

Catalytic synthesis of biodiesel from pongamia glabra over zirconia and its modified forms

Manjunatha Shyamsundar*, Sathgatta Zaheeruddin Mohamed Shamshuddin*[†], and Jaya Narayan Sahu**

*Chemistry Research Laboratory, HMS Institute of Technology, NH-4, Kyathsandra, Tumkur 572 104, Karnataka, India

**Department of Chemical Engineering, University of Malaya, Kuala Lumpur, Malaysia

(Received 20 June 2013 • accepted 12 September 2013)

Abstract—Zirconia & its modified forms such as Mo(VI)/ZrO₂, Pt-SO₄²⁻/ZrO₂, MgO & MgO-ZrO₂ mixed oxide were prepared by impregnation method. These catalysts were analyzed for surface acidity, surface basicity and crystallinity by using techniques such as TPD & powder X-ray diffraction. Mo(VI)/ZrO₂, Pt-SO₄²⁻/ZrO₂ were used as solid acid catalysts for esterification of pongamia glabra (karanja) oil to reduce the concentration of free fatty acid and MgO and MgO-ZrO₂ mixed oxide were used as solid base catalysts for transesterification of karanja oil to produce biodiesel. These zirconia catalysts were found to be highly efficient for the synthesis of biodiesel with more than 90% yield of biodiesel. These solid catalysts can be effectively reactivated and reused.

Key words: Mo(VI)/ZrO₂, Pt-SO₄²⁻/ZrO₂, MgO, MgO-ZrO₂, Transesterification, Biodiesel, Karanja Oil, Pongamia Glabra

INTRODUCTION

Biodiesel is a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, showing several advantages such as (a) biodegradable and nontoxic, (b) produce lower harmful emissions, (c) derived from agricultural surplus, which can also help to improve rural economies. Considering these advantages, there is a growing interest in expanding the biodiesel industry by focusing research on improving the yield and quality of biodiesel [1,2].

Commercially, biodiesel is produced by transesterification of vegetable oils such as sunflower, jatropha, soya bean oil, etc [3]. Transesterification reactions can be performed using homogeneous acid catalysts such as sulfuric acid, phosphoric acid or homogeneous base catalysts such as metal hydroxides, alkaline-earth oxides, etc [4]. Base catalysts are usually preferred over acid catalysts because of higher reaction rates and lower process temperatures required as compared to acid catalyzed transesterification [5]. However, the use of homogeneous catalysts requires neutralization and separation from the final reaction mixture leading to a series of environmental problems related to the use of high amounts of solvents and energy as well. Therefore, it is of interest to investigate the possibility of replacing homogeneous base catalysts by highly efficient solid base catalysts in transesterification reactions for biodiesel production.

Solid base catalysts are advantageous compared to liquid bases, such as ease of separation from the reaction mixture, easy regeneration, less corrosive, economical and eco-friendly.

One of the most important factors that affect the synthesis of biodiesel from vegetable oils using base catalysts is the concentration of free fatty acid (FFA) in oils. If vegetable oil contains more FFA, it may result in soap formation in presence of base catalysts, which

in turn decreases the yield of biodiesel. Therefore, FFA has to be removed from vegetable oils by esterification using acid catalysts. Since homogeneous acid catalysts such as sulfuric acid, phosphoric acid, etc., have disadvantages, the use of heterogeneous acid catalysts is preferred. Once FFA is removed, the vegetable oil can be converted to biodiesel by transesterification using base catalysts. Simultaneous esterification and transesterification in a single step, with a base catalyst is not possible due to soap formation, and with an acid catalyst it takes much longer time for completion.

Esterification of vegetable oils to reduce the % of FFA has been carried out over solid acid catalysts such as sulfated zirconia (SO₄²⁻/ZrO₂) by Sivanesan, et al [6]. Keeping in view the disadvantages of SZ [7], we used Mo(VI)/ZrO₂ and Pt-SO₄²⁻/ZrO₂ as solid acid catalysts for esterification to reduce the % of FFA from karanja oil. These zirconia catalysts also have been found to be effective for acid catalyzed reactions such as esterification, transesterification, and isomerization, to synthesize fine chemicals [8,9].

Synthesis of biodiesel from vegetable oils by transesterification has been studied over a wide range of solid base catalysts such as metal catalysts, resins, zeolites [10-12]. In case of some of the heterogeneous basic catalysts (for example, KOH/Al₂O₃, KOH/NaY, CaO) a part of the active sites are leached from the surface of the catalyst during transesterification and these loaded species could become responsible for a part of the catalytic activity and should be removed from the final product [13]. Xie et al., have used WO₃/AlPO₄, modified SBA-15 silica, KOH/NaX zeolite as solid catalysts for the transesterification of soya bean oil to synthesize biodiesel [14-16]. However, it is necessary to find a more efficient, easily prepared and economical catalyst for the transesterification of vegetable oils for commercial production of biodiesel. We synthesized biodiesel by using zirconia and its modified form such as MgO-ZrO₂, which is easy to prepare, economical and probably an efficient base catalyst. Zirconia and its modified forms are used in many industrially important acid catalyzed reactions [9]. But only a limited literature could be found over modified zirconia as catalysts in base catalyzed reactions.

[†]To whom correspondence should be addressed.

E-mail: em_es@rediffmail.com

Copyright by The Korean Institute of Chemical Engineers.

Since karanja (*Pongamia glabra*) trees are grown extensively in the southern part of India (especially in Karnataka State) and abundant availability of karanja seeds, karanja oil (k-oil) was selected for the present study to synthesize biodiesel. Further, karanja oil is less expensive compared to other vegetable oils, which makes the production of biodiesel more economical.

The emphasis of the present work is to evaluate the activity of modified zirconia catalysts such as Mo(VI)/ZrO₂ & Pt-SO₄²⁻/ZrO₂ as solid acid catalysts for esterification to reduce the percentage of FFA and MgO and MgO-ZrO₂ as solid base catalysts for transesterification to produce biodiesel from karanja oil. Reactivation and reusability studies on these zirconia catalysts were also taken up.

EXPERIMENTAL

1. Catalyst Preparation

1-1. Preparation of Zr(OH)₄

Zr(OH)₄ was prepared by precipitation of zirconyl nitrate with 1 : 1 ammonia solution. The precipitate of Zr(OH)₄ was filtered, washed with deionized water and dried in an air oven at 120 °C for 24 h.

1-2. Preparation of Mo(VI)/ZrO₂

Mo(VI)/ZrO₂ was prepared by impregnation method. 5.4 g zirconyl nitrate and 0.1 g ammonium molybdate were taken in a china dish. The mixture of these salts along with a limited amount of deionized water was mixed well for 1 h to form a paste. The resulting paste was dried in an air oven at 120 °C for 24 h.

1-3. Preparation of Pt-SO₄²⁻/ZrO₂

For the preparation of Pt-SO₄²⁻/ZrO₂ two impregnation steps were followed.

In the first step SO₄²⁻/ZrO₂ was prepared by impregnation of 3.0 g Zr(OH)₄ with 1.5 ml of 3 M H₂SO₄ solution. The resulting mixture was made into a fine paste by mixing the mixture for 1 h, which was then dried in an hot air oven at 120 °C for 24 h.

In the second step SO₄²⁻/ZrO₂ was mixed with known volume of 1.0 ml 1% H₂PtCl₆ solution. This mixture was mixed well for 1 h and made into a fine paste that was then dried in a hot air oven at 120 °C for 24 h to obtain Pt-SO₄²⁻/ZrO₂.

1-4. Preparation of MgO-ZrO₂ Mixed Oxide

Mixed oxide such as MgO-ZrO₂ was prepared by impregnation method. Typically, to prepare MgO-ZrO₂, 4.76 g of magnesium hydroxide was mixed with 5.06 g of zirconyl nitrate. This mixture was mixed well for 1 h and made into a fine paste by using deionized water. The resulting paste was dried in a hot air oven at 120 °C for 24 h.

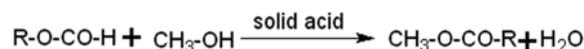
1-5. Preparation of MgO

MgO was prepared by using its magnesium nitrate. Magnesium nitrate was taken in a china dish and made a paste with deionized water. The paste was dried in an air oven at 120 °C for 24 h to obtain magnesium hydroxide.

Thus obtained catalysts were finally calcined in an air oven at 600 °C for 5 h in a muffle furnace before being used as catalysts. Calcined ZrO₂, Mo (VI)/ZrO₂, Pt-SO₄²⁻/ZrO₂, MgO and MgO-ZrO₂ are abbreviated as Z, MZ, Pt/SZ, MgO & MgZ, respectively.

2. Characterization of Catalysts

All the catalysts prepared for the present study were characterized for their physico-chemical properties such as surface acidity,



Scheme 1. Esterification of karanja oil over solid acid catalyst to reduce the percentage of FFA.

surface basicity and crystallinity. The total surface acidity (TSA) and total surface basicity (TSB) of the catalysts was measured by NH₃-TPD and CO₂-TPD methods, respectively. The crystallinity was analyzed by obtaining powder X-ray diffraction (PXRD) patterns recorded by X-ray powder diffract meter (Philips X'pert) using CuK α radiation ($\lambda=1.5418 \text{ \AA}$) using graphite crystal monochromator.

3. Biodiesel Synthesis from Karanja Oil (k-oil)

Biodiesel production involved two steps. The first step was the reduction of percent of FFA from k-oil by acid catalyzed esterification, and the second step was the production of biodiesel *via* base catalyzed transesterification. For both acid catalyzed esterification and base catalyzed transesterification reactions, one of the most favorable molar ratios of k-oil to methanol, i.e., 1 : 12, was used.

3-1. Step-1: Esterification over MZ and Pt-SZ Solid Acids

Since k-oil used for the present study consisted of high amount of high FFA (9%), it had to be reduced to a lesser value preferably below 2.5%. To reduce the concentration of FFA in k-oil, esterification reactions were carried out (Scheme 1).

Esterification of k-oil occurred in a 100 ml round bottomed (RB) flask fitted with a water cooled condenser. The reactions were performed by taking 50.0 g of the k-oil, 0.5 g of solid acid catalyst (Z or MZ or Pt-SZ) and calculated amount of methanol at a reaction temperature of 65 °C for 2 h. The percent of FFA in k-oil after the reaction was measured by determining its acid value by using the acid-base titration method as described elsewhere [7]. Acid value (conversion of FFA) is calculated by using the formula:

$$\text{Acid Value} = (X_1 - X_2) / X_1$$

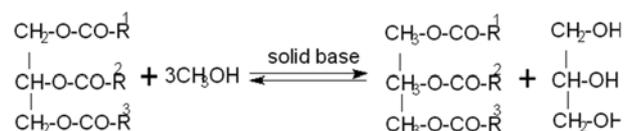
where, X₁ = volume of base required for pure k-oil.

X₂ = volume of base required for k-oil after esterification.

3-2. Step-2: Transesterification over ZrO₂, MgO and MgZ Solid Bases

The transesterification reaction of k-oil (after reducing the % of FFA in Step 1) was carried out in a RB flask fitted with a water cooled condenser. The reaction mixture consisted of 50.0 g of k-oil, 1 g of solid base catalyst (Z or MgO or MgZ) and calculated amount of methanol (Scheme 2). The mixture was heated on a magnetic stirrer-cum-heater at 65 °C using oil bath with constant stirring. After a stipulated reaction period (6 h) the catalyst was separated by filtration, the liquid product was heated to remove excess of methanol, and the remaining oil was allowed to settle overnight.

The lower layer consisting of glycerol and other impurities was drawn off and the upper layer consisting of biodiesel was washed



Scheme 2. Transesterification of karanja oil over solid base catalyst to synthesize biodiesel.

Table 1. Total surface acidity and Total surface basicity of different catalysts used in the present study

Catalyst	*TSA (mmoles/g)	*TSB (mmoles/g)
Z	0.32	0.09
MZ	1.34	-
Pt-SZ	1.49	-
MgO	-	0.96
MgZ	-	1.23

*Unit: (mmoles/g)

with hot de-ionized water at least five times. The final product of biodiesel was subjected for analysis over GC-MS (Hewlett-Packard) fitted with a capillary column (HP-624, 30 m×25 micro meter×0.25 micro meter).

RESULTS AND DISCUSSION

1. Catalyst Characterization

1-1. Total Surface Acidity and Total Surface Basicity

Solid acids such as Z, MZ and Pt-SZ were characterized for their physico-chemical properties such as total surface acidity (TSA) and crystallinity.

TSA values of these solid acids followed the order (Table 1):



Since pure zirconia is amphoteric [17], it consists of both acid as well as basic sites of different strengths. The TSA (overall acidity having different strengths) of pure zirconia was found to be least when compared to either MZ or Pt-SZ (Table 1, Column 2). Incorporation of Mo(VI) or Pt/SO₄²⁻ ions on ZrO₂ increased the TSA value drastically, which can be attributed to the formation of electron deficient states formed upon modification.

Total surface basicity (TSB) of solid bases used for the present work (Z, MgO and MgZ) was found to be in an order (Table 1, Column 3):



Pure zirconia was found to be least basic and MgZ had the highest TSB value. From the TPD experiments, we could only get total basicity or total acidity of solid catalysts, and TPD profiles for the concentration of different strength could not be obtained.

1-2. PXRD Analysis

PXRD patterns of solid acids and solid bases used in the present study are shown in Figs. 1 and 2, respectively. PXRD pattern of pure ZrO₂ consisted of both monoclinic (M) and tetragonal (T) reflections. However, incorporation of Mo(VI) or Pt/SO₄²⁻ ions in ZrO₂ resulted in a transition of monoclinic phase of ZrO₂ to tetragonal phase of ZrO₂. Both MZ and Pt-SZ consisted of only tetragonal phase of ZrO₂ with either very low or nil monoclinic phase.

However, in case of solid bases (MgO and MgZ), PXRD patterns of MgO and MgZ showed characteristic reflections of MgO (JCPDS 42-1164, 72-0597). The PXRD pattern of MgZ showed characteristic reflections due to MgO as well as reflections due to tetragonal zirconia (Fig. 2). Peaks due to monoclinic zirconia were not observed in the case of MgZ. This indicates that the incorpora-

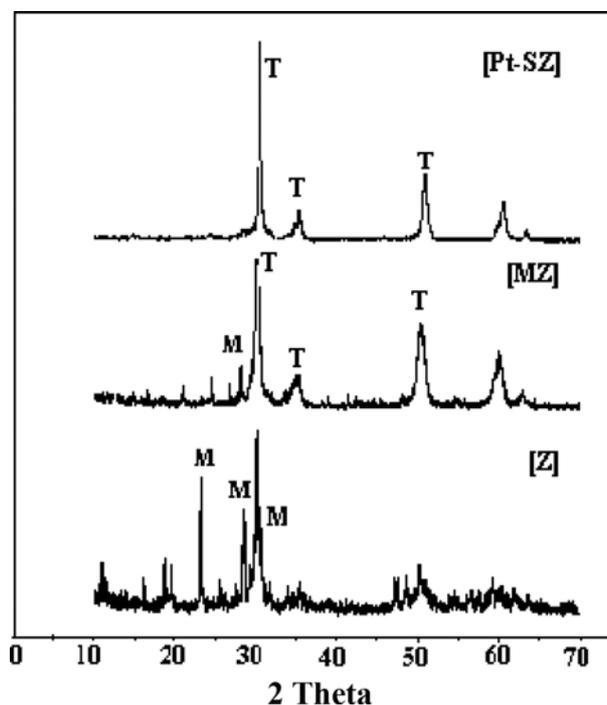


Fig. 1. PXRD patterns of Z, MZ and Pt-SZ [M- monoclinic ZrO₂, T- tetragonal ZrO₂].

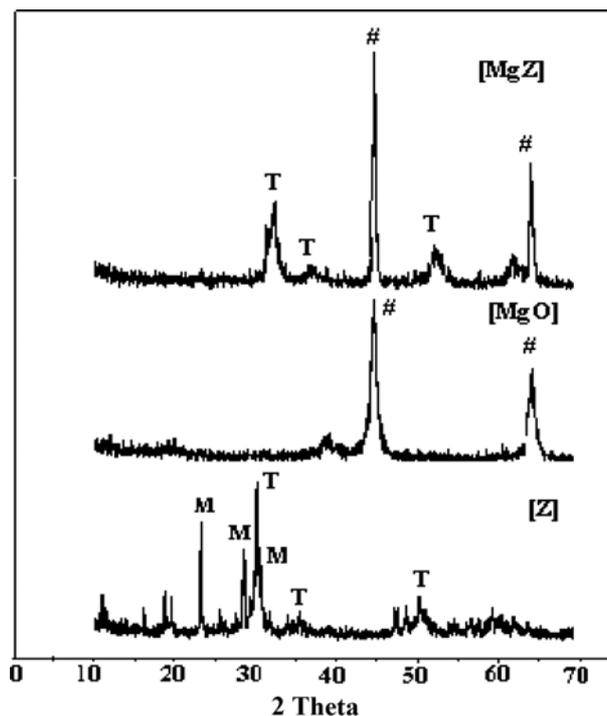


Fig. 2. PXRD patterns of Z, MgO and MgZ [M- monoclinic ZrO₂, T- tetragonal ZrO₂, # - MgO].

tion of either Mo(VI) or Pt/SO₄²⁻ or Mg(II) ions in ZrO₂ assists in a phase transition from monoclinic to tetragonal phase.

No other peaks corresponding to the formation of any compound between MgO and ZrO₂ were observed. This indicates that the catalyst is in the form of a mixed oxide, i.e., MgO-ZrO₂.

Table 2. Acid value and yield (%) of biodiesel over different catalysts

Catalyst	*Acid value (FFA value)	Yield of BD (%)
Z	3.1	32
MZ	2.1	-
Pt-SZ	1.9	-
MgO	-	67
MgZ	-	98

*Unit: mg KOH/g

Acid catalysts/Oil=0.5/50 (w/w), Oil to methanol ratio 1 : 12, FFA value

Base catalysts/oil=1/50 (w/w), Oil to methanol ratio 1 : 12, yield of biodiesel

2. Catalytic Activity of the Catalysts (in BD Synthesis)

2-1. Reduction of %FFA in k-oil

Among the solid acids used in the present study, Mo(VI)/ZrO₂ and Pt-SO₄²⁻/ZrO₂ were found to be highly active in the esterification of k-oil to reduce the percentage of FFA. A good correlation between the total surface acidity (TSA) and catalytic activity of solid acids was observed (Table 2). Since pure zirconia is least acidic showing less activity in esterification and Pt-SZ which is highly acidic was found to be most active for the reduction of % FFA via esterification.

However in case of Pt-SZ catalyst, during the reaction the color of the catalyst changed from white to brown which might be due to the decomposition of either the reactant or the product molecules during the reaction. This decomposition can be attributed to the very strong acid sites available in the Pt-SZ catalyst [7]. However, since pure zirconia and Mo (VI)/ZrO₂ consist of only weak and moderate acids sites [17,18], such discoloration of the catalyst was not observed.

2-2. Production of Biodiesel (BD)

In general, the catalytic activity of solid bases used in the present study followed the order similar to the order of their basicity:



Since zirconia is least basic compared to MgO or MgZ, it showed lowest yield of BD compared to MgO or MgZ catalysts (Table 2, Column 3). Even though MgO is a pure basic catalyst, it showed low yield of BD than over MgZ catalyst. Thus, a maximum yield of BD was achieved over MgZ catalyst.

The increased activity of MgZ towards the yield of BD can be attributed to the dispersion of MgO particles on ZrO₂ support, which results in the availability of more number of basic sites (active centers) required for transesterification reaction. Further, when pure MgO was used as a catalyst, the color of BD obtained was grayish and slightly more viscous than the BD obtained when the reactions were carried out over Z or MgZ catalysts. This might be due to the availability of very strong basic sites on pure MgO [19], which decomposes either the reactants or the product molecules and also results in the color change of pure MgO from pure white to grayish color. However, the extent of decomposition in case of MgZ was found to be much less as the amount of strong basic sites of MgO would be decreased when used in its mixed oxide form with zirconia.

It is reported [20] that the tetragonal phase of zirconia is more

catalytically active than in its monoclinic phase. Since MgZ consists of only tetragonal phase of zirconia, an enhanced catalytic activity has been observed when compared to pure zirconia.

It is also reported [18] that a triangular relationship exists between the total surface acidity, PXRD phase and catalyst activity of zirconia based solid *acid* catalyst. A similar relationship is observed in the present study, i.e., a relationship between total surface basicity, PXRD phase and catalyst activity of zirconia based solid *base* catalysts (Z and MgZ). Further, in the present work, pure zirconia consisting of both monoclinic and tetragonal phase was less basic and less catalytically active. But, MgZ catalyst which consists of only tetragonal phase of zirconia was found to be more basic and more catalytically active for BD synthesis.

This indicates that the tetragonal phase of zirconia is not only responsible for enhanced activity in an acid catalyzed reaction but also enhances the catalytic activity in *base* catalyzed reaction.

3. Reactivation and Reusability Studies of Solid Catalysts

The solid acids (Z, MZ, and Pt-SZ) and solid bases (Z, MgO, and MgZ) were reactivated after the first cycle of the reaction. The used catalyst was separated from the reaction mixture by filtration, thoroughly washed with methanol and dried in a hot air oven at 120 °C for 12 h. The solid catalyst was then calcined at 600 °C for 1 h in a muffle furnace before its use in the second reaction cycle. A similar procedure was repeated after every reaction cycle for reactivation of the solid catalyst.

3-1. Reusability of Solid Acids (Z, MZ, Pt-SZ) in Esterification

Among the solid acids used in the present study, Z and MZ were found to be more reusable and hence efficient catalysts for esterification of k-oil to reduce the concentration of FFA (Acid value) when used for five reaction cycles (Fig. 3). Though Pt enhances the stability of SO₄²⁻/ZrO₂ catalyst, Pt-SZ was found to lose its catalytic activity to a certain extent. However, the present study reveals that MZ is more active, stable and efficient solid acid catalyst when compared to Pt-SZ.

3-2. Reusability of Solid Bases (Z, MgO, MgZ) in Transesterification

As can be seen in Fig. 4, both Z and MgZ were found to be ef-

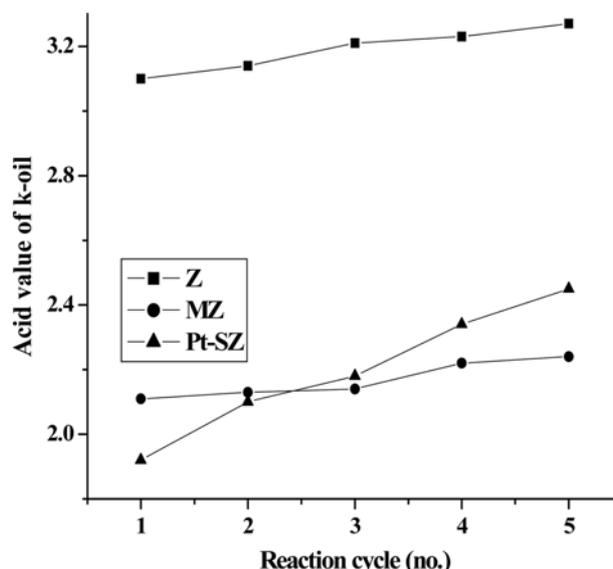


Fig. 3. Reusability of solid acid catalysts.

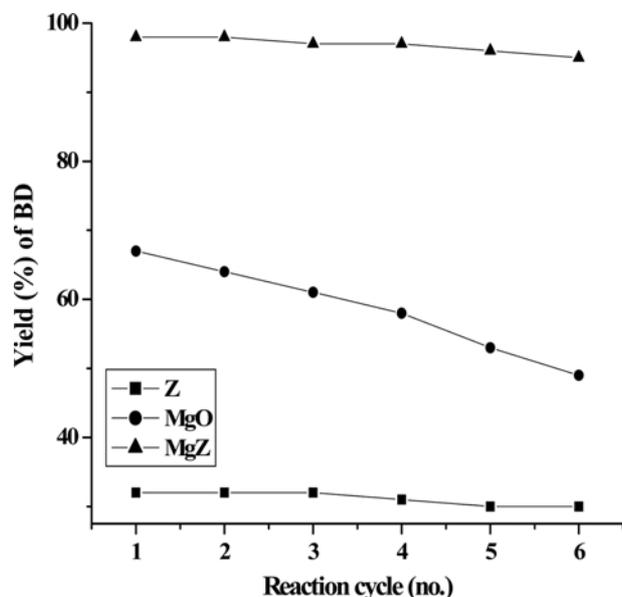


Fig. 4. Reusability of solid base catalysts.

efficient solid base catalyst for BD synthesis because not much change in the activity of Z or MgZ was observed when transesterification was carried for five reaction cycles.

However, over pure MgO, the yield (%) of BD decreased from 67% to ~45, when reused for six reaction cycles. This shows that the presence of ZrO_2 in MgZ catalysts improves the stability and activity of MgO and hence MgZ was found to be more reusable than pure MgO.

Further, it would be of great interest in biodiesel production to find a facile catalyst system which can be economical, efficient and ecofriendly (3e concept) [21]. In continuation with the work presented in this article, studies are being carried out to use catalyst carriers such honeycomb monoliths to coat zirconia and its modified forms [22], which would be an interesting step in the production of biodiesel. The use of honeycomb monoliths as catalyst carriers for zirconia and its modified forms are assumed to follow 3e concept.

CONCLUSIONS

Zirconia catalysts were found to be highly useful in biodiesel synthesis from *Pongamia glabra*. Zirconia modified with Mo(VI) or Pt/SO_4^{2-} was found to be efficient in acid catalyzed esterification to reduce the percentage of FFA, and zirconia modified with MgO are useful for base catalyzed transesterification to produce biodiesel. In particular, Mo(VI)/ ZrO_2 and MgO- ZrO_2 were found to be efficient, eco-friendly and economical solid catalyst for acid catalyzed esterification and based catalyzed transesterification reaction respectively. These zirconia based solid catalysts can be reactivated and reused for at least five reaction cycles. A triangular correlation be-

tween acid-basic property of zirconia and its modified forms, PXRD phases of zirconia and their catalytic activity was observed. In view of the efficiency of zirconia catalysts, further studies are being carried out to make the biodiesel production more economical, efficient and ecofriendly.

ACKNOWLEDGEMENTS

Authors are thankful to DST, New Delhi for funding through a major project, Department of Chemical Engineering, University of Malaya, Kuala Lumpur for PXRD analysis, IITM, Chennai for TPD analysis and Bangalore Test Center, Bangalore for GC-MS analysis.

REFERENCES

1. Y. Zhang, M. A. Dube, D. D. Mclean and M. Kates, *Bioresour. Technol.*, **90**, 229 (2003).
2. A. A. Refaat, *Int. J. Environ. Sci. Technol.*, **8**(1), 203 (2011).
3. F. Ma and M. A. Hanna, *A Review, Bioresour. Technol.*, **70**, 1 (1999).
4. H. Sanli and M. Canacki, *Energy Fuels*, **22**, 2713 (2008).
5. Y. C. Sharma, Bhaskar Singh and John Korstad, *Energy Fuels*, **24**(5), 3223 (2010).
6. K. V. Thiruvengadravi, J. Nandagopal, P. Baskaralingam, V. Sathya Selva Bala and S. Srivanesan, *Fuel*, **98**(1) (2012).
7. G. D. Yadav and J. J. Nair, *Micropor. Mesopor. Mater.*, **33**, 1 (1999).
8. M. Hino and K. Arata *Chem. Commun.*, **18**, 851 (1980).
9. B. M. Reddy, *Chem. Review*, **109**(6), 218 (2009).
10. G. J. Suppes, M. A. Dasari, E. Doskocil, J. Mankidy and M. J. Goff, *Appl. Catal.*, **257**, 213 (2004).
11. M. J. Ramos, A. Casas, L. Rodriguez, R. Romero and A. Perez, *Appl. Catal.*, **346**, 79 (2008).
12. M. E. Borges and L. Diaz, *Renewable and Sustainable Energy Reviews*, **16**(5), 2839 (2012).
13. K. Noiroj, P. Intarapong, A. Luengnaruemitchai and S. Jai-In, *Renew Energy*, **34**, 1145 (2009).
14. Wenlei Xie and Minglaing Fan, *Bioresour. Technol.*, **139**, 388 (2013).
15. Wenlei Xie and Dong Yang, *Bioresour. Technol.*, **60**, 119 (2012).
16. Wenlei Xie, Xiaoming Huang and Haitao Li, *Bioresour. Technol.*, **98**, 936 (2007).
17. K. Tanabe, *New solid acids and bases*, Academic Press, New York (1970).
18. N. Nagaraju and S. Z. Mohamed Shamshuddin, *J. Mol. Catal.*, **73**, 55 (2007).
19. W. N. Wan Omar and Nas Amin, *Fuel Process. Technol.*, **92**, 2397 (2011).
20. N. Nagaraju and S. Z. Mohamed Shamshuddin, *Catal. Commun.*, **7**(3), 593 (2006).
21. M. Shyamsundar and S. Z. Mohamed Shamshuddin, *Int. J. Innovative Research in Sci., Eng. Technol.*, **2**, 3 (2013).
22. S. Z. Mohamed Shamshuddin, M. Shyamsundar and N. Thimmaraju, *Comptes Rendus Chemie*, **15**(9), 799 (2012).