Ni, Co, Ni-Co/SiO_2 nanocomposites in the reaction of carbon dioxide methanation

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For highly effective carbon dioxide methanation mono- (Ni_{100}/SiO_2, Co_{100}/SiO_2) and bimetallic $Ni_{100-x}Co_x/SiO_2$ nanocomposites have been prepared. Mentioned nanocomposites were synthesized by the method of solvate stimulated modification of silica surface with nitrate solution of corresponding metals, further thermal decomposition and chemical reduction in the H_2/He flow. All samples were characterized with SEM EDX, N_2 adsorption and XRD analysis.

Table 1. Specific surface areas and $R_{p,V}$ of nanosilica and presented composites

Sample		S_{BET}, m^2/g	S_{meso}, m^2/g	$R_{p,V}$ nm
SiO_2		283	225	29.0
A1P	Ni_{100}/SiO_2 (o)*	214	200	16.7
	Ni_{100}/SiO_2 (r)**	216	200	16.2
A2P	Co_{100}/SiO_2 (o)	206	183	20.3
	Co_{100}/SiO_2(r)	219	203	20.6
A3P	$Ni_{50}Co_{50}/SiO_2$(o)	210	192	15.7
	$Ni_{50}Co_{50}/SiO_2$(r)	217	200	17.5
A4P	$Ni_{20}Co_{80}/SiO_2$(o)	231	222	15.6
	$Ni_{20}Co_{80}/SiO_2$(в)	218	202	17.3

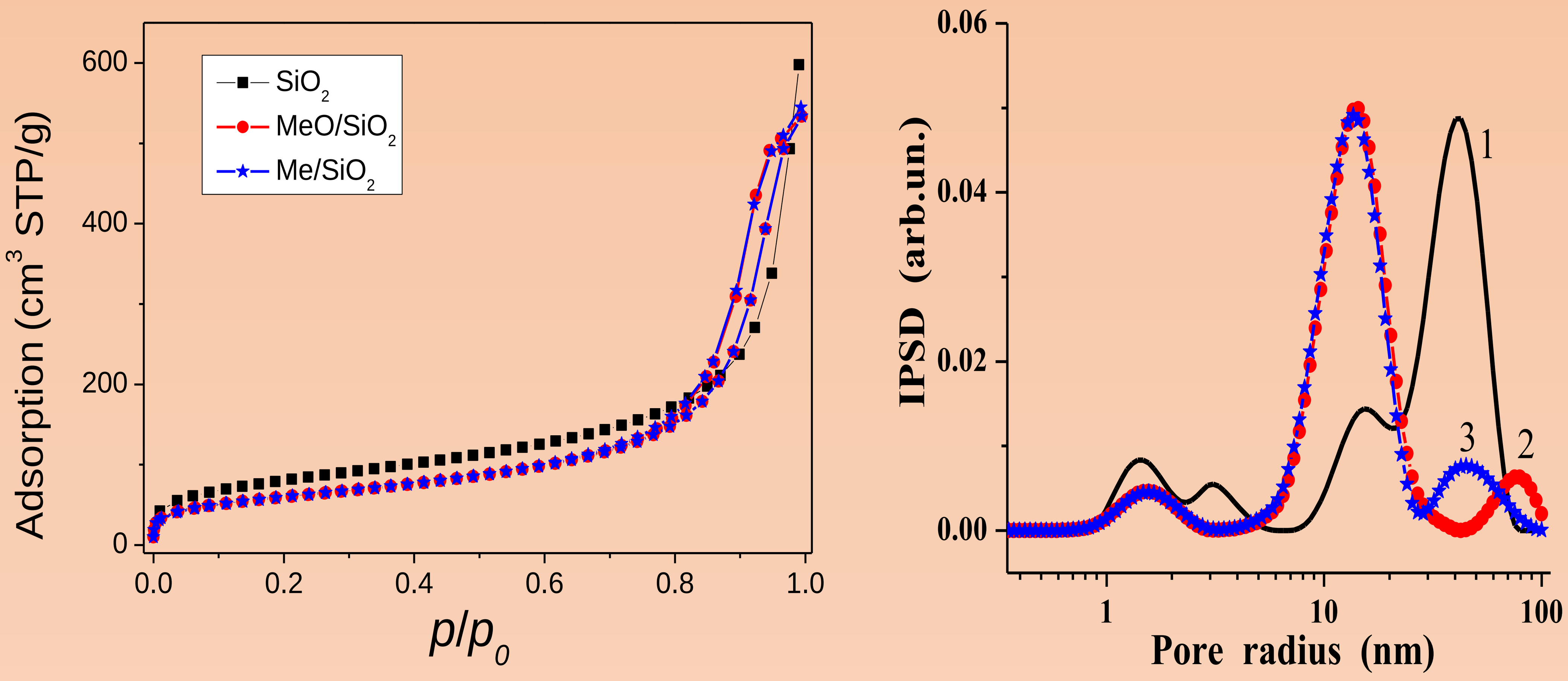
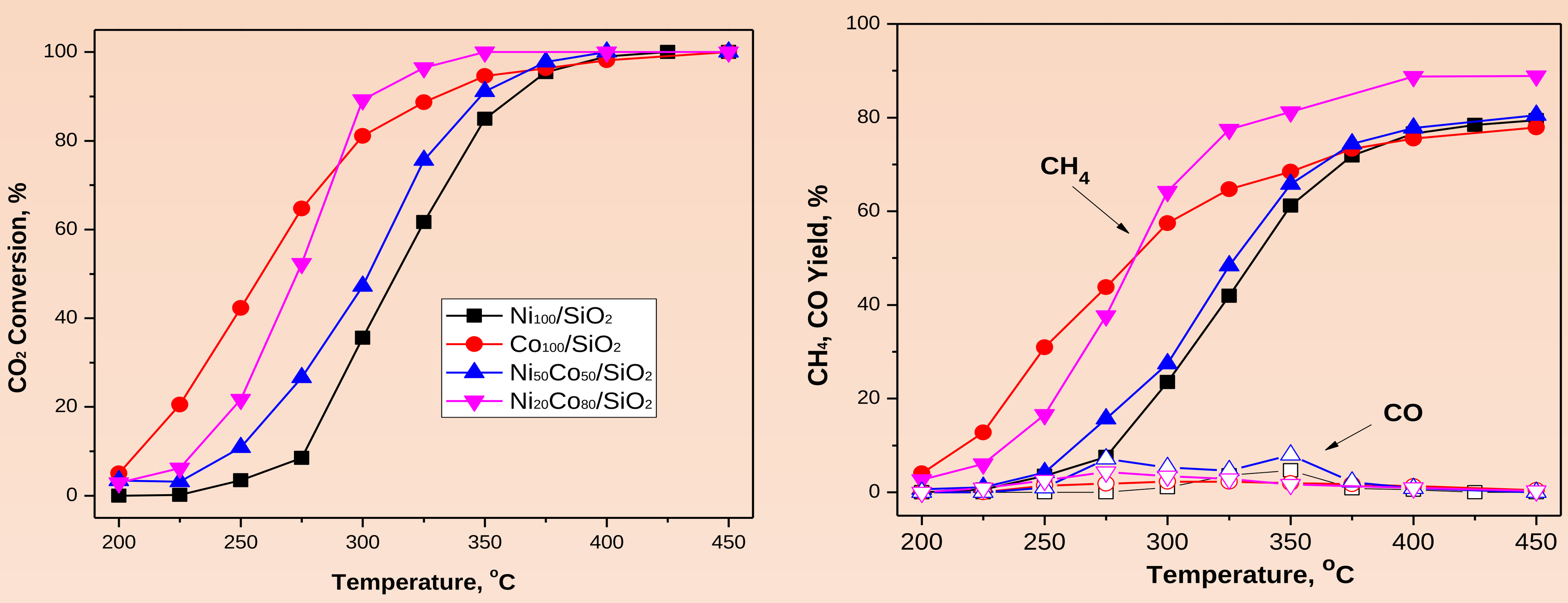


Fig. 1. Representative adsorption isotherm of nitrogen and incremental pore size distributions. In comparison, data for the nanosilica A-300 (1), the nanocomposites of MeO/SiO_2 (2) and Me/SiO_2 (3), where Me (metal) - Ni_{100}, Co_{100}, $Ni_{50}Co_{50}$, $Ni_{20}Co_{80}$, MeO – metal oxide

According to Table 1, the specific surface areas and pore volumes demonstrate a significant decrease after the formation of NiO and Co_3O_4 oxides. But, after the reduction of the respective metal oxides to metals, the composites showed a tendency to a slight increase in the specific surface area. The results of textural analysis (Fig.1) suggest preferential mesoporosity of the initial nanosilica and nanocomposites containing cobalt and nickel in the form of the metal oxides and metallic deposits



The result of catalytic test (Fig.1) showed that 100% conversion of CO_2 with CH_4 yield of about 79% can be reached over Ni_{100}/SiO_2 and Co_{100}/SiO_2 at atmospheric pressure and a reaction temperature of 450 °C. In the presence of $Ni_{50}Co_{50}/SiO_2$ and $Ni_{20}Co_{80}/SiO_2$, 100% CO_2 conversion was found at the lower reaction temperature of 400 °C. At this temperature, the yield of CH_4 is 79% and 88% for $Ni_{50}Co_{50}/SiO_2$ and $Ni_{20}Co_{80}/SiO_2$, respectively.

Fig. 2. Catalytic performance of mono- Ni_{100}/SiO_2, Co_{100}/SiO_2 and bimetallic $Ni_{100-x}Co_x/SiO_2$ under various reaction temperature.

From the data collected by the TPD MS method, we can estimate the state of reacted and adsorbed particles desorbed from the surface of the nanocomposites catalyst and to reproduce the course of elementary processes. During the TPD MS experiments, the TPD profiles of CO_2^+ (m/z 44), COH* (m/z 29), CO^+ (m/z 28), COOH* (m/z 45), and H_2O^+ (m/z 18) were registered (Fig. 2). For the CO_2 methanation on the Ni–Co/SiO_2 NC catalysts, both the nature of the metal active center and the hydrophilic surface groups of the nanosilica can play an important role. Most likely, for the Ni and Co monometallic particles and for the Ni–Co bimetallic particles that filled nanosilica, the methane formation happens directly at the metal active center with the participation of the surface silanol groups. These accessible silanol groups on the nanosilica play the role of adsorption centers for intermediate compounds in the mechanism of the methane formation. The surface silanol groups will participate in the formation of water at the recombining of oxygen and hydrogen atoms formed at the dissociation of CO_2 and H_2 on the metals.

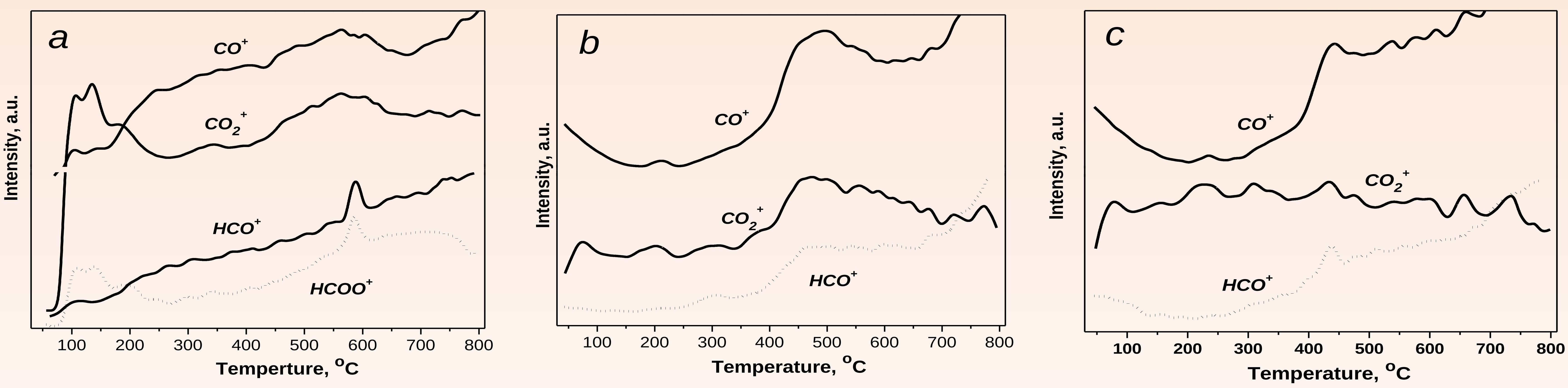


Fig. 3. TPD profiles of desorbed species from the surface of nanocomposite catalysts: **a** - Co_{100}/SiO_2, b - $Ni_{50}Co_{50}/SiO_2$ and c - $Ni_{20}Co_{80}/SiO_2$

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