Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 7, Issue, 10, pp.21644-21646, October, 2015

INTERNATIONAL JOURNAL
OF CURRENT RESEARCH

ISSN: 0975-833X

RESEARCH ARTICLE

KINETIC MODELING OF CATALYTIC REACTION

[1]Dr. Prafullachandra P. Tekale, [2,*]Dr. Smruti P. Tekale and [3]Dr. P. N. Pabrekar

[1]Department of Chemistry, G. N. Khalsa College, Matunga, Mumbai,
[2]Department of Applied Science, Vidyalankar Institute of Technology, Wadala, Mumbai
[3]Principal, ICLES' Motilal Jhunjhunwala College, Vashi, Navi Mumbai

ARTICLE INFO

Article History:
Received 27th July, 2015
Received in revised form
25th August, 2015
Accepted 15th September, 2015
Published online 31st October, 2015

Key words:
Kinetic modeling,
Hydrogenation,
LHHW model.

ABSTRACT

Chemical kinetic modelling is a concept for modelling chemical reactions by studying the reaction mechanism. The hydrogenation reaction of phenol was carried out using titnia supported ruthenium catalyst at 323 K and 2.07 Mpa hydrogen pressure. A Langmuir– data and a fundamental modeling approach that will enhance understanding of the reaction rate equations. Hinshelwood–Hougen–Watson (LHHW) model was proposed. The study provides both extensive and data and a fundamental modeling approach that will enhance understanding of the reaction rate equations.

Citation: Dr. Prafullachandra P. Tekale, Dr. Smruti P. Tekale and Dr. P. N. Pabrekar, 2015. "Kinetic modeling of catalytic reaction", *International Journal of Current Research*, 7, (10), 21644-21646.

INTRODUCTION

Chemical engineering processes are designed to transform raw materials to value added products via chemical reactions (Ranade 2002). Various engineering tools are used to understand the reaction mechanism (Elena et al., 2009). The first step would be systematic study of the reaction. Different kinetic parameters are varied to find the optimum reaction conditions where the conversion of the reactant is maximum. Based on this data a kinetic model is developed (Meyer et al., 2009, Stanislaus et al., 1994, Tekale et al., 2013). This facilitates the reaction engineers to carry the process to production level.

Experimental

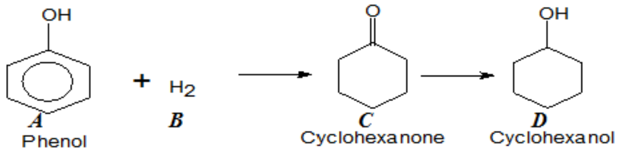
A systematic study of the hydrogenation reaction of phenol was carried out using titnia supported ruthenium catalyst at 323 K and 2.07 Mpa hydrogen pressure.

RESULT AND DISCUSSION

Kinetic model based on LHHW approach

The effect of speed of agitation on hydrotreatment of phenol was studied. At a speed of 1200 rpm, diffusion resistances were found to be absent. Also intraparticle diffusion was found to be absent. Hence an attempt was made to develop an intrinsic rate expression for phenol hydrogenation based on the Langmuir-Hinshelwood approach.

Hydrotreatment of phenol can be represented as follows:



Consider that the reaction occurs by the following series of elementary steps.

- Reversible adsorption of phenol.
- Reversible adsorption of hydrogen by a dissociative mechanism.
- Surface reaction between phenol and hydrogen adsorbed on the same type of active sites.
- Reversible reaction with more hydrogen further to form an intermediate.
- Fast reaction to give cyclohexanol.

The individual reactions according to this mechanism are:

***Corresponding author: Dr. Smruti P. Tekale**
Department of Applied Science, Vidyalankar Institute of Technology, Wadala, Mumbai

$A + X \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AX$ Fast

$B_2 + 2X \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} 2\,BX$ Fast

$AX + BX \xrightarrow{k_3} CX + X$ Slow

$CX + BX \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} DX + X$ Fast

$DX \underset{k_{-5}}{\overset{k_5}{\rightleftarrows}} D + X$ Fast

Assuming stationary steady state hypothesis, adsorption of A can be shown as

$k_1 C_A \varnothing_v = k_{-1} \varnothing_A$

where , $\varnothing_v$ = Fraction of vacant active sites

$\varnothing$ = Fraction of vacant active sites occupied by A

$$\varnothing_A = \frac{k_1}{k_{-1}} C_A \varnothing_V$$

$\varnothing_A = K_A C_A \varnothing_v$ ....(1)

where,

$K_A = \frac{k_1}{k_{-1}}$ Adsorption equilibrium constant for A.

Adsorption of B

$k_2 C_B \varnothing_v^2 = k_{-2} \varnothing_B^2$

$$\varnothing_B^2 = \frac{k_2}{k_{-2}} C_B \varnothing_v^2$$

$$\varnothing_B = \left(\frac{k_2}{k_{-2}} C_B\right)^{1/2} \varnothing_v$$

$\varnothing_B = (K_B . C_B)^{1/2} \varnothing_v$ ……………………(2)

where,

$K_B = \frac{k_2}{k_{-2}}$ = Adsorption equilibrium constant for B.

Desorption of D

$k_5 \varnothing_D = k_{-5} C_D \varnothing_v$

$$\varnothing_D = \frac{k_{-5}}{k_5} C_D \varnothing_V$$

$\varnothing_D = K_D C_D \varnothing_v$ ....(3)

where, $K_D = \frac{k_{-5}}{k_5}$ = Adsorption equilibrium constant for D.

For step 4 : $k_4 \varnothing_B \varnothing_C = k_{-4} C_D \varnothing_v$

$$\varnothing_C = \frac{\varnothing_D \varnothing_V \quad k_{-4}}{\varnothing_B \qquad k_4}$$

$$\varnothing_C = \frac{\varnothing_D \varnothing_V}{K_C \varnothing_B}$$

where

$$K_C = \frac{k_4}{k_{-4}}$$

From equation 1, 2 and 3 we get

$$\varnothing_C = \frac{K_D C_D \varnothing_V^{\,2}}{K_C (K_B C_B)^{1/2} \varnothing_V}$$

$$\varnothing_C = \frac{K_D C_D \varnothing_V}{K_C (K_B C_B)^{1/2}} \quad (4)$$

Since

$\varnothing_A + \varnothing_B + \varnothing_C + \varnothing_D + \varnothing_V = 1$ ……………………..(5)

$$K_A C_A \varnothing_V + (K_B C_B)^{1/2} \varnothing_V + \frac{K_D C_D \varnothing_V}{K_C (K_B C_B)^{1/2}} + K_D C_D \varnothing_v + \varnothing_v = 1$$

$$\varnothing_v \left[1 + K_A C_A + (K_B C_B)^{1/2} + \frac{K_D}{K_C \sqrt{K_B}} C_D C_B^{-1/2} + K_D C_D \right] = 1$$

$$\varnothing_V = \frac{1}{\left[1 + K_A C_A + (K_B C_B)^{1/2} + \frac{K_D}{K_C (K_B)^{1/2}} C_D C_B^{-1/2} + K_D C_D\right]} \quad \text{........(6)}$$

Assuming surface reaction between adsorbed phenol and hydrogen to be rate controlling

$$r_{overall} = k_3 \varnothing_A \varnothing_B$$

$$= k_3 K_A C_A (K_B C_B)^{1/2} \varnothing_v^{\,2}$$

$$r_{overall} = \frac{k_3 K_A (K_B)^{1/2} \quad C_A C_B^{1/2}}{\left[1 + K_A C_A + (K_B C_B)^{1/2} + \frac{K_D}{K_C (K_B)^{1/2}} C_D C_B^{-1/2} + K_D C_D\right]^2} \quad \text{.....(7)}$$

Assuming product adsorption to be weak, equation 7 can be simplified to the form

$$r_{overall} = \frac{k_3 . K_A (K_B)^{1/2} \quad C_A C_B{}^{1/2}}{[1+K_A C_A + (K_B C_B)^{1/2}]^2} \qquad \text{.........................(8)}$$

Equation 8 can be simplified further if we consider initial rates (r_0) only.

$$r_0 = \frac{k_3 K_A (K_B C_B)^{1/2} C_A}{[1+K_A C_A + (K_B C_B)^{1/2}]^2}$$

$$r_0 = \frac{C_A}{[\frac{(1+(K_B C_B)^{1/2}}{[k_3 K_A (K_B C_B)^{1/2}]^{1/2}} + (\frac{K_A}{[k_3 K_A (K_B C_B)^{1/2}]^{1/2}}) C_A]^2}$$

$$r_0 = \frac{C_A}{[P + Q C_A]^2} \qquad \text{..........................(9)}$$

where

$$P = \frac{(1+(K_B C_B)^{1/2}}{[k_3 K_A (K_B C_B)^{1/2}]^{1/2}} \qquad \text{.........................(10)}$$

$$Q = \frac{K_A}{[k_3 K_A (K_B C_B)^{1/2}]^{1/2}} = \frac{1}{[k_3 (K_B C_B)^{1/2}]^{1/2}} \qquad \text{............. (11)}$$

Thus

$$r_0 = \frac{C_A}{[P + Q C_A]^2} \qquad \text{................(12)}$$

Rearranging

$$[P + Q C_A]^2 = \frac{C_A}{r_0}$$

$$[P + Q C_A] = \sqrt{\frac{C_A}{r_0}}$$

$$P + Q C_A = R \quad \text{Where } R = \sqrt{\frac{C_A}{r_0}}$$

Thus $R = P + Q C_A$

Thus a linear form is obtained.

Table 1. Comparison between observed and predicted values of initial rates by LHHW model

Temperature K	P_{H2} MPa	$P_{sec}{}^{0.5}$	Q	$r_{observed}$ x 10^{-5}	$r_{predicted}$ x 10^{-5}
323	2.07	18.01	269.38	5	4.88
348	2.07	11.39	224.40	9	8.55
373	2.07	9.10	232.42	10	9.29

Conclusion

P and Q can be determined by using Least Square Method of data correlation i.e. by minimizing the square of the deviations between R and P + Q C_A. Value of R can be calculated for each n^{th} set of data. Also initial rates can be determined experimentally to check whether the experimental data fits into the model. Table 1 shows the values of P and Q at different temperature. Comparison of the initial rates showed that the observed values and the predicted values based on the above model are in good agreement. Thus the model can be validated.

REFERENCES

Elena Díaz, José A. Casas, Ángel F. Mohedano , Luisa Calvo, Miguel A. Gilarranz and Juan J. Rodríguez, 2009. *Ind. Eng. Chem. Res.*, 48, 3351.

Meyer C.I., Marchi A.J., Monzon A., Garetto T.F., 2009. *Applied Catalysis,* 367, 122.

Ranade, V., 2002. Computational Flow Modeling for Chemical Reactor Engineering, *Academic Press Publication*, pp 403.

Stanislaus A. and Cooper B. H., 1994. Catalysis Reviews: Science and Engineering, pp75.

Tekale S. and Tekale P., 2013. *Scholars Journal of Engineering and Technology,* 1, 187.

****