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NiCo-$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$ catalyst for dry reforming and partial oxidation of methane: effect of NiCo applying method on the conversion of methane to 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 metal precursors.

Support

$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$ was used as a support [Ceramics International 41 (2015) 8730-8734]. The synthesis is the same as for the co-precipitation method, only without the addition of nickel and cobalt salts.

Co-precipitation

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, dried at 150 °C for 12 h, and calcined in static air by heating at a rate of 4 °C min^{-1} from room temperature to 500 °C and kept at 500 °C for 1 h in a muffle furnace.

Impregnation

1.0000 g of support was dispersed into 30 ml of distilled water at 30 °C and stirred. This solution is referred as solution one. Solution two was prepared in parallel by dissolving of 0.2149 g $Ni(NO_3)_2 \cdot 6H_2O$ and 0.0538 g $Co(NO_3)_2 \cdot 6H_2O$ in 50 ml isopropanol at 30 °C. The solution two was added to the first solution and the mixture was stirred at 30 °C for 1 h, then the temperature was raised to 80 °C further

evaporating the solution. The solutions one, two, and mixture were subjected to ultrasonic treatment. The drying and calcination process is the same as in co-precipitation.

Core–shell

3.7049 g of polyvinylpyrrolidone (PVP 35000) was dissolved in 30 ml of distilled water at 30 °C for 10 min, then 1.0000 g of the support was dispersed into this system and stirred. This solution is referred as solution one. Solution two was prepared in parallel by dissolving of $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ in 50 ml of isopropanol at 30 °C. The solution two was added to the first solution and the mixture was stirred at 30 °C for 5 h, then the temperature was raised to 80 °C, evaporating until a gel formed. The solutions one and two were subjected to ultrasonic treatment, and after their mixing, the treatment was stopped. The drying and calcination process is the same as in co-precipitation.

Hydrothermal

The process is similar to the core-shell method, however, after mixing the two solutions for 20 min, the mixture was loaded into an autoclave and subjected to hydrothermal treatment at 120 °C for 5 h.

Catalytic activity

Partial oxidation and dry reforming of methane were performed using a single-pass plug-flow setup reactor including a fixed bed flow quartz reactor (inner diameter 18 mm) with an axial pocket for thermocouple (outer diameter 8 mm). The tip of the thermocouple [chromel-alumel (K)] was positioned in the center of the catalyst layer. Powdered catalysts precursors were pressed into pellets, grinded, and a fraction with 0.5–1 mm grains was used in further experiments. The catalyst precursor (0.2 g, layer height 1 mm) was placed on a quartz fiber substrate. 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. All of the tests were carried out at atmospheric pressure, using $CH_4/O_2 = 2$ or $CH_4/CO_2 = 1$ mixtures without any inert gas dilution. The catalyst precursor was preheated to 900 ºC in a stream of a gas mixture of CH_4 and CO_2 or O_2. Catalysts were tested in the temperature range of 600–950 °C with a GHSV 12 and 15 $L^1\ g^{-1}\ h^{-1}$ for POM and DRM, accordantly.

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 initial gas mixture and outlet gas were analyzed using two gas chromatographs. Helium was used as a carrier gas in both chromatographs. The first chromatograph was equipped with a TCD and two stainless steel columns that were 3 m in length and 3 mm in diameter. The first column was filled with Porapak Q (50–80 mesh, Waters Assoc., USA) and used to determine the content of air, methane, CO_2, ethane and ethylene. The second column was filled with 8% Na_2CO_3 supported on alumina and used to determine the content of air, methane, ethane, ethylene and C_{3+} hydrocarbons. The temperature of the columns during analysis was 80 °C. The second chromatograph was equipped with a TCD and a stainless steel column that was 2 m in length and 3 mm in diameter and packed with NaX zeolite (Gazprom Neftekhim Salavat, Russia). This column operates at ambient temperature and allows to determine the contents of hydrogen, oxygen, nitrogen, carbon monoxide and methane. The chromatograms were treated with an internal normalization method with a correction for the molecular weight of the components. Chromatographic peaks areas were multiplied by a molar correction coefficient and sum up. Corrected chromatographic peaks areas are divided on the sum of corrected areas that correspond to a molar ratio of each component. Due to the small difference in thermal conductivities of He and H_2, negative H_2 peaks can be occasionally observed. To solve this problem, we used the H_2 peak inversion procedure and special software for H_2 content calculation based on the results from analysis of model gas mixtures, composed from variable amounts of hydrogen, methane, CO and air. Graph of dependence of hydrogen vol% *vs*. ratio of hydrogen chromatographic peak in total chromatographic peaks area was build up and used to estimate H_2 content.

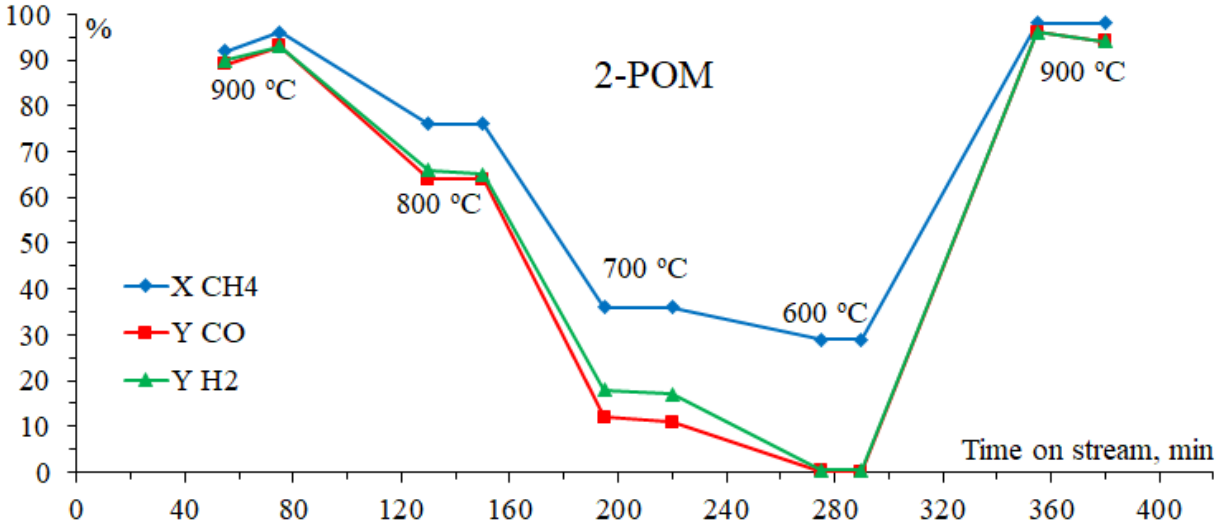
The powders were characterized by XRD (DRON-3M, CuK_α radiation), nitrogen sorption (TriStar 3000 Micromeritics, BET-BJH at 77K), TG-DSC (Netzsch STA 409 Luxx, 10 °C/min in air), SEM (TESCAN VEGA II SBU with INCA Energy 300 energy dispersive spectrometers).

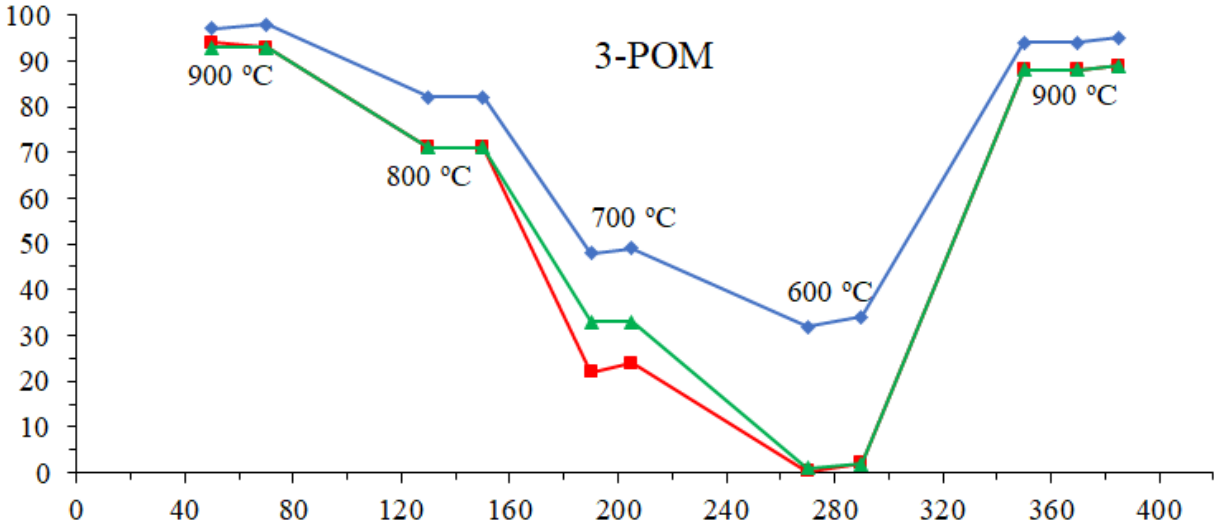
Catalysts 5 wt% NiCo-$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$ (Ni/Co = 80/20 mol), synthesized by various methods (f – fresh, p – used in partial oxidation of methane, d – used in dry reforming of methane)

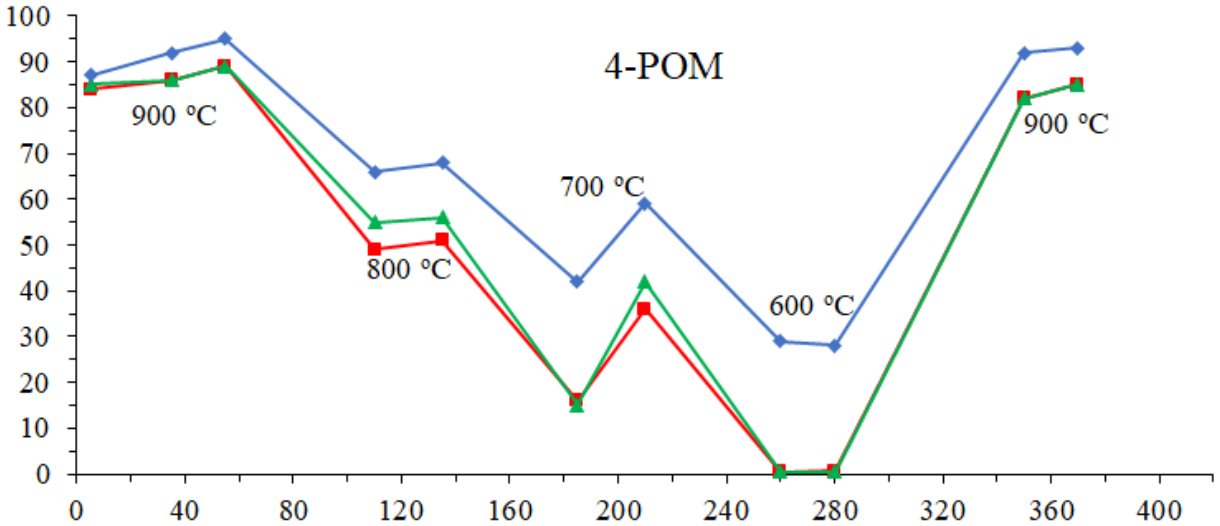
No	Method
1f	co-precipitation
1p	
1d	
2f	impregnation
2p	
2d	
3f	hydrothermal
3p	
3d	
4f	core–shell
4p	
4d	

Table S1 Composition of POM products at 900 °C (Selectivity/%).

No	C_2H_4	C_2H_6	C_{3+}	CO_2	CO
1f	0	0	0	0.4	99.6
2f	0	0	0	2.6	97.4
3f	0	0	0	3.8	96.2
4f	0	0	0	1.6	98.4


%
2-POM
900 °C
800 °C
700 °C
600 °C
900 °C
X CH4
Y CO
Y H2
Time on stream, min
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400


3-POM
900 °C
800 °C
700 °C
600 °C
900 °C
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400


4-POM
900 °C
800 °C
700 °C
600 °C
900 °C
0
10
20
30
40
50
60
70
80
90
100
0
40
80
120
160
200
240
280
320
360
400

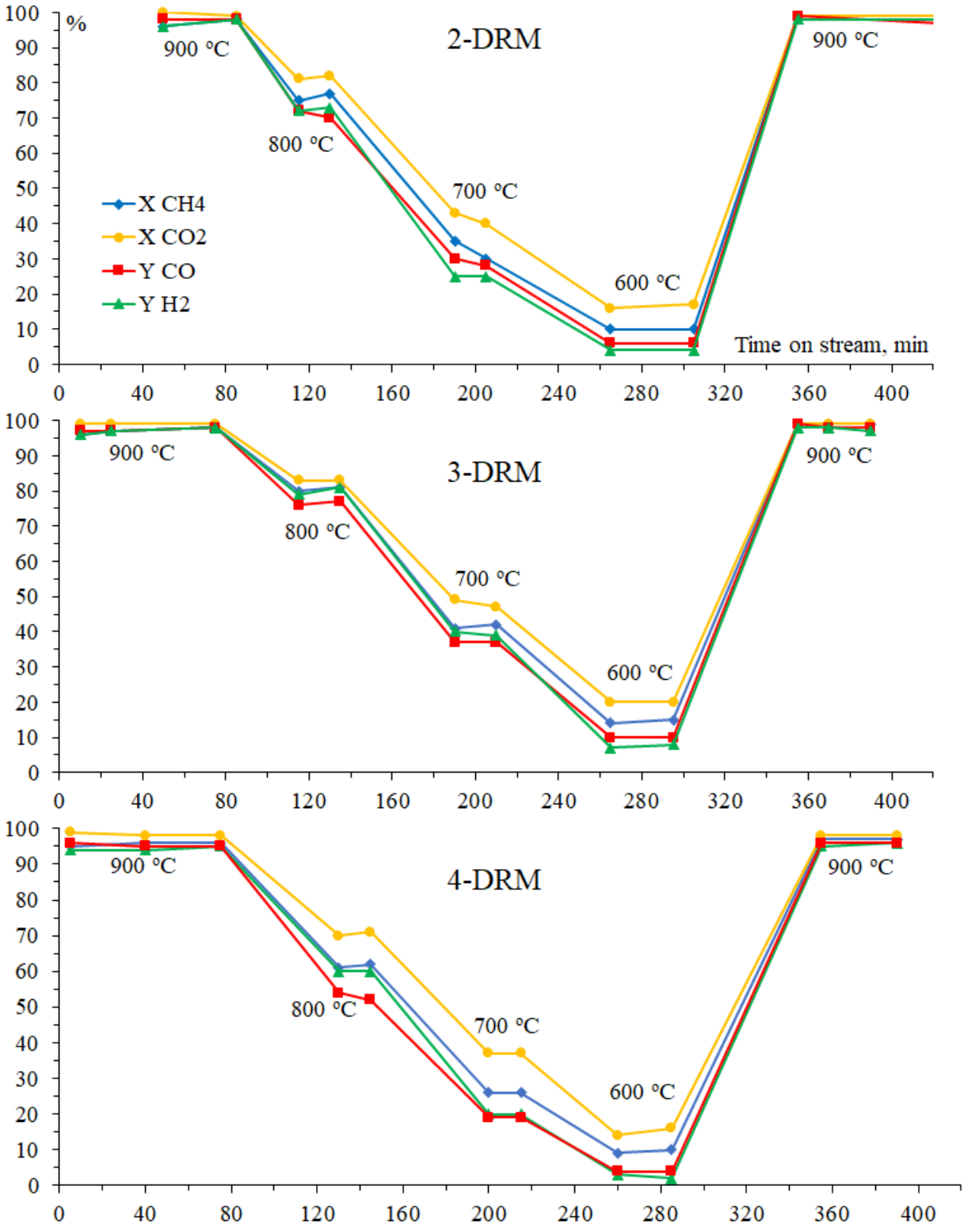
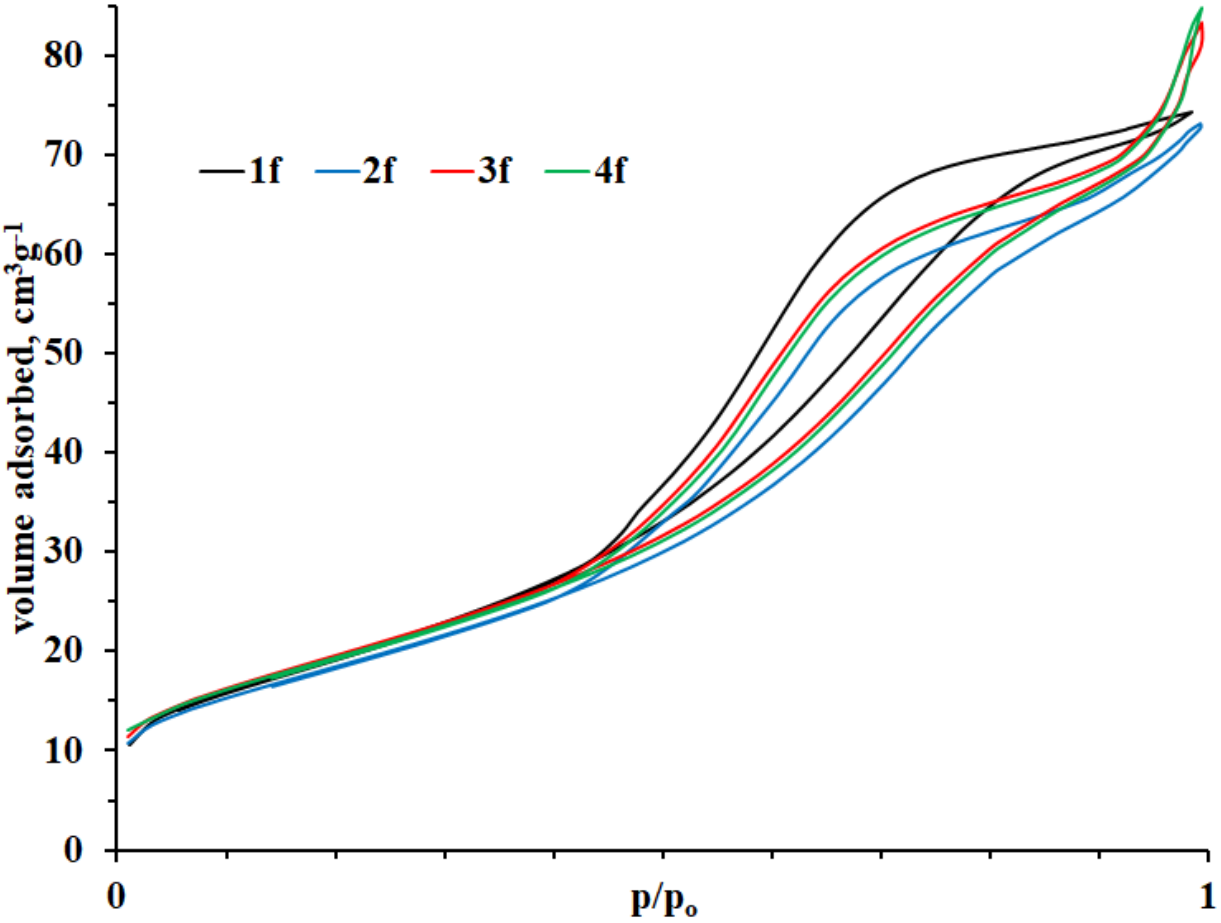
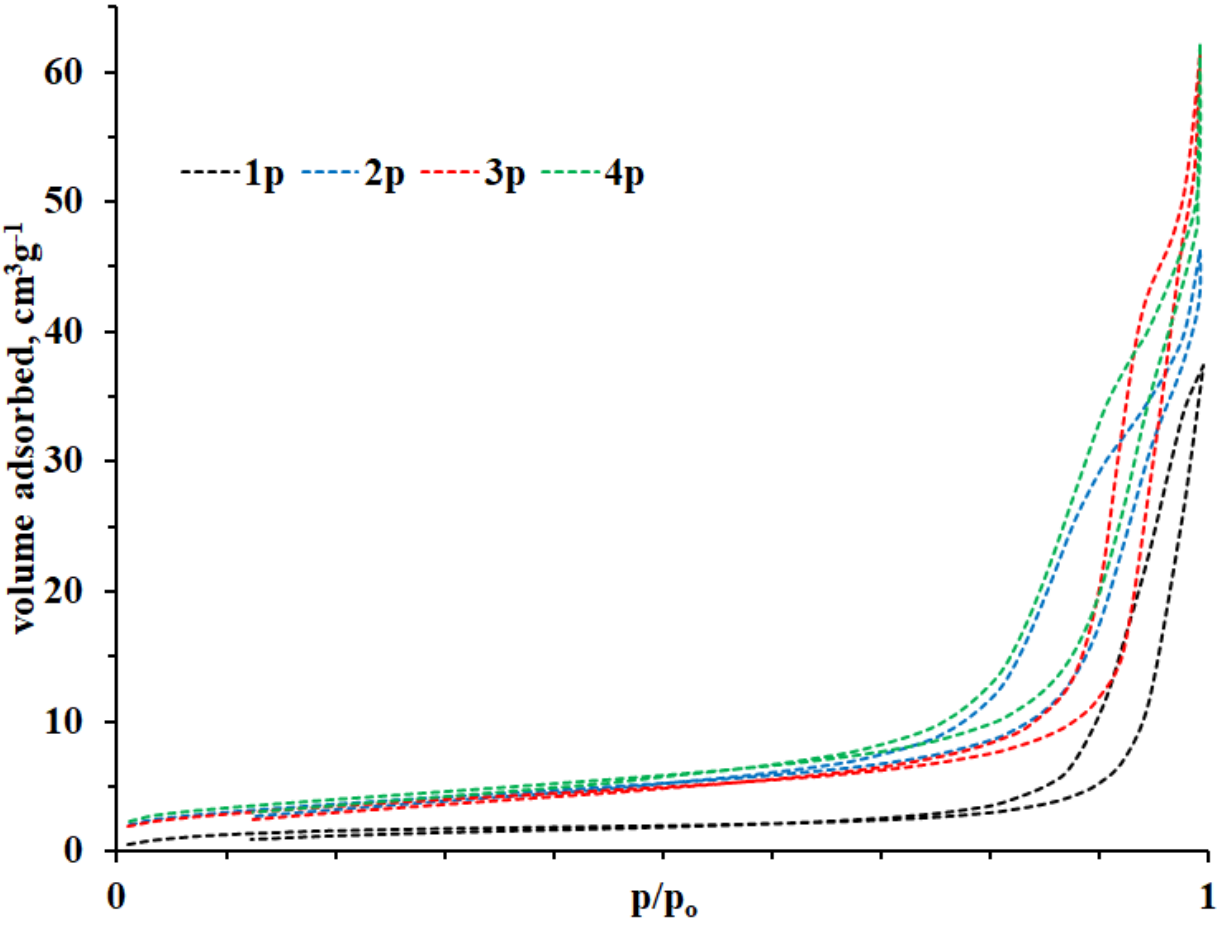


Figure S1 Catalytic activity (stability) of samples in POM or DRM.


1f
2f
3f
4f
volume adsorbed, cm3g-1
0
10
20
30
40
50
60
70
80
0
p/po
1


1p
2p
3p
4p
volume adsorbed, cm3g-1
0
10
20
30
40
50
60
0
p/po
1

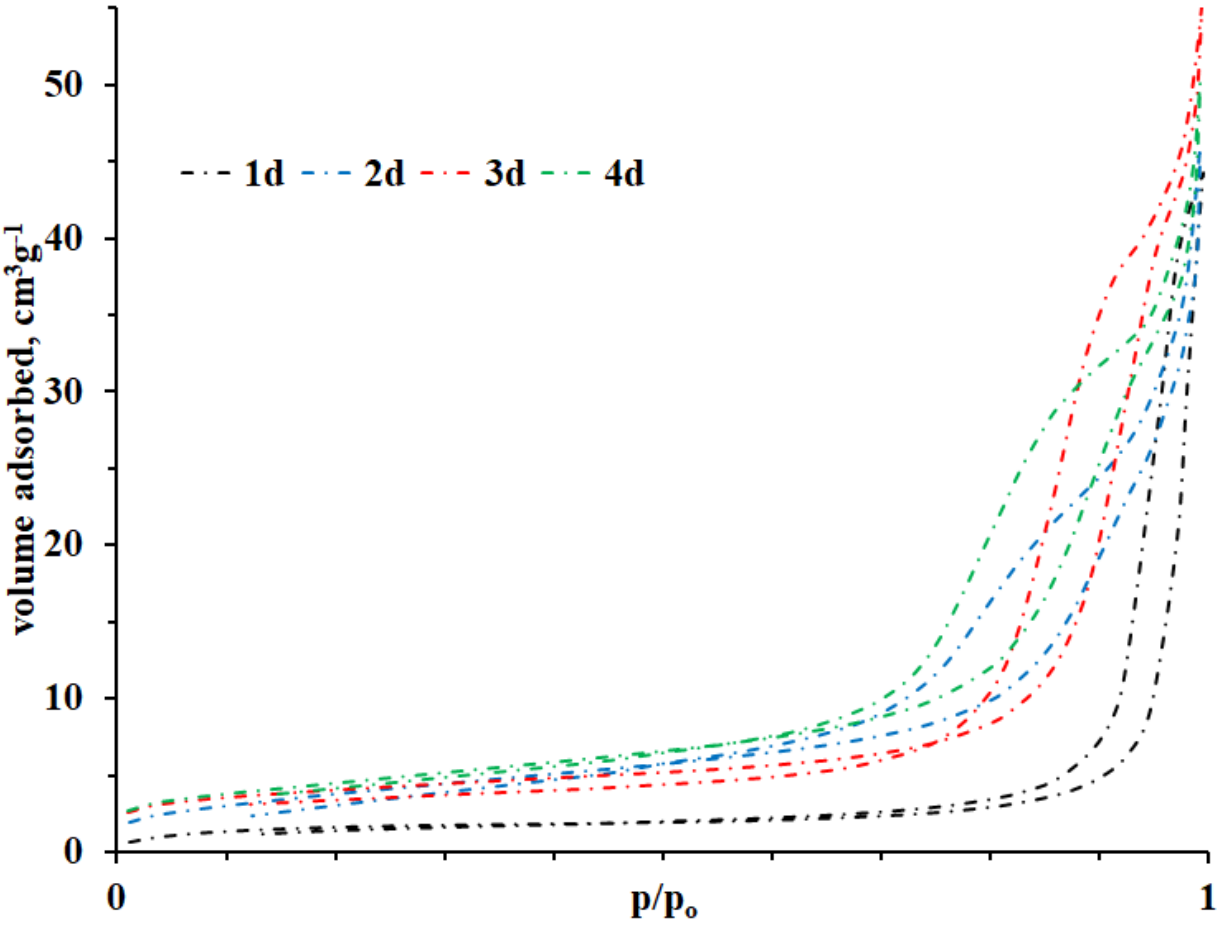
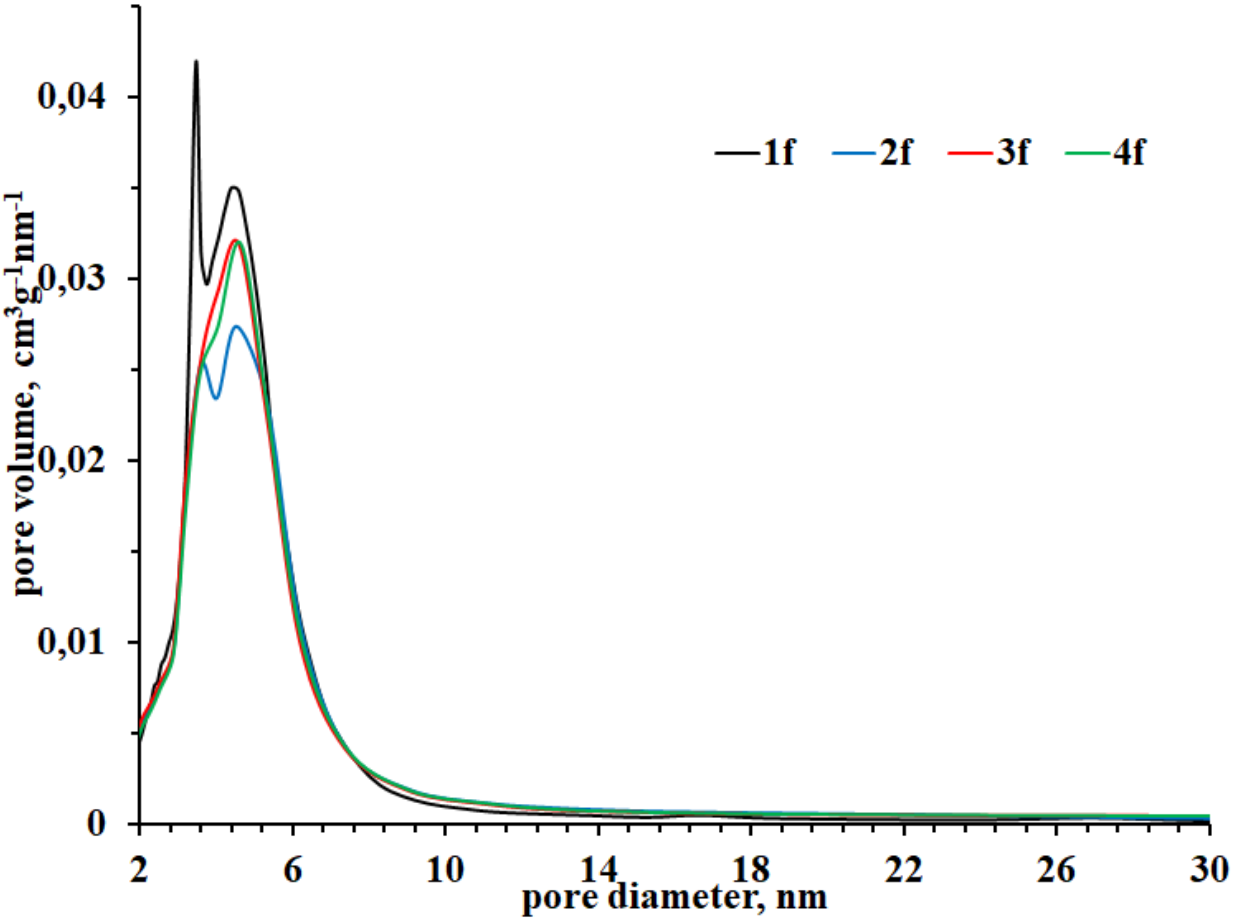
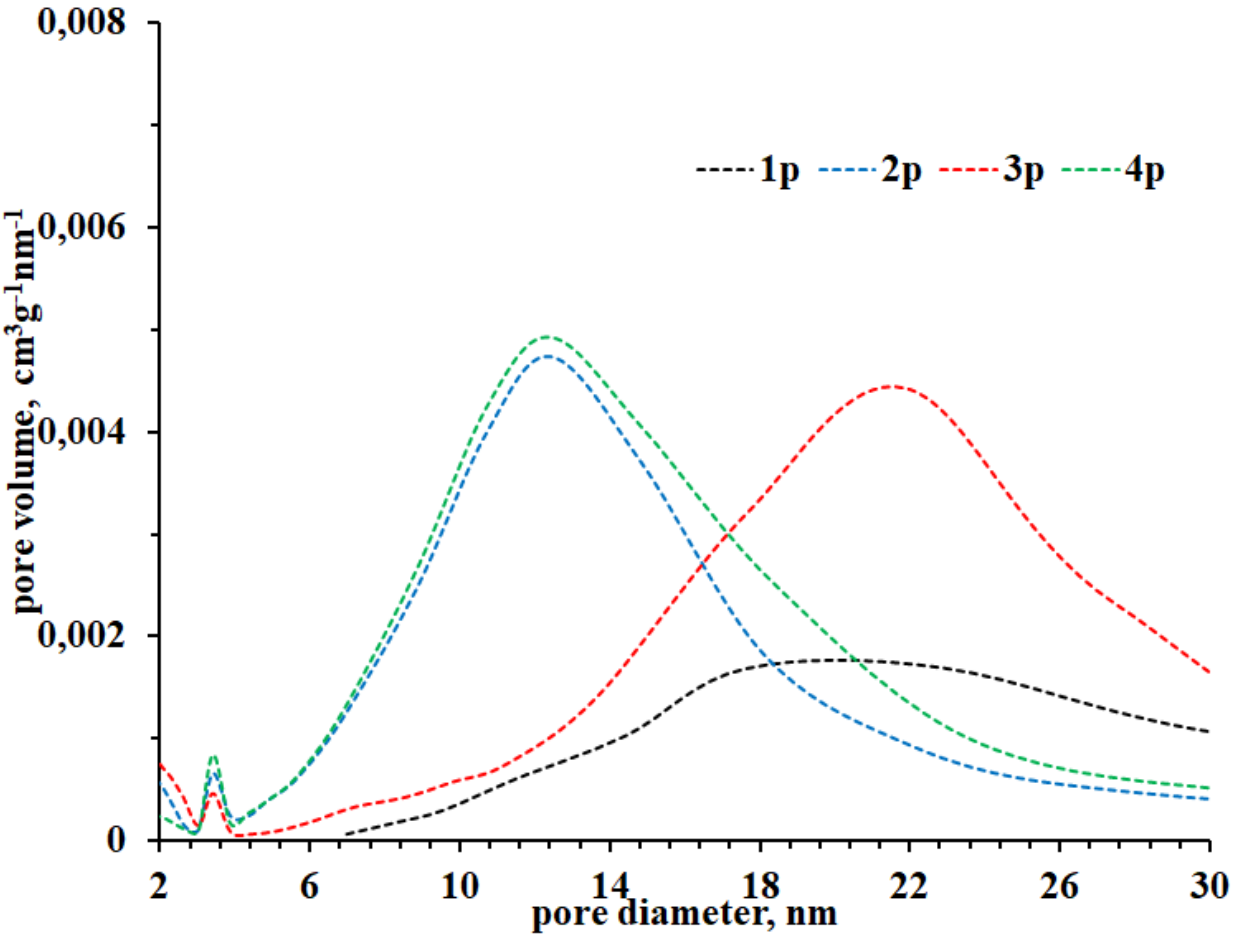


Figure S2 Nitrogen adsorption-desorption isotherms of the catalysts.


0,04
0,03
0,02
0,01
0
pore volume, cm3g-1nm-1
1f
2f
3f
4f
2
6
10
14
18
22
26
30
pore diameter, nm


0,008
0,006
0,004
0,002
0
pore volume, cm3g-1nm-1
1p
2p
3p
4p
2
6
10
14
18
22
26
30
pore diameter, nm

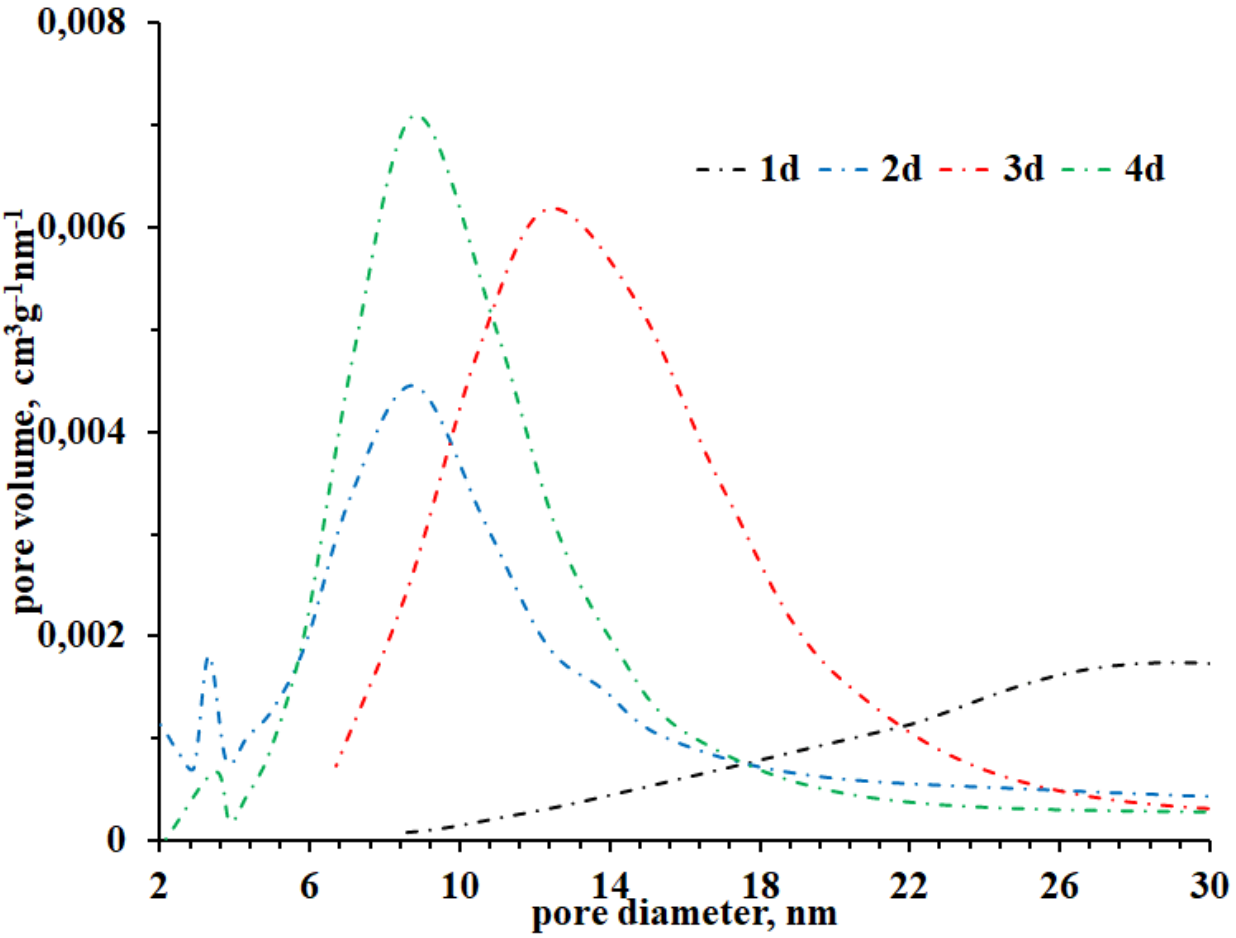


Figure S3 Pore size distributions of the catalysts.

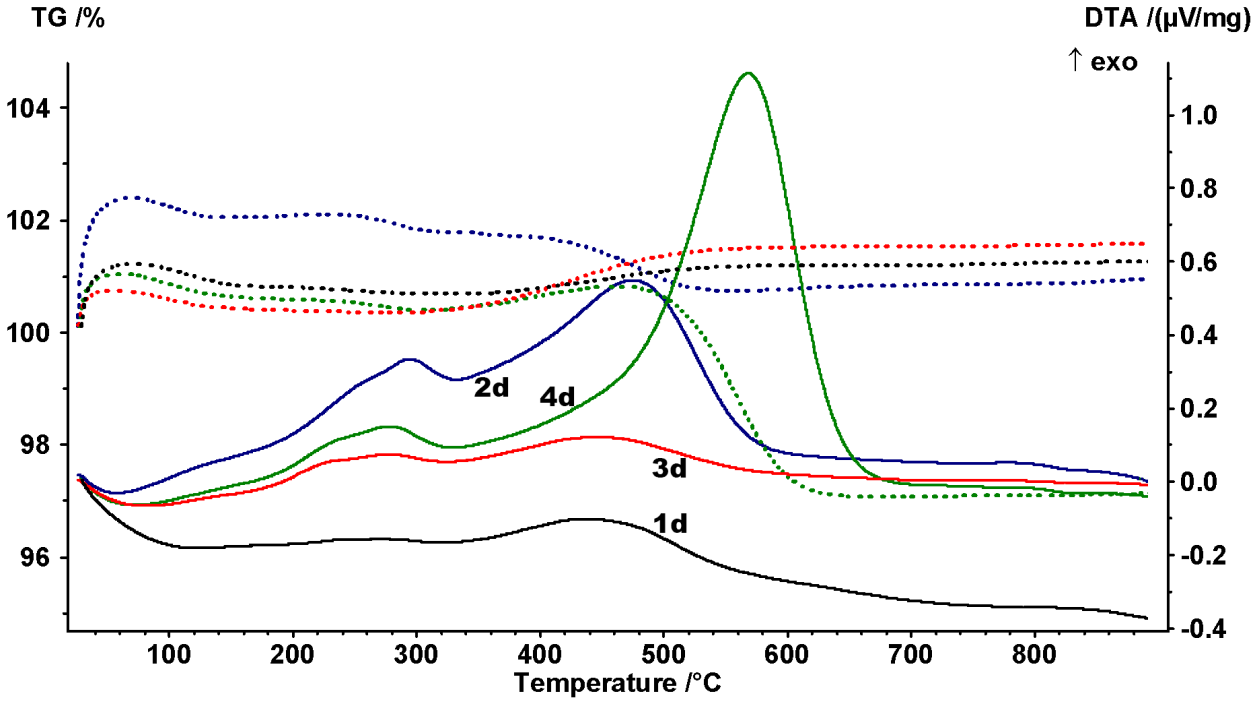


Figure S4 TG data of used catalysts after DRM.

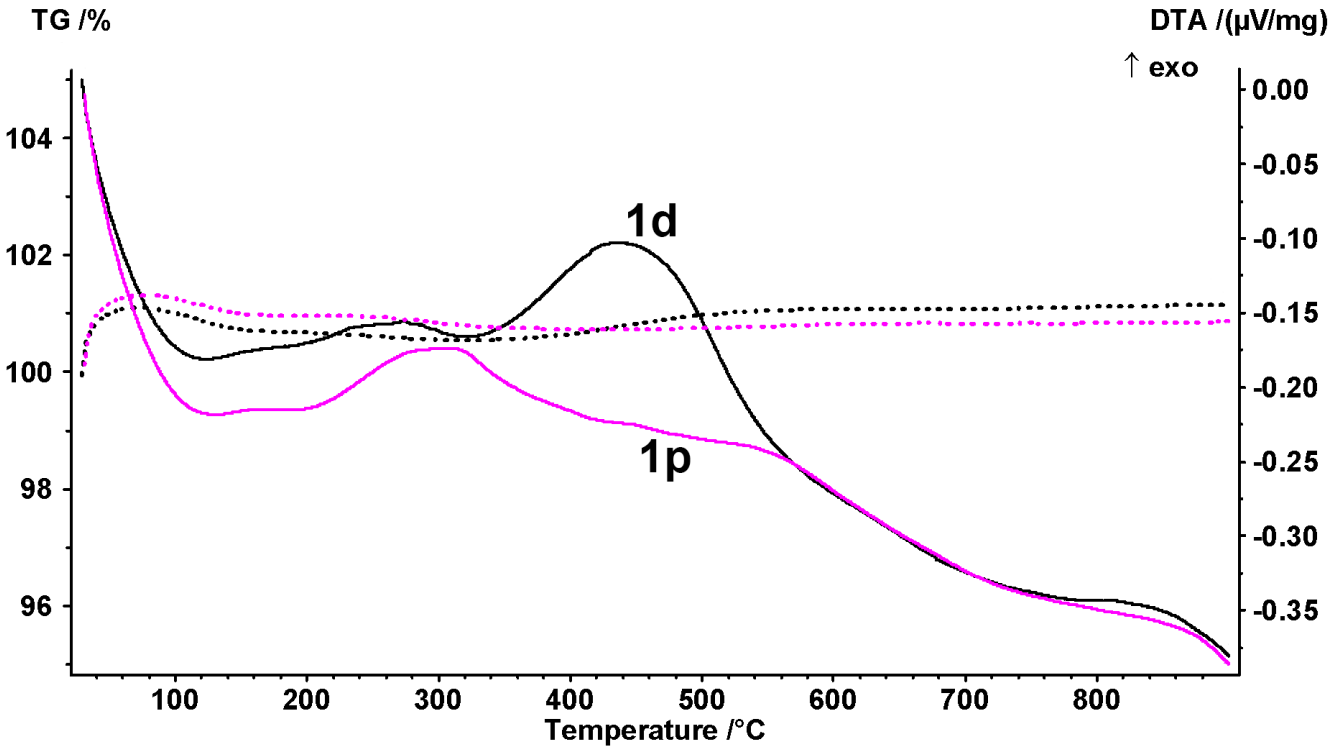


Figure S5 TG data of used catalyst 1 after DRM (1d) and POM (1p).

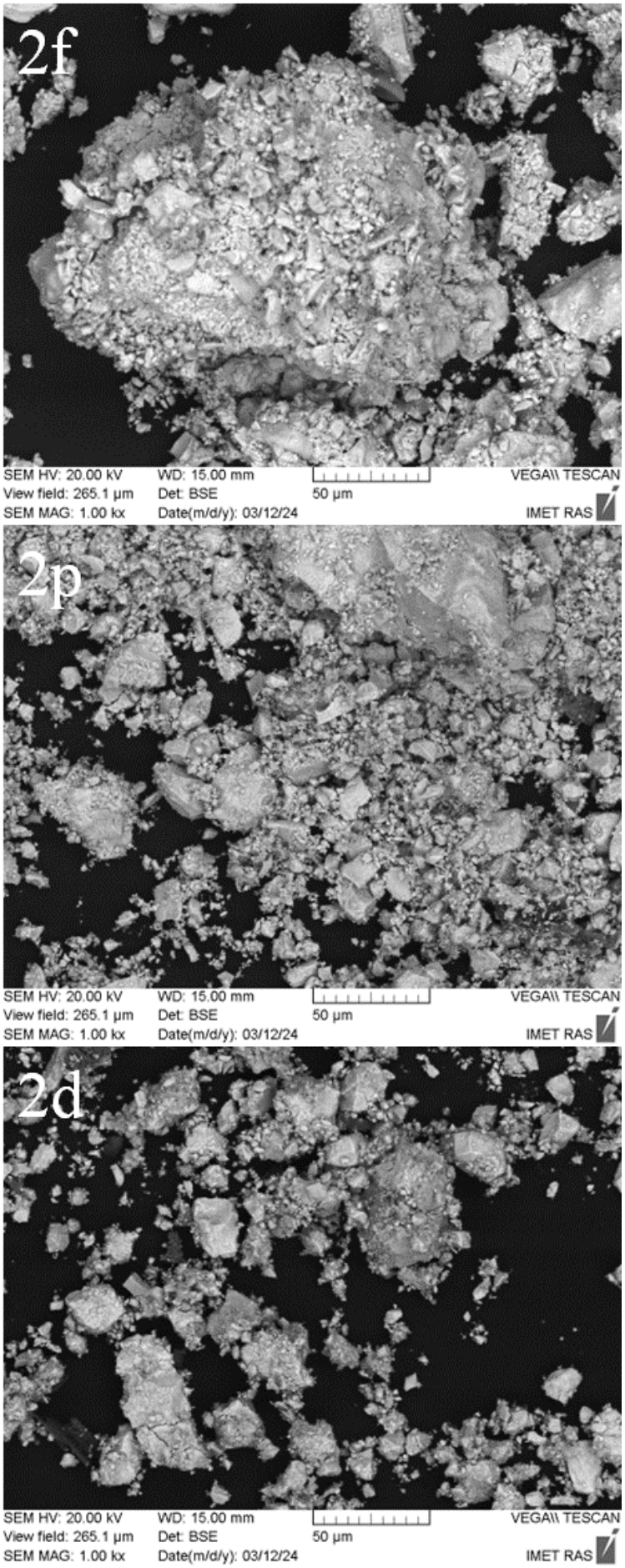


Figure S6 SEM images of catalyst 2 before and after CH_4 conversion.