

## Preparation and characterization of a strong solid base from waste eggshell for biodiesel production



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### ABSTRACT

A strong solid base catalyst was prepared from waste eggshell by KF modification and thermal treatment. The eggshell catalyst was characterized by Fourier-transform infrared spectra (FT-IR), X-ray diffraction (XRD), scanning electron microscope (SEM) and solid-state nuclear magnetic resonance (NMR) spectroscopy. The characterization results show that potassium hydroxide (KOH) formed from the modification process enhances the basicity and catalytic ability of the catalyst. The solid base catalyst from eggshell (SBES) exhibits excellent catalytic activity and stability in the transesterification reaction, which suggested that this catalyst would be potentially used as a solid base catalyst for biodiesel production.

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### Introduction

Eggshells are one of the vast by-products of food processing and manufacturing plants. Most of the waste eggshells are currently stockpiled on-site without any pretreatment. In addition, the emission of odor gas during its biodegradation seriously polluted the environment [1]. Thus, significant attentions were given to the recycling of these waste eggshells. Some researchers reported that the waste eggshell was used to prepare calcium phosphate bioceramics and a low-cost adsorbent for removal of ionic pollutant from the aqueous solution [2,3]. However, few papers have been reported to prepare solid base catalyst using the waste eggshell [4].

For the increasing price of petroleum and the environmental concerns, recyclable and environmental benign energy sources have been widely developed all over the world, in which biodiesel is one of the most promising fuel substitute in the future. As reported, biodiesel has already been commercially produced from renewable resources such as soybean oil by transesterification reaction using homogeneous strong bases or acids as catalysts [5–7]. Although the homogeneous base catalysts can catalyze biodiesel production with the fast reaction speed under mild reaction conditions, it still shows some disadvantages in the practical process. For example, it is hard to separate catalyst from

product [8]. Therefore, many attentions were focused on the solid base catalyst due to its convenience in separation and recycling [9].

The chemical composition of waste eggshell is mainly calcium carbonate as reported by other researcher [10]. Due to its intrinsic pore structure in eggshell surface and the amount in abundance, eggshell is a good raw material for the preparation of fine powder, which might pave the way for its utilization such as porous solid catalyst. In fact, the solid base catalysts derived from eggshell have been prepared by calcinations [4,11,12], the base strength of those catalysts is not strong enough and subsequently show relatively low activity in the application. Hence, the key questions in these catalysts, such as what method and which mechanism can improve their base strength and further to increase their catalytic activity, are still poorly understood. In this study, a strong solid base catalyst from waste eggshell (SBES) was prepared with chemical and thermal treatment. In addition, this solid base catalyst was also characterized by X-ray diffraction (XRD), Fourier-transform infrared spectra (FT-IR), temperature programmed desorption (TPD), scanning electron microscope (SEM) and solid-state nuclear magnetic resonance (NMR) spectroscopy.

### Experimental

#### Sample preparation

The waste eggshell sample was collected from a canteen of Wuhan University of Science and Technology. The eggshells were washed for three times, and then dried at 120 °C for 10 h. The dried

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eggshells were crushed and sieved to the particle size range of 100–150  $\mu\text{m}$ . Particle size analysis was performed by dry sieving with Taylor standard sieves.

The solid base catalyst from eggshell was prepared by KF modification and thermal treatment. Typically, 10.0 g of eggshell was immersed in 20 ml KF solution with the designed amount of KF for 5 h, then baked at 120 °C for 10 h, followed by calcination at the designed temperature for 12 h in a muffle furnace. The obtained catalyst was preserved in an airtight plastic bottle for further using. The catalyst with KF loading of 25 wt% and calcinations at 800 °C was chosen for all the sample characterization. CaO (from eggshell) was prepared by calcination the dried eggshell at 800 °C for 12 h. CaO (commercial) and MgO (commercial) were purchased from Shanghai Guoyao Company.

NaY catalysts were prepared by ion-exchange method using HY (Si/Al = 80, from Nankai University) as the starting material [13]. The ion-exchange process was carried out at 358 K using 100 ml NaOH solution (0.2 M) to exchange 10 g HY zeolite for 0.5 h. After the ion-exchange, the sample was washed thoroughly with deionized water, filtered, dried at 393 K overnight and then calcined in air at 823 K for 10 h.

Food-grade soybean oil supplied by commercial supermarket was used to carry out the transesterification reaction. The oil was purified and dried carefully before the catalytic test. According to GC (HP6890) analysis, the fatty acid compositions of the used soybean oil were as follows: palmitic acid, 12.6%; stearic acid, 5.8%; oleic acid, 26.7%; linoleic acid, 48.8%; and linolenic acid, 6.4%. The acid value of the oil was reduced to lower than 0.3 mg KOH/g and the water content below 10 ppm. The average molecular weight of the oil is 850.

#### Sample characterization

Surface area and porosity properties of the samples were obtained by  $\text{N}_2$  adsorption/desorption isotherms on a Micromeritics ASAP 2020 sorption analyzer. The amount of the basic site in the catalyst (Total basicity in Table 1) was determined by the indicator method [14].

The FT-IR spectra were performed on Impact 410, Nicolet Spectrometer with a resolution of 2  $\text{cm}^{-1}$ .

X-ray diffraction was recorded with a Philips X'PERT-Pro-MPD diffractometer.

The morphologies and dimensions of the samples were characterized by scanning electron microscope (SEM; Philips XL30).

The basic properties of the catalysts were characterized by the temperature programmed desorption (TPD) of  $\text{CO}_2$  measurement using a Micromeritics AutoChem II 2920 chemisorption analyzer.

The  $^{19}\text{F}$  NMR spectra were recorded on a Varian Infinityplus-400 spectrometer.

**Table 1**  
Textural properties and the catalytic performance of the various solid bases.

Catalysts	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{tot}}$ ( $\text{cm}^3/\text{g}$ )	Total basicity (mmol/g)	Yield (%)
SBES	19.96	0.046	1.65	99.1
CaO (from eggshell)	13.56	0.034	0.82	95.2
CaO (commercial)	11.63	0.029	0.88	93.6
MgO (commercial)	16.35	0.039	1.23	94.2
NaY	143.26	0.087	0.98	93.2

$S_{\text{BET}}$ , specific surface area from BET method;  $V_{\text{tot}}$ , total pore volume. Reaction condition: Catalyst/oil mass ratio: 2%; methanol/oil molar ratio: 12:1; reaction temperature: 65 °C, reaction time 2 h.

#### Catalytic reaction procedure

Transesterification reaction of soybean oil and methanol was performed as follows: at first, a 100 ml round-bottom flask was charged with 30.0 g of soybean oil (34.5 mmol, calculated from the average molecular weight of the rapeseed oil), 12.6 ml methanol and the eggshell catalyst. The mixture was stirred by a magnetic stirrer. All the transesterification reactions were performed under reflux with a water-cooled condenser. After the transesterification reaction was finished, the mixture was cooled in air and placed into a separation funnel, and then the mixture of the glycerol and methanol was separated. The oil phase FAME (fatty acids methyl esters, biodiesel) was quantitative analyzed in the presence of methyl salicylate as internal standard by HP6890 GC with a flame ionization detector (FID). The biodiesel yield was defined as a ratio of the actual weight of FAME (by HP6890 GC) to the theoretical weight of FAME (by calculation on the basis of soybean oil used in the reaction).

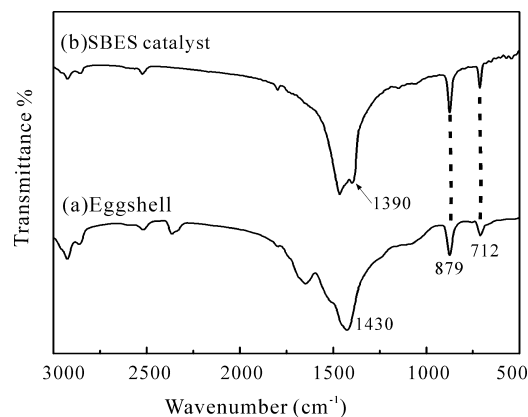
Repeated experiments of the transesterification reaction were performed to determine the catalytic stability of the catalyst. The catalyst was centrifuged from the mixture, and then directly used for the next cycle. The reaction conditions were used in each cycle as follows: catalyst/oil mass ratio: 2%; methanol/oil molar ratio: 12:1; reaction temperature: 65 °C; reaction time 2 h.

## Results and discussion

#### Catalyst characterization

Fig. 1 shows FT-IR spectra of SBES catalyst and eggshell. The strong peak at 1417  $\text{cm}^{-1}$  was attributed to carbonate minerals in eggshell [15]. Other two observable peaks at 712 and 875  $\text{cm}^{-1}$  were associated with the in-plane deformation and out-plane deformation modes of carbonate groups, respectively [15]. The band at 1390  $\text{cm}^{-1}$  in the spectrum of SBES catalyst was assigned to molecular  $\text{CO}_2$  adsorbed by the basic hydroxyl groups in the catalyst [16]. While no such peak appears in the spectrum of eggshell, which indicated that basic hydroxyl groups was generated via the reaction of KF and  $\text{CaCO}_3$  by calcination.

Fig. 2 illustrates the XRD patterns of the SBES catalyst and eggshell. The diffraction peaks at 29.4°, 36.3°, 43.2°, 47.3° and 48.5° in eggshell spectrum are ascribed to  $\text{CaCO}_3$  in the eggshell [10]. While in the spectrum of SBES catalyst, the typical peaks at 18.2°, 28.2°, 32.3°, 35.8° and 62.1° are attributed to CaO derived from  $\text{CaCO}_3$  in the eggshell by calcination [10]. The peaks (19.9°, 40.1°, 50.8°, 59.9° and 65.8°) arising from the crystal of  $\text{KCaF}_3$  can also be clearly observed, further indicative of occurrence of the reaction between KF and  $\text{CaCO}_3$  during the calcination process [17,18].



**Fig. 1.** FT-IR spectra of (a) eggshell and (b) the SBES catalyst.

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