JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Solvent Effects on Hydration of Cyclohexene over H-ZSM-5 Catalyst

Xianglei Shan, Zhenmin Cheng,* and Ying Li

State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

ABSTRACT: Hydration of cyclohexene over H-ZSM-5 catalyst was carried out in a batch autoclave reactor in the presence of different cosolvents. With ethylene glycol as the cosolvent, a cyclohexene conversion of 11.4 % was obtained, which is much higher than that of 8.2 % obtained without the cosolvent. To evaluate the solubility of cyclohexene in the presence of ethylene glycol, the liquid−liquid equilibria (LLE) data of cyclohexene + water + cyclohexanol + ethylene glycol were measured at 298.15 K. It was found that a modified UNIFAC model gives the best fits to the LLE data, and the solubility of cyclohexene has increased evidently. The kinetic behavior of the hydration reaction was then investigated in the temperature range from 383.15 to 413.15 K, with initial molar ratio of cyclohexene to ethylene glycol in the range from 2 to 20. The kinetic data were correlated with a simple pseudohomogeneous model and two heterogeneous ones based on the Langmuir−Hinshelwood−Hougen−Watson and Eley−Rideal mechanisms, respectively. The results showed that the addition of ethylene glycol does not change the reaction mechanism of cyclohexene hydration over H-ZSM-5 catalyst. Nevertheless, due to the solvation effect of ethylene glycol, the activation energy of the reaction was found decreased.

INTRODUCTION

Cyclohexanol is an important cyclic alcohol which is widely used in the production of nylon, plasticizer, and detergent.[1] Recently, the most economical and safe process for production of cyclohexanol is hydration of cyclohexene catalyzed by solid acid catalysts such as strongly acidic ion exchange resins and zeolites, which has many advantages such as high selectivity, small explosion hazards and convenient separation of the solid catalysts from the liquid mixture.[2−4] However, due to the low mutual solubility between cyclohexene and water, the reaction rate and the yield of cyclohexanol are substantially low. In order to improve the solubility of cyclohexene in the water, a possible alternative is the use of an organic cosolvent, which should also change the reaction equilibrium and kinetic behavior of the cyclohexene hydration.

It is evident that a proper cosolvent for cyclohexene hydration should satisfy some conditions. The cosolvent has to be helpful for dissolution of cyclohexene in the water and effective to improve the hydration reaction, and the cosolvent must be substantially inert under the reaction conditions. Also the separation of cosolvents from the reaction mixture should be convenient by conventional distillation. In the literature, some studies on the hydration of cyclohexene with different cosolvents have been reported. Panneman and Beenackers studied the solvent effects of sulfolane on the hydration of cyclohexene catalyzed by a strong acidic ion-exchange resin catalyst.[5−7] In their studies, the hydration reaction was carried out in a single liquid phase by presaturating water with cyclohexene. The solubility of cyclohexene was investigated with different water−sulfolane mixtures, and the solvent effects of sulfolane on the kinetics and chemical equilibrium of cyclohexene hydration were also studied by assuming the reaction system homogeneous. In addition, a patent by Yoshikazu and Tokitaka reported that cosolvents such as ethylene glycol monophenyl ether and isophorones could improve the solubility of cyclohexene in the water evidently.[8] Unfortunately, there is no information available in the published literature on an insight into the solvent effect on the adsorption of reactants on the surface of solid catalysts, which is meaningful for understanding the reaction mechanism of cyclohexene hydration catalyzed by heterogeneous catalysts.

It is well accepted that the pseudohomogeneous (PH) model is usually inadequate to disclose the mechanism of the reactions occurring on the heterogeneous catalysts. With the aim to understand the heterogeneous catalytic reactions more clearly, several representative models have been developed to describe the complex kinetic behaviors of the reactions catalyzed by a solid catalyst, including the Langmuir−Hinshelwood−Hougen−Watson (LHHW) model and its derived form, the Eley−Rideal (ER) model.[9−18] In our previous work,[19] the reaction kinetics and mechanism of cyclohexene hydration were studied based on the LHHW mechanism and the ER mechanism. It was demonstrated that cyclohexene hydration catalyzed by H-ZSM-5 belonged to the ER mechanism which accounted for the reaction between the adsorbed water and bulk cyclohexene in the aqueous phase. However, the solvent effect on the hydration of cyclohexene was not investigated. In this work, a series of organic solvents will be used to screen a suitable cosolvent for cyclohexene hydration catalyzed by H-ZSM-5 catalyst. In addition, three models based on different mechanisms will be applied to correlate the obtained kinetic data, to study the reaction kinetics of cyclohexene hydration in the presence of a cosolvent, and to understand the solvent effect on the adsorption behavior of the reactants on the surface of H-ZSM-5 catalyst.

EXPERIMENTAL SECTION

Chemicals and Materials. Cyclohexene was commercially supplied by Shanghai Gonghe Chemical Co., Ltd. with purity

Special Issue: Kenneth N. Marsh Festschrift

Received: February 1, 2011
Accepted: March 9, 2011
Published: March 21, 2011

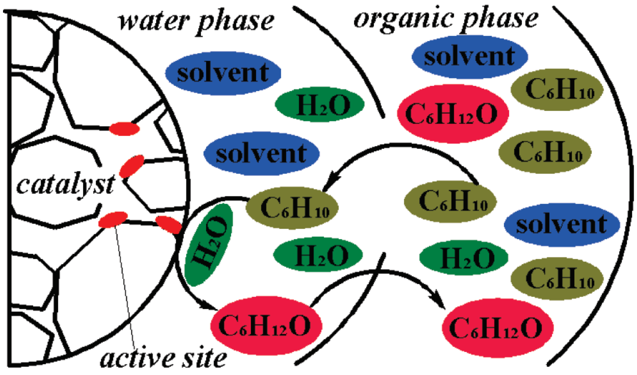

Figure 1. Schematic diagram of the cyclohexene hydration over the solid catalyst.

greater than 0.950 in mass fraction. Ethylene glycol (1,2-dihydroxyethane), 2-phenylethanol (2-phenylethanol), isophorone (3,5,5-trimethylcyclohex-2-en-1-one), butanone (2-butanone), sulfolane (thiolane 1,1-dioxide), and dimethyl sulfoxide (methylsulfinylmethane) were purchased from Sinopharm Chemical Reagent Co., Ltd. with purity greater than 0.990 in mass fraction. 3,3,5-trimethylcyclohexanone (3,3,5-trimethylcyclohexan-1-one) was purchased from Tokyo Kasei Kogyo Co., Ltd. with purity greater than 0.990 in mass fraction. All the liquid chemicals were verified by gas chromatography. The H-ZSM-5 catalyst ($SiO_2/Al_2O_3 = 25$) was supplied by Nankai University catalyst Co., Ltd. The catalyst was calcined at 773 K for 4 h and stored in desiccators for future use.

Apparatus and Procedure. The hydration reaction was carried out in a batch autoclave with a volume of 500 cm^3. For screening out the best cosolvent, the amounts of the different cosolvents were kept at 0.3 mol, and the detailed experimental procedure has been presented elsewhere.[19] In this work, the kinetic experiments were conducted over a temperature range of (383.15 to 413.15) K. Based on the preliminary experiments, the external mass transfer resistances were eliminated at a stirring speed of 1000 rpm, and the internal diffusion resistances were ignored due to the changeless conversion of cyclohexene with different catalyst particle sizes.

Cyclohexene hydration is a triphasic reaction system composed by the two liquid phases and the solid catalyst, and the reaction is conventionally considered to occur in the aqueous phase, a schematic diagram of the cyclohexene hydration over the solid catalyst is shown in Figure 1. In order to select a more accurate method to calculate the compositions in the aqueous phase, the liquid−liquid equilibria (LLE) experiments of the cyclohexene (CHE) + water (H_2O) + cyclohexanol (CHOL) + ethylene glycol (EG) system were performed at 298.15 K in a thermostatical Teflon tank with a volume of 50 cm^3. A total of 15 mL of cyclohexene, 15 mL of water, 1.5 mL of cyclohexanol, and the desired volume of ethylene glycol were added into the tank, and then the tank was placed in a water bath shaker for 2 h to reach the equilibrium. After the tank was kept static for 3 h for complete phase separation, the samples of the organic phase were withdrawn and analyzed.

A gas chromatograph (GC) equipped with a flame ionization detector (FID) was used to analyze the obtained samples. A capillary column of 60 m length was used for chromatographic analysis. The oven temperature was started at 393 K for 2 min, and then increased to 473 K at a rate of 15 K min^{-1} and hold for 20 min. The temperatures of injector and detector were set at 523 and 553 K, respectively. Nitrogen acted as the carrier gas at 0.07 MPa.

Table 1. Conversion of Cyclohexene, x_{CHE}, as a Function of Reaction Time, *t*, with Different Cosolvent Catalyzed by H-ZSM-5[a]

	t	x_{CHE}
solvent	min	%
no solvent	180	7.6
	240	8.2
isophorone	180	10.2
	240	10.4
3,3,5-trimethylcyclohexanone	180	9.4
	240	9.6
butanone	180	8.5
	240	8.9
ethylene glycol	180	10.9
	240	11.4
2-phenylethanol	180	9.1
	240	9.3
sulfolane	180	8.2
	240	8.6
dimethyl sulfoxide	180	6.9
	240	7.1

[a] Reaction conditions: cyclohexene, 150 mL; water, 150 mL; coslovent, 0.3 mol; H-ZSM-5, 30 g; temperature, 393.15 K; stirring speed, 1000 rpm.

RESULTS AND DISCUSSION

Screening of Cosolvent. With the aim to obtain a much more suitable cosolvent for the cyclohexene hydration catalyzed by H-ZSM-5, a series of solvents were selected by referring to the relevant literatures. The experimental results of cyclohexene hydration with different cosolvents are listed in Table 1.

It is observed from Table 1 that ethylene glycol (EG) is the best cosolvent for the cyclohexene hydration catalyzed by H-ZSM-5. In addition, isophorone and 3,3,5-trimethylcyclohexanone also gave relatively high conversions of cyclohexene. Unexpected is that sulfolane showed a poor ability to improve the conversion of cyclohexene, which is in disagreement with the conclusion obtained by Panneman and Beenackers.[5−7] It is probably caused by the different catalysts used and the discrepancy in characteristics of the reaction system. In this work, the ethylene glycol was selected as the cosolvent for cyclohexene hydration.

LLE Calculations. The relationship of liquid−liquid equilibrium can be represented with activity coefficient model. For every component *i* in the two liquid phases at equilibrium, the following equations must be satisfied:

$$x_i^{I}\gamma_i^{I} - x_i^{II}\gamma_i^{II} = 0 \tag{1}$$

$$x_i^{I}\phi\sum n_i + x_i^{II}(1-\phi)\sum n_i - n_i = 0 \tag{2}$$

$$\sum x_i^{I} - 1 = 0 \tag{3}$$

$$\sum x_i^{II} - 1 = 0 \tag{4}$$

where $\phi = n^{I}/\Sigma n_i$ is mole ratio of the moles in phase I to total moles in the system, n_i is the moles of component *i* in the system and n^{I} is the total moles in phase I. x_i^{I} and x_i^{II} are the mole fractions of component *i* in phases I and II, and γ_i^{I} and γ_i^{II} are the activity coefficients of component *i* in phases I and II.

For the liquid−liquid equilibria of the quaternary system of cyclohexene + water + cyclohexanol + ethylene glycol at 298.15 K, the influence of the volume of ethylene glycol, which varied from 0.4 to 4 mL, was studied. The mole ratios of cyclohexanol to cyclohexene in the organic phase were measured and the experimental data were correlated with a UNIFAC model, a modified UNIFAC model developed by Gmehling et al. (Mod. UNIFAC (Do)),[20] and a modified UNIFAC model developed by Larsen et al. (Mod. UNIFAC (La)).[21] The experimental results and the calculated values by the three models were shown in Figure 2. As shown in Figure 2, the Mod. UNIFAC (Do) model gives much better fits to the experimental data than the original UNIFAC model and the Mod. UNIFAC (La) model at all experimental conditions. Thus, the Mod. UNIFAC (Do) model was applied to calculate the concentration and corresponding activity coefficients of reactants in the further study. For the quaternary system of cyclohexene + water + cyclohexanol + ethylene glycol, the group information, structural parameters and interaction parameters are given in Tables 2, 3, and 4.

The reaction temperature of cyclohexene hydration is generally varied from 383.15 to 413.15 K. For the quaternary cyclohexene + water + cyclohexanol + ethylene glycol system at the reaction temperature, the variation of the mole fraction of cyclohexene in the aqueous phase with the volume of ethylene glycol was calculated by the Mod. UNIFAC (Do) model, which is shown in Figure 3. It is clear that addition of ethylene glycol leads to an evident increase of the solubility of cyclohexene in the aqueous phase. The higher the equilibrium temperature is, the better the capacity of ethylene glycol to improve the solubility of cyclohexene. Figure 3 also shows that the mole fraction of cyclohexene only increases slightly with the temperature, it is mainly because the temperature range investigated is narrow.

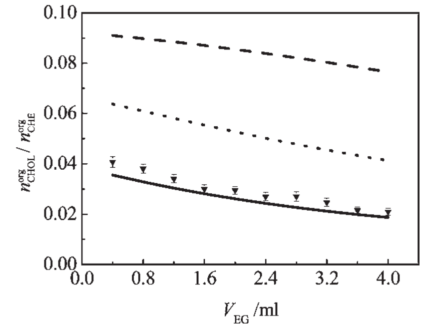

Figure 2. Effect of the volume of ethylene glycol, V_{EG}, on the mole ratio of cyclohexanol to cyclohexene in the organic phase, $n^{\mathrm{org}}_{\mathrm{CHOL}}/n^{\mathrm{org}}_{\mathrm{CHE}}$, of the cyclohexene (CHE) + water (H_2O) + cyclohexanol (CHOL) + ethylene glycol (EG) system at 298.15 K. ▼, experimental data; dash line, calculated values by UNIFAC; dot line, calculated values by Mod. UNIFAC (La); solid line, calculated values by Mod. UNIFAC (Do).

Chemical Equilibrium. The equilibrium constants for the hydration of cyclohexene can be calculated with the following equation:

$$K_{\mathrm{a}} = \frac{a_{\mathrm{CHOL}}}{a_{\mathrm{CHE}}a_{\mathrm{H_2O}}} = \frac{x_{\mathrm{CHOL}}}{x_{\mathrm{CHE}}x_{\mathrm{H_2O}}}\frac{\gamma_{\mathrm{CHOL}}}{\gamma_{\mathrm{CHE}}\gamma_{\mathrm{H_2O}}} \tag{5}$$

where K_{a} is the equilibrium constant in terms of activity, a_i is the activity of the *i*th component in the aqueous phase, and x_i and γ_i are the corresponding mole fraction and activity coefficient of the *i*th component in the equilibrium aqueous phase. Activity coefficients are calculated by the Mod. UNIFAC (Do) model.[20]

The thermodynamic equilibrium constant K_{a} is dependent on the temperature only. In Figure 4, the equilibrium constant at 393.15 K is plotted as the function of the added amount of ethylene glycol, which is expressed as the mole ratio of ethylene glycol to cyclohexene. As shown in Figure 4, the equilibrium constant is between 0.125 and 0.135, except a deviated value of 0.093 corresponding to a mole ratio of 0.5. The lower value is probably due to the decrease of the catalytic activity of H-ZSM-5 caused by the excess cosolvent, which is verified subsequently.

Equilibrium constants can also be expressed in terms of the standard Gibbs free energy of reaction ($\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\ominus}$)

$$K_{\mathrm{a}} = \exp\left(-\frac{\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\ominus}}{RT}\right) = \exp\left(-\frac{\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\ominus}}{RT} + \frac{\Delta_{\mathrm{r}}S_{\mathrm{m}}^{\ominus}}{R}\right) \tag{6}$$

where $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\ominus}$ and $\Delta_{\mathrm{r}}S_{\mathrm{m}}^{\ominus}$ are the standard enthalpy of reaction and standard entropy of reaction for the cyclohexene hydration. In Figure 5, the logarithm of equilibrium constants obtained is plotted as the function of the inverse absolute temperature. It is clear that the equilibrium constant decreased with temperature, which shows that the hydration of cyclohexene is an exothermal reaction. When the standard enthalpy of the reaction is assumed to be independent of temperature, the $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\ominus}$ and $\Delta_{\mathrm{r}}S_{\mathrm{m}}^{\ominus}$ of the hydration reaction can be obtained. With regression analysis, we

Table 3. Mod. UNIFAC (Do) Structural Parameters for the Quaternary Cyclohexene (CHE) + Water (H_2O) + Cyclohexanol (CHOL) + Ethylene Glycol (EG) System

	structural parameters[a]						
	−CH₂−	—CH=CH—	−OH (p)	−OH (s)	H_2O	*c*-CH₂	*c*-CH
R_k	0.6325	1.2832	1.2302	1.0630	1.7334	0.7136	0.3479
Q_k	0.7081	1.2489	0.8927	0.8663	2.4561	0.8635	0.1071

[a] From ref 20.

Table 2. Group Assignment by Mod. UNIFAC (Do) for the Quaternary Cyclohexene (CHE) + Water (H_2O) + Cyclohexanol (CHOL) + Ethylene Glycol (EG) System

	subgroup (main group number; subgroup number)[a]						
	−CH₂− (1; 2)	—CH=CH— (2; 6)	−OH (p) (5; 14)	−OH (s) (5; 81)	H_2O (7; 16)	*c*-CH₂ (42; 78)	*c*-CH (42; 79)
CHE	0	1	0	0	0	4	0
H_2O	0	0	0	0	1	0	0
CHOL	0	0	0	1	0	5	1
EG	2	0	2	0	0	0	0

[a] According to ref 20.

Table 4. Mod. UNIFAC (Do) Interaction Parameters for the Quaternary Cyclohexene (CHE) + Water (H_2O) + Cyclohexanol (CHOL) + Ethylene Glycol (EG) System

		interaction parameters[a]					
n	*m*	a_{nm}/K	b_{nm}	c_{nm}/K^{-1}	a_{mn}/K	b_{mn}	c_{mn}/K^{-1}
$-CH_2-$	—CH=CH—	189.66	−0.2723	0	−95.418	0.6171×10^{-1}	0
$-CH_2-$	−OH (p)	2777	−4.674	0.1551×10^{-2}	1606.0	−4.7460	0.9181×10^{-3}
$-CH_2-$	−OH (s)	2777	−4.674	0.1551×10^{-2}	1606.0	−4.7460	0.9181×10^{-3}
$-CH_2-$	H_2O	1391.3	−3.6156	0.1144×10^{-2}	−17.253	0.8389	0.9021×10^{-3}
$-CH_2-$	*c*-CH_2	−680.95	4.0194	-0.6878×10^{-2}	1020.8	−6.0746	0.1051×10^{-1}
$-CH_2-$	*c*-CH	−680.95	4.0194	-0.6878×10^{-2}	1020.8	−6.0746	0.1051×10^{-1}
—CH=CH—	−OH (p)	2649	−6.508	0.4822×10^{-2}	1566.0	−5.8090	0.5197×10^{-2}
—CH=CH—	−OH (s)	2649	−6.508	0.4822×10^{-2}	1566.0	−5.8090	0.5197×10^{-2}
—CH=CH—	H_2O	778.3	0.1482	0	−1301	4.072	0
—CH=CH—	*c*-CH_2	−78.19	0.1327	0	182.4	−0.303	0
—CH=CH—	*c*-CH	−78.19	0.1327	0	182.4	−0.303	0
−OH (p)	−OH (s)	0	0	0	0	0	0
−OH (p)	H_2O	−801.9	3.8240	-0.7514×10^{-2}	1460	−8.673	0.1641×10^{-1}
−OH (p)	*c*-CH_2	3856.0	−17.970	0.2083×10^{-1}	3246	−4.937	-0.1143×10^{-2}
−OH (p)	*c*-CH	3856.0	−17.970	0.2083×10^{-1}	3246	−4.937	-0.1143×10^{-2}
−OH (s)	H_2O	−801.9	3.8240	-0.7514×10^{-2}	1460	−8.673	0.1641×10^{-1}
−OH (s)	*c*-CH_2	3856.0	−17.970	0.2083×10^{-1}	3246	−4.937	-0.1143×10^{-2}
−OH (s)	*c*-CH	3856.0	−17.970	0.2083×10^{-1}	3246	−4.937	-0.1143×10^{-2}
H_2O	*c*-CH_2	274.37	−0.5861	-0.3001×10^{-3}	1632.9	−2.8719	0.3455×10^{-2}
H_2O	*c*-CH	274.37	−0.5861	-0.3001×10^{-3}	1632.9	−2.8719	0.3455×10^{-2}
c-CH_2	*c*-CH	0	0	0	0	0	0

[a] From ref 20.

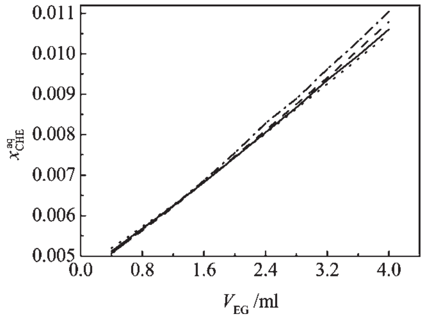

Figure 3. Mole fraction of cyclohexene in the aqueous phase, x^{aq}_{CHE}, as the function of the volume of ethylene glycol, V_{EG}, in the cyclohexene (CHE) + water (H2O) + cyclohexanol (CHOL) + ethylene glycol (EG) system, calculated by Mod. UNIFAC (Do). dot line, 383.15 K; solid line, 393.15 K; dash line, 403.15 K; dash and dot line, 413.15 K.

obtain eq 7

$$K_a = \exp\left(3421.7\frac{1}{T} - 10.739\right) \qquad (7)$$

From eq 7, we obtain a reaction enthalpy of −28.45 ± 12.13 kJ mol^{-1}, which is slightly lower than the value of −30.53 kJ mol^{-1} obtained in our previous work[19] with the same H-ZSM-5 catalyst. The slightly decrease is mainly due to the variation of the activity coefficient of cyclohexene and cyclohexanol as a function of their mole fractions.

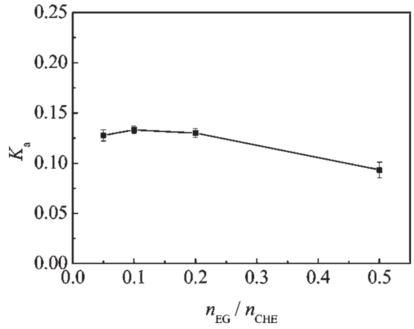

Figure 4. Equilibrium constants, K_a, as a function of the mole ratio of ethylene glycol to cyclohexene at 393.15 K.

Reaction Kinetics Results. In the present work, the kinetic behaviors of cyclohexene hydration catalyzed by the H-ZSM-5 were studied in the presence of the cosolvent ethylene glycol, which was proved to be the best cosolvent in various solvents selected. The effects of reaction temperature and initial mole ratio of cyclohexene to ethylene glycol on reaction kinetics were determined.

Effect of Reaction Temperature. The reaction temperature of the kinetic experiments was varied form 383.15 to 413.15 K with a constant initial mole ratio of cyclohexene to ethylene glycol (5:1). As shown in Figure 6, the maximum conversion of cyclohexene (11.4 %) was obtained at temperature 393.15 K, which is consistent with the optimum temperature for the cyclohexene hydration without the cosolvent ethylene glycol.[19] It is also observed that the reaction rate increases with the

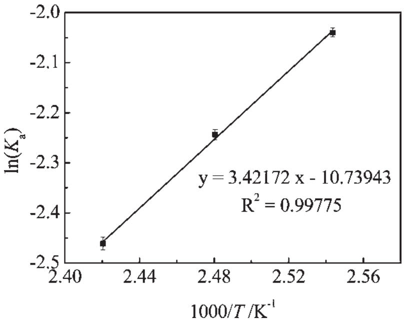

Figure 5. Logarithm of the equilibrium constants, $\ln(K_a)$, as a function of temperature.

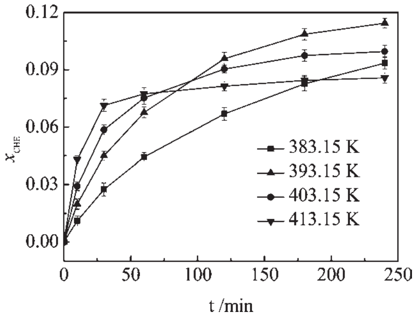

Figure 6. Effect of reaction temperature on the conversion of cyclohexene, x_{CHE}, catalyzed by H-ZSM-5 catalyst in the presence of cosolvent ethylene glycol. Cyclohexene, 150 mL; water, 150 mL; H-ZSM-5, 30 g; initial mole ratio of cyclohexene to ethylene glycol: 5:1.

increase of the temperature, and the highest conversion of cyclohexene decreases when the reaction temperature increases from 393.15 to 413.15 K. Similar behavior was noticed in the previous study[4,19] for cyclohexene hydration, which indicates that cyclohexene hydration is an exothermic equilibrium reaction.

Effect of Initial Mole Ratio of Cyclohexene to Cosolvent. The reaction was carried out over the H-ZSM-5 catalyst with the initial mole ratio of cyclohexene to ethylene glycol from 2 to 20 at temperature 393.15 K. The results are shown in Figure 7. With the initial mole ratio of cyclohexene to ethylene glycol decreased from 20 to 5, there is a progressive increase in the conversion of cyclohexene. This indicates that the increase of the amount of ethylene glycol in the certain range is helpful to improve the proceeding of cyclohexene hydration. However, with further decrease in the initial mole ratio to 2, a sharp decrease in the conversion of cyclohexene is observed. The inhibition effect might be due to the adsorption of ethylene glycol on the catalyst, which occupies too many active sites when excessive ethylene glycol is used. Based on the experimental results, an initial mole ratio of 5:1 of cyclohexene to ethylene glycol is considered optimum for cyclohexene hydration catalyzed by H-ZSM-5 catalyst.

Kinetic Modeling. In this work, the experimental data obtained at four temperatures were used in the kinetic modeling. In order to describe the kinetic behavior of cyclohexene hydration in the presence of the cosolvent ethylene glycol, a simple pseudohomogeneous (PH) model and two heterogeneous models based on the LHHW mechanism and ER mechanism, were applied to correlate with the kinetic data. The reaction equilibrium constant K_a determined experimentally is used in the models, and the temperature dependence of the rate constant is expressed by the Arrhenius law. In addition, the adsorption of ethylene glycol, as an inert adsorbed material, was taken into account in the two heterogeneous models. The rate expressions based on the three models are as follows:

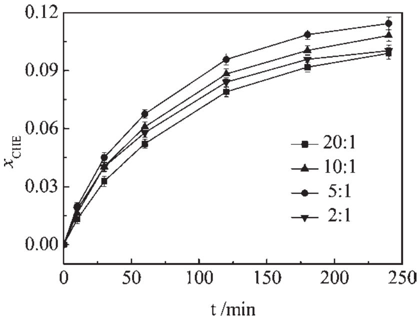

Figure 7. Effect of initial mole ratio of cyclohexene to ethylene glycol on the conversion of cyclohexene, x_{CHE}, catalyzed by H-ZSM-5 catalyst. Cyclohexene, 150 mL; water, 150 mL; H-ZSM-5, 30 g; reaction temperature: 393.15 K.

(1) PH Model

$$-r_{CHE} = k_0 \exp(-E/RT)(a_{CHE}a_{H_2O} - a_{CHOL}/K_a) \tag{8}$$

(2) LHHW Model

$$-r_{CHE} = \frac{k_0 \exp(-E/RT)(a_{CHE}a_{H_2O} - a_{CHOL}/K_a)}{(1 + K_{CHE}a_{CHE} + K_{H_2O}a_{H_2O} + K_{CHOL}a_{CHOL} + K_{EG}a_{EG})^2} \tag{9}$$

(3) ER Model

$$-r_{CHE} = \frac{k_0 \exp(-E/RT)(a_{CHE}a_{H_2O} - a_{CHOL}/K_a)}{1 + K_{CHE}a_{CHE} + K_{H_2O}a_{H_2O} + K_{CHOL}a_{CHOL} + K_{EG}a_{EG}} \tag{10}$$

where r_i is the reaction rate of ith component and T is the reaction temperature. k_0 is the preexponential factor, E is the activation energy of cyclohexene hydration, and K_i is the adsorption constant of ith component.

The values of the kinetic parameters, including the preexponential factor, activation energy, and adsorption constants, were obtained by minimizing the residual sum of squares (RSS) between the experimental and calculated values of reaction rate with a Levenberg–Marquardt (LM) optimization algorithm, which can be expressed as follows:

$$\text{RSS} = \sum (r_{i,\,\text{exp}} - r_{i,\,\text{calc}})^2 \tag{11}$$

In addition, the correlation coefficient (ρ^2) was obtained by the following equation for statistical test of the models:

$$\rho^2 = 1 - \sum (r_{i,\,\text{exp}} - r_{i,\,\text{calc}})^2 / \sum r_{i,\,\text{exp}}{}^2 \tag{12}$$

where the subscripts "exp" and "calc" denote the experimental and calculated values of reaction rate, respectively.

The values of the kinetic parameters and the results of the statistical analysis for the three models are listed in Table 5. As shown in Table 5, the PH kinetic model gives a larger RSS value

Table 5. Preexponential Factor, k_0, Activation Energy, E, Adsorption Constants of ith Component, K_i, Residual Sum of Squares, RSS, and Correlation Coefficient, ρ^2, for Cyclohexene Hydration over H-ZSM-5

model	parameter	value	RSS	ρ^2
1	k_0/mol s^{-1} kg cat^{-1}	$1.119 \times 10^{-3} \pm 1.094 \times 10^{-3}$	1.468×10^{-6}	0.9662
	E/kJ mol^{-1}	74.65 ± 11.67		
2	k_0/mol s^{-1} kg cat^{-1}	$1.556 \times 10^{-3} \pm 2.834 \times 10^{-3}$	9.125×10^{-8}	0.9979
	E/kJ mol^{-1}	67.94 ± 76.19		
	K_{CHE}	$6.707 \times 10^{-12} \pm 1.005 \times 10^{-4}$		
	K_{H2O}	$2.576 \times 10^{-11} \pm 6.733 \times 10^{-2}$		
	K_{CHOL}	5.965 ± 6.192		
	K_{EG}	0.3029 ± 0.9514		
3	k_0 /mol s^{-1} kg cat^{-1}	$1.353 \times 10^{-2} \pm 0.769 \times 10^{-2}$	9.455×10^{-8}	0.9979
	E /kJ mol^{-1}	67.23 ± 26.73		
	K_{CHE}	$6.968 \times 10^{-7} \pm 3.648 \times 10^{-7}$		
	K_{H2O}	3.166 ± 3.612		
	K_{CHOL}	126.8 ± 55.4		
	K_{EG}	27.63 ± 9.38		

(1.468×10^{-6}) and a smaller ρ^2 value (0.9662) than the other two heterogeneous models. It indicates that the heterogeneous models, which take into account the adsorption of reactants and product on the catalyst, are much more suitable to describe the realistic behaviors of cyclohexene hydration over the H-ZSM-5 catalyst in the presence of the cosolvent ethylene glycol. The same conclusion was also obtained in the previous study of the kinetics of cyclohexene hydration without cosolvent.[19] For the two heterogeneous models respectively based on the LHHW mechanism and ER mechanism, the RSS values are almost identical with the value of 9.125×10^{-8} and 9.455×10^{-8}. Thus, it is difficult to judge the realistic reaction mechanism merely based on the results of statistical analysis.

Based on the LHHW model, the adsorption constants of cyclohexene and water are determined to be 6.707×10^{-12} and 2.576×10^{-11}, respectively. The obtained adsorption constants of the reactants are so small that the adsorption of cyclohexene and water on the catalyst can be ignored for the LHHW model. This seems unreasonable in consideration of the assumption of the LHHW mechanism, which is proposed based on the adsorbed cyclohexene and adsorbed water. Because the obtained kinetic parameters are not physically meaningful, the LHHW model is discarded.

The model 3 is proposed based on the ER mechanism, which assumes that the cyclohexene hydration could proceed between an adsorbed reactant molecule and another reactant molecule in the bulk phase. The ER model gives physically meaningful parameters and satisfactory agreement between the experimental and calculated reaction rates, which can be seen in Figure 8. According to the ER model, the adsorption constant of water with a value of 3.166 is found to be greatly larger than that of cyclohexene (6.968×10^{-7}). It is suggested that the cyclohexene molecule existed in the aqueous phase could directly react with the water molecule adsorbed on the active sites of the H-ZSM-5 catalyst. In the previous work,[19] cyclohexene hydration without the cosolvent was also proved to follow the same ER mechanism. Thus it is concluded that the coslovent ethylene glycol does not change the reaction mechanism of cyclohexene hydration over the H-ZSM-5 catalyst.

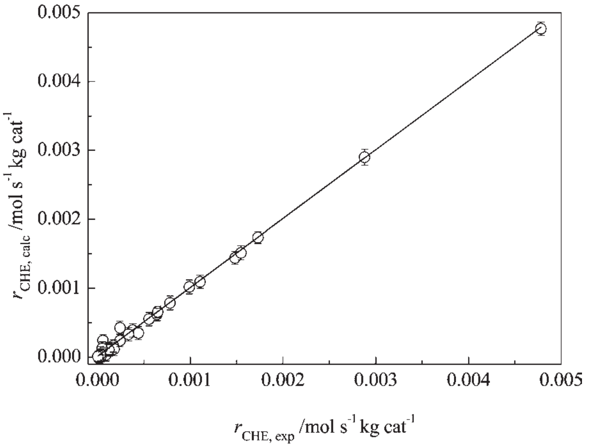

Figure 8. Calculated reaction rate of cyclohexene, $r_{CHE,calc}$, by ER model as a function of experimental rate of cyclohexene, $r_{CHE,exp}$, for cyclohenexe hydration catalyzed by H-ZSM-5 catalyst in the presence of the ethylene glycol.

According to the ER model, the cyclohexene hydration with ethylene glycol as the cosolvent has an activation energy of 67.23 kJ mol^{-1}, which is lower than that obtained in our previous work[19] for cyclohexene hydration without the cosolvent (77.69 kJ mol^{-1}). The decrease of the activation energy is mainly caused by the solvent effect of ethylene glycol. It is well-known that the polarity of cyclohexanol is largely stronger than that of cyclohexene molecule. Thus, the ethylene glycol, as a polar solvent, has the capacity to increase the reaction rate of cyclohexene hydration by the strong solvation effect with the polar cyclohexanol molecule.

In addition, the adsorption equilibrium of the components on the H-ZSM-5 catalyst is also influenced by the cosolvent ethylene glycol. As shown in Table 5, the adsorption constants of water, cyclohexanol, and ethylene glycol are found to be 3.166, 126.8, and 27.63, respectively. In the case of no cosolvent used in the cyclohexene hydration over the H-ZSM-5 catalyst, the adsorption constants of water and cyclohexanol were determined to be 19.95 and 146.6 in the previous work.[19] It is found that the adsorption of water and cyclohexanol are both weakened due to the existence of ethylene glycol.

CONCLUSIONS

Synthesis of cyclohexanol from hydration of cyclohexene over H-ZSM-5 catalyst was studied in the presence of a series of cosolvent. Among the various organic solvents, the ethylene glycol showed the best performance in improving the conversion of cyclohexene. Based on the liquid−liquid equilibria (LLE) experimental results of the quaternary system of cyclohexene + water + cyclohexanol + ethylene glycol at temperature 298.15 K, a modified UNIFAC model was used to determine the concentration and corresponding activity coefficients of reactants in the reaction system.

The reaction kinetics of the cyclohexene hydration over H-ZSM-5 catalyst, using ethylene glycol as the cosolvent, was studied in the temperature range from 383.15 to 413.15 K, and initial mole ratios of cyclohexene to ethylene glycol in the range from 2 to 20. Temperature of 398.15 K and initial mole ratio of 5:1 of cyclohexene to ethylene glycol were found to be optimum for cyclohexene hydration. Three kinetic models, including the PH model, the LHHW model, and the ER model, were applied to correlate the kinetic data obtained in this work. It showed that the ER model gave the best description of the experimental data, which suggests that the mechanism of cyclohexene hydration catalyzed by H-ZSM-5 is not changed by the cosolvent ethylene glycol. However, the activation energy, and the adsorption constants of water and cyclohexanol were found to be decreased due to the existence of ethylene glycol.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +86-21-64253529. Fax: +86-21-64253528. E-mail: zmcheng@ecust.edu.cn.

Funding Sources

The present work was conducted under support from the State Key Laboratory of Chemical Engineering in China via SKL-ChE-08C03 and partially from Natural Science Foundation of China via No. 20876043.

REFERENCES

(1) Misono, M.; Inui, T. New Catalytic Technologies in Japan. *Catal. Today* **1999**, *51*, 369–375.

(2) Ishida, H. Liquid-Phase Hydration Process of Cyclohexene with Zeolites. *Catal. Surv. Jpn.* **1997**, *1*, 241–246.

(3) Ogawa, H.; Xiuhua, H.; Chihara, T. Hydration of Cyclohexene by Alkyl-Immobilized H-ZSM-5 Catalyst in Decalin-Water System. *Chem. Lett.* **1998**, *55*, 121–123.

(4) Zhang, H.; Mahajani, S. M.; Sharma, M. M.; Sridhar, T. Hydration of Cyclohexene with Solid Acid Catalysts. *Chem. Eng. Sci.* **2002**, *57*, 315–322.

(5) Panneman, H. J.; Beenackers, A. A. C. M. Effect on the Hydration of Cyclohexene Catalyzed by Strong Ion-Exchange Resins. 1. Solubility of Cyclohexene in Aqueous Sulfolane Mixtures. *Ind. Eng. Chem. Res.* **1992**, *31*, 1227–1234.

(6) Panneman, H. J.; Beenackers, A. A. C. M. Effect on the Hydration of Cyclohexene Catalyzed by Strong Ion-Exchange Resins. 2. Effect of Sulfolane on the Reaction Kinetics. *Ind. Eng. Chem. Res.* **1992**, *31*, 1425–1433.

(7) Panneman, H. J.; Beenackers, A. A. C. M. Effect on the Hydration of Cyclohexene Catalyzed by Strong Ion-Exchange Resins. 3. Effect of Sulfolane on the Equilibrium Conversion. *Ind. Eng. Chem. Res.* **1992**, *31*, 1433–1440.

(8) Yoshikazu T.; Tokitaka, K. Process for the Preparation of Cyclohexanol. U.S. Patent 6,552,235, 2003.

(9) Lee, M.; Chou, P.; Lin, H. Kinetic of Synthesis and Hydrolysis of Ethyl Benzoate over Amberlyst 39. *Ind. Eng. Chem. Res.* **2005**, *44*, 725–732.

(10) Bożek-Winkler, E.; Gmehling, J. Transesterification of Methyl Acetate and n-Butanol Catalyzed by Amberlyst 15. *Ind. Eng. Chem. Res.* **2006**, *45*, 6648–6654.

(11) Delgado, P.; Sanz, M. T.; Beltrán, S. Kinetic Study for Esterification of Lactic Acid with Ethanol and Hydrolysis of Ethyl Lactate Using an Ion-Exchange Resin Catalyst. *Chem. Eng. J.* **2007**, *126*, 111–118.

(12) Mao, W.; Wang, X.; Wang, H.; Chang, H.; Zhang, X.; Han, J. Thermodynamic and Kinetic Study of Tert-Amyl Methyl Ether (TAME) Synthesis. *Chem. Eng. Process.* **2008**, *47*, 761–769.

(13) Kalló, D.; Mihályi, R. M. Mechanism of 1-Butene Hydration over Acidic Zeolite and Ion-Exchange Resin Catalysts. *Appl. Catal. A-Gen.* **1995**, *121*, 45–56.

(14) Kirumakki, S. R.; Nagaraju, N.; Chary, K. V. R. Esterification of Alcohols with Acetic Acid over Zeolites Hβ, HY and HZSM5. *Appl. Catal. A-Gen.* **2006**, *299*, 185–192.

(15) Yip, A. C. K.; Hu, X. Catalytic Activity of Clay-Based Titanium Silicalite-1 Composite in Cyclohexanone Ammoximation. *Ind. Eng. Chem. Res.* **2009**, *48*, 8441–8450.

(16) Marchi, A. J.; Paris, J. F.; Bertero, N. M.; Apesteguía, C. R. Kinetic Modeling of the Liquid-Phase Hydrogenation of Cinnamaldehyde on Copper-Based Catalysts. *Ind. Eng. Chem. Res.* **2007**, *46*, 7657–7666.

(17) Pour, A. N.; Housaindokht, M. R.; Tayyari, S. F.; Zarkesh, J. Kinetics of the Water-Gas Shift Reaction in Fischer−Tropsch Synthesis over a Nano-Structured Iron Catalyst. *J. Nat. Gas Chem.* **2010**, *19*, 362–368.

(18) Sert, E.; Atalay, F. S. Kinetic Study of the Esterification of Acetic Acid with Butanol Catalyzed by Sulfated Zirconia. *Reac. Kinet. Mech. Cat.* **2010**, *99*, 125–134.

(19) Shan, X.; Cheng, Z.; Yuan, P. Reaction Kinetics and Mechanism for Hydration of Cyclohexene over Ion-Exchange Resin and H-ZSM-5. *Chem. Eng. Res. Des.* submitted.

(20) Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties. *Ind. Eng. Chem. Res.* **1993**, *32*, 178–193.

(21) Larsen, B. L.; Rasmussen, P.; Fredenslund, A. A Modified UNIFAC Group-Contribution Model for Prediction of Phase Equilibria and Heats of Mixing. *Ind. Eng. Chem. Res.* **1987**, *26*, 2274–2286.