In Situ H$_2$ Reduction of Al$_2$O$_3$-Supported Ni- and Mo-Based Catalysts

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Abstract: Nickel (Ni)-promoted Molybdenum (Mo)-based catalysts are used for hydrotreatment processes in the chemical industry where the catalysts are exposed to high-pressure H$_2$ at elevated temperature. In this environment, the catalyst transforms into the active phase, which involves the reduction of the oxide. Here, we report on the first in situ study on the reduction of alumina supported Ni- and Mo-based catalysts in 1 mbar H$_2$ using ambient-pressure X-ray photoelectron spectroscopy (APXPS). The study confirms that mixing Ni and Mo lowers the reduction temperature of both Ni- and Mo-oxide as compared to the monometallic catalysts and shows that the MoO$_3$ reduction starts at a lower temperature than the reduction of NiO in NiMo/Al$_2$O$_3$ catalysts. Additionally, the reduction of Ni and Mo foil was directly compared to the reduction of the Al$_2$O$_3$-supported catalysts and it was observed that the reduction of the supported catalysts is more gradual than the reduction of the foils, indicating a strong interaction between the Ni/Mo and the alumina support.

Keywords: bimetallic catalysts; X-ray-based methods; NiMo-alumina; reduction; in situ; APXPS; catalysis; XANES

1. Introduction

Mo-based catalysts are widely used in catalytic hydrotreating processes and act as a workhorse in the chemical industry [1]. These catalysts are known to be efficient in the removal of the toxic and environmentally harmful sulfur in petroleum-based feedstock in the production of diesel and gasoline. However, the same type of catalyst has also been shown to be a suitable alternative for the valorization of biomass where the removal of oxygen is an essential reaction via hydrodeoxygenation (HDO) [2]. It has also been shown that the activity of the Mo-based catalysts in the HDO reaction can be improved by adding Ni and Co as promoters [3–5]. While Ni/Al$_2$O$_3$ catalysts have a high deoxygenation ability [6], Mo/Al$_2$O$_3$ catalysts showed higher selectivity and higher conversion for the

HDO route for various feedstocks [7]. NiMo/Al_2O_3 catalysts showed enhanced conversion for some feedstocks such as triglyceride compared to the monometallic catalysts.

In the chemical industry, the NiMo catalysts are most often introduced in the catalytic reactor as oxides, where Mo is in the Mo^{6+} oxidation state and the Ni in the Ni^{2+} oxidation state. In the presence of the reactants, inactive oxides transform into an active catalyst [8]. The transformation to the high-activity phase partly involves the reduction of the MoO_3 to either create vacancies and Mo^{5+} sites or the transformation into a sulfide if sulfur is present in the feedstock [9]. It has been suggested that Ni may facilitate the reduction of the MoO_3 by hydrogen spill over from the Ni to the MoO_3 [10–12]. Thus, Ni is acting as a promoter for the active site that enhances the formation of an undercoordinated Mo, and due to that, may be more active.

Due to their importance in the petrochemical industry, Mo-based catalysts have been studied in detail for decades [13–16], but the nature of the active site on an atomistic level in the catalytic HDO reaction of biomass is still under debate. Traditional characterization techniques for supported catalysts such as X-ray diffraction and transmission electron microscopy do not provide chemical information about the catalyst and are often limited to ex situ studies. These ex situ studies rely on the stability of the active phase of the catalyst and that the active site is also preserved outside the chemical process. In many cases, the active sites are not stable outside the reaction conditions of the chemical process and the characterization of the catalysts should therefore be studied *operando* or in situ.

In situ and *operando* studies of industrial catalysts are, however, challenging due to the structural complexity of the industrial catalysts, which contain only a few weight percent of the active metal well-dispersed on the oxide support. Simplified model systems, such as metal foils, are therefore often used to achieve information on an atomistic scale of the catalyst. Initially, these model catalysts were primarily studied in ultrahigh vacuum conditions, but the development of experimental techniques allows for in situ experiments under more realistic conditions. One of these experimental techniques is ambient-pressure X-ray photoelectron spectroscopy (APXPS), which is surface-sensitive and provides detailed chemical information about the catalyst. However, it is well-known that XPS studies of insulating materials such as Al_2O_3 are challenging due to their low electrical conductivity that leads to charging of the sample. The charging can be reduced by performing the measurements at elevated temperatures and in a gas atmosphere instead of vacuum as previously reported [17].

In this study, we characterize the reduction of alumina-supported monometallic Ni and Mo, and two bimetallic alumina-supported catalysts in situ, with the aim of investigating how the interaction of Ni and Mo influences the reduction of the active metals. To investigate how the interaction between the active metals and the support affects the reduction process, the results of the supported catalysts were compared to the reduction of oxidized Ni and Mo foils. The chemical surface properties of the catalyst were studied in situ with APXPS, and X-ray absorption near-edge structure (XANES) of the Ni and Mo K-edges was used as a complementary technique providing additional information on the oxidation state of the catalysts.

2. Results

2.1. Characterization of Al_2O_3-Supported Catalysts before Reduction Experiments

Four alumina-supported catalysts were characterized in this study: one pure Ni/Al_2O_3, one pure Mo/Al_2O_3 catalyst, and two bimetallic alumina-supported catalysts containing both Ni and Mo. The bimetallic samples were prepared with different Ni to Mo ratios and were denoted as NiMo(1:1) and NiMo(1:2) based on the measured atomic ratio of the two metals. Prior to the in situ APXPS and XANES reduction experiment, the specific surface area of the alumina-supported catalysts was estimated from nitrogen physisorption using the Brunauer–Emmett–Teller (BET) method [18]. The results presented in Table 1 show that the BET area decreases by approximately 8% after the impregnation of the alumina

support. Only a minor variation of the measured BET surface area is observed for the different catalysts.

Table 1. BET area of the Al_2O_3-supported catalysts.

Catalyst	BET Area in m^2/g
Mo/Al_2O_3	107
$NiMo(1:2)/Al_2O_3$	109
$NiMo(1:1)/Al_2O_3$	109
Ni/Al_2O_3	114
Al_2O_3	121

In addition, energy-dispersive X-ray spectroscopy (EDX) in scanning transmission electron microscopy (STEM) mode was used to achieve spatially resolved information about the metal content and distribution over the alumina support. Representative STEM/EDX images of the catalysts are shown in Figure 1 and the average composition obtained from STEM/EDX mapping is shown in Table 2. The atomic percent (at.%) of Ni in the bimetallic catalysts measured with EDX contains significantly less Ni than expected from the synthesis recipe. However, the pure Ni catalyst shows a Ni at.% in agreement with the expected Ni content, which indicates that the preceding impregnation with Mo hinders the impregnation of Ni. Alternatively, the lower concentrations observed by EDX could possibly be due to the low concentrations of the catalyst in the bulk Al_2O_3 and the agglomerated particles selected for the analysis.
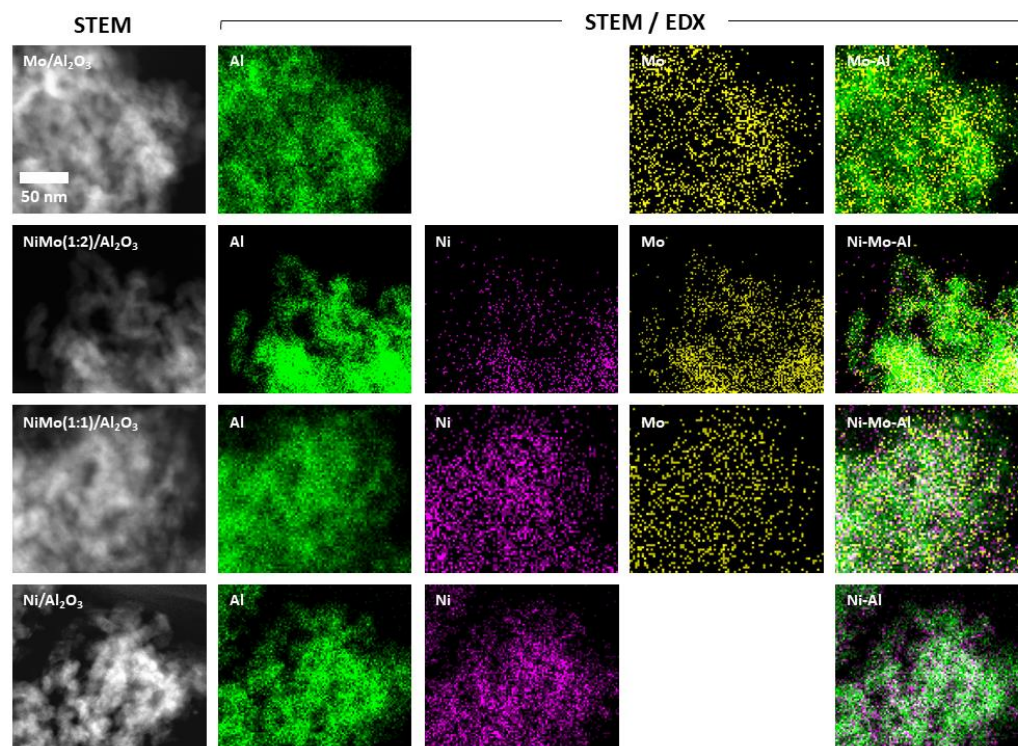
Figure 1. STEM micrographs and STEM-EDX maps of the alumina-supported catalysts. The first column on the left shows STEM images of the four catalysts. The following columns show the element-specific mapping of the STEM/EDX. The right column shows an overlay of the STEM/EDX mapping of Ni, Mo, and Al. Each row corresponds to one catalyst. The scale bar is 50 nm for all micrographs and maps. The mapping shows that Ni and Mo are homogeneously distributed in low concentrations over the bulk Al_2O_3.

Table 2. The average catalyst composition with standard deviation measured at three to four different locations on each catalyst using STEM/EDX.

Catalyst	Ni [at. %]	Mo [at. %]	Ni: Mo
Mo/Al$_2$O$_3$	-	2.95 ± 0.09	-
NiMo(1:2)/Al$_2$O$_3$	0.98 ± 0.17	2.03 ± 0.39	0.48 ± 0.17
NiMo(1:1)/Al$_2$O$_3$	1.37 ± 0.67	1.42 ± 0.33	0.96 ± 0.68
Ni/Al$_2$O$_3$	2.95 ± 1.47	-	-

2.2. In Situ H$_2$ Reduction Followed with Ambient-Pressure X-ray Photoelectron Spectroscopy

The reduction of the Ni and Mo catalysts supported on alumina and Ni and Mo foils were studied in situ using APXPS in 1 mbar of H$_2$. To evaluate the influence of the alumina support, the reduction of the alumina-supported catalysts was compared to the reduction of the metal foils under the same conditions. In addition, the behavior of monometallic-supported catalysts was compared to the bimetallic supported catalysts to investigate the effect of having two active metals impregnated on the support. In the study, the samples were heated stepwise and the Mo 3d, Ni 2p$_{3/2}$, and Al 2p core level were measured at each temperature. The high thermal stability of Al$_2$O$_3$ [19] allows the use of the Al 2p peak of the Al$_2$O$_3$ for binding-energy calibration to compensate for possible charging of the alumina support, which could otherwise cause unquantifiable shifts of the Mo 3d and Ni 2p$_{3/2}$. Figures S1 and S2 in the Supplementary Materials show the energy-calibrated Ni 2p$_{3/2}$ and Mo 3d APXPS spectra of the different catalysts over a temperature range of 100 °C to 600 °C. The spectra in which significant chemical changes were observed are analyzed in more detail and the fitted spectra are shown in Figures 2 and 3. An overview on the binding energies of Ni 2p$_{3/2}$ and Mo 3d fits for different catalysts in the literature is provided in Tables 3 and 4. These binding energies were used to constrain the fits of the APXPS spectra.

Table 3. Binding energies in eV for the Ni 2p$_{3/2}$ of alumina-supported and -unsupported pure Ni catalysts from the literature.

| Catalyst	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Ref.
NiO	853.7	855.4	860.9	864.0	866.3		[20]
NiOH	854.9	855.7	857.7	860.5	861.5	866.5	[20]
Ni	852.6	856.3	858.7				[20]
NiO/Al$_2$O$_3$	855.5–855.0	~862.2					[21]
Ni/Al$_2$O$_3$	853.0–852.	856.6–856.0					[21]
NiMoO$_4$/Al$_2$O$_3$	858.3	864.3					[22]
	856.2	862.0					[23]

Table 4. Binding energies in eV for the Mo 3d from the literature.

Catalyst	3d$_{5/2}$	3d$_{3/2}$	Ref.
MoO$_3$ (Mo^{6+})	232.5	235.8	[24,25]
Mo$_5$O$_{10}$ (Mo^{5+})	231.2	234.4	[24,25]
MoO$_2$ (Mo^{4+})	229.3	230.6	[24,25]
Mo$_2$C (Mo^{2+})	228.9	231.9	[25]
Mo (Mo^0)	228.3	231.5	[26]

Figure 2 shows the fits of the Ni 2p$_{3/2}$ for the Ni foil measured with a photon energy of 1800 eV and the Ni-containing Al$_2$O$_3$-supported catalysts measured with a photon energy of 1000 eV. In Figure 2a, the Ni 2p$_{3/2}$ spectra of Ni foil at 200 °C are fitted with five peaks with respective binding energies of 853.2 eV, 854.7 eV, 860.3 eV, 863.5 eV, and 865.8 eV. The interpretation of the Ni 2p photoemission line has been widely discussed in literature [20,27,28]. In summary, the five peaks observed in the spectra in Figure 2a can be assigned to different shielding effects of the Ni 2p core-hole after the photoexcitation

process. Details on these shielding mechanisms are discussed in the SI. The binding energy of the different peaks indicates that the surface of the Ni foil is oxidized and is predominately composed of NiO, but may also contain some Ni hydroxide.
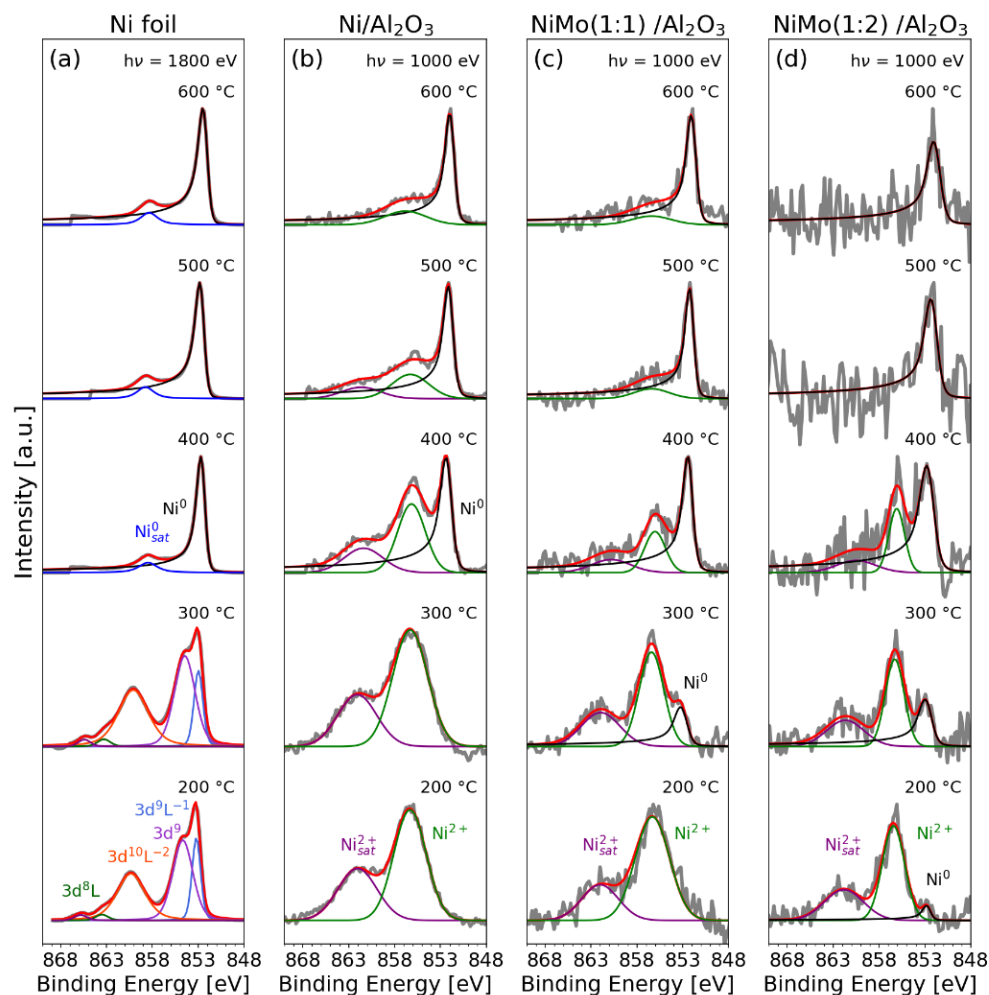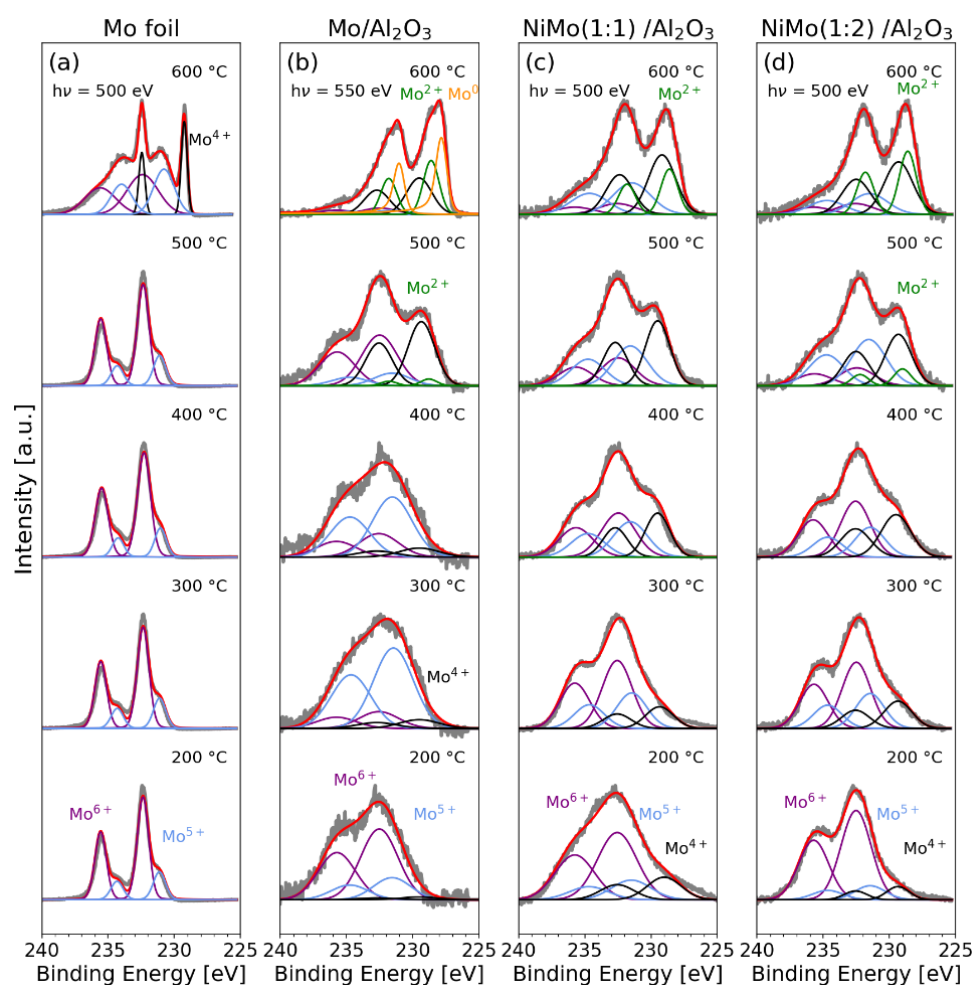

Figure 2. Ni $2p_{3/2}$ core-level spectra of (**a**) Ni foil, (**b**) Ni/Al$_2$O$_3$, (**c**) NiMo(1:1)/Al$_2$O$_3$, and (**d**) NiMo(1:2)/Al$_2$O$_3$ in 1 mbar H$_2$ at 200 °C, 300 °C, 400 °C, 500 °C, and 600 °C. The peak labels in the spectra in a) at 200 °C are a notation for the different final states of NiO resulting from the core-hole shielding mechanisms. These final states are labeled as $3d^aL^{-b}$, where a is the number of electrons in the Ni 3d core level, L refers to the ligand oxygen atoms, and $-b$ is the number of ligand electrons shielding the Ni core-hole by charge transfer to the Ni atom.

After heating the Ni foil to 400 °C, the multiplet structure assigned to NiO disappears. Instead, the peak at 852.7 eV with a small satellite component at 858.5 eV originating from the metallic Ni is dominating the Ni $2p_{3/2}$ spectrum. For these photoemission peaks, no further changes are observed. The binding energies of the observed peaks are in good agreement with the literature [20].

In general, the fitted Ni components of the supported Al$_2$O$_3$ catalysts are broader than the components observed for the Ni foil. The broadening of the peaks is likely due to non-well-ordered oxides and different oxides, which are all found within a narrow binding energy range and cannot be resolved in the spectra. Therefore, at 200 °C, only two components are used to fit the Ni $2p_{3/2}$ spectra for the Al$_2$O$_3$ supported catalysts: one main peak at 856.3 ± 0.1 eV and a satellite signal at 861.9 ± 0.1 eV. The binding energy of the main peak is too high to correspond to pure Ni-oxide or hydroxide and may indicate of a NiMoO$_4$ formation or NiOOH. [20]. Earlier studies of Ni-based Al$_2$O$_3$-supported catalysts

observed that the Ni 2p signal shifts due to interaction with the Al_2O_3 support [29,30]. The findings of these studies indicate that the Ni in the Al_2O_3-supported catalysts is in the +2 oxidation state corresponding to either $NiMoO_4$ or $NiAl_2O_4$ [14,21,23,29]. While the Ni/Al_2O_3 and the $NiMo(1:1)/Al_2O_3$ are still fully oxidized at 200 °C, a small amount of metallic Ni with a binding energy of 852.7 eV can be detected in the $NiMo(1:2)/Al_2O_3$ (Figure 2d). At 300 °C, the Ni foil and the Ni/Al_2O_3 remain fully oxidized while the reduction of both bimetallic catalysts has started. At 400 °C, the Ni foil is fully reduced to metallic Ni and metallic Ni begins to form in the Ni/Al_2O_3. At this temperature, the bimetallic catalysts are more reduced than the monometallic Ni/Al_2O_3. While heating the samples to 600 °C, the remaining Ni^{2+} component reduces further. A small amount of Ni^{2+} is still detectable in the $NiMo(1:1)/Al_2O_3$ and the Ni/Al_2O_3, while the $NiMo(1:2)/Al_2O_3$ appears to have reduced completely. This may, however, be due to the low statistics in the spectrum.

Figure 3 shows the Mo 3d core-level spectra for the alumina-supported catalysts and Mo foil measured at temperatures between 200 °C and 600 °C. At 200 °C, the spectra of all the catalysts are dominated by components with the binding energies 232.5 eV and 235.7 eV, which indicates Mo^{6+} corresponding to MoO_3 oxide or possibly $NiMoO_4$ in the bimetallic catalysts. The Mo/Al_2O_3 and the Mo foil, however, show a weak shoulder at 234.3 eV and 231.1 eV, which is attributed to a Mo^{5+} oxidation state.

Figure 3. Mo 3d core-level spectra of (**a**) Mo foil, (**b**) Mo/Al_2O_3, (**c**) $NiMo(1:1)/Al_2O_3$, and (**d**) $NiMo(1:2)/Al_2O_3$ in 1 mbar H_2 at 200 °C, 300 °C, 400 °C, 500 °C, and 600 °C. The spectra of the Mo foil, $NiMo(1:1)/Al_2O_3$, and $NiMo(1:2)/Al_2O_3$ were measured with a photon energy of 500 eV and the spectra of the Mo/Al_2O_3 were measured with 550 eV.

At 300 °C, additional components with the binding energies 229.5 eV and 231.8 eV are observed for the Mo/Al_2O_3. These components are attributed to the Mo^{4+} oxidation state [26,29,30] in a MoO_2 oxide and indicate that the reduction process has started. The spectrum at 400 °C is, however, dominated by the Mo^{5+} component that contributes to 75% of the total Mo 3d signal. This is highly interesting since the partially reduced Mo atoms are believed to be important in the catalysis process [31]. Increasing the temperature of the Mo/Al_2O_3 to 400 °C reduces the Mo^{5+} contribution to approximately 50% of the Mo 3d signal intensity and at 500 °C the Mo^{4+} and Mo^{6+} components dominate the spectrum. In addition, a new Mo^{2+} component is observed at binding energies 231.8 eV and 228.6 eV, which may be an indication of the formation of Mo_2C [25]. The corresponding C 1s spectra, however, show a peak at 284.0 eV, which is comparatively high for a carbide, which has been reported at binding energies of ~283.1 eV [25]. As the Mo/Al_2O_3 is heated further, metallic Mo is detected at 600 °C.

If we compare the reduction of the Mo/Al_2O_3 to the Mo foil, we can see that there is a significant difference in the reduction process. The Mo spectrum of the foil does not change significantly until the sample temperature reaches 600 °C and a distinct reduction of the Mo^{6+} to Mo^{4+} is observed. The good statistic in the spectra of the foil makes it possible to detect a clear broadening of the Mo^{6+} and Mo^{5+} when the Mo^{4+} is formed. This broadening could result from a Mo^{4+} satellite [26] at binding energies of 231.0 eV and 234.2 eV, but is not included in the fit due to the already complex fit of the spectra.

The results of the Mo foil and Mo/Al_2O_3 are compared to the reduction of the bimetallic catalysts shown in Figure 3c,d. In contrast to the Mo foil and Mo/Al_2O_3, the Mo^{4+} component can be identified already at 200 °C in the spectra originating from the bimetallic catalysts. Increasing the temperature further, the MoO_3 continues to reduce, and at 300 °C the spectra of the two bimetallic catalysts look very similar, both showing approximately 50% Mo^{6+} but only 30% Mo^{5+}, which is significantly lower compared to the monometallic Mo/Al_2O_3.

With increasing temperature, the reduction of the catalysts proceeds, and the Mo^{4+} component is continuously increasing. The larger amount of Mo^{4+} in both bimetallic catalysts as compared to Mo/Al_2O_3 is interpreted as the Ni content facilitating the reduction of Mo. Moreover, at 500 °C, a Mo^{2+} component is observed for $NiMo(1:2)/Al_2O_3$, but this component is surprisingly not observed for the $NiMo(1:1)/Al_2O_3$ until the catalyst reaches 600 °C.

To illustrate the temperature dependence of the reduction, the peak areas obtained from the APXPS spectra were plotted in Figure 4 as a function of temperature. Figure 4a shows the peak area of the NiO photoemission peak normalized to the total Ni $2p_{3/2}$ signal as a function of the temperature. It can be seen that a temperature of 300 °C is needed to start the reduction of the Ni/Al_2O_3 and the Ni foil. Further, the slope of the curve indicates that the reduction of the Ni/Al_2O_3 is more gradual than the reduction of the Ni foil. However, the two bimetallic catalysts (green and dark-cyan line in Figure 4a) start to reduce at a lower temperature than the monometallic catalyst or the Ni foil. The comparison of the two bimetallic catalysts indicates that the reduction of the $NiMo(1:2)/Al_2O_3$ begins before the reduction of the $NiMo(1:1)/Al_2O_3$, which suggests that a higher Mo content may facilitate the reduction of the NiO in the bimetallic catalysts.

Figure 4b shows the sum of the Mo^{6+} and Mo^{5+} peak area normalized by the total peak area of the Mo 3d signal as a function of temperature. At temperatures up to 400 °C, the reduction of the Mo/Al_2O_3 and the bimetallic catalysts progress at similar speeds, but at a temperature of approximately 400 °C and above, the reduction of the Mo/Al_2O_3 accelerates and advances faster than the reduction of the bimetallic catalysts. The reduction of the foil differs completely from the supported catalysts and a temperature of 600 °C is needed before a reduction of the Mo foil can be detected. It is, however, important to understand that the fitting of Mo 3d spectra is complex and the overlapping oxide peaks make the interpretation challenging. This may introduce an uncertainty in the quantification of the different oxidation states that are correlated to the fitted peak area in the spectra.
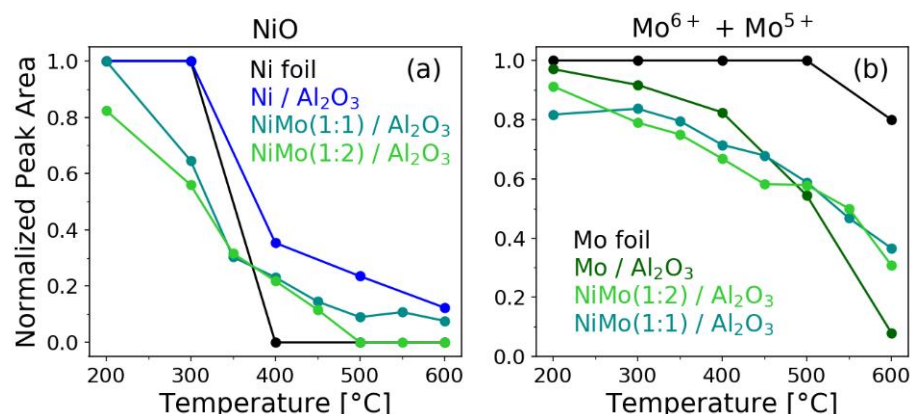
Figure 4. Peak area from XPS fits in Figures 2 and 3 as a function of temperature. In (**a**) the area of the NiO and (**b**) the sum of the Mo^{6+} and Mo^{5+} peak area normalized by the total peak area of the Ni $2p_{5/2}$ and Mo 3d, respectively.

2.3. In Situ H_2 Reduction Followed by XANES

The XANES data of the bimetallic NiMo(1:2)/Al_2O_3 were recorded in situ during heating from room temperature up to 600 °C while flowing of 4% H_2 diluted in N_2, at atmospheric pressure. The reduction experiment was repeated twice following the Ni K-edge and Mo K-edge, respectively, during the temperature ramp. A new sample was used for each experiment. The XANES of the bimetallic catalyst before and after the reduction was compared to NiO, Ni(OH)$_2$, NiOOH, MoO_2, MoO_3, and Na_2MoO_4 reference as well as the references of Ni and Mo metal foils (Figure 5a,b). The in situ measurements of the Ni K-edge and the Mo K-edge are shown in Figure 5c,d.

The initial XANES spectrum of Ni (called "NiMo(1:2)_start") has an edge energy E_{edge} of 8344.9 eV, which is very similar to the reference spectra of NiO and NiOOH with an E_{edge} of 8345.3 eV and 8344.1 eV, respectively (Figure 5a), where E_{edge} defined as the maximum in the first derivative of the adsorption spectrum. To analyze the composition of the catalyst prior to the reduction, linear combination fitting (LCF) was performed using the NiO, Ni(OH)$_2$, NiOOH, and metallic Ni reference spectra. This resulted in a composition of 65% NiOOH, 28% NiO, and 7% Ni(OH)$_2$ (shown in Figure S4c, in the Supplementary Materials). An alternative interpretation of the initial spectra is that the Ni is in the form of mainly NiO and that the spectra are smeared due to nanosized structures of the Ni on the Al_2O_3 support, resulting in not well-ordered NiO structures, as reported in [32].

In Figure 5b, the initial Mo K-edge spectrum is shown. The spectrum resembles that of MoO_3 (octahedral coordinated Mo^{6+}) and Na_2MoO_4 (tetrahedral coordinated Mo^{6+}). The prepeak is, however, more pronounced than for the MoO_3 XANES spectra, while less so than in the Na_2MoO_4 reference spectra, and with an energy in between the prepeak of MoO_3 and Na_2MoO_4. A LCF based on the available references resulted in a fitted composition corresponding to 69% MoO_4 and 31% MoO_3 (fit is shown in Figure S4a, in the Supplementary Materials). The presence of MoO_4 could indicate the presence of tetrahedral $NiMoO_4$ corresponding to β-phase $NiMoO_4$ [22].

The changes in the XANES spectra with temperature under a reducing environment is shown in Figure 5c,d. The induced change in chemical form is also illustrated in the inserts in Figure 5, showing the change in features in the Ni and Mo XANES spectra.

When the temperature of the catalyst is increased, small changes in the chemical state are observed for both Ni and Mo already below 200 °C (see inserts in Figure 5c,d). The intensity of the white line at 8343.5 eV decreases in the Ni spectrum, while the pre-edge peak in the Mo spectrum increases initially. We speculate that the increased intensity in the prepeak is a sign of structural changes into a more ordered tetrahedral structure of β-phase $NiMoO_4$. This would likely also affect Ni, but no Ni k-edge reference spectrum of $NiMoO_4$ was available.
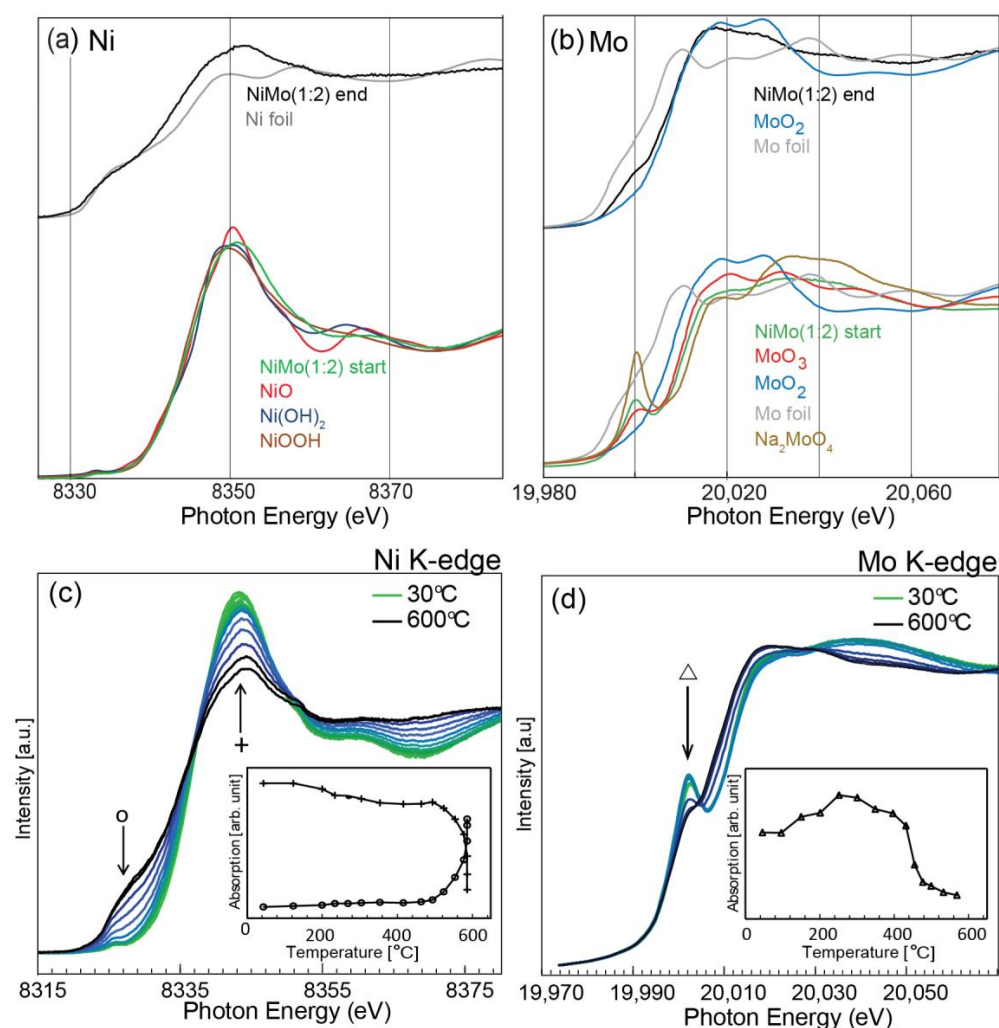
Figure 5. The normalized XANES spectra corrected for self-absorption, measured at room temperature and 600 °C, are shown together with XANES reference spectra in (**a**,**b**) for the Ni K-edge and the Mo K-edge, respectively. XANES in situ data showing the chemical transformation during the reduction of NiMo(1:2)/Al$_2$O$_3$ in the (**a**) Ni K-edge and (**b**) Mo K-edge. The absorption of specific energies marked with an arrow in the XANES spectra, as a function of temperature, is plotted in the inserted plots. In (**c**), the prepeak at 8328.5 eV is marked with o and at 8343.5 eV the white line marked with + is shown, and in (**d**) the absorption at 20,003 eV is shown.

A more rapid and pronounced reduction does not start until ~400–450 °C for Mo, and for Ni at slightly higher temperatures.

The end temperature of the XANES experiments was slightly below 600 °C. The final Ni and Mo spectra are plotted in Figure 5 together with selected references. The Ni spectrum shows an edge position of 8332.6 eV, which is slightly lower than metallic Ni. The features in the white line deviate from those of the metallic Ni, which could indicate the formation of an alloy with Mo, or the alumina substrate (the spectra resemble that reported for Ni-doped alumina) [33]. The LCF after the reduction showed ~80% metallic Ni and ~10% NiO and ~10% NiOOH, respectively (fit is shown in Figure S4d, in the Supplementary Materials). However, the edge position of the fitted spectra is too high in energy, indicating that the presence of Ni-oxides is overestimated and that the Ni after reduction is more likely metallic.

At 600 °C the Mo spectrum (E$_{edge}$ 20,007.6 eV with E$_{edge}$ defined as the energy at half the edge height of the adsorption [34]) shows that the Mo is still oxidized when compared to the XANES spectra of the Mo-foil (E$_{edge}$ 20,000 eV). From room temperature to 600 °C

the energy of the edge position shifts by ΔE 4.3 eV, initially being +0.6 eV higher than the edge of MoO_3. The E_{edge} after reduction is more similar to that of MoO_2 at 20,007.2 eV, the features above the adsorption edge differ from the MoO_2 and a small pre-edge peak remains visible. An LCF fitting suggests a composition of 18% MoO_3, 55% MoO_2, and 27% metallic Mo. The LCF gave the correct edge position, but shows some apparent difference in the structure of the white line (Figure S4b in the Supplementary Materials).

3. Discussion

Before the in situ reduction experiments, the oxidation state of the catalysts was characterized. The measurements indicate that the Ni in the supported catalysts was in the 2+ oxidation state corresponding to NiO or $NiMoO_4$ for the bimetallic catalyst. However, the presence of Ni hydroxides can not be excluded, since the APXPS spectra are challenging to interpret. Based on the APXPS measurements, the Mo was primarily in the 6+ oxidation state, which is related to MoO_3 or $NiMoO_4$. The XANES spectra of the initial Ni state could either be interpreted as nanostructure NiO or as NiOOH. For Mo, the XANES shows that as well as MoO_3, MoO_4 is also present, which supports the formation of β-phase $NiMoO_4$ [22]. For the bimetallic catalyst, both the APXPS and the XANES show the presence of $NiMoO_4$ and MoO_3 in the initial state of the catalyst, while it cannot be clearly determined whether there is additional NiO or NiOOH.

Above 400 °C, the APXPS spectra indicate that the majority of Mo is partially reduced and there is a mixture of different oxidation states. At the final reduction temperature at 600 °C, the Mo signal is dominated by Mo^{4+} and Mo^{2+}. The presence of Mo^{4+} is supported by the Mo XANES spectrum, which indicates a mixture of Mo oxides at the end of the experiment. The XANES measurements can neither confirm nor exclude the presence of Mo^{2+} due to a lack of a Mo^{2+} reference spectrum. According to the literature [35], Mo^{2+} in Mo_2C has a half-step energy of approximately 20,007.5 eV, which is in good agreement with the measured edge position for the NiMo(1:2) and could indicate Mo^{2+} in the XANES spectra. In summary, we can conclude from the APXPS and the XANES that Mo is not fully reduced to a metallic state, but a mixture of oxides and possibly carbides is present at 600 °C in a reducing atmosphere.

If we analyze the Ni spectra from the two techniques during the reduction, the APXPS results show that Ni is almost completely reduced above 500 °C. The XANES spectra for the NiMo(1:2) show, however, a rapid reduction just above 500 °C, indicating metal bonds with an E_{edge} similar to that of the Ni foil. However, the shape of the Ni XANES spectrum after reduction deviates from metallic Ni, and shows a similar shape as reported for Ni-doped Al [33]. This could indicate that Ni may have been incorporated in the Al_2O_3. Additionally, the APXPS showed a binding-energy shift of the Ni by 0.5 eV towards lower binding energies compared to the reference value for $Ni^{0.15}$ for all alumina-supported catalysts. A temperature of 600 °C is high enough to allow Ni bulk molecules to become mobile [36], which could result in the sintering of the Ni into larger clusters. For the bimetallic catalysts, the formation of a new alloy is possible. However, the observed binding-energy shifts could also be caused by an issue with the binding-energy calibration of the APXPS data.

4. Materials and Methods

The reduction of two bimetallic NiMo catalysts supported by Al_2O_3 was investigated with APXPS and compared to the reduction of monometallic Al_2O_3-supported Ni and Mo catalysts and the reduction of oxidized Ni and Mo foils.

4.1. Sample Preparation

4.1.1. Synthesis of Al_2O_3-Supported Catalysts

Four Al_2O_3-supported catalysts were characterized in this study. The catalysts were synthesized by incipient wetness impregnation of δ-Al_2O_3. We prepared two monometallic catalysts that contained only Mo or Ni as the active metal and two bimetallic catalysts with

different Ni:Mo ratios. The aimed Ni and Mo composition of the catalysts after production is shown in Table 5.

Table 5. The at. % of the Ni and Mo of the four Al_2O_3-supported catalysts from the synthesis solutions.

Catalyst	Ni [at. %]	Mo [at. %]	Ni [at. %]:Mo [at. %]
Mo/Al_2O_3	-	3.3	-
$NiMo(1:2)/Al_2O_3$	1.3	1.8	0.7
$NiMo(1:1)/Al_2O_3$	2.2	1.1	2.2
Ni/Al_2O_3	3.1	-	-

The synthesis of the Mo/Al_2O_3, Ni/Al_2O_3, and $NiMo(1:2)/Al_2O_3$ was described in a previous publication [37]. The $NiMo(1:1)/Al_2O_3$ was prepared as the $NiMo(1:2)/Al_2O_3$ with adjusted concentrations of the impregnation solutions as indicated in Table 5. The loading of the four catalysts ranged between 14.0 wt% and 4.9 wt% of Mo and between 3.4 wt% and 8.4 wt% for the Ni.

4.1.2. Metal Foils

The Ni and Mo foils with a purity of 99.99% (Sigma Aldrich, St. Louis, MO, USA) were used as references for the APXPS measurements where Ni 2p, Mo 3d, and O 1s core levels were probed.

4.2. Experimental Techniques
4.2.1. Nitrogen Physisorption

The nitrogen physisorption experiments were performed with a Micromeritics 3-flex system (Norcross, GA, USA) in dynamic physisorption mode. Prior to the measurement, the catalysts were degassed at 250 °C in high vacuum for 4 h. For the experiments, ~100 mg of the catalysts were probed at liquid nitrogen temperature, and the surface area was estimated using the equations suggested by Brunauer, Emmet, and Teller (BET) [18].

4.2.2. Transmission Electron Microscopy and Energy-Dispersive X-Ray Spectroscopy

Each sample was ground until a homogenous powder was obtained and sonicated in ethanol. Afterwards, a few drops of the solution were deposited on a holey carbon-film-coated Cu transmission electron microscopy (TEM) grid. JEOL 3000F operated at 300 kV was used for TEM and high-resolution transmission electron microscopy (HRTEM) imaging and scanning transmission electron microscopy (STEM) for energy-dispersive X-ray (EDX) spectroscopy. In STEM mode, a high-angle annular dark-field (HAADF) detector coupled with an EDX spectrometer (Oxford Instruments, Abingdon, UK) was used for elemental mapping. The data were processed and analyzed in the INCA software (Oxford Instruments, Abingdon, UK).

4.2.3. Ambient-Pressure X-ray Photoelectron Spectroscopy

The ambient-pressure X-ray photoelectron spectroscopy (APXPS) measurements were made at the HIPPIE beamline, MAX IV Laboratory [38]. The beamline is located at the larger ring of the synchrotron, which operates at 3 GeV with a ring current of 300 mA. The APXPS endstation is equipped with a ScientaOmicron Hipp-3 electron analyzer. The spectra were recorded with normal emission angle with a beam-incidence angle of 55°. The reduction of the oxidized catalysts was followed in situ in 1 mbar of H_2 while increasing the temperature of the catalysts stepwise.

The Ni 2p were collected with an excitation energy of 1000 eV and 1800 eV, while the Mo 3d core-level spectra were collected with lower photon energies of 500 eV and 550 eV. For binding-energy calibration, the Al 2p core level was used and the Al_2O_3 peak was calibrated to 74.6 eV and only minor charging was observed.

The APXPS spectra were fitted using the CasaXPS software package [39]. Details on the chosen line shapes are discussed in Supporting Information.

Finally, we would like to address the issue of beam damage. MoO_3 has previously been reported to be sensitive to beam damage, which causes a reduction in the oxides [40]. To minimize this effect, each spectrum of the Mo foil was collected at a fresh spot. For the alumina-supported catalysts, no beam damage was observed at room temperature and thus all spectra were collected at the same spot for the whole measurement series.

4.2.4. X-ray Absorption Near-Edge Structure

The XANES measurements were made using the Balder beamline (BL) at the MAX IV Laboratory. Balder BL is placed at the larger ring operating at 3 GeV and 300 mA [41]. Si111 crystals are used for monochromatizating, and the beam size is ~100 μm × 100 μm.

XANES spectra were measured at the K-edges of Ni (8333 eV) and Mo (20,000 eV). For references and initial state of the samples, spectra were recorded in transmission mode, while for the in situ studies, XANES spectra were recorded in fluorescence mode (the set-up used for heating did not allow transmission model measurements). The fluorescence mode data were collected using a seven-element silicon drift detector. In situ experiments were performed using a gas-flow cell (High Temperature Heating System—TS1500, Linkham Scientific Instruments, Redhill, UK) flowing a gas of 4% H_2 in N_2 over the sample during heating up to ~580 °C.

Several reference compounds (NiO, MoO_3, Mo_2O_3) were purchased (>99%) and tablets with an optical thickness of ~2.5 were prepared and pressed with BN as binder. The XAS spectra of the references were measured in transmission mode. For energy calibration, foils of Mo and Ni were used, also measured in transmission mode. The catalysts were measured in transmission mode before the in situ experiment to quantify and take into account the effect of self-absorption in fluorescence mode [42].

XANES data were preprocessed (summation, background subtraction, normalization, and correction of self-absorption) and further analyzed using the ATHENA software package [43].

5. Conclusions

The reduction of four Al_2O_3-supported catalysts, two with different Ni:Mo ratios, one monometallic Mo/Al_2O_3, and one monometallic Ni/Al_2O_3 catalysts, were compared to the reduction of Ni and Mo foil, respectively, in 1 mbar H_2. Characterization with TEM/EDX and BET showed that the active metals were well-dispersed on the alumina support and the strong interaction with the support was concluded to be the reason for the slow reduction observed for the supported catalysts as compared to the foils. In addition, we found that the Ni foil was completely reduced at 400 °C while the reduction of the alumina-supported Ni was still ongoing. The opposite behavior was found for the Mo, where the Mo-oxide on the foil was reduced at a significantly higher temperature as compared to the alumina-supported Mo. For the bimetallic catalysts, it was observed that the reduction of the MoO_3 starts at a lower temperature than the reduction of the NiO. Overall, we could conclude that at 600 °C in 1 mbar of H_2, the Ni is completely reduced to metallic Ni for all samples (supported and foils), while Mo was only partially reduced and a mixture of different oxide phases, mainly MoO_2, and possibly carbide was observed.

The reduction from Mo^{6+} to Mo^{4+} was observed at 200 °C in the bimetallic alumina supported catalysts and at 300 °C in the monometallic Mo/Al_2O_3, while it was only detected at 600 °C for the Mo foil. In our study, we found that during this reduction step, Mo^{5+} could be identified in the spectrum, which has been suggested to be the active phase of the Mo-based catalyst. This paves the way for future operando APXPS experiments where the nature of the active site can be explored.

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