

Biodiesel Production from Soybean Oil Catalyzed by K_2SiO_3/C

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Abstract: A solid base catalyst (K_2SiO_3/C) capable of microwave absorption was used for the transesterification of soybean oil under microwave radiation. The K_2SiO_3/C catalyst was prepared by an impregnation method that loaded K_2SiO_3 on carbon particles (1–3.5 mm diameter) followed by drying at 120 °C. The catalysts were characterized by X-ray diffraction, scanning electron microscopy-energy dispersive spectrometry, and the Hammett indicator method. K_2SiO_3 was well distributed on the support. The effects of reaction variables such as catalyst loading, molar ratio of methanol to oil, and reaction time (under microwave radiation and conventional heating) were studied. When the conventionally heated reaction was carried out at 65 °C with a methanol/oil molar ratio of 30:1 and a catalyst concentration of 24 wt%, the biodiesel conversion was 96.5% after 2.5 h reaction time. The same reaction reached equilibrium after 1.5 h under microwave radiation, and the conversion of biodiesel was 96.7%.

Key words: biodiesel; solid catalyst; potash water glass; carbon particle; microwave absorption

Global warming due to the heavy consumption of fossil resources and the depletion of natural resources is of increasing concern, and for sustainable development, biodiesel is of increasing attention as a source of renewable energy. The most common way to produce biodiesel is by transesterification. Although transesterification is relatively fast and has high conversions in homogeneous catalyst systems, these have some serious drawbacks [1] such as that the catalyst cannot be recovered and must be neutralized, and the separation of fatty acid methyl esters (FAME) from the catalyst during the process also generates large volumes of wastewater. These problems have led to the search for stable and more environmentally friendly solid catalysts. A literature survey indicated that alkali earth oxides, such as CaO, SrO, and MgO, are the main solid catalysts used for the transesterification reaction [2–4]. Alkali metals or alkali earth salts loaded on metal oxide such as KOH/ Al_2O_3 [5], KF/MgO [6], KI/MCM-41 [7], $Ca(NO_3)_2/Al_2O_3$ [8], and calcined Mg-Al hydrotalcites [9,10] have also been used in recent years.

In recent years, microwave (MW) technology has attracted the attention of researchers due to its unique molecular level

heating to give rapid thermal reactions [11]. Many studies on the application of MW dielectric heating have been reported with homogeneous and heterogeneous catalysts in biodiesel production [12,13]. In this study, a solid catalyst (K_2SiO_3/C) was evaluated as a nonconventional basic solid that can absorb microwave irradiation resulting in energy absorption. It is well known that carbon materials can strongly absorb microwave energy. Due to its non-uniformity, “hot spots” can be generated on the surface of carbon materials where the temperatures (above 1200 °C) are higher than at other places, and where chemical reactions can easily take place [14].

Alkali-silicate binders have been known for a long time and the mechanism of solidification in the sol-gel technique of materials preparation has been gradually understood [15]. A K_2SiO_3 solution used to supply basic sites supported on carbon particles for the transesterification reaction has not been reported. The catalytic performance of the K_2SiO_3/C catalyst was studied to provide a solid base catalyst for the production of biodiesel.

1 Experimental

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1.1 Preparation of the catalyst

The K_2SiO_3/C catalysts were prepared by an impregnation method. Typically, a required amount of K_2SiO_3 solution (reagent grade, 66.2%, Shimadzu's Pure Chemicals) was diluted with 200 ml deionized (DI) water at ambient temperature. The carbon particles (Taiwan Active Carbon Industry Co., dried at 80 °C for 3 h before being used), which was an irregular type of particle size 1–3.5 mm, was then added into the solution followed by vigorous mixing. The amount of K_2SiO_3 solution/carbon was varied from 10 wt% to 30 wt%. After equilibrating the mixture for 1 h, the resulting solution was dried in an oven at 120 °C for 24 h.

1.2 Transesterification reaction procedure

The transesterification reaction was performed in a 250 ml flat-bottom flask equipped with a reflux condenser and a magnetic stirrer. The transesterification reaction of soybean oil (Great Wall Enterprise Co.) and methanol (ACS grade, ECHO Chemical Co.) was carried out in the liquid phase under atmospheric pressure at 65 °C while stirring at 600 r/min for 0.5–3 h. The microwave reactions were carried out in a microwave synthesis reactor (CEM, MARS) working at 2.45 GHz and rated at 150 W. The temperature of the reaction mixture was maintained by a fiber optic temperature sensor (Model: Discover Fiberoptic, CEM; range: –50 to 250 °C). For the conventional heating method, a hot plate was used for heating the mixture in the flask. The heating power of the hot plate was 700 W.

After the transesterification reaction, DI water was added into the reaction mixture to stop the reaction. The supernatant was filtrated through a filter paper, and excess methanol and water were evaporated before the analysis of the FAMES.

1.3 Characterization of the catalyst

The basic strength of the samples (H_-) was determined by Hammett indicators [6]. The Hammett indicators for basic site strength used were: bromthymol blue ($H_- = 7.2$), phenolphthalein ($H_- = 9.8$), 2,4-dinitroaniline ($H_- = 15.0$), and 4-nitroaniline ($H_- = 18.4$). About 1 g of sample was shaken

with 10 ml methanol solution of the Hammett indicator and left for 1 h to achieve equilibration. The total number of basic sites was determined by titration with benzoic acid in methanol using phenolphthalein as the indicator [6]. The X-ray diffraction (XRD) characterization of the catalysts was performed on a MAC MXP18 powder X-ray diffractometer using $Cu K_\alpha$ radiation over a 2θ range from 20° to 80° with a step size of 0.04° at a scanning speed of 3°/min. The microstructures of the K_2SiO_3/C catalysts were observed by a field emission scanning electron microscope (SEM, JEOL JSM-7401F). The FAME concentration, used to express the biodiesel purity of the product, was determined by a gas chromatograph (Thermo trace GC ultra) equipped with a flame ionization detector and a capillary column (Tr-biodiesel (F), Thermo, 30 m × 0.25 mm × 0.25 μm). Nitrogen was used as the carrier gas. The amount of FAME was calculated by the internal standard (methyl heptadecanoate) method according to Chinese National Standards 15051. In order to quantitatively evaluate leaching of the solid base catalyst under the reaction conditions, some parts of the samples taken from the reactor were carefully filtered, and the residual methanol was evaporated in a rotary evaporator so that the FAME and glycerol were left as a separate phase. After the evaporation, the dry fraction was treated with 0.1 mol/L hydrochloric acid [16]. The resulting solution was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro Genesis) to determine the K concentration.

2 Results and discussion

The catalytic activities of carbon particles with different K_2SiO_3 loadings were measured. For comparison, the same reaction conditions shown in Table 1 were employed in all experiments. The reaction conditions were not optimized for the highest reaction conversion. Non-loaded carbon particles exhibited no activity. When K_2SiO_3 was loaded on the carbon particles, the supported catalysts showed catalytic activity. It can be concluded that the observed activities of the carbon supported catalysts were due to their basicity, i.e., a higher basicity result in a higher conversion.

Figure 1 shows the XRD patterns of ground original carbon particles and catalyst particles (loading of 30 wt% K_2SiO_3 solution). The carbon particles and prepared catalyst particles

Table 1 Properties of K_2SiO_3/C particles used as solid base catalyst for the transesterification of soybean oil with refluxing methanol

| Catalyst | K_2SiO_3 solution loading (wt%) | Basic strength | Basicity $H_- \geq 9.8$ (mmol/g) | Conversion* (%) |
|--------------|-----------------------------------|--------------------|----------------------------------|-----------------|
| Carbon | 0 | $H_- < 7.2$ | 0 | No reaction |
| K_2SiO_3/C | 10 | $7.2 < H_- < 9.8$ | 0 | 23.3 |
| K_2SiO_3/C | 15 | $9.8 < H_- < 15.0$ | 0.018 | 42.5 |
| K_2SiO_3/C | 20 | $9.8 < H_- < 15.0$ | 0.043 | 63.3 |
| K_2SiO_3/C | 25 | $9.8 < H_- < 15.0$ | 0.053 | 82.0 |
| K_2SiO_3/C | 30 | $9.8 < H_- < 15.0$ | 0.052 | 81.2 |

*Reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 24:1, catalyst amount 2 g, reaction time 3 h, at the methanol reflux temperature with conventional heating.

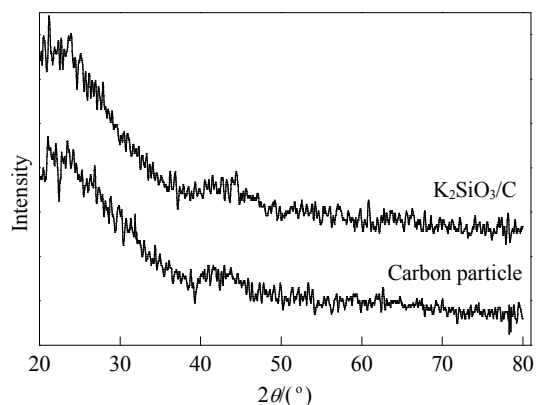


Fig. 1. XRD patterns obtained from ground original carbon particle and catalyst particle.

had the same XRD patterns which was identical to that of C (PDF 261077). No characteristic peak due to K_2SiO_3 or any new species such as KOH and SiO_2 was observed, indicating the high dispersion of K_2SiO_3 on the carbon support [17].

Figure 2 shows typical SEM and EDS mapping images of the K_2SiO_3/C catalyst (30% K_2SiO_3 solution loading) and a used K_2SiO_3/C catalyst. These showed that the morphology was irregular and diverse, with smooth surfaces, large pores, and convex surfaces. The distribution of K_2SiO_3 on the support surface was homogeneous even on the convex surfaces and in the large pores. K_2SiO_3 was found to be very effectively distributed on the surface of the support. In order to remove adsorbed species from the catalyst surface, the used K_2SiO_3/C catalysts were washed with anhydrous methanol and dried at 120 °C for 24 h before examination by SEM. K_2SiO_3 was found to be well distributed on the surface of the support even after the transesterification reaction.

In order to compare the microwave absorption ability of

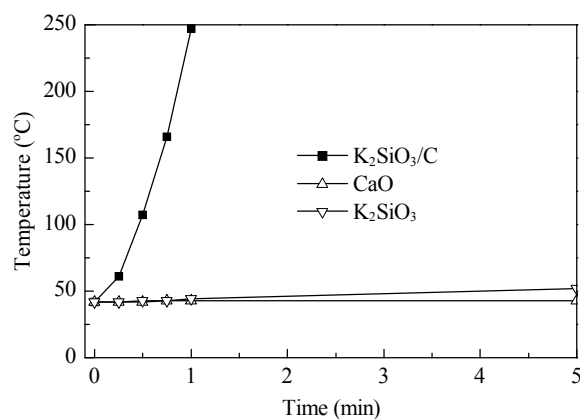


Fig. 3. Temperature profiles of K_2SiO_3/C , CaO, and K_2SiO_3 under 150 W microwave heating of 25 g sample.

carbon particles (30% K_2SiO_3 solution loading), CaO powder and K_2SiO_3 powder (K_2SiO_3 solution dried at 120 °C for 24 h and then well ground), a 25 g sample was placed in a glass reactor with an i.d. of 57 mm that was heated at 2.45 GHz with 150 W. The catalyst temperature was measured by a fiber optic temperature sensor located in the sample. In Fig. 3, it is clearly shown that K_2SiO_3/C is much more effective in absorbing microwave than K_2SiO_3 and CaO since it had a much higher temperature. Therefore, the K_2SiO_3/C catalyst showed a higher energy efficiency and would have a faster reaction rate to shorten the reaction time under microwave irradiation.

The variables investigated included the catalyst amount, alcohol/oil ratio, and reaction time for the K_2SiO_3/C catalyst (30% K_2SiO_3 loading). The catalyst amount was varied in the range of 1–6 g. As shown in Fig. 4, the conversion increased as the catalyst amount was increased to 1–3 g. The conversion reached a plateau value for the catalyst mass of 4–6 g.

In heterogeneous catalysis, mass transfer and reactant ad-

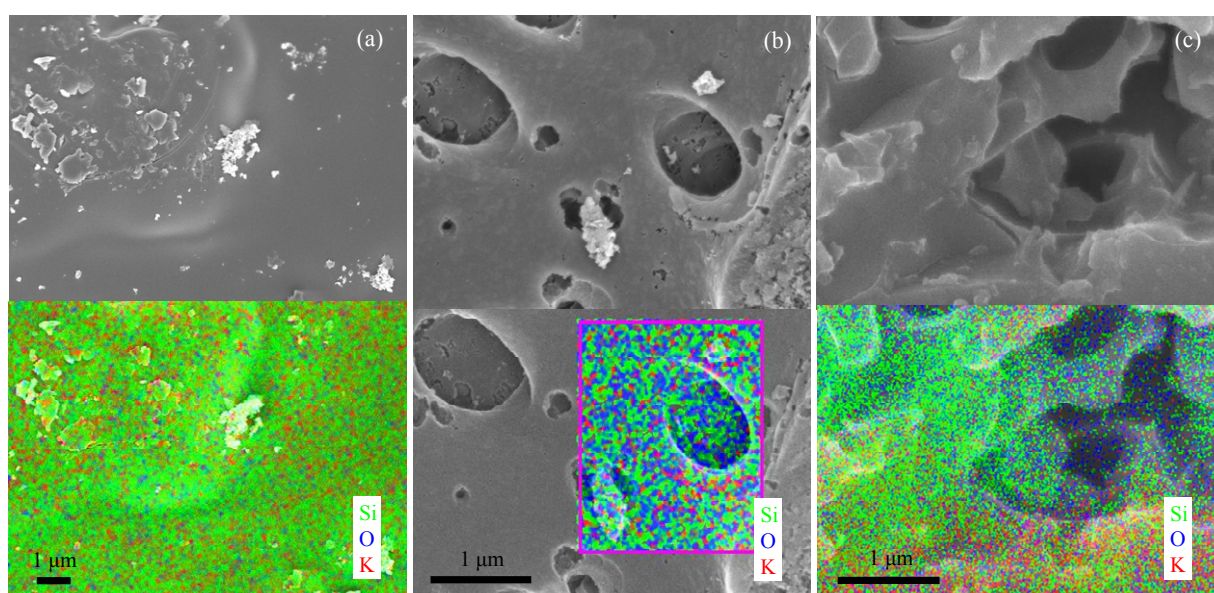


Fig. 2. SEM and EDS mapping of samples. (a) and (b) Fresh K_2SiO_3/C catalyst; (c) Used K_2SiO_3/C catalyst.

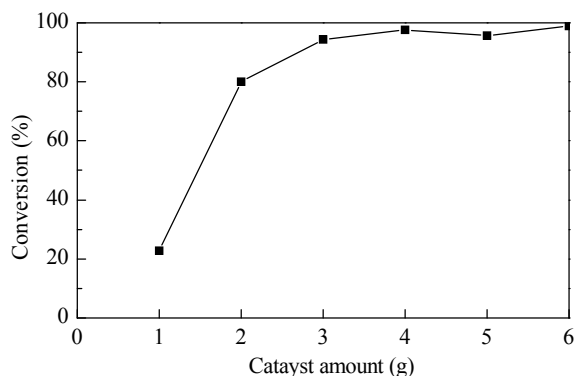


Fig. 4. Influence of catalyst amount on the conversion using conventional heating. Reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 24:1, reaction time 3 h, reaction temperature 65 °C.

sorption on the catalyst are very important; thus, a molar ratio higher than the stoichiometric molar ratio of methanol is needed to shift the equilibrium of the reaction. As shown in Fig. 5, when the methanol loading increased, the conversion increased considerably. The maximum conversion was 96.6% at the methanol/oil molar ratio of 36:1.

To study the effect of microwave radiation and conventional heating on the conversion, experiments were carried out using a K_2SiO_3/C catalyst. As shown in Fig. 6, the reaction reached equilibrium after 1.5 h under microwave radiation. The conversion of biodiesel was 96.7%. However, the reaction did not reach equilibrium when conventional heating was used for 2.5 h. The conversion of biodiesel was 96.5%. That is, a shorter time was needed under microwave radiation compared to conventional heating.

In order to study the stability of the K_2SiO_3/C catalyst, the samples were recovered by simple decantation. The remaining catalyst in the reactor was used to catalyze the next batch of soybean oil. A decline was observed in the conversion to methyl esters from 96.6% to 57.9%, indicating the decrease of catalytic activity. This lowered activity may be explained by the dissolution of K species in the heterogeneous K_2SiO_3/C catalyst. Glycerol covering of the surface of catalyst was also

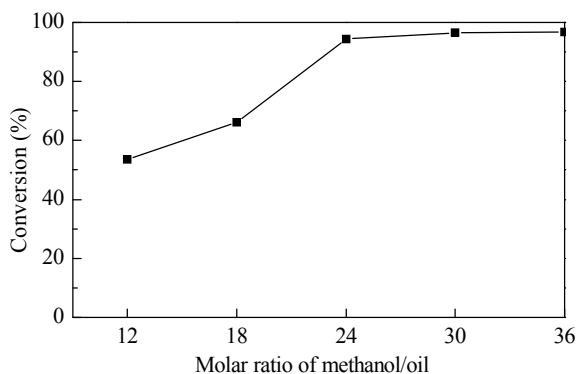


Fig. 5. Influence of methanol/oil molar ratio on the conversion using conventional heating. Reaction conditions: 12.5 g soybean oil, catalyst amount 3 g, reaction time 3 h, reaction temperature 65 °C.

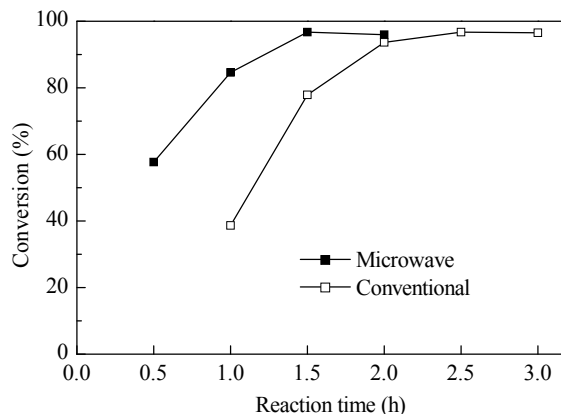


Fig. 6. Comparison of microwave radiation and conventional heating on the conversion. Reaction conditions: 12.5 g soybean oil, methanol/oil molar ratio 30:1, catalyst amount 3 g.

considered as the reason for the activity loss. The stability of the K_2SiO_3/C catalyst was better than that of a KOH/NaX [18] catalyst and KOH/MgO catalyst [19]. After a recycling experiment, it was found that the catalytic activity of the KOH/NaX catalyst and KOH/MgO catalyst decreased to 48.7% biodiesel conversion and 26.45% biodiesel yield, respectively.

The solubility of the catalyst was also a very important factor that should be taken into account to correctly interpret the performance and assess its practical use. This was a very important issue since neutralization and washing steps of the biodiesel produced would be necessary if any metal was found in it. Then, the possible advantage of using the heterogeneous catalyst for this process would be nullified. The results showed that only small quantities (free K^+ concentration was 3.1 ppm) existed in the biodiesel. The results obtained proved that the K_2SiO_3/C catalyst prepared has good potential for the biodiesel production from soybean oil.

3 Conclusions

The K_2SiO_3/C catalyst was prepared by an impregnation method. K_2SiO_3 was well distributed on the surface of the carbon particle and it was an effective base for the transesterification reaction. Furthermore, the K_2SiO_3/C catalyst has good microwave absorption ability and showed high energy efficiency to give a faster reaction rate to shorten the reaction time.

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