Phase Composition and Catalytic Reactivity of α–NiMoO$_4$ Reduced with Hydride Anion

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Abstract

An attempt was carried out to improving the catalytic performance of α–NiMoO$_4$ in partial oxidative dehydrogenation of alkanes, different catalyst samples were reduced by hydride anion H$^-$ using CaH$_2$ in temperature range (100-450°C). The catalytic performance of the resulting catalyst samples in the oxidative dehydrogenation of cyclohexane at different temperatures and at atmospheric pressure was investigated. Phase composition of molybdate and reduction products was analyzed by XRD. Reduction of α–NiMoO$_4$ with CaH$_2$ at temperatures above 200°C yielded reduction products, consisting of crystalline Ni and MoO$_2$, intermetallics compounds between Ni and Mo and incompletely reduced α–NiMoO$_4$. Whereas, reduction of α–NiMoO$_4$ with H$_2$ is not possible under the same conditions applied. Nickel molybdate catalyst; reduced with CaH$_2$ at 300°C, showed a high selectivity towards cyclohexene in reaction temperature range 300- 500°C, in comparison with that of parent α–NiMoO$_4$ and that of catalyst reduced with hydrogen. In view of the XRD results, the significant high selectivity of this catalyst towards cyclohexene was attributed to the fact that reduction by CaH$_2$ modified crystal structure "cell dimensions" of the incompletely reduced α–NiMoO$_4$. On the other hand, a synergetic effect between the new phases founded in this catalyst sample after reduction and the incompletely reduced α–NiMoO$_4$ was proposed.

1- Introduction

The discovery of new ways to master metal oxides selectivity in catalytic oxidation of alkanes is still a great challenge.[1] Different groups of investigators have done several trials in this field by adding gaseous promoters (Viz., CO, CO$_2$, NH$_3$, N$_2$O and H$_2$) into reaction feed.[2-4]. The presence of hydrogen brought about conspicuous changes in the selectivity of catalytic oxidation reactions, permitting the production of unexpected molecules .[5,6] The role of hydrogen in selective oxidation is attracting much attention, recent investigations suggested that hydrogen modifying the chemical state of the active sites of the catalysts.[6] Indeed, controlled reduction of metal oxides using hydrogen could offer new promising approach for modulating the nature of catalytic oxidation sites.

Nickel molybdate catalyst was widely investigated in connection with its industrial application in ODH of alkanes (C$_2$-C$_4$).[7-9] It is well known that, nickel molybdate formed principally in two phases α- and β phase, where Mo is octahedral coordination in α– phase and tetrahedral in β–phase. Previous investigations have shown that the catalytic performance of this catalyst is closely related to its molybdenum coordination.[10,11] An effective controlled reduction of α–NiMoO$_4$ using hydrogen gas can open a new gate to modulate Mo

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coordination and subsequently master catalytic performance. However, the mechanism of reduction of α–NiMoO₄ with H₂ is still debated, especially at temperatures below 500°C .[7,12,13] Therefore, there is clearly a need to use reducing agents that are effective at lower temperatures to avoid complete reduction of α–NiMoO₄ to their metals.

The hydride anion is one of the most powerful reducing agents known; the reduction potential of the H⁻/H₂ couple has been estimated at -2.25 V.[14] A variety of highly metastable oxides of specific electronic and magnetic properties were prepared by reduction of complex oxides by the hydride anion using different metal hydrides (viz.; LiH, NaH).[15-18] Recently, CaH_2 has been used as a powerful reducing agent in solid-state topotactic reduction, at lower temperatures than would be required for H₂ gas process.[19] In addition, CaH_2 has a higher decomposition temperature (~ 880°C) than the other solid hydrides, which could be used to carry out solid-state reduction over a wide temperature range. The development of a new synthetic route based on reduction of the metal oxide catalysts using CaH_2 can probably provide the possibility of modifying selectivity and/or activity of these catalysts in oxidative dehydrogenation (ODH) of alkanes.

In the present work an attempt, has been done to produce a change in the molecular structure "coordination" of α–NiMoO₄ by controlled reduction using CaH_2 at different temperatures.[19] The reactivity of all catalysts was tested for the oxidative dehydrogenation of cyclohexane as a model reaction, looking for a significant modification in catalytic performances. H₂ was also used to prepare a reference sample. The phase composition of the studied catalysts was investigated by XRD and the change in the structure "cell dimensions" of α–NiMoO₄ was analyzed.

2-Experimental

Pure stoichiometric α–NiMoO₄ was prepared by co-precipitation from aqueous solutions of 750 ml of 0.057 M ammonium heptamolybdate (Merck 99+%) and 750 ml of 0.4 M of nickel nitrate (Aldrich 99+%) in the thermo-regulated conditions at temperature of 63 °C and at pH = 6.0.[20]

Different α–NiMoO₄ samples were reduced using CaH_2 (Aldrich, 99.9%) following the reported procedure in literature.[19,21] α–NiMoO₄ sample was mixed and ground with CaH_2 in stoichiometric ratio in He-filled glove box, and then sealed in an evacuated Pyrex ampoule ($p < 2 \times 10^{-4}$ torr). The sealed reaction vessel was then heated for two periods of 3 days at 100°C. The byproduct (CaO) was removed from the produced solid by washing with a solution of 1M NH_4Cl in CH_3OH, in a Schlenk filter under a nitrogen atmosphere. The produced solid was then further washed with CH_3OH before drying under vacuum ($p < 1 \times 10^{-1}$ torr); the resulted catalyst was denoted NMH1. The complete removal of CaO from catalyst sample was confirmed by both X-ray diffraction (XRD) and Energy dispersive X-ray (EDX) analyses. Reduction of another α–NiMoO₄ samples was carried out at other temperatures 200, 300 and 450°C following the same procedure as above; the catalysts were denoted as NMH2, NMH3 and NMH4, respectively. Reference sample (denoted as NMH₂) was reduced by a gas mixture consisting of 5 % hydrogen in helium (40 ml/min) at 450°C for 4 h.

X-ray diffraction (**XRD**) measurements were performed using a Philips Pert-MPD (multipurpose X-ray diffractometer) employing Cu $K_{\alpha1, 2}$ radiation (λ = 1.5405 Å) for 2θ angles varying from 10° to 80°. The scan rate was 0.4 degree/min corresponding to a step size of 0.04° and a step time of 3 s. Cell dimensions analysis was performed with the program Win cell 1.1.

Particle size ($t(Å)$) of $\alpha-NiMoO_4$ was calculated by using Scherrer formula: $t(Å) = 0.92\ \lambda\ /B\ \cos\theta$; where B is the width at the half maximum of the peak at $2\theta = 28.817$ degree

Catalytic activity measurements were performed employing a conventional fixed-bed reactor system using air as the carrier gas for the cyclohexane feed.[22] The following reaction conditions were employed: catalyst weight, 0.2 g; flow rate of air, 20 ml/min; molar feed rate of cyclohexane, 4×10^{-3} mol/h; reaction temperature, 200–500°C.
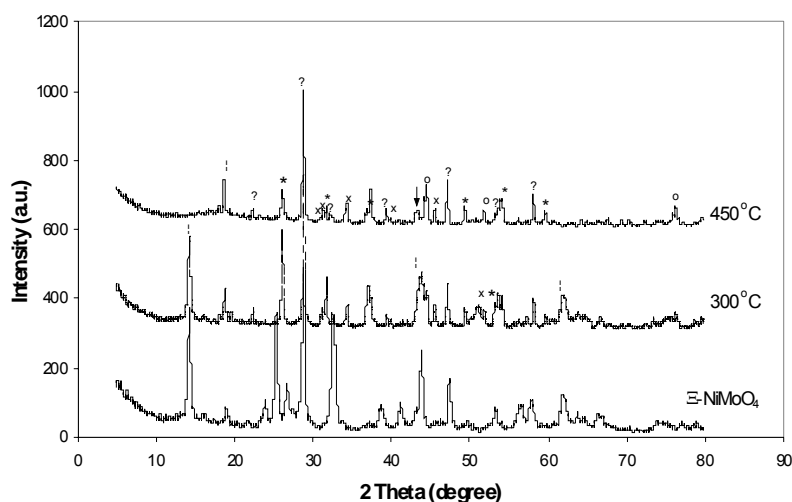
3- Results and Discussion

Fig. 1. XRD patterns of parent $\alpha-NiMoO_4$ and the samples reduced by CaH_2 at 300°C and 450°C. Peaks marked by the symbols "■", "*", "○" and "x" indicate those peaks assigned to $\alpha-NiMoO_4$, MoO_2, Ni and intermetallic compound between Ni and Mo, respectively.

Figure 1 shows the X-ray diffraction patterns of the parent nickel molybdate and samples reduced by CaH_2 at 300°C and 450°C. The prepared nickel molybdate showed a diffraction pattern which corresponds to pure $\alpha-NiMoO_4$ (JCPDS standard file, 33-0948). Reduction of $\alpha-NiMoO_4$ samples at 100°C and 200°C resulted in no observable change to the X-ray powder diffraction patterns of theses samples. However, reduction of $\alpha-NiMoO_4$ at 300°C (Figure 1(b)) produced the following phases: MoO_2 (JCPDS file 78-1071), Ni (JCPDS file 04-0850). In addition, the peaks characteristics of $\alpha-NiMoO_4$ were detected, which indicates no full conversion under these reaction conditions. Furthermore, new weak peaks of d spacing 4.52, 3.97, 2.89, 2.86, 2.60, 2.26, 1.99, 1.78, 1.65 Å were also detected, which are possibly referred to $MoNi_4$ (JCPDS file 03-1036) and/or MoNi (JCPDS file 48-1745) whose characteristic lines are almost coincident. Similar phases (MoO_2, Ni, $\alpha-NiMoO_4$ and NiMo intermetallics compounds) were detected in the XRD pattern of the sample reduced at 450°C (Figure 1 (c)). However, the following differences were observed between the diffraction pattern recorded at 300°C and that one recorded at 450°C: i) a significant decrease in the intensity of the peaks characteristic of incompletely reduced $\alpha-NiMoO_4$, ii) the peaks of $\alpha-NiMoO_4$ at $2\theta = 14.10°$, 43.94° and 62.20° disappeared completely, iii) the peaks characteristics of MoO_2 and Ni in NMH4 pattern have a higher intensity than that observed in the pattern of NMH3 sample, iv) one of the peaks characteristics of MoNi intermetallic compound also disappeared which at $2\theta = 51.20°$; and v) a new peak was appeared at $2\theta = 43.05°$ (d spacing = 2.09 Å), this peak probably due to $Mo_{1.24}Ni_{0.76}$ phase (JCPDS file 47-1129). These mentioned above observations indicating that reduction of $\alpha-NiMoO_4$ to MoO_2,

and Ni by CaH_2 is more effective at 450^oC than at 300^oC. In contrast, the X-ray diffraction pattern of sample reduced at 450^oC clearly presents only peaks due to α- $NiMoO_4$. However, the intensities of all the peaks decreased after reduction accompany with peaks broadening and increasing the background (Figure 2). In contrast, the XRD pattern of the sample reduced by H_2 at 450^oC showed only the peaks characteristics of α-$NiMoO_4$ with a significant decrease in their intensities (Figure 2).

Figure 3 represent the variation of cyclohexane conversion rate over catalysts under investigation (pure α-$NiMoO_4$, NMH_2, NMH3 and NMH4) with reaction temperature. It is clear that the parent α-$NiMoO_4$ catalyst exhibited the highest activity at reaction temperatures above 300^oC; where it has conversion rate ca. 2.0 times higher than that of the other catalysts. However, all catalysts studied were found to obey the same trend of the variation of cyclohexane conversion rate with reaction temperature namely, the conversion rate increased with increasing temperature, attained a maxima value at ca. 450^oC and then remained nearly constant up to 500 ^oC. On the other hand, catalyst samples reduced either with H_2 or CaH_2 afforded approximately the same conversion rate in the high temperature range 400-500 ^oC.
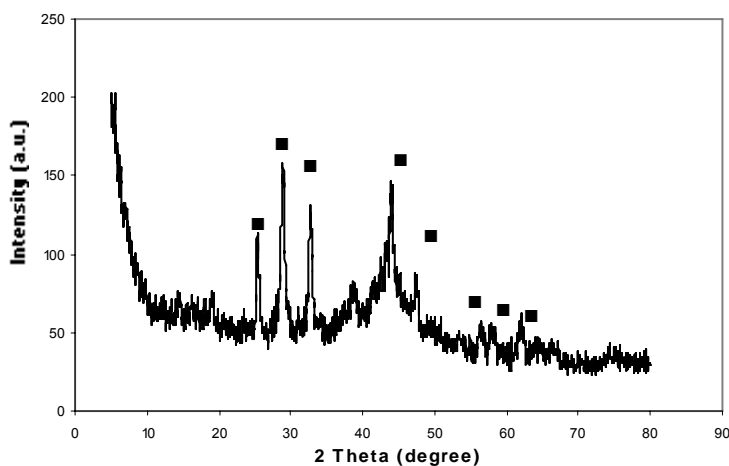

Fig. 2 . XRD patterns of α−$NiMoO_4$ reduced by H_2 at 450^oC. Peaks marked by the symbols "■", indicate those peaks assigned to α−$NiMoO_4$

The oxidation of cyclohexane over all catalysts understudy yielded cyclohexene, 1,3-cyclohexadiene and benzene as organic products as well as CO_2 and CO as inorganic carbon products. The patterns of distribution of the yielded reaction products (in wt %) over parent α-$NiMoO_4$, NMH_2, NMH3 and NMH4 catalysts as a function of reaction temperature are shown in Figure 4; because of the very low CO concentration, its yield was not taken into account. In the case of parent α−$NiMoO_4$ (Figure 4 (a)), benzene was the predominant product detected together with traces of cyclohexene, cyclohexadiene and CO_2 at all temperatures. The weight percentage of benzene increased with increasing temperature and reached a maximum at about 400^oC and then decreased at 450^oC. However, with NMH_2 catalyst (Figure 4 (b)), a significant decrease in the benzene weight percentage was observed which accompanied with an increase in cyclohexene (wt %) at all reaction temperatures, but benzene is still the predominant product above 350^oC.
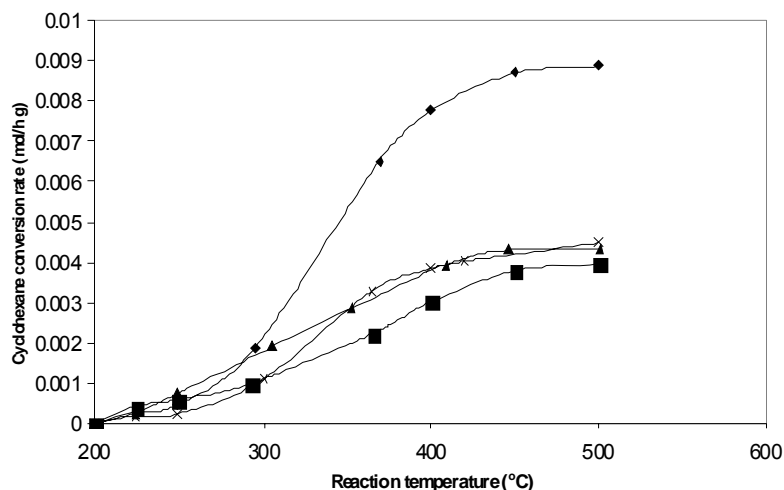
Fig. 3. Cyclohexane conversion rate over ($\blacklozenge$) parent $\alpha-NiMoO_4$ ($\blacksquare$) $\alpha-NiMoO_4$ reduced by H_2 at 450^oC, ($\blacktriangle$) $\alpha-NiMoO_4$ reduced by CaH_2 at 300^oC and (X) $\alpha-NiMoO_4$ reduced by CaH_2 at 450^oC.

On the other hand, the weight percentage of benzene attained a maximum at about 350^oC and then remained nearly constant up to 500^oC. In contrast, with NMH3 and NMH4 catalysts cyclohexene was the major product detected at all reaction temperatures, benzene and CO_2 were also detected in addition to cyclohexene, together with a very small trace of cyclohexadiene (Figure 4 (c and d)).
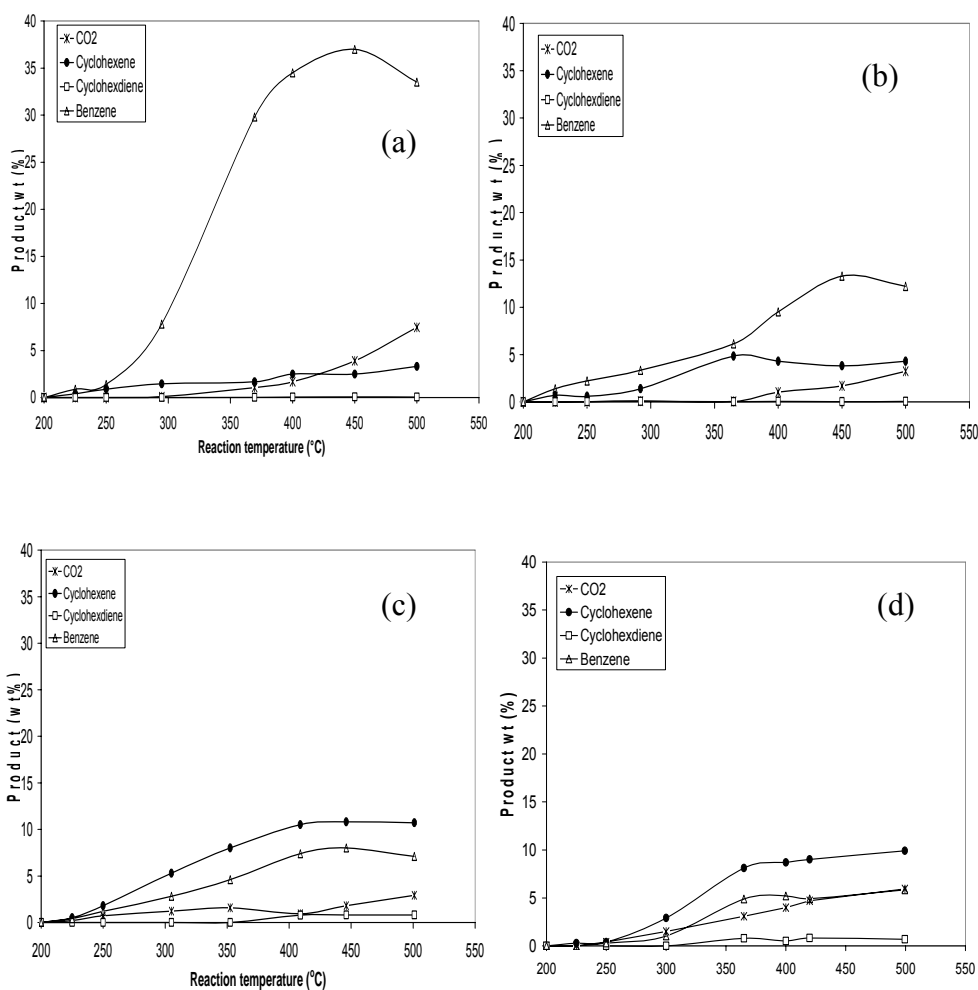
Fig. 4. Distribution of the reaction products in wt (%) of ODH of cyclohexane over (a) parent $\alpha-NiMoO_4$, (b) reference sample reduced by H_2 molecule at 450^oC and (c and d) samples reduced by CaH_2 anion at 300^oC and 450^oC respectively, as a function of reaction temperature.
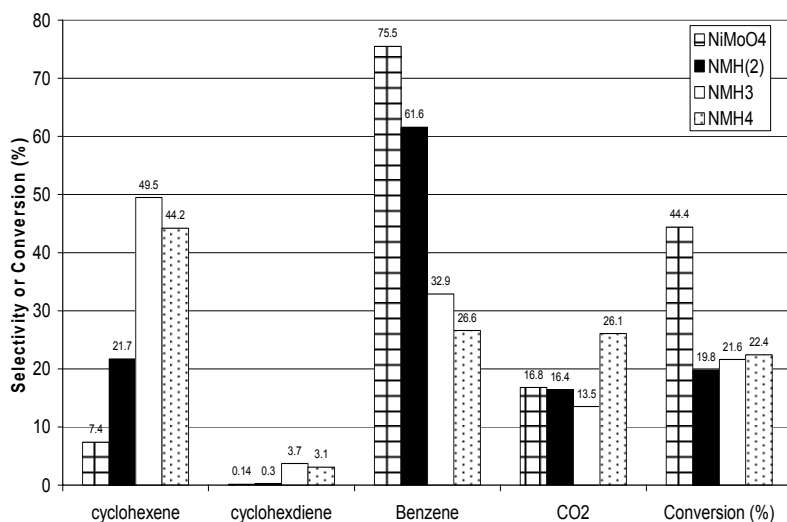

Fig. 5. Comparison of conversion of cyclohexane and selectivities of cycloexene, cyclohexadiene, benzene and CO_2 measured at 500^oC between studied catalysts.

The activity results for ODH of cyclohexane over studied catalysts at 500^oC are summarized in Figure 5. it is clear that parent α-NiMoO$_4$ exhibited the highest selectivity towards benzene selectivity (75.5%) with 44.4 % conversion. However, NMH3 catalyst is the most selective towards cyclohexene (49.5%) but with low conversion (21.6 %). Theses results verified that reduction of α-NiMoO$_4$ by CaH$_2$ leads to a significant modifications in catalytic performance. Similar tendencies were observed at the other reaction temperatures.

According to the XRD results of NMH3 and NMH4 catalysts, reduction of α-NiMoO$_4$ by CaH$_2$ produced MoO$_2$, Ni, intermetallic compounds of different Mo/Ni ratio and α-NiMoO$_4$"ICR". As already observed NMH3 and NMH4 catalysts have lower cyclohexane conversion than parent α-NiMoO$_4$. This may indicate that these phases are inactive. However the high selectivity of these catalysts towards cyclohexane might be affected by the presence of these phases. It seems that there is a synergetic effect between theses phase and α-NiMoO$_4$"ICR", but the exact role of these phases can not stated on the basis of this work.

On the other hand, significant changes were observed in the crystal structure "cell dimensions" of α-NiMoO$_4$"ICR" phase founded in NMH3 and NHM4 catalysts (Table 1). Where there is an expansion in the *"b"* and *"c"* axes and simultaneous contraction of the *"a"* axis were occurred, which accompanied with an increase in the $\alpha-NiMoO_4$ particles size. Such behaviour can be expected in $\alpha-to-\beta-$ NiMoO$_4$ transition induced by change in temperature. But these modifications are completely different than that observed in the above mentioned transition.[23,24] The marked changes in cell dimensions of $\alpha-NiMoO_4$ observed after reduction by CaH$_2$ may reflect a change in the coordination of Mo namely, a possible "metastable coordination". This phenomenon can give an explanation for the observed high

selectivity of these samples towards cyclohexene. It is important to mention that, no big change was observed in the estimated lattice parameters "cell dimension" of $\alpha-NiMoO_4$ sample reduced by H_2.

Table 1.
Calculated cell dimensions and particle size of parent $\alpha-NiMoO_4$ before reduction and after reduction with CaH_2 at different temperatures.

Catalyst	a [Å]	b [Å]	c [Å]	β	t (Å)
$\alpha-NiMoO_4$	9.5741	8.7440	7.6552	114.136	213.5
NMH3	8.9716	9.4902	8.7932	102.231	345.2
NMH4	9.0917	9.4502	8.7344	102.621	334.8

N.B. *the estimated cell dimensions of the parent $\alpha-NiMoO_4$ are very close to those reported in ref. [23].*

The outcome of the reactions of $\alpha-NiMoO_4$ with both CaH_2 and H_2 is completely different. This may be due to the difference between the two processes in both nature of reducing species and the reaction pathways. CaH_2 thermally decomposes at 880^oC mainly H^- may be present as reducing agent at the temperatures used (300 and 450^oC).[19, 25] Hayward et al., reported that reduction of metal oxides by H^- could produce metal oxide hydrides. In this case, one can not exclude that nickel molybdenum oxide hydride ($NiMoO_{4-x}H_x$) may be formed as an intermediate of specific molybdenum coordination.[19] The changes observed in the cell dimensions of the $\alpha-NiMoO_4$"ICR" may give an induction about the formation of this intermediate. The proposed intermediate might be converted to the detected intermetallic phases through disproportionation reaction with CaO.[19]

4. Conclusions

H^- anion is a promising reducing agent for activation of $\alpha-NiMoO_4$ in partial oxidative dehydrogenation of alkane (viz.., cyclohexane to cyclohexene) in comparison with H_2 molecule. Calcium hydride allowed the reduction of $\alpha-NiMoO_4$ to Ni and crystalline MoO_2 at 300^oC where H_2 was not effective. Nickel molybdenum oxide hydride was proposed to be an intermediate or starting compound of reduction of $\alpha-NiMoO_4$ with H^- anion. To clarify this hypothesis, further specific characterization studies are still required, which is beyond the frame of this work. In addition, optimization of reduction conditions is necessary to avoid transfer a large amount of $\alpha-NiMoO_4$ to other phases.

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