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Development of highly efficient solid acid catalysts supported on mesoporous KIT-6 for esterification of oleic acid

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Abstract−This study aimed at the synthesis of heterogeneous acid catalysts by incorporating 12 tungstophosphoric acid (HPW) over mesoporous silica support KIT-6 via impregnation and sol-gel methods to improve the catalytic efficiency of the esterification reaction. The catalytic activity of the KIT-6 supported catalysts was investigated for esterification of oleic acid in the presence of MeOH. Synthesized catalysts were analyzed using scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) and Fourier transform infrared (FTIR) spectroscopy techniques. Characterization results showed the variation in porosity, roughness, presence of SiO_2 and kegging structure after successful deposition of HPW over KIT-6 surface. Additionally, the textural property of synthesized catalysts was compared with highly active HPW and sulfated KIT-6. The ordered structure of mesoporous silica KIT-6 facilitated the dispersion of HPW resulting in better catalytic stability and activity. To evaluate the impact of synthesizing technique on catalytic activity and effectiveness of heterogeneous acid catalysts, loading of HPW over KIT-6 mesoporous silica was controlled between 10 to 30 wt%. Catalysts synthesized by impregnation and sol-gel methods showed the highest catalytic activity with 30-IM and 25-SG, respectively. The enhanced performance was ascribed to the improved textural property and amount of HPW, which led to higher activity, stability and reusability.

Keywords: 12 Tungstophosphoric Acid (HPW), KIT-6, Esterification, Impregnated, Sol-gel

INTRODUCTION

Energy is a basic element of the modern life and sustainable supplies of energy are of vital importance for the socio-economic growth of societies [1-5]. Enormous efforts have been documented recently regarding the production of energy from renewable sources due to continuous depletion of fossil fuel reserves and environmental concerns owing to the emission of greenhouse gases [6-10]. Esterification of carboxylic acid or transesterification of triglycerides in the presence of low molecular weight alcohol has attracted the attention concerning the novel routes to the synthesis of biofuels from the renewable feedstocks [11]. Among biofuels, biodiesel is recognized as a green fuel because it can be produced from renewable resources, with less toxic emission, low CO_x (x=1 or 2), better lubricity and biodegradability [12]. Biodiesel contains alkyl esters that can be synthesized from the esterification of fatty acids (FFA) in the presence of short-chain alcohols and suitable catalysts [13]. The esterification reaction is a key step for the production of biodiesel in the presence of alcohol and acid catalyst when raw material contains a very high amount of free fatty acids.

Edible oils, such as coconut oil, soybean oil and peanut oil, are the prime source of high-quality free fatty acids for the production of biodiesel. Recent studies have revealed that the utilization of edible oil as a feedstock is disadvantageous due to the high cost of refining the feedstock and questionable challenge to the food-fuel crisis. This obstacle can be overcome by selecting the non-edible oil feedstock such as oleic acid, vaccenic acid and elaidic acid for the production of biodiesel [14]. Among different non-edible oils, monounsaturated structured oleic acid has widely been used for the esterification reaction to produce biodiesel with the help of MeOH/EtOH and acid catalysts. In addition, mineral acid catalysts such as H_2SO_4, HCl or HBr act in the same liquid phase as a reaction mixture (homogeneous phase) and have widely been tested for the esterification reaction to produce biodiesel.

The application of homogeneous acid catalysts in the esterification reactions, owing to their astonishing catalytic activity and simple usage, dominates the biodiesel industry [15]. Although, these

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catalysts have acquired matchless catalytic activity, they are non-reusable, hazardous and corrosive to the process and pose serious potential threats to the environment. The acid-catalyzed esterification reaction would become even more important if hazardous, non-reusable and corrosive conventional homogeneous acid catalysts could be replaced by the eco-friendly, reusable and noncorrosive heterogeneous solid acid catalysts. The incorporation of heterogeneous acid catalysts into the esterification reaction for the production of biodiesel can lead to the higher yield of biodiesel production, easier catalyst separation from the final product, safety to the process and environment [16]. An ideal heterogeneous acid catalyst must possess a large interconnected pore structure for better mass transfer, hydrophobic surfaces and strong acid sites for better catalytic activity [17]. Several heterogeneous acid catalysts, such as sulfated zirconia, ion exchange resin, kaolins and heteropoly acids (HPAs), have been tested in the esterification reactions of FFA to produce biodiesel [18]. Each of the synthesized catalysts possesses unique physicochemical properties, interconnected porous structure, leaching stability to enhance process economy, and comparable catalytic activity. HPAs have accelerated appreciable research in acid-catalyzed reactions due to strong acidity, unique keggin structure and acceptable stability, specifically the 12-tungstophosphoric acid (HPW) among different synthesized HPAs [19,20]. HPW has emerged as the promising catalyst in various fields where its complex structure makes it suitable for various applications [21]. Inherently, HPW possesses keggin structure where PO_4^{-3} placed as central atom which is surrounded by 12WO6 to form a polyanion which is further neutralized by three protons.

Despite the enormous advantages of HPW in various fields, it is readily soluble in polar media and behaves like a homogeneous catalyst, specifically in the esterification reaction, non-porous and suffering from the very low surface area (<10 m^2/g) [22]. To overcome these limitations, large monovalent cations such as K^+, Cs^+ and NH_4^+ can be incorporated into heteropoly structure, which provides the surface area around 120 to 150 m^2/g and makes them highly insoluble towards polar media [23]. In addition, to enhance its surface area, heterogeneity and catalytic activity, it must be well dispersed over appropriate support, such as mesoporous silica such as MCM-41, SBA-15 and KIT-6 [24,25], silica-alumina [26] and zeolites [27]. Among siliceous materials, SBA-15 and KIT-6 have widely been studied and reported for biodiesel production. SBA-15 is inherently composed of a hexagonal framework of parallel mesoporous channels facilitating the mass transfer during reaction. Although the incorporation of macro-porous structure over the mesoporous SBA-15 showed positive correlation with esterification and transesterification reactions, low pore size (300 nm) limited mass transfer and acid site accessibility [28].

Enhancing the pore size, interconnectivity and other structural properties can directly influence the process efficiency positively. KIT-6 is drawing much more attention due to its unique three-dimensional mesostructured bi-continuous networks of the chiral channel [29-31]. KIT-6 have a high surface area and pore diameter, which helps in the efficient diffusion of reactant particles through the pores due to the interpenetrating structure as well as imperviousness to agglomeration [30]. Moreover, interconnected pore architecture $Ia\bar{3}d$ significantly increases the per-site activity of catalysts as well as pore accessibility to reduce the mass transfer barrier.

These advantageous characteristics of KIT-6 can help to encounter the limitations associated with HPW and enhance the heterogeneity and surface area of HPW when incorporated over the surface of support material.

Another class of heterogeneous acid catalysts is sulfated heterogeneous catalysts, which have drawn attention due to astonishing catalytic activity and high acidic strength. It is also well documented that several sulfated catalysts have been synthesized and characterized, such as sulfated zirconia, sulfated titania and sulfated mesoporous titania-silica that can be used as solid acid catalysts [32-34]. The presence of sulfate ions predominantly enhances the catalytic activity of synthesized catalysts. In another study on sulfated catalysts, focusing on synthesis temperature over activation energy reported that higher synthesis temperature (300-500 °C) reduced the catalytic activation energy (7.25-6.01 KJ/mol) [35].

Furthermore, the impact of catalyst synthesis technique is undeniable on the pore size, pore density and other textural properties of desired catalysts.

In this study, an attempt has been made to synthesize the supported (HPW/KIT-6) mesoporous solid acid catalysts with two different synthesis techniques, impregnation and sol-gel method, to analyze the effect on the catalytic activity towards the esterification reactions of oleic acid in the presence of methanol and synthesized catalysts. To the best of the authors' knowledge, the study involving the impregnation and sol-gel method to analyze the effect on the catalytic activity towards the esterification reactions has not been reported in the literature. Different synthesis techniques like impregnation and sol-gel method to incorporate HPW over the KIT-6 mesoporous silica support ultimately affect the structural properties of HPW in favor of esterification reaction of oleic acid for biodiesel production. Additionally, the influence of synthesis technique in terms of structural characteristics of synthesized catalysts has also been evaluated by comparing it with highly active pure HPW and sulfated KIT-6.

MATERIALS AND METHODS

1. Materials

Pluronic acid (P123), tetraethyl orthosilicate (TEOS, 98%), methanol (99.8%) and 12-tungstophosphoric acid (99%,) were purchased from Sigma Aldrich. Oleic acid (with 99.8% FFA,), HCl (37% w/w) and n-butanol (>99.5%) were purchased from AnalaR and used without further purification.

2. Preparation of Mesoporous Solid Acid Catalysts

2-1. Synthesis of KIT-6

Mesoporous silica support KIT-6 was prepared using the method reported by Soni et al. [36]. Typically, 11.8 g of HCl and 6 g of P123 were suspended in doubly deionized 217 g of water. The solution was heated at 35 °C with stirring speed of 850 rpm to get a clear solution, followed by the addition of 6 g of 1-butanol and stirred for 1 h. Furthermore, 12.90 g TEOS was added in the solution and reaction conditions were maintained for 24 h. To form the mesopores in the product, it was heated at 100 °C for 24 h in oven. The resultant product, semi-solid and white in appearance, was separated by filtration and dried in an oven at 60 °C for 12 h. The pure

SiO_2 product was obtained after calcination at 550 °C for 6 h with a heating rate of 2 °C/min.

2-2. HPW/KIT-6 by Impregnation Method

Different amounts of 12-tungstophosphoric acid (HPW) were dissolved in a mixture containing 1.5 g KIT-6 and 20 mL methanol to obtain the product containing 10, 15, 20, 25 and 30% HPW in the final composition and labelled as 10-IM, 15-IM, 20-IM, 25-IM and 30-IM. All the samples were kept on stirring for 24 h followed by centrifugation at 7,000 rpm for 15 min to separate products in the form of pellets. Finally, dried samples were calcined at 300 °C for 4 h to get final HPW/KIT-6 catalysts.

2-3. HPW/KIT-6 by Sol-gel Method

Firstly, a homogeneous solution of 217 g water, 11.8 g HCl, and 6 g P123 was obtained after stirring at a constant temperature of 35 °C. Secondly, 6 g of 1-Butanol was added into the first solution and after 1 h 12.8 g TEOS was also added dropwise 1 h interval. After 3 h stirring at 35 °C, the calculated amount of HPW was added in the solution to obtain the final weight percentage of HPW at 10, 15, 20, 25 and 30. The samples were stirred for 24 h and transferred to a Teflon bottle for hydrothermal treatment at 100 °C for 24 h. Solid products were recovered through filtration. The residues were dried, calcined at 550 °C for 5 h, and labelled as 10-SG, 15-SG, 20-SG, 25-SG, and 30-SG, respectively.

2-4. Sulfated KIT-6

Sulfated KIT-6 was prepared by the direct impregnation of sulfate group (SO_4^{2-}) on the surface of mesoporous support KIT-6. The 1.5 g KIT-6 was dissolved into 50 mL 1 M H_2SO_4 and stirred for 12 h at 30 °C. The solution was centrifuged, washed several times with double deionized water, product was oven-dried at 100 °C for 24 h, calcined at 450 °C for 2 h and labelled as sulfated KIT-6.

3. Experimental Procedure

The esterification of oleic acid was done by using synthesized heterogeneous acid catalysts in a 100 mL round bottom flask, equipped with double-walled reflux condenser, heating and magnetic stirrer plate. The reaction mixture employed comprises 5 g oleic acid (0.0177 mol) mixed with the 17 g methanol (0.531 mol). The reaction was at 65 °C for 6 h in the presence of 5 and 10 wt% of catalysts in oleic acid. The catalysts and excess methanol were separated out from the product after 6 h using a filtration and rotary evaporator, respectively. The obtained biodiesel samples were collected and analyzed by acid value test.

3-1. Heterogeneity Test

Heterogeneity of the synthesized sulfated catalysts was studied reusing the same catalyst in the esterification reaction at the identical reaction conditions for multiple cycles. For this purpose, the catalyst was reused in the next reaction cycle without any further treatment. In addition, the catalyst was also regenerated by washing with hexane to remove methyl ester, dried at 100 °C for 60 min, followed by treatment with 1 M H_2SO_4 for 12 h at 30 °C. The obtained catalyst was washed with water, dried and calcined at 450 °C for 2 h. This regenerated catalyst was charged into the esterification reaction to explore the effect of regeneration, leaching stability and the reusability under the same environment. The experimental results are presented in Table 4.

3-2. Characterization

Surface functional groups were identified by FTIR spectroscopy (THERMO Scientific, model-Nicolet 6700). FTIR spectra were recorded at a scan rate of 256 with a resolution of 04 cm^{-1} from 500 cm^{-1} to 4,000 cm^{-1}. To analyze the morphology of support and the effect of HPW anchored on a support material, SEM, (Tescan VEGA-3 LMU equipped with UTHSCSA image software) was used. The samples were coated with a gold film of 250 Å thickness before being put into the SEM chamber. The surface area, porosity and the pore volume of the synthesized catalysts were measured using Brunauer-Emmett-Teller (BET, Tristar II 3020) at the temperature of 77 K.

3-3. Acid Value Test

Acid value suggests the presence of carboxylic acid in the product. The sample (0.2-0.5 g) was mixed with 50 ml absolute ethanol and stirred for 30 min. A few drops of phenolphthalein (0.1%) as an indicator were added to a homogeneous mixture, which was neutralized with 0.1 N KOH till the solution turned to light pink.

$$\text{Acid Value} = \frac{\begin{array}{l}(\text{Volume of KOH used}) \times (\text{Normality of solution}) \\ \times (\text{Molecular weight of KOH})\end{array}}{(\text{Weight of sample})}$$

RESULTS AND DISCUSSION

Surface modification of low surface area HPW by dispersing it over the support with the higher surface area facilitated the active HPW by enhancing its surface area and heterogeneity, making it suitable for different applications, specifically in heterogeneous catalysis. The high surface area and the ordered pore structure of support was solely responsible for the better mass transfer in a reaction, which can be elucidated in terms of better heterogeneity and high catalytic activity. The low surface area HPW supported over mesoporous silica support KIT-6 resulted in the enhancement of their surface area, porosity and heterogeneity. Table 1 shows the BET surface area and pore volume of various synthesized mesoporous silica KIT-6 supported HPW catalysts in this study. The specific surface area of mesoporous silica KIT-6 was recorded as high as (619 m^2/g) with pore volume (0.735 cm^3/g). Results revealed that the pore structure and textural properties of synthesized HPW/KIT-6 are strongly under the influence of loading amount as well as synthesizing technique. The BET surface area of mesoporous silica KIT-6 gradually reduced from 619 m^2/g to 415.618 m^2/g and 231.608 m^2/g with the increasing HPW content over the support from 5 to 30%

Table 1. BET surface area and pore volume of synthesized catalysts

Support/ Supported catalysts	S_{BET} (m^2/g)	PV (cm^3/g)
HPW	<10	-
KIT-6	619	0.735
10-IM	577.595	0.658
15-IM	538.856	0.573
30-IM	415.613	0.449
10-SG	514.326	0.544
15-SG	454.392	0.441
30-SG	231.608	0.152
Sulfated KIT-6	434.027	0.448

by impregnation and a sol-gel method, respectively. This phenomenon of surface area reduction of support due to deposition of HPW has also been reported by Blasco et al. [34]. In comparison with the impregnated catalysts, the catalysts synthesized by sol-gel technique showed the least surface area and catalytic activity; the possible reason could be entrapped HPW materials into the structure of support which reduced the exposure of catalyst during the reaction.

Although 30-IM and 15-SG showed comparable surface area to sulfated KIT-6, higher catalytic activity of sulfated KIT-6 can explain the influence of the higher number of active sites and the nature of anion groups which take part in the reaction.

FTIR spectra of the support KIT-6 and the catalysts with highest catalytic activity, including 30-IM, 25-SG and sulfated KIT-6, are shown in Fig. 1. The KIT-6 exhibited peaks at ~800, 1,085, and 1,660 cm^{-1} ascribed to symmetrical and asymmetrical stretching vibration of TO_4 tetrahedra of mesoporous silica, similarly reported by Soni et al. [36]. Further, pure KIT-6 spectrum showed absorption peaks at 1,085 cm^{-1} and 1,165 cm^{-1}, describing the asymmetric vibration of Si-O-Si, which were also reported in previous study [37]. The FTIR spectrum of 30-IM and 25-SG showed the peaks at 1,080, 982, 897 and 800 cm^{-1}, indicating the presence of keggin anion: P-O in the central tetrahedron, terminal W=O, W-O-W cm^{-1} asymmetric vibration, respectively. In Fig. 1, peaks at 982, 897 and 800 cm^{-1} were affected due to the varying amount of HPW. These findings suggest that the native Keggin structure of HPW was unhurt during the synthesis of catalysts; similar findings have been reported in literature [38]. Further, FTIR spectrum suggested that the new peaks at 930, 990 and 1,300 cm^{-1} were of sulfate group

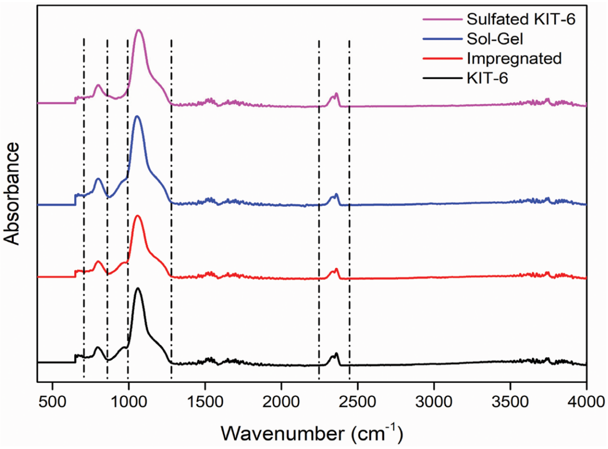

Fig. 1. FTIR spectra of various synthesized catalysts KIT-6, 30-IM; 25-SG; and Sulfated KIT-6.

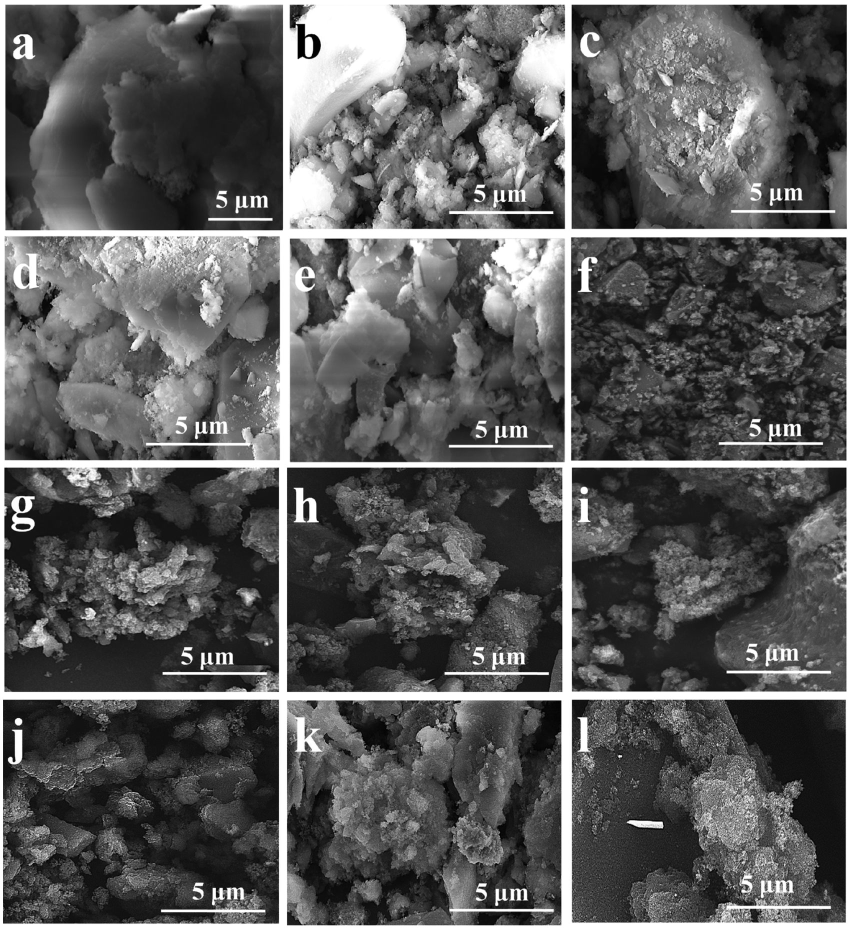

Fig. 2. Scanning electron microscope images of all synthesized catalysts; (a) KIT-6; (b) 10-IM; (c)15-IM; (d) 20-IM; (e) 25-IM; (f) 30-IM; (g) 10-SG; (h) 15-SG; (i) 20-SG; (j) 25-SG; (k) 30-SG; (l) Sulfated KIT-6.

as described in literature [39,40]. Spectra of sulfated KIT-6 indicated the absence of HPW peaks at 897 and 982 cm^{-1}, but the characteristic peaks of KIT-6 were still visible. It could be due to surface deposition of the sulfated group over the surface of KIT-6.

The SEM micrograph shown in Fig. 2(a) of mesoporous support KIT-6 shows well organized, smooth patchy surface with ordered structure, clear evidence of mesoporous silica. The surface morphology of HPW supported over mesoporous silica support KIT-6 through impregnation method (HPW/KIT-6 IM) was almost identical to each other, but there was a slight change in structure due to an increasing amount of HPW amount over support. In the images of impregnated catalysts, it can be seen that with the increase in the concentration of HPW from 5-30%, the HPW was deposited over KIT-6 in the mono-layer pattern. Due to high availability of HPW over the KIT-6 surface in the mono-layer fashion from the reaction in 30-IM catalyst as shown in Fig. 2(b)-(f), would be showing the highest catalytic activity. In Fig. 2(g)-(k), SEM investigation of HPW/KIT-6-SG showed that there might be a greater chance of agglomeration due to addition of the HPW during the structure development of KIT-6. These images confirm the presence of HPW (white particle) in the structure of KIT-6 and the concentration of dispersed HPW increasing continuously with the increasing percentage of HPW. Introduction of active sites of HPW into the structure of KIT-6 could be explained from the activity trend (maximum at 25 wt% HPW/KIT-6 SG) with the help of its dispersion mechanism. The catalytic activity started to decrease above 25 wt% HPW/KIT-6-SG because of non-uniform dispersion, agglomeration and the pore blockage of support due to excess amount of HPW, which hindered the accessibility of reactants to the active sites of catalysts that ultimately decreased the catalytic activity as shown in Fig. 2. The SEM images of sulfated KIT-6 (Fig. 2(l)) indicate the presence of a sulfate group in the form of the rough surface over the smooth surface of KIT-6.

ACTIVITY OF SYNTHESIZED ACID CATALYSTS

1. HPW Supported over KIT-6 (Impregnation)

Performance of the synthesized catalysts was tested for the pro-

Table 2. Esterification of oleic acid in the presence of synthesized catalysts (Impregnated)[a]

Serial No.	Catalysts name	Oleic acid conversion to FAME (%)[b]	
		5% Catalyst (with respect to oleic acid)	10% Catalyst (with respect to oleic acid)
1	KIT-6	4.33	-
2	10-IM	37.52	43.56
3	15-IM	43.34	50.76
4	20-IM	50.84	56.46
5	25-IM	57.36	62.85
6	30-IM	61.29	70.68

[a] Reaction Conditions: Reaction time 6 h; Oil/MeOH ratio 1 : 30; temperature 65 °C; catalyst loading into reaction mixture 5% and 10%.

[b] $$\text{Oleic acid conversion (\%)} = \frac{\text{intial acid value} - \text{final acid value}}{\text{initial acid value}} \times 100$$

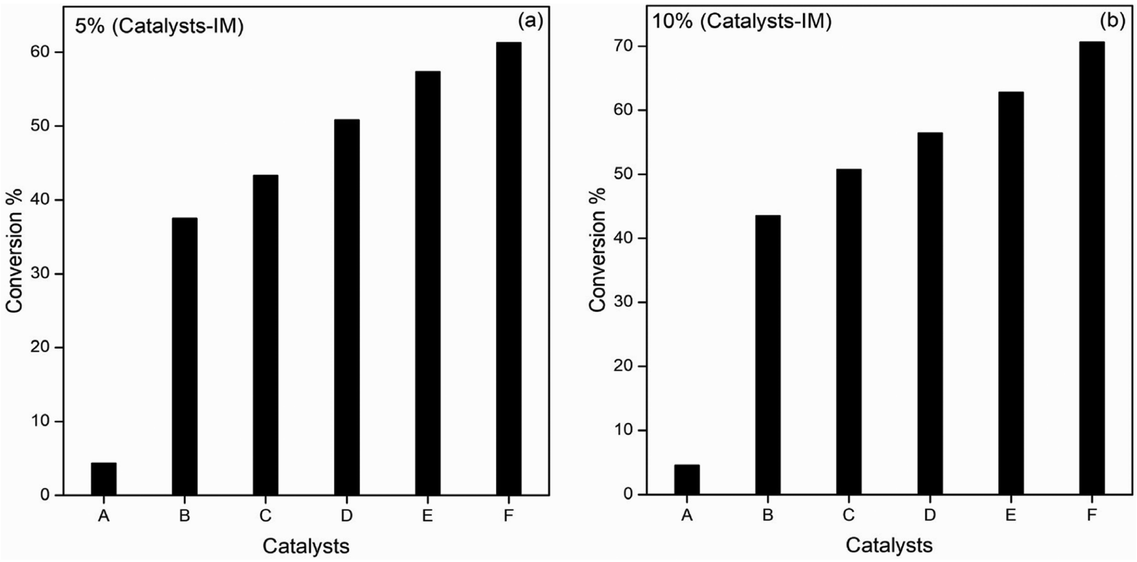

Fig. 3. Catalytic activity of various synthesized catalysts for the esterification reaction at oil/methanol molar ratio 1 : 30, 65 °C, 6 h and the catalyst loading (a) 5% (0.25 g) and (b) 10% (0.5 g) with respect to oleic acid. (A) KIT-6, (B) 10-IM, (C) 15-IM, (D) 20-IM, (E) 25-IM, (F) 30-IM.

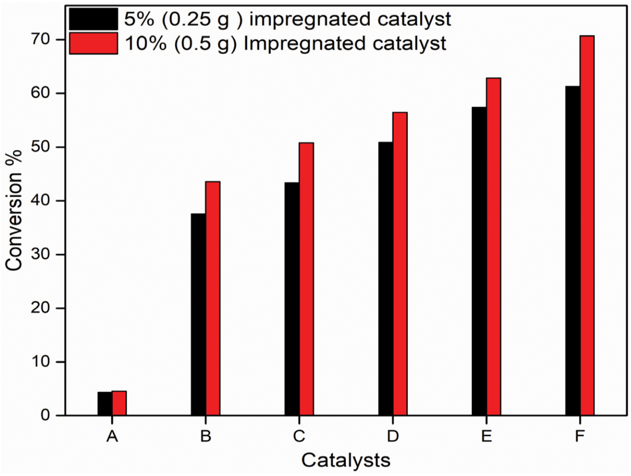

Fig. 4. Comparison of catalytic activity in esterification reaction among different synthesized catalysts by impregnation method (A) KIT-6, (B) 10-IM, (C) 15-IM, (D) 20-IM, (E) 25-IM, (F) 30-IM.

duction of biodiesel through esterification of oleic acid and the results are shown in Table 2 and Fig. 3. The catalytic activity was carried out at 5% (0.25 g), 10% (0.5 g) amount of catalysts to oleic acid into the reaction mixture. All catalysts proved active for this reaction and a few of them gave ester yield more than 70% at 65 °C after the 6 h reaction time. The catalytic performance of synthesized catalysts by using the impregnation method for esterification reactions is explained in Fig. 3(a), (b). Higher FAME conversion was achieved by slightly increasing the catalysts loading into the reaction mixture. With the increase in catalyst loading with respect to oleic acid from 5% (0.25 g) to 10% (0.5 g), conversion bars of FAME yields shifted from 61.29% to 70.68% at specified reaction conditions (Fig. 4). Catalytic activity of several catalysts was of following order, either by using 5% (0.25 g) or 10% (0.5 g): 30-IM> 25-IM>20-IM>15-IM>10-IM. Therefore, it was concluded from the comparison of the graph that 30-IM showed the highest performance with more than 70% FAME yield at 10% (0.5 g) catalyst dosage. The higher catalytic activity of 30-IM catalysts as compared to other synthesized catalysts by impregnation method could be attributed to uniform dispersion of HPW over the porous support KIT-6.

Table 4. Reuse activity of sulfated KIT-6 (10% with respect to oleic acid) in the esterification reaction at specified reaction conditions

Experiment #	Conversion (%)
1st run	91.50
2nd run	28.9
3rd run	16.3
Regenerated	83.43

2. HPW Supported over KIT-6 (Sol-gel)

The synthesized heterogeneous acid catalysts by sol-gel technique were tested in the esterification reactions with different catalyst loading into the reaction mixture and the effect of different loadings of catalysts is shown in the Table 3 and Fig. 5 The FAME conversion increased from 10-SG to 25-SG and then decreased in both cases either with 5% (0.25) or 10% (0.5) catalyst loading. The maximum FAME conversion achieved with the 25-SG catalyst was 46.52% and 53.55% with the slight increase in catalyst loading at 5% (0.25) and 10% (0.5) catalyst, respectively. (Fig. 6). It could be suggested from conversion graphs that the catalysts synthesized by sol-gel method showed the catalytic activity of the following order: 25-SG>20-SG>30-SG>15-SG>10-SG. This unexpected trend in lowering the catalytic activity of 30-SG catalysts was due to agglomeration and occupation of active sites of HPW into the support structure while synthesis. These unwanted phenomena lead to the poor accessibility of reactants to the active sites, which limits the mass transfer during the chemical reaction.

It could be concluded from the results that 30%HPW/KIT-6 IM and 25%HPW/KIT-6 SG catalysts showed the best catalytic activity among other synthesized catalysts at given reaction conditions. The catalysts synthesized from impregnation techniques showed better catalytic activity than sol-gel synthesized catalysts. During the impregnated catalysts synthesis, active HPW was impregnated over the silica support after successful synthesis of KIT-6. Higher activity indicated that most of HPW had attached to the surface and were available for reaction.

During the sol-gel synthesis of catalysts, HPW was added while

Table 3. Esterification of oleic acid in the presence of synthesized catalysts (sol-gel)[a]

Serial No.	Catalysts name	Oleic acid conversion to FAME (%)[b]	
		5% Catalyst[c]	10% Catalyst[c]
1	KIT-6	4.33	-
2	10-SG	36.44	38.31
3	15-SG	37.7	41.90
4	20-SG	40.58	46.88
5	25-SG	46.52	53.55
6	30-SG	37.41	43.41

[a] Reaction condition: Reaction time 6 h; Oil/MeOH ratio 1 : 30; temperature 65 °C; catalyst loading into reaction mixture 5% and 10%.

[b] Oleic acid conversion (%) $=\dfrac{\text{intial acid value}-\text{final acid value}}{\text{initial acid value}}\times 100$

[c] Catalysts with respect to oleic acid.

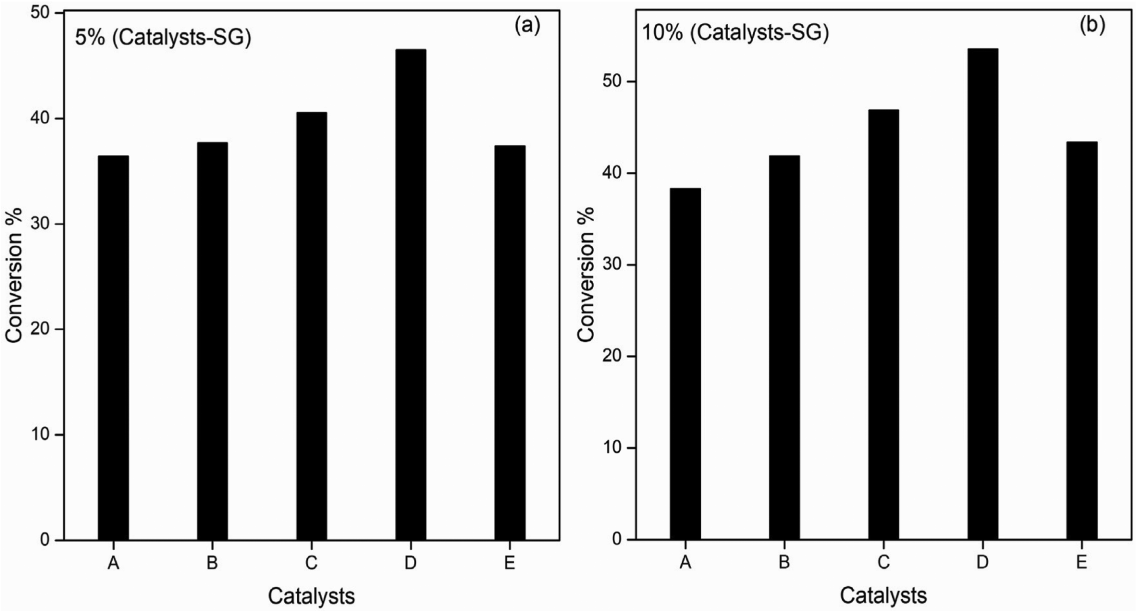

Fig. 5. Catalytic activity of several synthesized catalysts for the esterification reaction at specified reaction conditions and the influence of different catalyst loading (a) 5% (0.25 g) and (b) 10% (0.5 g) with respect to oleic acid (A) 10-SG (B) 15-SG, (C) 20-SG, (D) 25-SG, (E) 30-SG.

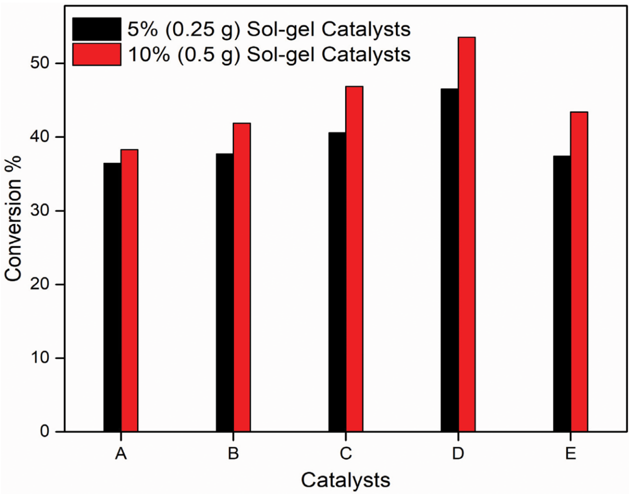

Fig. 6. Comparison of catalytic activity among different synthesized catalysts by a sol-gel method for the esterification of oleic acid at specified reaction conditions (A) 10-SG, (B) 15-SG, (C) 20-SG, (D) -SG, (E) -SG.

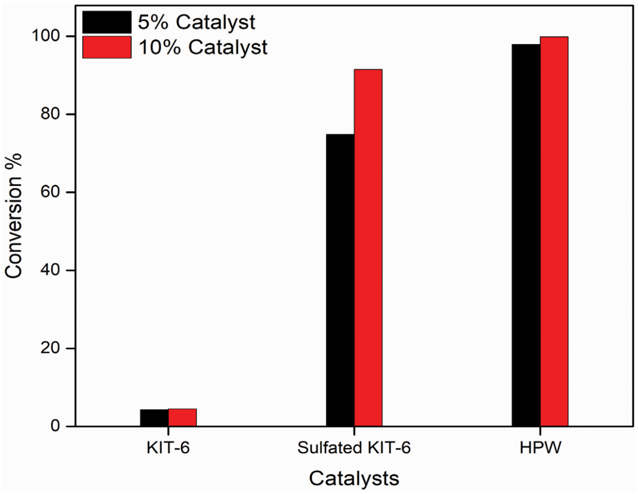

Fig. 7. Comparison of catalytic activity of different synthesized catalysts. KIT-6, Sulfated KIT-6, Pure HPW.

support synthesis, indicating that the major proportion of HPW had entrapped into the structure of support. Consequently, fewer active sites were available for reactions, hence catalytic activity decreased.

In comparison with other supported catalysts, the synthesized catalysts 30-IM showed comparable catalytic activity at comparatively milder reaction conditions, such as 10% catalyst loading and 1 : 20 oil : alcohol ratio. Supported heteropolyacids, such as HPMo/activated carbon and HSiW/SiO_2, showed 76% and 79% conversion with much higher catalyst loading and oil : alcohol ratio [41,42].

The sulfated catalyst has been considered as another class of heterogeneous acid catalysts and synthesized in this research for the comparison with other synthesized catalysts presented in Fig. 7. These plots clearly show the high catalytic activity of sulfated KIT-6 and pure HPW for the esterification reaction. After comparison, it may be suggested that among differently synthesized catalysts, 30-IM, 25-SG and sulfated catalysts show the highest catalytic activity among others, as shown in Fig. 8. Although sulfated catalysts are considered as one of the most active catalysts for biodiesel production, key drawbacks, such as fast deactivation and poor regeneration, are associated with it. During the esterification or transesterification reactions, the sulfate group leached out due to the presence of water or glycerol present in the reaction media as byproducts, respectively [43]. So, as the sulfate group leached out, the catalytic activity decreased.

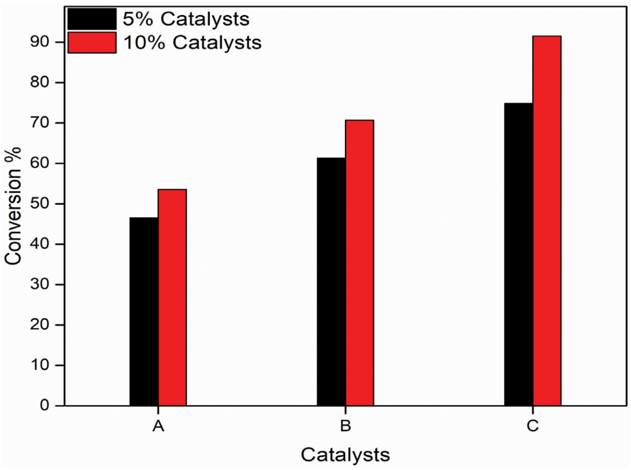

Fig. 8. Comparison of catalysts with highest catalytic activity (A) 25-SG (B) 30-IM (C) sulfated KIT-6.

CONCLUSION

Mesoporous solid acid catalysts were successfully synthesized via the impregnation and sol-gel method by anchoring the 12-tungstophosphoric acid (HPW) on the mesoporous silica KIT-6 support for the esterification of oleic acid with MeOH. The results showed that the method of loading the HPW over mesoporous support has a significant impact on the structure and catalytic activity of synthesized catalysts. Ordered structured mesoporous silica KIT-6 facilitated the dispersion of HPW, resulting in better catalytic stability and activity. The 30-IM and 25-SG catalysts synthesized by impregnation and sol-gel methods showed the highest catalytic activity. Dispersion of HPW beyond 30 and 25 wt% (SG) could be worse because of severe pore blockage and reduction in acid sites, which reduced the catalytic activity and disturbed the process economy. The structural features of synthesized catalysts compared with sulfated KIT-6 and pure HPW which were also prepared in this work. Results revealed that the KIT-6 and HPW structure remained intact and the synthesis process had a noticeable impact on the presence of active sites on catalysts, which can be elucidated in terms of FAME conversion. This structural comparison was carried out after comparing the various characterization results with already reported highly active sulfated catalyst and pure HPW. Among the synthesized catalysts, maximum FAME conversion obtained for the esterification reaction at 65 °C in 6 h with 10% catalyst with respect to oleic acid was 30% HPW/KIT-6-IM (70.68%)>25% HPW/KIT-6-SG (53.55%), indicating the effectiveness of impregnation methods over sol-gel method. Additionally, the catalytic activity of sulfated KIT-6 was evaluated by regenerated and charged into the same reaction at specified reaction conditions without major activity loss. Thus, mesoporous solid acid HPW/KIT-6 (impregnated) showed good catalytic activity with remarkable stability for the consecutive reaction.

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REFERENCES

1. A. Ahmed, M. S. Abu Bakar, R. Hamdani, Y. K. Park, S. S. Lam, R. S. Sukri, M. Hussain, K. Majeed, N. Phusunti, F. Jamil and M. Aslam, *Environ. Res.*, **186**, 109596 (2020).
2. A. Abdullah, A. Ahmed, P. Akhter, A. Razzaq, M. Zafar, M. Hussain, N. Shahzad, K. Majeed, S. Khurrum, M. S. A. Bakar and Y. K. Park, *Korean J. Chem. Eng.*, **37**, 1899 (2020).
3. S. Moogi, L. Nakka, S. S. P. Potharaju, A. Ahmed, A. Farooq, S. C. Jung, G. H. Rhee and Y. K. Park, *Int. J. Hydrogen Energy*, https://doi.org/10.1016/j.ijhydene.2020.08.190 (2020).
4. F. Jamil, M. Aslam, A. H. Al-Muhtaseb, A. Bokhari, S. Rafiq, Z. Khan, A. Inayat, A. Ahmed, S. Hossain, M. S. Khurrum and M. S. A. Bakar, *Rev. Chem. Eng.*, **36**, 2690 (2020).
5. T. Chowdhury, H. Chowdhury, A. Ahmed, Y. K. Park, P. Chowdhury, N. Hossain and S. M. Sait, *Sustainability*, **12**, 1 (2020).
6. S. H. Ansari, A. Ahmed, A. Razzaq, D. Hildebrandt, X. Liu and Y. K. Park, *Environ. Pollut.*, **266**, 115103 (2020).
7. S. Moogi, J. Jae, H. P. R. Kannapu, A. Ahmed, E. D. Park and Y. K. Park, *Bioresour. Technol.*, **315**, 123835 (2020).
8. T. Chowdhury, H. Chowdhury, N. Hossain, A. Ahmed, M. S. Hossen, P. Chowdhury, M. Thirugnanasambandam and R. Saidur, *J. Clean. Prod.*, **272**, 122818 (2020).
9. A. Ahmed, M. S. Abu Bakar, R. S. Sukri, M. Hussain, A. Farooq, S. Moogi and Y. K. Park, *Energy Convers. Manag.*, **42**, 556 (2020).
10. M. S. Abu Bakar, A. Ahmed, D. M. Jeffery, S. Hidayat, R. S. Sukri, T. M. I. Mahlia, F. Jamil, M. S. Khurrum, A. Inayat, S. Moogi and Y. K. Park, *Bioresour. Technol.*, **318**, 123913 (2020).
11. A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, **311**, 484 (2006).
12. N. Narkhede, S. Singh and A. Patel, *Green Chem.*, **17**, 89 (2015).
13. M. C. Math, S. P. Kumar and S. V. Chetty, *Energy Sustain. Dev.*, **14**, 339 (2010).
14. M. Zabeti, W. M. A. Wan Daud and M. K. Aroua, *Fuel Process. Technol.*, **90**, 770 (2009).
15. M. E. Borges and L. Díaz, *Renew. Sustain. Energy Rev.*, **16**, 2839 (2012).
16. Z. Yaakob, M. Mohammad, M. Alherbawi, Z. Alam and K. Sopian, *Renew. Sustain. Energy Rev.*, **18**, 184 (2013).
17. A. Talebian-Kiakalaieh, N. A. S. Amin and H. Mazaheri, *Appl. Energy*, **104**, 683 (2013).
18. M. K. Lam, K. T. Lee and A. R. Mohamed, *Biotechnol. Adv.*, **28**, 500 (2010).
19. M. Misono, *Catal. Rev. Sci. Eng.*, **29**, 269 (1987).
20. I. V. Kozhevnikov, *Catal. Rev.*, **37**, 311 (1995).
21. C. Baroi and A. K. Dalai, *Ind. Eng. Chem. Res.*, **53**, 18611 (2014).
22. J. S. Santos, J. A. Dias, S. C. L. Dias, F. A. C. Garcia, J. L. MacEdo, F. S. G. Sousa and L. S. Almeida, *Appl. Catal. A: Gen.*, **394**, 138 (2011).

23. Y. Yoshinaga, T. Suzuki, M. Yoshimune and T. Okuhara, *Top. Catal.*, **19**, 179 (2002).
24. I. V. Kozhevnikov, A. Sinnema, R. J. J. Jansen, K. Pamin and H. van Bekkum, *Catal. Lett.*, **30**, 241 (1994).
25. A. Ghanbari-Siahkali, A. Philippou, J. Dwyer and M. W. Anderson, *Appl. Catal. A: Gen.*, **192**, 57 (2000).
26. F. Marme, G. Coudurier and J. C. Védrine, *Micropor. Mesopor. Mater.*, **22**, 151 (1998).
27. J. Wang, Z. Lin, S.-Y. Han, M. Eum and C. W. Lee, *J. Ind. Eng. Chem.*, **9**, 281 (2003).
28. J. Dacquin, A. F. Lee and K. Wilson, *Green Chem.*, **12**, 296 (2009).
29. T. W. Kim, F. Kleitz, B. Paul and R. Ryoo, *J. Am. Chem. Soc.*, **127**, 7601 (2005).
30. H. Oveisi, C. Anand, A. Mano, S. S. Al-Deyab, P. Kalita, A. Beitollahi and A. Vinu, *J. Mater. Chem.*, **20**, 10120 (2010).
31. S. Moogi, I. G. Lee and K. R. Hwang, *Int. J. Hydrogen Energy*, **45**, 28462 (2020).
32. G. N. Shao, R. Sheikh, A. Hilonga, J. E. Lee, Y. H. Park and H. T. Kim, *Chem. Eng. J.*, **212**, 600 (2013).
33. S. Gopinath, P. S. M. Kumar, K. A. Y. Arafath, K. V. Thiruvengadaravi, S. Sivanesan and P. Baskaralingam, *Fuel*, **203**, 488 (2017).
34. T. Blasco, A. Corma, A. Martínez and P. Martínez-Escolano, *J. Catal.*, **177**, 306 (1998).
35. M. K. Lam, K. T. Lee and A. R. Mohamed, *Appl. Catal. B: Envion.*, **93**, 134 (2009).
36. K. Soni, B. S. Rana, A. K. Sinha, A. Bhaumik, M. Nandi, M. Kumar and G. M. Dhar, *Appl. Catal. B: Environ.*, **90**, 55 (2009).
37. A. Lapkin, B. Bozkaya, T. Mays, L. Borello, K. Edler and B. Crittenden, *Catal. Today*, **81**, 611 (2003).
38. Q. Y. Liu, W. L. Wu, J. Wang, X. Q. Ren and Y. R. Wang, *Micropor. Mesopor. Mater.*, **76**, 51 (2004).
39. J. Navarrete, T. Lopez, R. Gomez and F. Figueras, *Langmuir*, **12**, 4385 (1996).
40. L. K. Noda, R. M. De Almeida, L. F. D. Probst and N. S. Gonçalves, *J. Mol. Catal. A: Chem.*, **225**, 39 (2005).
41. J. Alca, G. Trautwein and J. P. Marco-lozar, *Appl. Cata. A: Gen.*, **468**, 432 (2013).
42. K. Yan, G. Wu, J. Wen and A. Chen, *Catal. Commun.*, **34**, 58 (2013).
43. M. José da Silva and A. Lemos Cardoso, *J. Catal.*, **36**, 169 (2013).