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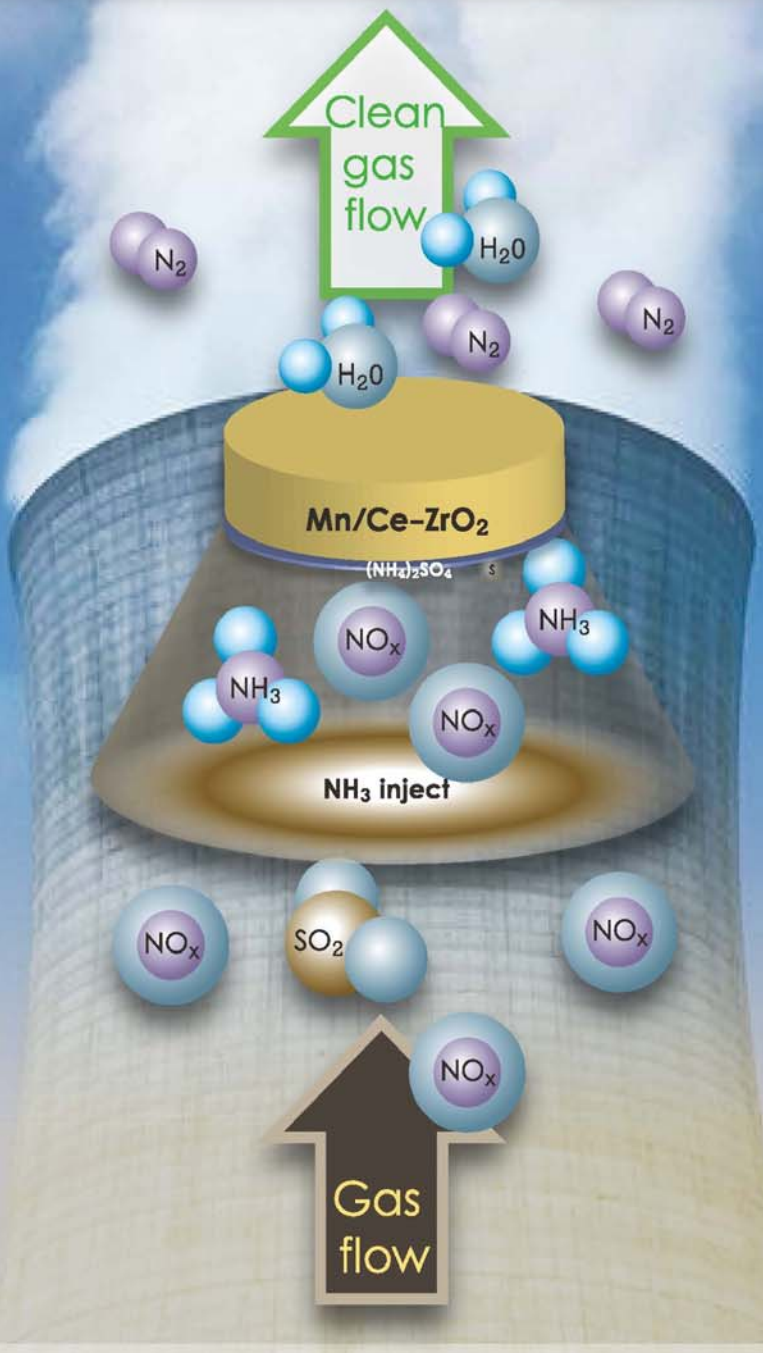

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Application of red mud as a basic catalyst for biodiesel production

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Abstract

Red mud was investigated in triglyceride transesterification with a view to determine its viability as a basic catalyst for use in biodiesel synthesis. The effect of calcination temperature on the structure and activity of red mud catalysts was investigated. It was found that highly active catalyst was obtained by simply drying red mud at 200°C. Utilization of red mud as a catalyst for biodiesel production not only provides a cost-effective and environmentally friendly way of recycling this solid red mud waste, significantly reducing its environmental effects, but also reduces the price of biodiesel to make biodiesel competitive with petroleum diesel.

Key words: red mud; basic catalyst; transesterification; biodiesel; industrial waste

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Introduction

Red mud is a solid waste residue formed after the caustic digestion of bauxite ores during the production of alumina (Antunes et al., 2012; López et al., 2011). Each year, about 90 million tons of red mud is produced globally. For every ton of alumina produced, the process can leave behind a third of a ton to more than two tons of red mud. Red mud is a highly alkaline waste material with a pH of 10–13 because of the sodium hydroxide solution used in the refining process. Red mud is mainly composed of fine particles containing aluminum, iron, silicon, titanium oxides and hydroxides. The red color is caused by the oxidized iron present, which can make up to 60% of the mass of the red mud. Because of the alkaline nature and the chemical and mineralogical species present in red mud, this solid waste causes a significant impact on the environment, and proper disposal of waste red mud presents a huge challenge where alumina industries are installed (López et al., 2011; Bhatnagar et al., 2011; Zhou and Haynes, 2010). Many attempts have been made over past years to find some practical applications for red mud. These major applications have included construction materials and ceramics (Yang and Xiao, 2008; Zhang et al., 2011a), surface treatment for carbon steel (Collazo et al., 2005), and a low-cost adsorbent for removal of pollutants from aqueous solutions or the gas phase (Zhou and Haynes, 2010; Zhao et al., 2009; Huang et al., 2008; Tor et al., 2009; Cengeloglu et al., 2007; Zhang et al., 2008; Yadav et al., 2010; Ma et al., 2009). In addition, red mud can also be employed as a catalyst for hydrogenation, hydrodechlorination and hydrocarbon oxidation (Karimi et al., 2010; Sushil and Batra, 2008; Balakrishnan et al., 2009; Oliveira et al., 2011).

Red mud can be classified as hazardous waste because of its caustic/saline/sodic nature (Zhou et al., 2010). On the other hand, the number and strength of base sites are highly pertinent parameters for the activity of heterogeneous base catalysts (Busca, 2010). Due to its alkaline nature, it is possible to prepare active basic catalyst from red mud. However, to the best of our knowledge, there is no report on the subject of basic catalyst prepared from red mud in the open literature.

The price of petroleum diesel has soared in recent years and the available reserves of this important fuel will eventually be exhausted if large-scale use continues, and greenhouse gas emission by the usage of fossil fuels is also becoming a greater concern. Therefore, research is now being directed towards the use of alternative renewable and environmentally friendly fuels that are capable of fulfilling an increasing energy demand (Verziu et al., 2009; Jiménez-Morales et al., 2011). Biodiesel is a renewable alternative to petroleum diesel that is composed of monoalkyl esters of fatty acids, and it has physical properties similar to

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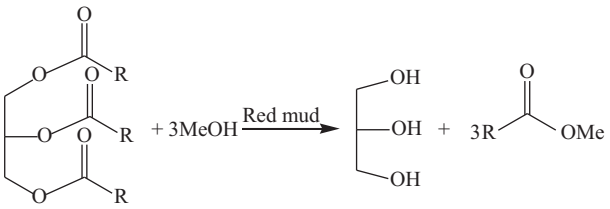
petroleum diesel but unique advantages including being renewable, biodegradable, non-toxic and low-emission. Biodiesel is generally produced by transesterification of vegetable oils or animal fats with short-chain alcohols (generally methanol) in the presence of basic or acid catalysts (**Scheme 1**). The cost of fabricating a catalyst can be an important factor in its industrial application. The production of biodiesel calls for an efficient and cheap catalyst to make the process economical and fully ecologically friendly, accordingly reducing its price and making it competitive with petroleum diesel (Verziu et al., 2009; Jiménez-Morales et al., 2011; Wei et al., 2009).



Scheme 1 Transesterification of vegetable oils or animal fats with short-chain alcohols (generally methanol) in the presence of catalysts.

In this work, we explored the possibility of the application of red mud as a basic catalyst in the catalytic process of biodiesel production (**Scheme 1**).

1 Experimental

1.1 Materials

The red mud used in this study was obtained from Shandong Aluminium Corporation China. It was dried at 100°C for 24 hr in an oven. Calcination was performed in a muffle furnace at different temperatures (200–1000°C) for 5 hr under static air after crushing the dried red mud. The obtained catalysts were labeled as Red mud-X with X from 1 to 10, where X corresponds to the calcination/drying temperature. For example, Red mud-1 corresponds to red mud dried at 100°C, and Red mud-2 corresponds to red mud calcined at 200°C.

1.2 Characterization methods

Elemental analysis was determined by an FEI Quanta 200 scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDS) capability.

X-ray diffraction patterns were recorded on a D/Max-3C X-ray powder diffractometer (Rigaku Co., Japan), using a Cu $K\alpha$ source fitted with an Inel CPS 120 hemispherical detector.

TGA experiments were carried out using a Q600 SDT thermal analysis machine (TA Instruments, USA) under a flow of nitrogen. The sample weight used was about 10 mg, and the temperature ranged from room temperature to 1000°C with a ramping rate of 20°C/min.

The nitrogen adsorption and desorption isotherms were measured at –196°C using a Micromeritics ASAP 2020 system. Specific surface areas of the samples were determined by nitrogen adsorption data in the relative pressure range from 0.06 to 0.30 using the BET (Brunauer-Emmett-Teller) equation. Total pore volumes were estimated from the amount of nitrogen adsorbed at a relative pressure of 0.995. Pore volume and pore size distribution curves were obtained from the analysis of the desorption branches of the nitrogen isotherms using the BJH (Barrett-Joyner-Halenda) method.

pH value was an important parameter which reflected the alkaline property of red mud (Liu et al., 2007). pH of red mud was determined according to the procedure in the literature (Liu et al., 2007). 1:5 (weight ratio of red mud/water) extracts were prepared. The pH in water extracts was determined by a calibrated pH meter.

1.3 Transesterification of soybean oil

The reactions were carried out in a 100-mL one-necked glass flask with a water-cooled condenser at 65°C under vigorous stirring. Typical reactions were performed with 29.4 mL of vegetable oil (100% soybean oil; Xi'an Jiali Grease Industrial Co., Ltd., Xi'an, China) and 27.8 mL of methanol (methanol/vegetable oil molar ratio 24:1) using 4 wt.% (catalyst/oil weight ratio) of red mud catalyst at 65°C for the specified time.

Reaction products were analyzed using the following procedure. The samples were separated from the catalyst and glycerol by centrifugation, with the separation of glycerol being achieved because it was insoluble in the esters and had a much higher density. The methanol was removed under vacuum and the product was added to chloroform-d for ^{1}H-NMR spectroscopy. Methyl ester could be readily determined quantitatively from the NMR spectra using the method described by Gelbard et al. (1995). The signal due to methylene protons adjacent to the ester group in triglycerides appears at 2.3 ppm and after reaction the methoxy protons of the methyl esters appear at 3.7 ppm. The yield (Y, %) of transesterification could be monitored using the areas of the signals of methylene and methoxy protons.

A simple equation is given as follows:

$$Y = \left(\frac{2A_{CH_3}}{3A_{CH_2}}\right) \times 100\% \quad (1)$$

where, A_{CH_3} is the area of the signal corresponding to the protons of the methyl esters (the strong singlet); and A_{CH_2} is the area of the signal corresponding to the protons of the methylene protons. The factors 2 and 3 are derived from the fact that the methylene carbon possesses two protons and the alcohol (methanol derived) carbon has three attached protons.

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2 Results and discussion

2.1 Characterization of red mud catalyst

2.1.1 Chemical composition of red mud

The variation in chemical composition between different red muds worldwide is high (Wang et al., 2008). The elemental analysis by EDS reveals that red mud contains calcium, silica, aluminum, iron, sodium, as well as an array of minor constituents, namely: K, Mg, and Ti (**Fig. 1**). It is noted that calcium was the major component followed by silica and alumina. The composition of the red mud was similar to the results reported by Zhao et al. (2009), who collected their red mud samples from the same site as we did. However, the composition of the red mud was different from others worldwide. In the red mud from India, the Ti content was the highest. In the red mud from other places, e.g. USA, Australia, Hungary and Germany, the Fe content was the highest (Wang et al., 2008).

2.1.2 XRD analysis

The XRD patterns of the red mud uncalcined and calcined within the interval 200–1000°C are shown in **Fig. 2a** and **b**, respectively. It can be seen that the major phases present in the uncalcined red mud were $CaCO_3$, Fe_2O_3, $CaTiO_3$, Ca_2SiO_4, and $Ca_3AlFe(SiO_4)(OH)_8$ (Zhang et al., 2011a, 2011b; Liu et al., 2011). Iron and aluminum hydroxide phases were commonly found to be present for red mud (Sushil et al., 2010). However, the result from our study was different. Through comparison of the XRD pattern with the standard patterns of iron and aluminum hydroxide phases, and with the reports by other authors who have collected red mud from the same source (Zhang et al., 2011b; Liu et al., 2011), it was found that the red mud did not contain iron and aluminum hydroxide phases. Fe_2O_3, $CaTiO_3$ and Ca_2SiO_4 phases were not affected by the heat treatment up to 1000°C. $Ca_3AlFe(SiO_4)(OH)_8$ could not be detected in the sample treated at 600°C, nor could crystalline $CaCO_3$ be detected within the temperature interval 800°C–1000°C. $Ca_2Al_2SiO_7$ and Fe_3O_4 were observed in the sample within the temperature interval 800°C–1000°C. This indicated that the structure of the red mud was affected by the calcination temperature.

2.1.3 TGA-DSC analysis

In order to explain the effect of calcination temperature, we investigated the calcination process of red mud with thermal gravimetric analysis technology. **Figure 3** exhibits TGA-DSC curves of red mud. They show two major steps for the mass loss with changing temperature. The first step occurred in the range of 80–600°C corresponding to the physically absorbed water and chemically bound water. As the red mud sample had been dried at 100°C before thermogravimetric analysis, most of the physically absorbed water dissipated in the drying process, and therefore the physically absorbed water measured in the TGA diagram was about 0.3% of the total weight over the temperature range of 80–105°C. The temperature range of 105–600°C with mass loss of 14.2% of the total weight was mainly related to the evaporation of chemically bound water. The second step with mass loss of 3.6% of the total weight could be detected in the range of 600–700°C, most likely corresponding to the release of CO_2 during the decomposition of carbonates. It is notable that one

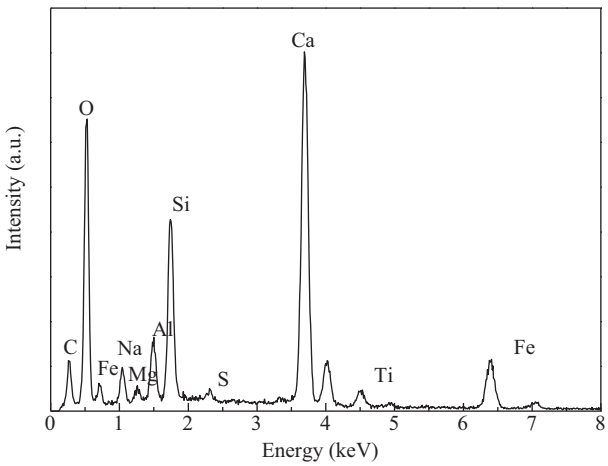

Fig. 1 EDS spectrum of red mud.

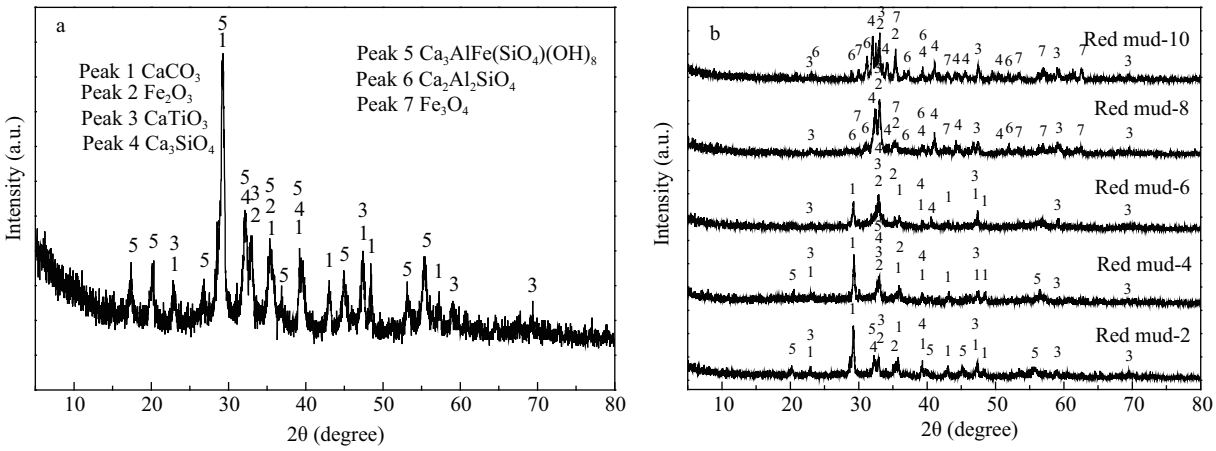

Fig. 2 Powder X-ray diffraction patterns of red mud at uncalcined (a) and calcined within the interval 200–1000°C (b).

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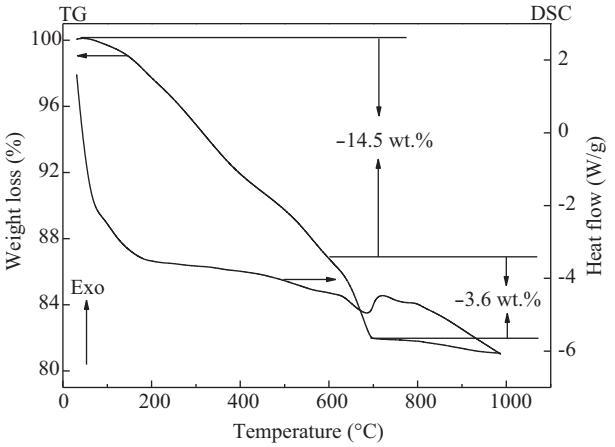

Fig. 3 TGA-DSC profiles of red mud sample.

endothermic peak (around 710°C) occurred within the interval 687–750°C, suggesting that one carbonate phase was present in the red mud sample (Liu et al., 2011).

2.1.4 BET surface area and pore size

The specific surface areas, pore volume and average pore diameter are shown in **Table 1**. The surface area of Red mud-1 was 23 m^2/g. The surface area of red mud calcined below 800°C was similar to that of Red mud-1. Red mud-10 (**Table 1**), which was calcined at 1000°C, had the lowest surface area (11 m^2/g). The decrease of Red mud-10 in surface area may be due to the collapse of pores at 1000°C.

2.1.5 Basicity of red mud

The pH of red mud was determined to be: 12.2 (Red mud-1, -4, -6); 12.0 (Red mud-2); 12.3 (Red mud-8). The pH of Red mud-10 was 11.5, which was slightly lower than that of other red mud samples. Compared with the fresh Red mud-2 (pH = 12.0), the used Red mud-2 (pH = 11.6) showed slightly lower basic strength. This indicated that a small amount of basic species was possibly leached during the biodiesel synthesis.

2.2 Effect of calcination temperature

To determine the influence of the calcination temperature on the activity of the red mud catalyst, red mud was calcined at different temperatures between 100 and 1000°C and then tested for the transesterification of soybean oil to produce biodiesel. **Figure 4** shows that the red mud sample calcined at 200°C was the most active catalyst. The highest biodiesel yield (> 94%) was obtained when the calcination temperature was 200°C. Above 200°C, the activity of red mud decreased with the calcination temperature. At calcination temperature 1000°C, the biodiesel yield went down to 20%. This suggested that the calcination temperature affected the activity of red mud. Structure analysis by TGA and XRD methods showed that the structure of red mud changed with calcination temperature. Therefore, the activity of red mud may change with its structure.

Table 1 Nitrogen physisorption data of the red mud calcined at different temperatures

Entry	Sample	Surface area[a] (m^2/g)	Pore volume[b] (cm^3/g)	Average pore diameter[b](nm)
1	Red mud-1	23	0.067	14.22
2	Red mud-2	21	0.063	17.47
3	Red mud-4	27	0.089	17.29
4	Red mud-6	19	0.074	22.08
5	Red mud-8	17	0.027	22.28
6	Red mud-10	11	0.005	15.61

[a] Calculated by the BET method, [b] calculated by BJH method from the desorption isotherm.
Red mud-1 to 10 corresponds to red mud dried at the temperature from 100 to 1000°C.

2.3 Effect of reaction variables

The yield of biodiesel was affected by reaction variables such as catalyst amount, methanol/oil ratio, or reaction time. These reaction variables were associated with the type of catalysts used (Ma and Hanna, 1999). Therefore, the effect of reaction variables was studied in the presence of red mud catalyst. For the following reactions, all the catalyst was prepared by calcining red mud at 200°C for 5 hr.

Figure 5a shows the effect of catalyst amount. The yield increased with increasing the catalyst loading up to 4 wt.%. Therefore, the optimum catalyst loading was found to be 4 wt.% in this system. **Figure 5b** shows the effect of the molar ratio of soybean oil to methanol. It indicates that the yield increased with increasing methanol/oil molar ratio, and reached a maximum value when the ratio was above 24:1. The stoichiometric ratio for transesterification is 3:1 (methanol/oil). Because this is a reversible reaction, an excess of methanol will increase the oil conversion by shifting this equilibrium to the production of methyl ester. The effect of reaction time was tested (**Fig. 5c**). The results showed that the yield increased with time, reaching

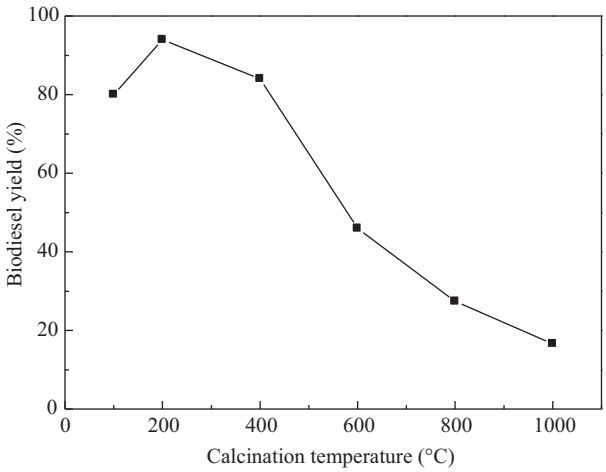

Fig. 4 Effect of calcination temperature on biodiesel yields. Reaction conditions: methanol to oil molar ratio 24:1; catalyst amount 4 wt.%; reaction temperature 65°C; reaction time 3 hr.

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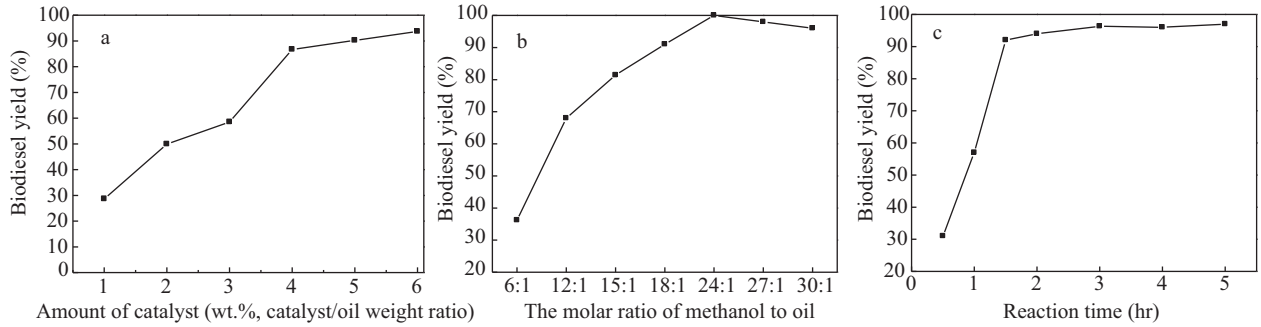

Fig. 5 Effect of reaction variables in the presence of Red mud-2. (a) amount of catalyst on biodiesel yields, conditions: methanol to oil molar ratio, 24:1; reaction temperature 65°C; reaction time 3 hr; (b) molar ratio of methanol to oil, conditions: catalyst amount 4 wt.%; reaction temperature 65°C; reaction time 3 hr; (c) reaction time, conditions: catalyst amount 4 wt.%; methanol to oil molar ratio 24:1; reaction temperature 65°C.

a maximum value (yield > 94%) after 3 hr.

The experimental results showed that a 24:1 molar ratio of methanol to oil, addition of 4 wt.% red mud catalyst (calcined at 200°C), and 65°C reaction temperature gave the best results, and the biodiesel yield exceeded 94% at 3 hr. This indicates that red mud could be a highly effective catalyst for transesterification of vegetable oil to produce biodiesel. The activity of red mud was slightly lower than that of KF-doped catalysts and eggshell catalyst, but was higher than that of MgO catalyst (Wei et al., 2009; Xu et al., 2010; Xu and Liu, 2011).

2.4 Recycling experiments for red mud catalyst

Attempts to reuse the red mud catalyst have not as yet been successful. The catalyst after one run showed extremely low activity (biodiesel yield, < 20%). As shown in the previous section, the pH of spent catalyst was lower than that of fresh material. The deactivation of red mud catalyst may be partly due to the decrease of basic strength. Another reason for the deactivation may be ascribed to the adsorption of reaction products during the reaction. The regeneration of red mud was investigated as follows. After being washed with THF, the used red mud was doped with NaOH. The doping amount of NaOH was 1.0 wt.% (NaOH/red mud weight ratio). Then the treated red mud was applied to the transesterification of soybean oil. The obtained yield was the same as that with the fresh red mud. The result showed that the activity of red mud could be regenerated.

2.5 Mechanism study

Efforts were made to clarify the mechanism and deactivation of red mud. Red mud-2 (0.5 g) and methanol (13.9 mL) were mixed. After stirring the mixture for 10 min, the methanol and Red mud-2 were separated by filtration. The pH and activity of the treated samples were tested (**Table 2**). The pH of treated methanol (i.e. filtrate) was 9.5, which was higher than that of fresh methanol (pH = 6.4; **Table 2**). The pH of treated Red mud-2 (i.e. precipitate) was 11.6, which was slightly lower than that of the fresh Red mud-2 (pH = 12.0). The change in the pH value of treated methanol and Red mud-2 may be ascribed to the leaching of soluble base. The soluble base leached from Red mud-2 and dissolved into the methanol phase, which resulted in the decrease of Red mud-2 pH and the increase of methanol pH. The activity of soluble base was tested (**Table 2**, entry 2). The obtained biodiesel yield was 0. The activity of insoluble base was also tested by using the precipitate Red mud-2 as catalyst; the obtained yield was 35% (**Table 2**, entry 4). The activity of both the insoluble base and soluble base was less than that of the fresh Red mud-2.

Table 2 Mechanism study of red mud as catalyst

Entry	Sample	pH	Biodiesel yield (%)
1	Methanol[a]	6.4	0[e]
2	Methanol[b]	9.5	0[e]
3	Red mud-2[c]	12.0	95
4	Red mud-2[d]	11.6	35

[a] Fresh methanol, [b] treated methanol (i.e., filtrate), [c] fresh Red mud-2 as catalyst, [d] treated Red mud-2 (i.e., precipitate) as catalyst, [e] in the absence of catalyst.
Reaction conditions: 29.4 mL of vegetable oil, 27.8 mL of methanol, 4 wt.% (catalyst/oil weight ratio) of catalyst, reaction temperature 65°C, reaction time 3 hr.

To characterize the soluble base, the experiment below was conducted. The soluble base was separated from red mud by liquid-solid extraction. A 10-mL of methanol was added to 5 g of Red mud-2. After stirring the mixture for 30 min at room temperature, the methanol and Red mud-2 were separated by filtration. Then 10 mL of fresh methanol was added to the precipitate for further extraction. The Red mud-2 was extracted with methanol four times under the same procedure. The extraction liquids were combined. After removing the methanol under vacuum, the soluble residue was obtained. The amount of soluble residue was 0.025 g, which meant that 0.5 wt.% of Red mud-2 was leached into methanol. The soluble species was characterized. As shown in **Fig. 6**, the soluble species mainly contained Na and O. The insoluble part of Red mud-2 was also characterized. The EDS spectrum of the treated Red mud-2 was the same as that of the fresh Red mud-2. Red mud-8 was tested by the same method as Red mud-2. It was found that the amount of soluble species for

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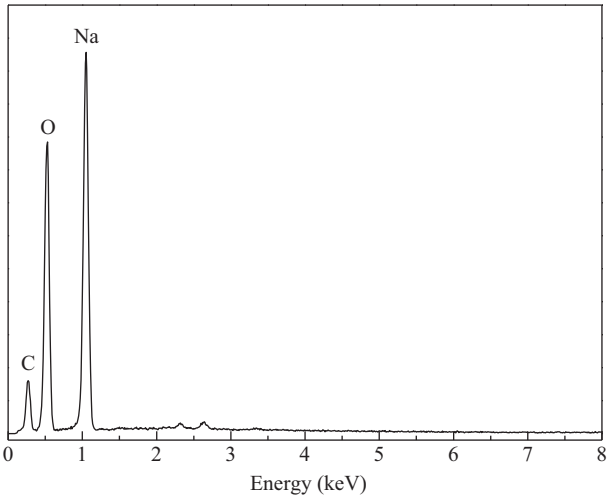

Fig. 6 EDS spectrum of the soluble species of Red mud-2.

Red mud-8 was 0.2 wt.%, which was half of that for Red mud-2. These results indicated that the amount of soluble species was low and changed with calcination temperature. The amount of soluble species was so low that it may have little effect on the pH value of red mud. This explained why the pH value of red mud did not change much when the calcination temperature increased up to 1000°C (pH 11–12). This result could also explain the reusability of red mud. The low activity of used red mud may be due to the loss of the soluble base. This result could also clarify the effect of calcination temperature. The amount of soluble species changed with calcination temperature. This is why the activity of red mud changed with calcination temperature although the pH value of red mud did not change much.

3 Conclusions

Red mud exhibited high activity towards the transesterification of vegetable oil with methanol to produce biodiesel. A 24:1 molar ratio of methanol to oil, addition of 4 wt.% red mud catalysts (calcined at 200°C), and 65°C reaction temperature gave the best results, and the biodiesel yield exceeded 94% at 3 hr. This method of reusing red mud waste to prepare catalyst could recycle the waste, minimize contaminants, and reduce the cost of the catalyst. This highly efficient and low-cost red mud catalyst could make the process of biodiesel production economical. In addition to biodiesel production, such environmentally friendly red mud catalysts should find application in a wide range of other important base-catalysed organic reactions.

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