New Task-Specific and Reusable ZIF-like Grafted H₆P₂W₁₈O₆₂ Catalyst for the Effective Esterification of Free Fatty Acids

Fatemeh Narenji-Sani, Reza Tayebee,* and Mohammad Chahkandi

ABSTRACT: The catalytic esterification of free fatty acids is an important reaction pathway for chemical synthesis and biodiesel production, wherein efficient heterogeneous catalysts are sought to replace mineral acids. Herein, the esterification of oleic acid together with some familiar fatty acids is demonstrated with methanol over a heterogeneous heteropolyacid-functionalized zeolite imidazolate framework [H₆P₂W₁₈O₆₂⁺/ZIF(H₄His.)⁷⁺]. This new heterogeneous catalyst (named as HPA/ZIF(His.) throughout the text) with an average particle size of 80 nm was prepared via condensation of histamine with zinc chloride and characterized by means of Fourier transform infrared (FT-IR), X-ray diffraction (XRD), UV−vis, energy-dispersive X-ray spectrometry, Brunauer−Emmett−Teller, thermogravimetric analysis (TGA), inductively coupled plasma - optical emission spectrometry (ICP-OES), and scanning electron microscopy. According to the performed characterizations, an HPA loading of 40.5 wt % is obtained for HPA/ZIF(His.) from ICP-OES analysis. Moreover, a typical type-IV isotherm with similar adsorption−desorption properties as seen for ZIF-8 is attained. In addition, TGA measurement confirms less stability of HPA/ZIF(His.) compared to that of pure ZIF(His.). The catalytic performance of the nanomaterial is evaluated with respect to temperature, catalyst loading, and methanol/oleic acid ratio and leads to a high yield of methyl ester (>90%) under reflux for 4 h. The preliminary kinetic studies confirm a pseudo-first-order kinetic model for the esterification of oleic acid. To explore the scope of the HPA/ZIF(His.) catalyst in methyl ester production, other free fatty acids with various chain lengths are also successfully tested. Although the nanocatalyst loses a part of its activity during reuse, however, it is stable over at least four recycles as confirmed by XRD and FT-IR. Eventually, the response surface methodology (RSM) is used as a statistical modeling approach to get the best-optimized reaction conditions compared to the performed single-variable benchmarking experiments. Therefore, the central composite design (CCD) and RSM attained a platform to determine the relationship among the reaction time, acid/methanol molar ratio, and catalyst dosage.

1. INTRODUCTION

Biofuels are important low-carbon energy feedstocks that have been considered as sustainable energy resources to replace fossil-fuel-derived counterparts.¹ Among these, biodiesel can be obtained by the transesterification and esterification of respective triglycerides and fatty acids of nonedible algal or plant oils under the catalytic action of some solid bases and acids.² Moreover, alkali-catalyzed processes for the production of biodiesel are not applicable for low-cost oils since these feedstocks should have <0.5% of free fatty acids and free of water. Besides, free fatty acids may react with alkaline catalysts and cause difficulties in the separation of biodiesel from the reaction mixture. However, energy-efficient commercial processes require high active site densities, achievable through porous support frameworks,³ and tunable acid/base strength and/or hydrophobicity.⁴

Metal–organic frameworks (MOFs) are an expandable group of ordered nanoporous materials with tunable porosity and chemical functionality.³–⁹ The tunable pore dimensions and diversity of organic linkers have opened a broad application for MOFs in gas adsorption,¹⁰ drug delivery,¹¹ molecular separation,¹² and catalysis.¹³,¹⁴ Crystalline porous zeolite imidazolate frameworks (ZIFs) are a category of MOFs comprising imidazole linkers coordinated to different transition metals such as Zn²⁺ and Co²⁺ in a tetrahedral surrounding through N atoms of the deprotonated imidazolate¹⁵–¹⁷ and exhibit excellent thermal and chemical stability in catalysis.¹⁸

Heteropolyacids (HPAs) are polyoxometalate inorganic cages that possess high Brønsted/superacidity and tunable redox activity,¹⁹,²⁰ one subset being the Wells−Dawson form with the general formula of H₂X₅M₁₈O₆₀, where M and X are the central and heteratoms, respectively. High stability and

Received: January 25, 2020
Accepted: April 15, 2020
Published: April 22, 2020

https://dx.doi.org/10.1021/acsomega.0c00358
ACS Omega 2020, 5, 9999−10010

© 2020 American Chemical Society
strong acidity observed for \( H_{6}X_{2}M_{18}O_{62} \) made these heteropolyacids effective and promise acidic catalysts for the esterification of fatty acids. However, the unsupported heteropolyacids are typically soluble in polar reaction media and, hence, unsuitable for chemical manufacturing due to the difficulty in separating them from the product stream. Several recent studies have shown that the catalytic efficiency of heteropolyacids can be improved following their dispersion over solid supports.\(^{21-23}\)

The esterification of free fatty acids such as oleic acid could be achieved with either homogeneous or heterogeneous acid catalysts. Some examples are acid-functionalized silica/ mesoporous silica, ion-exchange resins decorated with sulfonic acids, heteropolyacids, sulfated or mixed oxides, carbonaceous acidic materials, metal-involving molecular sieves, zeolites, and so on.\(^{24,25}\) Although some liquid inorganic or mineral acids have been known as good catalysts for esterification reactions, they present several drawbacks such as environmental unfriendliness, expensive separation and purification, corrosion to the equipment, nonreusability, long reaction time, or high reaction temperature.\(^{26}\) Therefore, new catalytic systems should be developed to overcome the above limitations and improve biodiesel production under a mild condition.

Herein, we explore grafting of \( H_{6}P_{2}W_{18}O_{62} \) over a new ZIF-8-like material (analogous to ZIF-8, in which a proton of imidazole is substituted with propylamine) to reach a highly stable catalyst in terms of chemical, physical, and thermal properties under the reaction conditions for the esterification of fatty acids. It is hoped that the pendant amino would facilitate ionic bonding of the primary or secondary HPA units (Figure 1), preventing leaching of the latter even in a methanol solvent, resulting in a stable heterogeneous acid catalyst for oleic acid esterification. Different reaction variables are optimized for esterification, and catalyst reutilization is further studied. The prepared catalyst is characterized before and after the reaction by various techniques.

2. RESULTS AND DISCUSSION

2.1. Characterization of ZIF(His.). The pure ZIF(His.) was synthesized under solvothermal conditions by mixing of \( \text{ZnCl}_2 \) and histamine dihydrochloride in methanol at room temperature for 48 h. Figure 2 shows the X-ray diffraction (XRD) pattern of the as-synthesized ZIF(His.), which was in good agreement with that observed for ZIF-8; the latter was prepared from an aqueous Zn salt and 2-methylimidazole organic linker.\(^{27}\) ZIF(His.) crystallites with mean diameters of 50 nm were the principle phases observed with sharp reflections at \( \sim 7.3, 10.1, 12.9, 17.5, \) and \( 19.2^\circ \) attributed to \( (011), (002), (112),(222), \) and \( (123) \) planes of ZIF-8 (JCPDS, 89-3739), respectively.\(^{28}\) It indicates that both samples would have the same structure. Figure 2d displays the XRD pattern of HPA/ZIF(His.). Strong diffractions at the...
$2\theta$ of 6.7, 9.8, 12.8, 17.2, and 18.1 confirmed the preservation of the ZIF(His.) structure after the immobilization of HPA. Some minor shifts may be due to the interaction of the heteropolyacid with the surface amine groups and presumably little deformation of the crystal structure. Observation of no specific diffractions for HPA confirmed high dispersion of the acid onto the surface of the ZIF nanostructure. The Debye–Scherrer equation was applied to estimate the crystallite size of HPA/ZIF(His.) based on the width of the powder diffraction peak (eq 1).

$$D = \frac{K \times \lambda}{\beta \times \cos \theta}$$

where $D$ is the particle size in nanometers, $K$ is shape factor and usually is 0.9, $\lambda$ is the wavelength of the radiation (1.54056 Å for Cu Kα radiation), $\theta$ is the peak position, and $\beta$ is the peak width at the half-maximum intensity. With these data and replacing the different $\theta$'s in eq 1, the average particle size of 80 nm was attained.

The UV–vis spectrum of the as-synthesized ZIF(His.) showed an intense absorption band at 387 nm (Figure 3), in accordance with that observed for ZIF-8 due to the characteristic absorption band of Zn$^{2+}$. The as-synthesized ZIF(His.) was white and absorbed across the whole UV–vis spectrum.

Scanning electron microscopy (SEM) images of the as-synthesized “ZIF(His.)” and HPA/ZIF(His.) (Figure 4a,b) showed inhomogeneous distributions of crystallites and particles spanning 50 nm to 1 μm, some of which had a plateletlike morphology. Compositional analysis by energy-dispersive X-ray spectrometry (EDX) indicated the presence of Zn and N for HPA/ZIF(His.) (Figure 4c) with the Zn/N atomic ratio of 0.395 consistent with the proposed structure in Figure 1 and the Zn/W ratio of 0.05 consistent with the HPA loading of 40.5 wt % from ICP.

The surface area and pore distribution of the as-synthesized HPA/ZIF(His.) were analyzed using nitrogen adsorption–desorption isotherms at 77 K (Figure 5). The corresponding isotherm showed an abrupt increase at relatively low pressure ($P/P_0 < 0.1$), indicating its microporous structure. It seems that HPA/ZIF(His.) obeys a typical type-IV isotherm with a hysteresis loop in the range of $P/P_0 = 0.7–0.9$, confirming the presence of mesopores. Moreover, the observation of high adsorption capacity at high relative pressure ($P/P_0 > 0.8$) suggested the coexistence of mesopores and macropores. These findings showed that HPA/ZIF(His.) may include all of the three types of micro-, meso-, and macroporous textures. This may be due to some structural changes originated from the propylamine branch. The pore size distribution of HPA/ZIF(His.) was calculated by the BJH method in the range of $P/P_0 = 0.7–0.9$.
1–100 nm (Figure 5B). This study indicated a nearly wide distributed pore structure.

The textural properties of “ZIF(His.)” and HPA/ZIF(His.) (fresh and recycled) including the Brunauer–Emmett–Teller (BET) surface area, total pore volume, and micropore volume are summarized in Table 1. Compared to that of “ZIF(His.)”, the HPA/ZIF(His.) nanocatalyst showed a decrease in BET surface area and micropore volume due to blocking of the cavity windows upon sequential grafting of HPA, indicating the presence of guest components on the surface of the “ZIF(His.)” framework. Moreover, an additional decrease in the BET surface area and total pore volume was also observed for the reused catalyst after 4 cycles. This was likely due to the agglomeration of the nanoparticles, which leads to the blockage of some pores. To ascertain similarities in adsorption–desorption behaviors of ZIF(His.) and ZIF-8, the textural properties of ZIF-8 and H₃PW₁₂O₄₀/ZIF-8 are now included in Table 1. Clearly, it can be envisaged that both ZIF(His.) and ZIF-8 show a similar trend in the examined textural properties.

Fourier transform infrared (FT-IR) spectra of histamine, ZIF(His.), and HPA/ZIF(His.) evidenced bands at 3133 and 2927 cm⁻¹ associated with C–H stretches of the imidazole ring and alkyl group, respectively (Figure 6). The peak at 1581 cm⁻¹ is ascribed to a C–N stretch within the imidazole ring. Bands in the spectral regions of 500–1350 and 1350–1500 cm⁻¹ are assigned to additional imidazole ring bends and stretches, respectively, while bands at 1140, 1637, and 3422 cm⁻¹ are attributed to P–O, W–O, and O–H stretches from the heteropolyacid, respectively.

To study the stability of ZIF(His.) and HPA/ZIF(His.) in this system, new data on TGA analysis is now added (Figure 7). TGA measurements confirmed less stability of HPA/ZIF(His.) compared to that of pure ZIF(His.). The TG curve of HPA/ZIF(His.) shows four weight-loss steps at 87.27, 171.93, 360.21, and 419.49 °C. The first two weight losses of ~25% are attributed to the release of guest H₂O and solvent.
molecules. On further heating, a weight loss of ∼34% between 360 and 419 °C may be ascribed to the decomposition of the organic linker and partial destruction of the heteropolyacid, which can lead to the eventual framework decomposition and formation of the corresponding simple oxides. This study showed that around 66% of the starting HPA/ZIF(His.) weight is remained up to 600 °C. Furthermore, the thermogravimetric analysis conducted in air indicated that HPA/ZIF(His.) particles have slightly lower stability than that of ZIF(His.) crystals. For ZIF(His.), a sharp weight loss step was observed at ca. 375 °C, corresponding to the decomposition of organic species, whereas the corresponding weight loss was started at ∼360 °C for HPA/ZIF. Therefore, a small decrease in the thermal stability of HPA/ZIF(His.) occurred after the incorporation of HPA.

2.2. Esterification of Oleic Acid. Fatty acids can be divided into saturated and unsaturated long-chain carboxylic acids, which are naturally found in animal fats and vegetable oils. Oleic acid is an unsaturated long-chain acid, and almost a high concentration of this acid is detected in various vegetable oils such as pecan, sunflower, grape seed, macadamia, peanut, sea buckthorn, sesame, and canola oils as shown in Figure 8.

2.3. Experimental Esterification Tests (Single-Variable Experiments for the Esterification Reactions). To optimize the esterification process, several variables such as reaction duration (1–24 h), catalyst dosage (0–50 mg), reaction temperature (25 °C reflux), and methanol/acid molar ratio (30:1–120:1) were investigated. Conversion increased with enhancing the methanol/acid ratio up to 60:1 (Figure 9), falling at a higher molar ratio can be attributed to competitive adsorption and coordination of both alcohol and organic acid at adjacent Brønsted acid sites. Hence, high alcohol concentrations would block the catalyst sites and inhibit acid adsorption.

After optimizing the MeOH/oleic acid molar ratio at 60:1, the effect of reaction temperature was explored to minimize methanol losses and optimize activity (Figure 10). As shown, the reaction temperature had a profound influence on the esterification reaction. It was found that conversion was improved from 0% at 25 °C to 86% under reflux conditions. In general, the esterification rate should be improved by temperature due to the shift of the reaction equilibrium.

The effect of reaction time was subsequently examined for oleic acid esterification with methanol. As observed, there was a monotonic steep increase in conversion with increasing the reaction duration. Therefore, the oleic acid conversion and the corresponding methyl ester yield were increased to ∼80 and 70%, respectively, over the first 3 h of reaction; beyond which a slower rise was observed until a plateau was reached at approximately 96% after 24 h (Figure 11). However, a further increase of the reaction time beyond 24 h did not enhance the conversion because of the equilibrium. Therefore, it could be concluded that the favorable reaction duration is 4 h.

The effect of catalyst dosage was monitored in the esterification reaction. First, no reaction was observed without the HPA/ZIF(His.) catalyst. As depicted in Figure 12, the acid...
conversion was monotonously increased along with the increment in catalyst amount until a maximum conversion of 86% was achieved at a catalyst loading of 50 mg (3.3 wt %). This phenomenon was due to the increased acidic sites involved in the catalytic reaction, thereby increasing the esterification efficiency. This observation indicated that the reactions were free from mass transport limitations. However, the esterification efficacy was slightly declined as the catalyst amount exceeded 80 mg. The excessive catalyst can enhance the viscosity of the reaction mixture, hindering the effective mass transfer of the catalyst and reagents, which consequently led to a diminished conversion. Based on these results, the optimal catalyst loading was 50 mg for the esterification reaction.

The HPA/ZIF(His.) catalyst performance for oleic acid esterification with methanol was benchmarked against a range of solid acids under identical reaction conditions (Figure 13). The unsupported H$_3$PW$_{12}$O$_{40}$, H$_5$PW$_{10}$V$_2$O$_{40}$, and H$_6$P$_2$W$_{18}$O$_{62}$ exhibited modest conversion and ester yields and the latter showed the best activity merely because of the higher accessible acid sites. In addition, the parent ZIF(His.) exhibited no catalytic activity. Moreover, UIO(66)-HPA behaved much better than SBA-HPA. Interestingly, HPA/ZIF-8 showed low catalytic activity, which may be due to the lower amount of loaded HPA on this material compared to that of ZIF(His.).

### 2.4. Effect of the Interactive Parameters

The major effects and two-factor interactions were calculated based on the response, and the “normal probability” curve (Figure 14) was drawn to find the factors that significantly affect the methyl ester production. Table 2 lists the results for experimental and predicted yields according to the introduced coded levels for each parameter. Experimental yields are attained in the laboratory, whereas the predicted data are obtained through the used software. Figure 14A, called the operational parameter deviation, shows the effect of independent variables on the esterification yield. Figure 14B shows the model’s capability in process optimization and presents the normal probability plot for the quadratic model. The plot of the residuals illustrated a normal distribution supporting the adequacy of the least-squares fit because most of the points follow a straight line.
Table 2. Experimental Design and Results of the CCD

| Run | Reaction time (h) | MeOH/OA molar ratio | Catalyst amount (mg) | Biodiesel yield (%) |
|-----|-------------------|----------------------|---------------------|---------------------|
| 1   | 3.00              | 60.00                | 0.07                | 91                  |
| 2   | 3.00              | 60.00                | 0.01                | 70                  |
| 3   | 4.50              | 85.00                | 0.03                | 75                  |
| 4   | 1.50              | 35.00                | 0.10                | 18                  |
| 5   | 4.50              | 35.00                | 0.10                | 21                  |
| 6   | 3.00              | 102.04               | 0.07                | 68                  |
| 7   | 3.00              | 60.00                | 0.07                | 88                  |
| 8   | 3.00              | 60.00                | 0.07                | 93                  |
| 9   | 1.50              | 85.00                | 0.10                | 28                  |
| 10  | 3.00              | 60.00                | 0.07                | 90                  |
| 11  | 4.50              | 85.00                | 0.10                | 56                  |
| 12  | 1.50              | 85.00                | 0.03                | 39                  |
| 13  | 4.50              | 35.00                | 0.03                | 63                  |
| 14  | 3.00              | 17.96                | 0.07                | 51                  |
| 15  | 0.48              | 60.00                | 0.07                | 33                  |
| 16  | 3.00              | 60.00                | 0.07                | 90                  |
| 17  | 5.52              | 60.00                | 0.07                | 98                  |
| 18  | 1.50              | 35.00                | 0.03                | 48                  |
| 19  | 3.00              | 60.00                | 0.07                | 89                  |
| 20  | 3.00              | 60.00                | 0.12                | 36                  |

Therefore, it is a suitable model to predict the most affecting parameters for the esterification efficiency. Moreover, it can be used to find the optimum conditions for the desired esterification process. Additionally, interactions between the variables can be clearly seen from the perturbation plot in Figure 14, which came up by default from Design-Expert software and perturbation theory using mathematical methods to find the optimized condition to solve the problem.45

To calculate regressions, Design-Expert software was used to obtain all models of its polynomial. The best model of the tables and analysis of variance (ANOVA) were selected, and a software-default quadratic model was proposed (Table 3). As the F-value is greater and the p-value is smaller, values of the relevant model were more accurate and only factors with a 95% level of confidence (p-value equal to 5% or less) were kept in the model. Thus, the best relationship between response and factors can be obtained and would be used for data analysis. A three-level factorial design was used to achieve all possible combinations of input variable that are able to optimize the response within the region of 3-D space. According to the analysis of variance (ANOVA), the quadratic model was found to be significant at p-value less than 0.05. Some values were not significant; hence, model reduction was done using the response surface methodology (RSM). The values are presented in Table 3. Fisher’s statistical analysis proved the adequacy of the developed model. However, based on the reported p-value for the lack-of-fit test (0.0002), it was concluded that the proposed model did not fit the response (Table 3).

Figure 15 confirms the pairwise interactions between the selected parameters. The interaction between the temperature and amount of catalyst was obvious. However, according to the performed experiments, the effect of temperature is crucial. It means that besides the value of other reaction parameters a least minimum temperature is needed to start the esterification reaction. Moreover, a concomitant increase in temperature can benefit methyl ester production. According to the performed RSM study based on the central composite design (CCD) and the corresponding statistical modeling approach, the optimum conditions were attained as 3.3 wt % of catalyst, 4 h reaction time, and acid/methanol molar ratio of 1:60 under reflux conditions.45

2.5. Hot Filtration Test. To prove that the catalytic activity was originated from HPA/ZIF(His.) and not from the leached HPA in the reaction solution, a hot filtration test was carried out. In this experiment, the esterification of oleic acid with methanol was performed under the optimum conditions for 2 h in the presence of HPA/ZIF(His.), affording 36% methyl ester yield. Thereafter, the heterogeneous catalyst was filtered and the reaction was continued with the filtrate for an extended time of 22 h. However, only a little increase in the product yield (8%) was achieved and the maximum final yield of 42% was achieved in the whole. To compare the catalytic activity of HPA/ZIF(His.) with HPA/ZIF-8, the latter was synthesized with the same amount of loaded HPA (~40 wt %), as confirmed by ICP. As is expected, the loading of HPA onto ZIF-8 occurs mainly via physical adsorption since there is no

Table 3. Analysis of Variance (ANOVA), Regression Coefficient Estimate, and Test of Significance for the Esterification Reaction

| Source          | Sum of squares | df | Mean square | F value | p-value prob. > F |
|-----------------|----------------|----|-------------|---------|-----------------|
| Model           | 12 573.28      | 9  | 1397.03     | 14.89   | 0.0001 significant |
| A - time        | 2680.12        | 1  | 2680.12     | 28.56   | 0.0003          |
| B - ratio       | 429.54         | 1  | 429.54      | 4.58    | 0.0581          |
| C - catal       | 1855.37        | 1  | 1855.37     | 19.77   | 0.0012          |
| AB              | 264.50         | 1  | 264.50      | 2.82    | 0.1241          |
| AC              | 50.00          | 1  | 50.00       | 0.53    | 0.4822          |
| BC              | 220.50         | 1  | 220.50      | 2.35    | 0.1563          |
| A²              | 1961.82        | 1  | 1961.82     | 20.90   | 0.0010          |
| B²              | 2740.04        | 1  | 2740.04     | 29.20   | 0.0003          |
| C²              | 3729.49        | 1  | 3729.49     | 39.74   | <0.0001         |
| Residual        | 938.47         | 10 | 93.85       | 62.27   | 0.0002 significant |
| Lack of fit     | 923.64         | 5  | 184.73      |         |                 |
| Pure error      | 14.83          | 5  | 2.97        |         |                 |
| Cor total       | 13 511.75      | 19 |             |         |                 |

https://dx.doi.org/10.1021/acsomega.0c00358
ACS Omega 2020, 5, 9999–10010
Lewis base site on the supporting material to warrant the grafting of HPA. Therefore, HPA/ZIF-8 was very susceptible to methanol as a strong polar solvent. Even, in this case, a significant increase in the yield of the produced ester (~24%) was achieved in the hot filtration test under similar reaction conditions selected for HPA/ZIF(His.). This amount correlates well with the obtained result for pure H$_6$P$_2$W$_{18}$O$_{62}$ in Figure 13. This finding clearly confirmed that nearly all of the physically adsorbed HPA on ZIF-8 (~20 mg with respect to 50 mg of HPA/ZIF-8) was leached from the surface of ZIF-8. This clear difference between ZIF-8 and ZIF(His.) in the grafting of HPA is the distinct novelty of this work. Thus, it is believed that the incorporation of the pendant amino group can provide a strong electrostatic interaction with HPA and ZIF(His.) and inhibits easy leaching of the heteropolyacid. These results affirmed the heterogeneous nature of the HPA/ZIF(His.) catalyst and no significant leaching of HPA during the course of the esterification reaction. FT-IR spectra and XRD patterns of the recycled catalyst were compared to those of the fresh one. In agreement with the results of recyclability, no obvious spectral change was detected for the recycled catalyst.

2.6. Studying Stability and Reusability of HPA/ZIF(His.). The stability and reusability of HPA/ZIF(His.) were assessed for oleic acid esterification with methanol over four consecutive reactions, with the spent catalyst washed with methanol and air-dried between each reaction. The oleic acid conversion and ester yield decreased from ~92% in the first run to ~73% after the fourth run, indicative of modest deactivation (Figure 16). Comparison of the FT-IR spectra and XRD patterns of the recycled HPA/ZIF(His.) after four consecutive reactions with those of the as-prepared catalysts evidenced good catalyst stability (Figures 16 and 17). UV–vis spectra of the fresh catalyst in methanol compared to those of the filtrate following the removal of the catalyst refluxed in methanol for 2 h demonstrated that only ~3% of the initial HPA was leached from HPA/ZIF(His.). The recovery rate of the catalyst in all reuse experiments was >90%.

2.7. Preliminary Kinetic Study. Furthermore, the reaction kinetics of oleic acid esterification were conducted at 40, 60, and 70 °C with 0.05 g of HPA/ZIF(His.) at the methanol/oleic acid molar ratio of 60:1 for 2 h. The noncatalyzed reaction rate was insignificant relative to that of the catalyzed system. The methyl ester yield at the above temperatures was plotted versus time, 0–120 min. The obtained data showed that ester yield increased with increasing the reaction time, and finally, a pseudo-first-order kinetic model was attained. This finding was in accordance with the previous reports using similar catalytic systems.

2.8. Catalytic Performance of HPA/ZIF(His.) for the Esterification of Other Free Fatty Acids. To explore the scope of the HPA/ZIF(His.) catalyst in the methyl ester production, further studies on the esterification of some free fatty acids with methanol were outlined (Figure 18). High conversions were achieved for lauric acid (98%), myristic acid (96%), stearic acid (91%), and palmitic acid (78%) under the optimum reaction conditions. Based on the results, the HPA/ZIF(His.) catalyst can effectively convert common free fatty acids with various chain lengths into the corresponding methyl esters.
2.9. Catalytic Activity of Different Catalysts in the Esterification of Oleic Acid. Catalytic performance of HPA/ZIF(His.) was compared to that of other reported catalytic systems in the esterification of oleic acid, as shown in Table 4. HPA/ZIF(His.) exhibited relatively high catalytic activity and almost the best efficacy among the titled catalysts, which have more or fewer drawbacks like relatively low conversion, high temperature, and relatively long reaction time in comparison with our catalyst that could be a promising catalyst for the industrial purposes.

3. CONCLUSIONS

Carboxylic acid esterification with methanol was investigated over HPA/ZIF(His.) as a solid acid composite catalyst comprising H₆P₂W₁₈O₆₂ supported over a ZIF-8-like structure bearing histamine instead of imidazole. This new heterogeneous catalyst with an average particle size of 80 nm was prepared via the condensation of histamine with zinc chloride and characterized by means of FT-IR, XRD, UV−vis, EDX, BET, TGA, inductively coupled plasma - optical emission spectrometry (ICP-OES), and SEM. According to the performed characterizations, an HPA loading of 40.5 wt % was obtained for HPA/ZIF(His.) from ICP-OES analysis. Moreover, the textural properties of this catalyst confirmed a typical type-IV isotherm with similar adsorption−desorption behaviors as seen for ZIF-8. In addition, TGA measurements confirmed less stability of HPA/ZIF(His.) compared to that of pure ZIF(His.). This study showed that around 66% of the starting HPA/ZIF(His.) weight is remained up to 600 °C. The attained optimum reaction conditions for oleic acid esterification over the HPA/ZIF(His.) catalyst were an alcohol/acid molar ratio of 60:1, using 50 mg of solid acid, under reflux and afforded the maximum conversion of 92% after 4 h. To explore the scope of the HPA/ZIF(His.) catalyst in the methyl ester production, other free fatty acids with various chain lengths were also successfully tested. The HPA/ZIF(His.) framework exhibited acceptable catalytic activity, good stability, and good reusability for at least 4 cycles. Moreover, a pseudo-first-order kinetic model was attained for the esterification of oleic acid. In addition, statistical RSM modeling is used to get the best-optimized reaction conditions compared to the performed experimental benchmarking. To prove that the catalytic activity was originated from HPA/ZIF(His.) and not from the leached HPA in the reaction solution, a hot filtration test was carried out. A series of experiments with HPA/ZIF(His.) and HPA/ZIF-8 showed that the loading of HPA onto ZIF-8 occurs mainly via physical adsorption, whereas the pendant amino group in HPA/ZIF(His.) can provide a strong electrostatic interaction to graft HPA on the surface of ZIF(His.) and

![Figure 17. FT-IR spectra of (a) as-prepared HPA/ZIF(His.) and (b) after 4 times reuse. (c) XRD pattern for the reused HPA/ZIF(His.).](image)

![Figure 18. Catalytic performance of HPA/ZIF(His.) for the esterification of some free fatty acids under the standard reaction conditions.](image)

Table 4. Comparing Efficacy of HPA/ZIF(His.) with Some Catalysts in the Esterification of Oleic Acid

| Catalyst (wt %) | temp. (°C) | acid/MeOH (molar ratio) | time (h) | conv. (%) | TON (h⁻¹) | ref |
|----------------|------------|------------------------|----------|-----------|-----------|-----|
| WO₃/USY (10)   | 200        | 1:6                    | 2        | 74        | 3.75      | 47  |
| HPW@ML-100 (5) | 111        | 1:11                   | 1        | 40        | 8         | 48  |
| CsSO₄⁺/ZrO₂ (5) | 150        | 1:1                    | 1        | 50        | 10        | 49  |
| Cu-SA (250 mg) | 70         | 1:10                   | 1        | 50        | 3         | 50  |
| sulphated Zr-KIT-6 (4) | 120 | 1:20                   | 3        | 85        | 7.08      | 51  |
| HCISO₄⁻/ZrO₂ (3) | 100        | 1:8                    | 12       | 99        | 2.75      | 52  |
| MFH4 (8)       | 160        | 1:60                   | 1        | 79        | 9.8       | 53  |
| HPA/ZIF(His.) (3.3) | 80        | 1:60                   | 1        | 25        | 7.5       | this work |

*Turn over number (TON) is calculated as [amount of product (g)/1 g of catalyst] per time.*
inhibits easy leaching of the heteropolyacid, as confirmed by FT-IR and XRD. Eventually, such a composite heterogeneous catalyst can offer a new opportunity for fatty efficient esterification and associated biodiesel production.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. All chemicals were analytical-grade and applied as received without further refinement. Anhydrous zinc chloride (98%), methanol, oleic acid (99%), potassium hydroxide (99%), phenolphthalein (97%), and histamine dihydrochloride (99%) were obtained from Merck and Fluka. Scanning electron microscopy (SEM) was performed on a VEGA TESCAN scanning electron microscope using samples dispersed in ethanol by ultrasonication and the resulting solution was dropped onto a carbon film supported on a copper grid. Selected areas were subjected to microanalysis using an Oxford Instrument EDX spectrometer. Fourier transform infrared (FT-IR) spectra were obtained on a 8700 Shimadzu Fourier transform spectrophotometer on diluted samples (10 wt %) pressed into KBr pellets. UV−visible spectra were recorded using a Photonon UV−visible array spectrophotometer. Elemental analyses were performed using a Thermo Finnigan Flash-1112 EA micro analyzer. X-ray diffraction patterns (XRD) were acquired on a Unisanits XMD300 diffractometer with Cu Ka radiation at 30 mA and 40 keV and a scanning rate of 3° min−1 in the 2θ domain from 5 to 80°. The chemical composition of the prepared material was determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES; model VARIAN VISTA-PRO). For this purpose, the samples were digested in 1 mL of HNO3 70% at 70 °C overnight. For the in situ synthesis of HPA/ZIF(His.), as the maximum absorbance at 259 nm was due to HPA, this figure clearly demonstrates the grafting of the heteropolyacid onto the surface of ZIF(His.) and that most of HPA had been adsorbed after 4 h.

4.2. Synthesis of ZIF(His.). Room-temperature synthesis of the new ZIF was attempted by mixing zinc chloride (anhydrous; 0.06 g; 0.05 mmol) with histamine dihydrochloride (0.21 g; 1.1 mmol) in warm methanol (50 °C, 13 mL). The reaction mixture was held for 24 h without disturbing the interface, and the resulting fine white powder was isolated and then washed with deionized water and air-dried at 70 °C. This material appears to possess a similar structure to ZIF-8 and for the purposes of this work is termed ZIF(His.), although additional characterizations such as single-crystal analysis is required to definitively prove that it is a new metal−organic framework material.

4.3. In Situ Synthesis of HPA/ZIF(His.). H₄P₂W₁₈O₆₂ was prepared according to a general standard method Na₃W₁₂O₴·2H₂O (100 g) was added to 350 mL of water, and the mixture was heated to boiling. Then, 150 mL of 85% H₃PO₄ was added and the resulting yellow-green solution was refluxed for 13 h. Then, the solution was cooled, and the product was precipitated by the addition of 100 g of solid KCl. Finally, the collected light green precipitate was redissolved in a minimum amount of hot water and allowed to be crystalized at 5 °C overnight. For the in situ synthesis of HPA/ZIF(His.), a solid mixture of H₄P₂W₁₈O₆₂ (0.04 g, 9 mmol), histamine (0.21 g, 1 mmol), and ZnCl₂ (0.13 g, 1 mmol) were dissolved in 13 mL of methanol. The solution was kept at RT for 24 h. After removing the mother liquor, methanol (5 mL) was added to wash the powder. Finally, white-green powders were collected, dried, and named as HPA/ZIF(His.). The HPA loading in this composite was calculated from the amount of W determined by ICP-OES (40.5 wt %). This amount results in an acid site loading of 9.26 × 10⁻⁵ mol/g. Figure 19 shows UV−vis spectral changes of the mother liquor during in situ impregnation of ZIF(His.) with H₄P₂W₁₈O₆₂.

![Figure 19](https://dx.doi.org/10.1021/acsomega.0c00358)

The crude ester, which was composed of the filtrate produced after filtering the reaction mixture and washing the spent catalyst, was transferred to a 10 mL tube and dried at 100 °C overnight to evaporate methanol. Then, the oil samples were placed in screw-capped glass vials for acid value analysis. From the acid value, the acid conversion was determined by eq 3. It should be mentioned that the produced ester is insoluble in methanol and can be easily separated from the bilayered reaction mixture and no further purification is needed.

\[
\text{conversion (\%)} = 1 - \frac{\text{AV}_{\text{final}}}{\text{AV}_{\text{initial}}} \times 100
\]

(3)
where $AV_{\text{final}}$ is the measure of the postraction acid value and $AV_{\text{initial}}$ is that of the initial reaction mixture. The methyl ester yield was determined from eq 4.

$$\text{yield (\%)} = \left( \frac{\text{mol of methyl ester}}{\text{mol of acid}} \right) \times 100$$

All experiments were repeated twice, and the listed yields were the average of two runs with a standard deviation of 0.01–6.80%.

4.4.1. Statistical Modeling Approach Using Response Surface Methodology. The Design-Expert version 10 software (Stat-Ease, Inc., Minneapolis) was used to optimize the esterification of oleic acid. Central composite design (CCD) was achieved to study the four-level factors, which required 30 experimental combinations. The levels were selected according to the retrieved results from a preliminary study. The analysis of variance (ANOVA) and regression analysis were performed, and the effects of independent factors on the esterification reactions were computed using statistical tools (Table 5).

### Table 5. Coded and Uncoded Levels of Design

| factors | reaction time (h) | MEOH/OA molar ratio | catalyst amount (mg) | temperature (°C) |
|---------|-------------------|----------------------|----------------------|------------------|
| uncoded levels | 2.5 & 4 & 6 | 30:1 & 60:1 & 90:1 | 30 & 50 & 80 | 45 & 78 & 110 |
| coded levels | −1 & 0 & +1 | −1 & 0 & +1 | −1 & 0 & +1 |

## AUTHOR INFORMATION

### Corresponding Author

Reza Tayebee — Department of Chemistry, Hakim Sabzevari University, Sabzevar 96179-76487, Iran; orcid.org/0000-0003-2907-1091; Phone: +98-571-44013212; Email: Rtayebee@hsu.ac.ir; Fax: +98-571-44410300

### Authors

Fatemeh Narenji-Sani — Department of Chemistry, Hakim Sabzevari University, Sabzevar 96179-76487, Iran; orcid.org/0000-0002-1766-9945

Mohammad Chahkandi — Department of Chemistry, Hakim Sabzevari University, Sabzevar 96179-76487, Iran

Complete contact information is available at https://pubs.acs.org/10.1021/acsomega.0c00358

## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work has been supported by the Iran National Science Foundation (INSF) and Hakim Sabzevari University. Special thanks to Prof A. F. Lee for his valuable comments and editing the primary drafts of this work.

## REFERENCES

1. Knothe, G. Biodiesel and renewable diesel: A comparison. Prog. Energy Combust. Sci. 2010, 36, 364–373.

2. Lee, A. F.; Bennett, J. A.; Manayil, J.; Wilson, C. K. Heterogeneous catalysis for sustainable biodiesel production via esterification and transesterification. Chem. Soc. Rev. 2014, 43, 7887–7916.

3. Woodford, J. J.; Dacquin, J. P.; Wilson, K.; Lee, A. F. Better by design: nanoengineered macroporous hydrotalcites for enhanced catalytic biodiesel production. Energy Environ. Sci. 2012, 5, 6145–6150.

4. Sánchez-Vázquez, R.; Pérez, C.; Iglesias, J.; Wilson, K.; Lee, A. F.; Melero, J. A. Zr-containing hybrid organic–inorganic mesoporous materials: Hydrophobic acid catalysts for biodiesel production. ChemCatChem 2013, 5, 994–1001.

5. Zhou, H. C.; Long, J. R.; Yaghi, O. M. Introduction to metal–organic frameworks. Chem. Rev. 2012, 112, 673–674.

6. Wang, Z.; Cohen, S. M. Postsynthetic covalent modification of a neutral metal-organic framework. J. Am. Chem. Soc. 2007, 129, 12368–12369.

7. Natarajan, S.; Mandal, S. Open-framework structures of transition-metal compounds. Angew. Chem., Int. Ed. 2008, 47, 4798–4828.

8. Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. Design and synthesis of an exceptionally stable and highly porous metal-organic framework. Nature 1999, 402, 276–279.

9. Yaghi, O. M.; O’Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular synthesis and the design of new materials. Nature 2003, 423, 705–714.

10. Morris, R. E.; Wheatley, P. S. Gas storage in nanoporous materials. Angew. Chem., Int. Ed. 2008, 47, 4966–4981.

11. Kahn, O. Chemistry and physics of supramolecular magnetic materials. Acc. Chem. Res. 2000, 33, 647–657.

12. Chen, B.; Liang, C.; Yang, J.; Contreras, D. S.; Clancy, Y. L.; Lobkovsky, E. B.; Yaghi, O. M.; Dai, S. A. Microporous metal-organic framework for gas-chromatographic separation of alkanes. Angew. Chem., Int. Ed. 2006, 45, 1390–1393.

13. Gascon, J.; Aktay, U.; Hernandez-Alonso, M. D.; van Klink, G. P. M.; Kapteijn, F. Amino-based metal-organic frameworks as stable, highly active basic catalysts. J. Catal. 2009, 261, 75–87.

14. Llabrés i Xamena, F. X.; Cirujano, F. G.; Corma, A. An unexpected bifunctional acid base catalysis in IRMOF-3 for Knoevenagel condensation reactions. Microporous Mesoporous Mater. 2012, 157, 112–117.

15. Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O’Keeffe, M.; Yaghi, O. M. Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks. Acc. Chem. Res. 2010, 43, 58–67.

16. Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, B. H.; O’Keeffe, M.; Yaghi, O. M. High-throughput synthesis of zeolitic imidazolate frameworks and application to CO2 capture. Science 2008, 319, 939–943.

17. Miralda, C. M.; Macias, E. E.; Zhu, M.; Ratnasamy, P.; Carreon, M. A. Zeolitic imidazole framework-8 catalysts in the conversion of CO2 to chloropropene carbonate. ACS Catal. 2012, 2, 180–183.

18. Morris, W.; Doonan, C. J.; Furukawa, H.; Banerjee, R.; Yaghi, O. M. Crystals as molecules: postsynthesis covalent functionalization of zeolitic imidazolate frameworks. J. Am. Chem. Soc. 2008, 130, 12626–12627.

19. Kozehevnikov, I. V. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. Chem. Rev. 1998, 98, 171–198.

20. Kirisci, L.; et al. Heteropolyacid-based heterogeneous photocatalysts for environmental application. Appl. Catal., A 2003, 256, 1–32.

21. Alsalme, A.; Alsharif, A. A.; Al-Enizi, H.; Khan, M.; Alshammary, S. G.; Alotaibi, M. A.; Khan, R. A.; Rafiq, M.; Siddiqui, H. Probing the catalytic efficiency of supported heteropoly acids for esterification: Effect of weak catalyst support interactions. J. Chem. 2018, 47, 10.

22. Shah, A. K.; Park, S.; Khan, H. A.; Bhatti, U. H.; Kumar, P.; Bhutto, A. W.; Park, Y. H. Citronellal cyclisation over heteropoly acid
supported on modified montmorillonite catalyst: effects of acidity and pore structure on catalytic activity. Res. Chem. Intermed. 2018, 44, 121.
(23) Frattini, L.; Isaacs, M. A.; Parlett, C. M. A.; Wilson, K.; Kyriakou, G.; Lee, A. F. Support enhanced α-pinene isomerization over HPIW/SBA-15. Appl. Catal. B: Environ. 2017, 200, 10–18.
(24) Pan, Y.; Alam, M. A.; Wang, Z. M.; Mu, W. J.; Zhang, Y.; Yuan, Z. H. Enhanced esterification of oleic acid and methanol by deep eutectic solvent assisted Amberlyst heterogeneous catalyst. Bioresour. Technol. 2016, 220, 543–548.
(25) Pan, Y.; Alam, M. A.; Wang, Z. M.; Mu, W. J.; Zhang, Y.; Yuan, Z. H. Enhanced esterification of oleic acid and methanol by deep eutectic solvent assisted Amberlyst heterogeneous catalyst. Bioresour. Technol. 2016, 220, 543–548.

(26) Li, T. T.; Li, Z. L.; Li, W.; Shi, C. J.; Wang, Y. Preparation and characterization of biomass carbon-based solid acid catalyst for the esterification of oleic acid with methanol. Bioresour. Technol. 2013, 133, 618–621.
(27) Zhang, H.; Li, H.; Pan, H.; Wang, A. P.; Souzanchi, S.; Xu, C. B.; Yang, S. Facile synthesis of polyoxometalates tethered to post Fe-BTC frameworks for esterification of free fatty acids to biodiesel. Appl. Energy 2018, 223, 416–429.
(28) Meng, X.; Yang, J.; Xu, X.; Zhang, L.; Nie, Q.; Xian, M. Biodiesel production from oleaginous microorganisms. Renewable Energy 2009, 34, 1–5.
(29) Li, Q.; Jiang, S.; Ji, S.; Ammar, M.; Zhang, Q.; Yan, J. Synthesis of magnetically recyclable ZIF-8@SiO2@Fe3O4 catalysts and their catalytic performance for Knoevenagel reaction. J. Solid State Chem. 2015, 235, 65–72.
(30) Zavadi, F.; Tayeeb, R. Preparation and characterization of ZnO/nano-clinoptilolite as a new nanocatalyst and studying its catalytic performance in the synthesis of 2-aminothiophenol via Gewald reaction. Microporous Mesoporous Mater. 2016, 231, 100–109.
(31) Kanaparthy, R.; Kanaparthy, A. The changing face of dentistry: nanotechnology. Int. J. Nanomed. 2011, 6, 2799.
(32) Youn, M. H.; Kim, H.; Jung, J. C.; Song, I. K.; Barateau, K. P.; Barateau, M. A. UV-vis spectroscopy studies of H2PMo12O40-xWO4-x heteropolyacid (HPA) catalysts in the solid state: Effects of water content and polyatom substitution. J. Mol. Catal. A: 2005, 247, 227.
(33) Schejn, A.; Aboulach, A.; Balan, L.; Falk, V.; Lalevée, J.; Medjahdi, G.; Schneider, R. Cu4+-doped zeolitic imidazolate frameworks (ZIF-8): efficient and stable catalysts for cycloadditions and condensation reactions. Catal. Sci. Technol. 2015, 1829–1839.
(34) Liu, S.; Li, C.; Yu, J.; Xiang, Q. Improved visible-light photocatalytic activity of porous carbon self-doped ZnO nanosheet-assembled flowers. CrystEngComm 2011, 13, 2533–2541.
(35) Yu, J.; Li, Q.; Liu, S.; Jaroniec, M. Ionic-liquid-assisted synthesis of uniform fluorinated B/C-codoped TiO2 nanocrystals and their enhanced visible-light photocatalytic activity. Chem. Eur. J. 2013, 19, 2433–2441.
(36) He, M.; Yao, J.; Liu, Q.; Wang, K.; Chen, F.; et al. Facile synthesis of zeolitic imidazolate framework-8 from a concentrated aqueous solution. Microporous Mesoporous Mater. 2014, 184, 55–60.
(37) Elrashidi, S.; Balbreche, Y.; Pessan, L. A. Ultem/ZIF-8 mixed matrix membranes for gas separation: transport and physical properties. Mater. Res. 2016, 19, 1.
(38) Zhong, H. X.; Wang, J.; Zhang, Y. W.; Xu, W. L.; Xing, W.; Xu, D.; Zhang, Y. F.; Zhang, X. B. ZIF-8 derived graphene-based nitrogen-doped porous carbon sheets as highly efficient and durable oxygen reduction electrocatalysts. Angew. Chem., Int. Ed. 2014, 53, 14235–14239.
(39) Wang, S.; Fan, Y.; Jia, X. Sodium dodecyl sulfate-assisted synthesis of hierarchically porous ZIF-8 particles for removing mercaptan from gasoline. Chem. Eng. J. 2014, 256, 14–22.
(40) Khan, N. A.; Biswa, N. B.; Sung, H. J. Heteropoly acid-loaded ionic liquid@ metal-organic frameworks: Effective and reusable adsorbents for the desulfurization of a liquid model fuel. Chemical Engineering Journal 2018, 334, 2215–2221.
(41) Rößler, C.; Esken, D.; Wittor, C.; Kobayashi, H.; Yamamoto, T.; Matsumura, S.; Fischer, R. A. Encapsulation of Biomimetic Nanoparticles into a Metal–Organic Framework: Preparation and Microstructure Characterization of Pd/Au@ZIF-8. J. Inorg. Chem. 2014, 5514–5521.
(42) Hu, X.; Zhou, Z.; Sun, D.; Wang, Y.; Zhang, Z. Esterification of fatty acids by zincic catalysts. Catal. Lett. 2009, 133, 90–96.
(43) Manique, M. C.; Silva, A. P.; Alves, A. K.; Bergmann, C. P. Application of hydrothermally produced TiO2 nanotubes in photo-catalytic esterification of oleic acid. Mater. Sci. Eng., B 2016, 206, 17.
(44) Essamalhi, Y.; Larzék, M.; Essaid, B.; Zahouily, M. Natural phosphate supported titania as a novel solid acid catalyst for oleic acid esterification. Ind. Eng. Chem. Res. 2017, 5821–5832.
(45) Chowdhury, S.; et al. Process optimization of silver nanoparticle synthesis using response surface methodology. Procedia Eng. 2016, 148, 992–999.
(46) Zhang, H.; Li, H.; Pan, H.; Liu, X.; Yang, K.; Huang, S.; Yang, S. Efficient production of biodiesel with promising fuel properties from Koelreuteria integrifoliola oil using a magnetically recyclable acidic ionic liquid. Energy Convers. Manage. 2017, 138, 45–53.
(47) Costa, A. A.; Braga, P. R. S.; Macedo, J. L.; de Dias, J. A.; Dias, S. C. L. Structural effects of WO3 incorporation on USY zeolite and application to free fatty acids esterification. Microporous Mesoporous Mater. 2012, 147, 142–148.
(48) Wang, H.; Chen, C.; Wu, Z.; Que, Y.; Feng, Y.; Wang, W.; Wang, L.; Guan, G.; Liu, X. Encapsulation of heteropolyanion-based ionic liquid within the metal-organic framework MIL-100 (Fe) for biodiesel production. ChemCatChem 2015, 7, 441–449.
(49) Greeca, M. L.; Dimian, A. C.; Tanase, S.; Subbiah, V.; Rothenberg, G. Sulfated zirconia as a robust superacid catalyst for multicomponent fatty acid esterification. Catal. Sci. Technol. 2012, 2, 1500–1506.
(50) Zhang, Q.; Wei, F.; Zhang, Y.; Wei, F.; Ma, P.; Zheng, W.; Zhao, Y.; Chen, H. 2017. Biodiesel production by catalytic esterification of oleic acid over copper (II)-alinate complexes. J. Oleo Sci. 2017, 66, 491–497.
(51) Gopinath, S.; Kumar, P. S. M.; Arafath, K. Y.; Thiruvengadavarl, K. V.; Sivanesan, S.; Baskaralingam, P. Efficient mesoporous SO3−/Zr-KIT-6 solid acid catalyst for green diesel production from esterification of oleic acid. Fuel 2017, 203, 488–500.
(52) Zhang, Y.; Wing-Tak, W.; Ka-Fu, Y. Biodiesel production via esterification of oleic acid catalyzed by chlorosulfonic acid modified zirconia. Appl. Energy 2014, 116, 191–198.
(53) do Nascimento, L. A. S.; et al. Comparative study between catalysts for esterification prepared from kaolins. Appl. Clay Sci. 2011, 51, 267–273.
(54) Tayeeb, R.; Nehzat, F.; Rezaei-Seresht, E.; Mohammad, P.; Rafiee, Z. E. An efficient and green synthetic protocol for the preparation of bis (indolyl) methanes catalyzed by H2P(W6O24)2−4H2O, with emphasis on the catalytic proficiency of Wells-Dawson versus Keggin heteropolyacids. J. Mol. Catal. A: Chem. 2011, 351, 154–164.
(55) International Organization for Standardization. ISO 660 Article.