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Supplementary Materials

Effect of Ce/Zr Composition on Structure and Properties of $Ce_{1-x}Zr_xO_2$ Oxides and Related Ni/$Ce_{1-x}Zr_xO_2$ Catalysts for CO_2 Methanation

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DFT+U Calculations

The face-centered cubic unit cell of fluorite type structure (space group: Fm $\bar{3}$ m) was used as the initial geometry in the calculations. $Ce_{1-x}Zr_xO_2$ supercells (x = 0.25, 0.50, 0.75) were built by replacing cerium atoms with zirconium ones (Figure S1).

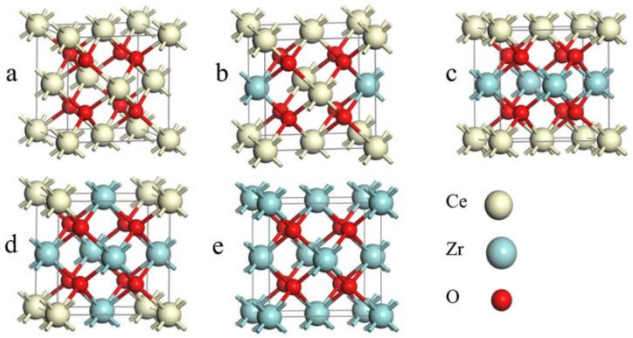

Figure S1. The models of fluorite $Ce_{1-x}Zr_xO_2$ unit cells: (**a**) x = 0, (**b**) x = 0.25, (**c**) x = 0.5, (**d**) x = 0.75, (**e**) x = 1.

XRD Quantitative Analysis of Ni/$Ce_{1-x}Zr_xO_2$ Catalysts Aged Under Reductive Conditions of CO_2 Methanation

The Rietveld refinement for quantitative analysis was carried out. The obtained data on amounts of detected crystalline Ni^0 phase were compared with XRF data on nickel loading in the catalysts (Table S1). It is seen that part of the loaded nickel in the catalysts is not detected by XRD analysis as crystalline phases. The fraction of undetectable nickel species in the catalysts decreases in order of Ni/$Ce_{0.9}Zr_{0.1}O_2$ > Ni/$Ce_{0.75}Zr_{0.25}O_2$ > Ni/$Ce_{0.5}Zr_{0.5}O_2$.

Table S1. Quantities of nickel compounds in the used $Ni/Ce_{1-x}Zr_xO_2$ catalysts according to XRD phase analysis and XRF analysis.

Sample	XRD Quantitative Phase Analysis by Rietveld Refinement			XRF Analysis	XRD Undetected ** (%)
	R_{wp} *	χ^2 *	Quantity of Ni^0 Phase (wt.%)	Ni Loading (wt.%)	
$Ni/Ce_{0.9}Zr_{0.1}O_2$	4.01	1.03	4.5(3)	10.5(1)	57
$Ni/Ce_{0.75}Zr_{0.25}O_2$	3.23	0.94	7.2(2)	10.1(1)	28
$Ni/Ce_{0.5}Zr_{0.5}O_2$	3.18	1.01	8.9(2)	10.9(1)	18

* Rietveld analysis agreement indices. ** Fraction of nickel compounds undetectable by XRD phase analysis.

TEM Study of $Ni/Ce_{1-x}Zr_xO_2$ Catalysts

The observed nickel containing particles in all the as-prepared $Ni/Ce_{1-x}Zr_xO_2$ catalysts were found to be NiO particles. Interplanar distances measured from selected area diffraction correspond to the NiO phase, as demonstrated by the example of the $Ni/Ce_{0.9}Zr_{0.1}O_2$ catalyst (Figure S2).

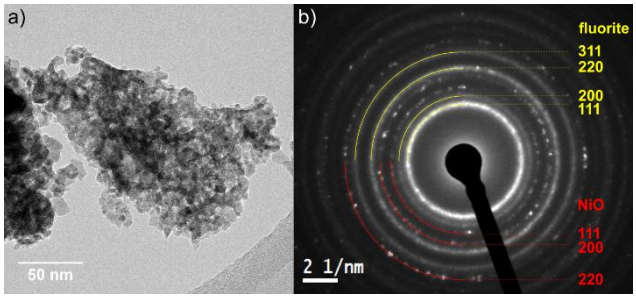

Figure S2. TEM image of as-prepared $Ni/Ce_{0.9}Zr_{0.1}O_2$ catalyst (**a**), electron diffraction pattern (**b**).

HAADF-STEM studies with EDX-mapping (Figure S3) of the spent catalysts indicated that highly dispersed nickel particles being in contact with support are preserved after catalytic reaction.

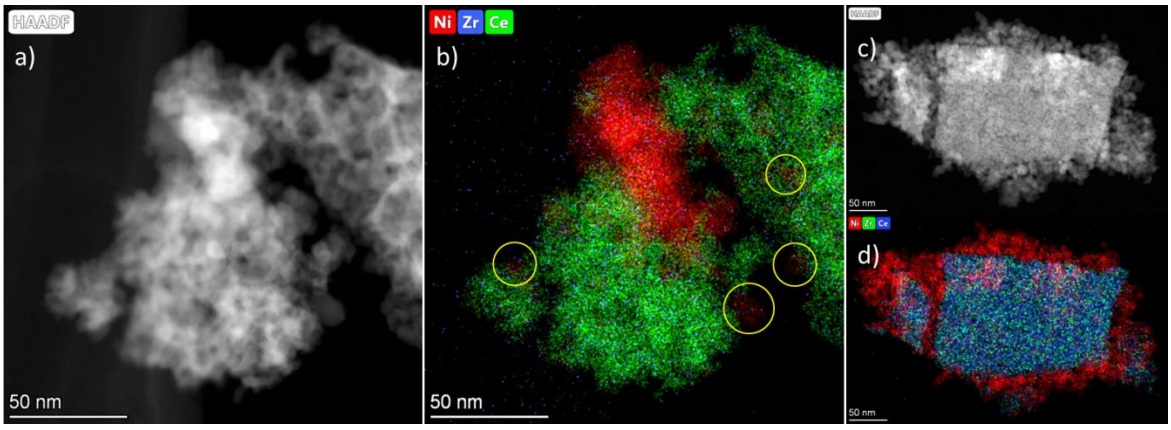

Figure S3. HAADF-STEM images and corresponding EDX-mapping patterns for aged $Ni/Ce_{0.9}Zr_{0.1}O_2$ (**a**,**b**) $Ni/Ce_{0.5}Zr_{0.5}O_2$ (**c**,**d**) catalysts.