Supporting information for

Structural insight into an atomic layer deposition (ALD) grown Al_2O_3 layer on Ni/SiO_2: impact on catalytic activity and stability in dry reforming of methane

Sung Min Kim[a], Andac Armutlulu[a], , Wei-Chih Liao[b], Davood Hosseini[a], Dragos Stoian[c], Zixuan Chen,[a] Paula M. Abdala[a], Christophe Copéret[b] and Christoph Müller[a,*]

[a] Department of Mechanical and Process Engineering, ETH Zurich, Leonhardstrasse 27, 8092 Zurich, Switzerland

[b] Department of Chemistry and Applied Sciences, ETH Zurich, Vladimir Prelog Weg 1-5, 8093 Zurich, Switzerland

[c] Swiss–Norwegian Beamlines, ESRF, BP 220, Grenoble, 38043, France

*Corresponding author. e-mail: muelchri@ethz.ch

Table of content

Table S1. The coordination[a] of Al sites in Al (0.4 nm)-Ni/SiO_2 and Al (4.0 nm)-Ni/SiO_2 after calcination and NH_3-treatment, and the distribution of Al_2O_3 and amorphous aluminosilicate (AAS) phase[b].

Catalyst	Treatment	Al coordination[a]			Al_2O_3		AAS			Al content[c] [mmol/g]	
		Al^{IV}	Al^{V}	Al^{VI}	Al^{IV}	Al^{VI}	Al^{IV}	Al^{V}	Al^{VI}	Al_2O_3	AAS
γ-Al_2O_3	Calcined	28	3	69	28	69	-	-	-	100	-
	NH_3-treated	28	3	69							
Al (0.4 nm)-Ni/SiO_2	Calcined	22	36	42	5	11	18	36	31	6 (16)	34 (84)
	NH_3-treated	48	41	11							
Al (4.0 nm)-Ni/SiO_2	Calcined	35	41	24	10	23	25	41	1	125 (33)	253 (67)
	NH_3-treated	39	38	23							

[a]The coordination of Al sites was fitted with the CzSimple model using the DMFit software with the assumption of all Al sites detected by ^{27}Al MAS NMR.[b] The Al^{IV} and Al^{VI} sites in Al_2O_3 was calculated using the coordination of Al^{VI} sites after NH_3 treatment, whereby a constant 3:7 ratio is available in γ-Al_2O_3 regardless of calcination and NH_3 treatments. The Al^{IV}, Al^{V}, and Al^{VI} sites in AAS were calculated by the subtraction of Al^{IV} and Al^{VI} in Al_2O_3. [c]Al content in calcined Al (0.4 nm)-Ni/SiO_2 and Al (4.0 nm)-Ni/SiO_2 was quantified by combination of elemental analysis and ^{27}Al NMR with the assumption that all Al species can be detected by ^{27}Al NMR. The parenthesis represented the relative ratio between Al_2O_3 and AAS

Table S2. Ni K-edge XANES-based linear combination fitting (LCF) quantification of $NiAl_2O_4$ (mol%) for the benchmarks and Al_2O_3 coated Ni-based DRM catalysts after calcination and DRM (10 h of TOS).

Catalyst	Calcination[a]	After DRM[b]
Ni/SiO_2	0	0
Ni/Al_2O_3	100	10
Al (0.4 nm)-Ni/SiO_2	0	0
Al (4.0 nm)-Ni/SiO_2	30	0
Al (4.0 nm)-Ni/Al_2O_3	100	9
Ni/Al (4.0 nm)-SiO_2	0	0
Ni/Al (4.0 nm)-Al_2O_3	100	10

[a]The benchmark catalysts Ni/SiO_2 and Ni/Al_2O_3 were calcined at 300 °C, while the ALD Al_2O_3-coated Ni catalysts were calcined at 800 °C. [b]The catalysts were completely reduced to metallic Ni^0 at 400–800 °C under 10 vol.% H_2/N_2 prior to DRM tests. The amount of $NiAl_2O_4$ was quantified after 10 h TOS under DRM conditions at 700 °C.

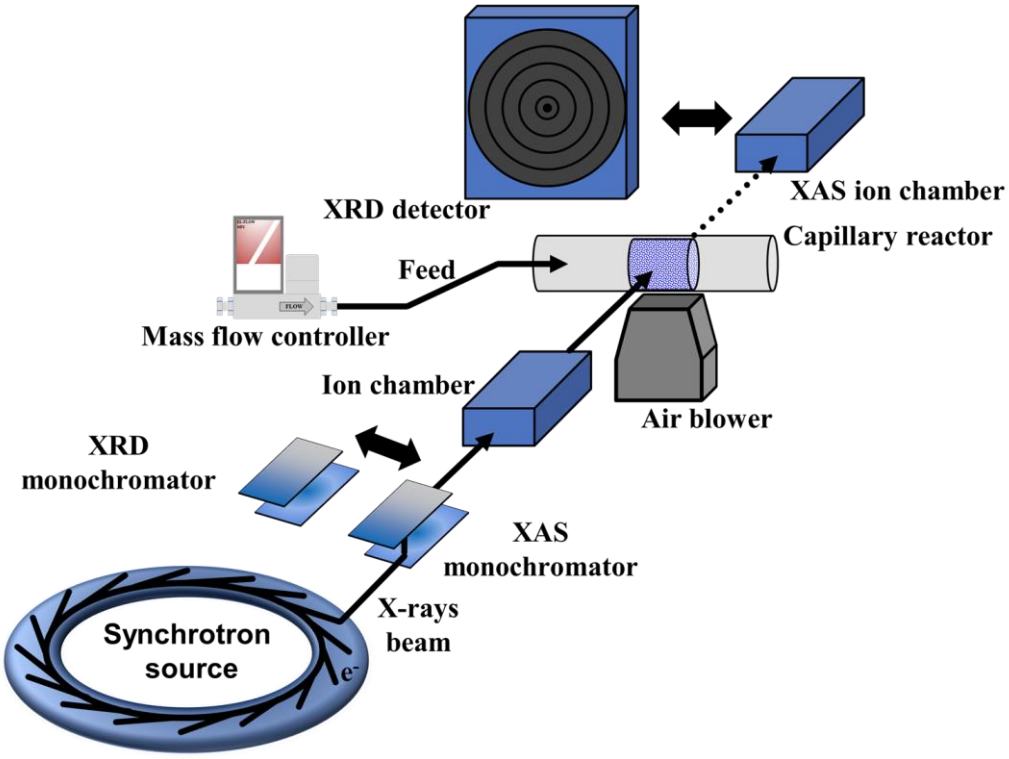

Figure S1. Schematic of the experimental setup for combined *in situ* XAS-XRD measurements BM31 beamline, SNBL at ESRF.

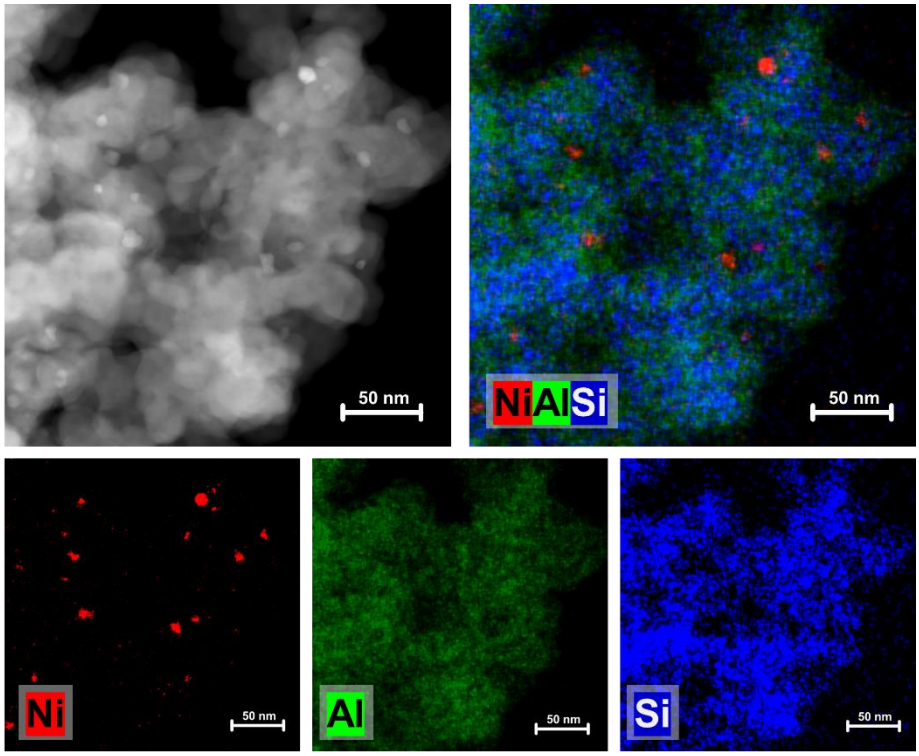

Figure S2. HAADF STEM with EDX analysis of Al (4.0 nm)-Ni/SiO_2 calcined at 800 °C

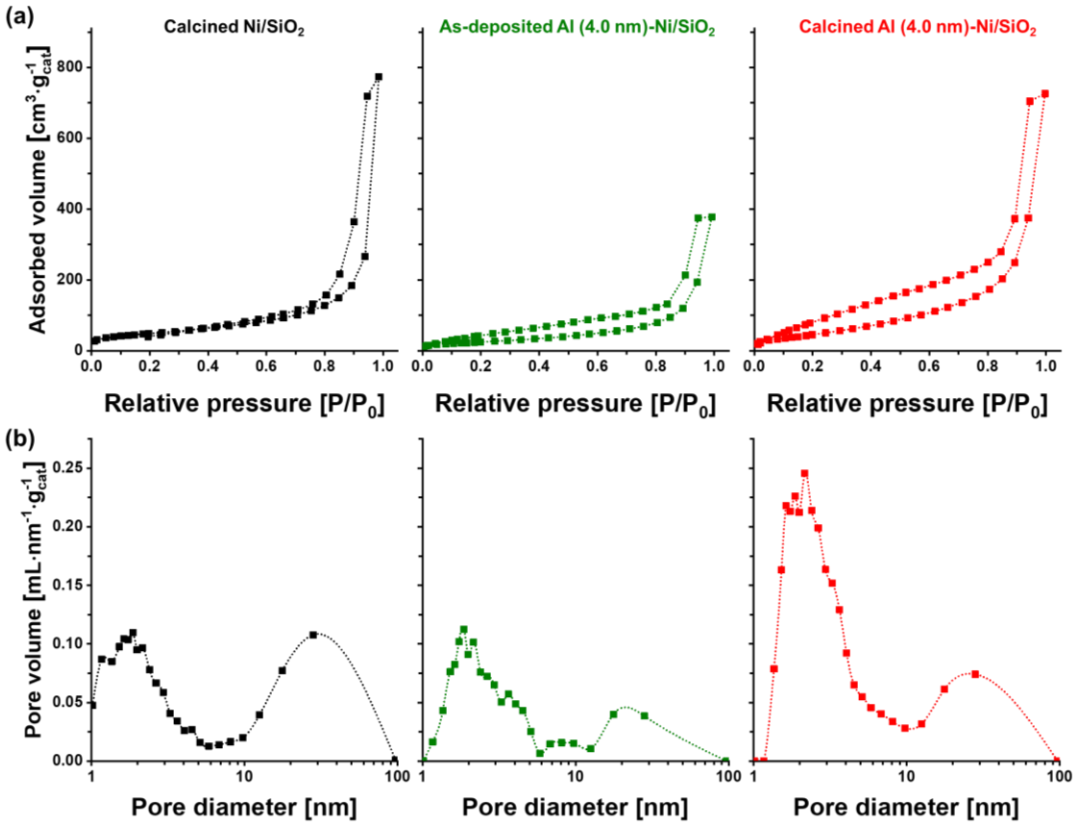

Figure S3. (a) N_2 isotherm and (b) BJH pore size of calcined Ni/SiO_2, as-deposited Al (4.0 nm)-Ni/SiO_2, and calcined Al (4.0 nm)-Ni/SiO_2.

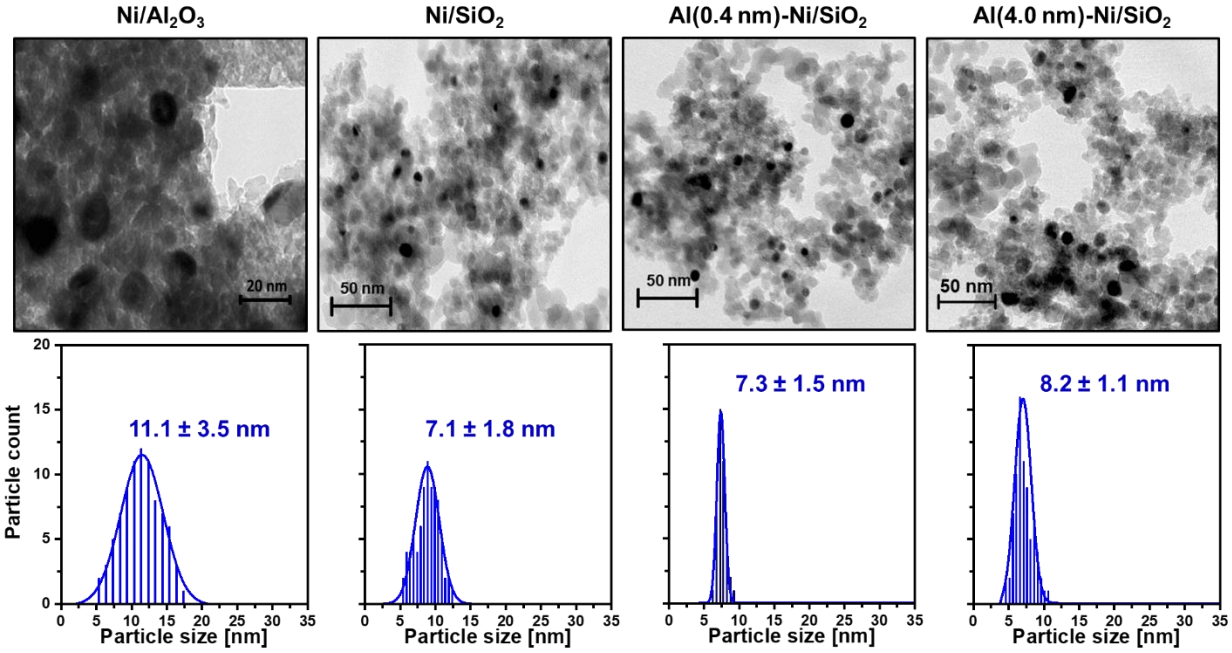

Figure S4. TEM images and particle size distribution of reduced Ni/Al_2O_3, Ni/SiO_2, Al (0.4 nm)-Ni/SiO_2, and Al (4.0 nm)-Ni/SiO_2.

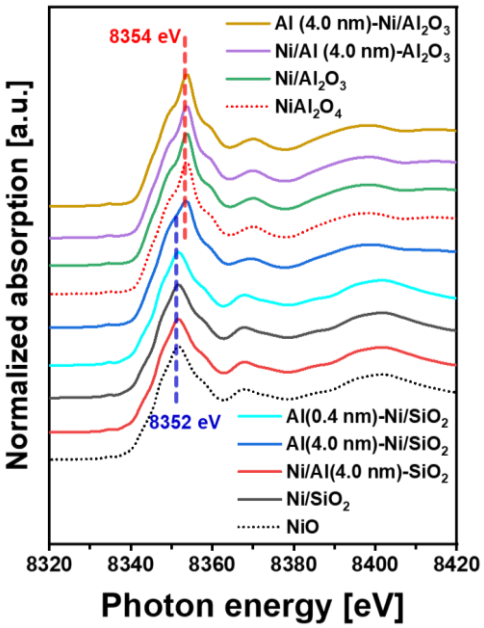

Figure S5. Ni K-edge XANES spectra for calcined Ni/SiO_2, Ni/Al_2O_4, Al (4.0 nm)-Ni/SiO_2, Ni/Al (4.0 nm)-SiO_2, Al (4.0 nm)-Ni/Al_2O_3, and Ni/Al (4.0 nm)-Al_2O_3. NiO and $NiAl_2O_4$ references plotted for comparison.

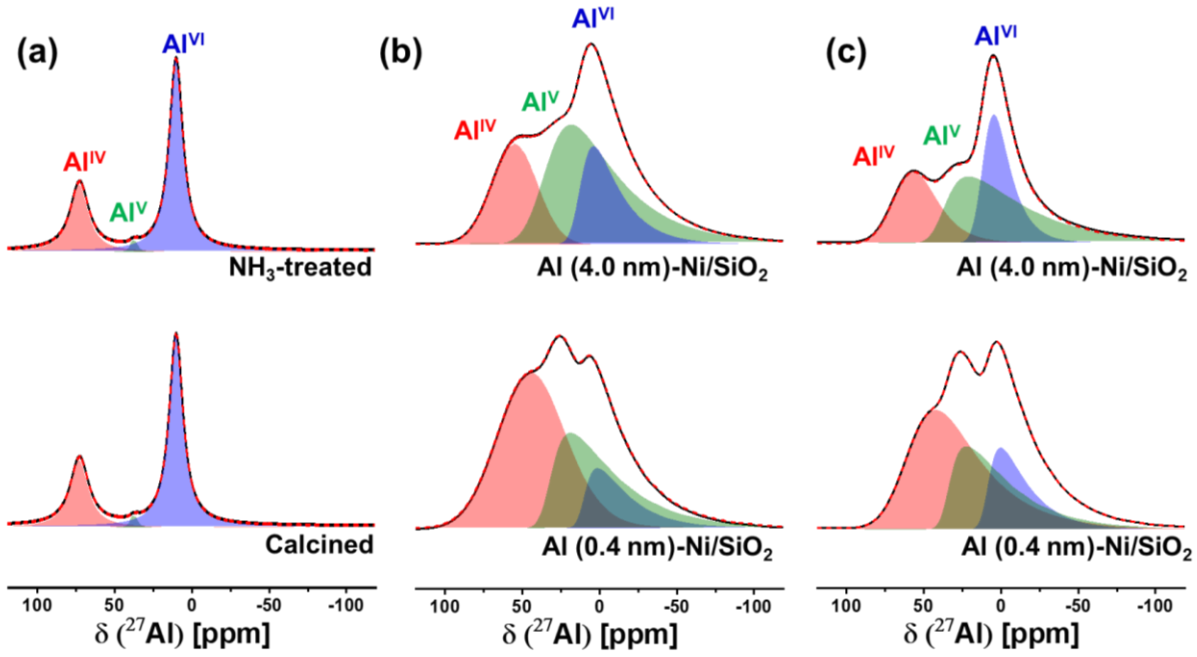

Figure S6. Solid-state ^{27}Al NMR spectra of (a) γ-Al_2O_3 after calcination and NH_3-treatment, and Al (0.4 nm)-Ni/SiO_2 and Al (4.0 nm)-Ni/SiO_2 after (b) NH_3 adsorption and (c) reduction.

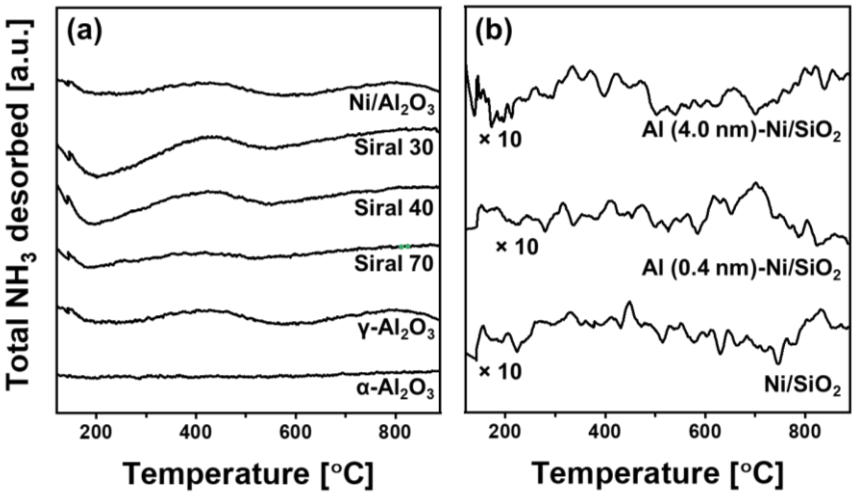

Figure S7. NH_3-TPD profile of (a) reference and (b) calcined materials.

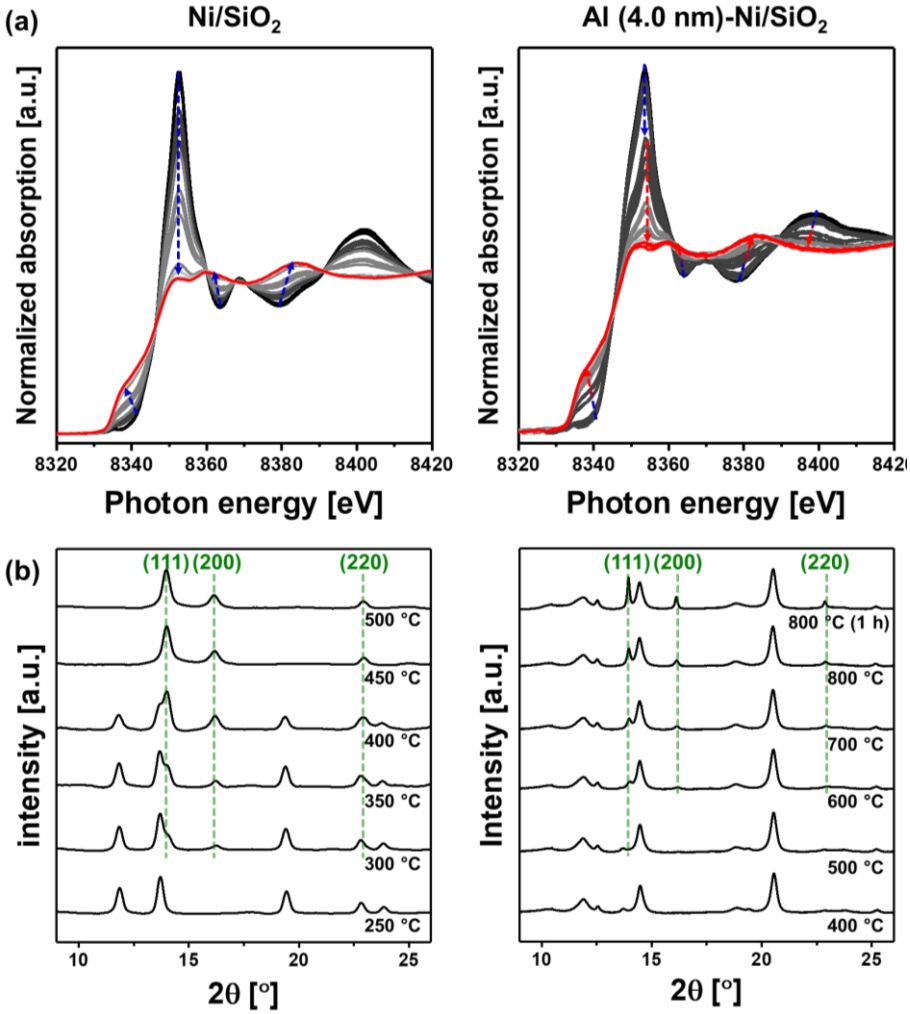

Figure S8. Combined (a) *in situ* Ni K-edge XANES and (b) *in situ* XRD of calcined Ni/SiO_2 and calcined Al (4.0 nm)-Ni/SiO_2 during reduction. The arrows in (a) indicate the change of XANES upon reduction. The dashed line in (b) represents (111), (200) and (222) Bragg reflections of Ni.

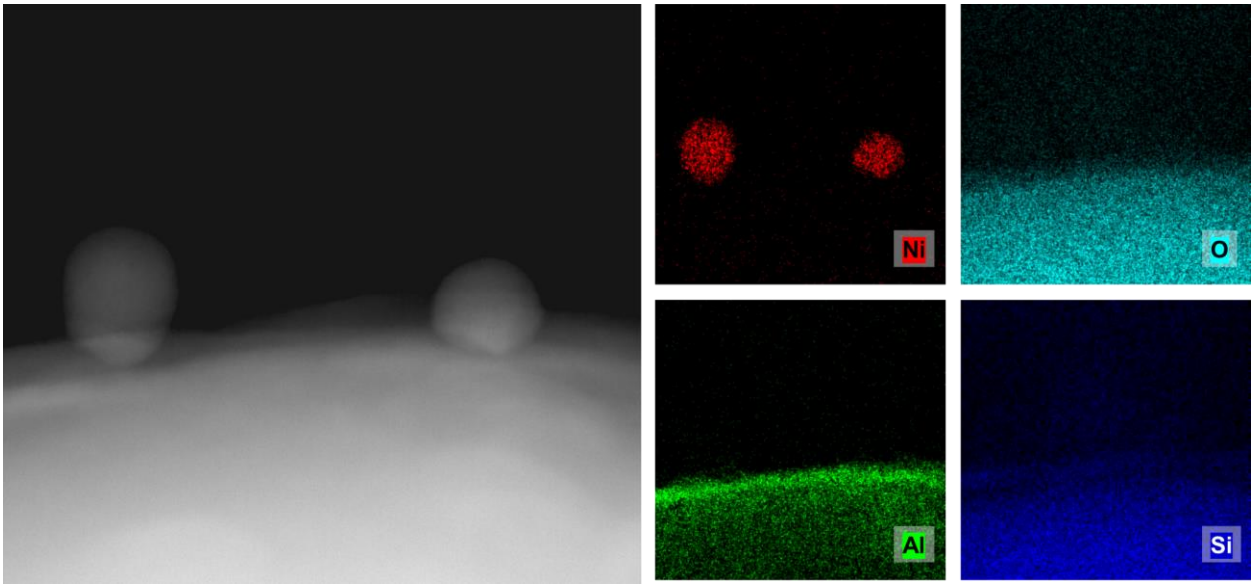

Figure S9. HAADF-STEM images with EDX mapping for reduced Al (4.0 nm)-Ni/SiO_2.

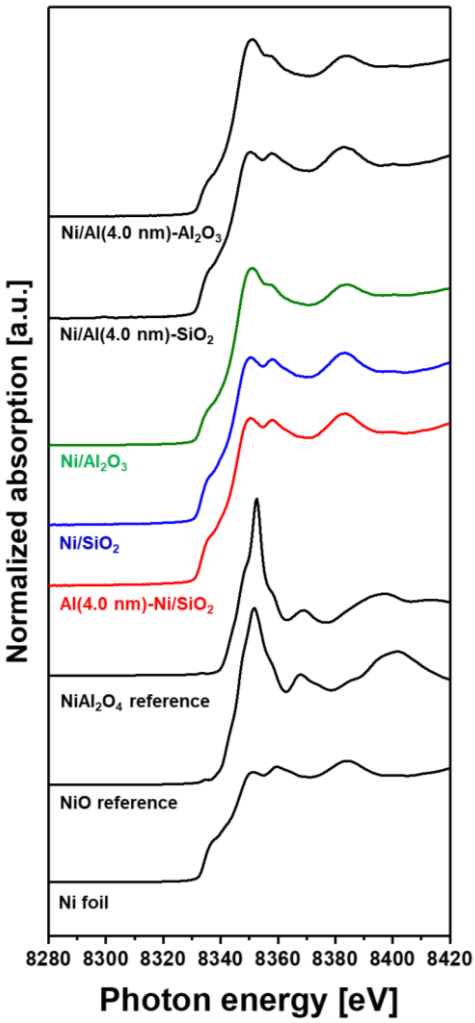

Figure S10. *Ex situ* Ni K-edge XANES for spent catalysts after 10 h of DRM and references.