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Effect of the oxidizing capacity of ceria-based support on the conversion of methane to syngas

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Synthesis

$Ce(NO_3)_3\cdot 6H_2O$, $Sm(NO_3)_3\cdot 6H_2O$, $Nd(NO_3)_3\cdot 6H_2O$, $Mn(NO_3)_2\cdot 4H_2O$, $Cu(NO_3)_2\cdot 3H_2O$, $ZrO(NO_3)_2\cdot 7H_2O$, $Ni(NO_3)_2\cdot 6H_2O$, $Co(NO_3)_2\cdot 6H_2O$, $Gd(NO_3)_3\cdot 6H_2O$, $TiCl_4$ (Acros Organics) were used as initial salts. Appropriate amounts of salts were dissolved in 500 mL distilled water containing nitric acid (pH=2) to give total concentrations of metals of 0.046 M. Then, the co-precipitation of hydroxides was carried out by addition of 2.5 M KOH solution up to pH 10 at 30°C under stirring. Ultrasonic processing (35 kHz, 150 W) was used during the dissolution of salts in distilled water and after precipitation. The resulting precipitates were filtered, washed with distilled water-ethanol solution (H_2O/C_2H_5OH=9 vol.), dried at 150°C for 12 h, and calcined in static air by heating at a rate of 4°C/min from room temperature to 500°C and kept at 500°C for 1 h in a muffle furnace. The initial molar ratio Ni/Co/Mn was 72/18/10 and their total number in catalyst was 5wt.% [S1-S3].

Characterization

All systems were characterized by XRD (Rigaku MiniFlex 600, CuK_α radiation; Mean crystallite size (d_{XRD}) was estimated by Scherrer equation taking into account the instrumental broadening using germanium as reference; Quantitative phase analysis was calculated by the Rietveld method), nitrogen adsorption-desorption method (TriStar 3000 Micromeritics, BET-BJH).

The catalytic activity of the samples in the oxidation of CO was determined by the flow method at atmospheric pressure. The process was conducted in a U-shaped quartz reactor at the total flow rate of 60 ml/min within a temperature range of 20-700°C. The temperature was measured with a thermocouple placed in the center of the catalytic bed. The catalyst sample mass was 0.3 g (was diluted for testing by quartz particles). The model gas mixture had the following composition, vol.%: CO – 1; O_2 – 2; N_2 – 97.

Partial oxidation and dry reforming of methane were performed using a single-pass plug-flow setup including a flow-fixed bed quartz reactor. The reactor was equipped with a pocket for a thermocouple, placed axially at the center of the reactor. All of the tests were carried out with 0.2 g of the catalyst (particles 0.5-1 mm), placed between quartz wool support and quartz pieces packing, at atmospheric pressure, using $CH_4/O_2=2$ or $CH_4/CO_2=1$ mixture without any inert gas dilution. Catalysts were tested in the temperature range of 750-980°C with a GHSV 10 and 12 $L^1g^{-1}h^{-1}$ for POM (CH_4+O_2) and DRM (CH_4+CO_2), accordantly. The initial gas mixture and outlet gas were analyzed using gas chromatography[S1-S3].

The catalytic properties of the synthesized samples in POM and DRM were investigated in a heated flow-through quartz reactor (inner diameter 18 mm, with a pocket for a thermocouple with a diameter of 8 mm). The end of the thermocouple was located in the center of the catalyst bed. The height of the catalyst bed is 1 mm. The particles are evenly distributed over the surface of the silica fiber substrate. They form an almost monolayer. During the POM, quartz particles were poured on top, which could get between the catalyst particles. No special dilution of the catalyst was done.

The carbon balance was evaluated in each experiment. Carbon losses associated with coke formation have been observed. The imbalance depended on the conditions of the experiment. With a high yield of synthesis gas in the POM, it did not exceed 0.5% of the mass. In experiments on the DRM was about 2% of the mass.

The catalysts were heated to a predetermined temperature in a stream of reagents for 1 h, kept for 1 h at this temperature, and within 15 min passed to another predetermined temperature, at which the experiment was also conducted for 1 h. During this hour, the composition of the exhaust gases was analyzed twice, recording the stability of the catalyst for an hour.

References

S1. I. V. Zagaynov, A. S. Loktev, A. L. Arashanova, V. K. Ivanov, A. G. Dedov, I. I. Moiseev, *Chem. Eng. J.*, 2016, **290**, 193.

S2. I. V. Zagaynov, A. S. Loktev, I. E. Mukhin, A. G. Dedov, I. I. Moiseev, *Mendeleev Commun.*, 2017, **27**, 509.

S3. I. V. Zagaynov, A. S. Loktev, I. E. Mukhin, A. A. Konovalov, A. G. Dedov, I. I. Moiseev, *Mendeleev Commun.*, 2019, **29**, 22.

Table S1

Sample	Composition
1	$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$
2	5 wt.% NiCoMn-$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$ (Ni/Co/Mn=72/18/10 mol.)
3	$Cu_{0.08}Mn_{0.02}Ce_{0.9}O_2$
4	5 wt.% NiCoMn-$Cu_{0.08}Mn_{0.02}Ce_{0.9}O_2$ (Ni/Co/Mn=72/18/10 mol.)
5	$Cu_{0.08}Mn_{0.02}Zr_{0.1}Ce_{0.8}O_2$
6	5 wt.% NiCoMn-$Cu_{0.08}Mn_{0.02}Zr_{0.1}Ce_{0.8}O_2$ (Ni/Co/Mn=72/18/10 mol.)
7	$Cu_{0.08}Mn_{0.02}Sm_{0.05}Ce_{0.85}O_2$
8	5 wt.% NiCoMn-$Cu_{0.08}Mn_{0.02}Sm_{0.05}Ce_{0.85}O_2$ (Ni/Co/Mn=72/18/10 mol.)
9	$Cu_{0.08}Mn_{0.02}Sm_{0.05}Zr_{0.1}Ce_{0.8}O_2$
10	5 wt.% NiCoMn-$Cu_{0.08}Mn_{0.02}Sm_{0.05}Zr_{0.1}Ce_{0.8}O_2$ (Ni/Co/Mn=72/18/10 mol.)

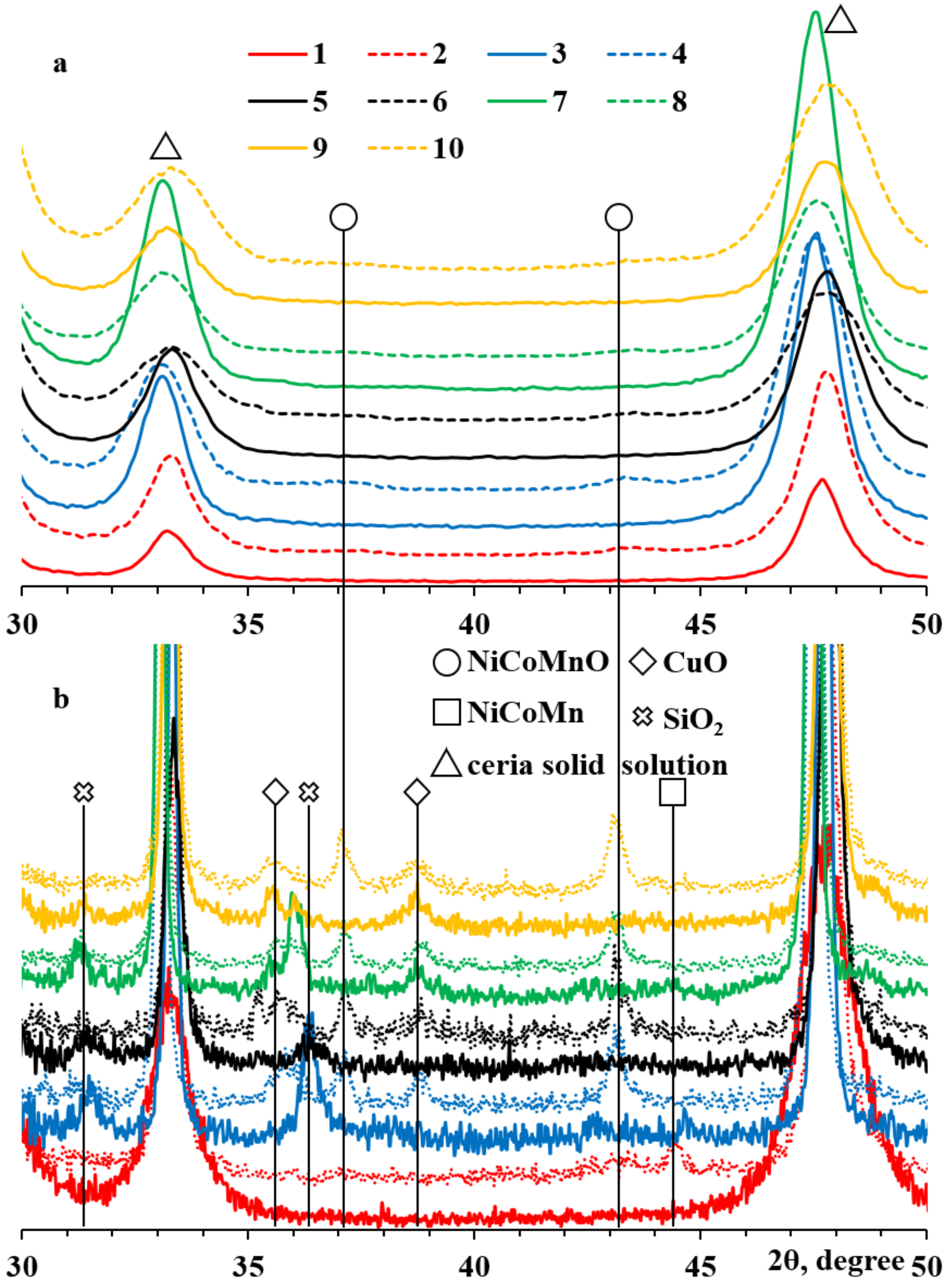

Figure S1 XRD patterns of fresh catalysts (a) and used after POM and DRM (b). SiO_2 from quartz pieces packing.

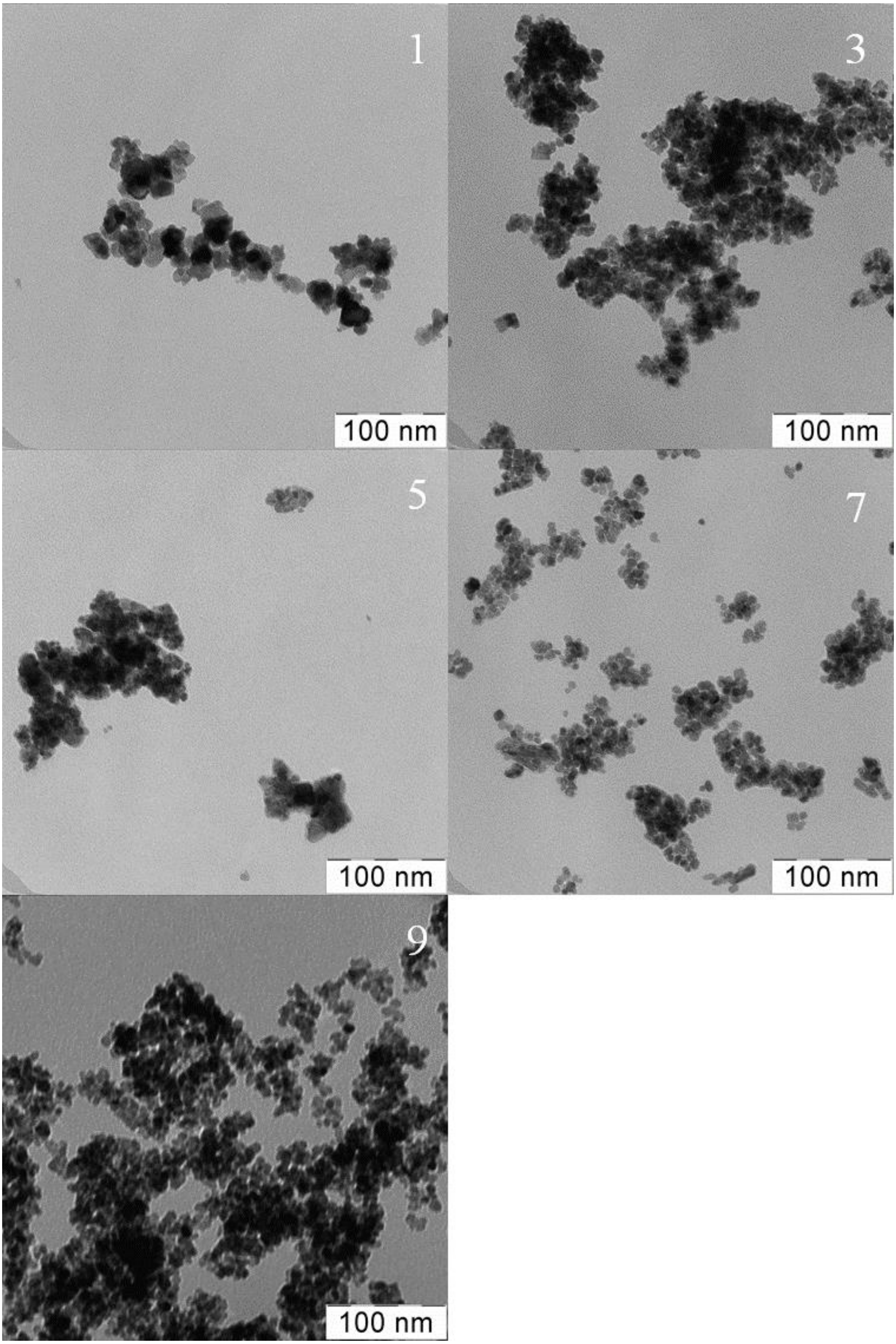

Figure S2 TEM images of fresh catalysts.