Co-Ni-Fe heterometallic nanocomposites with different component ratios in the catalytic CO_2 hydrogenation

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Today, the use of renewable energies and recycling of atmospheric gas-pollutants are progressively important way for development of new nanosized materials for ecological catalysis. In this framework, applying of methanation with small CO2 sources such as biogas plants provides such possibility. This leads to new research challenges with respect to the required catalysts and the overall process design. The ternary heterometallic catalysts could be the perspective materials for this purposes.

Synthesis procedure. A number of precursors for mixed metal nanosized Co-Ni–Fe catalysts with different metal ratios were prepared by the co-precipitation method. These ratios were chosen according to the Fe-Co-Ni ternary phase diagram [1] and correspond to the heterogeneity zones. To obtain a precursor with a defined ratio of metals, a mixture of pure metal powders was dissolved in concentrated HNO_3. When the metals were completely dissolved, the resulting nitrate solution was slowly concentrated at 100°C for 4 hours until the remaining solvent evaporated. The precipitated solid was calcined in a muffle at 250°C for 4 hours to obtain a mixture of metal oxide powders. The consequence procedures of drying-calcination-reduction provide the formation of Co-Ni-Fe nanosized materials that were tested in the catalytic conversion of CO_2 to methane. The thermodesorption procedure with MS analysis of desorbed particles from the surface of catalysts was applied for the reaction mechanism estimation.

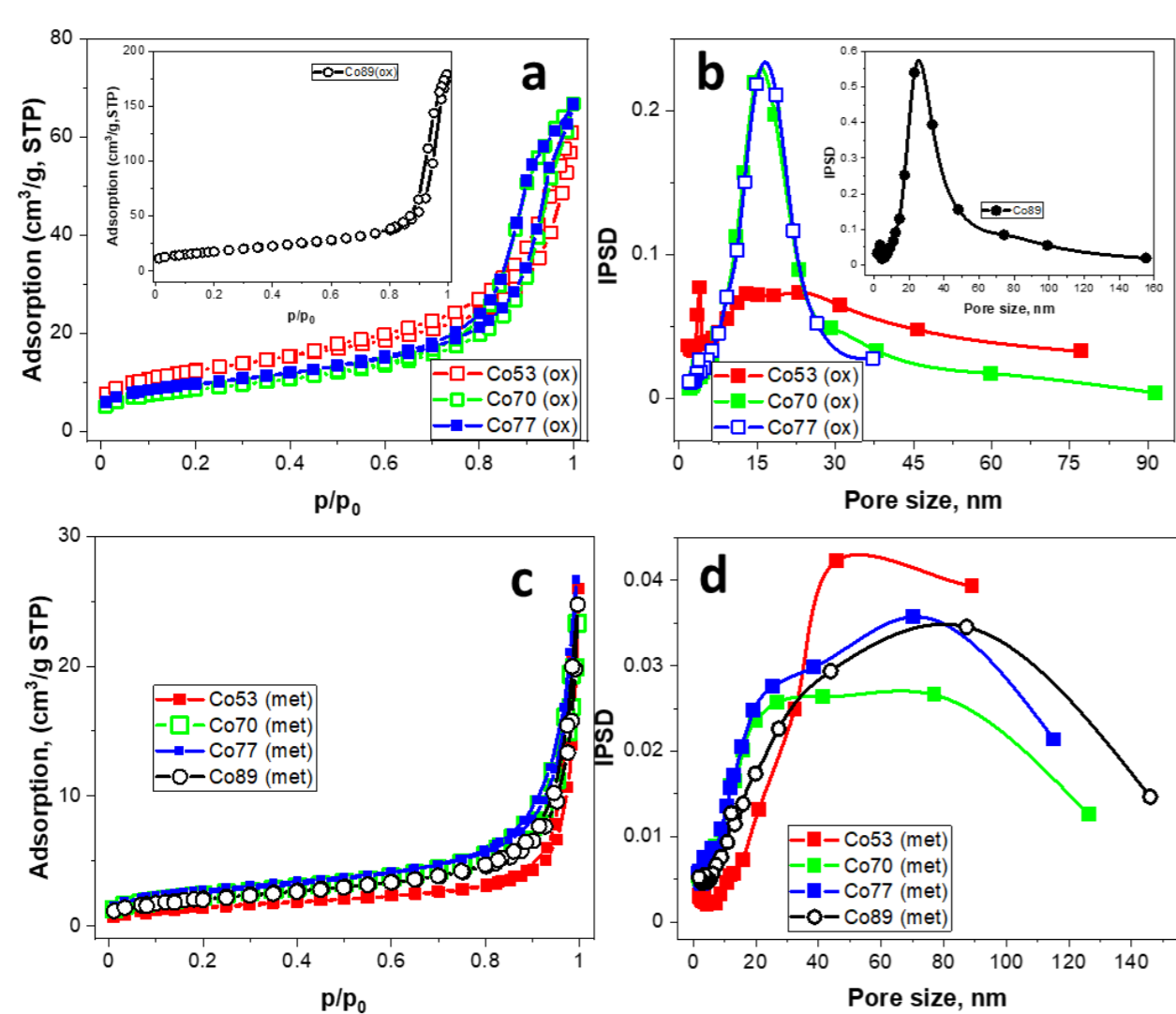## Structural and surface properties

Fig. 1. Nitrogen adsorption-desorption isotherm (a, c) and incremental pore size distribution (b, d) for the heterometallic composites in the oxide (a,b) and metallic (c, d) forms.

Sample	S_{BET}, m²/g	V_p, cm³/g	R_p, m³/g
Co53Ni37Fe9(ox)	43.2	0.097	8.3
Co53Ni37Fe9(met)	5.4	0.039	30.5
Co70Ni13Fe17(ox)	29.9	0.103	12.7
Co70Ni13Fe17(met)	8.5	0.036	16.5
Co77Ni17Fe6(ox)	33.7	0.095	11.2
Co77Ni17Fe6(met)	9.7	0.041	17.9
Co89Ni5Fe6(ox)	63.6	0.277	16.9
Co89Ni5Fe6(met)	7.6	0.038	19.4

Table 1. Textural characteristics of Co-Ni-Fe heterometallic composites in the oxide (a,b) and metallic (c, d) forms.

The results of N2 adsorption demonstrate a significant decrease in SBET value (Table 1) for metallic nanosized (NS) catalysts compared with their oxide precursors. Also, the porosity decreases as well as pore width is increased resulting in catalytic action.
SEM observation of a couple of catalysts showed a difference in surface morphology. A sponge-type surface was detected for the Co89Ni5Fe6 catalyst and more smoothed for Co77Ni17Fe6 one.
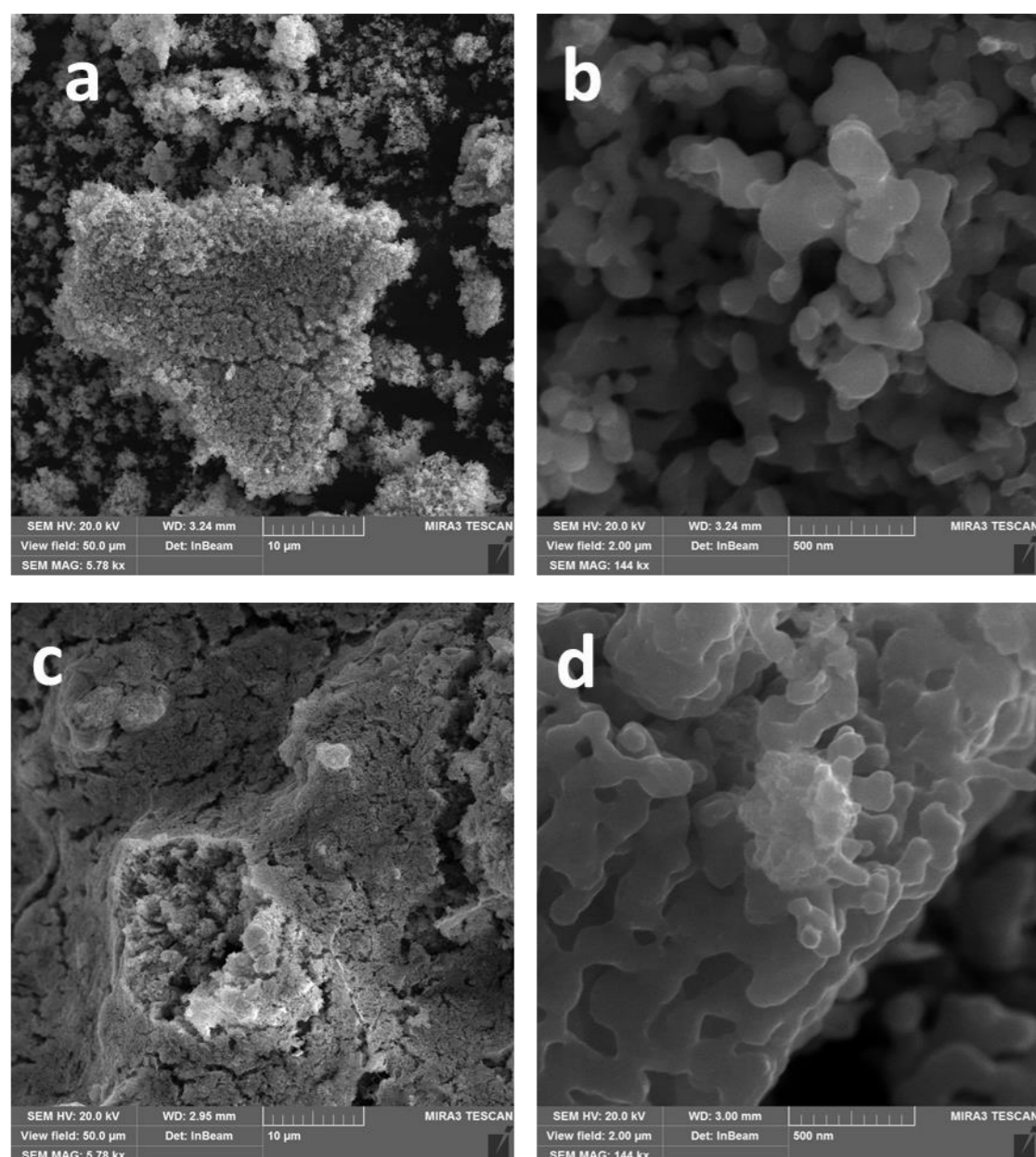

Fig. 2. SEM images of the Co89Ni5Fe6 (a,b) and Co77Ni6Ni23 (c,d) after xposured in the catalytic reaction.

Catalytic activity in the CO_2 hydrogenation
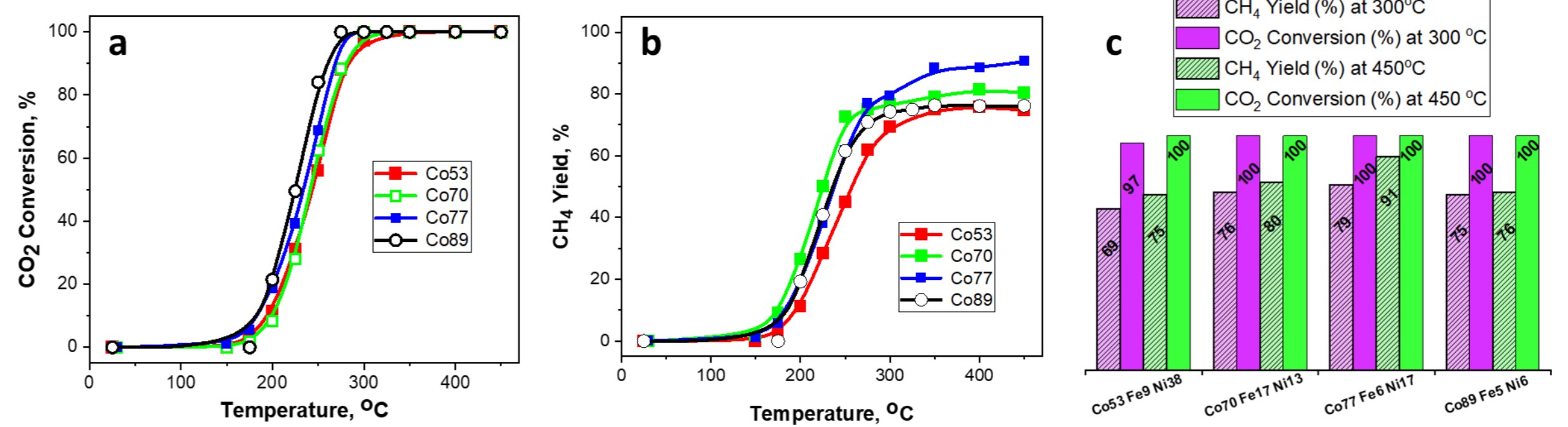

Fig. 3. GC results of the catalytic evaluation of Co-Ni-Fe bulk compounds in the reaction of CO_2 hydrogenation: CO_2 conversion and CH_4 yield as the temperature function (a, b) and sample diagram activity (c).

The catalytic behaviour of Co-Ni-Fe nanoparticles in the reaction of CO_2 hydrogenation was evaluated at the atmospheric pressure within the temperature range of 30-450 °C with GC registration of outlet gases. GC results present 100% of CO_2 conversion (Fig 3a) and 70-90% of CH_4 yield (Fig 3b) over tested catalysts. The diagram (Fig 3c) demonstrates the small increase in CH_4 yield with temperature growth. The most productive catalyst indicated is Co(77)Ni(17)Fe(06), where the numbers in the brackets correspond to the mass% of each metal.
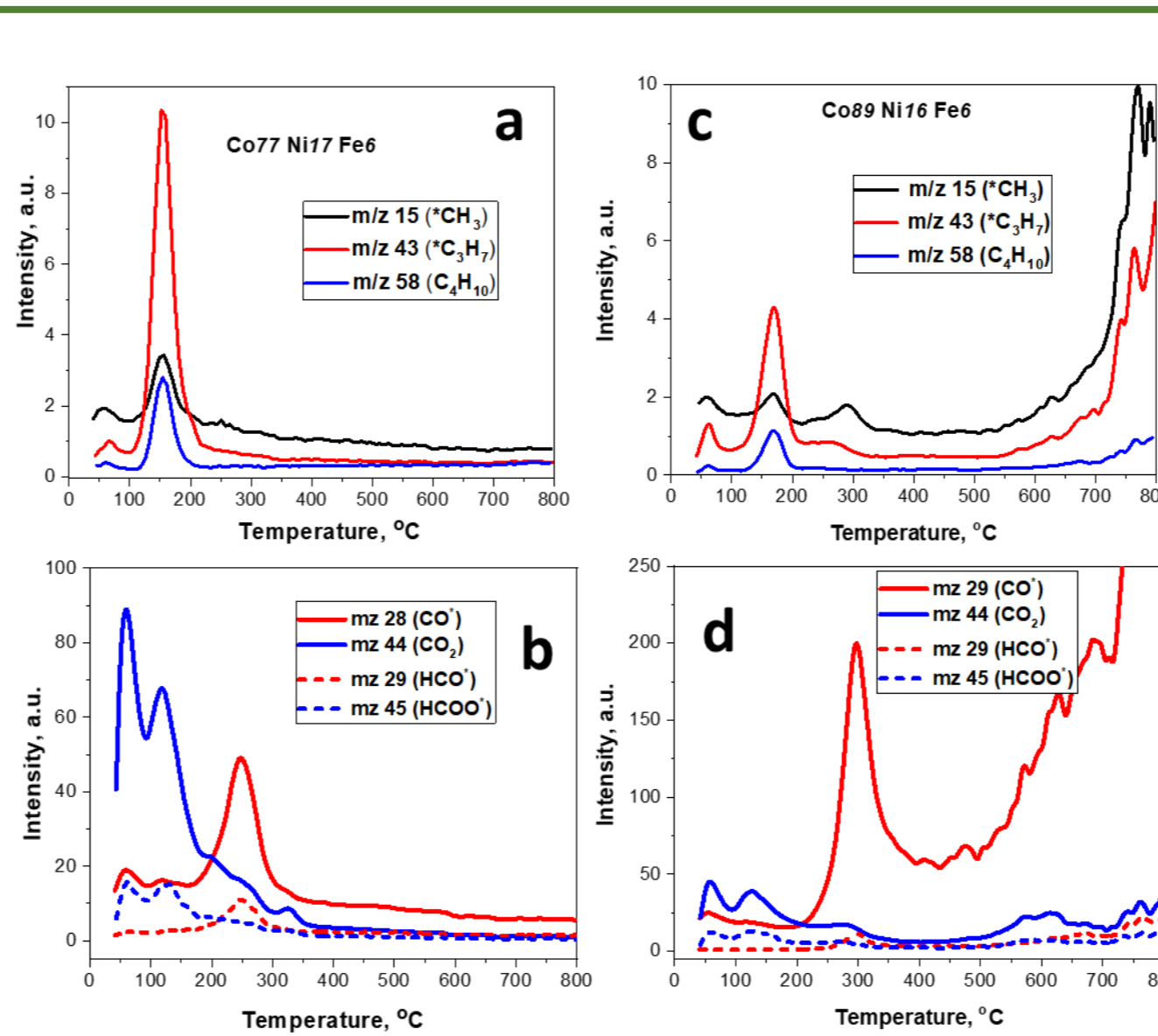

Fig. 4. TD profiles of the species desorbed from the surface of the NS catalysts Co77Ni17Fe6 (a,b) and CO89Ni16Fe6 (c,d).

The investigation of the state of the surface of Co-Ni-Fe compounds after their testing in catalytic CO2 hydrogenation was provided with the method of TPDMS. TD profiles of the species desorbed from the surface of catalysts with m/z28 (CO), and m/z44 (CO2) related with hydrogenated species with m/z 29 (HCO*) and m/z45 (HCOO*) can be offered to the process of methane formation according to the mechanism proposed in [2]. Additionally, the profiles with m/z=43 and 58 can be related to (C_3H_7*) and (C_4H_{10}) species associated with the reaction co-product butane. The observation of the TPD results demonstrates a significant difference for temperature ranges of desorbed species for catalysts Co77Ni17Fe6 and Co89Ni16Fe6 (Fig 4). The most intensive desorption pikes for Co77 are observed in the temperature range of 50-400 ºC while the intensity of TD profiles for sample Co89 is growing at the higher temperature. This indicates the species is strongly chemisorbed with the catalyst. surface

CONCLUSIONS

It was shown that the coprecipitation method using the nitrate solution of appropriate metals as the precursors can lead to te formation of ternary Co-Ni-Fe nanosized compounds that were effectively acting in the catalytc hydrogenation of CO_2. Resulting the synthesis it is possible to manage the porosity and morphology of NS heterometallic catalysts and affect the catalytic activity. The main product of CO_2 hydrogenation over presented materials is methane with a yield of 69-91% at the temperature range of 300-450 ºC. In addition, the TPDMS method allowed to the recognition of the butane formation as a co-product that was not detected by the GC apparatus.

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[2] Peter Strucks et al A short rewiev on Ni-Catalyzed methanation of CO2: reaction mechanism, catalyst deactivation, dynamic operation. *Chem. Ing. Tech.* 93 (2021) 1-12