Electronic supplementary materials *Mendeleev Commun.*, 2017, **27**, 509–511

Influence of the Ni/Co ratio in bimetallic NiCo catalysts on methane conversion into synthesis gas

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Synthesis

$Ce(NO_3)_3 \cdot 6H_2O$, $ZrO(NO_3)_2 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $TiCl_4$ (Acros Organics) were used as precursors. Appropriate amounts of salts were dissolved in 500 mL distilled water containing of nitric acid (pH=2) to give total concentrations of metals of 0.045 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 (10 min, 35 kHz, 150 W, Sapphire UZV-4.0) was used during 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.

Characterization

Powder XRD data were collected at room temperature (Rigaku MiniFlex 600, Japan) with CuK_α radiation. Specific surface area (S_{BET}) of the powders was measured by a conventional nitrogen adsorption method at 77K (TriStar 3000 Micromeritics). Pore-size distributions were calculated from desorption isotherm, using BJH method. TEM analyses were conducted on an Omega Leo-912AB transmission electron microscope with accelerating voltage of 100 kV. SEM analyses were conducted on a JEOL JSM-6390LA scanning electron microscope with accelerating voltage of 20 kV, equipped energy-dispersive X-ray spectrometer (EDS). Thermal analysis (TG-DSC) was carried out under air flow (20 ml/min) with Netzsch STA449F3. The samples were heated to 900°C at the rate of 20°C/min.

Partial oxidation and dry reforming of methane was performed using a single-pass plug-flow setup including a flow-fixed bed U-shaped quartz reactor (5 mm internal). The reactor was equipped with a pocket for a thermocouple, placed between inlet and outlet tubes. All of the tests were carried out with 0.2 g of catalyst (catalyst pellet particle size was 0.5 mm), placed at the bottom of U-tube, at atmospheric pressure, using $CH_4/O_2=2$ or $CH_4/CO_2=1$ mixtures without any inert gases dilution. Catalysts were tested in the temperature range of 850-950°C with a GHSV 10 and 12 $L^1g^{-1}h^{-1}$ for POM and DRM, accordantly.

The initial gas mixture and outlet gas were analyzed using gas chromatography. Detailed catalytic test is in previous paper [1].

References

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

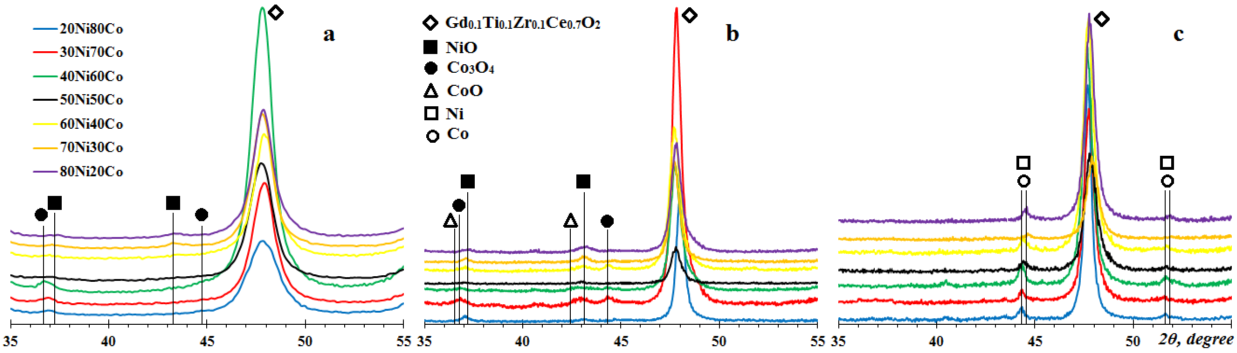

Figure S1 XRD patterns of fresh catalysts (a) and catalysts used after POM (b) and DRM (c).

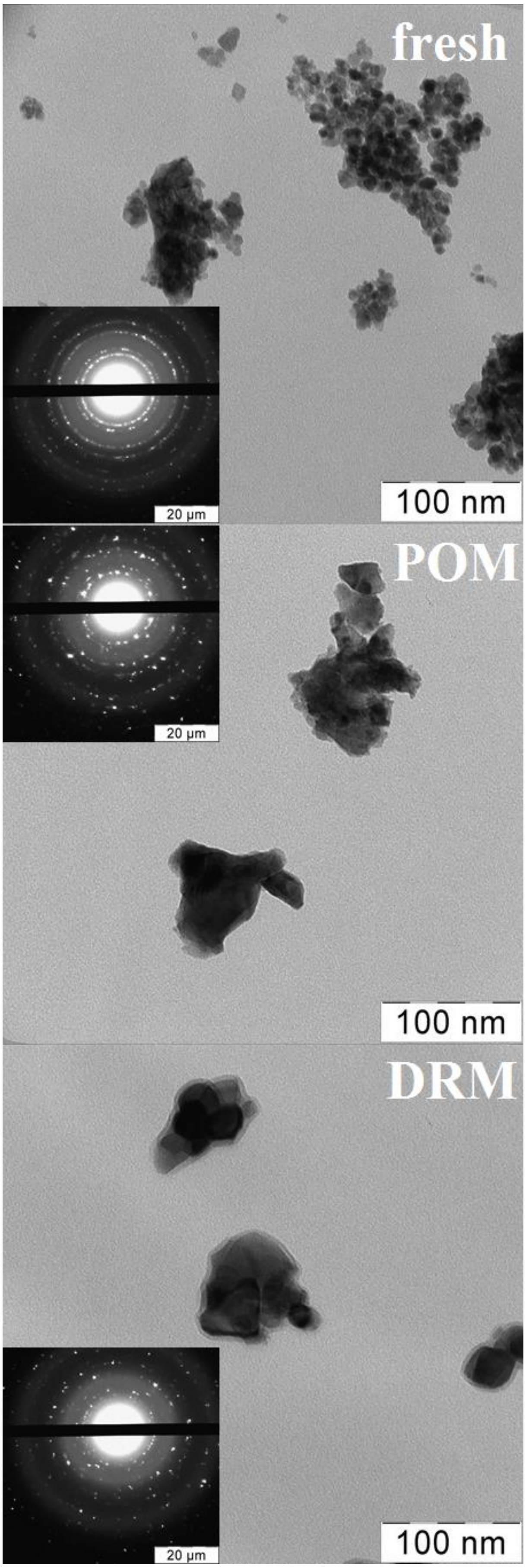

Figure S2 TEM pictures of fresh (a) and catalyst used after POM (b) and DRM (c) (sample 80Ni/20Co).

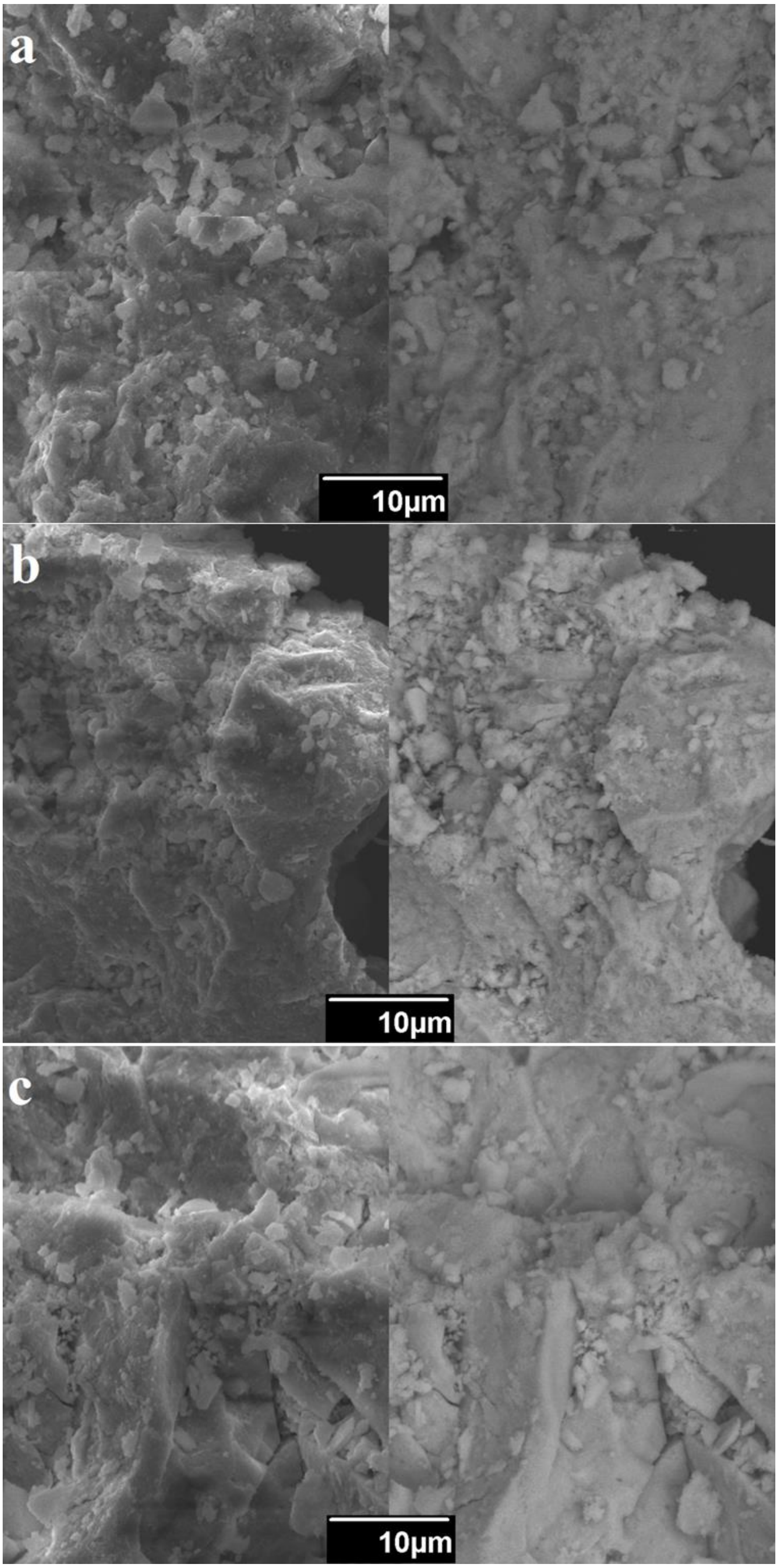

Figure S3 SEM pictures of fresh (a) and catalyst used after POM (b) and DRM (c) (sample 80Ni/20Co) in SE (left) and BSE (right) mods.