ALKYLATION OF DIPHENYL OXIDE WITH BENZYL ALCOHOL OVER H-ZSM5 ZEOLITE AS CATALYST

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Abstract

Friedel-Crafts alkylation using highly polluting homogeneous Lewis and Bronsted acids are ubiquitous in a variety of organic process industries. In many cases, very high conversions and selectivity can be achieved with aluminum chloride as catalyst and nitrobenzene as solvent. Even though, these acids pose several problems such as recovery and reuse of catalyst, poor selectivity, waste generation, and treatment, use of expensive acid-resistant material of construction, process hazards, etc. However, environmental concerns associated with aluminum chloride-nitrobenzene or BF_3-HF has encouraged development of new solid catalyst that can accomplish reactions under milder operating conditions with minimal harm to the environment and not only intensify the rates of reactions but also offer better product selectivity. Zeolites have been utilized for synthesis of fine chemicals involving shape selective catalysis leading to development of many industrial processes. The alkylation of diphenyl oxide with benzyl alcohol was studied over H-ZSM5 zeolite catalyst and it leads to industrially important products such as heat transfer fluids and perfumery compounds.

Keywords : Benzyl Diphenyl Oxide, Zeolites, H-ZSM5

I. INTRODUCTION

Organic process industry has of late realized the importance of heterogeneous catalysis because of strict environmental laws. Amongst different conversion process, the use of liquid phase acid catalysts is very common. In particular, Friedel-Crafts alkylation reactions are conducted by employing different homogeneous acid catalysts. These acids pose several problems in case of recovery and reuse of catalyst, poor selectivity, waste generation and treatment, use of expensive acid-resistant material of construction, process hazards, etc. Therefore, there is a continuous search for new solid catalyst that can accomplish reactions under milder operating conditions with minimal harm to the environment.

Zeolites have been utilized for synthesis of fine chemicals involving shape selective catalysis leading to development of many industrial processes. In the recent years, alkylation of aromatics in the liquid phase conditions over large pore zeolites like Y and dealuminated mordenite zeolites are widely used. The present work is concerned with the production of benzyl- diphenyl oxide. The alkylation of diphenyl oxide with a number of olefins, alcohols, and benzyl chloride leads to commercially important products, for instance, heat transfer fluids and perfumery compounds. Particularly the alkylation of diphenyl oxide with benzyl alcohol has not been reported in the literature, and the alkylated product has potential uses worthwhile to study systematically the Friedel-Crafts alkylation of diphenyl oxide with benzyl alcohol in the presence of zeolite catalysts.

Solid catalysts exhibit high activities and selectivity's for many kinds of reactions, including alkylation's, cyclizations and isomeriszations; however, many of these processes are carried out industrially by using liquid Catalyst. These applications can require nearly stoichiometric amounts of liquid catalyst for conversion to the desired product. Replacement of liquid catalysts with solid catalysts allows easier separation from the product as well as possible regeneration and reuse. Solid catalysts also have the added advantages of being noncorrosive and environmentally friendly, which allows easier disposal.

II. EXPERIMENTAL

Experimental Set- up

The alkylation reactions were carried out in a 250ml glass reactor, which is fully baffled and coupled with mechanical stirrer. It is provided with a four bladed turbine impeller and a reflux condenser. The desired speed of agitation of reaction mixture was achieved by controlling the speed of stirrer motor with a regulator and the speed of the stirrer is measured by laser tachometer. An electrically heated oil bath was used to heat the glass reactor and temperature of reaction mixture was measured by thermometer. The temperature of the oil bath was maintained by using a temperature controller and oil bath temperature was measured by thermocouple.

Experimental Procedure

Typical experiments were carried out by using 0.33mol (53.02ml) of diphenyl oxide and 0.066mol (6.91ml) of benzyl alcohol. The catalyst loading was100kg/m^3 of total reactants. The reactions were carried out at 120^{0}C for 3hrs. A speed of agitation of 1100 rpm was employed for the reaction. The samples of the reaction mixture were withdrawn periodically from the closed reactor and analysed on gas chromatogram.

Method of Analysis

The samples were analysed by gas chromatogram (Chemito 8510model with a flame ionization detector). A 2 m 3.2mm internal diameter stainless steel column packed with Chromosorb WHP impregnated with 10% SE-30 was used for analysis. Synthetic mixtures of the authentic compounds were used for calibration and quantification of the data

The conditions employed for G.C analysis are:

Injection temperature: 250^{0}C

Detector temperature: 260^{0}C

Program : 190^{0}C to 270^{0}C, 10^{0}C/min

The reaction mixture was also analysed on a HPLC and TLC. The result shows two peaks on HPLC chromatogram and two spots in TLC plate. From that we conclude an isomeric mixture (ortho and para) of benzyl-diphenyl oxide was obtained as the reaction product.

III. RESULTS AND DISCUSSION

The Friedel-Crafts alkylation of diphenyl oxide (B) with benzyl alcohol (A) in the presence of H-ZSM5 catalyst leads to the formation of an isomeric mixture of benzyl-diphenyl oxide, which was qualitatively confirmed by HPLC and TLC. The effect of various parameters was studied under otherwise similar condition at a standard temperature of 393 K.

Effect of Speed of Agitation

Since diphenyl oxide (B) was used in large excess over benzyl alcohol (A), there was a chance of external resistance for the transfer of benzyl alcohol from the bulk liquid phase to the external surface of the catalyst particle .Therefore, the speed of agitation was varied under otherwise similar conditions to determine the optimum speed at which there will be no effect of external resistance to mass transfer. The effect of speed of agitation was studied at a catalyst loading of 100kg/m^3 and at 393 K over the range of 700-1300 rpm .Fig 1 shows the conversion of benzyl alcohol at different time intervals for different speeds. It was found that the conversion remains practically the same at speeds beyond 1100 rpm, thereby indicating the absence of solid-liquid mass transfer resistance at that range. Hence, it is decided to carry on the further reactions at 1100rpm.Theoretical

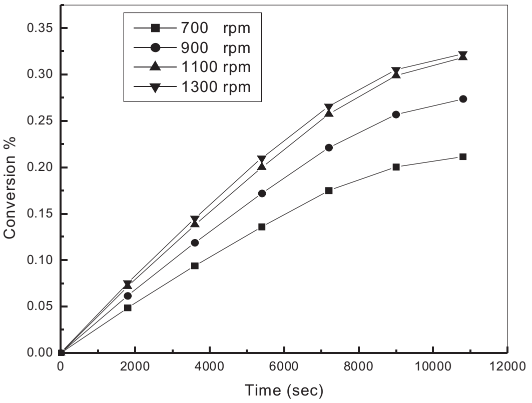

Fig. 1. Effect of speed of agitation on conversion of Benzyl alcohol

Effect of Particle Size

The reactions studied in this case involve two reactants in organic phase, which can be said to react on the surface of the catalyst to form product. Surface reaction control is further supported by the effect of particle size of the catalyst on the rate. The contribution of intra particle diffusion resistance was ascertained by studying the reaction for different particle sizes (1.5mm, 1.33mm and 85mm) by keeping the catalyst loading same. It is apparent from Fig 2 that the conversion remains practically the same within the range of the sizes. This shows intraparticle mass transfer resistance is insignificant. So, further reactions were carried out using 1.5 mm. catalyst particles.

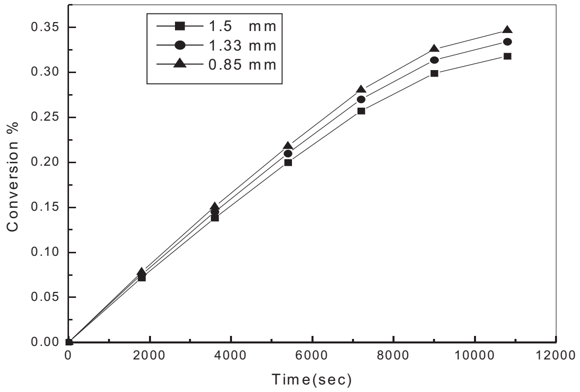

Fig. 2. Effect particle size on conversion of benzyl alcohol

Effect of Catalyst Loading

The effect of catalyst loading was studied by varying the loading from 50 kg/m^3 to 120 kg/m^3 .The plots of conversion as a function of time and the initial rate of reaction as a function of catalyst loading are shown in Figures 3 and 4 respectively. It is observed that both the conversion and rate of the reaction increases linearly with catalyst loading because of the increase in the available acid sites. This is a consequence of absence of both external and internal mass transfer resistance.

Fig 5 a plot of –ln (1-X_A) vs. time was made for this reaction at various catalysts loading. It can be seen that all of these plots show straight lines passing through the origin. Their linearity confirms the first order reaction.

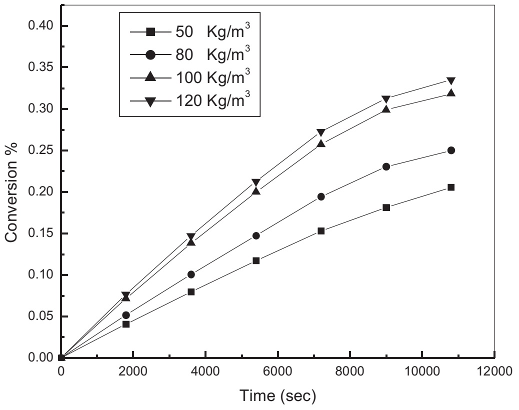

Fig. 3. Effect of catalyst loading on conversion of Benzyl alcohol

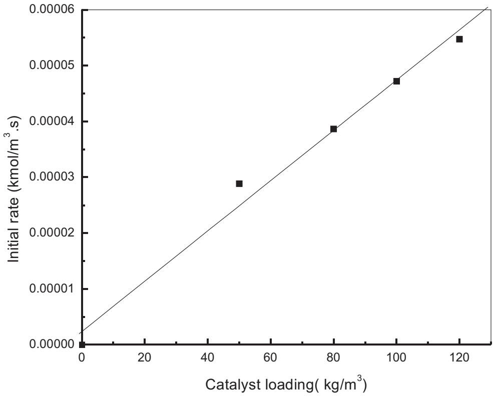

Fig 4. Plot of initial rate of reaction (r_{0i}) against catalyst loading (w)

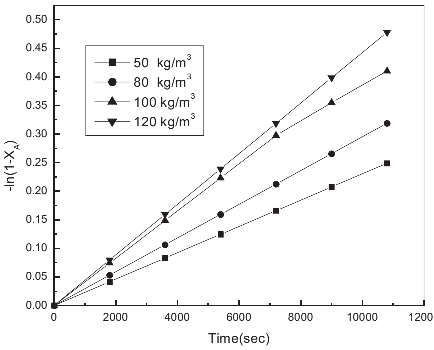

Fig. 5. First order reaction plots: effect of catalyst loading

Effect of Mole Ratio

The effect of mole ratio of the reactants was studied for different mole ratios (2:1, 3:1, 5:1 and7:1) of diphenyl oxide to benzyl alcohol under otherwise similar conditions. Fig 6 shows the plot of conversion of benzyl alcohol against time at different mole ratios .it was found that as the mole ratio of diphenyl oxide to benzyl alcohol was changed ,the conversion of diphenyl oxide remains practically the same ,which shows zero order dependence on diphenyl oxide but the conversion of benzyl alcohol slightly increases.

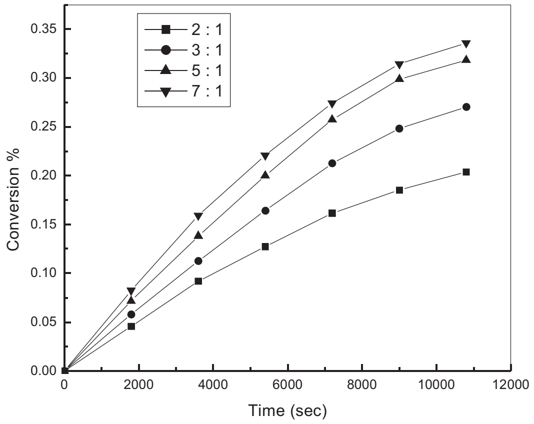

Fig. 6. Effect of mole ratio on conversion of Benzyl alcohol

4.6 Effect of Temperature

Effect of temperature was studied at four different temperatures of 373 K, 383 K, 393Kand 403 K under otherwise similar conditions and is as depicted in Fig 7 .It is seen that the conversion of benzyl alcohol is increased with increase in temperature of the reaction .Correspondingly ,plots of –ln (1-X_A) vs. time at different temperatures are made (Fig 8)

It can be seen that all of these plots show straight lines passing through the origin. Their linearity confirms the first order reaction.

Arrhenius plot ln(k) vs.1/T is shown in Fig 9. From this graph the slope of the curve the apparent activation energy was calculated. The activation energy was found to be 26.74kj/mol .The high value of activation energy again shows that the reaction was kinetically controlled and occurs at the surface of the catalyst.

From Fig 8 The rate constants was calculated ($k_{1)}$ at 373 K, 383 K, 393 K and 403 K are found to be 2.26 10^{-5} , 2.93 10^{-5}, 3.689 10^{-5} and 4.265 10^{-5} m^6 .kmol .kg^{-1} .s^{-1}

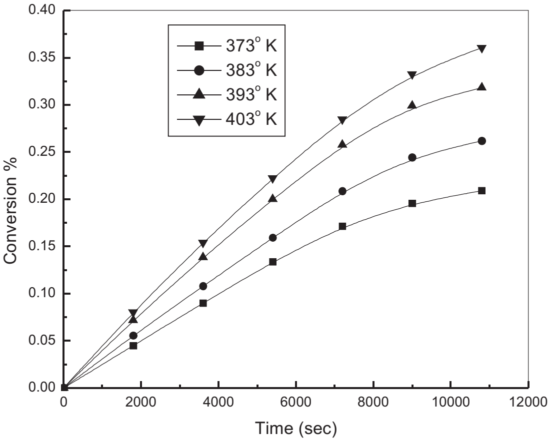

Fig. 7. Effect of temperatures on conversion of Benzyl alcohol

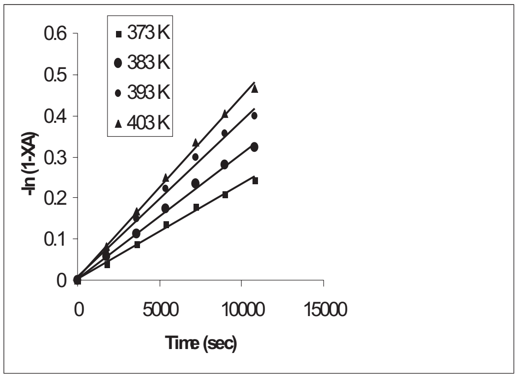

Fig. 8. Kinetic plots for various temperatures

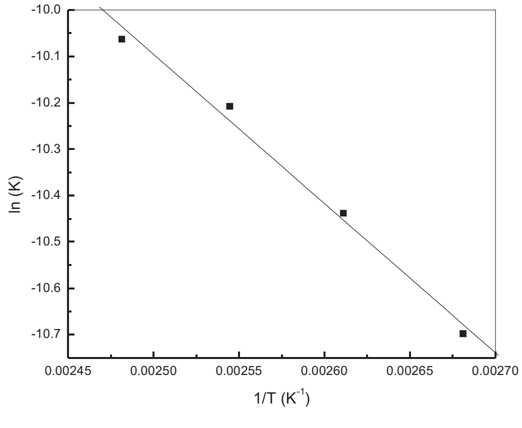

Fig. 9. Arrhenius plot Development of Model and Kinetics of the Reaction

In the case of present studies, it is essential to understand the reaction mechanism to develop a suitable model .The initial rate data could be analysed based on Langmuir –Hinshelwood-Hougen-Watson (LHHW) or Eley-Reidel mechanisms. For initial rate data, the following analysis is most appropriate.

1. Adsorption of benzyl alcohol(A) on a vacant site S is given by:

$$A + S \xleftrightarrow{K_A} AS \tag{4.5}$$

Similarly adsorption of diphenyl oxide (B) on a vacant site S is represented by:

$$B + S \xleftrightarrow{K_B} BS \tag{4.6}$$

2. Surface reaction of AS with BS, in the vicinity of the site, leading to formation of benzyl diphenyl oxide (ES) on the site.

$$AS + BS \xleftrightarrow{K2} ES + WS \tag{4.7}$$

Desorption of benzyle diphenyl oxide (ES), and water (WS)

$$ES \xleftrightarrow{1/K_E} E + S \tag{4.8}$$

$$WS \xleftrightarrow{1/K_w} W + S \tag{4.9}$$

The total concentration of the sites, C_t expressed as

$$C_t = C_S + C_{AS} + C_{BS} + C_{ES} + C_{WS}$$

or

$$C_t = C_S + K_A C_A C_S + K_B C_B C_S + K_E C_E C_S + K_W C_W C_S \tag{4.10}$$

Or the concentration of vacant sites,

$$C_S = \frac{C_t}{(1 + K_A C_A + K_B C_B + K_E C_E + K_W C_W)} \tag{4.11}$$

If the surface reaction (4.3) controls the rate of reaction, then the rate of reaction of A is given by

$$-r_A = -\frac{dC_A}{dt} = k_2 C_{AS} C_{BS} - k_2' C_{ES} C_{WS} \tag{4.12}$$

$$-\frac{dC_A}{dt} = k_2 K_A K_B C_A C_B C_S{}^2 - k_2' K_E K_W C_E C_W C_S{}^2 \tag{4.13}$$

$$= k_2 C_S{}^2 \left[K_A K_B C_A C_B - \frac{k_2' K_E K_W C_E C_W}{k_2} \right] \tag{4.14}$$

$$= \frac{k_2 C_t{}^2 \left\{ K_A K_B C_A C_B - \dfrac{K_E K_W C_E C_W}{\left(\dfrac{k_2}{k_2'}\right)} \right\}}{(1 + K_A C_A + K_B C_B + K_E C_E + K_W C_W)^2} \tag{4.15}$$

$$\frac{dC_A}{dt} = \frac{k_2 \left\{ K_A K_B C_A C_B - \dfrac{K_E K_W C_E C_W}{K2} \right\} C_t{}^2}{(1 + K_A C_A + K_B C_B + K_E C_E + K_W C_W)^2} \tag{4.16}$$

When the reaction is far away from equilibrium

$$\frac{dC_A}{dt} = \frac{k_2 Ct^2 K_A K_B C_A C_B}{(1+\sum k_i C_i)^2} \tag{4.17}$$

$$\frac{dC_A}{dt} = \frac{k_{R2} w C_A C_B}{(1+\sum k_i C_i)^2} \tag{4.18}$$

Where $k_{R2} w = k_2 C_t^2 K_A K_B$; *w* is catalyst loading. If the adsorption constants are very small, then the above equation reduces to

$$\frac{dC_A}{dt} = k_{R2} C_A C_B w \tag{4.19}$$

Let, the molar ratio of diphenyl oxide to benzyl alcohol, at time *t=0.* Then equation (4.18) can be written in terms of fractional conversion as

$$\frac{dX_A}{dt} = k_{R2} w C_{A0}(1-X_A)(M-X_A) = k_t C_{A0}(1-X_A)(M-X_A) \tag{4.20}$$

Which upon integration leads to

$$\ln\{(M-X_A)/M(1-X_A)\} = k_t C_{A0}(M-1)t \tag{4.21}$$

When M is other than unity.

For equimolar quantities of A and B, the integration of equation (4.11) yields the following

$$\frac{X_A}{1-X_A} = C_{A0} k_{R2} wt = k_1 t \tag{4.22}$$

When M>>1, equation (4.16) leads to a pseudo-first-order kinetics; hence, upon integration it becomes,

$$-\ln(1-X_A) = k_{R2} C_{B0} wt = k_1 t \tag{4.23}$$

Where $k_1 = k_{R2} C_{B0} w$

IV. CONCLUSIONS

The effects of different parameters on rates of alkylation of diphenyl oxide with benzyl alcohol catalysed by H-ZSM5 were studied systematically to establish the kinetics of reaction. This catalyst is reusable. It was seen that the external mass transfer resistance can be eliminated by providing adequate stirring and internal mass transfer resistance was absent. A LHHW model was tested which shows that the reaction is intrinsically kinetically controlled. The influence of temperature showed typical apparent activation energy for this reaction as 26.74 kj/mol

REFERENCES

[1] H.Scott Fogler., Elements of Chemical Reaction Engineering (Third edition).

[2] Smith J.M., Van Ness H.C and Abbott M.M., Introduction to Chemical Engineering Thermodynamics (Fifth edition).

[3] Robert Thornton Morrison and Robert Neilson Boyd., Organic chemistry (6th edition).

[4] Levenspiel O., Chemical Reaction Engineering (4th edition).

[5] S.M.Mukherji and S.P.Singh., Reaction mechanism in organic chemistry (Third edition).

[6] G.D.Yadav and Sonali Sengupta., *Friedel-Crafts Alkylation of Diphenyl oxide with Benzyl chloride*, Organic process research &Development .**6**, 252-262, (2002).

[7] Amrhein. C., Haghnia. G.H., Mosher. P.A., Amanios.Tand Torre.L.D.L., *Synthesis and properties of zeolites from coalflyash*.Environ.sci.engg. **30**, 735-742, (1996).

[8] Anderson. J. R., Foger. K, Mole. T, Rajadhyaksha. R. A and Sanders. J. V.,*Reactions on ZSM-5 type zeolite catalysts*. J. Catal. **58 ,**114-130, (1979).

[9] Bhat. Y. S., Halgeri. A. B and Rao. T. S. R. P., *Kinetics of toluene alkylation With methanol on HZSM-8 zeolite catalyst*, Ind.Eng.Chem.Res. Res., **28,**894-899, (1989).

[10] Chandavar K. H., Kulkarni. S. B and Ratnaswami. P., *Alkylation of benzene to propyl and isopropyl benzenes over ZSM-5 zeolite*. J.Chem.technol. *J. Chem.* **34 ,**165-173, (1984).

[11] Chandavar. K. H., Kulkarni. S. B and Ratnaswami. P., *Alkylation of benzene with ethanol over ZSM-5 zeolites*. Appl.cata. **4,** 287-295, (1982).

[12] Chandra. K. G and Sharma M. M., *Alkylation of phenol with MTBE and other tert- butyl ethers, Cation exchange resins as catalyst*.Catal.lett, **19,** 309-317, (1993).

[13] Chaudhuri, B and Sharma, M. M., *Alkylation of phenol with α-methylstyrene, propylene, butenes, isoamylene, l-octene, and diisobutyle heterogeneous vs homogeneous catalysts.* Ind .Eng.Chem.Res. **30** , 227-231,(1991).

[14] Cross. N. E., Kemball. C and Leach. H. F., *Isomerization of n-butenes over ion-exchanged*

*zeolites.*Advances in Chemistry Series , **102,**389-399, (1971).

[15] Deshmukh. A. R., Gumaste, A.S and Bhawal. B. M., *Alkylaion of benzene with long chain (C_8-C_{18}) linear primary alcohols over zeolite-Y*. Catal. **64**, 247-250, (2000)

[16] Engelhardt. J., Szanyi. J and Valyon J., *Alkylation of toluene with methanol on commercial X zeolite in different alkali cation forms.* J.Catal, **107,** 296-306, (1987)..

[17] Hathaway. P. E and Davis. M. E., *Base catalysis by alkali metal zeolites Alkylation with methanol*. J. Catal. **119,** 497-507, (1989).

[18] Kaeding, W. W., Weinstein, B. and Butter., *S. A. Selective alkylation of toluene* with e*thanol to produce para-Xylene.* J. Catal. **67** (1981), 159-174.

[19] Korenskii V. I., Kolenko. I. P and Skobeleva. V. D., *Alkylation of phenol by isobutylene in the presence of Vanadium compounds on γ-alumina.* Chem*.* Abstr. **57**, 2016-2020, (1991)

[20] Koshichii. V. A., Kozlikovskii. Y. B and Matyusha.A. A., *Alkylation of phenol with alcohols in the presence of alumina phenolate.* Org.Process. **24**,1508-1512, (1988),

[21] Krishnan. A. V, Ojha. K and Pradhan. N. C., *Alkylation of phenol with tertiary buty alcohol over zeolites.* Org. Proc. Res. Dev. **6**,132-137, (2002).

[22] Lee. D. B and Wang. I., *Kinetic analysis of ethylation of toluene on HZSM-5.* Ind. Eng. Chem. Prod. Res. Dev. **24**, 201-205, (1985).

[23] Velu. S and Swamy. C. S., Kinetics of the alkylation of phenol with methanol over magnesium-aluminum calcined hydrotalcite, Appl. Catal. A: General **145**, 225- 230(1996).

[24] Zhang. K. Zhang. H. Xu. G ., Xiang. S., Xu .D,Liu. S and Li. H., *Alkylation of phenol with tert-butyl alcohol catalyzed by large pore zeolites*. Appl. Catal. A: General, **207**,183-190, (2001).

[25] Sridevi. U., Rao. B. K. B and Pradhan. *N. C., Kinetics of alkylation of benzene with ethanol on $AlCl_3$-impregnated 13X zeolites.* Chem. Eng. J. **83**,185-189(2001).

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