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Methane Reforming with Carbon Dioxide on the Co/α-Al_2O_3 Catalyst: The Formation, State, and Transformations of Surface Carbon

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Abstract—The interactions of oxidized and reduced Co/α-Al_2O_3 (4 wt % CoO) with H_2, CH_4, CO_2, and O_2 and their mixtures are studied in flow and pulse regimes using a setup involving a DSC-111 differential scanning calorimeter and a system for chromatographic analyses. It is shown that treatment with hydrogen at 700°C results in the partial reduction of cobalt oxide to Co. Methane poorly reacts with the oxidized catalyst but readily reacts with the reduced catalyst to form H_2 and surface carbon. The initial surface carbon transforms into other forms, which block the cobalt surface to different extents and differ in the heats of reaction with CO_2. Carbon dioxide may react with the surface carbon to form CO (rapidly) and with metallic Co to form CO and CoO (slowly). Thus, the main route of methane reforming with carbon dioxide on Co/α-Al_2O_3 is the dissociative adsorption of CH_4 to form surface carbon and H_2 and the reaction of surface carbon with CO_2 to form CO via the reverse Boudouard reaction.

INTRODUCTION

Methane reforming with carbon dioxide to form syngas has been intensively studied in recent years. In most cases, efficient catalysts for methane reforming with carbon dioxide contain a platinum-group metal or nickel/cobalt. Review papers [1, 2] contain information on the relative activities of different metals, effect of supports, methods for catalyst preparation, and a number of other parameters. Previous reports from the Semenov Institute of Chemical Physics [3, 4] concerned methane reforming with carbon dioxide on Ni/MgO and Ni/Al_2O_3 systems. More recently, we found that the Co/Al_2O_3 system is another active catalyst of methane reforming with carbon dioxide. This work deals with a mechanistic study of methane reforming with carbon dioxide on Co/Al_2O_3 using *in situ* calorimetry and the unsteady flow of reactants. The potential of the method and its applications to hydrocarbon oxidation reactions were described in [5].

Currently, all researchers agree that the mechanism of methane reforming with carbon dioxide involves the dissociative adsorption of methane on the metal (Pt, Ni, etc.) surfaces:

$$CH_4 + M \longrightarrow M\text{–}C + 2H_2, \qquad \text{(I)}$$

where M is metal. Carbon formed in the reaction may transform into CO in the reaction with CO_2 molecules,

$$CO_2 + M\text{–}C \longrightarrow 2CO + M, \qquad \text{(II)}$$

or in the reaction with oxygen (reaction (IV)), which is a component of the catalyst or which is formed by CO_2 dissociation:

$$M + CO_2 \longrightarrow M\text{–}O + CO, \qquad \text{(III)}$$

$$M\text{–}O + M\text{–}C \longrightarrow 2M + CO. \qquad \text{(IV)}$$

It is known (see, for instance, [6, 7]) that all these reactions occur, but the question of what the pathway is the main in the course of catalysis is still open. Some researchers [6, 7] assume that this pathway is reactions (III) and (IV). In the previous paper [4], we showed for the Ni/Al_2O_3 catalyst that reaction (II) is much faster than reactions (III) and (IV) and therefore determines the main pathway of CO_2 conversion in the course of methane reforming with carbon dioxide. It was interesting to check this conclusion for other catalysts, e.g. Co/Al_2O_3.

The role of carbonaceous deposits in the process of methane reforming with carbon dioxide was studied by many authors, but this question also remains debatable. Some authors report [8–10] that carbonaceous deposits decrease the catalytic activity, although others assume that the activity is almost independent of cocking [11]. In a series of papers [11–14], using the methods of temperature-programmed oxidation and hydrogenation, the formation of two or three forms of carbon in the course of methane reforming with carbon dioxide has been shown. However, their nature was not completely clear (amorphous carbon, graphite, and metal carbides were suggested). The goal of this work is to characterize the thermochemical properties of carbonaceous deposits by measuring the heats of their reaction with CO_2 and to use these data to calculate the enthalpies of their formation and concretize the chemical nature of carbon forms. In [4], a similar task failed because of pronounced masking with the equilibrium adsorption of CO_2 on the support. To eliminate this effect, we chose a support with a lower specific surface area.

EXPERIMENTAL

A Co/α-Al_2O_3 sample was prepared by the impregnation of alumina with a solution of cobalt nitrate so that the concentration of CoO was 4 wt %. For the preparation of the support we used γ-Al_2O_3 (S_{sp} = 220 m^2/g), which was calcined at 1150°C for 20 h. According to XRD, the resulting material contained only α-Al_2O_3 without γ-Al_2O_3 and θ-Al_2O_3 admixtures and had a specific surface area of 6 m^2/g. Alumina impregnated with cobalt nitrate was dried at 120°C for 1 h and calcined in air at 850°C for 1 h.

The interaction of the sample with gaseous reactants was studied in a setup involving a DSC-111 differential scanning calorimeter and two gas chromatographs. A solid sample of the catalyst (100–150 mg) was charged into a flow quartz cell with an inner diameter of ~5 mm, which was placed into a measurement channel of the calorimetric block of DSC-111. Preliminary treatment of the samples involved heating in a flow of air at 700°C for 60 min. To study the reduced state of the catalyst, the sample was treated in a flow of hydrogen at 700°C for 30 min. The reaction of the sample with reactants was carried out in flow and pulse regimes. In the case of a pulse regime, the sample was constantly purged at a rate of 30 ml/min with specially cleaned helium. Reactant gas pulses (0.6 ml) were added to a helium flow using a six-way valve. The product flow was analyzed in two consecutive chromatographic columns. These columns were packed with Porapak N and zeolite 5A. A thermal conductivity detector was used. The system of analyses enabled us to determine CO_2, H_2, O_2, N_2, CH_4, CO, C_2H_6, and C_2H_4.

The concentrations of gaseous reactants and reaction products were expressed in terms of the ratio of the volume of a measured component to the initial pulse volume (in %). This value was convenient for further calculations, but the sum of concentrations of all components after the reaction was not equal to 100%.

RESULTS

The Reduction of 4% CoO/Al_2O_3 by Hydrogen and Reoxidation by Oxygen

The initial oxidized sample readily reacts with hydrogen in a flow at 700°C. A sharp positive peak (1–2 min) is seen on the heat evolution curve at the instant of hydrogen admission. Further treatment in a hydrogen flow for 30 min is not accompanied by a noticeable thermal effect and, therefore, by additional sample reduction. In further experiments, this treatment in hydrogen was used to obtain a reduced form of the catalyst. In the subsequent discussion below, we will use the following notation for the reduced sample: Co/Al_2O_3.

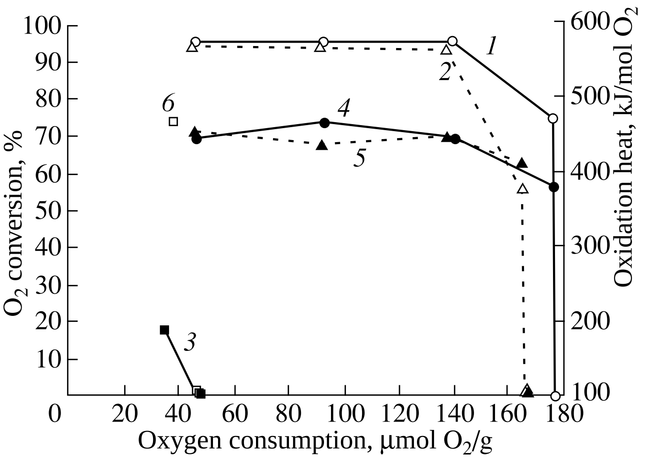

Fig. 1. (*1–3*) Oxygen conversion and (*4–6*) oxidation heats in the process of Co/Al_2O_3 reoxidation at (*1, 2, 4, 5*) 700°C and (*3, 6*) 100°C after reduction in a flow of hydrogen at 700°C.

The reduced sample rapidly reacts with air pulses at 700°C. A series of air pulses was accompanied by the almost complete conversion of oxygen (Fig. 1), which drastically decreases when oxidation ceases. In the course of oxidation, ~170 μmol O_2/g is consumed. The amount of O_2 consumed for oxidation is ~70% of all oxygen contained in supported cobalt oxide (assuming CoO stoichiometry). Figure 1 shows the results of two experiments on oxidation at 700°C to illustrate a scatter in the reduction degrees.

The oxidation is accompanied by intensive heat evolution. The heat of oxidation is 450–470 kJ/mol O_2 (Fig. 1) and decreases to 380–410 kJ/mol O_2 only at the end.

The amount of oxygen consumed in the reoxidation of the sample depends on the reaction temperature. If the catalyst is reduced by hydrogen at 700°C and then cooled to 100°C in a flow of helium, the reoxidation process completes more rapidly after the supply of air pulses (see Fig. 1). The full amount of consumed oxygen in this case is 49 μmol O_2/g and the heat of oxidation is 470 kJ/mol O_2.

The Interaction of CO_2 with Co/Al_2O_3

The reduced sample reacts with CO_2 pulses at 700°C to form CO (Fig. 2). The conversion of CO_2 in the first pulse is equal to 4.3% and then decreases to 2.0%. Obviously, the rate of cobalt oxidation is much lower than in the case of air pulses. After ten CO_2 pulses, the sample consumed ~60 μg-atom O/g, which is ~18% of the amount of oxygen consumed in the case of oxidation by air. We failed to measure the heats of these processes because of their low intensity.

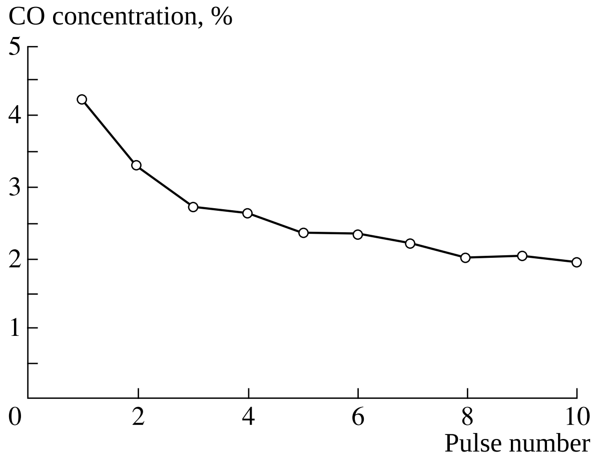

Fig. 2. CO formation in the reaction of reduced Co/Al_2O_3 with CO_2 pulses at 700°C.

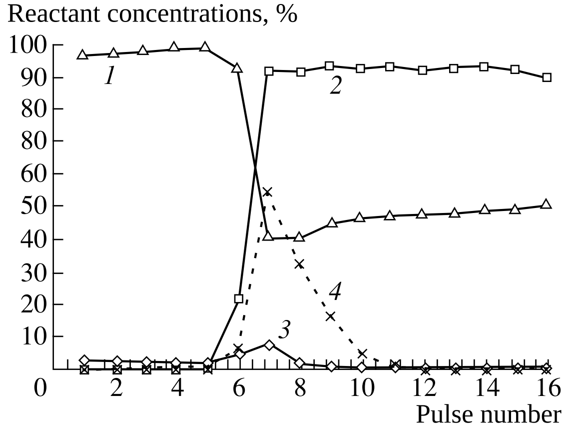

Fig. 3. Concentrations of (*1*) CH_4, (*2*) H_2, (*3*) CO_2, and (*4*) CO in the reaction between methane pulses with oxidized 4% CoO/Al_2O_3 at 700°C.

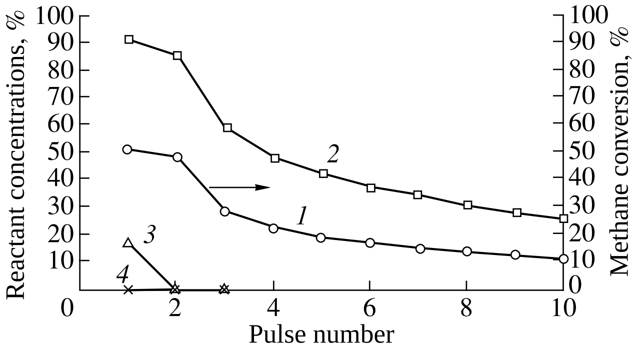

Fig. 4. (*1*) Methane conversion and the concentrations of (*2*) H_2, (*3*) CO, and (*4*) CO_2 with reduced Co/Al_2O_3 at 700°C.

The Interaction of Oxidized and Reduced Samples with Methane

Figure 3 shows the results of the interaction of methane pulses with the oxidized 4% CoO/Al_2O_3 sample. In the first pulse, methane consumption is 4.6% and decreases to 1.3% in a further four pulses. The main products are CO_2 and ethane (not shown in Fig. 3). Starting from the sixth pulse, methane conversion drastically increases and CO and H_2 appear in the products, and hydrogen becomes the main products of the reaction. The conversion of methane and the yield of carbon oxides are maximal in the seventh pulse. In further pulses, the conversion of methane gradually decreases. The formation of carbon oxides is completed after the tenth pulse.

The reoxidation of the sample in a flow of air at 700°C restores the initial state of the catalyst. However, after several reduction–reoxidation cycles, the properties of the sample in the reaction with methane gradually change. Specifically, the number of methane pulses increases and then intensive reduction begins.

The reduced Co/Al_2O_3 sample reacts with methane pulses at 700°C to form H_2 and CO (Fig. 4). The formation CO points to the additional reduction of cobalt oxide. The conversion of methane decreases with an increase in the number of pulses, which is probably due to surface carbon covering the surface. The initial rate of methane consumption and hydrogen formation decrease with the number of reduction–reoxidation cycles.

The rate of the decrease in the methane conversion with an increase in the number of pulses depends on the interval between pulses. Figure 5 shows the dependence of the hydrogen yield in the reaction of the reduced sample with methane pulses supplied every 10 min or every 20 s. It is seen that, in the second case (curve *2*), the amount of hydrogen decreases much more rapidly. A further increase in the interval between pulses to 10 min results in an increase in the yield of hydrogen up to the level of curve *1*.

The Interaction of CO_2 with Surface Carbon

Figure 6 shows data on CO formation in the consecutive admission of CH_4 and CO_2 pulses onto the Co/Al_2O_3 surface (with 10-min pulse intervals). In the first three pulses, CO_2 reacts with the sample reduced by hydrogen. Then, the pulses of CH_4 (products are not shown) and CO_2 follow in the sequence: 4, CH_4; 5, CO_2; 6–7, CH_4; 8–10, CO_2; 11, CH_4; 12–16, CO_2. It is seen that, after the reaction with methane, the catalyst reacts with CO_2 much more rapidly than before it (pulses 5, 8, and 12). The amount of evolved CO was double the amount of consumed CO_2; that is, the stoichiometry corresponded to the reaction

$$C + CO_2 \longrightarrow 2CO. \qquad (V)$$

However, after the second CO_2 pulse (pulses 9 and 13), the amount of CO corresponds to the reaction of CO_2 with the clean sample reduced by hydrogen. Pulses 8 and 12 are accompanied by a noticeable endothermic effect (56–57 kJ/mol CO).

In another experiment, the sample was kept in a flow of methane for 10 min at 700°C, and then a series of CO_2 pulses was supplied onto the cocked surface. The intensive formation of CO (Fig. 7) was observed in this case as well, and the conversion of CO_2 was ~50%. After twelve pulses, the surface carbon was completely consumed and the yield of CO dropped. Figure 7 shows the measured values of reaction heats (Q_{CO_2}). Under the conditions of a high CO yield, the heat is 60–70 kJ/mol CO.

The Interaction of Oxidized and Reduced Samples with the Pulses of the 49% CH_4 + 49% CO_2 + 2% N_2 Mixture

The oxidized 4% CoO/Al_2O_3 sample is practically inactive in methane reforming with carbon dioxide at 700°C, although the sample reduced by hydrogen provides high conversions of CH_4 (up to 80%) and CO_2 (up to 85%) at an almost constant activity (Fig. 8). The concentration of H_2 in Fig. 8 is probably underestimated because of the nonlinear dependence of the thermal conductivity detector signal intensity for H_2 in the range of high concentrations.

Figure 9 shows the results of a run with alternating pulses of $CH_4 + CO_2$ and methane supplied onto the reduced Co/Al_2O_3 sample. It is seen that after the reaction of the sample with five methane pulses (3–7), the conversion of methane and the concentration of H_2 in pulse 8 of the $CH_4 + CO_2$ mixture decrease compared to pulses 1 and 2. In further pulses of the mixture, the stationary activity is restored.

When reduced Co/Al_2O_3 was treated in a flow of methane for 10 min at 700°C and pulses of the mixture were supplied (the interval between a change of methane flow to a flow of helium and the first pulse of the mixture was ~30 min), a similar effect (a decrease in the conversion of methane and the yield of H_2) was not observed.

DISCUSSION

The results obtained demonstrate that the 4% $CoO/\alpha\text{-}Al_2O_3$ sample is readily reduced by hydrogen and reoxidized by oxygen at 700°C. It is known that metallic cobalt can be oxidized to CoO or Co_3O_4. The enthalpies of formation of these oxides are noticeably different [15] and the heats of oxidation should be

$$2Co + O_2 \longrightarrow 2CoO, \quad \Delta H = -479 \text{ kJ/mol } O_2, \qquad \text{(VI)}$$

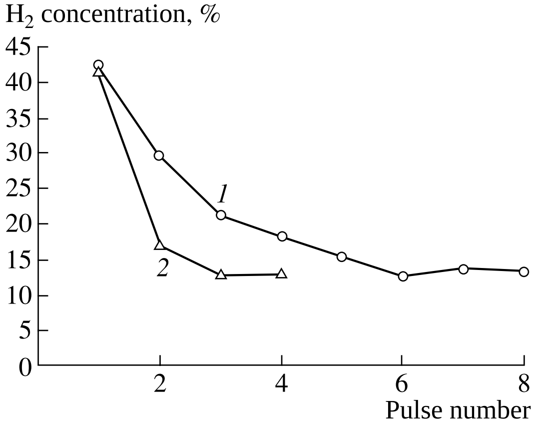

Fig. 5. Formation of H_2 in the reaction of methane pulses with reduced Co/Al_2O_3 at 700°C when intervals between pulses are (*1*) 10 min and (*2*) 20 s.

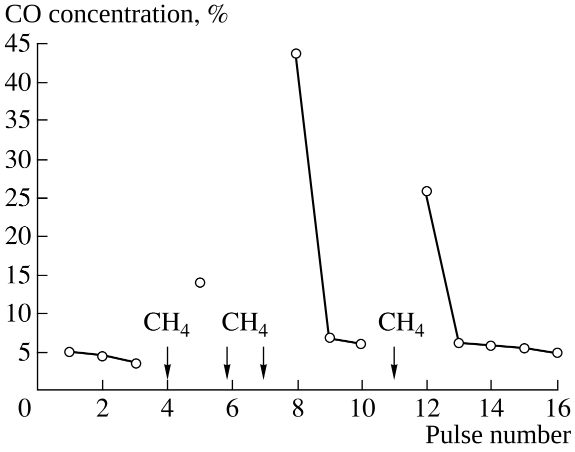

Fig. 6. CO formation in the reaction of alternating pulses of CO_2 (pulses 1–3, 5, 8–10, 12–16) and CH_4 (pulses 4, 6–7, 11) with reduced Co/Al_2O_3 at 700°C.

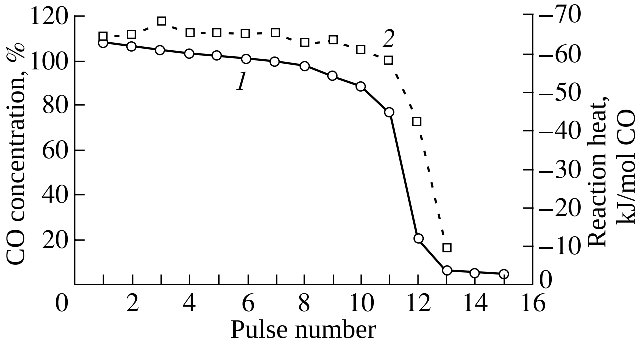

Fig. 7. (*1*) CO concentration; (*2*) reaction heat in the reaction of CO_2 pulses with Co/Al_2O_3 preliminarily treated in a flow of CH_4 at 700°C.

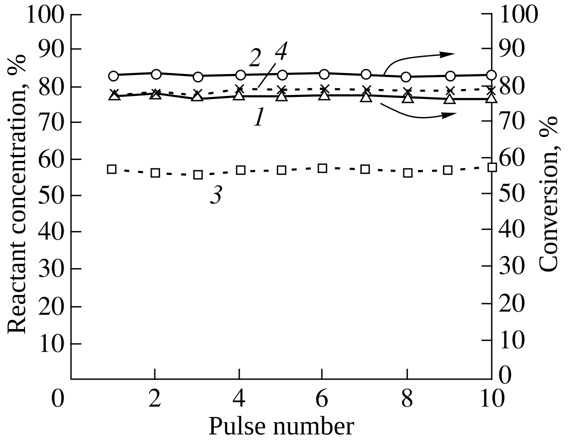

Fig. 8. The conversions of (*1*) CH_4 and (*2*) CO_2 and the concentrations of (*3*) H_2 and (*4*) CO in the reaction of reduced Co/Al_2O_3 with the pulses of the $CH_4 + CO_2$ mixture at 700°C.

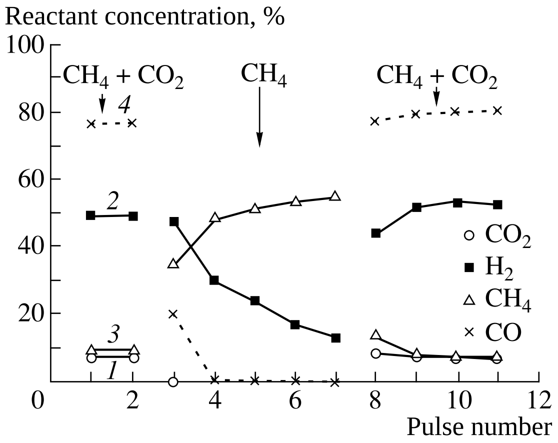

Fig. 9. The concentration of (*1*) CO_2, (*2*) H_2, (*3*) CH_4, and (*4*) CO in the reaction of alternating pulses of $CH_4 + CO_2$ (pulses 1–2, 8–11) and CH_4 (pulses 3–7) with reduced Co/Al_2O_3 at 700°C.

$$3Co + 2O_2 \longrightarrow Co_3O_4, \quad \Delta H = -395\ \text{kJ/mol } O_2, \qquad \text{(VII)}$$

$$6CoO + O_2 \longrightarrow 2Co_3O_4, \quad \Delta H = -142\ \text{kJ/mol } O_2. \qquad \text{(VIII)}$$

Although the corresponding values for supported phases may differ from the above values, the tabulated values of ΔH can be used to analyze experimental data when thermal effects differ substantially as in our case. The measured values (see Fig. 1) for the most part of consumed oxygen are close to the heat of reaction (VI). The measured heat corresponds to oxidation to Co_3O_4 only in the case of the last pulse. Therefore, we can assume that CoO is the main form of the oxidized cobalt in the sample. Proceeding from this finding and knowing the overall amount of oxygen consumed in the course of Co/Al_2O_3 reoxidation, we calculated that ~70% of the supported cobalt oxide is reduced in a flow of hydrogen at 700°C. It is likely that the rest of the cobalt oxide is not reduced because of a stronger binding to alumina. This conclusion agrees with the fact that only ~22% of the NiO supported on Al_2O_3 with a higher specific surface area (35 m^2/g rather than 6 m^2/g as in this work) is reduced under analogous conditions [4].

The high conversions of oxygen and the absence of a tail on the curve of conversion versus pulse number (Fig. 1) points to the fact that, at 700°C, the processes of reduction and reoxidation of cobalt oxide crystallites is not limited by diffusion and affect the whole bulk of crystallites. At 100°C, a different pattern is observed in the course of reoxidation. It is likely that only the surface of metallic cobalt crystallites is oxidized at this temperature. The fact that the apparent heat of oxidation is the same as at 700°C means that the reaction product (cobalt oxide) is the same. Therefore, the ratio of the amounts of oxygen consumed at 100 and 700°C is equal to the portion of cobalt atoms on the outer surface of crystallites. Using the results of a run where a portion of the 4% CoO/Al_2O_3 sample was consecutively reduced by hydrogen and reoxidized at 700 and 100°C, we obtain that this value was 25%.

It is interesting that the amount of cobalt on the outer surface of metallic cobalt crystallites (~25%) and the amount of supported cobalt oxide that is not reduced by hydrogen at 700°C (~30%) are close. Possibly, in this system, the barely reducible portion of cobalt oxide is the lower layer of the crystallite, which directly interacts with the alumina surface. It is reasonable to assume that the region of cobalt oxide contact with alumina is close in its chemical properties to the mixed oxide, cobalt aluminate. The fact that transition metal aluminates are reduced less readily than oxides was noted many times (see, e.g., [16]).

Our experiments show that the reduction–reoxidation processes result in a gradual change in the reactivity of supported cobalt compared to the initial sample. This reveals itself in the more difficult reduction of the oxidized sample by methane (an increase in the number of methane pulses before the beginning of intensive reduction) and in a decrease in methane conversion (and the hydrogen yield) in the course of the reaction between methane pulses with the reduced catalyst. It is probable that this effect is due to the gradual enlargement of cobalt particles due to the consecutive oxidative and reductive treatments at 700°C.

Similarly to the 6% Ni/Al_2O_3 catalyst [4], the reactivities of oxidized and reduced 4% CoO/Al_2O_3 samples in its reaction with CH_4 differ substantially. In the case of the oxidized sample, the initial period is noteworthy (the first five pulses), which is characterized by a combination of the complete oxidation of methane to CO_2 and H_2O and the oxidative coupling of methane:

$$CH_4 + 4|O| \longrightarrow CO_2 + 2H_2O, \qquad \text{(IX)}$$

$$2CH_4 + |O| \longrightarrow C_2H_6 + H_2O, \qquad (X)$$

where |O| is oxide oxygen.

The low conversion of methane and the absence of hydrogen from the reaction products suggest that metallic cobalt particles are absent. The source of active oxygen can be the Co_3O_4 admixture, which is reduced to CoO, or a portion of CoO that is capable of donating a certain amount of stoichiometric lattice oxygen without destruction and formation of metallic cobalt particles. When this source of oxygen exhausts, the reduction of cobalt oxide to metal begins, which results in a drastic increase in the methane conversion due to its decomposition on the metallic cobalt surface:

$$CH_4 \longrightarrow C + 2H_2. \qquad (XI)$$

If the sample was preliminarily reduced in a flow of hydrogen, reaction (XI) began from the start. Its rate was maximal in the first pulse (Fig. 4) and steadily decreased possibly because of metal surface coking.

The fact that a decrease in the rate of hydrogen evolution depends on the interval between methane pulses (Fig. 5) in the course of methane decomposition points to the effect of mass-transfer processes. It is most probable that carbon atoms formed on the metallic cobalt crystallites diffuse and form an ordered form of carbon, while the surface of cobalt particles is partially freed. This process manages to occur during 10-min intervals between methane pulses, whereas a 20-s interval is insufficient for the diffusion completion. Overall, the results obtained suggest the existence of three stages of surface carbon redistribution. At the first stage (0–20 s after the reduced sample contacted with methane), carbon (form A) covers the cobalt surface and strongly retards further methane decomposition. At the second stage (up to 10 min), most of the cobalt surface is freed and carbon atoms agglomerate (form B). Because the reactivity of metal is completely restored (Fig. 4), we may assume that carbon species contact the metal and block its surface. When a pulse of the $CH_4 + CO_2$ mixture follows a pulse of methane (pulse 8 in Fig. 9) a noticeable decrease in the conversion of methane and the hydrogen yield are observed. In further pulses of the $CH_4 + CO_2$ mixture, the catalytic activity is restored, pointing to the relatively fast cleaning of the surface from this form of carbon under the conditions of methane reforming with carbon dioxide. Finally, after a ~30-min interval between methane pulses and the pulses of the $CH_4 + CO_2$ mixture, even a substantial amount of carbon (>1000 μmol/g) (form C) does not affect the catalytic activity of the sample.

Comparison of the rate of deactivation in the reaction with methane for the sample preliminarily reduced with hydrogen (Fig. 4) and the sample freshly reduced by methane pulses (pulses 10–15 in Fig. 3) point to the fact that, in the second case, the rates of hydrogen evolution and methane conversion decrease more slowly. Because the formation of carbon oxides (pulses 10–15 in Fig. 3) is completed at this stage, this conservation of the rate of methane decomposition can barely be explained by the restoration of the cobalt surface at the expense of coke oxidation. It is possible that, in this case, cobalt surface cleaning due to diffusion and agglomeration of carbon atoms is more efficient because of the relatively small size of metal particles immediately after their formation.

Data obtained in this work on the heats of reaction between CO_2 and surface carbon can be used to characterize the latter species. According to the standard values of the heats of formation [15], the heat of reaction (V) with graphite carbon at 700°C is –85.3 kJ/mol CO. The measured values of the thermal effect of reaction (V) are noticeably lower. This means that the state of carbon formed in methane decomposition differs from the standard one (graphite). The enthalpy of its formation ΔH^{f}_{C} can be calculated using the formula

$$\Delta H^{f}_{C} = 2\Delta H^{f}_{CO} - \Delta H^{f}_{CO_2} + 2Q_{CO_2},$$

where ΔH^{f}_{CO} and $\Delta H^{f}_{CO_2}$ are the enthalpies of formation of CO and CO_2, and Q_{CO_2} is the measured heat of reaction (V). The measured values for Q_{CO_2} are equal to 57 kJ/mol (pulses 8 and 12 in Fig. 6; form B) and 70 kJ/mol for CO (Fig. 7, form C) correspond to the values ΔH^{f}_{C} 57 and 31 (form C) kJ/mol. According to literature data [15], the enthalpies of cobalt carbide Co_3C and Co_2C formation are 44.4 and 17.0 kJ/mol, respectively. The first of these is close to the value of ΔH^{f}_{C} for form C. At the same time, the amount of carbon formed after 10-min treatment with methane (form C) (~1000 μmol/g) is much larger than the amount of cobalt in the sample (530 μmol/g). Therefore, carbide Co_3C cannot be the main form of surface carbon in this case. When the amount of surface carbon is smaller (1–3 methane pulses, ~10-min interval, form B), it is comparable with the amount of reduced cobalt, but the value ΔH^{f}_{C} = 57 kJ/mol is noticeably higher than the tabulated enthalpy of carbide carbon formation.

An opinion has been expressed many times in the literature that carbon formed under the conditions of carbon dioxide reforming (completely or partially) on nickel catalysts is in the form of carbide Ni_3C. The reason for this claim is, for instance, data on the loss of magnetic properties of metallic nickel after catalyst treatment with methane [17]. Our data support the conclusion that the state of surface carbon substantially differs from its state in graphite in the enthalpy of formation ΔH^{f}_{C}. Although we failed to measure this value during the first 1–2 min after methane decomposition, we may state that it decreases from 57 to 31 kJ/mol at the time interval 10–30 min. It is likely that this is due to the transformation of the metastable form of carbon into a more stable form. At the same time, as shown above, none of the observed states can be assigned to the Co_3C phase. Data on a decrease in the rate of methane decomposition and its further reduction point to intensive diffusion of carbon atoms from the cobalt surface. Diffusion can occur either along the surface or through the bulk of metallic cobalt particles. In the latter case, the magnetic state of cobalt may change. Experiments on magnetization measurement probably show this particular effect. The form of carbon observed last (form C) and characterized by ΔH^{f}_{C} = 31 kJ/mol, which is still different from the value for graphite, possibly corresponds to nanotubes observed by several researchers.

Unlike for the Co/Al_2O_3 sample covered by carbon, the rate of CO_2 interaction with the sample reduced in a flow of hydrogen is relatively low at 700°C. The apparent yield of CO is at most 4–5% in the first 1–2 pulses of CO_2 (Fig. 2) and rapidly decreases to 2%. In the first pulse, the sample consumed ~10 μg-atom O/g. This means that the low conversion of CO_2 is determined by the low rate of reaction (III) rather than by the insufficient amount of reduced cobalt on the Co/Al_2O_3 surface, because 49 μmol O_2/g (or 98 μg-atom O/g) is consumed in the low-temperature oxidation of the sample. For the coked sample under analogous conditions in the reaction with CO_2 pulses, 20–120% CO is evolved (Figs. 4 and 6). Under conditions of catalytic methane reforming with carbon dioxide, the high conversion of CO_2 was also observed and the concentration of CO was ~80%. We obtained analogous results earlier [4] for the 6% Ni/Al_2O_3 sample. It is likely that in both systems, the main route of CO formation from CO_2 in methane reforming with carbon dioxide is reaction (II) of CO_2 with the surface carbon rather than a combination of reactions (III)–(IV).

CONCLUSION

Thus, in this work we showed that, on the 4% CoO/Al_2O_3 catalyst (as in the 6% Ni/Al_2O_3 system [4]) the main route of CO_2 transformation into CO in the process of methane reforming with carbon dioxide at 700°C is reaction (II), in which CO_2 directly reacts with the surface carbon. Carbon is formed by the decomposition of methane on the reduced cobalt. The initial form of carbon covers the surface cobalt crystallites and blocks further reaction with methane. Carbon agglomerates due to diffusion to form new states. Depending on time, one may isolate two such states, which have different heats of the reaction of CO_2 and the degree of cobalt blocking.

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