

## Supporting Information

# Transition metal pairs on ceria-promoted, ordered mesoporous alumina as catalyst for methane-CO<sub>2</sub> reforming reaction

Moom Sinn Aw,<sup>a</sup> Goran Dražić,<sup>b</sup> Petar Djinović,<sup>a,\*</sup> and Albin Pintar<sup>a</sup>

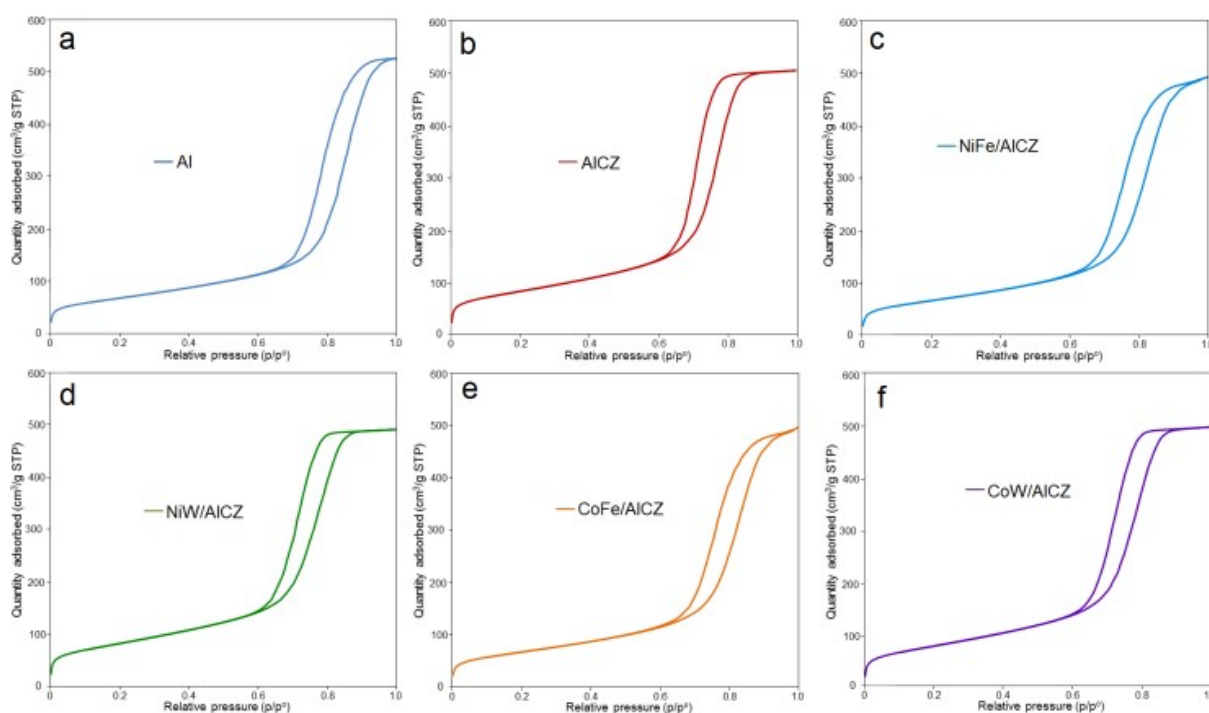
<sup>a</sup>Moom Sinn Aw, Petar Djinović, Albin Pintar, Laboratory for Environmental Sciences and Engineering, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

\*E-mail address: petar.djinovic@ki.si

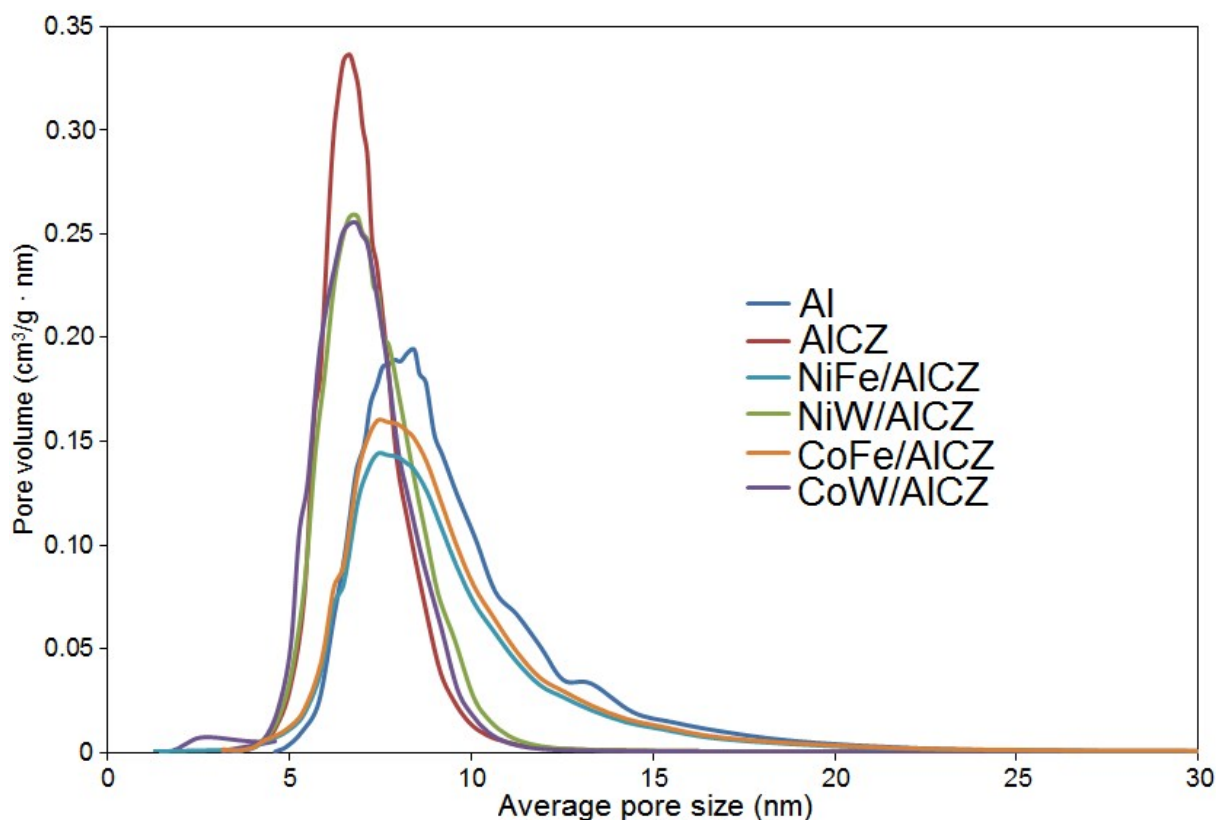
<sup>b</sup>Goran Dražić, Laboratory for Materials Chemistry, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia

**Table S1.** Chemical composition of catalysts measured by means ICP-MS analysis.

Sample	CeO <sub>2</sub> , wt. %	ZrO <sub>2</sub> , wt. %	Ni, wt. %	Co, wt. %	Fe, wt. %	W, wt. %
NiFe/AICZ	4.68	0.83	0.56	/	2.67	/
CoFe/AICZ	4.83	0.81	/	0.75	2.62	/
NiW/AICZ	5.59	0.77	0.66	/	/	1.92
CoW/AICZ	5.36	0.66	/	0.67	/	2.56

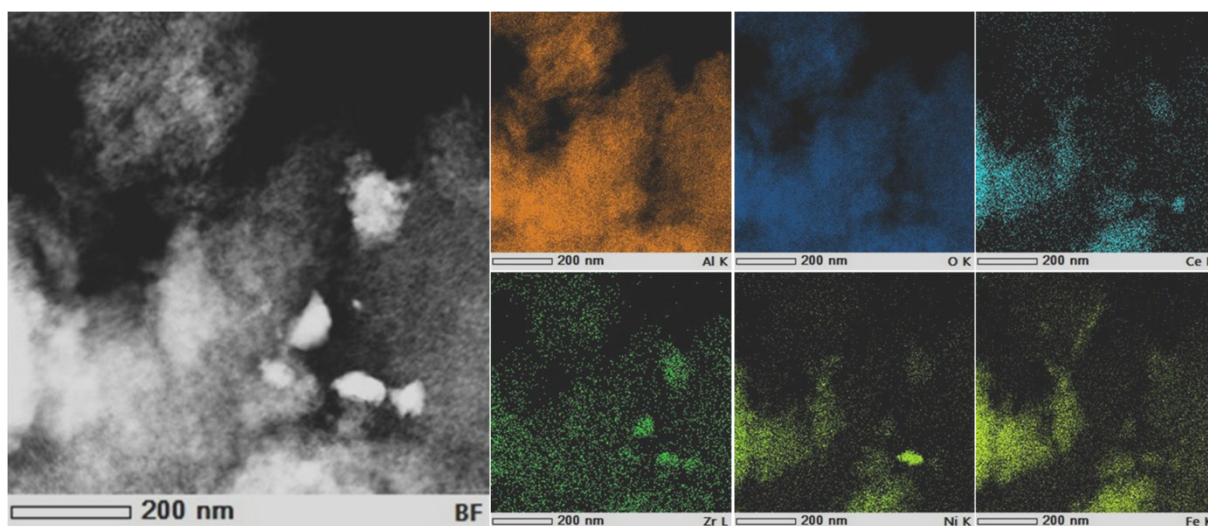


**Figure S1.** N<sub>2</sub> adsorption-desorption isotherms of a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, b) CeZr-promoted  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support and c-f) supported bimetallic catalysts.

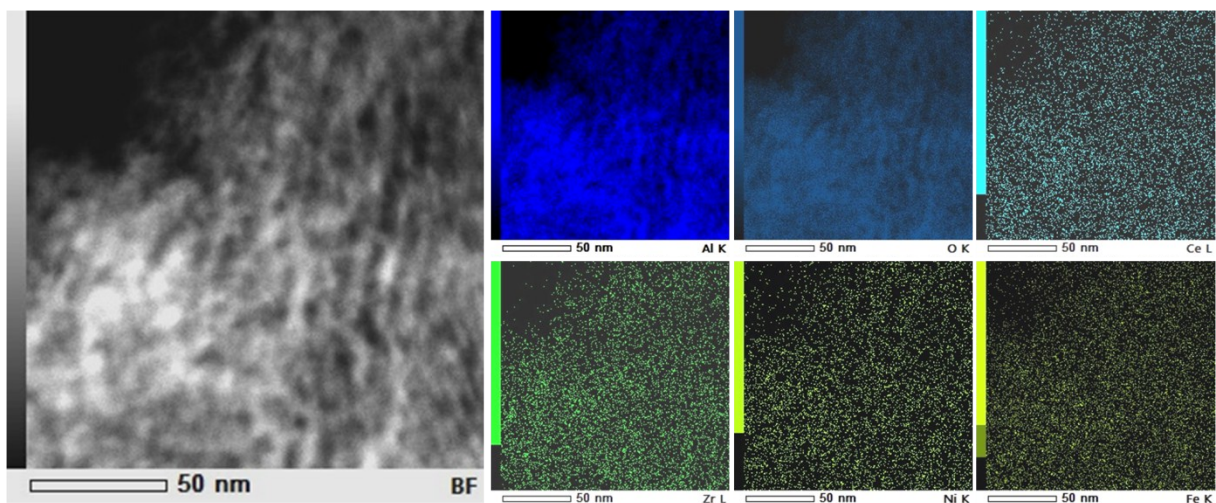


**Figure S2.** Fractional pore size distribution of supports and catalysts.

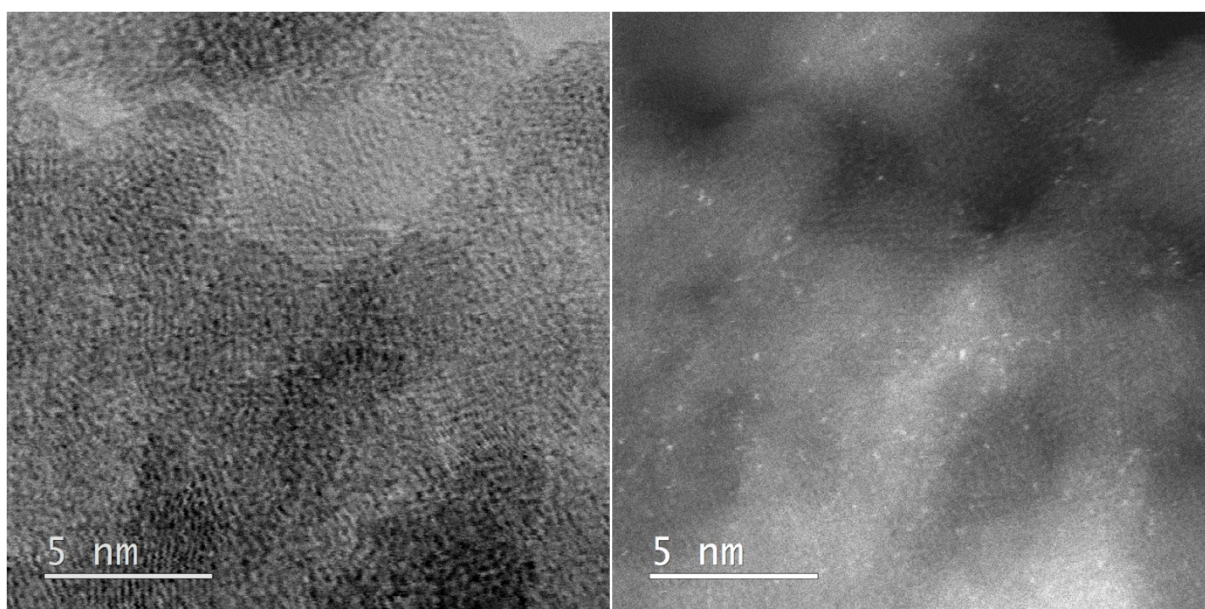
Regarding the reasons for morphological changes of catalysts after deposition of active metals: aqueous solutions of metal nitrate precursors which were used to impregnate Al and AICZ supports, were acidic (pH values of NiFe = 2.42, NiW = 4.55, CoFe = 2.20, CoW = 4.51 and CeZr = 2.54). Considering that no changes were identified after CZ deposition and its solution was as acidic as that of NiFe or CoFe, pH value of the impregnating solution likely plays a minor role in modification of Al.



**Figure S3a.** HAADF-STEM image of reduced NiFe/AICZ catalyst with corresponding EDXS elemental mapping depicting areas of non-homogeneous deposition of redox promoter ( $\text{CeO}_2$  rich zones) and nickel clustering.

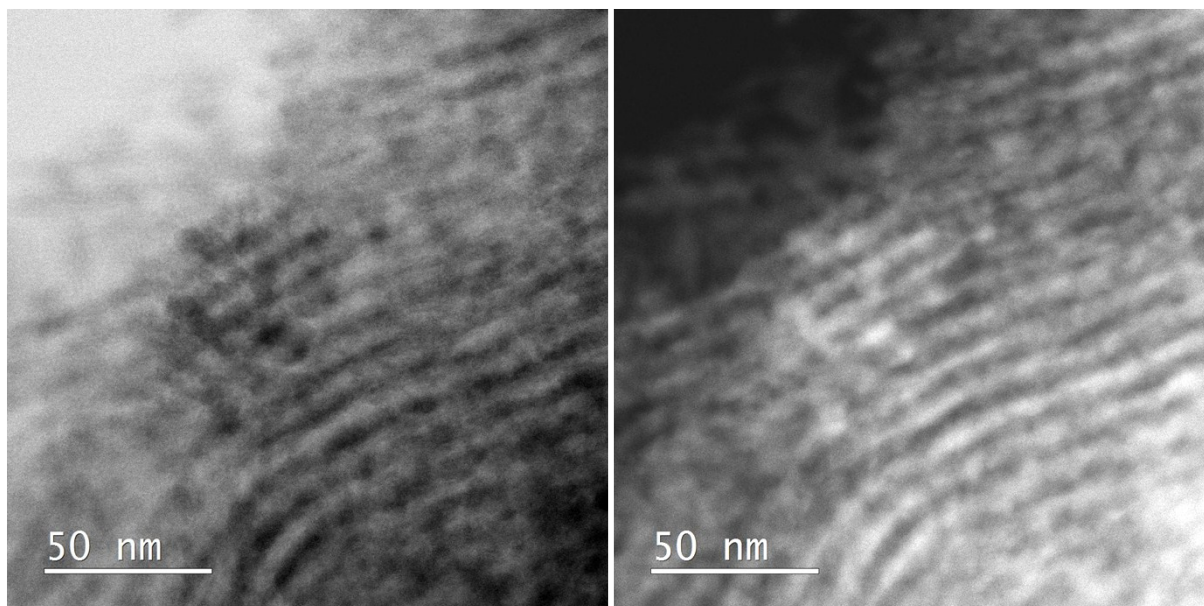


**Figure S3b.** HAADF-STEM image of reduced NiFe/AICZ catalyst with corresponding EDXS elemental mapping depicting areas of homogeneous deposition of redox promoter and active transition metals.

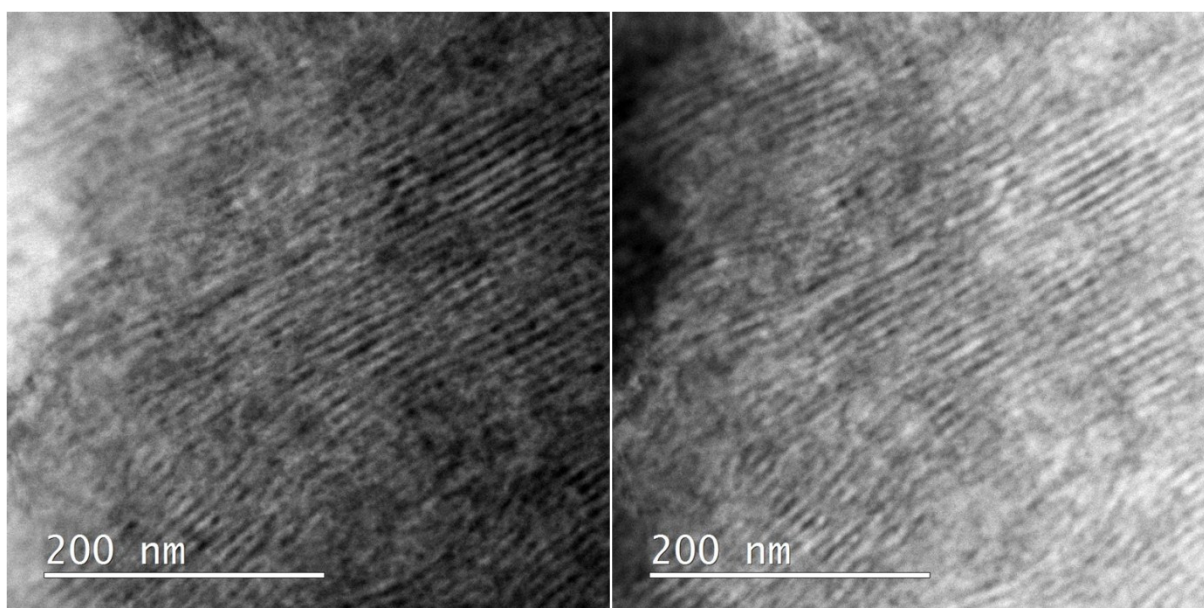


**Figure S3c.** ABF-STEM (left hand side) and HAADF-STEM (right hand side) image of reduced NiFe/AICZ catalyst. Atoms of heavier elements (Ce, Zr, Ni and Fe) appear as brighter spots.

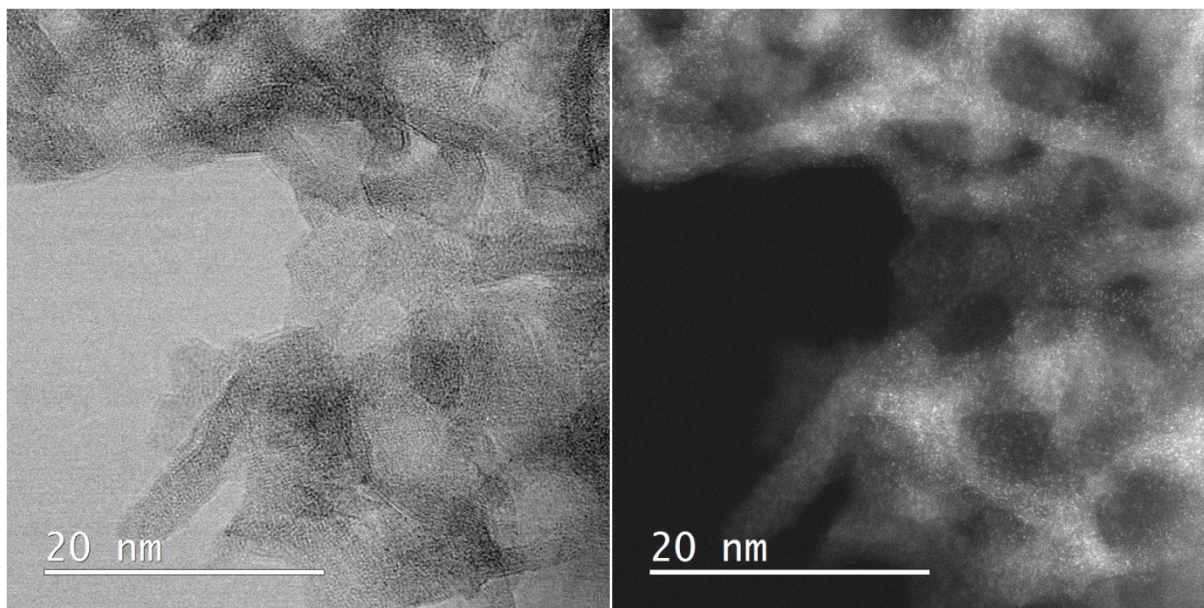




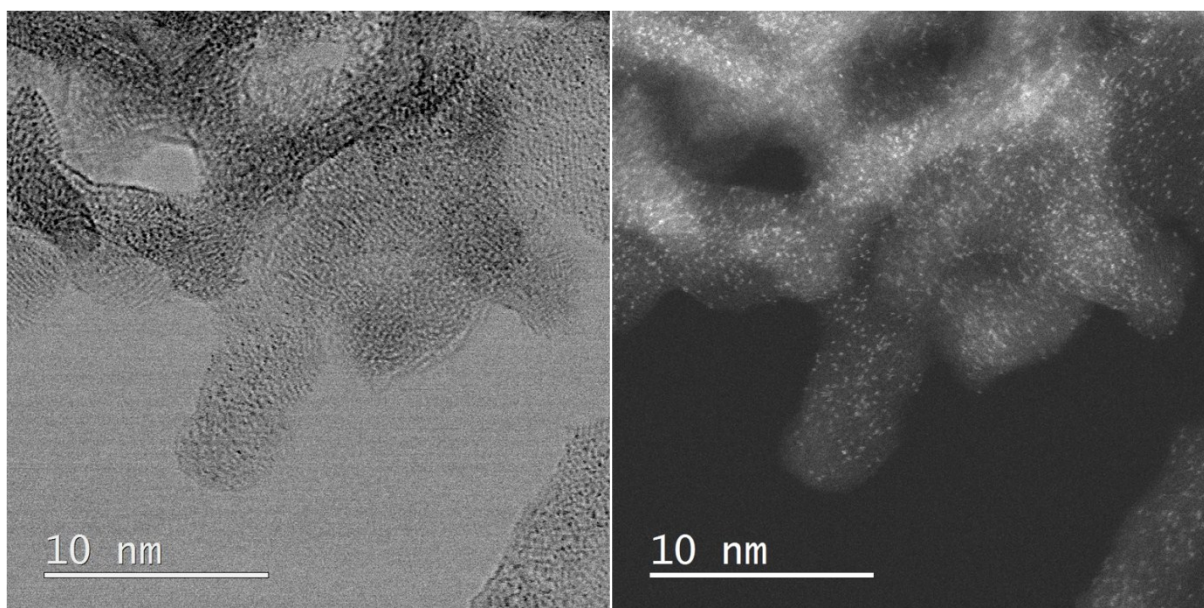
**Figure S3d.** ABF-STEM (left hand side) and HAADF-STEM (right hand side) image of reduced NiFe/AlCZ catalyst. The bright areas clearly indicate confinement of heavier elements (redox promoter and transition metals) inside the parallel cylindrical pores of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.



**Figure S3e.** ABF-STEM (left hand side) and HAADF-STEM (right hand side) image of reduced NiFe/AlCZ catalyst at smaller magnification. The bright areas clearly indicate confinement of heavier elements (redox promoter and transition metals) inside the parallel cylindrical pores of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support.

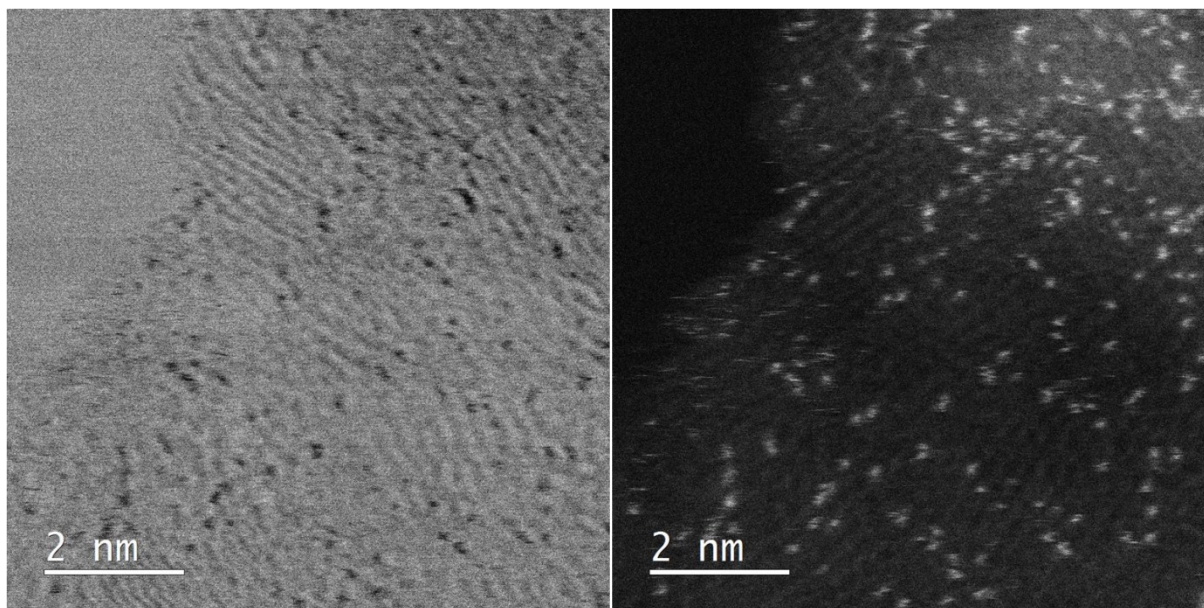


**Figure S3f.** ABF-STEM (left hand side) and HAADF-STEM (right hand side) image of reduced CoFe/AICZ catalyst at smaller magnification. Atoms of heavier elements (Ce, Zr, Co and Fe) appear as brighter spots.

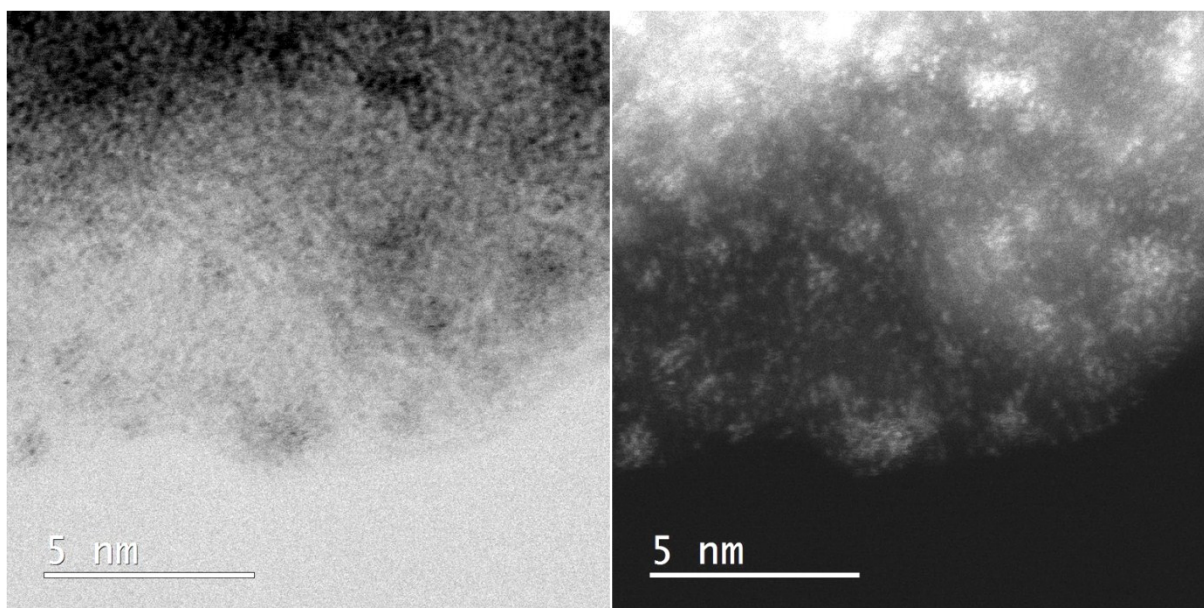


**Figure S3g.** ABF-STEM (left hand side) and HAADF-STEM (right hand side) image of reduced CoFe/AICZ catalyst at higher magnification. Atoms of heavier elements (Ce, Zr, Co and Fe) appear as brighter spots.





**Figure S3h.** ABF-STEM (left hand side) and HAADF-STEM (right hand side) image of reduced CoFe/AICZ catalyst at higher magnification. Individual atoms of heavier elements (Ce, Zr, Co and Fe) appear as brighter spots.



**Figure S3i.** ABF-STEM (left hand side) and HAADF-STEM (right hand side) image of reduced CoFe/AICZ catalyst. Atoms of heavier elements (Ce, Zr, Co and Fe) form clusters between 1 and 3 nm in size, which appear as brighter spots.

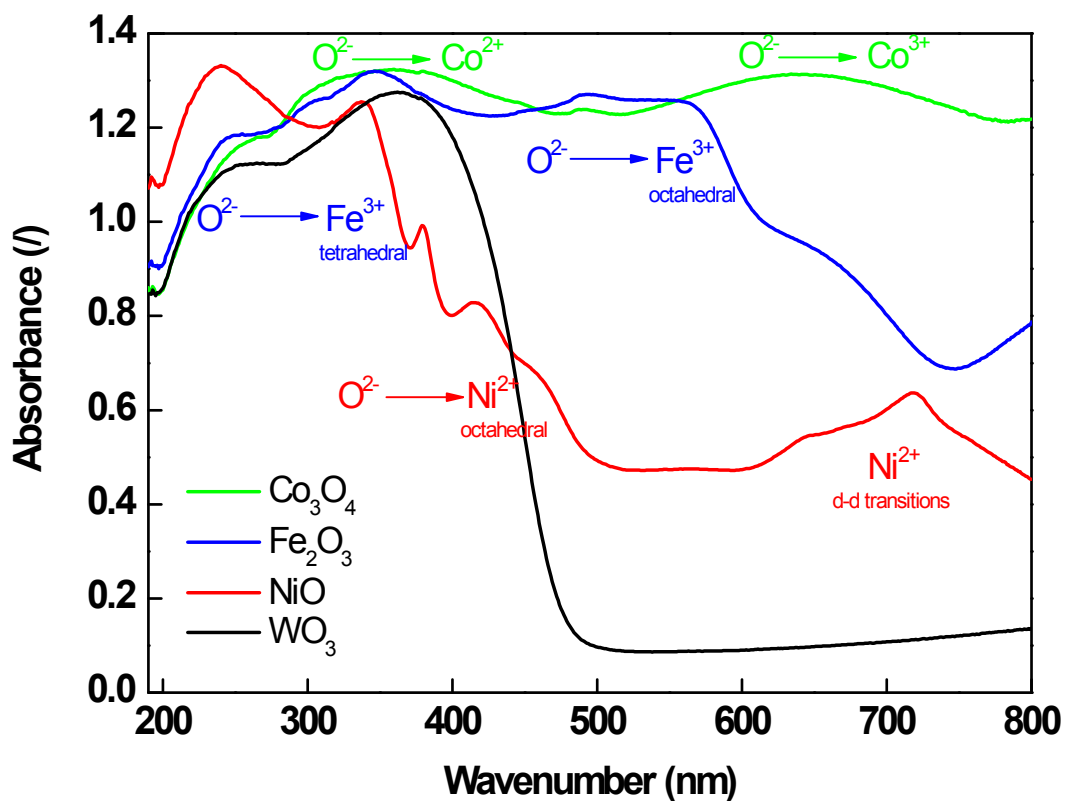


Figure S4. UV-Vis DRS spectra recorded against a Spectralon® background of individual transition metal oxides.

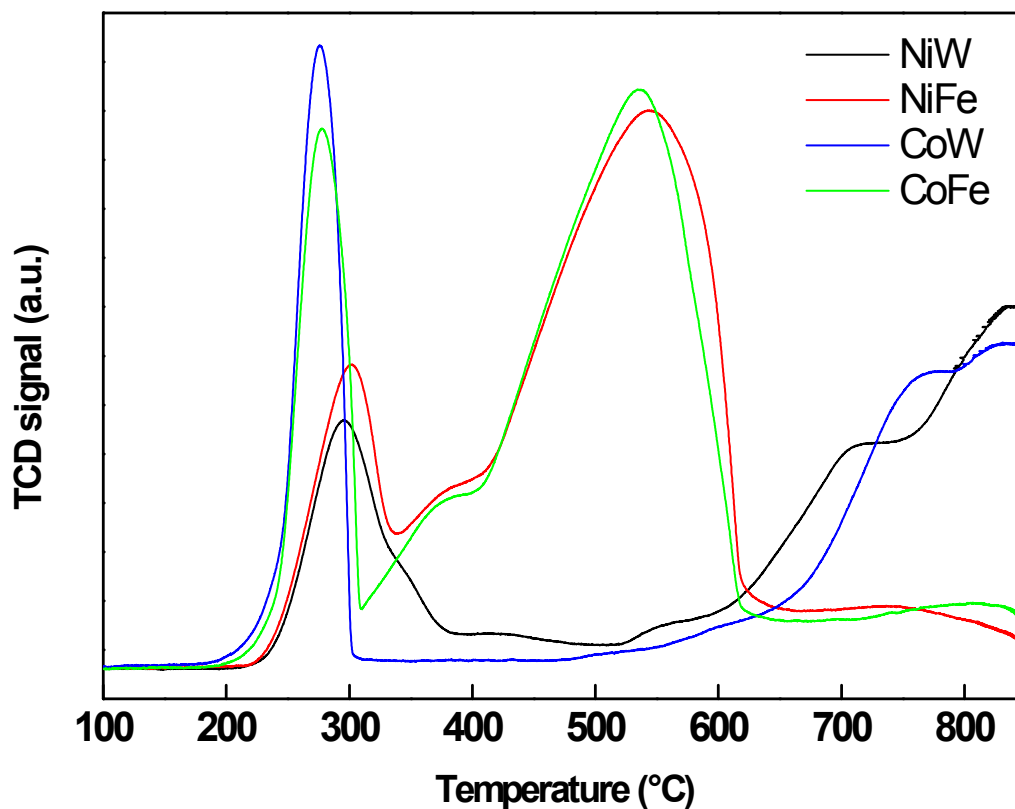
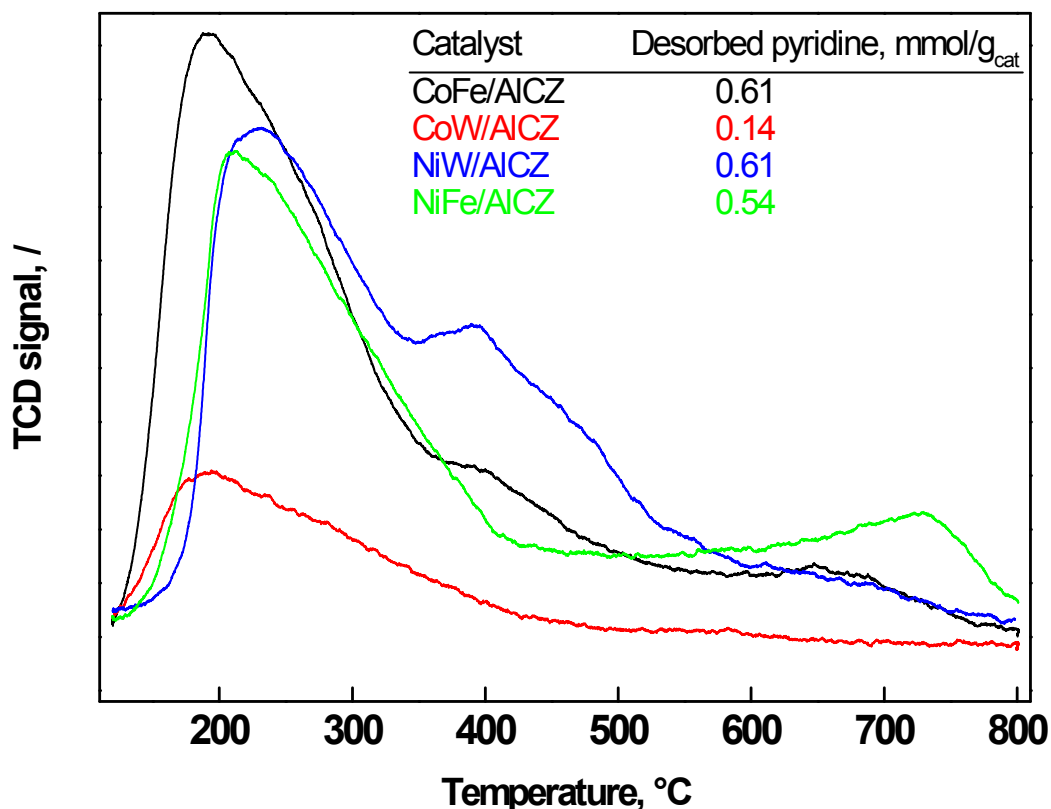


Figure S5.  $\text{H}_2$ -TPR profiles of physical mixtures of metal oxides:  $\text{NiO} : \text{Fe}_2\text{O}_3 = 1 : 4$ ,  $\text{Co}_3\text{O}_4 : \text{Fe}_2\text{O}_3 =$

1 : 4, NiO : WO<sub>3</sub> = 1 : 4, Co<sub>3</sub>O<sub>4</sub> : WO<sub>3</sub> = 1 : 4.

Based on the recorded H<sub>2</sub>-TPR profiles of bulk metal oxide physical mixtures, the following rationalization regarding the origins of individual contributions can be made: (i) reduction of bulk Co<sub>3</sub>O<sub>4</sub> takes place in a narrow temperature range between 200 and 300 °C; (ii) reduction of WO<sub>3</sub> is initiated at about 450 °C and extends well beyond 850 °C, which was the maximal temperature probed in the performed tests; (iii) reduction of bulk NiO takes place between 220 and 400 °C; (iv) reduction of Fe<sub>2</sub>O<sub>3</sub> occurs between 300 and 630 °C.



**Figure S6.** Pyridine TPD profiles of supported bimetallic catalysts.

In order to verify the possible correlation between acidity of catalysts and their tendency for carbon accumulation, the number and strength of acid sites was analyzed using pyridine temperature programmed desorption.

Measurements were performed with 100 mg of sample using a Micromeritics Autochem II 2920 apparatus. Prior to pyridine adsorption, the catalyst samples were reduced in 20 % H<sub>2</sub>/N<sub>2</sub> stream at 750 °C for 60 min, followed by cooling to 120 °C in 25 mL/min He flow. After temperature stabilization, samples were exposed for 30 min to a flow of He (25 ml/min) which was bubbled through a flask of pyridine, maintained at 50 °C. After saturation, the samples were maintained in He flow for 1 h. Pyridine TPD profiles were recorded during heating of samples from 120 to 800 °C with a 10 °C/min ramp.

Acid sites exhibiting weak, medium and strong bonding with pyridine can be observed from desorption peaks between: a) 120-350, b) 350-600 and c) 600-800 °C, respectively (Fig. S6). The CoFe/AICZ, NiW/AICZ and NiFe/AICZ catalysts exhibited the highest number of acid sites (0.54-0.61 mmol/g<sub>cat</sub>) and accumulated between 0.6 and 1.2 wt. % of carbon during the catalytic runs. The number of acid sites over CoW/AICZ catalyst was substantially lower (0.14 mmol/g<sub>cat</sub>). However, the amount of coke was the highest over this sample, namely 4.7 wt. %. Based on the lack of correlation between catalyst acidity and amount of accumulated coke, we can conclude that coke accumulation during methane-CO<sub>2</sub> reforming reaction is not predominantly associated with presence of acid sites in the tested solids, but rather with morphology of active metal clusters and especially redox properties of the promoted support.