



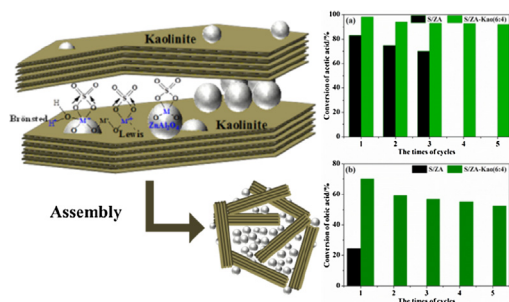
Full Length Article

Esterification for biofuel synthesis over an eco-friendly and efficient kaolinite-supported $\text{SO}_4^{2-}/\text{ZnAl}_2\text{O}_4$ macroporous solid acid catalystAnqi Wang¹, Junxia Wang^{*,1}, Can Lu, Mingliang Xu, Jianhang Lv, Xiuling Wu^{*}

Faculty of Materials Science and Chemistry, Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, China

GRAPHICAL ABSTRACT

An eco-friendly raw kaolinite was used as a novel support to synthesize a highly efficient S/ZAO macroporous solid acid catalyst for typical esterification reactions of oleic acid with methanol and acetic acid with *n*-butanol in the synthesis of green biofuels.



ARTICLE INFO

Keywords:

Bio-fuels
Biomass
Esterification
Kaolinite
Macroporous
Solid acid

ABSTRACT

A series of raw kaolinite-supported $\text{SO}_4^{2-}/\text{ZnAl}_2\text{O}_4$ (S/ZAO) macroporous solid acid catalysts were synthesized and applied in esterification of both oleic acid with methanol and acetic acid with *n*-butanol for the biofuels synthesis. The structures and acidic properties of S/ZAO catalysts were characterized by means of XRD, FE-SEM, EDS, BET, FT-IR (direct and NH_3 adsorbed), NH_3 -TPD, TG and XPS. The results indicated the mass ratio of ZnAl_2O_4 /kaolinite played a significant role in adjusting the active components dispersion, textural and acidic properties. The optimal S/ZAO(6:4) catalysts performed the macroporous structure and the high dispersion of active components, which might be the essential reason for its improved acid sites and reduced limitation of mass transfer. As a result, the macroporous solid acid exhibited superior conversion of 98.2% in acetic acid esterification and 70.1% in oleic acid esterification. The kinetic study demonstrated that the relatively lower values of activation energy over the S/ZAO(6:4) macroporous solid acid, further confirming that the macroporous solid acid was highly efficient for the biofuel synthesis via esterification. Moreover, the further investigation indicated the catalytic activities were closely related to the ratio of Brønsted acid sites on catalysts. Besides, S/ZAO(6:4) macroporous solid acid particularly displayed excellent reusability, which was due to its structural stability and high dispersion of active components.

* Corresponding authors.

E-mail addresses: wjx76@sina.com (J. Wang), xlwu@cug.edu.cn (X. Wu).¹ These authors contributed equally.

1. Introduction

In recent years, the increasing demand for fossil fuel has led to energy shortage and environmental degradation. Therefore, the development of renewable fuels has become a subject of great concern in the past decade [1,2]. Considering its practical application and economic benefits, biodiesel has developed into one of the most promising renewable fuels due to its outstanding advantages of high energy density, biodegradable, sustainable supply and non-toxicity. It is well known that biodiesel is mainly comprised of methyl esters, which can be synthesized by several types of biomass such as plant oils and waste cooking oils. Oleic acid, as a major component in various plant oils, belongs to long chain fatty acids and is widely applied in the esterification reactions for synthesis of methyl esters. Among them, the esterification reaction of oleic acid with methanol has attracted much attention in the perspective of high quality biodiesel products [3,4]. Apart from the biodiesel, the bio-oil is also widely used as another kind of renewable energy to replace the traditional fossil fuels. However, the crude bio-oil always contains various short chain acids, which results in its low pH value and its instability [5,6]. Therefore, acetic acid as a representative short chain acid in crude bio-oils must be removed so as to improve the quality of target bio-oil products because it might be up to 1–36%. Accordingly, numerous studies have shown that the esterification of acetic acid with alcohol, including *n*-butanol, is a key and efficient route to reduce the acidity and improve the stability of bio-oils [6]. Based on the above consideration, the esterification reactions of oleic acid with methanol and acetic acid with *n*-butanol have been extensively studied in recent years.

It is important to note that esterification reactions in the transformation from biomass to biofuels, including the reactions mentioned above, are traditionally catalyzed by homogenous acid catalysts (e.g. H_2SO_4), which have serious drawbacks of the corrosiveness, hazardous waste, complex separation and so on [3]. Compared to homogenous acid catalysts, sulfated metal oxides ($\text{SO}_4^{2-}/\text{M}_x\text{O}_y$) solid acids are a kind of heterogeneous catalysts and have the outstanding advantages of high activities, strong acidic properties, easy recovery and environmental friendliness [7]. For example, the $\text{SO}_4^{2-}/\text{ZrO}_2$ and $\text{SO}_4^{2-}/\text{TiO}_2$, as the most typical $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid acid catalysts, have been widely applied in the biodiesel production from oleic acid esterification and performed superior reactivity [8,9]. Nevertheless, $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid acid catalysts still suffer from rapid deactivation due to the sulfate leaching and coke deposition, which limit their application in industries [8,10]. To solve this problem, remarkable efforts have been devoted to the development of supported $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid acid catalysts, which are prepared by supporting $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ on suitable supports. Moreover, many reports have demonstrated that the introduction of the supports play significant roles in promoting the sulfur stability and the dispersion of the active species. As a result, supported $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid acid catalysts exhibit better catalytic performances than conventional $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid acid catalysts, making them more efficient and suitable for esterification reactions in the transformation from biomass to biofuels [11,12]. However, most of works have been focused on mesoporous silica such as MCM-41, SBA-15 and KIT-6 and so on. Few attempts have been tried to use the natural minerals of raw kaolinite as a novel support to prepare the supported $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid acid catalysts. As a common kind of natural minerals, the raw kaolinite has many considerable advantages of naturally abundant, widely available, nontoxic, eco-friendly and very cheap [13]. Moreover, the raw kaolinite has its own unique performance superiorities of large pore size, high mechanical, thermal stability and flake-like morphology, making it gain much attention in adsorbents, catalysts as well as catalyst supports [13,14]. As supports, the kaolinite has been employed in other catalysts. Kateřina et al. synthesized kaolinite/ZnO composites and revealed the kaolinite support efficiently improved the catalytic performances by restricting the leaching of surface active component [15]. Li et al. reported a heterogeneous $\text{g-C}_3\text{N}_4/\text{TiO}_2/\text{kaolinite}$ with high dispersion,

enlarged surface area and enhanced visible-light absorption ability [16]. Moreover, it is worthy to mention that the kaolinite and kaolinite-contained materials could perform macroporous structures [17,18]. This macroporous feature is always designed in solid acids, since it is important for facilitating the mass transfer in catalyzing the large molecule substances, such as the oleic acids with long carbon chains [19,20]. Therefore, using kaolinites to support active components is supposed to a facile, low-cost and efficient method to improve the catalytic performance of traditional $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$. In our previous work, we have been engaged in using spinel oxides of ZnAl_2O_4 as a new active component for the preparation of spinel-type sulfated ZnAl_2O_4 solid acid catalysts, which exhibited high catalytic activity in the esterification of *n*-butyl acetate [21]. However, pure $\text{SO}_4^{2-}/\text{ZnAl}_2\text{O}_4$ solid acid catalyst still have similar disadvantages of the relatively small surface area and poor reusability with other $\text{SO}_4^{2-}/\text{M}_x\text{O}_y$ solid acids. So, it is still a challenge to further improve the catalytic activities and reusability of $\text{SO}_4^{2-}/\text{ZnAl}_2\text{O}_4$, making it meets industrial demands. To date, there are few reports on esterification reactions in the transformation from biomass to biofuels over raw kaolinite-supported $\text{SO}_4^{2-}/\text{ZnAl}_2\text{O}_4$ ($\text{SO}_4^{2-}/\text{ZnAl}_2\text{O}_4$ -kaolinite, S/ZA-Kao) solid acid catalysts.

In the present work, an attempt had been made to use the eco-friendly raw kaolinite as a novel support to synthesize a highly efficient S/ZA-Kao macroporous solid acid catalyst for typical esterification reactions of oleic acid with methanol and acetic acid with *n*-butanol in the synthesis of biofuels. The influence of $\text{ZnAl}_2\text{O}_4/\text{kaolinite}$ mass ratio on the structures and acidic properties of various S/ZA-Kao catalysts were studied in detail. The relationship between the structures, properties and the activity results was systematically discussed by combining the characterizations and catalytic performances. Additionally, the efficiency of the macroporous solid acid was evaluated by further kinetic study of the two esterification reactions. It is well known that the reusability is of vital importance to heterogeneous acid for industrial application. Thus, the recycling test was taken in this work. Furthermore, the leaching study and characterization of used catalysts were employed to study the stability of sulfate species and explain the slight deactivation. Besides, a possible assembly structure of the kaolinite-supported macroporous solid acid and the reaction mechanism of esterification over catalysts were proposed. This work may provide referential values in the application of raw kaolinite in preparation of eco-friendly, low-cost and highly efficient catalysts and explore their application in the conversion from biomass to green biofuels.

2. Experimental

2.1. Catalyst preparation

The ZnAl_2O_4 was synthesized as same as our previous work [21]. Typically, the $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ at the 1:2 M ratio of Zn:Al were dissolved in ethanol with magnetic stirring. Then, 5 wt% (total mass of metal nitrates) of polyethylene glycol (PEG-2000) was added into the mixture solution. After continuous stirring at room temperature for 4 h, the solution was evaporated with further stirring in the water bath at 60 °C to obtain the sol. The resultant sol was dried in an oven at 120 °C overnight and then ground. The obtained powder was heated to 600 °C (10 °C·min⁻¹) for 5 h in air to obtain the spinel ZnAl_2O_4 .

The $\text{SO}_4^{2-}/\text{ZnAl}_2\text{O}_4$ -Kaolinite catalysts were simply prepared by impregnating the mixture of pre-synthesized ZnAl_2O_4 and raw kaolinite (Chemical composition of raw kaolinite in Table S1) with 1.5 mol·L⁻¹ $(\text{NH}_4)_2\text{SO}_4$ aqueous and stirred continuously at room temperature for 12 h. The mass ratios of ZnAl_2O_4 to kaolinite ratios were chosen 8:2, 6:4, 5:5, 4:6 and 2:8. The impregnated solid phase was separated by filtering and dried at 80 °C for 4 h. The dried samples were calcined at 450 °C for 3 h. The single $\text{SO}_4^{2-}/\text{ZnAl}_2\text{O}_4$ and $\text{SO}_4^{2-}/\text{kaolinite}$ were prepared by a similar method as composite without adding raw kaolinite or ZnAl_2O_4 . The calcined samples were the final catalysts and

Download English Version:

<https://daneshyari.com/en/article/6630044>

Download Persian Version:

<https://daneshyari.com/article/6630044>

[Daneshyari.com](https://daneshyari.com)