

# Combined Steam and CO<sub>2</sub> Reforming of Methane over Ni-Based CeO<sub>2</sub>-MgO Catalysts: Impacts of Preparation Mode and Pd Addition

Lyudmila Okhlopkova <sup>1</sup>, Igor Prosvirin <sup>1\*</sup>, Mikhail Kerzhentsev <sup>1</sup> and Zinifer Ismagilov <sup>1,2</sup>

<sup>1</sup> Borekov Institute of Catalysis SB RAS, Prospekt Akademika Lavrentieva 5, Novosibirsk 630090, Russia

<sup>2</sup> Institute of Coal Chemistry and Material Science, Prospekt Soviet 18, Kemerovo 650000, Russia

\* Correspondence: prosvirin@catalysis.ru; Tel.: +73833269774

## Physicochemical Methods for Studying Catalysts

The content of metals in the catalysts was determined by X-ray fluorescence spectroscopy using an ADVANT'X ARL analyzer (ThermoTechno Scientific, Switzerland). The textural characteristics of the catalysts (specific surface area ( $S_{\text{BET}}$ ), pore volume ( $V_{\text{pore}}$ ), and average pore diameter ( $D_{\text{pore}}$ )) were studied using an ASAP 2400 specific surface area analyzer (Micromeritics, United States) by measuring and processing isotherms of low-temperature nitrogen adsorption at 77 K. Diffraction (XRD) of the samples was carried out using an HZG-4C diffractometer (Freiberger Präzisionmechanik, Germany) with monochromatic CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The phase composition was determined from the obtained diffraction patterns by scanning the angle range  $2\theta = 10^\circ - 80^\circ$  with a step of  $0.1^\circ$  and an accumulation time of 6–15 s. Experiments on studying the phase composition of catalysts after activation were carried out ex situ. The unit cell parameters and crystallite sizes were calculated according to the Bragg-Wolfe and Debye-Scherrer equations, respectively. The distribution of elements and their size were obtained with a Themis-Z 3.1 instrument (TFS, USA) equipped with X-FEG-monochromator and CS/S double corrector, accelerating voltage 200 kV. Elemental analysis was performed with a Super-X EDS detector (energy resolution about 120 eV) in HAADF-STEM mode. Samples for the TEM study were prepared by ultrasonic dispersing in ethanol and subsequent deposition of the suspension upon a "holey" carbon film supported on a copper grid. Thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) were carried out in a NETZSCH STA 449C apparatus (NETZSCH Gerätebau GmbH, Germany) in a temperature range of 25–900°C.

X-ray photoelectron spectra (XPS) were received using SPECS spectrometer with a PHOIBOS-150-MCD-9 hemispherical energy analyzer (AlK $\alpha$  irradiation,  $h\nu = 1486.6 \text{ eV}$ , 150 W). The peak positions of Au4f<sub>7/2</sub> (BE= 84.0 eV) and Cu2p<sub>3/2</sub> (BE= 932.67 eV) were used for the pre-calibration of binding energy (BE) scale. Samples in the form of powder were loaded onto double-sided copper scotch. To take into account the effect of sample charging, the spectra were calibrated against the Ce3d U''' line of cerium (BE =916.7 eV). The survey photoelectron spectra (analyzer pass energy of 50 eV) and narrower spectral regions Mg2p, Mg2s, C1s, O1s, Ni2p and Ce3d (analyzer pass energy of 20 eV) were recorded. Analysis of the individual spectral regions was analyzed for determination of peak BE, chemical state of elements and calculation of elements atomic concentration ratios. Integral photoelectron peak intensities were corrected with theoretical sensitivity factors based on Scofield's photoionization cross sections.

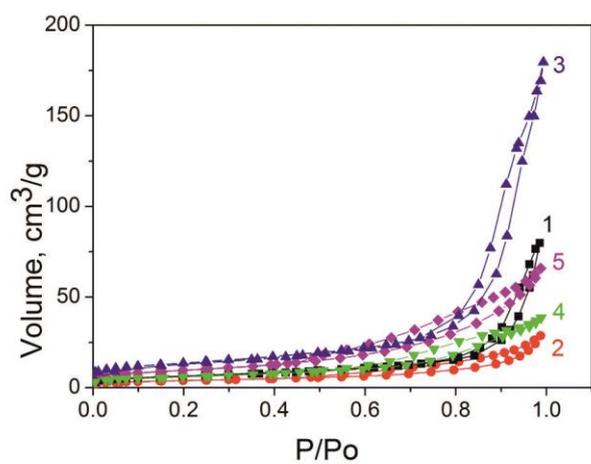


(a)

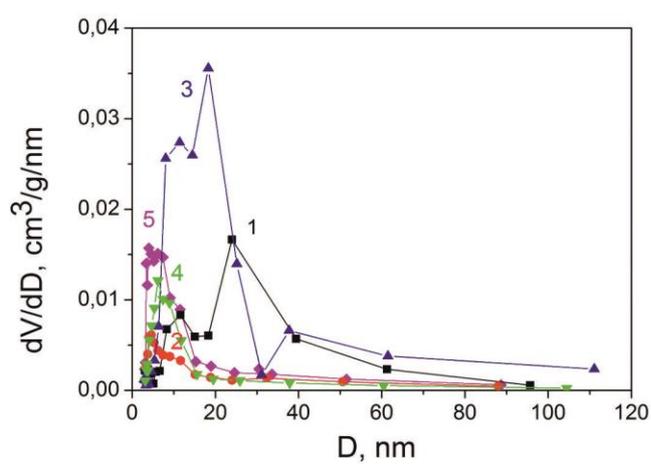


(b)

**Figure S1:** Photograph images of the CSMR (a) experimental equipment and (b) reactor



(a)



(b)

**Figure S2.** N<sub>2</sub> adsorption-desorption isotherms (a) and pore size distributions (b) of as-prepared catalysts calcined at 500°C. 1- Ni/CeMg-C-S-O; 2- Ni/CeMg-A-S-V; 3- Ni/CeMg-A-S-O; 4- Ni-Pd/CeMg-A-S-V; 5- Ni/CeMg-A-P-O.

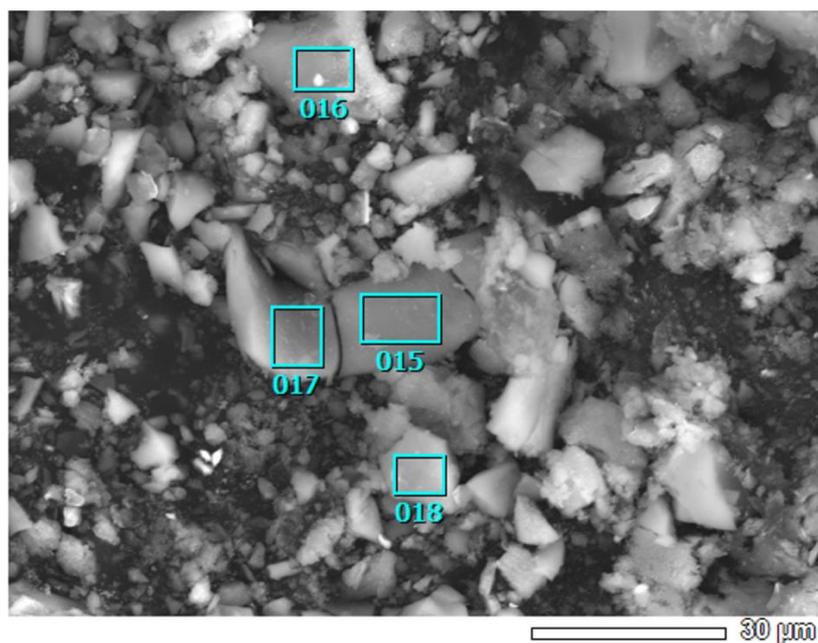


Figure S3. SEM images Ni/CeMg-C-S-O.

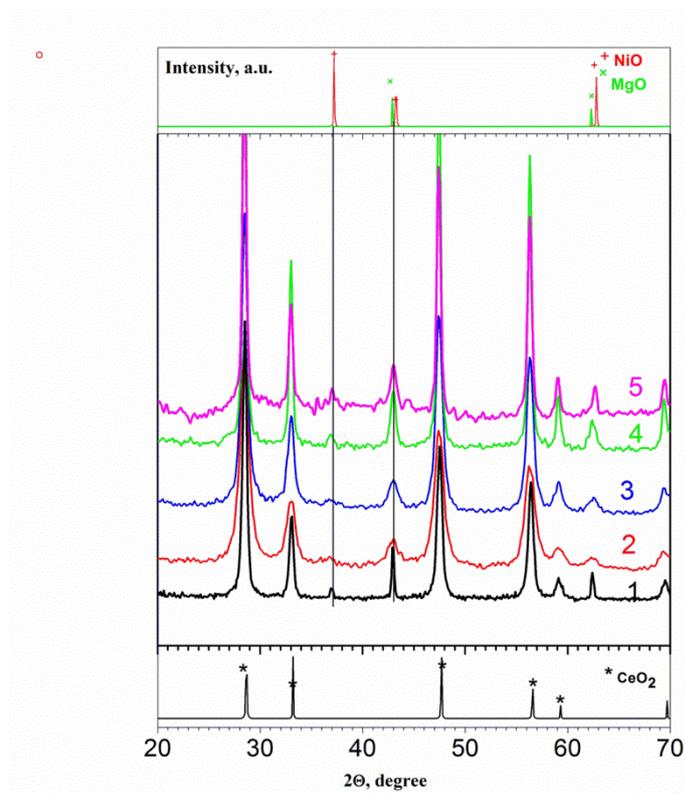
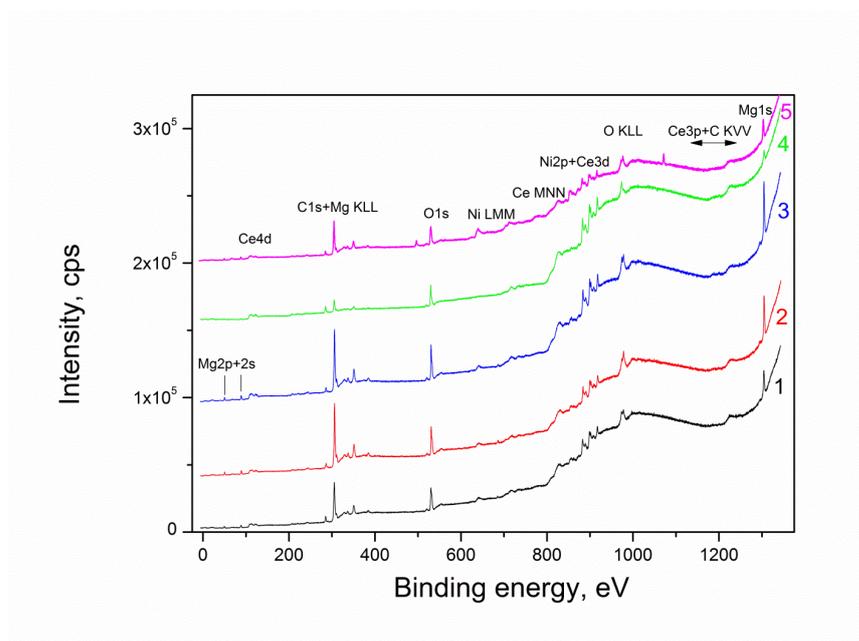
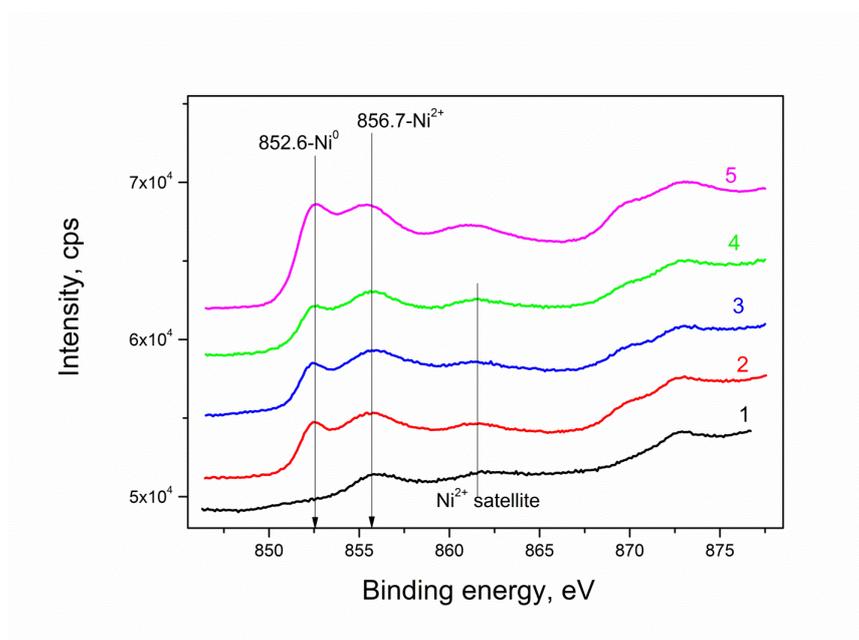


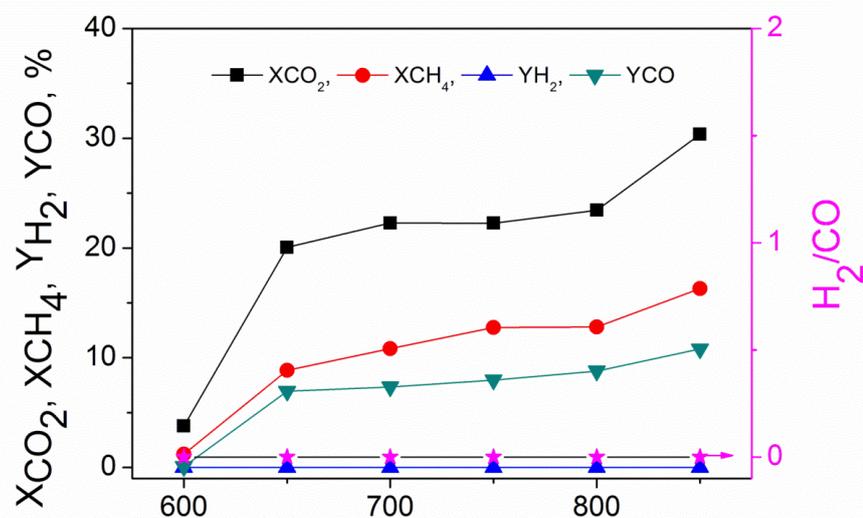
Figure S4. X-ray diffraction patterns of the as-prepared catalysts calcined at 500 C. 1- Ni/CeMg-C-S-O; 2- Ni/CeMg-A-S-V; 3- Ni/CeMg-A-S-O; 4- Ni-Pd/CeMg-A-S-V; 5- Ni/CeMg-A-P-O.



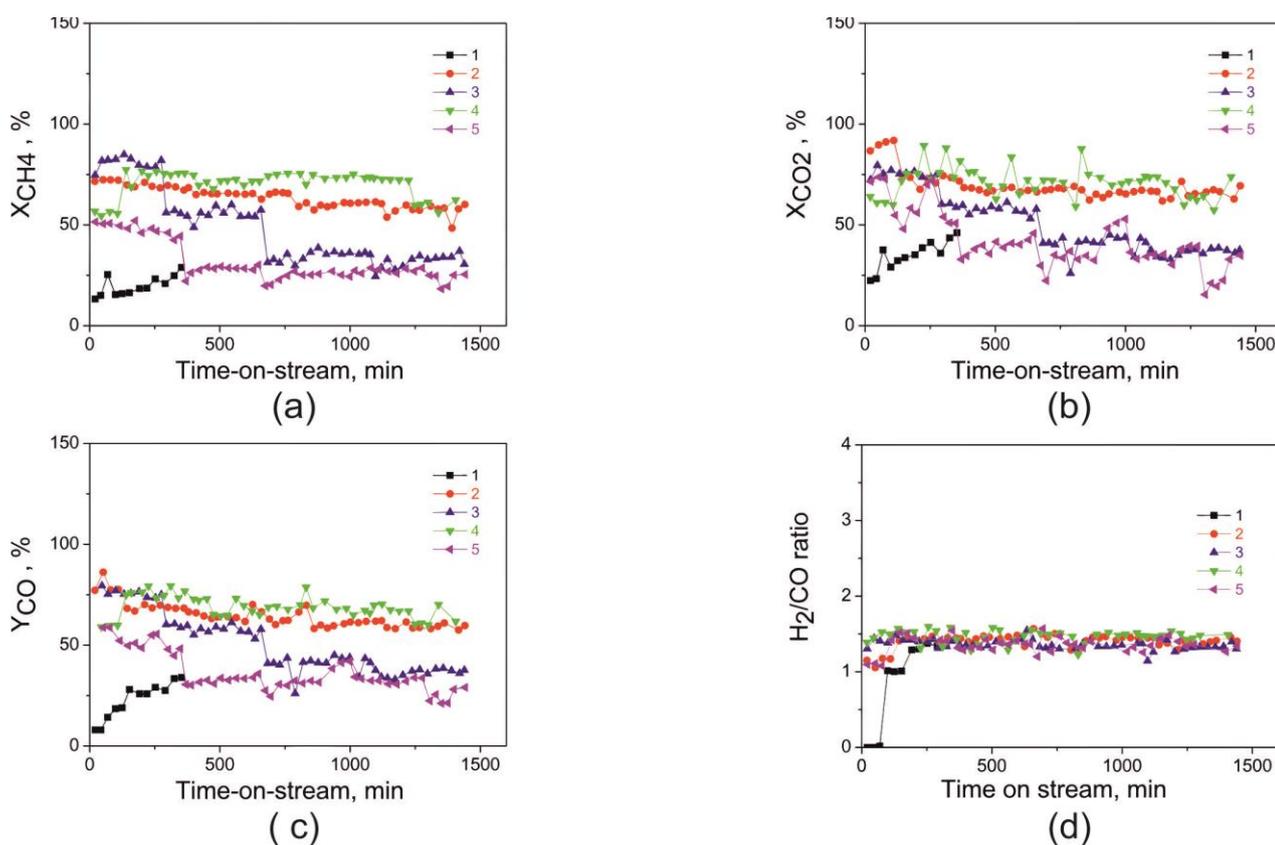
**Figure S5.** Survey X-ray photoelectron spectra of reduced catalysts. 1- Ni/CeMg-C-S-O; 2- Ni/CeMg-A-S-V; 3- Ni/CeMg-A-S-O; 4- Ni-Pd/CeMg-A-S-V; 5- Ni/CeMg-A-P-O.



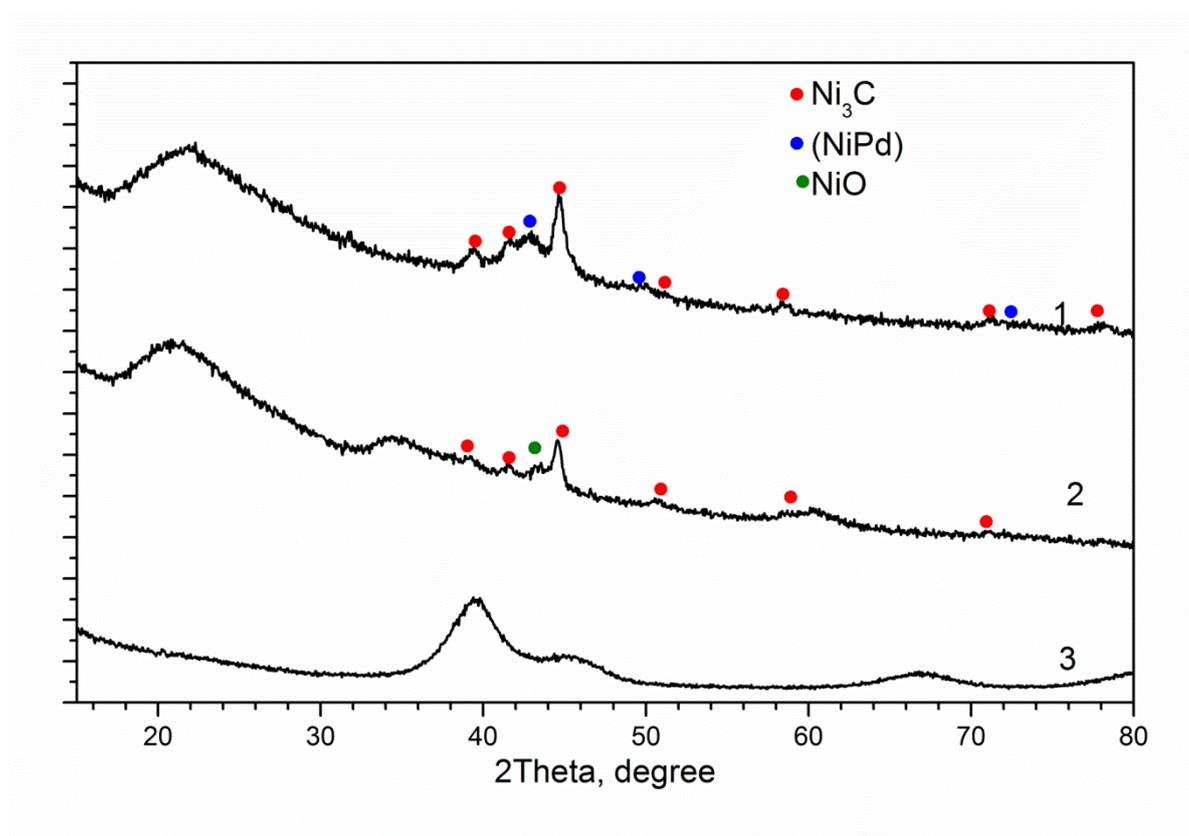
**Figure S6.** X-ray photoelectron spectra of Ni2p over reduced catalysts. 1- Ni/CeMg-C-S-O; 2- Ni/CeMg-A-S-V; 3- Ni/CeMg-A-S-O; 4- Ni-Pd/CeMg-A-S-V; 5- Ni/CeMg-A-P-O.



**Figure S7.** Temperature dependences of CO<sub>2</sub> and CH<sub>4</sub> conversions and H<sub>2</sub> and CO yields on catalyst Ni/CeMg-C-S-O.



**Figure S8.** (a) CH<sub>4</sub> conversion, (b) CO<sub>2</sub> conversion, (c) CO yield and (d) H<sub>2</sub>/CO ratio during CSMR at 750°C over M/Ce<sub>0.5</sub>Mg<sub>0.5</sub>O<sub>1.5</sub>. 1- Ni/CeMg-C-S-O; 2- Ni/CeMg-A-S-V; 3- Ni/CeMg-A-S-O; 4- Ni-Pd/CeMg-A-S-V; 5- Ni/CeMg-A-P-O.



**Figure S9.** Diffraction patterns of coloids stabilized by PVP and calcined at 573 K in vacuum at 10 mbar:  $\text{Ni}_{0.97}\text{Pd}_{0.03}$  (1), Ni (2), Pd (3).