2\text{O}_3$ catalyst particles is irregular and the average size of catalyst particles is 3.8 μm .

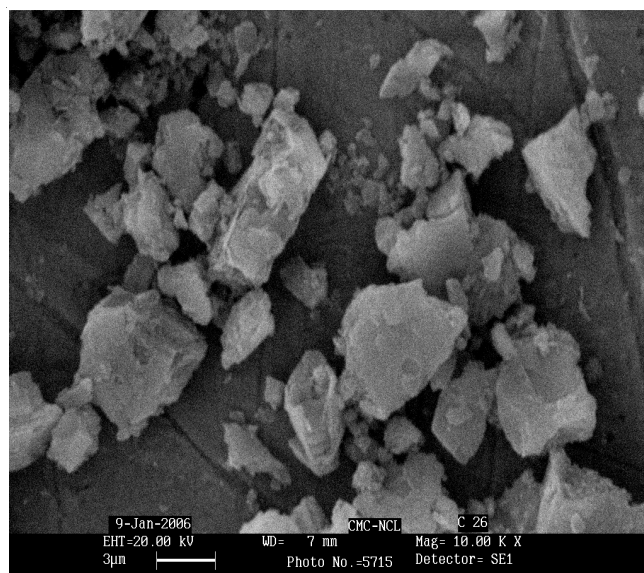


Fig. 1. SEM image of $\text{Ru-Sn/Al}_2\text{O}_3$ catalyst

XPS studies: The binding energy value for Ru, Sn and Al were observed to be 280.2, 487.2 and 74.6 eV, respectively as shown in Fig. 2. These binding energies confirm oxidation state of Ru, Sn and Al to be 0, II/IV and III respectively.

Preliminary reactions for hydrogenation of benzoic acid: Hydrogenation of benzoic acid with monometallic 5% $\text{Ru/Al}_2\text{O}_3$ catalyst gives hydrogenolysis products toluene and methyl cyclohexane along with cyclohexane carboxylic acid and cyclohexyl methanol [3]. From the proposed reaction pathway is depicted in **Scheme-I**.

When Sn was added to $\text{Ru/Al}_2\text{O}_3$ catalyst, the reaction profile for the hydrogenation of benzoic acid changes completely [3]. Hydrogenation of the aromatic ring was completely inhibited and the hydrogenation of carboxylic group was favoured to give benzyl alcohol as shown in Fig. 3.

The benzyl alcohol formed during hydrogenation does not undergo hydrogenolysis to give toluene and methyl cyclohexane as observed with $\text{Ru/Al}_2\text{O}_3$ catalyst. The 100% selectivity to benzyl alcohol is due to a change in adsorption properties of Ru on addition of Sn to $\text{Ru/Al}_2\text{O}_3$ catalyst, which inhibits the hydrogenolysis reaction as proposed by Toba *et al.* using TPR studies [13].

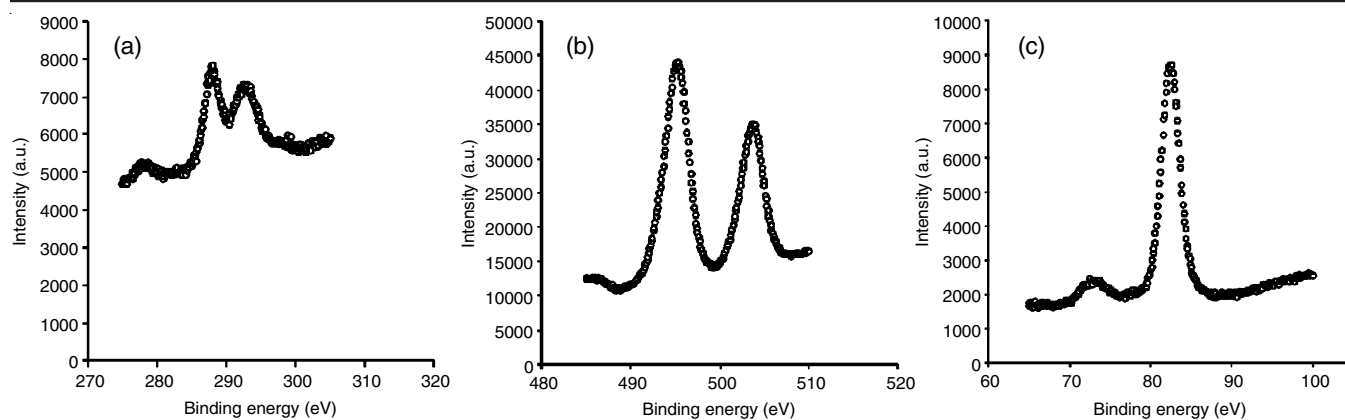


Fig. 2. XPS characterization for (a) Ru in Ru-Sn/Al₂O₃ catalyst, (b) Sn in Ru-Sn/Al₂O₃ and (c) Al in Ru-Sn/Al₂O₃ catalyst

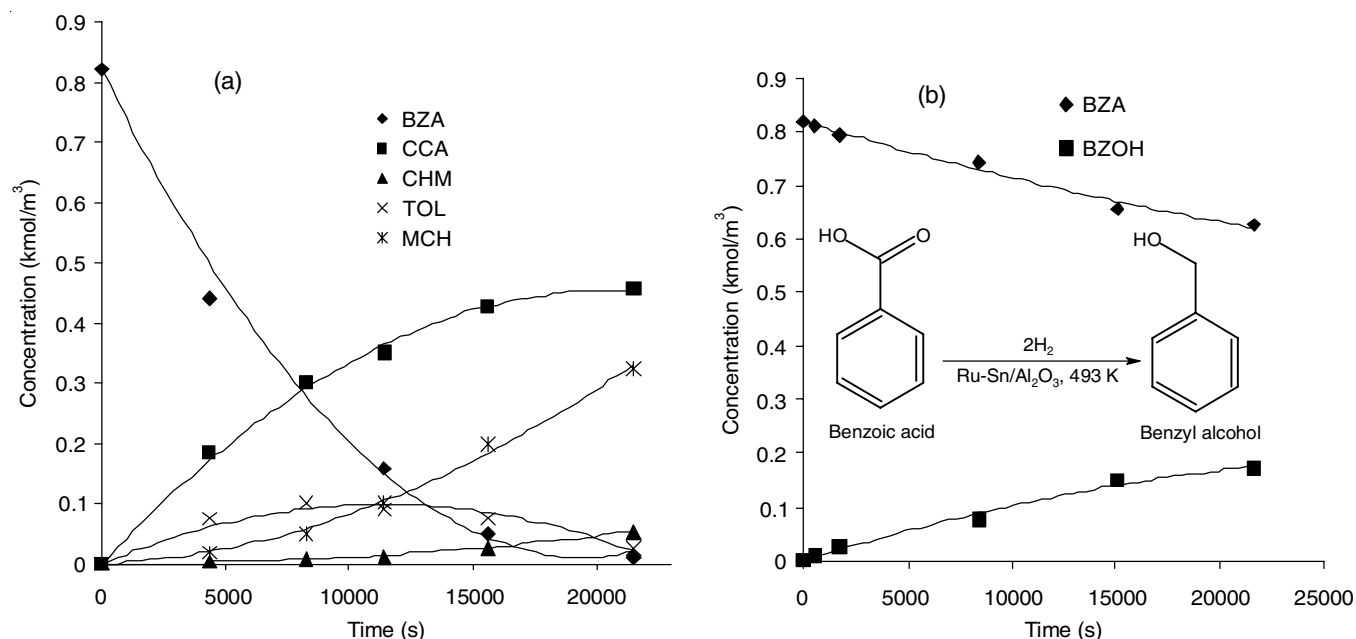
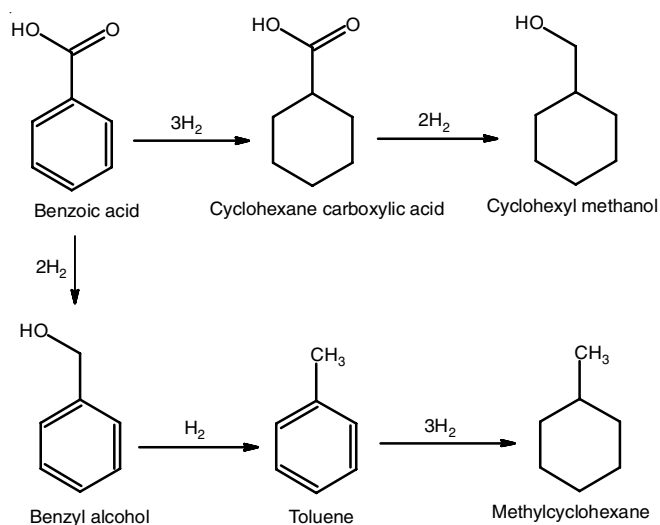


Fig. 3. Concentration time profile for hydrogenation of benzoic acid with 5% Ru/Al₂O₃ catalyst (a) and Ru-Sn/Al₂O₃ (Sn/Ru atomic ratio is 1:5) catalyst (b) (Reaction conditions: temperature = 493 K, hydrogen partial pressure = 6.89 MPa, catalyst = 5 kg m⁻³, benzoic acid = 0.82 kmol m⁻³, solvent = 1,4-dioxane, time = 6 h, agitation speed = 1000 rpm, total volume = 1.0 × 10⁻⁴ m³)



Scheme-I: Hydrogenation of benzoic acid with 5% Ru/Al₂O₃ catalyst

Recycle study for Ru-Sn/Al₂O₃ catalyst for hydrogenation of benzoic acid to benzyl alcohol: In order to confirm the stability of catalyst for hydrogenation of benzoic acid to benzyl alcohol, the catalyst was recycled under same reaction conditions.

In these experiments after end of reaction, the reactor was cooled to 313 K and the catalyst was allowed to settle down and supernatant solution was separated from the catalyst. The catalyst was washed with reaction solvent and the reactor was then charged with benzoic acid and 1,4-dioxane to carry out the recycle experiment. The catalyst recycle experiments were performed at 493 K and at a hydrogen partial pressure of 6.89 MPa. The catalyst was found to retain its activity for four recycles without affecting the conversion of benzoic acid and selectivity to benzyl alcohol as shown in Fig. 4. The overall cumulative turn over frequency (TOF) for the catalyst was found to be 2.73×10^{-3} kmol kg⁻¹ h⁻¹.

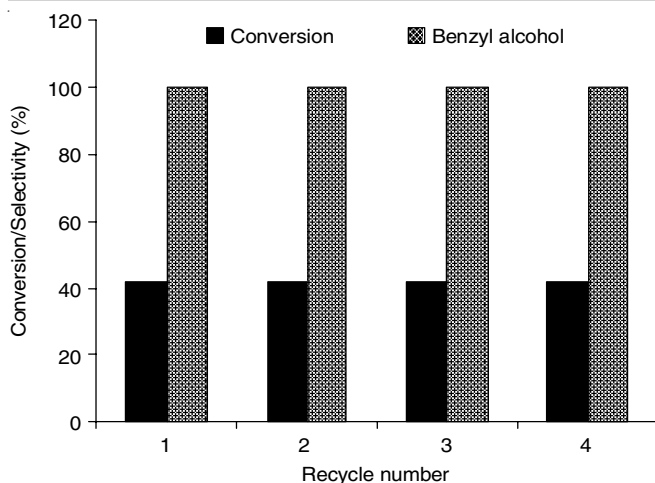


Fig. 4. Recycle study for Ru-Sn/Al₂O₃ catalyst for hydrogenation of benzoic acid (Reaction conditions: temperature = 493 K, hydrogen partial pressure = 6.89 MPa, catalyst = 10 kg m⁻³, benzoic acid = 0.41 kmol m⁻³, solvent = 1,4-dioxane, time = 6 h, agitation speed = 1000 rpm, total volume = 1.0 × 10⁻⁴ m³)

Mass transfer analysis for the hydrogenation of benzoic acid using Ru-Sn/Al₂O₃ catalyst: Hydrogenation of benzoic acid with Ru-Sn/Al₂O₃ catalyst is an example of a multiphase reaction involving gas, liquid and solid phases. So, this reaction involves (i) transfer of reactant (H₂) from gas into the liquid, (ii) the transfer of dissolved reactants (BZA and H₂) from liquid phase on to the catalyst surface, which is in a solid phase, (iii) intraparticle transfer of reactants to the catalytic site. If the rate of transport of reactants from one phase to the other is slower as compared to the intrinsic rate of reaction, then the rate of reaction is controlled by the rate of mass transport.

So, before commencing with the kinetic study, it was important to ensure that the reaction occurs in the kinetic regime. The effect of agitation speed on the rate of reaction was studied at 513 K in the range of 800-1500 rpm. The agitation speed had no effect on rate of hydrogenation as shown in Fig. 5, which confirms that gas-liquid mass transfer is not significant.

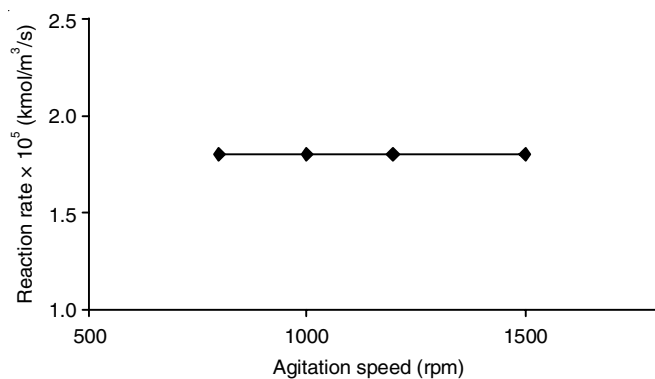


Fig. 5. A plot of initial rate of hydrogenation vs. agitation speed (Reaction conditions: temperature = 513 K, hydrogen partial pressure = 6.89 MPa, benzoic acid = 0.41 kmol m⁻³, catalyst = 10 kg m⁻³, solvent = 1,4-dioxane, time = 3 h, total volume = 1.0 × 10⁻⁴ m³)

Kinetic study for hydrogenation of benzoic acid to benzyl alcohol with Ru-Sn/Al₂O₃ catalyst: Kinetic study was carried out for chemoselective hydrogenation of benzoic acid

to benzyl alcohol using Ru-Sn/Al₂O₃ catalyst. In the prepared catalyst, the percentage of Ru & Sn in catalyst was 5% and 29% respectively. The Ru:Sn atomic ratio in the catalyst was 5.

In all experiments, the consumption of benzoic acid, hydrogen gas and formation of hydrogenation products were monitored for calculating liquid mass balance and gas balance, which was found to be more than 95%.

The kinetic study for hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al₂O₃ catalyst in 1,4-dioxane as solvent was carried out in the range of conditions (Table-1). The initial rates for hydrogenation were calculated as a function of formation of benzyl alcohol with time from the concentration-time profiles. These are initial rates for hydrogenation as they were obtained for low conversion of benzoic acid (conversion < 10-15%).

Reaction parameter	Range
Temperature	473-513 K
Catalyst concentration	5-20 kg m ⁻³
Substrate concentration	0.2-0.8 kmol m ⁻³
Pressure	3.8-8.8 MPa
Stirring speed	1200 rpm
Total charge	1.0 × 10 ⁻⁴ m ³
Reaction time	3 h

Effect of catalyst loading: The effect of catalyst concentration on the rate of hydrogenation of benzoic acid to benzyl alcohol was studied in the temperature range of 473-513 K, benzoic acid concentration of 0.41 kmol m⁻³ and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane as solvent. The rate was found to be linearly dependent on the catalyst concentration, indicating a first order kinetics with respect to the catalyst loading (Fig. 6).

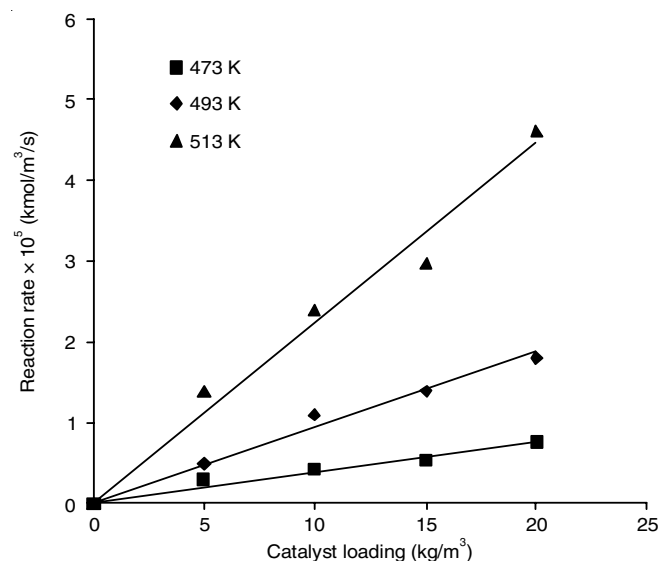


Fig. 6. Effect of catalyst loading on rate of hydrogenation of benzoic acid (Reaction conditions: hydrogen partial pressure = 6.89 MPa, benzoic acid = 0.41 kmol m⁻³, solvent = 1,4-dioxane, agitation speed = 1200 rpm, time = 3 h, total volume = 1.0 × 10⁻⁴ m³)

Effect of benzoic acid concentration: The effect of benzoic acid concentration on the initial rate of hydrogenation was investigated in the temperature range of 473-513 K, catalyst concentration of 10 kg m^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane as solvent. The rate for hydrogenation showed a first order dependence on the benzoic acid concentration (Fig. 7).

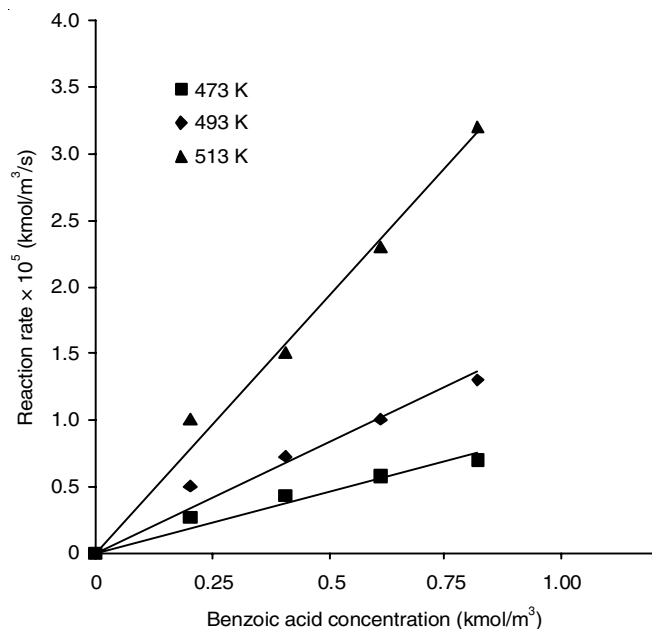


Fig. 7. Effect of benzoic acid concentration on rate of hydrogenation (Reaction conditions: hydrogen partial pressure = 6.89 MPa, catalyst = 10 kg m^{-3} , solvent = 1,4-dioxane, agitation speed = 1200 rpm, time = 3 h, total volume = $1.0 \times 10^4 \text{ m}^3$)

Effect of hydrogen partial pressure: The effect of hydrogen partial pressure on the rate of hydrogenation of benzoic acid to benzyl alcohol was studied in the temperature range of 473-513 K, catalyst concentration of 10 kg m^{-3} and benzoic acid concentration of 0.41 kmol m^{-3} in 1,4-dioxane as solvent. The rate was found to be linearly dependent on the hydrogen partial pressure, indicating first order kinetics (Fig. 8).

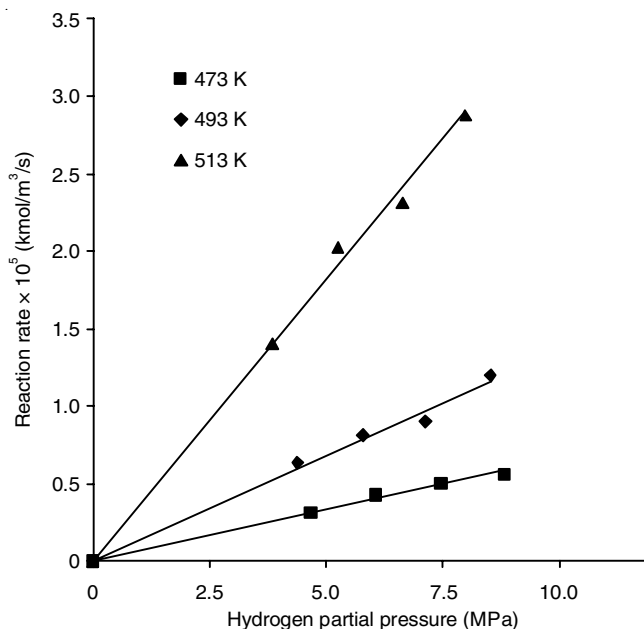


Fig. 8. Effect of hydrogen partial pressure on rate of hydrogenation (Reaction conditions: benzoic acid = 0.41 kmol m^{-3} , catalyst = 10 kg m^{-3} , solvent = 1,4-dioxane, agitation speed = 1200 rpm, time = 3 h, total volume = $1.0 \times 10^4 \text{ m}^3$)

Kinetic modeling: The rate data obtained were fitted to different rate equations based on Langmuir-Hinshelwood (L-H) type models and the results are shown in Table-2. In order to estimate the kinetic constants, the rate equation was subjected to a non-linear regression analysis using an optimization routine based on Marquardt's method [14]. The objective function is as given by the following formula:

$$\Phi = \sum_{i=1}^n (r_{\text{exp}} - r_{\text{mod}})_i^2$$

where r_{exp} is observed rate of hydrogenation and r_{mod} is the predicted rate of hydrogenation.

Model I was found to fit the observed rate data with reasonable agreement based on the Φ_{min} value. Model I was verified for hydrogenation of benzoic acid to benzyl alcohol by comparing theoretical rates predicted by model I with the

TABLE-2
RATE MODELS FOR HYDROGENATION OF BENZOIC ACID WITH Ru-Sn/Al₂O₃ CATALYST TO BENZYL ALCOHOL

Model	Rate equation	Temp. (K)	k	K _A	K _B	Φ_{min}
I	$R_{\text{H}} = k w A B$	473	1.72×10^{-7}	–	–	7.14×10^{-12}
		493	2.99×10^{-7}	–	–	4.07×10^{-11}
		513	8.65×10^{-7}	–	–	2.68×10^{-10}
II	$R_{\text{H}} = \frac{k w A B}{(1 + K_A A)}$	473	1.19×10^{-3}	0.37	–	3.16×10^{-10}
		493	2.43×10^{-3}	1.48	–	1.11×10^{-9}
		513	5.41×10^{-3}	2.43	–	1.23×10^{-8}
III	$R_{\text{H}} = \frac{k w A B}{(1 + K_B B)}$	473	1.05×10^{-3}	–	0.47	3.15×10^{-10}
		493	1.31×10^{-3}	–	-0.46	3.19×10^{-9}
		513	2.29×10^{-3}	–	-0.40	3.09×10^{-8}
IV	$R_{\text{H}} = \frac{k w A B}{(1 + K_A A)(1 + K_B B)}$	473	1.38×10^{-3}	0.40	1.34	2.37×10^{-10}
		493	2.79×10^{-3}	1.56	0.86	1.08×10^{-9}
		513	6.39×10^{-3}	2.53	0.78	1.19×10^{-8}

where, R_{H} = Initial rate of hydrogenation ($\text{kmol/m}^3/\text{s}$), k = Rate constant ($\text{m}^6 \text{ kg}^{-1} \text{ kmol}^{-1} \text{ s}^{-1}$), w = Catalyst concentration (kg/m^3), A = Benzoic acid concentration (kmol/m^3), B = Hydrogen concentration (kmol/m^3), K_A = Adsorption equilibrium constant for benzoic acid (m^3/mol) and K_B = Adsorption equilibrium constant for hydrogen (m^3/kmol).

experimental rates for the hydrogenation. For the comparison experimental and theoretical rates for the hydrogenation of benzoic acid to benzyl alcohol for a given parameter were plotted on the same graph as shown in Figs. 9-11.

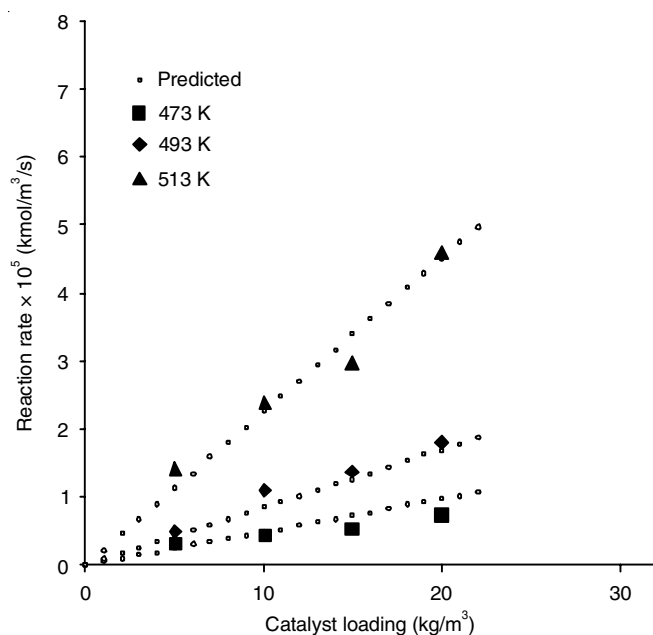


Fig. 9. Effect of catalyst loading on rate of hydrogenation: Comparison of experimental and predicted rates (Reaction conditions: hydrogen partial pressure = 6.89 MPa, benzoic acid = 0.41 kmol/m³, solvent = 1,4-dioxane, agitation speed = 1200 rpm, time = 3 h, total volume = 1.0 × 10⁻⁴ m³)

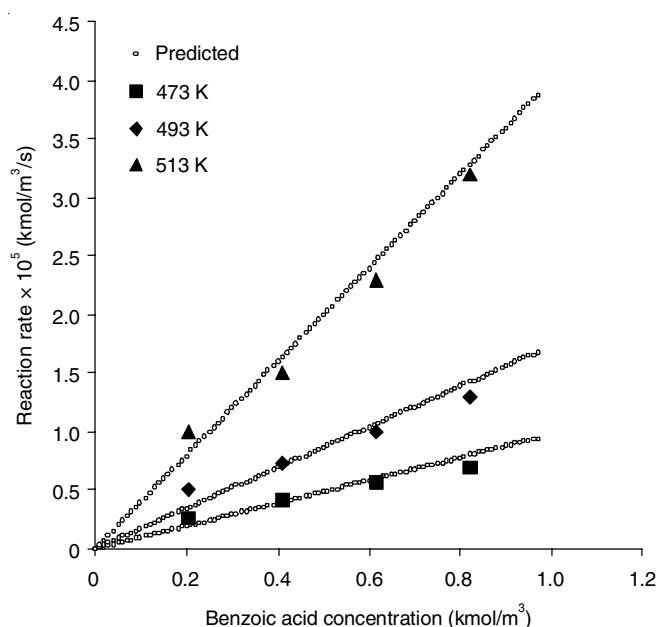


Fig. 10. Effect of benzoic acid concentration on rate of hydrogenation: Comparison of experimental and predicted rates (Reaction conditions: hydrogen partial pressure = 6.89 MPa, catalyst = 10 kg/m³, solvent = 1,4-dioxane, agitation speed = 1200 rpm, time = 3 h, total volume = 1.0 × 10⁻⁴ m³)

From Figs. 9-11, it is understood that model I predicts the rate of reaction with an error less than ± 5%. Based on the values of rate constant (k) for model I a plot of $\ln k$ versus $1/T$

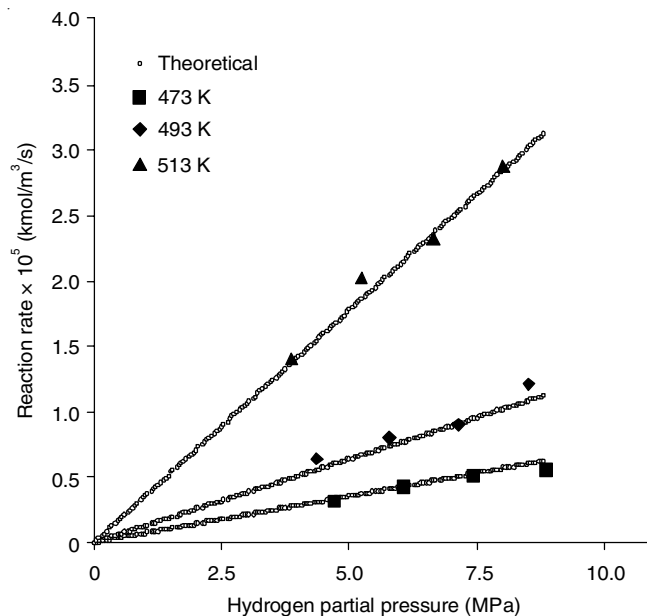


Fig. 11. Effect of hydrogen partial pressure on rate of hydrogenation: comparison of experimental and predicted rates (Reaction conditions: benzoic acid = 0.41 kmol/m³, catalyst = 10 kg/m³, solvent = 1,4-dioxane, agitation speed = 1200 rpm, time = 3 h, total volume = 1.0 × 10⁻⁴ m³)

(Arrhenius plot) is obtained as shown in Fig. 12. From the plot activation energy (E_a) for the hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al₂O₃ catalyst was found to be 81.64 kJ/mol.

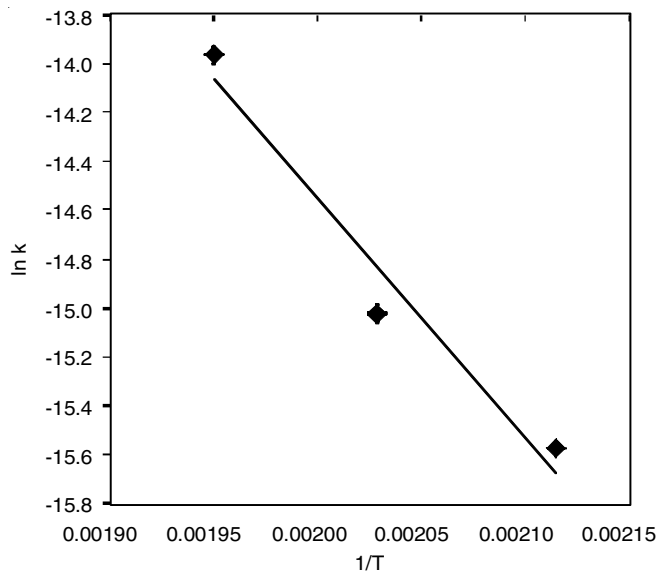


Fig. 12. Arrhenius plot for hydrogenation of benzoic acid with Ru-Sn/Al₂O₃ catalyst

From kinetic model I ($R_H = k w A B$), a dual site mechanism for hydrogenation of benzoic acid to benzyl alcohol over Ru-Sn/Al₂O₃ catalyst was confirmed as proposed by Kluson & Cerveny [15]. Dual site mechanism means two different types of active sites are present on the catalyst for hydrogenation of benzoic acid. The first-order dependence on benzoic acid and hydrogen partial pressure for hydrogenation indicates two

different catalytic sites present for the activation of -COOH group of benzoic acid and hydrogen.

Conclusion

The chemoselective hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al₂O₃ catalyst was studied in a laboratory scale slurry reactor. The Ru-Sn/Al₂O₃ catalyst was found to be stable for four recycles. The kinetics of hydrogenation of benzoic acid to benzyl alcohol with Ru-Sn/Al₂O₃ catalyst was investigated for initial rates. The initial rates were found to be first order with respect to catalyst, benzoic acid and hydrogen partial pressure indicating dual site mechanism for hydrogenation of benzoic acid to benzyl alcohol on Ru-Sn/Al₂O₃ catalyst. The rate equation $R_H = k w A B$ was found to predict the observed rates in good agreement. The activation energy for hydrogenation of benzoic acid to benzyl alcohol using Ru-Sn/Al₂O₃ catalyst was found to be 81.64 kJ/mol.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- S. Dutta, T. Bhattacharya, F.J. Geffers, M. Bürger, D. Maiti and D.B. Werz, *Chem. Sci.*, **13**, 2551 (2022); <https://doi.org/10.1039/d1sc05392b>
- B. Grömer, S. Yoshioka and S. Saito, *ACS Catal.*, **12**, 1957 (2022); <https://doi.org/10.1021/acscatal.1c04392>
- H. Wang and F. Zhao, *Int. J. Mol. Sci.*, **8**, 628 (2007); <https://doi.org/10.3390/i8070628>
- S.B. Shinde and R.M. Deshpande, *Nat. Volatiles. Essent. Oils*, **8**, 11628 (2021).
- M.J. Mendes, O.A.A. Santos, E. Jordao and A.M. Silva, *Appl. Catal. A Gen.*, **217**, 253 (2001); [https://doi.org/10.1016/S0926-860X\(01\)00613-5](https://doi.org/10.1016/S0926-860X(01)00613-5)
- R.M. Deshpande, V.V. Buwa, C.V. Rode, R.V. Chaudhari and P.L. Mills, *Catal. Commun.*, **3**, 269 (2002); [https://doi.org/10.1016/S1566-7367\(02\)00119-X](https://doi.org/10.1016/S1566-7367(02)00119-X)
- S. Shinde and R.M. Deshpande, *Asian J. Chem.*, **32**, 339 (2020); <https://doi.org/10.14233/ajchem.2020.22393>
- Y. Hara and K. Endou, *Appl. Catal. A Gen.*, **239**, 181 (2003); [https://doi.org/10.1016/S0926-860X\(02\)00388-5](https://doi.org/10.1016/S0926-860X(02)00388-5)
- X. Chen, Z. Wang, H. Daly, R. Morgan, H. Manyar, C. Byrne, A.S. Walton, S.F.R. Taylor, M. Smith, R. Burch, P. Hu and C. Hardacre, *Appl. Catal. A Gen.*, **593**, 117420 (2020); <https://doi.org/10.1016/j.apcata.2020.117420>
- Z. Zhu, Z. Lu, B. Li and S. Guo, *Appl. Catal. A Gen.*, **302**, 208 (2006); <https://doi.org/10.1016/j.apcata.2006.01.005>
- M. Guo, X. Kong and C. Li, Quiha Yang, *Commun. Chem.*, **4**, 1 (2021); <https://doi.org/10.1038/s42004-021-00489-z>
- Ibrahim, M. Riski and Rodiansono, *IOP Conf. Series: Mater. Sci. Eng.*, **980**, 012012 (2020); <https://doi.org/10.1088/1757-899X/980/1/012012>
- M. Toba, S. Tanaka, S. Niwa, F. Mizukami, Z. Koppány, L. Guzzi, K. Cheah and T. Tang, *Appl. Catal. A Gen.*, **189**, 243 (1999); [https://doi.org/10.1016/S0926-860X\(99\)00281-1](https://doi.org/10.1016/S0926-860X(99)00281-1)
- D.W. Marquardt, *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963); <https://doi.org/10.1137/0111030>
- P. Kluson and L. Cerveny, *Appl. Catal. A Gen.*, **128**, 13 (1995); [https://doi.org/10.1016/0926-860X\(95\)00046-1](https://doi.org/10.1016/0926-860X(95)00046-1)