Synthesis and Kinetics of the N-(2-Methyl-6-ethyl phenyl)-1-methoxypropyl-2-imine Schiff Base Catalyzed by NKC-9 Cation Exchange Resin

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ABSTRACT: The kinetics of condensation reaction of methoxyacetone with 2-methyl-6-ethyl aniline catalyzed by NKC-9 cation exchange resin was studied for the first time. The reaction temperature of Schiff base synthesis was determined in the range of 367.15 to 401.15 K by the batch experiments, and influences of reactant molar ratio, temperature, catalyst dosage, and particle size on the ultimate conversion were also studied. The dynamic data were used to be relevant with PH, ER(1), ER(2), and Langmuir Hinshelwood Hougen Watson homogeneity models. Model parameters, including reaction equilibrium constants, activation energy, enthalpy change, entropy change, and rate constants, were solved. The accuracy of the model was validated by means of both experimental proofs and standard deviation between the predicted and experimental data. Finally, a series of characterization tests such as Fourier transform infrared spectroscopy, X-ray diffraction, and polarizing microscopy were performed to investigate the structure and properties of NKC-9.

1. INTRODUCTION

Schiff bases,† also known as imines, are compounds containing C≡N groups formed by nucleophilic addition of carbonyl compounds and amino compounds. It is characterized by the simple synthesis method that lots of Schiff bases with variable structure and different properties can be derived from changing the substrate amine and ketone. Nowadays Schiff base compounds and their metal complexes have important applications in various fields, such as pharmacy,² catalysis,³ analytical chemistry,⁴ corrosion,⁵ and photochromism.⁶ They also have antibacterial, bactericidal, antitumor, antiviral, and other biological activities extensively applied in the medical field. In addition, the cobalt and nickel complexes of Schiff bases have been widely used as catalysts in the field of catalysis. Moreover, the Schiff base, as a good ligand in analytical chemistry, can be used for the identification and quantitative analysis of metal ions. In the field of corrosion, certain aromatic Schiff bases are often adopted as corrosion inhibitors of copper. In the field of photochromism, some Schiff bases containing characteristic groups also have unique applications.

N-(2-Methyl-6-ethyl phenyl)-1-methoxypropyl-2-imine (MEMI), as a kind of important Schiff bases, synthesized by heterogeneous catalysis was discussed for the first time as shown in Scheme 1. As an important pharmaceutical intermediate for the synthesis of metolachlor, industrial production can only be made by asymmetric hydrogenation of this Schiff base, so the prospects of MEMI for research and its practical value are very considerable. Generally, the metolachlor has two different configuration images, including the S configuration and the R configuration. Among them, the
metolachlor in the S configuration has herbicidal activity, but the metolachlor in the R configuration has no herbicidal activity. In the same case, the herbicidal activity of the S-metolachlor is 1.4–1.6 times that of metolachlor. As a common herbicide, S-metolachlor is commonly used in cash crops such as dry fields, orchards, and vegetable crops. Besides, it is specially suitable for weeding in paddy fields with many weeds, early germination, long growing season, and large weed growth area. On the other hand, half of the R configuration of the metolachlor has no pharmacological effect; however, it is also released to the environment. As a result, it not only causes pollution to the environment, but also increases the input of raw materials.

In general, the commonly catalysts used for synthesis of the Schiff bases are strong proton acid liquid, such as HCl, H$_2$SO$_4$, HF, H$_3$PO$_4$, and so forth. However, these catalysts can cause environmental pollution and equipment corrosion problems, increasing the purification difficulty and complexity of the desired product. Therefore, a variety of environmentally protective and efficient heterogeneous solid acid catalysts, such as acidic ion exchange resin (Amberlyst-47, Amberlyst-15, Indion-130 Dowex 50Wx2, Dowex 50Wx8 etc.),

10–12 which are used in acid catalytic reactions, have been developed from the perspective of eco-friendly economic benefits, including esterification, condensation, and etherification reaction. Qian

13 used cation exchange resin to catalyze ketonization of cyclohexanone with 1,4-butanediol. JagadeeshBabu

14 used cationic exchange resin to synthesize methyl acetate and studied its kinetics. Sharma

15 used Amberlyst-15 to catalyze the esterification of nonanoic acid with 1-propanol and so forth.

16–18

In our study, the NKC-9 cation-exchange resin as a heterogeneous catalyst was applied to realize the synthesis of Schiff base. At the same time, effects of the stirring rate, catalyst particle size, initial molar ratio of reactants, temperature, and catalyst loading factors on the performance of the catalyst were discussed in this paper through a series of experiments. The experimental data were processed by several kinetic models,

9,20 and the kinetic parameter rate equation based on the Langmuir Hinselwood Hougen Watson (LHHW) reaction mechanism was also established. The calculated reaction rate and the experimental measurement results were used to determine the kinetic model parameters by minimizing the residual sum of squares. The kinetics and thermodynamics of the catalytic preparation of the MEMI Schiff base which were studied and discussed in this paper would provide technical and data support for the subsequent industrial continuous production.

2. RESULTS AND DISCUSSION

2.1. Selection of Ion Exchange Resin Catalysts. In order to study the catalytic activity of strong acid cation-exchange resins D113, NKC-9, and 001*7, a preliminary comparison was made among these resins. As shown in Figure 1, MEA conversion in the presence of NKC-9 is highest when the reaction equilibrium is reached, which means a better catalytic effect than that of the other two resins. In addition, the equilibrium time of reaction catalyzed by NKC-9 resin is also relatively short. Therefore, NKC-9 was selected for further study of catalytic condensation reaction.

2.2. Kinetic Experiment and Optimization. 2.2.1. Effect of Catalyst Loading. The influence of the catalyst loading on the conversion was discussed under the same experimental conditions: the reaction temperature was 393.15 K, and the molar ratio of the reactants was 1:1.7. The catalyst loading range was from 0.020 g catalyst/g liquid mixture to 0.030 g catalyst/g liquid mixture. As shown in Figure 2, the reaction equilibrium time is significantly shortened with the presence of a catalyst compared with the blank experiment. When the catalyst loading increases from 0.020 g catalyst/g liquid mixture to 0.025 g catalyst/g liquid mixture, the MEA conversion measured at the same reaction time is significantly improved, which is due to the change of catalyst loading leading to the increase of available active sites. However, when the catalyst loading increases from 0.025 g catalyst/g liquid mixture to 0.030 g catalyst/g liquid mixture, the MEA conversion measured under the same reaction time is nearly the same. The findings indicated that the optimal catalyst loading is 0.025 g catalyst/g liquid mixture.
2.2.2. Effect of Reaction Temperature. The effect of different reaction temperatures on MEA conversion was investigated under the condition of 0.025 g catalyst/g liquid mixture and molar ratio of reactants 1:1.7. As shown in the Figure 3, MEA conversion increases with the increase of temperature before it reaches equilibrium, which indicates that high temperature facilitates the forward reaction. At the same time, it can be found that the higher the temperature, the faster the reaction reaches equilibrium, which suggests the forward reaction endothermic and more activation sites of ion-exchange resin emerging with a higher temperature. However, ion-exchange resin maybe easy to expand and fracture if the reaction temperature is too high. In conclusion, the optimal reaction temperature of this reaction is 393.15 K.

2.2.3. Effect of the Molar Ratio of Reactants. In order to determine the optimal reactants molar ratio, repeated tests were carried out under the same experimental conditions to investigate the effects of the molar ratio of reactants (1:1.5, 1:1.7, and 1:1.9) on the conversion of MEA. Now that MEA has a higher boiling point and takes a smaller proportion in the gas phase, the yield of the Schiff base can be precisely calculated based on MEA conversion. According to the principle of chemical equilibrium, the increasing amount of MOA can improve MEA conversion. As shown in the Figure 4, when the molar ratio of reactants is increased from 1:1.5 to 1:1.7, the chemical reaction equilibrium is significantly increased, which is partly due to the fact that reactants will promote the forward reaction. However, when the molar ratio goes from 1:1.7 to 1:1.9, the increase of the MEA conversion is not obvious. It is found that when the reaction is close to equilibrium, the higher the molar ratio of reactants is, the more difficult the separation of Schiff base will be, which hinders the forward progress of the reaction.

2.3. Elimination of Internal and External Diffusion. 2.3.1. Elimination of External Diffusion. In the process of studying dynamics, it is necessary to eliminate influences of internal and external diffusion. In order to eliminate the external diffusion influence, it is reasonable to determine the appropriate stirring speed under the optimal conditions of reaction temperature, molar ratio, and catalyst loading.

Figure 3. Effect of reaction temperature (catalyst loading, 0.025 g catalyst/g liquid mixture; MEA/MOA = 1:1.7; catalyst size, >45 mesh; stirring speed, 450 rpm).

Figure 4. Effect of MEA/MOA initial ratio (temperature, 393.15 K; catalyst size, >45 mesh; catalyst loading, 0.025 g catalyst/g liquid mixture; stirring speed, 450 rpm).

Figure 5. Effect of the stirring speeds on the conversion of MEA (temperature, 393.15 K; catalyst loading, 0.025 g catalyst/g liquid mixture; MEA/MOA = 1:1.7; catalyst size, >45 mesh).

Therefore, several tests were carried out under the same experimental condition by changing the rotating speed, including 350, 450, 500, and 550 rpm. The experimental results are shown in Figure 5. When the stirring speed increases from 350 to 450 rpm, the MEA conversion is significantly increased in the same reaction time. However, when the stirring speed increases from 450 to 550 rpm, the MEA conversion rate increases slowly. As a result, taking the wear and tear of the experimental equipment caused by rotating into consideration, 450 rpm was selected as the best condition.

2.3.2. Internal Diffusion Elimination. In order to eliminate the internal diffusion influence, the effect of the catalyst particle size on the conversion of MEA was investigated by repeated experiments with only change of particle size under the optimal reaction temperature, molar ratio of materials, catalyst loading, and appropriate stirring speed. Mesh 24, 30, 38, and 45 of the catalyst were selected as the experimental
objects. As shown in Figure 6, when the particle mesh increases from 24 to 38, the MEA conversion is significantly increased at the same time. However, when the particle mesh is greater than 38 mesh, the MEA conversion does not change obviously with the decrease of the catalyst particle size. It indicated that more active sites exposed will facilitate the reaction as the size of catalyst decreases.

2.4. Structural Characteristics of Fresh and Regenerated NKC-9 Resin.

2.4.1. FT-IR. The Fourier-transform infrared (FT-IR) spectra of a new regenerated NKC-9 cation-exchange resin catalyst are shown in Figure 7. The wide band in the range of 3200−3400 cm\(^{-1}\) is caused by the carbon bond expansion of vinyl. Several characteristic absorption peaks are observed at 500−1250 cm\(^{-1}\), which verify the existence of −SO\(_3\)H. In addition, in the FT-IR spectrum of the regenerated catalyst, the main peaks attributed to the fresh catalyst still exist. Therefore, it is found that the FT-IR spectra of two kinds of strong acid styrene cation-exchange resin catalysts are basically the same.

2.4.2. Scanning Electron Microscope. The surface structure of NKC-9 resin was characterized by a scanning electron microscope. As shown in the Figure 8, a large number of pores are distributed on the surface of the resin. Because of the existence of these pores, the reactant and catalyst can be condensed by means of adsorption, desorption, and other ways, and the contact area between reactants and the catalyst is also considerably increased, which is more conducive to the transformation of the reaction.

2.4.3. Optical Microscope. The optical microscope images of the fresh and used NKC-9 resin in a batch stirred reactor indicating the change of catalyst morphology are shown in Figure 9. Figure 9A shows the surface morphology of the fresh catalyst. It can be observed that the new catalyst is an irregular ball with a smooth and uniform surface. Figure 9B,C presents the surface morphology of the catalyst used in the reaction with a magnification of 35. From the Figure 9B,C, it is found that catalyst ball breaks into hemispheres and the cracks also appear on the catalyst surface. That is because in the reaction process, rapid stirring may lead to catalyst rupture or adsorption and deposition and collision in the catalytic process, which will also lead to catalyst rupture. The damage rate of ion-exchange resin calculated is about 3%.

2.4.4. Brunauer−Emmett−Teller. The pore conditions of the NKC-9 resin were determined by the Brunauer−Emmett−Teller (BET) test. Figure 10 shows the adsorption and desorption curves of NKC-9. It can be seen from the pore size distribution curve in Figure 11 that the pore size of the catalyst ranges from 20 to 100 nm. The specific surface area, pore volume, and average pore diameter of the catalyst calculated by the BET and BJH models are 27.387 m\(^2\)/g, 0.205 cm\(^3\)/g, and 29.928 nm, respectively.

2.4.5. X-ray Diffraction. The X-ray diffraction (XRD) patterns of the fresh and new regenerated NKC-9 catalyst were obtained using a power X-ray diffractometer (Rigaku Dmax-C) with Cu K\(_{α}\) radiation (\(k = 1.5405\) Å). The XRD patterns were scanned from 2θ = 10° to 90°. As is clearly shown in Figure 12, three broad peaks are found at the 2θ range of 18.4°, 28.3°, and 43.3° for the fresh NKC-9 catalyst. The other weak peaks can be attributed to monoclinic zirconia.
From the Figure 12, it is also found that the three main peaks at 18.4°, 28.3°, and 43.3° still present in the XRD pattern of the regenerated NKC-9. In addition, the XRD pattern of the regenerated NKC-9 catalyst is almost identical with that of the fresh NKC-9 catalyst, indicating the excellent regeneration performance of the NKC-9 catalyst.

2.5. Kinetics Model. Considering the non-ideal behavior of the reaction system in liquid phase, the activity \(a_i\) of the components was used to replace the mole fraction \(x_i\) in the equilibrium state. Thus, the thermodynamic equilibrium constant \(K_e\) was obtained by the UNIFAC group contribution method.\(^{21-23}\)

\[
K_e = \frac{a_{MEM1^2H_2O} \cdot x_{MEM1^2H_2O} \cdot y_{MEM1^2H_2O}}{a_{MOA} \cdot x_{MOA} \cdot y_{MOA}} = K_e \cdot \gamma
\]

(1)

As shown in Table S1, the equilibrium constant \(K_e\) of the reaction increases with the increase of reaction temperature, indicating that the reaction is endothermic. In \(K_e\) was also used to plot \(1/T\) to get the relation between reaction equilibrium and temperature. Therefore, the thermodynamics of the reaction is calculated by the van’t Hoff equation. As shown in Figure 13, the relation between the equilibrium constant and the temperature can be obtained as follows

\[
\Delta G^o = -RT \ln K
\]

\[
\Delta G^o = \Delta H^o - T\Delta S^o
\]

\[
\ln K_e = \left(\frac{-\Delta H^o}{RT}\right) + \left(\frac{\Delta S^o}{R}\right)
\]

(3)

(4)

\(\ln K_e\) is plotted with \(1/T\) in pairs as shown in Figure 14. The reaction equilibrium constant \(K_e\) within the temperature range of 366.15−401.15 K can be obtained by linear-fitting the \(\ln K_e−1/T\) curve as expressed in eq 5

\[
K_e = 4.686 \times 10^4 \exp\left(-\frac{2.347 \times 10^4}{RT}\right)
\]

(5)
The enthalpy change of reaction can be obtained by the Hoffmann equation. As shown in Table 1, this reaction is endothermic at 298.15 K because of $\Delta H^\circ = 23.474 \text{ kJ} \cdot \text{mol}^{-1}$. As a result of $\Delta G^\circ = -3.176 \text{ kJ} \cdot \text{mol}^{-1}$, the reaction can occur spontaneously at room temperature.

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Table 1. Enthalpy Change and Entropy Change at Room Temperature

| $T$/K | $\Delta H^\circ$ | $\Delta S^\circ$ | $\Delta G^\circ$ |
|------|-----------------|-----------------|-----------------|
| 298.15 | 23.474 kJ·mol$^{-1}$ | 89.417 J·mol$^{-1}$·K$^{-1}$ | -3.176 kJ·mol$^{-1}$ |

In the reaction process, reactants need to diffuse into the internal gap of catalyst particles, so the specific kinetic mechanism is required to describe the process of adsorption, surface reaction, and desorption in the rediffusion. Considering the different adsorption mechanisms of various kinetic models, it is proposed to adopt the following four kinetic models: pseudo-homogeneous (PH) model, Eley–Rideal (ER) model of adsorption reactant A or B, and LHHW model to verify the experimental kinetic data.

1. PH model

$$-r = A \exp\left(-\frac{E}{RT}\right)\left(\frac{\alpha_{\text{MOA}}\alpha_{\text{MEA}} - \alpha_{\text{MEMI}}\alpha_{\text{H}_2\text{O}}}{K_c}\right)$$

2. ER (1) (Eley–Rideal) model

$$-r = A \exp\left(-\frac{E}{RT}\right)\left(\frac{\alpha_{\text{MOA}}\alpha_{\text{MEA}} - \alpha_{\text{MEMI}}\alpha_{\text{H}_2\text{O}}}{1 + K_c\alpha_{\text{MOA}} + K_d\alpha_{\text{H}_2\text{O}}}ight)$$

3. ER (2) (Eley–Rideal) model

$$-r = A \exp\left(-\frac{E}{RT}\right)\left(\frac{\alpha_{\text{MOA}}\alpha_{\text{MEA}} - \alpha_{\text{MEMI}}\alpha_{\text{H}_2\text{O}}}{1 + K_c\alpha_{\text{MEA}} + K_d\alpha_{\text{H}_2\text{O}}}ight)$$

4. LHHW model

Derivation process

1. Adsorption of MOA

$$\text{MOA} + \sigma \xleftrightarrow[k_1]{k_{-1}} \text{MOA}\sigma$$

2. Adsorption of MEA

$$\text{MEA} + \sigma \xleftrightarrow[k_2]{k_{-2}} \text{MEA}\sigma$$

3. Adsorbed MOA and MEA reacted on the surface to produce adsorbed MEMI

$$\text{MOA}\sigma + \text{MEA}\sigma \xrightarrow[k_3]{k_{-3}} \text{MEMI}\sigma$$

4. Adsorbed MEMI was desorbed to form imine

$$\text{MEMI}\sigma \xrightarrow[k_4]{k_{-4}} \text{MEMI} + \sigma$$

5. Adsorbed H$_2$O was desorbed to form H$_2$O

$$\text{H}_2\text{O}\sigma \xrightarrow[k_5]{k_{-5}} \text{H}_2\text{O} + \sigma$$

From the normalized equation

$$\theta_i = \frac{K_{i\alpha_i}}{1 + \sum_{j=1}^{N} K_{j\alpha_j}}$$

$$\theta_{\text{MOA}} + \theta_{\text{MEA}} + \theta_{\text{MEMI}} + \theta_{\text{H}_2\text{O}} + \theta_V = 1$$

where $\sigma$ is the active site, and $K_1$, $K_2$, $K_3$, $K_4$, and $K_5$ are adsorption equilibrium constants of each component. Through simultaneous eqs 9–16, the following equation can be obtained

$$-r = A \exp\left(-\frac{E}{RT}\right)\left(\frac{\alpha_{\text{MOA}}\alpha_{\text{MEA}} - \alpha_{\text{MEMI}}\alpha_{\text{H}_2\text{O}}}{(1 + K_c\alpha_{\text{MOA}} + K_d\alpha_{\text{H}_2\text{O}})^2}\right)$$

The exchange capacity $q_t$ for each component with the resin at any time $t$ can be represented with the following equation

$$q_t = \frac{(C_s - C_o) v}{w}$$
where \( C_0 \) and \( C_v \) are the concentration of each component in aqueous solutions at time 0 and \( t \), respectively, and \( v \) is the volume of aqueous solution for each component. \( K_i \) is the adsorption equilibrium constant obtained from the Langmuir isothermal adsorption equation

\[
\frac{C_v}{q_v} = \frac{C_C}{q_m} + \frac{1}{q_m K_i}
\]  \( (19) \)

where \( q_m \) is the maximum adsorption capacity of the resin, and \( K_i \) represents the adsorption equilibrium constant. When the ion exchange reaches the dynamic equilibrium, \( q_v = q_m C_v = C_C \).

The reaction rate constant \( k_i \) and adsorption equilibrium constants of each component \( K_i \) from 369.15 to 401.15 K are presented in Table S2. The relationship between the forward reaction rate constant and temperature is shown in Figure 14 in terms of ln \( k_i - 1/T \). From the Figure 14, the reaction rate constant increases with the increase of temperature. Thus, the kinetic rate equation and data parameters of the condensation reaction can be obtained, which provides data support for the substitution of kinetic model data in the future. According to the Arrhenius equation

\[
k_i = A \exp\left(-\frac{E_i}{RT}\right)
\]  \( (20) \)

\[
\ln k_i = -\frac{E_i}{RT} + \ln A \tag{21}
\]

where \( k_i \) is the forward reaction rate constant, \( E_i \) is the activation energy, and \( A \) is the pre-exponential factor. Therefore, the relationship between the reaction rate constant \( k_i \) and temperature can be obtained by linear regression from Figure 14 as follows

\[
k_i = 6.727 \times 10^3 \exp\left(-\frac{1.584 \times 10^4}{RT}\right)
\]  \( (22) \)

Finally, the data of \( k_i, K_{1i}, K_{2i}, K_{4i}, K_{5i} \) and \( K_e \) are substituted into the expression 17 to obtain the condensation reaction rate expression.

\[
r = 6.457 \times 10^3 \exp\left(-\frac{1.571 \times 10^4}{RT}\right)\frac{a_{MOA}a_{MEA} - a_{MEOA}a_{MOE}}{K_e} \frac{1}{(1 + K_{4i}a_{MOA} + K_{5i}a_{MEA} + K_{5i}a_{MEOA} + a_{H_2O})^2}
\]  \( (23) \)

In the batch reaction process, the reaction rate of component \( i \) can be written according to the mass conservation as follows

\[
r_i = \frac{n_0}{m_{cat}} \frac{dx_i}{dt}
\]  \( (24) \)

The calculated reaction rate is expressed as \( r_{calc} \) and the experimental measured rate is expressed as \( r_{exp} \). The parameters of different kinetic models can be determined with the value of minimizing the sum squares of residues (SRSmin) according to the calculated reaction rate \( r_{calc} \) and experimental measured rate \( r_{exp} \).

\[
SRS_{min} = \sum_{i=1}^{N} (r_{exp} - r_{calc})^2
\]  \( (25) \)

The parity plot between calculated and experimental obtained reaction rates of LHHW model are shown in Figure 15. The regression data of the theoretical reaction rate of different kinetic models and the experimental measured reaction rate at different temperatures obtained using MATLAB software are presented in Table 2. As shown in Table 2, the SRSmin for LHHW model is the smallest in comparison with other models, so the LHHW model can be used to best represent the kinetic behavior of catalytic condensation reaction. According to Figure 15 and Table 2, which shows the comparison between the figure and SRS, LHHW < ER(2) < ER(1) < PH, so the LHHW model can better represent the kinetic behavior of catalytic condensation reaction.

Thus, the kinetic rate equation and the parameters of the condensation reaction of methoxyacetone with 2-methyl-6-ethyl aniline using NKC-9 as the catalyst are presented in Table S3. At the same time, we can get a plot of ln \( k_i \), ln \( K_{1i} \), ln \( K_{2i} \), ln \( K_{4i} \), and ln \( K_{5i} \) versus 1/T for condensation reaction shown in Figure S1.

**2.6. Recycling Performance of the Regenerated NKC-9 Catalyst.** The recycle times of the regenerated NKC-9 catalyst and its impact on the conversion of MEA is another important factor to characterize the performance of the cation-exchange resin, which is indicated in Figure S2. According to the abovementioned characterization results, the NKC-9 resin still keeps high catalytic activity in the recycling process. However, as can be seen from Figure 9, in the reaction process, rapid stirring may lead to catalyst rupture or adsorption, deposition, and collision in the catalytic process, which will also lead to the reduction of catalytic activity. Therefore, when
the catalyst was used for five times, the catalytic activity appeared to decline slowly.

3. CONCLUSIONS

In this study, MEMI was synthesized for the first time in a batch reactor using different ion-exchange resins: D113, NKC-9, and 001*7. In the meanwhile, the synthesis kinetics was studied to provide data support for future industrial continuous production. It was found that the NKC-9 cation-exchange resin had the most outstanding catalytic property among those investigated resins, and therefore it was chosen for further study. Thereafter, the optimal operating conditions of the catalytic reaction was determined at temperature of 393.15 K, catalyst loading of 0.025 g/g liquid mixture, and reactant molar ratio of 1:1.7. In addition, the influence of external diffusion of the reaction system was eliminated with the stirring speed of 450 rpm, while the influence of the internal diffusion could be wiped off with the catalyst particle size superior to 45 mesh. The thermodynamic equilibrium constant $K_e$ was obtained by the UNIFAC group contribution method at temperature range of 367.15 to 401.15 K. The reaction enthalpy change at 298.15 K is 23.47 kJ mol$^{-1}$, indicating that the reaction is endothermic, whereas the Gibbs free energy change calculated by Hoffman equations is 3.176 kJ mol$^{-1}$, suggesting that the reaction is spontaneous at room temperature.

Through the calculated reaction rate value and the regression of experimental dynamic data, it is shown that the LHHW model can best represent the kinetic process of Schiff base synthesis reaction. In addition, the study of thermodynamics and kinetics data will provide the optimal experimental base synthesis reaction. In addition, the study of thermodynamics, kinetic rate equation, and parameters related to kinetics and thermodynamics, kinetic rate equation, and parameters of the condensation reaction (PDF).

4. EXPERIMENT

4.1. Materials. 2-Methyl-6-ethyl aniline (chemical pure, Agricultural Development in Henan Agrochemical Co. Ltd.), methoxy acetone (chemical pure, Shandong Qiao Chang Chemical Co. Ltd.), toluene (analytical pure, Sinopharm Chemical Co. Ltd.), and D113, NKC-9, 001*7 Ion-exchange resins (Nankai University, China) were produced by chemical plants in China. The resin was pretreated before use. It was soaked in saturated NaCl solution for 8 h to remove impurities, then soaked in 5% dilute hydrochloric acid for 4 h to stimulate acidic sites, and finally washed with deionized water. The physical and chemical properties of cation-exchange resin are shown in Table S4.

4.2. Preparation of the Schiff Base. The synthesis of the Schiff base was carried out in a three-neck flask containing a water separator, a reflux condenser, a sampling device, and a thermometer. First, the reactant methoxacetone and 2-methyl-6-ethyl aniline were weighed and added to the volumetric flask, followed by toluene with water agent, and then the corresponding molecular weight of the ion-exchange resin was determined and it was added to the flask. The experiments at different conditions were carried out by adjusting the vacuum degree and changing the temperature of the reaction system. In the reaction process, syringe timing sampling was used for real-time detection by an Agilent gas chromatograph (7890B, Shanghai Lairui Scientific Instrument Co., Ltd.)

$n$-(2-Methyl-6-ethyl phenyl)-1-methoxypropyl-2-imide:

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.11–1.14 (3H, t), 1.67 (3H, s), 1.99 (3H, s), 2.30–2.41 (2H, m), 3.48 (3H, s), 4.19 (2H, s), 6.92–6.95 (1H, t), 7.00–7.05 (2H, q); $^{13}$C NMR (500 MHz, CDCl$_3$): $\delta$ 13.85, 16.93, 17.92, 24.42, 58.84, 123.11, 125.40, 125.96, 127.86, 131.73, 147.46, 169.51. As shown in Figures S3 and S4.

4.3. Analytical Methods and Characterizations. The yield of the target product was determined by GC (Agilent 7890B, Shanghai Lairui Scientific Instrument Co., Ltd.), and the specific conditions were shown as follows: chromatographic column: se-3 quartz capillary column, the column length was 50 m. The pre-column pressure of hydrogen and nitrogen carrier gas was 0.1 MPa, and that of air was 0.03 MPa. Injection volume: 0.1 μL; Sample temperature: 523.15 K; FID detection temperature: 553.15 K; keep application temperature: 353.15 K/5 min, after rising at a rate of 283.15 K/min to 573.15 K, keep 2 min. At the same time, benzyl alcohol was used as the internal standard to calibrate the actual content of each component. MEA conversion is defined as the ratio of the MEA conversion amount to MEA total amount.

It was found by gas chromatograph and NMR that no impurity peaks appeared except the peaks of products, raw materials and solvents. Therefore, this esterification reaction catalyzed by ion-exchange resins is thought to be without byproducts, approximately.

The calculation method of conversion ($X_i$) and yield ($Y_i$) is shown as formulas 26 and 27, where $n_i$ is the molar number of component $i$ and $n_{i,f}$ is the molar number of component $i$ after $t$ time.

$$X_i = \frac{n_{i,0} - n_{i,f}}{n_{i,0}} \times 100\% \quad i = (\text{MOA, MEA}) \quad (26)$$

$$Y_i = \frac{n_{i,f}}{n_{\text{MEA,0}}} \times 100\% \quad i = (\text{MEMI, H}_2\text{O}) \quad (27)$$

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01197.

Product NMR, reaction equilibrium constants and reaction rate constants related to kinetics and thermodynamics, kinetic rate equation, and parameters of the condensation reaction (PDF).

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NOMENCLATURE

ER (1) Eley–Rideal (1) ER (2) Eley–Rideal (2) LHHW Langmuir–Hinshelwood–Hougien–Watson

\[ X_i \] concentration of component \( i \)

PH pseudo-homogeneous

MOA methoxyacetone

\( \theta \) surface concentration of component \( i \)

MEA 2-methyl-6-ethyl aniline

\( x \) molar fraction of the component

\( \gamma \) pre-exponential factor

\( q_i \) each component with the resin at any time \( t \), mmol·g\(^{-1}\)

\( K_0 \) adsorption equilibrium constant of component \( i \)

\( q_m \) the maximum adsorption capacity of the resin, mmol·g\(^{-1}\)

\( K_e \) reaction equilibrium constant

\( C_0 \) the concentration of each component in aqueous solution at time \( t \), mmol·L\(^{-1}\)

\( r_{calc} \) the calculated reaction rate

\( v \) the volume of aqueous solution of each component, L

\( w \) the quality of the dry resin, g

GREEK LETTERS

\( a \) activity; \( \gamma \) activity coefficient; \( \theta \) stoichiometric coefficient

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