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Research article

Esterification of oleic acid by heteropolyacid/TiO_2–SiO_2 catalysts synthesized from less expensive precursors

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ABSTRACT: A series of 12-tungstophosphoric acid [HPW, $H_3PW_{12}O_{40}$ (HPW)] catalysts supported on mesoporous titania–silica composite (TSC) were prepared by impregnation method. Primarily, TSC with mesostructure was successfully prepared by a modified sol–gel process using a less expensive silica precursor (sodium silicate) and titanium oxychloride as a titania source. In order to develop catalysts with various properties, the HPW loading over mesoporous TSC was controlled between 5 and 50 wt%. The surface morphology and structural properties of the prepared catalysts were characterized using N_2 gas physisorption analysis, Fourier transform infrared spectroscopy, X-ray diffraction, ultraviolet spectroscopy, transmission electron microscopy, and scanning electron microscopy analysis. The X-ray diffraction and ultraviolet spectroscopy results were useful in determining the HPW dispersion on the support material. The catalytic activities of the samples were tested in liquid phase esterification of oleic acid with methanol. The results suggested that HPW dispersion on the support material was essential for the stability and performance of the catalysts during the esterification reaction. Even though the activity of the synthesized catalysts increased with increasing HPW loading, the homogeneity decreased in the samples with higher HPW content (30–50 wt%). The 20%HPW/TSC sample was found to be an active and catalytically stable catalyst, which was successfully regenerated and recycled for three consecutive runs.
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Keywords: 12-tungstophosphoric acid; titania-silica composite; esterification; dispersion

INTRODUCTION

Over recent years, various studies have been carried out to explore alternative energy sources because of fluctuating crude oil prices and serious environmental concerns. Biodiesel is a renewable and environmentally friendly fuel that can be considered as the best alternative of the depleting petro-diesel. Generally, it is produced by the esterification of free fatty acids and transesterification of triglycerides.[1,2] Esterification is also assumed as an essential step in the production of biodiesel from waste oils and greases, which usually contain high free fatty acids contents.[3,4] Conventional esterification reactions are carried out in the presence of strong acid catalysts such as sulfuric acid and hydrochloric acid, which are highly active,[5,6] but also very corrosive and usually require neutralization at the end of the reaction.[7] It is thought that environmentally benign heterogeneous catalysts can admirably eliminate the corrosion-related problems and harness easy separation of the catalysts from the products. Özbay *et al.*[8] demonstrated that ion exchange resins, such as Smopex-101, Amberlyst 15, and Amberlyst 16, can be utilized as promising heterogeneous catalysts for esterification reactions. Zirconium sulfate supported on silica have also been studied and assumed to be more effective than various other catalysts and a heterogeneous substitute for sulphuric acid for the esterification reaction.[9]

The utilization of mixed metal oxides has been reported extensively, either as active phases or as catalyst supports.[10–12] The unique textural properties as well as the generation of new acid sites in titania–silica mixed oxide are essential attributes that enhance its outstanding catalytic properties.[12,13] The acidic properties of the TiO_2–SiO_2 composite were investigated by Galán-Fereres *et al.* and found to be more acidic than TiO_2 and SiO_2 individual oxides.[13] It is a promising catalyst for various acid-catalyzed reactions such as isomerization[14] and dehydration,[15] because new bronsted acid sites are created when Ti–O–Si bonding is developed between two oxides. Gao *et al.*[12] described titania–silica composite as an excellent catalytic support material that possesses enhanced thermal and mechanical stability due to SiO_2 while preserving the catalytic performance of

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TiO_2. In our previous study, we successfully utilized the mesoporous TiO_2–SiO_2 composite to synthesize sulfated catalysts for the production of biodiesel from waste cooking oil.[16]

Heteropolyacids, in particular the most typical one, heteropoly tungstate ($H_3PW_{12}O_{40}$, hereafter HPW), have many applications as catalyst in acid-catalyzed reactions.[17–20] Nonetheless, bulk HPW is a non-porous material with inherently low surface area ($<5\ m^2g^{-1}$); the main drawback overlooks its extensive applications. A great aspect, beneficial in the field of heterogeneous catalysis, is the dispersion of HPW on high surface area support materials, which may also enhance its catalytic performance.

In the present study, different contents of HPW were exquisitely impregnated on TiO_2–SiO_2 composite to form heterogeneous catalysts suitable for esterification reactions. The sol–gel technique was used to form TiO_2–SiO_2 composite support utilizing titanium oxychloride and sodium silicate as titania and silica precursors, respectively. The loading amount of HPW on the composite was varied from 5 to 50 wt% in order to investigate the influence of HPW loading on the microstructure of TiO_2–SiO_2 and the catalytic activities of the formed HPW/TiO_2–SiO_2 catalysts. The recycled use of the best supported catalyst is particularly assessed in consecutive batch reaction tests. Moreover, the results of the present study are compared with previously reported results for the same esterification reactions performed under catalysis of sulfated titania–silica catalysts.

EXPERIMENTAL

Materials

Sodium silicate ($SiO_2/Na_2O = 3.27$) and 25 wt% $TiOCl_2$ were procured from Kukdong Chemicals Co. Ltd, South Korea. Methanol (99.8%), oleic acid (technical grade, 90%), 12-tungstophosphoric acid (reagent grade), and 60% HNO_3 were purchased from Aldrich, Korea. Ammonium hydroxide solution (28%) was bought from Dae-Jung Chemical and Metal Co. Ltd, South Korea. The reagents employed in the products analysis include heptane as solvent and methyl heptadecanoate (analytical reagent, Sigma-Aldrich) as internal standard. All the reagents used in this study were acquired from their commercial sources and utilized without further purification, unless otherwise stated.

Catalyst preparation

Titania–silica composite was synthesized by the sol–gel technique according to the procedure reported by Shao *et al.*[21] Briefly, ammonium hydroxide solution was added dropwise into a mixture of 8 g of $TiOCl_2$ and 8 g of deionized (DI) water to obtain a strong gel that was peptized in 0.02 M HNO_3 and stirred for 30 min to obtain a TiO_2 sol. Into another beaker, 5 g of Na_2SiO_3 was stirred in the double amount of DI water for 30 min. The preformed TiO_2 sol was reacted with sodium silicate solution at room temperature under vigorous stirring. The formed slurry was aged at a temperature of 80 °C for 4 h under constant stirring. After 4 h, the slurry was filtered and washed with an excess amount of water to remove Na^+ and NO^{3-} ions. Finally, the resulting products were oven-dried at 100 °C for 6 h and named as mesoporous TSC (titania–silica composite).

In order to prepare supported HPW catalysts, HPW solutions with different concentrations were prepared in DI water. Then, 8 g of TSC was added to the aforementioned solution, and the mixture was stirred overnight at room temperature. Further, the solvent was evaporated at 60 °C by using vacuum evaporator to obtain dry, free-flowing powder. Subsequently, the obtained powder was dried at 110 °C for 6 h and calcined at 300 °C. The prepared catalysts were denoted as *x*HPW/TSC ('*x*' represents the loading amount of HPW; 5, 10, 15, 20, 30, and 50 wt%).

20%HPW/TiO_2 was synthesized for comparison purposes. First, titanium hydroxide was prepared by the hydrolysis of $TiOCl_2$ by dropwise addition of aqueous ammonia solution. A known amount of titanium hydroxide powder was suspended in an aqueous solution of HPW. The suspension was dried to obtain white powder and then calcined at 300 °C. Sulfated titania–silica catalyst, SO_4^{2-}/TSC, was synthesized by impregnating preformed TSC with 1 M H_2SO_4 solution using the following method.[22] After 6 h stirring, the solids were separated by filtration and dried at 100 °C overnight. Further, the fine white powder was calcined at 450 °C for 3 h.

Esterification reaction

Liquid phase esterification reaction between oleic acid and methanol was carried out at 100 °C in a stainless steel autoclave equipped with magnetic stirrer and temperature controller. In a typical experiment, a reactor was charged with 15 g of oleic acid and 10 wt% of the catalyst (related to oleic acid). Because the esterification is a reversible reaction, it is generally performed in excess alcohol to shift the equilibrium to the product side. On the basis of preliminary tests, methanol to fatty acid molar ratio of 20 was found suitable for obtaining better conversions in this study. The reactor was pressurized up to 15 bars to maintain the liquid phase of reactants during the reaction. After 5 h of reaction time, the products were cooled down and excess methanol was separated using a vacuum evaporator. The reaction products were

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analyzed by gas chromatography apparatus using an Agilent 6890 gas chromatograph equipped with an AT-wax polyethylene glycol capillary column (30 m × 0.25 mm × 0.25 μm). The gas chromatograph oven temperature was kept at 150 °C for 1 min and then increased at a rate of 10 °C/min to 250 °C (10 min hold). Moreover, gas chromatography–mass spectrometry technique was used for qualitative identification of products and unreacted reactants. The turnover numbers (TONs) were calculated at the same reaction conditions as the moles of methyl oleate produced per mole of HPW in specified reaction time.

Catalyst stability test

The catalytic stability tests were carried out by boiling the *x*HPW/TSC catalysts in methanol at 100 °C for 5 h. It is noteworthy that a predetermined amount of *x*HPW/TSC was used to have the same amount of HPW in all stability tests. For example, 1.5 and 0.75 g of 5%HPW/TSC and 10%HPW/TSC, respectively, were boiled in methanol so that the both compounds had same quantity of 0.075 g of HPW. After 5 h, the supernatant was collected by centrifugation. The dissolution of HPW in the methanol was assessed by Ultraviolet-visible (UV-Vis) spectroscopy. It has been reported that an absorption band at a wavelength of 266 nm is characteristics of heteropoly anion, $PW_{12}O_{40}^{3-}$.[23]

The recycling tests were performed using 20%HPW/TSC catalyst. In this case, the catalyst was separated from the reaction mixture by simple filtration after 5 h reaction. Further, the catalyst was washed with hexane to remove any methyl esters or unreacted compounds present on the surface. It was dried at 100 °C overnight prior using in catalytic test. The recycling tests were carried out under the same reaction conditions as for the fresh catalysts.

Characterization

The Brunauer–Emmett–Teller (BET) surface area and the porosity of the samples were studied by a nitrogen adsorption instrument (Micrometrics ASAP 2020). Prior to measurements, the samples were degassed at 200 °C for 4 h. Infrared spectra of the samples were recorded with a resolution of 4 cm^{-1} using Nicolet 380 FT-IR instrument equipped with DTGS KB detector. The X-ray diffraction patterns of the samples were recorded by an X-ray Diffractometer (XRD-6000, Shimadzu) at accelerating voltage and current of 40 kV and 100 mA, respectively. The surface morphologies of the samples were observed by field emission scanning electron microscope (Hitachi S-4800, Japan) operated at an acceleration voltage of 15.0 kV. Transmission electron microscopy (Jeol JEM 2100 F, Korea) was used for further study of the material's morphology. A UV-Vis Spectrometer (Optizen 2021 UV-Korea) was used to acquire the absorption of leached HPW in methanol.

RESULTS AND DISCUSSIONS

Surface modification of the metal oxide facilitates formation of materials with improved surface structure of materials suitable for various applications especially in heterogeneous catalysis. Conventionally, most of titania–silica supports reported in the literature are essentially acquired through utilization of expensive and hazardous precursors hindering the substantial commercialization of the catalysts. Recently, we found that SO_4^{2-}/TiO_2–SiO_2 synthesized by surface modification of pre-synthesized TiO_2–SiO_2 composites is suitable in catalyzing esterification reactions.[16] Indeed, the present study extends the advantage of utilizing the composites obtained from less expensive silica precursor and titanium oxychloride to fabricate HPW/TiO_2–SiO_2 catalysts suitable for catalyzing various organic reactions. The low surface area HPW was impregnated on the TSC to increase their surface area and porosity, which are fundamental properties of heterogeneous catalysts.

Preliminarily, the effect of different HPW loading on mesoporous TSC was investigated by N_2 adsorption–desorption isotherms. Table 1 displays the distribution of the BET surface areas, average pore diameters, and pore volumes of mesoporous TSC, *x*HPW/TSC, and 20%HPW/TiO_2 obtained in the present study. The specific surface area of TSC was high (498 m^2/g) with an average pore size of 5.5 nm. As can be seen, the textural properties of *x*HPW/TSC samples are strongly influenced as the loading amount is varied. The BET surface areas of the samples are gradually decreased from 432 to 237 m^2/g when the HPW loading is

Table 1. Distribution of the surface area, pore diameter, and pore volume exhibited by the catalysts.

Catalyst	BET Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
TSC	498	5.5	0.82
5%HPW/TSC	439	5.8	0.61
10%HPW/TSC	404	5.8	0.53
15%HPW/TSC	363	7.1	0.51
20%HPW/TSC	347	7.98	0.48
30%HPW/TSC	295	7.3	0.42
50%HPW/TSC	237	5.02	0.31
20%HPW/TiO_2	65	7.4	0.19

BET, Brunauer–Emmett–Teller; TSC, titania–silica composite; HPW, $H_3PW_{12}O_{40}$.

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increased from 5 to 50 wt%. This behavior of surface area reduction with HPW loading on a mesoporous support has already been reported by Corma *et al.*[24] The average pore diameter of the HPW-supported samples is increased as the loading amount is increased except in 50%HPW/TSC. Sample 50% HPW/TSC exhibited smaller pore diameter suggesting that most of the HPW present on the surface of support material is in the form of agglomerates. It is notable that superior textural properties displayed in the samples with adequate amount of HPW. 20% HPW/TSC sample exhibits larger surface area (347 m^2/g) than the 20%HPW/TiO_2 (65 m^2/g), with larger pore volume and almost the same pore diameter. This suggests that impregnation of support materials with high surface area, large pore diameter, and pore volume eventually yields HPW-supported catalysts with high surface area as well. Figure 1 presents the N_2 adsorption–desorption isotherms and pore size distribution of the as-synthesized TSC-supported and HPW-supported samples with different loading amounts. All the samples exhibit a typical type IV isotherm, which is a characteristic of the mesoporous materials.[21] In addition, the samples possess a narrow pore size distribution even after 50wt% HPW loading. It can be inferred that well-defined mesoporous structures were obtained when mesoporous TSC was modified with HPW. Therefore, synthesis of a suitable mesoporous TSC prior to impregnation was essential to form HPW/TSC catalysts with superior properties.

Figure 2 illustrates the XRD patterns of mesoporous TSC-supported and HPW-supported samples with different loadings. It can be seen that the as-prepared TSC is amorphous with a broad but weak peak at ~26° indicating the existence of a bulk amount of TiO_2 in the silica.[25] No diffraction peaks corresponding to HPW can be observed in the XRD pattern for 20%HPW/TSC sample (Fig. 2b), suggesting that HPW was well dispersed in the mesoporous channels of TSC. Generally, bulk HPW exhibits characteristic crystalline peaks from 15° to 50° (not shown).[26] As the loading amount exceeds 20 wt%, some characteristics crystalline peaks of HPW gradually evolve. This is a clear justification that large crystals of HPW form into the pores of TSC, which subsequently lower the HPW dispersion. Most of the diffraction peaks of HPW can be seen for 50%HPW/TSC sample depicting that at this loading, agglomeration occurs; therefore, some HPW species are not impregnated on TSC support. It seems that the support surface area plays an important role in the better dispersion of active sites. It was reported that when MCM-41, with a surface area of 1200 m^2/g, was used as a support material for HPW, finely dispersed samples were obtained even though the loading reached a value as high as 50 wt%.[27] In addition, no crystalline phase of TiO_2 is seen for all samples at the calcination temperature 300 °C,

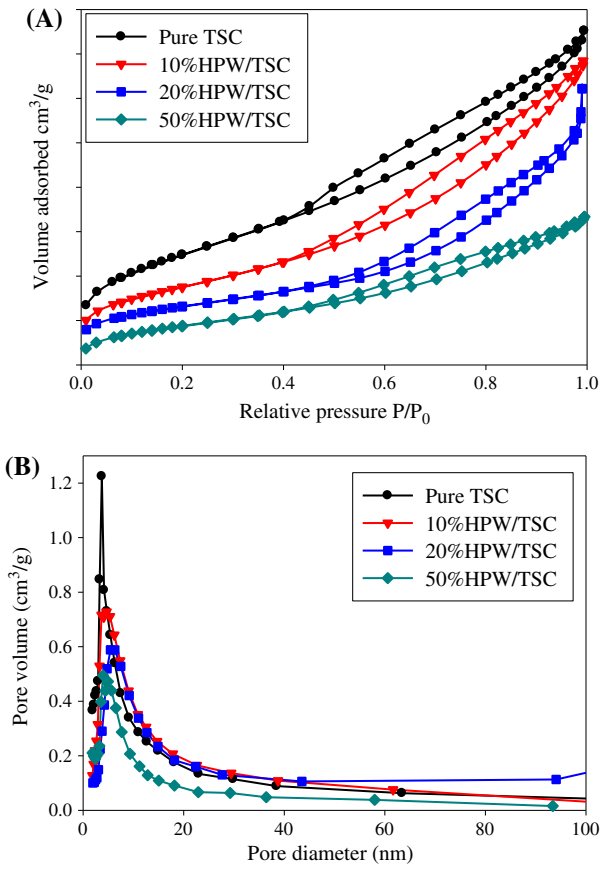


Figure 1. N_2 adsorption–desorption isotherms (A) and pore size distribution curves (B) for as-synthesized titania–silica composite (TSC) and supported samples with different $H_3PW_{12}O_{40}$ (HPW) loadings. This figure is available in colour online at www.apjChemEng.com.

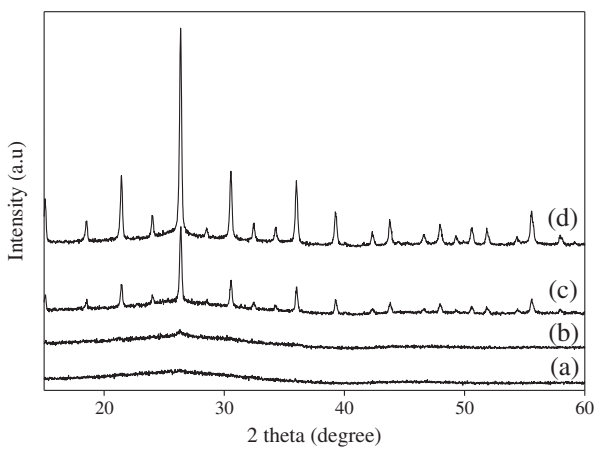


Figure 2. X-ray diffraction patterns of (a) mesoporous TSC, (b) 20%HPW/TSC, (c) 30%HPW/TSC, and (d) 50%HPW/TSC. TSC, titania–silica composite; HPW, $H_3PW_{12}O_{40}$.

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irrespective of the different HPW loading amounts, revealing that the TiO_2 exists in amorphous state.

The Fourier transform infrared spectra of as-synthesized TSC, supported samples, and bulk HPW are shown in Fig. 3. TSC sample exhibits two peaks around 785 and 1075 cm^{-1} assignable to the symmetric and the asymmetric stretching of Si–O–Si, respectively.[28] The vibration band observed at 940 cm^{-1} depicts the formation of Ti–O–Si linkage signifying the interaction of titania and silica to form a composite. In case of the supported samples, there are four peaks extending from 700 to 1100 cm^{-1} attributable to the characteristics absorption bands of the HPW Keggin structure.[21,28] These results reveal that the primary Keggin structure of HPW remained intact during the anchoring process at all loadings. The intensities of the Keggin structure corresponding bands are increased when the HPW loading amount is increased in the *x*HPW/TSC composites.

Morphologies of mesoporous TSC, 20%HPW/TSC, and 50%HPW/TSC were determined by field emission scanning electron microscopy, and the obtained images are presented in Fig. 4(A)–(C). The as-synthesized TSC is composed of spherical primary particles.[29] The surface morphology of 20%HPW/TSC sample is almost identical to the parent TSC but exhibits a more regular and uniform surface structure. It shows that the morphology of mesoporous TSC is largely retained as long as the HPW loading amount is up to 20 wt% and no separate agglomerates of HPW can be observed in the scanning electron microscopy image. In contrast, the surface of 50% HPW/TSC is found to be in aggregated form. Increased aggregation might be responsible for the lower specific surface area exhibited by this sample as a result of higher HPW loadings. The dispersion of HPW in the mesoporous TSC was further studied by transmission electron microscopy analysis 20 wt% loading as a representative sample (Fig. 4D). It can be seen that at this loading amount, the distribution of HPW in the sample is homogeneous.

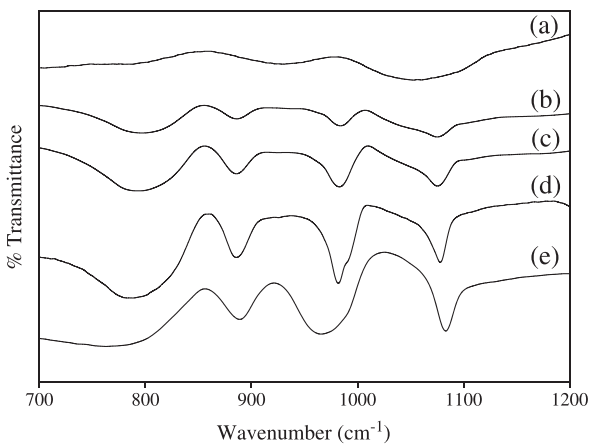


Figure 3. Fourier transform infrared spectra of (a) mesoporous TSC, (b) 20%HPW/TSC, (c) 30%HPW/TSC, (d) 50%HPW/TSC, and (e) bulk HPW. TSC, titania–silica composite; HPW, $H_3PW_{12}O_{40}$.

The supported catalysts, *x*HPW/TSC, were screened for the esterification of oleic acid with methanol at 100 °C. For the sake of comparison, 20%HPW/TiO_2 and sulfated-TSC catalysts were prepared and tested at the same reaction conditions. The conversions of oleic acid to methyl oleate and TON of the catalysts are presented in Table 2. The results show that the loading amount of HPW greatly influences the catalytic activity of the samples in the esterification reaction. The conversion of methyl oleate increases rapidly from 17.4% to 81% as the HPW loading is increased from 5 to 20 wt% in the samples. Interestingly, the activities continue increasing while the loading amount is further increased, reaching a maximum value of 93% at the loading of 50 wt%. It is worth noting that the conversion increase ratio was slightly increased when the loading was increased from 20 to 50 wt%. This suggests that the activity of as-synthesized *x*HPW/TSC samples is mainly associated with the amount of surface acid sites and specific surface areas. The increase of activities in the higher loading (≥30wt%) might be due to the aggregated HPW formation on the support surface. Because the conversion of 97.5% can be obtained when bulk HPW is used as a catalyst (Table 2), then using catalysts with higher loadings might be thought to facilitate both homogeneous and heterogeneous catalysis. Even though HPW is a strong Br nsted acid used as a catalyst at the specified reaction conditions, nonetheless, the reaction is homogeneous as the catalyst is readily soluble in methanol. Additionally, HPW supported on mesoporous TSC showed better catalytic activities than the same amount of HPW supported on pure titania. This might be attributed to the enhanced surface textural properties including higher surface area and pore volume and availability of maximum surface acid sites while using silica-modified titania as a support material for HPW. On the other hand, sulfation of mesoporous TSC gives a highly active catalyst for the esterification reaction. In the previous study, we found that the acidic properties of mesoporous TSC were remarkably enhanced by sulfate modification.[16]

The actual catalytic activities of the as-synthesized catalysts with different HPW loadings were elaborated by calculating the TON values (Table 2). The maximum TON value was found in the 20%HPW/TSC catalyst. This might be associated with the effective dispersion of HPW on the support surface, and thus the availability of maximum surface acid sites for the reaction. Hence, the loading of HPW/TSC should be 20 wt% to obtain highly dispersed and stable catalyst. All the supported HPW catalysts exhibited

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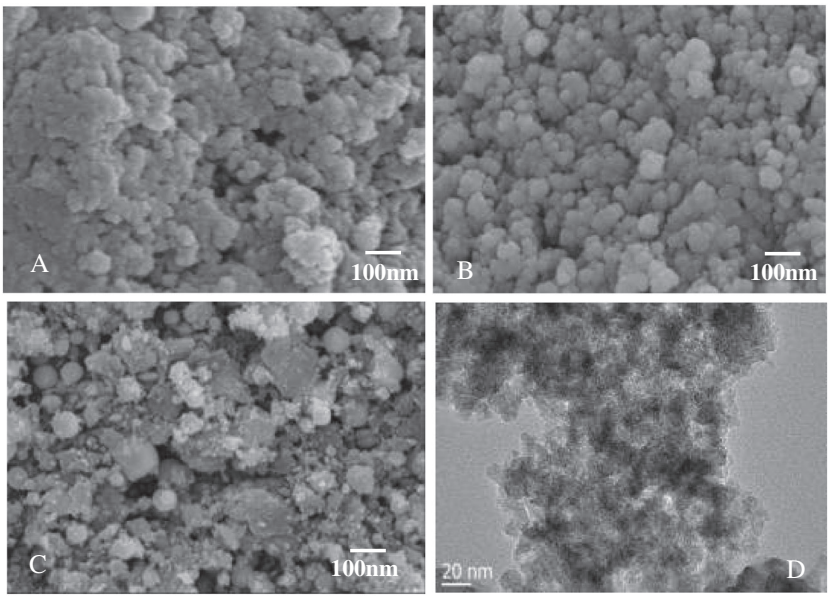


Figure 4. Field emission scanning electron microscopy images of (A) mesoporous TSC, (B) 20%HPW/TSC, and (C) 50%HPW/TSC and transmission electron micrograph of (D) 20%HPW/TSC. TSC, titania–silica composite; HPW, $H_3PW_{12}O_{40}$.

Table 2. Esterification reaction activities of bulk HPW and supported HPW catalysts with different loadings (reaction conditions: MeOH/oleic acid molar ratio 20, reaction time 5 h, temperature 100 °C).

Catalyst	Conversion (%)	TON ($M_{MO}M_{HPW}^{-1}h^{-1}$)
HPW	97.8	18.9
5%HPW/TSC	17	66
10%HPW/TSC	36.5	70.7
15%HPW/TSC	59	76.8
20%HPW/TSC	81	78.7
30%HPW/TSC	89	57
50%HPW/TSC	93	36
20%HPW/TiO_2	68	66
SO_4^{2-}/TSC	95	—

HPW, $H_3PW_{12}O_{40}$; TON, turnover number; TSC, titania–silica composite.

higher TON values than the bulk HPW toward the esterification reactions, implying that supported catalysts are economically more attractive than the bulk HPW. The increased catalytic activity upon higher loading of HPW may raise questions if the dissolution of HPW was happening during the reaction. Heteropoly acids can deposit on the support surface either in the molecular form or in the aggregate form. It has been suggested that as the loading of HPW was increased on the mesoporous TSC, the small HPW particles easily interact with each other to form large particles. Aggregated HPW particles are most probable to be leached out during the reaction. Dissolved HPW molecules can act as homogeneous catalyst, which might be a reason of higher activities in case of heavily loaded samples. Increased aggregation also implies the poor dispersion of the active sites. Hence, the optimum loading was determined by boiling the *x*HPW/TSC catalysts in methanol at 100 °C for 5 h and analyzing the supernatant by UV-Vis spectroscope. The results are presented in Fig. 5. All the samples showed a band around 266 nm, which is a characteristic for $PW_{12}O_{40}^{3-}$ anion.[23] Inspection of the supernatant concentrations revealed that all the catalysts suffered from HPW dissolution in methanol, but the effect was minimal in the case of lower loadings. On the other

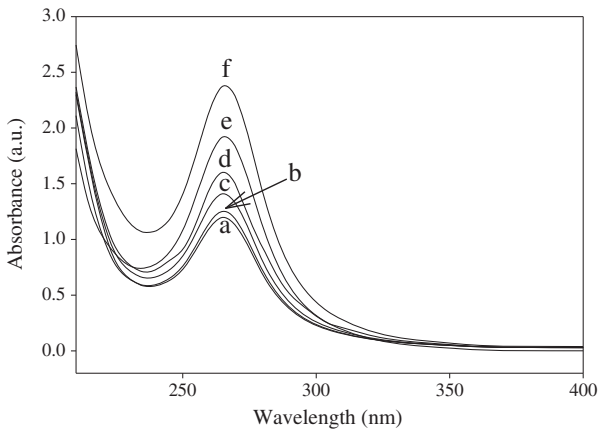


Figure 5. Ultraviolet-visible spectra of (a) 5%HPW, (b) 10%HPW, (c) 15%HPW, (d) 20%HPW, (e) 30%HPW, and (f) 50%HPW supported on mesoporous TSC. TSC, titania–silica composite; HPW, $H_3PW_{12}O_{40}$.

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hand, more intense peaks in case of higher loading of HPW indicate that more amounts of HPW were dissolved in the solution. These results are in good agreement with the XRD results that exhibit the crystalline phase of HPW as a result of aggregation when the loading is increased beyond 20 wt%.

Further, 20%HPW/TSC was selected for the regeneration and reusability tests in the esterification of oleic acid for three consecutive runs, and the results are presented in Fig. 6. For this purpose, after the first run completed, the catalyst was recovered by hot filtration and washed with hexane to remove the attached methyl esters and unreacted compounds from the catalyst surface. The catalyst was dried overnight at 100 °C prior using in the next run. The recovered catalyst was used for the second and third runs under the same reaction conditions. In the second run, the conversion sharply declined to about 9% of the first run. This partial activity loss with the recycled catalyst could be due to dissolution of physisorbed HPW during the first run and regeneration process. Interestingly, after the second run, the regenerated catalyst sustained its activity, which indicated that the HPW was strongly anchored on to the support surface. For comparison purposes, SO_4^{2-}/TSC catalyst was also tested at the same reaction conditions for three consecutive runs, and a drastic activity loss was observed (Fig. 6). The reusability tests of the 20%HPW/TSC catalyst were carried out for three consecutive runs only as the minor catalyst (fine powder) loss was unavoidable during the batch process.

Any textural and morphological changes in the used catalyst were also examined by scanning electron microscopy and BET analysis. For this purpose, the catalyst was recovered, washed with hexane, and dried before analysis. It can be seen in Fig. 7 that 20%HPW/TSC preserved most of its morphology during the esterification reaction performed at 100 °C. But, BET analysis showed that the surface area of the used catalyst was decreased (266 m^2/g) as compared with the fresh catalyst (347 m^2/g). It was proposed that the dispersion of HPW over support surface was affected after the first run, which caused a decrease in surface area. The non-uniform dispersion of HPW in the used catalyst was further confirmed by carrying the surface elemental analysis. Different concentrations of tungsten (main constituent of HPW) were obtained when Energy Dispersive using X-Ray (EDX) analysis was performed over various locations of the catalyst surface.

The influence of reaction temperature on the conversion of methyl oleate over 20%HPW/TSC has also been investigated, and the results are presented in Fig. 8. As expected, the conversion increases monotonically as the temperature is increased in the range of 80–120 °C. A maximum conversion of 95% is achieved at 120 °C.

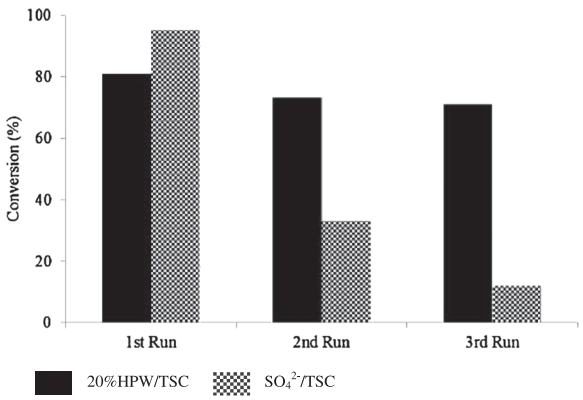


Figure 6. Reuse of 20%HPW/TSC in the esterification of oleic acid (MeOH/oleic acid ratio, 20; 100 °C; 5 h). TSC, titania–silica composite; HPW, $H_3PW_{12}O_{40}$.

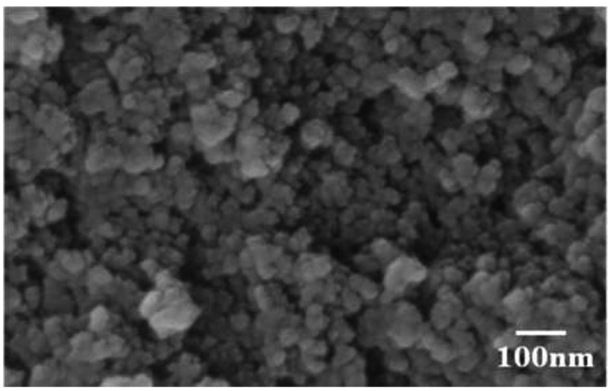


Figure 7. Scanning electron micrograph of 20%HPW/TSC catalyst separated after esterification reaction of oleic acid. TSC, titania–silica composite; HPW, $H_3PW_{12}O_{40}$.

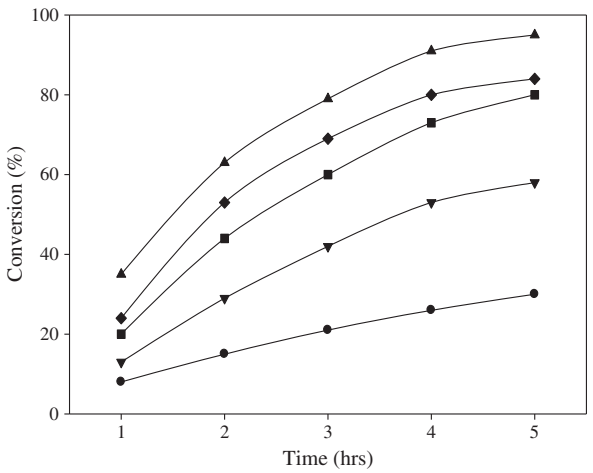


Figure 8. Plots of oleic acid conversion against the reaction time at different reaction temperatures: ●, 80 °C; ▼, 90 °C; ■, 100 °C; ♦, 110 °C; ▲, 120 °C (MeOH/Oleic acid molar ratio 20, catalyst 10 wt%).

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CONCLUSION

In the present study, mesoporous titania–silica composite was prepared from inexpensive precursors and used as a support material for the 12-tungstophosphoric acid to produce a strong acid catalyst for the esterification of oleic acid. The results revealed that the different loading of HPW had a strong impact on the structure of as-synthesized *x*HPW/TSC samples. The high surface area of mesoporous TSC support facilitated the better dispersion of HPW as long as the loading was up to 20 wt% and no clear diffraction peaks were detected. The UV and XRD data showed that the dispersion became worse when the loading was increased beyond 20 wt% of HPW. The catalytic activities of supported catalysts in liquid phase esterification reaction increased when the loading amount of HPW was increased. The catalytic stability was strongly dependent upon the loading amount of HPW. A maximum conversion of 95% was achieved at 120 °C in 5 h reaction over 20%HPW/TSC catalyst. This catalyst was easily regenerated and recycled for three consecutive runs without major activity loss.

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