

Sulphated Fe₂O₃-TiO₂ catalysed transesterification of soybean oil to biodiesel

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Sulphated Fe₂O₃-TiO₂ has been synthesized from ilmenite ore and calcined over 300-900 °C. The catalyst samples have been examined for acidity by adsorption of pyridine. The spectral studies reveal the presence of sulphate groups and both Brønsted and Lewis acid sites. The transesterification of soybean oil with methanol is studied over unsulphated and sulphated Fe₂O₃-TiO₂ catalysts with varying sulphate contents and the results are evaluated on the basis of acidity. The catalyst samples calcined below 500 °C show higher conversion of vegetable oil with significant yield of biodiesel which could be due to the greater affinity of hydroxyl groups of methanol on Fe₂O₃-TiO₂. The sulphated Fe₂O₃-TiO₂ samples calcined above 500 °C show lower conversion of biodiesel and this is proposed to be due to the removal of sulphate groups during calcination.

Keywords: Catalysts, Transesterification, Metal oxides, Sulphated metal oxides, Iron oxide, Titania, Ilmenite ore, Vegetable oils, Biodiesel

The need for non-toxic, economic, pollution free biodiesel prompts the exploration of renewable resources like vegetable oil. Presence of free fatty acids (FFA) and water in these oils preclude the use of homogeneous catalysts. Base catalysts react with FFA to produce soap and the reactivity is affected by the presence of water. In the production of ‘green fuel,’ heterogeneous acid catalysts are used to carry out the esterification and transesterification simultaneously using low cost feedstock. The catalysts do not affect the free fatty acid present in the feedstocks. Ecofriendly heterogeneous acid catalysts include heteropolyacids, sulphated metal oxides, tungstated zirconia, sulfonated carbonized sugar, sulfonic acid functionalized mesoporous silica, sulphated zirconia on SBA-15, etc.¹⁻⁴

Sulfonated carbons obtained by pyrolysis of sugar in nitrogen atmosphere and sulfonated Si/C material obtained through mesoporous silica SBA-15 are found effective in biodiesel production⁵⁻⁸. Chabukswar *et al.*⁹ showed that sulphuric acid was a better catalyst than sulfonated microcrystalline cellulose, but the solid catalyst enabled good conversion and reusability for esterification. Multifunctionalized ordered mesoporous carbon with hydrophilic groups and the hydrophobic framework showed improved catalytic activities for biodiesel production¹⁰.

Many metal oxides and sulphated metal oxides find application in various reactions¹¹⁻¹⁷ such as isomerisation, dehydration, alkylation, esterification and transesterification because of the possibility of their recovery for reuse and tailoring their properties by controlling various parameters such as acidity, pore size, surface area, etc. Higher conversion (over 90%) for both esterification of *n*-octanoic acid and transesterification of soybean oil with methanol was observed with the superacid catalyst, tungstated zirconia-alumina¹⁸. Sulphated zirconia (SZ) prepared by the solvent-free method was found to be an efficient catalyst for simultaneous transesterification and esterification of rapeseed oil in the presence of 10 wt% myristic acid. The presence of the latter significantly increases the initial reaction rate non-catalytically¹⁹. The same catalyst was also found to be more effective in the transesterification of soybean oil than the SZ prepared by precipitation method⁴. ZrO₂ supported La₂O₃ catalyst, prepared by the impregnation method, was examined in the transesterification reaction of sunflower oil with methanol to produce biodiesel. The results showed that the yields of fatty acid methyl esters (FAME) depend on their basicity²⁰. Catalytic activity of zirconia supported mixed metal oxides prepared by sol-gel process²¹ depends on metal composition. These catalysts can achieve simultaneous

esterification and transesterification reactions on feedstock of 33% FFA and 67% soybean oil to achieve FAME yields higher than 90%.

A pseudo-homogeneous second order reversible reaction model was proposed for the esterification of myristic acid with methanol in presence of triglycerides using sulphated zirconia as catalyst²². The catalytic performance of TiO₂ supported on SiO₂ was studied in batch and continuous reactors in the transesterification of vegetable oils with methanol²³. The catalyst failed in the life-time test in continuous tubular reactor in which a slow leaching process occurs deactivating the catalyst in 100-150 h. Mesoporous sulphated titania-silica composites S-TSC-450 and S-TSC-550 were evaluated for esterification of oleic acid and transesterification of waste oil with methanol to yield methyl esters. These catalysts possessed high catalytic activity comparable to pure H₂SO₄ implying the surface modification²⁴. A very high yield (>99.0%) of FAME from crude *Jatropha* oil using heterogeneous catalyst, FeO_x/SiO₂ was promoted via the acidic function of the catalyst under reaction condition²⁵.

Considering the catalytic activity of the metal oxides, especially iron and titanium oxide, the naturally occurring ilmenite ore, which is composed of iron and titania, has been chosen for the alcoholysis of the vegetable oil. Ilmenite is inexpensive sand available in plenty in southern coasts of Tamil Nadu. While considering metal oxide alone, the yield of biodiesel depends on factors such as acidity, basicity and lifetime of the catalyst employed. To overcome these problems, ilmenite ore was surface activated. The sulphated forms of both oxides are known for their catalytic activities. We have earlier reported the synthesis of sulphated Fe₂O₃-TiO₂ using ilmenite and H₂SO₄ as the starting materials²⁶ and its catalytic activity towards *tert*-butylation of phenol. The sulphation of ilmenite generates both Lewis acid and Brønsted acid sites. The catalytic activity of the present catalyst has been tested with transesterification of soybean oil. The effect of the sulphate group on the catalytic activity has been observed by varying the calcination temperature of the sample. Reusability and a one-step approach to achieve high biodiesel yield free from soap is the significant aim of this work.

Materials and Methods

Ball-milled Ilmenite (Kilburn Chemicals) ore was sulphated with conc. H₂SO₄ (36N, Qualigens, India) according to reported procedure²⁶. The SFT samples

calcined in muffle furnace at various temperatures are denoted as SFT-300, SFT-500, SFT-700 and SFT-900, where the numbers indicate the temperature of calcination. The soybean oil was procured from market and used as such. The acid value of the soybean oil was found to be 0.3 mg KOH/g.

Wide-angle XRD patterns of the as-synthesized and calcined materials were obtained on a Rigaku Miniflex II diffractometer, using CuK α irradiation. The composition of the catalysts was analysed using Rigaku XRF spectrometer. Pyridine adsorption-desorption measurements was used for the identification of Brønsted and Lewis acid sites of the catalyst. The thermal analyses of the samples were performed on PerkinElmer TG/DTA using alumina as the reference. The BET-surface area of the samples was measured using Micromeritics ASAP-2020 analyzer after the samples were degassed in vacuum at 300 °C for 3 h. For ready reference, the composition, crystallite size, BET-surface area, and pore volume of the SFT samples are given in Table S1 (Supplementary Data²⁶).

Transesterification of vegetable oil

The transesterification reactions were performed in Teflon-lined stainless steel (100 mL) autoclave using 10 g of soybean oil, catalyst (5-15 wt% of oil) and high methanol-to-oil molar ratio. Stirring and heating were performed on a heating plate with magnetic stirrer. The reactions were carried out at 100 °C for 2 h. At the end of the experiments, the autoclave was cooled and the catalyst was separated from the reaction mixture by centrifugation and filtration. Two separate liquid layers were formed. Unreacted methanol and glycerol formed the lower layer while the upper layer consisted of fatty acid alkyl esters (biodiesel). The layers were separated by decantation, washed with brine, dried with anhydrous magnesium sulphate and filtered. The products of the transesterification reaction were analysed on HPLC/Shimadzu CTO-20A equipped with UV-vis detector ($\lambda = 205$ nm) and Shim-Pack VP-ODS column (C-18, 250 mm, 4.6 mm i.d.)²⁷. The reproducibility of experiments was confirmed by three consecutive runs.

Results and Discussion

Catalytic studies

Transesterification of vegetable oil is well studied by several authors using superacid catalysts. It has been reported that the superacid catalysts such as

sulphated titania (ST) and sulphated zirconia showed high conversion of cotton seed oil to methyl ester¹⁷. The introduction of sulphate anions creates Brønsted acid sites. However, higher methyl ester yields were obtained for ST due to its higher specific surface area of 99.5 m²/g compared to 91.5 m²/g of SZ. High temperature of 230 °C and pressure of 10 Mpa with long time duration was needed to achieve high biodiesel yield. Below 250 °C, ST and SZ showed both strong Lewis and Brønsted acidity but when the temperature was increased to 450 °C, the Lewis and Brønsted acidity decreased slightly, but nevertheless remained relatively strong in the transesterification of cotton seed oil¹⁷. Several organic nucleophilic substitution and addition reactions can be catalysed by Fe³⁺ ion due to its Lewis acidity. It was reported²⁸ that the reduction in the yield of FAME using base catalyst CaO and Li-CaO from Jatropa oil can be increased markedly by the addition of Fe₂(SO₄)₃. The reduction in the yield of FAME using base catalyst, in general, may be due to soap formation which can be overcome by introducing acidic sites by surface modification or in presence of co-catalyst such as Fe₂(SO₄)₃. Methanolysis²⁹ of rapeseed oil with 2 wt% SO₄/Fe₂O₃ alone showed a yield of 80% at 220 °C. For FeOx/SiO₂ catalysts, the optimal iron loading was preferably 7 wt%, suggesting that low valent Fe site was more effective in the transesterification reactions than the higher oxidation sites²⁵. This prompted us to examine the catalytic activity of the unsulphated Fe₂O₃-TiO₂ and various sulphated Fe₂O₃-TiO₂ (SFT) materials for transesterification of soybean oil with methanol. Initially, the transesterification was carried out without catalyst and was found to proceed unfavourably. With unsulphated catalyst calcined at 500 °C, the conversion of soybean oil was found to be 24% over a period of 5 h. To improve the conversion of oil, the SFT catalysts calcined at various

temperatures have been tested and the results are summarised in Table 1. The SFT samples calcined at 300 °C and 500 °C were analysed on DRIFT spectra which revealed a broad absorption band between 800 and 1200 cm⁻¹ corresponding to sulphate groups³⁰. The peak observed at 1140 cm⁻¹ was attributed to asymmetric stretching of sulphate species³¹. On comparing the surface area of ST and SFT, the SFT samples have low surface area. The surface area values remained constant with temperatures up to 500 °C and showed insignificant change for SFT-700 and SFT-900 samples. However, transesterification of edible oil using SFT samples showed high conversion at 100 °C for 2 hours when compared with ST and SZ. Therefore, it appears that the presence of sulphate and Fe/Ti sites are responsible for Brønsted and Lewis acid sites of the SFT samples. XRD patterns of the SFT samples show the diffraction lines at 2θ(°) of 32.8, 34.9, 46, 48.8, and 56.7 due to the formation of FeTiO₃. The peak at 2θ of 54.5 is due to the presence of Fe₂O₃. The peak at 2θ of 18.2 may be due to Fe₂TiO₅ and the peak at 39.4 is due to Fe₂TiO₄. The enhanced catalytic effect due to the presence of Fe²⁺ in FeTiO₃ and Fe₂TiO₄ is confirmed and stabilization of different oxidation states of iron oxide is anticipated due to the high valency of titania. The data on the composition of the SFT samples determined by XRF method showed the presence of sulphate, silica, titania and iron oxides. The samples calcined up to 500 °C showed almost the same composition. Nevertheless, the calcination of the sample at 700 °C drastically decreased the sulphate content from 8.1% to 1.4%. The SFT-900 sample showed almost the same sulphate content as that of SFT-700. The weight loss obtained between 430 and 610 °C for the samples calcined between 300 and 500 °C may be due to the removal of sulphate groups. The study reveals the thermal stability of the sample up to 500 °C. The

Table 1 – Products and yields of transesterification reactions with SFT-500 catalyst. [React. cond.: SFT sample: 1.5 g; methanol-to-oil molar ratio (mol/mol): 1:20; react. temp.: 373 K; react. time: 2 h]

Sample	Soybean oil conv. (%)	Monoglyceride and fatty acids (%)	Diglyceride (%)	Triglyceride (%)	Biodiesel (%)
FT-500 ^a	23.6	4.20	16.6	76.4	2.80
SFT-300	100	7.54	1.06	traces	91.4
SFT-500	98.3	5.11	1.01	1.68	92.2
SFT-700	76.5	15.5	18.3	20.5	45.7
SFT-900	65.7	11.3	24.2	34.3	30.2

^aReact. time: 5 h.

thermograms of SFT-700 and SFT-900 showed that these samples do not contain adsorbed water molecules, hydroxyl groups and sulphates. The SFT samples calcined at 700 °C and 900 °C showed low intensity bands at 840 and 940 cm^{-1} ; other than that these samples exhibited no absorption bands in the region of 700–1300 cm^{-1} , showing the removal of sulphate groups from the samples. This was well observed from the fall in the yield of the biodiesel beyond the calcined temperature of 500 °C. The peak at $2\theta = 31.2^\circ$ due to iron titanium sulphate is observed for all the samples irrespective of the temperature of calcinations. In accordance with XRD measurements, the SFT samples calcined at 900 °C for 2 h showed significant absorptions at 1880, 2000, 2140 and 2245 cm^{-1} due to the formation of iron titanate and iron titanium sulphate. This is responsible for the reactivity of SFT-700 and SFT-900.

In biodiesel production, in addition to the calcination temperature, various factors such as acidity, methanol-oil feed ratio and reaction time influenced the oil conversion. The DFT studies on the structures of pyridine adsorbed SFT suggest that the sample is susceptible to adsorption of hydroxyl groups than water molecules in SFT sample³². This is also evidenced from the DRIFT spectral data of the SFT samples showing absorption bands at 3400 and 1640 cm^{-1} due to the stretching modes of adsorbed water and hydroxyl groups. The IR studies also revealed that the interaction between sulphate group and any other reactants is possible when SFT sample is used as an acid catalyst. The DRIFT spectra of the pyridine adsorbed SFT samples calcined at ≤ 500 °C shows both the pyridinium ion band at 1540 cm^{-1} and the band due to coordinated pyridine at 1485 cm^{-1} indicating the presence of both Brønsted and Lewis acid sites, respectively³². In addition, the intensity of bands at 1540 cm^{-1} for Brønsted acidity is greater than that at 1480 cm^{-1} (due to Lewis acid sites), thus indicating greater Brønsted acid sites in the samples. The adsorption of pyridine on SFT samples calcined at 700 and 900 °C showed no peaks at 1485 and 1540 cm^{-1} ; revealing the absence of Brønsted and Lewis acid sites on these samples. The increasing calcination temperature from 500 to 700 °C accounted for the removal of 82 wt.% of sulphate. This shows that the catalysts can be effectively used at less than 500 °C.

Adsorption of water or hydroxyl groups on Fe, Ti and/or S sites is the origin for the conversion of Lewis acid sites into Brønsted acid sites. It is expected that

methanol is adsorbed on the Lewis acid (Fe^{3+} and Ti^{4+}) and creates the Brønsted acidity. The approach of alcoholic groups towards Fe-sulphate site is more favourable than towards Ti-sulphate due to weaker Fe-sulphate bond. This was confirmed by the reaction of phenol with *tert*-butanol¹⁶. Acidic sites of the catalyst contribute to the methanol activation, forming a methoxide anion through the coordination of methanol oxygen with $\text{Fe}^{3+}/\text{Ti}^{4+}$ site as shown in Scheme 1. The keto group of triglyceride is activated by the Lewis site of the catalyst and subsequent attack of methoxy nucleophile on carbonyl carbon results in the formation of ester and diglyceride. The same mechanism is expected to operate and can result in the formation of fatty acid methyl ester and glycerol.

It is known that the methanolysis of vegetable oil requires three moles of methanol for each mole of oil. However, transesterification requires higher molar ratio than that of the stoichiometric ratio in order to produce more methyl esters. The effect of feed ratio on the product yield over SFT-500 was examined at 100 °C for a reaction time of 2 h. The reaction was performed by varying the feed ratio of methanol-to-oil ratio from 1:10 to 1:40 and the results are presented in Fig. 1. In acid catalysed transesterification, the triglyceride is converted into di- and mono-glyceride and subsequently into methyl esters. The conversion increases with increase in methanol-to-oil feed ratio, as the methanol is employed as nucleophile. It is well known that increasing the quantity of catalyst can increase rate of reaction and thereby higher conversion and yield. In this study, higher conversion is achieved

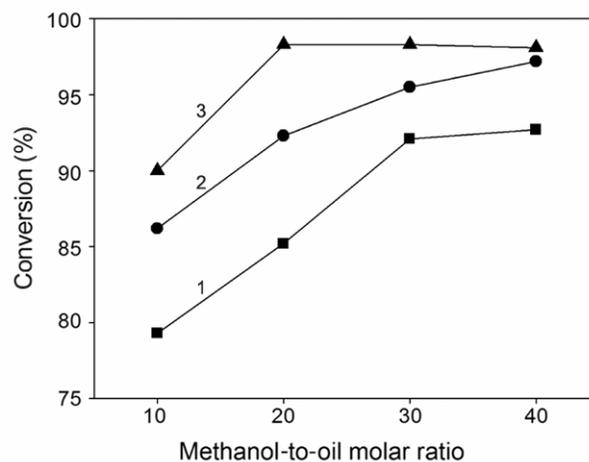


Fig. 1 – Effect of molar ratio of methanol-to-oil on oil conversion over SFT-500 at 373 K for 2 h. [Catalyst amt: 1 (■), 5 wt.%; 2 (●), 10 wt.%; 3 (▲), 15 wt.%].

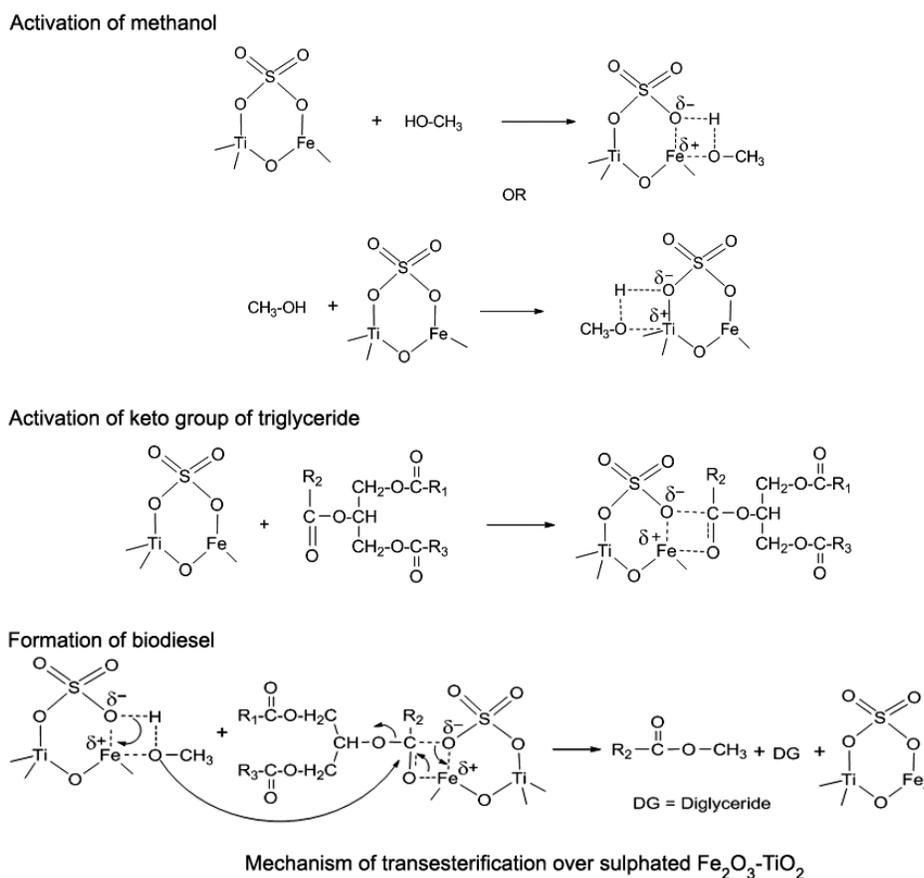
**Scheme 1**

Table 2 – Products and yields of transesterification reactions with SFT-500 catalyst. [React. cond.: SFT-500: 1.5 g; methanol-to-oil molar ratio (mol/mol): 1:20; react. temp.: 373 K]

Time (h)	Soybean oil conv. (%)	Monoglyceride and fatty acids (%)	Diglyceride (%)	Triglyceride (%)	Biodiesel (%)
0.5	44.8	5.90	18.6	55.2	20.3
1.0	70.3	9.10	10.1	29.7	51.1
1.5	85.6	15.6	4.30	14.4	65.7
2.0	98.3	5.11	1.01	1.68	92.2

with 1:20 feed ratio of oil-to-methanol with 15 wt% of catalyst loading. Methyl ester yield for a period of 2 h has been shown in Table 2 and Fig. 2. When the reaction was run for 1 h, the conversion is 70% for soybean oil. The conversion is 98% when the reaction was run for 2 h in an autoclave at 100 °C with SFT-500. Thus, the reaction time influences the biodiesel yield also.

Four successive runs of transesterification of vegetable oil were performed on SFT-500 in order to ascertain its reusability (Fig. 3). A decrease in conversion and product yield was observed with successive runs. The catalyst obtained from the above

reaction mixture was used again for the transesterification process. The catalyst used for the second run showed a conversion of 12% less than the conversion obtained for the first run. The catalyst used for the third run gave a conversion of 17% less than the conversion obtained during the first run. The catalyst used for the fourth run showed 20% lower conversion than the conversion obtained for the first run. After each run, the catalyst was filtered, washed with methanol, dried at 100 °C and thereafter measured for the sulphate content using XRF spectrometry. The sulphate content for runs 1, 2, 3 and 4 is respectively 8.1, 6.8, 5.3 and 4.7 wt%. The decreasing conversion

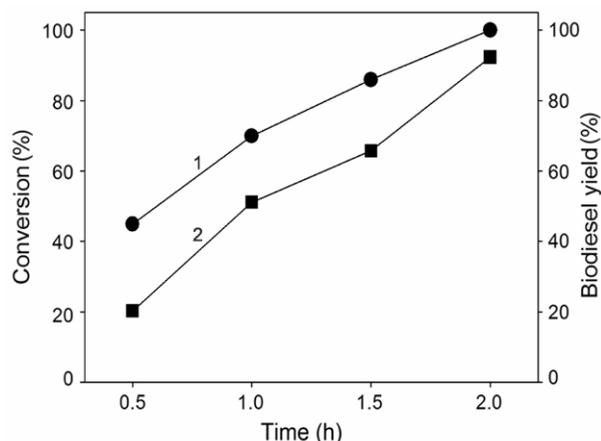


Fig. 2 – Effect of conversion of oil (1, ●) and FAME yield (2, ■) on SFT-500 as a function of time. [React. cond.: SFT-500: 1.5 g; methanol-to-oil molar ratio (mol/mol): 1:20; react. temp.: 373 K; react. time: 2 h].

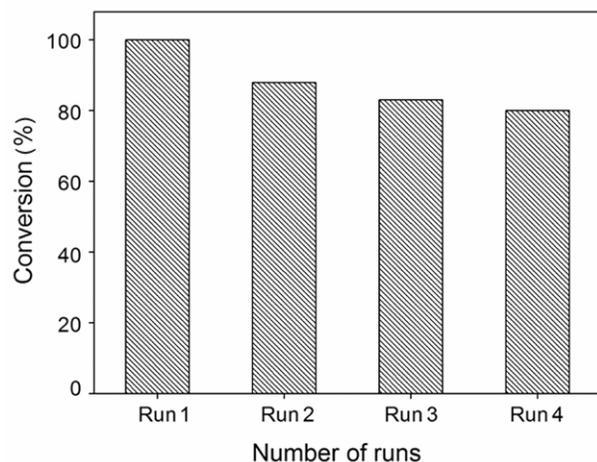


Fig. 3 – Effect of conversion and yield for four reaction cycles on SFT-500. [React. cond.: SFT-500: 1.5 g; methanol-to-oil molar ratio (mol/mol): 1:20; react. temp.: 373 K; react. time: 2 h].

with successive runs demonstrates the leaching of sulphates from the surface of the catalyst.

The evaluation of biodiesel formation on SFT-500, SFT-700 and SFT-900 shows that it is about 47% lower on SFT-700 and about 62% lower on SFT-900 than SFT-500. This observation demonstrates the removal of sulphates from the surface of the catalysts when calcined at 700 and 900 °C, thereby lowering the catalytic activity. The catalytic activity was evaluated for the milled ilmenite sand (FT-500); the biodiesel obtained on the fresh sand was 2.8%. This experiment explains the inevitability of sulphate groups for the catalytic activity.

Conclusions

In the present work, transesterification of vegetable oil using sulphated $\text{Fe}_2\text{O}_3\text{-TiO}_2$ was carried out. The XRD data reveals the existence of iron in high and low valent oxidation states. The combination of Fe_2O_3 and TiO_2 present in the catalyst strongly holds the sulphate on its surface which accounts for the catalytic activity of the samples, irrespective of the lower surface area. The pyridine adsorption-desorption studies revealed the presence of Brønsted and Lewis acid sites which are essential for the activation of alcohol and keto groups of triglycerides of oil respectively. Lewis acid is expected to accelerate the transesterification while Brønsted acid sites prevent soap formation leading to high conversion and high selectivity of the transesterification reaction. With successive runs, a decrease in the conversion was observed due to the leaching out of sulphate.

Supplementary Data

Supplementary data associated with this article, i. e., Table S1, is available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA_53A\(12\)_1493-1499_SupplData.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA_53A(12)_1493-1499_SupplData.pdf).

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References

- Narasimharao K, Brown D R, Lee A F, Newman A D, Siril P F, Tavener S J & Wilson K, *J Catal*, 248 (2007) 226.
- Lopez D E, Suwannakarn K, Bruce D A & Goodwin Jr J G, *J Catal*, 247 (2007) 43.
- Chen X R, Ju Y H & Mou C Y, *J Phys Chem C*, 111 (2007) 18731.
- Garcia C M, Teixeira S, Marciniuk L L & Schuchardt U, *Bioresour Technol*, 99 (2008) 6608.
- Toda M, Takagaki A, Okamura M, Kondo N J, Hayashi S, Domeni K & Hara M, *Nature*, 438 (2005) 178.
- Zong M H, Duan Z Q, Lou W Y, Smith T J & Wu H, *Green Chem*, 9 (2007) 434.
- Lou W Y, Zong M H & Duan Z Q, *Bioresour Technol*, 99 (2008) 8752.
- Dhainaut J, Dacquin J P, Lee A F & Wilson K, *Green Chem*, 12 (2010) 296.
- Chabukswar D D, Heer Parminder Kaur K S & Gaikar V G, *Ind Eng Chem Res*, 52 (2013) 7316.
- Chang B, Fu J, Tian Y & Dong X, *J Phy Chem C*, 117 (2013) 6252.
- Hino H & Arata K, *Chem Lett*, (1979) 477.
- Tanabe K, Kayo A & Yamaguchi T, *J Chem Soc Chem Commun*, (1981) 602.

- 13 Kayo A, Yamaguchi T & Tanabe K, *J Catal*, 83 (1983) 99.
- 14 Comelli R A, Vera C R & Parera J M, *J Catal*, 151 (1995) 96.
- 15 Jin T, Machida M, Yamaguchi T & Tanabe K, *Inorg Chem*, 23 (1984) 4396.
- 16 Joseph Antony Raj K, Prakash M G & Viswanathan B, *Catal Sci Tech*, 1 (2011) 1182.
- 17 Chen H, Peng B, Wang D & Wang J, *Front Chem Eng China*, 1 (2007) 11.
- 18 Furuta S, Matsuhashi H & Arata K, *Catal Commun*, 5 (2004) 721.
- 19 Rattanaphra D, Harvey A & Srinophakun P, *Top Catal*, 53 (2010) 773.
- 20 Sun H, Ding Y, Duan J, Zhang Q, Wang Z, Lou H & Zheng X, *Bioresour Technol*, 101(2010) 953.
- 21 Kim M, DiMaggio C, Salley S O & Simon Ng KY, *Bioresour Technol*, 118 (2012) 37.
- 22 Rattanaphra D, Harvey A P, Thanapimmetha A & Srinophakun P, *Renew Energ*, 36 (2011) 2679.
- 23 Di Serio. R. Tesser M, Casale L, D'Angelo A, Trifuoggi M & Santacesaria E, *Top Catal*, 53 (2010) 811.
- 24 Shao G N, Sheikh R, Hilonga A, Lee J E, Park Y H & Kim H T, *Chem Eng J*, 215-216 (2013) 600.
- 25 Suzuta T, Toba M, Abe Y & Yoshimura Y, *J Am Oil Chem Soc*, 89 (2012) 1981.
- 26 York R S, Joseph Antony Raj K, Subramanian V R & Viswanathan B, *Coll Surf A Phys Eng Asp*, 367 (2010) 140.
- 27 DaSilveira Neto B A, Alves M B, Lapis A A M, Nachtigall F M, Eberlin M N, Dupont J & Suarez P A Z, *J Catal*, 249 (2007) 154.
- 28 Endalew A K, Kiros Y & Zanzi R, *Energy*, 36 (2011) 2693.
- 29 Wang Z, Sun X, Sun G & Liu G, *China Oils Fats*, 32 (2007) 59.
- 30 Yamaguchi T, *Appl Catal*, 61(1990) 1.
- 31 Berger F, Beche E, Berjoan R, Klein D & Chambaudet A, *Appl Surf Sci*, 93 (1996) 9.
- 32 Joseph Antony Raj K, Prakash M G, Shanmugam R, Krishnamurthy K R & Viswanathan B, *Indian J Chem*, 50A (2011) 1050.