Esterification of levulinic acid into hexyl levulinate over dodecatungstophosphoric acid anchored to Al-MCM-41

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ABSTRACT
Aluminum-substituted MCM-41 (Al-MCM-41) were hydrothermally synthesised and used as supports to fabricate the mesostructured H3PW12O40 (HPW) solid acid catalysts via an impregnation method. The influences of various HPW loadings on the structures of the catalysts were verified by X-ray diffraction (XRD), nitrogen physisorption, scanning electron microscopy (SEM), transmission electron microscopy (TEM), ultraviolet–visible (UV–Vis) spectroscopy and Fourier-transform infrared spectroscopy (FT-IR) measurements and their acidities were evaluated by infrared of pyridine adsorption (Py-IR) and temperature-programmed desorption of ammonia (NH3-TPD) measurements. The optimisation of the reaction conditions for levulinic acid esterification with n-hexanol such as the reaction temperature and time, the reactant molar ratio, and the catalyst dosages was performed to maximise the conversion of levulinic acid. The effects of various HPW loadings on the conversion of levulinic acid were investigated under the optimised and harsh reaction conditions. The reusability of the catalysts was also investigated. The results showed that these catalysts retained the hexagonal mesoporous structure of Al-MCM-41 and the Keggin characteristic of HPW, although their textural parameters decreased with increasing loading of HPW. In particular, the catalysts were found to be efficient in the esterification of levulinic acid with n-hexanol, resulting in hexyl levulinate which could replace the petroleum-derived chemical feedstocks.

KEYWORDS
HPW/Al-MCM-41; mesoporous catalysts; esterification; levulinic acid; fuel additives

1. Introduction
In recent years, driven by the increasing global energy consumption and gradual depletion of fossil fuel resources, the utilisation of biomass as renewable natural resources and the conversion of it into valuable biofuels and feedstock chemicals have attracted considerable attention. It not only aimed at the development of effective and environmentally benign technology, but also solves the problem of agricultural and forestry waste use. [1–4] Among various chemicals synthesised from cellulose and cellulosic biomass, levulinic acid
(LA) and its esters are promising platform chemicals for a wide range of derivatives in the biofuel, polymer and special chemicals markets. In particular, hexyl levulinate can be used as fuel additives. However, the serious disadvantages of the typical mineral acids catalysts (HCl, H2SO4 and H3PO4) for LA esterification, such as poor recyclability, harsh reaction conditions and corrosion of equipment, restrict the practical applications. Therefore, the researchers have focused on the heterogeneous catalysts for LA esterification with ethanol or butanol, such as acidic zeolites, micro/meso-HZ-5, desilicated H-ZSM-5, the hydrothermal carbons (HTCs), sulphated oxides, heteropoly acid (HPA)/acid-treated clay montmorillonite (K10), and H3PW12O40/desilicated H-ZSM-5.

As for HPAs, the outstanding advantages such as strong Brønsted acidity, reversible multi-electron redox transformations, and high proton mobility across their discrete ionic structure ensure them to be widely used for scientific and industrial applications. However, the low thermal stability, low surface area and difficulties in separating them from reaction mixtures restrict them as catalyst. Those problems could be overcome by supporting or encapsulating them on suitable porous materials with high surface area, providing an opportunity for HPAs to be dispersed over a large surface area to enhance the catalytic activity. Among those porous materials, MCM-41 is one of the most widely studied mesoporous materials because of its pseudo-crystalline and textural properties. For example, its one-dimensional uniform mesopores with diameters of about 2–10 nm are organised in a hexagonal symmetry. In addition, since pure Si-MCM-41 has electrically neutral frameworks and consequently no Brønsted acidity which restricts its application as a catalyst, much effort has been devoted to enhance the surface acidity of MCM-41 through the direct incorporation of metal ions such as aluminum. The application of MCM-41 containing Al (Al-MCM-41) as catalysts is of great interest since the tetrahedrally coordinated Al can produce active sites for adsorption, ion exchange and catalysis. Till now, several groups have worked on the heterogeneous catalysts consisting of 12-tungstophosphoric heteropoly acid (H3PW12O40, HPW) and Al-MCM-41. For example, Wang et al. prepared Al-MCM-41 from tetraethylorthosilicate (TEOS) and aluminum tri-sec-butoxide and then used it to prepare Pt/H3PW12O40/Al-MCM-41 catalysts. Yang et al. also prepared Pt/H3PW12O40/Al-MCM-41 catalysts, in which Al-MCM-41 was prepared from fumed silica and aluminium sulphate. Both the catalysts exhibited excellent catalytic activity for n-heptane hydroisomerisation. Nandhini et al. prepared Al-MCM-41 from sodium metasilicate and aluminium sulphate and then used it to prepare H3PW12O40/Al-MCM-41 catalysts. The vapour phase alkylation of phenol with tert-butyl alcohol (TBA) and esterification of succinic anhydride with ethanol over the resultant catalysts were examined. Even so, no work has been reported on the synthesis and application of HPW/Al-MCM-41 in the esterification of LA.

In this work, Al-MCM-41 is prepared via a direct assembly process and used as supports to prepare a series of supported HPW catalysts. The chemical composition of Al-MCM-41 is measured by X-ray fluorescence analysis (XRF). The textural properties of the resulting catalysts (HPW/Al-MCM-41) are determined by N2 adsorption–desorption isotherms method. Their crystalline structure and surface morphological features are studied using X-ray diffraction (XRD), scanning electron microscopy (SEM), and
transmission electron microscopy (TEM). The acid properties of the catalysts are measured using the Fourier-transform infrared of pyridine adsorption (Py-IR) and temperature-programmed desorption of ammonia (NH$_3$-TPD) methods. The molecular structures of HPW/Al-MCM-41 are also studied using Fourier-transform infrared spectroscopy (FT-IR) and diffuse reflectance ultraviolet–visible spectroscopy (DR UV–Vis) techniques. For the first time, HPW/Al-MCM-41 was used as catalyst for the esterification of levulinic acid with n-hexanol. The optimisation of the catalytic reaction conditions including the reaction temperature and time, the reactant molar ratio, and the catalyst dosages was performed to maximise the conversion of levulinic acid. The effects of various HPW loadings on the conversion of levulinic acid were investigated under the optimised and harsh reaction conditions. The reusability of the catalysts was also investigated.

2. Experimental

2.1. Synthesis of HPW/Al-MCM-41 catalysts

Al-MCM-41 was synthesised via a hydrothermal process using TEOS as silica source and cetyltrimethylammonium bromide (CTAB) as template. Sodium hydroxide (NaOH) aqueous solution was used for hydrolysis and pH adjustment, and aluminum sulphate (Al$_2$(SO$_4$)$_3$·18H$_2$O) was used as aluminum source. Al-MCM-41 was synthesised from a synthesis gel with a molar content of 1Si:0.017Al:0.3CTAB:0.3NaOH:70H$_2$O. In brief, 1.60 g of CTAB was dissolved into 34.6 mL of NaOH solution (0.39 M) at 40 °C. 10.0 mL of TEOS was then added and the system was kept at stirring for 0.5 h. 0.51 g of Al$_2$(SO$_4$)$_3$·18H$_2$O was dissolved into 20 mL of H$_2$O and the resulting solution was added dropwise into the system described above. After stirred for 7 h, the mixture was transferred into a Teflon-lined stainless-steel autoclave and crystallised at 100 °C for 96 h. The resulting solid was filtered, washed with distilled water and dried at 60 °C. Finally, the samples were calcined in air at 500 °C for 6 h. The Si/Al molar ratio determined by XRF was found to change from 60 in the gels to 65 in the resulting Al-MCM-41 due to the partial leaching of aluminum species in the washing process.

Bulk HPW was synthesised via an improved diethyl ether extraction method reported elsewhere.[16]. HPW/Al-MCM-41 catalysts were prepared by an impregnation method. First, a desired amount of HPW was dissolved into 60.0 mL of H$_2$O. Then, 2.0 g of Al-MCM-41 was dispersed into the solution under continuous stirring. The resulting mixture was left on the magnetic stirrer for 24 h under vigorous stirring at room temperature and then the solvent was slowly vapourised at 50 °C. Finally, the materials were dried at 110 °C overnight and denoted as x wt.% HPW/Al-MCM-41 (x = 5, 10, 15, 20, 25, 30, 35, 40, and 45, respectively).

2.2. Characterisation of physicochemical properties

Surface areas, pore size distributions, total pore volumes and sorption isotherms of the samples were measured via N$_2$ adsorption—desorption at −196 °C using a Quantachrome NOVA 1000e surface area & pore size analyser. Samples were degassed at 250 °C under vacuum for 2 h to vapourise physisorbed water prior to data collection. Specific surface
areas were calculated by the BET (Brunauer–Emmett–Teller) method by using adsorption data ranging from $P/P^0 = 0.05$ to 0.35. The pore size distributions were obtained from desorption branch of the nitrogen isotherms by the BJH (Barret–Joyner–Halenda) method and the pore volume was accumulated up to $P/P^0 = 0.99$.

Powder XRD patterns were acquired on a Panalytical X’pertPro diffractometer operated at 40 kV and 40 mA. The Cu Ka radiation ($\lambda = 0.154$ nm) sources were calibrated against a crystalline Si standard.

FT-IR spectra were recorded on a Thermoscientific Nicolet 380 Fourier transform spectrometer at room temperature using a KBr pellet technique. Determination of the type and strength of the acid sites was done by the FT-IR with pyridine as probe molecule on the same spectrometer. Prior to contacting with pyridine, samples were calcined at 300 °C for 3 h. Then, the samples impregnated with pyridine were processed by ultrasonic treatment for 1 h and outgassed at 35 °C in a vacuum oven to remove the unabsorbed pyridine.

DR UV–Vis spectra were recorded in the wavelength range of 200–800 nm using a Varian Cary 5000 UV–Vis–NIR spectrophotometer. BaSO4 was used as the reference.

SEM images were recorded in a ZEISS SUPRA55 scanning electron microscope with an accelerating voltage of 15 kV. Samples were supported on aluminum stubs backed with carbon tapes.

TEM images were recorded on a JEOL JEM-2100 transmission electron microscope operated at an accelerating voltage of 200 kV. Finely ground samples were dispersed in ethanol by sonication for 15 min and dropped onto a copper grid coated with a holey carbon support film and dried in air.

The acidity of catalysts was studied by NH$_3$-TPD using a Tianjin XQ TP5080 auto-adsorption apparatus. A 50 mg of sample was pretreated in a helium atmosphere (30 mL/min, 500 °C, 1 h), cooled to 20 °C, and then loaded into the reaction cell. The samples were exposed to ammonia at 100 °C for 0.5 h and then purged with helium. The spectra were registered between 100 °C and 750 °C with a 10 °C/min temperature ramp. The NH$_3$ consumption was monitored by a TCD detector. Integration of the TCD traces in comparison with the area given by a known amount of NH$_3$ allowed for quantifying the total amount of acid sites per gram of the samples.

### 2.3. Catalytic reaction

The reaction for esterification of levulinic acid with $n$-hexanol was utilised to evaluate the catalytic properties of the x wt.% HPW/Al-MCM-41 catalysts (Scheme 1). The solid catalyst and levulinic acid (48.60 mmol) were dispersed into $n$-hexanol in a round-bottom flask equipped with a magnetic stirrer and a water-cooled condenser. After the reaction, the solid catalyst mixture was centrifuged out at 10,500 rpm for 20 minutes. Then, a rotary evaporation procedure was applied to remove the resulting water. The products of the reaction were analysed by a gas chromatograph (GC2010 II) equipped with an OV-1701 capillary column (30 m × 0.53 mm × 0.33 μm) and an FID detector. Naphthalene was used as the internal standard. 25 wt.% HPW/Al-MCM-41 was repeatedly used for six times to examine the recyclability of the solid acid catalysts. After each catalytic run, the catalysts were recovered from the reaction solution by centrifugation, washed with ethanol and dried at 70 °C.
3. Results and discussion

The structural properties and porosities of pure Al-MCM-41 and x wt.% HPW/Al-MCM-41 catalysts were studied by N\textsubscript{2} adsorption—desorption technique. The N\textsubscript{2} adsorption—desorption isotherms (Figure 1(a)) show the characteristic type-IV curves with sharp capillary condensation steps as well as H1-type hysteresis loops, which are typical features of highly ordered and well-reserved cylinder-type mesopores before or after HPW incorporation. The capillary condensation of N\textsubscript{2} molecules inside the uniform mesopores for all the samples appears in a similar relative pressure \((P/P^0)\) range of 0.20–0.35, consistent with the characteristic of the highly ordered mesoporous materials.\textsuperscript{[30,31]} All samples possess good structural ordering of mesopores indicated by the narrow pore size distribution with a unique peak centred at a pore diameter of 3.8 nm under the present conditions (Figure 1(b)). Furthermore, it is noticed that all the isotherms exhibit a large hysteresis loop at high relative pressures between \(P/P^0 = 0.45\) and 0.95, which is assigned to the solids with slit-shaped pores.\textsuperscript{[32]} The results of N\textsubscript{2} adsorption—desorption analysis illustrate that the Al-MCM-41 and HPW/Al-MCM-41 catalysts retain the typical mesoporous structure of MCM-41. Similar results were also found in our previous work on HPW/Al-MCM-48 materials.\textsuperscript{[33]}

The low-angle XRD patterns of pure Al-MCM-41 (Figure 2(a)) show three well-resolved XRD peaks due to the reflections of (1 0 0), (1 1 0), and (2 0 0) crystal planes, indicating the formation of well-ordered mesoporous structure of MCM-41 with a hexagonal symmetry.\textsuperscript{[34,35]} The spacing of (1 0 0) planes \((d_{100})\) and the lattice parameter \((a_0)\) are calculated to be 3.91 and 4.52 nm, respectively (Table 1). Meanwhile, the diffraction patterns of the HPW/Al-MCM-41 materials show the typical peaks of MCM-41. The unit cell parameters \((a_0)\) of the HPW/Al-MCM-41 materials are in the range of 4.41–4.54 nm (Table 1). These results suggest that they maintain the hexagonal lattice symmetry. The
decrease of intensities with increasing HPW loading is probably due to that part of the impregnated HPW species presented in the pores, especially in the microspores.[36]

The high-angle XRD patterns of pure Al-MCM-41, bulk HPW, and the resulting HPW/Al-MCM-41 materials are shown in Figure 2(b). Compared with that of bulk HPW, only a broad peak between 15° and 35° associated with the amorphous silica

Figure 1. N₂ adsorption—desorption isotherms (a) and pore size distributions (b) of Al-MCM-41 and x wt.% HPW/Al-MCM-41 materials.
appears for Al-MCM-41 and the HPW/Al-MCM-41 materials, suggesting that HPW species are well dispersed. Moreover, since the pore size of Al-MCM-41 is larger than that of HPW nanocrystals (∼1.2 nm), the impregnated HPW species are expected to present on the surface, inside the channels or at the pore walls of Al-MCM-41.

Figure 2. Low-angle (a) and high-angle (b) XRD patterns of Al-MCM-41 and x wt.% HPW/Al-MCM-41 materials.
As summarised in Table 1, all of the supported catalysts exhibit high surface areas ($S_{BET} > 490 \text{ m}^2/\text{g}$) and pore volumes ($V_p > 0.345 \text{ cm}^3/\text{g}$), even for those with high HPW loadings. The reasonable high surface area also indicates that the mesoporous structure of Al-MCM-41 is retained in those catalysts. On the other hand, it can be seen clearly in Table 1 that the HPW loading influences the textural properties of the HPW/Al-MCM-41 materials. The pure Al-MCM-41 exhibits the highest specific surface area ($S_{BET} = 1110 \text{ m}^2/\text{g}$) and pore volume ($V_p = 0.817 \text{ cm}^3/\text{g}$) and the $S_{BET}$ of $x$ wt.% HPW/Al-MCM-41 decreases from 1051 to 495 $\text{m}^2/\text{g}$ when $x$ is changed from 5 to 45. The corresponding $V_p$ changes from 0.739 to 0.346 $\text{cm}^3/\text{g}$. These changes could be attributed to the deposition of HPW species inside the pores and the dispersion of them on the surfaces of Al-MCM-41 channels.

Figure 3(a,b) shows the SEM images of Al-MCM-41 and 25 wt.% HPW/Al-MCM-41. One can see that both images demonstrate identical morphology of aggregated particles, indicating that the morphology of Al-MCM-41 is not affected significantly upon HPW addition in the typical HPW/Al-MCM-41 samples. The TEM images of Al-MCM-41 and 25 wt.% HPW/Al-MCM-41 shown in Figure 3(c,d) indicate similar abundant hexagonal pores. These results demonstrate that the supported HPW catalysts can retain the characteristic mesoporous structure of Al-MCM-41 and also support the fact that the HPW species are well dispersed.[36] However, compared with that of pure Al-MCM-41, the porous structure of HPW/Al-MCM-41 is unclear and less ordered, indicating to some extent a debasement of its ordered mesophase. The results are consistent with those of XRD characterisation.

As shown in the FT-IR spectra for Al-MCM-41 and $x$ wt.% HPW/Al-MCM-41 (Figure 4(a)), the appearance of the weak band at about 1231 $\text{cm}^{-1}$, which can be ascribed to the external asymmetric stretching vibrations of Si$-$O$-$Al group, confirms the incorporation of Al species in MCM-41.[37] Furthermore, comparing with that of HPW and Al-MCM-41, although the characteristic bands of HPW at 1082, 983 and 804 $\text{cm}^{-1}$ are masked by matching bands of Al-MCM-41 matrix framework, an absorbance of the corner-shared vibrations of W$-$O$-$W at 892 $\text{cm}^{-1}$ in the $x$ wt.% HPW/Al-MCM-41 samples gradually increases with increasing $x$, which could be used to identify the existence of Keggin phase. Similar results are also found in our previous work for HPW/Al-MCM-48.[33]

Table 1. Textural and structural characteristics of Al-MCM-41 and $x$ wt.% HPW/Al-MCM-41 catalysts.

| Sample   | $S_{BET}$ (m$^2$/g) | $V_p$ (cm$^3$/g) | $D_a$ (nm) | $d_{100}$ (nm) | $a_0$ (nm) | $\delta$ (nm) | Keggin-anion density$^a$ (HPW nm$^{-2}$) |
|----------|---------------------|------------------|------------|----------------|------------|--------------|-------------------------------------|
| Al-MCM-41| 1110                | 0.817            | 2.947      | 3.914          | 4.521      | 1.574        | —                                   |
| $x = 5$  | 1051                | 0.739            | 2.811      | 3.828          | 4.421      | 1.610        | 0.010                               |
| $x = 10$ | 990                 | 0.675            | 2.727      | 3.819          | 4.411      | 1.684        | 0.021                               |
| $x = 15$ | 924                 | 0.630            | 2.728      | 3.846          | 4.442      | 1.714        | 0.034                               |
| $x = 20$ | 774                 | 0.533            | 2.756      | 3.850          | 4.447      | 1.691        | 0.054                               |
| $x = 25$ | 748                 | 0.529            | 2.828      | 3.840          | 4.435      | 1.607        | 0.070                               |
| $x = 30$ | 676                 | 0.471            | 2.784      | 3.902          | 4.507      | 1.723        | 0.093                               |
| $x = 35$ | 602                 | 0.411            | 2.727      | 3.876          | 4.477      | 1.750        | 0.122                               |
| $x = 40$ | 561                 | 0.387            | 2.762      | 3.928          | 4.537      | 1.775        | 0.149                               |
| $x = 45$ | 495                 | 0.346            | 2.795      | 3.843          | 4.539      | 1.744        | 0.190                               |

$S_{BET}$, specific surface; $V_p$, total pore volume; $D_a$, mean pore diameter obtained from the desorption isotherms by the BJH method; $a_0$, unit-cell parameter determined from the position of the (1 0 0) diffraction line as $a_0 = 2d_{100}/\sqrt{3}$; $\delta$, pore wall thickness calculated as $\delta = a_0 - D_a$. $^a$The density of Keggin ion was expressed as number of Keggin anions per square nanometer.[43]

Keggin–anion density (HPW nm$^{-2}$) = \frac{[\text{HPW loading (wt.%) x 100}]}{S_{BET} \text{ surface area of catalyst (m}^2/\text{g}) \times 2.88 \times 10^{22}}
The DR UV–Vis spectra of Al-MCM-41, bulk HPW and \(x\) wt.% HPW/Al-MCM-41 \((x = 5, 25, 45)\) were recorded to understand the nature of HPW species presented in the supports (Figure 4(b)). A broad group of signals can be observed in the spectrum of bulk HPW, which can be assigned to oxygen to metal (\(O^2− \rightarrow W^{6+}\)) charge transfer in \([PW_{12}O_{40}]^{3−}\) anion.[16,38] Al-MCM-41 shows a weak peak located at about 200 nm which is attributed to the charge transfer transition of the framework of tetrahedral aluminum atoms, and a band with low intensity at 220–270 nm corresponding to a small amount of extra frameworks of aluminum species.[39] Compared to pure Al-MCM-41, the HPW/Al-MCM-41 catalysts exhibit an obvious absorption in the range of 220–370 nm, suggesting the presence of undegraded HPW species in the supports. In other words, the Keggin phase remains intact upon loading HPW in Al-MCM-41.

The chemisorption of pyridine followed by IR studies is usually a useful probe to detect the presence and nature of acid sites in a catalyst since the information on the strength of Lewis and Brönsted acid sites can be obtained from pyridine thermodesorption.[22,40] According to the previous literature such as [41], 1650–1400 cm\(^{-1}\) absorbed region is ascribed to the vibrations of pyridine molecules interacting with both Lewis acid centres and silanols. Pyridine adsorbed on strong Lewis sites appears at 1623 and 1455 cm\(^{-1}\) and pyridine adsorbed on weak Lewis sites appears at 1575 cm\(^{-1}\). The pyridinium ring

![Figure 3. SEM images of Al-MCM-41 (a) and 25 wt.% HPW/Al-MCM-41 materials (b); TEM images of Al-MCM-41 (c) and 25 wt.% HPW/Al-MCM-41 material (d).](image-url)
vibrations appear at 1545 and 1639 cm\(^{-1}\) due to the proton transfer from Brönsted acid sites to pyridine. The band at 1492 cm\(^{-1}\) is assigned to pyridine associated with both Brönsted and Lewis sites. As shown in Figure 4(c), Al-MCM-41 exhibits obvious Lewis acid sites and weak Brönsted acid sites. However, the obvious bands attributed to pyridine adsorbed on the Brönsted acid sites (about 1540 cm\(^{-1}\)) and Lewis acid sites (about 1445 cm\(^{-1}\)) are detected for the x wt.% HPW/Al-MCM-41 catalysts. Another band (at about 1488 cm\(^{-1}\)) resulting from pyridine’s interaction with both Lewis and Brönsted acid sites is also observed. Furthermore, the intensity attributed to Brönsted acid sites increases with increasing HPW loading in the resulting catalysts since HPW is a strong Brönsted acid.[42]

Therefore, the incorporation of HPW in the Al-MCM-41 supports greatly enhances the Brönsted acidity.

Figure 4(d) shows the typical NH\(_3\)-TPD curves of x wt.% HPW/Al-MCM-41 catalysts (x = 25, 45) which characterise the distributions of acid sites in the resulting materials. The NH\(_3\)-TPD curves of Al-MCM-41 and bulk HPW are also shown in Figure 4(d). Al-MCM-41 shows a desorption peak around 165 °C, which is associated with the Lewis and Brönsted acid sites with weak acidic strength resulting from the tetrahedral aluminum in the framework.[24,39] Bulk HPW exhibits two peaks at ca. 170 °C and 550 °C, which are ascribed to the weak strength acid sites corresponding to the desorption of physisorbed ammonia and the strong strength acid sites representing the desorption of chemisorbed ammonia, respectively. Ammonia desorption occurs in the temperature range of

![Figure 4. FT-IR spectra (a), DR UV–Vis spectra (b), Py-IR spectra (c) and NH\(_3\)-TPD profiles (d) of Al-MCM-41, x wt.% HPW/Al-MCM-41, and bulk HPW.](image)
120 °C—400 °C in the curves for both HPW/Al-MCM-41 samples, revealing that the
surface acid sites are of weak or medium strength for the resulting supported catalysts.
Furthermore, the peak width and area for the 45 wt.% sample are larger than that of
the 25 wt.% one, indicating that the total acidic amount increases with increasing
HPW loading in the catalysts. The total concentration of acid sites obtained by inte-
gration of the ammonia desorption amounts is 0.0189, 0.0747, 0.1127, and
0.2754 mmol/g for pure Al-MCM-41, 25 wt.%, 45 wt.% HPW/Al-MCM-41, and bulk
HPW, respectively.

In order to maximise the LA conversion esterified with n-hexanol, the reaction
parameters such as reaction temperature, reaction time, molar ratio between hexanol
and LA and catalyst dosages are optimised for the 25 wt.% HPW/Al-MCM-41 catalysts.
It is well known that the increase of reaction temperature facilitates molecular colli-
sion and the miscibility of the reactants, or enhances the reaction rate and increases
the conversion of the reactants. As shown in Figure 5(a), the LA conversion is only
34.0% at 60 °C and then increases with increasing reaction temperature until it
reaches up to 100% at 100 °C. Therefore, the optimum temperature is 100 °C under
the reaction conditions. The effects of reaction time on LA conversion are shown in
Figure 5(b). It can be seen that the conversion of levulinic acid after 2 h of reaction is
43.7% and the value increases with increasing reaction time. 100% conversion is

Figure 5. Influences of (a) reaction temperatures, (b) reaction time, (c) hexanol-to-LA molar ratios
and (d) catalyst dosage on LA conversion over 25 wt.% HPW/Al-MCM-41 catalysts. The reaction
conditions are as follows: catalyst dosage 0.40 g, hexanol-to-LA molar ratio 5, time 10 h, temper-
ature 100 °C.
reached after the 10-h reaction. Thus, 10 h is found to be optimum and hence it is used further to optimise other parameters. Because the esterification reaction is reversible, an excess amount of hexanol used could favour the conversion of LA. The hexanol-to-LA molar ratio is varied in the range of 1/C0 to 5 and the results are depicted in Figure 5(c). The conversion is found to increase from 72.1% to 100% with the increase in the mole ratio from 1 to 5. Thus, the hexanol-to-LA molar ratio is optimised to be 5 under the reaction conditions. It can be explained by the fact that the active sites which promote the transformation of the reactant should increase with increasing amount of catalysts. The influence of catalyst dosage on LA conversion is shown in Figure 5(d). The conversion of LA increases from 54.2% to 100% as the amount of catalyst increases from 0.10 to 0.40 g. Thus, the appropriate catalyst dosage is selected to be 0.40 g.

Figure 6(a) shows the values of LA conversion of the x wt.% HPW/Al-MCM-41 catalysts under the optimised reaction conditions described above (catalyst dosage 0.40 g, hexanol-to-LA molar ratio 5, temperature 100 °C, time 10 h). The conversion shows a minimum value at x = 5. With increasing HPW loading up to 20 wt.%, the LA conversion is found to increase from 27.0% to 92.8%. The conversion reaches up to 100% when the HPW loading increases further (x ≥ 25), demonstrating that these HPW/Al-MCM-41...
catalysts exhibit superior catalytic activities for the esterification of LA with n-hexanol under the reaction conditions. The effects of HPW loading on the LA conversion under harsh reaction conditions are further investigated and the results are shown in Figure 6(b,c) ((b) catalyst dosage = 0.20 g, hexanol-to-LA molar ratio 2, temperature 70 °C, time 3 h; (c) catalyst dosage 0.25 g, hexanol-to-LA molar ratio 2, temperature 90 °C, time 3 h). It is found that the value of LA conversion increases with increasing HPW loading. However, when the HPW loading is increased to be larger than 30 wt.%, no significant improvement in the conversion of LA with increasing HPW loading can be observed, as shown in Figure 6 (c). The difference in the catalytic activity of the x wt.% HPW/Al-MCM-41 catalysts may be explained by their pore textural structures, the loading and the state of HPW species, which essentially affect the relative amount of active acidic sites in the catalysts and this may be expressed with the Keggin-anion density. As shown in Table 1, the parameters of pore textural structure (i.e. surface area and pore volume) decrease with increasing HPW loadings. However, the total acidity exhibits the opposite trend. Thus, the influences of pore texture and total acidity on the Keggin-anion density could be different. In addition, the excess concentration of catalyst limits the further increase in interphase mass transfer rate, which restricts the enhancement in catalytic activity.[7]

Although the esterification of LA with alcohols could proceed without catalyst since LA itself shows strong acidity capable of catalysing the reaction, our blank experiment shows that only 3.1% of LA conversion can be yielded in the absence of catalysts at 100 °C after 10 h, indicating that the reaction is significantly accelerated by the HPW/Al-MCM-41 catalysts.

The stability of the catalyst is an important aspect of any industrial process. For this reason, we examine the recyclability of the 25 wt.% HPW/Al-MCM-41 catalyst. As shown in Figure 6(d), the LA conversion is decreased from 100% to 97.2% in the second cycle of reaction. This is mainly due to the partial leaching of HPW species which have weak interaction with the Al-MCM-41 supports. Meanwhile, the as-synthesised hexyl levulinate deposited on the catalysts, perhaps, was not washed out thoroughly. These residual species may cover the catalytic sites of the catalysts and therefore decreased the catalytic activity. Even so, the conversion is maintained to be relatively stable without apparent decrease in the rest of successive cycles. After six cycles of reaction, the value is still around 93.3%. The results indicate that the x wt.% HPW/Al-MCM-41 catalysts are efficient catalysts with excellent recycling stability. In addition, the N₂ adsorption–desorption isotherm for the reused catalysts is similar to those of Al-MCM-41 and the fresh one shown in Figure 7(a), indicating that the reused catalysts still maintained the mesoporous structure of Al-MCM-41. On the other hand, the textural parameters of the reused catalysts ($S_{\text{BET}} = 830 \text{ m}^2/\text{g}$, $V_p = 0.574 \text{ cm}^3/\text{g}$) are larger than those of the fresh one ($S_{\text{BET}} = 748 \text{ m}^2/\text{g}$, $V_p = 0.529 \text{ cm}^3/\text{g}$). The relative intensity of the bands attributed to Brønsted acid sites becomes weak in the Py-IR spectrum for the reused catalysts (Figure 7(b)). This is mainly caused by the partial leaching of HPW species.

Comparing with the HSiW/MCM-41 catalysts for LA esterification with n-hexanol,[43] the resultant HPW/Al-MCM-41 materials show obvious better catalytic activities, indicating that the HPW/Al-MCM-41 are more efficient in the production of hexyl levulinate fuel additives.
4. Conclusion

Mesoporous solid acid catalysts consisting of Al-MCM-41 and the supported HPW are synthesised. The results show that the well-dispersed HPW can be entrapped within Al-MCM-41 with a loading as high as 45 wt.%. The hexagonal phase of mesoporous MCM-41 remains almost unchanged upon the loading of HPW, while its long-range

Figure 7. N$_2$ adsorption—desorption isotherms (a) and Py-IR spectra (b) of Al-MCM-41, HPW, the fresh and the reused 25 wt.% HPW/Al-MCM-41 catalysts.
order, surface area and pore volume decrease significantly. The reaction parameters for the esterification of levulinic acid with \( n \)-hexanol are optimised. When the catalyst dosage is 0.40 g, the hexanol-to-LA molar ratio, the reaction temperature and time are 5, 100 °C and 10 h, respectively. Furthermore, it is found that the structural characteristics and HPW loadings significantly affect the catalytic activities of the HPW/Al-MCM-41 catalysts. The conversion of levulinic acid increases with the increasing HPW loadings. Remarkably, 100% conversion can be reached under the optimum conditions if the loading is not less than 25 wt.%. This work demonstrates that the synthesised mesoporous HPW/Al-MCM-41 catalysts are promising ones for bio-ols upgrading applications, with excellent recyclability.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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