

## Production of biodiesel from soybean oil catalyzed by attapulgite loaded with $C_4H_5O_6KNa$ catalyst

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**Abstract**—Biodiesel is a green, safe, renewable alternative fuel, which is of great significance to solving the problem of energy shortage and environmental pollution. A series of solid base catalysts were prepared with the support of attapulgite (ATP), the load of  $C_4H_5O_6KNa$  by impregnation method, and were used to catalyze transesterification of soybean oil with methanol to biodiesel. The activities of prepared catalysts were investigated compared to pure ATP. The optimal conditions for the catalyst preparation were investigated: molar ratio of Na : ATP was 1.7 : 1 and calcination temperature was 400 °C. The prepared catalysts were characterized by several techniques such as Fourier transform infrared spectroscopy, scanning electron microscopy, transmission electron microscopy,  $N_2$  adsorption-desorption measurements, X-ray diffraction and the Hammett indicator method. The prepared solid base catalyst can be separated from reaction system effectively and easily. The effects of the molar ratio of methanol to oil, reaction temperature and amount of catalyst on the biodiesel yield were investigated. The experimental results showed that a 22 : 1 molar ratio of methanol to oil, 10.0% of catalyst amount, 65 °C of reaction temperature and 3.0 h of reaction time gave the best results. The catalyst has longer lifetime and maintained sustained activity after being used for five cycles.

Key words: Transesterification, Biodiesel, Attapulgite, Solid Base Catalyst

### INTRODUCTION

Traditional fossil resources, which will be exhausted shortly, are supplying the majority of the energy needs of the world nowadays. Therefore, finding alternative fuels has attracted considerable attention in recent years. Among these alternative fuels, biodiesel is a promising nontoxic and biodegradable fuel arising from biomass. Fatty acid methyl esters (FAME) show great potential as diesel substitutes, and they are known as the sources of biodiesel, which are synthesized by direct transesterification of vegetable oils with a short-chain alcohol in the presence of a catalyst [1-3]. Currently, most commercial processes used for biodiesel synthesis employ a homogeneous catalyst such as NaOH [4,5] and KOH [6]. Georgogianni et al. reported the production of biodiesel from the soybean frying oil using 2% NaOH as catalyst [5]. It can give a high yield of methyl esters (95%) after a short reaction time (20 min) because the homogeneous base catalyst can significantly accelerate the transesterification reaction. However, it is considerably costly to separate homogeneous catalysts from the reaction mixture [7-10], and purification steps are time consuming and not environmentally benign because a large amount of waste water is produced during these steps [11]. Therefore, conventional homogeneous catalysts are expected to be replaced in the near future by environmentally friendly heterogeneous catalysts, mainly because of environmental constraints and simplifications in the existing processes.

Heterogeneous catalysis is an economically and ecologically important field in catalysis research because these catalysts have many advantages: they are noncorrosive, environmentally benign and present fewer disposal problems. They are also much easier to separate from liquid products and can be designed to give higher activity, selectivity and longer catalyst lifetimes [12-14]. As a result, research on chemical reaction using heterogeneous catalysts had increased over the past decade. Researchers found many solid heterogeneous acid- and alkali-catalysts for biodiesel synthesis. Various carbohydrate-derived and a carbon-based solid acid catalyst have good catalytic activity to high free fatty acid-containing waste oils. However, as the catalytic activity of a base is higher than that of an acid and acid catalysts are more corrosive, base catalysis is preferred to acid catalyzed routes, and is thus most often used commercially [15].

Attapulgite [ $Mg_3Si_8O_{20}(OH)_2(OH_2)_4 \cdot 4H_2O$ , ATP] or Palygorskite is a hydrated magnesium aluminum silicate that exists in nature as a fibrous mineral [16]. It is widely used in petroleum, chemical, building materials, paper, medicine and agriculture due to its special chemical and physical properties and processing properties. In addition, it is a natural, cheap and its rough surface results in a relatively high surface area which can be a good carrier. In this work, a new type of catalyst for biodiesel preparation with  $C_4H_5O_6KNa$  as active component on ATP support was prepared using the impregnation method, and a screening of the reaction conditions was carried out by examining the effect of the concentration of catalyst, the initial methanol/oil, catalyst/oil molar ratio, reaction temperature and time. To the best of our knowledge, this is the first time that the preparation and application of a catalyst  $C_4H_5O_6KNa$ /attapulgite are reported.

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## EXPERIMENTAL

### 1. Materials

Methanol, sodium chloride (NaCl), sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), sodium nitrate ( $\text{NaNO}_3$ ), sodium biphosphate ( $\text{NaH}_2\text{PO}_4$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), sodium tartric ( $\text{C}_4\text{H}_5\text{O}_6\text{Na}$ ) and sodium potassium tetrahydrate ( $\text{C}_4\text{H}_4\text{O}_6\text{KNa}\cdot 4\text{H}_2\text{O}$ ) were purchased from Sinopharm Chemical Reagent Co. Ltd., (Shanghai, China). Soybean oil was obtained from Jinlongyu Company (Fujian, China). ATP was obtained from a Clay Factory. All solvents were AR grade and were used without purification.

### 2. Preparation of Catalyst

The ATP was carried out by acid treatment and the process was as follows. The attapulgite was deposited in a hydrochloric acid solution (100 mL, 2 mol/L) in a flask, and stirred magnetically for 100 min at 60 °C. Then, the solution was vibrated with the aid of an ultrasonic instrument for 10 min at room temperature. After the supernatant was removed, the residue was centrifuged and washed with distilled water several times until pH=7 and dried under vacuum at 100 °C for 12 h. After grinding, the pretreated attapulgite solid was obtained and stored in desiccator.

The catalyst was prepared by incipient wetness impregnation with different concentration of aqueous tartaric acid potassium sodium solution. For this purpose, the required amount of aqueous tartaric acid potassium sodium solution was slowly added to the carrier and kept 24 h. After impregnation, the catalyst was dried for 12 h at 100 °C, and then the solid was calcined in a muffle furnace at designed temperature for 12 h before use for the reaction. The solid base catalyst was obtained.

### 3. Catalyst Characterizations

The Hammett indicator method was used to determine the basic strength of the catalyst [17,18]. Basic strength was expressed by an acidity function ( $H_-$ ) defined by Eq. (1):

$$H_- = \text{p}K_{BH} + \log \frac{[B^-]}{[BH]} \quad (1)$$

where  $[BH^-]$  and  $[B^-]$  are the concentrations of the indicator and its conjugated base, respectively, and  $\text{p}K_{BH}$  is the logarithm of the dissociation constant of the indicator used.

The indicators used were as follows: bromothymol blue ( $\text{p}K_{BH}=7.2$ ), phenolphthalein ( $\text{p}K_{BH}=9.8$ ), and 2,4-dinitroaniline ( $\text{p}K_{BH}=15.0$ ) [19,20]. Typically, 300 mg of the catalyst was mixed with 1 mL of a solution of Hammett indicators diluted in 10 mL methanol and allowed to sit for at least 2 h. After equilibration, the color of the catalyst was noted. The basic strength of the catalyst was taken to be higher than the weakest indicator that underwent a color change and lower than the strongest indicator that underwent no color change. To measure the basicity of solid bases, the method of Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous ethanol solution) titration was used [21].

FT-IR spectra of the samples were obtained between 4,000 and 400  $\text{cm}^{-1}$  on a KBr powder with an FTIR spectrometer (AVATAR 360, Nicolet, Madison, USA). A minimum of 32 scans was signal-averaged with a resolution of 2  $\text{cm}^{-1}$  in the 4,000–400- $\text{cm}^{-1}$  range. Scanning electron microscopy (SEM) images were obtained with 20-kV accelerating voltage with a field emission scanning electron microscope (S-4800, HITACHI Corp., Tokyo, Japan). The morphol-

ogy of the particles was observed by transmission electron microscopy (TEM) (TECNAI-12, Philips Company, Eindhoven, Netherlands) with an acceleration voltage of 120 kV.

The component on the surface of samples was measured by energy dispersive X-ray spectrometer (EDX) (S-4800, Hitachi High-Tech, Japan). X-ray diffraction (XRD) patterns of selected samples were recorded by reflection scan with nickel-filtered Cu  $K\alpha$  radiation (D8, Bruker-AXS, Germany). The X-ray generator was run at 40 kV and 70 mA. All the XRD measurements were performed at  $2\theta$  values between 5 and 80°.

The nitrogen adsorption and desorption isotherms were measured at –196 °C using a NDVA2000e analytical system made by Quantachrome Corporation (USA). The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. Pore size and pore volume were calculated by Barrett-Joyner-Halenda (BJH) method.

### 4. Transesterification Reaction

The transesterification reactions were performed at 60 °C in a 125 mL three-neck reaction flask equipped with a condenser by refluxing 10 mL of methanol (247 mmol) with 10.0 g of soybean oil (commercial edible grade, acid value=0.976 mg KOH/g, saponification index=188.6 mg KOH/g, and average molecular weight=896.88 g/mol) and 1.0 g of catalyst. After the reaction completion, the samples were separated from catalyst and glycerol by centrifuge. The glycerol could be separated because it was insoluble in the esters and had a much higher density. Then methanol was removed using rotary evaporation, and the obtained product was analyzed by gas chromatography (GC) to determine the biodiesel yield.

### 5. Analysis Methods

Reference materials and samples were analyzed by a 7890A gas chromatograph (Agilent Technology Inc. USA), equipped with a flame-ionization detector (FID) and an HP-5 capillary column (30 m×0.32 mm×0.25  $\mu\text{m}$ ). The carrier gas was nitrogen. The oven temperature ramp program was 135 °C for 10 min, 170 °C at 10 °C/min, and held for 10 min. 250 °C at 25 °C/min, and held 2 min. The flow rate of hydrogen was 30 mL/min and the flow rate of air was about 400 mL/min. Temperatures of the injector and detector were 280 and 300 °C. The injection was performed in split mode with a split ratio of 10 : 1. Biodiesel yield was quantified in the presence of tricaprylin as an internal standard. The biodiesel for each sample was analyzed by dissolving 10  $\mu\text{m}$  of biodiesel sample and 8  $\mu\text{m}$  tetradecane as the internal standard into 1 mL of n-hexane and injecting 1  $\mu\text{m}$  of this solution in GC, in the same condition described as above. The biodiesel yield was calculated from the content of methyl esters analyzed by GC with the following Eq. (2):

$$\text{Biodiesel yield} = \frac{m_{\text{tricaprylin}} A_B f_{\text{tricaprylin}}}{A_{\text{tricaprylin}} m_s} \quad (2)$$

where  $m_{\text{tricaprylin}}$ =weight of the internal standard,  $A_B$ =peak area of FAME,  $f_{\text{tricaprylin}}$ =response factor,  $A_{\text{tricaprylin}}$ =peak area of the internal standard, and  $m_s$ =weight of the sample [22].

Sulfur content of biodiesel was determined by inductively coupled plasma emission spectrometer (ICP) using Intrepid XP Radial ICP-OES (VISTA-MPX, Varian, USA) with a concentric nebulizer and CCD detectors technology.

Flash point was determined by a closed-cup tester (BF-02, Dalian North Analytical Instruments Co., Ltd.), by the standard ASTM D 93. The acid number, which is expressed as mg KOH/g, was deter-

mined by titration with 0.01 N potassium hydroxide for the mixture of tested fuel and chemical reagents until the appearance of the color pink. Cetane number was determined by the standard ASTM D6890. Kinematic viscosity was determined by an SYD-265D Kinematic Viscometer (Shanghai Changji Geological Instruments Co., Ltd.) by the standard ASTM D445. The amount of water was measured with a coulometric Karl Fisher titration instrument, according to ASTM D 6304 standard, based on the reduction of iodine by sulfur dioxide in the presence of water. The other properties of biodiesel, such as density at 20 °C and ash content, followed PRC standards: GB/T 2540, SH/T0248 and ASTM D482, respectively.

## RESULTS AND DISCUSSION

### 1. Screening of Catalyst Preparation

Due to the high activity of the catalysts in the transesterification reaction of soybean oil, the influence of catalyst preparation conditions on the conversion of soybean oil was studied to find a higher activity catalyst.

#### 1-1. The Effect of ATP Loaded with Different Sodium Compound on the Biodiesel Yield

A series of Na-compound/ATP catalysts with molar ratio Na : ATP=2.5 : 1 were prepared by the impregnation method. The catalytic activity screening of ATP loaded with different sodium compounds ( $NaCl$ ,  $Na_2S_2O_3$ ,  $NaNO_3$ ,  $NaH_2PO_4$ ,  $NaHCO_3$ ,  $C_4H_5O_6Na$  or  $C_4H_4O_6KNa$ ) in the soybean oil transesterification was performed and the results are summarized in Table 1. Different catalysts were tested in the transesterification reaction under the same reaction conditions. As shown in Table 1, the activities of the catalysts correspond to basic strength and base total amount of the catalysts. The pure ATP,  $NaCl/ATP$ ,  $Na_2S_2O_3/ATP$  and  $NaNO_3/ATP$  samples are found to be weak basic, possessing  $H_L$  values  $H_L < 7.2$  and exhibited no activity. Loading  $NaH_2PO_4$ ,  $NaHCO_3$ ,  $C_4H_5O_6Na$  or  $C_4H_4O_6KNa$  onto the support material (ATP) promoted basic strengths of the catalysts. The biodiesel yield is also low for catalysts with low base strength ( $H_L$ ) in the range of  $7.2 < H_L < 9.8$ , such as  $NaH_2PO_4/ATP$ ,  $NaHCO_3/ATP$  and  $C_4H_5O_6Na/ATP$ . Especially, the prepared  $C_4H_4O_6KNa/ATP$  catalyst demonstrates the superior catalytic activity compared to the other catalysts. It has the strongest base strength and

**Table 1. Catalytic activity and basic strength of ATP loaded with different sodium compounds**

Catalyst	$H_L$	$B_{(Total)}$ (mmol/g)	Yield/wt%
ATP	$H_L < 7.2$	-	No reaction
$NaCl/ATP$	$H_L < 7.2$	-	No Reaction
$Na_2S_2O_3/ATP$	$H_L < 7.2$	-	No Reaction
$NaNO_3/ATP$	$H_L < 7.2$	-	No Reaction
$NaH_2PO_4/ATP$	$7.2 < H_L < 9.8$	0.09	<10
$NaHCO_3/ATP$	$7.2 < H_L < 9.8$	0.12	11.5
$C_4H_5O_6Na/ATP$	$7.2 < H_L < 9.8$	0.41	33.06
$C_4H_4O_6KNa/ATP$	$9.8 < H_L < 15.0$	0.59	69.33

Transesterification condition: molar ratio of methanol/oil, 22 : 1; catalyst amount, 10.0 wt%; reaction time, 2 h; reaction temperature, 60 °C. Catalyst preparation condition: molar ratio, Na : ATP=2.5 : 1; calcination temperature, 400 °C; reaction pressure, 1 atm

**Table 2. The effect of molar ratio of Na : ATP on the biodiesel yield**

Catalyst	Molar ratio (Na : ATP)	$H_L$	$B_{(Total)}$ (mmol/g)	Yield/wt%
ATP	-	$H_L < 7.2$	-	No reaction
ATP-0.8-400	0.8	$9.8 < H_L < 15.0$	0.28	23.9
ATP-1.3-400	1.3	$9.8 < H_L < 15.0$	0.68	79.8
ATP-1.7-400	1.7	$9.8 < H_L < 15.0$	0.89	89.28
ATP-2.1-400	2.1	$9.8 < H_L < 15.0$	0.67	77.67
ATP-2.5-400	2.5	$9.8 < H_L < 15.0$	0.59	69.33

Transesterification condition: molar ratio of methanol/oil, 22 : 1; catalyst amount, 10.0 wt%; reaction time, 2 h; reaction temperature, 60 °C. Catalyst preparation condition: calcination temperature, 400 °C; reaction pressure, 1 atm

gave the highest biodiesel yield. The base total amount of solid base catalyst was also obtained. The results showed that the biodiesel yield increases with base total amount increase. In addition, for catalysts with the similar basic strength ( $7.2 < H_L < 9.8$ ), the one with higher base total amount shows stronger catalytic activity. Based on these results, the catalytic activity is in the following order:  $C_4H_4O_6KNa/ATP > C_4H_5O_6Na/ATP > NaHCO_3/ATP > NaH_2PO_4/ATP$ . Therefore, the basic strength and base total amount could help us to select the suitable solid base catalyst. In this paper, the solid base catalyst  $C_4H_4O_6KNa/ATP$  was selected and further studied as the catalyst for transesterification of soybean oil to biodiesel.

#### 1-2. The Effect of Molar Ratio of Na : ATP on the Biodiesel Yield

The effects of molar ratio of Na : ATP in the solid base catalysts on their catalytic activities were investigated with the molar ratio of Na : ATP ranging from 0.8 : 1 to 2.5 : 1 (Table 2). The ATP does not present any particular catalytic activity, most likely due to the lack of strong basic sites on which the transesterification reaction could occur. However, the loading of  $C_4H_4O_6KNa$  onto the ATP produced a dramatic increment of basic strengths on the  $C_4H_4O_6KNa/ATP$  catalyst, resulting in an increase in the biodiesel yield. As shown in Table 2, when the loading amount of  $C_4H_4O_6KNa$  increased, the biodiesel yield increased and the highest yield of 89.28% was obtained at a molar ratio of Na : ATP 1.7 : 1. However, when the molar ratio of Na : ATP was over 1.7 : 1, the biodiesel yield did not increase significantly, which could be because the ATP was loaded with too much  $C_4H_4O_6KNa$ ; the  $C_4H_4O_6KNa$  could not be well dispersed and, for this reason, not all but only a part of the loaded  $C_4H_4O_6KNa$  could be decomposed. Moreover, the excess  $C_4H_4O_6KNa$  would cover the basic sites on the surface of the catalysts, resulting in a lowered catalytic activity. It demonstrated that the catalyst sample (ATP-1.7-400) had the highest base total amount, reaching 0.89 mmol/g. Therefore, the molar ratio of Na : ATP of 1.7 : 1 was selected and further studied as the catalyst for transesterification of soybean oil to biodiesel.

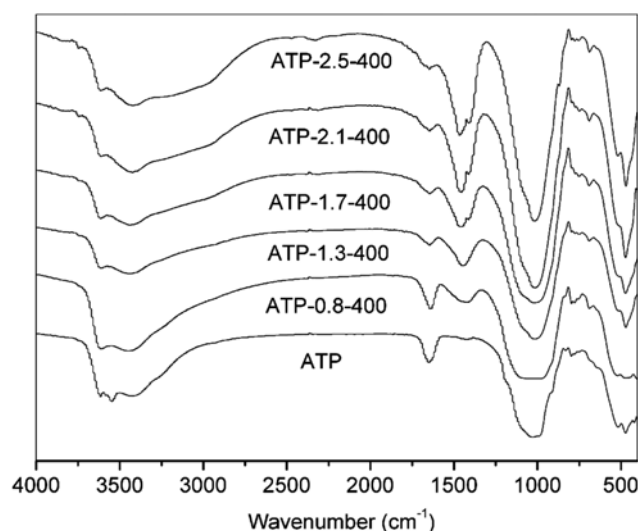
#### 1-3. The Effect of Calcination Temperature on the Biodiesel Yield

The effect of different calcination temperature on the biodiesel yield was investigated and listed in Table 3. The calcination temperature ranged from 200 °C to 600 °C. As shown in Table 3, obviously, with the increase of the calcination temperature, the biodiesel yield increases gradually, mainly because the corresponding sodium compounded gradually decomposition, and formed the base active

**Table 3. The effect of calcination temperature on the biodiesel yield**

Catalyst	Calcination temperature (°C)	H-	B <sub>(Total)</sub> (mmol/g)	Yield/wt%
ATP-1.7-300	300	9.8<H<15.0	0.64	74.18
ATP-1.7-350	350	9.8<H<15.0	0.78	81.88
ATP-1.7-400	400	9.8<H<15.0	0.89	89.28
ATP-1.7-450	450	9.8<H<15.0	0.49	58.05
ATP-1.7-500	500	9.8<H<15.0	0.38	31.72
ATP-1.7-600	600	9.8<H<15.0	0.17	11.95

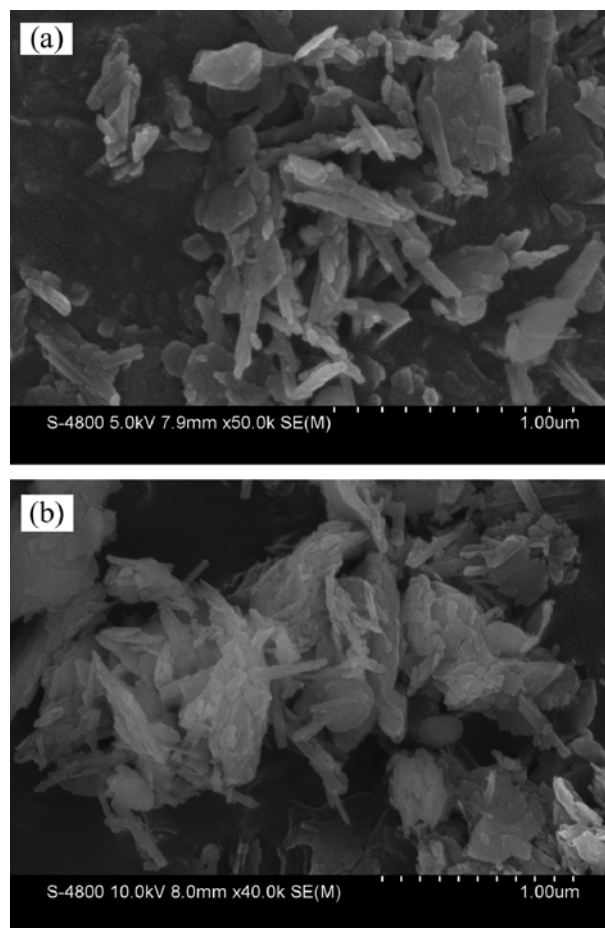
Transesterification condition: molar ratio of methanol/oil, 22 : 1; catalyst amount, 10.0 wt%; reaction time, 2 h; reaction temperature, 60 °C. Catalyst preparation condition: molar ratio, Na : ATP=1.7 : 1; reaction pressure, 1 atm

**Fig. 1. FT-IR spectra of catalysts calcined at various molar ratio of Na : ATP.**

sites. The biodiesel yield was the highest when the calcination temperature was 400 °C. However, with further increase in temperature, the biodiesel yield reduced instead. This is mainly because when the calcination temperature was over 450 °C, the loaded  $C_4H_4O_6KNa$  could be decomposed and got a good dispersion on the surface of the carrier attapulgite, which led to a loss of base active sites. Therefore, the calcination temperature of 400 °C was selected and further studied as the catalyst for transesterification of soybean oil to biodiesel.

## 2. FT-IR Spectra Analysis

FT-IR spectra of catalysts calcined at various molar ratios of Na : ATP were recorded and shown in Fig. 1. The broader band at around 3,300–3,600  $cm^{-1}$  could be partly assigned to the stretching vibration of hydroxy group which linked with Mg, Al inside the structure of the tetrahedron. Also, the absorption band of Si-O-Si is observed at around 980–1,080  $cm^{-1}$  which is completely the same with the absorption band of attapulgite. Moreover, all the samples show an absorption band at 1,415  $cm^{-1}$  that could be attributed to the absorption band of C=O ( $CO_3^{2-}$ ), while this C=O absorption band is not observed on attapulgite without loaded  $C_4H_4O_6KNa$ . Further, as the molar ratio of Na : ATP increases, the intensity of the 1,415  $cm^{-1}$

**Fig. 2. SEM images of (a) ATP and (b) ATP-1.7-400.**

band increases. This is mainly because under the high molar ratio of Na : ATP, the  $C_4H_4O_6KNa$  could be decomposed into  $K_2CO_3$  and  $Na_2CO_3$ . Moreover, FT-IR spectra were almost unchanged after molar ratio of Na : ATP of 1.7 : 1.

## 3. SEM and TEM Analysis

SEM images of (a) ATP and (b) ATP-1.7-400 are shown in Fig. 2. Evidently, no important difference is observed between pure ATP and ATP-1.7-400 catalyst samples, thus suggesting a good dispersion of  $C_4H_4O_6KNa$  on the surface of attapulgite. Based on the obtained results, after loading of  $C_4H_4O_6KNa$ , attapulgite retained its structure, which was important for catalysis, and therefore the sodium species was found highly distributed upon the surface of the support. TEM images of (a) ATP and (b) ATP-1.7-400 are shown in Fig. 3. From the TEM image of ATP, that the ATP consists of irregular ellipsoid and needle composition. In the TEM image of ATP-1.7-400, under high calcination temperature, the  $C_4H_4O_6KNa$  could be decomposed and evenly distributed in the carrier ATP.

The pure ATP and  $C_4H_4O_6KNa$ /ATP catalyst sample were selected for EDX analysis to determine the components of on the surface of ATP and catalyst. The results are shown in Table 4. Typically, plenty of Al and Si was observed. As mentioned, some  $SiO_2$  and  $Al_2O_3$  in ATP may act as catalyst for the decomposition of  $K_2CO_3$  and  $Na_2CO_3$ . Moreover, the sodium and potassium contents of the catalyst are much higher than that of the pure ATP support, indicating that the new formed materials are sodium and potassic compounds. Even

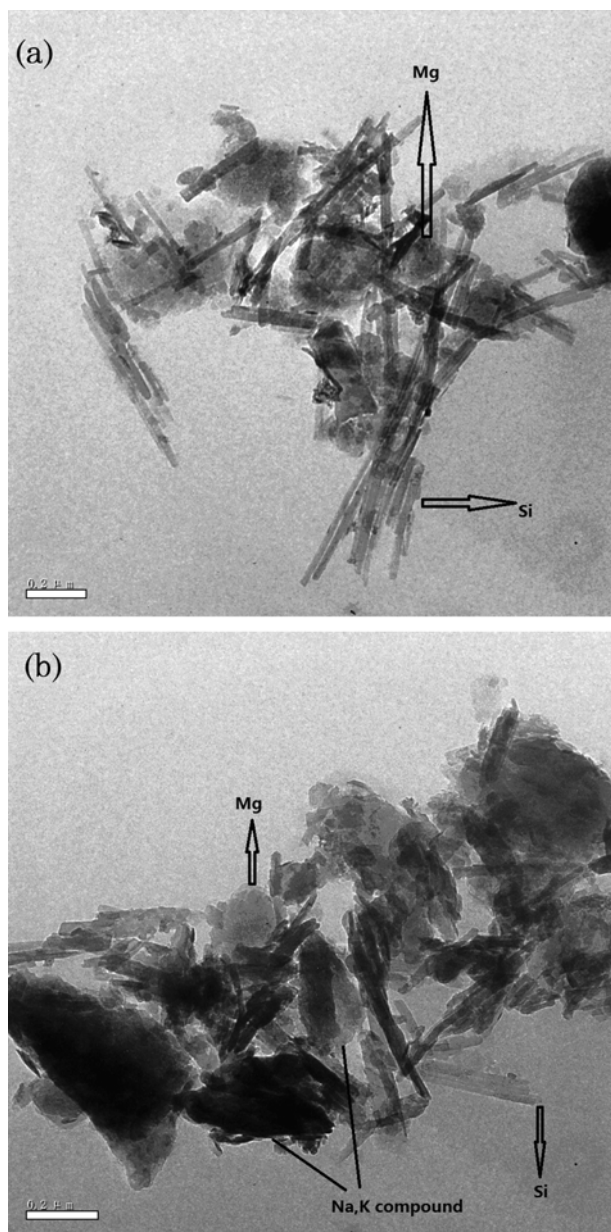


Fig. 3. TEM images of (a) ATP and (b) ATP-1.7-400.

though there is no obvious new material found in Fig. 2(b), the contents of sodium and potassium increased from 0.183% to 9.006%, and from 1.849% to 14.78% are also high, which suggests that the loaded sodium and potassium are more evenly dispersed in the ATP support.

#### 4. Nitrogen Physical Adsorption Analysis

To characterize the specific surface area, pore size and pore vol-

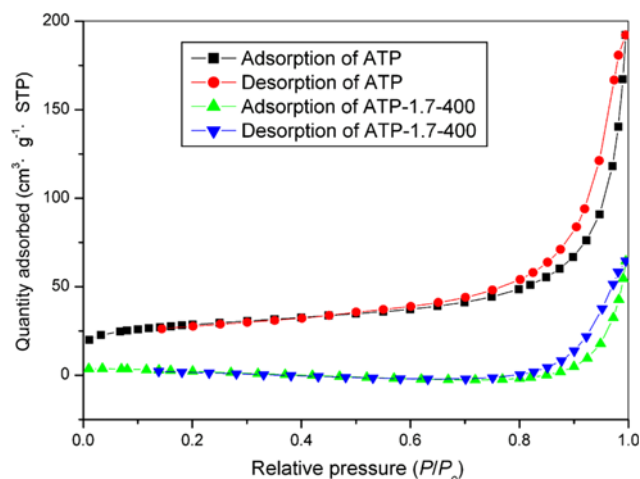


Fig. 4. Nitrogen adsorption-desorption isotherms of ATP and ATP-1.7-400 ( $p$ : Pressure of adsorbate;  $p_0$ : Saturated vapor pressure of liquid adsorbate at adsorption temperature; STP: Standard temperature and pressure).

Table 5. The results of nitrogen physical adsorption

Sample	Surface area ( $m^2/g$ )	Pore volume ( $m^3/g$ )	Pore size (nm)
ATP	101	0.18	73
ATP-1.7-400	8	0.05	246

ume of the ATP and ATP-1.7-400 catalyst, nitrogen adsorption and desorption isotherms were carried out. Fig. 4 illustrates the  $N_2$  adsorption-desorption isotherms for the ATP and ATP-1.7-400 samples. As shown, the isotherms are type III isotherms. Table 5 shows the specific surface area, pore size and pore volume of the sample calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. As shown, the surface area of the catalyst was smaller than that of ATP. The reason is that catalyst preparation methods involve a calcination step at high temperature. The low surface area and high density base active sites of the catalyst indicate that most of the base active sites were in the interior of the catalyst. If the pore size of this catalyst is small, the entry of a bulky organic molecule reactant such as soybean oil will be obstructed. Since the average pore size of the ATP-1.7-400 catalyst is 246.4720 nm, which is big, reactants can easily diffuse into the interior of the catalyst. This allows reactants to contact with more base active sites, and the catalyst has better activity.

#### 5. XRD Analysis

Fig. 5 shows the XRD patterns of the ATP and ATP-1.7-400 catalyst samples. As shown, when the mole ratio of Na : ATP was 1.7, the characteristic diffraction peaks ( $2\theta=19.9^\circ$ ,  $27.9^\circ$  and  $35.3^\circ$ ) of

Table 4. EDX analysis of ATP and  $C_4H_9O_6KNa/ATP$  catalyst

Sample	Surface atomic concentration (%)										
	Si	Al	Fe	Na	K	Ca	Mg	Mn	Ti	O	C
ATP	29.25	6.97	5.783	0.183	1.849	1.983	5.407	0.243	0.792	47.542	-
Catalyst	20.94	4.99	4.139	9.006	14.78	1.419	3.870	0.173	0.567	38.901	1.218

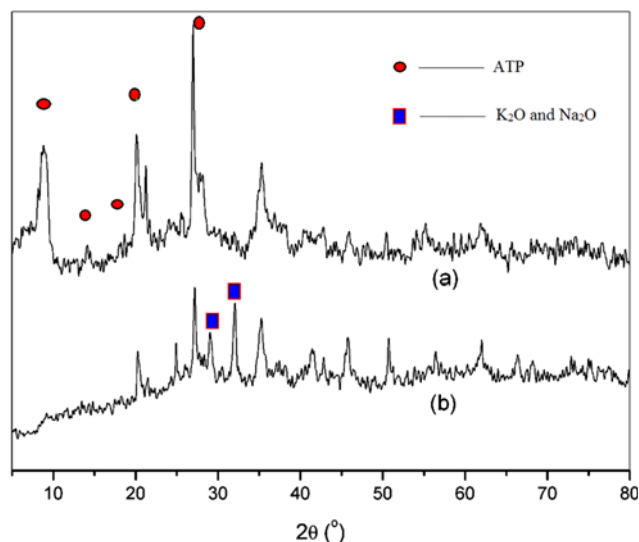


Fig. 5. XRD patterns of (a) ATP and (b) ATP-1.7-400.

the ATP support were registered on both the XRD patterns of ATP and ATP-1.7-400 catalyst. However, a species such as  $K_2O$  and  $Na_2O$  ( $2\theta=31^\circ$ ) was observed at catalyst, indicating good dispersion of  $C_4H_4O_6KNa$  on ATP support. In  $2\theta=8.6^\circ$  was the diffraction peak of the crystal plane (110) whose crystal plane spacing was 1.064 nm in the attapulgite structure. Moreover, the diffraction peak disappeared in the pattern of the ATP-1.7-400 catalyst. The phenomenon can result from the incorporation of  $Na^+$  and  $K^+$  ions into the vacancies in the structure of the ATP support and change the structure (refer to the TEM photograph of the ATP-1.7-400 catalyst Fig. 3(b)). The  $Na^+$  and  $K^+$  ions of  $C_4H_4O_6KNa$  could insert in the vacant sites of ATP, accelerating dissociative dispersion and decomposition of  $C_4H_4O_6KNa$  to form basic sites in the activation process. The more sodium and potassium compounds are loaded on the ATP, the more free vacancies decrease, which results in the low surface area of the catalyst (Table 5), and the surface enrichment of sodium and potassium species that is probably considered to be the active sites for base-catalyzed reactions. When the amount of  $Na^+$  and  $K^+$  ions loaded on ATP was below the saturation uptake of ATP, it could have been well dispersed. As a result, the number of basic sites together with the activities of the catalysts would increase with the increase of the mole ratio of  $Na : ATP$ . When too much  $C_4H_4O_6KNa$  was loaded on the ATP, the  $C_4H_4O_6KNa$  could not be well dispersed and, in this case, not all but only a part of the loaded  $C_4H_4O_6KNa$  could be decomposed. Moreover, as mentioned in the preceding sections, the excess  $C_4H_4O_6KNa$  would cover the basic sites on the surface of the catalysts, resulting in a lowered catalytic activity (Table 2) [23].

## 6. Transesterification of Soybean Oil Catalyzed by ATP-1.7-400

### 6-1. Effect of Molar Ratio of Methanol/Soybean Oil on the Biodiesel Yield

Transesterification is a reversible reaction. The amount of methanol must be in excess to force the reaction towards the formation of biodiesel. Fixing the reaction temperature at  $65^\circ C$ , the catalyst amount was 10.0 wt% and reaction time was 3.0 h and the reaction pressure was 1 atm; the biodiesel from soybean oil was conducted

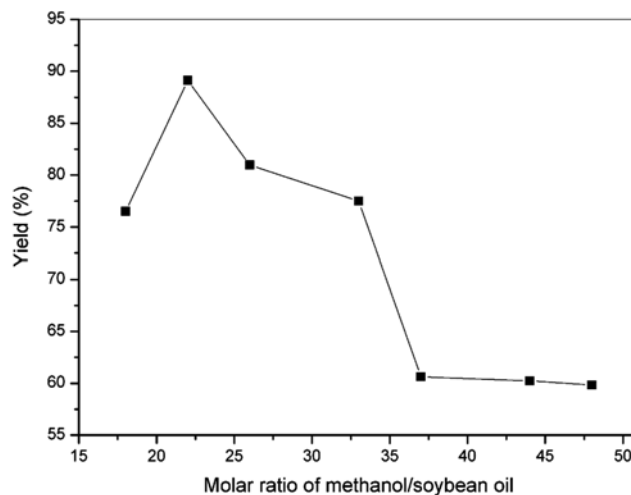


Fig. 6. The effect of molar ratio of methanol/soybean oil on the biodiesel yield.

at various molar ratios of methanol/soybean oil, and the results are shown in Fig. 6. With the molar ratio of methanol/soybean oil increasing, the biodiesel yield increases. And when the molar ratio is 22 : 1, the biodiesel yield is the highest. However, with a further increase in the molar ratio, the biodiesel yield changes little. The decrease in conversion is mainly due to excess methanol favoring the conversion of triglycerides into monoglycerides. The monoglycerides enhance the solubility of glycerol in biodiesel, and the glycerolysis of biodiesel takes place, and triglycerides conversion decreases. Therefore, the optimum molar ratio of methanol/soybean oil is 22 : 1.

### 6-2. Effect of Catalyst Amount on the Biodiesel Yield

Fixed molar ratio of methanol/soybean oil was 22 : 1, the reaction temperature was  $65^\circ C$  and reaction time was 3.0 h and the reaction pressure was 1 atm, a series of transesterification reactions carried out at various catalyst amounts. The effect of the catalyst amount on the biodiesel yield was investigated and the result is shown in Fig. 7. The catalyst amount was varied in the range of 5.0-20.0 wt%. As shown in Fig. 7, the biodiesel yield increases firstly with the increase of catalyst amount from 5.0 to 10.0 wt%. But, with catalyst amount further increase, the biodiesel yield decreases. This is possi-

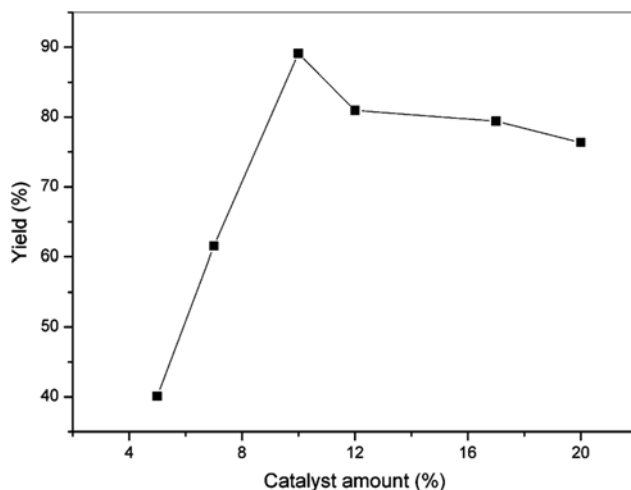


Fig. 7. The effect of catalyst amount on the biodiesel yield.



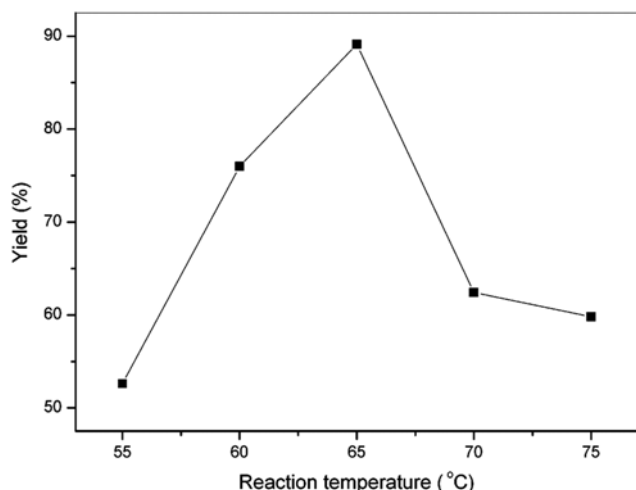


Fig. 8. The effect of reaction temperature on the biodiesel yield.

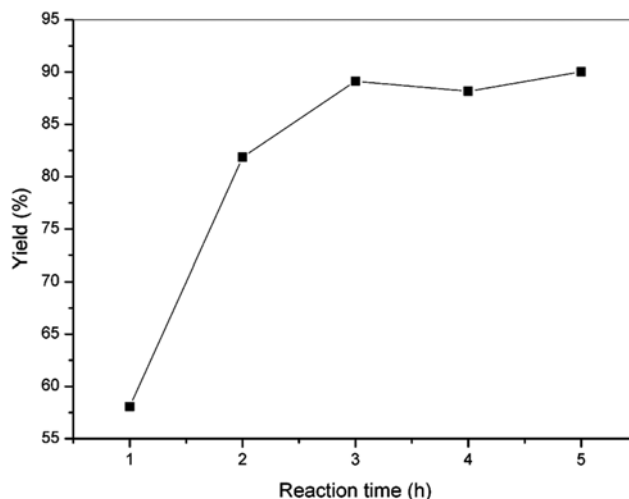


Fig. 9. The effect of reaction time on the biodiesel yield.

bly due to a mixing problem involving reactants, products and solid catalyst [24]. Therefore, the optimum catalyst amount is 10.0%.

#### 6-3. Effect of Reaction Temperature on the Biodiesel Yield

Reaction temperature can influence the reaction rate and biodiesel yield. The effect of reaction temperature on the biodiesel yield was obtained at the fixed molar ratio of methanol/soybean oil 22 : 1, the catalyst amount 10.0% and reaction time 3.0 h, and the reaction pressure was 1 atm. The results are shown in Fig. 8. In the present work, the reaction temperature was varied within a range from 55 to 75 °C. From Fig. 8, the results indicate that the reaction rate is slow at low temperature and the biodiesel yield is only 52.6% at 55 °C after 3 h of reaction time. The biodiesel yield increased with the increase of reaction temperature to nearly 90% at 65 °C. However, if the reaction temperature exceeds the boiling point of methanol, the methanol will vaporize and form a large number of bubbles, which inhibits the reaction on the three-phase interface [25]. Therefore, the optimum reaction temperature for the transesterification of soybean oil to biodiesel is considered to be 65 °C.

#### 6-4. Effect of Reaction Time on the Biodiesel Yield

Fixing the molar ratio of methanol/soybean oil at 22 : 1, the catalyst amount was 10.0% and the reaction temperature was 65 °C and the reaction pressure was 1 atm; the biodiesel from soybean oil was conducted at various reaction times and the results are shown in Fig. 9. The reaction time varied from 0.5 to 5.0 h. With the reac-

tion time increase, the biodiesel yield increases. However, with further increase in the reaction time, the biodiesel yield remains almost constant as a result of near equilibrium conditions after 3.0 h. In this experiment, 3.0 h of reaction time is chosen as the suitable time.

#### 6-5. Effect of Repeated Use of $C_4H_9O_6KNa$ /ATP Catalyst on the Biodiesel Yield

Compared with homogeneous catalyst, the superior advantages of heterogeneous solid catalyst are their easy recovery and good reusability. The prepared solid base catalyst, which is insoluble in both methanol and biodiesel system, can be separated from the reaction system effectively and easily. Therefore, it is quite necessary to evaluate the reusability of the as-prepared catalyst, especially from the viewpoint of practical application. The prepared catalyst was separated and centrifuged from the liquid reaction mixture after reaction completion, and then the catalyst was heated by centrifuging, separating, washing thoroughly with methanol from the reaction mixture in a muffle oven at 400 °C for 12 h before next use.

When the molar ratio of methanol/soybean oil was 22 : 1, reaction temperature was 65 °C, reaction time was 3.0 h and catalyst amount was 10 wt% and the reaction pressure was 1 atm, the reusability of catalyst is shown in Fig. 10. It can be seen that the process was repeated 1-5 times, and the yield of biodiesel changed little. The obtained results could prove that the prepared catalyst is stable for biodiesel production from soybean oil and can be repeatedly

Table 6. Comparison of properties of the obtained biodiesel and the standards of biodiesel in China, Europe and the United States

Item	Obtained biodiesel	CHINA GB/T 20828-2007	USA ASTMD 6751-03	EUROPE EN 14214
Density (kg L <sup>-1</sup> )	0.852 (20 °C)	0.82-0.90 (20 °C)	0.82-0.90 (20 °C)	0.86-0.90 (15 °C)
Flash point (°C)	166	>130	>130	>120
Cetane value	56	≥49	≥47	>51
Sulfur content (w/w, %)	0.003	<0.05	<0.0015	<0.001
Acid value (KOH) (mg g <sup>-1</sup> )	0.21	<0.8	<0.8	<0.5
Water content (w/w, %)	0.04	<0.05	<0.05	<0.05
Kinematic viscosity (mm <sup>2</sup> S <sup>-1</sup> )	3.12	1.9-6.0	1.9-6.0	3.5-5.0
Ash content (w/w, %)	0.013	<0.05	<0.05	<0.05

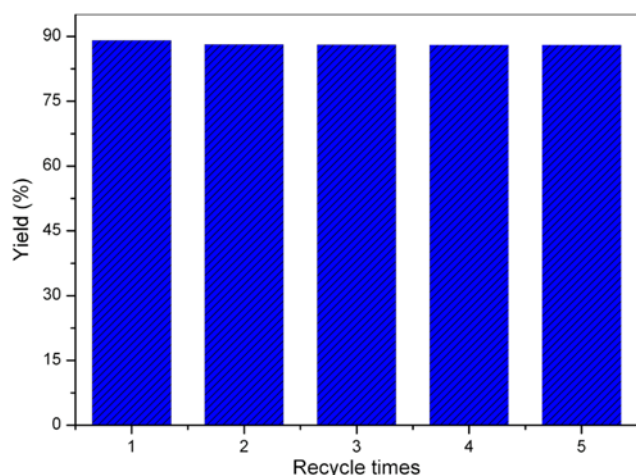


Fig. 10. The effect of recycle times of catalyst on the biodiesel yield.

used.

To find the reason for the little deactivation of the catalyst, the leakages of sodium and potassium to biodiesel were investigated. Sodium and potassium ion concentration in the solution obtained from transesterification with  $C_4H_4O_6KNa/ATP$  catalyst were found to be 15 ppm. That is the main reason for the deactivation of solid catalyst. However, the leakage of sodium and potassium ion was little enough and would not affect the activity of the catalyst. Therefore, it is generally believed that the catalyst is heterogeneous and can be repeatedly used.

### 7. The Properties of Biodiesel

The properties of biodiesel, density, cetane number, flash point, cold filter plugging point, acid number, water content, ash content and total glycerol content, were determined and listed in the Table 6, which shows comparisons of the obtained biodiesel and the standards of biodiesel in China, Europe and the United States. The properties of the prepared biodiesel, in general, show many similarities. Therefore, the obtained biodiesel from the soybean oil is rated as a realistic fuel as an alternative to diesel.

## CONCLUSIONS

(1) Attapulgite loaded with sodium potassium tartrate tetrahydrate, which was prepared by impregnation of powdered attapulgite with an aqueous solution of sodium potassium tartrate tetrahydrate followed by calcination at a high temperature, showed high catalytic activities for the transesterification reaction.

(2) The optimal catalyst preparation conditions were determined to be: calcination temperature of 400 °C, molar ratio of Na : ATP to 1.7 : 1, the biodiesel yield is the highest.

(3) The catalyst was tested by FI-IR, SEM, TEM XRD, EDX,  $N_2$  adsorption-desorption measurements and the Hammett indicator method. The results showed a good dispersion of  $C_4H_4O_6KNa$  on the support of attapulgite.

(4) The catalyst ATP-1.7-400 was investigated for transesterification of soybean oil with methanol to biodiesel. The best reaction conditions were found to be: catalyst amount 10%, molar ratio of

methanol/soybean oil 22 : 1, reaction temperature 65 °C and the reaction time 3.0 h.

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