Kinetics and Catalysis, Vol. 42, No. 4, 2001, pp. 533–538. From Kinetika i Kataliz, Vol. 42, No. 4, 2001, pp. 588–593.

Original English Text Copyright © 2001 by Han, Li, Lin.

Intrinsic Kinetics of the Alkylation of Benzene with Propylele over β Zeolite Catalyst[1]

M. Han*, X. Li, and S. Lin*****

** Department of Chemical Engineering, Tsinghua University, Beijing 100084, China*

*** Chemical Research Center, Beijing Institute of Clothing Technology, Beijing 100029, China*

**** National Heavy Oil Research Laboratory, University of Petroleum, Beijing 102200, China*

Received January 5, 2000

Abstract—The kinetics of benzene alkylation with propylene over H β zeolite catalyst was investigated in an autoclave with a stirrer, as internal and external diffusion resistance were eliminated. A Langmuir-Hinshelwood type kinetic model was proposed on the basis of the experiments. The model parameters were evaluated, and the model was justified by variance analysis and residual analysis.

1. INTRODUCTION

Alkylation of benzene with propylene is an industrially important reaction for the production of cumene, an intermediate for production of acetone and phenol. The traditional processes, which use solid phosphoric acid or $AlCl_3$ catalyst, suffer from corrosion and environmental problems. A new process, using β zeolite catalyst that is not corrosive and does not require periodic regeneration, has been industrialized in Beijing Yanshan Petrochemical in 1998.

The industrial process is carried out in a fixed-bed bubble reactor where it is difficult to eliminate external and internal diffusion resistance. To study the intrinsic kinetics, an autoclave with a stirrer was used in this paper.

In this reaction system when the resistance of external and internal diffusion is eliminated and the reaction temperature is constant, the concentration of propylene in the liquid phase is determined by both its partial pressure in the vapor phase and by the concentration of other components. Thus, the concentration of propylene correlated to kinetic equations cannot be substituted by the partial pressure of propylene. Unfortunately, the concentration of propylene obtained by sampling in the kinetic experiments is lower than its true concentration in the liquid phase because of the flash evaporation of propylene in the liquid phase due to the abrupt decompression during sampling. To overcome this difficulty, a calculating method is developed that is briefly described in the next paragraph.

When reactions are slow at constant pressure and temperature, eliminating the resistance of external and internal diffusion ensures that the gas and liquid phases are at equilibrium or close to equilibrium. The relative concentrations of benzene, isopropylbenzene, and diisopropylbenzenethe liquid phase can be measured by GC. Given the known temperature and pressure, the concentration of components in the liquid and vapor phases can be calculated by the Soave equation of state [1].

In addition, the mass transfer in this study includes external diffusion transfer and internal diffusion transfer (micropore diffusion in crystals and macropore diffusion in pellets). The basic theory of diffusion coupled with a chemical reaction in a catalyst pore was put forward by Thiele [2] and Zeldovich [3] sixty years ago. Two excellent reviews published by Wheeler [4, 5] in the 1950s extended these basic ideas to show how diffusional resistance can modify kinetic behavior and catalyst selectivity for a range of simple model systems. Although in the subsequent years there have been numerous publications extending these ideas to more complex kinetic systems, the basic theoretical framework remains very much as delineated by Wheeler. In the prior development of the subject, conventional macroporous catalysts in which transport occurs mainly by the well-known Knudson and molecular diffusion mechanisms were the focus.

However, there are two important ways in which the behavior of a zeolite catalyst subject to intracrystalline diffusion limitation may be expected to be different [6]: (1) Intracrystalline diffusion is an activated process so that the diffusivity varies with temperature according to the Arrhenius equation and the diffusion activation energy may be comparable with the activation energy of a chemical reaction; (2) reaction occurs in the adsorbed phase, the Henry law is inapplicable, and the apparent reaction order differs from the true order.

To determine whether or not the kinetic model of chemical reaction is intrinsic, it is necessary to eliminate both macropore and micropore diffusion.

---

[1] This article was submitted by the authors in English.

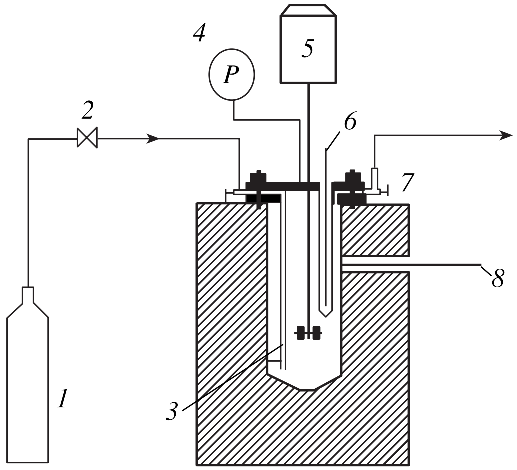

Fig. 1. Schematic diagram of apparatus for intrinsic kinetics. (*1*) Propylene cylinder; (*2*) regulator; (*3*) propylene pipe; (*4*) pressure gauge; (*5*) stirrer; (*6*) thermocouple; (*7*) sampling valve; (*8*) heater.

2. EXPERIMENTAL

2.1. Materials

The samples of β zeolite with Si/Al = 35 were kindly provided by Dr. Guanhua Liu, Beijing Petrochemical Scientific Research Institute, and the crystal sizes were about 1.0, 0.8, 0.5 and 0.2 μm. Commercial catalyst pellets, 3 mm in diameter, made of β zeolite (roughly 0.2 μm, measured with a JSM-35C scanning electron microscope), were supplied by Beijing Dongda Cemical Factory.

Propylene was provided by Yanshan Petrochemical Ltd., with at least 99.95% purity. Benzene was purchased from the Beijing Chemical Reagent Company, with at least 99.0% purity.

2.2. Methods

Kinetic experiments were carried out in a 100-ml stainless steel autoclave with stirrer. This reactor was equipped with automatic temperature controller, adjustable speed stirrer, and the device for liquid sampling. The schematic diagram of the experimental apparatus is shown in Fig. 1.

The catalyst was dried at 773 K for 4 h in dry air, cooled in a desiccator, and then loaded into an Ample bottle. The bottle and 80 of benzene were charged into the reactor. After the desired temperature was attained, the system was pressurized with propylene to a level required for the experiments and maintained for 0.5 h. Then, the Ample bottle was broken and the reactions started while the stirrer was switched on. To maintain a constant pressure in the reactor, propylene was fed through a pressure controller from the cylinder. The kinetic experiment conditions are listed in Table 1.

Table 1. Kinetic experimental conditions

No.	Temperature (K)	Weight of catalyst (mg)	Pressure (MPa)
1	433	21	0.725
2	415	66.7	0.500
3	406	42	0.420
4	393	200	0.310
5	353	500	0.255

3. RESULTS AND DISCUSSION

3.1. Preliminary Experiments

Some experiments showed that no alkylation took place without a catalyst, indicating the absence of any homogeneous reaction in the reactor. The reproducibility of the rates was found with 3–5% error from several repeated experimental runs. It was verified by various experiments with different sizes of catalyst pellets and adjustable stirring speed, that the resistance of internal and external diffusion could be eliminated when the diameter of catalyst pellets is ~0.15 mm (Fig. 2) and the stirring intensity is =800 rpm (Fig. 3). Figure 4 shows that the intracrystalline diffusion resistance could be eliminated when the crystal size is ≤0.8 μm. That is similar to Bellussi's conclusion [7]. In this study, the intrinsic kinetic experiments were performed at a stirring intensity of 1000 rpm using catalyst pellets smaller than 0.1 mm and a crystal diameter of the β zeolite catalyst is roughly 0.2 μm.

3.2. Intrinsic Kinetic Model

According to the experimental results from *in situ* IR, reaction–ion trap detector (ITD) [8] and coke characterization [9], the mechanism of alkylation is as follows: propylene adsorbed at active sites reacts with adsorbed aromatic hydrocarbons, such as benzene and isopropylbenzene, and so does the adsorbed diisopropylbenzene react with the adsorbed benzene.

In addition, in heterogeneous reaction, if the adsorption of reactants or products is a rate-determining step (RDS), the selectivity of the products will be controlled by the thermodynamics of the system and remain constant regardless of the reaction time at the same reaction temperature; whereas, if the reaction is RDS, the selectivity will be dominated by the kinetics of the system and will vary with the reaction time [10]. We found in experiments (Fig. 5) that the selectivity varies with the reaction time, so it could be deduced that the reactions are RDSs.

The alkylation of benzene and propylene can be described by two independent reactions:

$$\mathrm{B} + \mathrm{P} \rightleftarrows \mathrm{I}, \qquad \text{(I)}$$

$$\mathrm{I} + \mathrm{P} \rightleftarrows \mathrm{D} \qquad \text{(II)}$$

We experimentally found that these two independent reactions are reversible and conclude that (1) the mechanism of the system is that adsorbed propylene reacts with adsorbed aromatic hydrocarbons; (2) the reactions are RDSs; (3) the two independent reactions are reversible.

The rate equation is deduced from the following reaction scheme [11]:

1. $\mathrm{B} + \mathrm{Z} \rightleftarrows \mathrm{BZ}$
2. $\mathrm{P} + \mathrm{Z} \rightleftarrows \mathrm{PZ}$
3. $\mathrm{BZ} + \mathrm{PZ} \overset{w_1}{\rightleftarrows} \mathrm{IZ} + \mathrm{Z}$ (RDS)
4. $\mathrm{IZ} + \mathrm{PZ} \overset{w_2}{\rightleftarrows} \mathrm{DZ} + \mathrm{Z}$ (RDS)
5. $\mathrm{IZ} \rightleftarrows \mathrm{I} + \mathrm{Z}$
6. $\mathrm{DZ} \rightleftarrows \mathrm{D} + \mathrm{Z}$

where B, P, I and D represent the benzene, propylene, isopropylbenzene and diisopropylbenzene, and Z represents an active site. The following rate equations can then be derived:

$$\begin{cases} w_1 = \dfrac{k_1 C_\mathrm{B} C_\mathrm{P} - k_{-1} C_\mathrm{I}}{(1 + K_\mathrm{P} C_\mathrm{P} + K_\mathrm{B} C_\mathrm{B} + K_\mathrm{I} C_\mathrm{I} + K_\mathrm{D} C_\mathrm{D})^2}, \\ w_2 = \dfrac{k_2 C_\mathrm{I} C_\mathrm{P} - k_{-2} C_\mathrm{D}}{(1 + K_\mathrm{P} C_\mathrm{P} + K_\mathrm{B} C_\mathrm{B} + K_\mathrm{I} C_\mathrm{I} + K_\mathrm{D} C_\mathrm{D})^2}, \end{cases} \qquad (1)$$

where K_B, K_P, K_I and K_D stand for the adsorption equilibrium constants for the steps 1, 2, 5 and 6 respectively, k_1 and k_2 represent the reaction rate constants for the steps 3 and 4.

3.3. The Concentration of the Components in Liquid Phase and in Vapor Phase

For a component in a mixture at a given temperature and pressure on the saturation condition,

$$f_i^\mathrm{L} = f_i^\mathrm{V} \qquad (2)$$

(Superscripts L and V refer to the liguid and gas phases, respectively).

The fugacity coefficient of a component in both vapor phase and liquid phase is given by [1]:

$$\ln\frac{f_i}{Px_i} = \frac{b_i}{b}(x-1) - \ln(Z - B^*) - \frac{A^*}{B^*}\left(2\frac{a_i^{0.5}}{a^{0.5}} - \frac{b_i}{b}\right)\ln\left(1 + \frac{B^*}{Z}\right), \qquad (3)$$

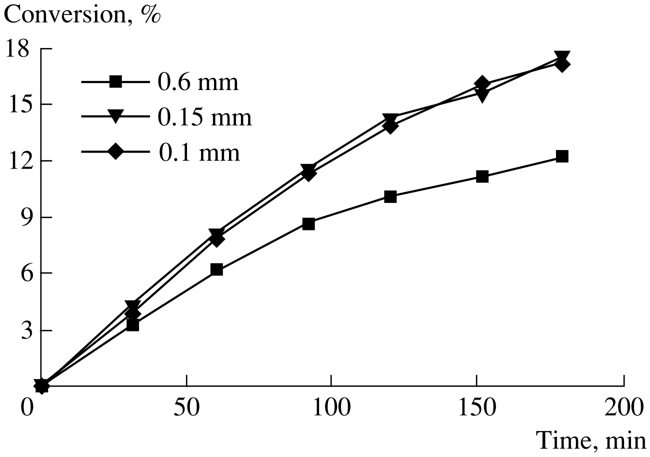

Fig. 2. Effect of catalyst pellet sizes on the conversion of B (in %). Conditions: Stirring intensity is 1000 rpm, $T = 433$ K, $P = 0.71$ MPa, 21 mg catalyst.

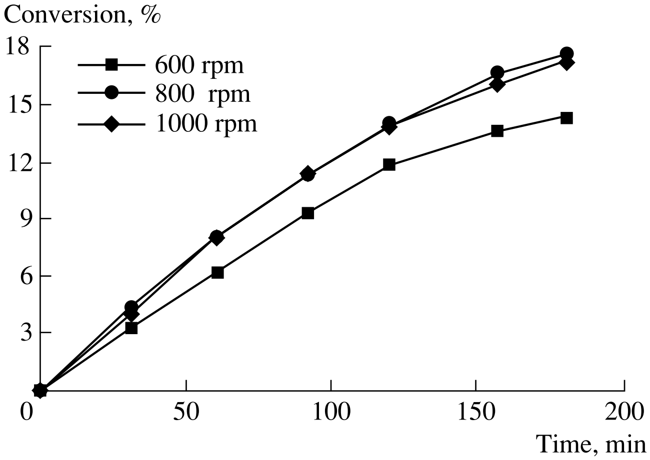

Fig. 3. Effect of the stirring rate on the conversion of B%. Conditions: Particle size is 0.1 µm, $T = 433$ K, $P = 0.71$ MPa, 21 mg catalyst.

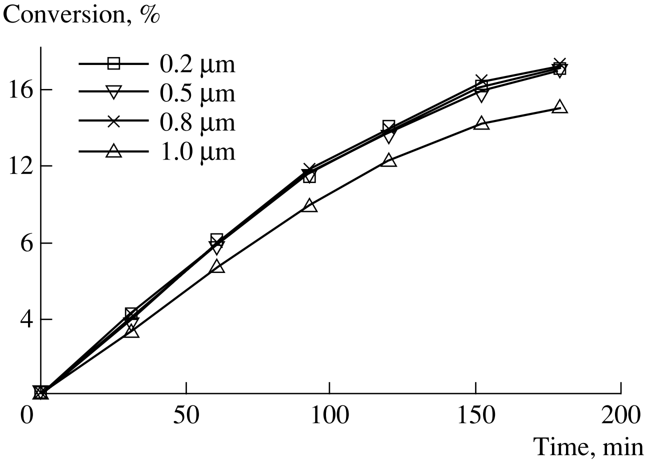

Fig. 4. Effect of the crystal size on the conversion of B (in %). Experimental conditions: particle size, 0.1 µm; $T = 433$ K; $P = 0.71$ MPa; catalyst loading, 21 mg.

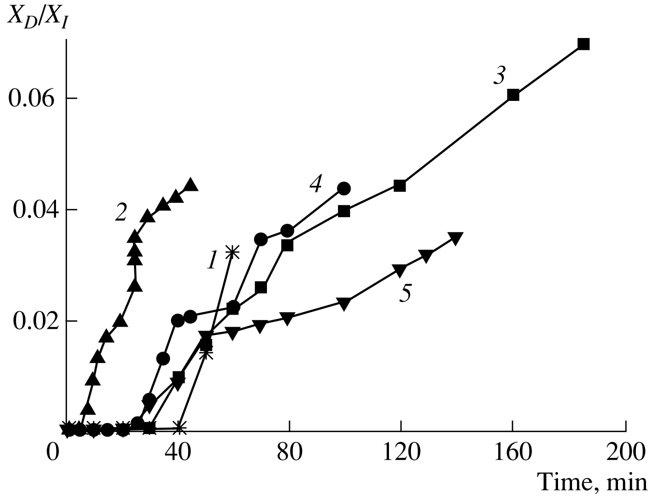

Fig. 5. The variety of selectivity with the reaction time (for nos. *1–5* see Table 1).

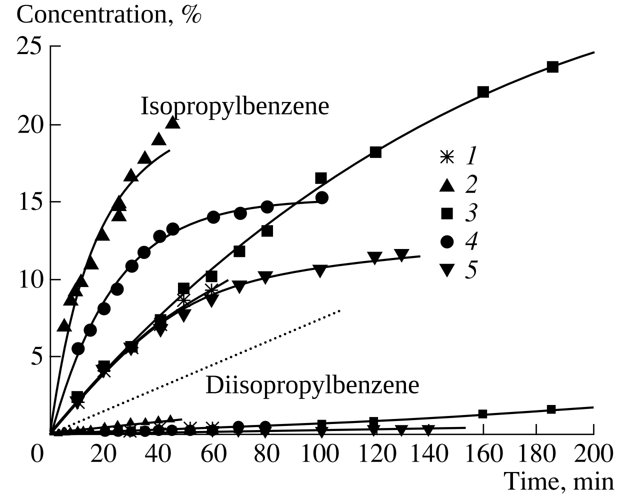

Fig. 6. Comparison of concentrations in liquid phase simulated by kinetic model and detected by GC. Conditions: Particle size is 0.1 μm, $T = 433$ K, $P = 0.71$ Mpa, 21 mg catalyst. Points are experimental data and curves are calculated.

where x_i are the molar ratios of the components in liquid phase,

$$\frac{a_i^{0.5}}{a^{0.5}} = \frac{a_i^{0.5} T_{\mathrm{cr},\,i}/P_{\mathrm{cr},\,i}^{0.5}}{\sum_{i=1}^{4} x_i a_i^{0.5} T_{\mathrm{cr},\,i}/P_{\mathrm{cr},\,i}^{0.5}}, \tag{4}$$

$$\frac{b_i}{b} = \frac{T_{\mathrm{cr},\,i}/P_{\mathrm{cr},\,i}}{\sum_{i=1}^{4} x_i T_{\mathrm{cr},\,i}/P_{\mathrm{cr},\,i}}, \tag{5}$$

$$A^* = 0.42748\frac{P}{T^2}\left(\sum_{i=1}^{4} x_i \frac{T_{\mathrm{cr},\,i} a_i^{0.5}}{P_{\mathrm{cr},\,i}^{0.5}}\right)^2, \tag{6}$$

$$B^* = 0.08664\frac{P}{T}\sum_{i=1}^{4} x_i \frac{T_{\mathrm{cr},\,i}}{P_{\mathrm{cr},\,i}}, \tag{7}$$

Table 2. Physical property data of propylene, benzene, isopropylbenzene, and diisopropylbenzene

Components	T_{cr}, K	P_{cr}, atm	ω
Propylene	365.0	45.6	0.148
Benzene	562.1	48.3	0.212
Isopropylbenzene	631.0	31.7	0.330
Diisopropylbenzene	712.4	20.5	0.415

$$a_i^{0.5} = 1 + m_i(1 - T_{Ri}^{0.5}), \tag{8}$$

$$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2, \tag{9}$$

$$Z^3 - Z^2 + Z(A^* - B^* - B^{*2}) - A^*B^* = 0. \tag{10}$$

and the compressibility factor Z is obtained by solving Eq. (12). (The smallest root must be taken for a liquid phase and the greatest one for a vapor phase.)

According to experimental data on temperature, pressure and relative concentrations x_3/x_2, x_4/x_2 of B, I, D in liquid phase, the concentration of the components in vapor phase and liquid phase based on the vapor–liquid equilibrium can be calculated by following steps:

1) Input initial values, x_1, y_1, y_2, and y_3 (y_i are the molar ratios of the components in vapor phase);

2) x_i and y_i (i = 1, 2, 3, 4) can be calculated by Eqs. (11) and (12), using experimental data on the relative concentrations x_3/x_2, x_4/x_2.

$$\sum_{i=1}^{4} x_i = 1, \tag{11}$$

$$\sum_{i=1}^{4} y_i = 1, \tag{12}$$

3) By applying Eqs. (3)–(10), f_i^{L} and f_i^{V} are obtained from data in Table 2, x_i, and y_i (i = 1, 2, 3, 4);

4) If $S = \left|f_i^{\mathrm{L}} + -f_i^{\mathrm{V}}\right| > 10^{-7}$, choose a new initial value (x_1, y_1, y_2, and y_3) that makes $\Delta S = |S - S_0| < 0$, let $S = S_0$, and go back to step 2;

5) If $S < 10^{-7}$, the values of x_i and y_i (i = 1, 2, 3, 4) are accepted to be final.

3.4. Estimating Parameters of the Rate Equation

Since the Gauss-Newton method for parameter estimation is restricted by suitable selection of initial values, we adopt the Hooke-Jeeve method to estimate the parameters of ordinary differential equations of the kinetic model. The target function is the sum of the squared deviation between model prediction and experimental data.

3.5. The Verification of Conspicuousness of the Model

According to the theory of mathematical statistics, the validity of the model can be verified through the variance analysis and residual analysis [12]. The results of the variance analysis are shown in Table 3.

Because $F_1 = 2.3 < F_{0.05}\,(34.3) = 8.65$, and $F_2 = 54.3 > F_{0.05}\,(14.37) = 1.97$, the variance analysis suggests that the confidence of the model is more than 95%.

Comparison of experimental and simulated kinetic data detected by (Fig. 6) shows very good agreement with the experimental data.

In addition, the scatter of the residual analysis versus the quality of the catalyst, the pressure and the temperature is random [13], which indicates the suitability of the model. The model parameters are as follows:

$$
\begin{aligned}
k_1 &= 2.90 \times 10^7 \exp(-3.91 \times 10^3/T),\\
k_{-1} &= 2.91 \times 10^6 \exp(-7.65 \times 10^3/T),\\
k_2 &= 3.80 \times 10^7 \exp(-4.31 \times 10^3/T),\\
k_{-2} &= 4.50 \times 10^6 \exp(-7.85 \times 10^3/T),\\
K_\mathrm{P} &= 0.768 \exp(3.18 \times 10^3/T),\\
K_\mathrm{B} &= 0.019 \exp(2.33 \times 10^3/T),\\
K_\mathrm{I} &= 0.426 \exp(2.34 \times 10^3/T),\\
K_\mathrm{D} &= 0.108 \exp(2.62 \times 10^3/T).
\end{aligned}
\tag{13}
$$

3.6. Activation Energy

From the parameters of Eq. (13), it is found that the activation energy of reaction (2) is greater than that of reaction (1), which is due to shape selective catalysis. Because the diameter of the molecule of diisopropylbenzene is bigger than that of isopropylbenzene, diisopropylbenzene is formed more difficulty than isopropylbenzene in intracrystal pores of catalyst, which hinders the reaction of isopropylbenzene with propylene.

3.7. Selectivity Trend

We see from the instantaneous selectivity of isopropylbenzene (Eq. (14)), that the selectivity of isopropylbenzene is influenced by the temperature and the concentration of isopropylbenzene, and that a high temperature and a high concentration of isopropylbenzene are not beneficial to the selectivity to isopropylbenzene; this has been testified by the results of the accelerated aging of the catalyst [9].

$$
\begin{aligned}
S_\mathrm{I} &= \frac{w_1 - w_2}{w_1} = 1 - \frac{w_2}{w_1} = 1 - \frac{k_2 C_\mathrm{I} C_\mathrm{P} - k_{-2} C_\mathrm{D}}{k_1 C_\mathrm{B} C_\mathrm{P} - k_{-1} C_\mathrm{I}}\\
&\approx 1 - \frac{k_2 C_\mathrm{I}}{k_1 C_\mathrm{B}} = 1 - 1.31 \exp(-0.4 \times 10^3/T) \frac{C_\mathrm{I}}{C_\mathrm{B}}.
\end{aligned}
\tag{14}
$$

In order to obtain a high conversion and a high selectivity to isopropylbenzene, the promising reactor for this reaction should be used to enable simultaneous separation of the product isopropylbenzene.

Table 3. Results of variance analysis

Item	Sum of squares	Degree of Freedom	Sum of mean squares	Ratio	$F_{0.05}$
Total sum	$\sum_{i=1}^{M+n-1} (y_1 - \bar{y})^2 = 0.6481$	51			
Regression	$\sum_{i=1}^{M+n-1} (\hat{y}_1 - \bar{y})^2 = 0.618$	14	0.0442	54.3	1.97
Residual error	0.0301	37	8.1×10^{-4}		
Deviation from regression	0.0290	34	8.5×10^{-4}	2.3	8.65
Error	0.0011	3	3.7×10^{-4}		

4. CONCLUSION

The alkylation of benzene and propylene over β zeolite catalyst has been studied in an autoclave with a stirrer over a temperature range of 353–433 K. Some kinetic experiments have been carried out under the condition of eliminated internal and external diffusion resistance. Based on the observation and the study of the mechanism of the alkylation, an intrinsic kinetic model based on the theory of Langmuir adsorption has been proposed. On the basis of experimental data, the kinetic parameters of the rate equations have been evaluated. Variance analysis and residual analysis have been performed and the results show that the kinetic model is applicable.

REFERENCES

1. Soave, G., *Chem. Eng. Sci.*, 1972, vol. 27, p. 1197.
2. Thiele, W., *Ind. Eng. Chem.*, 1939, vol. 31, p. 916.
3. Zel'dovich, Ya.B., *Zhur. Fiz. Khim.*, 1939, vol. 13, p. 163.
4. Wheeler, *Catalysis*, Emmett, P.H., Ed., New York: Reinold, 1955, vol. 2, p. 123.
5. Wheeler, *Adv. Catal.*, 1951, vol. 3, p. 249.
6. Kärger and Ruthven, D.M., *Diffusion in Zeolities and other Microporous Solids*, New York: Wiley, 1992, p. 538.
7. Bellussi, G., Pazzuconi, G., Perego, C., *et al.*, *J. Catal.*, 1995, vol. 157, p. 227.
8. Han, M., Lin, S., Chen, S., Zhang, J., *Petrochem. Eng.*, 1999, vol. 28, p. 1.
9. Han, M., Lin, S., Chen, S., Zhang, J., *Petrochem. Eng.*, 1999, vol. 28, p. 73.
10. Li, Z., *Basis of Reaction Kinetics of Heterogenous*, Beijing: Beijing University, 1990.
11. Li, S., *Chemical and Catalytic Reaction Engineering*, Beijing: Chemical Industry Press, 1986.
12. Zhu, Z., Dai, Y., *Data Proceeding of Chemical Datas and Experiment Designing*; Beijing: Hydrocarbon Processing Press, 1989.
13. Han, M., Study of the Alkylation of Benzene with Propylene over β Zeolite Catalyst, *Ph.D. Dissertation*, Beijing: University of Petroleum, 1997.