

# Bimetallic NiFe and CoFe nanoparticles deposited on mixed fumed oxides in the reaction of CO<sub>2</sub> hydrogenation

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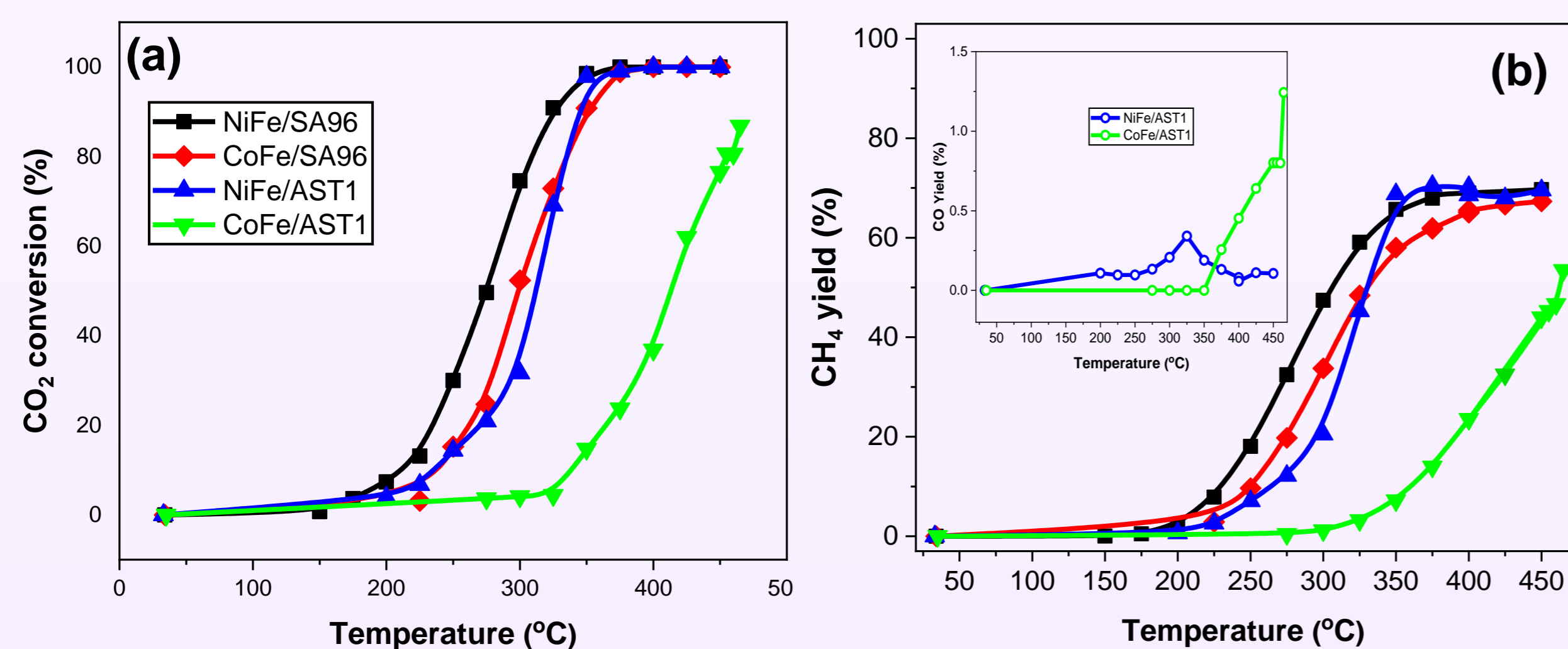
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**Introduction.** Carbon dioxide remains the main component of greenhouse gases present in the atmosphere. To date, there are two main approaches to emission reduction to capture CO<sub>2</sub> in geological formations to reduce its amount or convert CO<sub>2</sub> into low-carbon fuels: energy-to-gas (E-G) and energy-to-liquid (E-L) technology. The CO<sub>2</sub> methanation reaction has a number of advantages over other chemical processes, since CH<sub>4</sub> gas can be directly transported through existing gas pipelines, and it can also be used as a fuel or raw material for the production of various chemicals. Nanocomposites (NCs) based on silica or alumina with NiFe or CoFe bimetallic nanoparticles (NPs) are prominent CO<sub>2</sub> hydrogenation catalysts. In order to achieve a better catalytic effect, the bimetallic composition of NiFe and CoFe was deposited on the surface of mixed bi- (Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>) and ternary- (Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>/TiO<sub>2</sub>) industrial fumed oxides marked as SA96 and AST1, respectively.

**Preparation of composites.** The application of active metals to the surface of the SA96 ( $S_{\text{BET}} = 65 \text{ m}^2/\text{g}$ ) and AST1 ( $S_{\text{BET}} = 90 \text{ m}^2/\text{g}$ ) media was carried out by the method of solvation-stimulated modification of the media surface with aqueous solutions of salts followed by drying, calcination and recovery in a flow of a hydrogen-helium mixture (50 vol.% H<sub>2</sub>, 50 vol.% He) for 2 hours at atmospheric pressure and a temperature determined by according to the TGA. The amount of active mass was 11 wt.% of the mass of the carrier. The catalytic study was performed with the supply of a gas mixture of 2%CO<sub>2</sub>–55%H<sub>2</sub>–43%He and chromatography control. The crystal structure and surface porosity of the samples after the catalytic test were determined by XRD and low-temperature nitrogen absorption methods.

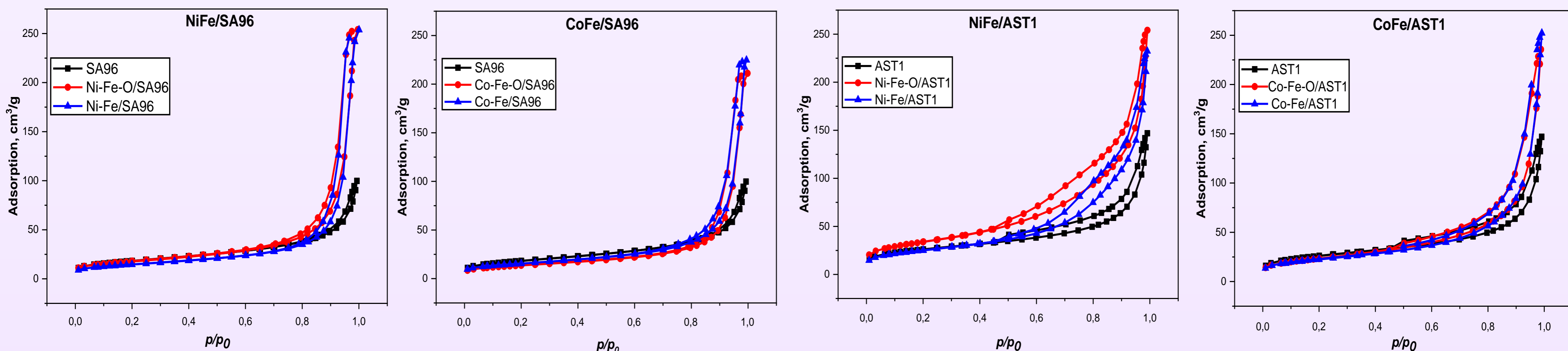
## Catalytic performance data



The catalytic experiment was carried out on a flow bed glass reactor at atmospheric pressure and a total gas flow rate of 0,1 l/min. The reaction gas mixture of CO<sub>2</sub>/H<sub>2</sub> balanced with He in a composition's ratio of 2/55/43 vol.% was applied over the studied nanocomposite catalyst within the temperature range of 25-450 °C. The structure and properties of composites in the oxide and metallic form were investigated with TG, XRD, nitrogen adsorption and TD MS methods. The results of the catalytic study showed that the application of Co-Fe and Ni-Fe active mass on the surface of fumed carrier SA96 is more promising compared to similar catalysts applied to carrier AST1 due to the absence of carbon monoxide among the reaction products.

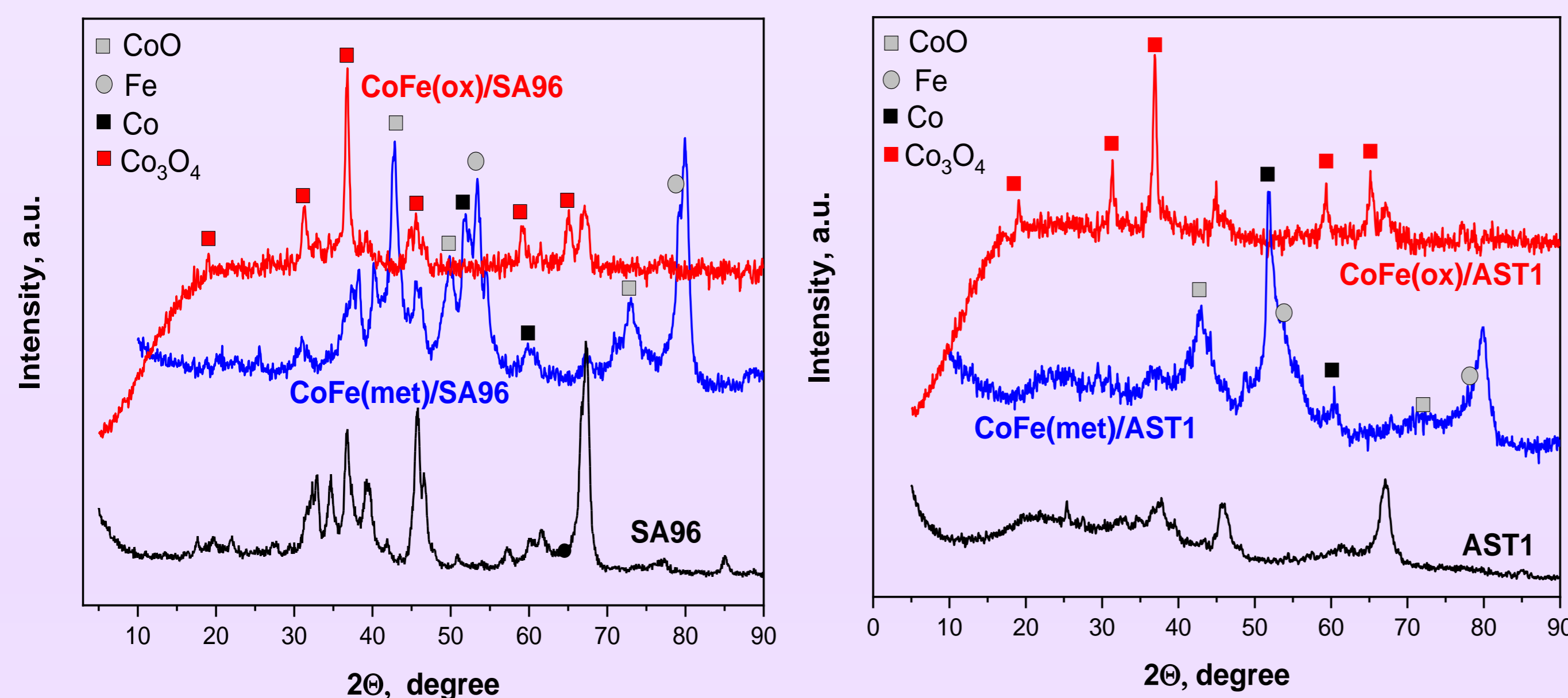
**Fig. 1.** Catalytic performance data of bimetallic nanocomposites based on synthetic fumed oxide carriers under various reaction temperature (CO yield is shown inside the figure).

## Low-temperature adsorption of nitrogen



**Fig. 2.** Nitrogen adsorption-desorption isotherms for NiFe and CoFe samples supported on SA96 and AST1.

## X-Ray diffraction



**Fig. 3.** XRD patterns of CoFe/SA96 and CoFe/AST1 samples in oxidized and reduced forms compared to the initial carriers.

## Conclusions

The obtained nitrogen adsorption-desorption isotherms for the studied catalysts have a sigmoid shape with a narrow hysteresis loop, which is characteristic of mesoporous materials. For both carriers, the application of Co/Fe active mass contributes to the increase of the adsorption capacity after recovery, while the application and recovery of Ni/Fe active mass has practically no such effect.

The method of X-ray phase analysis shows that the low degree of crystallinity of the original AST1 carrier does not contribute to the formation of the active phase of the catalyst. Both in the case of Co-Fe active mass and in the case of Ni-Fe active mass deposited on AST1, after catalysis, the diffractograms show a high content of the dominant metal oxides CoO and NiO. These factors can explain the low catalytic activity of these samples in the methanation reaction. The size of the crystallites varies between 7-34 nm.