Preferential CO Oxidation over Pt- and Rh-Catalysts under Conditions of Strong CO Adsorption[1]

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Abstract—Reaction of preferential CO oxidation is studied over Rh-, Pt-catalysts in a flow reactor made of quartz. In the experiments, the following parameters were monitored: catalyst bed temperature at the inlet to the catalyst bed and the outlet, residual CO content (with IR-analyzer), residual O_2 content (GC analysis). In CO absence from the reaction gas, H2 is easily oxidized over Rh and Pt, and the reaction proceeds in the mode of catalytic surface ignition (CSI) with the "hot spot" at the inlet to the catalyst bed. Appearance of CO in gas at temperatures at least below 200°C leads to slow deactivation of the catalysts. The possibility of CSI mode realization under PROX conditions over a Rh-catalyst is shown. The key component of the reaction in this case is O_2—its residual content in CSI mode is less than 100 ppm. It is found that in CSI mode, a decrease in temperature increases selectivity of the reaction. Disestablishment of CSI (extinction) is accompanied over a Rh-catalyst by oscillations in catalytic activity. Possible mechanism of this oscillation phenomenon is proposed in connection with catalyst deactivation by CO at the inlet to the catalyst bed and with CSI at the outlet.

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Various processes employing hydrogen (fuel cells for cars and stationary units, hydrogenation processes including ammonia synthesis, gas separation by membranes of Pt-group metals) are sensitive to presence of CO in H_2. Development of these technologies in recent decades has led to intensive research on purification of hydrogen and hydrogen-containing gases obtained by oxidative conversion of hydrocarbon raws from CO admixture.

According to literature, the process of catalytic CO oxidation to CO_2 (preferential CO oxidation, or PROX CO if in H_2 presence) is the most efficient, in particular, over systems based on noble metals of Group VIII.

Studies of preferential CO oxidation started in the 1960s with the purpose of bettering the pre-treatment of the reaction gas of ammonia synthesis. Nowadays, such research is focused on the prospects of PEM fuel cells, platinum anodes of which are poisoned by CO admixture.

One of the possible applications for fuel cells is automotive transport, the demand existing for a quite compact unit of hydrogen generation/purification with a sufficiently high throughput. This gives an incentive for the development of a highly active and selective catalyst of CO removal. According to the evaluations made in [1], a ~50 kW fuel cell would require a throughput of 60 m^3/h of hydrogen-containing gas at hydrogen content ~ 65 vol %. Purification of such gas down to some dozens ppm of CO (initial CO content being ~1 vol %) requires addition of oxygen above the stoichiometric amount (0.5 vol %).

Because the reactions of CO, H_2 oxidation are strongly exothermic, a combination of high throughput and significant content of oxygen in gas leads to substantial release of heat. Correspondingly, when the heat flow created by reaction surpasses the heat flow dissipated from the reaction zone, a spontaneous transfer of the reaction into the outer diffusion region may take place resulting in a sudden increase in temperature and also in conversion of the key component. This phenomenon has been called the catalyst surface ignition (CSI) by Frank-Kamenetskii [2].

As we have shown for Ru-based catalysts [3], also Pt−Ru [4], PROX CO can change into the CSI mode. In this mode, a significant temperature gradient is established along the catalyst bed.

Surface ignition and extinction is described for Pt- and Rh-catalysts in a number of works: for Rh/SiO_2 in stepwise heating/cooling [5]; for honeycomb Pt-catalysts in linear heating/cooling [6, 7]; in stepwise increase/decrease in O_2 concentration in initial mixture [7, 8].

In works [9, 10], a small change in temperature led in certain situations to rapid growth of CO conversion in PROX CO over a Pt- [9] and a Rh-catalyst [10]. The authors connected the observed phenomenon with ignition. Still, the role of ignition in these experiments through possible changes in temperature profile of catalysts were not taken into consideration.

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[1] The article was translated by the authors.

If Ru-catalysts are known for strong adsorption of oxygen [3, 11], then for Pt and Rh it is strong adsorption of CO that is typical, as follows from reference and this very work. This feature is the reason for catalyst deactivation observed over Pt [9, 12–14] and Rh [12].

In this work, the effect of strong CO adsorption on PROX CO is studied over Pt-, Rh-catalysts. Experiments were performed in the set-up used earlier for the studies of PROX CO [3, 4, 11].

EXPERIMENTAL PROCEDURE

Preparation of Catalysts and Gas Mixtures

Crushed commercial extrudates of γ-Al_2O_3 (Ryazan NPZ, Russia, type A-64k; specific surface 200 m^2/g; fraction 0.200–0.315 or 0.250–0.315 mm) were used for support. Alumina was calcined in air for 2 h at 500°C before impregnation with active component.

Hexachloroplatinic acid or rhodium chloride were dissolved in excess of distilled water. Alumina was put into the solutions and kept there until the color of the liquid disappeared. After that the excess of liquid was decanted, the sample was rinsed with water and dried at 120°C.

Catalyst loading was 0.20–0.23 g (no dilution of catalyst by inert packing was used). The catalyst was reduced after loading by hydrogen-containing gas with admixture of 1% O_2. Catalyst activation will be considered in detail in a separate paper.

Activation was monitored by residual oxygen content at the reactor outlet in the course of linear heating. The final stage of activation was performed in hydrogen, at a temperature higher than the mark for complete oxygen conversion by ~30–50°C, but not higher than 270°C.

Initial gas mixtures were composed after preliminary evacuation of the gas cylinder and controlled by pressure of components (with digital manometer of precision 0.01 atm). Following gases were used: H_2 (standard TU 6-20-00209585-26-07), CO_2 (standard GOST 8050-85), N_2 (Grade B, standard TU 6-21-39-79); CO was prepared by decomposition of formic acid.

Special gas mixtures were composed by Balashikha Oxygen Plant for calibration and fine-tuning of IR-analyzer, in particular, for its CO channel—the bulk component was He or N_2, and CO content was in the range 8 ppm—0.8 vol %.

Catalytic Experiments

Experiments were performed in a flow set-up with quartz reactor [3, 4]. Gas flow rate was measured by digital flow meter IRG-1000 (discreteness 1 ml/min) and calculated for normal conditions (760 Torr, 0°C). Gas exiting the reactor was dried if the original mixture contained water (at 0°C) and split in two streams by precision valves for IR and GC analyses. GC analysis was performed on CO, CH_4, O_2 (TCD, zeolite 13 X). Content of CO and CO_2 in the main part of split flow was monitored for dried gas by 2-channel IR analyzer BINOS 100 (CO channel: range 0–9999 ppm, discreteness 1 ppm; CO_2 channel: range 0–25 vol %, discreteness 0.1 vol %).

The error in CO concentration measured in gas was determined by the errors in preparation of calibration gas mixtures. At small contents of CO (~20 ppm and less) it did not exceed 1–2 ppm.

Quartz reactor was of tubular form in order to heat the vapor-gas mixture at high flow rates (ID ~ 0.5 cm while that of the oven ~50 cm). Reaction gas was fed to the inlet of the reactor. For the placing of catalyst the reactor was fitted with a quartz matt insert. Height of the catalyst bed was ~1.4–1.6 cm. Two measuring chromel-copel thermocouples (case OD = 0.1 cm, stainless steel) were inserted into the catalyst bed through a joint connection and fixated at 1–2 mm from surfaces of the catalyst bed.

Accuracy of temperature measurements was 0.1°C. For studies of Rh-catalysts, an additional thermocouple was placed at ~25 mm above the top of catalyst bed measuring gas temperature.

Oven temperature was controlled by a multichannel processing unit through a thermocouple placed near the electric spiral in the oven case. Different channels of the processor were used for controlling the temperature of catalyst bed in two spots (inlet to the catalyst bed—"top," outlet—"bottom"), gas temperature; also for processing the analogue signal of the CO channel of IR analyzer.

O_2 conversion was calculated from the areas of corresponding chromatographic peaks (small changes in gas space velocity connected to H_2 and CO transformation were neglected).

Selectivity of O_2 consumption in CO oxidation was calculated usually as follows:

$$S = 0.5 C_{CO}^0 X_{CO}/(C_{O_2}^0 X_{O_2}), \qquad (1)$$

where X_{CO}, X_{O_2}—conversion of CO, O_2; C_{CO}^0, $C_{O_2}^0$—initial concentration of CO, O_2.

EXPERIMENTAL RESULTS

H_2 Oxidation over Pt and Rh: CO Influence

Effect of CO on oxidation of hydrogen over Pt is illustrated in Fig. 1 as the reduced catalyst was subjected at room temperature to alternating feeds of two gas mixtures, one containing O_2, H_2, N_2 and another, CO, O_2, H_2, N_2. (Catalyst which had performed in PROX CO was reduced before these experiments at 270°C in H_2 flow for 2 h.)

Hydrogen is easily oxidized over Pt when the mixture with just O_2, H_2, N_2 is fed on. The moment when
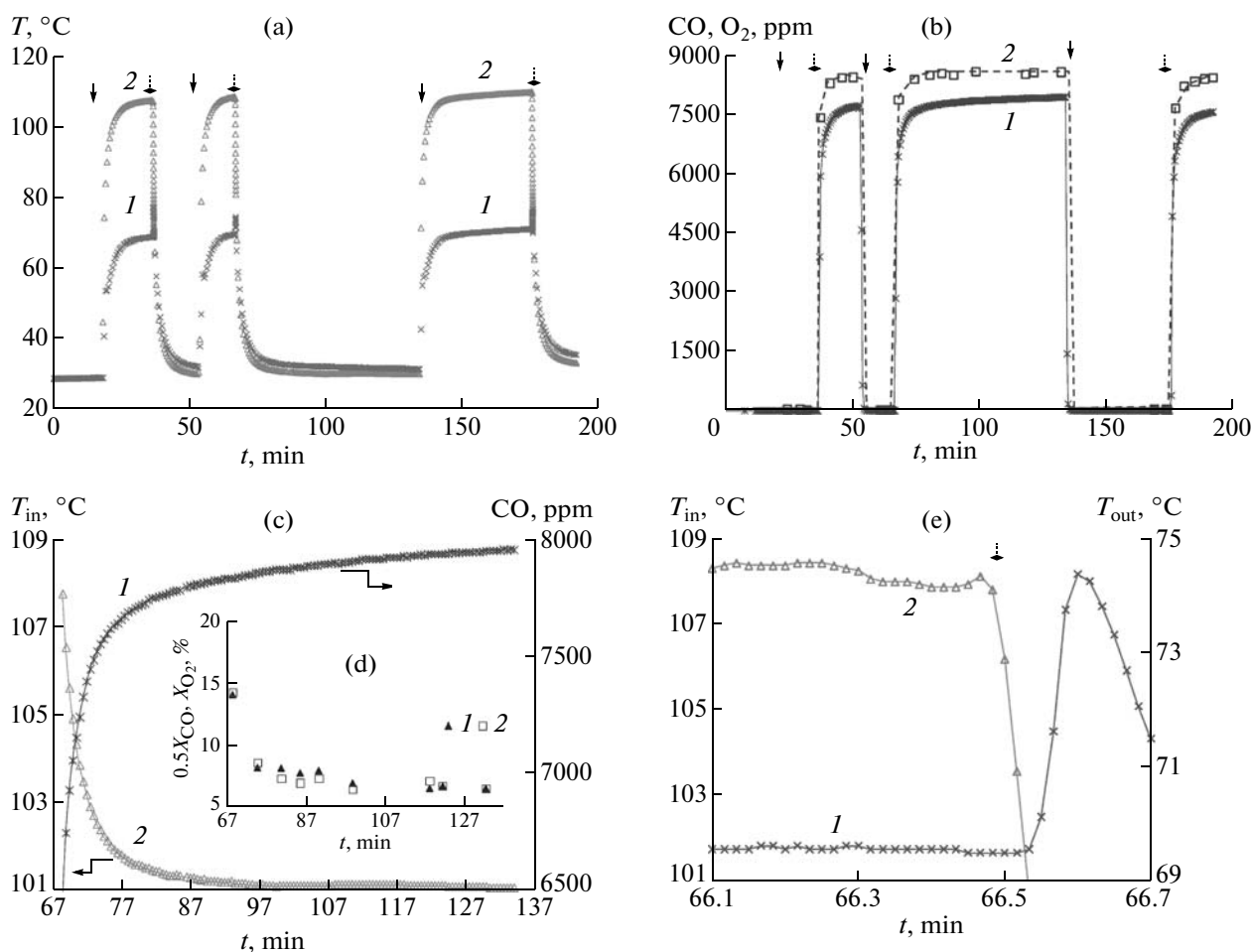
Fig. 1. Behavior of 1% Pt/Al$_2$O$_3$ in alternated feeds of two gas mixtures, one with CO, one without. Solid arrow points at the starting moment of the first mixture feed, composition, vol %: O$_2$—1, H$_2$—60, N$_2$—rest; dashed arrow, the second mixture: O$_2$—0.92, CO—0.93, H$_2$—62, N$_2$—rest. Gas flow rate 48 l (g Cat)$^{-1}$ h^{-1}. (a) Records of temperature in the catalyst bed. *1, 2*—Temperature at the bottom and the top of the catalyst bed, correspondingly; (b) record of residual content of CO (*1*) and O$_2$ (*2*); (c–e) a switch was made at 66 min to the CO-containing mixture: (c) record of residual content of CO (*1*) and of temperature at the top (*2*); (d) record of halved value of CO conversion (*1*) and of O$_2$ conversion (*2*); (e) record of temperature at the bottom (*1*), at the top (*2*).

this mixture was switched on after reduction in hydrogen (Fig. 1a, 18 min) showed a sharp increase in catalyst temperature: ~107°C at the top, ~69°C at the bottom. In this, a decrease in oxygen content was detected at the outlet down to ~40 ppm (Fig. 1b, 25 min). Appearance of CO in gas (switching of feed mixtures occurred at 36 min) led first to rapid, then to slow decrease in catalyst temperature (Fig. 1a). Repeated runs without CO (Fig. 1a, 53 and 134 min) and with CO (Fig. 1a, 66 and 175 min) reproduced the patterns already seen: catalyst heated up in gas mixture without CO and cooled down when CO was in the gas mixture. Thus, catalyst deactivated in contact with CO, regaining its activity quickly from the moment CO was excluded from the gas mixture—just like a freshly-reduced sample (Figs. 1a, 1b).

The manner in which catalyst activity declines with time when CO is present in gas can be seen from Figs. 1c, 1d which show the range 67–137 min. Residual CO content grew slowly with time after the change in gas composition (a delay shorter than 2 min should be mentioned for IR-analyzer), while catalyst temperature did otherwise. In Fig. 1d, conversion of oxygen is compared to halved value of CO conversion. At equal concentrations of CO and O$_2$, the ratio of values mentioned above gives the selectivity of O$_2$ consumption in CO oxidation (Fig. 1d, curve *1*). As seen from the figure, the curves of O$_2$ conversion and halved value of CO conversion lay in close proximity, which gives selectivity ~1. This means that oxygen is consumed only in CO oxidation (appearance of CO$_2$ is confirmed by the data from the CO$_2$ channel of IR-analyzer).
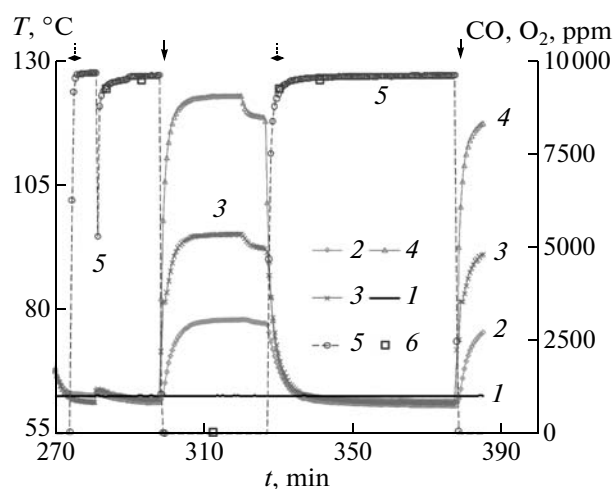
Fig. 2. Behavior of 1% Rh/Al_2O_3 in alternated feeds of two gas mixtures, one with CO, one without. Solid arrow points at the starting moment of the mixture feed, composition, vol %: O_2—1, H_2—60, N_2—rest; dashed arrow, the mixture: O_2—0.97, CO—0.97, H_2—63, N_2—rest. Temperatures of: oven (*1*), gas (over the top) (*2*), bottom (*3*), top of the catalyst bed (*4*) correspondingly; *5, 6*—residual content of CO (*5*) and O_2 (*6*) correspondingly. In the range 274–280 min reactor was bypassed. Gas flow rate ~42 l (g Cat)$^{-1}$ h^{-1}.

After the switch of gas to CO-containing one, there was a rapid decline in temperature at the top while temperature at the bottom increased after some delay and gradually went through a maximum. The delay between the start of temperature decline at the top and aforementioned temperature maximum at the bottom was ~0.1 min (Fig. 1e).

Reduced Rh-catalyst behaves similarly (Fig. 2). Thus, a switch from H_2 to a mixture composed of (vol %): 0.97 O_2, 0.97 CO, 63 H_2, balance—N_2 (bypassing the reactor at first) at constant oven temperature ~63°C (curve *1*) has led first to a small overheat along the catalyst bed starting from 280 min (curves *3*, *4*). Nevertheless, after some minutes temperatures of bottom and top (curves *3*, *4*), and also residual contents of CO, O_2 (curve *5* and a set of experimental points *6*, correspondingly) almost returned to initial values. Then, when at 297 min the CO-containing mixture was switched to the mixture which does not contain CO, temperature of top (curve *4*) rose in a jump and topped that of the bottom (curve *3*) by 28 K; in this, almost complete consumption of oxygen (~40 ppm, 312 min) was observed. A small reduction in temperature at 320 min was connected with the decrease in gas flow rate from 46 to 42 l (g Cat)$^{-1}$ h^{-1}. Return to CO-containing mixture at 326 min "killed" the reaction while the repeated run with CO-free mixture "kickstarted" it. Note that there is a delay not exceeding 2 min between the records of gas temperature (curve *2*) and temperature of catalyst bed at the
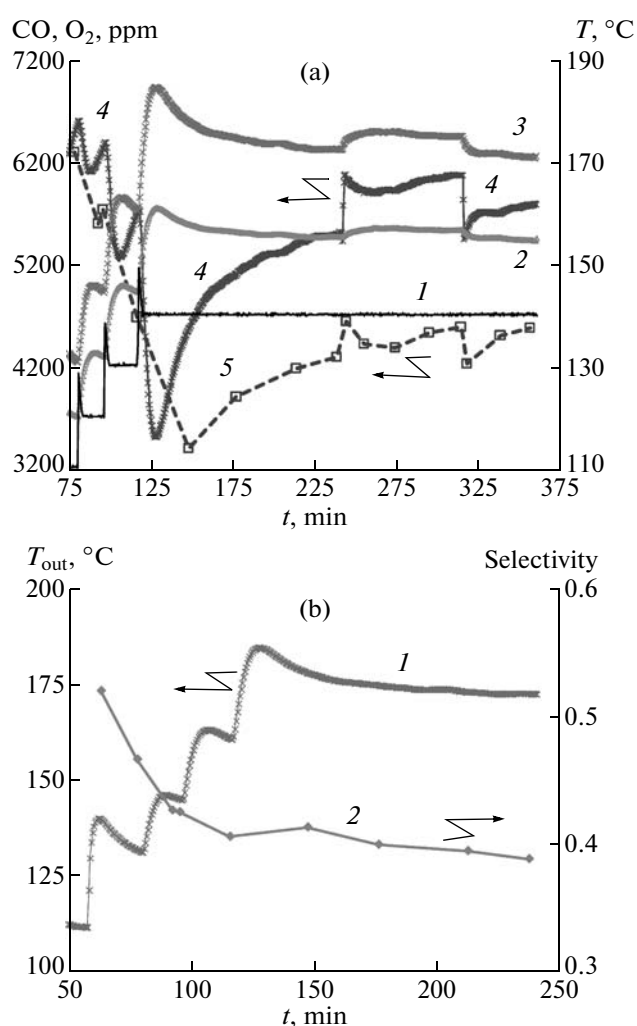

Fig. 3. PROX CO over 1% Pt/Al_2O_3. In the ranges 0–241 min, 314 min—forward the gas composition was, vol %: O_2—0.75, CO—0.75, H_2—56, CO_2—18, H_2O—22, N_2—rest. Gas flow rate 85 l(g Cat)$^{-1}$ h^{-1}. In the range 241–314 min the gas composition was, vol %: O_2—0.77, CO—0.77, H_2—57, CO_2—0, H_2O—21, N_2—rest. Gas flow rate 97 l(g Cat)$^{-1}$ h^{-1}. Records obtained in stepwise heating and prolonged exposure to temperature are shown for: (a) temperatures of: oven (*1*), top (*2*), bottom (*3*) correspondingly; residual content of CO (*4*) and O_2 (*5*); (b) temperature at the bottom (*1*); selectivity (*2*).

top—heating/cooling of catalyst affects heat transfer in the reactor which is reflected by the thermocouple measuring the gas temperature.

1% Pt/Al₂O₃ in Preferential CO Oxidation

Behavior of a Pt-catalyst in a prolonged run at constant oven temperature is depicted in Fig. 3. After heating in H_2 flow up to 111°C and switching on the vapor flow, hydrogen was changed for the feed gas. Oven temperature was increased stepwise (curve *1*) by

10 K. As seen from Fig. 3a (a fragment of the record starting from 75 min is shown), after each step in temperature the residual CO content (curve *4*) decreased first then grew monotonously.

Prolonged exposure at oven temperature 140°C showed that transition to the steady state takes quite a time (Fig. 3a). For example, at exposure of 2 h (range 120−240 min) a gradual increase in residual contents of CO, O_2 was observed (curves *4, 5*), as well as a decline in temperature both at top and bottom (curves *2, 3*). (Let us note that in absence of the reaction in the catalyst layer time of transition into a new steady state at a change in oven temperature does not exceed 10−15 min.)

A switch to the mixture which does not contain CO_2 (range 241−314 min; gas flow rate was increased) has led only to small changes in behavior of the catalyst, while the return to the previous mixture (and gas flow rate) restored the pattern where residual contents of CO, O_2 grew monotonously.

Selectivity of O_2 consumption in CO oxidation in this case, unlike in that depicted in Fig. 1d, is much lower than unity (Fig. 3b, curve *2*), its decrease occurring first of all with an increase in catalyst temperature (Fig. 3b, curve *1*).

It should be noted that the same kind of changes with time (an increase in residual CO content) happened when the experiment was conducted in absence of water vapor.

Thus, in the same manner as in the case depicted in Fig. 1, the catalyst undergoes slow deactivation when CO is present in reaction gas.

1% Rh/Al₂O₃ in Preferential CO Oxidation

Activity curves depicting the catalyst deactivation were obtained for 1% Rh-catalyst; they were shown to be similar to those for a Pt-catalyst. Experimental data are illustrated in Figs. 4a, 4b. The catalyst was reduced before the experiment, heated to oven temperature ~90°C (curve *1*, Fig. 4a) and subjected to gas mixture of the composition (vol %): CO—1.0, O_2—1.0, H_2—60, N_2—rest (Fig. 4a, 29 min). This resulted in an initial increase in catalyst temperature (curves *3, 4*, Fig. 4a). Still, during the next ~ 30 min the catalyst deactivated almost completely: its temperature fell (Fig. 4a) and residual contents of CO, O_2 grew (curves *2* and *3*, Fig. 4b). Further increase in temperature of the oven up to 106°C (range 72−104 min) allowed the observation of a temperature increase for top and bottom of the catalyst bed (curves *3, 4*, Fig. 4a) and sharp decrease in residual contents of CO, O_2 (Fig. 4b). Yet again, exposure at constant oven temperature (106°C, range 106−352 min) has led to a decrease in catalyst temperature and a monotonous growth in residual CO, O_2 contents (Fig. 4b). The result was gradual deactivation of the catalyst.
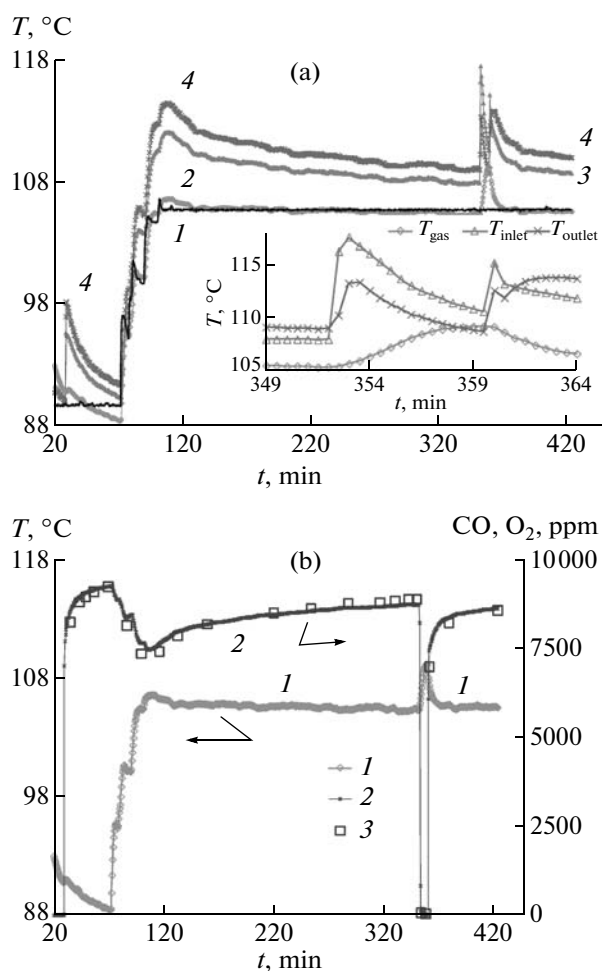
Fig. 4. PROX CO over 1% Rh/Al₂O₃. In the ranges 0−351.6 min, 359.7 min—forward the gas composition was, vol %: O_2—1.0, CO—1.0, H_2—60, N_2—rest. In the range 351.6−359.7 min the gas composition was, vol %: O_2—1, H_2—60, N_2—rest. Gas flow rate 261 (g Cat)$^{-1}$ h^{-1}. Records obtained in stepwise heating and prolonged exposure to temperature are shown for: (a) temperatures of: oven (*1*), gas (over the top) (*2*), bottom (*3*), top of the catalyst bed (*4*) correspondingly. In the insert, a record of temperature upon changing the gas feed is shown. (b) Temperature of gas (over the top) (*1*); residual contents of CO (*2*) and O_2 (*3*).

As witnessed by curve *2* in Fig. 4a, temperature of gas is close to that of oven. It is affected only slightly by an overheat at the top of catalyst bed.

Switch of feed gas from the one with CO to that without (range 351.6−359.7 min) has led to transition of the hydrogen oxidation reaction into CSI mode in the same manner as shown in Fig. 2. In this, the catalyst temperature first grew in a jump, first of all at the top, then a decline took place (yet the gas temperature continued to grow). This contrasting temperature pattern, growth in gas temperature at the decline in catalyst temperature at the top, testifies to spreading of hydrogen oxidation into the gas phase (refer to the
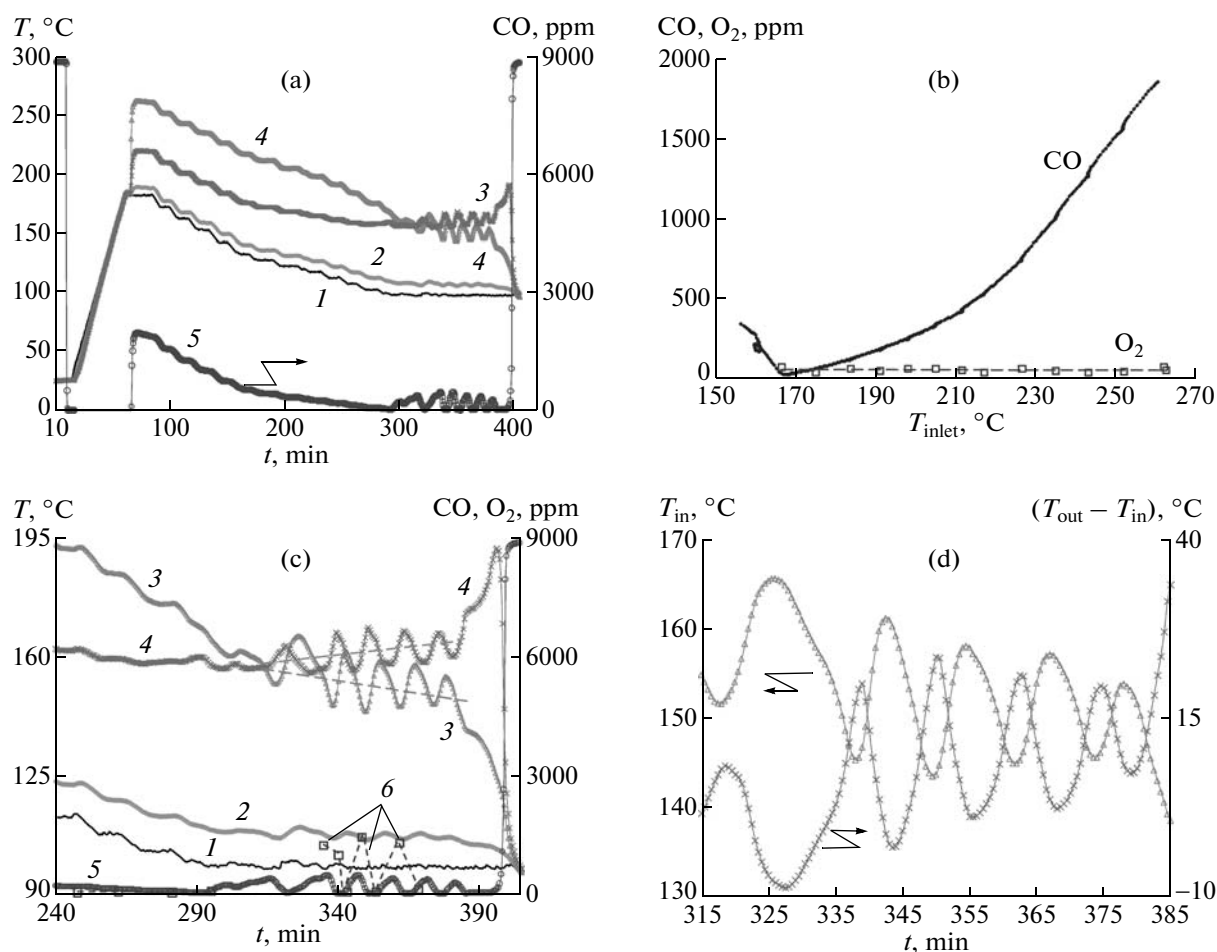
Fig. 5. PROX CO over 0.2% Rh/Al_2O_3. Gas composition, vol %: O_2—1.47, CO—0.89, H_2—71, CO_2—23, N_2—rest. Gas flow rate 50 l (g cat)$^{-1}$ h^{-1}. Before 9.5 min, reactor was bypassed; in the range 9.5–65.5 min the catalyst was in H_2 flow, after which the feed gas was switched on. (a) Complete record of the experiment; (b) temperature dependence of residual contents of CO and O_2 in CSI mode; (c, d) incomplete records of the range where oscillations were observed; Temperatures of: oven (*1*), gas (over the top) (*2*), bottom (*3*), top of the catalyst bed (*4*) correspondingly; *5, 6*—residual content of CO (*5*) and O_2 (*6*) correspondingly.

insert to Fig. 4a for detailed temperature records.) It should be noted that this effect is confirmed by independent experiments as well. At 359.7 min, the gas mixture containing CO was fed onto the catalyst resulting in return of the oxidation reaction back to the domain of catalyst bed as gas temperature almost leveled with the oven temperature. Insert to Fig. 4a shows small increases in temperature of catalyst bed first at the top, then at the bottom. They show at shrinking of reaction zone from gas phase back to the catalyst bed and to a quick drift of the "hot spot" downstream connected with catalyst deactivation. Further experimental treatments continued the deactivation pattern.

Transition of the Reaction into the Oscillation Mode

During a decrease in oven temperature in CSI mode over 0.2% Rh/Al_2O_3 we observed appearance of oscillations in the time range directly preceding sur-

face extinction (Figs. 5a−5c). Considering the positive effect of O_2 on catalyst activity in CO oxidation, we have increased the O_2/CO ratio in the experiments up to 1.65.

The catalyst was introduced into the CSI mode at higher temperature: it was heated in H_2 flow up to 183°C, then after the switch to feed gas (65 min, Fig. 5a) and the establishment of CSI mode the oven temperature was gradually decreased (curve *1*, Fig. 5a). After feeding of the feed gas oxygen conversion reached 99.6%, while temperature of the top grew to ~261 and that of the bottom, to ~220°C (86 min, Fig. 5a)—that is, the reaction proceeded at the top of the catalyst bed. When the oven temperature was lowered (stepwise, with exposure at each step ~10–15 min) down to 103°C (271 min), oxygen conversion remained the same but the selectivity was affected significantly. Thus, dependence of residual CO content on temperature at the top went through a minimum

(~40 ppm) during a decrease in oven temperature (Fig. 5b where data from the range 87–314 min were employed). As seen from Fig. 5b, temperature decrease in the chosen range did not affect the residual content of O_2, which remained at the level below 100 ppm. This testifies to reaction proceeding in CSI mode. A conclusion can be made also that it is oxygen which is the key component of the reaction. Residual content of CO went through a minimum when temperature of the top was 167.3°C. When the catalyst temperature reached 156.6°C both at top and bottom, CO content was at ~360 ppm (Fig. 5a). Growth in residual CO content means the surface extinction has started.

As in the case of Ru-catalysts [3], the positive effect of temperature decrease on reaction selectivity can be confirmed.

It should be noted that presence of CO_2 in gas in noticeable amounts did not lead in this case to formation of methane, i.e., hydrogenation of carbon dioxide (in absence of carbon monoxide which has been consumed in oxidation reaction) did not proceed.

As noted above, a decrease in oven temperature from 103 to 99°C (curve 1, 285 min, Fig. 5a) has made the temperatures of top and bottom of the catalyst bed closer. As a drift of "hot spot" was indicated here as well, surface extinction in the end could have been expected. Nevertheless, the process of extinction turned out to be more complicated.

During extinction, oscillations of ~12 min period appeared (see a fragment of a record in Fig. 5c), in behavior of both the catalyst bed temperature (curves 3, 4) and of residual contents of CO (curve 5) and O_2 (curve 6). Starting from 335 min, temperature drop in these oscillations (curves 3, 4) was 10–15 K. It should be noted that the oscillations were not connected in any way to the performance of the oven, as its temperature fluctuated by less than 1.5 K at much higher frequency. Oscillation mode remained intact for ~1 h, after which the catalyst surface extinction settled in completely.

It is seen that in each oscillation, a decrease in temperature at the bottom coincided with an increase at the top in an anti-phase manner. A better way to notice this would be the comparison of dynamics of temperature at the top versus the difference between the temperatures of bottom and top (Fig. 5d). As seen from Fig. 5d, the latter curve moves down at an increase in temperature at the top, up if otherwise.

In our opinion, decreases in temperature at the top happen due to catalyst deactivation caused by strong CO adsorption. A decrease in activity at the top, on one hand, leads to extinction of oxidation reactions: residual oxygen content increases (~1000 ppm, at 340, 348, 360 min, Fig. 5c). On another hand, consumption of CO in coverage of metallic Rh surface in the frontal layer (the top) increases the ratio O_2/CO in gas which enters the layers downstream. This, in turn,

promotes oxygen conversion, culminating in CSI at the bottom (residual O_2 content drops down to ~100 ppm: 343, 353, 368 min, Fig. 5c). In the course of CSI, rising temperature at the bottom assists temperature growth at the top. Now this latter overheat is favorable for the process of oxygen adsorption being preferable over that of CO—but the state of insufficient coverage of Rh surface with CO molecules is not stable, so the cycle is repeated.

Oscillations of temperature in the catalyst bed were accompanied not only by oscillations of residual O_2 content (curve 6, Fig. 5c), but also by those of CO (curve 5) due to the temperature dependence of selectivity noted above. Besides, during the oscillations a change in temperature at the top affects the gas temperature (curve 2) so there is a small delay in the record of the latter (~0.5 min) which otherwise follows the same pattern as the former.

It can be seen that in the course of oscillations a gradual drift of the "hot spot" downstream took place (trends of dynamics of average temperature values at the top/bottom are shown by dashed lines in Fig. 5c). Oscillations continued until the temperature at the top decreased at 385.5 min to the critical point of extinction. As extinction started at the top, "hot spot" drifted to the bottom at last, after which extinction established there as well. This was accompanied by a sharp maximum in the temperature dependence (curve 4, 396.5 min) and a sudden increase in residual contents of CO (curve 5) and O_2 (~14000 ppm, this experimental point is not shown in Fig. 5c) almost to the initial values.

Thus, the mechanism behind this oscillation phenomenon can be attributed to a combination of such factors as high exothermicity of occurring reactions, strong adsorption of CO, the extension of catalyst bed and presence of two reactants able to react with oxygen, H_2 and CO in this case.

DISCUSSION

Deactivating effect of CO

In the case when only hydrogen and oxygen are present in gas, oxygen adsorbs on the metal (Pt, Rh) surface and oxidizes hydrogen easily at almost complete conversion (Figs. 1, 2). In the steady state this corresponds to the "hot spot" placement at the top. Appearance of CO in gas leads to "extinction" of hydrogen oxidation as most of active metal centers end up covered with CO molecules. Further switch to the gas mixture not containing CO quickly restores the catalytic activity. This result is in agreement with the data of experiments where hydrogen-free gas mixtures were studied over 2.9% Pt/Al_2O_3 [15]. It has been shown there that a switch of gas flow at 300 K from CO/Ar/He to O_2/Ar/He leads to a quick (dozens of seconds) disappearance of linear forms of adsorbed CO due to formation of CO_2.

It is evident that the rate of metal deactivation by CO molecules depends on metal content in the sample, temperature, concentrations of CO and O_2 in gas, gas flow rate.

In the experiment described above (see Fig. 1e) the "quick" step of deactivation, drift of "hot spot", took ~0.1 min. At higher temperatures this step can take more time. In our opinion, quick initial deactivation of 5% Pt/γ-Al_2O_3 observed in [13] after a switch at 90°C and gas flow rate 190 000 h^{-1} from hydrogen to the composition of (vol %): H_2—45, CO—1, O_2—1, He—rest, was connected to strong adsorption of CO and not to the formation of carbonaceous deposits as the authors of that work have stated.

In [16], ellipsomicroscopy was used to obtain the picture of Pt monocrystal surface in order to study CO oxidation over the plane (111). It was found that CO at 403 K forms "islands" on the metal surface, and when CO is not fed on anymore (O_2 being present in gas) these CO "islands" end up "eaten away" by oxygen. It can be supposed that in our experiments CO also forms "islands" when adsorbing over the metal surface, and that its interaction with oxygen is possible only on the boundaries of these "islands." As follows from the data in Fig. 1d, selectivity of O_2 consumption in CO oxidation at temperatures close to the room one is close to unity, i.e., H_2 oxidation does not take place. At an increase in temperature the coverage of surface with CO molecules decreases which promotes adsorption of both O_2 and H_2 and leads to a decrease in selectivity (see Fig. 3b).

As noted above, at a certain temperature it is possible for H_2 oxidation reaction to spread into gas phase (see the insert to Fig. 4a) which presents an analogy to the heterogeneous-homogeneous mechanism of H_2 oxidation over Pt [17].

Thus, under certain conditions PROX CO proceeds over Pt- and Rh-catalysts due to a combination of, on one hand, strong CO adsorption, on the other hand, CO oxidation by oxygen. This combination ensures slow gradual growth of dynamics of residual CO, O_2 contents at a temperature increase (Figs. 3, 4).

This slow deactivation is in agreement with the data on PROX CO over Pt [9, 18] and Pt, Rh [12]. Thus, according to [18], there was a slow insignificant decrease in CO, O_2 conversions over 5% Pt/γ-Al_2O_3 at 65°C in the course of ~80 h. According to [9], when the mixture of CO, O_2, H_2 was fed onto a Pt-catalyst, deactivation occurred during the first 2 h with an additional 5% decrease in activity in the course of next 10 h. Stability of Pt-, Rh-catalysts in PROX CO over a 33 h run is considered in [12] for Pt at 200°C, Rh at 150 and 250°C. CO conversion decreased over time exponentially: in the case of Rh at 150°C by 70% from the initial value (by 30% at 250°C); by 50% in the case of Pt.

As follows from the discussion above, deactivating effect of CO regarding Pt-, Rh-catalysts can be reduced by an increase in O_2 content in gas and/or an increase in temperature.

For transfer of the reaction into CSI mode, the easiest way would be to follow the procedure employed by us in [3] in a study of Ru-catalysts. It makes sense in the search for temperature window corresponding to the minimum in residual CO content to perform a switch from H_2 to feed gas at such temperature at which the deactivating influence of feed gas components is minimal. All that is left to do in order to find that minimum in residual CO content would be to lower the temperature. Data illustrated in Fig. 5 were obtained precisely in this way (considering the positive effect of oxygen denoted above, an increased value of O_2/CO ratio was chosen).

Conditions of Catalyst Surface Ignition and Extinction under Strong Adsorption of CO

As follows from the theoretical consideration in [2], ignition starts when heat flow generated by the reaction starts to exceed the flow of removed heat and this excess of heat in the system is preserved at an increase in temperature. Accordingly, extinction begins when this situation is reversed. CO by its strong adsorption on metal surface lowers the surface area available for the reaction, so catalytic activity decreases as does the amount of heat generated in the reaction. This leads to an increase in critical temperatures of ignition and extinction.

This thesis can be illustrated by a comparison of Figs. 2 and 5c. As seen from Fig. 2, in CO absence from the gas feed CSI is observed at the top and its stability is preserved at relatively low temperature (~123°C; gas flow rate 46 l $(g\ Cat)^{-1}\ h^{-1}$). At the same time, under the condition of a similar gas flow rate but for a gas containing CO (Fig. 5c) already at ~156°C (315 min), a drift of "hot spot" to the bottom occurs which is followed by jumps in residual oxygen content up to the level of 1000−1400 ppm. This means that the driving force behind the extinction upon reaching the temperature of ~156°C in the reaction zone (Fig. 5c) is the decrease in heat generated by oxidation reactions caused by the catalyst deactivation due to strong adsorption of CO molecules. Basically, this also confirms the appearance of oscillations in the system. It is typical that the transition into oscillation mode started with the drift of "hot spot" downstream.

A practical conclusion can be made that placement of the "hot spot" at the top of catalyst bed is the condition of stable catalytic performance in CSI mode.

CONCLUSIONS

Preferential oxidation of CO is a reaction which can be realized in a special macrokinetic mode—catalyst surface ignition. This mode can be maintained in a steady state if the balance of heat generated by the

reaction and heat removed (with the gas flow and through the reactor walls) is preserved.

It can be proposed that for each specific design of the catalytic unit (with peculiar characteristics of heat exchange) it is possible to determine the ratio O_2/CO, gas flow rate, catalytic activity which will provide the required minimal value of residual CO content in stable performance of the catalyst in CSI mode.

Obtained data allow the conclusions that, first, it makes sense to utilize such design of the catalytic unit where the heat removal through the reactor walls and hydraulic resistance are at their minimums and, second, in the course of reaction proceeding in CSI mode at the upper layer of the catalyst bed other layers which are placed downstream should not be active in side reactions, in particular in methane formation.

First requirement can be obeyed by the use of catalyst in the form of mesh or honeycomb structure, the second—by selection of catalyst composition and reaction conditions.

What would be the best strategy for achieving the stable performance of noble metal-based catalysts in PROX CO? Evidently, in the light of disclosed data there would be a difference in approach in order to achieve the minimal value of residual CO content for, on one hand, Ru-based catalysts and on another, for Pt-, Rh-based ones.

If for Ru-catalysts it is required to seek optimal conditions above a certain critical temperature at minimal ratio O_2/CO in order to avoid ruthenium oxidation, for Pt- and Rh-catalysts optimal conditions should be sought at maximal allowed value of O_2/CO.

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REFERENCES

1. Han, Y.-F., Kahlich, M.J., Kinne, M., and Behm, R.J., *Phys. Chem. Chem. Phys.*, 2002, vol. 4, p. 389.

2. Frank-Kamenetskii, D.A., *Diffuziya i teploperedacha v khimicheskoi kinetike* (Diffusion and Heat Transfer in Chemical Kinetics), Moscow: Nauka, 1967.

3. Rozovskii, A.Ya., Kipnis, M.A., Volnina, E.A., Samokhin, P.V., and Lin, G.I., *Kinet. Katal.*, 2008, vol. 49, no. 1, p. 99 [*Kinet. Catal.* (Engl. Transl.), vol. 49, no. 1, p. 92].

4. Rozovskii, A.Ya., Kipnis, M.A., Volnina, E.A., Lin, G.I., and Samokhin, P.V., *Kinet. Katal.*, 2007, vol. 48, no. 5, p. 750 [*Kinet. Catal.* (Engl. Transl.), vol. 48, no. 5, p. 701].

5. Kiss, J.T. and Gonzalez, R.D., *J. Phys. Chem.*, 1984, vol. 88, p. 898.

6. Arnby, K., Törncrona, A., Andersson, B., and Skoglundh, M., *J. Catal.*, 2004, vol. 221, p. 252.

7. Arnby, K., Assiks, J., Carlsson, P.-A., Palmqvist, A., and Skoglundh, M., *J. Catal.*, 2005, vol. 233, p. 176.

8. Skoglundh, M., Thormählen, P., and Andersson, B., *Top. Catal.*, 2004, vols. 30−31, p. 375.

9. Kahlich, M.J., Gasteiger, H.A., and Behm, R.J., *J. Catal.*, 1997, vol. 171, p. 93.

10. Galletti, C., Fiorot, S., Specchia, S., Saracco, G., and Specchia, V., *Top. Catal.*, 2007, vol. 45, nos. 1−4, p. 15.

11. Rozovskii, A.Ya., Kipnis, M.A., Volnina, E.A., Samokhin, P.V., Lin, G.I., and Kukina, M.A., *Kinet. Katal.*, 2009, vol. 50, no. 5, p. 718 [*Kinet. Catal.* (Engl. Transl.), vol. 50, no. 5, p. 691].

12. Han, Y.-F., Kahlich, M.J., Kinne. M., and Behm, R.J., *Appl. Catal., B*, 2004, vol. 50, p. 209.

13. Sirijaruphan, A., Goodwin, J.G., and Rice, R.W., *J. Catal.*, 2004, vol. 221, p. 288.

14. Grisel, R.J.H., Slyconish, J.J., and Nieuwenhuys, B.E., *Top. Catal.*, 2001, vols. 16−17, nos. 1−4, p. 425.

15. Bourane, A. and Bianchi, D., *J. Catal.*, 2002, vol. 209, p. 114.

16. Colen, R.E.R., Christoph, J., Pena, F., and Rotermund, H.H., *Surf. Sci.*, 1998, vol. 408, p. 310.

17. Pyatnitskii, Yu.I., Azatyan, V.V., Boldyreva, N.A., and Shaprinskaya, T.M., *Khim. Fiz.*, 1988, vol. 7, no. 2, p. 235.

18. Avgouropoulos, G., Ioannides, T., Papadopoulou, Ch., Batista, J., Hocevar, S., and Matralis, H.K., *Catal. Today*, 2002, vol. 75, p. 157.