Application Peculiarities of *in situ* XPS and Mass Spectrometry Methods to Study Concentration Hysteresis in Methane Oxidation over Alumoplatinum Catalysts

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Abstract

Concentration hysteresis in methane oxidation over alumoplatinum catalysts was studied by in situ XPS and mass spectrometry. It was determined that the activation of catalysts was accompanied by partial reduction of platinum the boundaries of existence of concentration hysteresis and effect on them of the particle size of the active component were defined.

Key words: X-ray photoelectron spectroscopy (XPS), mass spectrometry, concentration hysteresis, alumoplatinum catalysts

INTRODUCTION

Hysteresis phenomena, *i. e.* dependencies of properties of the functioning system not only on acting on the system parameters but also on the prehistory of this condition of the system are commen in heterogeneous catalysis and usually associated with the nonlinearity of the mechanism of the catalytic process. Detecting the causes of such hysteresises is an active tool in studying the mechanism of the process. Relatively recently, a new phenomenon that is concentration hysteresis in methane oxidation on alumoplatinum catalysts was detected [1–3]. Thus, under identical external conditions (temperature and partial reagent pressure), there are two stable stationary system conditions with low and high catalytic activities that can be fulfilled under identical external conditions depending on the direction of changing the reagent ratio (O_2 and CH_4). By changing parameters of proceeding concentration hysteresis, it is possible to increase methane conversion from 10 to 90 %.

Thus, the study of the phenomenon of concentration (kinetic) hysteresis depending on such factors as the particle size of the active component, type of the used carrier, sample preparation method *etc.* in perspective will allow managing the activity and selectivity of catalysts in methane oxidation.

For this, one must obtain the detailed information of the adsorption layer composition, active component condition, change of nanoparticles morphology directly during catalytic reactions with simultaneous testing catalytic properties of the catalyst under study.

Practical implementation of such an approach has a number of methodological diffi-

culties, one of which consists in the problem of pressure gap well known in the field of surface science. In fact, most physicochemical methods of surface research operate under conditions of high and ultra-high vacuum, when the rate of proceeding of most catalytic reactions is extremely low. Additionally, the action of the reaction medium may lead to a change of the charge state of the active component [4, 5]. This may lead to the formation on the surface of new (not registered under ultrahigh vacuum conditions) active centres that can substantially differ from original and be responsible for catalytic properties of the system under study. Another problem arising when using the approach proposed is the "dimensional effect" consisting in a change in electron, adsorption and catalytic properties depending on the particle size of the active component.

A promising solution of these problems is the joint use of physicochemical methods in the *in situ* mode at the pressures of the reaction mixture above the sample of several orders of magnitude higher ($10^{-1}-10$ mbar), than in standard experiments used in the field of surface science ($10^{-6}-10^{-9}$ mbar) and applied catalysts with a narrow distribution of particles of the active component by sizes as research objects.

Precisely such an approach was used in this work when studying the nature of concentration hysteresis in methane oxidation on alumoplatinum catalysts. To solve this problem *in situ* XPS (determining the charge state of the active component) and mass spectrometry (analyzing a change in the composition of the gas phase above the sample surface) methods directly during the catalytic oxidation of methane were used.

EXPERIMENTAL

Research objects

As research object, 1 mass % Pt/γ-Al_2O_3 catalyst was selected with the particle size of the active component of (2±0.2) nm and the crust distribution of platinum along the carrier granule. The size of the catalyst grain granule amounted to 0.25−0.5 mm. Earlier, it was shown that this catalyst demonstrated a high catalytic activity in the reaction of low temperature methane oxidation, as well as high redox lability [6, 7]. To study a possible effect of the particle size on existence boundaries of concentration hysteresis, experiments were carried out with 1 mass % Pt/Al_2O_3 with the particle size of the applied active component of (8±1) nm.

Sample preparation technique

All catalysts were prepared by the impregnation method that is based on adsorption of the precursor onto the carrier surface from an aqueous solution of platinum (II) nitrate ($Pt(NO_3)_2$) [6] followed by calcination of the samples in a flow of oxygen at a temperature of 400 °C. Prior to the reaction in the sample with the particle size of 2 nm, platinum was present as oxide (PtO_2). The applied platinum was reduced in a flow of hydrogen at 600 °C to the metal state in a sample with a medium size of applied particles of 8 nm before the reaction.

X-ray photoelectron spectroscopy

X-ray photoelectron spectra were removed using a VG ESCALAB High Pressure photoelectron spectrometer with AlK_α radiation ($h\nu = 1486.6$ eV). This spectrometer allows recording photoelectron spectra at a pressure of the gas or reaction mixture above the sample up to 0.1 mbar [5].

This is reached using a special high pressure cell that is built in into a camera of the spectrometer analyser and compacted with viton rings. To create pressure drop between the cell and other parts of the spectrometer two-stage differential pumping of electron lenses and the analyzer, X-ray gun and quadrupole mass spectrometer using high performance diffusion pumps. There are two small diameter (3−5 mm) openings in the cell for the entrance of X-ray radiation and the exit of photoelectrons into the analyzer, and also for gas inlet or the reaction mixture.

Preliminarily, the energetic scale of the spectrometer was calibrated relatively to the Au4$f_{7/2}$ lines (binding energy $E_b = 84.0$ eV),

$Ag3d_{5/2}$ (368.3 eV) and $Cu2p_{3/2}$ (932.7 eV). Calibrating the removed photoelectron spectra in situ experiment was carried out according to the $Al2s$ line (119.3 eV) from the carrier (γ-Al_2O_3) that was used as an internal standard. To increase the reliability of the resulting spectral information, the analysis of the bond energy value and the peak shape of each scan was additionally carried out followed by their averaging. This procedure was necessary for minimizing possible effects caused by both the uneven charging of the sample, and possible adsorption of hydrocarbons under the action of the reaction mixture, X-ray radiation, and possible adsorption of hydrocarbons from vapours of diffusion oil onto the catalyst surface during *in situ* experiments. The measurement of photoelectron spectra was carried out with a step on the bond energy in 0.1 eV and the time of accumulation of 1 s. The number of scans for measurable spectra was determined as a compromise between the time of accumulation and the quality of the resulting averaged signal. It is noteworthy that the condition of platinum remained stable during the entire experiment (the recording time of the spectra is up to 8 h) in all key points of hysteresis. An analysis of photoelectron spectra was carried out according to the $Pt4f$ + $Al2p$, $Al2s$, $C1s$ and $O1s$ lines. The error in determining the bond energy value amounted to 0.1 eV. The survey spectra were recorded with the energy transmittance HV = 100 eV, separate regions – 20 eV. The determination of the relative content of elements was performed on the surface of catalysts and the ratio of atom concentrations was carried out according to integral intensities of photoelectron lines that were corrected for appropriate atomic sensitivity factors [8].

The temperature control during experiments was performed using a chromel-alumel thermocouple soldered-in to the sample holder body. All in situ experiments presented in this work were carried out at a temperature of (460±0.6) °C that was selected based on the available literature data [1−3].

Mass spectrometric measurements

A QME-220 quadrupole mass spectrometer with independent differential pumping of the Pfeiffer production (Germany) was used for the analysis of the purity of connected gases (methane and oxygen), analysis of a change in the gas phase over the sample surface during a catalytical reaction and the determination of the boundaries of existence of concentration hysteresis. The secondary electron multiplier that ensures high device sensitivity was an ion detector. The delay between measurement points amounted to 0.5 s, which was enough to reach the required scan rate by the measured masses. During experiments, the measurement of the following signals was conducted: H_2 (m/z 2), CH_4 (m/z 15 and m/z 16), H_2O (m/z 18), CO (m/z 28), O_2 (m/z 16 and m/z 32) and CO_2 (m/z 44).

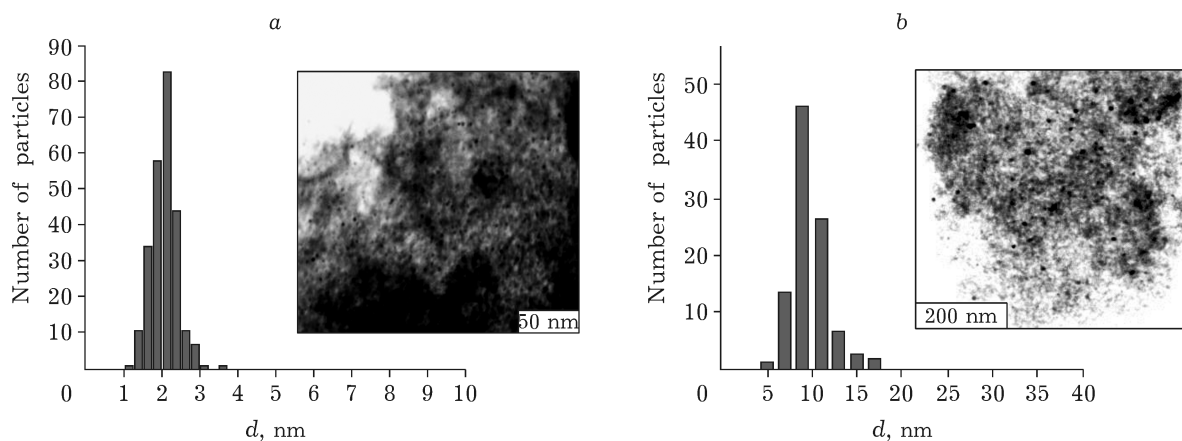The overlap of the reactants was performed using SEC-Z512MGX (Horiba, Japan) gas con-

Fig. 1. HREM images and distribution histogram of applied platinum particles by size for 1 mass % Pt/Al_2O_3 samples: $a - d_{Pt}^{av} = 2$ nm, $b - d_{Pt}^{av} = 8$ nm.

Pt4*f* + Al2*p*

74.5 Al$_2$O$_3$,

74.9 PtO$_2$

71.2

Pt/Al$_2$O$_3$, *d* = 2 nm

Pt/Al$_2$O$_3$, *d* = 8 nm

66   68   70   72   74   76   78   80   82   84
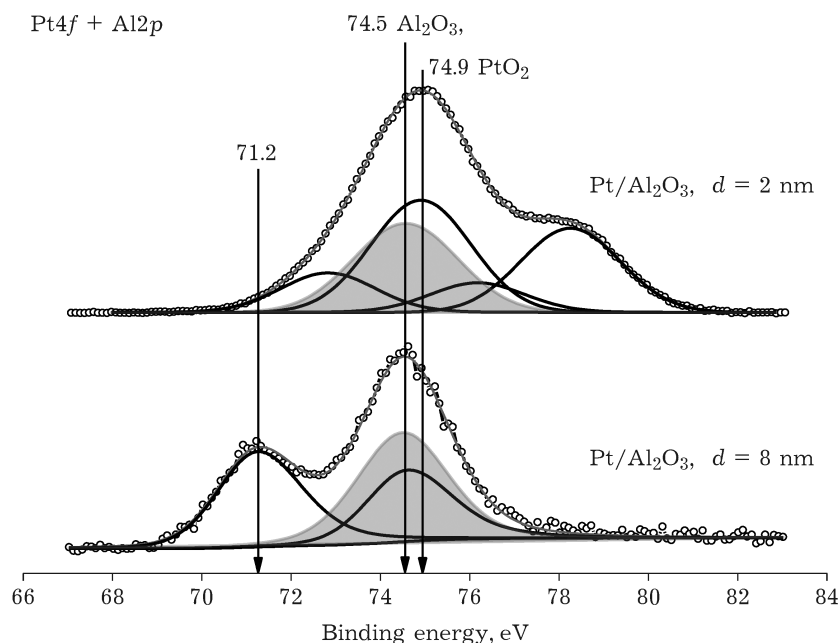
Binding energy, eV

Fig. 2. Photoelectron spectra of a Pt4*f* + Al2*p* region of initial aluminoplatinum catalysts.

sumption precision regulators. To measure the reaction mixture pressure in a catalytic cell, a Baratron MKS-121A absolute pressure transducer (MKS, the USA) operating in a pressure range from 10^{-3} to 1 mbar was applied.

All experiments were conducted at constant methane concentrations in the reaction mixture ($P(CH_4) \sim 0.008$ mbar), the concentration of oxygen was varied in a pressure range from 0.002 to 0.2 mbar.

RESULTS AND DISCUSSION

Distribution by size of applied platinum particles by high resolution electron microscopy

High resolution electron microscopy (HREM) demonstrated that the prepared samples possessed a narrow size distribution of applied platinum particles (Fig. 1). The average nominal particle size (d_{Pt}^{av}) of 2 and 8 nm will be used further in the work.

75.1 Pt^{4+}
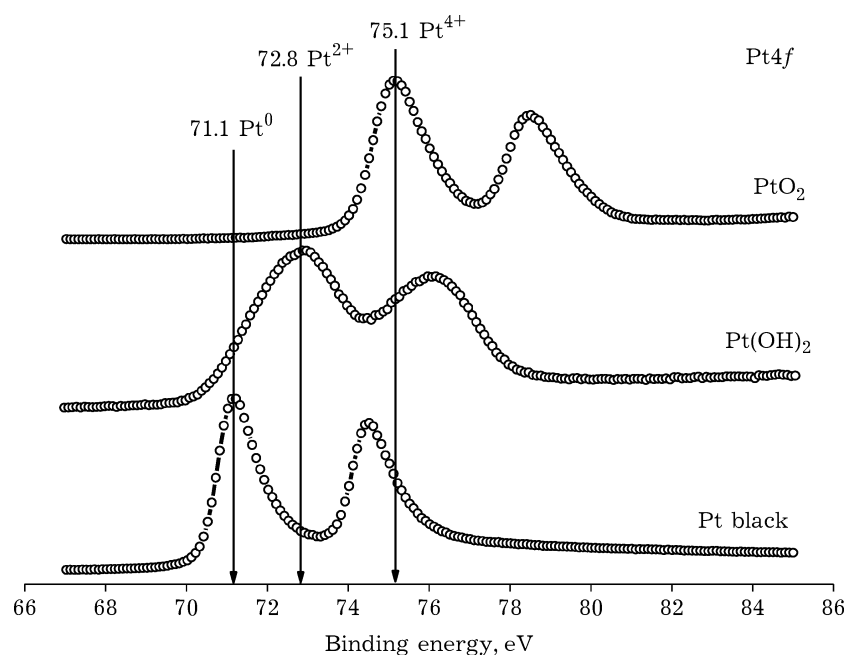
72.8 Pt^{2+}

Pt4*f*

71.1 Pt^0

PtO$_2$

Pt(OH)$_2$

Pt black

66   68   70   72   74   76   78   80   82   84   86

Binding energy, eV

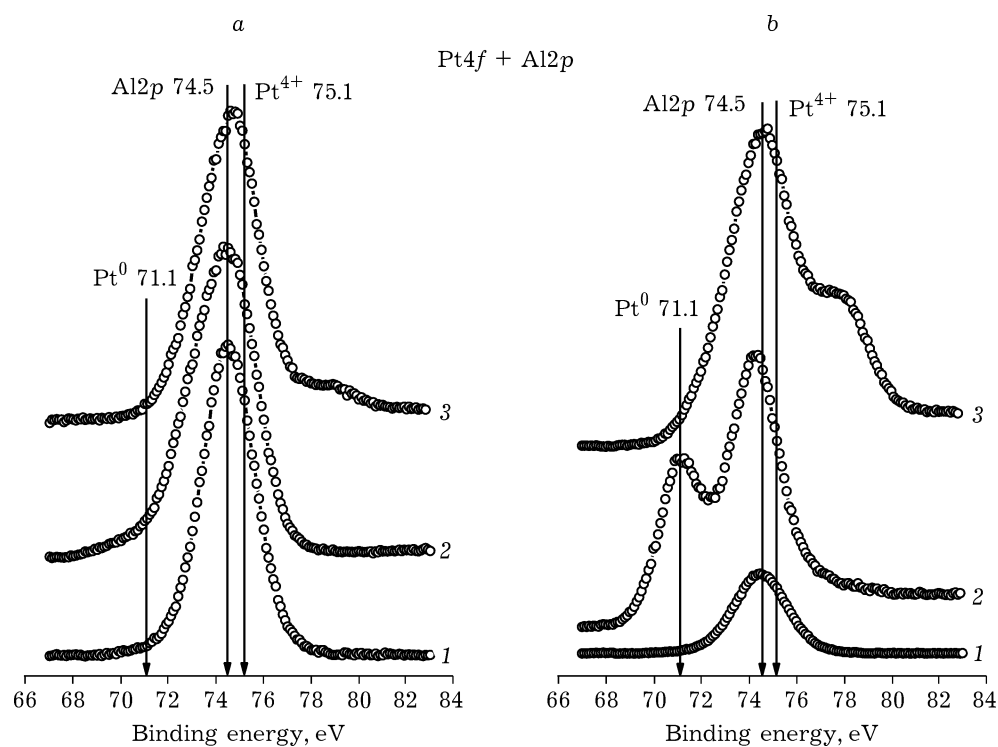Fig. 3. XPS spectra of reference platinum compounds.

Fig. 4. XPS Al2*p* + Pt4*f* spectra of aluminoplatinum catalysts (1 mass % Pt/γ-Al$_2$O$_3$) with uniform (*a*) and crust distribution (*b*) of the active component along the granule.

Ex situ XPS study of alumoplatinum catalysts and reference samples

The study of all samples was carried out by the XPS method to determine the initial state of platinum in the catalyst. Analysis of spectra measured demonstrated that platinum for Pt/γ-Al$_2$O$_3$ sample (d_{Pt}^{av} = 2 nm) is present completely in the oxide state, and for Pt/γ-Al$_2$O$_3$ sample (d_{Pt}^{av} = 8 nm) platinum is present in the form of metal (Fig. 2).
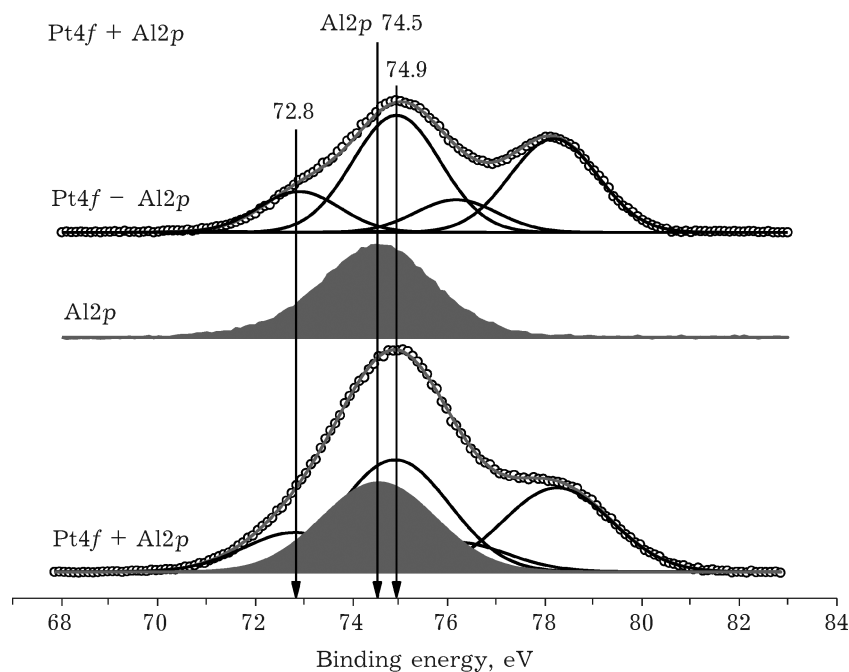

Fig. 5. Isolation of the Pt4*f* signal from the total Pt4*f* + Al2*p* spectrum.

Photoelectron spectra of a number of reference platinum compounds with various oxidation levels of Pt (0, 2+, 4+) were measured to further analyze changes of the charge state of applied platinum in the process of methane oxidation (Fig. 3). This should significantly increase the reliability of spectral information obtained directly when conducting *in situ* measurements during methane oxidation and at the subsequent decomposition of photoelectron peaks into individual spectral components.

It must be said that when studying platinum states on the surface of Pt/γ-Al₂O₃ catalysts by the XPS method, their analysis is largely hampered, firstly, due to a low platinum content in the composition of the catalyst (usually, within 1 mass %), and secondly, due to overlapping of platinum spectral lines Pt4*f* and aluminum Al2*p*. Spectra of the Pt4*f* + Al2*p* region for samples with the uniform and crust platinum distributions are presented in Fig. 4, respectively. As can be seen from the given Fig. 4, *a*), at the uniform platinum distribution along the granule, the platinum signal is so low intense that the identification of its charge state is all the more difficult, under *in situ* conditions, when the peak intensity drops significantly due to scattering of photoelectrons in the gas phase. However, at the crust distribution of platinum (see Fig. 4, *b*), the intensity of the Pt4*f* signal is comparable to that of the Al2*p* peak, which makes these samples suitable for the study by the XPS method, including *in in situ* mode.

To solve the problem of isolating the Pt4*f* signal from the total (Pt4*f* + Al2*p*) spectrum spectra of Al2*p* and Al2*s* regions from (γ-Al₂O₃) carrier *in situ* mode, *i. e.* directly under conditions of the existence of concentration hysteresis, from which their spectral characteristics were determined, preliminarily, the spectra were normalized along the Al2*s* line from the samples under study. The resulting parameters of the Al2*p* peak were further used when decomposing the Pt4*f* + Al2*p* region. The isolation of the Pt4*f* signal from the total spectrum for the initial surface of the Pt/γ-Al₂O₃ sample with d = 2 nm that was concluded in subtracting the Al2*p* peak from the carrier preliminarily normalized along the Al2*s* line for the measured sample from the total Pt4*f* +

Al2*p* spectrum is presented in Fig. 5 as an example. It is noteworthy that *in situ* experiments conducted using a carrier (γ-Al₂O₃) demonstrated both a complete absence of the carrier activity in methane oxidation and that of concentration hysteresis.

When conducting *in situ* experiments special attention was paid to analyzing the C1*s* peak, since it is well known that under the influence of the methane-oxygen reaction medium, considerable carbonization of the sample surface may occur, which leads to blocking of active centers of the catalyst and, consequently, catalytic properties of the system under study are worsened [9−11]. In order to assess a possible effect of adsorbed carbon on catalytic properties of the samples under study during concentration hysteresis in methane oxidation, C1*s* spectra in a flow of methane at 500 °C and of oxygen at room temperature (the pressure of the reagents amounted to 0.01 mbar), the C1*s* spectrum from methane gas phase was also recorded (Fig. 6). Analysis of the measured spectra demonstrated that in a flow of oxygen on the catalyst surface, carbon with a value of E_b = 284.8 eV that is typical for hydrocarbons was present; this may be associated with the fact that a part of oil from diffusion pumps falls into a high pressure cell. The C1*s* peak with the value of the bond energy of 284.5 eV that is typical for graphite-like sediments on the sam-
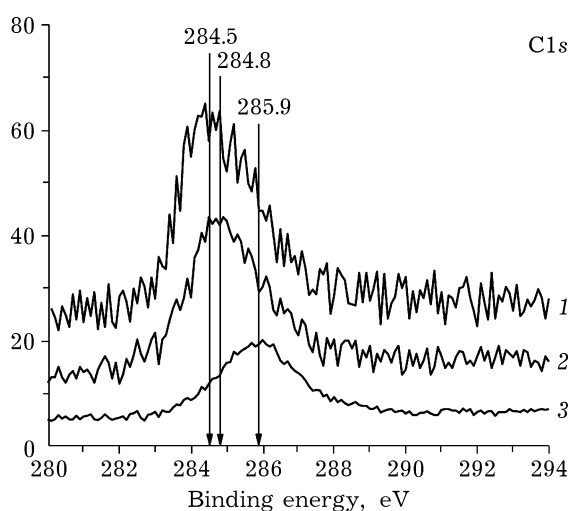

Fig. 6. XPS C1*s* spectra of a 1 mass % Pt/γ-Al₂O₃ sample, d_{Pt}^{av} = 2 nm, recorded in atmosphere: *1* − methane (P = 0.01 mbar, T = 500 °C), *2* − oxygen (P = 0.01 mbar, T = 30 °C) in the presence of the catalyst; *3* − spectrum of the gas phase (P(CH₄) = 0.01 mbar, T = 30 °C).

ple surface is observed in a methane atmosphere. However, it should be taken into account that additional peaks from the methane gas phase and from carbons on the surface are also present in the composition of this peak. It can also be seen that the difference in integral intensities of appropriate peaks (in an atmosphere of methane and oxygen) is comparatively low. Based on this, one can conclude that blocking the sample surface by carbon sediments, which might lead to worsening catalytic properties, *i. e.* carbonization, was not observed.

In situ study of the Pt/γ-Al$_2$O$_3$ sample with d_{Pt}^{BV} = 2 nm

In situ experiments carried out under conditions close to testing in a catalytic reactor at the atmospheric pressure [1−3] (temperature and change range of the reagent ratio) demonstrated the availability of concentration hysteresis (Fig. 7, *a*). The direction of the arrows in Fig. 7,

a schematically demonstrates the direction of the content change of oxygen in the reaction mixture at the constant content of methane.

The measurement of photoelectron spectra during proceeding the reaction was conducted simultaneously with controlling concentrations of the components of the gas phase occurs in the *in situ* mode. Analysis of XRE spectra demonstrated that at transition of a catalyst of into the activated state, a shift of the Pt4f line of platinum to the side of lower values of the bond, which testifies a change in its charge state (see Fig. 7, *b*). This suggestion is confirmed by the results of decomposing the Pt4f spectra into separate components (Pt^0 − E_b = 71.1−71.2 eV, Pt^{2+} − E_b = 72.4−72.5 eV, Pt^{4+} − E_b = 74.7−74.8 eV). That is, one may argue that a transition of a catalyst into the active state is accompanied by partial reduction of platinum.

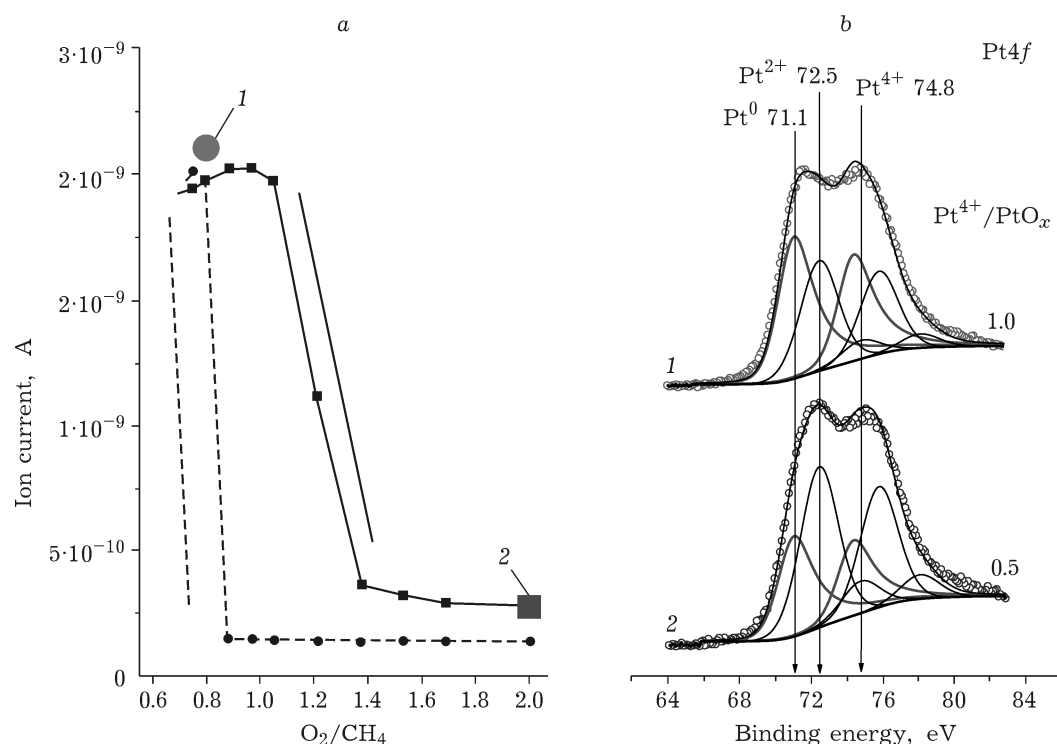Analysis of a change in the ratio of atomic concentrations of platinum and aluminium in

Fig. 7. Concentration hysteresis in the methane oxidation reaction over a 1 mass % Pt/γ-Al$_2$O$_3$ catalyst (d_{Pt}^{av} = 2 nm) accompanied by a change in electronic state of supported platinum: *a* − level of total ion current from CO and CO$_2$ corresponding to methane conversion in oxidation reaction during a decrease and a subsequent increase in the oxygen content in the mixture; the direction of the arrows schematically shows the direction of a change of the oxygen content; *b* − photoelectron Pt4f spectra measured in the active (*1*) and inactive (*2*) states of platinum under concentration hysteresis conditions.

active and inactive phases of hysteresis demonstrated that minor sintering of particles of the active component under concentration hysteresis conditions was observed for this sample (Pt/Al ratio drops at activating the catalyst from 0.4 to 0.3).

In situ study of the Pt/γ-Al$_2$O$_3$ sample with d_{Pt}^{av} = 8 nm

There is a significant narrowing of the hysteresis loop for the sample with the particle size d_{Pt}^{av} = 8 nm (Fig. 8, *a*), however, a shift of the Pt4f line from 72.1 to 71.6 eV is observed (see Fig. 8, *b*), which, as in case of the sample with the particle size of 2 nm, testifies partial reduction of platinum. Narrowing the hysteresis loop may be due to both the mutual effect of the size effect and a change in the surface of the catalyst active component, available for the reaction [5, 12−17].

This catalyst shows good thermal stability under concentration hysteresis conditions at 460 °C, which is confirmed *via* analysis of a change in the ratio of atomic Pt/Al concentrations (~0.1) in active and inactive phases of hysteresis.

CONCLUSION

Experiments conducted by XPS and mass spectrometry methods directly during methane oxidation over alumoplatinum catalysts allowed making a correlation between a change of the charge state of platinum and the system transition from low-active into the highly active state. It was determined that activation and reversible deactivation of alumoplatinum catalysts was driven by partial reduction and oxidation of the active component. The ratio of the metallic and oxide forms of platinum significantly differs for low-active and highly active state, including at the same oxygen/methane ratio.

The size effect of applied particles of the active component on the hysteresis loop width
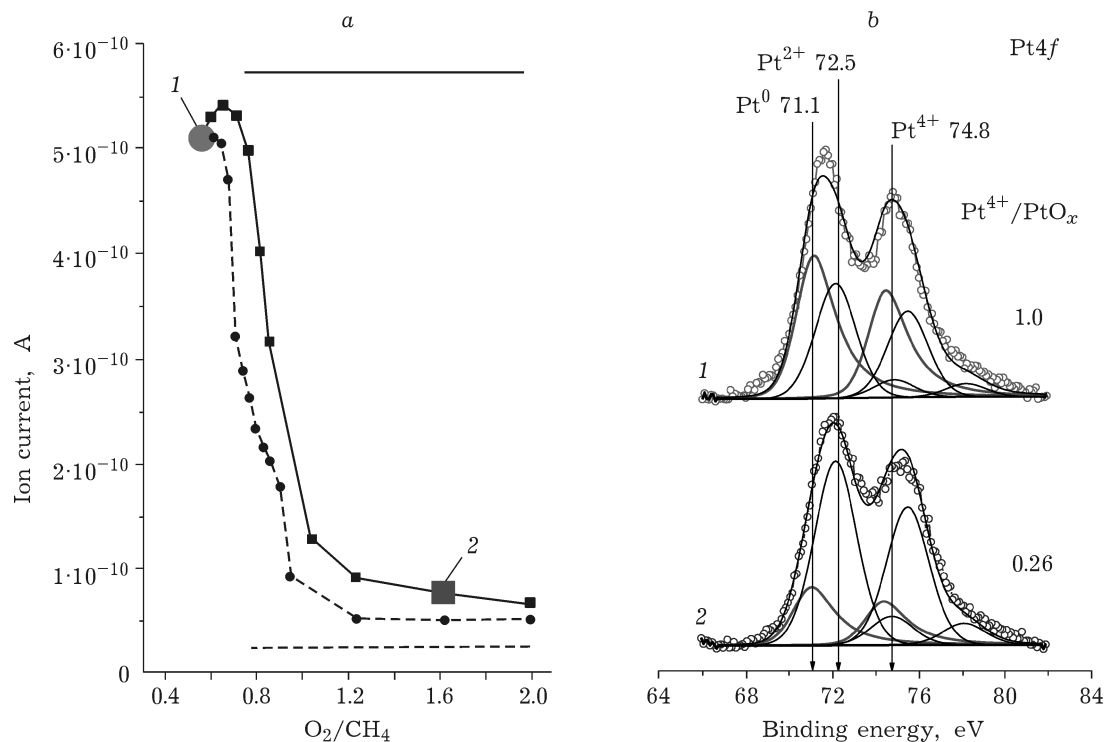

Fig. 8. Concentration hysteresis in the methane oxidation reaction over a 1 mass % Pt/γ-Al$_2$O$_3$ catalyst (d_{Pt}^{av} = 8 nm) accompanied by a change in the electronic state of applied platinum: *a* − level of total ion current from CO and CO$_2$ corresponding to methane conversion in oxidation reaction at a decrease and a subsequent increase in the oxygen content in the mixture; the direction of the arrows schematically shows the direction of a change in the oxygen content; *b* − photoelectron Pt4f spectra measured in the active (*1*) and inactive (*2*) states of platinum under concentration hysteresis conditions. The process conditions: P(CH$_4$) = 0.008 mbar, P(O$_2$) = 0.02 to 0.002 mbar, T = 460 °C.

was detected. An increase in the size of platinum particles leads to narrowing of the hysteresis loop, which may be associated with by a change in the area of the active component, available for the reaction. Varying the particle size of the active component provides an opportunity to manage the sample activity and selectivity in methane oxidation depending on concentration hysteresis conditions.

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