Kinetics and Catalysis, Vol. 43, No. 4, 2002, pp. 555–560. Translated from Kinetika i Kataliz, Vol. 43, No. 4, 2002, pp. 601–607.

Structure of a Platinum–Alumina Catalyst Prepared from the Carbonyl Cluster $H_2[Pt_3(CO)_6]_5$

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Received December 26, 2001

Abstract—The state of a platinum carbonyl cluster in an initial aqueous acetone solution and its transformations on the surface of aluminum oxide in the course of catalyst preparation were studied by EXAFS spectroscopy. It was found that water enters the polynuclear framework of the dissolved cluster (the Pt–O distance is 2.55 Å, where O is the oxygen atom of water). Structural changes in the supported cluster in the course of catalyst preparation exhibited a strong interaction of platinum with alumina (the Pt–O distance is 1.92–1.95 Å), beginning at the step of $H_2[Pt_3(CO)_6]_5$ adsorption. This interaction was retained upon the subsequent high-temperature treatments of the catalyst. The structures of samples prepared from platinum carbonyl and chloroplatinic acid were significantly different. In the former case, a surface prototype was formed from the initial cluster; in the latter case, the sample consisted of platinum metal clusters of a considerable size.

INTRODUCTION

Transition metal clusters are considerably different in nature from mononuclear complexes, which are frequently used as the precursors of supported metal catalysts. The use of cluster complexes, especially, carbonyls, is often responsible for the higher activity, selectivity, dispersity, and thermal stability of supported catalysts. In addition, because of their structure peculiarities, clusters are of considerable interest as model catalyst precursors for solving fundamental problems in heterogeneous catalysis. The use of clusters different in nuclearity, composition, and structure provides an opportunity to create surface ensembles of active metal atoms with certain structures and thus gain further insight into the structure of active centers of real catalysts. Thus, the studies of catalysts based on carbonyl clusters are of both scientific and practical interest. This is particularly true of the cluster analogs of practically important catalysts such as platinum–alumina catalysts, which are used in hydrocarbon conversion (reforming), automobile-exhaust emission control, and so on.

Du *et al.* [1] found that the Pt/Al_2O_3 catalyst prepared from the platinum carbonyl cluster $[N(C_2H_5)_4]_2[Pt_3(CO)_6]_5$ was more stable in the process of *n*-heptane conversion (773 K) as compared with the traditional catalyst from H_2PtCl_6. In this case, supported platinum was stable in a highly disperse state. Handy *et al.* [2] noted a higher selectivity of a catalyst prepared from $[MePPh_3]_2[Pt_3(CO)_6]_5$ in neopentane hydrogenolysis as compared with a traditional analog. The transformations of supported clusters were also studied in the cited publications using IR spectroscopy, chemisorption, and electron spectroscopy. It was found that the cluster adsorbed on Al_2O_3 in freshly prepared samples retained its structure in a vacuum or inert atmosphere at low temperature. On heating up to 370 K in a vacuum, the initial cluster underwent an irreversible structural rearrangement accompanied by the removal of bridging CO groups. It was found by transmission electron microscopy (TEM) that in this case clusters were formed whose size (~1 nm) was close to the size of the initial Pt_{15} cluster.

In the publications cited above, the transformations of the supported cluster and its decarbonylation products were considered without taking into account its interaction with the support, which strongly affects the catalytic properties of the supported catalyst. Kolosov *et al.* [3] attempted to evaluate the interaction of platinum with the support in a $2\%Pt/\gamma\text{-}Al_2O_3$ catalyst prepared from $H_2[Pt_3(CO)_6]_5$ by constructing radial distribution functions. They concluded that a platinum phase with an fcc lattice (Pt_{met}) was absent from the surface, whereas a stable surface compound of platinum with alumina was formed. Its structure was constructed assuming the complete decomposition of the cluster and almost monoatomic distribution of platinum over the surface of the support.

In this work, the structure of the $Pt/\gamma\text{-}Al_2O_3$ catalyst in the course of its preparation from a platinum carbonyl cluster, beginning with a solution and ending with high-temperature treatments of the solid-phase sample in various atmospheres, was studied by EXAFS spectroscopy. The 15-atomic anionic carbonyl cluster $[Pt_3(CO)_6]_5^{2-}$, one of the series of the Chini carbonyl anions $Pt_3(CO_6)]_n^{2-}$ (n = 2–5), which were precipitated with heavy organic anions [4], was used as a parent compound for preparing catalysts. In our case, the negative charge of the cluster was compensated by protons. The proton form $[Pt_3(CO)_6]_5H_2$ of the cluster can be prepared from the polymeric platinum dicarbonyl $[Pt(CO)_2]_m$, which was historically the first carbonyl cluster of Pt^0 [5, 6]. Based on published data [4], its formula can be written as $H_2[Pt_3(CO)_6]_{\sim 10}$; that is, the platinum dicarbonyl is a higher nuclearity analog of Chini cluster ions and its negative charge is compensated by protons.

Note that, in contrast to analogs precipitated with organic cations, the use of the proton form of the carbonyl cluster makes it possible to prepare high-purity model platinum catalysts by the low-temperature decarbonylation of the supported cluster.

EXPERIMENTAL

Initial $H_2[Pt_3(CO)_6]_{\sim 10}$ cluster. The initial $H_2[Pt_3(CO)_6]_{\sim 10}$ cluster (Pt_{30}) was prepared by the reduction of an aqueous solution of chloroplatinic acid ([Pt] ≅ 2 mg/ml) with carbon monoxide at room temperature and atmospheric pressure for $\tau \geq 2$ h in accordance with the reaction

$$30H_2PtCl_6 + 121CO + 61H_2O$$
$$= H_2[Pt_3(CO)_6]_{\sim 10} + 61CO_2 + 180HCl.$$

In this case, platinum was quantitatively precipitated from the solution as a dark cherry precipitate of Pt_{30}. The completeness of the reaction was monitored by measuring the amounts of absorbed CO, released CO_2, and formed HCl, which were practically consistent with the reaction stoichiometry.

$H_2[Pt_3(CO)_6]_5(Pt_{15})$ carbonyl cluster. The $H_2[Pt_3(CO)_6]_5(Pt_{15})$ carbonyl cluster (Pt_{15}) was prepared from the Pt_{30} cluster. For this purpose, the dark cherry precipitate of Pt_{30} was rapidly filtered off, washed with water to remove Cl^- ions, and transferred into a flask with acetone (reagent grade), which was filled with carbon monoxide. Water (3 vol %) was added to the resulting suspension of Pt_{30} in acetone, and the contents were allowed to stand until the complete dissolution of the initial cluster and the formation of Pt_{15}, which was identified by the IR spectrum: ν(Pt–CO) = 2050 cm^{-1} (the stretching vibration frequency of terminal CO groups) and $\nu(\mu_2\text{-CO})$ = 1870 cm^{-1} (bridging CO groups) [4]. The concentration of platinum in the working solution was 6 mg/ml.

Note that the solutions thus prepared are characterized by a high stability in a carbon monoxide atmosphere, where they can be stored for a long time in a hermetically sealed apparatus.

Supported Pt/γ-Al_2O_3 catalysts. The supported γ-Al_2O_3 catalysts were prepared by the adsorption of the Pt_{15} cluster on γ-Al_2O_3 (S_{sp} = 195 m^2/g), which was calcined at 773 K, from an aqueous acetone solution in a CO atmosphere at room temperature. Acetone containing 3 vol % water was poured over the support fraction with a particle size of 0.2–0.5 mm. The resulting suspension was evacuated to completely remove air from the pores of the support, and a cluster solution containing platinum in an amount required for preparing 2 wt % Pt/Al_2O_3 was introduced with intense stirring. After adsorption, the samples were subjected to various thermal treatments.

EXAFS spectroscopy. The platinum L_3-edge EXAFS spectra were measured at the EXAFS Station of the Siberian Synchrotron Radiation Center (Novosibirsk) [7]. The initial clusters in solution and the supported 2% Pt/γ-Al_2O_3 catalysts were examined. The spectra of clusters were measured in a CO atmosphere. The reduced catalysts were placed in hermetically sealed cells with beryllium windows out of contact with air. The catalysts that were dried and calcined in air were examined in air. Platinum metal was used as a model compound with the known structure. All spectra were measured at room temperature. The oscillating part of $\chi(k)$ was separated using standard techniques [8]. The data were analyzed by simulation according to a standard procedure with the use of the EXCURV-92 program [9]. The EXAFS spectra were simulated in a wavenumber range of 3.5–12.0 Å^{-1}. The table summarizes the structural data for all compounds.

In addition to EXAFS spectra, XANES data were also used. The XANES region involves transitions to unoccupied $d_{5/2}$ symmetry upper levels and to ionized states with energies up to 100 eV above the ionization potential. This spectrum region provides information on the charge state of the element and on the symmetry of its environment. In this work, we used the so-called white line for determining the effective charge state of platinum. A maximum that appears because of transitions to vacant states near the Fermi level is designated the white line; it manifests itself in the spectrum as a peak at the absorption edge. The height of this peak with reference to the absorption edge correlates with the effective positive charge at the platinum atom.

RESULTS AND DISCUSSION

$H_2[Pt_3(CO)_6]_5$ Cluster in an Aqueous Acetone Solution

The platinum carbonyl cluster $H_2[Pt_3(CO)_6]_5$ in an aqueous acetone solution was prepared by the interaction of the higher nuclearity species $H_2[Pt_3(CO)_6]_{\sim 10}$ with the solvent. The solubility of the latter cluster in dry acetone is low, and the major portion of it occurred as a suspension. The cluster can be completely dissolved only by the addition of water. In this case, the color of the solution changed from initial brown to intense grass green. The IR spectrum of the resulting solution exhibited lines with ν(Pt–CO) = 2050 cm^{-1} and $\nu(\mu_2\text{-CO})$ = 1870 cm^{-1}, which are characteristic of the $[Pt_3(CO)_6]_5^{2-}$ cluster. This 15-atomic carbonyl cluster

EXAFS data for the initial cluster and its decarbonylation products on the surface of γ-Al_2O_3 in the course of catalyst preparation

Sample no.	Sample	Distance, Å	Coordination number	Debye factor $\times 10^{-4}$, Å^2	Distance assignment	*R*-factor
1	$H_2[Pt_3(CO)_6]_5$	1.85	1.6	137	Pt–C	5.2
	Aqueous acetone solution	2.68	1.7	41	Pt–Pt	
		2.55	4.3	137	Pt–OH_2	
2*	Pt/γ-Al_2O_3	1.92	0.8	14	Pt–O	9.9
	Drying in an Ar atmosphere at room temperature	2.07	0.8	14	Pt–O	
		2.72	3.4	95	Pt–Pt	
3*	Pt/γ-Al_2O_3	1.95	1.3	14	Pt–O	7.0
	Drying in air at room temperature	2.10	1.1	14	Pt–O	
		2.75	2.8	91	Pt–Pt	
4*	Pt/γ-Al_2O_3	1.92	2.6	76	Pt–O	–
	Drying in air at 120°C	2.71	5.7	119	Pt–Pt	
5*	Pt/γ-Al_2O_3	1.93	2.2	87	Pt–O	–
	Reduction with H_2 at 500°C	2.77	4.4	81	Pt–Pt	
6*	Pt/γ-Al_2O_3	1.94	2.9	30	Pt–O	–
	Calcination in air at 500°C	3.04	2.2	19	Pt–Al	
		3.96	0.9	11	Pt–Al	
7	Pt/γ-Al_2O_3 from H_2PtCl_6	2.77	7.7	76	Pt–Pt	–
	Reduction with H_2 at 500°C	3.92	2.9	96	Pt–Pt	
		4.68	3.8	90	Pt–Pt	

* Samples 2–6 were prepared from $H_2[Pt_3(CO)_6]_5$.

is one of the series of the dianionic carbonyl Chini clusters $[Pt_3(CO_6)]_n^{2-}$ ($n = 2$–5) [4].

The formation of $H_2[Pt_3(CO)_6]_5$ from $H_2[Pt_3(CO)_6]_{\sim 10}$ takes place by the interaction of the latter with water present in the reaction solution in an amount of ~3%. At [Pt] = 6 mg/l, the molar ratio $[H_2O] : [Pt] \cong 50$. It is well known [4] that water acts as a reducing agent with respect to the high-nuclearity cluster $[Pt_3(CO)_6]_{\sim 10}^{2-}$ to convert it into the lower nuclearity species $[Pt_3(CO)_6]_5^{2-}$ as follows:

$$H_2[Pt_3(CO)_6]_{\sim 10} + H_2O = 2H_2[Pt_3(CO)_6]_5 + 0.5O_2.$$

According to Calabrese *et al.* [10], the structural unit of the $[Pt_3(CO)_6]_5^{2-}$ cluster precipitated with a heavy organic cation $[E(R_4)]_2[Pt_3(CO)_6]_5$ (E = N, H, or As; R = alkyl or aryl) is a triangle of platinum atoms with three terminal and three bridging CO groups. The platinum triangles arranged in parallel planes one above the other form a trigonal prismatic cluster framework slightly distorted by a helical twisting. The structure of the $[Pt_3(CO)_6]_5^{2-}$ cluster is characterized by two Pt–C distances from bridging (2.03 Å; coordination number of 2) and terminal (1.80 Å; coordination number of 1) CO groups and by two Pt–Pt distances, intratriangular (2.66 Å; coordination number of 2) and intertriangular (3.08 Å; coordination number of 1.6).

The results of this study obtained by EXAFS spectroscopy for the cluster in solution (table, Fig. 1) are significantly different from the above data for the cluster in a solid state. The radial atomic distribution (RAD) curve for the dissolved cluster (Fig. 1, curve *1*) exhibits all peaks corresponding to distances in an individual triangle of platinum atoms: a Pt–Pt distance of 2.68 Å, which is in complete agreement with X-ray diffraction data [10], although with a somewhat underestimated coordination number (1.7 in place of 2), and platinum–

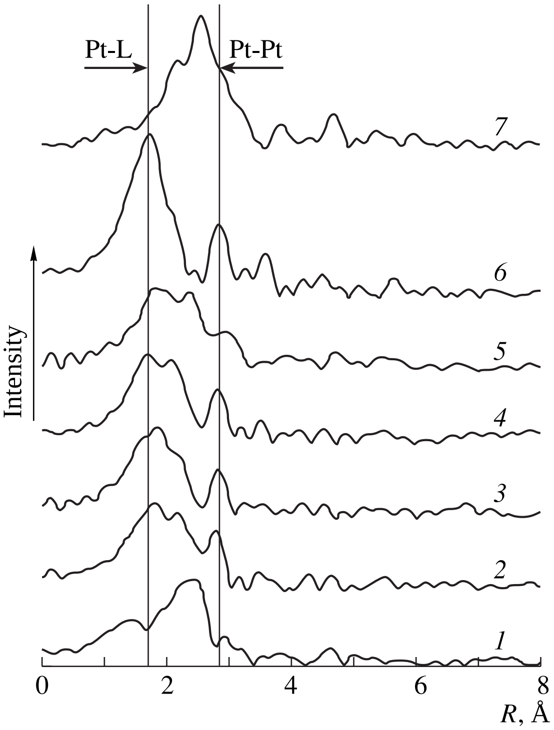

Fig. 1. Fourier transform amplitudes of the Pt L_3-edge EXAFS spectra of samples 1–7 (see the table).

ligand distances. Because EXAFS spectroscopy cannot resolve closely spaced peaks, one platinum–carbon distance was taken in the simulation. Because the coordination number for bridging CO groups is greater than that for terminal groups, the distance was found closer to 1.80 Å. Because of this, the coordination number for the Pt–ligand distance was also underestimated.

Thus, the structure of the $[Pt_3(CO)_3(\mu_2\text{-}CO)_3]_5^{2-}$ fragment of the dissolved cluster determined by EXAFS spectroscopy is in complete agreement with the structure found for the solid cluster $[As(C_6H_5)_4]_2[Pt(CO)_3(\mu_2\text{-}CO)_3]_5$, which was precipitated with a heavy organic cation [10].

However, the RAD curves for the solution did not exhibit a peak due to a Pt–Pt distance of ~3.08 Å, which corresponds to the interplanar spacing between Pt_3 triangles in a solid state. The absence of the Pt–Pt distance between Pt_3 fragments can result from a higher mobility of the cluster in solution and from its interactions with the solvent, especially with water molecules. In turn, this results in both the separation of Pt triangles and a disorder when individual Pt_3 fragments can be turned through different angles with respect to one another. The results of studying of the ^{195}Pt NMR spectra of the dianionic Chini clusters $[Pt_3(CO_6)]_n^{2-}$ (n = 2–5) in acetone and tetrahydrofuran solutions also suggested the high mobility of the cluster [11]. It was found that in the presence of n internal triangles in a cluster ($n \geq 3$) the following phenomena take place: (1) the rapid rotation of Pt_3 triangles about the threefold axis of the cluster framework and (2) the rapid intermolecular exchange of Pt_3 fragments. In this case, an enhanced mobility of $[Pt_3(CO)_6]_5^{2-}$ toward external Pt_3 exchange was noted.

The EXAFS results are indicative of another difference between the structures of the dissolved cluster and its solid analog. The spectrum of the dissolved cluster exhibited a long Pt–O distance (2.55 Å) with a coordination number higher than 4 (table), which is consistent with a distance between the Pt atom and the solvation molecules of water, which was absent from the previously studied Chini anions $Pt_3(CO_6)]_n^{2-}$ (n = 2–5) synthesized in dried solvents. The occurrence of this distance is consistent with gel formation at a high water concentration in a solution of the cluster; this phenomenon will be described below. The results obtained allowed us to assume that water enters the structure of the dissolved $[Pt_3(CO)_6]_5^{2-}$ cluster. The number of water molecules associated with the cluster was estimated at ~18. In addition to the coordination of water molecules to platinum atoms (a distance of 2.55 Å), the cluster can also be hydrated by the formation of hydrogen bonds with polar CO groups. In this context, an interesting feature in the behavior of $[Pt_3(CO)_6]_5^{2-}$ in an aqueous acetone solution should be noted. It consists in the formation of a viscous intensely colored green gel as the water content was increased up to ~25–50 vol %. That is, although the cluster solution was diluted with water, it was cross-linked by hydrogen bonds with the participation of solvation water molecules.

Supported Cluster

The structure of the cluster formed after the adsorption of $[Pt_3(CO)_6]_5^{2-}$ on γ-Al_2O_3 followed by drying at room temperature in an argon atmosphere (sample 2) or air (sample 3) is considerably different from that of the dissolved cluster. The RAD curves of the above samples (Fig. 1) did not exhibit the peak that was observed for the cluster in solution and corresponded to the Pt–O distance 2.55 Å, where O is the oxygen atom of water molecules coordinated to platinum. At the same time, the RAD curve exhibited peaks corresponding to Pt–O distances of 1.92 and 2.07 or 1.95 and 2.10 Å for samples 2 and 3, respectively, and the coordination number for the first coordination sphere of platinum (the Pt–O bond) decreased.

To attribute the obtained distances to certain bonds of the cluster, its chemical properties should be taken into account. Under conditions of preparing both samples, the structure of the initial cluster was affected by its interactions with the support and solvation water. Along with this, in sample 3, the cluster underwent decarbonylation due to the oxidation of CO ligands with atmospheric oxygen to CO_2. Upon the drying of samples both in an argon flow and in air, the color of the supported cluster was changed. The intensely green sample obtained after impregnation with a solution of $[Pt_3(CO)_6]_5^{2-}$ turned brown in the course of drying in both carbon monoxide and argon atmospheres. Handy *et al.* [2] noted that this cluster supported on alumina is unstable in the presence of moisture not only in air but also in an inert atmosphere, as supported by the disappearance of bands due to CO ligands at room temperature. This is likely due to the conversion of carbon monoxide on a wet sample. Consequently, samples 2 and 3 should be almost identical.

The Pt–O and Pt–C distances cannot be distinguished by EXAFS spectroscopy. Therefore, in the interpretation of EXAFS data, the following versions cannot be excluded: (1) the partial retention of CO groups, that is, the presence of Pt–C and Pt–O distances and (2) the presence of two Pt–O distances, one of which is shorter and the other longer than 2.0 Å. However, the chemical behavior of the carbonyl cluster indicates that in a damp atmosphere all CO groups were removed after blowing with both argon and air. This is particularly true of air-dried sample 3. Note that the structural characteristics of samples 2 (Ar) and 3 (air) are very similar. Only the coordination numbers for Pt–Pt and Pt–O distances are different; this can be due to experimental errors. This fact provides support to the assignment of the distances 1.92 and 2.07 or 1.95 and 2.10 Å to Pt–O bonds in samples 2 or 3, respectively.

Figure 2 demonstrates the XANES spectra in the L_3-edge region for the $[Pt_3(CO)_6]_5^{2-}$ cluster in an aqueous acetone solution and for samples 2 and 3 prepared from this solution. As mentioned above, the L_3-edge is characterized by the so-called white line, that is, transitions to vacant $d_{5/2}$ states. The intensity of this line, that is, its height above the absorption edge, is indicative of the charge state of platinum atoms. In the metal, platinum exhibits the $d_{9.65}S_{0.35}$ configuration, and it is characterized by a much lower white-line intensity than that of platinum ions. In the carbonyl clusters, although platinum formally occurs in a zero-valent state, its electronic state is much different from that of the metal; that is, a redistribution of electrons between *d*- and *s*-states takes place with a decrease in the number of *d*electrons. As can be seen in Fig. 2, the effective charge of platinum in the cluster evaluated by $d_{5/2}$ states remained unaffected after supporting on a carrier, because the white-line height remained unchanged. However, the shape of the absorption region above the ionization potential (XANES region) strongly changed, and it was identical for the samples dried in air and in an inert gas. The constancy of the white line and identical changes in the XANES region for samples 2 and 3 allowed us to suggest that the cluster underwent minimum structural changes in the course of drying at room temperature. Changes in the XANES spectra can be attributed to the appearance of Pt–Pt bonds between Pt_3 triangles, as evidenced by an increase in the coordination number for this distance up to 3.4.

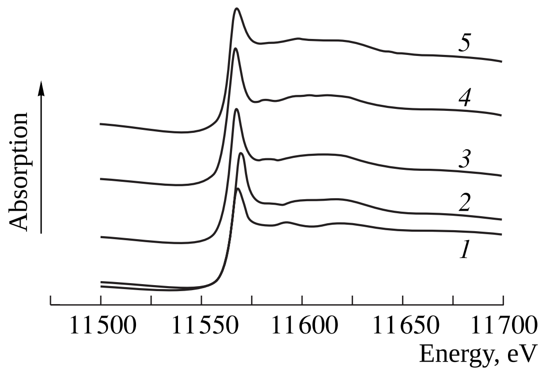

Fig. 2. Pt L_3-edge XANES spectra of samples 1–5 (see the table).

A conceivable model of the surface compound is an almost decarbonylated Pt_{15} cluster, which interacts with the support surface through a lateral face of the framework. This interaction provides a minimum energy of the cluster–support system because of the maximum interaction of Pt_{15} with the support. It is likely that in this case several shorter bonds of platinum atoms with the surface oxygen of the support lattice were formed (distances of 1.92 and 1.95 Å) to provide a reasonable stability of the cluster structure. This hypothesis was additionally supported by the results from thermally treated samples, which are considered below. The longer Pt–O distances (2.07 and 2.10 Å) can be ascribed to the remaining molecules of chemisorbed water, the distance to which was shortened because of a partial degradation of the solvation sphere.

Dehydrated Sample

Sample 4 was dehydrated in air at 393 K. The RAD curve exhibited only two peaks; one of them was ascribed to the Pt–ligand distance, and the other, to the Pt–Pt distance. This thermal treatment would be expected to result in the complete dehydration of the sample and in the complete removal of CO groups. That is, only oxygen was present in the first coordination sphere of platinum. The retention of the short distance 1.95 Å and the complete disappearance of the distance 2.1 Å allowed us to assume (see above) that the distances 2.07 and 2.1 Å in samples 2 and 3, respectively, are ascribed to the Pt–O bond, where O is the oxygen of the remaining chemisorbed water. An increase in the coordination number for the Pt–Pt distance is also indicative of a more highly ordered structure of the cluster due to the removal of ligands and of the appearance of Pt–Pt interactions between adjacent triangles with a distance approximately equal to that within a triangle. The structural data are consistent with the above model of the Pt_{15} cluster bound to the support through a lateral face.

Samples after High-Temperature Treatments

Two samples reduced at 773 K were studied; one of them (5) was prepared from platinum carbonyl, and the other (7), from chloroplatinic acid. The structures of these samples were essentially different. Evidently, sample 7 consisted of large platinum metal clusters. This follows from the fact that a peak due to the platinum–ligand distance is absent from the RAD curve and there are three peaks due to the Pt–Pt distance corresponding to platinum metal with coordination numbers typical of clusters 16–20 Å in diameter. The structure of sample 5 is identical to the structure of sample 4, which was not subjected to high-temperature treatments. This fact is indicative of the strong interaction of the platinum carbonyl cluster with the support in the latter sample. Severe reduction conditions (773 K) did not degrade it. This was also demonstrated by the retention of the intense white line at the *L*-edge of sample 5, although its intensity is lower than that in the initial clusters (Fig. 2).

Data on the structure of sample 6, which was calcined in air at 773 K, provide indirect evidence for the strong interaction of cluster platinum with the support. It can be seen that calcination completely degraded the cluster and platinum ions were dissolved in the support; it is likely that they were trapped in so-called forbidden octahedral positions. This follows from the presence of the Pt–Al distance 3.96 Å, which is absent from the ordinary spinel structure.

Note that the strong interaction took place even at the first stage of catalyst preparation, that is, starting from the adsorption of the cluster on alumina. This follows from the constant Pt–O distance (1.92–1.95 Å), which was observed in all samples (2–6) not subjected to thermal treatment (2, 3) or subjected to moderate (4) or high temperatures (5, 6). This manifests itself in an important catalyst property such as high dispersity, which is stable to high temperatures, that is, in the almost complete absence of the sticking of platinum supported from the carbonyl cluster up to 773 K [12].

It follows from the results of this study that the nature of the starting compound has a strong effect on the formation of platinum supported on Al_2O_3. Compounds that contain platinum in a low oxidation state, as is the case in the carbonyl clusters, should be used as initial materials for preparing a finely dispersed catalyst stable to sticking.

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