

Carbon Dioxide Reforming of Methane over Co-Ni Catalysts

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Low-percentage catalysts for dry reforming of methane (DRM) with Ni and Co deposited on a glass fiber support by the “solution combustion” (SC) method have been developed. Particle size and state of the active component were studied by XRD, TPR, TEM, SEM and AFM. The active component was shown to be dispersed in the near-surface layer of support as nanoparticles of size 10–20 nm, which have a Co₃O₄ or (Co,Ni)Co₂O₄ spinel structure depending on the catalyst composition. Spinel structure of the active component is resistant to carbonization and provides high catalytic activity toward DRM.

1. Introduction

In recent years, much attention has been given to the problem of uncontrollable CO₂ emission to the atmosphere upon combustion of fossil hydrocarbons, which causes the so-called “greenhouse effect” (Ross, 2005; Ismagilov et al., 2010). Main components of a greenhouse gas are water vapor, CO₂, CH₄ and O₃ (Intergovernmental Panel on Climate Change, 2001). Utilization of CO₂ and CH₄ is of great interest because these substances can be used as reactants for dry reforming of methane to yield hydrogen or synthesis gas (Ma and Trimm, 1996; Liu et al., 2000; Ismagilov et al., 2007 a), which are a valuable feedstock for the production of ultraclean fuels (Dry and Hoogendoorn, 1981). Rostrup-Nielsen (1993) reported most of the catalysts for DRM process to consist of Ni, Co and noble metals deposited on the oxide supports. The problem of carbon deposition due to side reactions of CH₄ decomposition and CO disproportionation (Boudouard reaction) (Ismagilov et al., 2007 b; Fan et al., 2009) stimulates a search for new catalytic systems and alternative methods of their synthesis. The aim of this work was to develop the low-percentage catalysts with Ni and Co oxides deposited on a glass fiber support by the “solution combustion” (SC) method (Mukasyan and Dinka, 2007) and to reveal the effect of active components nanostructure on their activity in the DRM reaction.

2. Experimental

2.1 Catalyst synthesis

The catalysts were synthesized by impregnating the KS-11-LA glass fabric with aqueous solutions of cobalt and nickel nitrates doped with glycine (to initiate the SC reaction) at a molar ratio of MeO/glycine = 1/4. Then the impregnated glass fabric was dried under a lamp at 100 °C and calcined at 400 °C. Thus, three series of catalysts were synthesized: *C1* – containing 0.2 to 1.5 wt.% CoO, *C2* – containing 0.5 to 1.5 wt.% CoO + NiO at a ratio of CoO/NiO = 50/50, and *C3* – with 1.2 wt.% CoO + NiO at CoO/NiO ratios of 70/30, 60/40, 30/70 and 0/100. In the text, samples are designated as C_n-x-y/z, where C_n is a catalyst series, x is a MeO content, and y/z is a CoO/NiO ratio.

2.2 Study of catalytic activity

The catalytic activity in the DRM process was examined using a vertical quartz flow reactor with the inner diameter of 10 mm under the following conditions: CH₄, 50%; CO₂, 50%; temperature, 600-800 °C; flow rate, 60 cm³/min; gas hourly space velocity, 1440 h⁻¹; and time of activity measurement, 5 h.

2.3 Physicochemical examination of samples

Specific surface area (S_{sp} , m²/g) of the samples was determined by the BET method on a SORBI N4.1 instrument. X-ray phase analysis was performed using an HZG-4 diffractometer with CoK_α radiation in 2θ angle range of 20-80° at a scanning rate 1 deg/min.

The particle size and state of the active components were estimated by HRTEM using a JEM 2010 (JEOL, Japan) microscope with the lattice resolution 0.14 nm connected to a Phoenix EDAX spectrometer for microanalysis. An additional assessment of catalyst dispersity was made by AFM using a SolverP47Bio instrument. The catalyst morphology was examined by SEM on a JSM 6460LV (JEOL, Japan) microscope. The H₂-TPR studies of the catalysts pretreated in situ in O₂ or Ar at 400°C were carried out with 10 % H₂/Ar mixture, feed rate 30 cm³/min, heating at a rate of 10°C/min from 30 to 800 °C. Carbon content was determined using an Elementar Vario EL Cube analyzer.

3. Results and Discussion

3.1 Physicochemical properties of catalysts

Specific surface area of the tested samples is near 1.0 m²/g, which is close to geometrical surface of the glass fiber catalyst support.

Diffraction pattern of the catalysts is represented by the X-ray amorphous phase of support and spinel phases of the Co₃O₄ for series *C1* catalysts (Fig. 1, curve 1) and (Co,Ni)Co₂O₄ for series *C2*. For series *C3* catalysts, as the NiO concentration increases above 50%, along with the spinel phase there appears a NiO phase (Fig. 1, curve 2), which is a single phase in the sample C3-1.2-0/100. Particle size of the active components for all catalysts, as determined from the coherent scattering region and calculated by the Scherrer formula, is 20 nm.

As shown by SEM, the catalysts are represented by filaments 7-8 μm in diameter. Particles of the active component cannot be visualized by this method; however, EDX spectra of various parts of the catalyst have the lines of Co and/or Ni. The atomic content of the detected elements corresponds to the introduced amount.

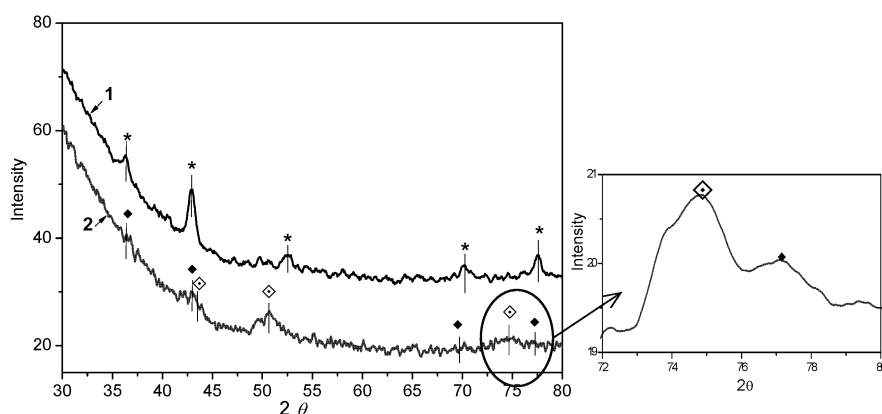


Figure 1: XRD pattern of the catalysts: 1 – C1-1.0-100/0 (* – Co_3O_4); 2 – C3-1.2-30/70 (◇ – NiO , ◆ – $(\text{Ni,Co})\text{Co}_2\text{O}_4$).

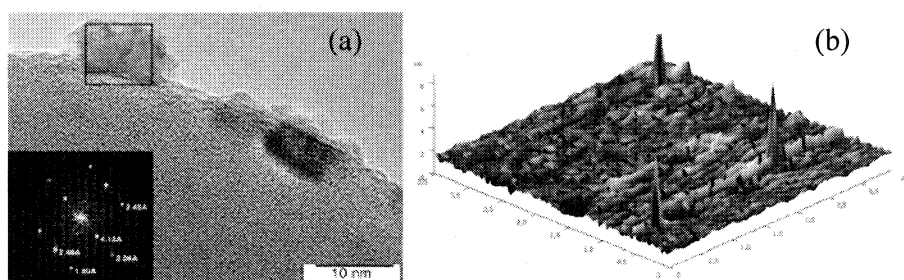


Figure 2: HRTEM (a) and AFM (b) images of catalyst C3-1.2-60/40.

According to TEM, irrespective of the catalyst composition, the active component forms as particles of size 10-20 nm (mainly 10 nm). One may see from Fig. 2a that particles of the active component in catalyst C3-1.2-60/40 have the size of *ca.* 10 nm, are distributed separately from one another and fixed in the near-surface layer of glass fiber. The observable interplanar distances are close to those of NiCo_2O_4 : (111) 4.6846Å, (222) 2.3423Å, (311) 2.4465Å, and (331) 1.8615Å (JCPDS diffraction data, PDF # 73-1702). As shown by EDX analysis, a particle contains virtually equimolar amounts of Ni and Co. Note that the particles are strongly retained on the support surface. In a special experiment with pronounced mechanical effect followed by ultrasonic treatment, we managed to detach some particles from the support. An AFM image (3D view) of these 8 nm particles is presented in Fig. 2b.

The H_2 -TPR analysis of catalysts pretreated in Ar and having different CoO/NiO ratio of active component, 100% CoO (C1-1.2-100/0), 100% NiO (C3-1.2-0/100), and 50%CoO/50%NiO (C2-1.2-50/50), (Fig. 3a) revealed that the temperature of H_2 consumption maximum increases in the following order: $\text{NiO} < \text{NiO/CoO} < \text{CoO}$. The catalysts containing spinel phase are reduced by two-step scheme $(\text{Co,Ni})\text{Co}_2\text{O}_4 \rightarrow$

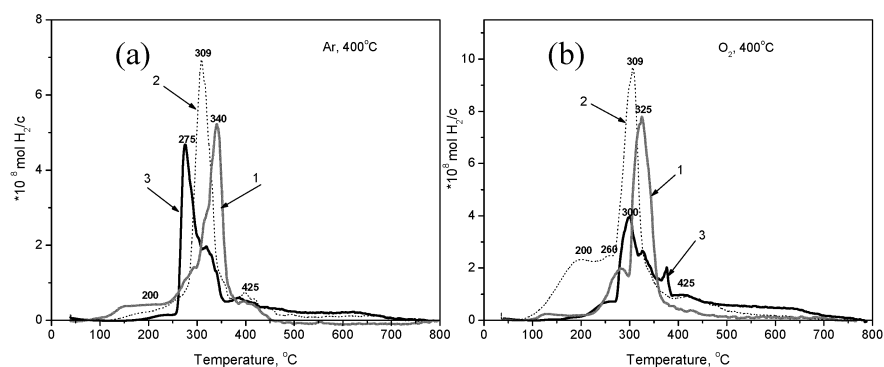


Figure 3: TPR curves for the catalysts: 1 – C1-1.2-100/0, 2 – C2-1.2-50/50, and 3 – C3-1.2-0/100 after pretreatment at 400 °C in Ar (a) and O₂ (b).



Upon treatment in an oxygen medium (Fig. 3b), this trend persists; however, the H₂ consumption maximum for nickel catalysts shifts by 25 °C to a high-temperature region, probably due to interaction with support in the oxidative atmosphere. It agrees with lower value of the experimental H₂ consumption than one of required for NiO reduction to Ni. Meanwhile, the cobalt catalysts oxidized to Co₂O₃ are reduced at a 25 °C lower temperature as compared to the Ar-pretreated catalysts containing Co₃O₄ spinel. The presence of several TPR peaks for these catalysts (Fig. 3b, curves 1, 2) indicates the three-step reduction by a scheme Co₂O₃ → Co₃O₄ → CoO → Co, the NiO phase reduced together with CoO (Fig.3, curve 2).

3.2 Catalytic activity of samples in the DRM reaction

A study of series *C1* catalysts in the DRM reaction revealed a dependence of their catalytic activity on the concentration of active components. As seen from Fig. 4, the conversion of initial reactants (Fig. 4a) and the yield of H₂ and CO (Fig. 4b) increase with increasing the content of Co oxides in the catalysts.

For catalysts of series *C2*, a direct dependence of activity on the total concentration of Ni and Co oxides is not observed. In this series, a maximum activity was shown by catalyst C2-0.8-50/50 (Fig. 5a, 5b).

Catalysts of series *C3*, which comprise not only the spinel phase, but also NiO with the concentration higher than 50%, are more active at low temperatures as compared to catalysts of series *C1* and *C2*. As the reaction temperature is raised to 700-800°C, conversion of initial reactants attains 80%, but the yield of target products does not exceed 35-40%, due to side reactions and formation of carbon.

After the DRM reaction, carbon content of the catalyst samples was measured. It was found that samples of series *C1* and *C2* have no more than 0.13-0.20 wt.% of carbon, which corresponds to its content in the initial catalysts before the reaction. In catalysts of series *C3*, the amount of carbon deposits on the catalyst surface increases from 0.5 to 5.7 wt.% as the concentration of NiO in the samples grows from 60 to 100%.

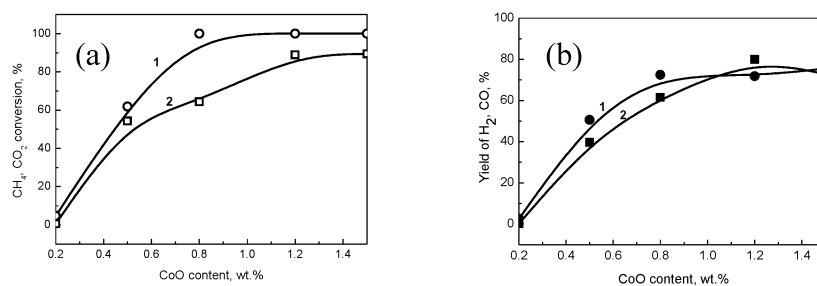


Figure 4: Conversion (a) of CO₂ (1) and methane (2); yield of the reaction products (b) CO (1) and H₂ (2) versus the concentration of Co oxides in the catalysts of series C1.

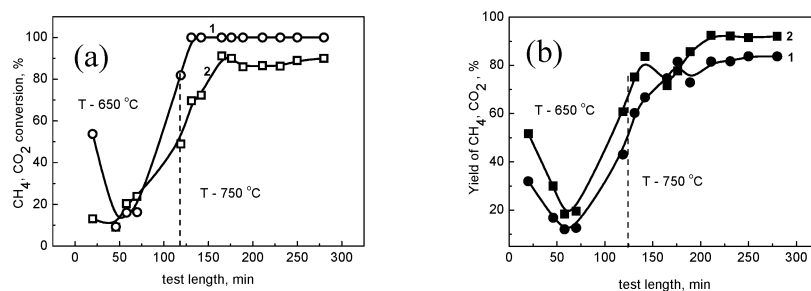


Figure 5: Conversion (a) of CO₂ (1) and methane (2); yield of the reaction products (b) CO (1) and H₂ (2) versus time on stream at 650-750°C on catalyst C2-0.8- 50/50.

A comparison of the obtained results with the literature data demonstrates that activity of the developed catalysts based on Co oxides or mixed Co and Ni oxides with the total content of active component not higher than 1.5 wt.% is comparable with the activity of CoO_x/MgO catalysts, which contain 12-30 wt.% of cobalt oxides (Ruckenstein and Wang, 2000; Choudhary et al., 2006).

4. Conclusion

Glass fiber catalysts based on Ni and Co oxides with the total content of oxides not exceeding 1.5 wt.% for the reaction of carbon dioxide reforming of methane have been developed. The catalysts were synthesized by the “solution combustion” method providing a uniform distribution of the active component in the near-surface layer of support as individual nanoparticles of size 10-20 nm. Depending on the composition of supported catalysts, the active component forms as Co₃O₄ and (Co,Ni)Co₂O₄ spinels or as NiO. It was shown that spinel structure of the active component prevents the formation of carbon deposits and provides high activity of the catalysts in the DRM reaction.

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