Development of Alumina Supported Alkaline Catalysts Used for Biodiesel Production

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The transesterification of canola oil with methanol was studied in a heterogeneous system, using γ-Al_2O_3 supported alkaline catalysts. All the catalysts were prepared by incipient-wetness impregnation of an aqueous solution of alkaline compounds on γ-Al_2O_3 support. The effects of alkaline compound, methanol/canola oil molar ratio, reaction temperature, catalyst amount, and reaction time in biodiesel production were investigated. The catalyst with KOH loaded on γ-Al_2O_3 gave the highest basicity and the best catalytic activity for this reaction. The highest FAME yield obtained was 89.40%.

Key Words: Biodiesel, canola oil, heterogeneous catalyst, Al_2O_3 supported catalysts.

Introduction

Alkyl esters of long chain fatty acids are called biodiesel. Biodiesel is obtained by transesterification of the triglycerides found in vegetable oils and animal fats with an excess of a primary alcohol (most commonly methanol) in the presence of a homogeneous or heterogeneous catalyst.[1,2] Homogeneous catalytic systems have many drawbacks. Removal of these catalysts to purify the biodiesel fuel and glycerol as a by-product is difficult and requires a large amount of water. Consequently, a considerable amount of wastewater is inevitably produced. To overcome these problems, transesterification over environmentally benign solid catalysts is a promising route.[3−5] Heterogeneous catalysts could be easily separated from the reaction mixture by filtration and then reused. Moreover, they are less corrosive, leading to safer, cheaper, and more environmentally friendly operations. For developing a process of biodiesel production with environmental benignity, much interest has been focused on solid base catalysts for transesterification of vegetable oils with methanol.[4,6] Heterogeneous

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catalysts have been investigated more and more in relation to biodiesel production as a means to overcome the problems caused by using homogeneous catalysts, and it is suggested that using heterogeneous catalysts can produce a favourable yield of biodiesel.[2] A number of articles on the development of heterogeneous catalysts for biodiesel production have been published. For example, KNO_3/Al_2O_3,[7] $Na/NaOH/\gamma$-Al_2O_3,[8] KI/Al_2O_3,[9] calcined Mg–Al hydrotalcites,[10,11] zeolite and metal catalysts,[12,13] Eu_2O_3/Al_2O_3,[14] and Li/CaO[15,16] have been developed to promote the transesterification of vegetable oils.

In the present study, we investigated the possibility of using γ-Al_2O_3 supported alkaline compounds as heterogeneous catalysts for the transesterification of canola oil with methanol. The effects of various factors such as mass ratio of catalyst to oil, reaction temperature, reaction time, and molar ratio of methanol to canola oil were studied to optimise the reaction conditions.

Experimental

Catalyst preparation and characterisation

All the catalysts were prepared by incipient wetness impregnation of γ-Al_2O_3 with an aqueous solution of alkali metal compound. Amounts of alkali metal compounds, such as NaOH, LiOH, KOH, Na_2CO_3, K_2CO_3, were 10 wt.% of the catalysts prepared. The catalysts were dried at 393 K for 16 h and calcined at 773 K for 5 h. Basic strength of the solid bases (H_-) was determined using Hammett indicators. About 50 mg of sample was shaken with an appropriate volume of a methanol solution of Hammett indicator and left to equilibrate for 2 h, after which no further colour changes were observed. In these experiments, the following Hammett indicators were used: dimethylaminoazobenzene (H_-=3.3), phenolphthalein (H_-=8.2), 2,4-dinitroaniline (H_-=15), and nitroaniline (H_-=18.4). To measure the basicity of the catalysts, the method of Hammett indicator–benzene carboxylic acid titration was used.[17] X-ray powder diffraction patterns were obtained from calcined catalyst samples with a Rigaku D/MAX-Ultima+/PC X-ray diffractometer using $CuK\alpha$ radiation at 40 kV and 40 mA and a scan speed of 2 °C/min. Surface areas were measured using Brunauer-Emmett-Teller (BET) surface area measurement (QuantaChrom, Autosorb-1-C). Prior to the adsorption measurements, the samples were dried at 110 °C for 3 h.

Transesterification reaction

Commercial edible grade canola oil was obtained from a market. A 250 cm^3 three-necked glass flask with a water-cooled condenser was charged with 50 g of canola oil, different volumes of anhydrous alcohol, and varied amounts of catalyst. The mixture was refluxed for the required temperature and 9 h of reaction time under stirring at 1000 rpm. After the reaction, the solid catalyst was separated by filtration. The liquid was put into a separating funnel and was kept at ambient temperature for 24 h, after which 2 liquid phases appeared. The upper layer was biodiesel and the lower layer was glycerol. The content in FAME (fatty acid methyl esters) of the upper layer was determined by following the European regulated procedure EN 14103.

Results and Discussion

Catalyst characterisation

The base strengths of γ-Al$_2$O$_3$ modified with different alkali compounds were measured using Hammett indicators. As evident in the Table, loading of NaOH, KOH, LiOH, K$_2$CO$_3$, or Na$_2$CO$_3$ on the surface of alumina could induce the base strength (H_-) in the range of 9.8–15.0. γ-Al$_2$O$_3$ loaded with KOH exhibited a high basicity more than other alumina modified samples. Among the catalysts tested, γ-Al$_2$O$_3$ loaded with KOH exhibited comparatively high activity and the FAME yield obtained was 82.29%. As shown in the Table, when γ-Al$_2$O$_3$ was loaded with alkali compounds, total surface areas of all catalysts were reduced due to coverage of alkaline compounds on the porous surface of γ-Al$_2$O$_3$. Moreover, as seen in the Table, basicity is much more important in the activity of the catalysts prepared for the transesterification reaction of canola oil rather than total surface area.

Table. Catalytic activities and base strengths of γ-Al$_2$O$_3$ support loaded with different alkali metal compounds.

Catalysts	Basic strength (H_-)	Basicity (mmol/g)	BET surface area (m^2/g)	FAME Yield (wt.%)
$\gamma-$Al$_2$O$_3$	< 7.2	-	120-190	0.7
NaOH/γ-Al$_2$O$_3$	15>H$_-$>9.8	1.56	49.64	73.44
LiOH/γ-Al$_2$O$_3$	15>H$_-$>9.8	0.40	90.60	8.99
Na$_2$CO$_3$/γ-Al$_2$O$_3$	15>H$_-$>9.8	1.66	89.57	74.57
K$_2$CO$_3$/γ-Al$_2$O$_3$	15>H$_-$>9.8	1.70	89.12	76.56
KOH/γ-Al$_2$O$_3$	15>H$_-$>9.8	1.76	80.98	82.29
Reaction conditions: methanol/oil molar ratio 6:1, catalyst amount of 3 wt.%, reaction temperature 333 K, reaction time 9 h.				

Figure 1 shows the XRD patterns of KOH/γ-Al$_2$O$_3$, LiOH/γ-Al$_2$O$_3$, NaOH/γ-Al$_2$O$_3$, K$_2$CO$_3$/γ-Al$_2$O$_3$, and Na$_2$CO$_3$/γ-Al$_2$O$_3$. The characteristic peaks of alumina ($2\theta = 37.0°$, $46.0°$, and $66.7°$) were almost unchanged on the XRD patterns regardless of the alkaline compound, indicating that alumina still retained its amorphous structure.[9] Due to the interaction of alkali compound and γ-Al$_2$O$_3$, the formation of new crystal phases was observed. From XRD patterns of the KOH/γ-Al$_2$O$_3$ and K$_2$CO$_3$/γ-Al$_2$O$_3$ catalysts only the presence of a K$_2$Al$_2$O$_4$ phase was observed. Similarly, a NaAlO$_2$ phase was observed from the XRD patterns of the NaOH/γ-Al$_2$O$_3$ and Na$_2$CO$_3$/γ-Al$_2$O$_3$ catalysts. These K$_2$Al$_2$O$_4$ and NaAlO$_2$ phases were probably the cause of the catalytic activity and basicity of the catalysts, since a lithium aluminate (LiAlO$_2$) phase was not observed from the XRD patterns of the LiOH/γ-Al$_2$O$_3$ catalyst, which has lowest basicity and catalytic activity.

Transesterification Reaction

As seen in the Table, 6 different γ-Al$_2$O$_3$ catalysts loaded with different alkali metal compounds were used in the transesterification of canola oil. Reaction conditions were as follows: molar ratio of methanol to oil 6:1,

catalyst amount of 3 wt.%, reaction temperature 333 K, and reaction time 9 h. Although γ-Al_2O_3 support was inactive, the addition of alkali metal compounds to the support improved the catalyst activity. Among the catalysts tested, γ-Al_2O_3 loaded with KOH exhibited comparatively high activity and the FAME yield obtained was 82.29%. Therefore, in the rest of the study in order to investigate the effects of other parameters this catalyst was used.
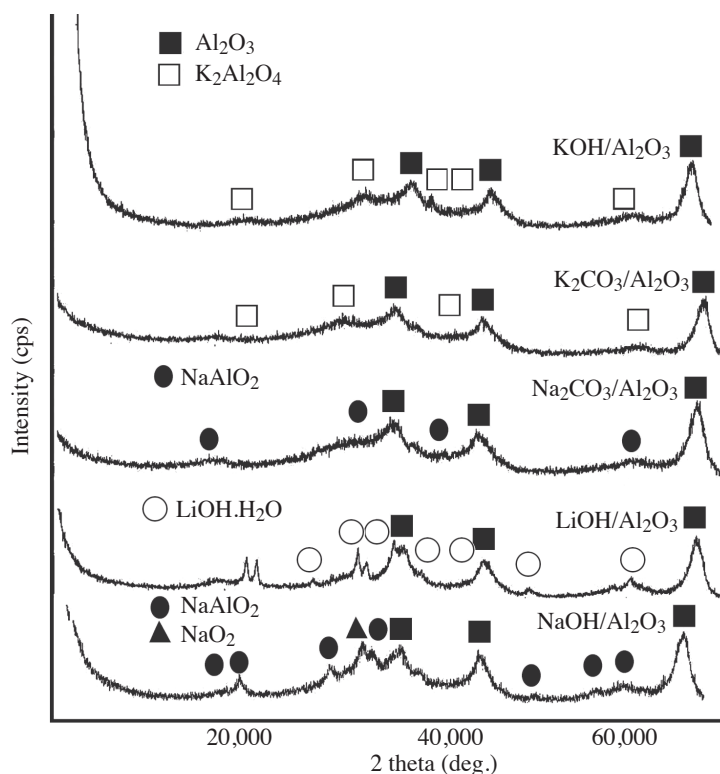

Figure 1. XRD patterns of the prepared catalysts.

The effects of methanol/canola oil molar ratio, reaction temperature, reaction time, and amount of catalyst in biodiesel production were investigated. The stoichiometric ratio for transesterification requires 3 mol of methanol and 1 mol of triglyceride. Since this is an equilibrium reaction, an excess of methanol will increase the conversion of oil and FAME yield by shifting this equilibrium to the right side. Therefore, the effects of methanol/canola oil molar ratio on catalyst activity and FAME yield were studied at 4 different ratios (6:1-15:1) higher than the stoichiometric ratio using 10% KOH/γ-Al_2O_3 catalyst.

As seen in Figure 2, the highest FAME yield of 89.40% was obtained in the reaction carried out at a 12:1 methanol/canola oil molar ratio. Similar results were reported in the literature for different heterogeneous catalysts. For example, Lingfeng et al.[1] studied KF/γ-Al_2O_3 in the transesterification of cottonseed oil with methanol and found that the ester yields increased as the percentage of methanol increased, with the best results being for a molar ratio of 12:1. According to Lingfeng et al., for a methanol/oil molar ratio less than 12:1 the reaction was incomplete, and at 15:1 methanol/oil molar ratio the separation of glycerol was difficult, since the excess methanol hindered the decantation by gravity so that the apparent yield of esters decreased because part of the glycerol remained in the biodiesel phase. Hence, the best results were obtained for an

intermediate methanol/oil molar ratio of 12:1. Yan et al.[18] studied CaO/MgO as a solid base catalyst to catalyse the transesterification of rapeseed oil with methanol. They found that both molar ratios of 3:1 and 6:1 gave poor conversions in heterogeneous catalysis, and a higher molar ratio of methanol to oil resulted in conversions higher than 90%. It was reported that excess methanol can promote the transesterification reaction forward and also extract products, such as glycerine and methyl esters, from the system to renew the surface of the catalyst. Although our results suggest that the optimal molar ratio is 12:1, in order to eliminate excess methanol usage because of environmental and economical reasons, the minimum possible amount of methanol to oil ratio (6:1) was used in the rest of the study. The FAME yield of 82.29% was achieved when the molar ratio was 6:1.
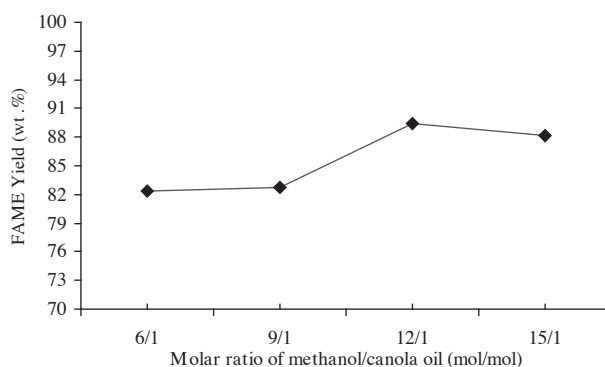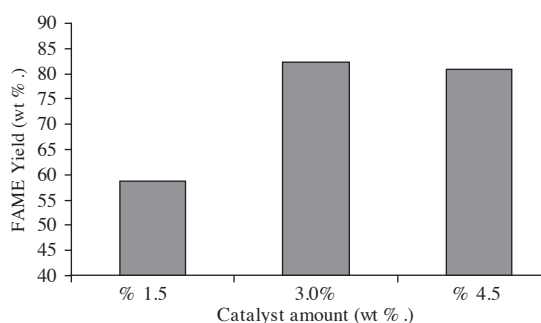

Figure 2. Effect of methanol/oil molar ratios on the FAME yield. Reaction conditions: reaction time, 9 h; catalyst amount, 3 wt.%; temperature, 333 K.

Effects of reaction temperature were investigated at 3 different reaction temperatures: room temperature, 333 K (slightly less than boiling temperature), and reflux temperature of methanol (338 K). The catalyst used in this experiment was 10% KOH/γ-Al$_2$O$_3$. Figure 3 shows the effect of reaction temperature on the FAME yield. As shown, the transesterification reaction is strongly influenced by the reaction temperature. The FAME yield increased with increase in the reaction temperature from room temperature to 333 K and 338 K. The FAME yields at 333 K and 338 K were 82.29% and 79.99%, respectively. A similar result was observed in the literature. In the study by Ma et al.,[2] the heterogeneous base catalyst (K/KOH/Al$_2$O$_3$) was used in the transesterification of rapeseed oil with methanol and the effect of the reaction temperature of transesterification in the range of 30-65 °C was investigated. It was reported that 84.52% yield was obtained at 60 °C.
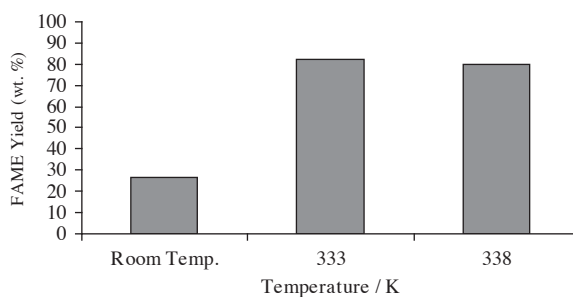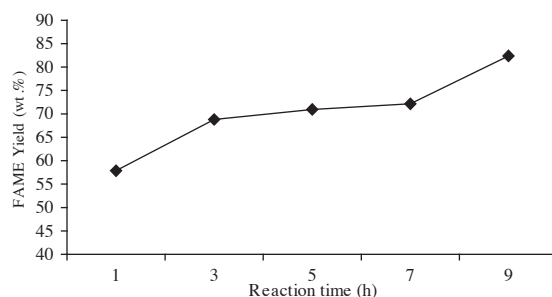

Figure 3. Effect of reaction temperature on the FAME yield. Reaction conditions: methanol/oil molar ratio, 6:1; catalyst amount, 3 wt.%; reaction time, 9 h.

The effect of catalyst loadings on FAME yield was investigated at a 6:1 molar ratio of methanol to canola oil at 60 °C for 9 h by using 10% KOH/γ-Al$_2$O$_3$ catalyst. The catalyst amount referenced to the starting oil weight was varied in the range of 1.5-4.5 wt.%. As shown in Figure 4, FAME yield increased with an increase in catalyst amount from 1.5% to 3%. However, with further increases in catalyst amount FAME yield slightly decreased, which was possibly due to a mixing problem involving reactants, products, and solid catalyst. When increasing the amount of loading catalyst, the slurry (mixture of catalyst and reactants) became too viscous, giving rise to a problem of mixing. In addition, when the catalyst loading amount was not enough, maximum production yield could not be achieved. To avoid this kind of problem, the optimum amount of catalyst loading was investigated. The catalyst amount of 3 wt.% was found to be optimum for the conditions studied.

Figure 4. Effect of catalyst amount on the FAME yield. Reaction conditions: methanol/oil molar ratio, 6:1; temperature, 333 K; reaction time, 9 h.

The effect of reaction time on FAME yield was studied at 60 °C. The reaction time was varied in the range 1-9 h. As seen from Figure 5, after 1 h of reaction time, FAME yield increased significantly and reached 57.75%. With a further increase in reaction time, FAME yield increased and the highest FAME yield of 82.29% was obtained after 9 h of reaction time.

Figure 5. Effect of reaction time on the FAME yield. Reaction conditions: methanol/oil molar ratio, 6:1; catalyst amount, 3 wt.%; temperature, 338 K.

Conclusions

The catalyst 10 wt.% KOH loaded on γ-Al$_2$O$_3$, which has the highest basicity, gave the best catalytic activity for transesterification of canola oil in this study. When the reaction was carried out at 60 °C, with a molar ratio

of methanol to canola oil of 12:1, and a catalyst amount 3%, the highest FAME yield of 89.40% was obtained after 9 h of reaction time. This result indicates that $KOH/\gamma\text{-}Al_2O_3$ catalyst needs to be improved because the FAME yield is less than 96.5%, which does not meet the European Standard for biodiesel (EN 14214).

Acknowledgements

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