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YOUNG SCIENTISTS' SCHOOL

Selective Methanation of CO in the Presence of CO_2 in Hydrogen-Containing Mixtures on Nickel Catalysts

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Abstract—The screening of commercial nickel catalysts for methanation and a series of nickel catalysts supported on CeO_2, γ-Al_2O_3, and ZrO_2 in the reaction of selective CO methanation in the presence of CO_2 in hydrogen-containing mixtures (1.5 vol % CO, 20 vol % CO_2, 10 vol % H_2O, and the balance H_2) was performed at the flow rate WHSV = 26000 cm^3 (g Cat)$^{-1}$ h^{-1}. It was found that commercial catalytic systems like NKM-2A and NKM-4A (NIAP-07-02) were insufficiently effective for the selective removal of CO to a level of <100 ppm. The most promising catalyst is 2 wt % Ni/CeO_2. This catalyst decreased the concentration of CO from 1.5 vol % to 100 ppm in the presence of 20 vol % CO_2 in the temperature range of 280–360°C at a selectivity of >40%, and it retained its activity even after contact with air. The minimum outlet CO concentration of 10 ppm at 80% selectivity on a 2 wt % Ni/CeO_2 catalyst was reached at a temperature of 300°C.

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INTRODUCTION

In recent years, low-temperature proton-exchange membrane fuel cells (PEMFCs) have been considered as attractive devices for transport power generation (as an alternative to internal combustion engines) or portable (electronic instrumentation and communication facilities) and fixed applications (main and standby power supply devices, in particular, in hard-to-reach areas). Either pure hydrogen or a hydrogen-containing mixture can serve as fuel for PEMFCs. This mixture is generated on site in a fuel processor from traditional hydrocarbon materials (natural gas, propane–butane mixtures, gasoline, and diesel fuel) or oxygen-containing compounds (alcohols and ethers) using catalytic (steam, oxygen, or autothermal) conversion followed by the steam conversion of CO. The hydrogen-containing mixture thus prepared usually contains 0.5–2 vol % CO, which is a poison for the PEMFC anode, and its concentration in the mixture should be decreased to a level of <10 ppm (in the case of a Pt anode) or 100 ppm (Pt–Ru anode) [1–3]. The selective oxidation of CO in hydrogen-containing mixtures is an efficient process for the removal of carbon monoxide. In the past 15 years, much effort has been directed toward the development of stable, highly active, and selective catalysts for this reaction all round the world. As a result, a large number of various systems mainly containing Au, Pt, Ru, Rh, Co, and Cu supported on various carriers have been proposed [2, 3].

However, the process of selective CO oxidation is associated with a number of problems. To determine the amount of oxygen to be supplied to the reactor inlet, the inlet concentration of CO should be continuously monitored. Otherwise, the desired degree of removal will not be reached in an oxygen deficiency or an additional amount of hydrogen will be consumed in an excess of oxygen to decrease the process efficiency. In addition, nitrogen will also be supplied to the reactor if air will be used as a source of oxygen to result in an undesirable dilution of the gas mixture.

Another possible way of removing CO from a hydrogen-containing gas is the selective methanation of CO

$$CO + 3H_2 = CH_4 + H_2O, \quad \Delta H^\circ = -206 \text{ kJ/mol}. \tag{I}$$

The advantages of selective CO methanation over selective oxidation consist in that it is not necessary to add oxygen (air) to the reaction mixture and the resulting methane, which is not a poison for PEMFCs, can further be used in an afterburner of anodic gases. Because the initial concentration of CO is low, the amount of hydrogen consumed for CO methanation is also small. The main problem is the side methanation of CO_2

$$CO_2 + 4H_2 = CH_4 + 2H_2O, \quad \Delta H^\circ = -165 \text{ kJ/mol}. \tag{II}$$

Because the concentration of CO_2 in the hydrogen-containing mixture usually is 15–20 vol %, considerable hydrogen losses can occur. The reverse reaction of steam CO conversion can also facilitate an increase in the concentration of CO:

$$CO_2 + H_2 = CO + H_2O, \quad \Delta H^\circ = 41 \text{ kJ/mol.} \quad (III)$$

The preliminary adsorption removal of CO_2 (analogous to industrial processes of hydrogen production) is often inappropriate because of a considerable increase in the size of a fuel processor. Thus, highly active and selective catalysts for CO methanation are required; these catalysts should prevent the occurrence of CO_2 methanation reactions and the reverse reaction of steam CO conversion.

The process of selective CO methanation in the presence of CO_2 has long been known [4]. It has been found that ruthenium- and nickel-containing catalysts are sufficiently effective for performing the selective methanation of CO. Interest in studies in this area has quickened in the past few years [5–22]. The majority of researchers are agreed that Ru [5–15] and Ni [13–22] systems are the most promising catalysts, the properties of which can be changed using various supports, promoting additives, and preparation techniques. It is believed that nickel catalysts rank below ruthenium catalysts in performance characteristics because they require a long reductive pretreatment, are pyrophoric, and rapidly lose activity in contact with air. At the same time, their main advantage (which is a crucial factor for use in a fuel processor for widespread applications) is much lower cost, as compared with ruthenium systems.

In this context, it is pertinent to develop stable nonpyrophoric, active, and highly selective catalysts containing no expensive precious metals for the selective methanation of CO in the presence of CO_2.

An analysis of publications devoted to selective CO methanation on Ni-containing catalysts allowed one to recognize several supports: MgO [13], Al_2O_3 [13, 15], TiO_2 [13], and ZrO_2 [13, 19]. Among them, Ni/ZrO_2 systems exhibited the best characteristics. It was found [15, 19] that the main factor affecting process selectivity is the dispersity of supported nickel particles and the degree of nickel interaction with the support. Thus, in the series of test samples with various nickel concentrations (from 0.6 to 15 wt %), a 1.6 wt % Ni/ZrO_2 catalyst was found most effective; the dispersity of nickel particles in this catalyst was high [19]. At a concentration of Ni in the catalyst higher than 3 wt %, the agglomeration of nickel particles was observed, which resulted in a decrease in the process selectivity.

The domestic know-how for the development of nickel catalysts for the methanation of carbon oxides also suggests a considerable effect of nickel concentration and dispersity on the properties of catalysts [23–25]. Thus, for a series of nickel–alumina (NKM-1, which is currently referred to as NIAP-07-01 in accordance with technical specifications) and nickel–alumina–calcium catalysts (NKM-2A and NKM-4A, which are currently referred to as NIAP-07-02) developed at the Novomoskovsk Institute of Nitrogen Industry in cooperation with the Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, a correlation of the specific surface area of nickel with activity, thermal stability, and agglomeration resistance of supported particles was demonstrated [24, 25]. Unfortunately, the catalytic properties of these catalysts under the reaction conditions of selective CO methanation remained unstudied. Recently, we proposed nickel–cerium catalysts that exhibited high activity and selectivity in the reaction of selective CO methanation in the presence of CO_2 in hydrogen-containing mixtures [17, 18].

In this work, we synthesized nickel-containing catalysts on CeO_2, ZrO_2, and γ-Al_2O_3 supports, studied their catalytic properties in the reaction of selective CO methanation in the presence of CO_2 in hydrogen-containing mixtures, and compared their activity with that of commercial samples of nickel–alumina and nickel–alumina–calcium catalysts manufactured at the Novomoskovsk Institute of Nitrogen Industry.

EXPERIMENTAL

Preparation of the Catalysts

The table lists the catalysts, their main compositions, and specific surface areas.

The NiCe, NiCeAl, NiAl, and NiZr catalysts were prepared by incipient wetness impregnation.

Cerium oxide was prepared from cerium nitrate by calcination in air at 400°C for 2 h. The specific surface area of CeO_2 was 82 m^2/g.

γ-Al_2O_3 as spherical granules 0.25–0.50 mm in diameter was used. The specific surface area of γ-Al_2O_3 was 120 m^2/g.

To prepare the CeO_2/γ-Al_2O_3 support, γ-Al_2O_3 was impregnated with a required amount of an aqueous solution of cerium nitrate and then dried in air at 110°C for 2 h and calcined at 400°C for 2 h.

Zirconium oxide was prepared by precipitation from an aqueous solution of zirconyl nitrate at a constant value of pH 10. A 5% aqueous solution of ammonia was used as a precipitating agent. The resulting precipitate was filtered off and washed with water and then with ethanol on filter. The resulting mass was dried in air for two days and then calcined in air at 500°C for 4 h.

The resulting supports were impregnated with an aqueous solution of a nickel salt and dried in air for 2 h at 110°C. The preparation procedure was described in more detail elsewhere [17].

Before performing the catalytic experiments, the resulting powdered NiCe and NiZr catalysts were pelletized and crushed, and a fraction with a particle size of 0.25–0.50 mm was taken.

In this work, we studied nickel-containing catalysts taken from several pilot batches manufactured at the Novomoskovsk Institute of Nitrogen Industry: NIAP-

Characteristics of the commercial and synthesized nickel catalysts for CO methanation

Sample	Catalyst	Concentration of Ni, wt %	S_{BET}, m^2/g	Support components
Series of synthesized catalysts				
NiCe	2 wt % Ni/CeO_2	1.9	75	CeO_2
NiCeAl	2 wt % Ni/8 wt % CeO_2/Al_2O_3	1.9	115	γ-Al_2O_3, CeO_2
NiAl	2 wt % Ni/γ-Al_2O_3	1.8	120	γ-Al_2O_3
NiZr	2 wt % Ni/ZrO_2	1.9	35	ZrO_2
Commercial methanation catalysts manufactured at the Novomoskovsk Institute of Nitrogen Industry				
NIAP-07-02	Pellets	28.6	209	γ-Al_2O_3, $CaCO_3$, CA_2^*
NKM-2A (t)	Pellets	30.6	137	AlOOH, γ-Al_2O_3, $CaCO_3$, CA_2
NKM-2A (e1)	Extrudates 1 mm in diameter	14.3	149	$CaCO_3$, γ-Al_2O_3, CA_2, gibbsite
NKM-2A (e2)	Extrudates 1.5 mm in diameter	7.7	177	AlOOH, γ-Al_2O_3, $CaCO_3$, CA_2
NKM-4A (k)	Ring	27.3	156	$CaCO_3$, γ-Al_2O_3, CA_2, graphite, $Al(OH)_3$, boehmite
NKM-4A (t)	Pellets	27.6	178	$CaCO_3$, γ-Al_2O_3, CA_2, graphite
NKM-4A (e1)	Extrudates 1 mm in diameter	13.4	235	γ-Al_2O_3, boehmite, $CaCO_3$

*Notation used in the chemistry of cements: C = CaO, A = Al_2O_3, CA_2—calcium dealuminate.

07-02, NKM-4A (k), NKM-4A (t), NKM-4A (e1), NKM-2A (t), NKM-2A (e1), and NKM-2A (e2). The table summarizes the concentrations of nickel in the samples and the main composition of the catalysts. The procedures used for the preparation of these catalysts were described elsewhere [24, 25]. To perform the catalytic experiments, commercial catalysts were crushed and a fraction with a particle size of 0.25–0.5 mm was taken.

Before performing the experiments, all of the catalyst samples were prereduced immediately in a reactor in a flow of 5% H_2 in He at 400°C for 2 h.

The concentrations of main components in the catalysts were determined using inductively coupled plasma atomic emission spectrometry on an Optima instrument.

The specific surface areas (S_{BET}) of samples were determined on an ASAP-2400 instrument from full isotherms of low-temperature nitrogen adsorption at −196°C.

Catalytic Experiments

The reaction of selective CO methanation in the presence of CO_2 in hydrogen-containing mixtures was studied in a quartz flow reactor at atmospheric pressure. The reactor was a U-shaped tube 40 cm in length with inner and outer diameters of 3 and 5 mm, respectively. A weighed portion (0.25 g) of a catalyst was placed in the reactor. To avoid the release of flour catalyst particles with a gas flow to the offtake capillary system, a filter was arranged at the reactor outlet. The reaction temperature was determined using a Chromel–Alumel thermocouple placed at the center of a catalyst bed.

The compositions of gas mixtures at the reactor inlet and outlet were analyzed using a Kristall 2000 chromatograph equipped with a flame-ionization detector with a methanizer containing an NKM-4 nickel catalyst. The test mixture was separated on a column packed with Porapak Q. The sensitivity of the determination of CO, CO_2, CH_4, and other gaseous hydrocarbon concentrations was 1 ppm. Error in the concentration measurements was no higher than ±3 rel. %.

In the course of reaction, we monitored the formation of not only methane but also other hydrocarbons. We found that, under the reaction conditions used, the total concentration of hydrocarbons other than methane was no higher than a few ppm.

The course of the reaction of selective CO methanation was characterized by the inlet CO concentration, the outlet CH_4 concentration, and selectivity (S), which was calculated from the equation

$$S = \frac{F_{CO}^{in} - F_{CO}^{out}}{F_{CH_4}^{out}} \times 100\%, \qquad (1)$$

where F_{CO}^{in} is the molar concentration of CO at the reactor inlet; F_{CO}^{out} and $F_{CH_4}^{out}$ are the molar concentrations of CO and CH_4, respectively, at the reactor outlet.

Selective CO methanation was studied using a gas mixture with the following composition: CO, 1.5 vol %; CO_2, 20 vol %; H_2O, 10 vol %; and the balance H_2. The supply rate of the mixture (standard temperature and pressure) on a catalyst weight basis (WHSV) was 26000 cm^3 $(g\ Cat)^{-1}$ h^{-1} in all of the experiments.

To prevent the formation of volatile $Ni(CO)_4$, the formation of which is thermodynamically possible at $T < 150°C$, the reaction was performed over the tem-

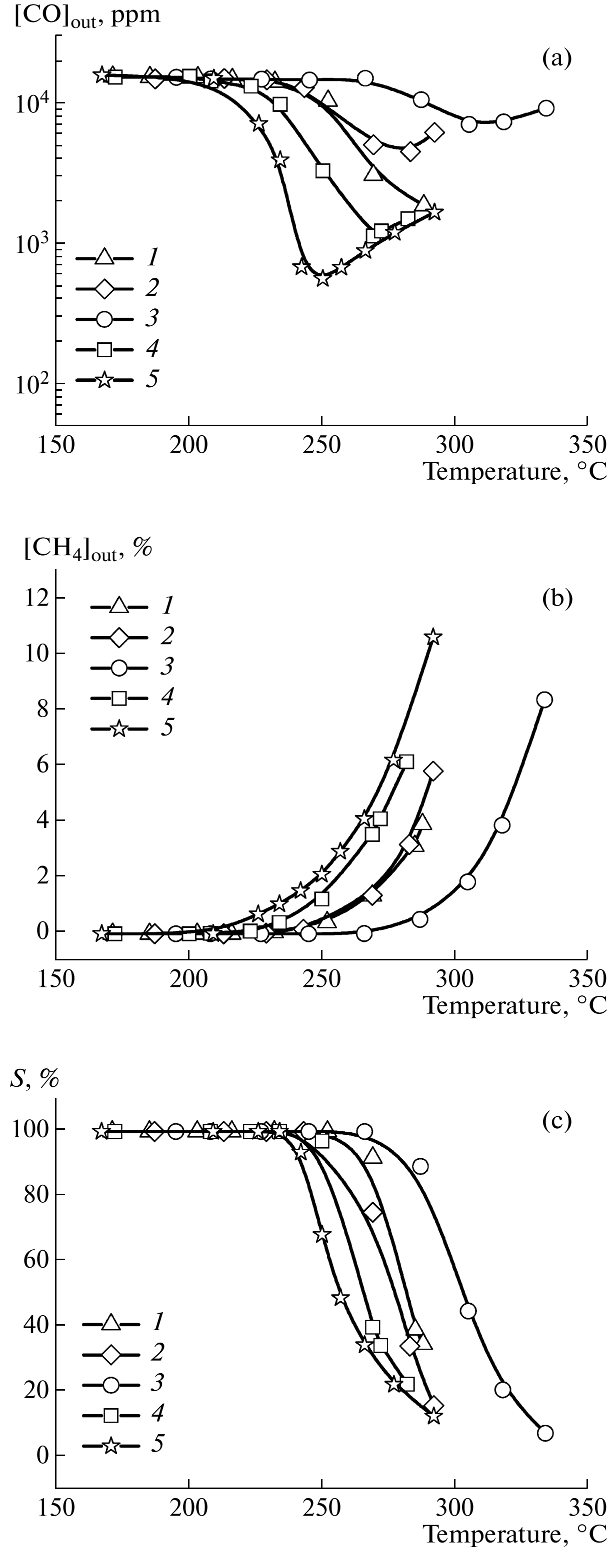

Fig. 1. Temperature dependence of the concentrations of (a) CO and (b) CH_4 at the reactor outlet and (c) selectivity in the course of the reaction of selective CO methanation in the presence of CO_2 in a hydrogen-containing mixture on the commercial catalysts (*1*) NKM-4A (k), (*2*) NKM-4A (t), (*3*) NKM-2A (e2), (*4*) NKM-2A (t), and (*5*) NIAP-07-02.

perature range of 170–400°C. Initially, the reactor was heated to 170°C in a flow of He; thereafter, the reaction mixture was supplied and the catalytic experiments were started.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of (a) the outlet concentration of carbon monoxide, (b) the outlet concentration of methane, and (c) selectivity for the commercial catalysts NIAP-07-02, NKM-4A (k), NKM-4A (t), NKM-2A (t), and NKM-2A (e2). The catalysts NKM-2A (e1) and NKM-4A (e1) were found inactive under reaction conditions, and they are not given in Fig. 1.

It can be seen that catalysts containing 27.3–30.6 wt % Ni exhibited high activity; among them, NIAP-07-02 was found the most active (the CO and CH_4 outlet concentration curves were shifted to the region of lower temperatures with respect to other catalysts). This catalyst decreased the concentration of CO to 570 ppm at 250°C. The selectivity of CO methanation was as low as 68% at the specified temperature. This is reasonable taking into account the fact that these systems were initially developed for the combined removal of CO and CO_2 from a hydrogen-containing gas mixture.

According to published data [24, 25] for the NKM-1 (an analog of the catalyst NIAP-07-02), NKM-2A, and NKM-4A series, the optimum compositions of catalysts for the methanation of CO and CO_2 present in a hydrogen-containing mixture in amounts of 0.3–2.5 vol % contained ~27.5 wt % Ni. In this case, the maximum specific surface area of nickel, thermal stability, and catalyst strength were reached. Nevertheless, as can be seen in Fig. 1, the test commercial catalysts did not allow us to reach the required degree of CO removal in the reaction of selective CO methanation in the presence of CO_2 in spite of a near-optimum composition.

Figure 2 shows the results of testing the catalytic activity of NiCe, NiCeAl, NiAl, and NiZr samples. It can be seen that the NiAl catalyst exhibited the lowest activity and selectivity. The methanation reactions of CO and CO_2 were not observed on this catalyst until a temperature of ~350°C. A further increase in the temperature resulted in the formation of methane because of both CO and CO_2 methanation. In this case, the fraction of reacted CO_2 rapidly increased, and this manifested itself in a decrease in selectivity to 60% even at 420°C. It is most likely that the low activity of this catalyst was related to the formation of inactive nickel aluminate on the catalyst surface and the hindered reduction of nickel to the metal state [24, 25].

The NiZr catalyst exhibited a low activity (the concentration of CO at the reactor outlet decreased to 1 vol % at 350°C, Fig. 2); the reaction selectivity was 100%. The high selectivity of NiZr catalysts in the reaction of selective CO methanation in the presence of CO_2 was also demonstrated previously [13, 19].

The supporting of cerium oxide onto the surface of alumina had a positive effect on the activity and selectivity of the NiAl catalyst. As can be seen in Fig. 2, on the NiCeAl catalyst, a minimum concentration of CO at the reactor outlet (1600 ppm) was observed at 380°C and 70% selectivity. Note that 100% selectivity was observed on this catalyst to a temperature of 330°C. We call attention to the fact that Xavier et al. [26] observed previously an increase in the activity of the Ni/Al_2O_3 catalyst in the CO methanation reaction upon doping with cerium oxide. Xavier et al. [26] related this effect to an increase in the dispersity of nickel in the presence of cerium oxide; in turn, this resulted in a decrease in the temperatures required for the reduction of supported particles and the methanation of CO. Barrault et al. [27] also observed a decrease in the reduction temperature of nickel particles supported on CeO_2, as compared with the Ni/γ-Al_2O_3 and Ni/SiO_2 systems. On the whole, this is consistent with the results of this work.

Among the synthesized samples containing 2 wt % Ni, the NiCe catalyst exhibited the best catalytic characteristics. It provided the occurrence of the selective CO methanation reaction in the presence of CO_2 with 100% selectivity to a temperature of 260°C, at which the concentration of CO at the reactor outlet was 0.4 vol % (see Fig. 2). The minimum CO concentration of 10 ppm at the reactor outlet was reached at 300°C and 80% selectivity. A further increase in the temperature resulted in a gradual increase in the outlet concentration of CO and a decrease in selectivity, which were as high as 60 ppm and 40% at 360°C, respectively. Note that this catalyst decreased the concentration of CO to <100 ppm over the temperature range of 280–360°C at >40% selectivity; this makes it possible to use the resulting hydrogen-containing mixture for feeding PEMFCs with Pt–Ru anodes.

It is well known that nickel-containing catalysts are pyrophoric systems, and they often lose activity in contact with air because of the agglomeration of the active component. To reveal the effect of air (oxygen) on the catalytic properties of the NiCe system, we performed the following experiments: After performing standard catalytic experiments, the reactor with the NiCe catalyst was cooled in a reaction atmosphere to 160°C and then purged with an inert gas (1 min) and air to cool it to 25°C; then, it was repeatedly heated to 160°C (2 h) and purged with an inert gas (1 min). After this treatment, a reaction mixture was supplied to the reactor and catalytic experiments were performed.

Figure 3 shows the temperature dependence of the outlet concentrations of CO and CO_2 and selectivity in the course of the reaction of selective CO methanation on the NiCe catalyst immediately after contact with air (the measurements were performed as the temperature was increased from 160 to 360°C) and in the subsequent experiment (the measurements were per-

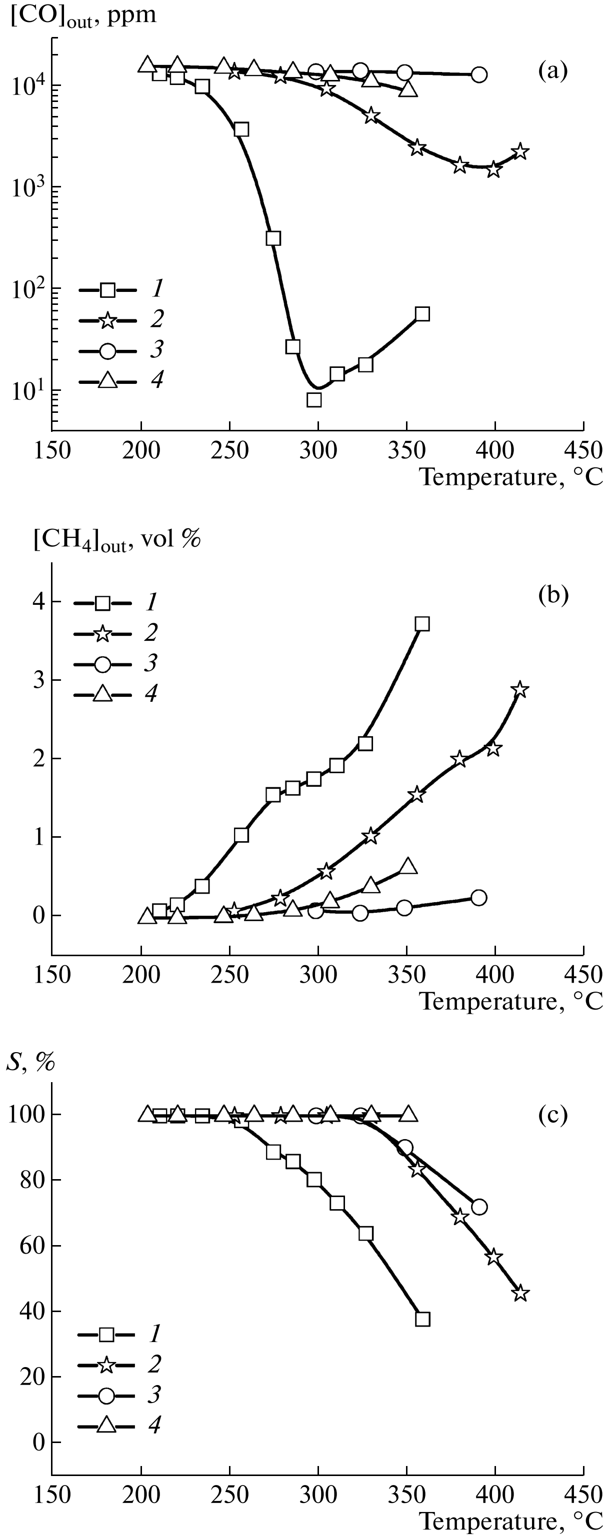

Fig. 2. Temperature dependence of the concentrations of (a) CO and (b) CH_4 at the reactor outlet and (c) selectivity in the course of the reaction of selective CO methanation in the presence of CO_2 in a hydrogen-containing mixture on the catalysts (*1*) NiCe, (*2*) NiCeAl, (*3*) NiAl, and (*4*) NiZr.

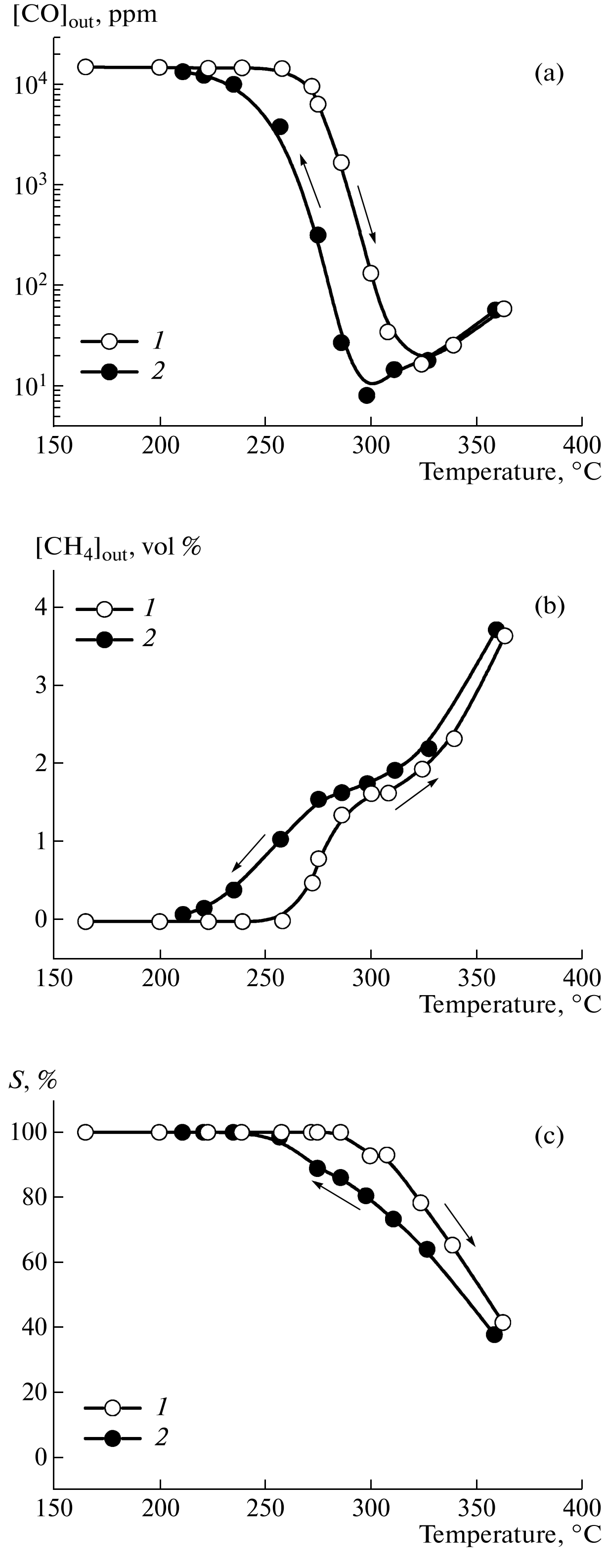

Fig. 3. Temperature dependence of the outlet concentrations of (a) CO and (b) CH_4 and (c) selectivity in the course of the reaction of selective CO methanation in the presence of CO_2 in a hydrogen-containing mixture on the NiCe catalyst (*1*) immediately after contact with air and (*2*) in the subsequent experiment.

formed as the temperature was decreased from 360 to 160°C). It can be seen that the activity of the NiCe catalyst (Figs. 3a, 3b) measured immediately after contact with air was lower than that in the subsequent experiment. This was most likely due to the surface oxidation of supported nickel particles in air; then, these particles were reduced immediately in the reaction atmosphere. Note that, in the subsequent experiment, the observed temperature dependence of the outlet concentrations of CO and CH_4 and selectivity was consistent with that obtained in standard catalytic experiments (Fig. 2). In the following temperature increase–decrease cycles over the range of 160–360°C without contact with air, changes in the activity of the NiCe catalyst were not observed.

This suggests that the NiCe catalyst is stable to agglomeration in air, and it recovers its activity in the reaction of selective CO methanation without any additional pretreatment immediately before the action of a reaction atmosphere.

CONCLUSIONS

The study of the catalytic properties of NKM-2A and NKM-4a (NIAP-07-02) commercial methanation catalysts did not allow us to recommend them for use in the reaction of selective CO methanation in the presence of CO_2. Among the test systems, 2 wt % Ni/CeO_2 is the most promising catalyst. This catalyst retained its activity after contact with air and decreased the concentration of CO from 1.5 vol % to 100 ppm in the presence of 20 vol % CO_2 over the temperature range of 280–360°C at >40% selectivity. The minimum CO outlet concentration of 10 ppm at 80% selectivity was reached at 300°C.

It is reasonable to focus the subsequent studies on the optimization of the composition and preparation procedure of the NiCe system in order to increase its activity and to extend the range of conditions under which the reaction of selective CO methanation occurs in the presence of CO_2.

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REFERENCES

1. O’Hayre, R., Cha, S.-W., Colella, W., and Prinz, F.B., *Fuel Cell Fundamentals*, New York: Wiley, 2006, p. 304.
2. Trimm, D.L., *Appl. Catal., A*, 2005, vol. 296, p. 1.
3. Farrauto, R.J., Liu, Ye., Ruettinger, W., Ilinich, O., Shore, L., and Giroux, T., *Catal. Rev.*, 2007, vol. 49, p. 141.
4. Rehmat, S. and Randhava, S., *Ind. Eng. Chem. Prod. Res. Dev.*, 1970, vol. 9, p. 512.

5. Görke, O., Pfeifer, P., and Schubert, K., *Catal. Today*, 2005, vol. 110, p. 132.
6. Xu, G., Chen, X., and Zhang, Z.-G., *Chem. Eng. J.*, 2006, vol. 121, p. 97.
7. Zhang, Z.-G. and Xu, G., *Catal. Commun.*, 2007, vol. 8, p. 1953.
8. Galletti, C., Saracco, G., Specchia, S., and Specchia, V., *Int. J. Chem. React. Eng.*, 2007, vol. 5, p. 110.
9. Dagle, R.A., Wang, Y., Xia, G.-G., Strohm, J.J., Holladay, J., and Palo, D.R., *Appl. Catal., A*, 2007, vol. 326, no. 2, p. 213.
10. Panagiotopoulou, P., Kondariges, D.I., and Verykios, X.E., *Appl. Catal., A*, 2008, vol. 344, p. 45.
11. Panagiotopoulou, P., Kondariges, D.I., and Verykios, X.E., *Appl. Catal., B*, 2009, vol. 88, p. 470.
12. Galletti, C., Specchia, S., Saracco, G., and Spechia, V., *Chem. Eng. Sci.*, 2010, vol. 65, p. 590.
13. Takenaka, S., Shimizu, T., and Otsuka, K., *Int. J. Hydrogen Energy*, 2004, vol. 29, p. 1065.
14. Choudhury, M.B.I., Ahmed, S., Shalabi, M.A., and Inui, T., *Appl. Catal., A*, 2006, vol. 314, p. 47.
15. Men, Y., Kolb, G., Zapf, R., Hessel, V., and Löwe, H., *Catal. Today*, 2007, vol. 125, p. 81.
16. Krämer, M., Duisberg, M., Stöwe, K., and Maier, W.F., *J. Catal.*, 2007, vol. 251, p. 410.
17. RF Patent 2323044.
18. Badmaev, S.D. and Snytnikov, P.V., *Int. J. Hydrogen Energy*, 2008, vol. 33, p. 3026.
19. Liu, Q., Dong, X., Mo, X., and Lin, W., *J. Nat. Gas Chem.*, 2008, vol. 17, p. 268.
20. Minyukova, T.P., Itenberg, I.Sh., Demeshkina, M.P., Shtertser, N.V., and Yur'eva, T.M., *Khim. Interes. Ust. Razv.*, 2005, vol. 13, p. 793.
21. Minyukova, T.P., Boronskaya, N.A., Khasin, A.A., and Yur'eva, T.M., *Katal. Prom—sti.*, 2008, special issue, p. 24.
22. Minyukova, T.P., Itenberg, I.Sh., Khassin, A.A., Sipatrov, A.G., Dokuchits, E.V., Terent'ev, V.Ya., Khristolyubov, A.P., Brizitskii, O.F., and Yurieva, T.M., *Chem. Eng. J.*, 2007, vol. 134, p. 235.
23. Berezina, Yu.I., in *Spravochnik azotchika* (Nitrogen Engineer's Handbook), Mel'nikov, E.Ya., Ed., Moscow: Khimiya, 1986, p. 333.
24. Golosman, E.Z., Efremov, V.N., Kreindel', A.M., Sobolevskii, V.S., and Yakerson, V.I., *Khim. Prom—st.*, 1997, vol. 2, p. 22.
25. Golosman, E.Z., Efremov, V.N., Kreindel', A.M., Sobolevskii, V.S., and Yakerson, V.I., *Khim. Prom—st.*, 1997, vol. 3, p. 27.
26. Xavier, K.O., Sreekala, R., Rashid, K.K.A., Yusuff, K.K.M., and Sen, B., *Catal Today*, 1999, vol. 49, p. 17.
27. Barrault, J., Alouche, A., Paul-Boncour, V., Hilaire, L., and Percheron-Guegan, A., *Appl. Catal.*, 1989, vol. 46, p. 269.