Supplementary Information SI

Deconvolution of APXPS spectra

Ni 2p spectra

The electronic structure of Ni 2p is complex and still under debate. The main component in the spectrum at 853.7 eV is attributed to the Ni^{2+} in NiO. The core level shift is due to the shielding of the core hole by an electron originating from the ligand oxygen ($3d^9L^{-1}$, L: ligand) [27]. The shoulder at higher binding energy is more controversial. It is believed to originate either from non-local screening of the core hole by a next to nearest-neighbor oxygen atom ($3d^8L(3d^8L^{-1})$)[27] or multiplet screening [44] or Ni^{3+} in the form of Ni_2O_3 [45]. The satellite features at + 7 eV and + 10 eV are assigned to the screening of the core hole by two electrons originating from the neighboring ligand oxygen ($3d^{10}L^{-2}$) and the unscreened hole ($3d^8$) [27]. Additionally, to these 4 peaks which can be assigned to different shielding effects based on DFT, we observed an additional fifth peak with a binding energy of 865.8 eV which has also been observed in previous experimental studies [20,28].
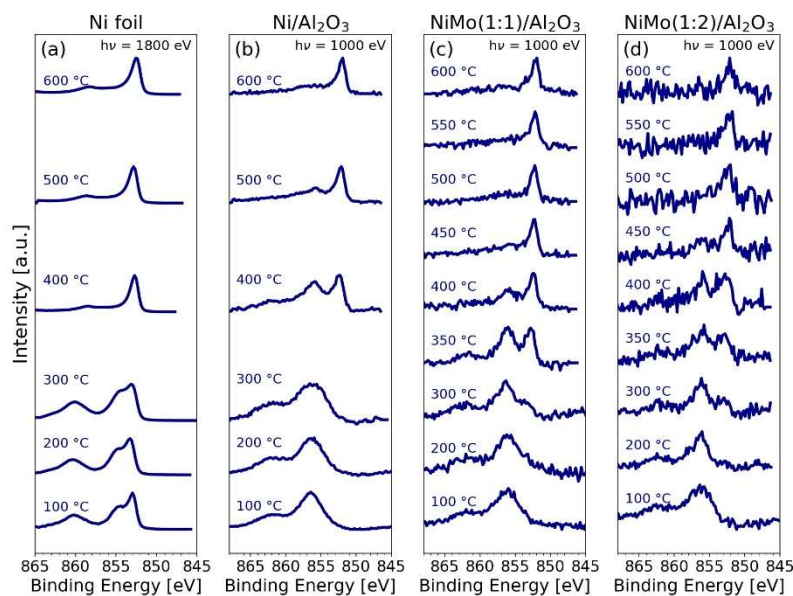
For the deconvolution of the Ni $2p_{3/2}$ spectra of the Ni foil a Shirley background was used while the supported catalysts were fitted with a linear background. The photoemission peaks originating from oxidized nickel were represented by a sum of a Gaussian and Lorentzian while the asymmetric nature of the metallic Ni was represented by a Doniach Sunjic function.

The observed binding energies for the oxidized Ni foil were 0.4 eV lower than the reported binding energies for NiO in literature [20,28]. We speculate that this is due to crystal defects in Ni foil. Similar shifts to lower binding energy for Ni foils have previously been reported in the literature [46].
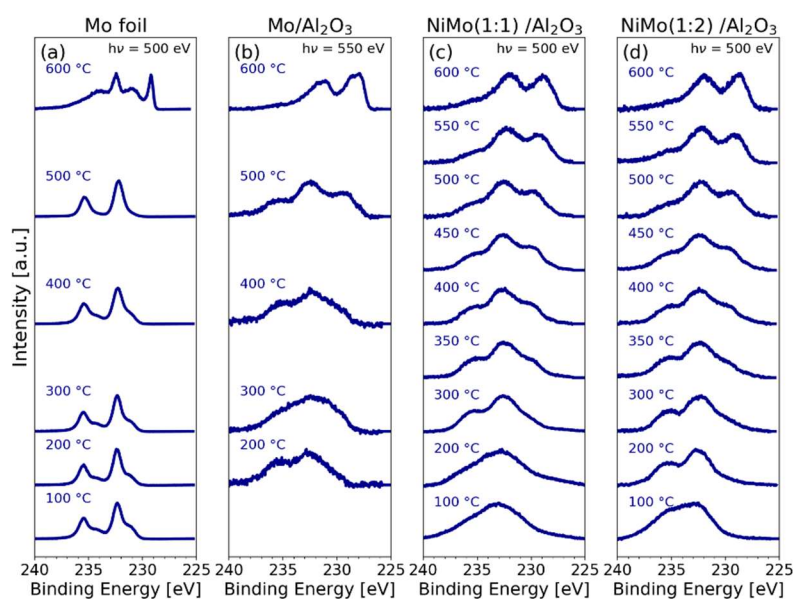
Mo 3d spectra

A Shirley background was subtracted from the Mo 3d spectra. The photoemission peaks were fitted using a sum of a Gaussian and Lorentzian for the oxidation state 6+, 5+, 4+ and 2+ while the metallic peaks were represented using a Doniach Sunjic line shape. In the fit, the spin-orbit splitting between the $3d_{5/2}$ and $3d_{3/2}$ was fixed to 3.2 eV and the peak area ratio of these two components was fixed to 3:2. The FWHM of the 6+ and 5+ were constrained to be equal while the 4+ and metallic oxidation state showed a lower FWHM which agrees with the Mo 3d deconvolution presented in [31].
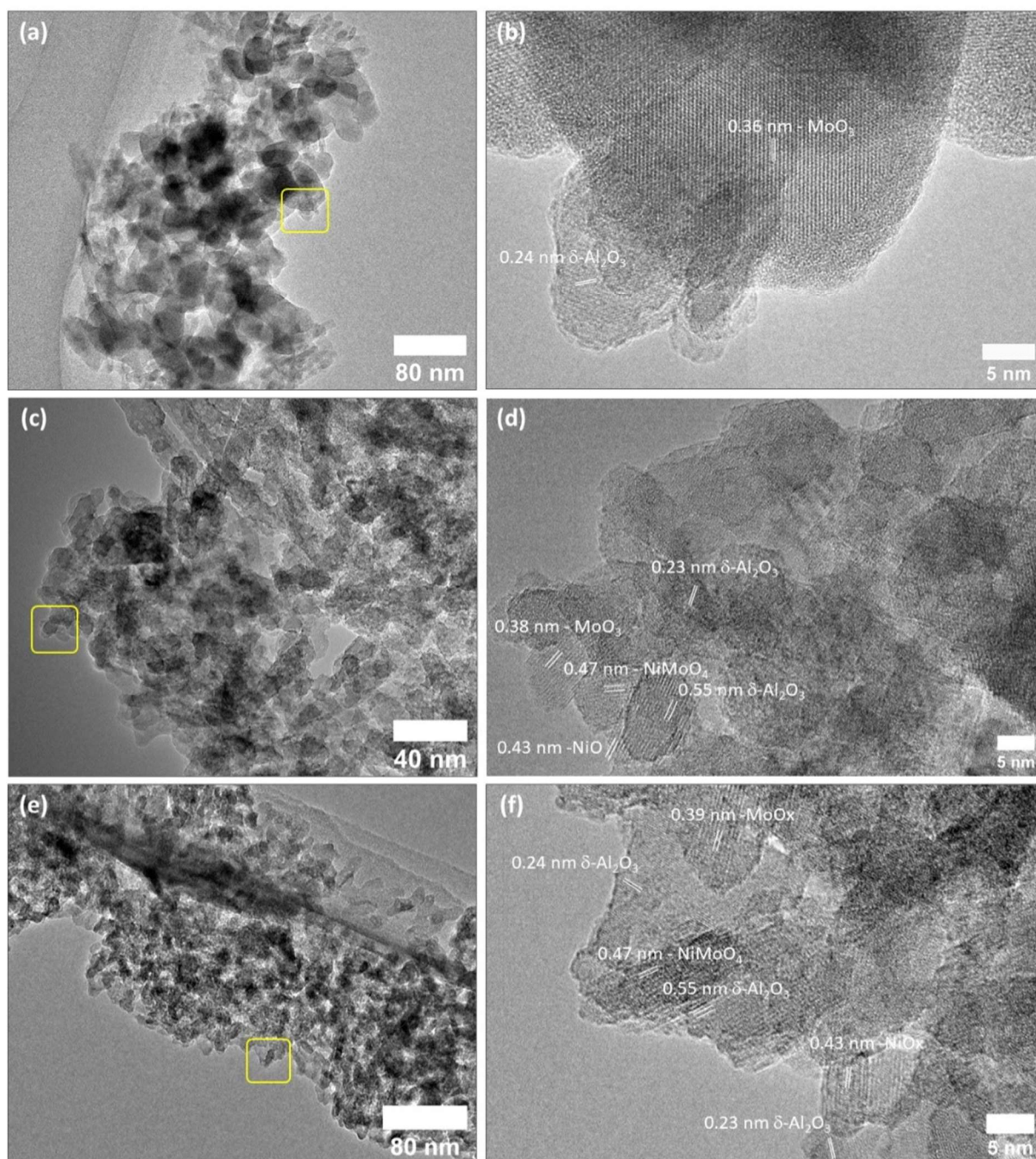
Figure S1. Ni 2p$_{3/2}$ core level of **(a)** Ni foil, **(b)** Ni/Al$_2$O$_3$, **(c)** NiMo(1:1)/Al$_2$O$_3$, and **(d)** NiMo(1:2)/Al$_2$O$_3$ at different temperatures in 1 mbar H$_2$.

Figure S2. Mo 3d core level of **(a)** Mo foil, **(b)** Mo/Al$_2$O$_3$, **(c)** NiMo(1:1)/Al$_2$O$_3$, and **(d)** NiMo(1:2)/Al$_2$O$_3$ at different temperatures in 1 mbar H$_2$. The Mo 3d spectra in **(a)**, **(c)** and **(d)** were measured with a photon energy of 500 eV and **(b)** was measured with a photon energy of 550 eV.

TEM images

TEM and HRTEM images of the Al_2O_3 supported catalysts are shown in Figure S3. Lattice constants of 0.24 and 0.56 nm corresponding to bulk d-Al_2O_3 were found in all of the catalysts [47]. Mo/Al_2O_3 (Figure S3 b) and Ni/Al_2O_3 (Figure S3 h) before reduction show lattice constants consistent with their oxides MoO_3 of 0.36 nm [48] and NiO of 0.41 nm [49], respectively. Moreover, $NiMoO_4$ with a lattice constant of 0.47nm was identified in both bimetallic catalysts NiMo(1:1)/Al_2O_3, and NiMo(1:2)/Al_2O_3. (Figure S3 d and f).
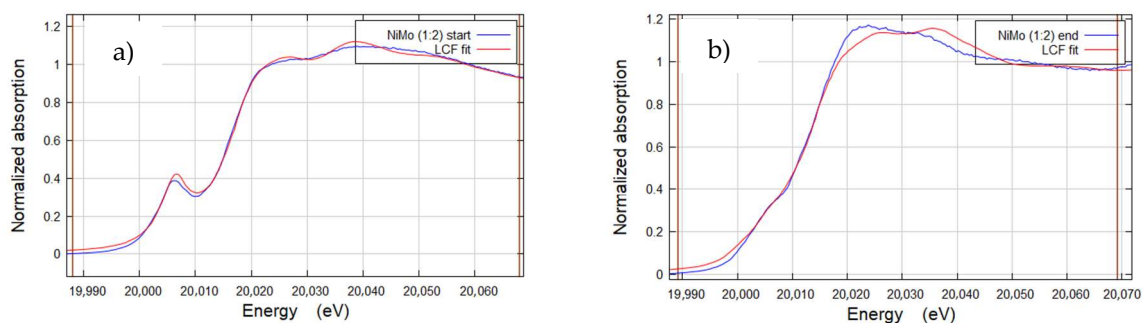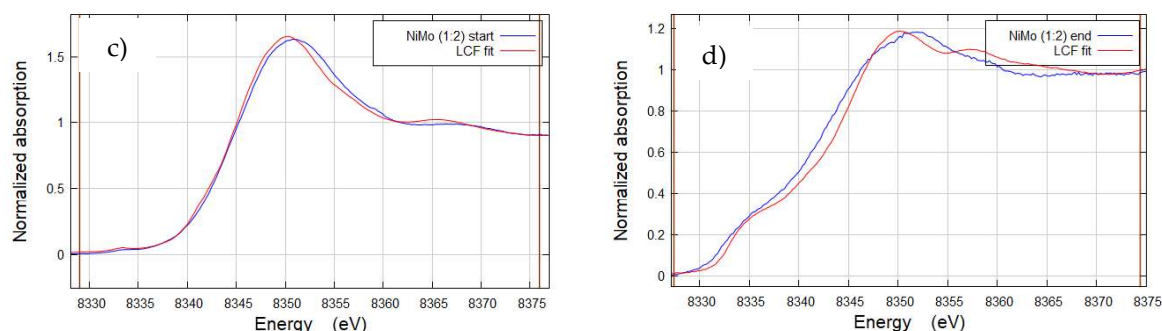
Figure S3. TEM (left) and HRTEM (right) images of (a)(b) Mo/Al₂O₃, (c)(d) NiMo(1:2)/Al₂O₃, (e)(f) NiMo(2:1)/Al₂O₃, and (g)(h) Mo/Al₂O₃.
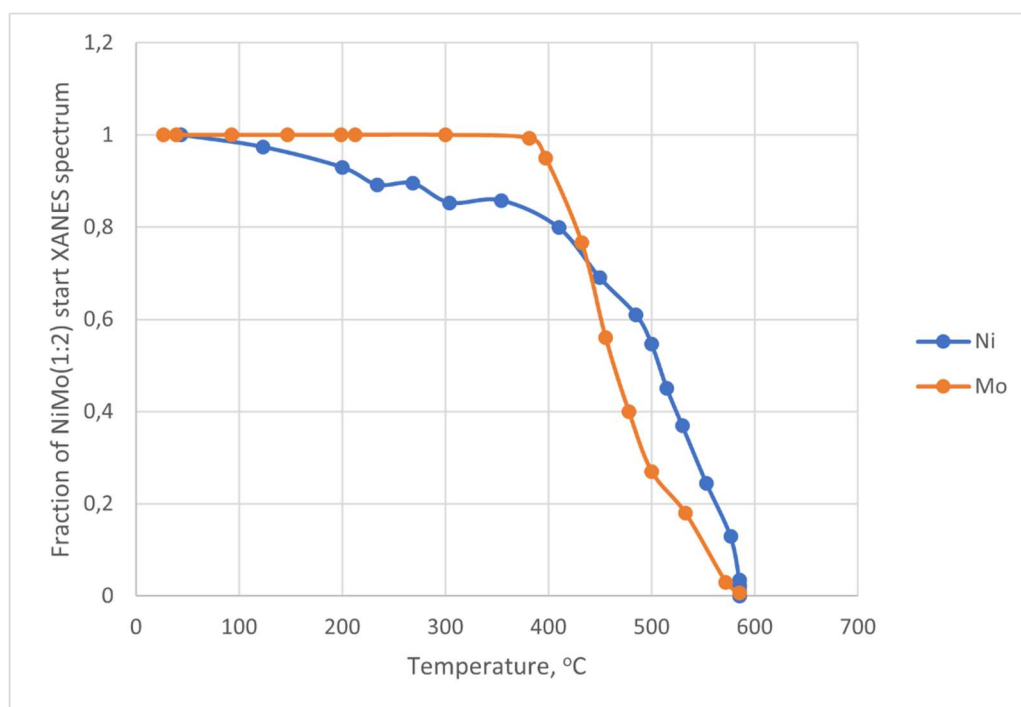
LCF of XANES data

The Linear Combination Fitting (LCF) was performed for the XANES spectra measured at the start and end of the reduction experiment for both the Ni and Mo K-edge. In Fig a) and b) the Mo Kedge spectra of NiMo(1:2) catalyst are shown together with the LCF fit for the start and end spectra. The references used were MoO_2, MoO_3, Mo metal, and Na_2MoO_4, representing the presence of MoO_4^{2-}. The data show that Mo is initially highly oxidized and the pre-edge is well pronounced at the beginning of the experiment (Fig S4a) indicating the presence of MoO_3 and MoO_4. The composition from the resulting fit is presented in the main text. In Fig S4b) the XANES spectrum at the highest reduction temperature of the NiMo(1:2) catalyst is shown. The LCF shows that additional references would be needed to achieve a perfect fit with the measured Mo XANES data. However, the edge position is well described by the fit. We speculate that a Mo^{2+} is present at the end of the experiment but no reference XANES data of Mo^{2+} was measured. However, the edge position is in good agreement with the Mo^{2+} spectrum reported in the literature [35]. The corresponding Ni K-edge spectra measured at the start and end of the experiment were fitted including the Ni metal, NiO, NiOOH, and $Ni(OH)_2$. In Fig S4c) the starting spectrum of NiMo(1:2) is shown. It is clear that the Ni is oxidized. The deviation of the fitted curve could be due to the nanostructures. In Fig S4 d) the Ni spectrum at 600 °C is shown together with the LCF fit. For this Ni spectrum, the edge-position of the fitted spectra does not match the measured spectra, leading to an overestimation of the oxidation state. The reason for the low quality of the fit may be the interaction with Mo- or Al compounds, or the formation of a carbide, which is not included as references in the LCF.

Figure S4. The measured Ni and Mo K-edge spectra measured at the start and end of the reduction of the NiMo(1:2) catalyst plotted together with the result from the Linear Combination Fitting (LCF). The references include the Ni metal, NiO, NiOOH, and Ni(OH)$_2$ as well as MoO$_2$, MoO$_3$, Mo metal and Na$_2$MoO$_4$. In a) the Mo k-edge at the start temperature, in b) the end temperature, in c) the Ni k-edge at the start temperature, and in d) the end temperature.

Figure S5. The fraction of the starting XANES K-edge spectrum of Ni and Mo in the NiMo(1:2) as a function of temperature.

In Fig S5 the result from a LCF, using the start and end spectra, of the XANES spectra from various temperatures indicates at what temperature the Ni and Mo are reduced, with a turning point at around 400°C. At temperatures below 400 °C, Mo is preserved as at the starting point which was highly oxidized while Ni is reducing slowly. When the catalyst reached 400 °C and above the data suggests that the Mo and Ni are reduced at a similar rate.