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Kinetics of the Transesterification Reaction Catalyzed by Solid Base in a Fixed-Bed Reactor

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Kinetics of the transesterification reaction catalyzed by solid base in a fixed-bed reactor was studied in this paper. The transesterification reaction between palm oil and methanol was catalyzed by KF/Ca−Mg−Al hydrotalcite solid base, which made it a complicated liquid−liquid−solid heterogeneous reaction. Isopropyl ether was used to obtain a homogeneous reactant system, and then liquid−liquid mass-transfer limitations were eliminated. Experimental results showed that, when the feed rate was faster than 0.3 mL/min, liquid−solid external diffusion mass-transfer limitations were negligible and, when the diameter of the catalyst particle was not larger than 0.18 mm, liquid−solid internal diffusion mass-transfer limitations could be neglected as well. Then, intrinsic reaction rates of this transesterification under different space velocities, temperatures, and concentrations were measured in a fixed-bed integral reactor. An intrinsic kinetic model was developed on the basis of the Eley−Rideal mechanism according to the experimental data, which indicated a new mechanism of the transesterification reaction catalyzed by solid base. The transesterification reaction occurred between methanol adsorbed on solid base active sites and glyceride from the liquid phase. The surface reaction of triglyceride with adsorbed methanol was assumed to be rate-determining. The model calculation agreed well with experimental data. Regression of experimental data indicated that the transesterification reaction was an endothermic reaction and the activation energy was 111.6 kJ/mol.

1. Introduction

The energy crisis and environmental pollution are two main issues all over the world. As a potential substitute of fossil energy, biodiesel [fatty acid methyl ester (FAME)] becomes more and more attractive because of its environmental benefits and the fact that it is made from renewable resources,[1,2] which can alleviate both of the two problems.

Among all biodiesel production methods that use different catalysts or different reactors, the process of the transesterification reaction catalyzed by solid base in a fixed-bed reactor is a potential industrial technology because of its significant advantages, such as continuous production, simple purification, and convenient operation.[3,4] In our recent study, it was found that supported hydrotalcite showed high activity of catalyzing the transesterification reaction of vegetable oil with methanol and the yield of biodiesel could reach 90% in 10 min.[5,6] To obtain the relatively high biodiesel yield in a short retention time, KF/Ca−Mg−Al hydrotalcite was chosen as the catalyst in this paper.

Chemical kinetics is a guideline to reactor design and the mechanism study of the reaction. Studying the kinetics of the transesterification reaction in a fixed bed will give some advice on the continuous production of biodiesel. Some kinetic models of the transesterification reaction catalyzed by solid base have been reported. Singh et al.[7,8] investigated the transesterification using heterogeneous metal oxide catalysts, such as MgO, CaO, BaO, PbO, MnO_2, and Na-based mixed metal oxide, in a high-temperature batch reactor and estimated and compared their kinetic parameters (rate constants and orders) to each other. Huang et al.[9] investigated the transesterification of crude soybean oil with methanol catalyzed by $Mg(OCH_3)_2$. Their kinetic model was expressed as the following three significant controlled regions: a mass-transfer controlled region in the internal surface of the heterogeneous catalyst, an irreversible chemical reaction controlled region on the pseudo-homogenous fluid body, and a reversible equilibrium chemical reaction controlled region near the transesterification equilibrium stage.

Dossin et al.[10] investigated the transesterification of ethyl acetate with methanol over magnesium oxide as the solid base catalyst. Their intrinsic kinetic model based on a three-step Eley−Rideal mechanism was proposed according to the kinetic data obtained in a perfectly mixed slurry batch reactor. They believed that the transesterification occurred between

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the methanol adsorbed on solid base free sites and the ethyl acetate from the liquid phase. Among the three steps, methanol adsorption, surface reaction, and ethanol desorption, methanol adsorption was assumed to be the rate-determining step. In another paper,[11] the three-step Eley−Rideal model of the transesterification reaction between triolein and methanol to methyl oleate was chosen to simulate the continuous production of biodiesel from rapeseed oil.

Hsieh et al.[12] investigated the continuous production of biodiesel using Ca-based solid base in a fixed-bed reactor. A Langmuir−Hinshelwood model of transesterification was established according to the experimental data. The overall reaction was described as the adsorption of methanol and vegetable oil, a series of surface reactions, and desorption of FAME and glycerol, and one of the surface reactions was assumed to be rate-determining.

The transesterification of vegetable oil and methanol via solid base is a complicated liquid−liquid−solid heterogeneous reaction. The overall reaction process consists of the intrinsic reaction, interliquid mass transfer, and liquid−solid external and internal mass transfer. Liu et al.[13] established a heterogeneous liquid−liquid−solid model and a liquid−solid model on the transesterification of soybean oil to biodiesel with methanol using solid base catalysts, in which the intrinsic reaction was considered as pseudo-first-order kinetics with a huge molar excess of methanol.

Until nowadays, however, no intrinsic kinetic models of transesterification between vegetable oil and methanol catalyzed by solid base have been reported. Before measuring the intrinsic kinetic data, the limitations of mass-transfer effects must be excluded. The transesterification procedure of methanol with oil catalyzed by solid base includes three mass-transfer processes: mass transfer on the liquid−liquid interface of methanol to oil and external and internal diffusion of the catalyst. When co-solvent is added into the oil and methanol mixture, the reactants will turn into a solvent that has no liquid−liquid interface, so that the liquid−liquid mass transfer can be eliminated.[14,15] Guan et al.[16] proposed some ethers as co-solvents, such as dimethyl ether, diethyl ether, tert-butyl methyl ether, and tetrahydrofuran, in biodiesel production. Meng et al.[17] suggested that isopropyl ether was also an ideal co-solvent for this heterogeneous system. Liquid−solid external and internal mass-transfer resistances can be excluded by the method of an increasing feed rate and a decreasing diameter of the catalyst particle, respectively.

In this paper, interliquid mass transfer and liquid−solid external and internal mass-transfer limitations were eliminated, and then the intrinsic kinetic model of the transesterification between palm oil and methanol catalyzed by KF/Ca−Mg−Al hydrotalcite was established according to experimental data obtained in a fixed-bed integral reactor. The model was based on the Eley−Rideal mechanism, and it indicated a new mechanism of the transesterification catalyzed by solid base.

2. Experimental Section

2.1. Materials and Catalyst Preparation. Palm oil was purchased from the Nanjing Runtai market. CH_3OH was purchased from Nanjing Chemical Reagent Co., Ltd. $(CH_3)_2$-$CH-O-CH(CH_3)_2$ was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. KOH was purchased from Guangdong Guanghua Chemical Factory Co., Ltd.

The KF/Ca−Mg−Al hydrotalcite solid base catalyst was prepared by the procedure described in our previous work.[18]

2.2. Apparatus and Procedure. A fixed-bed integral reactor apparatus was purchased from Tianjin Pengxiang Technology Co., Ltd. The kinetic experiments were conducted in a 12 mm (inner diameter) stainless-steel reactor equipped with a thermowell to insert the thermocouple into the center of the bed. With this arrangement, the reaction temperature could be controlled with a precision of 1 °C and the length of the isothermal section is at least 50 mm. A measured amount of catalyst sample was placed in the isothermal section of the reactor.

In the feed section, isopropyl ether solution of the methanol and palm oil mixture was introduced by a high-performance metering pump into a preheater. The preheater and reactor were set at the same temperature. The products were collected after a water-cooled trap and analyzed offline by a gas chromatograph (Ouhua GC 9160) equipped with a DB-5Ht capillary column (15 m × 0.25 mm × 0.25 mm) via a flame ionization detector (FID). Nitrogen was used as a carrier gas with a flow rate of 2 mL/min. The temperature of the injector and detector were 523 and 633 K.

The FAME yield (equal to the conversion of palm oil, when selectivity of the reaction was considered to be a unit) in each experiment was calculated according to its content in the composition, as analyzed by gas chromatography (GC). The yield was defined as the ratio of the weight of FAME, determined by GC, to the weight of the whole production.

The acid value, saponification value, and average molecular weight of palm oil were determined according to GB/T5530-2005, GB/T5534-2008, and GB/15680-2009, respectively.

3. Results and Discussion

The plug flow pattern for continuous operations is one of the characteristics that are crucial for carrying out a kinetic experiment correctly to obtain intrinsic reaction rates. In our Experimental Section, the diameter of the reactor was 10 times greater than the diameter of the catalyst particle, while the length of the catalyst bed was 100 times greater than the diameter of the catalyst particle. Then, a plug flow pattern could be achieved.[19]

It was found that conversion of palm oil over KF/Ca−Mg−Al hydrotalcite catalyst in fixed bed reactor was almost constant during a period of 8 h, then all the kinetic experiments were carried out under steady-state conditions and the conversions were measured after the reaction run for 3 h.

Acid value and saponification value were 0.3726 mg of KOH/g and 198.2992 mg of KOH/g, respectively. Average molecular weight of palm oil was calculated using acid value and saponification value (according to GB/15680-2009). The average molecular weight was 850.3149 g/mol and with this value, the molar number of palm oil could be measured accurately.

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3.1. Eliminating Mass-Transfer Resistances. Isopropyl ether was added into the reactant mixture and homogeneous system was obtained, which meant that mass transfer resistances between the oil-methanol phases disappeared.

The "retention time" was defined as the ratio of the catalyst weight (W) to the volume feed rate (V). In these experiments, the catalyst weight was increased proportionally with the increasing of the volume feed rate; therefore, the retention time (W/V) could keep constant, which meant that all of these reactions were under the same reaction time. Under the constant retention time, when conversions of the reactant did not change along with the feed rates, the liquid−solid external diffusion mass-transfer resistances could be neglected. Figure 1 shows conversions of the same retention time with different feed rates. As a result, to avoid external diffusion limitations, the feed rate should be controlled faster than 0.3 mL/min.

When conversions of the reactant did not change along with the diameter of the catalyst particle, the liquid−solid internal diffusion mass-transfer resistances could be neglected. Results in Table 1 show that, when the diameter of the catalyst was not larger than 0.18 mm, the conversions hardly changed and, in this case, internal diffusion limitations were negligible.

3.2. Intrinsic Kinetic Model. The transesterification reaction can be represented as eq 1.

$$\text{palm oil} + 3\text{methanol} \leftrightarrow 3\text{FAME} + \text{glycerol} \quad (1)$$

The intrinsic kinetic experiments were conducted in the absence of mass-transfer limitations. The reaction rate of

the transesterification reaction catalyzed by solid base is defined as eq 2.

$$r_p = -\frac{dF_p}{dW} = -\frac{dF_{p0}(1-x)}{dW} = F_{p0}\frac{dx}{dW} = \frac{dx}{d(W/F_{p0})} \quad (2)$$

The cubic B spline function was used to fit kinetic data and calculate reaction rates at experimental points. The results are presented in Table 2.

The Eley−Rideal mechanism model was used to derive a rate equation for the transesterification reaction of palm oil and methanol in the fixed-bed reactor. According to this model, the reaction consisted of three steps: the adsorption of methanol, a series of surface reactions of adsorbed methanol with glyceride from the liquid phase, and the desorption of glycerol. Equation 3 describes the overall reaction of triglyceride (A) and methanol (B) to form three FAME (C) and glycerol (D). The elemental steps of the transesterification are proposed in eqs 4−8. It was assumed that only methanol and glycerol adsorbed on active sites of the KF/Ca−Mg−Al hydrotalcite solid base catalyst. At first, methanol (B) adsorbed on the active sites of the catalyst. Then, triglyceride from the liquid phase reacted with one molecule of adsorbed methanol to generate one FAME (C) and diglyceride (E). The diglyceride further reacted with adsorbed methanol to generate one monoglyceride (F) and one more FAME (C). Finally, the monoglyceride reacted with adsorbed methanol to generate the last FAME (C) and adsorbed glycerol (D). Glycerol (D) eventually desorbed from the active sites of the catalyst.

$$A + 3B \leftrightarrow 3C + D \quad (3)$$

$$B + \sigma \leftrightarrow B\sigma \quad (4)$$

$$B\sigma + A \rightarrow C + E + \sigma \quad (5)$$

$$B\sigma + E \leftrightarrow C + F + \sigma \quad (6)$$

$$B\sigma + F \leftrightarrow C + D\sigma \quad (7)$$

$$D\sigma \leftrightarrow D + \sigma \quad (8)$$

$$r_p = \frac{k\left(C_A C_B - \frac{1}{K}\frac{C_C^3 C_D}{C_B^2}\right)}{1 + K_B C_B + K_D C_D} \quad (9)$$

It was reported by Hattori et al.[20] that the surface reaction should be assumed to be rate-determining when solid super base catalysts were used to catalyze transesterification. Noureddini et al.[21] showed that the reaction of triglyceride with methanol was slower than those of di- and monoglycerides. Therefore, eq 5 was assigned to be rate-determining. All of the other steps were assumed to be equilibrium states. Equation 9 was derived to be the rate equation of the overall reaction after a reasonable mathematical procedure. The method of multiple nonlinear regressions was used to estimate
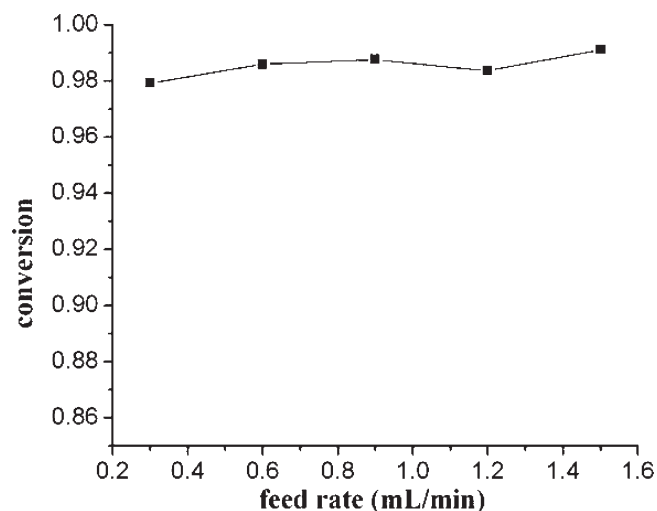

Figure 1. Liquid−solid external diffusion effects (T, 333 K; c_{p0}, 0.3983 mol/L; m, 12; W/V, 3.3333 g min mL^{-1}).

Table 1. Liquid−Solid Internal Diffusion Mass-Transfer Effects (T, 333 K; c_{p0}, 0.3983 mol/L; m, 12; W, 3 g; V, 0.9 mL/min)
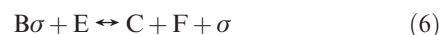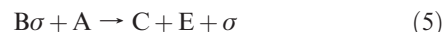
d_p (mm)	0.83−0.38	0.38−0.25	0.25−0.18	0.18−0.15	<0.12
x (%)	65.89	94.78	97.84	98.20	98.76

Table 2. Intrinsic Kinetic Data and Calculation of Reaction Rates (T, 333 K; c_{p0}, 0.3983 mol/L; m, 12; W, 3 g)

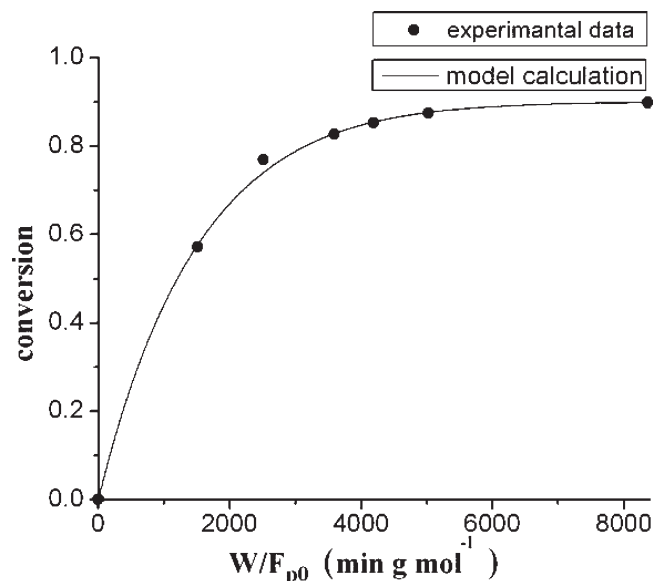| V (mL/min)		5	3	2.1	1.8	1.5	0.9
F_{p0} (×10^{-3}, mol min^{-1})		1.9915	1.1949	0.8364	0.7169	0.5975	0.3585
W/F_{p0} (×10^3, min g mol^{-1})		1.5064	2.5107	3.5867	4.1845	5.0213	8.3689
x	0	0.5716	0.7696	0.8294	0.8591	0.8661	0.8843
$dx/d(W/F_{p0})$ (×10^{-3}, mol min^{-1} g^{-1})	0.5185	0.2485	0.1274	0.0417	0.0069	0.0068	0.0063

Figure 2. Experimental data and model calculation of kinetics (*T*, 333 K; c_{p0}, 0.3983 mol/L; *m*, 12; *W*, 3 g).

Table 3. Regression of Model Parameters under Different Temperatures (c_{p0}, 0.3983 mol/L; *m*, 12; *W*, 3 g; *V*, 0.9 mL/min)

T (K)	*k* (L^2 mol^{-1} g^{-1} min^{-1})	*K*	K_B (L/mol)	K_D (L/mol)	*x* (%)
333	0.00112	0.220	0.52	1.04	88.43
328	0.00045	0.140	0.82	1.84	67.24
325	0.00026	0.080	0.90	2.94	48.79
318	0.00014	0.064	1.03	3.65	31.82
313	0.00008	0.043	1.35	4.34	13.83

the four model parameters (*k*, *K*, K_B, and K_D). Experimental data and model calculation are compared in Figure 2.

As Figure 2 shows, model calculation agreed well with experimental data, which means that the Eley−Rideal mechanism model was appropriate to describe the kinetics of the transesterification reaction between palm oil and methanol catalyzed by KF/Ca−Mg−Al hydrotalcite solid base in a fixed-bed reactor. Similarly, model parameters of other temperatures were regressed, and the results were showed in Table 3.

As Table 3 shows, rate constants increased with the increase of the temperature, which obeyed the Van't Hoff law. Reaction equilibrium constants also increased with the increase of the temperature, which means that the transesterification of palm oil with methanol was an endothermic reaction and was consistent with the literature reported.[12] The kinetic data were found to obey the Arrhenius law in the temperature range investigated.

$$k = A e^{-E_a/RT} \qquad (10)$$

$$\ln k = \ln A + \left(-\frac{E_a}{R}\right)\frac{1}{T} \qquad (11)$$

The parameters of the Arrhenius model were estimated by mean of linear regression. Figure 3 shows a good linear relationship of the two variables (ln *k* and 1/*T*) in eq 11 (correlation coefficients is 0.986).
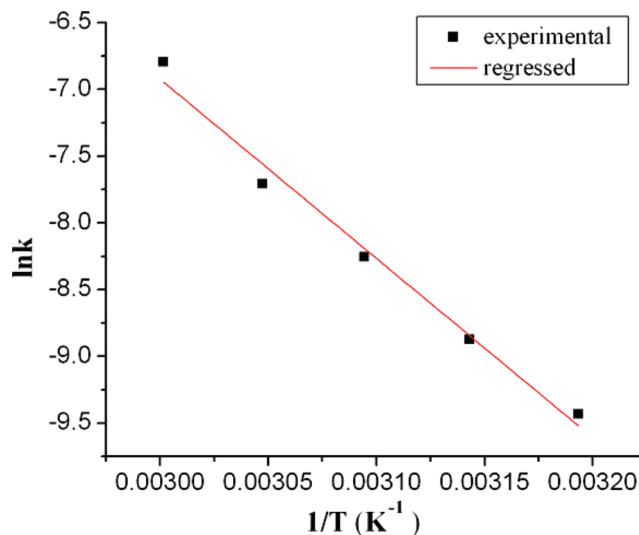
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Figure 3. Regression of rate constants.

Table 4. Verification of Model Calculations (*T*, 333 K; *m*, 12; *W*, 3 g; *V*, 0.9 mL/min)

molar ratio of palm oil/methanol	3:1	6:1	12:1	18:1	30:1
model calculation (%)	40.65	65.53	89.81	95.66	96.43
experimental data (%)	43.25	73.80	88.43	95.84	98.32

The activation energy was estimated to be 111.6 kJ/mol. It can be concluded that, in the presence of the KF/Ca−Mg−Al hydrotalcite solid base catalyst, conversion of the reaction increased significantly along with the increase of the reaction temperature. This conclusion was confirmed in the experiment; when the reaction temperature was 313 K, the conversion was only 13.83%, and when the reaction temperature was 333 K, the conversion could reach 88.43%. As a result, the reaction temperature was a key factor impacting the transesterification at the view of both kinetic and thermodynamic aspects. The value of adsorption equilibrium constants (K_B and K_D) decreased with the increase of the temperature because of the exothermic adsorption process. In addition, all adsorption equilibrium constants of methanol under different temperatures were less than that of glycerol, which could be explained by the fact that the hydroxyl value of methanol was smaller.

3.3. Verification of the Model. Model calculation and experimental conversion under different molar ratios of palm oil/methanol are compared to each other in Table 4. The deviation was less than 10%, which implies that the kinetic model can predict conversion of transesterification within a certain range.

4. Conclusion

Isopropyl ether was a perfect co-solvent of the palm oil and methanol system and was added to the methanol−oil mixture to obtain a homogeneous reactant system, so that liquid−liquid mass-transfer limitations were eliminated. When the feed rate was faster than 0.3 mL/min, external diffusion mass-transfer limitations were negligible, and when the diameter of the catalyst particle was less than 0.18 mm, the internal diffusion mass-transfer limitations could be neglected as well.

Under the conditions of eliminating all mass-transfer limitations, an Eley−Rideal mechanism model was proposed to

describe the kinetic performance of the transesterification in a fixed-bed reactor and the surface reaction of triglyceride with adsorbed methanol was assumed to be the rate-determining step. Parameters of the model were regressed according to experimental data. The new mechanism model could reflect the kinetics of the transesterification catalyzed by KF/Ca−Mg−Al hydrotalcite solid base in a fixed-bed reactor reasonably, and the model calculation agreed well with the experimental data. With the intrinsic kinetic model described in this paper, the biodiesel technology of the transesterification reaction catalyzed by solid base in a fixed-bed reactor can be studied further.

Nomenclature

A = pre-exponential factor ($L^2 \, mol^{-1} \, g^{-1} \, min^{-1}$)

c_i = concentration of component i ($mol \, L^{-1}$)

c_{i0} = initial concentration of component i ($mol \, L^{-1}$)

d_p = diameter of the catalyst particle (mm)

E_a = activation energy ($kJ \, mol^{-1}$)

F_i = mole feed rate of component i ($mol \, min^{-1}$)

F_{i0} = initial mole feed rate of component i ($mol \, min^{-1}$)

k = reaction rate constant of transesterification ($L^2 \, mol^{-1} \, g^{-1} \, min^{-1}$)

K = reaction equilibrium constant

K_i = adsorption equilibrium constant of component i ($L \, mol^{-1}$)

m = molar ratio of palm oil/methanol

R = gas constant ($J \, mol^{-1} \, K^{-1}$)

r_p = reaction rate of transesterification ($mol \, g^{-1} \, min^{-1}$)

T = reaction temperature (K)

V = volume feed rate ($mL \, min^{-1}$)

W = weight of catalyst (g)

x = conversion of the transesterification reaction

σ = void molar fraction of adsorption on the catalyst surface