Solvent-Free Hydrodeoxygenation of Triglycerides to Diesel-like Hydrocarbons over Pt-Decorated MoO2 Catalysts

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ABSTRACT: In the present work, the solvent-free hydrodeoxygenation of palm oil as a representative triglyceride model compound to diesel-like hydrocarbons was evaluated in a batch reactor using Pt-decorated MoO2 catalysts. The catalysts with various Pt loadings (0.5−3%) were synthesized by an incipient wetness impregnation method. The metallic Pt and MoO2 phases were detected in the XRD patterns of as-prepared catalysts after the reaction and acted as active components for the deoxygenation reactions. The XPS experiments confirmed the existence of metallic Pt and PtOx species. The XANES investigation of Mo L3-edge spectra elucidated a change in the valence state by the transformation of MoO3 into MoO2 species after the deoxygenation reaction. The TEM observation revealed the formation of Pt nanoparticles in the range of 1−3 nm decorated on MoO2 species. The number of acid sites increased with stronger metal−support interactions on increasing the Pt loading. The catalytic performance of the MoO2 catalyst significantly improved with a small amount of Pt decoration. However, the further increase in Pt loading did not relatively increase the deoxygenation activity due to the formation of the agglomerated Pt particles. The high performance of the decorated catalysts could be attributed to the moderate acidity from the Pt dispersed on MoO2 toward decarbonylation and decarboxylation reactions.

1. INTRODUCTION

Currently, the utilization of bioresources from agricultural feedstocks for alternative biofuel production has been recognized as an effective process due to the depletion of fossil fuel and global environmental problems. Compared with the various types of bioresources such as lignocellulosic biomass and carbohydrates, vegetable oils, fatty acids, and animal fats have been generally used as starting materials for biofuel production due to their low functionalization degree and simple chemical structure compared with lignocellulosic materials.1,2 Diesel-like hydrocarbons produced via hydrodeoxygenation of triglycerides and fatty acids from agricultural oil feedstock have been recommended as a sustainable replacement for diesel-based petroleum because their fuel properties are comparable to those of the fossil diesel.3−6 Generally, the deoxygenation of oil feedstock containing triglycerides and/or fatty acids in the presence of hydrogen and suitable catalysts could produce diesel-like n-alkanes under moderate conditions (temperature 300−400 °C and H2 pressure 20−50 bar).7−12 Hydrodeoxygenation (HDO), decarboxylation (DeCO), and decarbonylation (DeCO2) are the three major reaction pathways occurring in the deoxygenation process.13,14 HDO leads to the elimination of oxygen by generating water and produces n-alkanes with a carbon number similar to that of the fatty acid component in the oil feed. DeCO and DeCO2 pathways result in the oxygen removal by producing the carbon monoxide and water or carbon dioxide, respectively, with the n-alkanes shorter by one carbon atom compared with the original fatty acid.

Various transition metal and metal sulfide catalysts have been utilized for the hydrodeoxygenation of triglycerides, fatty acids, and other oxygenated biomass compounds, especially in liquid-phase reactions under a hydrogen atmosphere such as NiMoS2,15−17 CoMoS2,16,18 Ni1,17,19−23 Co1,7,24 Pd19,25−27 and Pt1,27−29 supported on various materials such as Al2O3, TiO2, SiO2, zeolites, and carbon. In the case of transition metal sulfide catalysts, the sulfiding of the oil feedstock is required to retard the catalyst deactivation.24,30 In particular, sulfur leaching due to the small amount of water generated from HDO and DeCO reactions leads to a shortened catalyst lifetime and sulfur contamination in the liquid product.31
Among the other catalysts, sulfur-free monometallic catalysts such as Ni- and Co-based catalysts exhibited high activity toward DeCO₂ and DeCO reactions compared with the NiMo and CoMo sulfides supported on Al₂O₃ catalysts. However, the formation of a large amount of coke during deoxygenation was the major reason for catalyst deactivation. In addition, precious-metal-based catalysts such as Pt and Pd have been extensively investigated for hydrodeoxygenation with and without a solvent due to their high activity under mild conditions. In fact, the Pt- and Pd-based catalysts are favorable for DeCO and DeCO₂ routes with a lower hydrogen consumption than for the HDO route. Thus, the utilization of these kinds of catalysts under solvent-free conditions and limited hydrogen supply in a batch reactor is crucial for further investigation. Recently, transition metal oxides such as MoO₃-x have been reported as active components for oxygen removal from small oxygenated compounds, mainly palmitic acid and oleic acid via HDO under a moderate hydrogen pressure. The oxygen vacancies on the MoO₃-x surface occurred by the reaction between hydrogen and the generated water via HDO, and DeCO has been reported as the active site for breaking the C–O bond. In particular, molybdenum dioxide, MoO₂, has been confirmed to be an active component for the C–O and C=O breakings for palmitic acid hydrodeoxygenation. Nevertheless, the deoxygenation of triglycerides using molybdenum oxides under solvent-free conditions was limited because of the complexity of the reaction pathway via the hydrogenation and hydrogenolysis reactions to produce fatty acids and, subsequently, n-alkane production through HDO, DeCO, and DeCO₂ reactions. To the best of our knowledge, the investigation of the effect of Pt-decorated molybdenum oxide in the form of MoO₂ on the solvent-free hydrodeoxygenation of triglycerides has never been reported in the literature.

Therefore, we investigated the solvent-free hydrodeoxygenation of triglycerides to diesel-like hydrocarbons over the Pt-decorated MoO₃ catalysts in a batch reactor. Extensive characterizations of catalysts using N₂ sorption, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure (XANES), NH₃ temperature-programmed desorption (NH₃-TPD), H₂ temperature-programmed reduction (H₂-TPR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were carried out to comprehend the correlation between the structural and textural properties and deoxygenation activities of the synthesized catalysts. Their catalytic performances were systematically compared in terms of the triglyceride conversion, gasoline and diesel yields, the relative involvement of HDO (hydrodeoxygenation) and DeCO/DeCO₂ (decarbonylation and decarboxylation) activities, and n-alkane product distribution.

2. RESULTS AND DISCUSSION

2.1. Textural Properties by BET. The N₂ sorption experiments were first conducted to investigate the textural properties of the calcined samples. The N₂ adsorption and desorption isotherms of all of the samples are exhibited in Figure 1a. According to the IUPAC classification, it can be found that both the bare MoO₃ and Pt-decorated MoO₃ samples exhibited a type II isotherm with H3-type hysteresis loops. The pore size distribution calculated from the adsorption branches of the isotherms using the BJH model reveals the presence of uniform mesopores and an average pore diameter for all of the samples except for the 3%Pt-decorated MoO₃ catalyst (Figure 1b).

Table 1 summarizes the specific surface area, average pore diameter, and pore volume of the calcined samples. The BET surface area and pore volume of the bare MoO₃ were 3.63 m² g⁻¹ and 0.0039 cm³ g⁻¹, respectively. A small increase in the surface area from 3.91 to 4.57 m² g⁻¹ with a larger pore volume in the range of 0.0043–0.0065 cm³ g⁻¹ was observed on increasing the Pt loading from 0.5 to 2%. The pore diameter was in the range of 43–57 nm for the Pt loading in the range of 0.5–2%. Interestingly, an increase in the Pt loading of up to 3% led to a significant increase in the BET surface area of up to 22.46 m² g⁻¹ accompanied by the highest pore volume of 0.1217 cm³ g⁻¹. This may be due to the formation of small pores with an average pore diameter of 21.7 nm, resulting in the enlargement of the catalyst surface area.

2.2. Phase Identification by XRD. The XRD patterns of all of the fresh catalysts are exhibited in Figure 2. The XRD analyses confirmed the formation of the α-MoO₃ phase (JCPDS No. 05-0508) after the calcination of ammonium heptamolybdate in the air at 500 °C for 5 h. The decoration of Pt species into as-synthesized MoO₃ samples resulted in the existence of the diffraction peak of metallic Pt at 2θ = 39.8° to the (111) plane of the face-centered cubic structure (PDF#04-0802). The disappearance of the diffraction peak at 2θ =
46.2° corresponding to the (200) plane of Pt was due to the overlap with the diffraction peak of MoO$_3$. As demonstrated in Figure 2, the diffraction peak intensity of Pt seemed to be increased with Pt loadings, implying the larger catalyst particle formation.

The catalysts after the reaction tests were subsequently characterized by XRD to identify the active components for the hydrodeoxygenation reaction (Figure 3). Interestingly, the diffraction peaks at 2θ = 26.3, 37.2, 54.4, 60.2, and 67.5° assigned to the planes (011), (020), (022), (031), and (−231) of the MoO$_2$ phase, respectively (JCPDS: 65-1273), were observed for all of the spent catalysts. It should be deduced that MoO$_3$ was completely in situ reduced to MoO$_2$ during the reaction. This was similar to the previous study where the MoO$_3$ was transformed into the MoO$_2$ phase at 400°C under the high pressure of H$_2$.$^{41}$ Furthermore, the diffraction peak of metallic Pt at 2θ = 39.8° (111) still presented after the reaction and metallic Pt acted as an active site in hydrodeoxygenation reactions. In the case of the 0.5%Pt/MoO$_3$ sample, the diffraction peak of metallic Pt could not be detected due to the low amount of Pt loading. Similar to the fresh catalysts, the diffraction peak of Pt (111) observed in decorated samples became shaper, indicating the growth of metal particles with increasing Pt loading.

2.3. Pt Surface Investigation by XPS. The XPS analysis was conducted to confirm the form of Pt species before and after the reaction. The XPS survey spectra of the fresh and spent 1%Pt/MoO$_3$ samples show characteristic peaks of O, C, Pt, and Mo elements (see Figure S1a,b). The presence of carbon could be ascribed to the sample preparation from the carbon tape or coke deposition of the spent sample. As displayed in Figure 4, the XPS profiles of Pt 4f spectra of the fresh and spent samples exhibited the characteristic peaks of Pt 4f as two distinguished peaks of Pt 4f$_{7/2}$ and Pt 4f$_{5/2}$ doublets for both samples, indicating that the Pt species predominately existed on the MoO$_2$ species. The peaks were deconvoluted into two oxidation states of metallic Pt$^0$ and oxidized Pt$^{2+}$. In the case of fresh 1%Pt/MoO$_3$, two peaks occurred at 71.3 and 73.4 eV for Pt$^0$ and those of Pt$^{2+}$ appeared at 72.7 and 76.2 eV. The 4f peaks of Pt$^0$ for the spent 1%Pt/MoO$_3$ appeared at 70.2 and 73.5 eV and those of Pt$^{2+}$ occurred at 71.4 and 74.7 eV. The shift observed in 4f peak positions of Pt in the presence of the spent 1%Pt/MoO$_3$ to lower binding energies was due to a change in the electronic structure of metal oxide to metallic species during the deoxygenation. A shift in electron transitions to lower binding energies was reported for the supported Pt−WO$_3$,$^{42}$ and Pt−MoO$_3$,$^{35}$ catalysts. As summarized in Table 2, the presence of a high amount of the Pt$^0$ state was observed for the spent 1%Pt/MoO$_3$, confirming that the
Table 2. Peak Assignment, Binding Energy, and Relative Area of Deconvoluted Peaks from Pt 4f Spectra of the Fresh and Spent 1%Pt/MoO₃ Catalysts

| catalyst         | peak  | binding energy (eV) | relative area (%) |
|------------------|-------|---------------------|-------------------|
| fresh 1%Pt/MoO₃  | Pt⁰   | 71.3/73.4           | 64.4              |
|                  | Pt⁺   | 72.7/76.2           | 35.6              |
| spent 1%Pt/MoO₃  | Pt⁰   | 70.2/73.5           | 85.9              |
|                  | Pt⁺   | 71.4/74.7           | 14.1              |

2.4. Mo Oxidation State by XANES. To further investigate the oxidation state of Mo in MoO₃ and 1%Pt/MoO₃ samples before and after the deoxygenation experiments, the X-ray absorption near-edge structure (XANES) analysis was conducted. Figure 5 exhibits the normalized and first-derivative Mo L₃-edge XANES spectra of all of the Mo standards and the MoO₃ and 1%Pt/MoO₃ catalysts before and after the deoxygenation reaction. The edge position, white line, and spectral features were used to identify the form of samples compared with the Mo foil, bulk MoO₂, and bulk MoO₃ standards. As demonstrated in Figure 5, the edge and shape of the spectra of the as-prepared MoO₃ and 1%Pt/MoO₃ samples by the decomposition of ammonium heptamolybdate at 500 °C have almost the same characteristic features as the bulk MoO₃ standards, indicating the complete transformation of ammonium heptamolybdate into the bulk MoO₃ sample. This observation is in agreement with the XRD analysis of all of the fresh samples. In contrast, it was found that the adsorption edges of the MoO₃ and 1%Pt/MoO₃ catalysts after the deoxygenation reaction shifted to lower energy. As demonstrated in the first-derivative spectra in Figure 5, the transformation of MoO₃ to MoO₂ forms was clearly detected by the spectral features and edge position. These results implied that a change in the valence state occurred during the deoxygenation process and the MoO₂ form acted as an active component for the reaction.

2.5. Support and Metal Interaction by H₂-TPR. The H₂ temperature-programmed reduction (H₂-TPR) experiments were conducted to investigate interactions of the Pt and Mo species using calcined samples (Figure 6). The H₂-TPR profile of MoO₃ exhibited two major reduction peaks in the wide temperature range of ca. 630−900 °C, indicating the reduction behavior of pure MoO₃ to metallic Mo. The sharp peak at ca. 780 °C is due to the reduction of MoO₃ to MoO₂ and the broad peak at a higher temperature of ca. 855 °C is assigned to the reduction of MoO₂ to metallic Mo, which was consistent with the previous study. The H₂-TPR profiles of all of the Pt-decorated MoO₃ catalysts showed a reduction peak at around 260 °C, confirming the characteristic reduction of surface PtOₓ, which was detected by the XPS analysis. A H₂ consumption at ca. 500 °C for all of the decorated samples might correspond to the H₂ spillover from the Pt species to MoO₃ resulting in the partial reduction to MoO₃−ₓ. This suggested that the Pt loading had strong metal−support interactions. In addition, the reduction peak of MoO₃ to metallic Mo at high temperatures in the wide range of ca. 700−900 °C was quite different from that of bare MoO₃, suggesting that the Pt species changed the reduction behavior of MoO₃ species. Although the reduction peaks of MoO₃ to MoO₂ occurred at temperatures higher than 700 °C, the MoO₂ phase was reduced in the presence of H₂ at the same temperature range of ca. 630−900 °C, indicating the reduction of MoO₂ to MoO₁−ₓ. The lower H₂ consumption for the 2 and 3%Pt-supported MoO₃ samples was expected to be due to the lower metal dispersion and agglomeration of the higher PtOₓ contents. This observation was in agreement with a former investigation.

2.6. Acidity by NH₃-TPD. The acidity of the bare MoO₃ and Pt-decorated MoO₃ catalysts was examined using NH₃ temperature-programmed desorption (NH₃-TPD). The catalysts were first in situ reduced in the presence of H₂ at the same reaction temperature to change the surface PtOₓ to metallic Pt before NH₃-TPD implementation. As exhibited in Figure 7, it was found that the NH₃ desorbed in the wide temperature range of 70−250 °C for the bare MoO₃ and 0.5−2%Pt-decorated MoO₃ catalysts and at 100−275 °C for the 3%Pt-decorated MoO₃ catalyst. These characteristic desorption peaks were ascribable to NH₃ desorption on acidic sites of the pre-reduced catalysts. The peak intensity of ammonia desorption for 0.5−3%Pt-decorated MoO₃ catalysts was much lower than that of the bare MoO₃ sample.
higher than that for bare MoO₃. This NH₃ desorption behavior implied that the number of acidic sites on the catalyst surface relatively increased by the decoration of Pt species into the MoO₃ species. In addition, the desorption peak of ammonia for the 3%Pt-decorated MoO₃ catalyst shifted to higher temperatures, indicating that the ammonia strongly adsorbed on the catalyst surface, implying stronger acidic sites generated for the higher Pt loading. Based on the literature, it was reported that the high hydrodeoxygenation activity was due to the synergetic effect between acidic and metallic sites. It was evident that the calculated number of acidic sites significantly increased with Pt loading and the calculated values using the ammonia standard are summarized in Table 1.

2.7. Morphology by SEM. SEM observations were performed to further study on the morphology of the as-prepared catalysts. The SEM images of the fresh and spent MoO₃ and 1 and 3%Pt/MoO₃ catalysts are represented in Figure 8. It can be seen that MoO₃ consists of the angular-shaped particles with different particle sizes, similar to the previous study. The microstructures of the fresh catalysts did not change by the addition of Pt species into the MoO₃ species. On the other hand, the irregularities of angular-shaped particles were detected, in particular, the observation of micropores for the Pt-decorated MoO₂ catalysts (see Figure S2b,c) after the hydrodeoxygenation experiments. It has been reported that H₂-reduced MoO₃ catalysts were accompanied by an increased specific surface area, which was the highest when MoO₃ was reduced to MoO₂ by reduction degrees of 60−70% at 400 °C. This may be due to the formation of a porous structure inside the large angular-shaped particles observed in this present study. Moreover, as shown in Figure S3a,b, the results of EDS measurements of the prepared Pt-decorated catalysts before and after the reaction revealed the existence of Pt species on the MoO₃ species.

2.8. Particle Size Distribution by TEM. The spent 1%Pt/MoO₃ catalyst was selected to examine the particle size distribution of Pt by TEM measurements due to the highest activity among the other catalysts (Figure 9). TEM images exhibited the spherical shape and uniform dispersion of metallic Pt decorated on MoO₂ species in the narrow range of 1−3 nm. Furthermore, the observed lattice fringes of ca. 0.0224, 0.225, and 0.234 nm correspond to the Pt(111) plane, indicating that the Pt species located on MoO₂ species have a face-centered cubic (fcc) (111) lattice spacing. This was consistent with the XRD analysis. Moreover, some agglomerated Pt particles with an average metal particle of 3.3 ± 0.6 nm were detected in the fresh 3%Pt/MoO₃ sample (see Figure S4).

2.9. Catalytic Performance of the Pt-Decorated MoO₂ Catalysts. The solvent-free hydrodeoxygenation of refined palm oil as the representative triglyceride model compound was conducted under the following conditions; a temperature of 400 °C, an initial H₂ pressure of 40 bar, and a reaction time of 3 h over the bare MoO₃ and Pt-decorated MoO₃ catalysts. The bare MoO₃ catalyst was initially investigated by varying the reaction temperatures to 370, 400, and 430 °C to find a suitable reaction temperature since the temperature significantly affected the conversion and product yields. As demonstrated in Table S2, the triglyceride conversion was 100% for all of the temperatures, indicating that the triglyceride completely transformed into oxygenated intermediates and desired products. The liquid product obtained from the deoxygenation reaction at a reaction temperature of...
370 °C became solidified under ambient conditions and mainly consisted of fatty acids and a small amount of fatty acid alcohols. This result was confirmed by GC−MS analysis. This result suggested that the hydrogenation of carbon double bonds in unsaturated triglycerides occurred, followed by the carbon−oxygen bond cleavage toward the hydrogenolysis of saturated triglycerides to generate the primary oxygenated intermediates (fatty acids and fatty acid alcohols) and propane.\textsuperscript{1,52} Subsequently, the produced fatty acids underwent hydrodeoxygenation (HDO), decarbonylation (DeCO), and decarboxylation (DeCO\textsubscript{2}) to generate \textit{n}-alkanes. The gasoline and diesel yields obtained were only 1 and 3%, respectively, at 370 °C. The increase in the reaction temperature significantly improved the deoxygenation activities. As revealed in Table S2, the total product yields increased from 4 to 22.3% with the temperature increasing from 370 to 430 °C. However, the decrease in the diesel yield from 10.1 to 8.8% on increasing the temperature from 400 to 430 °C would be associated with the promotion of cracking due to the formation of light hydrocarbons at a high reaction temperature (430 °C). Therefore, the reaction temperature of 400 °C was chosen to investigate the effect of Pt decoration on MoO\textsubscript{2} by varying the Pt loading.

Figure 10 shows the product yields and reaction rates over the bare MoO\textsubscript{2} and Pt-decorated MoO\textsubscript{2} catalysts. The solvent-free hydrodeoxygenation reaction over all of the catalysts resulted in a 100% conversion of triglycerides with different product yields (Figure 10a). Over all of the Pt-decorated catalysts, the diesel- and gasoline-range \textit{n}-alkane yields significantly increased compared with that on bare MoO\textsubscript{2}, implying that the hydrodeoxygenation reaction proceeded over Pt metallic sites accompanied by MoO\textsubscript{2} species in the presence of hydrogen. By comparing the catalytic activities with various Pt loadings, the hydrodeoxygenation activities in terms of total product yields decreased in the order of 1%Pt/MoO\textsubscript{2} (56.4%) > 2%Pt/MoO\textsubscript{2} (55.2%) > 3%Pt/MoO\textsubscript{2} (54.5%) > 0.5%Pt/MoO\textsubscript{2} (46.2%) > MoO\textsubscript{2} (18.4%). It should be noted that the increase in Pt loading from 0.5 to 1% resulted in an increase of gasoline and diesel yields probably due to the sufficient Pt loading and cooperative effects between Pt and MoO\textsubscript{2} phases. However, the further increase in the Pt loading from 2 to 3% seemed to decrease the product yields although the number of acidic sites significantly increased. This could be due to the fact that the large amount of Pt is likely to partially cover the active MoO\textsubscript{2} sites, causing the agglomeration of larger Pt particles, resulting in a reduction of the \textit{n}-alkane production rate (see Figure 10b), which was calculated based on the summation of desired products against the amount of catalyst and time.

Furthermore, the reusability of the 1%Pt/MoO\textsubscript{2} catalyst was investigated at a temperature of 400 °C, an initial H\textsubscript{2} pressure of 40 bar, and a reaction time of 3 h. The spent catalyst was rinsed with hexane to remove the oil product and dried overnight at 100 °C before the second and third hydrodeoxygenation tests. It was found that the triglyceride conversion remained constant at 100%; meanwhile, the gasoline and diesel yields dropped after the third consecutive experiment (see Figure S5a,b). The degradation of the catalyst after the first run was likely due to the formation of organic impurities on the active sites during the deoxygenation under solvent-free conditions.\textsuperscript{53} To evaluate the hydrodeoxygenation behavior using the bare MoO\textsubscript{2} and Pt-decorated MoO\textsubscript{2} catalysts, the percentage relative involvements of HDO and DeCO/DeCO\textsubscript{2} reactions are estimated and depicted in Figure 11a. As reported in the
literature, DeCO and DeCO₂ were the major reaction pathways compared with HDO over the Pt-based catalysts. It was found that the percentage relative involvement of DeCO/DeCO₂ was significantly greater than that of HDO over all of the catalysts, suggesting that DeCO and DeCO₂ were the major reaction pathways for all of the catalysts. By comparison with the percentage relative involvement of HDO, the bare MoO₃ was highly selective to HDO among the other decorated catalysts. The reducible transition metal oxides such as MoO₃ and MoO₄ species have been suggested as the catalysts for C=O and C−O bond scission in oxygenated biomass compounds toward hydrodeoxygenation. In contrast, the addition of Pt into MoO₂ resulted in a noteworthy increase in the percentage relative involvement of DeCO and DeCO₂, indicating that the active Pt sites promoted the active MoO₂ sites at higher Pt loading (Figure 11a). As summarized in Table S3, the C_{16} and C_{18} fatty acids are the major fatty acid components in the representative triglycerides used in this study. Therefore, as demonstrated in Figure 11b, the n-alkanes of n-C₁₅ and n-C₁₇ were found as the major constituents of the deoxygenated product due to the high selectivity of DeCO and DeCO₂ reactions over the Pt-decorated MoO₂ catalysts.

2.10. Deoxygenated Product Analysis by FTIR. To confirm the removal of oxygen atoms in refined palm oil, the functional groups of the liquid products were analyzed by Fourier transform infrared (FTIR) spectroscopy (see Figure 12). The peaks at 1704 cm⁻¹ in the FTIR spectrum correspond to the carboxylic functional groups of fatty acids. On the other hand, the carbonyl groups and ester groups of triglycerides were detected in the FTIR spectrum at 1746 and 1165 cm⁻¹, respectively. In the deoxygenation process, triglycerides were first hydrogenolyzed to fatty acids and further deoxygenated to n-alkane. Palmitic acid and stearic acid are major oxygenated intermediates detected by GC−MS analysis. The FTIR spectrum of refined palm oil exhibited the adsorption peaks corresponding to triglycerides. Interestingly, for the liquid product after the deoxygenation process, the peaks intensity of triglycerides and fatty acids in the FTIR spectrum significantly decreased with an increase in the Pt loading. This result confirmed that the triglyceride and fatty acids partially converted into n-alkanes under solvent-free conditions via DeCO and DeCO₂ reactions.

3. CONCLUSIONS

We have successfully prepared the Pt-decorated MoO₂ catalysts with various Pt loadings (0.5−3%) by an incipient wetness impregnation method and their catalytic activities for triglyceride hydrodeoxygenation were investigated without solvent addition in a custom-made shaking-batch-type reactor under the following operating conditions: temperature, 400 °C; initial H₂ pressure, 40 bar; and reaction time, 3 h. Using XRD, XPS, and XANES investigations, it was confirmed that the active components for hydrodeoxygenation under solvent-free conditions were in the form of metallic Pt and MoO₂ generated during the reaction. The number of acidic sites obtained from NH₃-TPD significantly increased by the addition of Pt species into the MoO₂ species. In addition, stronger metal−support integration was achieved by Pt decoration. It was found that the catalytic performance of MoO₂ for triglyceride hydrodeoxygenation was significantly improved by the decoration of a small amount of Pt with the uniform distribution on the MoO₂ phase. Moreover, a large amount of Pt species cause a slight decrease in product yields, suggesting that the excess Pt species are likely to partially cover the active MoO₂ sites and cause the agglomeration of larger Pt particles. High decarbonylation (DeCO) and decarboxylation (DeCO₂) activities, as the major pathways in the deoxygenation, were observed, attributed to the moderate acidity from the Pt dispersed on MoO₂.

4. EXPERIMENTAL SECTION

4.1. Catalyst Synthesis. Molybdenum trioxide (MoO₃) was synthesized by dissolving 10 g of ammonium heptamolybdate ([NH₄]₆Mo₇O₂₄·4H₂O, Carlo Erba, purity 99.0%) in 50 mL of deionized water. The resultant solution was heated and stirred at 110 °C until a solid powder formed. The obtained solid was combusted at 350 °C for 2 h. Finally, the obtained sample was calcined at 500 °C for 5 h in stagnant air.

The various Pt loadings (0.5−3%) decorated on as-prepared MoO₃ catalysts were prepared by an incipient wetness impregnation method using the corresponding Pt precursor as 3.4 wt % diaminodinitriplatinum(II) in dilute ammonium hydroxide (Sigma Aldrich). The samples were dried at 110 °C after impregnation overnight and subsequently calcined at 500 °C for 5 h in stagnant air.

4.2. Catalyst Characterizations. The specific surface area, total pore volume, and average pore diameter of the as-synthesized samples before the reaction were determined by a nitrogen adsorption and desorption technique at −196 °C (BEL Japan, Bel Sorp mini II). The samples were degassed, and the moisture content was removed at 150 °C for 12 h before N₂ sorption implementation.

The phase identification of as-synthesized samples before and after the deoxygenation tests was confirmed by X-ray diffraction (XRD) performed on an X-ray diffractometer (D8 ADVANCE, Bruker, Ltd., Germany) using Cu Kα radiation over the range of 10° < 2θ < 80°.

The form of Pt decorated on MoO₂ was quantitatively analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis ULTRA DLD (Kratos) spectrometer equipped with an Al Kα radiation source. The C 1s feature at 284.8 eV was used to calibrate the binding energy of Pt 4f.

The X-ray absorption near-edge structure (XANES) was used to further investigate the Mo oxidation state. XANES

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spectra at the Mo L3-edge (2500–2550 eV) were acquired in the transmission mode at Beamline 8 of the Synchrotron Light Research Institute (SLRI), Thailand, using InSb(111) double-crystal monochromators for scanning the photon energy. Normalization of the XANES spectra was performed using the ATHENA program.58

The H2 temperature-programmed reduction (H2-TPR) was performed to investigate support–metal interactions using BELCAT-B Instruments, Japan, using approximately 100 mg of calcined samples. To remove the moisture content, the samples were first heated to 190 °C for 30 min under an inert gas before H2-TPR implementation. The reduction behavior was analyzed by the temperature-programmed method using a 5 vol % H2/Ar at a heating rate of 10 °C min⁻¹ in the temperature range of 100–1000 °C. The H2 consumption was recorded using a thermal conductivity detector (TCD).

The acidity of the synthesized catalysts was determined by NH3 temperature-programmed desorption (NH3-TPD) technique using the same instrument as for H2-TPR. The samples were initially pre-reduced at 400 °C for 2 h in 5 vol % H2/Ar to transform the surface PtO into Pt phases. NH3 adsorption was subsequently conducted for 2 h after cooling the samples to 50 °C in an inert gas, followed by the excess NH3 removal under the supply of He for 1 h. The temperature-programmed desorption was carried out in the range of 50–400 °C at a heating rate of 10 °C min⁻¹ under the supply of He. The peak intensity from a thermal conductivity detector (TCD) was used to calculate the number of acidic sites from the amount of NH3 desorption compared with the NH3 standard.

The morphologies of the catalysts before and after the reaction were examined by field-emission scanning electron microscopy (FE-SEM) on a JEOL, JSM-7600F, instrument equipped with an energy-dispersive X-ray spectrometer (EDS; X-Max® 50, Oxford Instruments).

The particle size distribution and morphology of the Pt-decorated catalyst after the reaction were observed by field-emission transmission electron microscopy (FE-TEM) at 300 kV on a JEOL, JEM-3100F, instrument. The sample preparation was performed by dispersing the catalyst powder in ethanol for 20 min under ultrasonic conditions and subsequently dropping the solution on a carbon-coated Cu grid at least three times.

4.3. Catalytic Deoxygenation Evaluation. A locally available refined palm oil with a low free-fatty-acid content was employed as a model compound for triglycerides, and their catalytic deoxygenations under solvent-free conditions were conducted in a stainless-steel shaking-batch-type reactor with an internal volume of 10 cm³. The fatty acid compositions of the feedstock were experimentally determined via the transesterification of refined palm oil with methanol over a sodium phosphate (NaP04) catalyst corresponding to the fatty acid methyl ester (FAME) composition. The fatty acid compositions are listed in Table S3. In the deoxygenation activity evaluation, 2 g of refined palm oil with 20 wt % as-synthesized catalysts without the pre-reduction process was loaded into the stainless-steel reactor. Subsequently, the air inside the reactors was removed to prevent explosion and oil combustion by H2 purging three times, and they were pressurized to an initial H2 pressure of 40 bar. The sealed reactors were immediately placed into an electric furnace at an operating temperature of 400 °C for 3 h with a shaking speed of 150 rpm to minimize the effect of mass transfer resistance. After the deoxygenation test, the reactor was suddenly stopped by subjecting the reaction to initial conditions by quenching in an ice-cool bath. The experiments were conducted in duplicate and the average values are presented.

4.4. Analysis of the Deoxygenated Liquid Product. The deoxygenated liquid products were filtrated to remove the catalyst and were subsequently analyzed by a gas chromatography (GC) system equipped and a flame ionization detector (FID) (Clarus 580, Perkin Elmer) with a capillary column (DB-1HT, 30 m × 0.32 mm × 0.1 μm). The quantities of n-alkanes ranging from n-C8 to n-C18 and unreacted triglycerides (TGs) in the liquid product were calculated using the calibration curves of n-alkane and triglyceride standards. The GC conditions were similar to those of a previous study.1,7,11 The triglyceride conversion, gasoline yield, and diesel yield were defined by the following equations:

\[
\text{conversion} (\%) = \frac{\text{weight percent of TG in feed} - \text{weight percent of TG in product}}{\text{weight percent of TG in feed}} \times 100
\]

\[
\text{gasoline yield} (\%) = \frac{\text{total weight percent of n-C8 to n-C12 in product} \times 100}{\text{total weight percent of C16 and C18 fatty acids in feed}}
\]

\[
\text{diesel yield} (\%) = \frac{\text{total weight percent of n-C13 to n-C17 in product} \times 100}{\text{total weight percent of C16 and C18 fatty acids in feed}}
\]

To directly evaluate the involvement of hydrodeoxygenation (HDO), decarbonylation, and decarboxylation (DeCO/DeCO2) reactions, the percent relative involvements of HDO and DeCO/DeCO2 reactions were calculated using eqs 4 and 5.

\[
\text{relative involvement of HDO (\%)} = \frac{\text{weight percent of n-C16 and n-C18 in product}}{\text{weight percent of n-C15 to n-C18 in product}} \times 100
\]

\[
\text{relative involvement of DeCO/DeCO2 (\%)} = \frac{\text{weight percent of n-C15 and n-C17 in product}}{\text{weight percent of n-C15 to n-C18 in product}} \times 100
\]

In addition, the n-alkane product distribution of each component was calculated according to a previous study62 using eq 6.

\[
\text{n-alkane product distribution (\%)} = \frac{\text{weight percent of single component n-alkane (Cn)}}{\text{total weight percent of n-C8 to n-C18 in product}} \times 100
\]

Furthermore, to confirm the deoxygenation activities under solvent-free conditions, the functional groups of the refined palm oil, n-alkane standard, and products were identified by...
Fourier transform infrared (FTIR) spectroscopy (Jasco FT/IR 6800).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00326.

XPS survey spectra of the fresh and spent Pt-decorated catalysts, calculated H₂ consumption from H₂-TPR experiments, SEM images of the spent catalysts with high magnification, EDS measurements, TEM image of fresh 3%Pt/MoO₃, effect of reaction temperature over the bare MoO₃ catalyst, reusability study of the 1%Pt/MoO₂ catalyst in the three consecutive experiments, and fatty acid composition of refined palm olein (PDF).

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**Notes**

The authors declare no competing financial interest.

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