Interesterification for biofuel synthesis over HJ-2[#] caly-supported SO₄²⁻/ZrO₂ solid acid catalyst

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Abstract. This study makes use of soybean oil to produce biodiesel using SO₄²⁻/ZrO₂-HJ-2[#] caly solid acid catalyst (SZ-HJ-2[#]). It was through coprecipitation and impregnation method that the catalyst was prepared which was then characterized by means of FE-SEM, XRD, EDS, BET, FT-IR, ICP-MS, NH₃-TPD and XPS. The catalytic property of the synthesized catalyst was determined by using it to produce biodiesel from soybean oil. A study was carried out to find the effect of the different preparation condition of catalyst affecting the process. For SZ-HJ-2[#], Optimized condition of 0.5 mol/L(zirconium salt solution), 1.5 mol/L (the concentration of sulfuric acid impregnating solution) and 450°C(calcination temperature). Optimized conditions of 8.32:1 methanol to soybean oil molar ratio and catalytic loading of 1 wt% at 55°C with a stirring rate of 500 rpm for a reaction duration of 10 h gave a maximum yield of 89.6 wt%. Moreover, the further investigation indicated the catalytic activities were closely related to the ratio of Brönsted acid sites and intensity on catalysts. Besides, the excellent performance of the catalyst during recycling was shown by conducting reusability study.

1 Introduction

In recent years, the increasing demand for fossil fuel has led to energy shortage and environmental degradation^[1]. According to the BP's statistics show that the oil reserve and production ratio in 2019 is only 49.9 years^[2]. The development of cheap and eco-friendly energy source has become one of the main challenges of the current century^[3,4]. Biodiesel as a clean renewable fuel is considered a good alternative for nonrenewable petroleum-based fuel, which has outstanding advantages of high energy density, biodegradable, sustainable supply and non-toxicity^[5].

Biodiesel is generally produced by the transesterification of vegetable oil^[6], animal fat, recycled oil^[7], etc., with methyl alcohol in the presence of a catalyst including basic, acidic or enzymatic catalysts. Therefore, the choice of catalyst is crucial. Conventionally homogeneous basic catalysts such as NaOH and KOH are used. However, there are drawbacks associated with homogeneously catalyzed processes, including corroding equipment, not being reusable and not being easy to separate. Heterogeneous catalysts, on the other hand, makes product separation easier and the reusable^[8]. So far, solid acid catalysts, one kind of heterogeneous catalysts, are widely applied in transesterification reactions^[9].

SO₄²⁻/ZrO₂ (SZ) is one of the SO₄²⁻/M_xO_y type solid super acids, which has the advantages of strong acidity, high activity, easy separation, good thermal stability and regeneration stability^[10]. Nevertheless, SO₄²⁻/M_xO_y solid

acid catalysts still suffer from rapid deactivation due to the sulfate leaching and coke deposition, which limit their application in industries.^[11, 12] To solve these problems, some researchers supported SZ on a molecular sieve with a high specific surface area, such as a MFI framework of ZSM-5^[13], ordered mesoporous molecules of MCM-41^[14] and SBA-15^[15]. However, the stability of catalyst will be affected. Consequently, it remains a big challenge to develop high active and stable heterogeneous catalysts for transesterification reactions. Hangjin 2[#] clay, which is composed of two layers of silica-oxygen tetrahedra and a layer of aluminum (magnesium)-oxygen octahedra, is a 2:1 type of clay minerals, with the advantages of small particle size and large specific surface area^[16]. It has a larger specific surface area, average pore size and total pore volume than montmorillonite and kaolin^[17]. In addition, Hangjin 2[#] clay is inherently acidic. Therefore, it will be an excellent support of solid acid catalysts^[18].

Herein, we realized the improved catalytic activity and stability of solid acid catalyst by synthesizing SO₄²⁻/ZrO₂-Hangjin 2[#] Clay (SZ-HJ-2[#]) with co-precipitation-impregnation method. The influence of zirconium solution concentration, sulfuric acid impregnation solution concentration and roasting temperature during the preparation of the catalyst on the structures and acidic properties of SZ-HJ-2[#] catalyst were studied in detail. The relationship between the structures, properties and the activity results was systematically discussed by combining the characterizations and catalytic performances. It is well known that the reusability is of

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vital importance to heterogeneous acid for industrial application. Thus, the recycling test was taken in this work. Furthermore, characterization of used catalyst were employed to study the stability of sulfate species and explain the slight deactivation. This work may provide referential values in the application of raw HJ-2[#] clay in preparation of eco-friendly, low-cost and highly efficient catalysts and explore their application in the conversion from biomass to green bio-fuels.

2 Materials and Methods

2.1 Materials

HJ-2[#] clay was supplied from Hangjin Banner, Ordos City, Inner Mongolia Autonomous Region, China. It was screened for 200 mesh and dried. The average molecular weight of Soybean oil was obtained at 883.46 g/mol based on the acid value (0.16 mg KOH/g) and saponification value (190.66 mg KOH/g)(see the method of calculation in the Supporting Information). $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (A.R) was purchased from Shanghai Macklin Biochemical Co., Ltd. Analytically pure methanol, petroleum ether and 25%~28% ammonia were obtained from Tianjin Dengke Chemical Reagent Co. Ltd. H_2SO_4 (95-98.0%) was purchased from Sinopharm Chemical Reagent Co. Ltd.

2.2 Synthetic procedures

The In this study, the $\text{SO}_4^{2-}/\text{ZrO}_2$ -HJ-2[#] cally solid acid (SZ-HJ-2[#]) catalyst was prepared by coprecipitation and impregnation. Firstly, 10 g HJ-2[#] clay was mixed with 500 mL 3 mol/L H_2SO_4 , and stirred at 90°C for 4 h. After stirring, the product was washed with water to pH= 5~6 of the filtrate and dried. The product obtained at this time was activated white clay. Secondly, after mixing the activated white clay with different concentrations of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ solution (0.1 mol/L, 0.3 mol/L, 0.5 mol/L, 0.7 mol/L, 0.9 mol/L) at 5:1 (g/mL) for 1 hour, the pH of the mixture was adjusted to 9~10 with 6mol/L $\text{NH}_3 \cdot \text{H}_2\text{O}$ and aged 24 h, the Cl⁻ was removed by water washing (assay with AgNO_3 solution) and dried, followed by precalcined at 400°C for 3 h. The composite carrier obtained was called Zr/HJ-2[#] and then impregnated with different concentrations H_2SO_4 solution (0.5 mol/L, 1.0 mol/L, 1.5 mol/L, 2.0 mol/L, 2.5 mol/L) for 4 h and aged 24 h. Finally, the samples were calcined at different temperatures (250°C, 350°C, 450°C, 550°C, 650°C) for 3 h to obtain SZ-HJ-2[#] catalysts.

2.3 Catalytic Activity

Catalytic activities were tested for biodiesel synthesis. 50g of soybean oil, 18.83 mL of methanol and 2.5 g of SZ-HJ-2[#] were put into a reactor and reacted at 60°C for 6 h. After extraction, washing and drying, the mass of

biodiesel obtained was recorded, The catalyst activity was expressed in terms of biodiesel yield and the yield Y(%) was calculated as follows^[19].

$$Y(\%) = \frac{m_2}{m_1} \times 100$$

where m_1 is the initial mass of soybean oil and m_2 is the mass of biodiesel in the product.

3 Results and Discussion

3.1. Catalyst characterization

Figure 1. SEM images of HJ-2[#] (a), activated clay(b), Zr/HJ-2[#] before precalcined(c), Zr/HJ-2[#](d), SZ-HJ-2[#](e) and SZ-HJ-2[#] after 5 times use(f)

The general morphologies and microstructures of sample were investigated by SEM analysis as shown in Figure 1. The raw Hangjin 2[#] clay(HJ-2[#])(Figure 1a) exhibited typically plate-like morphology which was formed by many parallel nanoflakes. After the sulk morphology of the activated clay as shown in Figure 1b. The smaller bulk were stuck together with some relate activation, there was an obvious fragmentation in semble needles and flakes. After the introducing of Zr (Figure 1c), the number of fine particles decreased significantly, and the particles showed irregular morphology, relatively rough surface, and a large number of free growing small grains. After the precalcination (Figure 1d), the grains grew larger result from recrystallization. Impregnated by sulfuric acid and calcined, SZ-HJ-2[#] (Figure 1e) were prepared. The catalysis were block and the surface was loose and uneven. In addition, the aggregation of catalyst is serious.

Figure 2. EDS mapping images of SZ-HJ-2[#](a) and SZ-HJ-2[#] after 5 times use(g)(The percentages in the legend are weight percentages)

Table 1. Font styles for a reference to a journal article.

Element	Fresh	Used
C	2.08	15.86
O	54.74	57.92
Al	7.37	2.21
Si	25.48	13.40
Zr	3.05	5.38
S	3.29	4.57
K	2.70	0.66
Ti	0.48	--
Fe	0.81	--

According to mapping images in Figure 2(a), the SZ-HJ-2[#] catalysts well maintained the block morphologies and the roughly surface. The distinction of four elements(Si, S, Zr and Al) was given by the mapping image, respectively (Figure 2). The four elements(Si, S, Zr and Al) in SZ-HJ-2[#] catalysts were highly dispersing. It suggested that the experiment condition would facilitate the high dispersion of active components. EDS analysis results were carried out on SZ-HJ-2[#] in Table 1. Combined with the elemental analysis for the region, the ratio of S and Zr atomic percentages in the fresh catalyst and the used catalyst were 1.08 and 0.85, respectively. It suggested that the content of S decreases on the surface of used SZ-HJ-2[#]. SO₄²⁻ was an important condition for the formation of acid sites to sustain the activity in SZ-HJ-2[#]. Therefore, the reduction of S content will seriously affect the catalytic activity of catalysts. Meanwhile, SZ-HJ-2[#] catalysts still contain some Fe and Ti.

XRD measurement was used to further explore the structural insight by analyzing the crystallographic structure, as shown in Figure 3. The activated clay samples showed the characteristic peaks of raw HJ-2[#] (JCPDS No.14-0164), moreover, some impurity peaks including CaCO₃ at 29.38° disappeared after the treatment of sulfuric acid.

Figure 3. XRD patterns of each sample

The strongest diffraction peaks at 20.84° and 26.62° of SiO₂ (PDF#89-8934) were clearly displayed in all samples associated with the activated clay, indicating the structures of the activated clay were well maintained in supported catalysts. Comparing with SZ (Zirconia impregnated with sulfuric acid), the peak 2θ=30.16° of t-ZrO₂ (PDF#88-1007) did not occur in SZ-HJ-2[#] catalysts. It was implied that the Zr in the catalyst may form Zr-O-Si bond on the surface and facilitate to form the efficient catalysts. Introducing ZrO₂ and H₂SO₄ might result in the aggregation of the block structure as shown in FE-SEM morphology in Figure 1. Compared with the peak height of the curve, the impurity was obviously decreased by the SZ loading and almost disappeared in SZ-HJ-2[#] catalyst. The intensity of SiO₂ peaks sharply decreased when introducing the SZ components. As determined by XRD, it also proved that the structure of SZ-HJ-2[#] was different from HJ-2[#] and SZ.

The N₂ adsorption-desorption isotherms of the SZ-HJ-2[#] catalyst was shown in Figure 4 to study the texture. According to the IUPAC classification, the isotherm was ascribed to the representative type IV adsorption-desorption with the hysteresis loop in the relative pressure (P/P₀) ranging from 0.7 to 0.99, reflecting the presence of the macro-porous structure. The hysteresis loop was assigned to the type H3, which represented the formation of slit-shape pores due to the flakes [20,21]. Thus, it suggested that the macro-porous structure in SZ-HJ-2[#] catalyst were generated from the flake-like HJ-2[#] supports, which had been also observed in other HJ-2[#]-based materials[22]. The formed macro-porous structure

had been reported to significantly promote the mass transfer during the reaction and consequently improved the catalytic activities^[23]. Besides, it also performed the

surface areas was 32.07 m²/g, average pore size was 19.14 nm and pore volume was 0.0817 cm³/g.

Figure 4. BET patterns of each sample

FT-IR studies were carried out for the structure of samples (Figure 5a). By compared to the raw HJ-2[#], the activated clay, Zr/HJ-2[#] and SZ-HJ-2[#] catalysts exhibited some intense bands in the range of 1000-1200 cm⁻¹ due to the strong interaction between sulfate species and metal ions. Among them, the bands at 1088 and 1053 cm⁻¹ were assigned to the stretching of S=O bond, indicating that a chelating bidentate structure had been formed between surface sulfate species and Zr ions and contained amount of Brönsted acid^[24]. It was noted that the band of S=O stretching was shifted to high wavenumber gradually by introducing of Zr ions, implying that there might be some synergistic interaction between Zr and HJ-2[#] components influencing the molecular structure of species. These bands were correlated to surface active sites and explained the superior catalytic activities. The bands at 1026 and 987 cm⁻¹ were assigned to Si-O vibrations^[25]. The widen absorption peak in Zr/HJ-2[#] and SZ/HJ-2[#] at 1026 cm⁻¹ appeared obviously, and the location of the peak occurred red shift it to a certain extent compared to the HJ-2[#] (987 cm⁻¹). It was shown that the three-dimensional structure of the silicon oxide was broken and the content of amorphous SiO₂ increases. It suggested that Zr has doped into the structure of HJ-2[#]. The bands at 1637 and 3350 cm⁻¹ were due to OH bending vibrations and stretching vibrations, respectively of water that was adsorbed from the air on the surface of the catalyst^[26]. Additionally, the spectra of HJ-2[#] displayed strong band around at 798 cm⁻¹ was characteristic of Si-O structure. It further confirmed the HJ-2[#] structure was maintain in catalysts well, which

was consistent with the XRD results (see Figure 3). Besides, the weak bands at 3654 and 3568 cm⁻¹ were due to the stretching vibration of -OH on surface metal ion which were easily covered by the broad band from water molecules.

To understand the amount and strength of acid sites, the SZ and SZ-HJ-2[#] catalysts were investigated by NH₃-TPD, as shown in Figure 5(b). It is well acknowledged that the area of desorption peak represents the amount of acid sites, while desorption temperature indicates the acid strength. Generally, the strength of acid sites is classified into weak (< 250°C), medium (250-400°C) and strong (> 400°C) strength^[27]. The broad peak of SZ-HJ-2[#] catalyst indicated the existence of weak and medium strength acid sites on the surface. As for the SZ and SZ-HJ-2[#], it implied that the supports could generate a few strong acid sites after sulfate activation. Among them, the SZ possessed more the strong acid sites than SZ-HJ-2[#] catalyst. By comparing the peak area of SZ-HJ-2[#] (1789.5) with SZ (2977.0), it was suggested that the number of acid sites in SZ-HJ-2[#] is significantly less than that in SZ, but the intensity of acid sites in SZ-HJ-2[#] is higher than that in SZ.

Figure 5. (a) FT-IR patterns of each sample. (b) NH_3 -TPD patterns of SZ-HJ-2[#] and SZ

Chemical valence states were detected by XPS analysis, as shown in Figure 6. The binding energy spectrum of sulfur elements can be divided into 169.0 eV and 170.0 eV, both of which assigned to the sulfur oxidation state of +6.^[28] The S 2p peak has closely spaced spin-orbit components ($\Delta=1.16$ eV). Effect of spin-orbit splitting, either splitting between components or asymmetric peak shape can often be observed. The S 2p_{3/2} peak were at 168.9 and 169.3 eV in SZ-HJ-2[#] and SZ, respectively. The high oxidation state was necessary to prove the formation of bidentate sulfate species, confirming that catalyst possessed acid sites, which may be the main source of the formation of different acid centers in the catalysts. The peaks at 183.2 eV and 185.6 eV were corresponded to Zr 3d_{3/2} and Zr 3d_{5/2} in the sample before calcined due to the formation of Zr-O-Si. The binding energy of Zr decreased slightly after calcined due to part of the Zr-O-Si bond formed ZrO₂. Furthermore, the peak of Zr 3d_{3/2} at 183.55 eV, which shifted to high bonding energy of 0.55 eV (the bond energy of Zr-O-Si was 183 eV). This was because Zr in SZ-HJ-2[#] was affected by the strong electron-absorbing action of SO₄²⁻, which reduced the density of the outer electron cloud of Zr, weakened the shielding effect, and increased the electron binding energy, indicating that strong interaction is formed between Zr and SO₄²⁻. While, the peak of Zr 3d_{3/2} (183.55 eV) in SZ was lower than that of SZ-HJ-2[#] because it was only affected by sulfate radical but not affected by electron absorption of Si. By comparison, it indicated that the density of electron

cloud in the outer layer of Zr atom in SZ-HJ-2[#] was lower than that in SZ, thus the SZ-HJ-2[#] had stronger acidity. The results of NH_3 -TPD test also showed that the acid strength of SZ-HJ-2[#] was higher.

Figure 6. High-resolution XPS spectra of Zr 3d and S 2p in each sample

3.2 Catalytic performances

The optimization of preparation of SZ-HJ-2[#] process was carried out by the controlling variable method. Several offers were presented to optimize the conditions that the parameters are chosen such as the concentration of zirconium salt solution (cZr), the concentration of sulfuric acid impregnating solution (cH₂SO₄) and the calcination temperature of catalyst. In the present study (see Figure 7(a), (b) and (c)), optimum conditions were chosen as 0.5 mol/L, 1.5 mol/L and 450 °C, respectively. The experimental biodiesel yield of 89.6% was achieved with adopting above SZ-HJ-2[#].

Figure 7. Single-factor and cycle experimental data

3.3 Reusability

The reusability of SZ-HJ-2[#] in optimum conditions was assessed in Figure 7(d). After each reaction, the catalyst was washed two times with methanol and petroleum ether and then dried at 90 $^{\circ}C$ for 3 h. According to Figure 7(d), the catalyst keeps its activity for the fourth use. The yield decreased to 72.3% (NO. 4) which could be caused by either the solubility of some sulfate ions on the catalyst surface in mixture products, or the fillings of the catalysts pore spaces. However, the yield sharply reduces after the fifth used (NO. 5). The cause of the decrease has been attributed to the leaching of active phases and poisoning of catalyst surfaces with the reactants and products produced in the interesterification reaction^[29–31]. In the present study, the effects of reactant and product, probably, were meaningfully eliminated by washing methanol and petroleum ether of used catalyst after each reaction. Therefore, the leaching of active phases may be the main reason for deactivation of SZ-HJ-2[#].

Table 2. Font styles for a reference to a journal article

Element		Zr	Al	C
Weight %	Fresh	9.94	4.19	0.12
	Used	9.35	4.02	0.77

In order to explore the cause of deactivation of SZ-HJ-2[#], a series of structural characterizations of the SZ-HJ-2[#] which has used for 5 times was carried out such as FE-SEM, EDS, BET, FT-IR, XPS and ICP-MS. According to the SEM (see Figure.1f) and mapping image, the morphology and element distribution of SZ-HJ-2[#] catalyst did not change significantly before and after catalysis reaction. The N₂ adsorption-desorption isotherms of the used SZ-HJ-2[#] catalyst were shown in Figure 4. The isotherm was ascribed to the representative type IV adsorption-desorption, reflecting the presence of the macro-porous structure. The hysteresis loop was still assigned to the type H3, which represented the formation and structure of used SZ-HJ-2[#] was consistent with that before catalysis.

EDS analysis results were carried out on used SZ-HJ-2[#] in Table 1. It can be found that the composition of surface element changes greatly. By analyzing the relative content, it can be seen that the relative content of Zr increases, while the content of Si, Al and S decreases in varying degrees on the surface of used SZ-HJ-2[#]. According to the ICP-MS date (see Table 2), the overall elemental content of the catalyst does not change significantly, so this elemental loss may be more on the surface of the catalyst. SO₄²⁻ was an important condition for the formation of acid sites to sustain the activity in SZ-HJ-2[#], therefore, the reduction of S content will seriously affect the catalytic activity of catalysts. As evidenced from infrared (IR) spectra(see Figure 5), the stretching vibration peaks of S=O bond near 1088 cm⁻¹ and 1053 cm⁻¹ were obviously wider, indicating that the S=O bond is indeed damaged. Besides, the XPS analysis of used SZ-HJ-2[#] is shown that the shift of S 2p peak to high electron binding energy obviously. It indicated that the chemical environment has changed though S was still +6 and Si-O-Zr bond still existed. In addition, EDS had shown that the content of C increased rapidly. Combined with XPS analysis, it can be considered that there was carbon deposition on the surface of the catalyst, which was also one of the reasons for catalyst deactivation.

4 Conclusions

SZ-HJ-2[#] solid acid catalysts by using the raw HJ-2[#] clay as supports were synthesized and applied in esterification of soybean oil with methanol for the biofuels synthesis. The optimal SZ-HJ-2[#] solid acid well maintained the effective structures of both HJ-2[#] clay and SO₄²⁻/ZrO₂ components. These structures brought about the most intensity acid sites and the easier mass transfer in the reaction. As a result, the SZ-HJ-2[#] solid acid performed the best catalytic activities of 89.6% conversion of soybean oil. Moreover, the relationship between acidic properties and activities clearly indicated the intensity of Brönsted acid on catalysts were favorable for the esterification reactions. Besides, the SZ-HJ-2[#] solid acid showed an excellent performance in reusability conversion of soybean oil in the fifth cycle. The excellent reusability was due to the stable surface sulfate and Brönsted acid sites in the recycling process. The present work indicated that the raw HJ-2[#] clay was constructive in synthesizing a low-cost and eco-friendly, efficient solid acid, which is of vital significance for production of green bio-fuels.

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