

Supporting Information

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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Figure S1

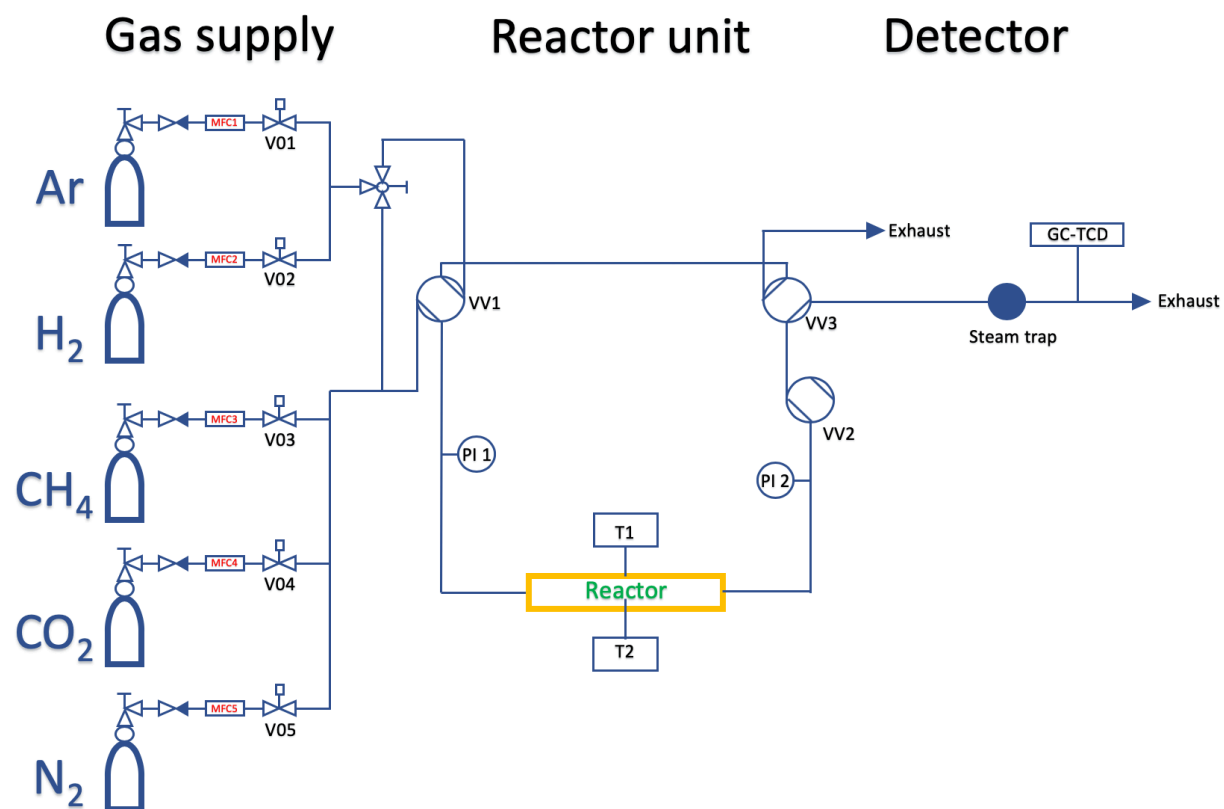


Figure S1: Flow scheme of the reactor used for the DMR activity measurements.

Figure S2

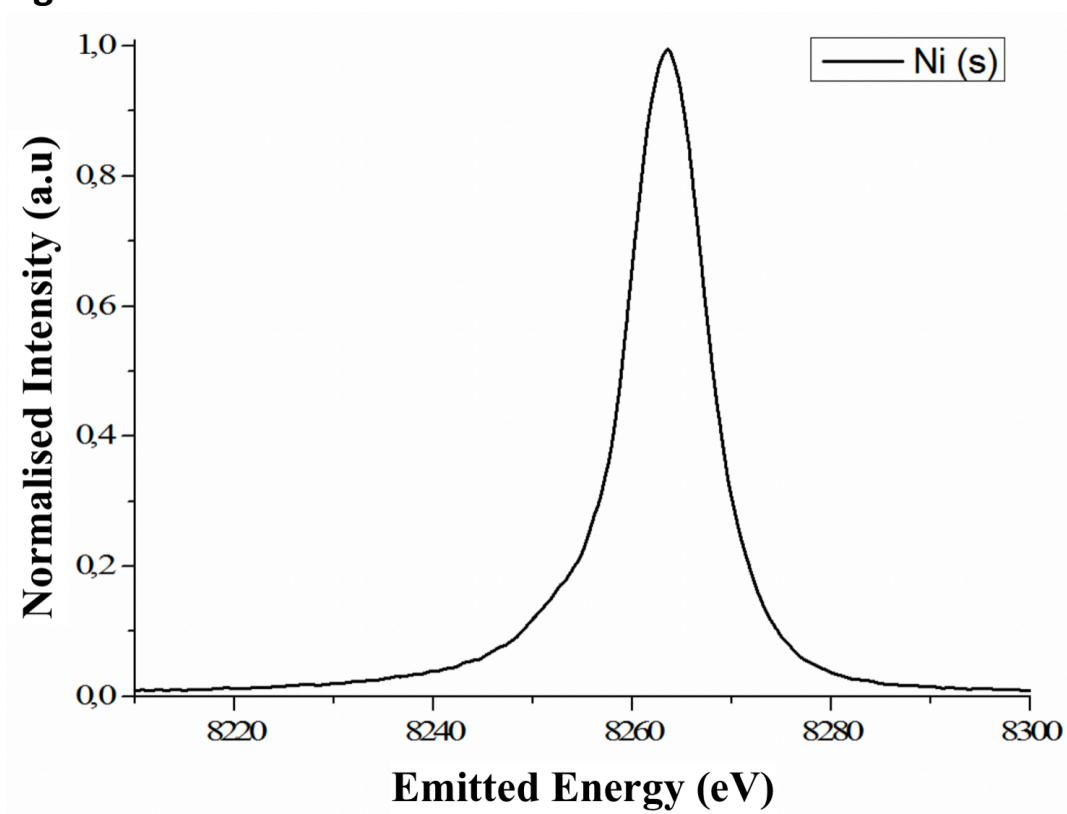


Figure S2: Reference Ni XES spectra of Ni foil.

Figure S3

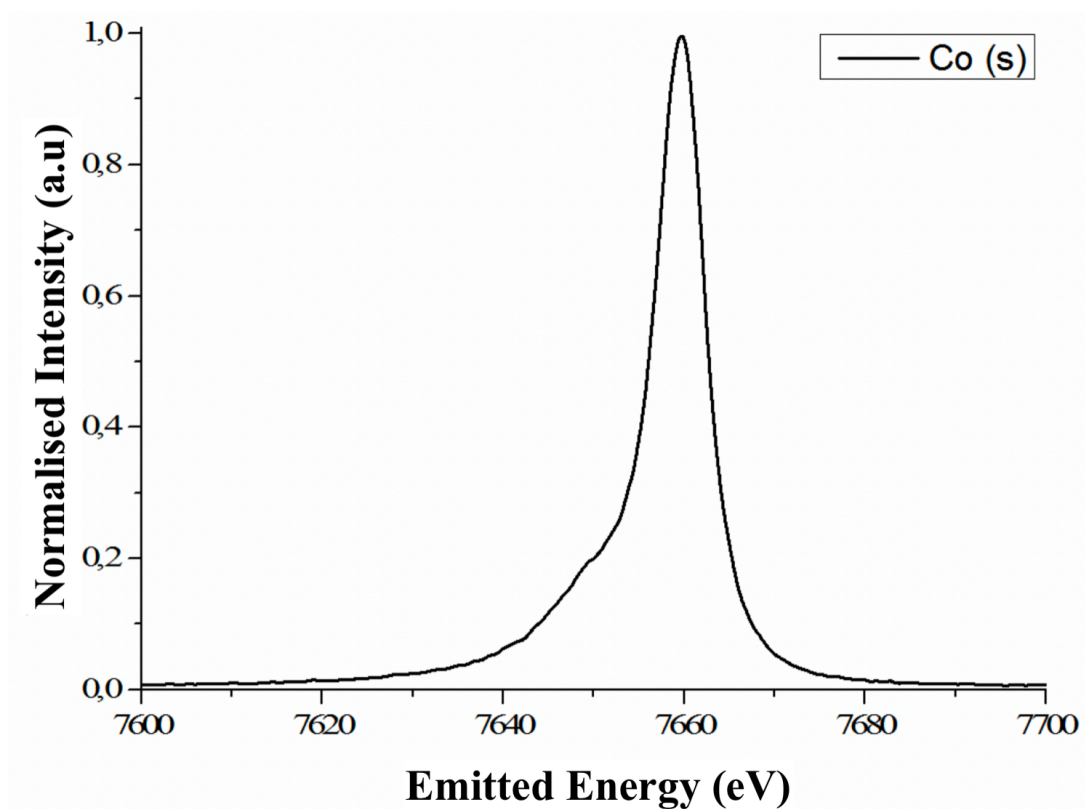


Figure S3: Reference Co XES spectra of Co foil.

Figure S4

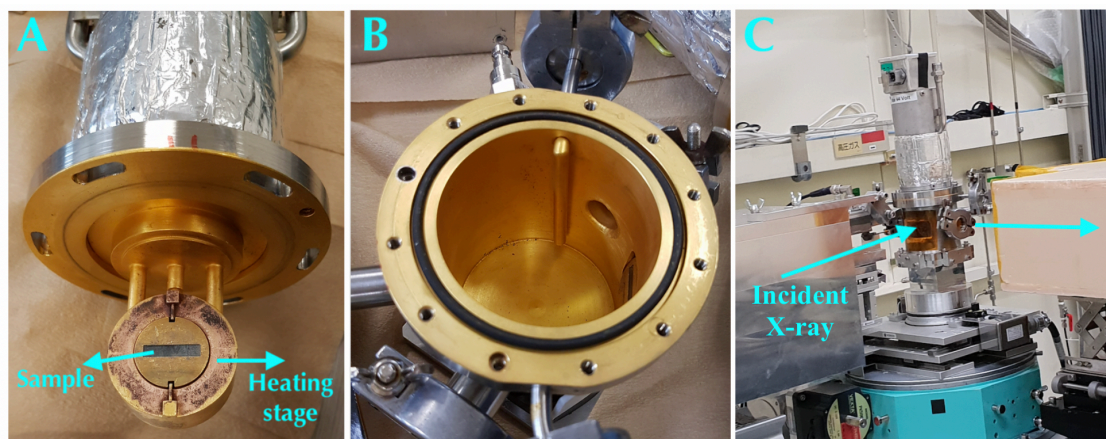


Figure S4: A) The sample powder is pressed into a pellet that is located in the sample holder. The heating stage allows heating up to 600°C. B) image showing that interior of the used reactor. C) Operational reactor setup used in this experiment. During this process the Incident X-ray beam enters the reactor from the window covered with Kapton tape and the scattered emission is measured from the 90° angle.

Figure S5

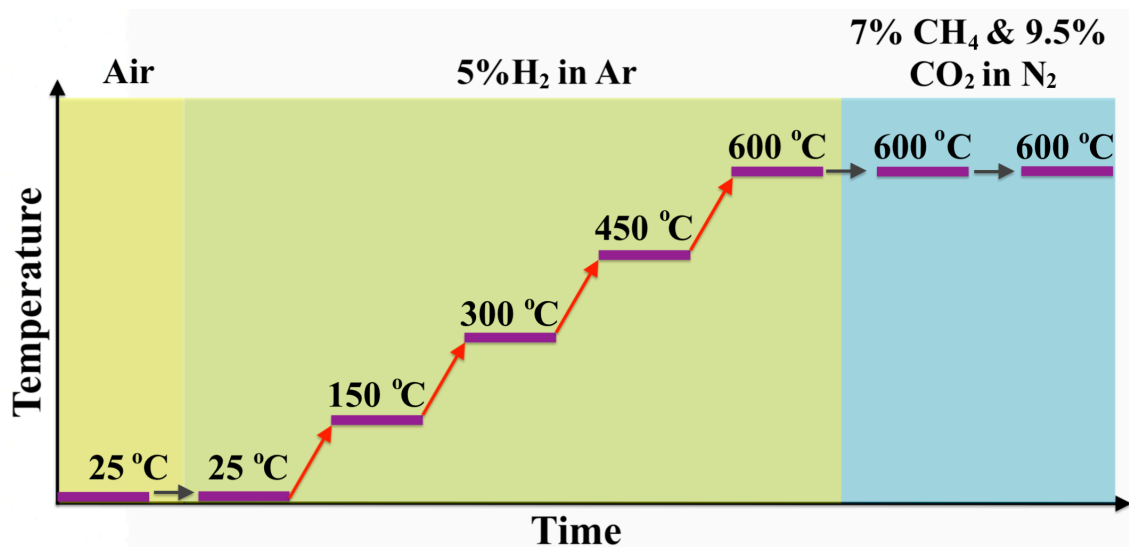


Figure S5: Schematic illustration of the hard X-ray experiments. In the first stage of the experiment the calcined samples were measured at 25 °C under air. The next step involves heating the sample under reducing conditions. In the last step the sample is exposed to DMR conditions.

Table S1

Table S1: Stabilized conversion/yield values for the NiCoO/ γ -Al₂O₃ and NiO/ γ -Al₂O₃ DMR catalysts.

	NiCoO/ γ -Al ₂ O ₃	NiO/ γ -Al ₂ O ₃
<i>CH₄ Conversion (%)</i>	79	46
<i>CO₂ Conversion (%)</i>	71	43
<i>H₂ Yield (%)</i>	70	39
<i>CO Yield (%)</i>	73	44
<i>H₂O Yield (%)</i>	9	5

Figure S6

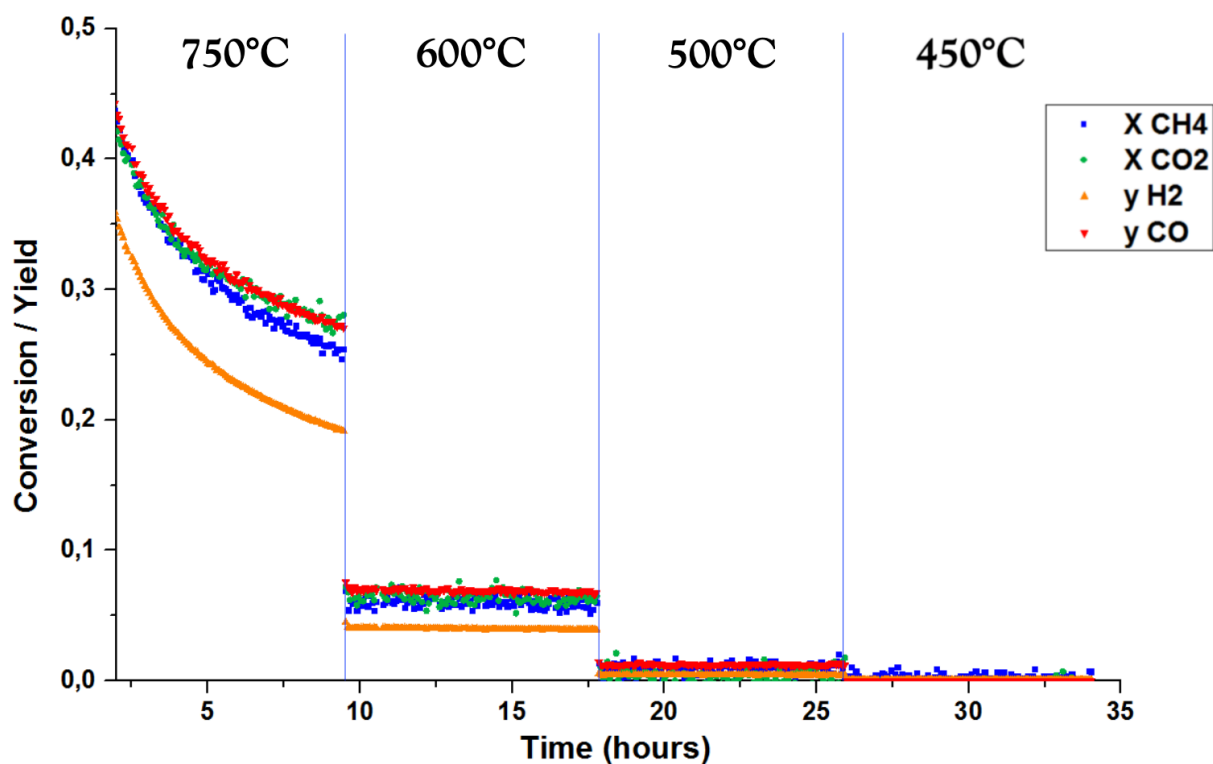


Figure S6: Conversion/Yield values of the NiCoO catalyst during the DMR experiment at 750 °C, 600 °C, 500 °C and 450 °C with 7% CH₄, 9.5 % CO₂ in N₂ and a flow rate of 490 mL/min.

Figure S7

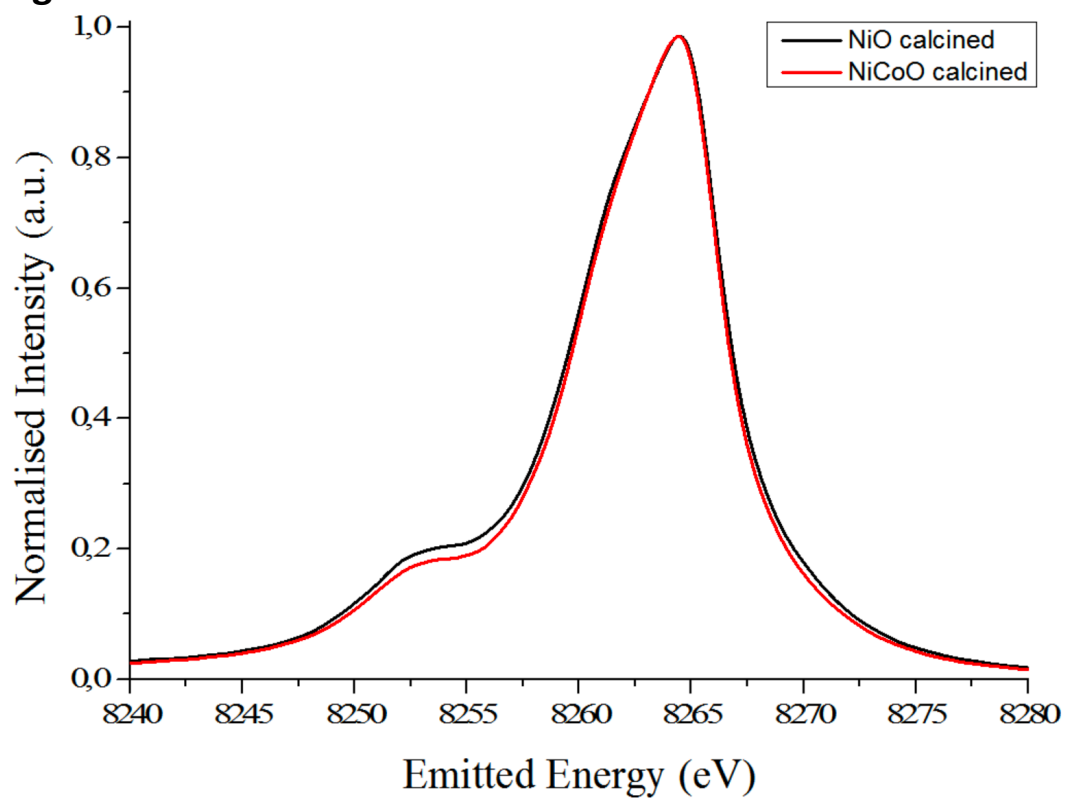


Figure S7: Overlay of the XES spectra for the NiO and NiCoO calcined catalysts.

Table S2

Table S2: $K\beta_{1,3}$ peak position for both NiO/ γ -Al₂O₃ and NiCoO/ γ -Al₂O₃ catalysts measured under activation and DMR conditions.

	NiO/ γ -Al ₂ O ₃	NiCoO/ γ -Al ₂ O ₃
<i>Calcined</i>	8264.50 eV	8264.44 eV
<i>Reduced at 150 °C</i>	8264.45 eV	8264.14 eV
<i>Reduced at 300 °C</i>	8263.72 eV	8263.32 eV
<i>Reduced at 450 °C</i>	8263.57 eV	8264.10 eV
<i>Reduced 600 °C</i>	8263.48 eV	8263.99 eV
<i>DMR 5 hours</i>	8263.40 eV	8263.68 eV

Figure S8

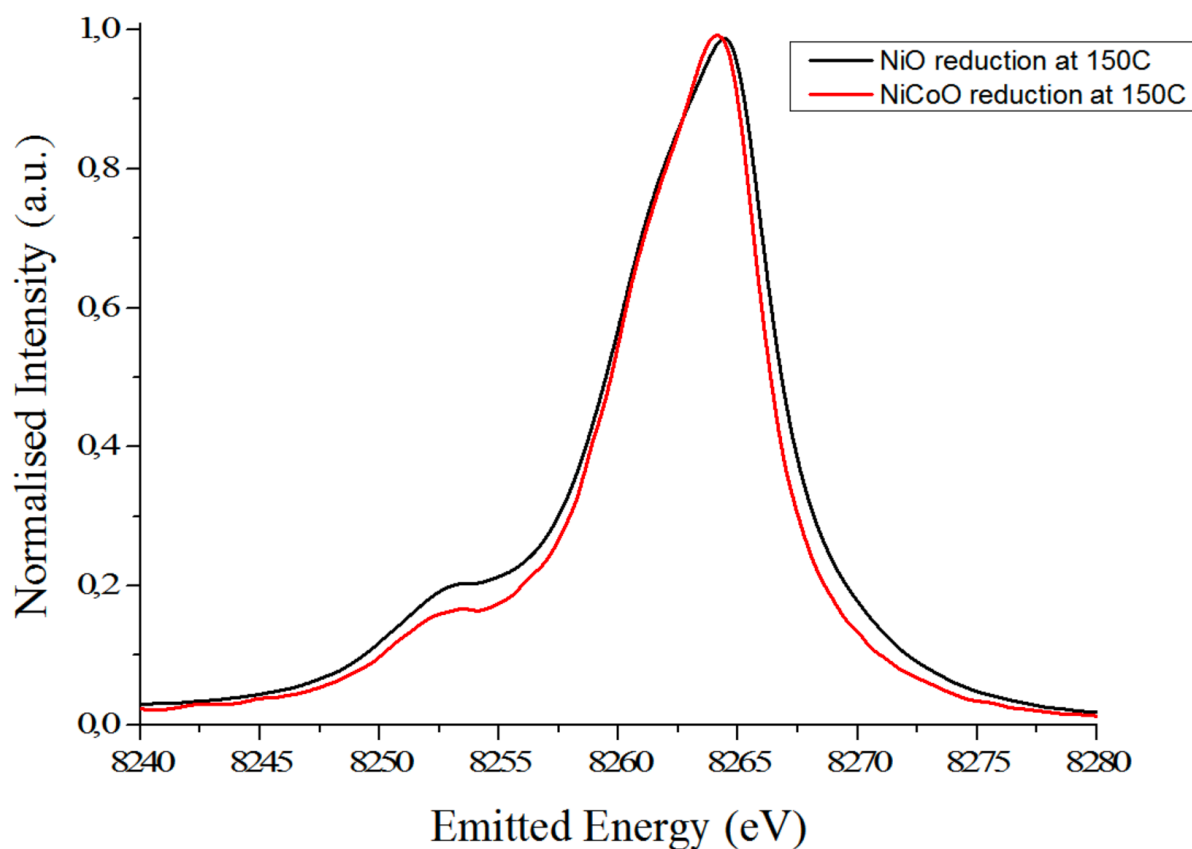


Figure S8: Overlay of the XES spectra for the NiO and NiCoO catalyst after being reduced at 150 °C.

Figure S9

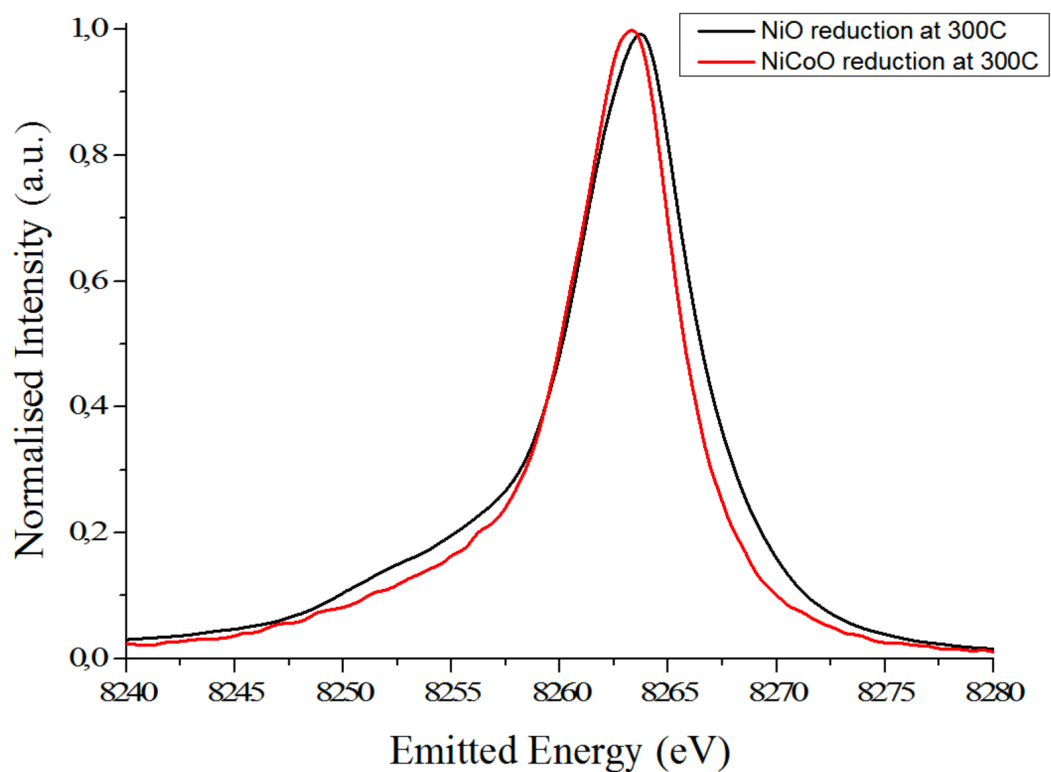


Figure S9: Overlay of the XES spectra for the NiO and NiCoO catalyst after being reduced at 300 °C.

Figure S10

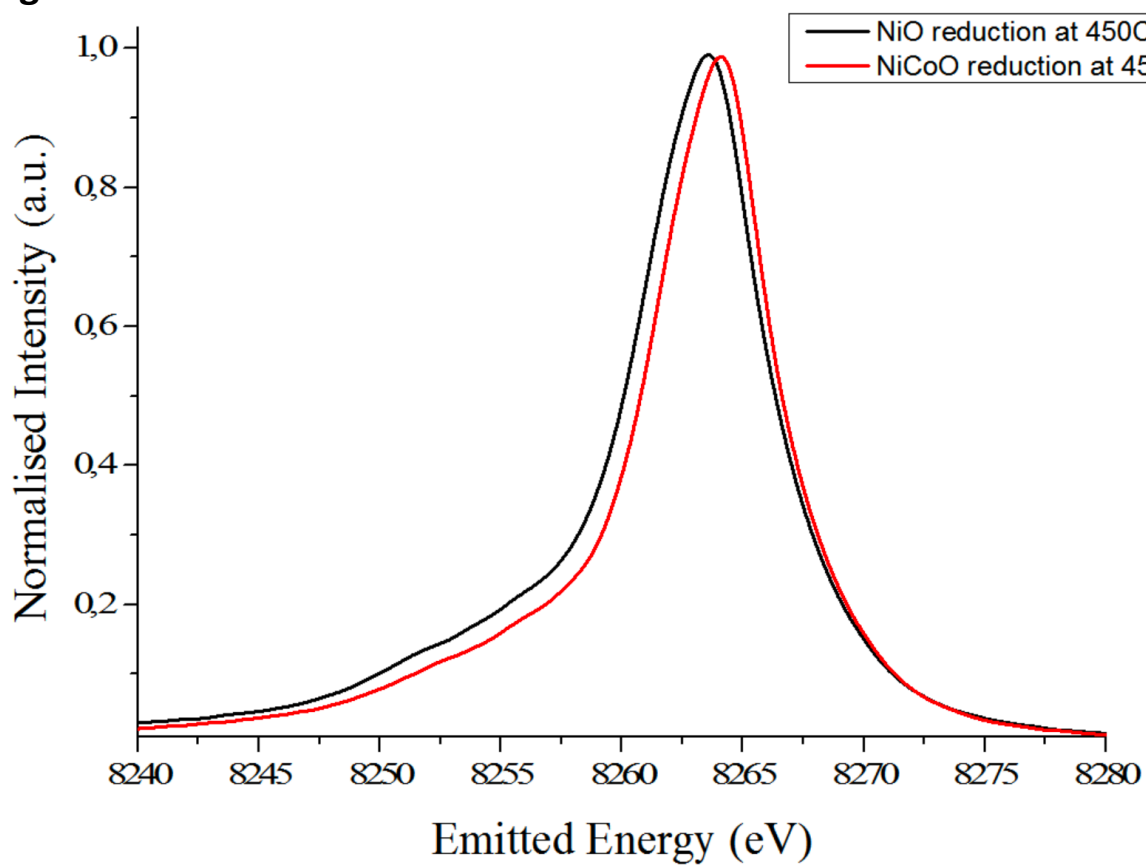


Figure S10: Overlay of the XES spectra for the NiO and NiCoO catalyst after being reduced at 450 °C.

Figure S11

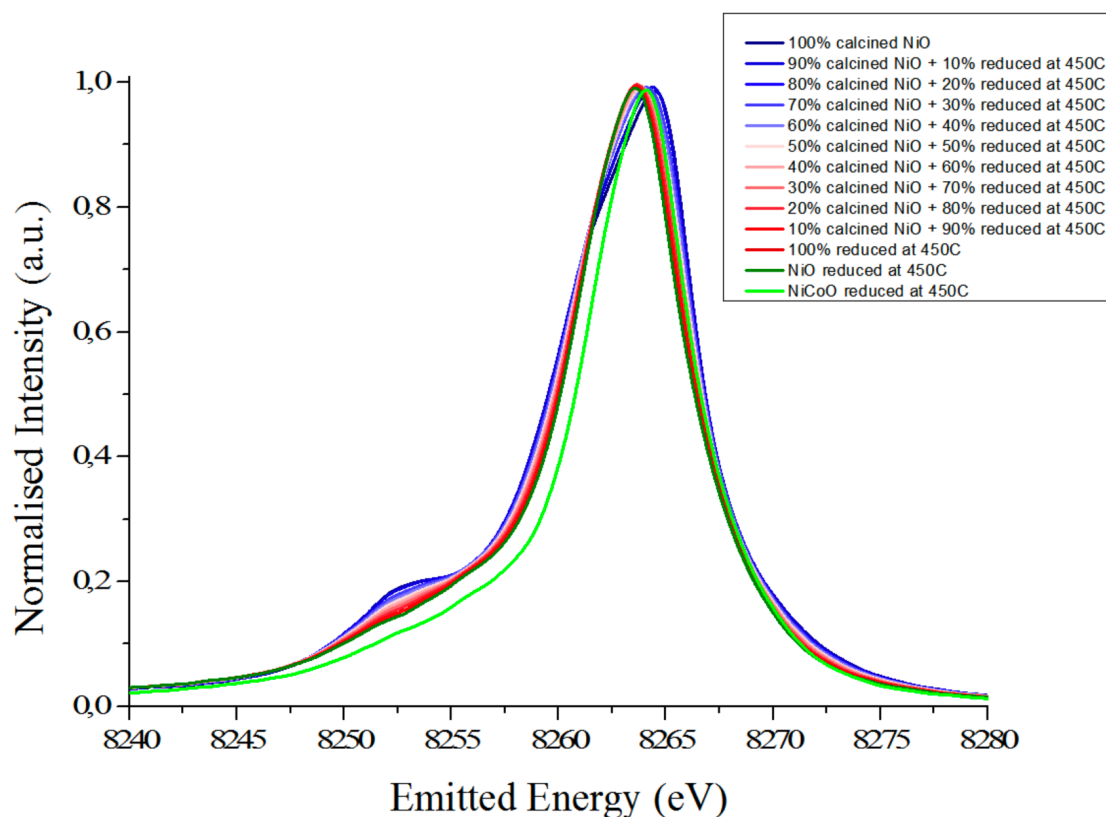


Figure S11: A combination of NiO XES spectra showing the calcined NiO (dark blue), the fully reduced NiO (dark green) and NiCoO (light green) at 450°C. Furthermore, several average spectra were obtained by mixing the spectra of the calcined and reduced NiO sample at 450 °C.

Figure S12

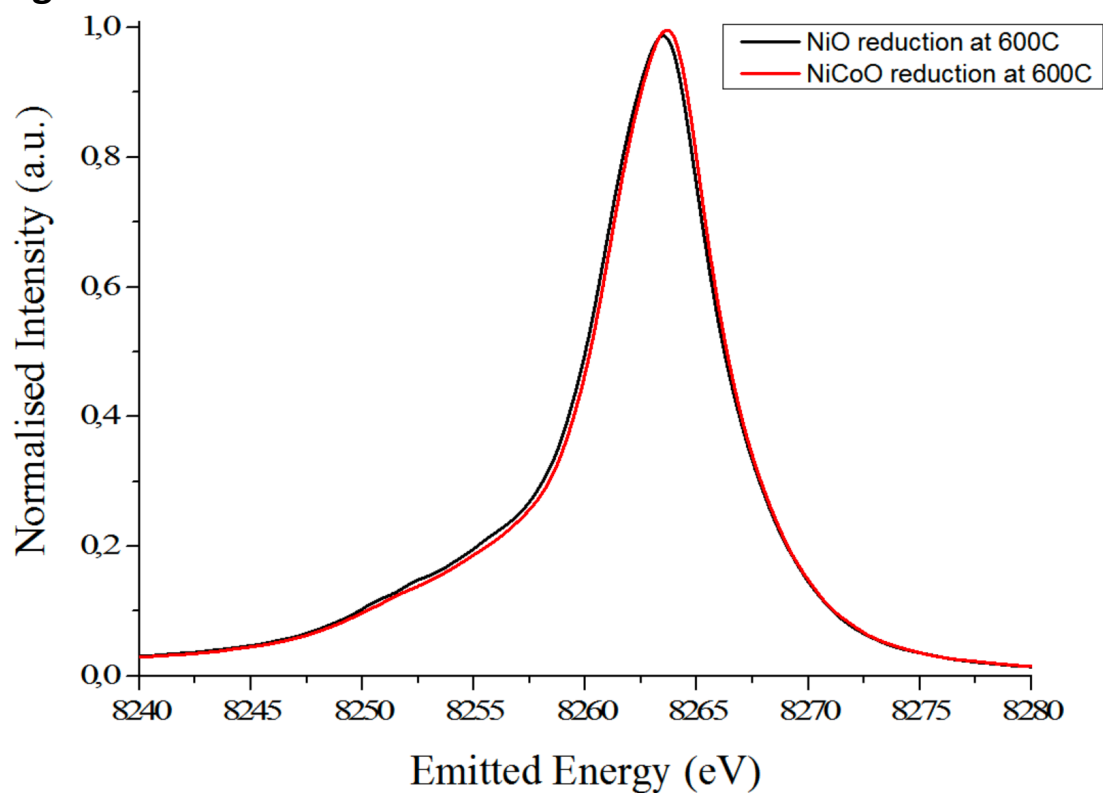


Figure S12: Overlay of the XES spectra for the NiO and NiCoO catalyst after being reduced at 600 °C.

Figure S13

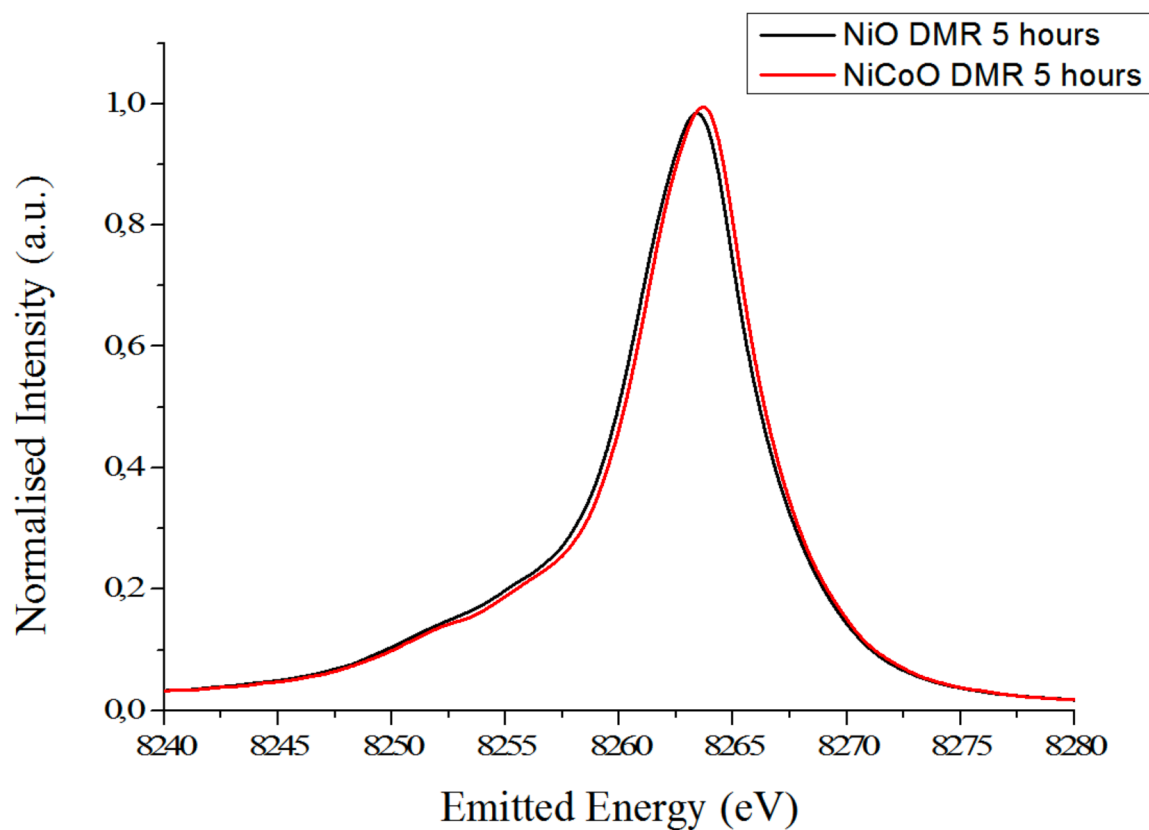


Figure S13: Overlay of the XES spectra for the NiO and NiCoO catalyst after being exposed to DMR conditions for 5 hours.

Figure S14

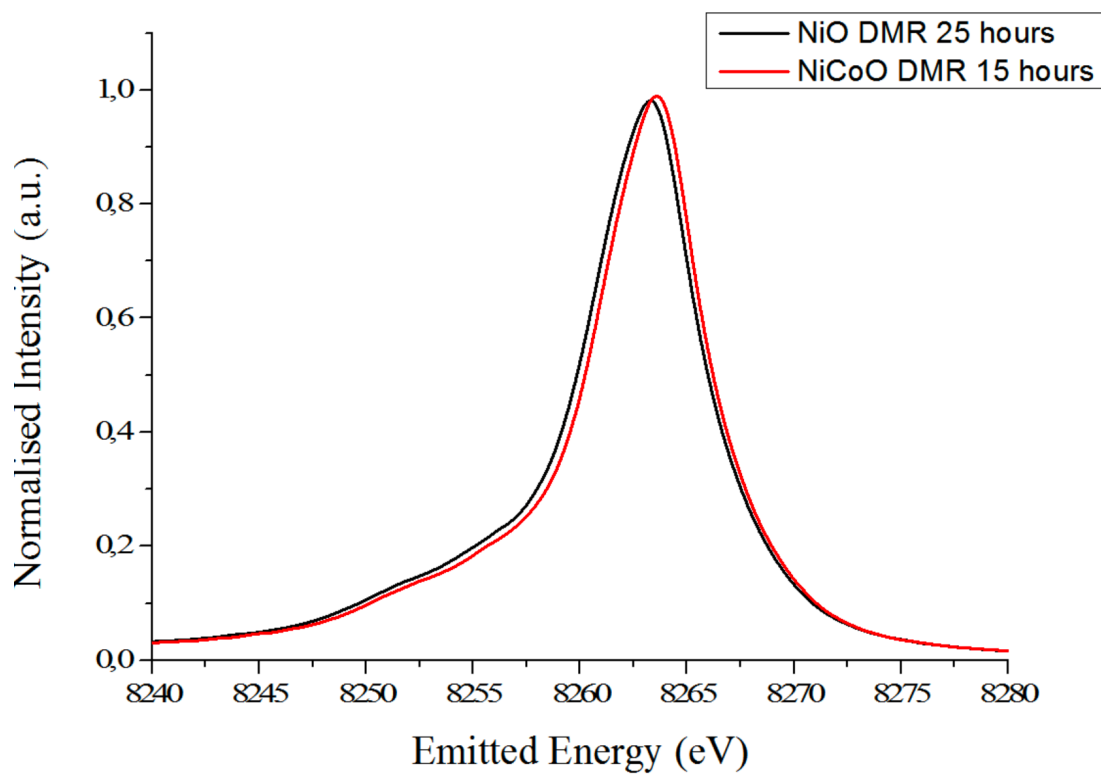


Figure S14: Overlay of the XES spectra for the NiO and NiCoO catalyst after being exposed to DMR conditions for 25 and 15 hours respectively.

Figure S15

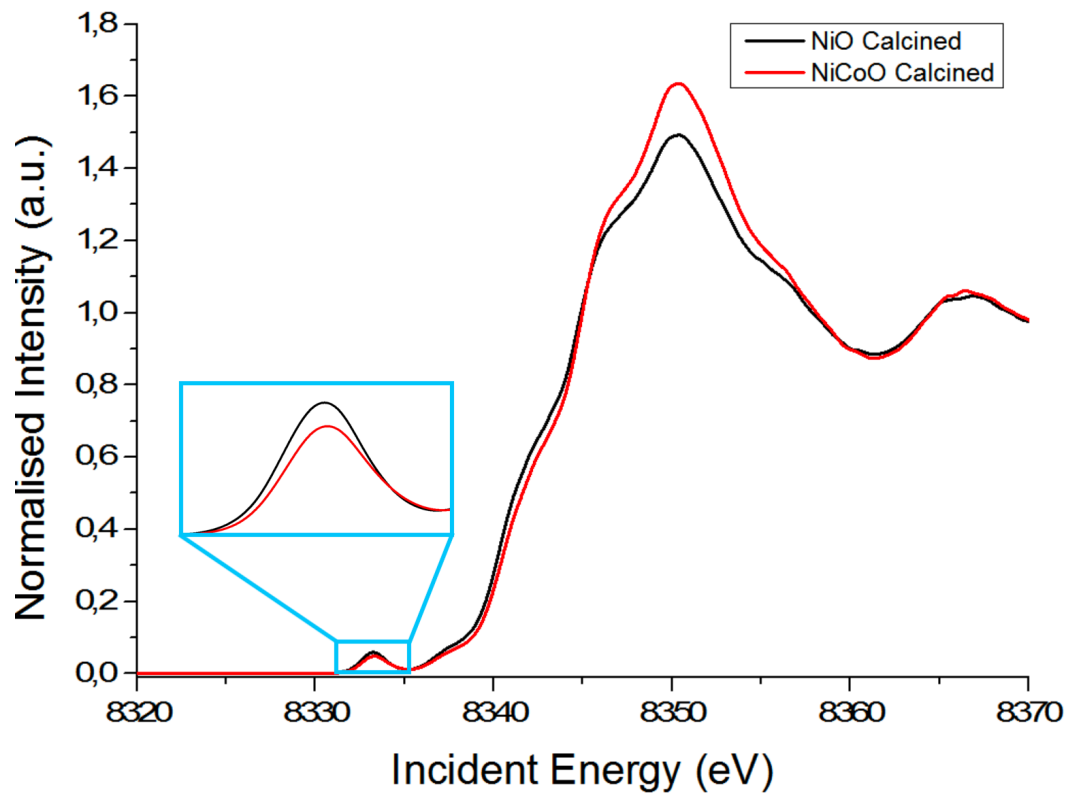


Figure S15: Overlay of the HERFD spectra for the NiO and NiCoO calcined catalysts.

Figure S16

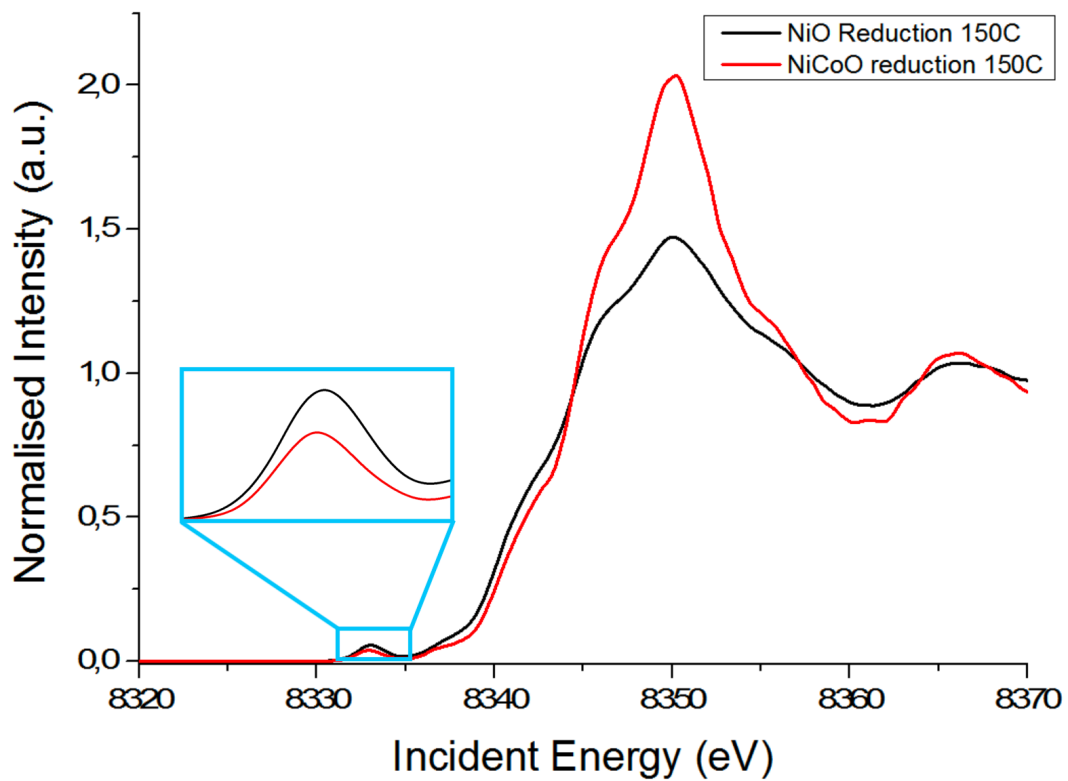


Figure S16: Overlay of the HERFD spectra for the NiO and NiCoO catalyst after being reduced at 150 °C.

Figure S17

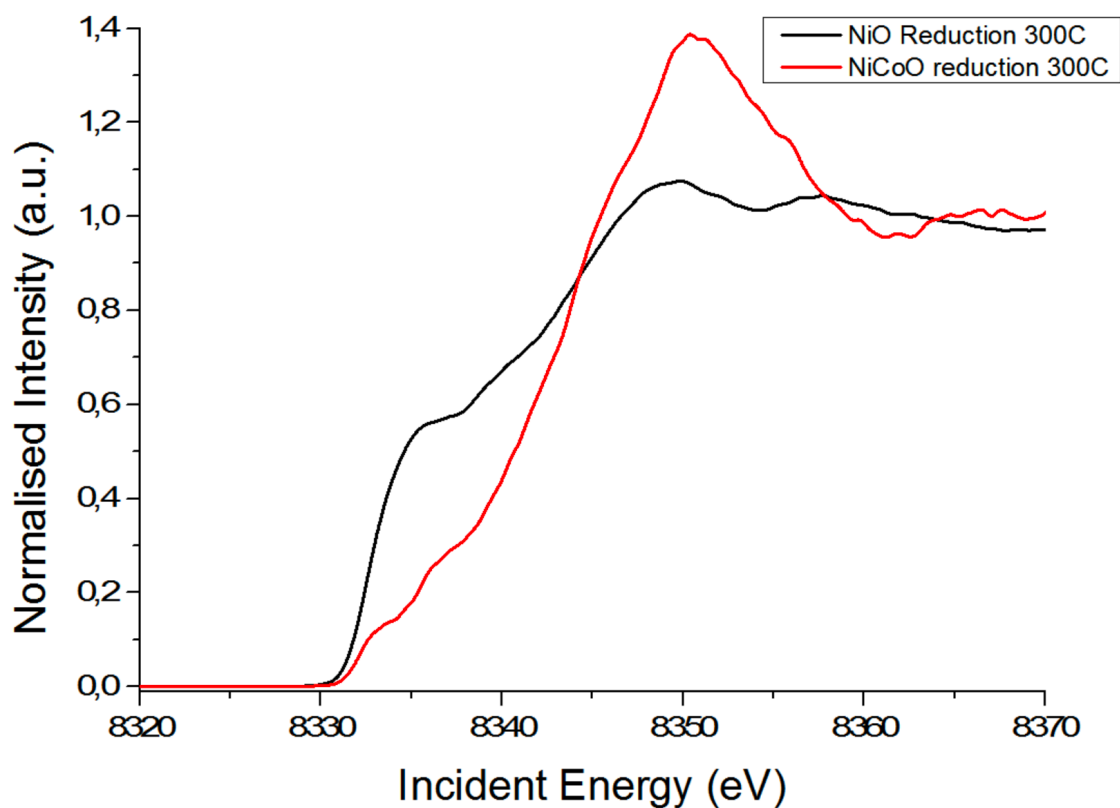


Figure S17: Overlay of the HERFD spectra for the NiO and NiCoO catalyst after being reduced at 300 °C.

Figure S18

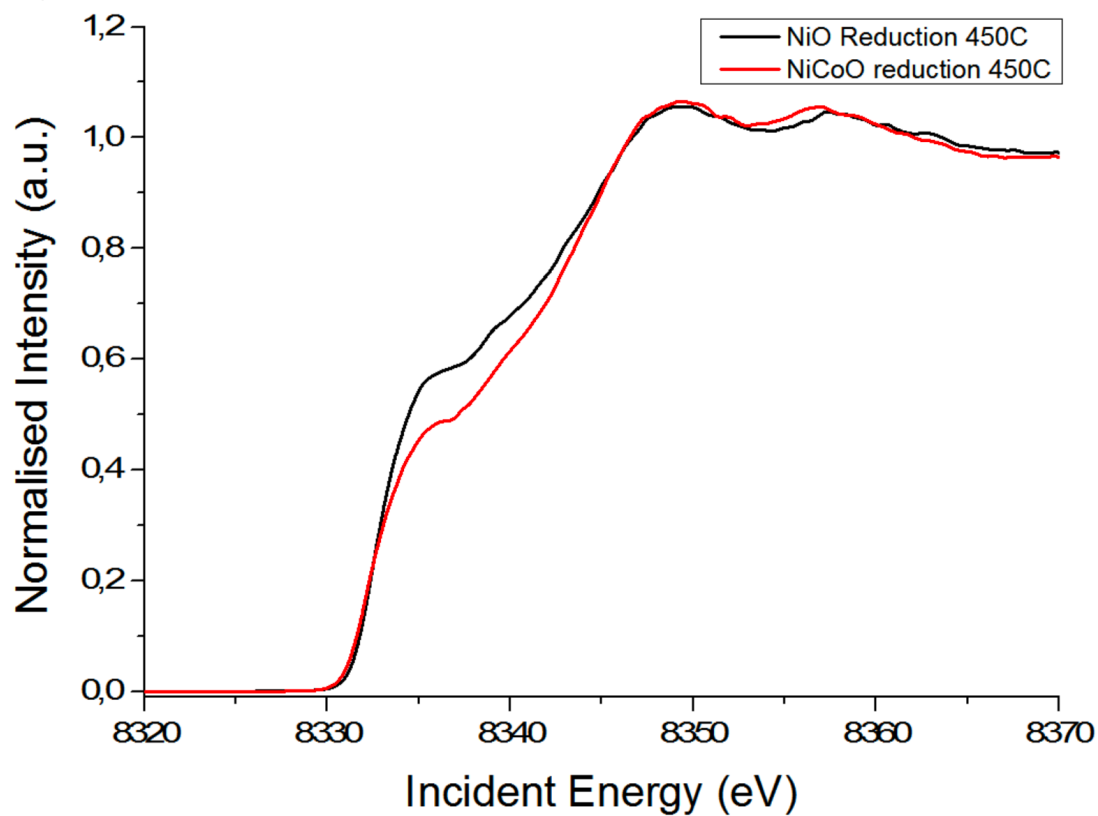


Figure S18: Overlay of the HERFD spectra for the NiO and NiCoO catalyst after being reduced at 450 °C.

Figure S19

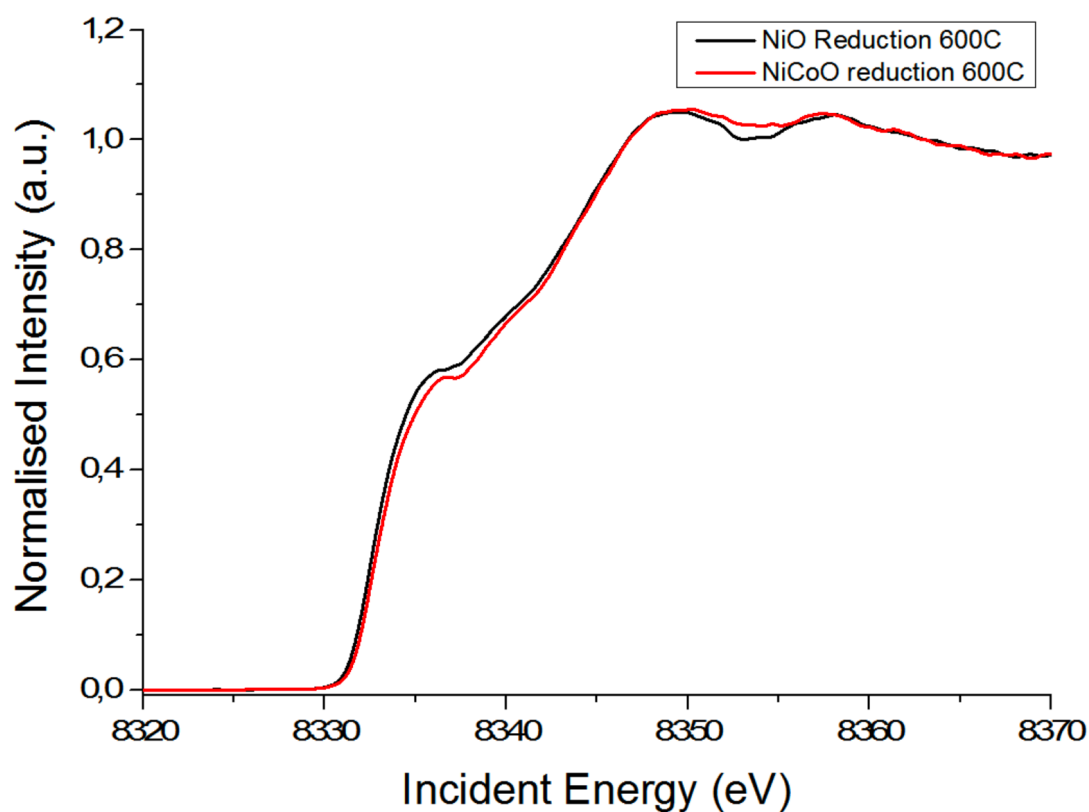


Figure S19: Overlay of the HERFD spectra for the NiO and NiCoO catalyst after being reduced at 600 °C.

Figure S20

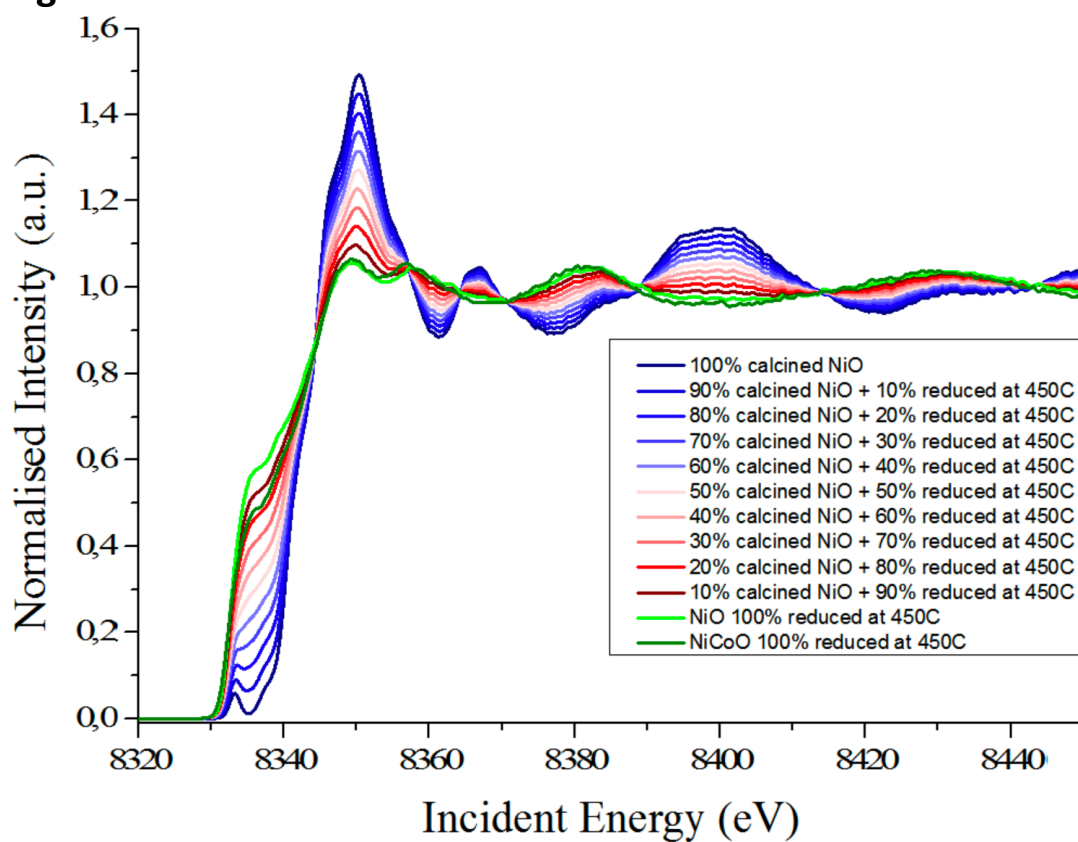


Figure S20: A combination of NiO HERFD spectra showing the calcined NiO (dark blue), the fully reduced NiO and NiCoO at 450 °C.

Figure S21

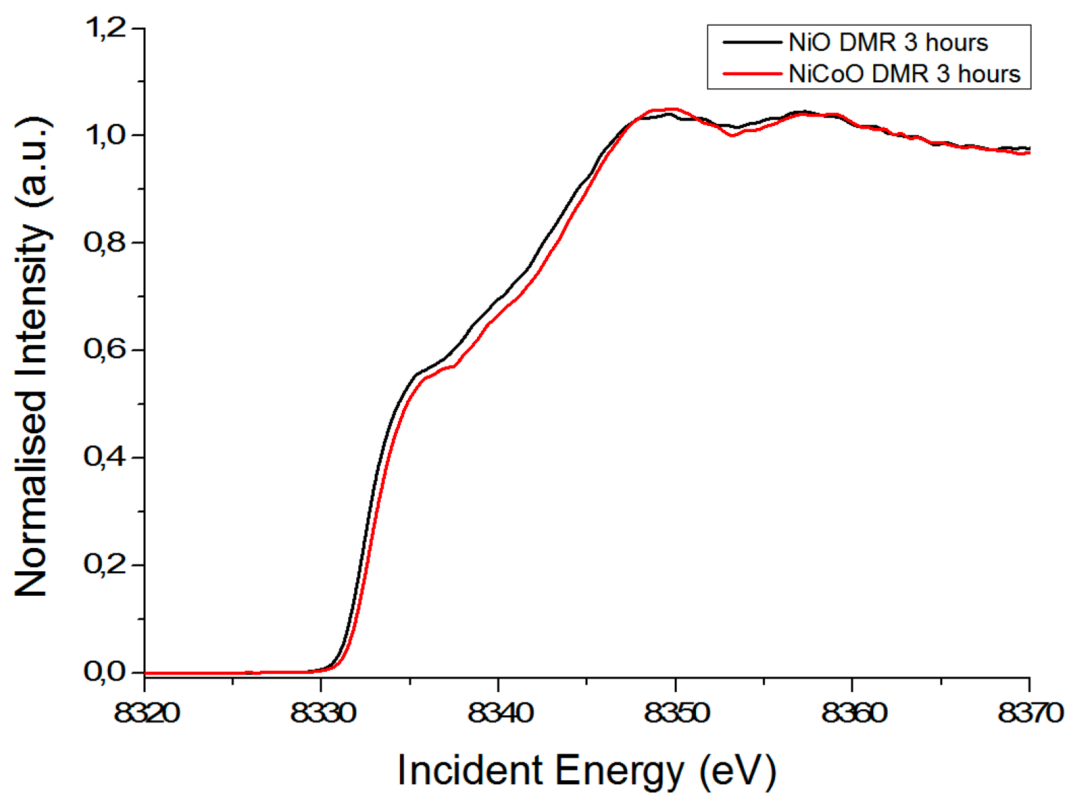


Figure S21: Overlay of the HERFD spectra for the NiO and NiCoO catalyst after being exposed to DMR conditions for 3 hours.

Figure S22

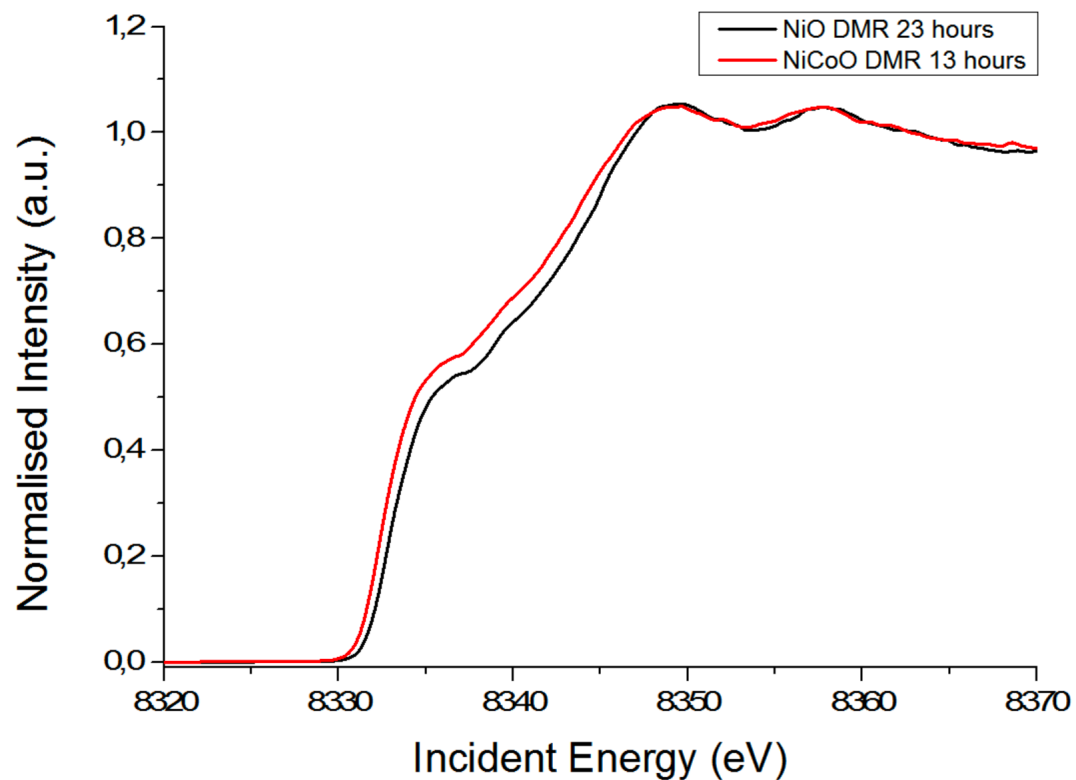


Figure S22: Overlay of the HERFD spectra for the NiO and NiCoO catalyst after being exposed to DMR conditions for 23 and 13 hours respectively.

Figure S23

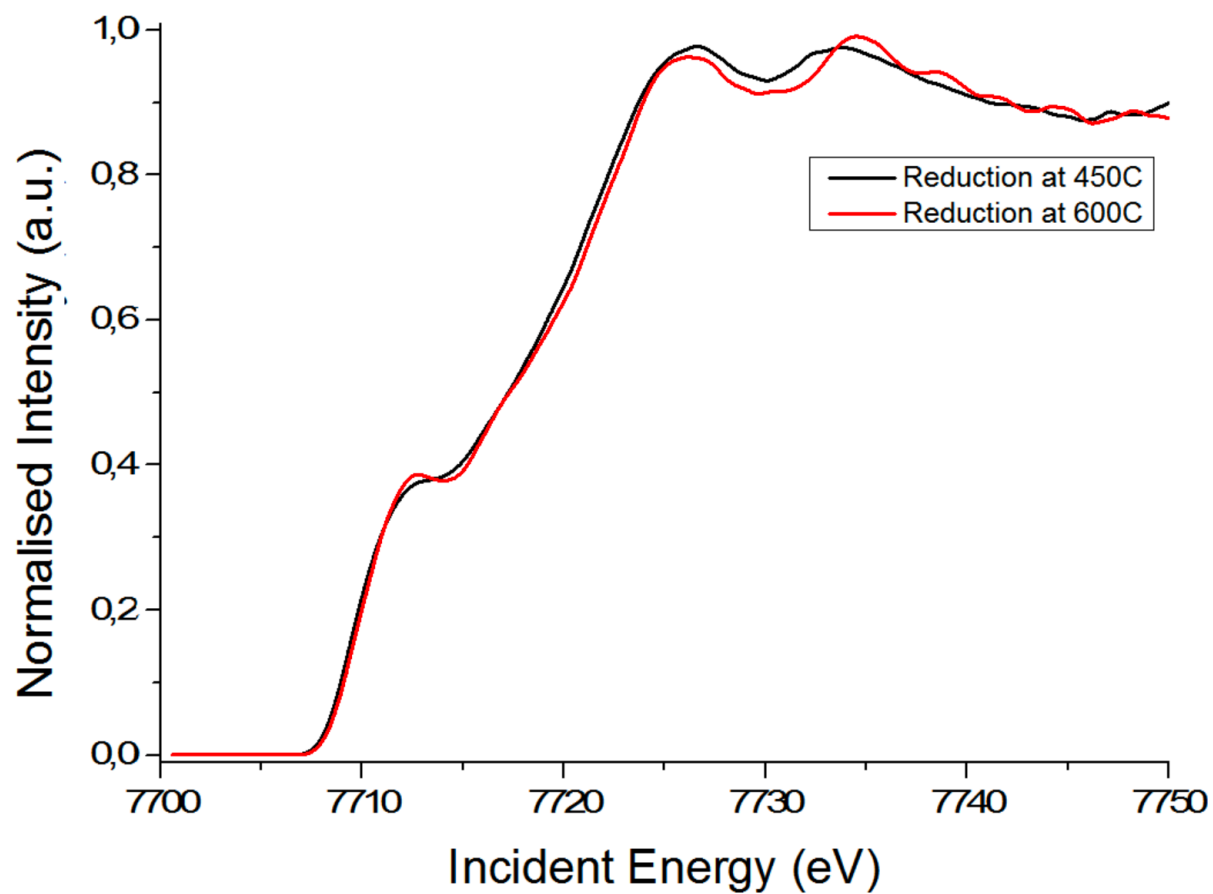


Figure S23: Overlay of the NiCoO HERFD spectra for the catalyst reduced at 450 and 600 °C.