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ABSTRACTS

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Synthesis and Study of Nickel Catalysts Based on Ordered SBA-15 Modified with CeO₂-MnO_x Binary Oxides in the DRM Process

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Recently, mesoporous nanostructured materials have been used to develop heterogeneous catalysts for application in catalytic reforming due to their high specific surface and low density [1]. Ni-based catalysts supported on mesoporous supports, such as MCM-41, SBA-15 meso-Al₂O₃ and so on, are well known for their high activity and resistance to coke formation. Interaction with the support matrix favours the stabilization of Ni metal as dispersed nanoparticles and allows to lower the amount of introduced metal. However, at elevated temperatures, Ni nanoparticles (NPs) tend to diffuse from mesoporous channels onto the outer surface of the support due to the weakening interaction of the Ni-support [2]. A possible solution to this problem is the use of modifiers oxides that enhance the Ni-support interaction. High catalytic performance can be achieved by combining Ni/SBA-15 with binary oxides of La, Ce, Mn [3].

The present work is devoted to study the interaction of the nickel nitrate precursor with the support, SBA-15 and SBA-15 modified with binary oxides of CeO₂-MnO_x at different molar ratio of Ce/Mn, and to reveal the effect of the supports and their interaction with Ni on the catalytic performances in dry reforming of methane (DRM).

Mesoporous SBA-15 with a regular pore size (4-8 nm) was prepared by template synthesis using a surfactant of PEO20PPO70PEO2 (Pluronic P123 triblock copolymer). SBA-15 surface modification with CeO₂-MnO_x/SBA-15 binary oxides was carried out by the incipient wetness impregnation using aqueous solutions of Ce(NO₃)₃*6H₂O and Mn(NO₃)₂*6H₂O with the addition of citric acid solution.

After calcination of the supports at 500 °C, Ni (10wt. %) was deposited by wetness impregnation and the resulting catalysts were calcined at 800 °C.

The physical chemical properties, the catalytic activity and the long-run stability of prepared catalysts have been evaluated in DRM reaction. The characterization of both fresh and spent catalysts was carried out using low-temperature N₂ adsorption/desorption, XRD, SAXS, TGA, H₂-TPR, Raman and TEM analyses.

After loading nickel over unmodified SBA-15 (Ni/SBA-15) a monomodal pore size distribution, with an average diameter of 5.3 nm, was found.

Based on the results of small-angle X-ray diffraction (SAXS), it was confirmed that the original structure of SBA-15 was preserved for this sample, however, the wall thickened due to the incorporation of Ni²⁺ into the SBA-15 structure. According to XRD data, the average crystal size was estimated, NiO particles of 18 nm and Ni⁰ particles of 15 nm were detected. H₂-TPR experiments

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showed that the formation of Ni NPs in an H₂/Ar flow occurs in the temperature range of 400-725°C with a reduction extent of 82%.

In the SBA-15 modified by CeO₂-MnO_x binary oxides MnO_x was well dispersed in the CeO₂ lattice with the formation of a Ce_{1-x}Mn_xO_{2-δ} solid solution, according to XRD characterization. With an increase in the molar ratio of Ce to Mn (from 0.25 to 9) and the deposition of NiO on the corresponding supports, the defects of the CeO₂ crystal lattice increased due to the incorporation of MnO_x and/or NiO into the structure (a change in the lattice parameter of d₁₁₁ (CeO₂). Moreover, the addition of MnO_x to CeO₂ has a strong effect on the NiO particles size that varies from 7.5 to 11.4 nm for the Ni/CeO₂-MnO_x/SBA-15 catalysts. TPR experiments revealed that reduction of NiO NPs interacting with CeO₂-free SBA-15 occurs between 300-400 °C, whereas NiO stabilized by Ce_{1-x}Mn_xO_{2-δ} solid solution is reduced at higher temperature, above 400 °C.

The DRM catalytic tests at gradient temperature performed between 400°C to 800 °C showed high catalytic conversion of CH₄ and CO₂ for the Ni/CeO₂-MnO_x/SBA-15 sample with a molar ratio of Ce/Mn = 9 (Fig.1 b). This catalyst also exhibits stable conversion of CH₄ and CO₂ (long run stability tests at 650 °C during 24 and 80 h, Fig.1 c). The incorporation of Mnⁿ⁺ cations into CeO₂ structure led to enhanced Ni-support interaction and increased concentration of oxygen vacancies in the support structure, thus, diminishing the content of carbonaceous deposits. According to TGA data, the sample weight loss after long run tests at 650 °C, for 24 h and 80 h, were 0 and 19 wt. %, respectively.

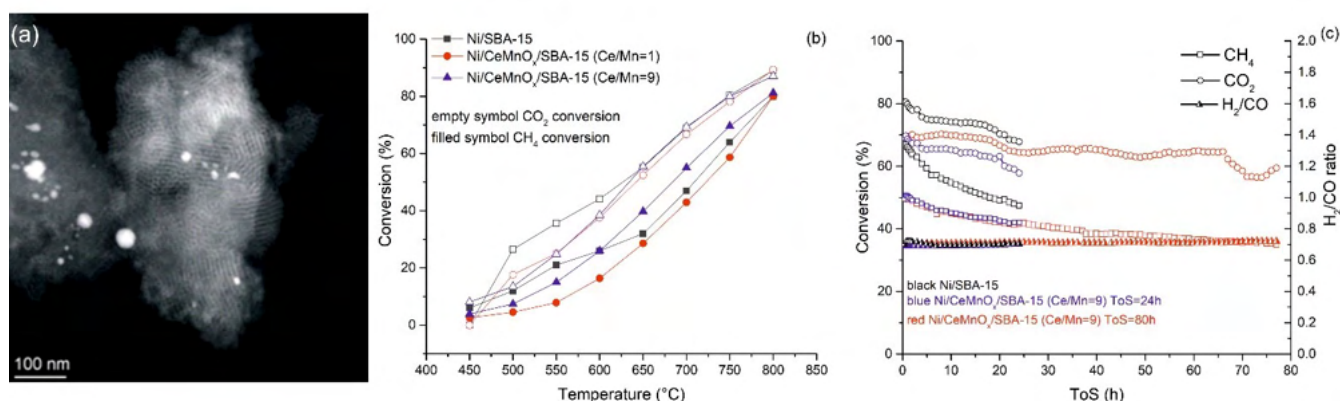


Fig. 1. TEM HR image of Ni/SBA-15 (a); temperature dependences of CH₄/CO₂ conversions (b); long run stability tests at 650 °C for Ni/SBA-15 during 24 h and for Ni/CeMnO_x/SBA-15 (Ce/Mn=9) during 24 h and 80 h (c)

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