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Trimetallic NiCoM catalysts (M = Mn, Fe, Cu) for methane conversion into synthesis gas

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Synthesis

The catalyst preparation methods have a strong influence over physical-chemical properties and performance of catalysts, so for this goal, the co-precipitation method was used as one of more simple and effective method. $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $ZrO(NO_3)_2 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $TiCl_4$ (Acros Organics) were used as the raw materials. Appropriate amounts of salts were dissolved in 500 mL distilled water containing nitric acid (pH=2) to give total concentrations of metals of 0.0458 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 was 80/20 and their total number in catalyst was 5wt.%, the appropriate amount of third metal was added, so composition of the active component was Ni/Co/M=72/18/10 (for 10 mol.% M content) or Ni/Co/M=64/16/20 (for 20 mol.% M content) [1, 2].

Characterization

All systems were characterized by XRD (Rigaku MiniFlex 600, CuK_α radiation; Mean crystallite size (dXRD) 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), TEM (Omega Leo-912AB), SEM (Carl Zeiss NVision 40), TG-DSC (Netzsch STA 409 Luxx, 10°C/min in air).

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 $CH_4/CO_2=1$ 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 [1, 2].

References

1. I.V. Zagaynov, A.S. Loktev, A.L. Arashanova, V.K. Ivanov, A.G. Dedov, I.I. Moiseev, Ni(Co)-$Gd_{0.1}Ti_{0.1}Zr_{0.1}Ce_{0.7}O_2$ mesoporous materials in partial oxidation and dry reforming of methane into synthesis gas, Chem. Eng. J. 290 (2016) 193–200.

2. I.V. Zagaynov, A.S. Loktev, I.E. Mukhin, A.G. Dedov, I.I. Moiseev, Influence of Ni/Co ratio in bimetallic NiCo catalysts in methane conversion into synthesis gas. Mendeleev Commun. 27 (2017) 509-511.

Table S1. Catalytic activity of samples.

DRM				
Sample	Conversion, %		Yield, %	
	CH_4	CO_2	CO	H_2
850°C				
20Mn	90	92	86	91
10Mn	95	95	92	92
20Fe	32	55	27	40
10Fe	72	82	64	77
20Cu	87	89	85	88
10Cu	92	92	91	91
900°C				
20Mn	95	96	95	97
10Mn	97	97	97	99
20Fe	68	81	74	58
10Fe	88	91	89	88
20Cu	94	96	94	94
10Cu	96	95	95	95
950°C				
20Mn	97	96	96	98
10Mn	98	97	97	100
20Fe	94	95	95	94
10Fe	97	93	94	96
20Cu	97	95	96	97
10Cu	98	97	97	97
POM				
Sample	Conversion, %		Yield, %	
	CH_4	O_2	CO	H_2
850°C				
20Mn	90	97	87	89
10Mn	90	97	90	90
20Fe	44	97	52	53
10Fe	36	96	20	28
20Cu	67	97	60	62
10Cu	79	97	74	75
900°C				
20Mn	94	97	93	94
10Mn	95	98	94	94
20Fe	81	97	77	75
10Fe	77	97	72	74
20Cu	87	98	85	87
10Cu	87	97	89	88
950°C				
20Mn	95	98	94	95
10Mn	97	98	97	97
20Fe	94	97	93	91
10Fe	93	97	93	93
20Cu	93	98	93	93
10Cu	94	97	93	93

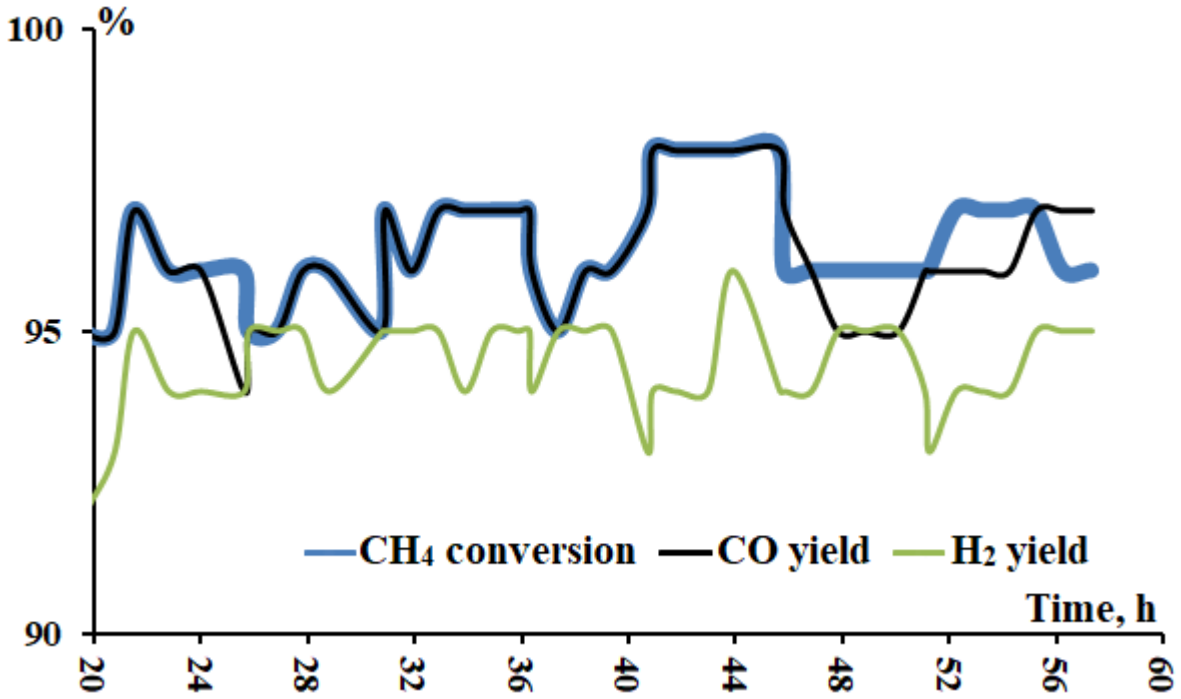

Figure S1. Conversion of methane and yields of products formed during POM of sample 10Mn at 900°C.

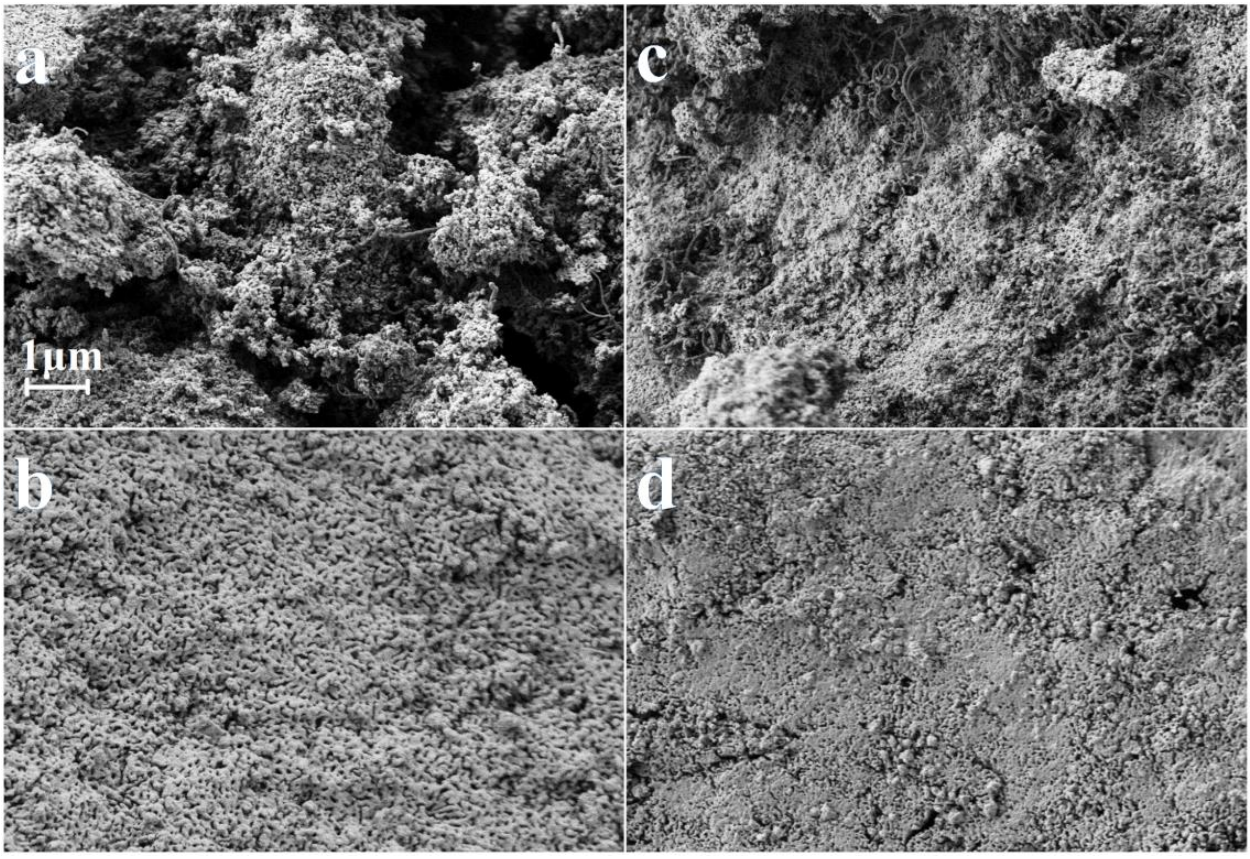

Figure S2. SEM microphotos of used catalysts after DRM (a, c) and POM (b, d) for samples 10Mn (a, b) and 20Mn (c, d).

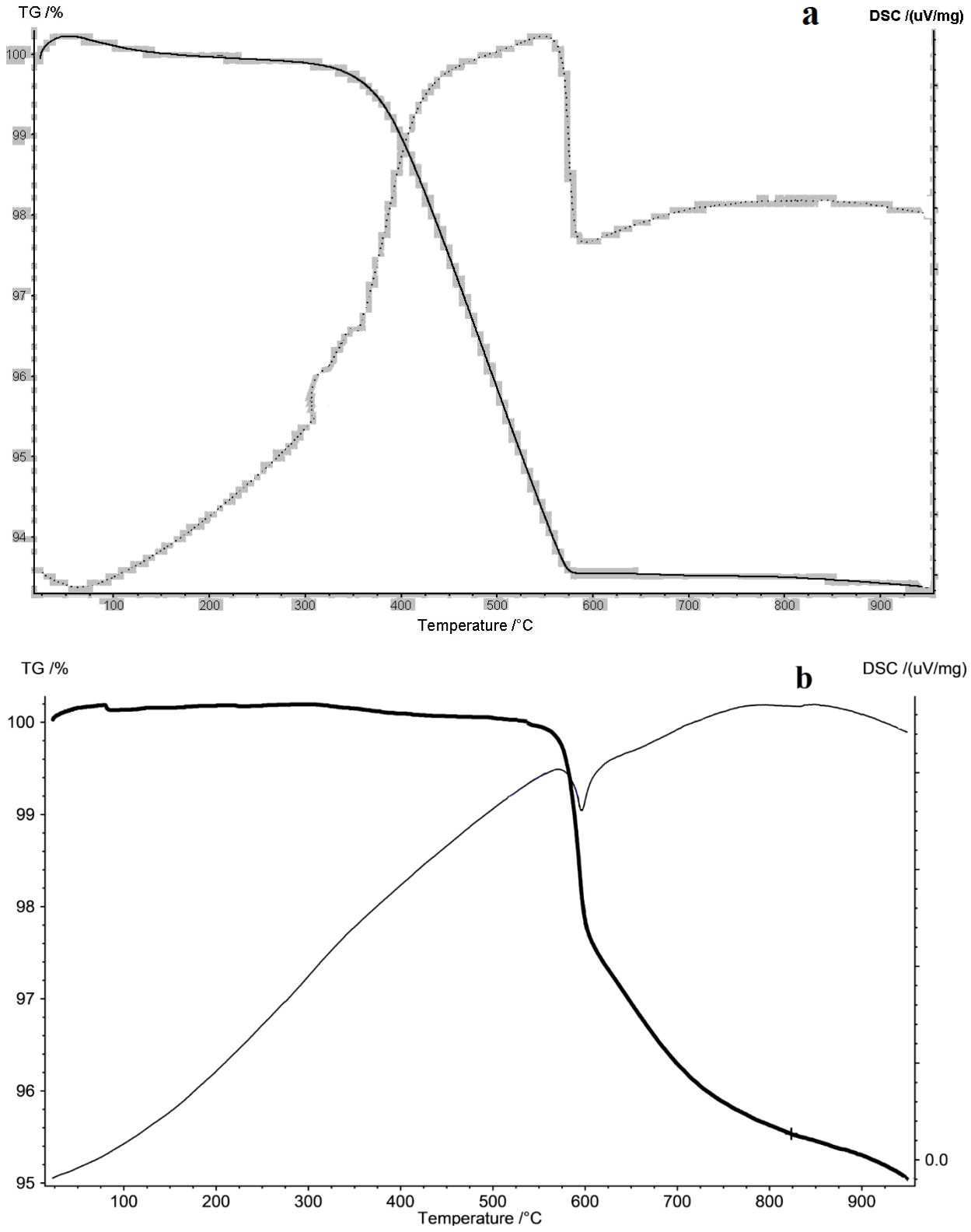

Figure S3. TG-DSC data of used catalysts after POM (a) and DRM (b) for samples 10Mn.