



Porous nickel-based catalysts for combined steam and carbon dioxide reforming of methane



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ABSTRACT

X-ray diffraction, low-temperature nitrogen adsorption, and electron microscopy combined with energy dispersive X-ray microanalysis were used for studying the effect of synthesis conditions on the phase composition and texture of a porous nickel ribbon with a MgO underlayer and of nickel catalysts supported on it. The MgO underlayer was prepared by impregnation of a nickel ribbon with a Mg(NO₃)₂ solution and subsequent calcination at 550 °C in air or H₂. Catalysts were synthesized by additional supporting of nickel onto supports by its impregnation with a solution of Ni(NO₃)₂ or a mixture of solutions Ni(NO₃)₂ and Mg(NO₃)₂. In supported reduced catalysts (750–900 °C, H₂), the phase of nickel and the solid solution of NiO in MgO were observed. A considerable part of nickel crystallites was epitaxially bound with MgO. The nickel-based catalysts were tested in combined steam and carbon dioxide reforming of methane to synthesis gas (750 °C, CH₄/CO₂/H₂O/N₂ = 35/23/39/3, GHSV = 62.5 L/g h). The catalysts with the MgO underlayer completely covering the nickel ribbon showed stable activity throughout the test period (18 h). After the reaction, in these catalysts on the large crystallites of nickel ribbon, dispersed nickel crystallites (5–10 nm) epitaxially bound with MgO appeared; no carbon deposits were found in them. The resistance of these catalysts to carbonization was attributed both to the formation of nickel crystallites epitaxially bound with MgO and to the formation of the MgO underlayer that covers the nickel ribbon and prevents its contact with the reaction medium.

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1. Introduction

Currently, combined steam and carbon dioxide reforming (SCDR) of methane to synthesis gas attracts much attention. In comparison with dry reforming of methane, the use of steam in the feed for CO₂-reforming reduces the formation of carbon [1–3]. By changing the H₂O/CO₂ ratio in the reaction feed, the H₂/CO product ratio can be controlled [1–3], and this makes it possible to produce synthesis gas with the H₂/CO ratio of about 2, which is suitable for the methanol and Fisher–Tropsch syntheses [4]. The SCDR of methane enables the production of synthesis gas from such renewable energy sources as biogas, whose main components are methane, carbon dioxide and water.

Analysis of published data shows that the main direction of development of catalysts for SCDR of methane is associated with supported nickel catalysts. Nickel catalysts are active and selective in this process and are less expensive than catalysts containing platinum group metals. The characteristic drawback of nickel catalysts is their carbonization, which leads to a decrease in their activity [1,3,5–9].

The carbonization of nickel catalysts can be diminished by the addition of promoters, such as calcium oxide [1,6,7,9], magnesium oxide [3,5,7], oxides of rare earth elements [7], and by optimization of synthesis methods [10].

The implementation of the endothermic reactions of SCDR of methane requires an intensive heat transfer from an external source into the reaction zone and the equalization of the temperature inside the catalyst bed. It means that the catalysts for these reactions must have high thermal conductivity, which can be imparted by the use of metallic supports [11,12]. A number of catalysts on such supports were tested in the steam reforming of methane: nickel composite catalyst reinforced with a stainless steel gauze [13,14], a nickel catalyst supported onto an oxide underlayer deposited on porous nickel [15], a composite nickel catalyst obtained by the capsulation of lanthanum nickelate particles in metal-ceramics [16], a nickel catalyst supported on a porous nickel plate with an underlayer of MgO [17].

According to the literature available, the use of MgO as an underlayer for the nickel catalysts is very promising: it has high thermal stability, reduces carbonization because of basic properties, and it easily forms solid solutions with NiO owing to the similarity of the structural parameters, which facilitates the formation of dispersed crystallites of reduced nickel [4,18]. A number of supported nickel catalysts with a MgO underlayer have been studied: nickel catalysts

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supported on metal foams [19], porous nickel plate [17], α - Al_2O_3 [5], and Al_2O_3 - SiO_2 [7,8].

In this paper, we reported some aspects of formation of nickel catalysts supported on a porous nickel ribbon with a MgO underlayer and the catalytic properties of obtained catalysts in the SCDR of methane to synthesis gas. The use of a catalyst support in the form of a porous nickel ribbon [20] allowed us to impart the high thermal conductivity and mechanical strength to the nickel catalysts and to produce structured catalysts.

2. Experimental

2.1. Catalyst preparation

Nickel catalysts were prepared on a 0.1 mm thick porous nickel ribbon (pNirb) obtained by rolling of a nickel powder followed by calcination at 1200 °C in a H_2 flow [21]. The ribbon nickel support had a specific surface area of 0.15 m^2/g and the total pore volume of ca. 0.1 cm^3/g . The MgO underlayer (6 wt.%) was prepared by impregnating the support with a $\text{Mg}(\text{NO}_3)_2$ solution followed by drying and then by calcination at 550 °C under air (support I) or in flowing H_2 (support II). The decomposition of $\text{Mg}(\text{NO}_3)_2$ in air is a usual method for the preparation of MgO support [5,8,19,22], but in the case of a nickel support, it can lead to loosening of the nickel surface [23,24]. Therefore, to reduce the loosening of the nickel ribbon surface, decomposition of $\text{Mg}(\text{NO}_3)_2$ in the case of support II was carried out in a H_2 flow. Catalysts I were prepared by supporting of nickel on support I via its impregnation with a $\text{Ni}(\text{NO}_3)_2$ solution. Catalysts II were prepared on support II via its impregnation with a mixture of $\text{Ni}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ solutions. After impregnation, all the catalysts were dried and then calcined at 450 °C in a N_2 flow. The prepared catalysts were reduced in flowing H_2 at 750 °C (catalysts I) or at 900 °C (catalysts II). The content of supported nickel in the reduced catalysts was 1–5 wt.%; the content of MgO in catalysts II was 7–10 wt.%.

2.2. Characterization

The specific surface area and the pore radius distribution were determined by low-temperature nitrogen adsorption at 77 K using an ASAP-2400 (Micromeritics, USA) precision instrument. The error of the evaluation of the specific surface area did not exceed 5 rel.%. For some samples, the total pore volume and the pore radius distribution were determined using mercury porosimetry. Particle morphology was examined by scanning electron microscopy (SEM) and by transition electron microscopy (TEM) with the respective use of JSM-6460LV and JEM-2010 (JEOL Co., Japan) instruments with a lattice resolution of 0.14 nm. The energy dispersive X-ray microanalysis (EDX) of some samples was performed using an EDAX energy dispersive spectrometer with a Si(Li) detector with an energy resolution of 130 eV. Crystal faces were indexed by high resolution TEM (HRTEM) of lattice fringe images. Phase analysis was carried out using X-ray diffraction patterns taken with an ARLXTRACT (Thermo, Switzerland) instrument (monochromatized $\text{Cu K}\alpha$ radiation).

2.3. Catalytic activity

Catalyst activity in the SCDR of methane was evaluated by the flow method under atmospheric pressure at 750 °C using a conventional continuous flow quartz reactor with an inner diameter of 14 mm. The initial reaction mixture comprised of 35 vol.% of methane, 23 vol.% of CO_2 , 39 vol.% of H_2O , and 3 vol.% of N_2 . According to [1–3], such feed composition allows a production of synthesis gas with the H_2/CO ratio of about 2. The feed rate of the initial mixture was 25.0 L/h. For the catalytic activity measurements, ribbon

Table 1
Unit cell parameters of oxide phases in the samples.

Catalyst	a_{MgO} (Å)	$a_{\text{Ni}_x\text{Mg}_{1-x}\text{O}^a}$ (Å)	a_{NiO} (Å)
pNirb + 6.0% MgO (I)	4.215	–	4.178
pNirb + 6.0% MgO (II)	4.219	–	–
3.0% Ni/(pNirb + 6.0% MgO)(I)	–	4.207	–
4.6% Ni/(pNirb + 6.0% MgO)(I)	–	4.205	–
1.0% Ni/(pNirb + 6.7% MgO)(II)	–	4.210	–
2.7% Ni/(pNirb + 8.6% MgO)(II)	–	4.208	–
4.0% Ni/(pNirb + 10.4% MgO)(II)	–	4.208	–
MgO	4.211 ^b	–	–
NiO	–	–	4.177 ^c

^a $\text{Ni}_x\text{Mg}_{1-x}\text{O}$ – assumed solid solution of NiO in MgO.

^b According to Ref. [26].

^c According to Ref. [27].

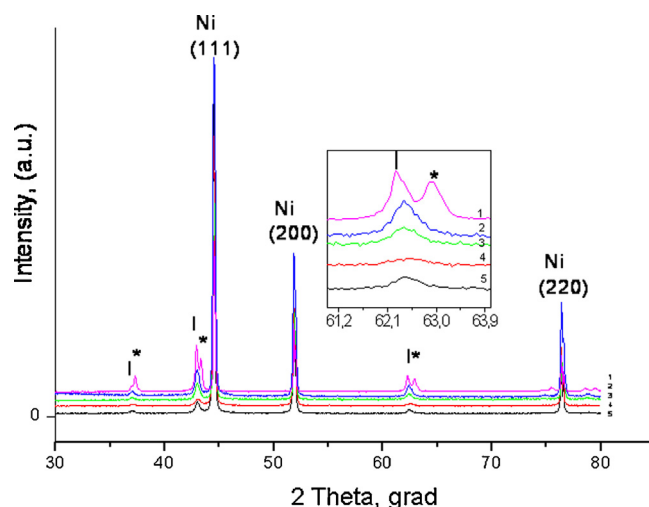


Fig. 1. XRD pattern of samples: 1 – pNirb+6.0% MgO (I), 550 °C, air; 2 – 4.0% Ni/(pNirb + 10.4% MgO) (II), 900 °C, H_2 ; 3 – 2.7%Ni/(pNirb + 8.6% MgO) (II), 900 °C, H_2 ; 4 – 3.0% Ni/(pNirb + 6.0% MgO) (I), 750 °C, H_2 ; 5 – 4.6% Ni/(pNirb + 6.0% MgO) (I), 750 °C, H_2 . The insert – fragment of XRD patterns of samples. Denoted as (I) and (*) location of diffraction peaks of MgO and NiO, respectively.

catalysts were cut to pieces (1.5 mm \times 1.5 mm \times 0.1 mm). Catalyst samples weighing 0.40 g were used in the tests. A commercial catalyst for steam reforming of methane NIAP-18 (10.5 wt.% Ni/ Al_2O_3) [25] was used for the comparison. The catalyst sample weighing 0.40 g was tested in the form of a 0.25–0.50 mm fraction. Before the activity measurements, the samples were reduced at 750 °C in flowing H_2 . Then the reaction mixture was substituted for hydrogen and measurements were taken after keeping the catalysts in the reaction mixture for 1 h. The catalyst bed temperature was controlled with a thermocouple mounted in the reactor at the level with the catalyst bed. The temperature evaluation error was ± 2 °C. The composition of reaction mixtures was analyzed chromatographically with an error less than 10%.

Catalytic activity measurements in the empty reactor showed that the methane conversion in this case was less than 1%.

3. Results and discussion

3.1. Phase composition and texture of initial catalysts

X-ray diffraction data showed that the metallic support contains only the nickel phase, whereas support I additionally contains phases of NiO and MgO with the unit cell parameter $a = 4.215$ Å (Table 1). Diffraction peaks of the oxide phases are very weak compared with the diffraction peaks of nickel (Fig. 1). In addition,

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