Preparation of Na doped SiO_2 solid catalysts by the sol-gel method for the production of biodiesel from jatropha oil

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A new solid catalyst, Na/SiO_2, which have come in demand recently due to environmental concerns is prepared using the sol gel method by transesterification of jatropha oil with methanol to produce a biodiesel fatty acid methyl ester. Na/SiO_2 with a loading of 50 : 50 molar ratio Na/Si, calcined at 600 °C exhibited the best catalytic activity for the reaction. The conversion of vegetable oil is found to be 99%. The optimum reaction conditions are achieved at the reflux temperature of methanol (65 °C), with a 1 : 15 molar ratio of methanol to oil and a catalyst amount of 6 wt%. The catalyst showed high activity under mild conditions and at a relatively short reaction time of 45 min.

1. Introduction

Biodiesel, due to increase in the price of petroleum and crude products, and due to environmental concerns about air pollution caused by the combustion of fossil fuels, has attracted considerable attention during the past decade as a renewable, biodegradable, and non-toxic fuel.[1] Biodiesel is usually produced by transesterification of vegetable oils or animal fats with methanol or ethanol.[2] In many countries, as edible oils are not in surplus of supply, there is a need to search for alternative starting oils such as from non-edible oil seeds. Jatropha oil, due to the presence of toxic phorbol esters is considered a non-edible oil.[3] *Jatropha curcas* is a low-growing tree, can be grown on barren land under harsh conditions and can be cultivated as part of the strategy for reclaiming degraded lands.[4] The economic evaluation has shown that the biodiesel production from *J. curcas* is very profitable provided the by-products of the biodiesel production can be sold as valuable products, especially for countries with large agricultural areas. There are several disadvantages associated with the commonly used alkali-catalyzed transesterification.[5] The liquid alkaline catalyst is corrosive, cannot be recovered from the reactor and is instead neutralized and disposed of as a waster stream. Jatropha oil contains about 14% free fatty acid (FFA), which is far beyond the limit of the 1% FFA level that can be converted into biodiesel by transesterification using an alkaline catalyst. These homogeneous catalyst-based processes thus involve elaborate process steps for removal of FFAs[6] and water from the feedstock and a catalyst from the products. When FFAs are present, they react with the homogeneous alkali catalysts, form unwanted soap by-products and deactivate the catalyst. In addition, water, sometimes present in non-edible, unrefined or waste vegetable oils also leads to the deactivation of homogeneous catalysts. Therefore, the development of heterogeneous catalysts that can eliminate the additional running costs and other problems associated with the homogeneous catalysts is highly desired.[7]

There have also been several reports on the use of heterogenous base or acid catalysts[8] for biodiesel production. Being a heterogeneous basic catalyst, guanidine has the advantage of not producing soaps and thus allowing for an easy phase separation.[9] $Na/NaOH/\gamma\text{-}Al_2O_3$ showed almost the same catalytic activity as NaOH under the optimum reaction conditions.[10] The Esterfip-HTM process involving a heterogeneous solid catalyst consisted of a mixed oxide of zinc and aluminium with a spinel structure, which was developed by the petroleum Institute of France.[11] The Esterfip-HTM process did not involve the neutralization and purification processes; therefore, the polluted water and the running costs were considerably reduced. When commercial CaO was used as a catalyst, the conversion rate of vegetable oil achieved was up to 95.5% after 300 min of reaction.[12] KF/CaO showed a higher activity in transesterification of vegetable oil with methanol as compared to CaO. CaO, dipped in an ammonium carbonate solution becomes a solid super-base and leads to 93% conversion in optimal conditions.[13] Leaching of metal ions was encountered in the case of basic zeolite X and ETS-10 catalysts. A range of catalysts including Mg/Al hydrotalcites, alkali nitrate and alkali carbonate-loaded Al_2O_3, polymer resins, sulfated-tin and zirconia oxides and tungstated-zirconia have also been reported.[8] Most of these catalysts lose their activity on recycle and/or require pretreatment of the feedstock to remove the FFAs and water.

In the present work, a new solid catalyst, Na/SiO_2 is prepared by the sol gel method for transesterification of jatropha oil with methanol to produce a fatty acid methyl ester. The Na/SiO_2 of various Na/Si molar concentrations, calcined at different temperatures is used as an efficient alternative to homogeneous and other reported solid catalysts for jatropha oil transesterification. X-Ray diffraction patterns of the catalyst

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samples are analyzed to get an idea of the structure of the catalyst showing maximum conversion.

2. Results and discussion

Na/SiO$_2$ of various Na/Si compositions, calcined at various temperatures is used for the biodiesel production by transesterifcation using methanol. The reaction parameters are optimized to get maximum conversion. Except for the Na/Si molar ratio study, the system selected for optimization is Na/SiO$_2$ with a Na/Si molar ratio of 50 : 50 calcined at 600 °C. Catalyst loading indicates the weight percentage of catalyst with oil.

2.0 Effect of the Na/Si molar ratio

At lower loading of Na on SiO$_2$, there is not much conversion for the transesterification of jatropha oil using methanol. So we selected high Na/Si molar ratios for the present study. The ratio increased from 40 to 60%. The results are shown in Fig. 1. From the plot it is clear that a 50/50 molar ratio of Na/Si is optimum giving a maximum conversion.

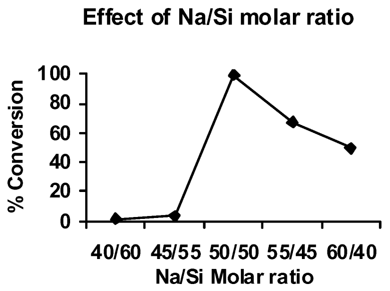

Fig. 1 Effect of the Na/Si molar ratio on fatty acid methyl ester production with a catalyst amount of 6 wt%, oil/methanol molar ratio 1 : 15 and reaction temperature of 65 °C at a 45 min run.

2.1 Effect of time

The reaction time is varied from 0 to 60 min with an interval of 15 min. From the time *vs* conversion plot in Fig. 2, it is clear that conversion increases with time and after 45 min reaches more than 99% and becomes almost constant after 60 min, and so a 45 min duration is selected for further studies.

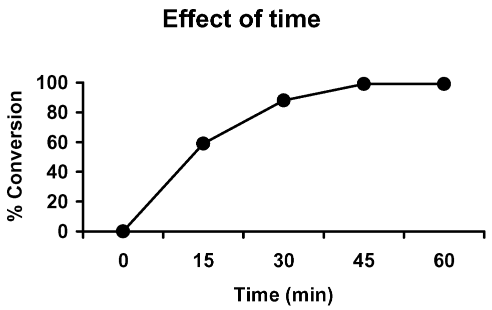

Fig. 2 Optimization of the reaction time with a catalyst amount of 6 wt% and an oil/methanol mol ratio of 1 : 15 at a reaction temperature of 65 °C.

This result is promising since the present catalyst shows very good activity within 45 min of run. Usually the reaction time is greater for many reported solid acids[14,15] and even reaches 26 h.

2.2 Effect of the weight percentage of catalyst/oil

The weight percentage of catalyst to oil is varied from 2 to 6% (based on the weight of the vegetable oil), and the highest percentage selected for the present study shows a maximum yield. The results are shown in Fig. 3. High percentage of 6 wt% or more is shown by KNO$_3$/Al$_2$O$_3$ and some other solid catalysts.[10,16,17] The highest conversion obtained in their study was 84% where the reaction time selected was 6 h.

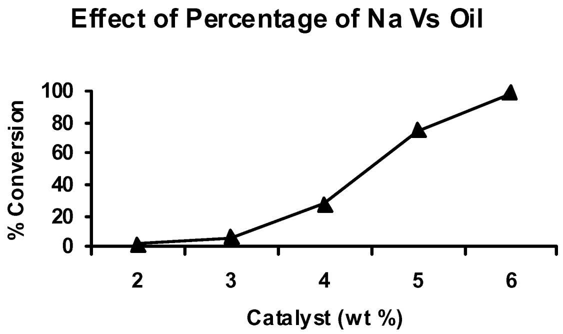

Fig. 3 Influence of the catalyst/oil ratio on biodiesel production with an oil/methanol mol ratio of 1 : 15 at a reaction temperature of 65 °C for a 45 min run.

2.3 Effect of methanol/oil molar ratio

The molar ratio of alcohol *vs* oil is varied from 6 to 15 and at a molar ratio of 15, the conversion is found to be maximum as seen from Fig. 4. Transesterification of soybean oil catalyzed by potassium loaded on alumina as a solid-base catalyst show 15 as the optimum molar ratio, where the catalyst weight was 6.5% for 8 h run.[18] Even though the molar ratio is found to be the highest when compared to many reports, the low reaction time favours the present technique. Excess methanol can be recovered after use.

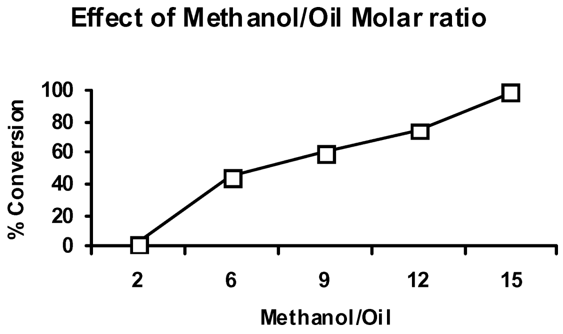

Fig. 4 Influence of the methanol/oil molar ratio on oil conversion with a catalyst amount of 6 wt%, at a reaction temperature of 65 °C and a 45 min run.

2.4 Effect of calcination temperature

Among the various molar ratios of Na/Si, a molar ratio of 50 : 50 gives maximum conversion and thus we selected this system. Its calcination temperature is varied from 400 to 800 °C with an interval of 100 °C. It is found that a calcination temperature of 600 °C is optimum for the present study. The results are shown in

Table 1 Effect of calcination temperature of catalysts for the transesterification of jatropha oil with a catalyst amount of 6%, oil/methanol molar ratio 1 : 15, reaction temperature 65 °C and reaction time 45 min

Calcination temperature/°C	% Conversion
400	21.43
500	38.13
600	99.02
700	54.2
800	27.71

Table 2 Effect of the reaction temperature on the transesterification of jatropha oil with a catalyst amount of 6% and an oil/methanol molar ratio of 1 : 15 for a 45 min run

Temperature/°C	% Conversion
RT	20.67
40	36.59
50	60.07
60	85.04
65	99.02

Table 1. Soyabean oil conversion over KF/ZnO catalysts[19] also shows the same trend in activity with calcination temperature.

2.5 Effect of temperature

The temperature of the reaction is varied from room temperature to the reflux temperature of methanol and in agreement with reports; maximum conversion is obtained at 65 °C as evident from the results shown in Table 2

2.6 Catalyst reusability

The catalyst was recycled to study reusability. After the first run, the catalyst was filtered, washed with methanol and dried. Then the catalyst was used in the second run, *etc*. In the first run, the conversion is 99.02% and in the second run it decreases to 93.1%. In the third run the conversion is 81.71%. In the fourth run, the conversion decreases to 71.62%. So we can use the same catalyst at least three times even without a high temperature treatment of the catalyst to recover its activity. The decreased activity after subsequent runs raised the question of leaching. In order to clarify this, reusability tests was also repeated after activation at 600 °C for 2 h. This was done to ensure the complete removal of any contaminants that may block the active sites of the catalyst, which has a poisoning effect.

Up to the 4th cycle there was only a minute decrease in activity as seen from the results shown in Table 3, whereas in the 5th cycle there is 7.99% decrease in activity. Thus the present catalyst can be effectively used at least for four repeated cycles without much change in activity. We did the XRF analysis of the used samples also to know whether any leaching had occurred or not. The results are the same as the fresh catalysts which eliminates the question of leaching.

From the results of the above studies it is clear that the present systems are found to be a promising catalyst for transesterifcation of jatropha oil. In many cases the use of co-solvent for maximum conversion is reported.[8,10,17] Here even without the presence of any co-solvent, a maximum activity of 99.02% is shown by the catalyst having a Na/Si molar ratio of 50 : 50 which is calcined at 600 °C under optimized reaction conditions.

Table 3 Reusability results of the catalyst activated at 600 °C under optimum conditions

No of clycle	% Conversion
1st	99.02
2nd	98.90
3rd	97.35
4th	97.17
5th	91.11

Table 4 Effect of FFA content on the conversion of jatropha oil

% FFA Content	% Conversion
0.17	99.64
3.6	99.02
4.23	98.90

Table 5 Transesterifcation of jatropha oil in the presence of added water

Amount of water added/wt%	% Conversion
—	99.02
2	98.11
3	97.68
4	97.63
5	97.32

2.7 Effect of FFA and moisture

It is reported that FFAs, when present, inhibited the transesterification on solid-base catalysts.[8] The highest activity of the above catalysts indicates that the catalyst is not affected by FFA and the water content in the reactants. For the present study the FFA content was 3.36%. We repeated the experiments with other jatropha oils with different FFA content and it was found that the conversion was only slightly affected with FFA as shown in Table 4.

Most of the heterogeneous catalysts are adversely affected by the presence of water. The experiment is also done with oils having a different moisture content in order to study the effect of moisture on conversion. It is found that the decrease in activity is not significant with increasing the moisture content (Table 5).

2.8 Effect of the support metal

The influence of other supports on the activity of Na dopant is also investigated using MgO, CaO and Al_2O_3 as the supports (Na/support metal molar ratio 50 : 50, calcination temperature 600 °C, reaction time 45 min, the catalysts are prepared by the impregnation method) The reaction is run at optimum conditions. It is seen from the results shown in Table 6 that activity is not comparable with that of the Na/SiO_2 catalyst of the present study. In the case of Na/CaO, formation of soap occurs which shows the leaching of Na from the support during the reaction which is not recommended for a heterogeneously catalyzed reaction.

Table 6 Effect of the supports on the transesterification reaction of jatropha oil

Catalyst	% Conversion
Na/SiO_2	99.02
Na/Al_2O_3	40.29
Na/MgO	57.01
Na/CaO	65.98

2.9 X-Ray diffraction analysis

XRD patterns of the present samples are taken to find the improved activity of our optimum catalyst as well as its decreased activity with change in calcination temperature and Na/Si molar ratio. Lower calcination temperature is not recommended since it does not allow a complete removal of the surfactant. It is found that the optimum catalyst, calcined at 600 °C shows a $Na_2Si_2O_5$ structure with more of δ-$Na_2Si_2O_5$ as evident from JCPDS data (JCPDS card number 00-022-1396). Small amounts of α, β and γ forms of $Na_2Si_2O_5$ are also found to be present as seen in the XRD profile.

Weak diffraction of Na_2SiO_3 (JCPDS No. 00-016-0818) is also observed in the sample. The XRD pattern of the optimized catalyst is shown in Fig. 5. Change in the calcination temperature from 600 to 700 °C as well as 500 °C, results in an amorphous structure, but at a higher calcination temperature of 800 °C the structure is found to be that of α-$Na_2Si_2O_5$ (XRD patterns are not shown). Thus it may be assumed that a particular structure contributes to the highest activity of the optimum catalyst. Change in the molar ratio of Na/Si is also not favourable to attain this particular structure which may be the reason for the decreased activity with change in the Na/Si molar ratio.

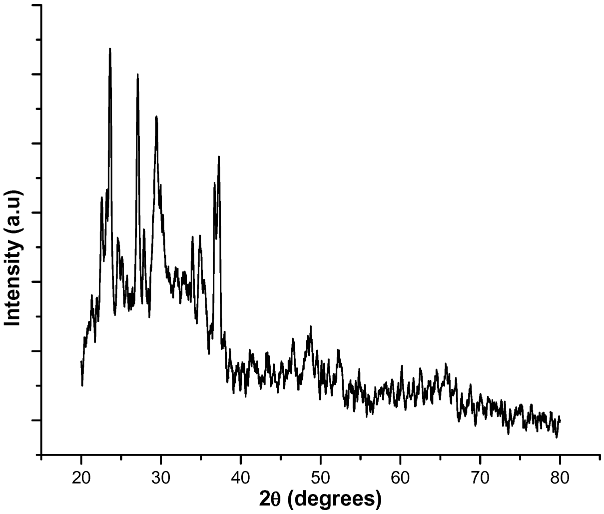

Fig. 5 X-Ray diffraction pattern of the catalyst with a Na/Si molar ratio of 50 : 50 which is calcined at 600 °C.

Fuel properties of biodiesel are important to be determined to ensure the quality of the biodiesel obtained. The properties of biodiesel were compared with European Standard EN14214. It is clearly shown in the Table 7 that the measured values were in the range of EN14214.

Table 7 Fuel properties of biodiesel obtained at optimum conditions

Parameters	Methods	Unit	EN14214	Biodiesel
Ester content	EN14103	% m/m	96.5 min	99.02
Free glycerol	EN14105	% m/m	0.02 max	<0.01
Total glycerol	EN14105	% m/m	0.25 max	0.05
Acid value	EN14104	mgKOH/g	0.50 max	0.11
Iodine value	EN14111	mgI/100 g	120 max	97
Water content	EN ISO 12937	mg/kg	500 max	0.0826

3. Experimental

3.0 Preparation of the catalysts

The desired amount of NaOH (Merck) is added to a mixture of 40 ml ethanol (Merck) and 40 ml distilled water. To this 20 g pluronic P123 (Sigma Aldrich) is also added and mixed thoroughly for 1 h. Tetraethylorthosilicate (20 g, Aldrich) is introduced to the above mixture dropwise and is again mixed for 1 h. The transparent sol obtained is then dried at 80 °C for 48 h. Calcination is done at various temperatures for 6 h.

3.1 Transesterificaton of jatropha oil

The experiment is carried out in a 25 ml round bottom flask equipped with a reflux condenser and a magnetic stirrer. 4.0 g of the jatropha oil (extract of the oil from the seed using the Soxhlet method with n-hexane as solvent) is mixed with the catalyst and then the required amount of methanol is added. The reaction is stirred vigorously using a magnetic stirrer to minimize the limitation of mass transfer.

3.2 Fatty acid methyl ester content (biodiesel) analysis

After the reaction, the solid catalyst is separated by centrifugation. The liquid is put into a separating funnel and is kept at ambient temperature for 6 h, after which two liquid phases appeared. The upper layer is biodiesel and the lower layer is glycerol. The upper layer is separated and analyzed using SRI gas chromatograph equipped with FID detector. Prior to analyzing the methyl ester content of the samples, 0.1 mg of the reaction mixture is weighed and mixed using 100 μl MTSFA (Aldrich) at room temperature for 30 min, and dissolved in 8 ml n-heptane.

4. Conclusions

A promising catalyst is proposed for biodiesel production by transesterifcation of oils with high FFA content. To the best of our knowledge the Na/SiO_2 catalyst of the present study with a Na/Si ratio of 50 : 50, calcined at 600 °C, yields maximum biodiesel production from jatropha oil when compared with any reported solid catalysts, even under mild conditions of operation with a low reaction time. There is little change in the catalytic activity of the reused catalyst even after five repeated cycles. The major advantages of the present system include operational simplicity, mild reaction conditions, low reaction time, high conversion and reusability.

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