Nanocomposites NiFe(CoFe)/Silica(Alumina) for the catalytic hydrogenation of CO_2

Dyachenko A., Ischenko O., Pryhunova O., Borysenko M., Bonarowska M.

Taras Shevchenko National University of Kyiv, 64/13 Volodymyrs'ka str., Kyiv, Ukraine, O.O. Chuiko Institute of Surface Chemistry National Academy of Science of Ukraine, 17 General Naumov Str, Kyiv, 03164, Ukraine

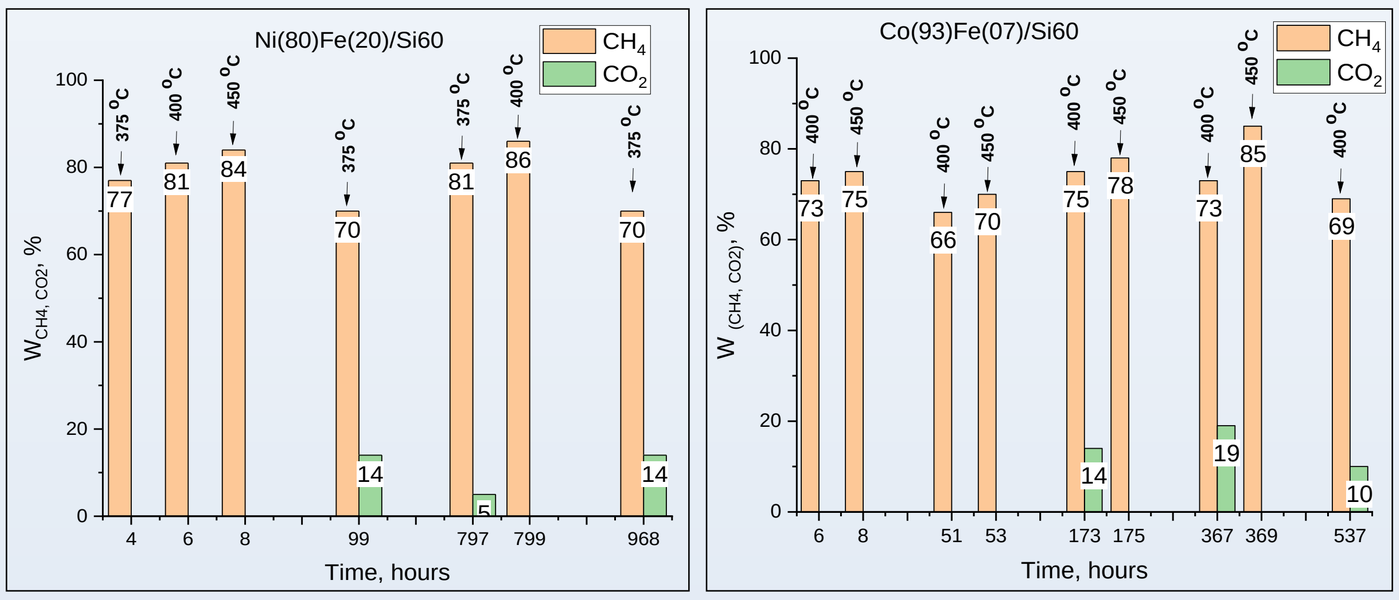
Institute of Physical Chemistry of Polish Academy of Sciences, 44/52 Kaspzaka, 01-224 Warsaw, Poland.

E-mail: dyachenko.alla@yahoo.com

Introduction. Climate change caused by global warming is one of the significant threats to civilization today. Excess greenhouse gases, 73 % of which is CO_2, cause global warming. Therefore, the conversion and use of carbon dioxide is an attractive and promising solution. The hydrogenation of CO_2 to methane has a number of advantages, as it can be directly injected into existing natural gas pipelines, as well as used as a fuel or feedstock for the production of chemicals. Among a wide range of catalysts, two-component systems based on transition d-metals occupy a special place.

Preparation of composites. Pyrogenic SiO_2 (marked Si-60) and Al_2O_3 with a specific surface area of about 80 m^2/g were used as carriers for the synthesis of applied bimetallic Ni–Fe, Co–Fe catalysts. The application of the active mass to the surface of the carrier was carried out by the method of mechanochemical treatment followed by drying, calcination, and recovery in a flow of a hydrogen-helium mixture (50 vol.% H_2, 50 vol.% He) for 2 hours at atmospheric pressure and temperature determined according to TGA data. The amount of active mass was 12 wt.% of the mass of the carrier. The long-time catalytic test was carried out with the supply of a gas mixture of 2%CO_2–55%H_2–43%He and chromatography controlled. 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 results of catalytic activity showed that all samples contribute to 100% conversion of carbon dioxide at a temperature of 350-400 °C, the maximum yield of methane is 75-84%. Carbon monoxide was not detected chromatographically. The catalytic activity of the samples was also studied over time. The long-time catalytic test demonstrates the high stability of the catalysts during 5 weeks of operation in the CO_2 methanation reaction. The catalytic reactor operated in the following mode: 8 hours of operation in the methanation process in the temperature range of 350-450 °C, then the catalyst was kept in the reaction mixture at room temperature for 1 week. This cycle was repeated 3-4 times for each catalyst. After 1-2 months of research, the yield of methane decreased by 11-15%.

Fig 1. Dependencies of changes in catalytic activity at 375-450 °C over time for samples $Ni_{80}Fe_{20}$/Si60 and $Co_{93}Fe_7$/Si60.

Low-temperature adsorption of nitrogen

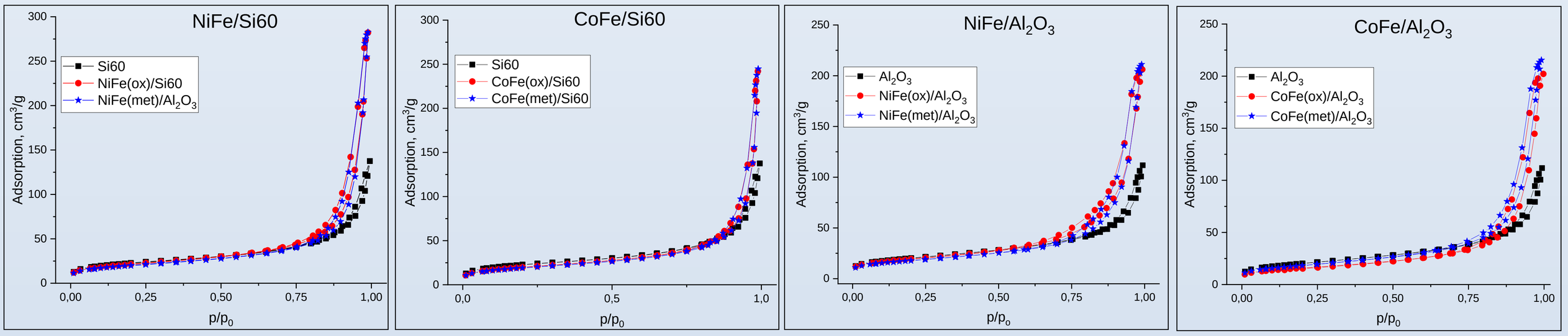


Fig. 2. Nitrogen adsorption isotherms for NiFe and CoFe samples supported on SiO_2 and Al_2O_3.

X-Ray diffraction

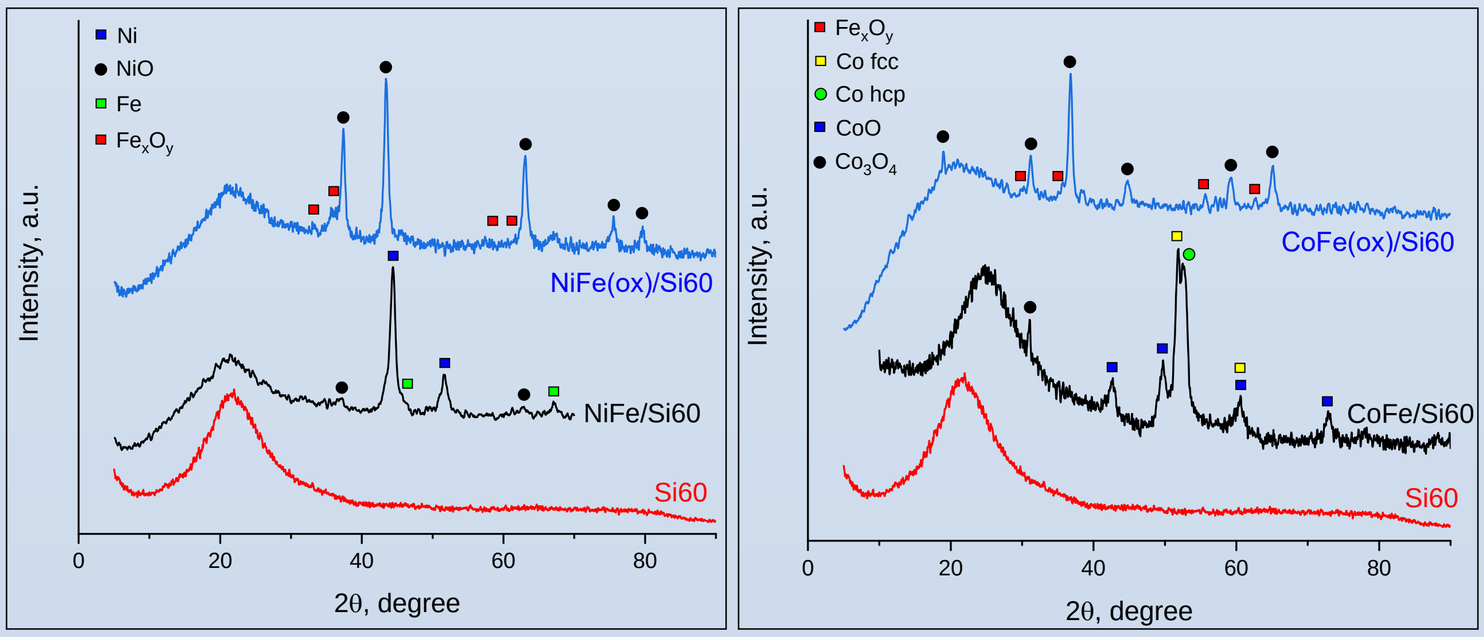


Fig.3. Diffractograms of NiFe/Si60 and CoFe/Si60 samples in oxidized and reduced forms, compared with the diffractogram of the Si60 carrier.

Conclusions

The appearance of nitrogen adsorption isotherms indicates the macroporosity of the studied samples, on the surface of which unlimited multilayer adsorption occurs. In the region of high pressures, a significant increase in adsorption is observed, which is explained by the process of adsorbate condensation.

The XRD results of the study show a wide halo in the range of 2Θ angles from 5° to 40°, which corresponds to the matrix of amorphous silica. NiO, Fe_2O_3, and Fe_3O_4 cubic syngonium oxide phases were registered for the NiFe/Si60 sample. For the sample CoFe/Si60 in the oxidized form, we observe the reflexes of the crystalline phase Co_3O_4 of cubic syngonia, as well as the phases of iron oxides Fe_2O_3 and Fe_3O_4 of cubic syngonia. CoO and Co_3O_4 phases of cubic syngonium were registered in the reduced form. Reflections from a face-centered cubic cobalt crystal (Co fcc) and reflections from a hexagonal close-packed cobalt crystal (Co hcp) were also recorded. The size of the crystallites is about 13-29 nm.