

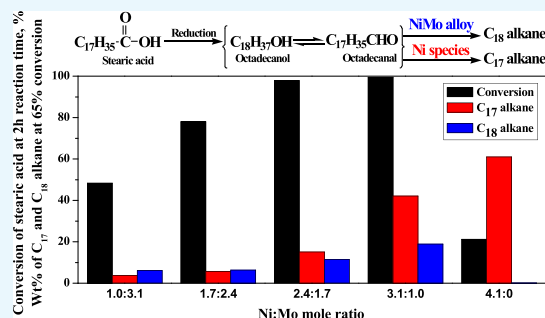
Role of NiMo Alloy and Ni Species in the Performance of NiMo/Alumina Catalysts for Hydrodeoxygenation of Stearic Acid: A Kinetic Study

Pankaj Kumar, Sunil K. Maity,*^{id} and Debaprasad Shee

Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Kandi, Sangareddy 502285, Telangana, India

Supporting Information

ABSTRACT: The hydrodeoxygenation (HDO) of vegetable oil and fatty acid is extremely important for the sustainable production of diesel-range hydrocarbons. The present work depicts the role of Ni/Mo (mole) in the performance of alumina-supported NiMo catalysts for the HDO of stearic acid. Both Ni and NiMo alloy coexist in the NiMo catalysts depending on the Ni and Mo content. With increasing Ni/Mo (mole), the NiMo alloy content in the catalyst increases with the simultaneous decrease in the Ni content. The activity of NiMo catalysts thus enhances with increasing Ni/Mo (mole). The reaction follows a decarbonylation route over Ni sites and a HDO route over NiMo alloy species. C₁₇ and C₁₈ alkanes are thus observed as the dominating hydrocarbon product over Ni and NiMo alloy-rich catalysts, respectively. The activity of the NiMo catalyst further enhances with increasing reaction temperature and metal (Ni + Mo) loading. The selectivity to alkanes was, however, not affected by metal loading. A suitable kinetic model was further established based on the reaction mechanism to relate the kinetic data.



1. INTRODUCTION

In the past few decades, considerable attention has been devoted to renewable resources to reduce dependency on finite fossil fuels. These efforts are intended to achieve energy security of the world in a sustainable manner. The renewable resources also play an important role in preserving a healthy environment. Currently, transportation fuels consume about 28% of the world's energy.¹ A significant effort has thus been made to produce transportation fuels from renewable carbon-neutral resources such as biomass. The use of biomass for biofuels will further boost the growth of agriculture-based industries and improvement in the rural economy. Several national-level policies are thus framed to promote biofuels. For example, India targeted about 20% blending of biofuels (bioethanol and biodiesel) with transportation fuels.² Following the 2nd commitment of the Kyoto protocol, the countries are now targeting 18% reduction of greenhouse gas emission between 2013 and 2020.³

Three different classes of biomass are used in the biorefinery: triglycerides, sugar and starch, and lignocellulosic. Among these, the triglyceride is simple in structure with low functionality and oxygen content and a long-chain linear hydrocarbon backbone.¹ The triglycerides are mainly composed of C₁₆ and C₁₈ fatty acids.⁴ Hence, it is an ideal feedstock for the diesel-range transportation fuel. Trans-esterification is one such well-accepted technology for the production of transportation fuels from triglycerides known as biodiesel. A significant advancement has thus been made in the production of biodiesel from triglycerides.⁵ The biodiesel has,

however, the maximum limit of 20% blending with diesel for application in unmodified combustion engines because of its unfavorable cold flow properties. Furthermore, it delivers lower fuel mileage because of the presence of oxygen in the structure.⁵ The removal of oxygen from triglycerides is thus vital in producing diesel-range hydrocarbons (green diesel) for direct use in a diesel engine. The pyrolysis and catalytic cracking are two potential processes in the production of green diesel from triglycerides.⁶ However, these processes provide a low yield of green diesel and high yield of gaseous products.

Hydrodeoxygenation (HDO) is another process for the manufacturing of green diesel from triglycerides in high yield. This process is analogous to the hydroprocessing technology used in the petroleum refinery and carried out over supported metal catalysts in the presence of hydrogen.⁷ The likelihood of the retrofitting with petroleum refinery production facilities is an added advantage of this process.⁸ The triglycerides can be converted to green diesel through two alternative approaches: direct HDO of triglycerides and HDO of fatty acids derived from triglycerides. In the latter approach, the triglycerides are generally (catalytically or noncatalytically) hydrolyzed to corresponding fatty acids.⁹ Following the latter approach, the present work is focused on the HDO of stearic acid (C₁₇-COOH) as a model fatty acid.

Received: December 21, 2018

Accepted: January 24, 2019

Published: February 7, 2019

Table 1. Physicochemical Properties of the Catalysts^a

catalyst	surface area, m ² /g		pore volume, cm ³ /g		crystallite size, nm	MD	Sm
	cal	red	Cal	red			
γ -Al ₂ O ₃	243		0.86				
4.1MoAl	57	90	0.36	0.49		0.07	0.30
1.0Ni3.1MoAl	103	86	0.56	0.57	31.3 ^c	0.05	0.36
1.7Ni2.4MoAl	109	94	0.54	0.53	39.4 ^c	0.11	0.55
2.4Ni1.7MoAl	123	118	0.56	0.55	41.3 ^c	0.22	1.45
3.1Ni1.0MoAl	146	123	0.58	0.56	44.9 ^c	0.50	3.31
4.1NiAl	169	135	0.57	0.51	44.8 ^d	1.01	6.70
1.8Ni1.2MoAl	126	122	0.52	0.54		0.30	1.8
1.2Ni0.8MoAl	132	127	0.56	0.61		0.35	1.94
0.9Ni0.6MoAl	137	131	0.54	0.57		0.36	2.01

^acal = calcined; red = reduced; MD = metal dispersion, %; Sm = metallic surface area, m²/g metal. ^bCalculated using the Debye–Scherrer equation. ^cNiMo alloy. ^dNi.

A vast number of works have been reported in the past on the HDO of numerous model fatty acids such as decanoic, dodecanoic, lauric, palmitic, stearic, oleic, and linoleic.^{4,10–18} Similar to hydrotreatment, the sulfided form of supported metal catalysts has also been employed for the HDO of vegetable oil and fatty acids.^{13,19–21} These catalysts are, however, accompanied with sulfur contamination of green diesel and deactivation because of sulfur leaching.²² The sulfur-free-supported metal catalysts have thus attracted huge attention for this process. HDO has also been studied over noble metal (Pt, Pd, Ru, etc.) catalysts.^{23–28} For example, Pd/C demonstrated high catalytic activity for the HDO of fatty acids.²⁴ These catalysts are, however, highly expensive. On the other hand, the transition metals (Ni, Co, NiMo, and CoMo) are inexpensive with high catalytic activity and stability. Hence, these catalysts have been reported extensively for this reaction by various research groups.^{4,29–34} For example, HDO of C₁₇-COOH was studied over SiO₂, γ -Al₂O₃, and HZSM-5-supported Ni catalyst.⁴ The C₁₇ alkane was reported as the main product over Ni/ γ -Al₂O₃. The HY, γ -Al₂O₃, and SiO₂-supported Ni catalysts were also reported for the HDO of C₁₇-COOH and conversion of C₁₇-COOH of 94, 43, and 46% was achieved at 90 min of reaction time, respectively.³⁵

The deoxygenation pathway depends on the nature of active sites present in the catalyst. The decarbonylation pathway is dominant over Ni catalysts. This route produces alkane with one carbon less than the fatty acid.^{4,17,35} The reaction, however, follows the HDO pathway over bimetallic catalysts (NiMo and CoMo).³⁶ The nonsulfided NiMo/ γ -Al₂O₃ showed the higher yield of green diesel from sunflower oil and waste cooking oil compared to the sulfided catalyst.³⁷ The nonsulfided CoMo/ γ -Al₂O₃ catalyst showed high catalytic activity with 100% hydrocarbon product containing 74% paraffin from sunflower oil.

The atomic composition of Ni and Mo in the supported NiMo catalyst is a governing factor to obtain the catalytically active NiMo alloy species.^{33,37–39} Wang et al. studied the effect of Ni/Mo (mole) and metal loading on structure, reducibility, and metal dispersion.⁴⁰ The detailed study on Ni/Mo (mole) is, however, scarcely available in the literature. The present work is thus focused on the preparation of alumina-supported NiMo catalysts with different Ni/Mo (mole). These catalysts were further characterized by several techniques to understand the formation of various active surface species. The HDO activity and product selectivity over these catalysts were then qualitatively correlated with the structural information. For

optimum Ni/Mo (mole), the study was then extended to different metal (Ni + Mo) loadings to obtain the optimum metal loading. The kinetics play an important role in the reactor design.^{4,25,40–42} The kinetics of HDO over monometallic catalysts were reported by various research groups in the past.^{4,24,41,43,44} The kinetic model for the HDO of fatty acids over the bimetallic catalyst is, however, scarcely available in the literature. Hence, a suitable kinetic model was developed in this work for the HDO of C₁₇-COOH over the alumina-supported NiMo catalyst.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. **2.1.1. BET Surface Area.** Table 1 shows Brunauer–Emmett–Teller (BET) surface area and pore volume of γ -Al₂O₃ and NiMo catalysts. The surface area of γ -Al₂O₃ was 243 m²/g with a pore volume of 0.86 cm³/g. Both calcined and reduced NiMo catalysts showed lesser surface area and pore volume compared to γ -Al₂O₃. The surface area of both calcined and reduced NiMo catalysts was further decreased with increasing Mo content and metal (Ni + Mo) loading. The drop in surface area with increasing Mo content and metal loading might be due to the greater coverage of the alumina surface or pore blockage by the high atomic weight Mo (and/or Ni) metal/metal oxide species. Excepting 4.1MoAl, the surface area of the reduced NiMo catalyst was, however, lower than that of the corresponding calcined catalyst. It might be due to the additional sintering of metals during reduction. In the case of 4.1MoAl, the MoO₃ clusters were formed during calcination. During reduction, these MoO₃ clusters were reduced to dispersed Mo or molybdenum oxide, resulting in a slight increase in the surface area.⁴⁰

2.1.2. Pulse Chemisorption. The metal dispersion and metallic surface area of NiMo catalysts were declined with increasing Mo content and metal (Ni + Mo) loading in the catalyst (Table 1). It might be due to the enrichment of MoO₃ clusters with increasing Mo content, leading to the formation of Al₂(MoO₄)₃. The Raman spectra further confirmed the presence of Al₂(MoO₄)₃ in the calcined NiMo catalyst (Figure 1). Giordano et al. also reported augmentation of the MoO₃ cluster with increasing MoO₃ content on alumina.⁴⁵ The decrease in metal dispersion and metallic surface area with increasing metal loading might be due to agglomeration of metals at higher metal loading.

2.1.3. Raman Spectroscopy. Figure 1 shows Raman spectra of calcined NiMo catalysts under ambient conditions. Raman

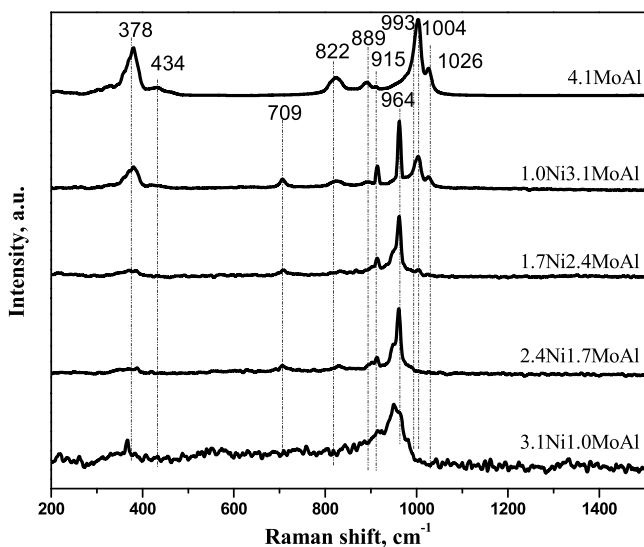


Figure 1. Raman spectra of calcined NiMo and Mo catalysts.

bands at ~ 993 , 1004 , and 1026 cm^{-1} were characteristics of Mo=O bond vibration of three MoO_4 units present in $\text{Al}_2(\text{MoO}_4)_3$. Tian et al. also observed similar bands in Raman spectra of bulk $\text{Al}_2(\text{MoO}_4)_3$ ⁴⁶ and reference therein. The Raman bands at 822 , 889 , and 915 cm^{-1} were attributed to the asymmetric stretching of three MoO_4 units present in $\text{Al}_2(\text{MoO}_4)_3$ ⁴⁶ and reference therein. These bands became intense with increasing Mo content. These results implied the enrichment of $\text{Al}_2(\text{MoO}_4)_3$ with increasing Mo content in the NiMo catalyst. The bands appeared at 434 and 378 cm^{-1} were due to asymmetric and symmetric bending modes of isolated MoO_4 units. Raman bands at 709 and 964 cm^{-1} were attributed to the NiMoO_4 species.⁴⁷ These bands were observed in all calcined NiMo catalysts. Moreover, these bands became sharp and intense with increasing Mo content in the NiMo catalyst. The strong MoO_4 bands in $1.0\text{Ni}3.1\text{MoAl}$ suggested a high concentration of $\text{Al}_2(\text{MoO}_4)_3$. Liu et al. also reported similar observation.⁴⁸ For the NiMo catalyst, the Raman bands corresponding to bridging Mo–O–Mo bonds were absent in the Raman shift region of $200\text{--}300$ and $500\text{--}800\text{ cm}^{-1}$. These results further confirmed the presence of different isolated MoO_4 units of $\text{Al}_2(\text{MoO}_4)_3$.

2.1.4. UV–Vis–NIR Spectra. Figure S2 shows UV–vis spectra of calcined NiMo catalysts. The UV–vis band appeared at 263 nm was assigned to the O^{2-} to Mo^{6+} ligand to metal charge transfer of the isolated MoO_4 units present in $\text{Al}_2(\text{MoO}_4)_3$.⁴⁶ The UV–vis absorption band at 263 nm in 4.1MoAl is relatively strong compared to that in the NiMo catalysts. This band became intense with increasing Mo content in NiMo catalysts. This result shows that the formation of $\text{Al}_2(\text{MoO}_4)_3$ was increased with increasing Mo content in the NiMo catalyst. The UV–vis band appeared at 621 nm was attributed to NiAl_2O_4 .⁴³ This band was intense in $3.1\text{Ni}1.0\text{MoAl}$. This result indicated that the formation of NiAl_2O_4 was increased with an increase in the Ni/Mo (mole).

2.1.5. Powder XRD. Figure 2A shows powder X-ray diffraction (XRD) pattern of calcined NiMo catalysts. The characteristic diffraction peaks at 2θ of 45° ($4\ 0\ 0$) and 65.5° ($4\ 4\ 0$) corresponded to the NiAl_2O_4 species [PDF#781601]. The previous studies also reported NiAl_2O_4 in the Ni/alumina catalyst.^{49,50} NiAl_2O_4 is, however, very difficult to distinguish from $\gamma\text{-Al}_2\text{O}_3$ [45.8° ($4\ 0\ 0$) and 67.3° ($2\ 2\ 0$)] because of

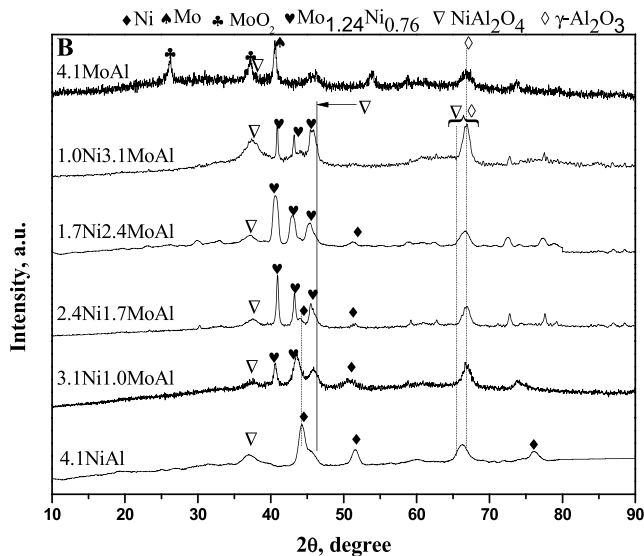
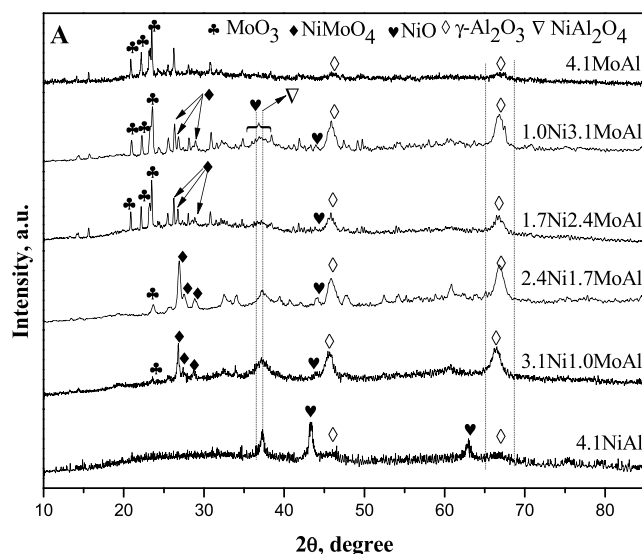


Figure 2. Powder XRD pattern of (A) calcined and (B) reduced NiMo catalysts with different Ni/Mo mole ratios.

overlapping diffraction peaks. The broad peaks at 2θ of $45^\circ\text{--}47^\circ$ and $65^\circ\text{--}67^\circ$ were thus considered as the combined diffraction peak of NiAl_2O_4 and $\gamma\text{-Al}_2\text{O}_3$. The broad peaks appeared at 2θ of $37^\circ\text{--}38^\circ$ were considered as combined diffraction peaks of NiO and NiAl_2O_4 . The calcined NiMo catalysts revealed characteristic NiO peaks at 2θ of 37.16° ($1\ 1\ 1$), 43.54° ($2\ 0\ 0$), and 62.98° ($2\ 2\ 0$) [PDF#750197].^{4,51} The intensity of NiO peaks at 2θ of 37.16° and 43.54° was increased with increasing Ni/Mo (mole) and practically disappeared in $1.7\text{Ni}2.4\text{MoAl}$ and $1.0\text{Ni}3.1\text{MoAl}$. The MoO_3 diffraction peaks appeared at 2θ of 20.81° ($1\ 1\ 1$), 23.15° ($0\ 0\ 2$), 23.30° ($0\ 2\ 0$), 23.49° ($2\ 0\ 0$), and 26.3° ($2\ 1\ 0$) [PDF#800347].^{51–53} These peaks became intense with increasing Mo content in the catalyst. The calcined NiMo catalysts additionally showed NiMoO_4 species diffraction peaks at 2θ of 24.28° ($0\ 1\ 1$), 25.46° ($1\ 1\ 0$), and 31.15° ($1\ 1\ 1$) [PDF#860362]. The NiMoO_4 species was also reported in previous studies.^{54,55} The NiMoO_4 species peaks were sharp and intense for $2.4\text{Ni}1.7\text{MoAl}$ and weak for both higher and lower Mo content in the catalyst. The intensity of the

characteristic NiO and NiMoO₄ species peaks was increased with increasing metal loading as shown in Figure S1. The characteristic NiO peak at 2θ of 43.58° (2 0 0) was absent in 0.9Ni0.6MoAl (Figure S1). It might be due to the existence of dispersed NiO below the detection limit of powder XRD or NiO was completely consumed for the formation of NiMoO₄ species.

Figure 2B shows the powder XRD pattern of reduced NiMo catalysts. The reduced 4.1NiAl showed three characteristic Ni peaks at 2θ of 44.48° (1 1 1), 51.83° (2 0 0), and 76.352° (2 2 0) [PDF#701849].^{4,51} The intensity of Ni peaks was decreased gradually with decreasing Ni/Mo (mole) and disappeared in 1.0Ni3.1MoAl. It might be due to complete consumption of Ni in the formation of NiMoO₄ or the crystallite size of Ni was below the detection limit of powder XRD. Wang et al. also reported an increase in the intensity of the NiMoO₄ diffraction peak with decreasing Ni/Mo (mole).⁴⁰ The reduced 4.1MoAl showed Mo peaks at 2θ of 40.47° (1 1 0) and molybdenum dioxide (MoO₂) at 2θ of 26.26° (1 1 1) and 37.21° (2 0 0). The reduced 3.1Ni1.0MoAl displayed diffraction peaks of the NiMo alloy (Mo_{1.24}Ni_{0.76}) at 2θ of 40.63° (4 0 1), 43.73° (3 1 3), and 45.58° (2 0 4) [PDF#471129]. These peaks were intensified with the increasing Mo content up to 1.7Ni2.4MoAl and decreased slightly with the further increase in Mo content (1.0Ni3.1MoAl). The intensity of NiMo alloy diffraction peaks was increased with increasing metal loading as shown in Figure S1. Mo and MoO₂ were, however, not observed in reduced NiMo catalysts. This result implies that the presence of Ni enhances the reducibility of MoO₂. The absence of Mo diffraction peaks might be due to complete consumption of Mo in the formation of the NiMo alloy or the quantity of Mo was below the detection limit of powder XRD. NiAl₂O₄ was observed at 2θ of 37.16°. The intensity of this peak was weak for all the catalysts. The peak associated with Ni was also observed in 1.8Ni1.2MoAl and 2.4Ni1.7MoAl (Figure S1).

2.1.6. Temperature-Programmed Reduction (TPR) Profile.

Figure 3 shows the temperature-programmed reduction (TPR) profile of calcined NiMo catalysts. 4.1NiAl exhibited three characteristic reduction peaks at T_{\max} of 657, 703, and 1014 K. The first peak at ~657 K was characteristics of the reduction of bulk NiO with a weak interaction with support. The bulk NiO reduction peak was, however, absent in all NiMo catalysts excepting 3.1Ni1.0MoAl. The bulk NiO reduction peak in 3.1Ni1.0MoAl was observed at a slightly lower temperature than the corresponding peak in 4.1NiAl. The second reduction peak at ~703 K was due to the reduction of dispersed NiO with a strong interaction with the support. The third high-temperature reduction peak at ~1014 K was attributed to the reduction of NiAl₂O₄. NiAl₂O₄ was also observed in the powder XRD pattern of the calcined Ni catalyst (Figure 2). The reducible NiAl₂O₄ was observed in the calcined NiMo catalyst with high Ni content only (3.1Ni1.0MoAl). NiAl₂O₄ was also reported by Li et al. at T_{\max} of 1064 K and Kumar et al. at T_{\max} of 950 K.^{4,56}

4.1MoAl displayed three characteristic reduction peaks at T_{\max} of 694, 796, and ~989 K. The first reduction peak was associated with the partial reduction of MoO₃ to MoO₂. The second reduction peak was due to the reduction of MoO₂ to Mo. The reduction peak at ~989 K might be due to the reduction of Al₂(MoO₄)₃.⁵⁷ The presence of Al₂(MoO₄)₃ in 4.1MoAl and NiMo catalysts with high Mo content was also confirmed by Raman spectroscopy as discussed in the previous section.

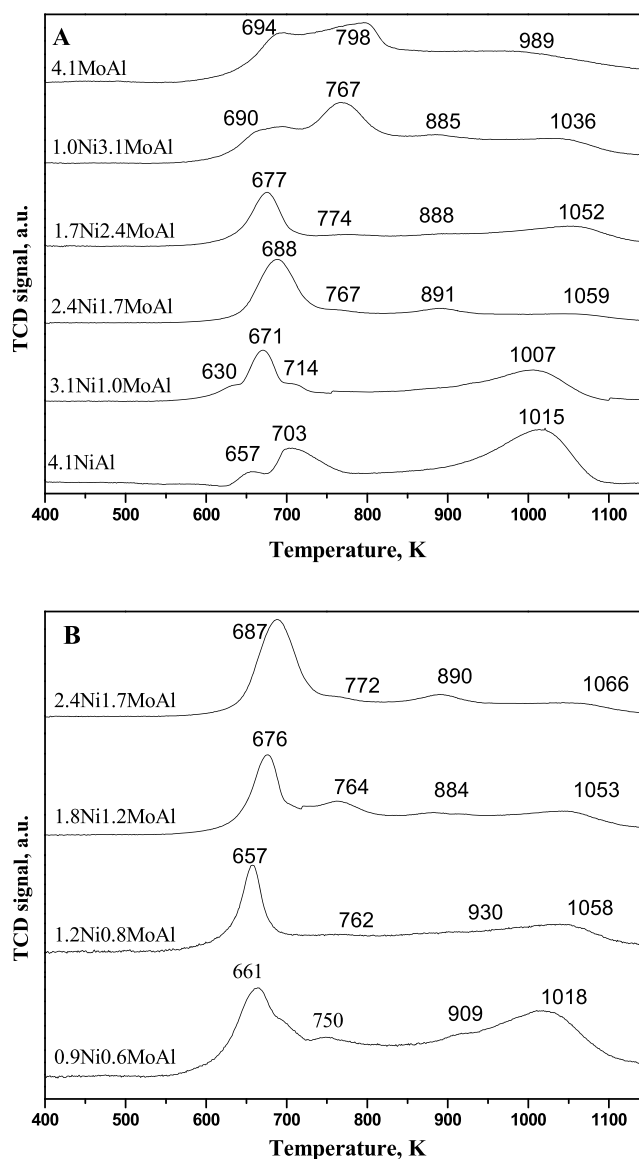


Figure 3. TPR profile of NiMo catalysts with different (A) Ni/Mo mole ratio and (B) metals loading.

The calcined NiMo catalysts exhibited four distinct reduction peaks at T_{\max} of 661–695, 750–774, 886–891, and 989–1058 K depending on Ni/Mo (mole) and metal loading. The dispersed NiO, MoO₃, and NiMoO₄ are reduced over a narrow temperature range (Figure 3A), and hence, their reduction peaks are often indistinguishable. The first reduction peak at 661–695 K was thus considered as the simultaneous reduction of dispersed NiO, MoO₃, and NiMoO₄. For the NiMo catalyst with high Ni content such as 3.1Ni1.0MoAl, this peak was weak and broad. On the other hand, the MoO₃ diffraction peak was weak in calcined 3.1Ni1.0MoAl (Figure 2). Therefore, this reduction peak might be attributed to the simultaneous reduction of dispersed NiO and NiMoO₄ in 3.1Ni1.0MoAl. For the NiMo catalyst with moderate Ni and Mo content such as 2.4Ni1.7MoAl and 1.7Ni2.4MoAl, this reduction peak was sharp and intense. The powder XRD pattern of these catalysts revealed the weak diffraction peaks of MoO₃ and NiO. This reduction peak for these catalysts was thus due to the reduction of NiMoO₄ predominately. The NiMoO₄ diffraction peak also became sharp and intense with

Table 2. Effect of Ni/Mo Mole Ratio on Product Distribution^a

Catalyst	product distribution at 65% conversion of stearic acid, wt %									
	all products						only hydrocarbons			
	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₇ -CHO	C ₁₈ -OH	C ₁₅	C ₁₆	C ₁₇	C ₁₈
4.1NiAl	0.4	3.7	61.0	0.1		34.8	0.6	5.6	93.6	0.2
1.0Ni3.1MoAl	0	0.1	3.6	6.1	1.3	88.8	0	1.0	36.7	62.3
1.7Ni2.4MoAl	0	0.1	5.6	6.3	1.4	85.4	0	1.6	46.3	52.1
2.4Ni1.7MoAl	0.1	0.1	15.1	11.5	1.8	71.4	0.4	0.4	56.3	42.9
3.1Ni1.0MoAl	0.2	0.2	42.1	18.9	0.9	37.7	0.3	0.3	68.6	30.8

^aAll reaction conditions are same as Figure 4.

The catalytic activity of these catalysts was thus due to both Ni and NiMo alloy species. On the other hand, the NiMo catalyst with high Mo content (1.7Ni2.4MoAl and 1.0Ni3.1MoAl), only NiMo alloy species was observed in powder XRD (Figure 2B). The catalytic activity of these catalysts was thus mainly due to NiMo alloy species. The TPR profile of the NiMo catalyst too showed that the reduction peak corresponding to NiMoO₄ species was weak for both high and low Ni content (3.1Ni1.0MoAl and 1.0Ni3.1MoAl) and quite intense for moderate Ni and Mo content (2.4Ni1.7MoAl and 1.7Ni2.4MoAl) (Figure 3A). The increasing trend of catalytic activity of the NiMo catalyst with increasing Ni content up to 2.4Ni1.7MoAl was thus due to the enrichment of highly active NiMo alloy species. The activity of 3.1Ni1.0MoAl was, however, not enhanced much compared to 2.4Ni1.7MoAl as observed from the initial reaction rate enhancement factor.

Table 2 shows the effect of Ni/Mo (mole) on the product distribution for a fixed conversion of C₁₇-COOH. For 4.1NiAl, the C₁₇ alkane was the primary hydrocarbon product with an insignificant quantity of the C₁₈ alkane. This result indicates that the reaction primarily follows the decarbonylation pathway over the Ni catalyst. On the other hand, the wt % of the C₁₈ alkane was increased with increasing Mo content in NiMo catalysts with the simultaneous decrease in the C₁₇ alkane. The C₁₇ alkane was the dominated hydrocarbon product for NiMo catalysts with high Ni content such as 3.1Ni1.0MoAl and 2.4Ni1.7MoAl. The C₁₈ alkane was, however, observed as the leading hydrocarbon product for the NiMo catalyst with high Mo content such as 1.7Ni2.4MoAl and 1.0Ni3.1MoAl. Powder XRD of the reduced NiMo catalyst exhibited the decline in intensity of Ni diffraction peaks with increasing Mo content and disappeared in 1.0Ni3.1MoAl (Figure 2B). On the other hand, the NiMo alloy diffraction peaks were intensified with increasing Mo content up to 2.4Ni1.7MoAl (Figure 2B). These results indicate that the reaction follows two different pathways simultaneously over two different active sites present in the NiMo catalyst. The reaction follows the decarbonylation pathway over the Ni sites and HDO route over NiMo alloy species.

At 65% conversion of C₁₇-COOH, the wt % of C₁₈-OH was quite high with the insignificant quantity of alkanes over NiMo catalysts (Table 2). Moreover, the wt % of C₁₈-OH was enhanced with increasing Mo content in the catalyst. For a better understanding of catalytic activity, the wt % of alkane (C₁₅-C₁₈) product at various conversions of C₁₇-COOH was calculated as presented in Figure 4B. The NiMo catalyst with the highest Mo content (1.0Ni3.1MoAl) exhibited the lowest catalytic activity for converting intermediate oxygenated compounds (C₁₈-OH and C₁₇-CHO) to alkanes. The catalytic activity toward alkanes was increased with increasing

Ni content in the NiMo catalyst. Despite the lowest conversion of C₁₇-COOH (Figure 4A), 4.1NiAl showed the highest catalytic activity toward alkanes. This result shows that reduction of C₁₇-COOH to C₁₈-OH is quite fast over NiMo alloy species compared to Ni sites of the catalyst, leading to the higher conversion of C₁₇-COOH over NiMo catalysts. The conversion of C₁₈-OH to alkanes is, however, relatively fast over Ni center than NiMo alloy species, resulting in higher wt % of the alkane product over the Ni catalyst. A small quantity of C₁₇-CHO was further noticed over the NiMo catalyst. C₁₇-CHO was, however, absent over 4.1NiAl. It might be due to the faster rate of decarbonylation of C₁₇-CHO over Ni center of the catalyst.

The optimum Ni/Mo (mole) in the NiMo catalyst can be deduced based on either catalytic activity or selectivity to hydrocarbon products. 3.1Ni1.0MoAl showed the highest catalytic activity (Figure 4), and hence, it might appear as the best catalyst. On the other hand, the C₁₇ alkane was the leading hydrocarbon product over 3.1Ni1.0MoAl and 2.4Ni1.7MoAl (decarbonylation route), whereas the C₁₈ alkane was the dominating hydrocarbon product over 1.7Ni2.4MoAl and 1.0Ni3.1MoAl (HDO route) (Table 2). Therefore, 3.1Ni1.0MoAl and 1.0Ni3.1MoAl may apparently be deliberated as the suitable catalysts for C₁₇ and C₁₈ alkane-rich products, respectively. The formation of the C₁₇ alkane is, however, associated with loss of one carbon with a slightly lower yield of green diesel. On the basis of this factor, 1.0Ni3.1MoAl may be considered as the appropriate catalyst for selective HDO of fatty acids. The decarbonylation route, however, consumes less hydrogen than the HDO route (Scheme 1). On the basis of this consideration, 3.1Ni1.0MoAl may be considered as the suitable catalyst for selective decarbonylation of fatty acids. On the other hand, green diesel with mixed hydrocarbons is desirable to obtain better fuel properties. The ratio of C₁₇/C₁₈ was about 1.3 over 2.4Ni1.7MoAl. Therefore, 2.4Ni1.7MoAl was considered as the optimum catalyst in the present study. Ni/Mo (mole) of 3:2 was thus considered for the remaining studies.

2.3.2. Effect of Metal Loading. For a fixed Ni/Mo (mole) of 3:2, metal (Ni + Mo) loading in the NiMo catalyst was varied to obtain optimum metal loading. Figure 5 shows the conversion of C₁₇-COOH over these catalysts. The conversion of C₁₇-COOH was improved with increasing metal loading. At 60 min of reaction time, the conversion of C₁₇-COOH was about 41% over 0.9Ni0.6MoAl and reached about 72% for 2.4Ni1.7MoAl. The initial reaction rates were 1.5×10^{-5} , 1.7×10^{-5} , 1.9×10^{-5} , and 2.6×10^{-5} kmol/m³ s over 0.9Ni0.6MoAl, 1.2Ni0.8MoAl, 1.8Ni1.2MoAl, and 2.4Ni1.7MoAl, respectively. The initial reaction rate enhancement factors were 1.1, 1.3, and 1.8 for increasing metal loading

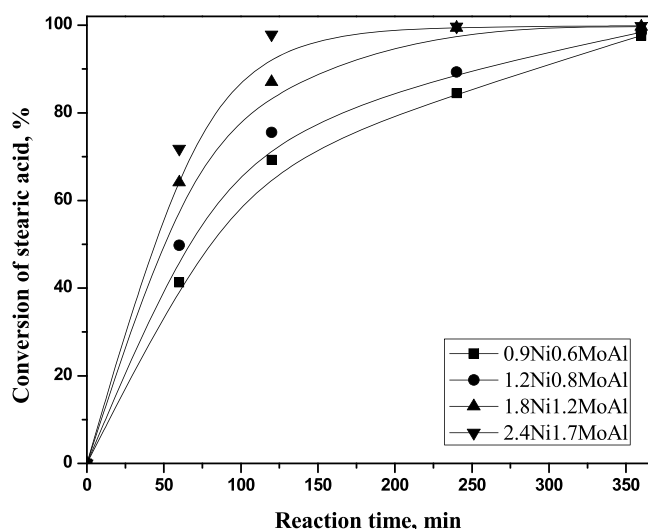


Figure 5. Effect of metals loading on conversion of stearic acid. Reaction conditions: concentration of stearic acid = 0.18 kmol/m³, *n*-dodecane = 100 mL, catalysts = 0.5 (w/v) %, 573 K, and initial hydrogen pressure = 20 bars.

from 1.5 to 4.1 mmol/g alumina, respectively. The increase in catalytic activity with increasing metal loading was due to the increase in active sites (Ni and NiMo alloy species) in the reduced NiMo catalyst (Figure S1B). The increase in the concentration of Ni and NiMo alloy species with increasing metal loading is also reflected by the increasing trend of the metallic surface area per gram of the catalyst (Table 1). Table 3 shows the effect of metal loading on wt % of products. The wt % of C₁₈-OH was dropped with increasing metal loading with the simultaneous increase in wt % of alkanes. The catalytic activity was enhanced with increasing metal loading, leading to the increase in the conversion of C₁₈-OH to alkanes. The product distribution was, however, practically unaffected by metal loading excepting 2.4Ni1.7MoAl. The wt % of the C₁₇ alkane was, however, dominated over 2.4Ni1.7MoAl. It may be due to the appreciable amount of Ni in 2.4Ni1.7MoAl, which is responsible for the decarbonylation route. The Ni was detected in powder XRD of reduced 2.4Ni1.7MoAl and 1.8Ni1.2MoAl only (Figure S1B).

2.3.3. Reproducibility, Recyclability, and Regeneration Ability of 2.4Ni1.7MoAl. Two separate reaction runs were conducted under similar reaction conditions to demonstrate the reproducibility of reaction results as shown in Table 4. The conversion of C₁₇-COOH and product distribution was almost similar in these two reaction runs. These results confirmed the repeatability of reaction results. To check the recyclability, the spent catalyst from these reaction mixtures was filtered and repeatedly washed with ethanol to remove

adsorbed organic compounds. The filtered catalyst was then dried overnight at 373 K. Another reaction run was then carried out using this dried spent catalyst. The conversion of C₁₇-COOH over the dried spent catalyst was much lesser than the fresh catalyst. The lower catalytic activity of the dried spent catalyst might be due to the carbonaceous deposition on the active sites. The dried spent catalyst was then regenerated by calcination and reduction at 973 K. The activity of this regenerated spent catalyst was subsequently tested for the HDO of C₁₇-COOH. The conversion of C₁₇-COOH and wt % of products over the regenerated spent catalyst was quite similar to that of the fresh catalyst (Table 4). These results demonstrate the regeneration ability of the NiMo catalyst for the HDO of C₁₇-COOH.

2.4. Kinetic Model. In this work, we proposed a kinetic model for the HDO of C₁₇-COOH (A) over NiMo catalysts based on the reaction of Scheme 1. The reaction was assumed as first order with respect to compounds in the liquid phase and partial pressure of hydrogen (*p*_{H₂}). The dehydrogenation of C₁₈-OH (B) to C₁₇-CHO (C) is a reversible reaction. However, we observed only a small quantity of C₁₇-CHO in this work. This was due to the faster rate of the decarbonylation reaction. A pseudo-steady-state hypothesis was thus adopted for the calculation of C₁₇-CHO concentration during the reaction (eq 1).

$$\begin{aligned} \frac{dC_C}{dt} = 0 &= k_2C_B - (k_2/k_{eq})C_Cp_{H_2} - k_4C_C \Rightarrow C_C \\ &= \frac{k_2C_B}{(k_2/k_{eq})p_{H_2} + k_4} \quad \text{where } k_{eq} = k_2/k_{-2} \end{aligned} \quad (1)$$

Equations 2–5 show the rate of formation of A, B, C₁₈ alkane (D), and C₁₇ alkane (E), respectively.

$$\frac{dC_A}{dt} = -k_1C_Ap_{H_2} \quad (2)$$

$$\frac{dC_B}{dt} = k_1C_Ap_{H_2} - k_2C_B + (k_2/k_{eq})C_Cp_{H_2} - k_3C_B \quad (3)$$

$$\frac{dC_D}{dt} = k_3C_B \quad (4)$$

$$\frac{dC_E}{dt} = k_4C_C \quad (5)$$

We calculated the equilibrium constant (*k*_{eq}) of the C₁₈-OH dehydrogenation reaction based on standard Gibbs free energy change ($\Delta G_{298K}^0 = 34.7$ kJ/mol): $\Delta G_{298K}^0 = -RT \ln(k_{eq})$. The hydrogen is consumed in the HDO of C₁₇-COOH. The partial pressure of hydrogen thus reduces with the progress of the reaction. It was calculated based on the following equation:

Table 3. Effect of Metal Loadings on Product Distribution^a

catalyst	product distribution at 70% conversion of stearic acid, wt %									
	all products						only hydrocarbons			
	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₇ -CHO	C ₁₈ -OH	C ₁₅	C ₁₆	C ₁₇	C ₁₈
0.9Ni0.6MoAl	0	0	2.9	3.2	1.4	92.5	0	0	47.5	52.5
1.2Ni0.8MoAl	0	0.1	8.4	9.4	1.0	81.1	0	0.6	46.9	52.5
1.8Ni1.2MoAl	0.1	0.2	10.6	10.9	1.4	76.8	0	1.4	48.6	50.0
2.4Ni1.7MoAl	0.2	0.3	16.7	12.6	1.4	68.8	0	1.7	56.0	42.3

^aAll reaction conditions are same as Figure 5.

Table 4. Reproducibility, Recyclability, and Regeneration Ability over 2.4Ni1.7MoAl for the HDO of Stearic Acid^a

experiment	conversion of stearic acid, % ^b	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₇ -CHO	C ₁₈ -OH
Reproducibility							
run 1	97.5	0	0.4	27.5	20.9	0.7	50.5
run 2	94.2	0	0.8	26.9	20.3	0.8	51.2
Recyclability of Spent Catalyst							
run 3	77.7	0	0	9.7	5.2	1.1	84.0
Reusability of Regenerated Spent Catalyst							
run 4	98.5	0.1	0.2	27.9	22.8	0.6	48.4

^aReaction conditions: concentration of stearic acid = 0.18 kmol/m³, *n*-dodecane = 100 mL, catalysts = 0.5(w/v)%, 543 K, and initial hydrogen pressure = 20 bars. ^bConversion of stearic acid at 120 min.

$$p_{H_2} = p_{H_2}^0 - \nu(2C_B + C_C + 3C_D + C_E)RT/V \quad (6)$$

where ν and V represent the volume of liquid and gas, respectively.

The rate constants of the kinetic model were calculated using kinetic data by a nonlinear regression algorithm. The ordinary differential equations (eqs 2–5) were integrated using the RK4 method. The rate constants were estimated by minimizing the below objective function.

$$OF = \sqrt{\sum_{i=1}^n ((C_{A,i}^E - C_{A,i}^C)^2 + (C_{B,i}^E - C_{B,i}^C)^2 + (C_{D,i}^E - C_{D,i}^C)^2 + (C_{E,i}^E - C_{E,i}^C)^2)} \quad (7)$$

2.5. Kinetic Studies. HDO of C₁₇-COOH was carried out at five different temperatures (493–553 K) over 2.4Ni1.7MoAl as shown in Figure 6. The conversion of C₁₇-COOH was

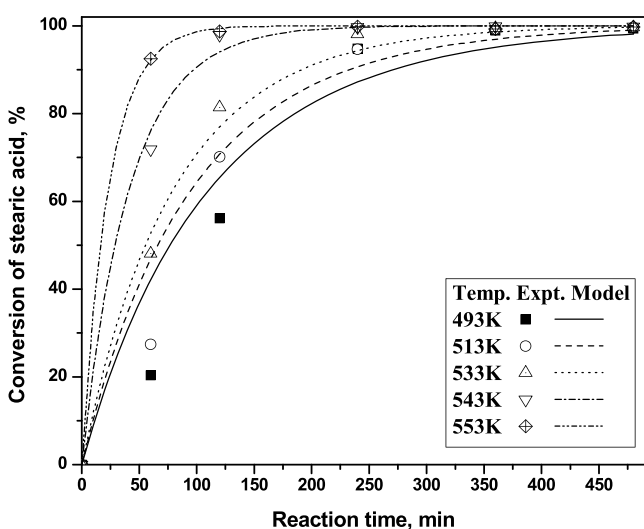


Figure 6. Effect of reaction temperature on conversion of stearic acid. Reaction conditions: concentration of stearic acid = 0.18 kmol/m³, *n*-dodecane = 100 mL, catalysts = 0.5 (w/v) % 2.4Ni1.7MoAl, and initial hydrogen pressure = 20 bars.

enhanced with increasing reaction temperature as expected. The conversion of C₁₇-COOH at 60 min of reaction time was about 20% at 493 K and increased to about 92% at 553 K. The initial reaction rates were 8.8×10^{-6} , 1.2×10^{-5} , 1.4×10^{-5} , 2.6×10^{-5} , and 2.9×10^{-5} kmol/m³ s at 493, 513, 533, 543, and 553 K, respectively. With respect to 493 K, the initial reaction rate was enhanced by factors of 1.4, 1.6, 2.9, and 3.3 for 513, 533, 543, and 553 K, respectively. The apparent activation energy was found to be 38.7 kJ/mol from the

Arrhenius plot of $\ln(\text{initial rate})$ versus $1/T$. Table 5 shows the effect of reaction temperature on wt % of products for a fixed conversion of C₁₇-COOH. The wt % of C₁₈-OH was dropped with increasing reaction temperature with the concurrent increase in wt % of alkanes. With increasing reaction temperature, the reaction rate was enhanced, resulting in the increase in conversion of C₁₈-OH to alkanes.

The rate constants of the kinetic model (eqs 1–7) were then obtained based on these kinetic data. The pre-exponential factor and activation energy were calculated using the Arrhenius law. The activation energy for the rate constant, k_1 , was quite low compared to the other rate constants (Table 6). The reduction of C₁₇-COOH to C₁₈-OH is thus quite a fast reaction, resulting in the high conversion of C₁₇-COOH even at a low reaction temperature. Because of high activation energy, the conversion of C₁₈-OH to alkanes (by decarbonylation and HDO route) was appreciable only at higher reaction temperatures especially at 543 K and above (Table 5). Therefore, the wt % of alkanes became significant at higher reaction temperatures only. The conversion of C₁₇-COOH was further calculated based on these rate constants. The calculated C₁₇-COOH conversion was then matched with the reaction results as shown in Figure 6. The calculated C₁₇-COOH conversion matched reasonably well with reaction results.

3. CONCLUSIONS

The NiMoO₄ and NiMo alloy species were observed in calcined and reduced NiMo catalysts, respectively. These species were significant in NiMo catalysts with Ni/Mo (mole) of 2:3 and 3:2. On the other hand, the Ni content was substantial in the NiMo catalyst with high Ni/Mo (mole) and decreased gradually with the drop in Ni/Mo (mole). The activity of the NiMo catalyst for the HDO of C₁₇-COOH was enhanced with increasing Ni/Mo (mole). It was due to the enrichment of highly active NiMo alloy species with increasing Ni/Mo (mole). The reaction followed two RPs simultaneously over two different active centers present in the catalyst: decarbonylation over Ni and HDO over NiMo alloy species. The C₁₇ alkane was the primary hydrocarbon product over 4.1NiAl. The C₁₈ alkane was the dominating hydrocarbon product over the NiMo catalyst with Ni/Mo (mole) of 1:3 and 2:3. The C₁₇ alkane was, however, the leading hydrocarbon product for higher Ni/Mo (mole). For a fixed Ni/Mo (mole), the catalytic activity of the NiMo catalyst was enhanced with increasing metal (Ni + Mo) loading without altering the product distribution. A power law-based kinetic model was established based on the proposed reaction scheme. The activation energy was relatively low for the reduction of C₁₇-COOH to C₁₈-OH (12.1 kcal/mol) compared to the

Table 5. Effect of Reaction Temperature on Product Distribution^a

temperature, K	product distribution at 70% conversion of stearic acid, wt %						all products				only hydrocarbons			
	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₇ -CHO	C ₁₈ -OH	C ₁₅	C ₁₆	C ₁₇	C ₁₈	C ₁₅	C ₁₆	C ₁₇	C ₁₈
493	0	0	1	1.1	0.6	97.3	0	0	47.6	52.4	0	0	47.6	52.4
513	0	0	1.9	1.8	0.8	95.7	0	0	51.4	48.6	0	0	51.4	48.6
533	0	0	3.7	3.1	1.2	91.7	0	0	54.4	45.6	0	0	54.4	45.6
543	0.2	0.3	16.7	12.6	1.4	68.8	0	1.7	56.0	42.3	0	1.7	56.0	42.3
553	0.1	0.3	24.1	23.2	1.5	51.1	0	0.6	50.5	48.6	0	0.6	50.5	48.6

^aAll reaction conditions are same as Figure 6.

Table 6. Estimated Parameters of the Kinetic Model

temperature, K	$k_1 \times 10^5, \text{s}^{-1} \text{bar}^{-1}$	$k_2 \times 10^3, \text{s}^{-1}$	$k_3 \times 10^5, \text{s}^{-1}$	k_4, s^{-1}	$k_{\text{eq}} \times 10^4$
493	0.417	1.08	0.283	0.67	2.11
513	0.467	1.25	0.633	1.17	2.93
533	0.533	1.58	1.33	1.50	3.97
543	1.03	2.33	6.00	7.08	4.59
553	1.83	5.67	11.17	9.58	5.28
pre-exponential factor, unit of k	8.00×10^{-1}	6.18×10^{17}	1.39×10^{24}	3.62×10^{25}	
activation energy, kcal/mol	12.1	45.9	66.2	57.2	
R ²	0.74	0.84	0.92	0.88	

decarbonylation of C₁₇-CHO (57.2 kcal/mol) and HDO of the C₁₈-OH (66.2 kcal/mol) route. The wt % of alkanes was thus trivial at low reaction temperature and enhanced with an increase in the reaction temperature.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. Alumina (Al)-supported NiMo catalysts are abbreviated as aNibMoAl, where *a* and *b* signify the millimoles of Ni and Mo per gram of support, respectively. These catalysts were prepared by an incipient wetness coimpregnation method. The metal precursors equivalent to *a* and *b* mmol/g alumina of Ni (nickel nitrate hexahydrate, $\geq 97\%$, Merck Specialties Pvt. Ltd.) and Mo (ammonium molybdate tetrahydrate, 99.98%, Sigma-Aldrich) were first dissolved in distilled water. The volume of water used in this method was slightly more than the pore volume of γ -Al₂O₃ (Alfa Aesar). This solution was then added dropwise to the measured quantity of γ -Al₂O₃ with constant stirring for about 1 h. This wet catalyst was first dried at ambient temperature, followed by drying in a hot-air oven at 373 K for about 12 h. The dried catalyst was then calcined at 973 K for about 6 h in a muffle furnace. The calcined catalysts were finally reduced by hydrogen at 973 K for 3 h in a tubular furnace. These catalysts are represented as the NiMo catalyst throughout this article for simplicity of the discussion.

4.2. Catalyst Characterization. The catalysts were characterized to determine the specific surface area and pore volume (Micromeritics ASAP 2020), reducibility, reduction temperature (T_{max}), metal dispersion, and metallic surface area (Micromeritics AutoChem II 2920). For BET, the catalyst was degassed under vacuum (10^{-5} Torr) at 523 K for 6 h. The nitrogen adsorption/desorption isotherms were measured at 77 K. The BET surface area was then calculated from nitrogen adsorption isotherm in the relative pressure (P/P_0) range of 0.05–0.3. The pore volume was considered as the volume of liquid nitrogen adsorbed at $P/P_0 = 1.0$ ca. For H₂-TPR studies, the calcined catalyst (20 mg) was first pretreated by argon (30 mL/min) at 473 K for 3 h. The H₂-TPR studies were then carried out using 10 vol % H₂-Ar gas mixture (30 mL/min) in

the temperature range of 323–1073 K with a heating rate of 5 K/min. For H₂-pulse chemisorption studies, the calcined catalyst was first reduced by 10 vol % H₂-Ar (30 mL/min) at 923 K for 2 h and then pretreated using pure He (30 mL/min) at 323 K for 3 h. The H₂-pulse chemisorption studies of the reduced catalyst were then carried out at 323 K using 10 vol % H₂-Ar gas. The metal dispersion and metal surface area were obtained from the amount of hydrogen chemisorbed.

Powder XRD pattern of the catalysts was recorded in the 2θ range of 10–90° in a Phillips X-ray diffractometer (X-PERT Pro PAN analytical) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 45 kV and 30 mA current with a scanning rate of 1°/min. The Raman spectra of calcined catalysts were obtained under ambient condition using a Raman spectrometer system (Bruker, Senterra) equipped with a confocal microscope and 1200 grooves/mm grate. The samples were excited with a 532 nm laser (20 mW), and the spectra were acquired in the 200–1100 cm⁻¹ region at a resolution of 20 cm⁻¹. A thin wafer of the pure sample was made for Raman analysis. UV–vis–NIR spectra of the calcined NiMo catalysts were recorded in a UV–vis–NIR spectrometer (PerkinElmer UV–vis–NIR spectrometer, Lambda-1050) equipped with diffuse reflectance accessories (Harrick scientific Products Inc., USA) in the wavelength range of 250–800 nm using BaSO₄ as a reference under ambient condition.

4.3. Reaction Setup and Procedure. Catalytic HDO of C₁₇-COOH ($\geq 97\%$, Merck Specialties Pvt. Ltd.) was studied in a high-pressure batch reactor. The reactor is enclosed in an electrically heated furnace. The reactor consists of a four-blade impeller, a thermocouple, and a temperature and rotations per minute regulator. The reactor was maintained within ± 1 K using a PID temperature controller. For a typical reaction, 5 g of C₁₇-COOH (0.18 kmol/m³) was dissolved in 100 mL *n*-dodecane ($\geq 99\%$, Sigma-Aldrich). The C₁₇-COOH solution and 0.5 g catalyst (0.5 (w/v) %) were then added into the reactor. The hydrogen was purged a few times to remove air from the reactor. The reactor was initially pressurized to 20 bars hydrogen at room temperature. The reactor was heated to a specified reaction temperature at a constant stirring speed of

1200 rpm. The reactor pressure was increased to about 31 bar at the reaction temperature of 543 K. The initial liquid sample was taken immediately after attainment of the specified reaction temperature. The conversion of C₁₇-COOH was calculated based on this initial reaction sample. Further reaction samples were collected at different reaction times. The products in the reaction sample were identified by GC-MS (GCMS-QP2010 Ultra) and quantified using an off-line GC-FID (Shimadzu, GC-2014).⁴ The wt % of products and unreacted C₁₇-COOH were calculated based on the known concentration of internal standard, *n*-dodecane. The product distribution term used in the article is expressed as wt % of the individual products.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b03592.

Powder XRD pattern of calcined and reduced NiMo catalysts with different metal (Ni + Mo) loading and UV-vis spectra of NiMo catalysts with different Ni/Mo mole ratios (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sunil_maity@iith.ac.in. Phone: +91-40-2301-6075. Fax: +91-40-2301 6003.

ORCID

Sunil K. Maity: 0000-0002-1832-5060

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are thankful to the Department of Science and Technology, New Delhi, India, for funding this project (DST/TSG/AF/2010/65-G dated 17.11.2011).

■ NOMENCLATURE

aNiMoAl, catalyst with *a* and *b* mmol of Ni and Mo metals per gram of γ -Al₂O₃ (Al), respectively; C₁₇-COOH, stearic acid; C₁₇-CHO, octadecanal; C₁₈-OH, 1-octadecanol; HDO, hydrodeoxygenation; RP, reaction pathway

■ REFERENCES

- (1) Maity, S. K. Opportunities, recent trends and challenges of integrated biorefinery: Part I. *Renewable Sustainable Energy Rev.* **2015**, *43*, 1427–1445.
- (2) Government of India. *National Policy on Biofuels*, 2008.
- (3) United Nations Climate Change. Kyoto Protocol. <https://unfccc.int/process-and-meetings/the-kyoto-protocol/what-is-the-kyoto-protocol> (accessed 2012).
- (4) Kumar, P.; Yenumala, S. R.; Maity, S. K.; Shee, D. Kinetics of Hydrodeoxygenation of Stearic Acid Using Supported Nickel Catalysts: Effects of Supports. *Appl. Catal., A* **2014**, *471*, 28–38.
- (5) Wang, W.-C.; Thapaliya, N.; Campos, A.; Stikeleather, L. F.; Roberts, W. L. Hydrocarbon Fuels from Vegetable Oils via Hydrolysis and Thermo-Catalytic Decarboxylation. *Fuel* **2012**, *95*, 622–629.
- (6) Wang, H.; Lin, H.; Zheng, Y.; Ng, S.; Brown, H.; Xia, Y. Kaolin-Based Catalyst as a Triglyceride FCC Upgrading Catalyst with High Deoxygenation, Mild Cracking, and Low Dehydrogenation Performances. *Catal. Today* **2019**, *319*, 164–171.

(7) Furimsky, E. Catalytic Hydrodeoxygenation. *Appl. Catal., A* **2000**, *199*, 147–190.

(8) Bezegegianni, S.; Dimitriadis, A.; Meletidis, G. Effectiveness of CoMo and NiMo Catalysts on Co-Hydroprocessing of Heavy Atmospheric Gas Oil-Waste Cooking Oil Mixtures. *Fuel* **2014**, *125*, 129–136.

(9) Ngaosuwan, K.; Lotero, E.; Suwannakarn, K.; Goodwin, J. G.; Praserthdam, P. Hydrolysis of Triglycerides Using Solid Acid Catalysts. *Ind. Eng. Chem. Res.* **2009**, *48*, 4757–4767.

(10) Liu, M.; Shi, Y.; Bi, Y.; Xing, E.; Wu, Y.; Huang, S.; Yang, M. Influence of Porosity on Product Distribution over Co/H-ZSM-22 Catalysts in the Upgrading of Palmitic Acid. *Energy Technol* **2018**, *6*, 406–415.

(11) Brillouet, S.; Baltag, E.; Brunet, S.; Richard, F. Deoxygenation of Decanoic Acid and Its Main Intermediates over Unpromoted and Promoted Sulfided Catalysts. *Appl. Catal., B* **2014**, *148-149*, 201–211.

(12) Bernas, H.; Eränen, K.; Simakova, I.; Leino, A.-R.; Kordás, K.; Myllyoja, J.; Mäki-Arvela, P.; Salmi, T.; Murzin, D. Y. Deoxygenation of Dodecanoic Acid under Inert Atmosphere. *Fuel* **2010**, *89*, 2033–2039.

(13) Coumans, A. E.; Hensen, E. J. M. A Model Compound (Methyl Oleate, Oleic Acid, Triolein) Study of Triglycerides Hydrodeoxygenation over Alumina-Supported NiMo Sulfide. *Appl. Catal., B* **2017**, *201*, 290–301.

(14) Ayodele, O. B.; Togunwa, O. S.; Abbas, H. F.; Daud, W. M. A. W. Preparation and Characterization of Alumina Supported Nickel-Oxalate Catalyst for the Hydrodeoxygenation of Oleic Acid into Normal and Iso-Octadecane Biofuel. *Energy Convers. Manage.* **2014**, *88*, 1104–1110.

(15) Peroni, M.; Lee, I.; Huang, X.; Baráth, E.; Gutiérrez, O. Y.; Lercher, J. A. Deoxygenation of Palmitic Acid on Unsupported Transition-Metal Phosphides. *ACS Catal.* **2017**, *7*, 6331–6341.

(16) Yang, L.; Carreon, M. A. Deoxygenation of Palmitic and Lauric Acids over Pt/ZIF-67 Membrane/Zeolite 5A Bead Catalysts. *ACS Appl. Mater. Interfaces* **2017**, *9*, 31993–32000.

(17) Besse, X.; Schuurman, Y.; Guilhaume, N. Hydrothermal Conversion of Linoleic Acid and Ethanol for Biofuel Production. *Appl. Catal., A* **2016**, *524*, 139–148.

(18) Ding, S.; Li, Z.; Li, F.; Wang, Z.; Li, J.; Zhao, T.; Lin, H.; Chen, C. Catalytic Hydrogenation of Stearic Acid over Reduced NiMo Catalysts: Structure–activity Relationship and Effect of the Hydrogen-Donor. *Appl. Catal., A* **2018**, *566*, 146–154.

(19) Arora, P.; Ojagh, H.; Woo, J.; Grennfelt, E. L.; Olsson, L.; Creaser, D. Investigating the Effect of Fe as a Poison for Catalytic HDO over Sulfided NiMo Alumina Catalysts. *Appl. Catal., B* **2018**, *227*, 240–251.

(20) Boonyasuwat, S.; Tscheikuna, J. Co-Processing of Palm Fatty Acid Distillate and Light Gas Oil in Pilot-Scale Hydrodesulfurization Unit over Commercial CoMo/Al₂O₃. *Fuel* **2017**, *199*, 115–124.

(21) Kaluža, L.; Kubička, D. The Comparison of Co, Ni, Mo, CoMo and NiMo Sulfided Catalysts in Rapeseed Oil Hydrodeoxygenation. *React. Kinet., Mech. Catal.* **2017**, *122*, 333–341.

(22) Zhao, C.; Brück, T.; Lercher, J. A. Catalytic Deoxygenation of Microalgae Oil to Green Hydrocarbons. *Green Chem.* **2013**, *15*, 1720–1739.

(23) Mondal, S.; Singuru, R.; Chandra Shit, S.; Hayashi, T.; Irlé, S.; Hijikata, Y.; Mondal, J.; Bhaumik, A. Ruthenium Nanoparticle-Decorated Porous Organic Network for Direct Hydrodeoxygenation of Long-Chain Fatty Acids to Alkanes. *ACS Sustainable Chem. Eng.* **2017**, *6*, 1610–1619.

(24) Hachemi, I.; Murzin, D. Y. Kinetic Modeling of Fatty Acid Methyl Esters and Triglycerides Hydrodeoxygenation over Nickel and Palladium Catalysts. *Chem. Eng. J.* **2018**, *334*, 2201–2207.

(25) Patil, S. J.; Vaidya, P. D. On the Production of Bio-Hydrogenated Diesel over Hydrotalcite-like Supported Palladium and Ruthenium Catalysts. *Fuel Process. Technol.* **2018**, *169*, 142–149.

(26) Janampelli, S.; Darbha, S. Effect of Support on the Catalytic Activity of WO_x Promoted Pt in Green Diesel Production. *Mol. Catal.* **2018**, *451*, 125–134.

- (27) Kaylor, N.; Xie, J.; Kim, Y.-S.; Pham, H. N.; Datye, A. K.; Lee, Y.-K.; Davis, R. J. Vapor Phase Deoxygenation of Heptanoic Acid over Silica-Supported Palladium and Palladium-Tin Catalysts. *J. Catal.* **2016**, *344*, 202–212.
- (28) Chen, H.; Zhang, X.; Zhang, J.; Wang, Q. Tuning the Decarboxylation Selectivity for Deoxygenation of Vegetable Oil over Pt-Ni Bimetal Catalysts via Surface Engineering. *Catal. Sci. Technol.* **2018**, *8*, 1126–1133.
- (29) Imai, H.; Kimura, T.; Terasaka, K.; Li, X.; Sakashita, K.; Asaoka, S.; Al-Khattaf, S. S. Hydroconversion of Fatty Acid Derivative over Supported Ni-Mo Catalysts under Low Hydrogen Pressure. *Catal. Today* **2018**, *303*, 185–190.
- (30) Santillan-Jimenez, E.; Loe, R.; Garrett, M.; Morgan, T.; Crocker, M. Effect of Cu Promotion on Cracking and Methanation during the Ni-Catalyzed Deoxygenation of Waste Lipids and Hemp Seed Oil to Fuel-like Hydrocarbons. *Catal. Today* **2018**, *302*, 261–271.
- (31) Srifa, A.; Kaewmeesri, R.; Fang, C.; Itthibenchapong, V.; Faungnawakij, K. NiAl₂O₄ Spinel-Type Catalysts for Deoxygenation of Palm Oil to Green Diesel. *Chem. Eng. J.* **2018**, *345*, 107–113.
- (32) Cao, Y.; Shi, Y.; Bi, Y.; Wu, K.; Hu, S.; Wu, Y.; Huang, S. Hydrodeoxygenation and Hydroisomerization of Palmitic Acid over Bi-Functional Co/H-ZSM-22 Catalysts. *Fuel Process. Technol.* **2018**, *172*, 29–35.
- (33) Kordouli, E.; Pawelec, B.; Bourikas, K.; Kordulis, C.; Fierro, J. L. G.; Lycourghiotis, A. Mo Promoted Ni-Al₂O₃ Co-Precipitated Catalysts for Green Diesel Production. *Appl. Catal., B* **2018**, *229*, 139–154.
- (34) Zhang, H.; Lin, H.; Zheng, Y. The Role of Cobalt and Nickel in Deoxygenation of Vegetable Oils. *Appl. Catal., B* **2014**, *160–161*, 415–422.
- (35) Hachemi, I.; Kumar, N.; Mäki-Arvela, P.; Roine, J.; Peurla, M.; Hemming, J.; Salonen, J.; Murzin, D. Y. Sulfur-Free Ni Catalyst for Production of Green Diesel by Hydrodeoxygenation. *J. Catal.* **2017**, *347*, 205–221.
- (36) Chen, N.; Gong, S.; Qian, E. W. Effect of Reduction Temperature of NiMoO_{3-x}/SAPO-11 on Its Catalytic Activity in Hydrodeoxygenation of Methyl Laurate. *Appl. Catal., B* **2015**, *174–175*, 253–263.
- (37) Kordouli, E.; Sygellou, L.; Kordulis, C.; Bourikas, K.; Lycourghiotis, A. Probing the Synergistic Ratio of the NiMo/ γ -Al₂O₃ Reduced Catalysts for the Transformation of Natural Triglycerides into Green Diesel. *Appl. Catal., B* **2017**, *209*, 12–22.
- (38) Chen, H.; Wang, Q.; Zhang, X.; Wang, L. Effect of Support on the NiMo Phase and Its Catalytic Hydrodeoxygenation of Triglycerides. *Fuel* **2015**, *159*, 430–435.
- (39) Nag, N. K. A Comparative Study on the Msperslon and Carrier-Catalyst Interaction of Molybdenum Oxides Supported on Various Oxides by Electron Spectroscopy for Chemical Analysis. *J. Phys. Chem.* **1987**, *91*, 2324–2327.
- (40) Wang, Y.; Xiong, G.; Liu, X.; Yu, X.; Liu, L.; Wang, J.; Feng, Z.; Li, C. Structure and Reducibility of NiO-MoO₃/ γ -Al₂O₃ Catalysts: Effects of Loading and Molar Ratio. *J. Phys. Chem. C* **2008**, *112*, 17265–17271.
- (41) Jenišťová, K.; Hachemi, I.; Mäki-Arvela, P.; Kumar, N.; Peurla, M.; Čapek, L.; Wärnå, J.; Murzin, D. Y. Hydrodeoxygenation of Stearic Acid and Tall Oil Fatty Acids over Ni-Alumina Catalysts: Influence of Reaction Parameters and Kinetic Modelling. *Chem. Eng. J.* **2017**, *316*, 401–409.
- (42) Rozmysłowicz, B.; Kirilin, A.; Aho, A.; Manyar, H.; Hardacre, C.; Wärnå, J.; Salmi, T.; Murzin, D. Y. Selective Hydrogenation of Fatty Acids to Alcohols over Highly Dispersed ReOx/TiO₂ Catalyst. *J. Catal.* **2015**, *328*, 197–207.
- (43) Yenumala, S. R.; Maity, S. K.; Shee, D. Reaction Mechanism and Kinetic Modeling for the Hydrodeoxygenation of Triglycerides over Alumina Supported Nickel Catalyst. *React. Kinet., Mech. Catal.* **2016**, *120*, 109–128.
- (44) Zhou, L.; Lawal, A. Kinetic Study of Hydrodeoxygenation of Palmitic Acid as a Model Compound for Microalgae Oil over Pt/ γ -Al₂O₃. *Appl. Catal., A* **2017**, *532*, 40–49.
- (45) Giordano, N.; Bart, J. C. J.; Vaghi, A.; Castellan, A.; Martinotti, G. Structure and Catalytic Activity of MoO₃ · Al₂O₃ Systems: I. Solid-State Properties of Oxidized Catalysts. *J. Catal.* **1975**, *36*, 81–92.
- (46) Tian, H.; Wachs, I. E.; Briand, L. E. Comparison of UV and Visible Raman Spectroscopy of Bulk Metal Molybdate and Metal Vanadate Catalysts. *J. Phys. Chem. B* **2005**, *109*, 23491–23499.
- (47) Ozkan, U.; Schrader, G. L. NiMoO₄ Selective Oxidation Catalysts Containing Excess MoO₃ for the Conversion of C₄ Hydrocarbons to Maleic Anhydride. *J. Catal.* **1985**, *95*, 137–146.
- (48) Liu, H.; Cheung, P.; Iglesia, E. Effects of Al₂O₃ Support Modifications on MoO_x and VO_x Catalysts for Dimethyl Ether Oxidation to Formaldehyde. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3795–3800.
- (49) Al-Ubaid, A.; Wolf, E. E. Steam Reforming of Methane on Reduced Non-Stoichiometric Nickel Aluminate Catalysts. *Appl. Catal.* **1988**, *40*, 73–85.
- (50) Kordouli, E.; Pawelec, B.; Bourikas, K.; Kordulis, C.; Fierro, J. L. G.; Lycourghiotis, A. Mo Promoted Ni-Al₂O₃ Co-Precipitated Catalysts for Green Diesel Production. *Appl. Catal., B* **2018**, *229*, 139–154.
- (51) Dhanala, V.; Maity, S. K.; Shee, D. Roles of Supports (γ -Al₂O₃, SiO₂, ZrO₂) and Performance of Metals (Ni, Co, Mo) in Steam Reforming of Isobutanol. *RSC Adv.* **2015**, *5*, 52522–52532.
- (52) Liu, J.; Liu, C.; Zhou, G.; Shen, S.; Rong, L. Hydrotreatment of Jatropha Oil over NiMoLa/Al₂O₃ Catalyst. *Green Chem.* **2012**, *14*, 2499–2505.
- (53) Liu, J.; Fan, K.; Tian, W.; Liu, C.; Rong, L. Hydroprocessing of Jatropha Oil over NiMoCe/Al₂O₃ Catalyst. *Int. J. Hydrogen Energy* **2012**, *37*, 17731–17737.
- (54) Hernández-Huesca, R.; Mérida-Robles, J.; Maireles-Torres, P.; Rodríguez-Castellón, E.; Jiménez-López, A. Hydrogenation and Ring-Opening of Tetralin on Ni and NiMo Supported on Alumina-Pillared α -Zirconium Phosphate Catalysts. A Thiotolerance Study. *J. Catal.* **2001**, *203*, 122–132.
- (55) Kukushkin, R. G.; Bulavchenko, O. A.; Kaichev, V. V.; Yakovlev, V. A. Influence of Mo on Catalytic Activity of Ni-Based Catalysts in Hydrodeoxygenation of Esters. *Appl. Catal., B* **2015**, *163*, 531–538.
- (56) Li, C.; Chen, Y.-W. Temperature-Programmed-Reduction Studies of Nickel Oxide/alumina Catalysts: Effects of the Preparation Method. *Thermochim. Acta* **1995**, *256*, 457–465.
- (57) Qu, L.; Zhang, W.; Kooyman, P. J.; Prins, R. MAS NMR, TPR, and TEM studies of the interaction of NiMo with alumina and silica-alumina supports. *J. Catal.* **2003**, *215*, 7–13.
- (58) Taromi, A. A.; Kaliaguine, S. Green Diesel Production via Continuous Hydrotreatment of Triglycerides over Mesoporous γ -Alumina Supported NiMo/CoMo Catalysts. *Fuel Process. Technol.* **2018**, *171*, 20–30.