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Hydrocarbon Oxidation with an Oxygen–Hydrogen Mixture: Catalytic Systems Based on the Interaction of Platinum or Palladium with a Heteropoly Compound

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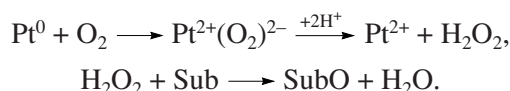
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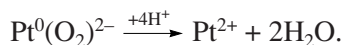
Abstract—A series of studies of hydrocarbon oxidation by the $O_2 + H_2$ mixture in the presence of catalytic systems based on Pt or Pd and a heteropoly compound (HPC) is reviewed. The catalytic systems were prepared from Pd(II) complexes with the heteropoly tungstate anions $PW_{11}O_{39}^{7-}$ and $PW_9O_{34}^{9-}$, the complex salt $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$, mixtures of H_2PtCl_4 or H_2PtCl_6 with $H_{3+n}PMo_{12-n}V_nO_{40}$ ($n = 0–3$) heteropoly acids, or supported platinum dispersed in HPC solutions. The interaction of metal ions and particles with HPCs in the initial state and after thermal and redox treatments was investigated by NMR, IR spectroscopy, XPS, EXAFS, HREM, and TPR. The catalytic systems were tested in the liquid-phase oxidation of alkanes, cyclohexane, cycloalkenes, benzene, toluene, and phenol with the $O_2 + H_2$ mixture at low temperatures. Effective supported catalysts based on platinum nanoparticles associated with the redox-active HPCs $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}$ were prepared for gas-phase benzene oxidation into phenol. The oxidation mechanism includes the interaction between dioxygen and platinum (or palladium) and the participation of the HPC in the formation of active oxygen species of radical nature.

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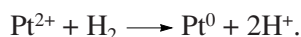
The stoichiometric mixture of oxygen and hydrogen attracts continuous interest as an oxidizer that is environmentally friendly and, at the same time, allows the oxidation process to be carried out under mild conditions. Oxidation in this case consists of the incomplete reduction of the oxygen molecule by hydrogen and further oxygen reduction by the substrate. The reductive activation of oxygen is known to take place on platinum-group metals, most readily on platinum and palladium. Electron transfer from the reduced metal surface to oxygen yields peroxide-type species and hydrogen peroxide [1–5], which can react with the substrate (Sub):



Along with reacting with the substrate, the peroxide can undergo reduction on the metal to yield water:



The metal ions undergo back reduction under the action of hydrogen, and this results in a steady state of the metal surface:



Some additions, such as the Cl^- ion and V(V) and Cu(II) oxides, stabilize the ionic state of the metal, thus dimin-

ishing the nonproductive reduction of the peroxide and favoring its interaction with the substrate [6–10].

It was found that heteropoly compounds (HPCs), which are widely known in oxidative catalysis [11–15], can serve as active admixtures in oxidations with the $O_2 + H_2$ mixture. Platinum or palladium and various HPCs have been used in two-component catalytic systems. Pt–HPC and Pd–HPC systems proved more active in oxidations with the $O_2 + H_2$ mixture than HPC-free Pt–V oxide catalysts [17].

This article, devoted to the nature of the catalytic action of Pt–HPC and Pd–HPC two-component systems in oxidations with $O_2 + H_2$, presents a survey of works by a large group of researchers from the Institute of Catalysis. The main focus is placed on the interaction between the platinum-group metal ions and the HPC. The oxidation mechanism has been investigated for a wide variety of hydrocarbons, such as alkanes, cyclohexane, cycloalkenes, benzene, toluene, and phenol.

We will consider the following systems obtained from various combinations of platinum or palladium with an HPC: (1) Pd(II) complexes with heteropoly tungstate anions (HPAs); (2) the complex salt $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$; (3) carbon-supported platinum dispersed in a HPC solution; (4) Pt(II) or Pt(IV) chloride complexes with phosphomolybdic acid, including those supported on silica gel.

Along with Pd(II) complexes with the unsaturated HPAs $\text{PW}_{11}\text{O}_{39}^{7-}$ and $\text{PW}_9\text{O}_{34}^{9-}$ as sodium and tetrabutylammonium (TBA) salts, the metal-substituted HPAs $\text{PW}_{11}\text{O}_{39}\text{Co}(\text{H}_2\text{O})^{5-}$, $\text{PW}_{11}\text{O}_{39}\text{Mn}(\text{H}_2\text{O})^{5-}$, $\text{PW}_{11}\text{O}_{39}\text{Fe}(\text{OH})^{5-}$, $\text{PW}_{11}\text{O}_{39}\text{Cr}(\text{OH})^{5-}$, $\text{PW}_{11}\text{TiO}_{40}^{5-}$, $\text{PW}_{11}\text{ZrO}_{40}^{5-}$, and $\text{PW}_{11}\text{VO}_{40}^{4-}$ and the heteropoly molybdate anions $\text{PMo}_{12}\text{O}_{40}^{3-}$ and $\text{PMo}_{12-n}\text{V}_n\text{O}_{40}^{(3+n)-}$ ($n = 1, 2$, or 3) have been employed as oxidation catalysts.

Liquid-Phase Oxidations with the $\text{O}_2 + \text{H}_2$ Mixture in the Presence of Pd(II) Complexes with Heteropoly Tungstate Anions

There are HPCs in which Pd(II) is incorporated in the HPA structure [18–21]. The Pd(II) ions in these complexes are considered to have a tetragonal or pentagonal coordination environment. In our works, we used Pd(II) complexes with the $\text{PW}_{11}\text{O}_{39}^{7-}$ and $\text{PW}_9\text{O}_{34}^{9-}$ heteropoly anions and characterized these complexes by IR and NMR spectroscopy [22–24].

The interaction between equimolar concentrations of palladium(II) sulfate and $\text{Na}_7\text{PW}_{11}\text{O}_{39}$ at pH 2 yields the mononuclear anion $[\text{PW}_{11}\text{O}_{39}\text{Pd}]^{5-}$ (^{31}P : $\delta = -13.2$ ppm) and the dinuclear anion $[(\text{PW}_{11}\text{O}_{39}\text{Pd})_2\text{O}]^{12-}$ (^{31}P : $\delta = -12.8$ ppm); at pH 4, the latter anion is more abundant. Less than 30% of the phosphorus introduced remains in the form of free heteropoly tungstates containing no Pd(II). The Pd(II) ions not coordinated to the HPC stay in the solution as Pd–HPC association species [22]. A series of solutions of coordination compounds has been prepared from palladium(II) sulfate and $\text{Na}_9\text{PW}_9\text{O}_{34}$ at pH ~ 4 [23, 24]. The $[\text{Pd}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ anion (^{31}P : $\delta = -12.4$ ppm; ^{183}W : $\delta = -69.6$ and -85.5 ppm (2 : 1)) was obtained at Pd(II)/ $\text{PW}_9\text{O}_{34}^{9-} = 3 : 2$. According to ^{31}P NMR data, 80% of the phosphorus taken for the synthesis was incorporated in this complex and the rest of the phosphorus was present as minor amounts of the phosphate anion (~ 0 ppm), $[(\text{PW}_{11}\text{O}_{39}\text{Pd})_2\text{O}]^{12-}$ (-12.8 ppm), and $\text{PW}_{12}\text{O}_{40}^{3-}$ (-15.3 ppm). At a larger Pd(II)/ $\text{PW}_9\text{O}_{34}^{9-}$ ratio of 3 : 1, complexes with the average composition $[\text{Pd}_3(\text{PW}_9\text{O}_{34})_2 \cdot \text{Pd}_3\text{O}_x\text{H}_y]^{m-}$ are obtained, again characterized by a ^{31}P NMR signal at -12.4 ppm. Extra palladium ions, probably as oligomerized hydroxo complexes, are associated with heteropoly anions and, because of this, stay in the solution. Other metal ions were introduced into the heteropoly tungstate complex together with Pd(II) ions [23, 24]. At Pd(II)/Fe(III)/ $\text{PW}_9\text{O}_{34}^{9-} = 2 : 1 : 2$ and pH 4, the components react to yield the $[\text{PdFe}_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ anion (^{31}P : broad peak at $\delta = -66$ ppm, 82% of the phosphorus introduced), a smaller amount of the $[\text{Pd}_2\text{Fe}(\text{PW}_9\text{O}_{34})_2]^{11-}$ anion (^{31}P : broad peak at $\delta =$

-40 ppm, 12%), and minor amounts of phosphate ions. The complex $[\text{Pd}_2\text{Cu}(\text{PW}_9\text{O}_{34})_2]^{12-}$ (^{31}P : broad peak at $\delta = -22$ ppm) was obtained at Pd(II)/Cu(II)/ $\text{PW}_9\text{O}_{34}^{9-} = 2 : 1 : 2$ and pH 4. These Pd-containing heteropoly anions belong to the $\text{M}_3(\text{A}-\alpha\text{-PW}_9\text{O}_{34})_2^{m-}$ structure type, as was demonstrated by the IR spectra of their cesium salts precipitated from the solution.

The sodium salts of the Pd(II)-containing HPAs are readily reducible with hydrogen at 30°C , yielding palladium metal (Pd_{met}). The only exception is the $[\text{Pd}_2\text{Cu}(\text{PW}_9\text{O}_{34})_2]^{12-}$ anion, whose reduction is slow and is accelerated only upon the formation of palladium metal [23].

In the presence of the Pd(II) HPA complexes, hydrogen is oxidized by oxygen in aqueous solution and benzene is oxidized into phenol by the $\text{O}_2 + \text{H}_2$ mixture in the aqueous complex solution–benzene two-phase system [22, 23].

Figure 1 plots the yields of the H_2 and C_6H_6 oxidation products for various HPCs. In the oxidation of hydrogen into water, the oxidation product yield depends on the nature of the HPC. The complex $[\text{Pd}_3(\text{PW}_9\text{O}_{34})_2 \cdot \text{Pd}_3\text{O}_x\text{H}_y]^{m-}$ affords a higher oxidation product yield than $[\text{Pd}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ owing to the larger number of palladium particles accessible to the reactants. In benzene oxidation, the mononuclear Pd(II)-containing HPA is more active than the dinuclear and trinuclear HPAs if the observed difference in activity is not due to the change in the acidity of the aqueous solution from pH 2 to pH 4. The palladium species weakly bonded to the HPA do not make any significant contribution to benzene oxidation (as distinct from hydrogen oxidation): the anions $[\text{Pd}_3(\text{PW}_9\text{O}_{34})_2 \cdot \text{Pd}_3\text{O}_x\text{H}_y]^{m-}$ and $[\text{Pd}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ are equal in catalytic activity. In benzene oxidation, the bimetallic complex $[\text{PdFe}_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ is the most active and affords the highest selectivity in terms of hydrogen consumption for phenol formation versus nonproductive hydrogen oxidation into water. The complex $[\text{Pd}_2\text{Cu}(\text{PW}_9\text{O}_{34})_2]^{12-}$ turned out to be inactive in oxidation.

Performing the catalytic oxidation of benzene over several hours, we observed only partial palladium reduction yielding a metal precipitate. As was demonstrated by a ^{31}P NMR study of the reaction solutions [22], the palladium weakly associated with the HPA undergoes reduction, while the Pd(II) incorporated in the HPC structure stays in the solution.

The above data elucidate the nature of the promoting effect of unsaturated HPAs on the catalytic properties of palladium in benzene oxidation. This effect is due to the formation of palladium complexes with the HPA. The Pd(II) ions incorporated in the HPA are reduced by hydrogen, and the resulting Pd_x^0 particles are oxidized rapidly by oxygen owing to the stabilization of one or three Pd(II) ions in the heteropoly anion structure. The stabilizing effect exerted by metal ions in

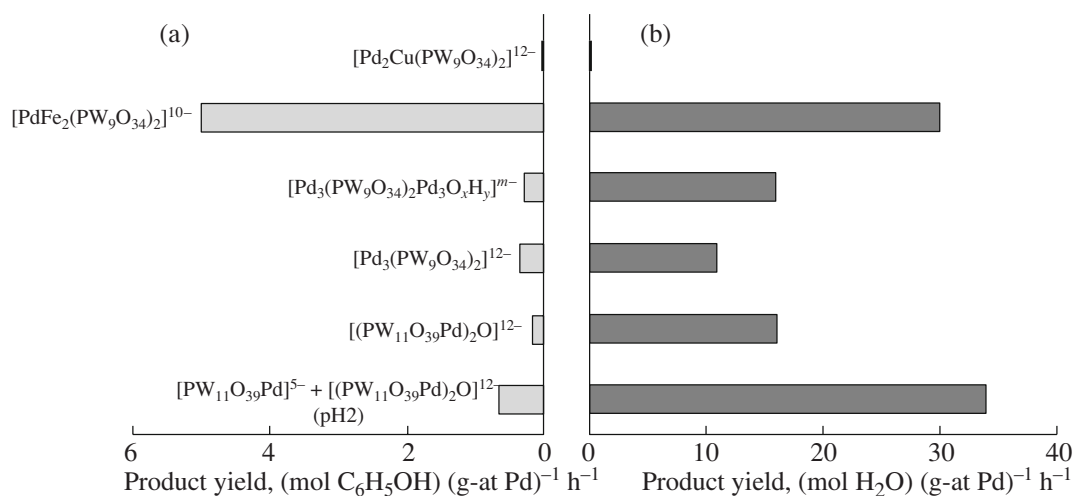
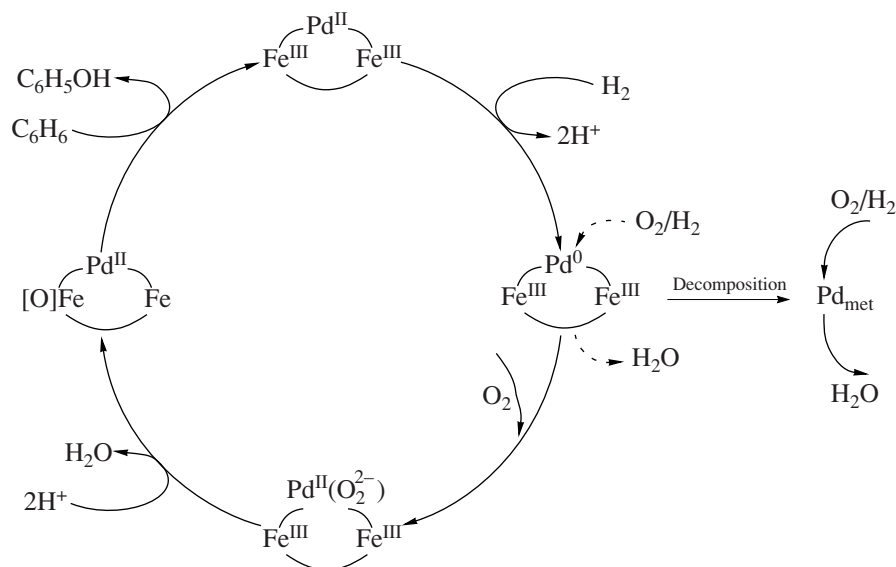


Fig. 1. Oxidation of (a) benzene into phenol and (b) H₂ into H₂O in the presence of sodium salts of Pd(II)-containing heteropoly tungstate anions. Conditions: O₂ + H₂ (1 : 2), pH 4, reaction time of 1 h; (a) 0.3 ml of a 0.01 M solution of the complex, 1 ml of benzene, *T* = 25°C (20°C for [PW₁₁O₃₉Pd]⁵⁻ and [(PW₁₁O₃₉Pd)₂O]¹²⁻); (b) 5 ml of a 0.01 M solution of the complex, *T* = 20°C.

the HPA structure on small molecules and peroxide species is well known [25, 26]. It can be assumed that the interaction between Pd(0) and oxygen on oxidized palladium ions in the HPA structure yields active peroxide species, which then undergo further conversions to oxidize the substrate. The promoting

role of the ions of the second metal in the HPA, namely, iron ions, is that they participate in the formation of active oxygen species. The complete system of redox reactions taking place in benzene oxidation by the O₂ + H₂ mixture can be represented as follows [25].



Scheme 1. Redox reactions in the system consisting of an aqueous solution of the sodium salt of [PdFe₂(PW₉O₃₄)₂]¹⁰⁻ and benzene under the action of the O₂ + H₂ mixture.

This reaction mechanism was verified by a study of SiO₂-supported sodium salts of the HPAs as catalysts for benzene and cyclohexane oxidation with the O₂ + H₂ mixture in acetonitrile [27]. The yield of the products—phenol or cyclohexanol + cyclohexanone—is

higher with the catalysts prereduced with hydrogen at 100°C. As was demonstrated by XPS, this reduction does not affect W(VI) in the heteropoly tungstate.

Figure 2 plots the yields of the products forming in the presence of systems prepared from various precu-

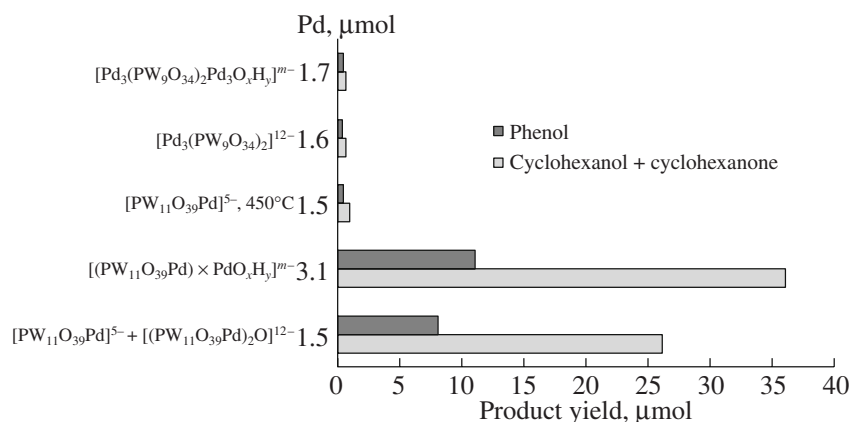


Fig. 2. Yields of the benzene and cyclohexane oxidation products obtained using silica gel-supported sodium salts of Pd-containing heteropoly tungstate anions. Conditions: 30 mg of catalyst, 1 ml of CH_3CN , 0.1 ml of cyclohexane or benzene, $\text{O}_2 + \text{H}_2$ (1 : 2), 30°C, 1 h.

sors. At nearly equal degrees of dispersion of the palladium metal resulting from the reduction of the initial complexes ($\text{CO}_{\text{ads}}/\text{Pd} = 0.23\text{--}0.31$), the highest product yield was achieved with systems based on Pd(II) incorporated in the $\text{PW}_{11}\text{O}_{39}^{7-}$ structure. As in the case of dissolved catalysts, the palladium ions weakly bonded to the HPA (“extra” palladium ions) have no significant effect on the yield of the hydrocarbon oxidation products. Calcination of the catalysts at a high temperature (450°C) breaks the heteropoly tungstate structure and, accordingly, causes a decrease in the product yield. Unlike the dissolved catalysts, the supported catalyst prepared from the Pd(II) complex with the $\text{PW}_9\text{O}_{34}^{9-}$ anion shows a low activity. This can be explained by the difficulties in the “assemblage” of the catalyst after the reduction of the complex anion $[\text{Pd}_3(\text{PW}_9\text{O}_{34})_2]^{12-}$ on the support surface.

Catalytic Systems Based on Platinum and the Heteropoly Acid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ for Hydrocarbon Oxidation with the $\text{O}_2 + \text{H}_2$ Mixture

Heteropoly molybdate ions are stronger oxidizers than heteropoly tungstate ions. Therefore, it would be expected that the molybdenum ions in Pt-HPC and Pd-HPC two-component systems would participate in redox reactions involved in hydrocarbon oxidations by the $\text{O}_2 + \text{H}_2$ mixture. At the same time, as was noted in earlier works [28, 29], metal-substituted heteropoly molybdates, unlike heteropoly tungstates, do not form in aqueous solutions. However, polyoxomolybdates stabilize both Pd(II) in the region of its hydrolytic instability [30, 31] and colloidal solutions of platinum-group metals [32], implying that platinum and palladium interact with heteropoly molybdate ions. We studied hydrocarbon oxidation by the $\text{O}_2 + \text{H}_2$ mixture in the presence of platinum and the redox-active phosphomolybdate anion. We tested the following three model

catalytic systems based on different starting compounds: (1) silica- or carbon-supported platinum dispersed in a solution of the $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ acid or its TBA salt, (2) alumina-supported platinum and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ reduced with hydrogen, and (3) the complex salt $[\text{Pt}(\text{NH}_3)_4][\text{H}_2\text{PMo}_{12}\text{O}_{40}]_2 \cdot 7\text{H}_2\text{O}$ heat-treated at 300°C for removal of water and ammonia and reduced with hydrogen. Oxidation reactions were carried out in acetonitrile at 35°C [33, 34].

System 1 is active in the oxidation of cyclohexane into cyclohexanol and cyclohexanone. In the absence of the HPC, platinum catalyzes only the conversion of O_2 and H_2 into water. The HPC modifies the platinum surface, thus slowing down this reaction and favoring substrate oxidation. To attain a comparable catalytic activity with systems 2 and 3 ($\sim 30 \text{ mol (g-at Pt)}^{-1} \text{ h}^{-1}$), it is necessary to prereduce platinum with hydrogen. The yield of the cyclohexane oxidation products depends on the solvent, the substrate concentration, the amounts of Pt and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, and the O_2 and H_2 partial pressures [34]. The oxidation of hydrocarbons with these catalytic systems yields secondary alcohols and ketones. The amount of products obtained in the presence of system 3 increases in the following order: n -butane < pentane < hexane < isobutane \ll cyclohexane [34]. The relative yields of the oxidation products of linear and branched hydrocarbons and the fact that secondary carbon atoms are oxygenated more readily than primary carbon atoms suggest that the oxidation reaction proceeds via a free-radical mechanism.

The nature of the active form of the catalyst can be elucidated by comparing the oxidation product yields obtained using the $[\text{Pt}(\text{NH}_3)_4][\text{H}_2\text{PMo}_{12}\text{O}_{40}]_2 \cdot 7\text{H}_2\text{O}$ precursor treated in different ways [33, 34]. Catalytic activity is shown by the substance resulting from the reduction of the salt at 115°C. The samples strongly reduced at 150–200°C are inactive, but they gain activity upon oxidative treatment with dry or, preferably, humid air. In activated samples, metallic and oxidized

Table 1. Literature data on the activity of catalytic systems for benzene hydroxylation with the O₂ + H₂ mixture

Catalyst	Conditions	Productivity, mol phenol/(g-at Pt or Pd) h ⁻¹	Benzene conversion, %	Reference
Liquid-phase oxidation				
(Pd–Cu)/SiO ₂	25°C	4	0.02	[35]
Pt/V ₂ O ₅	HOAc, 60°C	67	0.07	[36]
(Pd, Pt–V ₂ O ₅)/SiO ₂	HOAc, 60°C	46	0.14	[37]
Pt/ZrO ₂ + V(acac) ₃	HOAc, 60°C	400	0.45	[38]
Pt, Rh, Ir, Pd or Ru + V ₂ O ₅ , Y ₂ O ₃ , Nb ₂ O ₅ , WO ₃ , La ₂ O ₃ or MoO ₃ /SiO ₂	HOAc, 60°C	264	0.60	[39]
Pd/Ti silicates	H ₂ O + HCl, 25°C	13	0.13	[40]
Pd/Al ₂ O ₃ + V(acac) ₃ or FeCl ₂	HOAc, 65°C	50	2.30	[10]
Gas-phase oxidation				
(Pd–Cu)/SiO ₂	200°C	80	0.90	[41]
Pt/VO _x /SiO ₂ or Pd/VO _x /SiO ₂	(150–200)°C	60	0.68–0.97	[17]
Pd membranes	(150–200)°C	–	3–13	[42]

platinum is observed by XPS and HREM and reversible changes in the oxidation state of molybdenum take place [33]. The retention of the heteropoly molybdate structure is also essential for catalysis. The deactivation of the catalyst occurs at 600°C, when the HPA structure breaks down.

The studies of the properties of the Pt–heteropoly molybdate systems have demonstrated that these systems are promising for oxidations with the gaseous O₂ + H₂ mixture.

Gas-Phase Oxidation of Benzene into Phenol with the O₂ + H₂ Mixture over Catalysts Containing Platinum-Group Metals and Heteropoly Molybdates

Our screening covered supported catalysts of composition (0.1 or 0.2% M + 20% HPC)/SiO₂, where M is a Group VIII metal and HPC is H_{3+n}PMo_{12–n}V_nO₄₀ (n = 0–3), H₃PMo₆W₆O₄₀, or H_{3+n}PW_{12–n}V_nO₄₀ (n = 0–3) [16]. The gas-phase oxidation of benzene was carried out in a fixed-bed catalytic reactor at 200°C, a residence time of 0.05 s, and a feed composition of O₂/H₂/C₆H₆/N₂ = 5.5 : 5.5 : 33 : 56. The highest phenol formation rate, 270–380 mol (g-at M)⁻¹ h⁻¹, was observed for M = Pt or Pd and HPC = H₃PMo₁₂O₄₀ or H₄PMo₁₁VO₄₀. In terms of this parameter, the catalytic system based on Pt or Pd and one of the HPCs is superior to nearly all of the known liquid-phase systems (with acetic acid as the solvent) and gas-phase systems for hydrocarbon oxidation with the O₂ + H₂ mixture (Table 1).

The optimum temperature for this reaction is 200°C. At lower temperatures, there can be phenol condensa-

tion on the catalyst. Raising the temperature to 250°C causes a decrease in the phenol yield.

For two silica gel brands with specific surface areas of 400 and 200 m²/g (SiO₂(400) and SiO₂(200)) and the optimum HPC content of 20%, the phenol yield as a function of the platinum content passes through a maximum at 0.5 and 1% Pt, respectively. The productivity of the catalyst per gram-atom of Pt increases as the platinum content is decreased (Fig. 3). This is explained by the fact that, at low platinum contents, the support is dominated by fine, highly reactive metal particles.

Under our test conditions, the phenol selectivity was 95–98% at a benzene conversion of 0.3%. The only by-product was biphenyl. No carbon oxides were detected in the exit gas by gas chromatography, and no resinous compounds accumulated in the cold trap.

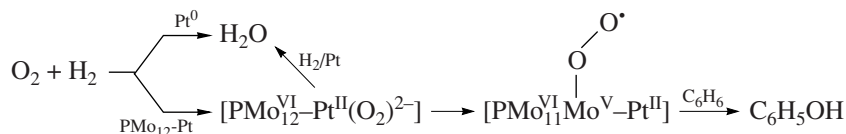
At equimolar amounts of O₂ and H₂ in the gas mixture, the oxygen conversion (see numbers in Fig. 3b) is about 50%. The number of moles of hydrogen consumed per mole of the resulting phenol increases as the hydrogen content of the gas mixture is increased, ranging between 20 and 100. Therefore, most of the hydrogen is spent on water formation.

The possible ways of controlling the process are illustrated in Table 2. The benzene conversion can be raised from 0.3 to 1.3% by decreasing the proportion of benzene in the gas mixture; however, this will reduce the productivity of the catalyst (entry 1). The introduction of water vapor into the gas flow increases the benzene conversion and the productivity of the catalyst (entry 2). Raising the oxygen and/or hydrogen concentration in the water-containing gas mixture, it is possi-

ble to attain a rather high benzene conversion (4.4%) at a high catalyst productivity (entries 3–5).

The reaction mechanism that we suggest is presented in Scheme 2. The first step of this mechanism is oxygen adsorption on platinum yielding peroxo species. These species are then transferred to the HPC to form electrophilic oxygen. This oxygen is most likely of free-radical

nature and is active in benzene oxidation into phenol. A parallel reaction is nonproductive hydrogen oxidation into water. It follows from Scheme 2 that, for enhancing the selectivity in terms of the consumption of the $O_2 + H_2$ mixture for substrate oxidation, it is necessary to ensure a high degree of dispersion of platinum so as to maximize the metal cluster–HPC contact area.



Scheme 2. Mechanism of benzene oxidation in the presence of $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2$.

In order to elucidate the nature of the platinum–HPC interaction, we studied the conversions of platinum and phosphomolybdic acid at the stage of preparation of the gas-phase benzene oxidation catalyst [43]. A solution of H_2PtCl_4 or H_2PtCl_6 and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (1 : 1 mol/mol)

was dried, and the resulting solid was calcined at 450°C (to remove most of the chlorine) and was reduced with hydrogen at 300°C . The product was stored in humid air. According to IR spectroscopic data, the resulting samples contained the $\text{PMo}_{12}\text{O}_{40}^{3-}$ anion. As was demonstrated by chemical analysis and XPS, calcination without reduction yielded water-soluble association species (solution acidity of pH 2) of average composition $(\text{Pt}_n^{\text{II}}\text{Cl}_m\text{O}_x\text{H}_y)(\text{H}_3\text{PMo}_{12}\text{O}_{40})$ ($n = 0.3\text{--}0.8$, $m = 0.2\text{--}1.0$) (**I**). Solid association species **I** retained the Keggin structure of the heteropoly molybdate anion, as was found by IR spectroscopy. According to TPR data, the reduction of molybdenum(VI) in **I** is catalyzed by platinum and occurs at $100\text{--}300^\circ\text{C}$.

The samples subjected to deep reduction at 300°C (**II**) were soluble in water, and platinum(0) stabilization took place in the solution. Metallic platinum precipitated from the solution upon molybdenum oxidation into the hexavalent state.

The solid samples that were stored in air after reduction were the mixed-valence association species $(\text{Pt}_{1-n}^0\text{Pt}_n^{\text{II}}\text{Cl}_m\text{O}_x\text{H}_y)(\text{H}_{3+p}\text{PMo}_{12-p}^{\text{VI}}\text{Mo}_p^{\text{V}}\text{O}_{40})$ (**III**). In the X-ray photoelectron spectra of **III**, the individual $\text{Pt } 4f_{7/2}$ doublets at 73.8 and 72.4 eV were assigned to Pt(II) and to Pt(0) associated with the heteropoly anion, respectively. The individual $\text{Mo } 3d_{5/2}$ doublets at 233.6 and 232.3 eV were assigned to Mo(VI) and Mo(V) ions in the heteropoly anion [44]. The intensity ratio of these doublets (1 : 5) suggests that the HPA contains two Mo(V) ions and ten Mo(VI) ions, implying that $p = 2$ in **III**.

The EXAFS method was used to study the coordination environment of platinum in association species **I** and **III** [43]. In the radial distribution curve for **I**, peaks at 2.0 and 2.3 Å with an intensity ratio of 3 : 1 correspond to the oxygen and chlorine atoms in the first coordination sphere of platinum. These peaks are characteristic of square-planar coordination. No Pt–Pt distances characteristic of oxide structures (3.0–3.15 Å) were observed. Weak Pt–heavy atom (Pt or Mo) peaks

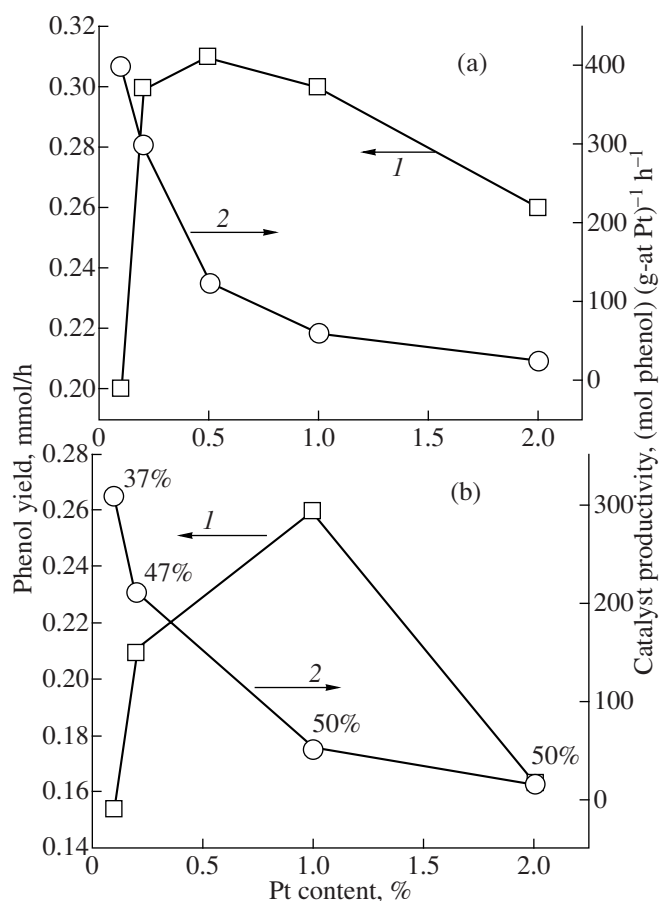


Fig. 3. Effect of the platinum content of the catalyst on the (1) phenol yield and (2) catalyst productivity. Catalysts: (a) (0.1 g Pt–20% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2(400)$) and (b) (0.1 g Pt–20% $\text{H}_3\text{PMo}_{12}\text{O}_{40}/\text{SiO}_2(200)$). $\text{O}_2/\text{H}_2/\text{C}_6\text{H}_6/\text{N}_2 = 5.5 : 5.5 : 33 : 56$; flow rate, 160 ml/min; $T = 200^\circ\text{C}$. O_2 conversion (%) is indicated at some points.

Table 2. Phenol yield, hydrogen consumption selectivity, benzene conversion, and productivity (P) of (Pt–H₃PMo₁₂O₄₀)/SiO₂ catalysts

Entry	Catalyst	Gas composition, O ₂ /H ₂ /C ₆ H ₆ /H ₂ O, %; the balance is N ₂	Phenol yield, mol/h	Hydrogen consumption selectivity, mol H ₂ /mol phenol	Benzene conversion, %	P , (mol phenol) × (g-at Pt) ^{−1} h ^{−1}
1	(1% Pt–20% PMo ₁₂)/SiO ₂ (400), 1.3 g	5.5 : 5.5 : 6.0 : 0	0.25	70	1.3	4
2	(1% Pt–20% PMo ₁₂)/SiO ₂ (400), 1.3 g	5.5 : 5.5 : 6.0 : 22	0.39	30	2.0	6
3	(0.2% Pt–20% PMo ₁₂)/SiO ₂ (100), 1.5 g	5.0 : 9.0 : 5.0 : 15	0.61	12	2.8	40
4	(0.2% Pt–20% PMo ₁₂)/SiO ₂ (100), 1.5 g	14 : 9.0 : 5.0 : 15	0.65	29	3.0	40
5	(0.2% Pt–20% PMo ₁₂)/SiO ₂ (100), 1.5 g	9.0 : 9.0 : 5.0 : 15	0.96	11	4.4	60

Note: The flow rate is 130 ml/min in entries 1 and 2 and 174 ml/min in entries 3 and 4; $T = 200^\circ\text{C}$.

were observed between 3.5 and 4.3 Å. As judged from the bonding pattern, **I** contains polynuclear Pt(II) hydroxo complexes [45]. The spectrum of **III** indicated the formation of platinum metal particles ~25 Å in size and suggested the presence of some Pt(II). HREM examination of **I** supported on SiO₂ and reduced with hydrogen revealed ~20-Å Pt_{met} particles both on the SiO₂ surface and in contact with the HPC [43].

Thus, the stabilization of Pt(II) is not due to its incorporation into the heteropoly molybdate structure, but is likely due to the electrostatic interaction or the formation of hydrogen bonds between Pt_n^{II}Cl_mO_xH_y and HPA. The fine platinum metal particles can be stabilized by adsorption on the HPA surface.

Furthermore, tests of **I** supported on SiO₂ in the gas-phase oxidation of benzene [43] demonstrated that, for this reaction to occur, the catalytic system must contain both mixed-valence Pt–HPC association species, which activate oxygen molecules, and fine particles of platinum metal, which catalyze the reduction of the Pt–HPC association species by hydrogen.

Effect of the HPC Composition on the Product Yield in Oxidation with the O₂ + H₂ Mixture and on the Mechanism of Oxygen Transfer in the Pt–HPC System

According to Scheme 2, HPC not only modifies platinum particles, but also participates in oxygen transfer from Pt(II) peroxide to the substrate. In order to verify this hypothesis, we studied the effect of the HPC composition on the product yield in liquid-phase oxidation with the O₂ + H₂ mixture at 15–35°C in acetonitrile in the presence of the Pt/SiO₂ (Pt/C) + HPC catalytic system [34, 46–49]. Various HPCs as acids or TBA salts were dissolved in CH₃CN under the reaction conditions, and they underwent partial adsorption on the catalyst.

Cyclohexane oxidation [34, 47] in the presence of 1% Pt/SiO₂ and various heteropoly tungstates (H₃PW₁₂O₄₀, H₅PW₁₁TiO₄₀, H₅PW₁₁ZrO₄₀, H₄PW₁₁VO₄₀, TBA-PW₁₁O₃₉Mn(H₂O), TBA-PW₁₁O₃₉Cr(OH), and TBA-PW₁₁O₃₉Co(H₂O)) yields small amounts of cyclohexanol and cyclohexanone (up to 6 mol (g-at Pt)^{−1} h^{−1}). The product yield is ~3 times higher in the presence of two salts, namely, TBA-PW₁₁O₃₉, which is capable of adding peroxide species, and TBA-PW₁₁O₃₉Fe(H₂O), which activates hydrogen peroxide under similar conditions [26]. For heteropoly molybdates that can generate radicals from hydrogen peroxide, the product yield changes in the order TBA-PMo₁₂O₄₀ ≈ H₃PMo₁₂O₄₀ < H₄PMo₁₁VO₄₀ < H₅PMo₁₀V₂O₄₀ > H₆PMo₉V₃O₄₀ and reaches 20 mol (g-at Pt)^{−1} h^{−1}. This finding is in agreement with the fact that the redox potential of HPC increases in this order [50], reaching its optimum value for H₅PMo₁₀V₂O₄₀. These data are consistent with the free-radical mechanism of oxidation by the O₂ + H₂ mixture in the presence of the Pt–HPC catalytic system.

Cyclohexene oxidation with the O₂ + H₂ mixture in CH₃CN on the catalytic system 5% Pt/C + HPC at 25°C was used as a test reaction in elucidating the nature of the reactive oxygen species generated in the presence of various HPCs [46–48]. In the presence of tetrahexylammonium chloride without an HPC, cyclohexene oxidized at the allyl carbon atom to yield cyclohexenol, cyclohexenone, hydrogenation products of allyl oxidation, and minor amounts of secondary products. The cyclohexene oxide yield was about 1% of the total product yield [48]. This result is consistent with the free-radical mechanism of cyclohexene oxidation [51]. Under the same conditions but in the presence of a heteropoly tungstate, the epoxide yield was higher, specifically, 7–9% for TBA-PW₁₁O₃₉^{7−} and TBA-PW₁₁O₃₉Fe(OH) and 20–30% for H₅PW₁₁TiO₄₀ and

Table 3. Product composition data (mol %) for toluene oxidation with the O₂ + H₂ mixture

Entry	Catalytic system, oxidizer	Benzyl alcohol + benzaldehyde	<i>o</i> -Cresol	<i>m</i> -Cresol	<i>p</i> -Cresol
1	H ₄ PMo ₁₁ VO ₄₀ + Pt/SiO ₂ , O ₂ + H ₂	43	33	18	6
2	TBA ₄ PMo ₁₁ VO ₄₀ + Pt/SiO ₂ , O ₂ + H ₂	35	43	17	5
3	TBA ₄ HW ₁₁ Fe(OH)O ₃₉ + Pt/SiO ₂ , O ₂ + H ₂	48	35	11	6
4	Fe ²⁺ _{aq} + H ₂ O ₂ [53]	90	7	0.5	2.5
5	TBA ₄ PMo ₁₁ VO ₄₀ + H ₂ O ₂ [54]	53	30	14	3
6	TBA ₄ PMo ₁₁ VO ₄₀ + H ₂ O ₂	21	55	9	15

Note: Entries 1–3: 0.1 ml toluene, 1 ml CH₃CN, 50 mg Pt/SiO₂, 10 mg HPC, O₂ : H₂ = 1 : 2, *T* = 30°C, reaction time of 1 h. Entry 6: 0.2 ml toluene, 2 ml CH₃CN, 0.2 ml ~30% H₂O₂, 20 mg HPC, *T* = 65°C, reaction time of 1 h. Entry 4: toluene suspension in an aqueous solution of FeSO₄ + H₂O₂, room temperature. Entry 5: two-phase system consisting of 0.2 mmol HPC in 20 ml CH₃CN and 20 ml toluene + 4 ml 30% aqueous H₂O₂, room temperature.

H₅PW₁₁ZrO₄₀. Small amounts of the epoxide were also observed in the presence of phosphovanadomolybdc acids H_{3+n}PMo_{12-n}V_nO₄₀ (*n* = 0–2) and their TBA salts. In the presence of the redox-active heteropoly molybdates, we observed a lower total yield of chromatographically identifiable products. Experimental data suggest that cyclohexene oxidation in the presence of HPCs occurs mainly via a free-radical mechanism.

In the presence of the heteropoly anions PW₁₁O₃₉⁷⁻, PW₁₁TiO₄₀⁵⁻, and PW₁₁ZrO₄₀⁵⁻, which are known to catalyze olefin epoxidation by hydrogen peroxide [26, 52], electrophilic attack takes place along with the free-radical route.

There has been a comparative study of the action of redox-active HPCs in the oxidations of aromatic compounds with hydrogen peroxide and the O₂ + H₂ mixture under similar conditions [49]. In the former case, we used a solution of an HPC and aqueous H₂O₂ in CH₃CN and *T* = 65°C; in the latter case, a solution of an HPC in CH₃CN + Pt/SiO₂, the O₂ + H₂ (1 : 2) mixture, and *T* = 30°C.

In the presence of H₄PMo₁₁VO₄₀ or a TBA salt of PMo₁₁VO₄₀⁴⁻ or PW₁₁O₃₉Fe(OH)⁵⁻, the relative substrate activity in terms of the total product yield increased with an increasing number of electron-donor groups in the substrate molecule (benzene < toluene ≪ phenol) for both epoxidation with H₂O₂ and oxidation with the O₂ + H₂ mixture.

These oxidations yielded products typical of radical reactions. The oxidation of benzene produced phenol. The further conversion of phenol yielded hydroquinone in the case oxidation with the O₂ + H₂ mixture and 1,4-benzoquinone in the case of H₂O₂. The absence of biphenyl among the products suggests that the intermediate radicals are bound to the catalyst and do not pass into the bulk of the reacting mixture.

The main product of phenol oxidation with the O₂ + H₂ mixture was hydroquinone, while phenol oxidation

with H₂O₂ produced 1,4-benzoquinone and a minor amount of hydroquinone.

Table 3 lists product composition data for toluene oxidations with the O₂ + H₂ mixture and with H₂O₂ in the presence of an HPC or Fenton's reagent. Toluene oxidation with the O₂ + H₂ mixture nearly always takes place both at the aromatic ring, yielding cresols, and at the methyl group, yielding benzyl alcohol and benzaldehyde. In oxidation in the presence of Fenton's reagent, the methyl group is more susceptible to attack by the OH• radical [53] (Table 3, entries 1–3 versus entry 4). In toluene oxidation with the O₂ + H₂ mixture, the hydroxylation of the aromatic ring took place mainly at the *ortho* position, which is typical of Fenton's system. The proportion of *para*-cresol was smaller, and, accordingly, the proportion of *meta*-cresol was larger. The product ratio in toluene oxidation with the O₂ + H₂ mixture was the same as was obtained by Nomiya et al. [54] in the two-phase system aqueous H₂O₂–CH₃CN solution of TBA-PMo₁₁O₄₀ at 25°C (entry 5). In toluene oxidation with H₂O₂ under our conditions (solution of H₂O₂ and an HPC in CH₃CN, 65°C), the proportions of the products were different (entry 6). This difference is explained by the fact that both oxidation with hydrogen peroxide and oxidation with the O₂ + H₂ mixture are due not to free OH• radicals, but to intermediate radicals bonded to the HPC, whose formation depends on the composition of the catalytic system and on the reaction conditions.

Thus, the oxidations of aromatic compounds with the O₂ + H₂ mixture and with H₂O₂ proceed in essentially similar ways. The slight difference arises from the way in which the O₂ + H₂ oxidizer is used, specifically, the presence of platinum-activated hydrogen, which is a strong reductant. The reductive medium prevents secondary oxidation, allowing the O₂ + H₂ mixture to be used in selective phenol synthesis.

CONCLUSIONS

The oxidations of hydrocarbons with the $O_2 + H_2$ mixture are complicated processes involving platinum metal catalysts and modifying admixtures. Their mechanism has not been completely elucidated as yet. The studies of the two-component systems consisting of Pt or Pd and an HPC have provided a better understanding of how to select catalysts for these reactions. Using HPCs, it is possible to design catalytic systems based on various types of component interaction ranging from the coordination bond in Pd-containing HPCs to weak adsorption effects. In the most active systems, there is interaction between the platinum metal and the HPC. Although this interaction may be weak, it ensures a high degree of dispersion of the metal. Furthermore, electron transitions and active oxygen transfer from platinum to the cocatalyst occur readily in these systems.

Due to the diversity of compositions and properties of HPCs, it is possible to vary the nature of active oxygen species to some extent and, therefore, the activity of the system toward hydrocarbon substrates. The most active systems for hydrocarbon oxidation involve oxygen species of radical nature.

The properties of the Pt–HPC and Pd–HPC catalytic systems are similar in wide ranges of physical states of the catalyst (solution, monolith, and supported solid) and reaction conditions (temperature and the phase composition of the reactants), suggesting the oxidation mechanism is the same.

The study of the general catalytic characteristics of these systems allowed us to recommend them for use in gas-phase benzene hydroxylation.

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