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Influence of the Mobility of Oxygen in a Complex Oxide Carrier on the Mechanism of Partial Oxidation of Methane

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Abstract—The catalytic partial oxidation of methane was studied over single channels of monolith catalysts Pt/PrCeZrO/α-Al_2O_3 and Pt/GdCeZrO/α-Al_2O_3 using the temporal analysis of products (TAP) and kinetic transients. Effects of catalyst composition, oxidation state, time offset between O_2 and CH_4 pulses on activity, selectivity and dynamics of product formation were elucidated. Realization of the direct pyrolysis–CH_4 partial oxidation route was reliably established. This route is favored by optimum lattice/surface oxygen mobility and reactivity controlled by the dopant type (Gd, Pr) and oxidation state of the complex cerium/zirconium oxide.

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INTRODUCTION

In the medium term the greater accessibility of natural gas compared to oil resources has stimulated development of technologies for its processing into valuable products [1]. In industry natural gas is used for manufacture of syngas (a mixture of CO and H_2) which is processes into high-cost products (alcohol, synthetic fuels, ammonia).

The manufacture of syngas by endothermic methane steam reforming features a high capital capacity and a low energy efficiency [2, 3]. Exothermic partial oxidation of natural gas is energetically more efficient [4]. Moreover, with oxygen as oxidizer, the H_2/CO ratio in the resulting syngas is close to two, which is quite suitable for the manufacture of methanol or liquid fuels [3].

Two reaction routes have been suggested for the catalytic partial oxidation of methane into syngas [5–7]:

(1) complete oxidation of part of methane into CO_2 and water, followed by steam and carbon dioxide reforming of the remaining methane molecules;

(2) direct pyrolysis–selective oxidation of natural gas.

In the first route, all oxygen is produced, with a strong heat release, in a narrow inlet part of the catalytic layer, after which the temperature falls down sharply in the main part of the catalytic layer due to endothermic steam and carbon dioxide methane reforming reactions. Probably, high temperatures at the inlet and efficient heat transfer along the catalyst layer in the endothermic zone pose serious problems in terms of catalyst stability and reactor design. In this connection of interest is to develop reactors operating at short contact times, in which syngas is manufactured by the pyrolysis–direct oxidation scheme [8–10]. Recent research show that the use such active components as precious metals (platinum, rhodium) applied to complex oxides of the fluorite structure (Ce–Zr–Me–O, Me = Pr, Gd, La) can favor direct oxidation of methane into syngas [11, 12]. The question of whether the reaction mechanism depends on such factors as mobility of oxygen in the lattice of oxide carriers or short-lived surface compounds is still under discussion. One of the reasons for the limited knowledge of the active component structure–catalyst activity interrelationship is that short-contact-time and high-temperature reaction mechanisms are difficult to study. In conventional reactors, reliable results are hardly obtainable because of heat and mass transfer which take place even in dilute mixtures and at high feed rates. On the other hand, use of spectral methods (IR spectroscopy, etc.) is prevented by strong radiation of samples at operating temperatures and extremely short lifetimes of intermediate surface compounds.

The pulse method of studying the dynamics of product formation on pulse feeding the reagents in a vacuum (Temporal Analysis of Products, TAP) seems to provide one of the most promising approaches for mechanistic studies [13, 14]. This method allows one to assess the effect of the oxidation level of a catalyst on its activity in direct methane oxidation, which is a challenging problem in the case of fast reactions at atmospheric pressure. The TAP technique makes it possible to fix a certain oxidation level of a catalyst and then to test the reactivity of the latter by its exposure to small methane pulses which scarcely affect the surface. Since the quantities of reactants in a pulse are very small, the TAP technique allows the effect of the oxidation level of the surface to be explored without complicating heat transfer effects. TAP data should be analyzed together with steady-state characteristics of catalyst activity at atmospheric pressure and with results of non-steady-state relaxation experiments on changing one mixture to another [15].

Until now TAP has been applied for research on powered catalysts placed as thin layers between layers of inert particles [13, 14]. For partial oxidation of natural gas at short contact times, block catalysts have been suggested, in which active components are applied as a thin layer onto walls of a ceramic or metallic carrier. The way in which active components (for example, platinum metals) are applied on even such relatively inert carriers as corundum or zirconium dioxide much affects their dispersity and reactivity. Active component–carrier interactions take even greater significance when these materials have a complex chemical composition [12]. The kinetics of the partial oxidation of methane into syngas at short contact times on block catalysts was proposed to be described using small structural elements of the blocks, such as short triangular channels (hollow trihedral prisms) [16]. This allows, due to the small amount of applied catalyst, to minimize and control temperature gradients and to provide required gas flow over the channel. This structural element is similar in design to Forzatti's reactor [17] in which the catalyst layer has the shape of a ring on the surface of inner inert ceramic tube, and narrow intertube space is bounded by gas flow. However, Forzatti's reactor was used exclusively for steady-state kinetic studies on hydrocarbon oxidation at atmospheric pressure.

In the present communication we report the first results of TAP and relaxation research on the mechanism of partial oxidation of methane on a complex active component Pt/Ce–Zr–Me–O (Me = Gd, Pr) incorporated in a block catalyst. Physicochemical and catalytic properties of powdered catalysts have been studied in detail and described in [11, 18–22].

First we studied the oxidized state of catalyst surface. This is important for understanding processes that occur at the inlet of block catalysts, where the highest oxygen concentration and temperatures are observed, and the catalyst works with maximum performance. At a low primary selectivity of the partial oxidation of methane, the final conversion of methane will be determined by the endothermic steam and carbon dioxide conversions of methane unreacted with oxygen. Under adiabatic conditions, these processes are controlled by a fairly slow heat transfer from the inlet part of the layer, which requires large-size reactors. Since oxygen adsorption occurs much faster than methane conversion on the surface [23], then, obviously, the active component in the inlet part of the layer will be mostly present in the oxidized state. Thus, the first criterion to rely on in choosing an active component for partial methane oxidation at short contact times is high primary CO selectivity of the oxidized surface.

EXPERIMENTAL

The preparation of complex fluorite-type $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_x$ and $Gd_{0.3}Ce_{0.35}Zr_{0.35}O_x$ oxides by a modified Pekini technique is described in [18–22]. The choice of these compositions was motivated by the fact that the mobility of oxygen in their lattices, as estimated by means of dynamic isotope exchange [11, 21, 22], is much different. After decomposing in air the complexes of metals with esters derived from polyethylene glycol and citric acid were calcined in air at 500°C for 4 h. The resulting powders were used for applying on corundum carrier channels (see below) and also as carriers for disperse Pt catalysts. Platinum was applied by impregnation (by moisture capacity) from an H_2PtCl_6 solution followed by drying and calcination at 500°C for 2 h.

Separate structural elements of block catalysts were cut out of a honeycomb block carrier (α-Al_2O_3) calcined at 1300°C (specific surface area 3 m^2 g^{-1}) as triangular channels (length 10 mm, wall thickness 0.2 mm, and triangle side length 2.33 mm) [16].

Powdered $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_x$ and $Gd_{0.3}Ce_{0.35}Zr_{0.35}O_x$ mixed oxides were peptized in a weak nitric acid (pH ~3) doped with 3 wt % of polyethylene glycol as surfactant for ultrasonication (T-25 disperser), until a stable zol with the solid phase concentration of 10 wt % formed. This zol was used for impregnating channels. After every impregnation stage the samples were calcined at 900°C in air, and the whole procedure was repeated until the applied oxide concentration reached 8–10 wt %. Platinum (1.4 wt %) was applied by impregnation (by moisture capacity) from an H_2PtCl_6 solution followed by drying and calcination in air 900°C.

Oxygen–surface bond strength was characterized by means of temperature-programmed desorption (TPD). Powdered active component, 20 mg, was placed in an isothermal zone of a high-temperature TAP reactor between layers of ground quartz (fraction 0.25–0.5 mm).

The same reactor was used to study the catalytic activity of separate structural elements (10 mm in length) under dynamic vacuum conditions. The reference gas in all experiments was argon. Before experiments, samples were heated to 800°C and treated with O_2/Ar pulses to remove residual carbon. The catalytic properties were assessed at 700°C by feeding pulses of O_2/Ar and CH_4/Ar mixtures (component ratio 1:1 in each mixture). First an oxygen pulse was fed and then, after a short delay (so-called flushing–testing mode), a methane pulse. The ratio between oxygen and methane pulses was such that the quantity of methane was double that of oxygen at a pulse size of 4.1×10^{15}–6.8×10^{15} molecules. Before TAP experiments with oxygen the sample was treated with O_2/Ar pulses (pulse size 3.6×10^{14}–2.4×10^{15} molecules) until dynamic saturation at every temperature. After that, not interrupting pulse feeding, the temperature was lowered to 250°C. Before starting temperature-programmed heating at a rate of 20°C/min, the sample was exposed to high vacuum for 10 min to remove weakly bound oxygen. Analysis of responses was performed on a quadrupole mass spectrometer with continuous control of *m/e* 32 (O_2), 16 (CH_4), 44 (CO_2), 28 (CO), 2 (H_2), and 40 (Ar). The CO responses were obtained from an analysis of *m/e* 28 ion currents minus the contribution of ionized fragments of CO_2 molecules, after the corresponding expansion of the ion currents of these molecules according to their fragmentation scheme.

Steady-state catalytic activity data at atmospheric pressure and short contact times were obtained in flow quartz reactors by the procedures described in detail in [12, 16]. The component concentrations were determined by chromatography and by means of infrared absorption sensors for CO, CO_2, and CH_4, a conductometric sensor for oxygen, and a polarographic sensor for hydrogen. The samples were preconditioned under O_2 at 700°C for 1 h.

Relaxation experiments at atmospheric pressure were performed in the same device in small quartz reactors. After preconditioning oxygen was displaced with helium (control by the zero point of the oxygen sensor) and then helium was displaced with a required reaction mixture. The composition of the mixture was continuously analyzed. Control experiments with a single-channel fragment of the corundum carrier showed that, at gas flow rates of about 30 l h^{-1}, the purge time of the system is no longer than 2–4 s.

RESULTS AND DISCUSSION

Steady-State Catalytic Characteristics

The catalysts studied in the range 650–800°C at a stoichiometric methane/oxygen ratio in the starting mixture (CH_4 4.5–20%) and contact times 4–15 μs ensured complete oxygen conversion. The conversion of methane and the selectivity in syngas varied over a wide range depending on the conditions of the process and the nature of the catalyst. Table 1 lists activity and selectivity data for the catalysts studied (contact time 15 ms, starting mixture 7% CH_4 + 3.5% O_2 in N_2.

Effect of temperature on the conversion and selectivity of partial oxidation of methane in the pulse mode. Pulse composition: 7% CH_4 and 3.5% O_2 in argon; contact time 15 ms

T, °C	Conversion, %	CO selectivity, %	H_2 selectivity, %	H_2/CO
		Pt/PrCeZrO		
650	52.9	43.5	72.5	2.5
700	60.6	60.6	81.8	2.1
750	72.9	74.9	89.6	2.0
800	87.6	81.8	94.1	2.0
		Pt/GdCeZrO		
650	35.7	9.6	27.6	4.3
700	57.8	41.5	70.4	2.6
750	83.9	73.7	90.8	2.2
800	94.5	83.5	95.3	2.1

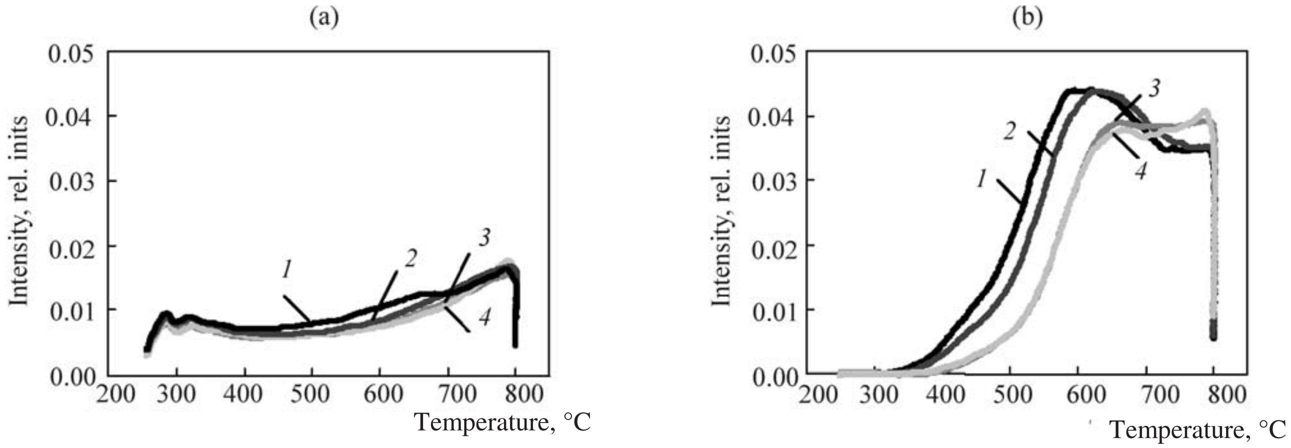

Fig. 1. Oxygen thermodesorption curves for samples doped with (a) gadolinium and (b) praseodymium, after their dynamic saturation with oxygen at (*1*) 550, (*2*), 600, (*3*) 650, and (*4*) 700°C.

In the lower temperature region, the methane conversion and CO selectivity of the praseodymium-doped sample are higher. At temperatures of about 800°C, the methane conversion and CO and H_2 selectivity of both samples are close to equilibrium values. The H_2/CO ratio at lower temperatures is higher than the equilibrium value 2 and approaches it as the temperature increases. This is probably associated with the preferential oxidation of CO to CO_2, on account of the fact that CO is retained on the catalyst surface, whereas hydrogen is readily desorbed into the gas phase. At higher temperatures, the H_2/CO ratio gets close to equilibrium [16].

The gadolinium-doped catalyst in steady-state conditions is more active at lower temperatures, which is manifested in the prevalence of complete oxidation and lower CO and H_2 selectivity. Dynamic isotope exchange data point to a higher mobility of oxygen in the praseodymium-doped complex oxide lattice [21]. These results are slightly unexpected and suggest a fairly intricate reaction mechanisms and presence of surface oxygen species differing from each other by bond strength, mobility, and reactivity. Obviously, insight in these aspects can be gained by means of nonsteady-state kinetic techniques, primarily TAP.

TAP Study of Partial Methane Oxidation

Oxygen Desorption under Dynamic Vacuum Conditions

The implementation of TAP for catalysts with a high oxygen capacity involves a number of problems. Platinum catalysts strongly adsorb oxygen, which prevents obtaining well-defined responses on oxygen pulses at thin coatings. At sufficiently thick coatings, oxygen slowly desorbs, which gives rise to the so-called "background effect:" Desorption appears as a continuous slowly descending tail above the background. Such a slow vacuum desorption affects the oxidation level of the surface and prevents complete saturation of the surface with oxygen, which can be realized when the gas phase is equilibrium with oxygen at a certain pressure. At the same time, dynamic saturation of the catalyst surface with oxygen, depending on pulse size and feeding rate. Under equilibrium conditions the desorption rate of oxygen is equal to the rate of its adsorption at pulse feeding, defined as the ratio of the quantity of oxygen adsorbed from a pulse to the time delay between two pulses.

To assess the oxygen–surface bond strength and oxygen mobility, we performed TPD experiments. The corresponding TPD patterns of oxygen after dynamic surface saturation at varied temperatures are shown in Fig. 1.

The gadolinium-doped sample features low-temperature oxygen desorption, whereas the praseodymium-doped sample begins to evolve oxygen above 350°C. Thus, doping the cerium/zirconium mixed oxide with gadolinium gives rise to more reactive weakly bound oxygen species which should be the first to take part in oxygen transfer to platinum over the carrier surface. At the same time, the total quantity of desorbed oxygen and the desorption intensity at high temperatures are higher for praseodymium-doped sample. This correlates with a greater mobility of oxygen in this sample, as follows from estimates by dynamic isotope oxygen heteroexchange [11, 21].

Under dynamic saturation conditions, the higher mobility of lattice oxygen during treatment provides a deeper penetration of oxygen into fluorite-type carrier particles, which reveals itself in its higher effective oxygen capacity. It should be noted that the dynamic isotope exchange technique [11, 20–22] failed to detect a weakly bound oxygen species on the surface of the gadolinium-doped sample. This species appears as a strong shoulder at ~250°C on the principal peak at ~280–290°C in the spectrum of the temperature-programmed reduction (TPR) of platinum-promoted samples of the given series with hydrogen [21]. In the spectrum of the praseodymium-doped sample, this shoulder is almost lacking, and the intensity of the principal TPR peak is several times higher than in the case of gadolinium.

Both catalysts are sufficiently active and selective in the partial oxidation of methane at temperatures above 600°C [18–20]. Obviously, under these conditions, oxygen desorption from the catalyst surface takes place, which makes impossible continuous coating of the surface with oxygen or its saturation. On the other hand, it is the mobility of oxygen in the lattice of fluorite-type oxides that is one of the most important factors that enhances activity of applied platinum in the partial methane oxidation to CO, compared to inert carriers.

To develop an approach to assessing the reactivity of a catalyst as a function of its oxidation level, let us identify three different states of a surface.

(1) “Evacuated” (gas-free) surface is fairly readily formed by vacuum treatment at high temperature, when the maximum possible quantity of oxygen is removed without a reducer. Such surface can simulate the state of a catalyst in the absence of oxygen.

(2) “Oxidized” state in TAP conditions is attained on dynamic saturation. This state can be simulated by any frontal layer at the catalyst inlet, where the oxygen concentration in the mixture is maximal. Probably, the low selectivity of methane conversion into CO and H_2 at the oxidized state of the catalyst will result in strong overheats. However, since the real reaction mixture contains methane, and the inlet temperature can be higher than 1000°C [23], it is obvious that the completely oxidized state is rarely realized in practice.

(3) As the catalyst is exposed to a big series of oxygen and methane pulses fed in succession in a 1:2 ratio, steady-state selectivity is attained. Such treatment brings the catalyst surface closest to the “working state” for partial methane oxidation at atmospheric pressure. The “working state” (WS) is not identical to the traditional steady state which takes place on prolong contact of catalyst with a flow of the reaction mixture of constant composition at certain temperature and pressure.

Research into the effect of small deviations of the surface from the WS gives information on the reaction mechanism. The state of the catalyst surface can be changed by exposure of the catalyst in the WS to oxygen pulses. This experimental strategy was realized in studying structural elements of block catalysts containing active Pt layer on the cerium/zirconium complex oxide doped with Pr or Gd. The WS was attained by feeding oxygen (1 part) and methane (2 parts) pulses at 0.5 s intervals (flashing–sample series). The oxidation level of the catalysts was varied by exposure to varied number of oxygen pulses. For reactivity assessment of the catalytic surface we used characteristics of the first 24 pulses in the flushing–sample mode after the oxidative series. All experiments on methane oxidation were performed at 700°C.

Praseodymium-doped Catalyst

The response of catalyst surface on methane and its oxidation products (H_2, CO, and CO_2) as a function of the deviation from the WS is shown in Fig. 2.

The response of unconverted methane (Fig. 2a) slightly decreases with increasing number of oxygen pulses. The decreased responses of H_2 and CO (Figs. 2b and 2d) and increased response of CO_2 (Fig. 2c) suggest that the CO selectivity decreases with increasing number of oxygen pulses, whereas the selectivity with respect to complete oxidation products increases. It should be noted that CO forms fairly slowly, as follows from the extended response for the WS. A fairly strong CO response is already observed at a “zero” time. This CO formation is associated with conversion of tightly retained CH_x fragments remaining after the preceding methane pulse in the “flushing–sample” sequence. Even though it is not quite clear, whether such a too slow CO formation and, as a result, insufficiently complete removal of CH_x fragments from the catalyst surface under conditions of TAP experiments, means that carbon deposits are also accumulated at atmospheric pressure; however, the very fact that CH_x fragments are present in the Pr-doped sample in the WS casts no doubts.

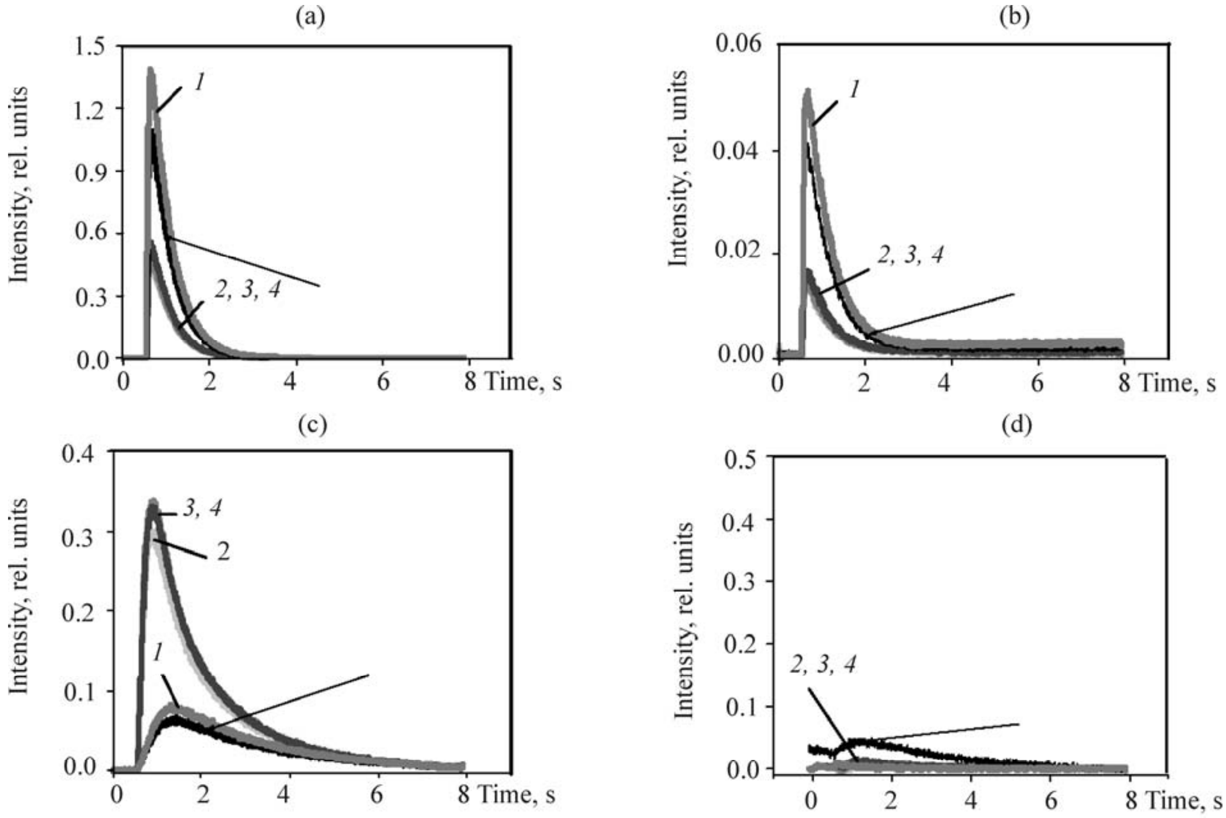

Fig. 2. Dynamics in the yields of (a) methane, (b) hydrogen, (c) CO_2, and (d) CO on exposure to methane pulses of the catalyst surface preliminarily treated with oxygen pulses. Number of oxygen pulses: (*1*) 5, (*2*) 20, (*3*) 50, and (*4*) 100. Catalyst: 1.4 wt % $Pt/Pr0_{.3}Ce_{0.35}Zr_{0.35}O_x/Al_2O_3$; 700°C; (WS) working state.

The results obtained at a great number of oxygen pulses (50 and 100) show that a stable hydrogen yield can be obtained even if the catalyst is highly oxidized. It should be noted that CO is always slowly firmed with this catalyst, which is likely to be explained by stabilization of CH_x fragments or CO molecules on the surface due to strong binding with high-charge Pr^{4+} cations. The fact that, as the oxidation level of the surface increases, CO formation is suppressed in preference to hydrogen formation suggests that such fragments scarcely contain hydrogen atoms, i.e. consist of carbon atoms or CO molecules.

Gadolinium-doped Catalyst

The effect of the oxidation level of the catalyst on its activity and selectivity is shown in Fig. 3.

Considerable responses of all the products suggest that CO formation occurs much faster than in the case of the praseodymium-doped sample. Moreover, comparison of the shapes of the CO and CO_2 responses shows that CO is formed as a primary product, since its signal sharply increases already during methane pulse. By contrast, CO_2 is a secondary product: It is formed slower. Noteworthy, H_2 and CO are formed almost concurrently, and no CO signal is observed at a zero time. Obviously, with the gadolinium-doped catalyst, methane transformations are not accompanied by accumulation of carbon particles on the surface. Comparison of these results with the oxygen TPD curves leads us to suggest that the higher rate of conversion of CH_x fragments into CO for this sample is associated with the presence of weakly bound surface oxygen species. Actually, as the oxidation level of the surface increases, the CO and H_2 responses increases after 20 oxygen pulses. It should be noted that in this case, too, the CO and H_2 responses have “tails,” implying decomposition of oxygen-containing, probably formate, complexes or oxygen diffusion from the bulk of the catalyst to its surface. With the praseodymium-doped sample, such CO and hydrogen

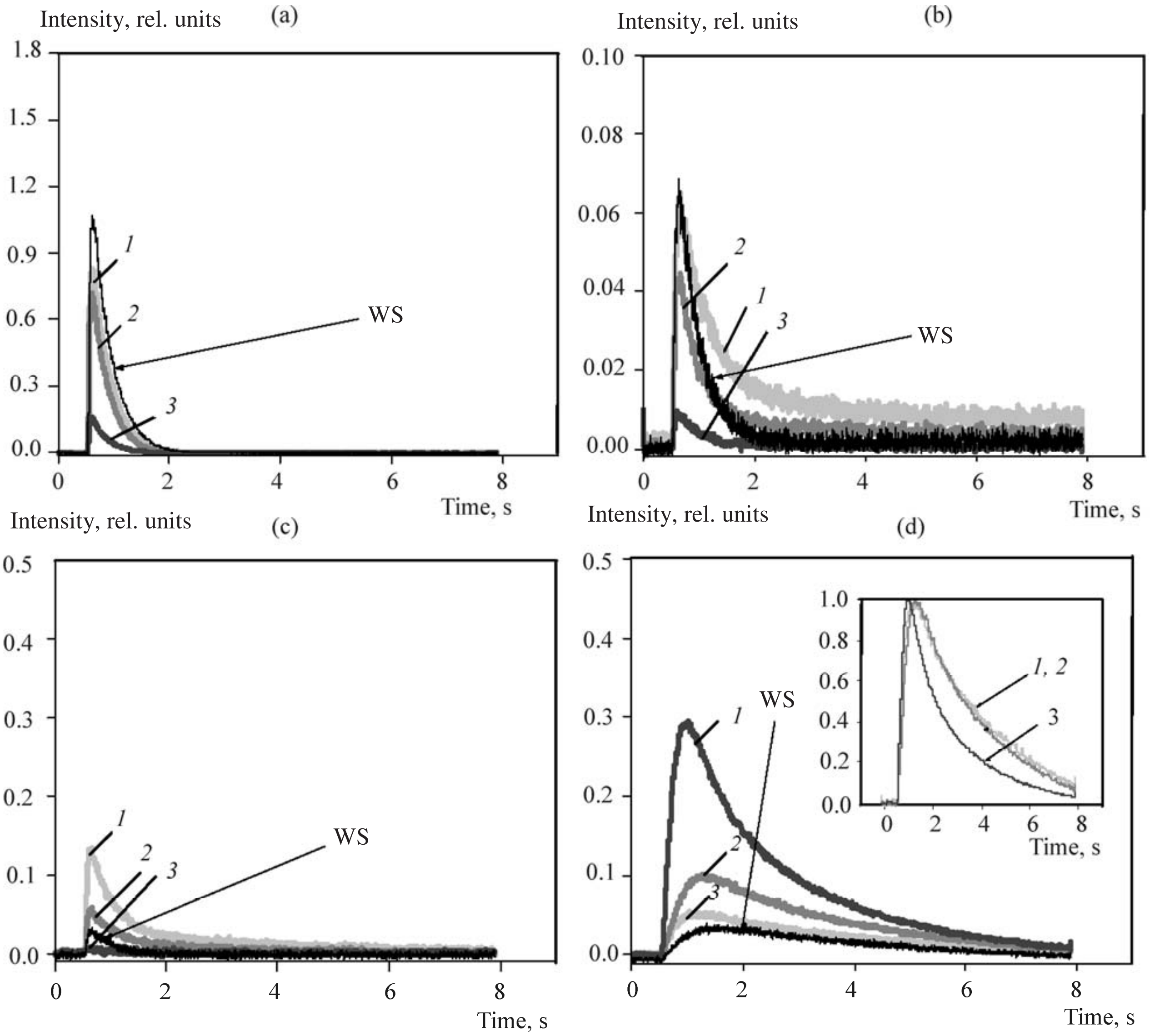

Fig. 3. Responses of (a) methane, (b) hydrogen, (c) CO, and (d) CO_2 to methane pulses for the “working” state of the catalyst after a series of 20–100 oxygen pulses. Catalyst: 1.4 wt % $Pt/Gd_{0.3}Ce_{0.35}Zr_{0.35}O_x/Al_2O_3$; 700°C. Number of oxygen pulses: (*1*) 20, (*2*) 50, and (*3*) 100.

liberation “tails” on a partially oxidized surface were lacking (Figs. 2b and 2d).

Further increase of the number of oxygen pulses decreases the intensity of CO and H_2 responses, whereas methane oxidation is much accelerated. Preliminary feeding of 100 oxygen pulses provides almost complete profound oxidation of methane. It is interesting to note that the normalized CO_2 response curves point to its much faster formation, implying that a different reaction mechanism is possible. Probably, this is associated with enhanced coating of platinum with oxygen, since saturation of the fluorite-like carrier surface with oxygen and the low mobility of oxygen in this oxide lattice hinders oxygen spillover.

Effect of Delay between Oxygen and Methane Pulses

In the experiments with varied delay between oxygen and methane pulses we studied the degree of oxygen spillover. Obviously, spillover occurs very fast on the “working” catalyst surface. To suppress spillover, the catalyst surface was enriched with oxygen to attenuate CO selectivity. With the Pr-doped catalyst, 5 oxygen pulses proved to be sufficient for this purpose, and with the Gd-doped system, 75 pulses were fed.

The effects of 0.1-, 0.5-, and 1-s delays between O_2 and CH_4 pulses were studied for both the catalysts.

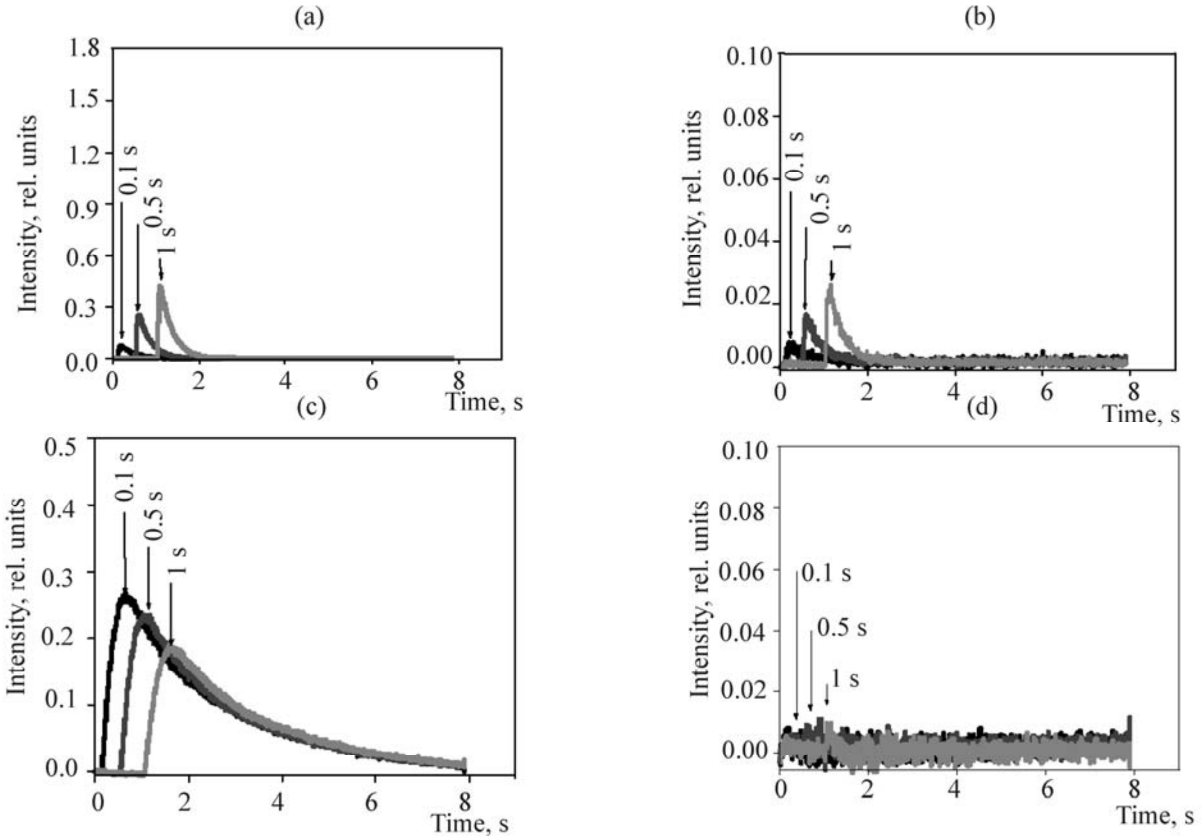

Fig. 4. Effect of pulse delay on the responses of (a) methane, (b) hydrogen, (c) CO_2, and (d) CO on exposure of the oxidized catalyst to methane pulses. Catalyst 1.4 wt % $Pt/Gd_{0.3}Ce_{0.35}Zr_{0.35}O_x/Al_2O_3$; after treatment with 75 oxygen pulses at 700°C.

Figures 4 and 5 compare product selectivities at varied pulse delays.

As seen, the H_2 selectivity of the Gd-doped catalyst is much dependent on pulse delay and decreases with decreasing pulse delay. The selectivity of the Pr-doped catalyst is only slightly dependent on pulse delay. Probably, the latter catalyst provides a more stable partial oxidation route due to a high mobility of lattice oxygen and accumulation of excess oxygen in bulk complex oxide particles, which compensates for its increased concentration in the gas phase. The sensitivity of the Gd-doped catalyst to pulse delay is probably explained by the occurrence on the oxide carrier surface of short-lived weakly bound oxygen species which, once an oxygen pulse has been fed, fast oxidize platinum-activated methane to CO_2. The limited mobility of oxygen in the gadolinium-containing complex oxide lattice preserves reactive oxygen on the surface. Moreover, as the pulse delay with the Pr-doped sample is decreased, sharp CO peaks characteristic of primary products and diffuse CO_2 peaks characteristic of secondary products of methane conversion.

The above information shows that the catalyst efficiency in partial oxidation of methane is determined by the relative contributions of the mobility of lattice oxygen and oxygen spillover between platinum and carrier. With the Gd-doped catalyst, the presence of a moderate quantity of oxygen on the platinum surface favors fast CO formation. Since hydrogen is mostly fast released (except for the Gd-doped sample, when its surface oxidation level slightly deviates from the WS), we can suggest that hydrogen is primarily formed due to fast dissociation of methane on the platinum surface, which requires no oxygen to occur. Even though one cannot a priory exclude the possibility that methane dissociates due to reaction with high-charge Pr^{4+} cations on the carrier surface, this issue should be further explored using a platinum-free carrier. On the other hand, hydrogen and CO are readily oxidized when there is much oxygen on the surface. In terms of the selectivity of methane oxida-

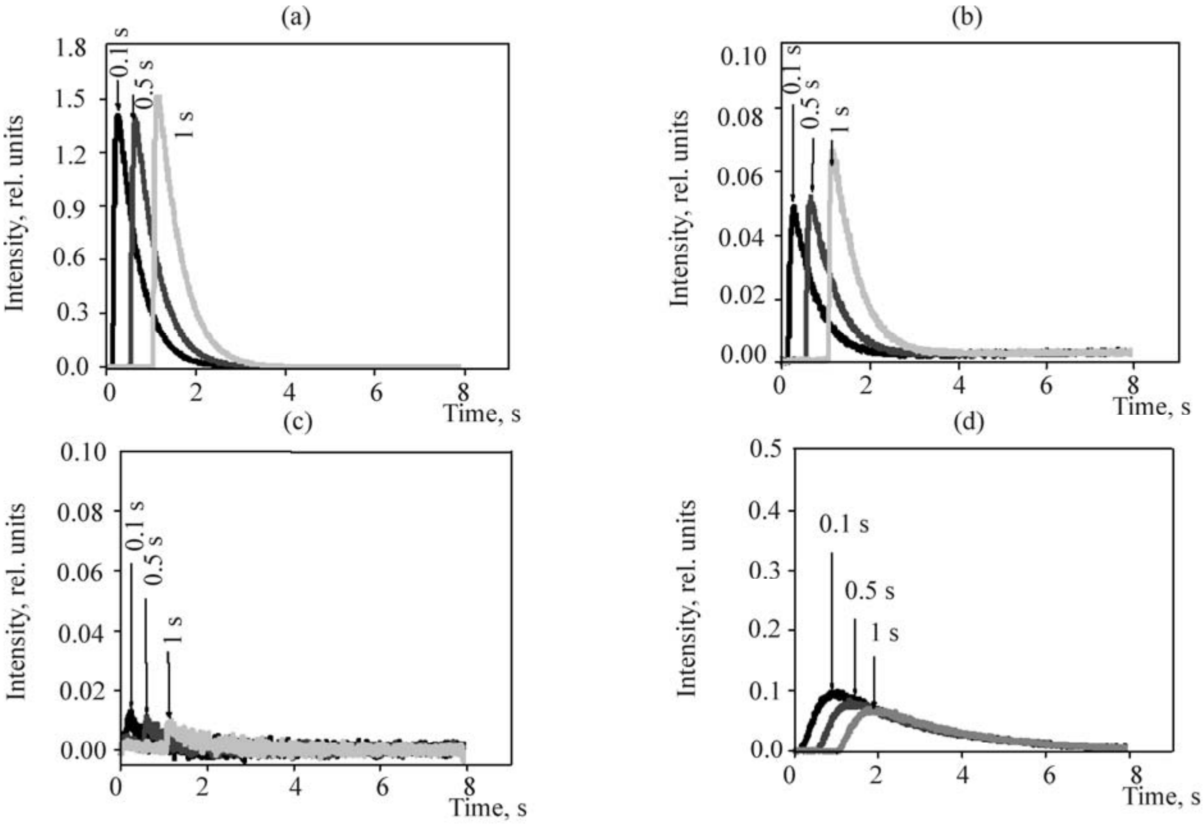

Fig. 5. Responses of (a) methane, (b) hydrogen, (c) CO_2, and (d) CO on methane pulses fed with various delay times. Catalyst 1.4 wt % $Pt/Pr_{0.3}Ce_{0.35}Zr_{0.35}O_x/Al_2O_3$; after treatment with 5 oxygen pulses at 700°C.

tion to CO, a mobile lattice oxygen is important for effective transfer of excess oxygen to the bulk of carrier particles, which decreases the oxygen coating of the surface. An optimal catalyst should combine a high mobility of lattice oxygen with a small number of active surface centers that ensure fast oxidation of CH_x fragments into CO.

Relaxation Experiments

Dynamic vacuum TAP data allow us to explain, to a first approximation, the difference in catalytic activity and selectivity between the Gd- and Pr-promoted catalysts. To assess the steady state of the surface at varied component pressures, we performed relaxation experiments at atmospheric pressure. Typical results of such experiments at 650°C and contact time 15 ms are shown in Fig. 6 and 7. Decreased contact time had no effect on the observed relaxations.

Of undeniable interest for understanding the reaction mechanism is the fact that the concentrations of hydrogen and CO pass through a maximum at fairly long (up to 600 s) relaxation times (Fig. 6). Much stronger changes are observed with the Gd-doped sample; therewith, the steady-state concentration of CO_2 (complete oxidation product) is established within much a shorter time. These results provide direct evidence for the importance of a certain intermediate catalyst oxidation level for the formation of partial methane oxidation products, which is consistent with TAP data. The higher mobility of lattice oxygen in the Pr-doped sample can be a factor that stabilizes the CO selectivity in time.

Analysis of initial relaxations (Fig. 7) allows certain conclusions as to the reaction mechanism [11] and compare them with TAP data. Thus, the large delay in the appearance of methane in the gas phase for the Gd-doped sample suggests stronger retention of methane on its oxidized surface compared to the Pr-doped sample. The same was observed in the TAP experiments, after the exposure of the “working” surface to 100 oxygen pulses (Fig. 3). With the Gd-doped sample, no CO or H_2 appear in the gas phase within 10 s, whereas traces of CO_2 are detectable. In

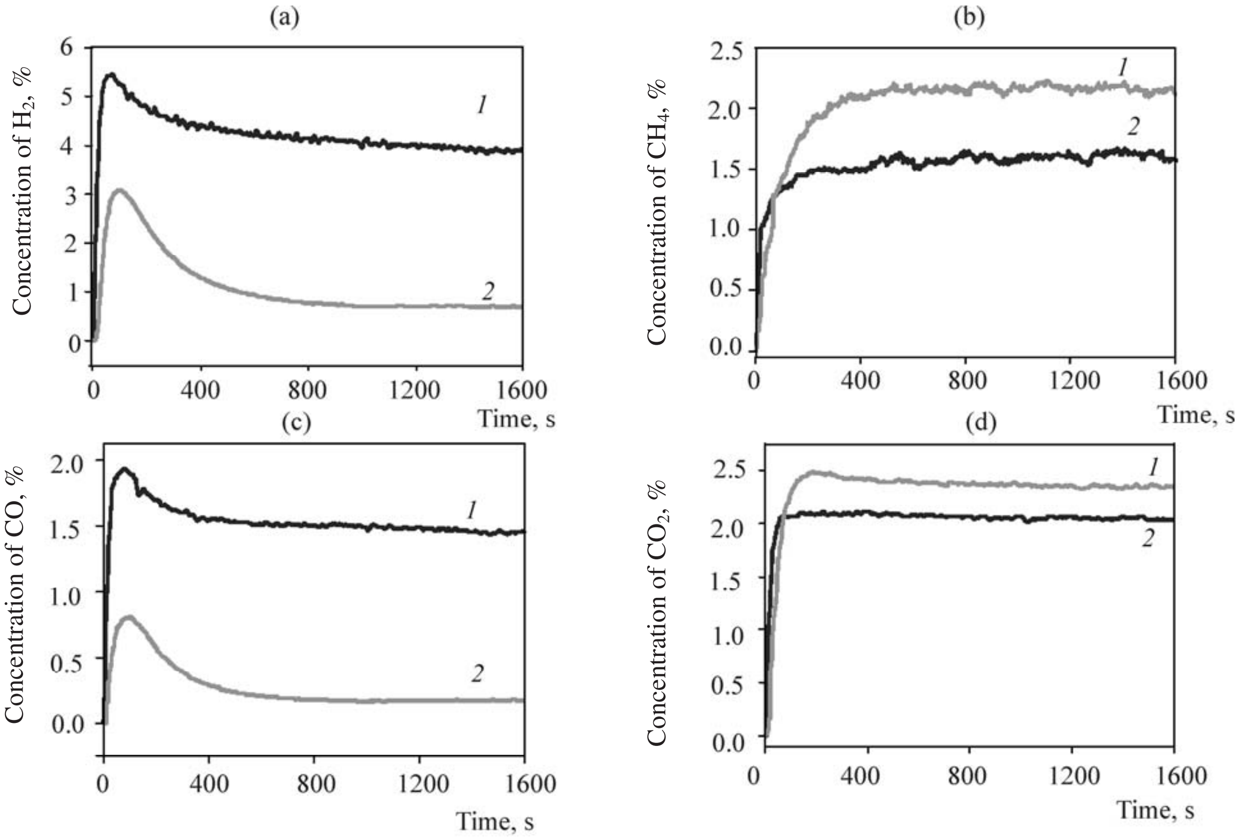

Fig. 6. Dynamics in the concentrations of (a) H_2, (b) CH_4, (c) CO, and (d) CO_2 in partial oxidation of methane for catalysts doped with gadolinium or praseodymium. Mixture 7% CH4 + 3.5% O_2 in N_2; contact time 15 ms; 650°C. Catalyst: (*1*) Pt/PrCeZrO and (*2*) Pt/GdCeZrO.

view of the TAP data, active oxidation of methane with weakly bound oxygen to form complexes (for example, carbonate–carboxylate) that decompose with liberation of complete oxidation products: CO_2 and H_2O. Hydrogen and CO in the gas phase appear almost simultaneously at contact times longer than 15 s, which can be explained both by consumption of weakly bound oxygen and by decomposition of surface complexes like formate ones.

In the case of the Pr-doped sample, hydrogen and CO appear almost simultaneously with methane, and CO_2 appears after a certain delay. These results show that even on the oxidized surface of this sample CO is formed by the primary pyrolysis–direct methane oxidation process, whereas complete oxidation products, by subsequent oxidation of CO and hydrogen. These results are nicely consistent with TAP data.

CONCLUSION

The effect of the oxidation level of the surface on the regularities of the oxidation of methane into CO and H_2 on platinum applied on complex cerium/circonium fluoride-type carries depends on the nature of the promoter cation in the carrier. In praseodymium-doped systems, CO formed in all the conditions studied. Hydrogen liberated shortly, and its quantity was only slightly dependent on the oxidation level of the sample. Moreover, the simultaneous presence of oxygen and methane introduced in pulses with short intervals does not result is a loss of CO and H_2 selectivity. Carbon monoxide is fairly slowly formed on a partially reduced "working" smple surface, probably, because CO or CH_x fragments are fairly strongly retained on the surface containing high-charge praseodymium cations. The Gd-doped sample does not retain CO. When the surfaces of both samples are in

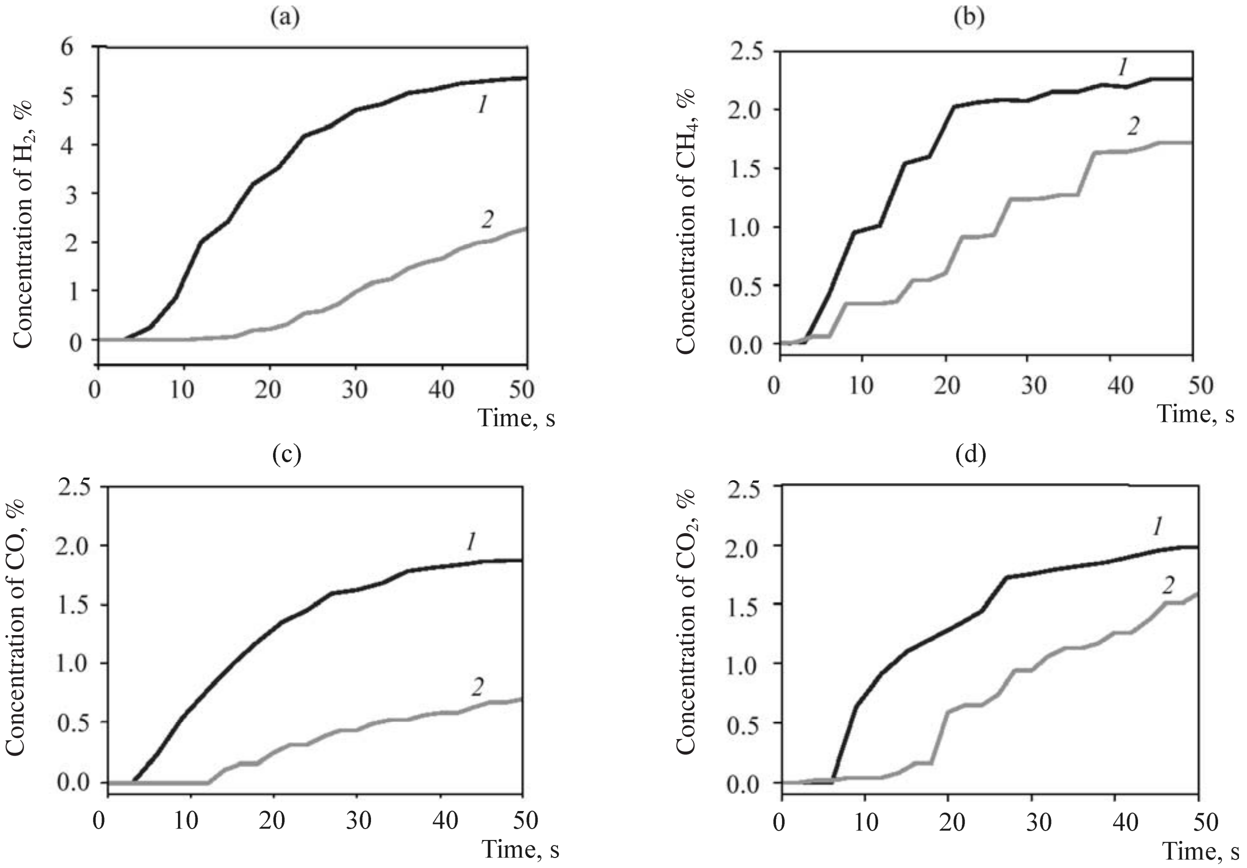

Fig. 7. Dynamics in the concentrations of (a) H_2, (b) CH_4, (c) CO, and (d) CO_2 in the initial period. Feeding the mixture of 7% CH_4 + 3.5% O_2 in nitrogen on oxidized samples; contact time 15 ms; 650°C. Catalyst: (*1*) Pt/PrCeZrO and (*2*) Pt/GdCeZrO.

the "working" state, the intensities and rates of hydrogen liberation compare with each other, implying that hydrogen is primarily formed by methane dissociation on platinum. When the surface of the Gd-doped sample in the WS was slightly more oxidized, "delayed" relaxations of hydrogen liberation are observed, on account of decomposition of formate-type surface complexes. In a general case, the increased surface oxidation level for the Gd-doped sample decreases the selectivity of partial oxidation until CO and H_2 disappear completely.

Comparing the catalytic characteristics of the samples were should note that under TAP conditions in dynamic vacuum the the surfaces of both samples in the WS can have much different oxidation levels, since a fixed oxidation level is impossible to ensure in view of the constant oxygen desorption at the working temperature. In terms of the reaction mechanism, one should separate the effects of surface oxygen and of the oxygen introduced together with methane or that fed in pulses with short delays after methane pulses. The latter circumstance was clearly demonstrated with the Gd-doped sample.

The results of TAP experiments are nicely consistent with the steady-state activities and kinetic relaxation characteristics of the samples at atmospheric pressure and provide clear evidence for the efficiency of the employed complex of methods for mechanistic research on partial oxidation of methane at short contact times.

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