

CO₂ Hydrogenation to Renewable Methane on Mg-doped Ni-Cu and Ni-Co modified mesoporous SiO₂ prepared from rice husks

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The growing demands of modern society for an increasingly high standard of living, together with the intensive industrialization, lead to the high consumption of energy and natural resources, which in turn exacerbates environmental problems related to climate change and deterioration of atmospheric air quality, mainly due to acid and greenhouse gas emissions in the atmosphere, depletion of natural deposits of minerals and fossil fuels, disposal of waste on soil terrains, generation of polluted wastewater and infiltration of toxic components into soils and groundwater [1]. Environmental protection and climate change management set high challenges for the development of efficient low-carbon and waste-free energy technologies, while imposing the principles of a circular economy in key industrial productions. A leading concept in the transition to green energy and achieving carbon neutrality are the technologies for capturing and utilizing carbon emissions (Carbon Capture and Utilization, CCU) through their conversion into synthetic fuels (syngas), as well as obtaining fuels or precursors for their production via chemical transformation of waste biomass [2]. Reducing the energy intensity of these processes to achieve economic and technological expediency, as well as ensuring a high degree of conversion of the raw material to fuels, requires the application of catalysts.

In this study, Mg-doped bimetallic Ni-Cu and Ni-Co modified mesoporous SiO₂, obtained from rice husks, are prepared and studied in the CO₂ hydrogenation to renewable methane.

The initial mesoporous silica is prepared by citric acid treatment of rice husks followed by calcination at 500 °C without using organic template. The procedure is environmentally friendly and economically efficient. The incipient wetness impregnation technique with nickel and cobalt, or nickel and copper salts, is applied for the loading of 10 wt.% and 5 wt. % metals, respectively. Mg-doped Ni-Cu and Ni-Co modified mesoporous SiO₂ catalysts were prepared by a two-step procedure in which Mg salt is added either before or after the modification with Ni and Co/Cu. XRD patterns of the Ni/Co(Cu) bimetallic and Mg-doped Ni/Co(Cu) modified catalysts after reduction at 400°C show the formation of Ni⁰, NiO and Cu⁰ nanoparticles. The calculated parameters based on the nitrogen physisorption isotherms of the initial mesoporous silica and metal-containing varieties are presented in Table 1. The initial mesoporous silica is distinguished by a high specific surface area (364 m²/g) and a content of mesopores with a narrow size distribution and a maximum at around 3.5 nm. The impregnation procedure results in a decrease of the specific surface area of the modified mesoporous silicas, which is proportional to the amount of added metals. Most probably the deposition of metal particles in the pores is the reason for the surface area changes (Table 1). Additionally, we cannot exclude also the formation of metal oxide nanoparticles on the external surface of the silica carrier.

Table 1. Physico-chemical properties of the studied samples

Samples	Reducibility, %	BET Surface Area, (m ² /g)	Total Pore Volume, (cm ³ /g)	W _{BJH} D, (nm)
SiO ₂	-	364	0.47	3.5
10Ni5Co/SiO ₂	100	267	0.33	3.5
10Ni5Cu/SiO ₂	100	266	0.34	3.6
10Ni5Co1.5Mg/SiO ₂	80.9	216	0.29	3.6
10Ni5Cu1.5Mg/SiO ₂	87.1	213	0.30	3.5
1.5Mg10Ni5Co/SiO ₂	71.8	205	0.32	3.5
1.5Mg10Ni5Cu/SiO ₂	86.9	214	0.31	3.7

The influence of the Ni and Co/Cu content, the addition of Mg and the sequence of the Mg addition on the reduction properties of the catalysts are followed by temperature programmed reduction (TPR) analysis. TPR results show that the doping with Mg after the modification with Ni and Co leads to a stronger interaction of the metals with the support. The opposite effect of Mg doping is detected for Ni/Cu-containing catalysts. The mesoporous structure of the applied carrier influences positively the formation of finely dispersed nickel oxide and copper/cobalt oxide species in the pores of the carrier. XPS study revealed that the surface became rich in nickel for Mg-doped Ni-Co supported SiO₂ catalysts. The obtained catalysts were tested in CO₂ hydrogenation to methane. The non-doped samples show lower activity than the Mg-doped ones.

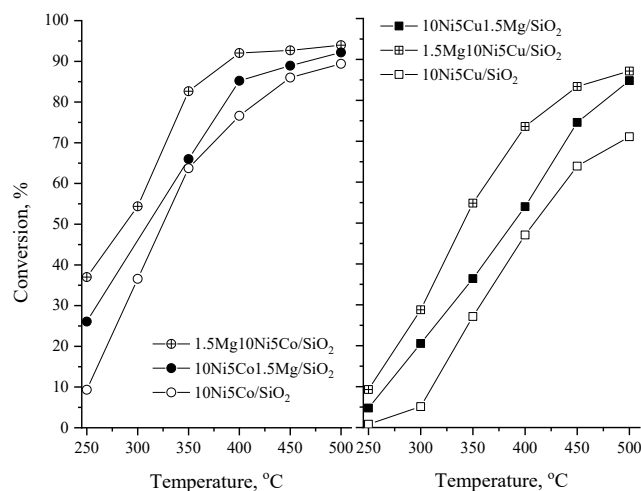


Figure 1. Catalytic activity vs. temperature for the studied catalysts ($\text{H}_2:\text{CO}_2 = 4:1$; $\text{GHSV} = 60,000 \text{ mL gc}^{-1} \text{ h}^{-1}$)

Among the studied catalysts the modification with Co as a second metal results in higher activity than with that of the catalysts containing Cu as a second metal. The use of copper as a modifier makes agglomeration of metallic nanoparticles more probable, thus decreasing the accessible number of active sites on the surface. The selectivity to methane is following the same trend as the activity, which is due to the stepwise reaction in which CO was an intermediate in the process of CH₄ formation [3]. The highest activity and high selectivity for methane formation were registered for 1.5Mg10Ni5Co/SiO₂ material, reaching the equilibrium conversion and 100% selectivity at 400 °C. Stability and re-usability of the latter catalyst in 3 reaction cycles show that it is appropriate for practical application.

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