



Article Highly Efficient Catalytic Hydrodeoxygenation for Aliphatic Acid to Liquid Alkane: The Role of Molybdenum

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Abstract: A series of NiM/SiO₂ (M = Ce, Co, Cu, Fe, Sn, Zr, Mo) catalysts are prepared and used in the selective hydrodeoxygenation (HDO) of aliphatic acid to produce alkanes with the same number of carbon atoms as the reactant (alkane-Cx). The results indicate the introduction of Mo promotes the hydrodehydration of aliphatic alcohol and suppresses the decarbonylation of aliphatic aldehyde. The selective to alkane-Cx is more than 70% in the case of a complete conversion of aliphatic acid. A mechanism study proves that, due to the higher electronegativity of Mo, electrons transfer from Ni to Mo easily and facilitate the reduction of Mo, and the partially reduced Mo species is favorable for the hydrodehydration of aliphatic alcohol. Meanwhile, the adsorption of alcohol on Mo is more favorable than on the Ni site, and the hydrogen bond between hydroxyl hydrogen and O atoms on the catalyst improves the adsorption stability of aliphatic alcohol. Further COHP analysis indicates that the C-OH bond was activated when alcohol was adsorbed on the Ni₅/MoO₂ surface, which promoted the hydrodehydration of aliphatic alcohols and improved carbon atom utilization.

Keywords: hydrodeoxygenation; DFT; Ni-Mo catalyst; aiphatic acid; dodecane

1. Introduction

Replacing traditional fossil fuels with biomass fuels is one of the effective ways to reduce carbon emissions and provides one solution to solve the energy problem [1,2]. Biodiesel can be one choice for the production of biomass fuels [3]. Aliphatic acid methyl esters (FAMEs) produced by the transesterification of triglycerides are considered the first generation of biodiesel, but the high viscosities and low cloud points limit their utilization [4–6]. While long-chain aliphatic hydrocarbons produced by hydrodeoxygenation (HDO) are considered to be second-generation biodiesel, the conversion of aliphatic acids is generally considered to be harder than the formation of them from triglycerides during the HDO process. Thus, aliphatic acids are often selected as the model compound in the mechanism study.

In the HDO process of aliphatic acids, aliphatic acids with n carbon atoms are first converted into aliphatic aldehydes, and aliphatic aldehydes are further converted into aliphatic hydrocarbons with n-1 carbon atoms through hydrodecarbonylation [7–10]. Take the HDO of lauric acid as an example; the reaction pathway is shown in Scheme 1. There are three ways to produce alkanes. For the decarbonylation process, the main reaction includes Equations (1)–(3). The catalysts and high H₂ pressure during the HDO promote the methanation of CO (Equation (3)). Alkanes with one carbon atom less than the reactant aliphatic acid (Alkanes-Cx-1) can be produced through the decarboxylation of aliphatic acid or the decarbonylation of aliphatic aldehyde [11]. The hydrodehydration process includes Equations (4) and (5). Alkanes with the same carbon atoms as the reactant (alkanes-Cx) are produced through the hydrodehydration of aliphatic alcohol. The competition between decarbonylation and hydrodehydration determines the products distribution [12–14]. It can be concluded that it will take four moles of H₂ and lose one mole of C for the HDO of one mole of saturated aliphatic acids to produce alkanes through decarbonylation.



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Scheme 1. Reaction pathway of the HDO of lauric acid (dotted arrows represent the minor reactions).

However, for the hydrodehydration process, only three moles of H_2 will be costed, and all the C atoms in the aliphatic acids can be retained into alkanes. Considering both the carbon utilization and the H_2 consumption, it is meaningful to promote the hydrodehydration process in the HDO of aliphatic acid purposefully.

$$R-COOH + H_2 \rightarrow R-CHO + H_2O \tag{1}$$

$$R-CHO \rightarrow R-H + CO \tag{2}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3}$$

$$R-COOH + 2H_2 \rightarrow R-CH_2-OH + H_2O \tag{4}$$

$$R-CH_2-OH + H_2 \rightarrow R-CH_3 + H_2O \tag{5}$$

Much research has been done on the catalytic hydrogenation mechanism of aliphatic acids and the selectivity of products. In order to improve the conversion rate of aliphatic acids and the selectivity of alkane in the products, many scholars focus on the development of high-efficiency catalysts. These catalysts include sulphided catalysts [12,13], noble metal catalyst [14], non-noble metal catalyst [15], etc. Presulfide catalysts require a certain amount of sulfur in the substrate to maintain catalytic activity. With the process of the reaction, the sulfur element is continuously lost. Not only is the activity of the catalyst reduced but also the substrate will be polluted. For the HDO of aliphatic acids with noble metal catalysts, such as Pt/γ -Al₂O₃ and Pt/C, some catalysts have been used to improve the selectivity of alkanes in the catalytic hydrogenation of aliphatic acids [16,17]. The selectivity of alkanes- C_{x-1} is generally higher than that of alkanes- C_x among all alkane products, and this result remains unchanged with several different carriers [18,19]. The traditional non-noble catalyst was used for the hydrogenation of aliphatic acids to alcohols. Compared to noble metal catalysts, non-noble transition metal catalysts are more attractive in industrial magnification. Ni is often used as a catalyst for the HDO process because of its high catalytic activity and low price [20,21]. The single metal Ni catalyst has high hydrogenation activity, but its deoxygenation activity is poor. Therefore, it is necessary to improve the deoxygenation activity of the Ni-based catalyst by proper modification. Recent studies have shown that bimetallic catalysts have superior catalytic properties than single metallic catalysts. Reduced transition metal catalysts, such as Ni, Fe, Cu, and Zn have attracted much attention due to their excellent catalytic performance [22,23]. Therefore, it is necessary to improve the deoxygenation activity of the Ni-based catalyst by proper modification. Mo, an inexpensive transition-metal, has many special properties, such as

high conductivity, high melting point, and chemical stability [24]. The HDO of guaiacol [25] and furfural [26] with Ni-Mo catalysts also proved the effect of Mo in the hydrogenolysis of C-O, reminding us that the synergetic effect between Ni and Mo should be studied in depth in order to obtain more favorable catalysts for the production of alkanes- C_x .

Therefore, a series of NiM/SiO₂ (M = Ce, Co, Cu, Fe, Sn, Zr, and Mo) bimetallic catalysts are synthesized, and their catalytic effects on the decarbonylation and hydrode-hydration are compared under the same reaction conditions. Afterwards, the NiMo/SiO₂ bimetallic catalyst, which possesses the best hydrodehydration activity, is selected to further explore the influence of the Mo doping amount on the catalytic effect. Combined with the catalyst characterization and DFT calculation results, the mechanism of Ni-Mo bimetallic sites on the HDO of aliphatic acid and the activation of the C-OH bond is studied.

2. Results and Discussion

2.1. Catalyst Synthesis and Characterization

A series of metals was doped into the Ni₅/SiO₂ to prepare the Ni₅M₁/SiO₂ catalysts and the activities on the HDO of lauric acid were tested; the results are shown in Figure 1a. It was clear that the activities of all the Ni₅M₁/SiO₂ except Ni₅Sn₁/SiO₂ on the HDO were better than Ni₅/SiO₂, with which the conversion of lauric acid was 25%. The introduction of Fe and Mo resulted in a 100% conversion of lauric acid, but the presence of Sn resulted in only a 7.2% conversion of lauric acid. And the introduction of Ni resulted in a higher dodecane selectivity, which was more favorable for the atom economy. As undecane and dodecane were the products of the conversion of lauryl alcohol through decarbonylation and hydrodehydration; lauryl alcohol was selected as the reactant to study the effect of the doped metal on the selectivity of the two products. The results are shown in Figure 1b. The conversion of lauryl alcohol with all the catalysts reached 100%, except Ni₅Cu₁/SiO₂ and Ni₅Sn₁/SiO₂. And Ni₅Mo₁/SiO₂ showed the best performance for the production of dodecane, with 35.5% selectivity. Based on the results above, the effect of the Mox doping into the Ni₅/SiO₂ catalyst on the HDO of aliphatic acid and the hydrodehydration of aliphatic alcohol was further studied.



Figure 1. Effect of metal doping on the conversion and product selectivity of (**a**) lauric acid and (**b**) lauryl alcohol.

The theoretical mental load was calculated in this way. A total mass of 1 g of catalyst was used in each experiment, with the loading of Ni always controlled at 10%wt, Taking the Ni₅Mo₁ catalyst as an example, the total mass of Ni is 0.1 g (10^{-3} moles), and under a molar ratio of Ni:Mo = 5:1, the total mass of Mo is 0.2 g (2×10^{-4} moles), resulting in a theoretical loading of Mo is 2%wt.

The accurate metal loading amount of the Ni₅Mox/SiO₂ was analyzed by ICP-OES and listed in Table 1. The results show that the actual load of Ni is close to the theoretical load of 10wt%, while the load of Mo is lower than the theoretical value in the bimetallic catalyst, but close to the theoretical metal load in the Mo/SiO₂ catalyst. The relative atomic mass of Mo is relatively large, so with the doping of Mo, there may be some loss during the catalyst preparation process. However, it is still within a reasonable range, indicating that Ni and Mo metals can be well-loaded on the carrier material. The dispersion of Ni/SiO₂, Mo/SiO₂, and Ni₅Mox/SiO₂ was measured by N₂O titration at the reaction temperature, and the results were displayed in Table 1. The dispersion of Ni/SiO_2 and Mo/SiO_2 was measured for comparation. As the dispersion of pure Mo catalyst was only 0.19%, the dispersion of the bimetallic catalysts measured was mainly due to Ni. Compared with the pure Ni (35.40%) catalyst, the dispersion of Ni_5Mo_1/SiO_2 (36.05%) only showed a little increase. Further increase of Mo content resulted in the gradual decrease of the dispersion. And the dispersion was only 9.80% for Ni_5Mo_{10}/SiO_2 . The decrease in dispersion can be attributed to the active sites of Ni being covered by Mo. It was generally considered that the main role of the Ni site in the bimetallic catalysts was to promote the dissociation of H₂. Reduction of Ni dispersion might result in lower hydrogenation activity.

Table 1. Accurate metal loading and Ni dispersity of Ni/SiO₂, Mo/SiO₂, and Ni₅Mox/SiO₂.

	Theory Metal Loading, wt%		Actual Metal Loading, wt% 1		Disporsity % 2
	Ni	Мо	Ni	Мо	Dispersity, 78
Ni	10	-	10.55	-	35.40
Ni5Mo1	10	2	9.88	1.45	36.05
Ni ₅ Mo ₃	10	6	10.65	5.20	17.89
Ni ₅ Mo ₅	10	10	10.47	8.70	17.85
Ni ₅ Mo ₇	10	14	9.28	10.24	10.25
Ni5Mo10	10	20	9.66	16.23	9.80
Мо	-	10	-	10.12	0.19

 1 Metal loading amount was determined by ICP-OES. 2 Dispersity of Ni was calculated based on the N₂O-titration results.

The XRD patterns of the different catalysts after calcination and reduction were displayed in Figures 2a and 2b, respectively. As was expected, nickel silicate was synthesized according to the peak located at 34.0°, 35.7°, and 60.9°, which were attributed to the (200), (131), and (135) surfaces of nickel silicate [27]. With the introduction of Mo, the peaks belonging to MoO_3 (PDF 05-0508) became obvious, which indicated that the Mo species tended to agglomerate with the increase of content [28]. Compared with the Mo/SiO_2 , the presence of the NiMoO₄ phase (PDF 12-0348) in the Ni₅Mox/SiO₂ samples, as shown in Figure 2a-1, proved the strong interaction between Ni and Mo after calcination [29]. After being reduced at 600 °C, nickel silicate was converted to Ni, as shown in Figure 2b, although the weak peaks at 34.0° and 35.7° indicated the incomplete reduction of nickel silicate. With the increase of Mo content, the main peak decreased gradually from 44.2° in Ni/SiO₂ to 43.4° in Ni₅Mo_{12.5}/SiO₂, as performed in Figure 2b-1, which proved the formation of NiMo alloy. However, when the content of Mo was higher than that of Ni, several peaks located at 40.5°, 58.6°, and 73.7° appeared, which can be attributed to the (110), (200), and (211) surfaces of reduced Mo. And the gradually sharp peak with the increase of Mo content indicated the agglomeration of the Mo phase. The disappearance of the MoO_3 phase indicated the total reduction of Mo species in the bulk phase.



Figure 2. XRD patterns of Ni/SiO₂, Ni₅Mox/SiO₂, and Mo/SiO₂ after calcination (**a**) and reduction (**b**). (**a-1,b-1**) were the partially enlarged details of (**a**,**b**).

TEM images of the catalysts are displayed in Figure 3. The particle-size distribution was also given. For the Ni₅Mox/SiO₂ samples, with the increase of Mo content, the average particle size decreased first, then increased. For the Mo/SiO₂ catalyst, as shown in Figure S1, TEM results show that there are only a few Mo particles on the catalyst surface, and most Mo particles exist in a random form, which meets well with the sharp XRD peak of this sample that the Mo tended to agglomerate when the content was high. The small amount of Mo particles also presented in the enlarged image of Mo/SiO₂ indicated that when the content of Mo is low, the dispersion of Mo was well with a smaller particle size, which resulted in the reduced average particle size from 3.25 nm to 2.38 nm in Ni₅Mox/SiO₂ (x is from one to seven). But for Ni₅Mo₁₀/SiO₂, much agglomerated Mo in the catalyst increased the average particle size of 3.99 nm.

HAADF-STEM images and the corresponding EDX elemental maps were obtained to illustrate the element distribution, as shown in Figure 4. The formation of Ni-Mo alloy can be further verified by the close match of the two elements. Compared with Mo, the distribution of Ni is more concentrated on the particles [30]. This might indicate that there is a strong interaction between Mo species and SiO₂. The unique interaction between the carrier and Mo can be explained. The well-dispersed Mo in this study also agrees with this view. Meanwhile, it can be seen that with the increase in Mo content, the distribution of the Mo element is relatively more concentrated, and the Mo element in Ni_5Mo_{10} is obviously concentrated. However, the distribution of Ni elements gradually becomes more dispersed. It can be seen that there is an obvious local aggregation of Ni in Ni_5Mo_5 and Ni_5Mo_7 , and the distribution of Ni is more dispersed in Ni_5Mo_{10} .



Figure 3. TEM images and nanoparticles size distribution of Ni_5Mox/SiO_2 (x = 1 (**a**), 3 (**b**), 5 (**c**), 7 (**d**), 10 (**e**)) and (**f**) Mo/SiO₂.



Figure 4. HAADF-STEM images and corresponding EDX elemental mapping of (**a**). Ni₅Mo₁/SiO₂, (**b**) Ni₅Mo₇/SiO₂, and (**c**) Ni₅Mo₁₀/SiO₂.

The electronic property and the chemical state of the reduced catalysts were characterized by XPS, and the spectra were displayed in Figure 5. The peaks at 853.2 and 856.4 eV in Figure 5 were ascribed to $2p_{3/2}$ peaks of Ni⁰ and Ni²⁺, respectively. The area of Ni^0 increased when Mo was added (Table 2), which indicated that the Mo species might promote the reduction of the Ni precursor [31]. XSP spectra of Mo 3d were displayed in Figure 5b, and the valence distribution of Mo was listed in Table 2. In the Ni_5Mo_1/SiO_2 , only oxidation states of Mo were observed. With the increase in Mo content, the proportion of Mo^{6+} decreased from 40.42% in Ni_5Mo_1/SiO_2 to 18.62% in Mo/SiO_2 . It can be seen that in the Ni₅Mo_X catalyst, Ni loses electrons to form NiO, resulting in an increase in the Ni^{2+} content in the catalyst. It is also related to the relatively strong electronegativity of Mo (Ni: 1.88, Mo: 2.16). The transfer of electrons from Ni to Mo leads to an increase in the electron-cloud density near Mo. With the increase in Mo loading, the proportion of Mo⁵⁺ gradually increases, resulting in more reduced states of Mo [32]. The presence of reduced Mo species can promote the generation of oxygen vacancies, thereby enhancing the activity of the catalyst. Additionally, compared with Mo/SiO₂, the introduction of Ni promotes the reduction of Mo and then brings up the content of Mo⁰. Considering the XPS result of Ni 2p, the oxidation resistance of NiMo alloy may be better than monometallic Mo. Therefore, there is a tendency for electron transfer from Ni to Mo in NiMo bimetallic catalyst, resulting in the promotion of Mo reduction and a decrease in electron-cloud density near the Ni site. XPS spectra of Si 2p and O 1s are also shown in Figure 5c,d. The peak at 103.8 eV for Si 2p can be attributed to the Si in SiO₂ [33]. After the introduction of Mo, another peak located at 102.8 eV appeared after the peak split. This peak might be attributed to the Si in SiMoOx [34], which can also explain the appearance of this peak in Mo/SiO₂. The change of the O 1s spectra shown in Figure 5d can indicate that the electronic environment of O also changed with the Mo.



Figure 5. (a) Ni 2p, (b) Mo 3d, (c) Si 2p, and (d) O 1s XPS spectra of the reduced samples.

Catalysts	Ni ⁰	Ni ²⁺	Mo ⁰	Mo ³⁺	Mo ⁴⁺	Mo ⁵⁺	Mo ⁶⁺
Ni	9.55	90.45	-	-	-	-	-
Ni ₅ Mo ₁	19.44	80.56	0.00	16.81	17.92	24.85	40.42
Ni ₅ Mo ₃	16.61	83.39	4.72	10.57	27.62	17.42	39.67
Ni5M05	17.53	82.47	5.52	16.32	25.49	19.89	32.79
Ni5M07	12.57	87.43	8.15	16.15	25.10	25.58	25.02
Мо	-	-	7.54	19.91	28.21	25.72	18.62

Table 2. Chemical state of Ni and Mo by XPS¹, %.

¹, calculated by the peak area of XPS.

Raman spectra of the catalysts before and after reduction are displayed in Figure 6. The peaks located at 373 cm^{-1} and 491 cm^{-1} in the calcinated Ni/SiO₂ can be attributed to the presence of nickel silicate and NiO, respectively [35]. With the introduction of Mo elements, the peak belonging to NiO gradually disappeared, which is consistent with the reported result that the NiO peak was obvious only when the MoO3 content was low [36]. The peak at 808, 905, and 955 cm⁻¹ indicated the presence of β -NiMoO₄ [37,38]. Compared with the larger NiMoO4 particle in the literature, the blue shift of these peaks meant that the particle size in this study was smaller than that in the literature. Further increase in the Mo content resulted in the shift of peaks above to 823, 898, and 953 cm^{-1} , which are consistent with the reported results of the simultaneous presence of NiO and MoO_3 [29]. For the Mo/SiO_2 before reduction, the peaks at 665, 814, and 991 cm⁻¹ meant that the Mo is mainly presented in the form of MoO₃ in catalyst [39]. In summary, the interaction between Ni and Mo in the Ni_5Mox/SiO_2 catalysts is strong, and the forms of MoOx were different in the catalysts. After reduction, there was still a weak NiO peak at about 500 cm^{-1} in Ni/SiO₂ and Ni₅Mox/SiO₂, which can be caused by oxidation during the passivation process. But the NiO peak disappeared and a new peak, which belonged to NiMoO₄, located at about 950 cm⁻¹, appeared in Ni₅Mo₃/SiO₂ and Ni₅Mo₅/SiO₂. However, the Raman spectra for Ni₅Mo₇/SiO₂, Ni₅Mo₁₀/SiO₂, and Mo/SiO₂ were still similar to those for the catalysts before reduction. This result indicated that the NiMo species on the surface might still be oxidized and possess strong interaction with each other. In summary, the interaction between Ni and Mo in the Ni_5Mo_X/SiO_2 catalysts is strong, the electron acquisition ability of Mo is enhanced, and more reduced Mo ions exist in the different forms of MoO_X in the catalysts.



Figure 6. Raman spectra of the catalysts after calcination (a) and reduction (b).

H₂-TPR was performed to investigate the reducibility of the catalysts, and the results can also prove the intensity of the interaction between Ni and Mo species. The profiles of Ni/SiO₂, Mo/SiO₂, and Ni₅Mox/SiO₂ were performed in Figure 7. Three obvious peaks located at 445, 552, and 717 °C were observed in the Mo/SiO₂. They were generally attributed to the conversion from Mo⁶⁺ to Mo⁵⁺, Mo⁵⁺ to Mo⁴⁺, and Mo⁴⁺ to Mo⁰ [40,41].

The peaks located at 350 °C and 600 °C in the profile of Ni/SiO₂ were attributed to the reduction of NiO and nickel silicate [42]. As most Ni was in the form of nickel silicate, the reduction peak of NiO was small. After the introduction of Mo, the reduction of nickel silicate became harder as the reduction peak moved to about 650 °C, which can be attributed to the transfer of electrons from Ni to Mo species because of the stronger electronegativity of Mo. And with the increase of Mo content, the electron-transfer effect between Ni and Mo is enhanced. Some oxides of Mo, such as MoOx, take electrons from the metal Ni to obtain nickel oxide to balance the electricity price of the catalyst in medium Mo and Ni. With the increase of Mo content, the reduction peak increases gradually, which can be attributed to the reduction of NiMoO₄, according to the XRD results. As was generally considered, the reduction of NiMoO₄ occurred in a wide temperature range [43,44]. The reduction peak in the range from 300 °C to 550 °C can be attributed to the reduction of the mixture of NiMoO₄ and excess MoO₃.



Figure 7. TPR profiles of Ni/SiO₂, Mo/SiO₂, and Ni₅Mox/SiO₂.

2.2. Evaluation of the Ni₅Mox/SiO₂ Catalysts

The performance of the Ni_5Mo_x/SiO_2 was evaluated and the reaction results of lauric acid are shown in Figure 8a. Mo greatly promoted the conversion of lauric acid. Compared with pure Ni catalyst, the conversion of lauric acid with Ni_5Mo_1/SiO_2 increased from 9.73% to 94.27%, and this promotion was further enhanced to 98.36% with Ni_5Mo_3/SiO_2 . For comparation, Ni/SiO₂ and Mo/SiO₂ were mixed physically to prepare the Ni₅Mo₃ mix sample and used in the HDO of lauric acid. As shown in Figure 8a, the conversion was 52.57%, which was higher than that of Ni/SiO₂ but much less than that of Ni₅Mo₃/SiO₂. This result indicated that the interaction between Ni and Mo played an important role in the HDO of lauric acid. And the stronger interaction in Ni₅Mo_x/SiO₂ than physically mixed NiMo catalyst greatly promoted the conversion of lauric acid. However, a further increase in the Mo content in Ni_5Mo_x/SiO_2 resulted in the reduction of lauric acid conversion. For the Ni_5Mo_{10}/SiO_2 , the conversion of lauric acid was only 53.67%. According to the N_2O titration results, the dispersion of Ni reduced with the increasing Mo content. This might result in a decrease in the density of active sites for hydrogenation, and the reduction of the catalytic activity. According to the reaction path in Scheme 1, lauric acid was converted to lauryl alcohol in the HDO first. After that, it was converted to undecane and dodecane through decarbonylation and hydrodehydration, respectively. Thus, lauryl alcohol was selected as the reactant to study the effect of Mo content on the selectivity to dodecane, and the results are shown in Figure 8b. Complete conversion can be reached with all the Ni_5Mo_x/SiO_2 catalysts except Ni_5Mo_{10}/SiO_2 , with which the conversion was 96.28%. With the increase of the Mo doping content, the selectivity to dodecane increased gradually and reached 78.58% with Ni_5Mo_{10}/SiO_2 . The results indicated that the Mo in the NiMo alloy played an important part in the increase of dodecane selectivity. However, the dispersion

of the Ni site was inhibited when the Mo content was high, which reduced the conversion of lauric acid, as shown in the case of Ni_5Mo_{10}/SiO_2 as the catalyst. To balance the activity and dodecane selectivity, Ni_5Mo_7/SiO_2 was selected in the next study.



Figure 8. (a) Mo content on the conversion of lauric acid, (b) Mo content on the conversion of lauryl alcohol and product selectivity with Ni_5Mox/SiO_2 , (c) initial H_2 pressure on the conversion of lauric acid and product selectivity with Ni_5Mo_7/SiO_2 , and (d) stability test of Ni_5Mo_7/SiO_2 .

The effect of H₂ initial pressure on the HDO of lauric acid was studied with Ni₅Mo₇/SiO₂. As performed in Figure 8c, H₂ initial pressure had no significant effect on the conversion of lauric acid within the study range. However, the selectivity of dodecane increased with the H₂ initial pressure and reached the plateau when pressure was above 4.67 MPa. This result can be explained easily as the dissociation of H₂ was an important step in the HDO. The stability of the Ni₅Mo₇/SiO₂ in the HDO of aliphatic acid was tested. The results are shown in Figure 8d. Complete conversion of lauric acid was reached with the fresh catalyst, and the selectivity to dodecane and undecane was 56.57% and 42.91%, respectively. Almost no lauryl alcohol and only a small amount of lauryl laurate were detected in the products. The conversion of lauric acid almost remained unchanged when the catalyst was reused six times. The selectivity to dodecane reduced a little when the catalyst was reused and eventually stabilized at about 50%. It can be concluded that the Ni₅Mo₇/SiO₂ possesses satisfactory stability in the HDO of lauric acid.

2.3. DFT Calculation

Three relaxed slabs for adsorption are displayed in Figure 9. For the Ni (111) slab, only one kind of Ni site exists. For the MoO_2 (011) slab, four kinds of O sites, as marked by the red cycle in the figure, and one kind of Mo site need to be studied. For the Ni_5/MoO_2 slab, the bottom Ni atoms tended to interact with MoO_2 (011) through the nearest Mo and O atoms. In addition to the same sites with the MoO_2 (011), the Ni sites in the Ni_5/MoO_2 model also need to be studied.



Figure 9. The slab model of (a) Ni (111), (b) MoO_2 (011), and (c) Ni_5/MoO_2 used in the adsorption.

The adsorption of methanol on different surfaces and sites was studied first, and the most stable adsorption configurations for each situation were displayed in Figure 10. On the Ni (111) surface, methanol was prone to adsorb on the top site of Ni via an O atom with an adsorption energy of -0.66 eV, as shown in Table 3. On the MoO₂ (011) surface, four kinds of O sites and one kind of Mo site were tested for the adsorption of methanol, and the most stable one was the top site of Mo via O atom of methanol with the adsorption energy of -1.81 eV. The adsorption of methanol on the Mo site of the Ni₅/MoO₂ model was similar to that of MoO_2 , but the adsorption energy reduced a little to -1.61 eV. Compared with the Ni (111) surface, the adsorption energy of methanol on the Ni site of the Ni_5/MoO_2 model increased to -0.88 eV. It can be concluded that the adsorption of methanol on MoO_2 was most stable [45]. The adsorption of methanol on the Ni(111) surface is the most unstable [46]. When the Ni₅ cluster was supported on MoO₂, the adsorption energy of methanol reduced a little. The adsorption of methanol on Ni₅ was stronger than on the Ni (111) surface but still much lower than the adsorption energy on MoO_2 . This result indicated that the interaction between Ni and MoO2 affected the adsorption of methanol, and it tended to adsorb on the MoO₂ site.

The adsorption energy of H showed a completely opposite trend to that of methanol, as performed in Table 3, which can be caused by the different adsorption configurations, as shown in Figure 11. The H was prone to be adsorbed on the fcc site of Ni with the energy of -0.64 eV and -0.26 eV for Ni (111) and Ni site of Ni₅/MoO₂, respectively. However, H tended to be adsorbed on the top site of Mo in the MoO₂ and Mo site of Ni₅/MoO₂ models, and the adsorption energy was 0.10 eV and 0.13 eV, respectively. This result indicated the unstable adsorption of H on the MoO₂, which meant that the activation of H₂ is unlikely to have occurred on the MoO₂ sites. Thus, the H₂ was prone to be activated on the Ni site even in the Ni₅/MoO₂ model. To balance the adsorption of methanol and the activation of H₂, the conjunction sites of Ni and MoO₂ may possess a stronger promoting effect on the HDO of methanol.



Figure 10. Most stable adsorption configuration and energy of methanol on slabs ((**a**): Ni (111) surface, (**b**): MoO₂ (011) surface, (**c**): Mo site of Ni₅/MoO₂ surface, and (**d**): Ni site of Ni₅/MoO₂ surface).

	NI: (111)	M-O (011)	Ni ₅ /MoO ₂	
	N1 (111)	MOO_2 (011)	MoO ₂ Site	Ni Site
Methanol H	−0.66 eV −0.64 eV	−1.81eV 0.10 eV	−1.61 eV 0.13 eV	−0.88 eV −0.26 eV

 Table 3. Adsorption energy of methanol and H atom on different surfaces and sites.



Figure 11. Most stable adsorption configuration and energy of H on slabs ((**a**): Ni (111) surface: 0.66 eV, (**b**): MoO₂ (011) surface: 1.81 eV, (**c**): Mo site of Ni₅/MoO₂ surface:1.61 eV, and (**d**): Ni site of Ni₅/MoO₂ surface: 0.88 eV).

Deformation charge-density analyses of the stable adsorption configurations were taken, and the results are shown in Figure 12. For the adsorption of methanol on Ni (111) in

Figure 12a, the electron density decreased near the O-Ni bond, but only increased slightly in the middle of the bond. However, the electron density around O and Ni increased, indicating that the stability of the adsorption was relatively low. In contrast, when methanol was adsorbed at the Ni site in Ni₅/MoO₂, the electron density of the O-Ni bond increased significantly, indicating that the adsorption of methanol became more stable, which was consistent with the calculated results of adsorption energy. As can be inferred from the stable adsorption configuration of methanol on the MoO₂ site, the H of hydroxyl tended to interact with the O atoms in MoO₂. Figure 12c,d showed that after methanol was adsorbed on the MoO₂ site, the electron density of hydroxyl H decreased, while the electron density of O that interacted with MoO₂ increased.



Figure 12. Deformation charge-density results of the adsorption of methanol on (**a**) Ni (111), (**b**) MoO₂ (011), (**c**) MoO₂ site of Ni₅/MoO₂, and (**d**) Ni site of Ni₅/MoO₂ (Arrows indicate side view direction).

A COHP analysis was taken on the C-OH bond of the methanol in gaseous and stable adsorbed states. As the spin polarization of the systems containing Ni had little influence on methanol, the spin up orbit was selected here for analysis and comparison. The analysis result of methanol in a gaseous state was shown in Figure 13a. As the ICOHP was -2.92 eV, the C-OH bond was stable in free methanol. When methanol was adsorbed on Ni (111), the Fermi level increased and some of the antibonding orbitals became lower than the Fermi level. Compared with the gaseous state, the stability of the C-OH bond became weaker as the ICOHP was -1.15 eV. When methanol was adsorbed on MoO_2 (011), the dispersion of antibonding orbitals above the Fermi level intensified and some of them fell below the Fermi level, which weakened the ICOHP to -0.28 eVand further activated the C-OH bond. However, when methanol was adsorbed on the surface of Ni_5/MoO_2 , the ICOHP of the C-OH bond was 0.59 eV and 0.37 eV for the adsorption on the Ni and MoO₂ site, which indicated that the C-OH bond was very weak. Meanwhile, the adsorption on the MoO_2 site resulted in the more diffuse antibonding orbitals of the C-OH bond near the Fermi level, indicating a stronger interaction between methanol and MoO₂. In conclusion, the MoO₂ sites of Ni_5/MoO_2 were more favorable for the activation of the C-OH bond of methanol.



Figure 13. COHP results of the C-OH bond in (**a**) gas methanol and adsorbed on (**b**) Ni (111), (**c**) MoO₂ (011), (**d**) Ni site of Ni₅/MoO₂, and (**e**) MoO₂ site of Ni₅/MoO.

3. Discussion

Based on the previous study on the reaction pathway of the HDO of aliphatic acid, it is favorable for carbon utilization and reducing the H2 consumption if the decarbonylation of aliphatic aldehyde was suppressed, but the hydrodehydration was promoted simultaneously. NiM/SiO₂ (M = Ce, Co, Cu, Fe, Sn, Zr, and Mo) catalysts were prepared by introducing the second metal into Ni/SiO₂. Evaluation results indicated that the Ni₅Mo₁/SiO₂ catalyst promoted the conversion of lauric acid from 25.76% to 100%, and the selectivity to dodecane increased from 2.30% to 19.33%. A further study showed that, with the increase of Mo content in the catalysts, the conversion of lauric acid increased first and then decreased; however, the selectivity to dodecane increased in the catalytic hydrogenation of lauryl alcohol, which indicated that Mo plays an important role in the catalytic hydrogenation of lauryl alcohol. Considering both the conversion of lauric acid and the selectivity to dodecane, the Ni_5Mo_7/SiO_2 was selected as the suitable catalyst, resulting in the total conversion of lauric acid with 59.63% selectivity to dodecane. And the selectivity can be further increased to more than 70% with higher H_2 initial pressure. The stable activity of Ni₅Mo₇/SiO₂ was proved as the lauric acid can be totally converted to alkanes after the catalyst had been used six times. The selectivity to dodecane also remained stable, which reduced from 56.57% with a fresh catalyst to about 50%. For comparation, monometallic Ni/SiO₂ and Mo/SiO₂ were mixed with the molar ratio of Ni and Mo of 5:3 and used in the HDO of lauric acid. Although the conversion of lauric acid was promoted compared with the Ni/SiO₂ only, the activity is much weaker than that of Ni₅Mo₃/SiO₂, which indicated that the interaction between Ni and Mo in the bimetallic catalyst played an important role. Strong interaction between Ni and Mo was proven based on the XPS characterization results, which promoted the reduction of the Mo precursor and resulted in the higher content of Mo species with lower valance, but the electron density around the Ni sites was reduced in the DFT calculation. According to the calculated dispersion results, the dispersion of Ni reduced with the increase of Mo content. As the Ni sites were favorable for the dissociation of H_2 in the HDO process, the lower dispersion may reduce the hydrogenation activity of the catalysts with higher Mo content. Thus, the Mo content needs to be controlled for the dispersion of Ni. The mechanism study indicated that the alcohol tended to adsorb on the Mo site, which can be caused by the hydrogen bond formed by the O near the Mo site with the hydroxyl H in the alcohol. Further COHP analysis proved that when alcohol was adsorbed on Ni_5/MoO_2 , the ICOHP of the C-OH bond changed from -2.92 eV in a gaseous state to a positive value, which meant that the bond had been fully activated. Additionally, compared with the monophase MoO₂ surface, the introduction of the Ni5 cluster further activated the C-OH bond. The calculation results above demonstrated that the introduction of Mo into the Ni-based catalyst promoted the adsorption of aliphatic alcohol, the intermediate of the HDO of aliphatic acid, and the

C-OH bond can be activated, which was facilitated for the hydrodehydration of aliphatic alcohol and the production of alkanes-Cx.

4. Materials and Methods

4.1. Catalyst Preparation

Several catalysts marked as NixMy/SiO₂ (M = Fe, Cu, Co, Sn, Zr, Ce, Mo) were prepared, and the x and y indicated the molar ratio of Ni and M. For the preparation of the catalysts with M being Fe, Cu, Co, Sn, Zr, and Ce, the deposition–precipitation method was used. The solution with a metal-ion concentration of 0.1 M was prepared and dropped into the SiO₂ support slowly with stirring. Then, 1M urea solution was added slowly into the solution above, so the molar ratio between urea and metal ion was 10:1. After being heated for 8 h with stirring, the sediment was filtered and washed with deionized water and dried in the oven for 12 h at 80 °C. For the preparation of NixMoy/SiO₂, in order to increase the dispersion of Mo, ammonium carbonate was selected as the precipitant because of the low decomposition temperature, as the (NH₄)₆Mo₇O₂₄·4H₂O cannot be precipitated by the deposition–precipitation method, the water was evaporated with a rotary evaporator, and the product was dried in the oven for 12 h at 80 °C. Then, all catalysts were calcinated at 550 °C in N₂ for 4 h. Before being used, the catalysts were reduced at 600 °C in pure H₂ for 2 h and passivated in 1%O₂/N₂ after the reduction temperature was reduced to room temperature.

4.2. Catalyst Characterization

The metal loading amount was determined by a Varian VISTA-MPX inductively coupled plasma optical emission spectrometer (ICP-OES, Palo Alto, CA, USA). It was operated under 15 kW high-frequency emission power and 15 mL/min plasma airflow rate. About 50 mg of catalysts were dissolved in 1 mL HF first, and aqua regia was added if the catalyst was difficult to dissolve. After the catalyst was completely dissolved, 15 mL saturated H3BO3 solution was added to complex the HF. Finally, the solution was diluted to 50 mL. The phase information of the catalysts was determined by X-ray diffraction (XRD). XRD patterns were collected with a Panalytical X'Pert Pro (Malvern, UK) equipped with Cu K α radiation run at 40 kV and 40 mA in the range of $2\theta = 10$ to 80° with a scanning rate of 0.17 °/s. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM) morphology images high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDS) of the catalysts were collected on a JEOL JEM-F200 (Tokyo, Japan) field emission transmission electron microscope with an electron energy of 200 kV. Passivated catalysts were sonicated in ethanol and then dispersed on an ultrathin Cu grid-supported carbon film. To get a clean surface in the HAADF and mapping, a beam shower was taken for 30 min to clean the surface contamination. H2 temperature programmed reduction (H2-TPR) was conducted with Micromeritics AutoChem II 2910 equipped with a TCD detector (Micromeritics Instrument Corporation, Norcross, GA, USA). Typically, a 50 mg calcinated catalyst was loaded in the U-type tube. After pretreatment at 200 °C for 1 h and cooling to room temperature, the catalyst was heated to 750 $^{\circ}$ C at 10 $^{\circ}$ C/min under 10% H₂/Ar. Signals were recorded during the heating process. Dispersion of Ni in the catalysts was determined by the N_2O titration with a Micromeritics AutoChem 2910. After being loaded in the tube, the catalyst was reduced at 600 °C for 1h and then cooled to 90 °C. Then, the sample was treated with N_2O for 1h to oxidize the metals of the outer layer. After that, the system was heated to 300 $^{\circ}$ C in Ar and then titrated by 10% H₂/Ar. Dispersion of Ni can be calculated by the H2 consumption. X-ray photoelectron spectra (XPS) of the passivated catalysts were performed on a ThermoFisher Scientific K-Alpha+ (Waltham, MA, USA) at 5×10^{-8} Pa, and Al Ka X-ray radiation was the X-ray source. C1s binding energy at 284.8 eV was taken as a reference value to calibrate the binding energy. Raman analysis of the NixMoy/SiO₂ was performed on a HORIBA LabRAM HR Evolution (Kyoto, Japan) equipped with a laser beam of 532 nm. Spectra were collected by 10 accumulated scanning signals, where

each scan time was 10 s. The Vienna Ab-initio Simulation Package (VASP) with projector augmented wave (PAW) was used to understand the adsorption of aliphatic alcohol and the activation of hydroxyl on Ni and Mo. Generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) was used to treat the exchange-correlation potential of electrons. The kinetic cutoff energy for electronic states was expanded on a plane-wave basis and was set as 450 eV. The energy and force tolerances for geometry optimization were 10^{-6} eV and 0.02 eV/Å, respectively. Only the gamma point was used to sample the first Brillouin zone. For the model containing a Ni atom, the spin-polarization effect was considered in the calculation. Grimme's DFT-D3 method was used to take van der Waals interaction in the adsorption model into consideration. The optimized lattice constant of Ni is 3.516 Å, which is close to 3.524 Å from the standard XRD PDF 04-0850. Ni/SiO₂ was represented by a p ($4 \times 4 \times 4$) Ni (111) slab with a 20 A vacuum region being built, and the bottom two layers of the atom were fixed before surface relaxation. In the construction of the NiMo model, most Mo in Ni₅Mo₇/SiO₂ exists in an incomplete reduced valence state. Therefore, the NiMo surface model is constructed by MoO_2 (011). MoO_2 was selected as the model form of partial reduction [47,48]. After cell optimization, the lattice parameters for MoO₂ were $\alpha = \gamma = 90^{\circ}$, $\beta = 120^{\circ}$, a = 5.55 Å, b = 4.88 Å, and c = 5.65 Å. A p (4 × 4 × 2) MoO_2 (011) slab with a 20 Å vacuum region was used to represent the Mo/SiO_2 . During the relaxation and calculation, the bottom layer of MoO_2 was relaxed. As for the Ni_5Mo_x/SiO_2 catalyst, the Ni₅ cluster supported by MoO₂ (011) was used to represent it.

The adsorption energies of alcohol and H were calculated by the following formula

$$E_{ads} = E_{slab + adsorbate} - E_{slab} - E_{adsorbate}$$

where E_{ads} , $E_{slab+adsorbate}$, E_{slab} , and $E_{adsorbate}$ represented the adsorption energy, energy of the adsorption model, energy of the slab, and energy of the adsorbate. For alcohol, the adsorbate energy represented the value in the gas. Methanol, the simplest alcohol, was selected as the probe molecule as the main concern was the activation of the C-OH bond. For the adsorption of H, 1/2 of the H₂ gas energy was used to represent the energy of the H atom.

4.3. Catalytic Reactions and Product Analysis

The catalysts were evaluated in a 100 mL autoclave equipped with mechanical agitation. In a typical run, the catalyst (0.02 g), reactant, tridecane (internal standard, same mass as the reactant), and n-decane (18 g) were mixed in the clave. Then, 5 MPa H₂ were pressed into the clave 3 times to replace the air in it; and then, 3.5 MPa H₂ was pressed in. After leak hunting, the reactor was heated to the desired temperature with 500 rpm stirring. After the reaction, the liquid product was collected and filtered for the off-line analysis. The solid catalyst was also collected, washed with ethanol, and dried for further characterization. Quantitative analysis of the liquid product was taken by gas chromatography analysis with a Beifen SP-3420A (Beijing, China) equipped with a flame-ionization detector (FID) and KB-1 capillary column (30 m × 0.25 mm × 0.25 µm). Qualitative analysis of aliphatic acid catalytic hydrogenation products was taken on an Agilent GC-7890B MSD-5799A (Palo Alto, CA, USA) gas chromatography-mass spectrometry equipped with an FID detector and an Agilent HP-INNOWAX capillary column (50 m × 0.2 mm × 0.4 µm).

5. Conclusions

Through the characterization of the catalyst series, there is an interaction between Ni and Mo sites: the incorporation of Mo significantly promotes the adsorption process of the aliphatic acids on the catalyst surface. In the process of further conversion of aliphatic alcohols to alkanes, Mo incorporation significantly promoted the activation of C-OH bonds and ultimately improved the selectivity of hydrodeoxygenation products. The stability evaluation results of Ni₅Mo₇/SiO₂ showed that the catalyst could still achieve complete conversion of lauric acid after repeated use six times. And the selectivity of dodecane was finally maintained at about 50%. The DFT calculation results show that the incorporation of

Mo in the Ni-based catalyst can promote the adsorption of alcohols on the catalyst surface. The COHP analysis results show that the Mo site can significantly activate the C-OH bond, thereby promoting the conversion of aliphatic alcohols to aliphatic hydrocarbons through hydrodeoxygenation. However, due to the decrease of the electron-cloud density at the Ni site, the H_2 dissociation process is inhibited to a certain extent. Therefore, the boundary position of Ni and Mo sites is conducive to the dissociation of H₂ and the adsorption of aliphatic alcohols, thereby promoting the formation of carbon alkane and improving the utilization of carbon atoms. The NiMo interaction can significantly improve the carbon atom utilization and reduce the hydrogen consumption in the process of aliphatic acid forming alkanes by HDO. However, the increase in the doping amount of Mo leads to a rapid decline in the dispersion of Ni, thus weakening the hydrogenation activity. Therefore, it is necessary to further prepare highly dispersed NiMo catalysts, and the NiMo bimetallic cluster catalysts are undoubtedly ideal, but the preparation difficulty is relatively high; for example, cluster metal catalysts suffer from poor stability, as they are prone to aggregation and inactivation issues. Moreover, the production process requires strict control over the reaction temperature and pressure. Furthermore, the application range of cluster catalysts is limited, necessitating the need to study and optimize different reaction systems to broaden the scope of catalyst application. So, further research is needed.

Supplementary Materials: The following supporting information can be downloaded at: https:// www.mdpi.com/article/10.3390/catal13101329/s1, Figure S1: TEM image of Mo/SiO₂; Figure S2: XRD patterns of Ni₅M₁/SiO₂; Figure S3: XRD patterns of Ni/SiO₂, Mo/SiO₂ and NixMo₅/SiO₂; Table S1: Accurate metal loading and Ni dispersity of Ni/SiO₂, Mo/SiO₂, and Ni5Mox/SiO₂; Table S2: Chemical state of Ni by XPS a, %; Table S3: Chemical state of Mo by XPS a, %; Table S4: Effect of Mo content on the conversion of lauric acid and product selectivity.

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