Surface Investigation of Tungstophosphoric Acid Supported on Ordered Mesoporous Aluminosilicates for Biodiesel Synthesis

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ABSTRACT: Aluminosilicates with ordered hexagonal mesopores denoted as MAS-7 and MAS-9 with uniform size were synthesized from zeolite β assembly and ZSM-5 precursors, respectively, with P123 as a surfactant, via the cooperative self-assembly pathway. A series of 12 tungstophosphoric acid (TPA) supported on MAS-7 and MAS-9 (H₃PW₁₂O₄₀/MAS-7/MAS-9) catalysts for biodiesel production were synthesized via the wet impregnation technique. The characterization of the supports and catalysts was done using N₂ adsorption–desorption analysis, X-ray diffraction (XRD), and pyridine adsorption Fourier transform infrared and Raman spectroscopies. Also, the ²⁹Si magic-angle spinning and cross-polarization/MAS nuclear magnetic resonance (NMR) techniques were employed to study MAS-7/MAS-9 and the supported solid acid catalyst surfaces. The nitrogen sorption analysis and XRD patterns indicated the formation of well-defined mesoporous materials, whereas IR spectroscopy confirmed the presence of four distinct types of OH groups with varying degrees of acidity. ²⁹Si MAS NMR signified a stronger interaction between the framework of mesoporous aluminosilicates and H₃PW₁₂O₄₀. The X-ray absorption near-edge spectra of L₁- and L₃-edge tungsten showed that W in the H₃PW₁₂O₄₀/MAS-9 sample exists as W⁶⁺, indicating the tungsten environment similar to that of H₂WO₄ with O₃ symmetry. The catalytic activity of the synthesized catalysts was investigated for biodiesel synthesis using unrefined green seed canola oil as a feedstock, giving a methyl ester yield of 76.5–88.7 wt % under optimized reaction conditions. The catalyst activities were strongly correlated with the surface chemistry of the TPA-supported MAS-7 and MAS-9 catalysts.

1. INTRODUCTION

One of the routes leading to the production of green fuel is the transesterification/esterification of vegetable oil/animal fat to produce biodiesel. The green properties of these fuels are the result of the fact that they are obtained from naturally derived compounds. Hence, this fuel is substantially free of sulfur and aromatic compounds and thus leads to a significant reduction in greenhouse gas emissions.

The transesterification reaction is often catalyzed by the addition of either base or acid catalysts. In case of the alkali-catalyzed transesterification reaction, there are several problems associated with the catalysts, including the product separation from the catalyst and the formation of soap from the free fatty acids (FFAs) present in the feedstock, thus making them undesirable for cheap feedstock. Different catalyst systems have been used to promote these reactions.

Institut Francais du Petrole has developed an EsterFipH process for the transesterification reaction using solid catalysts based on zinc aluminate. The main advantage of the process is that it produces a high-quality glycerol but requires partially refined vegetable oil to avoid the operating problems. Also, the Refining Hydrocarbon Technology developed a process where FFA is first esterified using an acid catalyst, and later the transesterification reaction is carried over a fixed bed of solid basic catalysts. However, the main problem associated with the solid basic catalysts is the leaching of catalysts into glycerol.

The heterogeneous solid acids were found to be more useful for the low-quality or unrefined oils than their solid base analogues and are expected to enhance the esterification of FFA and transesterification of triglycerides simultaneously. It is highly desirable to synthesize biodiesel from low-cost feedstock to avoid the cost associated with the refined vegetable oil. This cost can account for up to 85% of the biodiesel production cost.

Considering the heterogeneous solid acid catalysis, supported heteropoly acids (HPAs) have achieved enormous
interest in biodiesel synthesis because of their structural mobility and super acidity. As HPAs lack thermal stability and have a low surface area, they are incorporated on acidic/neutral carriers like Al₂O₃ or SiO₂. When compared to the other HPAs, 12 tungstophosphoric acid (HPW, TPA, H₃PW₁₂O₄₀) has a higher acidity. Atia et al. reported that alumina- and aluminosilicate-supported heteropolyacids are more active than the silica-supported catalysts for glycerol dehydration. As far as zeolites are concerned, they possess high thermal stability and acidity related to their unique Al in building units, but small pore size restricts their use when large molecules are involved during the catalytic reaction. However, in the case of mesoporous aluminosilicates with an ordered pore structure, low acid strength and thermal stability are of primary concern. In such a scenario, the zeolite molecules can be assembled into a framework structure such that the salient features of the zeolite and mesoporous aluminosilicate materials are maintained. Hence, the mesoporous aluminosilicates MAS-7 and MAS-9 were synthesized via the P123 surfactant with the as-formed zeolite β and the precursors of ZSM-5. Further, these mesoporous aluminosilicates can serve as a support for HPA owing to their exposed surface area available and ordered mesoporosity, in turn improving the acidity of the catalysts.

In the existing literature, aluminosilicates with ordered mesoporosity assembled directly from the zeolite precursors are yet to be explored for the synthesis of biodiesel. This work focuses on TPA-impregnated mesoporous materials with zeolite nanocrystallites like MAS-7 and MAS-9 as new catalysts for the biodiesel synthesis in a batch reactor. This manuscript provides detailed insights into the surface chemistry of the catalysts when TPA is incorporated on MAS-7 and MAS-9 supports and its correlation with the catalytic activity.

A series of 5–45 wt % TPA on MAS-7/MAS-9 catalysts were prepared by the wet impregnation technique. The synthesized supports and catalysts were employed for the biodiesel synthesis from low-quality oils such as unrefined green seed canola oil. It is accessible in large quantities in the western provinces of Canada. The synthesized catalysts facilitated simultaneous transesterification and esterification reactions.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Supports and Catalysts

2.1.1. Surface Analysis. The synthesized catalysts, 0–45 wt % TPA/MAS-7, had a high surface area in the range of 374–998 m²/g. For 0–45 wt % TPA/MAS-9, it ranged from 333 to 740 m²/g. The introduction of the HPW anions significantly changes the surface characteristics as the surface area decreases with an increase in the HPW content. From Table 1, it can be seen that as more TPA anions are incorporated, more depositions occurred on the external surface and resulted in the lowering of the surface area. However, in the case of 25% TPA/MAS-7 and 15% TPA/MAS-9, an increase in micropore area was observed which might be due to the development of abnormalities in the pores. Also, for the other catalysts, a decrease in micropore and mesopore areas and pore volume was observed after HPW loading, thus suggesting that HPW is deposited in the mesoporous channels and dispersed well on the surface of supports with ordered mesopores. In the case of MAS-7, the average pore size, as well as the unit cell parameter, hardly showed any change with TPA loading, but the values obtained slightly varied from the values of MAS-7/MAS-9. The reason behind this phenomenon can be explained by the fact that MAS-7/MAS-9 possesses both micropores and mesopores.

The t-plot analysis showed that MAS-7 and MAS-9 possessed microporous areas of 131.5 and 124.1 m²/g, respectively. MAS-7 and MAS-9 possessed microporosities of 0.07 and 0.04 cm³/g, respectively, whereas for the synthesized samples TPA/MAS-7/MAS-9, they varied in a nonsystematic way with TPA loading, but the values obtained slightly varied from the values of MAS-7/MAS-9. The reason behind this phenomenon can be explained by the fact that MAS-7/MAS-9 possesses both micropores and mesopores.

2.1.2. Adsorption Isotherm. The isotherms of N₂ for pure MAS-7 and MAS-9 and TPA-supported catalysts are shown in Figures 1 and 2. The isotherms of all the catalysts are of type IV as per the International Union of Pure and Applied Chemistry categorization, marked by a step increase because of capillary condensation (relative pressure of 0.2–0.4), and exhibited the H1 hysteresis loop characteristic of mesoporous solids, with closure at around p/p₀ = 0.45 and 0.54 for MAS-7 and MAS-9, respectively. The adsorption isotherms of TPA-impregnated MAS-7 catalysts hardly varied significantly, indicating that the mesoporosity of MAS-7 was unaffected by TPA loading, that is, for 5–45 wt % TPA/MAS-7, the shapes of the isotherms were similar to that of MAS-7, and the main part of the

### Table 1. Textural Properties of the Mesoporous Aluminosilicate Supports and TPA-Supported Catalysts

| Catalyst       | S_{BET} (m²/g) | S_{A} (m²/g) | S_{M} (m²/g) | D_{p} (nm) | V_{micro} (cm³/g) | V_{meso} (cm³/g) | d_{homo} (nm) | a₀ (nm) |
|----------------|----------------|--------------|--------------|------------|------------------|-----------------|----------------|--------|
| MAS-7          | 998            | 131.6        | 866.3        | 4.2        | 0.07             | 1.1             | 1.1            | 11.0   |
| 5% TPA/MAS-7   | 833            | 102.2        | 731.2        | 4.1        | 0.05             | 1.0             | 0.9            | 10.2   |
| 15% TPA/MAS-7  | 739            | 55.0         | 684.0        | 4.4        | 0.03             | 0.9             | 0.8            | 10.3   |
| 25% TPA/MAS-7  | 574            | 74.6         | 499.1        | 4.5        | 0.04             | 0.7             | 0.7            | 10.4   |
| 35% TPA/MAS-7  | 503            | 62.0         | 440.4        | 4.4        | 0.03             | 0.6             | 0.6            | 10.4   |
| 45% TPA/MAS-7  | 374            | 28.3         | 355.7        | 4.5        | 0.01             | 0.5             | 0.5            | 9.9    |
| MAS-9          | 740            | 74.1         | 665.7        | 8.5        | 0.04             | 1.5             | 1.5            | 9.8    |
| 5% TPA/MAS-9   | 649            | 43.4         | 605.9        | 8.7        | 0.02             | 1.4             | 1.4            | 1.0    |
| 15% TPA/MAS-9  | 551            | 181.0        | 370.3        | 11.0       | 0.09             | 0.8             | 0.7            | 10.4   |
| 25% TPA/MAS-9  | 426            | 69.6         | 356.5        | 8.0        | 0.04             | 0.9             | 0.8            | 9.9    |
| 35% TPA/MAS-9  | 574            | 74.6         | 499.1        | 4.5        | 0.03             | 0.7             | 0.7            | 10.4   |
| 45% TPA/MAS-9  | 339            | 39.2         | 300.3        | 10.4       | 0.02             | 0.8             | 0.7            | 10.3   |

*a₀, unit cell parameter determined from the position of the (100) diffraction line as a₀ = 2d_{100} √3; S_{BET}—surface area calculated by the BET method; S_{M}—micropore area; S_{A}—external surface area; D_{p}—mean pore diameter; V_{micro}—micropore volume; V_{meso}—total pore volume; V—mesopore volume.
The hysteresis loop remained at the same relative pressure. For 15−45 wt % TPA/MAS-9, the desorption branches extended to a lower relative pressure \( (p/p_0 = 0.45) \) compared to that of 5 wt % TPA/MAS-9 and MAS-9. It has been reported that HPW anions may occupy or block the mesopores of the aluminosilicates, thus increasing the average pore size and decreasing the surface area.\(^{11}\)

2.1.3. X-ray diffraction. The small-angle X-ray diffraction (XRD) patterns \((0.5−10^\circ)\) of MAS-7 possessed the strongest and weak diffraction peaks at 0.87° and 1.5°, ascribing to the (100) and (110) crystal planes, typical of the \(P6_{3}mm\) well-ordered hexagonal arrays of mesopores\(^{12}\) (Figure S1). The sharp (100) diffraction peaks for MAS-7 and MAS-9 at \(2\theta = 0.87\) and 0.9, respectively, gave the \(d\)-spacing values of 11.0 and 9.8 nm. The cell parameters \(a_0\) were 12.7 and 11.3 nm, respectively, for MAS-7 and MAS-9 based on the relationship \(a_0 = 2d_{100}/\sqrt{3}\). The wall thickness values calculated using the equation “wall thickness = \(a_0\)−pore diameter” were found to be 8.5 and 2.8 nm for MAS-7 and MAS-9, respectively. It has been reported that longer reaction duration and higher temperatures result in enlarged pore size and decreased wall thickness.\(^{13}\) However, MAS-7, which was synthesized at a higher temperature of 140°C as compared to MAS-9 (synthesized at 100°C), had a greater wall thickness and smaller pore size. The other factor, which can play a role in increasing wall thickness, is the nature of silica.\(^{14}\) Fumed silica, which is used in the synthesis of MAS-7, has a smaller unit of silicates and possesses a lower degree of polymerization with higher diffusion rates in solution as well as aggregates, resulting in the formation of thicker walls.

For the supported catalysts, hardly any change in the planes corresponding to the long-range structural ordering of MAS-7 and MAS-9 after HPW impregnation was observed. Hence, it can be concluded that the supports MAS-7 and MAS-9 retained their symmetry even after TPA loading.

The wide-angle diffraction patterns for HPW in bulk, supports, and 5−45 wt % TPA/MAS-7/MAS-9 catalysts are shown in Figures 3 and 4. A broad peak was observed at a \(2\theta\) value of 22.8° corresponding to an amorphous structure of silica, which was more pronounced in case of the MAS-7 and TPA/MAS-7 catalysts compared to that of the TPA-supported MAS-9 catalyst. It can be attributed to the source of silica used in the preparation of both the supports, which was fumed silica.
in case of MAS-7 and tetraethyl orthosilicate (TEOS) for MAS-9. This peak was observed up to the loadings of 25 and 15 wt % for MAS-7 and MAS-9 supports, respectively. The absence of the characteristic peaks of HPW at these loadings signified that HPW was well-distributed on the support surface and also inside the hexagonal channels and in the aluminosilicate pore walls, as the pore size of MAS-7 and MAS-9 (4.2 and 8.5 nm) is higher than that of the HPW (1.9 nm) crystals. As the loading increases from 25 to 45 wt %, peaks related to TPA gradually occur. As the XRD patterns are related, irrespective of the presence or absence of clear crystals, the diffraction patterns for TPA on MAS-7 and MAS-9 show that TPA introduced is precisely distributed on the MAS-7 and MAS-9 surfaces at a higher loading of 15 wt %. As the loading of TPA increases, some TPA exists as a crystal phase.

2.1.4. Raman Spectral Analysis. Further, the nature of impregnated HPW was studied using Raman spectroscopy. The spectra of TPA supported on MAS-7 and MAS-9 are shown in Figures 5 and 6. The crystalline HPW shows the characteristic bands at 1009.8 cm\(^{-1}\) (symmetric stretching of PO\(_4\) sites), 991 cm\(^{-1}\) \([\text{antistretching } (\nu_{as}) \text{ of } \text{W}=\text{O}=\text{W}]\), and 931 \([\nu_{as} (\text{W}=\text{O}−\text{W})]\), which is in good agreement with the literature data.\(^{15,16}\) The low-intensity bands appearing at 538 and 516 cm\(^{-1}\) are attributed to W=O−W \{symmetric stretching \([\nu(s)]\)\} and O−P−O \{asymmetric deformation \([\nu(as)]\)\}.\(^{37}\) After the impregnation of TPA into the MAS-7 and MAS-9 lattices, the peaks corresponding to the PO bond and W=O vibrations were broadened; therefore, a broad peak was seen in the range of 921–1053 cm\(^{-1}\). For 5 wt % loadings, the characteristic keggin bands for supported HPW are hardly observed, whereas 15 and 25 wt % loadings show only broad- and low-intensity main bands at about 985 and 1010 cm\(^{-1}\), suggesting an interaction of the keggin unit and the MAS-7/MAS-9 framework.

However, in the case of 35 and 45 wt % TPA loadings, sharp and higher intensity peaks were observed resembling that of pure TPA, thus indicating that the keggin unit environment is identical to that of HPW and hence confirms the retainment of the keggin structure even after anchoring to the supports. However, for 45 wt % TPA/MAS-7, additional peaks occurred at 710 and 804 cm\(^{-1}\), attributed to the presence of crystalline WO\(_3\).\(^{18}\) This suggests that despite the retainment of the keggin unit, there was some tungsten oxide formation on the surface.

2.1.5. \(^{29}\text{Si}\) Magic-Angle Spinning (MAS) and CP/MAS NMR Studies. The interaction of impregnated TPA with the mesoporous aluminosilicate framework was studied via \(^{29}\text{Si}\) nuclear magnetic resonance (NMR). \(^1\text{H} \rightarrow \text{^{29}Si}\) cross-polarization (CP, via dipolar coupling) detects the NMR signal of silicon nuclei that are close to protons, which makes it a reliable and sensitive technique for the detection of silicon nuclei at or close to the surface of the MAS-7/MAS-9 materials. Figure 7B,D shows the \(^{29}\text{Si}\) CP/MAS NMR spectrum of the support MAS-7 and the synthesized catalyst TPA/MAS-7 sample obtained at room temperature. The spectra showed three \(^{29}\text{Si}\) signals at about −93, −102, and −110 ppm, reflecting the presence of Q\(_2\), Q\(_3\), and Q\(_4\) units (Figure 7B,D).\(^{19}\) A dominating resonance is observed at −102 ppm, and it is ascribed to Si* nuclei within the X silicon linkages of XOSi*(OSi)\(_3\) (Q\(_3\)), where X is H or TPA. The shoulder at −93 ppm resembles the silicon atoms on the surface with two siloxane bonds and either single- or hydrogen-bonded germainal silanol sites, SiO\(_2\)\(^*\)(SiOX)\(_2\) (Q\(_4\)), whereas at −110 ppm the resonance is due to the hydroxyl-free Q\(_4\) (siloxane) units—no heterolinkages (either Si−O−H or Si−...
O−TPA). Note that this signal at −110 ppm dominates the 29Si MAS NMR spectra of the corresponding system (Figure 7A,C), which makes sense as there are much more silicon atoms inside the framework than on the surface. The reason leading to a weak 29Si signal for the Q3 unit in the CP/MAS spectra is that the signal intensities of the CP/MAS spectra rely on the number of protons and the dipolar coupling strength (i.e., the distance) between 1H and 29Si, rather than on the amount of silicon nuclei. Therefore, CP/MAS is not a suitable technique for quantitation. 29Si MAS NMR should be applied for this purpose.

Figure 7A,C shows the 29Si MAS NMR spectra with proton (1H) decoupling of MAS-7 and TPA/MAS-7. The signal at about −110 ppm, originated from Q4 units, dominates the spectra, especially for MAS-7. The signals from Q3 and Q4 can be clearly seen in the 29Si MAS spectrum of TPA/MAS-7. The spectra were therefore deconvoluted into three components, with the 29Si chemical shifts at about −93, −102, and 110 ppm corresponding to the silicon nuclei in the Q2, Q3, and Q4 units, respectively. Using the signal intensities from spectral deconvolution (Table 2), the fractional population of the surface germinal hydroxyl silanol sites and isolated silanol sites was calculated. From the fractional populations, we can calculate the surface SiOH concentration and the number of OH groups per square nanometer (σOH).

According to Leonardelli,19 if the different chemical species in Q2, Q3, and Q4 are proportioned as x, y, and z, the number of OH groups, assuming that all the hydroxyl groups are on the outer surface, measured by the Brunauer−Emmett−Teller (BET) method, is given by

$$\eta_{OH} = \frac{f_x(1 + f_g)}{S} \frac{N_A}{60 + 9f_g(1 + f_g)}$$

where $f_g = x/(x + y)$, $f_x = x + y$, and $N_A$ is the Avogadro number. The concentrations of $x$, $y$, and $z$ can be given as $x = f_g y = f(1 - f_g)$, $y = 1 - f_g$. The $\eta_{OH}$ values for the supports MAS-7 and MAS-9 and the synthesized catalysts, as well as the distribution of Q2, Q3, and Q4 units and their relative values, are shown in Table 2. The intensity redistribution of these silicon sites is thought to be due to the reactions of the surface SiOH groups with TPA. During impregnation, the protons of TPA (H3PW12O40) are transferred to the OH groups of the silica surface, mainly with the germinal silanols of the support. Thus, the terminal W−O groups within the keggin unit interact with the surface (AlO)(HO)Si(OSe)3 groups via W−O−Si(Al) covalent bonding. Hence, the variation in the distribution of Q4 units in the supported catalysts was observed because of the formation of heterolinkages. Also, the distribution of Q3 unit in the TPA-supported catalysts was found to increase, which could be probably due to the conversion of two germinal units into silanol sites (Q4) upon subsequent dehydroxylation. Therefore, a higher value of (Q3 + Q4)/Q4 was observed for the TPA-supported catalysts, thereby suggesting an interaction between the framework of mesoporous aluminosilicates and TPA. A similar kind of distribution of Q3, Q4, and Q5 units was observed for the TPA/MCM-41 catalysts.19

2.1.6. Hydroxyl Framework and Lewis and Bronsted Acidity. Figure 8A shows the infrared (IR) νOH spectra of the

![Figure 8. FTIR spectra of the hydroxyl stretching vibrations between 3820 and 3550 cm⁻¹ of the mesoporous aluminosilicates (A) MAS-7 and (B) pyridine-desorbed MAS-7 at 150 °C.](image_url)

Table 2. Quantification of Peak Areas in the 29Si MAS NMR Spectra of Mesoporous Aluminosilicates and TPA-Supported Catalysts and the Number of Hydroxyl Groups per Unit Area²

|          | $Q_2$ % (SiO)₂* (SiO)X₂ | $Q_3$ % XOSi* (OSi)₃ | $Q_4$ % (SiO)₄*Si | (Q3 + Q4)/Q4 | $\eta_{OH}$/nm² |
|----------|-------------------------|----------------------|-----------------|--------------|----------------|
| MAS-7    | 7.2                     | 32.1                 | 60.8            | 0.6          | 4.3            |
| TPA/MAS-7| 2.1                     | 41.5                 | 56.4            | 0.8          | 7.5            |
| MAS-9    | 13.3                    | 37.8                 | 48.9            | 1.0          | 7.7            |
| TPA/MAS-9| 11.3                    | 42.8                 | 45.8            | 1.2          | 17.5           |

²X = H/TPA.
mesoporous aluminosilicate MAS-7 before exposure to the pyridine (Py) atmosphere. The band appearing at 3741 cm$^{-1}$ can be assigned to the external silanols, whereas the other having a vibrational frequency of 3600 cm$^{-1}$ is associated with the Bronsted acidity, and the intensity of this band corresponds to the aluminum content of the zeolite and with the extent of proton exchange. Further, the relative intensity of external silanol when correlated with that of the Bronsted acid band indicates smaller primary crystallites and higher external surface area and agrees well with the BET and XRD analyses. The $\nu$OH spectra also show the occurrence of a weak band and a broadband at 3778 and 3652 cm$^{-1}$, respectively, ascribed to small noncharged extra-framework aluminum and to the OH stretching vibrations of Al$-$OH, where Al would be linked with the framework by chemical bonds.

Figure 8B represents the $\nu$OH spectra of the pyridine-desorbed MAS-7 sample.

The signal at 3600 cm$^{-1}$ reappeared after pyridine desorption at 150 °C, shifting to a lower wavenumber, thus indicating an interaction with the bridging OH group, whereas the band at 3720$-$3652 cm$^{-1}$ was found to be absent. The disappearance of the band at 3720$-$3652 cm$^{-1}$ perhaps is due to the adsorption of pyridine on the Al hydroxyl species with the subsequent dispersal of $\nu$OH vibration. Also, the band appearing at 3778 cm$^{-1}$ was found to be completely removed, and hence it can be concluded that it is fully available for pyridine adsorption. On the basis of the weak base interaction, it has been reported that the band at 3778 cm$^{-1}$ associated with the Al$-$OH species is moderately acidic. Moreover, the bands in the region 3880$-$3700 cm$^{-1}$ are usually present on aluminum oxides, in which Al is present in the tetrahedrally coordinated part. Hence, it can be proposed that OHS are present over the tetrahedral Al cations and are also associated with the formation of Lewis sites (because of the coordinatively unsaturated Al$^{3+}$ cations). On the other hand, the band at 3746 cm$^{-1}$ of the OH vibration stretching of silanol remains unaltered. Isernia reported a similar observation.

To conclude, MAS-7 showed four distinct types of OH groups with varying degrees of acidity, except for the terminal OH groups. The occurrence of these different OH groups on the metal oxide surface can promote the bonding to metal sites of different coordinations. Hence, this allows us to propose that the interaction of the HPW keggin structure can take place at these sites.

The identity of the acidic sites (Bronsted and Lewis acids) present in mesoporous aluminosilicates and HPW-supported catalysts with varying loadings has been deduced from the IR spectra of the framework vibrations of the adsorbed pyridine (Figures 9 and 10). The pyridine adsorption on MAS-7 and MAS-9 yields IR bands at 1448, 1602, and 1634 cm$^{-1}$. The peak at 1448 cm$^{-1}$ corresponds to the hydrogen-bonded pyridine and hence ascertainment of the surface OH group accessibility (donor H-bond sites), whereas the bands at 1602 and 1634 cm$^{-1}$ indicate the formation of LPy species (exposing the unsaturated metal sites) and Bronsted acid sites, respectively. The intensity at 1535 cm$^{-1}$, attributed to the formation of BPY species, resulted in an increased intensity at higher HPW loading (>25 wt % for MAS-7 and >15 wt % for MAS-9). The increase in Bronsted acidity with increasing HPW surface coverage can correspond to the polytungstate clusters, which can delocalize the protons among the neighboring tungsten trioxide species. Their occurrence was noticed in the Raman spectra by the presence of W$-$O$-$W bands at a loading of 45 wt % (Figure 5F). Similarly, the occurrence of the peaks at 1486 and 1624 cm$^{-1}$, corresponding to the formation of adjacent Lewis and Bronsted and Lewis acidic sites, was observed at higher TPA loadings.

2.1.7. W L$^1$- and L$^3$-Edge X-ray Absorption Near-Edge Spectra. 2.1.7.1. W L$^1$-Edge. The W L$^1$-edge spectra exhibit prominent features referred to as white line, which arises from the electronic transition from the 2p$^{3/2}$ state to the 5d unoccupied states accompanied by several excitations for the hybridized W 5d$-$O 2p conduction band. Figure 11(I) depicts the L$^1$-edge spectra of tungsten for the reference samples (A) H$_2$WO$_4$ (B) Na$_3$WO$_4$$\cdot$H$_2$O, and the synthesized catalyst sample (C) 45 wt % TPA/MAS-9. The W L$^3$ spectrum of TPA/MAS-9 was found to be similar to that of H$_2$WO$_4$ but different from that of Na$_3$WO$_4$$\cdot$H$_2$O. Hence, it can be said that 45 wt % TPA/MAS-9 exhibits O$_h$ symmetry as H$_2$WO$_4$ exhibits O$_h$ symmetry, whereas Na$_3$WO$_4$ showed $T_d$ symmetry. H$_2$WO$_4$ shows a broad peak, whereas an unsymmetrical peak is
observed for Na₂WO₄. These dissimilarities in the white line shape are because of the ligand field splitting of the 5d states of tungsten. Yamazoe et al. stated that the splitting of the 5d orbitals of the tungsten tetrahedral unit is smaller than that of an octahedral unit. The second-order derivative spectra were used to describe the splitting of the 5d orbitals in t₂g (dₓz, dᵧz, d₀z) and e₉ (dₓ²−y², dₓy). Figure 11(II) shows the second-order derivative spectra (X-ray absorption near-edge spectra, XANES) of W L₃ of 45 wt % TPA/MAS-9 and the reference samples. The ligand field splitting was more readily observed for tungstic acid (H₂WO₄) in the second-order derivative plot, and the energy gap indicates the d-orbital splitting. H₂WO₄ has nearly an octahedral symmetry, and the lower energy peak is referred to as a transition to orbital t₂g vacancy, whereas the peak at higher energy is ascribed to the excitation to an orbital e₉ vacancy. The crystal field splitting (Δd = E(e₉) − E(t₂g)) for H₂WO₄ and 45 wt % TPA/MAS-9 was found to be 3.5 and 4.09 eV, respectively, whereas the WO₄ units, as in case of Na₂WO₄, show a minima in lower energy as the 5d orbital split is small in the tetrahedral tungsten unit. The crystal filed splitting or the energy gap for Na₂WO₄ between the shoulder and the large peak was found to be 1.5 eV, which is pretty much closer to the value reported in the literature.

2.1.7.2. L₁-Edge. The pre-edge feature in the W L₁ spectra is ascribed to the 2s to d−p orbital transition, sensitive to the W bonding environment symmetry. For tetrahedral symmetry, the unoccupied p orbitals strongly hybridize with the d band, but not for regular octahedral symmetry.

As the 2s → 5d transition is formally dipole-forbidden, regardless of the symmetry, however, in case of distortion from the ideal symmetry, the hybridization of 5p/5d orbitals makes 2s → 5d transition possible, and therefore the pre-edge peak of Na₂WO₄ having the tetrahedral units of W is much more intense than the other reference samples (Figure 12).

Curve-fitting for W L₁-edge was done using an arctangent and Lorentz function similar to the pre-edge peak derivation from the L₃-edge (Figure S3). As H₂WO₄ and 45 wt % TPA/MAS-9 lack the hybrid d and p orbitals, mainly quadrupole electron transition could take place from 2s to t₂g and e₉ orbitals of 5d. Hence, the pre-edges of H₂WO₄ and 45 wt % TPA/MAS-9 were fitted with two Lorentz functions, whereas the pre-edge of Na₂WO₄ was fitted with one Lorentz function.

2.1.7.3. Conjoint W L₁- and L₃-Edge XANES. On plotting the pre-edge area of the L₁-edge versus L₃-edge energy gap split, it was observed that 45 wt % TPA/MAS-9 and H₂WO₄ with octahedral coordination comprised a smaller pre-edge area and a large energy gap, as shown in Figure 13, whereas Na₂WO₄·H₂O with a tetrahedrally coordinated W is recognized with a small energy gap (L₃-edge) and a larger pre-edge area (L₁-edge).

Figure 11. W L₃ XANES spectra (I) and second derivative spectra (II) of (A) H₂WO₄ (B) Na₂WO₄·H₂O, and (C) 45 wt % TPA/MAS-9.

Figure 12. W L₁-edge XANES (A) H₂WO₄ (B) Na₂WO₄·H₂O (C) 45 wt % TPA/MAS-9. 45 wt % TPA/MAS-9 and H₂WO₄ with W in octahedral symmetry show small pre-edge peaks.

Figure 13. Relationship between the area of the pre-edge peak in L₁-edge XANES and the splitting of the minima in the L₃-edge XANES second derivatives: (A) H₂WO₄ (B) Na₂WO₄·H₂O, and (C) 45 wt % TPA/MAS-9.
Consequently, from the W L$_3$ edge, L$_3$ edge, and combined analysis, it was confirmed that tungsten in the synthesized catalyst samples exists as W$^{6+}$, residing in an octahedral environment. In three-dimensional heteropolytungstates, WO$_x$ octahedral are connected within the wrapped surface and not by the central atom. The terminal group, W=O of TPA, interacts with the surface hydroxyls of the mesoporous framework (congruent with the $^{29}$Si NMR studies), leading to the formation of larger polyanions. These larger heteropolyanions generate Bronsted acidity by effectively delocalizing the negative charge and aid in the release of protons effectual for the transesterification and esterification reactions. This also agrees well with the pyridine-adsorbed Fourier transform infrared (FT-IR) spectroscopy measurements, in which an increase in Bronsted acidity was found at higher TPA loadings corresponding to the polyanion clusters.

### 2.2. Catalytic Activity

#### 2.2.1. Effects of TPA Loading on MAS-7 and MAS-9

The effects of TPA loading varying from 5 to 45 wt % in MAS-7 and MAS-9 supports on methyl ester yield were investigated (Figures 14 and 15). In this study, the operating parameters of reaction were fixed at 2.57 wt % (loading of catalysts), methanol-to-oil molar ratio of 20:1, 200 °C, and 8 h.

![Figure 14. TPA loading screening for MAS-7 (2.57 wt % catalyst, methanol-to-oil molar ratio of 20:1, 200 °C, 4 MPa, and 8 h).](image)

#### 2.2.2. Effects of Surface Acidity on Catalytic Activity

Figure 16A,B shows the quantitative correlation of surface acidity with the catalytic activity (methyl ester yield and FFA conversion) as a function of different TPA loadings for MAS-7 and MAS-9, respectively. The results indicated a direct relationship between the catalytic activity and the total surface acidity of the catalysts, that is, the catalytic activity increases with the total surface acidity. Figure 16A shows that 25 wt % TPA-supported MAS-7 exhibits a higher catalytic activity and can be related to the highest total surface acidity because of the better dispersion of the keggin anions on the surface of the catalyst, with an optimum surface area and pore diameter facilitating the simultaneous transesterification and esterification reactions.

However, with the higher amount of TPA loading on the catalyst surface, hardly any significant increase was found in the catalytic activity and can be interpreted by the surface area, and pore volume decreases with the amount of TPA loading (Table 1) and the decreasing accessibility by the triglyceride molecules.

The supported solid acid catalysts gave the methyl ester yield between 60 and 79 wt % in 8 h as compared to MAS-7 that only showed 41 wt %. It is well-known that acidity favors the transesterification and esterification reactions. Hence, with the low HPW loading, expectedly a low activity of 5 wt % TPA/MAS-7 was observed in comparison to other TPA on MAS-7/MAS-9 catalysts because of the lower number of acidic sites. However, 25 wt % TPA/MAS-7 showed a higher activity as compared to 35 wt % TPA/MAS-7 and 45 wt % TPA/MAS-7.

The results in Figure 14 suggest that at a HPW loading higher than 25 wt %, the acidic sites ingrained in the mesopores could have been unavailable because of the plugged mesopores, confirmed by the BET analysis, leading to an insignificant increase in the yield of ester.

Hence, the activities of the two catalysts did not significantly increase the methyl ester yield as compared to the 25 wt % TPA/MAS-7 catalyst in which most of the HPW anions were well-dispersed on to the support. This optimum dispersion was confirmed by the XRD analysis (Figure 3D). Hence, 25 wt % TPA loading was found to be optimum for the MAS-7 support.

For the support MAS-9, despite higher HPW loading, 45 wt % TPA/MAS-9 showed reduced activity as compared to 35 wt % TPA/MAS-9 (Figure 15). For instance, to obtain a methyl ester of 72, 35 wt % TPA/MAS-9 required only 5 h, whereas 45 wt % TPA-supported catalysts required up to 6 h. The maximum ester yield obtained in 8 h was 89.7 wt % at a TPA loading of 35 wt % in the case of MAS-9 support.

### 2.2.3. Statistical Analysis

The ester yield was determined at different combinations of the catalyst weight, alcohol/oil ratio, and reaction time for the 25 wt % TPA/MAS-7 catalyst. Table 3 gives the minimum and maximum limits of each factor used. The quadratic model equation was derived using response surface design of experiments (DOE) for determining the combinations of these three factors giving the maximum ester yield. The model has an R-square value of 0.90, meaning it is capable of explaining 90.3% of variations in the yield. The

![Figure 15. TPA loading screening for MAS-9 (2.57 wt % catalyst, methanol to oil molar ratio 20:1, 200 °C, 4 MPa, and 8 h).](image)
The maximum ester yield predicted by the model is 76.7% (95% confidence interval—66.8, 86.6%), with the optimal settings of factors being 5.5 wt % of the catalyst, 14.9:1 methanol/oil ratio, and 10 h of reaction time. However, it was seen from the Pareto chart of standardized effects (Figure 17) and the main effect plots of yield for factors and their interactions (Figure 18) that only the methanol/oil ratio and the reaction time have a statistically significant impact on the ester yield. The catalyst weight when varied between 1 and 10 wt % did not have any statistically significant impact on the ester yield. However, at 5.5 wt % catalyst, the ester yield is maximized. Previous researchers have also reported that the catalyst loading did not influence the ester yield significantly.26

Table 3. Factor and Limits for DOE

| factor          | unit | minimum | maximum |
|-----------------|------|---------|---------|
| catalyst weight | wt % | 1       | 10      |
| methanol/oil    | Mol  | 6:1     | 25:1    |
| reaction time   | H    | 4       | 10      |

The yield of ester increased with the increase in reaction time, whereas for methanol/oil molar ratio, it increased until the midpoint, and after that decreased. A similar trend was observed by the authors Xie and Li.27 The catalyst 35 wt % TPA/MAS-9 gave an ester yield of 88.7 ± 4.2 wt % at the above-optimized conditions. Polyyoxometalate supported on various meso/macroporous oxides resulted in 82–96% of oleic acid conversion at 200 °C. The most stable catalysts against the leaching of active material were heteropolyacid supported on 3.5% SiO2–ZrO2 and SiO2–Al2O3.28 The use of HPMo/Nb2O5 resulted in 99.7% ester yield at conditions of 20 wt % catalyst loading, 90:1 ethanol-to-oil molar ratio, a reaction temperature of 210 °C, and a reaction time of 4 h.29 Phosphotungstic acid-functionalized magnetic nanoparticles (HPW-PGMA-MNPs) gave 98% FAME yield after 24 h at 122 °C, with the catalyst loading of 4 wt % and 33:1 methanol/grease molar ratio.30

2.2.4. Reusability Study of the Supported Catalysts. The separated catalyst was washed with tetrahydrofuran (THF) for the removal of nonpolar and polar components and then subsequently regenerated by drying at 100 °C for 24 h. The results obtained for the first three cycles are presented in Figure 19 along with the surface acidity (mole of H+/g) of the catalysts. Reduction of 3.3 and 4% in the catalytic activity was observed for 35 wt % TPA/MAS-9 and 25 wt % TPA/MAS-7, respectively, after the first reuse. However, not a significant decrease in the ester yield was observed from the successive reaction runs.

The presence of active material in the present study, that is, HPW was monitored by UV–vis based on 253 nm absorption, ascribed to the transfer of the charge terminal/bridging oxygen 2p to the tungsten 5d orbital (W=O=W and W=O=W).31 For the leaching of TPA in methanol, a calibration curve was constructed with the standard solution of HPW in methanol at concentrations of 1.5, 3.1, 6.2, and 12.4 ppm. The concentration of the catalysts before and after the reaction was deduced from the curve obtained. The results hardly showed any significant leaching (0.002 and 0.001%) of the active phase from the supports MAS-7 and MAS-9 and can be associated to the interaction of the keggin anion with the supports, confirmed by the 29Si NMR studies. This study is supported by Kozhevnikov11 who stated that the reaction was truly heterogeneous and that the leaching of active phase was negligible.

Bala et al.32 showed that the PTA/KIT-5 catalysts exhibited the highest conversion of 83% for used cooking oil and 100% for palmitic acid at optimum conditions, and their catalyst recycling studies indicated 22% loss in conversion at the end of four cycles because of the leaching of acid from the framework. TPA-supported cesium-containing Niobia (TPA/Cs1.0/Nb2O5) when employed for the esterification of palm fatty acid distillate (PFAD) gave an ester yield of 90% at 65 °C after 8 h, with 15 wt % catalyst loading and 15:1 methanol/PFAD ratio. However, the catalysts showed poor reusability, marked...
by 15% decrease in the catalytic activity, at the fifth run because of the blockage of active sites and the alteration in the structure of the catalysts. Moreover, the catalysts were unable to reactivate via calcination.33 The 20% H3PW/ZrO2 catalyst with an oleic acid conversion of 88% in 4 h at 100 °C with 1:6 oleic acid/ethanol molar ratio and 10 wt % catalyst loading resulted in the leaching of 8 wt % of H3PW after the first reuse.34

3. CONCLUSIONS

H3PW12O40 on MAS-7/MAS-9 catalysts were synthesized by wet impregnation. As per the BET analysis, the mesoporosity of the synthesized catalysts was found to be preserved after the impregnation of TPA at a loading as high as 45 wt %. XRD and Raman studies confirmed the retention of the keggin anions on the support, whereas 29Si NMR suggested a stronger interaction between the framework of mesoporous aluminosilicates and H3PW12O40. Hence, no leaching of TPA from the support was observed. X-ray absorption fine structure spectroscopy of W L3 and L1 edges indicated that W in the TPA-supported catalysts is in an octahedral-like coordination, and hence the system was effective for the transesterification and esterification reactions. The synthesized catalysts showed suitable physicochemical properties for the biodiesel production. The acidic strength of TPA/MAS-9 was higher than that of TPA/MAS-7, as the precursor of MAS-9 was more acidic than the MAS-7 precursor. The 35 wt % TPA/MAS-9 and 25 wt % TPA/MAS-7 showed catalytic activities of 88.7 and 76.5 wt %, respectively, with unrefined green seed canola oil under optimized reaction conditions. Further, the catalysts separated by filtration and drying at 100 °C confirmed their reusability without a considerable decrease in activity.

4. EXPERIMENTAL SECTION

4.1. Synthesis of MAS-7 and MAS-9 Supports. Hydrothermally stable mesoporous aluminosilicates MAS-7 and MAS-9 with ordered hexagonal structures were synthesized from the assembly of a triblock polymer surfactant (P123, Fisher Scientific) with a precursor of zeolite β and ZSM-5 in a strongly acidic media, according to the report by Han et al.10 and Xia et al.12 The procedure for the synthesis of MAS-7 and MAS-9 is as follows: (1) The zeolite β precursor solution was prepared by mixing 0.4 g of NaOH, 0.83 g of NaAlO2, and 16.8 g of fumed silica into 75 mL of tetraethylammonium hydroxide (1 M in water, Aldrich) with the molar ratios of 1.0/60/2.5/22/800 for Al2O3/SiO2/Na2O/TEAOH/H2O. The mixture thus obtained was aged at 140 °C for 4 h. (2) The precursor solution with ZSM-5 was obtained by adding 0.35 g of NaAlO2 in 14 mL of tetrapropylammonium hydroxide solution (1 M in water, Aldrich) and 24 mL of TEOS (>98%, Aldrich) with 68 mL of water. The molar ratios of Al2O3/SiO2/Na2O/ (TPA)2O/H2O were maintained at 1.0/50/1.0/7/1800. The precursor solution was then aged at 100 °C for 3 h. (3) 10 g of the polymer surfactant (P123) was dissolved in acidified water (265 mL of water mixed with 98 mL of 10 M HCl). The precursor solution was then aged at 100 °C for 3 h. (4) The white product obtained was then filtered, dried in an oven, and calcined at 550 °C for 5 h for template removal.

4.2. Preparation of TPA/MAS-7/MAS-9 Catalysts. A series of 5−45 wt % TPA-anchored MAS-7/MAS-9 catalysts were prepared using a wet impregnation method. A 10 mL of
the methanolic solution of TPA was used to impregnate 1 g of MAS-7/MAS-9 supports. The samples were stirred at room temperature, oven-dried at 110 °C, and were further calcined.

4.3. Catalyst Characterization. The BET isotherms were assessed using Micromeritics ASAP 2000. The samples were degassed at 300 °C for 3 h. The surface area was obtained with the BET method. The pore size distribution was obtained with the help of the Barrett–Joyner–Halenda model.

The low-angle and wide-angle diffractograms were obtained on a D8 Advance powder diffractometer [monochromatic Cu Kα (λ = 1.54 Å) radiation]. The supports and catalyst samples were scanned from 1.5° to 10° and 10–90° with a 2θ step size of 0.01.

For FTIR spectroscopy of pyridine adsorption, the measurements were performed on a Fourier transform spectrometer (Vertex 60 Bruker, Germany) in the region 4000–400 cm⁻¹, with a resolution of 4 cm⁻¹. The Raman spectra of the catalysts were obtained on a Renishaw system 2000 spectrometer (785 nm).

The 29Si NMR technique was applied to study the chemical environment of 29Si nuclei in these mesoporous aluminosilicates. The Si solid-state NMR experiments were carried out on an AVANCE III HD Bruker spectrometer operated at 99.36 MHz (1H frequency at 500.13 MHz), with a Doty CP-MAS probe of 4 mm. Both 29Si MAS and CP/MAS (cross-polarization) experiments were carried out at 6 kHz spinning speed, along with 1H decoupling. For 29Si MAS experiments, 1024–4096 scans were accumulated for different samples, with a 45° pulse and a 5 s recycle delay. For 29Si CP/MAS experiments, 2048–4096 scans were accumulated for different samples, with a 2 s recycle delay and a 5.0 ms of contact time. The 29Si chemical shifts are referenced to a 4,4-dimethyl-4-silapentane-1-sulfonic acid sodium salt at 0 ppm.

The XANES analysis was carried out to study the environment of W in TPA-supported catalysts. The X-ray absorption spectra were obtained on the IDEAS beamline at Canadian Light Source Inc., Canada. A Ge(220) double-crystal monochromator was employed to cover the energy range of tungsten L1− and L3−-edges in transmission mode and fluorescence yield using a Si drift detector. The reference compounds, such as Na2WO4, H2O and H3WO4 were measured in transmission mode for comparison and energy calibration. All XANES data were processed using the Athena program.

The total surface acidity of the synthesized supports and TPA-impregnated catalysts was determined by acid–base titration. A 100 mg of catalyst was dissolosed in 20 mL of NaOH (0.1 M). The solution was agitated at room temperature for 3 h to facilitate ion exchange. The supernatant obtained after centrifugation was titrated with 0.1 M HCl using phenolphthalein indicator. The surface acidity was indicated in terms of moles of H⁺/g of the catalyst.

4.4. Catalyst Activity. The performance of the synthesized catalysts was determined via simultaneous transesterification and esterification of green seed canola oil (FFA content—3.74 wt %). A 100 mL of the Parr reactor was used to carry out the reaction. Green seed oil of 35 g was preheated to 60 °C. A weighed amount of catalysts was introduced into the reactor vessel followed by methanol. The preliminary experiments for the catalysts were conducted at 200 °C, methanol-to-oil molar ratio of 20:1, 2.5 wt % catalyst (weight of the catalysts based on green seed canola oil), and 600 rpm.

After the reaction, the contents were filtered to separate the catalysts. For ester phase analysis, high-performance liquid chromatography was used (Agilent Technologies). A Hewlett-Packard 1100 series was employed in ester content analysis. Two Phenogel columns (5 μm, 100 Å, 300 × 7.80 mm) with a column temperature of 24 °C were used. THF at 1 mL/min for 20 min was used as the mobile phase. The detector temperature was maintained at 35 °C, whereas the sample injection consists of 20 μL. The following eq 2 determines the ester yield (wt %)

\[
\text{Ester yield (wt %)} = \frac{\text{methyl ester weight in ester phase}}{\text{ester phase weight}} \times 100
\]

The acid value (AV) of the produced biodiesel was calculated as per the AOCS-D6751 method, and eq 3 determines the conversion of FFA.

\[
\text{Conversion (\%)} = \frac{\text{AV(initial)} - \text{AV(final)}}{\text{AV(initial)}} \times 100
\]

The leaching test of the TPA-supported mesoporous aluminosilicates was performed with methanol as the solvent. Methanol is one of the reactants in transesterification and esterification reactions, and TPA is highly soluble in the polar solvent. Hence, the supported catalysts were evaluated by adding 50 mL of methanol to 0.02 g of the solid at room temperature and kept under magnetic stirring for 1 h. An aliquot was withdrawn at regular intervals using a 1 mL syringe with a 0.2 μm filter. The concentration of TPA was measured by a UV–vis spectrophotometer (UV mini 1240 Shimadzu), with the scanning range of 200–800 nm wavelength.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01931.

Low-angle XRD patterns for MAS-7 and MAS-9; curve-fitted W L3-edge XANES spectra of Na2WO4, and the fitting data for the W L3 XANES spectra using Athena software (PDF)

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**Notes**

The authors declare no competing financial interest.

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