Kinetics of Hydrogenation of Lauric Acid in a Batch Slurry Reactor Using Ru-Sn/TiO₂ Catalyst

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Ru-Sn catalyst was prepared in-house by impregnation method. This catalyst was found to be stable for four recycles. The rate of hydrogenation of lauric acid (LAC) using Ru-Sn/TiO₂ catalyst was found to be linearly dependent on catalyst loading, lauric acid concentration and hydrogen partial pressure. The rate data obtained from kinetic study were fitted to simple rate equation based on Langmuir-Hinshelwood (L-H) type model. Based on kinetic data the hydrogenation of lauric acid over Ru-Sn/TiO₂ catalyst is proposed to occur by dual site mechanism the activation energy for hydrogenation of lauric acid to lauryl alcohol (LAOH) using Ru-Sn/TiO₂ catalyst was found to be 77.2 kJ/mol.

Key Words: Hydrogenation, Kinetics, Ru-Sn/TiO₂ catalyst, Langmuir-Hinshelwood model.

INTRODUCTION

In the last decade, supported ruthenium-tin catalysts have been intensively studied because of their activity and high chemoselectivity in the hydrogenation of unsaturated aldehydes, esters and carboxylic acids to corresponding alcohols[1]. A general conclusion drawn from the studies devoted to Ru-Sn catalyst systems is that ionic tin species, *i.e*., Lewis acid sites, activate the carbonyl group in hydrogenation reactions, by polarizing the C=O bond[2], followed by hydrogenation, which leads to their highly chemoselective behaviour.

Mendes *et al*.[3], have studied the performance of different supported ruthenium-tin catalysts for the liquid phase hydrogenation of oleic acid to unsaturated alcohol. Titania supported Ru-Sn catalyst prepared by impregnation showed better performance than the alumina supported sol-gel Ru-Sn catalyst. Ruthenium supported on alumina is more active for the hydrogenation of C=C bond, whereas the titania supported catalyst is more active for hydrogenation of the carboxylic group. The introduction of tin to Ru/TiO₂ catalyst resulted in almost total suppression of the C=C bond hydrogenation[4].

The beneficial effect of TiO₂ was attributed to the TiO₂₋ₓ species on the metal and Ti^{n+} ions that promote the hydrogenation in the desired direction[4]. The enhanced activity of transition metal catalysts supported on reducible oxides for selective hydrogenation of the C=O bond is generally attributed to an interaction of the oxygen end of the C=O bond with exposed cations of the oxide supports. In case of titania these sites can be Ti^{3+} cations or oxygen vacancies. These cations or oxygen vacancies are created *via* spill-over hydrogen activated by the metal during high temperature reduction. The improved performance of metal catalysts with the addition of promoters such as tin is attributed to the presence of promoter cations on the surface of metal, which activate the C=O bond through the interaction with the lone pair of electron of the carbonyl group oxygen[4].

Besides oxide supported, carbon supported Ru-Sn catalysts[5] also find application in hydrogenation reactions.

Despite the detailed studies on supported Ru-Sn catalyst for chemoselective hydrogenation reactions, there is a need to further investigate the kinetics of hydrogenation reaction using Ru-Sn catalyst.

In this work, the kinetic study for hydrogenation of lauric acid to lauryl alcohol was investigated using Ru-Sn/TiO₂ catalyst. A semi empirical model has been developed which fits the observed rate within experimental error. The activation energy for hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO₂ catalyst was calculated using this rate model. From the kinetic data general mechanism for hydrogenation of carboxylic acids over Ru-Sn catalyst is proposed.

EXPERIMENTAL

Lauric acid, 1,4-dioxane and RuCl₃·3H₂O, stannous chloride (SnCl₂·2H₂O) were procured from SD Fine Chemicals Ltd. (India). Catalyst support titania was procured from Aldrich Chemicals (USA). Authentic standards of reaction products

like lauryl alcohol were procured from Aldrich Chemicals (USA). Lauryl laurate ester was prepared from lauric acid and lauryl alcohol by esterification reaction. Crude lauryl laurate was separated on column, purified and was used as authentic standard. Hydrogen and nitrogen of 99.9 % purity were obtained from Indian Oxygen Ltd., Mumbai, India.

Catalyst preparation: The catalyst (5 % Ru-29 % Sn/ TiO_2) was prepared by impregnation method followed by calcination and reduction.

For preparing these catalysts, a homogeneous solution of required amount of $RuCl_3 \cdot 3H_2O$ and $SnCl_2 \cdot 2H_2O$ was prepared in 50 mL water. To this solution, 10 g of required support (TiO_2) 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 excess 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 silica glass reactor placed in a furnace as shown in Fig. 1, under constant flow of hydrogen gas (5 mL/min) for 12 h. After the reduction period, the silica glass reactor was cooled under nitrogen flow to room temperature. The reduced catalyst was transferred into a 50 mL container and stored in the dessicator under nitrogen.
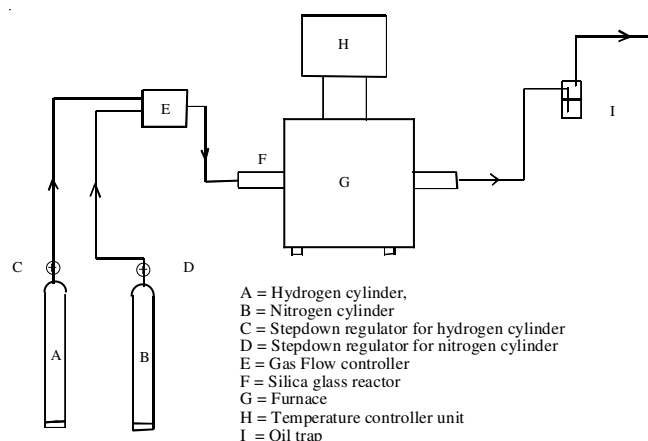

Fig. 1.   Schematic diagram of silica glass reactor set-up for catalyst reduction

A = Hydrogen cylinder,
B = Nitrogen cylinder
C = Stepdown regulator for hydrogen cylinder
D = Stepdown regulator for nitrogen cylinder
E = Gas Flow controller
F = Silica glass reactor
G = Furnace
H = Temperature controller unit
I = Oil trap

General procedure

Reactor set-up for high pressure reactions: The reactions were carried out in a 50 mL capacity high stainless steel alloy steel reactor supplied by Parr Instruments Co. USA. The reactor was provided with a double bladed variable speed stirrer with a magnetic drive and automatic temperature control by means of an external electrically heated jacket and internal cooling coils. A gas inlet/outlet as well as liquid outlet provided a facility for sampling of liquid contents in the reactor. For safety purpose, a high pressure-high temperature cut-off facility was also provided to the reactor, in addition to rupture disc. The autoclave was designed to operate at a temperature up to 623 K and 150 bar pressure.

The reactor was connected to a hydrogen reservoir held at a pressure higher than that of the reactor, through a constant

pressure regulator. Hydrogen gas was supplied to the reactor from this reservoir through a non-return valve. The gas consumed during the course of the reaction was determined from the observed pressure drop in the reservoir at different time intervals. A transducer connected to a pressure readout system was used to monitor pressure in the reactor and the hydrogen reservoir. A schematic of the reactor assembly is shown in Fig. 2.
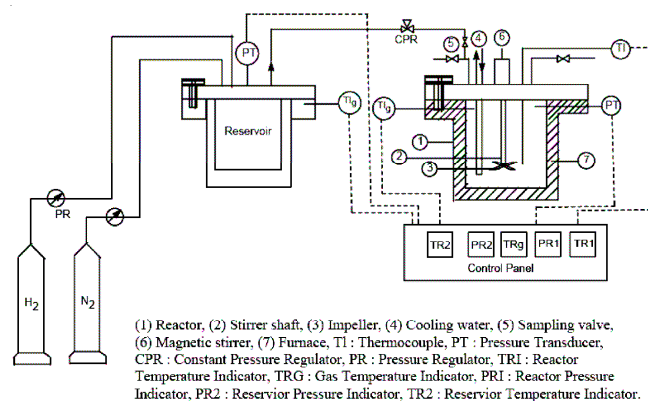

(1) Reactor, (2) Stirrer shaft, (3) Impeller, (4) Cooling water, (5) Sampling valve, (6) Magnetic stirrer, (7) Furnace, TI : Thermocouple, PT : Pressure Transducer, CPR : Constant Pressure Regulator, PR : Pressure Regulator, TRI : Reactor Temperature Indicator, TRG : Gas Temperature Indicator, PRI : Reactor Pressure Indicator, PR2 : Reservoir Pressure Indicator, TR2 : Reservior Temperature Indicator.

Fig. 2.   Schematic diagram of reactor set-up for high pressure hydrogenation reactions

Experimental procedure for high pressure reactions: In a typical hydrogenation experiment, known quantities of the substrate, catalyst and solvent were charged into a clean and dry reactor. The contents were flushed with nitrogen followed by hydrogen (2-3 times). The contents in the autoclave were heated to a desired temperature under slow stirring. After the desired temperature was attained, the autoclave was pressurized to the requisite pressure with hydrogen and the reaction was started by adjusting the agitation speed to 1200 rpm. The hydrogen consumption was determined from the drop in the hydrogen pressure in the reservoir vessel as a function of time. The liquid samples were withdrawn at specific time intervals and analyzed for reactant and product concentrations. At the end of the reaction, the autoclave was cooled to room temperature and a gas sample was withdrawn for analysing the gas phase products. The gas phase analysis was essential to ensure that cracking of the products to hydrocarbons was negligible. Following this, the contents in the reactor were discharged and the liquid sample was analyzed for reactants and products.

Detection method

Analysis: The various hydrogenation products formed during the reaction were identified using GC-MS (Agilent GC 6890 with 5973 mass selective detector instrument).

For quantitative analysis, samples from the reaction mixture were filtered to remove the catalyst and analyzed by gas chromatography (Agilent Systems 6890 GC). For analysis, a HP INNOWax, polyethylene glycol capillary column (30 m × 320 µm × 0.25 µm) along with flame ionization detector was used on Agilent 6890 gas chromatograph controlled by HP Chemstation software, equipped with an auto sampler unit. Calibration for the hydrogenation products was done using external standard method[6].

RESULTS AND DISCUSSION

Kinetic study for hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO$_2$ catalyst: In order to study the kinetics of hydrogenation of lauric acid to lauryl alcohol using Ru-Sn/TiO$_2$ (5 % Ru-29 % Sn/TiO$_2$, *i.e.*, Sn/Ru ratio is 5) catalyst in 1,4-dioxane as solvent, several experiments were carried out in the range of conditions shown in the Table-1. The rates for hydrogenation were calculated from the observed concentration-time profiles. These were essentially initial rates of hydrogenation as they were obtained for low conversion of lauric acid (conversion < 10-15 %).

TABLE-1
RANGE OF REACTION CONDITIONS FOR
HYDROGENATION OF LAURIC ACID TO LAURYL
ALCOHOL WITH Ru-Sn/TiO$_2$ CATALYST

Reaction parameter	Range
Temperature	453-493 K
Catalyst concentration	4-16 kg m^{-3}
Substrate concentration	0.2-0.5 k mol m^{-3}
Pressure	3-9 MPa
Stirring speed	1200 rpm
Total charge	2.5×10^{-5} m^3
Reaction time	2 h

Effect of catalyst loading: The effect of catalyst concentration on the rate of hydrogenation of lauric acid to lauryl alcohol was studied in the temperature range of 453-493 K, lauric acid concentration of 0.4 k mol m^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane as solvent. The results are shown in Fig. 3. The rate was found to be linearly dependent on the catalyst concentration, indicating first order kinetics.
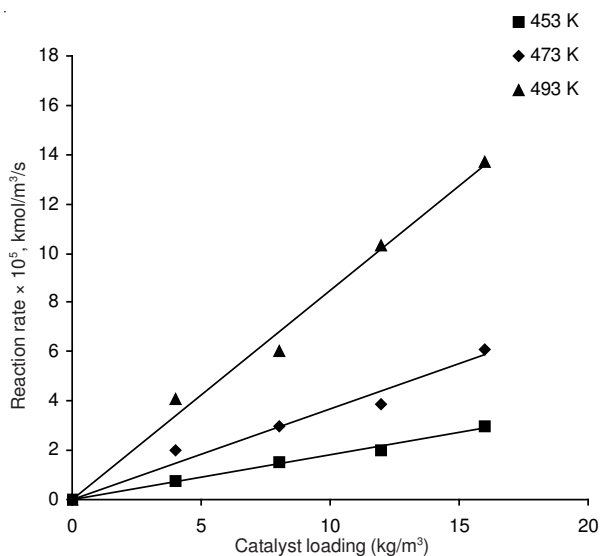

Fig. 3. Effect of catalyst loading on rate of hydrogenation of lauric acid

Effect of lauric acid concentration: The effect of lauric acid concentration on the initial rate of hydrogenation was investigated in the temperature range of 453-493 K, catalyst concentration of 8 kg m^{-3} and hydrogen partial pressure of 6.89 MPa and 1,4-dioxane as solvent. The results are shown in Fig. 4. The hydrogenation rate showed a first order dependence on lauric acid concentration.
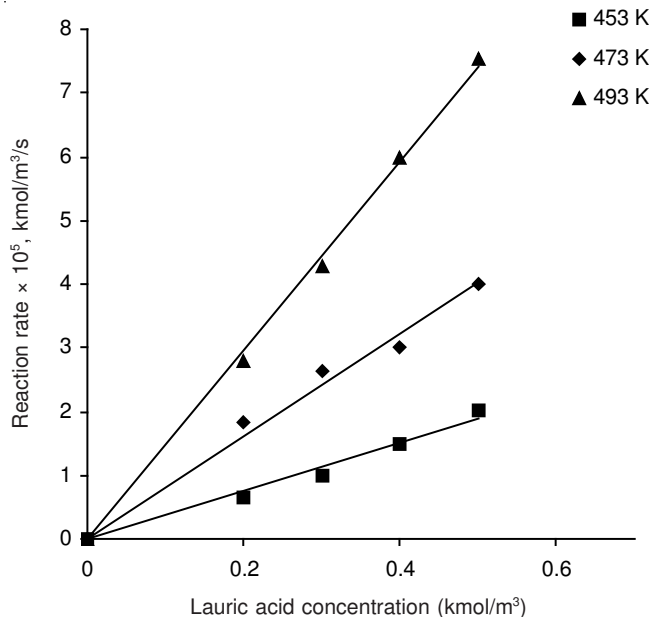

Fig. 4. Effect of lauric acid concentration on rate of hydrogenation

Effect of hydrogen partial pressure: The effect of hydrogen partial pressure on the rate of hydrogenation of lauric acid to lauryl alcohol was studied in the temperature range of 453-493 K, catalyst concentration of 8 kg m^{-3} and lauric acid concentration of 0.4 k mol 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. The results for effect of hydrogen partial pressure are shown in Fig. 5.
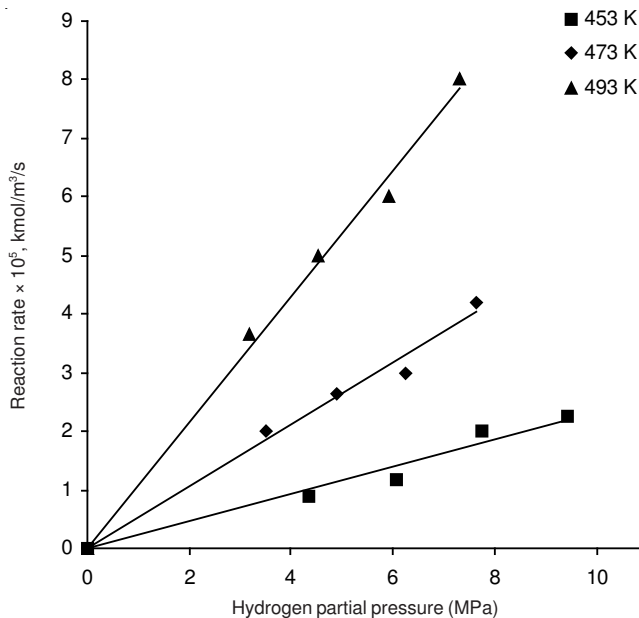

Fig. 5. Effect of hydrogen partial pressure on rate of hydrogenation

Kinetic modeling: The rate data obtained from kinetic study were fitted to simple rate equation based on Langmuir-Hinshelwood (L-H) type model given 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[7]. The objective function was chosen as follows:

<div align="center">TABLE-2</div>
<div align="center">RATE MODEL FOR HYDROGENATION OF LAURIC ACID WITH Ru-Sn/TiO, CATALYST TO LAURYL ALCOHOL</div>

Model	Rate equation	T (K)	k	K_A	K_B	Φ_{min}
I	$R_H = kwAB$	453	6.87×10^{-7}	–	–	9.89×10^{-11}
		473	1.53×10^{-6}	–	–	3.33×10^{-10}
		493	3.60×10^{-6}	–	–	5.32×10^{-10}
II	$R_H = \dfrac{kwAB}{(1+K_A A)}$	453	7.50×10^{-5}	0.45	–	9.61×10^{-10}
		473	9.08×10^{-5}	-0.22	–	3.32×10^{-10}
		493	1.42×10^{-4}	-0.023	–	7.03×10^{-10}
III	$R_H = \dfrac{kwAB}{(1+K_B B)}$	453	4.03×10^{-5}	–	-10	5.27×10^{-10}
		473	1.00×10^{-4}	–	0.063	3.33×10^{-10}
		493	1.42×10^{-4}	–	-0.026	7.06×10^{-10}
IV	$R_H = \dfrac{kwAB}{(1+K_A A)(1+K_B B)}$	473	-5.11×10^{-2}	-1.46×10^{3}	-4.01×10^{-5}	2.28×10^{-10}
		493	-2.29×10^{-2}	-5.96×10^{4}	-6.03×10^{-4}	6.09×10^{-10}
		513	1.53×10^{-4}	-3.53×10^{-2s}	-3.39	7.02×10^{-10}

Where, R_H = Initial rate of hydrogenation (kmol/m^3/s), k = Rate constant, w = Catalyst concentration (kg/m^3), A = Lauric acid concentration (kmol/m^3), B = Hydrogen concentration (kmol/m^3), K_A = adsorption equilibrium constant for lauric acid (m^3/kmol) and K_B = adsorption equilibrium constant for hydrogen (m^3/kmol).

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

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

The models proposed in Table-1 were discriminated using Φ_{min} values. The model I had the lowest Φ_{min} values and hence was accepted. To verify the model I for hydrogenation of lauric acid to lauryl alcohol, the theoretical rates for hydrogenation of lauric acid to lauryl alcohol were obtained using model I and compared with the experimental rate for hydrogenation as shown in Figs. 6-8.
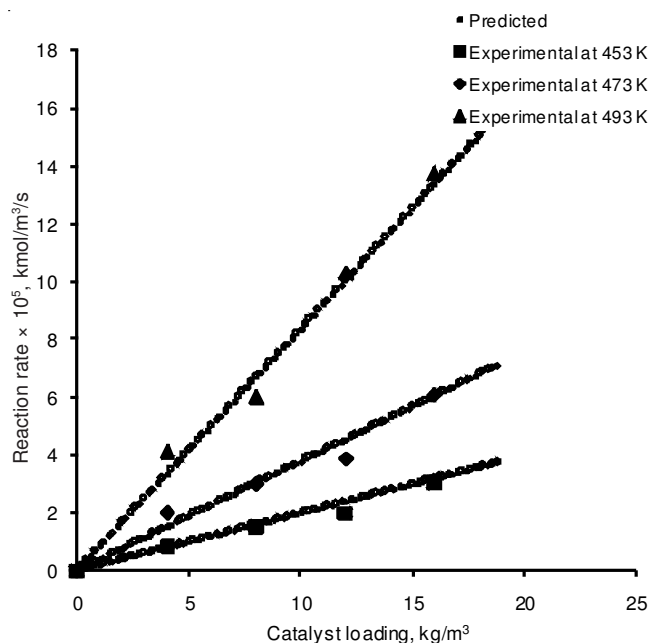

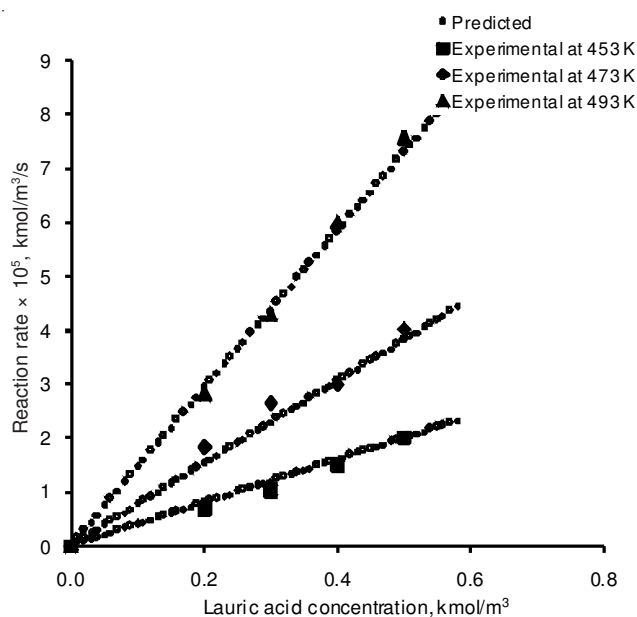Fig. 6. Comparison of experimental and predicted effect of catalyst loading on rate of hydrogenation

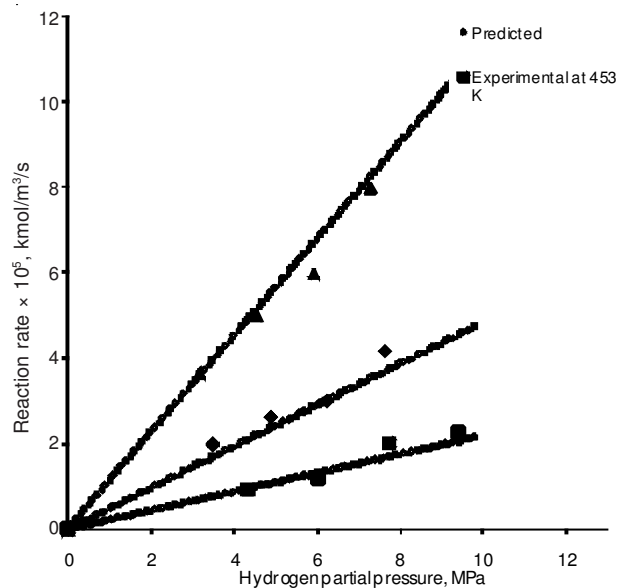Fig. 7. Comparison of experimental and predicted effect of lauric acid concentration on rate of hydrogenation

Fig. 8. Comparison of experimental and predicted effect of hydrogen partial pressure on rate of hydrogenation

From Figs. 6-8, it is observed that model I predicts the rate of reaction with an error less than ± 5 % which is within the range of experimental error. Based on the values of rate constant (k) of this equation, ln k *versus* 1/T was plotted (Fig. 9). From Fig. 9 the activation energy for hydrogenation of lauric acid to lauryl alcohol using Ru-Sn/TiO$_2$ catalyst was found to be 77.2 kJ/mol.
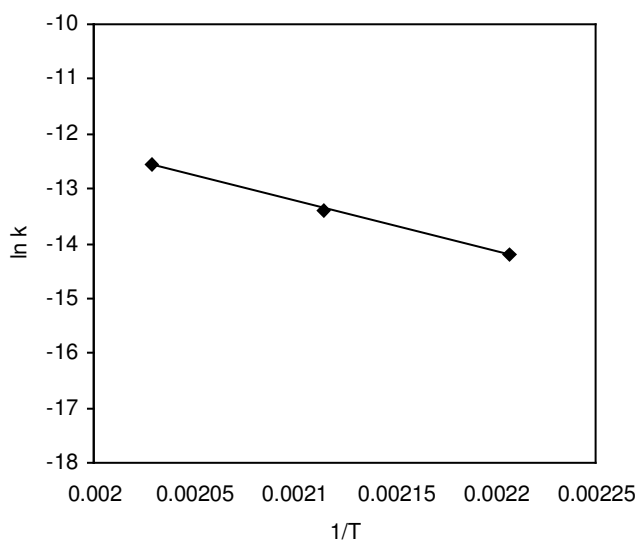
Fig. 9. Arrhenius plot for hydrogenation of lauric acid with Ru-Sn/TiO₂ catalyst

From kinetic study the dual site mechanism proposed by Kluson and Cerveny[8] was confirmed for the hydrogenation of lauric acid with Ru-Sn/TiO₂ catalyst. The mechanism for hydrogenation with this catalyst is a dual site mechanism, as the hydrogenation shows first order dependence on the two reaction parameters, lauric acid and hydrogen.

Conclusion

The hydrogenation of lauric acid to lauryl alcohol using Ru-Sn catalyst was studied in a laboratory scale slurry reactor. The Ru-Sn/TiO₂ catalyst was found to be stable for four recycles for the hydrogenation of lauric acid in 1,4-dioxane. The kinetics of hydrogenation of lauric acid to lauryl alcohol with Ru-Sn/TiO₂ catalyst was investigated in a temperature range of 453-493 K, hydrogen partial pressure between 3-9 MPa, catalyst loading between 4-16 kg/m³, initial lauric acid concentration between 0.2-0.5 kmol/m³. The rates were first order with respect to catalyst, lauric acid and hydrogen indicating dual site mechanism for hydrogenation of lauric acid to lauryl alcohol on Ru-Sn/TiO₂ catalyst. The following rate equation was found to predict the rates in good agreement with the experimental data.

$$R_H = kwAB$$

where, w, A and B are catalyst loading, lauric acid concentration and hydrogen concentration, respectively. The activation energy for hydrogenation of lauric acid to lauryl alcohol using Ru-Sn/TiO₂ catalyst was found to be 77.2 kJ/mol.

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