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The Mechanism of Methane Reforming with Carbon Dioxide: Comparison of Supported Pt and Ni (Co) Catalysts

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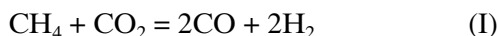
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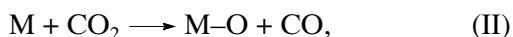
Abstract—The interaction of the catalyst 5.16 wt % Pt/ α -Al₂O₃ with CH₄, CO₂, O₂, and CH₄ + CO₂ pulses is studied using a setup involving the differential scanning calorimeter DSC-111 and a system for chromatographic analysis. Comparison of the results obtained with analogous data on Ni/Al₂O₃ and Co/Al₂O₃ suggests that methane activation occurs via a common pathway via dissociative chemisorption on the metal surface with the formation of H₂ and carbon on all the catalysts studied. Carbon dioxide activation on Pt/Al₂O₃ differs from its activation on Ni(Co)/Al₂O₃. It follows from the enthalpy of formation that carbon on Pt/Al₂O₃ is graphite-like in contrast to carbide carbon on Ni(Co)/Al₂O₃. This graphite carbon is more stable and less reactive.

INTRODUCTION

Methane reforming with carbon dioxide



is one of the promising processes for natural gas conversion. The mechanism of this reaction was studied by many authors (see, for instance, the review papers [1, 2]), but some important details of the process remain debatable. Among the catalysts for reforming methane, supported platinum-group metals or nickel/cobalt are the most active. Earlier we studied the mechanism of CO₂ reforming of methane on Ni/Al₂O₃ [3] and Co/Al₂O₃ catalysts [4], using a method combining the measurement of sample reactivity toward the pulses of separate reactants (CH₄, CO₂, H₂, and O₂) and their mixtures and continuous measurements of the calorimetric effect of these reactions. The results obtained made it possible to compare the rates of various routes of methane and CO₂ activation discussed in the literature [1, 2]. It was shown that, in contrast to the widespread opinion in the literature, CO₂ activation in the course of methane reforming does not occur via the oxidation of metallic nickel/cobalt and further interaction of surface oxygen with surface carbon,



but rather occurs via the direct interaction of CO₂ with carbon:



Moreover, it was shown that the state of carbon formed in methane decomposition on nickel/cobalt changes with time from a monolayer coverage to clusters and greater particles. Using calorimetric measurements of the heat of reaction (IV), we managed to determine the

enthalpies of formation ΔH_C^f of these forms of carbon. It was found that these values are noticeably higher than the values of ΔH_C^f for graphite and are close to that for carbide carbon. Since the chemical properties of platinum radically differs from the properties of nickel/cobalt, it was interesting to carry out an analogous study of the mechanism of CO₂ reforming of methane on Pt/Al₂O₃ and compare results with data for Ni (Co) catalysts.

EXPERIMENTAL

A sample 5.16 wt % Pt/ α -Al₂O₃ was prepared by the impregnation of alumina with a solution of H₂PtCl₆. Initial γ -Al₂O₃ ($S_{sp} = 220 \text{ m}^2/\text{g}$) was calcined at 1150°C for 20 h. According to XRD data, the resulting product contained only α -Al₂O₃ without admixtures γ -Al₂O₃ and θ -Al₂O₃ and had a specific surface area of 5 m²/g. The necessary amount of H₂PtCl₆ was dissolved in water, and the resulting solution was used to impregnate Al₂O₃. Then, the sample was dried at 120°C for 1 h and calcined in air for 1 h at 350°C.

The interaction of the sample with gaseous reactants was studied using a setup involving a differential scanning calorimeter DSC-111 and two gas chromatographs. The solid sample (100–150 mg) was loaded into a flow-type quartz cell, which was placed in a measuring channel of the calorimetric unit of DSC-111. Preliminary treatment of the samples included heating in a flow of air at 700°C for 60 min. To study the reduced state of a catalyst, the sample was treated in a flow of hydrogen at 700°C for 30 min. The interaction of the samples with reactants was carried out in flow and pulse regimes. In the case of the pulse regime, the sample was purged with specially purified helium pass-

Table 1. Data on oxygen consumption in alternating reduction (by an H₂ flow) and oxidation (air pulses) of the fresh sample Pt/Al₂O₃

Run	Temperature, °C		O ₂ amount, μmol	Q _{O₂} , kJ/mol O ₂	O*/PtO, mol %
	reduction	oxidation			
1	500	500	22.6	—	17.0
2	500	500	19.0	291	14.4
3	500	100	12.0	264	9.0
4	500	500	14.8	293	11.2
5	700	700	5.0	377	3.8
6	500	500	5.0	395	3.8

* The ratio of oxygen g-atoms consumed to the amount of PtO formed in the complete oxidation of supported platinum (264.5 μmol/g), %.

ing at a rate of 30 ml/min. The pulses of reaction gases (0.6 ml) were supplied into a flow of helium using a six-way valve. The flow that passed through a sample was analyzed using two chromatographs equipped with columns packed with Porapak N and zeolite 5 Å and thermal conductivity detectors. The system of analysis allowed us to determine the concentrations of CO₂, H₂, O₂, N₂, CH₄, CO, C₂H₆, and C₂H₄.

To characterize the concentration of gaseous reactants and reaction products, we used the ratio of each of the components to the initial pulse volume (as a percentage). This value was convenient for further calculations, but the sum of all the gaseous components after the reaction was not equal to 100%.

RESULTS

Reduction of Pt/Al₂O₃ by Hydrogen and Reoxidation by Oxygen

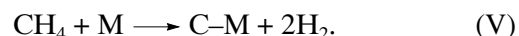
It was shown earlier [3, 4] that a comparison of redox properties of a catalyst at different temperatures makes it possible to characterize the state (the oxidation state) and the dispersity of the supported metallic component of the catalyst (the approach used by us is described in the subsequent discussion of the results below). Reduction was carried out in a flow of H₂ at 500 and 700°C. Then, the reduced sample was oxidized by a series of pulses of air, and oxygen consumption and the reaction heat were measured. The results are shown in Table 1.

It follows from this table that the amount of oxygen consumed was maximal (22.6 μmol O₂/g) in the course of the first reduction–oxidation run at 500°C. In the course of further runs at 500°C (Table 1, runs 2, 4), this value continuously decreased to 14.8 μmol O₂/g. A decrease in the oxidation temperature (run 3) also led to some decrease in oxygen consumption. The heat of oxidation practically remained constant (runs 2, 4). An increase in the temperature to 700°C led to a drastic

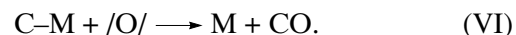
decrease in the amount of oxygen consumed (run 5). A decrease in the temperature to 500°C (run 6) did not restore the previous value. At the same time, the specific heat of oxidation drastically increased. However, taking into account a small amount of absorbed oxygen, the unusually high (~380 kJ/mol O₂) specific heat may be a result of measurement error.

Interaction of Pt/Al₂O₃ with Methane

In the interaction of Pt/Al₂O₃ with methane pulses at 700°C, the formation of hydrogen via the following reaction is observed:



After the reaction with methane, Pt/Al₂O₃ contains coke, which is rapidly removed in the form of CO₂ when oxygen pulses are admitted. Platinum surface blocking with coke leads to a rapid decrease in the amount of hydrogen evolved with the number of pulses (Fig. 1). After the first methane pulse, CO is also formed via the reaction of surface coke with the residual oxygen of the catalyst:



Preliminary treatment of the sample affects the formation of H₂ and CO. Figure 1 shows data on the formation of H₂ and CO in the reaction of Pt/Al₂O₃ with a series of methane pulses after preliminary reduction of the sample by hydrogen (1), reduction and reaction with seven pulses of CO₂ (2), reduction and reaction with one air pulse (3). It is seen that the results of runs 1 and 2 are almost identical: the yield of hydrogen drastically decreases from the first methane pulse to the second. Despite long treatment in a flow of H₂, the sample contained a certain amount of bound oxygen, which reacts with methane to form CO. Additional treatment with CO₂ pulses leads to practically no increase in the concentration of oxygen in the sample. Conversely, after the reaction with an air pulse, the amount of bound

oxygen in the sample increases, which leads to an increase in the amount of CO (Fig. 1, run 6). Simultaneously, the yield of H₂ in the first CH₄ pulse decreases, but it increases (compared to runs 1 and 2) when the second methane pulse is supplied (curve 3).

Figure 2 shows the results of the study of the effect of the time interval between CH₄ pulses on the amount of H₂ formed (we took a fresh portion of the catalyst for this run; therefore, the dependence of H₂ yield on the pulse number differs from the results presented in Fig. 1). It is seen that the dependences of H₂ on the pulse number when the time intervals between CH₄ pulses are 20 s and 10 min are very close.

Interaction with CO₂

When CO₂ pulses are supplied to the Pt/Al₂O₃ sample treated in a standard manner at 700°C, CO₂ consumption or CO formation was not seen (Fig. 3, pulses 1, 2). Preliminary treatment with methane leads to a drastic increase in CO₂ consumption and CO formation. Figure 3 shows CO formation in a series of CO₂ pulses (Fig. 3, pulses 6–8, 12–14) after the preliminary reaction of Pt/Al₂O₃ with three CH₄ pulses at 700°C (Fig. 3, pulses 3–5, 9–11). Carbon monoxide is formed in an amount that is twice as large amount as the CO₂ consumed, in agreement with the reaction stoichiometry



At a higher concentration of carbon, the concentration of CO increases (Fig. 4) but remains lower than 4.5–5.0%. When CO evolution is completed (Fig. 4, curve 1), further air pulses do not lead to CO₂ formation, which indicates that Pt/Al₂O₃ is cleaned of surface carbon by a series of CO₂ pulses.

Interaction with the CH₄ + CO₂ Mixture

Figure 5 shows the results of interaction of Pt/Al₂O₃ with pulses of the mixture 49%CH₄ + 49%CO₂ + 2%N₂ at 700°C. The maximal H₂ and CO formation is observed in the first pulse and then noticeably decreases. The admission of two air pulses (Fig. 5, pulse 11) restores the initial catalyst activity, whereas a pulse of 100% CH₄ (pulse 14) leads to a drastic decrease in the amount of H₂ and CO (pulse 15). In further pulses, the catalyst activity increases but does not reach the initial value.

Determination of the Enthalpy of Formation of Surface Carbon

In the preceding paper [4], to determine the enthalpy of surface carbon formation ΔH_C^f on Co/Al₂O₃, we measured the heat of reaction (VII). In this work, we made similar attempts, but they were unsuccessful because of the low intensity of the thermal signal in these runs (this is due to the lower reaction rate on

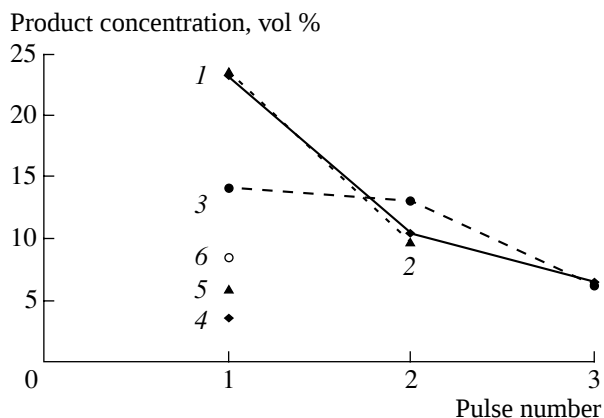


Fig. 1. Formation of (1–3) H₂ and (4–6) CO in the interaction of Pt/Al₂O₃ with CH₄ pulses at 700°C: (1, 4) sample preliminarily treated with H₂; (2, 5) reduced sample reacted with seven CO₂ pulses; (3, 6) reduced sample reacted with an air pulse.

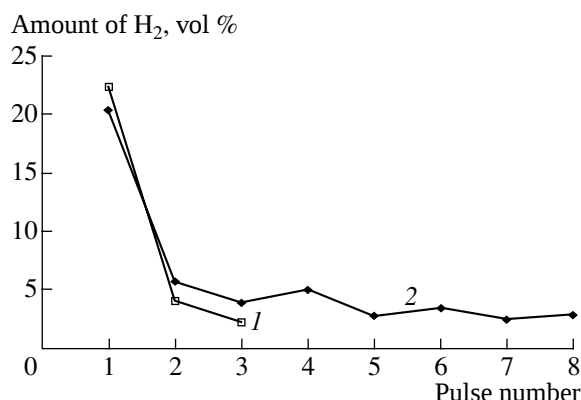


Fig. 2. Formation of H₂ in the reaction of Pt/Al₂O₃ with the series of CH₄ with intervals between pulses of (1) 20 s and (2) 10 min.

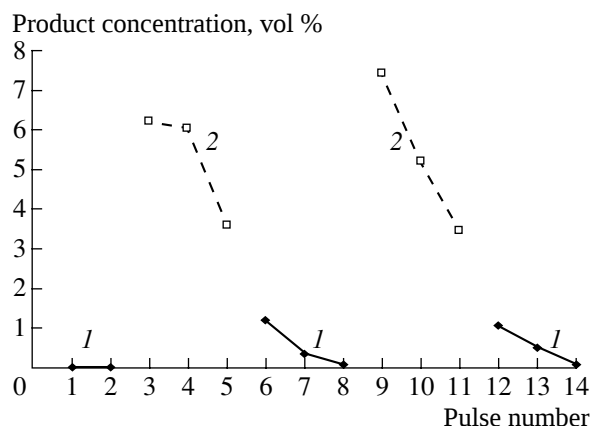


Fig. 3. Formation of (1) CO and (2) H₂ in the interaction of Pt/Al₂O₃ with the pulses of (1) CO₂ and (2) CH₄ at 700°C.

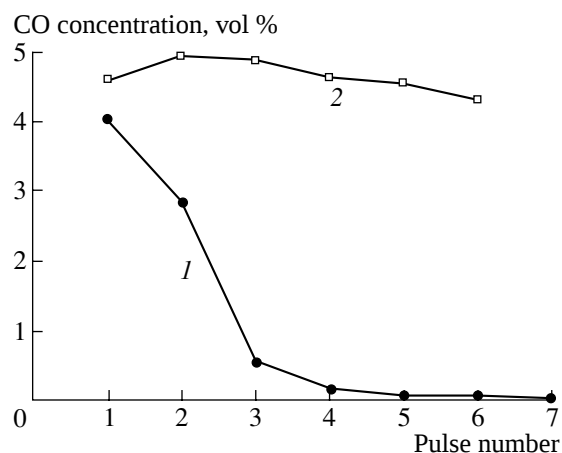
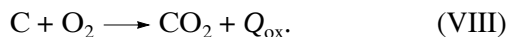


Fig. 4. Formation of CO in the interaction of CO₂ pulses with Pt/Al₂O₃ at 700°C after catalyst treatment by (1) two methane pulses at 700°C and (2) a methane flow at 700°C for 10 min.

Pt/Al₂O₃ at a relatively low specific heat of the reaction). Therefore, to determine ΔH_C^f , we measured the heat of carbon oxidation Q_{ox} :



Because for the Pt/Al₂O₃ system the intensity (and, correspondingly, the heat) of O₂ interaction with supported platinum at 700°C is rather low, it can be neglected and the thermal effect can be assigned to reaction (VIII) of coked Pt/Al₂O₃. The value of ΔH_C^f was calculated by the formula $\Delta H_C^f = Q_{ox} + \Delta H_{CO_2}^f$, where $\Delta H_{CO_2}^f$ is the enthalpy of CO₂ formation at 700°C (taken from handbook [5]). Table 2 shows the experimental and calculated data for ΔH_C^f . The average value over the two measurements is -4 kJ/mol and close to zero taking into account the scatter of values. This is typical of graphite carbon.

Table 2. O₂ consumption and heat evolution Q measured in the oxidation of Pt/Al₂O₃ with surface carbon at 700°C and the calculated values of the specific heat of oxidation Q_{ox} and ΔH_C^f

O ₂ , μmol	Q, mJ	Q _{ox} , kJ/mol O ₂	ΔH_C^f , kJ/mol
1.67	671.5	403	8
1.29	487.6	379	-16
Average			-4

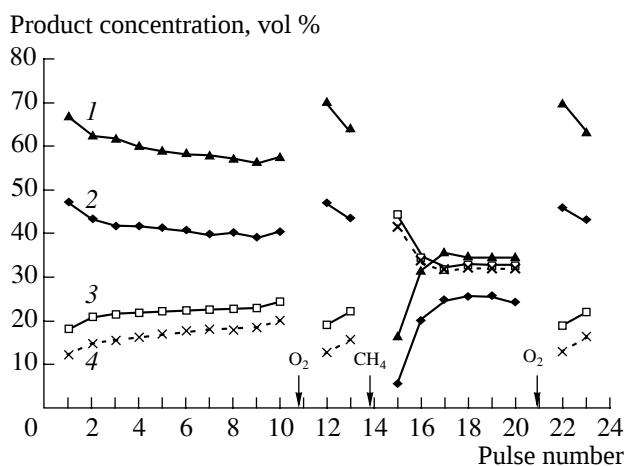


Fig. 5. Amounts of (1) CO, (2) H₂, (3) CH₄, and (4) CO₂ in the products of reaction of Pt/Al₂O₃ with pulses of the mixture 49%CH₄ + 49%CO₂ + 2%N₂ at 700°C.

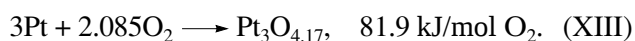
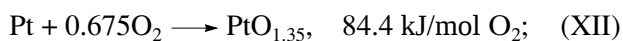
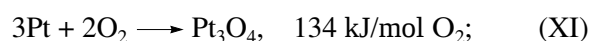
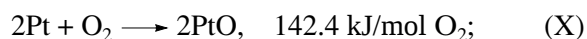
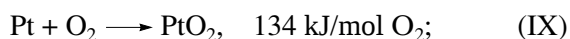
DISCUSSION

The State of Supported Platinum

In previous papers [3, 4], it was shown that, at temperatures of CO₂ reforming of methane (~700°C), supported nickel/cobalt can transform into oxides (NiO and CoO) or reduces to metallic particles by treatment with air or hydrogen, respectively. In an inert atmosphere, the resulting surface compounds are stable and allow reliable measurements of the amount of oxygen consumed and the oxidation heat to be made. The ratio of the amount of O₂ consumed by oxidation of nickel and cobalt catalysts (preliminarily reduced by hydrogen) at 100°C to the amount of O₂ consumed at 700°C characterizes the fraction of surface metal atoms in supported particles. Specifically, for the Co/Al₂O₃ sample, whose properties are compared in this work with the properties of Pt/Al₂O₃, the fraction of surface cobalt atoms measured in this way was 25%. Analogous experiments carried out using platinum catalysts show another pattern. Even the heating of the initial oxidized sample in a flow of helium to 500–700°C leads to the reduction of platinum particles. Correspondingly, the amount of oxygen consumed in the interaction of the reduced Pt/Al₂O₃ sample with air pulses at 700°C (see Table 1) is significantly smaller than the amount required for the complete oxidation of supported platinum into PtO. Oxidation at a low temperature (100°C) gives almost the same amount of consumed oxygen (Table 1). According to the conventional methods for measuring the surface area of supported platinum [6], the amount of chemisorbed H₂, O₂, or CO at 20–100°C corresponds to the number of surface metal atoms. It is likely that in our experiments on Pt/Al₂O₃ oxidation at both 100 and 700°C, O₂ chemisorbs without platinum oxide formation. Because we failed to oxidize all of the supported platinum in the experiment, in order to estimate the fraction of the surface atoms, the amount of

adsorbed oxygen was divided by the amount of oxygen in PtO calculated from the amount of platinum supported in the course of preparation. The results presented in Table 1 show that on the alumina used in these experiments the dispersity of supported platinum is only 17% after heating the fresh catalyst at 500°C. It continuously decreases in the course of oxidation–reduction treatments at 500°C and drastically decreases to ~4% after heating the sample to 700°C. Such an effect of a decrease in the dispersity of supported platinum in the course of sample heating above 700°C is known from the literature [7, 8].

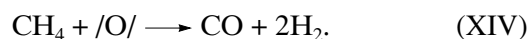
Data on the heat of oxidation (Table 1) characterize the energetics of this surface oxygen on Pt/Al₂O₃. According to the data on the enthalpies of platinum oxide formation [9], the heats of their formation in platinum oxidation should be



The values 260–290 kJ/mol O₂ measured by us are at least two times higher than those expected for possible platinum oxides. This fact suggests that the state of chemisorbed oxygen in the oxidized state of supported platinum differs from its state in platinum oxides. Sen and Vannice [10] compiled a set of data on the experimental heats of oxygen adsorption on Pt/SiO₂, which belong to the interval 210–290 kJ/mol O₂. Results obtained in this work agree well with these data.

The Mechanism of CO₂ Reforming of Methane on Pt/Al₂O₃

The mechanisms of CO₂ reforming of methane discussed in the literature differ in the degree of detail provided and in the choice of routes for methane and CO₂ activation. Usually, methane activation is considered as dissociative adsorption of methane on metallic particles (V) or reaction of CH₄ oxygen in various states on the catalyst surface:

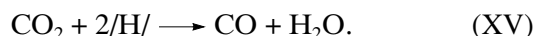


Three variants are possible for CO₂ activation:

(1) Two-step oxidation of metal and the further reaction of bound oxygen with surface carbon (reactions (II) and (III));

(2) Immediate interaction of CO₂ with surface carbon (IV); and

(3) The reaction of CO₂ with adsorbed hydrogen:



Earlier we showed [3, 4] that in the process of CO₂ reforming of methane on Ni/Al₂O₃ and Co/Al₂O₃, reaction (V) is the main route of methane activation, while reaction (XIV) is the secondary route. Carbon dioxide activation on these catalysts occurs via the second route (IV). Results obtained in this work make it possible to draw the same conclusion for Pt/Al₂O₃ catalysts as well.

The reactivities of Pt/Al₂O₃ and Ni(Co) catalysts toward methane are different [3, 4]. The latter are characterized by a rather low reactivity (complete oxidation of methane) in the oxidized state and high reactivity (dissociative chemisorption of methane) in the reduced state. Pt/Al₂O₃ actively reacts with methane after both reductive and oxidative treatments. The amount of H₂ formed in the first pulse of methane CH₄ is comparable with the amount of H₂ in the reaction of Pt/Al₂O₃ with the pulses of the CH₄ + CO₂ mixture. That is, as in the case of Ni(Co) catalysts, reaction (V) is the main route of methane activation. Treatment with air at 700°C (even for a long time) does not lead to a decrease in the conversion of CH₄, and a small amount of adsorbed oxygen held by Pt/Al₂O₃ at 700°C is removed after the first pulse of CH₄ in the form of CO and H₂O (a decrease in the amount of H₂) (Fig. 1, pulse 1). In this case, the residence time of CO in chromatography increases by ~1 min compared to the standard time required for CO analysis under the given conditions. This delay means that the CO evolved noticeably later than the time of contact of the CH₄ pulse with the sample (~1 s). It is likely that the relatively low rate of CO formation is due to diffusional limitations of the reaction of surface carbon and catalyst oxygen, as in the case of Ni/Al₂O₃ [3]. This reaction retards platinum surface coking, and this is clear from the higher activity of Pt/Al₂O₃ in the second pulse of CH₄.

In the reactions in the pulses of the CH₄ + CO₂ mixture, the catalytic activity of Pt/Al₂O₃ and Ni(Co)/Al₂O₃ also has different responses to the addition of oxygen. Air pulses increase the catalytic activity of Pt/Al₂O₃ toward CO₂ reforming of methane (Fig. 5), but they lead to a decrease in the conversion of CO₂ on Ni/Al₂O₃ [3] in an analogous experiment. This difference is explained by the fact that in the series of successive pulses of the CH₄ + CO₂ mixture, the catalytic activity of Pt/Al₂O₃ continuously decreased (Fig. 5, pulses 1–10) because of catalyst poisoning by coke. The introduction of oxygen leads to the fast oxidation of coke and the restoration of the initial catalytic activity. In the case of the Ni/Al₂O₃ system [3], CH₄ + CO₂ pulses do not lead to catalyst coking and a decrease in its activity under analogous conditions. In contrast, a pulse of air leads to the considerable oxidation of the nickel surface. This bound oxygen efficiently oxidizes surface carbon in the subsequent pulses of the CH₄ + CO₂ mixture and thus retards the activation of CO₂ via reaction (IV).

At 700°C the reactivity of Pt/Al₂O₃ toward CO₂ is much lower than the reactivity toward reduced Ni(Co) catalysts for which a 2–3% conversion of CO₂ into CO was observed [3, 4]. In the case of Pt/Al₂O₃, no CO formation was detected. This is probably due to the insufficiently high value of the binding energy of oxygen with the platinum surface, which can be judged from the value of the heat of oxidation, kJ/mol O₂: $Q_{ox} = 260\text{--}290$ (Pt/Al₂O₃), $470\text{--}490$ (Ni/Al₂O₃) [3], and $450\text{--}470$ (Co/Al₂O₃) [4]. This means that, as in the case of the Ni(Co) system, the activation of CO₂ via reactions (II) and (III) does not play an important role in CO₂ reforming of methane.

The rate of CO₂ reaction with surface carbon (IV) on Pt/Al₂O₃ is much higher than the rate of reaction (II). However, it is an order of magnitude lower than the rate of the analogous reaction on the Ni(Co) samples, and the maximal conversion of CO₂ (~2.5%) is much lower than the CO₂ conversion under conditions of catalysis at the same temperature (70–80%). It is likely that this is due to different properties of the surface carbon on Pt/Al₂O₃. Because a decrease in the rate of methane decomposition with an increase in the number of CH₄ pulses is due to site blocking with coke on the surface of metallic particles, the effect of the time interval between CH₄ methane pulses on the dependence of the H₂ yield on the number of pulses would point to the motion of surface carbon for the time between pulses. It was shown for Co/Al₂O₃ [4] that, in the interval 10–20 min after the formation of surface carbon in the decomposition of methane, carbon diffusion with the formation of its more stable form and a cleaning of the cobalt surface are observed. In this case the value of the enthalpy of formation (30–60 kJ/mol [4]) for this carbon is close to carbon in cobalt carbide. Conversely, in the case of Pt/Al₂O₃, the formation of H₂ in the series of CH₄ pulses with intervals between pulses 20 s and 10 min is practically identical (Fig. 2). This means that the form of carbon formed during first seconds after methane decomposition is rather stable under the reaction conditions. Calorimetric measurements suggest that the value of ΔH_C^f for this carbon is close to zero, and this value characterizes it as graphite carbon, in contrast to carbide carbon on Co/Al₂O₃.

Different states of carbon on platinum and nickel catalysts have been observed many times using microscopy, although in all cases the sample contained a large amount of carbon after long treatment under reaction conditions. These results suggest that, when the amount of coke in nickel and cobalt systems is large, the formation of carbon filaments and nanotubes is observed [11, 12]. On platinum, large agglomerates with an undefined indeterminate shape and containing graphite-like impurities are formed [13, 14]. Zaikovskii *et al.* [11] proposed a mechanism for carbon nanotube formation on

nickel according to which the process occurs via the intermediate formation of nickel carbide. In our experiments with a small amount of coke, there are only precursors of these bulk carbon particles, but the results agree well with the published data.

Different reactivities of carbon on Pt/Al₂O₃ and Ni(Co)/Al₂O₃ reveal themselves in different catalytic stabilities of these samples. In the pulse regime at 700°C, the catalytic activity of Ni(Co)/Al₂O₃ in CO₂ reforming of methane was stable and high [3, 4]. The activity of Pt/Al₂O₃ noticeably decreases with the number of pulse (Fig. 5). Additional coking of the Pt/Al₂O₃ catalyst due to a 100% CH₄ pulse decreases the yield of CO and H₂ (Fig. 5, pulse 15). In further pulses of the CH₄ + CO₂ mixture, the catalytic activity increases but does not restore the initial value. In the case of Co/Al₂O₃ in an analogous experiment [4], additional catalyst coking only lead to a slight reversible decrease in the catalytic activity.

Earlier we concluded that the interaction of CO₂ with the carbide carbon (IV) is the main route of CO₂ activation on Ni(Co) catalysts [3, 4]. In the case of Pt/Al₂O₃, the rate of reaction between CO₂ and graphite carbon cannot be responsible for the apparent conversion of CO₂ under catalytic conditions. The carbon species that has a shorter lifetime (less than a second) on Pt/Al₂O₃ is probably more reactive toward CO₂ than graphite carbon, and such short-lived carbon is the main intermediate in CO₂ reforming of methane.

Thus, in the course of CO₂ reforming of methane, carbon formed by methane decomposition (reaction (V)) participates in two competing processes: (1) a reaction with CO₂ (IV) to form CO and (2) an agglomeration with the formation of stable carbon. In the case of Ni(Co)/Al₂O₃ catalysts, this stable form of carbon is carbide carbon. It is highly reactive toward CO₂ and is an active intermediate of CO₂ reforming of methane. Moreover, carbide carbon does not block the surface of metallic particles. In the case of Pt/Al₂O₃, carbon is stabilized right on the platinum surface in a graphite-like state and blocks the catalytic sites. The reactivity of graphite carbon toward CO₂ is an order of magnitude lower than the reactivity of carbide carbon. This prevents it from being an active intermediate of CO₂ reforming of methane.

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