

A novel method for the preparation of biodiesel by transesterification of rapeseed oil using $K_2O/\gamma-Al_2O_3$ nano-solid-base catalyst

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Abstract

A novel method was developed for the preparation of biodiesel by transesterification of rapeseed oil and methanol using $K_2O/\gamma-Al_2O_3$ nano-solid-base catalyst. The influences of catalysts preparation conditions and transesterification conditions on the esterifiable ratio of rapeseed oil were studied. Under the optimum condition, the transesterification yield could achieve 94%.

Key words: biodiesel, nano-solid-base, rapeseed oil

Introduction

Biodiesel is obtaining more and more attention as an attractive fuel due to the depleting fossil fuel resources. The significance as a new energy source now results from its environmental benefits and the fact that it is made from renewable resources (Meher et al., 1984; Ayhan, 2003). Chemically produced biodiesel is mono-alkyl esters of long chain fatty acids derived from vegetable oils and animal fats by transesterification of triglycerides with methanol in the presence of catalysts (Xie et al., 2006; Zhang et al., 2005).

In the conventional method, the commonly used catalysts are sodium or potassium hydroxide, and a large amount of wastewater was produced to separate and clean the catalysts and the products. For the development of an environmentally benign process and the reduction of the production cost, heterogeneous catalysts have been studied in recent years (Kim et al., 2004; Sun et al., 2006). Compared with conventional solid base catalysts, nano-solid-base catalysts have been shown great advantages in transesterification (Zhu et al., 2004). The feed stock like rapeseed oil is widely planted all over China, and the "double zero" rapeseed oil is a new breed cultivated in HuBei province which is very suitable for the preparation of biodiesel. So it could be a promising feedstock in biodiesel production. Here it is reported an easy strategy to generate a novel nano-solid-base catalyst $K_2O/\gamma-Al_2O_3$ derived from $\gamma-Al_2O_3$ supported KNO_3 calcined in high temperature and is successfully applied to prepare biodiesel from rapeseed oil.

Experimental

Materials

Water free refined edible rapeseed oil is used in the reactions. KNO_3 and methanol are all analytical pure and the $\gamma-Al_2O_3$ is chemical pure of nano-grain.

Catalyst preparation

K_2O/Al_2O_3 nano-solid-base catalyst is prepared according to pestle-calcination method with some modifications (Zhu et al., 1996). Briefly, designed amount of KNO_3 was mixed with 10g nano- $\gamma-Al_2O_3$ powder, and then a certain amount of distilled water was added. After fully blended, the mixtures were decanted to evaporation dish which were then calcined in muffle for a certain time at the fixed temperature, therefore a series of $K_2O/\gamma-Al_2O_3$ nano-solid base catalysts were obtained. XRD and TEM methods were employed for the catalysts characterization.

Transesterification procedure

A 250ml three-neck glass flask with a water-cooled condenser and an automatic stirrer was charged with 50ml rapeseed oil, a certain amount of methanol and an appropriate amount of catalyst. The mixture was vigorously stirred and reacted for a required time at the fixed temperature. After the transesterification finished, the catalyst was filtered, and then the biodiesel could be separated from the glycerol with a funnel while the residual methanol was distilled from the liquid phase by decompression distillation. Biodiesel yield determination is based on the gas chromatography.

Results and discussion

The process of transesterification is affected by many factors. The main factors include the mode of catalysts preparation, such as loading ratio, calcination temperature and calcination time, and the transesterification condition such as the amount of catalyst in the reaction system, molar ratio of methanol to oil, reaction temperature and reaction time (Xie et al., 2006; Cui & Liu, 2005).

Influence of loading ratio of KNO_3 on $\gamma-Al_2O_3$ on the transesterification

Fig.1 showed the influence of the loading ratio of KNO_3 on $\gamma-Al_2O_3$ on the transesterification yield. A maximum

transesterification yield was obtained at 70 wt. % KNO_3 loading ratio, and further increase of the loading ratio of KNO_3 led to the lower of the transesterification yield. The possible reason might be the formation of multilayer deposition due to the excessive amount of K_2O on the surface of $\gamma\text{-Al}_2\text{O}_3$, which could lead to the decrease of activated points (Zhu et al., 1997). So the suitable loading ratio of KNO_3 was nearly 0.7.

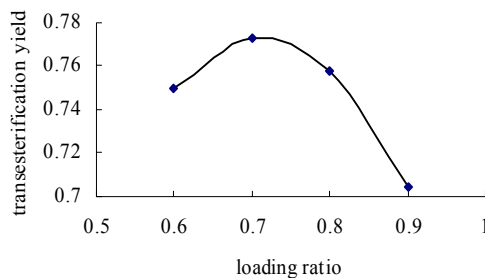


Fig.1. Influence of loading ratio of KNO_3 on $\gamma\text{-Al}_2\text{O}_3$ on transesterification yield (calcination temperature 600°C , calcination time 4h)

Influence of calcination temperature on transesterification

In the process of the solid catalyst preparation, calcinations of catalyst in high temperature makes for the reciprocity between carrier and activated ingredient which forms new crystal lattice, that is a new activated center, so the calcination temperature makes great importance to the catalytic activity. As illustrated in Fig.2, with increasing calcination temperature, the conversion was increased. Biodiesel conversion reached its maximum value at around a calcination temperature of 600°C . However, the conversion gradually decreased as the calcination temperature increasing beyond 600°C . It is maybe that higher temperature sintered the activated ingredient and lowered the catalytic activity (Meng & Xin, 2005). So the appropriate calcination temperature was 600°C .

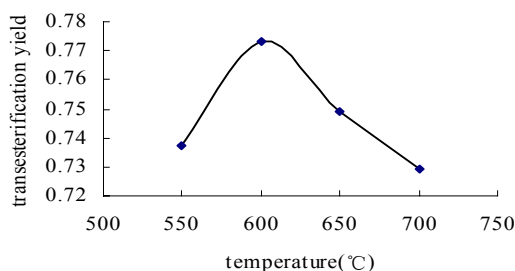


Fig.2. Influence of calcination temperature on transesterification yield (loading ratio of KNO_3 on $\gamma\text{-Al}_2\text{O}_3$ 0.7, calcination time 4h)

Influence of calcination time on transesterification

The influence of calcination time on catalytic efficiency of the catalyst was shown in Fig.3. With prolonging the calcination time from 2h, biodiesel yield gradually increased, and when calcination time was very close to 3h, the maximum conversion is achieved, which indicated that KNO_3 had been totally decomposed. But continually prolonging the calcination time led to the dropping of the esterifiable ratio. The reason is maybe that the new-formed crystal lattice was destroyed when the calcination time is too long and it depressed the catalytic efficiency. So the calcination time was approximately 3h.

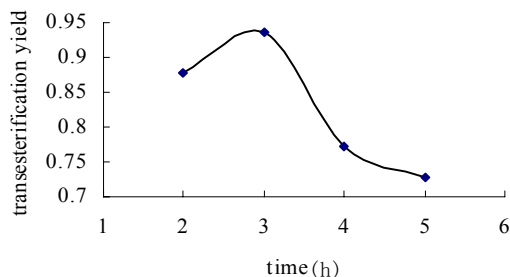


Fig.3. Influence of calcination time on transesterification yield (loading ratio of KNO_3 on $\gamma\text{-Al}_2\text{O}_3$ 0.7, calcination temperature 600°C)

The main conditions influenced the esterifiable ratio, including the catalyst dosage, molar ratio of methanol to oil, reaction temperature, and reaction time. Here orthogonal experiment was adopted to analyze the influences of each factor and screen out the optimum reaction condition.

Table1 Design table of orthogonal experiment

| Number | A | B | C | D |
|---------|-------------------------|--------------------------------|---------------------------|-------------------|
| Factor | Catalyst dosage (wt. %) | Molar ratio of methanol to oil | Reaction temperature (°C) | Reaction time (h) |
| Level 1 | 2 | 8:1 | 60 | 2 |
| Level 2 | 3 | 12:1 | 70 | 3 |
| Level 3 | 4 | 16:1 | 80 | 4 |

Table2 Intuitionistic analytic table of orthogonal experiment

| Number | A | B | C | D | Yield |
|-----------------|-------------------------|--------------------------------|---------------------------|-------------------|-------|
| Factor | Catalyst dosage (wt. %) | Molar ratio of methanol to oil | Reaction temperature (°C) | Reaction time (h) | |
| Experiment 1 | 1 | 1 | 1 | 1 | 0.640 |
| Experiment 2 | 1 | 2 | 2 | 2 | 0.914 |
| Experiment 3 | 1 | 3 | 3 | 3 | 0.804 |
| Experiment 4 | 2 | 1 | 2 | 3 | 0.904 |
| Experiment 5 | 2 | 2 | 3 | 1 | 0.898 |
| Experiment 6 | 2 | 3 | 1 | 2 | 0.900 |
| Experiment 7 | 3 | 1 | 3 | 2 | 0.916 |
| Experiment 8 | 3 | 2 | 1 | 3 | 0.833 |
| Experiment 9 | 3 | 3 | 2 | 1 | 0.936 |
| Average value 1 | 0.786 | 0.820 | 0.791 | 0.825 | |
| Average value 2 | 0.901 | 0.882 | 0.918 | 0.910 | |
| Average value 3 | 0.895 | 0.880 | 0.873 | 0.847 | |
| Pole difference | 0.115 | 0.062 | 0.127 | 0.085 | |

From table 2, it was seen that the value of pole difference $C > A > D > B$, that was to say, influences reaction temperature > catalyst dosage > reaction time > molar ratio of methanol to oil. Choosing the maximum value of the average value of each condition, the optimum condition assemblance was $A_2B_2C_2D_2$, which was catalyst dosage 3wt. %, molar ratio of methanol to oil 12:1, reaction temperature 70°C, and reaction time 3h.

Increase of the catalyst dosage could promote the conversion of biodiesel. But too much base catalyst in the reaction system would lead to saponification reaction, which was unexpected (Liu et al., 2006). So the adequacy catalyst dosage of 3wt. % was chosen. The products of biodiesel and glycerin were difficult to separate if lacking of methanol, but properly increase of the molar ratio of methanol to oil to dilute the reaction liquid is feasible. Too much methanol didn't increase biodiesel yield indeed, also it is wasteful, and so the suitable molar ratio of methanol to oil could be 12:1. Esterifiable ratio increased markedly as the rising of reaction temperature. But when the temperature continually increases, the conversion decreased. The reason was maybe that the boiling point of methanol is 64.7°C, and higher temperature causes volatilization, which reduces the molar ratio of methanol to oil in the reaction system and goes against the process of transesterification (Li & Zeng, 2005). So the suitable reaction temperature was 70°C. As the reaction time goes by, the conversion of biodiesel increased also. The transesterification velocity was very rapid at the beginning of the reaction. When the reaction reached the balance point, the reaction speed slowed down gradually and got to the kinetics balance, which was similar to the kinetics process of homogeneous transesterification. The reaction time was chosen 3h from the results of the orthogonal experiment.

Comparison of general parameters of the quality of biodiesel with Germany Standard (DIN V51606)

Table 3 Comparison of general quality parameters of biodiesel with Germany Standard

| Parameters | Biodiesel sample | Germany (DIN V51606) |
|--|------------------|----------------------|
| Density (g/cm ³ , 15 °C) | 0.883 | 0.875~0.900 |
| Kinematic viscosity (mm ² /s, 40°C) | 5.0 | 3.5~5.5 |
| Neutralization (mg/g, KOH) | 0.317 | ≤0.5 |
| Sulphur content (wt. %) | 0.007 | ≤0.01 |
| Ash (wt. %) | 0.015 | ≤0.03 |
| CFPP (°C) | -5 | ≤0 |

From table3, it is showed that the general quality parameters of the prepared biodiesel sample basically accord with Germany Standard (DIN V51606) (Han et al., 2002).

Conclusions

$K_2O/\gamma-Al_2O_3$ is an attractive and promising nano-solid-base catalyst for the production of biodiesel from rapeseed oil.

The catalyst with 70wt. % of KNO_3 loading on $\gamma\text{-Al}_2\text{O}_3$, which was calcined at 600°C for 3h, was found to be the optimum catalyst and gives the best catalytic activity in the transesterification reaction. When the reaction was carried out at a molar ratio of methanol to oil of 12:1, catalyst dosage 3wt. %, reaction temperature 70°C , and the reaction time 3h, the conversion of rapeseed oil to biodiesel can reach the maximum value of nearly 94%.

The easy preparation, favorable catalytic activity, mild reaction condition, shorter reaction time as well as the easy removal of solid catalyst for the transesterification emphasize the advantage of $\text{K}_2\text{O}/\gamma\text{-Al}_2\text{O}_3$ as nano-solid-base catalyst, and it is an environmentally benign process, which can minimize the production of pollutants.

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