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# A comparative study on the catalytic performance of different types of zeolites for biodiesel production

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## HIGHLIGHTS

- Different kinetic models were used to describe the esterification over zeolites.
- Al was verified to detect the leaching of active component of zeolite.
- The Cassie–Baxter model was used to study the effect of hydrophobic property.
- The Thiele modulus was used to investigate the effect of zeolite pore size.
- Microporous and micro-mesoporous zeolites were compared in biodiesel production.

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## ABSTRACT

Microporous zeolites (BEA type Beta zeolite and MFI type ZSM-5 zeolite) and micro-mesoporous zeolites (MFI type ZRP-5 zeolite) with various Si/A1 ratios were employed in the esterification of oleic acid with ethanol. The effect of pore size on the internal mass transfer limitation was investigated by Thiele modulus calculation. The results showed that the zeolites with high Si/Al ratios had better catalytic performance, and of these three zeolites at the same Si/A1 ratios, the ZRP-5 zeolite exhibited the lowest internal mass transfer limitations but the worst catalytic performance. Through the comparison of the Eley–Rideal model and the Langmuir–Hinshelwood model, it was indicated that on the surface of hydrophilic ZRP-5 zeolites, the adsorption of the polar ethanol molecules were more favorable than the adsorption of oleic acid molecules, resulting in less coverage of oleic acid molecules on the surface of zeolites and lower conversion rate of esterification. Moreover, the Cassie–Baxter model and the water adsorption capacity test were used to further validate the assumption of kinetic model. The highest conversion rate of 73.6% was achieved when the reaction was catalyzed by high hydrophobic Beta (50) zeolites under optimized conditions of the molar ratio of oleic acid to ethanol of 1:20, catalyst loading of 0.167 meq/g (oleic acid), temperature of 78.0 °C, reaction time of 10.0 h and stirring speed of 600 rpm. The conversion rate of oleic acid remained above 70.0% after five runs and there was no apparent loss of the active component (Al) from the zeolite.



## 1. Introduction

Biodiesel, a biodegradable fuel to replace traditional petroleum-derived diesels, has gaining much attention because of its renewability, non-toxic and low greenhouse gases emissions [1]. Generally, biodiesel is produced by the transesterification using alkaline catalysts [2]. However, the alkaline-catalyzed process suffers from serious limitations that the presences of free fatty acids (FFAs) and water in the feedstock may lead to the formation of soaps, increasing the product viscosity and separation difficulty of downstream products [3]. Compared with alkaline catalysts, the acid catalysts are known to react with the low-quality resources containing high FFAs and/or water under normal conditions. Moreover, the acid catalysts are effective for both esterification and transesterification reactions [4]. Some types of heterogeneous acid catalysts such as the zirconium sulfate [5], ion exchange resins [6], silica supported tin oxides [7] and tin oxide supported $WO_3$ [8]

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have been used for biodiesel production recently. In contrast to the homogeneous catalysts, the heterogeneous catalysts have the advantages of non-corrosion, environmental friendliness, and easy removal from the products, showing the promising potentials for industrial biodiesel productions [9].

As one kind of the solid acids, zeolites are crystalline and porous materials with high specific surface area. Chung et al. [10] compared different microporous zeolites for reduction of free fatty acids in waste cooking oil in esterification reaction (ZSM-5, faujasite, beta and silicalite zeolites). Due to the limitation of the narrow channels, large molecules (like oleic acid molecule, length ~2.4 nm and height ~0.3 nm) cannot access the internal active sites of microporous zeolites. Moreover mesoporous zeolites can be potentially used in biodiesel production and attract many attentions. However, mesoporous zeolites show weaker catalytic activity, which seriously limit their extensive uses. In order to improve the catalytic activities of mesoporous zeolites, various approaches were used to modify mesoporous zeolites including phenylsulfonic acid functionalized SBA-15 zeolite [11], 12-tungstosilicic acid functionalized SBA-15 zeolite [12] and Al supported MCM-41 zeolite [13]. By contrast, micro-mesoporous zeolites have the advantages over either microporous zeolites or mesoporous zeolites [14]. And there were few reports about comparative studies on the catalytic performance of microporous and micro-mesoporous zeolites with various Si/Al ratios for biodiesel production. Besides, to meet the needs of theoretical researches and practical applications, multiple models were developed to describe the process of reaction. Jiang et al. [15] reported a pseudo-homogeneous model to describe the reaction progress of biodiesel production. Merchant et al. [16] compared the Langmuir–Hinshelwood model and the Eley–Rideal model on the biodiesel syntheses catalyzed by cation exchange resins. Konno et al. [17] used the Thiele modulus and the effectiveness factor to study the influence of mass transfer limitation. Han et al. [18] studied the wetting state on the surface of ZSM-5 zeolites using Cassie–Baxter model. However, to investigate the influence of pore size and hydrophobicity on catalysis performance of zeolites, there were few reports discussing the correlation between mass transfer model, wetting state model and kinetic model.

In this study, oleic acid and ethanol were chosen as the model compounds for biodiesel production over zeolites, because both of them are renewable raw materials [19]. The zeolites included microporous zeolites (BEA type Beta zeolites and MFI type ZSM-5 zeolites) and micro-mesoporous zeolites (MFI type ZRP-5 zeolite) with various Si/Al ratio. Several models including the Cassie–Baxter model, the Thiele modulus, the Langmuir–Hinshelwood model and the Eley–Rideal model were used to discuss the correlation between physical prosperities of zeolite (the pore size and the pore surface hydrophilicity) and the performance of catalyst based on the experimental results. The influencing factors of esterification including reaction temperature, Si/Al ratios of zeolites, zeolite loading, the reusability of zeolites and molar ratio of oleic acid to ethanol were analyzed.

## 2. Experimental section

### 2.1. Materials

The zeolites of ZRP-5 (Si/Al = 25), ZRP-5 (Si/Al = 50), ZSM-5 (Si/Al = 25) and ZSM-5 (Si/Al = 50) were kindly supplied by Sinopec Catalyst Co., Ltd., Zibo, China. The Beta (Si/Al = 25) zeolite and Beta (Si/Al = 50) zeolite were purchased from the Catalyst Plant of Nankai University, Tianjin, China. The oleic acid was obtained from Shuangshuang Chemical Reagent Co., Ltd., Yantai, China. Ethanol and $NH_4Cl$ were purchased from Tieta Chemical Reagent Co., Ltd., Laiyang, China. All the reagents were analytically pure.

All H-type zeolites were prepared from Na-type zeolites by following the ion exchange procedure reported by Patel et al. [20]. The Na-type zeolite was added to a 2 M $NH_4Cl$ solution at the mass ratio of 1.0:1.0, and the mixture was stirred at 80.0 °C for 2.0 h. Then, the samples were washed twice with the ultrapure water (resistance 18.2 MΩ, deionized and distilled from the Ulupure UPT-2-401 pure water system), subsequently filtered and dried at 100.0 °C for 12.0 h, and finally calcined at 550.0 °C for 6.0 h. The prepared zeolites were denoted by their Si/Al ratio in the parenthesis after each zeolite name.

### 2.2. Characterization

Prior to testing, all samples were calcined at 500.0 °C for 6.0 h to remove the templates and moisture. The infrared spectra were recorded by using a Nicolet 5700 FTIR (Thermo Electron, USA) in the scanning range of 4000–400 $cm^{-1}$ with the KBr pellet method. XRD spectra were obtained by using a D8 Advance XRD instrument (Brucker, Germany) with a Cu Kα ($\lambda$ = 1.5418 Å) radiation and collected in the range of $2\theta$ = 3–60°. The pore size, pore volume and surface area of the samples were measured at −196.0 °C by $N_2$ sorption (ASAP 2020 system, Micrometitics, USA). Atomic absorption spectroscopy (AA-6601F Shimadzu, Japan) was used to study the leaching of Al from zeolites. The rigorous leaching test was conducted by studying the filtrate at the reaction temperature before the completion of reaction [21]. The reaction mixture was separated by simple filtration.

The particle size distribution analysis was performed using a JL 9200 laser particle size analyzer (Jinan Winner Particle Instruments Stock Co., Ltd., China). The samples were introduced into the dispersion module with ultrapure water as the solvent and sonicated for 1 min at 70 W and 40 kHz. The apparent contact angle of the zeolites was characterized by JY-82 contact angle measuring device (Chengde Dingsheng Testing Machine Equipment Co., Ltd., China) at room temperature. Prior to the measurement, the powder samples (0.2 g) were pressed into tablet under 30.0 MPa for 20 min. Every sample was tested several times and three results which the difference between each other was less than 0.5° were taken into average.

The semi-quantitative analysis of hydrogen ion contents in the zeolite samples was performed by measuring the ion exchange capacity (IEC), namely the number of milli-equivalents of ions (hydrogen ion) in 1.0 g of zeolites. The values of IEC was determined following the method described by Zhu et al. [22]. All samples were measured in duplicate within the error of 3.0%.

### 2.3. Evaluation of catalytic performance of zeolites

The reaction was carried out in a three-necked 250 ml round-bottomed flask, fitted with a water refluxing condenser. The temperature was controlled using a heating jacket which was connected to a thermocouple. The oleic acid, ethanol and zeolites were placed directly into the reactor, and the mixture was stirred at a constant rate by the magnetic agitator in the course of the reaction. When the reaction was completed, the zeolites were separated by filtration, and the excess ethanol was removed by using a rotary evaporator. After that, the zeolites were washed twice with ethanol and dried at 70.0 °C overnight. The recovered zeolites were charged for the next run. The initial acid value of oleic acid (198.73 mg KOH/g) and the acid value of the reacted mixture were determined by titrimetry following the procedure described by Ding et al. [23]. The conversion rates of oleic acid were calculated by Eq. (1).

$$X = \frac{S_0 - S_n}{S_0} \times 100\% \quad (1)$$