Catalytic systems based on platinum and heteropoly compounds for oxidation of hydrocarbons with a dioxygen—dihydrogen gaseous mixture

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The oxidation of cyclohexane, saturated and aromatic hydrocarbons with an O_2—H_2 gaseous mixture was applied to study the catalytic properties of bicomponent systems based on platinum and heteropoly compounds (HPC). The consumption of gases and the yield of the products depend on the surface area, accessibility of the platinum species to the reactant, and composition of the HPC. The solid Pt samples suspended in an HPC solution, the Pt(5%)—PMo_{12}/Al_2O_3 bicomponent supported system, and the solid bicomponent sample prepared from the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ complex salt were used as catalysts. Among the catalysts with the same molar compositions of the active components, the bicomponent materials are much more active in the oxidation than a combination of the Pt catalyst with an HPC solution. The bulk catalyst is a crystalline solid substance with the HPC structure with incorporated Pt species. Molybdenum is predominantly oxidized, and platinum is present in both the reduced and ionic states. The oxidation of saturated hydrocarbons affords alcohols and ketones. The yield of the positional isomers of the oxygenated products increases in the series primary ≪ secondary< tertiary C-atoms. Benzene and toluene are converted into the corresponding phenols in equal yields. The scheme proposed for oxidation assumes the participation of the active hydroxyl radical.

Key words: hydrocarbons, platinum, heteropoly compounds, oxygen, hydrogen, oxidation.

Conjugated oxidation of hydrocarbons occurs at relatively low temperatures and is characterized by high selectivity of transformation of the initial organic substrate into the desired product. These features follow from the oxidation mechanism that implies that coreduction generates an active oxidant, which can easily react with the substrate. The role of the coreducing agent plays either the second substrate molecule (in autooxidation reactions) or another organic compound, *e.g.*, ascorbic acid, hydrazobenzene, thiols, and aldehydes. Since the reaction needs the stoichiometric amount of the coreducing agent to occur, replacement of organic compounds by simple inorganic reducing agents, such as carbon oxide and dihydrogen is preferable.[1—7]

The catalytic oxidation of hydrocarbons with a O_2—H_2 was a subject of considerable interest in recent years. Previously, we studied the possibility to design bicomponent catalytic systems for hydrocarbon oxidation in the O_2—H_2 medium. The catalytic systems consisted of platinum metals and heteropoly compounds (HPC). Platinum functioned as an activator of dioxygen catalyzing the partial reduction of dioxygen to the peroxide form, whereas HPC were involved in the reaction of this peroxide oxygen with the substrate

$$O_2 + H_2 \xrightarrow{[Pt]} [O] + H_2O, \tag{1}$$

$$[O] + S \xrightarrow{[HPC]} SO,$$

where [O] is the peroxide compound; S and SO are the initial and oxidized forms of the organic substrate, respectively.

The catalytic systems active in oxidation by the O_2—H_2 gaseous mixture were developed[8,9] from the Pt^{II} and Pd^{II} complexes with the $PW_{11}O_{39}{}^{7-}$ heteropolyanions. The catalysts were used in both homogeneous and heterogeneous oxidation of benzene and cyclohexane. In the case of heterogeneous version, the complexes were supported on the silica surface. They exhibited a high activity after reductive pretreatment. In this work, we used HPC of different composition and determined those that could most efficiently be applied as components of

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catalytic systems for oxidation by the O_2—H_2 gaseous mixture.

The purpose of this work is to study the catalytic properties of bicomponent systems based on Pt and HPC in the oxidation of cyclohexane as well as saturated and aromatic hydrocarbons by the O_2—H_2 gaseous mixture.

Experimental

Preparation of catalysts. The metallic platinum powder was prepared by the reduction of chloroplatinic acid H_2PtCl_6.

The characteristics of the catalysts obtained by the impregnation of various supports by a solution of H_2PtCl_6 are presented below.

Catalyst*	Support
Pt(1%)/SiO_2(280)	KSK silica
Pt(5%)/SiO_2(280)	KSK silica
Pt(5%)/SiO_2(45)	Hydrothermally pretreated KSK
Pt(5%)/C(300)	Pyrocarbon (Sibunit)
Pt(5%)/Al_2O_3(300)	γ-Al_2O_3

Powders of the supports were impregnated with an aqueous solution of H_2PtCl_6, and water was evaporated. Then the samples were dried at 100 °C and calcined at at 300 °C, except for the Pt(5%)/C(300) sample that was not subjected to calcination. Then all samples were reduced for 1 h in an H_2 flow at 300 °C. The catalysts prepared were stored in air in the room, and their properties remained unchanged for 1—2 weeks.

To prepare the supported Pt(5%)—PMo_{12}/Al_2O_3 sample, the corresponding amounts of H_2PtCl_6 and $H_3PMo_{12}O_{40}$ in an aqueous solution were mixed in the 1 : 1 molar ratio, and this solution was used for impregnation of the support. The sample was dried at 100 °C, calcined in air at 300 °C, and reduced for 1 h in an H_2 flow at 150 °C.

The solid Pt—PMo_{12} catalyst was prepared from the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ salt. The latter was synthesized by mixing an 0.1 *M* solution of the platinum ammonia complex $[Pt(NH_3)_4]Cl_2$ and an 0.1 *M* solution of $H_3PMo_{12}O_{40}$ in the equimolar ratio. A precipitate was separated by centrifuging, washed with water, and dried at ~20 °C. The salt that formed was calcined in air at 300 °C, reduced in an H_2 flow at 150 °C, and repeatedly heated in a wet air at 150 °C.

Characterization of catalysts. Elemental analysis of the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ salt was performed by the X-ray fluorescence method: Mo, 52.5%; P, 1.4%; Pt, 4.94%; the molar ratio Pt : Mo : P = 0.55 : 12 : 1 was close to that in the molecular formula. The content of P and the content of Mo in a solution at the end of the reaction was determined by the photocolorimetric method, *i.e.*, content of phosphorus was determined from the concentration of the phosphorus-molybdenum-vanadium complex, and the content of MO was found from the concentration of the Mo^V complex with thiocyanate ions.[10,11]

Thermogravimetric analysis was carried out on a Q 1500D derivatograph. Measurements were performed at a heating rate of 10 deg min^{-1}. IR spectra were recorded on a Specord IR-75 instrument in KBr pellets.

The surface of the supports was measured from the adsorption of N_2 at 77 K. The specific surface area S_{Pt} (m^2 (g-at. Pt)$^{-1}$) was determined from transmission electron microscopy (TEM) data and calculated using the equation

$$S_{Pt} = 6 \cdot 10^{-4} m \left(\sum_i n_i d_i^2\right) / \left[\rho\left(\sum_i n_i d_i^3\right)\right],$$

where n_i is the number of Pt species with the diameter d_i (cm), ρ is the density of metallic platinum (21.46 g cm^{-3}), and *m* is the atomic weight of platinum (195 g g-at.$^{-1}$).

TEM images of the surface of the platinum catalysts were obtained on a JEOL 2010 instrument with a lattice resolution of 1.4 Å and an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) were detected at ~20 °C on an ES-2401 instrument using a Mg-Kα source.

Catalytic experiments. The catalytic reaction was carried out in a glass flask under an atmospheric pressure and at a temperature of ~35 °C, and the exact value of temperature was maintained using a thermostat. A mixture of solid and liquid components of the system as a vigorously stirred suspension was brought to the contact with the gas phase containing the O_2 and H_2 gases necessary for the reaction. The amount of the consumed gas was measured using a gas burette. The products of hydrocarbon oxidation were analyzed on a Kristall 2000 chromatograph with an HC-5 capillary column (30 m × 0.53 mm, DB-1701, JW Scientific Inc.) and a flame-ionization detector. In addition, LC-MS analysis (CV-2091 spectrometer) was used to identify the oxidation products.

Results and Discussion

Catalytic systems with different platinum catalysts. The catalytic systems under study contained platinum and HPC. The efficiency of the systems in oxidation with an O_2—H_2 gaseous mixture was estimated in model reactions with hydrocarbons using cyclohexane as a standard reactant. Initially a heteropoly acid $H_3PMo_{12}O_{40}$ was used in combination with various platinum catalysts, including the metallic platinum powder and platinum supported on the porous carriers in the form of H_2PtCl_6 and then reduced by hydrogen. Oxidation by a O_2—H_2 gaseous mixture was carried out in a suspension of the solid Pt catalyst in a solution of the heteropoly acid in MeCN. According to chromatographic analysis, cyclohexanol and cyclohexanone were almost the only products of cyclohexane oxidation with the ratio varying from 10 : 1 to 20 : 1. The main transformations of cyclohexane were described by the equation

$$\begin{tikzcd} C_6H_{12} + O_2 + H_2 \arrow[r] & C_6H_{11}OH + H_2O \arrow[d, "+1/2\ O_2"] \\ & C_6H_{10}O + H_2O\ . \end{tikzcd} \qquad (2)$$

Oxidation consumed a much greater amount of the dioxygen—dihydrogen mixture than the stoichiometric

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* Hereafter figures in parentheses at the support indicate the surface area of the support (m^2 g^{-1}).

Table 1. Yields (μmol) of the products of cyclohexane[a] oxidation and the amount of the reacted gases (m/μmol) in systems containing different Pt catalysts

Entry	Catalyst	S_{Pt} /m^2 (mol Pt)$^{-1}$	m	Yield	
				I[b]	II[c]
1	No catalyst		300	1	0
2	Pt (powder)	$2.7 \cdot 10^3$	1050	17	1
3	Pt(5%)/SiO_2(280)	$8.4 \cdot 10^3$	1960	19	1
4	Pt(5%)/SiO_2(45)	$6.5 \cdot 10^3$	2000	24	2
5	Pt(5%)/C(300)	$3.5 \cdot 10^4$	2300	31	3
6	Pt(5%)/Al_2O_3(300)	$1.7 \cdot 10^4$	3200	19	1

[a] Reaction conditions: 1 mL of MeCN; 0.1 mL of cyclohexane; 6 mg of $H_3PMo_{12}O_{40}$; T = 35 °C; O_2—H_2 (1 : 2), reaction time 1 h. In all experiments the content of Pt in the mixture was 2.6 μmol.

[b] Cyclohexanol.

[c] Cyclohexanone.

value. This indicated that water formation occurred intensely in parallel with reaction (2).

Using the data in Table 1, the amounts of reacted dioxygen and dihydrogen can be compared with oxidation products that formed on different platinum catalysts. In all experiments, the catalytic systems contained equal molar amounts of Pt and $H_3PMo_{12}O_{40}$ (see Table 1). The Pt(5%)/C(300) catalyst with the highest surface of supported platinum is the most active in cyclohexane oxidation among the catalysts with similar surface areas (equal accessibilities of the platinum surface to the reactants, see Table 1, entries *3*, *5*, and *6*).

The catalysts for entries *3* and *4* were prepared using silica with different surface areas (280 and 45 m^2 g^{-1}). The latter exhibited a higher activity in cyclohexane oxidation despite a lower surface area of platinum. Moreover, the dispersed platinum powder is comparable in activity with the supported samples, whose surface (calculated per mole of Pt) was much higher than the Pt powder surface. Therefore, the activity of the system is determined, to a great extent, by the accessibility of the platinum species to the reactants.

Catalytic systems containing HPC with different compositions. In the absence of HPC, the platinum samples exhibited the intense consumption of an H_2—O_2 gaseous mixture. However, the gases were consumed to reduce dioxygen to water, and no product of cyclohexane oxidation was observed. In the presence of HPC, the transformation of the gases into water was still considerable (Table 2), namely, not more than 20% reacted gases were consumed to oxidize cyclohexane (see Table 2, entry *7*) with the most part of gases transformed into water. Nevertheless, Pt partially lost its ability to catalyze the reduction of dioxygen to water due to the interaction of the HPC with its surface.

Table 2. Yields (μmol) of the products of cyclohexane[a] oxidation and the amount of the reacted gases (m/μmol) in systems containing the Pt(1%)/SiO_2(280) catalyst (55 mg) and different HPC

Entry	HPC	m	Yield	
			I[b]	II[c]
1	Without HPC	10000	<1	0
2	$H_3PMo_{12}O_{40}$	2860	25.2	1.1
3	$H_6P_2Mo_{18}O_{62}$	1520	26.7	3.2
4	$H_3PMo_6W_6O_{40}$	1740	6.5	0.6
5	$H_3PW_{12}O_{40}$	2050	3.8	0.7
6	$H_5PW_{11}Ti^{IV}O_{40}$	1120	4.1	6.7
7	$H_5PW_{11}Zr^{IV}O_{40}$	315	13.9	5.8
8	$H_4PW_{11}V^{V}O_{40}$	1295	11.9	1.2
9	α-1,2,3-$H_6PW_9V_3O_{40}$	940	19.8	1.6
10	$H_5PMo_{10}V_2O_{40}$	1830	74.4	3.5
11	$H_4PMo_{11}VO_{40}$	1695	55.7	2.1
12	$H_6PMo_9V_3O_{40}$	1295	6.5	0

[a] Reaction conditions: 1 mL of MeCN; 0.1 mL of cyclohexane; 7—8 mg of HPC (Pt : HPC = 1 : 1); T = 35 °C; O_2—H_2 (1 : 2), reaction time 1 h.

[b] Cyclohexanol.

[c] Cyclohexanone.

On forming water the heteropoly compounds with different compositions may deactivate platinum in different ways. Therefore, the surface deactivation can be explained by the oxidation of metallic platinum by the heteropoly acid. Among HPC listed in Table 2, the strongest oxidants are the P—Mo and P—Mo—V compounds, whereas the strongest deactivation effect was observed for the P—W heteropoly acids modified by the Ti^{IV}, Zr^{IV}, and V^{V} transition metal ions. It is most likely that the formation of water is suppressed by the high adsorptivity of multi-charged heteropolyanions rather than the oxidative activity. Due to the high absorptivity, the Pt species, when contacted with the HPC-containing reaction solution, are covered by a shell of the adsorbed heteropolyanions. At the same time, it is known that the reduction of molecular oxygen with hydrogen proceeds through the step of dioxygen adsorption on the metal. The adsorbed heteropolyanions restrict the accessibility of dissolved dioxygen to the platinum surface thus suppressing dioxygen reduction. Therefore, the adsorption of the heteropolyanions determines the consumption of gases: the higher the adsorption, the lower the consumption of gases.

It is possible that the role of adsorption of the heteropolyanions in the process is not confined to reduction in the amount of inefficiently consumed O_2 and H_2. Coverage of the metal surface by the heteropolyanions changes the relation between the forms of adsorbed oxygen along with a decrease in dioxygen adsorption. This makes the dissociative adsorption of oxygen[12] preceding the reduction of molecular oxygen to water less probable and, by contrast, favors adsorption in the molecular form, whose reduction affords peroxide compounds. Thus, the probability of hydrogen peroxide formation becomes higher in the presence of HPC.

The presence of HPC suppresses water formation, moreover, it initiates the oxidation of cyclohexane. The data in Table 2 do not exhibit correspondence between the opposite effects of HPC in the water formation and cyclohexane oxidation. This suggests that the deactivating effect of HPC and their ability to oxidize hydrocarbons are not directly related.

The highest yield of the products of cyclohexane oxidation was obtained for the the P—Mo and P—Mo—V HPC with the number of vanadium atoms ≤2, *i.e.*, for the HPC with the specific ability to generate homolytic processes on contact with hydrogen peroxide. These were numerously exemplified in the literature by catalytic oxidation *via* the homolytic decomposition of hydrogen peroxide (see, *e.g.*, Ref. 13). By analogy to these processes, we can assume that in our case the HPC initiates peroxide decomposition to form the $HO^•$ radicals capable of reacting with various hydrocarbons.

Bicomponent solid catalysts. In the systems considered, the catalytically active species involving platinum and HPC are formed due to the contact of the platinum surface with a solution of HPC. We succeeded in forming the platinum species surrounded with the heteropolyanions as solid particles and comparing their effect with that of the systems consisting of the solid Pt catalyst and dissolved HPC.

The solid samples containing both active components (Pt and $H_3PMo_{12}O_{40}$) were the supported $Pt—PMo_{12}/Al_2O_3$ sample and the solid catalyst obtained from the salt of the $[Pt(NH_3)_4]^{2+}$ complex cation and P—Mo heteropolyanion, *viz.*, $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$. In both cases, the conditions of thermal and reductive treatment were selected in such a way that the samples gained the catalytic activity in oxidation. The samples were heated and reduced under mild conditions (300 and 150 °C, respectively). Thermogravimetric analysis of the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ complex salt showed that at temperatures <400 °C the change in the HPC composition is associated with a loss of water of crystallization and ammonia and does not affect the molecular structure of the heteropolyanion. The unchanged structure of the the $PMo_{12}O_{40}{}^{3-}$ heteropolyanion is also confirmed by the IR spectroscopic data, namely, the bands characteristic of the heteropolyanion (ν/cm^{-1}: 1060 (PO_4 group), 960 (Mo=O bond in the heteropolyanion), and 862 and 790 (vibrations of the linear and angular Mo—O—Mo bonds, respectively)) appeared in the spectra of both the initial $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ complex salt and solid catalysts based on this salt.

The charges of platinum and molybdenum in the bicomponent solid catalysts were determined using XPS. The spectrum of the solid catalyst prepared from the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ complex in the region of Pt 4f signals contained the band from Pt^0 at 71.5 eV and a less intense band from Pt^{2+} at 72.5 eV. The bands from molybdenum Mo 3d appeared at 233.2 and 236.3 eV corresponded to Mo^{6+}.[14] Thus, the active catalysts contained platinum in both the metallic and ionic states, and the heteropoly compound was predominantly in the oxidized form.

The results of catalytic tests of the solid bicomponent catalysts and comparative tests of the Pt(5%)/SiO_2 catalyst with the dissolved heteropoly acid (Fig. 1) showed that although the composition of active components and reactants was the same in all three systems, the yield of the products of cyclohexane oxidation was higher in the presence of the solid bicomponent catalysts.

The reaction medium partially dissolved the solid catalyst, *viz.*, about 50% HPC transferred to a solution during 1 h of the reaction. The shape of the curve describing product accumulation with time shows that the rate of cyclohexane oxidation gradually decreases during ~1 h from the beginning of the reaction (Fig. 2, *a*). After that the oxidation products were accumulated for another several hours but with a lower rate. When another bicomponent $Pt—PMo_{12}/Al_2O_3$ catalyst was used, the heteropoly compound was not transferred to a solution in a noticeable amount due to the strong adsorption on

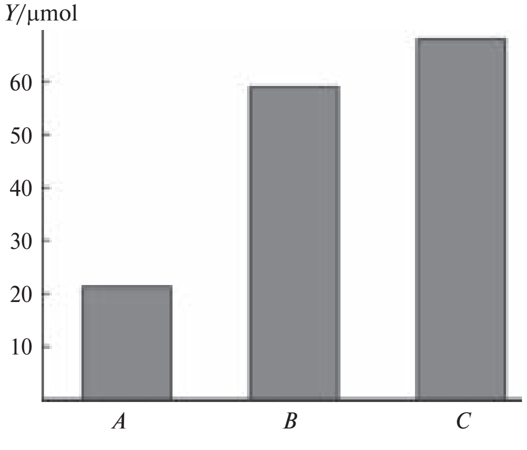

Fig. 1. Yields of the products of cyclohexane oxidation (*Y*) in the Pt(5%)/SiO_2 catalytic systems (10 mg) in a solution of $H_3PMo_{12}O_{40}$ (6 mg) (*A*), Pt(5%)—PMo_{12}/Al_2O_3 supported catalyst (10 mg) (*B*), and Pt—PMo_{12} solid catalyst (10 mg) (*C*). Oxidation conditions: 0.1 mL of C_6H_{12}, 1 mL of MeCN, $H_2—O_2$ (2 : 1), *T* = 35 °C, reaction time 1 h.

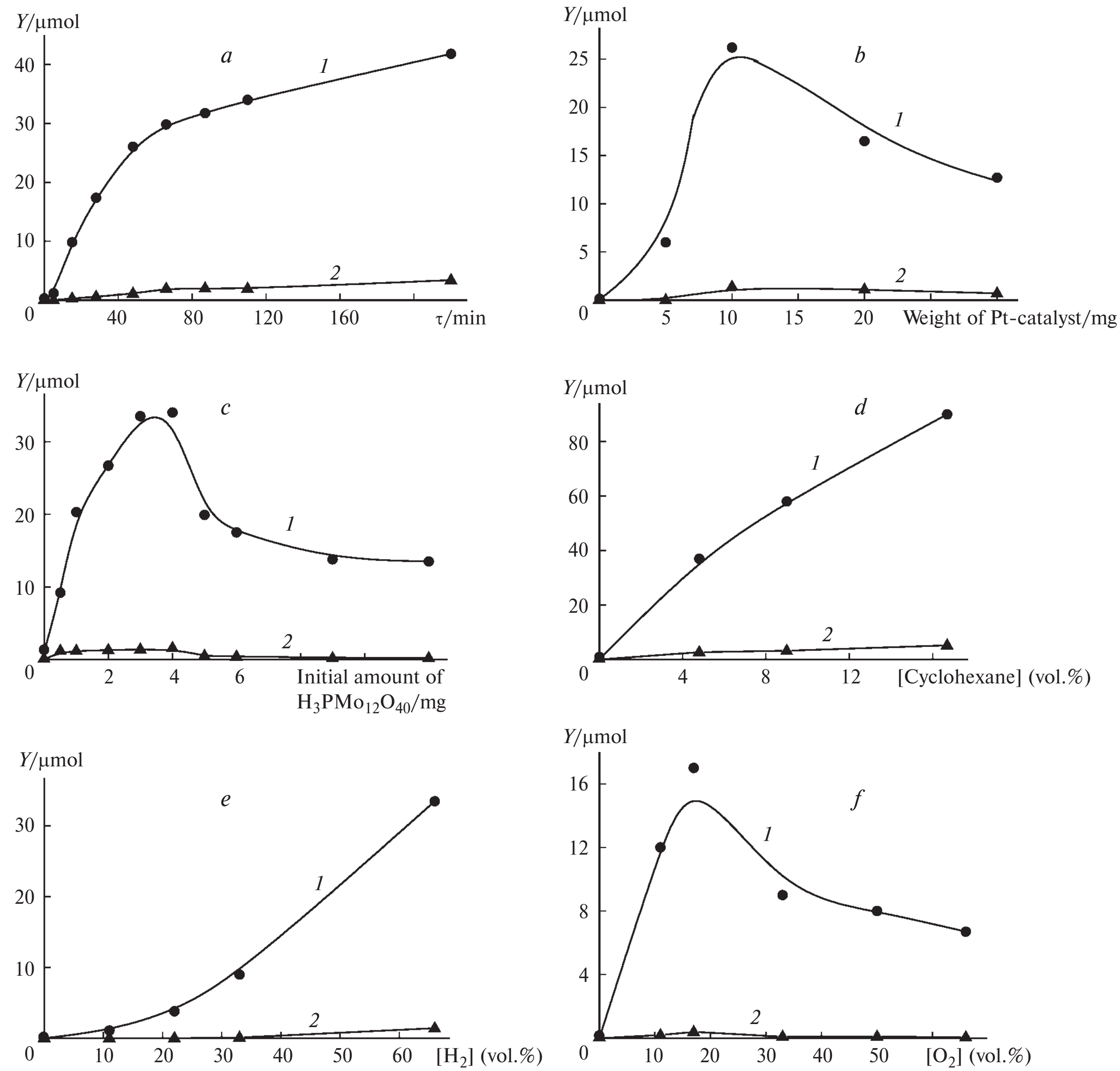

Fig. 2. Yields (*Y*) of cyclohexanol (*1*) and cyclohexanone (*2*), *viz*., products of cyclohexane oxidation, for different parameters: reaction time (*a*) (10 mg of the Pt—PMo_{12} solid catalyst, H_2—O_2 (2 : 1)); weighed samples of the 5%Pt/SiO_2(45) catalyst (*b*) (3 mg of $H_3PMo_{12}O_{40}$, H_2—O_2 (2 : 1)); amounts of dissolved acid $H_3PMo_{12}O_{40}$ (*c*) (10 mg of the 5%Pt/SiO_2(45) catalyst; H_2—O_2 (2 : 1)); concentrations of cyclohexane in the reaction mixture (*d*) (10 mg of the Pt—PMo_{12} solid catalyst, H_2—O_2 (2 : 1)); content of H_2 (*e*) (gas composition: H_2 (varied), O_2 (33%), N_2 (the rest), 10 mg of the 5%Pt/SiO_2(45) catalyst; 3 mg of $H_3PMo_{12}O_{40}$, and content of O_2 in the gas phase (*f*) (gas composition: O_2 (varied), H_2 (33%), N_2 (the rest), 10 mg of the 5%Pt/SiO_2(45) catalyst, 3 mg of $H_3PMo_{12}O_{40}$). Conditions in all experiments: 1 mL of MeCN, $T = 35$ °C, reaction time 1 h (except *a*), 0.1 mL of C_6H_{12} (except *d*).

the support. Platinum remained in the solid state and was not found in reaction solutions obtained in the presence of the catalysts of both types.

Thus, the Pt- and HPC-based catalytic systems for oxidation could include either the solid Pt catalyst and soluble heteropoly acid or the solid catalyst containing both components. In the first case, the active surface was formed by the reaction solution containing the heteropoly acid. Hydrogen peroxide or other peroxide compounds are generated on the Pt surface

$$O_2 + H_2 = H_2O_2, \qquad (3)$$

and HPC is involved in the oxidation of the organic substrate

$$C_6H_{12} + H_2O_2 = C_6H_{11}OH + H_2O. \qquad (4)$$

A minor amount of cyclohexanone is formed due to the secondary oxidation of cyclohexanol on metallic platinum (see Eq. (2)).

Reaction (4) can occur both on the surface, where the HPC species are localized, and in a solution containing dissolved forms of HPC. The first variant corresponds, to a great extent, to the specific features of reaction observed in this work. Indeed, the concentration of HPC in a solution was the highest when a solution of the heteropoly acid was used. However, in spite of this fact, the system with dissolved HPC was least active. In the case of the $Pt—PMo_{12}$ bulk sample, its gradual dissolution during the reaction did not increase the rate of product formation, which should be expected for the dissolved HPC involved in catalysis. Moreover, it retarded oxidation. The peroxide species that formed on the surface, evidently, react with the substrate directly on the catalyst surface rather than escape into the reaction bulk.

Variation of reaction conditions and substrate. Of the organic solvents used, MeCN proved to be optimal solvent for the reaction (Fig. 3). Regardless of the solvent, the molar ratio the oxidation products, *viz.*, cyclohexanol and cyclohexanone, remained unchanged. The yield of cyclohexanol in AcOH was higher than that in MeCN but the amount of the $O_2—H_2$ gaseous mixture consumed per mole of the formed oxidation product increased strongly. Correspondingly, the selectivity to the oxidant decreased. Probably, the more intense consumption of the gases is associated with a low adsorption of the heteropolyanions on platinum because the heteropoly acid exists in AcOH in the associated form.

The yields of cyclohexanol and cyclohexanone changed insignificantly (only by 30—40%), when the temperature was varied in the 20—50 °C interval, attaining the highest value at 35 °C.

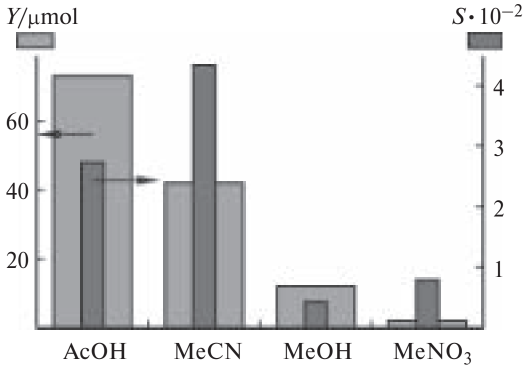

Fig. 3. Yields of the products (Y) and selectivity (S/moles of product per mole of O_2) of cyclohexane oxidation for various solvent. Oxidation conditions: 10 mg of the $Pt—PMo_{12}$ solid catalyst, 1 mL of MeCN, 0.1 mL of C_6H_{12}, T = 35 °C, $H_2—O_2$ (2 : 1), reaction time 1 h.

For the systems containing the solid Pt catalyst and dissolved heteropoly acid, we studied the relationships of the amounts of the oxidation product to the weight of the Pt catalyst at a constant content of $H_3PMo_{12}O_{40}$ (see Fig. 2, *b*) and to the content of the acid at a constant weight of the Pt catalyst (see Fig. 2, *c*). In both cases, the plots were described by the curves with maxima. The maximum yield was obtained at a content of 0.5—0.6 g-at. Pt per g-mole of $H_3PMo_{12}O_{40}$.

An increase in the initial amount of cyclohexane in a mixture with MeCN increased the yield of the oxidation products (see Fig. 2, *d*) if the content of cyclohexane in a mixture was at most 20 vol.%. The liquid phase laminated and oxidation was retarded at the C_6H_{10} : MeCN ratio > 0.2.

Changing the ratio of H_2, O_2, and N_2, we found that an increase in the partial dihydrogen pressure increases the yields of the oxidation products (see Fig. 2, *e*). The high content of dioxygen in the gas mixture decreases the yields of the oxidation products. The $H_2 : O_2$ ratio about 2, *i.e.*, close to stoichiometric for water formation, was optimum. Probably, in excess dioxygen the excessive oxidation of the platinum surface occurs to decrease its activity.

In addition to cyclohexane, we studied the oxidation of several saturated hydrocarbons and the oxidation of benzene and toluene. The relative reactivity of each hydrocarbon can be estimated from the data in Fig. 4. Isobutane is more reactive than *n*-butane, and cyclohexane is more reactive than *n*-hexane and *n*-pentane. The products of oxidation of saturated hydrocarbons consisted of isoalcohols and ketones, whereas the products

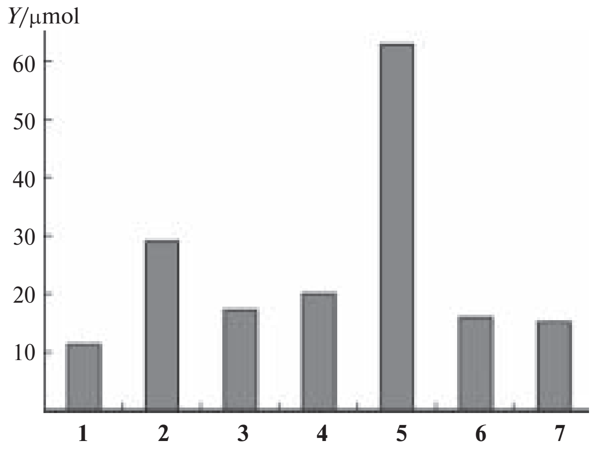

Fig. 4. Yields of the products (Y) of oxidation of butane (**1**), isobutane (**2**), pentane (**3**), hexane (**4**), cyclohexane (**5**), benzene (**6**), and toluene (**7**). Oxidation conditions: 10 mg of the $Pt—PMo_{12}$ solid catalyst, 1 mL of MeCN, $O_2—H_2$ (1 : 2), and 0.1 mL of liquid hydrocarbon or the $O_2—H_2—$hydrocarbon (1 : 2 : 2) gaseous mixture in the case of butane and isobutane, T = 35 °C, reaction time 1 h.

of oxygenation at the terminal carbon atom were almost absent. According to the composition of the products of oxidation of *n*-butane and isobutane, the change in the reactivity of the carbon atoms can be presented as tertiary > secondary ≫ primary C-atoms. Benzene and toluene transformed into the corresponding phenols with an insignificant difference in the yields of oxidation products.

The reactivities of hydrocarbons and composition of positional isomers in the oxidation products indicate radical oxidation. This conclusion follows from comparison of the catalytic properties of different HPC. The reaction mechanism involving active radical intermediates can be presented as the following scheme of reactions, for example, for cyclohexane:

$$\mathrm{Pt^0 + O_2 \rightleftharpoons Pt^0\,(O_2)_{ads}}, \tag{5}$$

$$\mathrm{Pt^0\,(O_2)_{ads} + H^+ \longrightarrow (Pt{-}OOH)^+}, \tag{6}$$

$$\mathrm{2\,(Pt{-}OOH)^+ + Pt^0 + 4\,H^+ \longrightarrow}$$
$$\mathrm{\longrightarrow 2\,(Pt{-}{}^{\bullet}OH)^{2+} + Pt^{2+} + 2\,H_2O}, \tag{7}$$

$$\mathrm{(Pt{-}OOH)^+ + [Mo^{5+}] + 2\,H^+ \longrightarrow}$$
$$\mathrm{\longrightarrow (Pt{-}{}^{\bullet}OH)^{2+} + [Mo^{6+}] + H_2O}, \tag{7´}$$

$$\mathrm{(Pt{-}{}^{\bullet}OH)^{2+} + C_6H_{12} \longrightarrow Pt^{2+} + {}^{\bullet}C_6H_{11} + H_2O}, \tag{8}$$

$$\mathrm{(Pt{-}{}^{\bullet}OH)^{2+} + {}^{\bullet}C_6H_{11} \longrightarrow Pt^{2+} + C_6H_{11}OH}, \tag{9}$$

$$\mathrm{Pt^{2+} + H_2 \longrightarrow Pt^0 + 2\,H^+}, \tag{10}$$

$$\mathrm{2\,[Mo^{6+}] + H_2 \xrightarrow{[Pt]} 2\,[Mo^{5+}] + 2\,H^+}. \tag{11}$$

Steps (5) and (6) occur on the platinum surface. On contacting the platinum species and HPC, dioxygen adsorbed on platinum becomes reducible to form peroxide compounds. The latter react with the reduced platinum to form hydroxyl radicals (7), which oxidize hydrocarbon without escaping into the reaction volume (reactions (8) and (9)). If the system contains a redox-active HPC, such as $H_3PMo_{12}O_{40}$, peroxyl radicals are generated more rapidly in reaction (7´) with the molybdenum ions in the reduced form of HPC. The platinum surface is reduced by dihydrogen (reaction (10)), and HPC is reduced by dihydrogen on the platinum surface (11).

Thus, in this work we demonstrated the possibility to design catalytic compositions from platinum and HPC for hydrocarbon oxidation by a mixture of gaseous dioxygen and dihydrogen. The development of active catalytic systems needs contact between the Pt species and heteropolyanions. This can be achieved by the suspension of the Pt catalyst in a solution of HPC or (more efficiently) by using bicomponent solid catalysts containing platinum and heteropolyanions. Due to their unique chemical properties, HPC suppress the reduction of molecular oxygen to water and modify the platinum surface thus increasing the probability of forming peroxide species. Finally, the HPC participates in the formation of hydroxyl radicals active in oxidation from the peroxide.

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