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In situ X-ray emission and high-resolution X-ray absorption spectroscopy applied to Ni-based bimetallic dry methane reforming catalysts†

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The promoting effect of cobalt on the catalytic activity of a NiCoO Dry Methane Reforming (DMR) catalyst was studied by a combination of *in situ* K β X-ray Emission Spectroscopy (XES) and K β -detected High Energy Resolution Fluorescence Detected X-ray absorption spectroscopy (HERFD XAS). Following the calcination process, Ni XES and K β -detected HERFD XAS data revealed that the NiO coordination in the NiCoO catalyst has a higher degree of symmetry and is different than that of pure NiO/ γ -Al₂O₃. Following the reductive activation, it was found that the NiCoO/ γ -Al₂O₃ catalyst required a relatively higher temperature compared to the monometallic NiO/ γ -Al₂O₃ catalyst. This finding suggests that Co is hampering the reduction of Ni in the NiCoO catalyst by modulation of its electronic structure. It has also been previously shown that the addition of Co enhances the DMR activity. Further, the K β XES spectrum of the partly reduced catalysts at 450 °C reveals that the Ni sites in the NiCoO catalyst are electronically different from the NiO catalyst. The *in situ* X-ray spectroscopic study demonstrates that reduced metallic Co and Ni are the primary species present after reduction and are preserved under DMR conditions. However, the NiCo catalyst appears to always be somewhat more oxidized than the Ni-only species, suggesting that the presence of cobalt modulates the Ni electronic structure. The electronic structural modulations resulting from the presence of Co may be the key to the increased activity of the NiCo catalyst relative to the Ni-only catalyst. This study emphasizes the potential of *in situ* X-ray spectroscopy experiments for probing the electronic structure of catalytic materials during activation and under operating conditions.

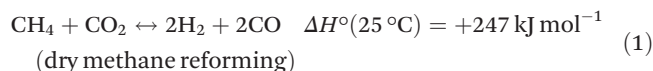
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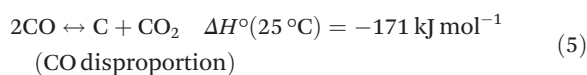
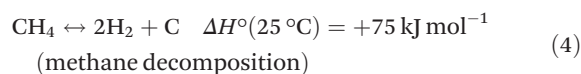
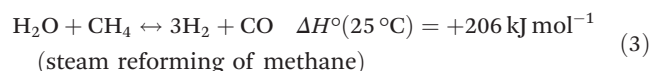
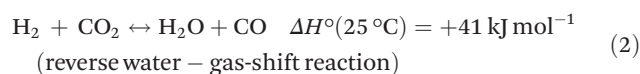
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1. Introduction

The development of catalysts that enable environmentally friendly means for the production of fuels is currently a subject of intense research.^{1–3} These efforts are motivated not only by the depletion of fossil fuels, but also the emission of greenhouse gases, which are known to have a devastating impact on the environment.^{4–6} One reaction that has been receiving increasing attention due to its high potential for converting CH₄ and CO₂ to syngas (H₂ and CO) (reaction 1) is the Dry Methane Reforming (DMR) process.^{7,8}



In addition, various undesired side reactions (reactions (2)–(5)) can occur during the DMR reaction that eventually lead to carbon deposition on the active phase.



Due to the carbon deposition side reactions, the active sites are gradually blocked, leading to catalyst deactivation.⁹ In the literature, numerous studies aimed at preventing coke for-

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2.3 TPR

In an earlier study, the details of the TPR experimental setup and the reduction profile for the NiCoO/ γ -Al₂O₃ catalyst were reported.²⁴ Additionally, the TPR profile of the NiO/ γ -Al₂O₃ was measured by filling a quartz cell with 64 mg of the calcined catalysts. In this experiment, the temperature was increased to 850 °C, with a temperature ramp of 6 °C min⁻¹ in a flow of 4.6% H₂ in Ar, 84.1 mL min⁻¹ total. The H₂ consumption was measured by a thermal conductivity detector (Hydros, Rosemount).

2.4 DMR activity tests

The DMR activity for the NiCoO/ γ -Al₂O₃ sample was reported in an earlier publication.²⁴ The experimental setup for measuring the activity of the NiO/ γ -Al₂O₃ DMR catalysts has been described in detail elsewhere by Tillmann *et al.*,^{24,36} Fig. S1.† Based on both the obtained data from STXM study,²⁴ on the NiCoO/ γ -Al₂O₃ catalyst and the limitation of the hard X-ray reactor, additional DMR catalytic activity data were collected at 750 °C, 600 °C, 500 °C, and 450 °C.

2.5 Synchrotron based experiments

In situ XES and HERFD data for the NiCoO/ γ -Al₂O₃ and NiO/ γ -Al₂O₃ catalyst were obtained at the Taiwan beamline BL12XU at the SPring-8 synchrotron facility (8 GeV, 99 mA).³⁷ The beamline has four main optical elements, a high heat-load Si (111) double-crystal pre-monochromator, a four-bounce channel-cut Si (220) monochromator, a cylindrical Si collimating mirror and a toroidal Pt-coated focusing mirror. A Pt-coated mirror was used to focus the beam both vertically and horizontally to ~ 80 (V) \times 120 (H) μm^2 at the sample position. The incident energy was calibrated with references to the first inflection points of Ni and Co foils at 8333 eV and 7709 eV, respectively. A crystal spectrometer aligned in a Rowland geometry was utilized to detect the fluorescence from the sample. The Ni K β (1s3p) emission spectra using a 1 m radius spherically bent Si (551) analyzer. For the Co K β measurements, a Ge (444) analyzer was used. A He-filled path was used between the sample and spectrometer to reduce signal attenuation and emitted X-rays. The signal selected by the spectrometer crystals was collected using an energy-resolving Si detector. A set of four Ni K β XES spectra were collected in the emission energy region of 8220 to 8335 eV using an incident energy of 8450 eV. The Co K β emission was collected from 7615 to 7700 eV energy range using a 7800 eV excitation energy (Fig. S2 and S3†). All XES spectra were normalized to the energy maximum of the K $\beta_{1,3}$ peak. Co and Ni XES data were calibrated by setting the K β maximum of Co₃O₄ and NiO to 7649.1 and 8264.8 eV,³⁷ respectively.

The HERFD spectra were measured by setting the spectrometer to the maximum of the K $\beta_{1,3}$ XES peak. For Co and Ni HERFD data, four sets of scans in the region from 7700 to 7900 eV and 8320 to 8450 eV were selected, respectively. This protocol was repeated for each step of the *in situ* experiment.

To validate the quality of the collected data, radiation damage studies were conducted by measuring multiple XES

and HERFD spectra during 3 h exposure. To avoid beam damage, filters were inserted before the sample to attenuate the incident beam until no observable damage in the pre-edge or edge region was observed.

2.5.1 Sample preparation. The sample preparation step involved placing a pressed pellet of the catalysts powders in the sample holder shown in Fig. S4a.† Next, the holder was fixed inside the heating stage and afterwards the reactor was sealed. Fig. S4c† shows how the incident window is covered with Kapton tape to prevent gas leakage.

2.5.2 Data collection. First, the K β XES and HERFD of the freshly calcined samples were measured. Then, the catalyst activation was followed by measured the XES and HERFD XAS by reducing the samples under 5% H₂ in Ar flow and gradually increasing the temperature from 25 °C to 600 °C, Fig. S5.† The selected temperature range is based on the limits of the reactor and is within the operating regime of the catalyst. Finally, for the DMR reaction the temperature was kept at 600 °C under the flow of the DMR gas mixture (7% CH₄ & 9.5% CO₂ diluted in N₂).

3. Results

The STEM data in Fig. 1a show the formation of small coalesced nanoparticles for the calcined NiCoO/ γ -Al₂O₃ sample, as previously demonstrated.²⁴ The elemental distributions for the Ni (green) and oxygen (blue) for the NiCoO sample are shown in Fig. 1b and c. Based on the Co-EDX image (in Fig. 1d) and the Ni-EDX image (1b), rather unequal distributions for Ni and Co on the γ -Al₂O₃ support are seen. These observations are also consistent with STEM-EDX and STXM results from an earlier study which demonstrated the existence of Ni-rich domains and a variable distribution of Co through the NiCoO/ γ -Al₂O₃ particle.²⁴ These data also suggest a similar morphology for both NiO/ γ -Al₂O₃ and NiCoO/ γ -Al₂O₃ samples (Fig. 1a and e).

The STEM-EDX images for the NiO/ γ -Al₂O₃ sample indicates rather homogeneous distributions for nickel (green) and oxygen (blue) on the support (Fig. 1f and g).

To follow the reduction and conversion of the oxides to the metallic active phase, TPR profiles were obtained for the NiO/ γ -Al₂O₃ (Fig. 2) and NiCoO/ γ -Al₂O₃ (Fig. SI.5 of ref. 24) DMR catalysts. For the NiCoO sample, there are two prominent reduction peaks. There is a relatively small peak at 265 °C which is assigned to the reduction of Co³⁺ species to Co²⁺ (ref. 38 and 39) followed by the main reduction peak at 325 °C where both Ni²⁺ and Co²⁺ are reduced to their metallic states.^{40,41} This result is consistent with *in situ* Ni and Co L-edges spectra for this catalyst.²⁴ However, from the TPR profile of the NiO catalyst in Fig. 2, a single peak reduction is observed at 317 °C which corresponds to the reduction of Ni²⁺ to the metallic nickel.^{42,43} By comparing the TPR profiles for both samples, it appears that the reduction of Ni²⁺ in the NiO sample initiates at a relatively lower temperature. These data suggest that due to the presence of cobalt in the NiCoO catalyst



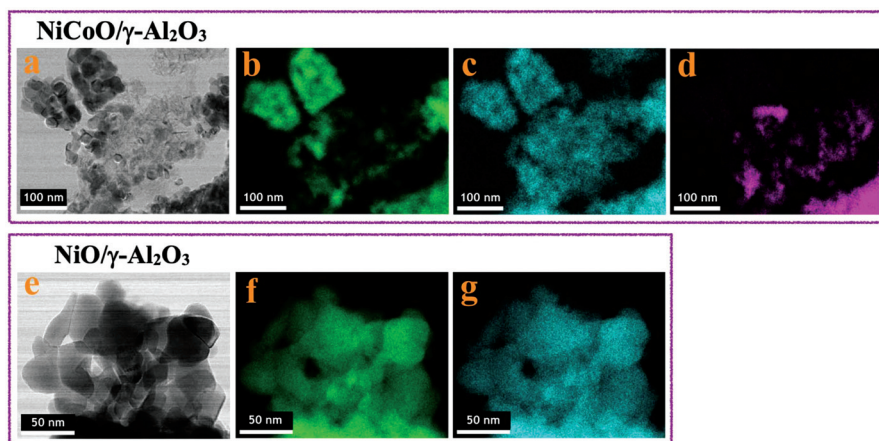


Fig. 1 STEM-EDX images of the; (a–d) NiCoO/ γ -Al₂O₃ and (e–g) NiO/ γ -Al₂O₃ samples after the calcination step at 400 °C. (b and f) nickel (green); (c and g) oxygen (blue); (d) cobalt (purple).

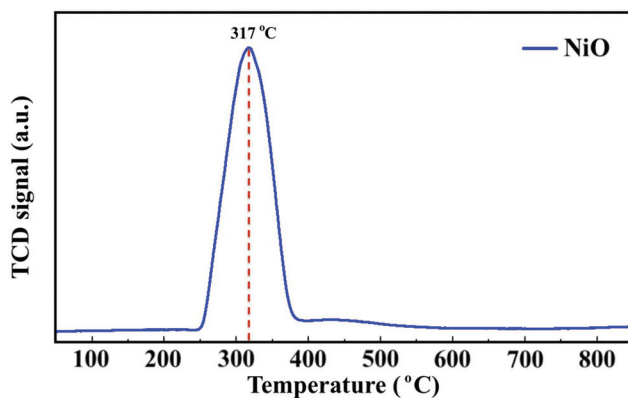


Fig. 2 H₂ TPR profile of the NiO/ γ -Al₂O₃ catalyst.

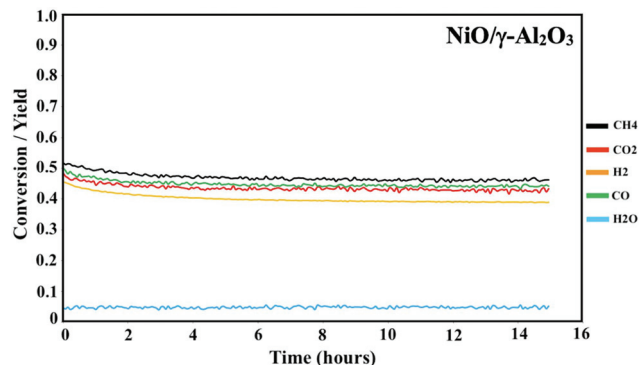


Fig. 3 Activity profile of the NiO/ γ -Al₂O₃ DMR catalysts for 15 hours under methane reforming conditions. Prior to the DMR activity measurements, the catalyst was activated for 20 minutes under 10% H₂ in N₂ with a flow rate of 100 mL min⁻¹. The DMR experiment was performed at 800 °C under 7% CH₄ and 9.5% CO₂ in N₂ and a flow rate of 490 mL min⁻¹. DMR activity profiles for the NiCoO/ γ -Al₂O₃ catalysts were measured in our previous study.²⁴

the reduction temperature is modulated and therefore Ni²⁺ is reduced at relatively higher temperature as compared to the monometallic NiO catalyst.

3.1. DMR activity experiments

Prior to the DMR activity measurements, the catalysts were activated by reducing the oxides at 850 °C for 20 minutes under 10% H₂ in N₂. The DMR activities of the NiCoO/ γ -Al₂O₃,²⁴ and NiO/ γ -Al₂O₃ catalysts (Fig. 3) were obtained at 800 °C under dynamic flow of the DMR gas mixture (7% CH₄ & 9.5% CO₂ diluted in N₂). The conversion values for NiO and NiCoO systems vary substantially with NiCoO at ~90%,²⁴ and NiO at only ~50%. The initial activity of the NiCoO catalyst is similar to other recently reported highly active DMR catalyst systems.^{44,45} Table S1† summarizes the stabilized conversion/yield values for the NiCoO and NiO catalysts under DMR conditions for 15 hours. These data suggest that following the DMR experiment, the activity of both catalysts has stabilized and thus suggests a high resistivity against coke formation.

The DMR activity data shows that the presence of cobalt in the NiCoO DMR catalysts has a promoting effect on the cata-

lytic activity, resulting in an almost two-fold higher conversion when compared to the monometallic NiO catalyst. In addition, to understand the effect of temperature on the catalytic activity of the NiCoO catalyst additional DMR activity tests at 750 °C, 600 °C, 500 °C and 450 °C under a continuous flow of DMR gas mixture (7% CH₄, 9.5% CO₂ in N₂) for 35 hours were performed (Fig. S6†). This data shows that decreasing the DMR reaction temperature dramatically reduces the achieved conversion which may be enhanced by the increase in the rate of coke deposition on the active phase.⁴⁶ Nonetheless the activity data for the NiCoO catalyst collected at 600 °C shows modest DMR activity, indicating that the X-ray spectroscopic data correspond to an operating catalyst.

3.2. Ni K β XES of NiCoO/ γ -Al₂O₃ vs. NiO/ γ -Al₂O₃

Fig. 4 shows the Ni K β mainline XES spectra (Ni 3p to 1s) for both the NiO/ γ -Al₂O₃ and NiCoO/ γ -Al₂O₃ catalysts in their cal-



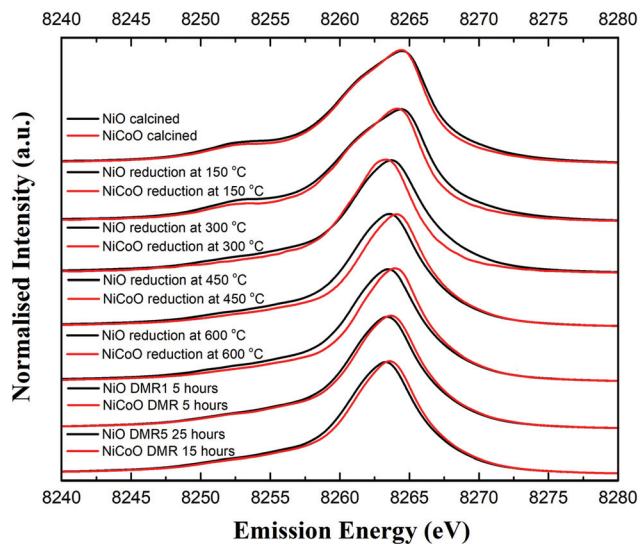


Fig. 4 Ni K β XES spectra of the NiO/ γ -Al $_2$ O $_3$ and NiCoO/ γ -Al $_2$ O $_3$ samples obtained under ambient, reductive activation, and DMR conditions.

cined form, during the reductive activation step, and during the DMR reaction. The black and grey spectra correspond to the Ni XES for the freshly calcined NiO and NiCoO samples, respectively. The spectra exhibit subtle differences with the K $\beta_{1,3}$ maxima occurring at 8264.5 eV and 8264.4 eV, for the NiO and NiCoO, respectively. Both calcined samples also exhibit a K β' feature at \sim 8253.1 eV, which is typical for a triplet ($S = 1$) Ni $^{2+}$ oxide species (Fig. S7 \dagger).⁴⁷ The slight differences in the mainline position could reflect modulations in site symmetry and/or covalency of the Ni site.^{33,48}

The samples were activated by flowing 5% H $_2$ in Ar gas and by gradually increasing the temperature from 25 °C to 600 °C. The selected temperature range for the reduction is based on the previously collected TPR data (Fig. 2), which revealed a full reduction of the active phase at $T < 500$ °C. To follow the reduction of the Ni sites and make a correlation with the TPR data, XES spectra were measured in a selected temperature range. First, following the reduction of the metal oxides at 150 °C and 300 °C, the Ni XES peak for the NiO sample shifts by -0.05 and -0.78 eV, respectively to lower emission energies and the K β' peak at 8253 eV has largely vanished (Fig. 4 and Table S2 \dagger). This is consistent with the reduction of Ni $^{2+}$ to Ni 0 . Upon complete reduction a d 10 configuration is reached and the p-d exchange, which gives rise to the K β' feature, is no longer present. Next, by increasing the temperature to 450 °C and 600 °C, the Ni XES K $\beta_{1,3}$ peak position for NiO shifts to lower emission energies, which indicated the full reduction of NiO-Al $_2$ O $_4$ at $T > 400$ °C (Fig. 2).⁴⁹ This is consistent with *in situ* STXM data for the NiCoO sample which showed that full reduction occurs at 500 °C.²⁴ Finally, due to the reduction of NiO-Al $_2$ O $_4$ sites to metallic Ni at 600 °C, the Ni K $\beta_{1,3}$ emission peak shifts by ~ -1 eV relative to the emission spectrum for the calcined sample to 8263.48 eV.

Fig. 4 shows that the Ni K $\beta_{1,3}$ XES peak for the NiCoO sample at 150 °C and 300 °C shifts by -0.30 eV and -1.12 eV, respectively, relative to the emission spectrum of the calcined sample. Based on a previous study, the full reduction of Co ions in NiCoO is proposed to proceed by a two-step process whereby first Co $^{3+}$ (O_h) is reduced to Co $^{2+}$ and its electronic and spin configurations changes from a 3d 6 , $S = 2$ to 3d 7 , $S = 3/2$. Subsequently at elevated temperatures the remaining Co $^{2+}$ (T_d) and Co $^{2+}$ (O_h) are fully reduced to metallic Co.²⁴ Following the reduction at $T \leq 300$ °C the XES spectra of the NiO vs. the NiCoO samples have different spectral shape and peak positions (Fig. 4 and S8, 9 \dagger). At 450 °C the shift in the emission spectra of NiCoO is reversed and moves towards higher emission energies. Further, by increasing the reduction temperature to 450 °C the Ni XES peak position for the NiO is shifted by additional -0.53 eV to lower energies with respect to the NiCoO spectrum and its K β' peak intensity is slightly higher, thus suggesting the formation of distinct Ni species (Fig. S10 \dagger). To understand the origin of this behavior and test if the sample at 300 °C is simply a mixture of both the oxide phase and reduced Ni, the emission spectra for the calcined and reduced NiO sample at 450 °C were averaged in different ratios (Fig. S11 \dagger). The K β spectrum of the reduced NiCo catalyst at 450 °C is clearly different from any of other spectra presented in Fig. S11 \dagger , indicating that this is not simply a partially converted species, but rather that the NiCoO sample has a Ni site that is electronically distinct from the Ni only catalyst. Further, upon full reduction of the Ni ions in NiCoO at 600 °C the K $\beta_{1,3}$ XES peak position for the sample at 600 °C is shifted by -0.45 eV relative to the calcined sample. This energy shift is smaller when compared to the NiO case and thus suggests a different reduction mechanism for the Ni ions in NiCoO. Further, the K $\beta_{1,3}$ XES peak position for the fully reduced monometallic catalyst is shifted by ~ -0.5 eV relative to the bi-metallic catalyst at 600 °C (Fig. S12 and Table S2 \dagger). These results confirm that the fully reduced NiO and NiCoO are not identical at 600 °C.

Finally, the XES spectra collected under dynamic flow of DMR gas mixture at 600 °C for both NiCoO and NiO indicate that a dominantly metallic Ni phase remains during the course of catalysis (Fig. 4). This observation is further supported by the XES data analysis in Fig. S13 and S14. \dagger However, it is important to note that even during the DMR reaction the spectra of both catalysts remain somewhat different from each other, with the NiCoO catalyst appearing slightly more oxidized than the NiO catalyst at all stages. The changes that occur in the Ni local geometric and electronic structure may be key to understanding the increased activity of the NiCo catalyst relative to the Ni-only catalyst.

3.3. Ni K β HERFD of NiCoO/ γ -Al $_2$ O $_3$ vs. NiO/ γ -Al $_2$ O $_3$

The Ni K β -detected HERFD XAS spectra for the calcined NiCoO/ γ -Al $_2$ O $_3$ and NiO/ γ -Al $_2$ O $_3$, during the reductive activation, and under DMR conditions are shown in Fig. 5. The Ni K-edge HERFD spectra for the calcined NiO and NiCoO samples are different in terms of their spectral shapes and



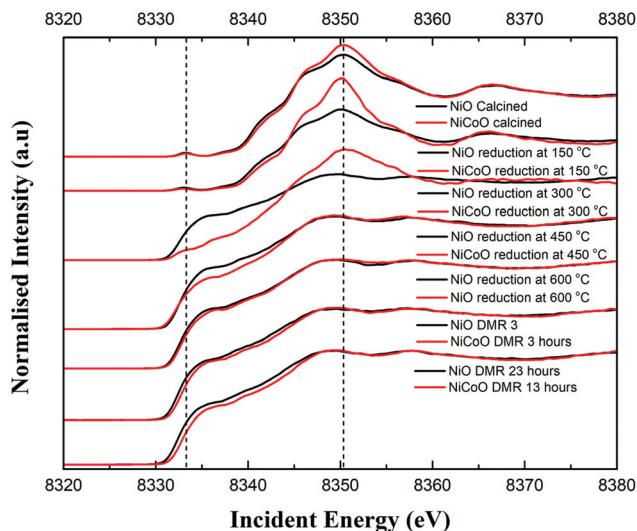


Fig. 5 Ni K β -detected HERFD XAS spectra of NiO/ γ -Al₂O₃ and NiCoO/ γ -Al₂O₃ collected for the freshly calcined samples, during the reduction/activation step, and under DMR conditions. The pre-edge and main edge peak positions have been indicated with dashed lines.

their K-edge peak positions is at 8350.37 eV and 8350.40 eV, respectively. The pre-edge of the NiO catalyst has a higher intensity than the NiCoO catalyst, which suggests that the former has a more distorted local structure (Fig. S15 \dagger).^{48,50} The sensitivity of the pre-edge intensity to the local geometric structure derives from symmetry allowed Ni p-d mixing, which occurs as the site deviates from ideal centrosymmetry. In addition, based on the pre-edge peak position, rising edge position, and spectral shape of the Ni K-edge HERFD for the calcined NiCoO and NiO samples, the Ni-site in both calcined catalyst is best described as Ni²⁺.^{48,51} Ni HERFD XAS data acquired during the catalyst activation in the temperature range from 150 °C to 600 °C are shown in Fig. S16–19 \dagger . Due to the induced reduction of the Ni at 150 °C, the K-edge peak positions for both catalysts equally shift by -0.3 eV relative to the spectra for the calcined samples (Fig. 5). In contrast to the NiCoO case, following the reductive activation at 300 °C the pre-edge feature of the NiO sample diminishes and its K-edge peak position shifts to lower energies indicating a further reduction of the Ni and consistent with loss of oxygen from the crystal structure.

The most striking difference during the catalyst activation step is the full reduction of the Ni ions in the NiO catalyst at just below 300 °C, while for the NiCoO catalyst the full conversion to the metallic state just occurs at just below 450 °C (Fig. 5). We note that a one-to-one comparison to the TPR temperatures is limited by the 150 °C temperature steps that were taken for the XAS measurements.

To test if the more oxidized appearance of the Ni K-edge HERFD in the NiCoO catalyst (at 300 °C) is simply a result of incomplete conversion, a similar data analysis as in the case of XES spectra was performed by mixing the HERFD spectra of the calcined NiO and reduced sample at 450 °C (Fig. S20 \dagger).

This analysis reveals that the EXAFS region of the spectrum for the reduced NiCoO samples at 450 °C and any of the obtained mixed spectra are not superimposable with the NiCoO catalyst at 300 °C. Therefore, we propose that this species in NiCoO is very likely a distinct Ni species, which results from the presence of Co in the catalyst. In addition, the overlaid HERFD spectra for the NiO and NiCoO samples at 450 °C indicate a different electronic structure (Fig. S18 \dagger). The HERFD spectra for reduced NiO and NiCoO at 600 °C remain distinct from each other. While both catalysts appear to be comprised of dominantly reduced metallic Ni, the NiCoO catalysts shows a slightly larger contribution of oxidized Ni (Fig. S19 \dagger). Finally, HERFD data were continuously collected during exposure to DMR conditions and revealed the high stability of Ni in its metallic state under the DMR conditions (Fig. 5 and S21, 22 \dagger).

3.4. Co K β HERFD of NiCoO/ γ -Al₂O₃

Co K β HERFD spectra for the NiCoO/ γ -Al₂O₃ catalyst in the calcined form, activated form, and under the DMR conditions are presented in Fig. 6. Based on the HERFD spectrum and previous Co L-edge XAS data,²⁴ the Co species in the freshly calcined sample is consistent with Co₃O₄.⁵² At 150 °C, the reduction of Co³⁺ (*O_h*) sites to most probably Co²⁺ oxide initiates, and the Co K-edge HERFD white line position dramatically shifts from 7729.8 eV to 7726.96 eV ($\Delta E = 2.8$ eV). In the following step, Co HERFD data collected at 300 °C shows an additional shift of +1.6 eV to higher energies which is assigned to the reduction of the remaining Co²⁺ species to metallic cobalt. Following the full reduction to metallic Co at 450 °C and 600 °C, the Co HERFD spectrum white line peak position is shifted from 7730 eV to 7726.5 eV (Fig. S23 \dagger). Finally, upon exposing the NiCo catalyst to DMR conditions for 8 h the HERFD spectra remain unchanged and confirms the stability of metallic Co under the DMR conditions.

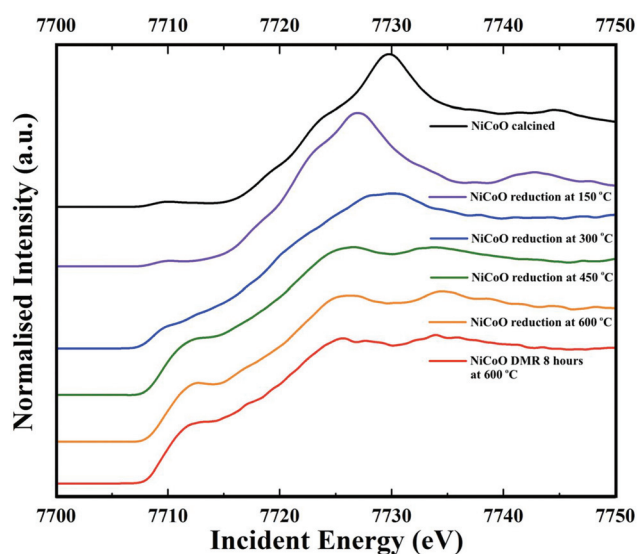


Fig. 6 Co K β -detected HERFD spectra of the NiCoO/ γ -Al₂O₃ sample measured under ambient, reduction activation (5% H₂ in Ar), and DMR (7% CH₄ and 9.5% CO₂ diluted in N₂) conditions.



4. Conclusion

We studied the structural and electronic properties of NiO/ γ -Al₂O₃ and NiCoO/ γ -Al₂O₃ DMR catalysts in the calcined and reduced states and *in situ* under DMR conditions. DMR activity measurements revealed a significantly higher activity for the bimetallic NiCoO catalyst compared to the pure NiO catalyst. *In situ* XES spectroscopy for the calcined DMR catalysts showed subtle differences in the Ni K β mainline spectral shape and positions, which are attributed to differences in site symmetry and/or covalency of the Ni sites upon addition of Co. Further, during the course of the reduction/activation of the catalyst, and also during the DMR reaction, the NiCoO catalyst appears to be slightly more oxidized when compared to the NiO catalyst. K β -detected HERFD XAS data revealed that the structure of the NiCoO/ γ -Al₂O₃ catalyst is less distorted (based on the pre-edge intensities) relative to the NiO/ γ -Al₂O₃ catalyst. In addition, Co in NiCoO was identified as being structural analogous to Co₃O₄. Based on both Ni K β XES and HERFD spectra, it was shown that due to the presence of Co in the NiCoO sample, the Ni ions under reductive activation conditions are reduced at relatively higher temperatures as compared to the NiO catalyst. Following the reduction of the NiCoO catalyst at 300 °C, a Ni species with a distinct geometric and electronic structure is formed. At 600 °C, both catalysts are activated and the metal oxides are largely reduced to the metallic phase. Both catalysts remain unchanged during DMR, but distinct differences remain between the Ni-only and the NiCo catalyst, which provide experimental evidence that the presence of Co modulates the Ni geometric and electronic structure.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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