Reductive activation of dioxygen in catalytic systems including platinum and heteropoly compounds: oxidation of cyclohexane

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Catalytic action of the system based on platinum and heteropoly compound (HPC) was studied in the oxidation of cyclohexane with O_2/H_2 gases to produce cyclohexanol and cyclohexanone. The active composition was represented by a solid bi-component catalyst prepared from the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ complex salt through calcination and redox treatments. The bi-component catalysts were characterized by HREM, XPS, and IR spectroscopy. The active samples consisted of undestroyed crystalline HPC with finely dispersed Pt species, which contained both metallic and ionic states. Reversible Mo^{6+}/Mo^{5+} electron transfer in HPC was easily realized under conditions of catalytic reaction. Based on the state of the active catalysts, a scheme of O_2/H_2 activation and cyclohexane oxidation was suggested. According to the scheme, oxidation proceeded *via* radical hydroxyl intermediate.

KEY WORDS: oxidation; cyclohexane; hydrocarbons; platinum; heteropoly compound.

1. Introduction

Selective conversion of hydrocarbons with gaseous oxygen to oxygenated compounds is considered as an attractive but in many cases an impracticable idea. Oxidation of inert saturated hydrocarbons into alcohols and ketones and aromatic hydrocarbons into phenols needs severe conditions [1–4], which give rise to secondary oxidation, often leading to C–C bond cleavage and, thus, resulting in reduced selectivity to hydrocarbon. A group of selective processes is limited to rather specific cases; among these is the commercial process of cyclohexane oxidation into cyclohexanol and cyclohexanone using cobalt catalyst [5]. Actual studies concern application of solid Fe, Co, and Mn catalysts [6]; in some cases these allow selectivity control, owing to the specific pore structure of the catalyst [7,8].

Oxyfunctionalization of hydrocarbons without cleavage of C–C bonds proceeds smoothly under ambient conditions under the action of single-oxygen donors. Hydrogen peroxide and other peroxy compounds in the presence of transition metal compounds as catalysts can be used for conversion of saturated hydrocarbons to oxygenated products [6,9,10] and benzene to phenol [11–13]. In many cases a disadvantage of the processes is low selectivity relatively to the peroxy compound resulting from the peroxide decomposition.

"Monooxygenase-like" catalysts are capable of oxidizing hydrocarbons with gaseous oxygen in the presence of an organic compound as reducing agent, for instance, ascorbic acid [14]. Because of stoichiometric consumption, the reducing agent should be selected from less expensive chemicals. Zinc and iron metals in acid [15] and carbon monoxide [16] were used for this purpose. More recently hydrogen has attracted much attention as a co-reducer. The appropriate catalytic systems using the O_2/H_2 oxidant have been described for hydroxylation of aromatics [17,18], oxygenation of methane [19] and other hydrocarbons [20,21].

Our previous studies were concerned with design of bi-component catalytic systems for hydrocarbon oxidation with the mixture of O_2/H_2 gases. The active O_2/H_2 oxidation systems were constructed on the bases of Pd(II) and Pt(II) complexes with tungstophosphate heteropoly anions [22,23]. Appropriate homogeneous and heterogeneous versions were applied to test benzene and cyclohexane conversion. The silica-supported complexes showed enhanced activity after reductive treatment prior to catalysis.

Later on, the scope of the heteropoly compound (HPC) tested in O_2/H_2 oxidation of cyclohexane was extended to P–Mo and P–Mo–V HPC [24]. One of the most effective compositions of Pt with molybdophosphoric HPC is represented in the present study.

2. Experimental

2.1. Catalyst preparation

A $1\%Pt/SiO_2$ sample was prepared by impregnation of silica (powdered SiO_2, $S = 280\,m^2/g$) with an aqueous

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solution of H_2PtCl_6, water was evaporated, the sample was kept at 100 °C to dryness, calcined at 300 °C and finally subjected to 1 h treatment in H_2 flow at 300 °C.

The solid bi-component Pt–PMo_{12} samples were started from $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ complex salt, for which 0.1 M solutions of $[Pt(NH_3)_4]Cl_2$ and $H_3PMo_{12}O_{40}$ were mixed in equal volumes. After centrifugal separation the precipitate formed was washed with water and left to dry at room temperature. The Pt–PMo_{12} catalysts were obtained through calcinations of the complex salt in air, reduction in H_2 flow, and in some cases following heating in wet air.

2.2. *Characteristics of the catalysts*

Analysis of the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ complex salt made by the X-ray fluorescent method gave Pt 4.94%, Mo 52.5%, P 1.4%, which corresponded to the ratio of Pt : Mo : P = 0.55 : 12 : 1 and agreed with the given formula.

Dissolving of the bi-component catalysts was estimated in solution after catalysis. For this purpose, phosphorus and molybdenum were determined by photocolorimetry [25,26]. Platinum dissolved was determined by atomic absorption spectroscopy.

Thermogravimetric and differential thermal analysis (TG-DTA) was performed on Q 1500D derivatograph at a rate of heating of $10^\circ\,\mathrm{min}^{-1}$. Infrared (IR) spectra were recorded as KBr pellets on a Specord IR-75 spectrometer. HREM images were obtained on a JEOL 2010 instrument with lattice resolution of 1.4 Å and accelerating voltage of 200 kV.

XPS data were registered on a VG ESCALAB HP instrument using a low-power (200 W) Mg K_α radiation source. The samples were transported from atmosphere. The spectra were obtained at room temperature in vacuum ($P \approx 10^{-9}$ torr), and the binding energy was corrected against C(1s) (284.8 eV) as a standard. Identification of chemical states was made according to [27].

2.3. *Catalytic experiments*

Catalytic reactions were carried out in a glass flask at a controlled temperature and atmospheric pressure. Components of the catalytic systems formed a suspension that was intensively stirred to provide a contact with a gaseous phase containing oxygen and hydrogen. The volume of the gas consumed was fixed on a gas buret connected with the reactor and filled with the mixture of gases $O_2/H_2 = 1/2$ (v/v).

Oxygenated products were analyzed by gas chromatography using Crystal 2000m equipment supplied with an HP-5 (crosslinked 5% PH ME siloxane) capillary column 30 m × 0.25 mm and a flame ionization detector. For identification of the products, a chromatomass spectrometric technique was additionally used (CV-2091 spectrometer).

3. Results and discussion

In the absence of HPC, the 1%Pt/SiO_2 sample produced intensive consumption of the O_2/H_2 gases without remarkable oxidation of cyclohexane. Adding HPC caused considerably lower consumption of the gases and gave rise to conversion of cyclohexane to form cyclohexanol and cyclohexanone in ratios of 10 : 1 to 20 : 1 respectively. The yield of the oxygenated products was dependent on the HPC composition. Maximum yield was obtained in the systems containing redox-active P–Mo and P–Mo–V HPC with one or two V atoms [24]. See figure 1.

As we tentatively believed, a necessary condition for the system to operate in hydrocarbon oxidation is

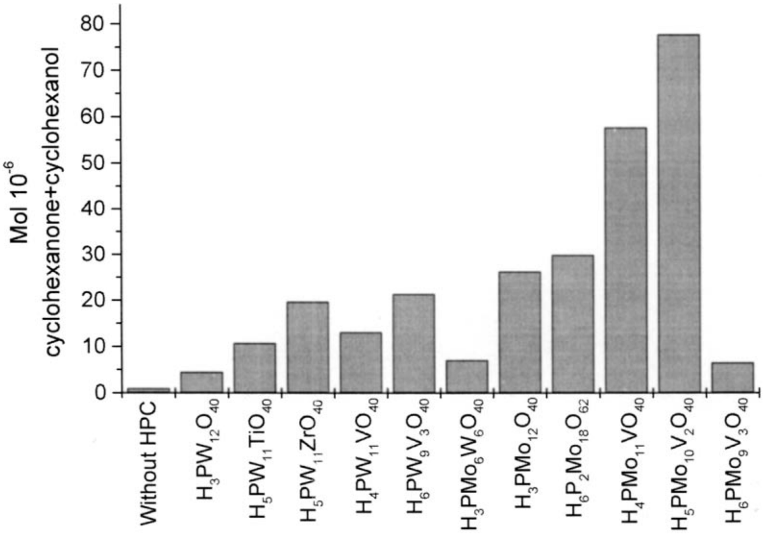


Figure 1.

Table 1
Effect of pre-treatments of the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2{\cdot}7H_2O$ salt on catalysis. Conditions of catalytic testing: 10 mg of the Pt-PMo_{12} sample, 1 ml CH_3CN, 0.1 ml C_6H_{12}, $T = 35\,^{\circ}C$, $O_2/H_2 = 1/2$, $t = 1$ h.

No.	Calcination (°C)	H_2 reduction (°C)	Additional activation	Cyclohexanol + cyclohexanone (μmol)
1	no	no	no	0
2	300	115	no	41
3	300	200	no	0
4	300	200	$O_2 + H_2O$, 100 °C	33
5	300	150	$O_2 + H_2O$, 100 °C	63
6	400	150	no	0
7	400	150	$O_2 + H_2O$, 100 °C	72
8	600	150	no	0
9	600	150	$O_2 + H_2O$, 100 °C	0

appropriate contact between the components. In the catalytic system consisting of 1%Pt/SiO_2 and HPC solution the contact was organized under reaction conditions as a result of adsorption of HPC on the Pt species. In the following study we prepared a solid substance containing Pt species surrounded with heteropoly anions.

We synthesized a salt of $[Pt(NH_3)_4]^{2+}$ complex cation and a P–Mo heteropoly anion of composition $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2{\cdot}7H_2O$, and used the salt as a precursor of the solid catalysts. Being originally inactive (No. 1 in table 1), the salt developed catalytic activity after a series of thermo and reductive treatments.

It was found that optimum temperatures of calcination lie in the range 300–400 °C. The calcined samples became active in oxidation just after mild H_2 reduction (No. 2 in table 1) or needed additional treatment in a wet air (Nos. 3–7). The additional oxidative treatment resulted in increasing the yield of the oxygenated products and even made active slightly over-reduced samples. When we calcined the salt at temperatures as high as 600 °C, the sample was kept inactive after all the following procedures (Nos. 8 and 9).

The TG profile in figure 2, spectrum 1, shows a loss of crystallization water and ammonia at 155 and 325 °C, respectively. The effects corresponded to exo- and endothermic peaks on the DTA profile (figure 1, spectrum 2). In the range of low temperature we observed no TG and DTA peaks which could indicate any transformation of the HPC molecular structure. Only at 605 °C did an intensive exothermic peak with no weight loss appear, caused by substantial decomposition of the heteropoly anion structure. We can certainly conclude that calcination of the sample at 300–400 °C kept heteropoly anions undestroyed.

This conclusion was supported by IR spectroscopy. In the IR spectrum of the starting $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2{\cdot}7H_2O$ salt, characteristic bands of the heteropoly anions were observed at $\nu = 1060\,cm^{-1}$ (PO_4 group), $\nu = 960\,cm^{-1}$ (Mo=O bond in the heteropoly anion), and $\nu = 862$ and $785\,cm^{-1}$ (two vibration frequencies of Mo–O–Mo linear and angular bonds) (figure 3, spectrum 1). Minor changes in the spectrum can be noted after low-temperature calcination and reduction, confirming retention of

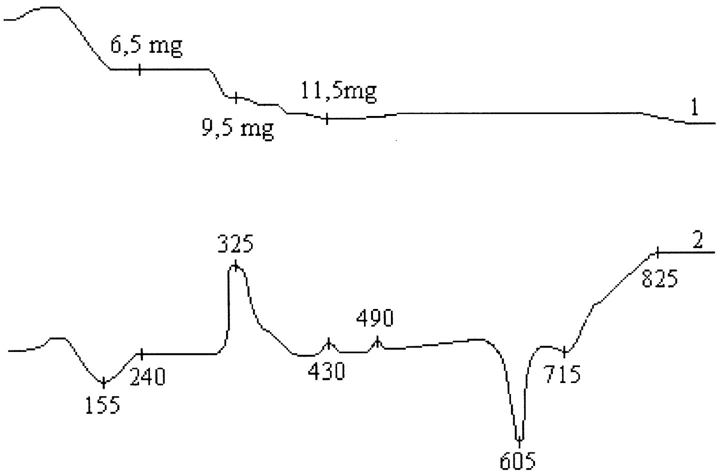


Figure 2. TG (spectrum 1) and DTA (spectrum 2) profiles of the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2{\cdot}7H_2O$ salt.

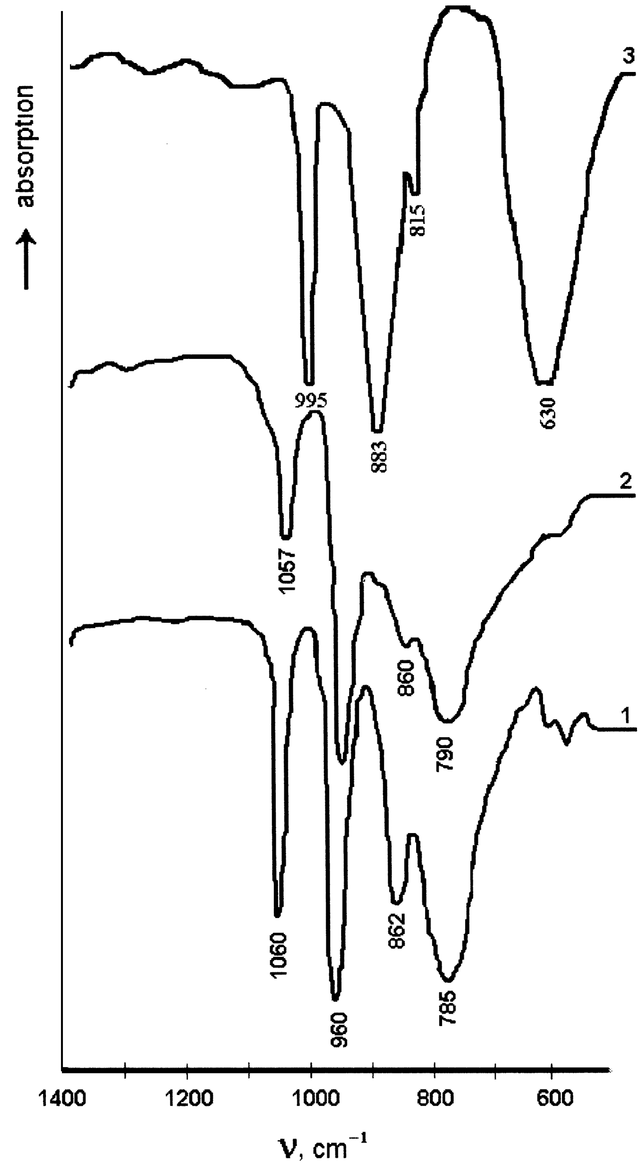


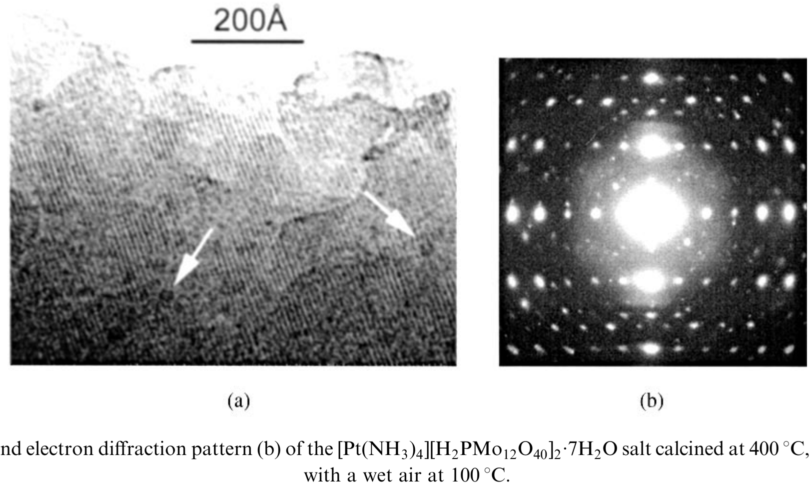
Figure 3. IR spectra of the starting $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ salt (spectrum 1), the salt passed through calcination at 400 °C, H_2 reduction at 150 °C (spectrum 2) and the salt after calcination at 600 °C (spectrum 3).

the molecular structure of the heteropoly anion for the samples active in oxidation (figure 3, spectrum 2). The spectrum of the salt calcined at 600 °C included the series of bands at $\nu = 995$, 883, 815, and 630 cm^{-1} (figure 3, spectrum 3) identical to those reported for MoO_3 [28].

Keeping undestroyed the heteropoly anions, some changes of the salt composition under low-temperature treatment were accompanied by reduction of Pt(II) and resulting fixation of Pt metal species surrounded by the HPC. The HREM image represents the active samples as consisting of flat, well-defined crystallites and finely-dispersed Pt species (figure 4(a)). Selected electron diffraction patterns (figure 4(b)) are very probably indications of the structure of P–Mo heteropoly acid with basic lattice parameters of 8.2 and 3.4 Å [29].

According to XPS data, platinum in the sample reduced at 115 °C can be considered as mainly Pt(II) bonded with the HPC with only a small possible admixture of Pt(0), the state corresponding to a peak of Pt $4f_{7/2}$ at $E = 72.7$ eV (spectrum 2 in figure 5). Increasing the temperature of hydrogen treatment resulted in the appearance of a peak of metal Pt $4f_{7/2}$ at $E = 71.5$ eV (spectrum 1). After oxidative treatment the reduced sample included superposition of oxidized and metallic Pt $4f_{7/2}$ doublets, to which were attributed bands at $E = 71.5$ and 73.2 eV (spectrum 3). High-temperature reduction converted Mo(VI) in the HPC into a mixture of Mo(VI) and Mo(V) (Mo $3d_{5/2}$ bands at $E = 233.2$ and 231.3 eV), which was recovered back to Mo(VI) after oxidative treatment (spectrum 3). From XPS data it became clear that catalytic activity of the samples is associated with the presence of both Pt^0 and Pt^{2+} ions (as seen in spectrum 3). Owing to retention of the HPC structure, redox transfer of Mo^{5+}/Mo^{6+} ions is reversible and easily realized under conditions of catalysis.

We compared the yields of the oxygenated products obtained in the presence of the bi-component "Pt + HPC solution" and solid Pt–PMo_{12} catalysts (figure 6). Providing equal composition of the active



(a) (b)

Figure 4. HREM image (a) and electron diffraction pattern (b) of the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2 \cdot 7H_2O$ salt calcined at 400 °C, reduced at 150 °C and treated with a wet air at 100 °C.

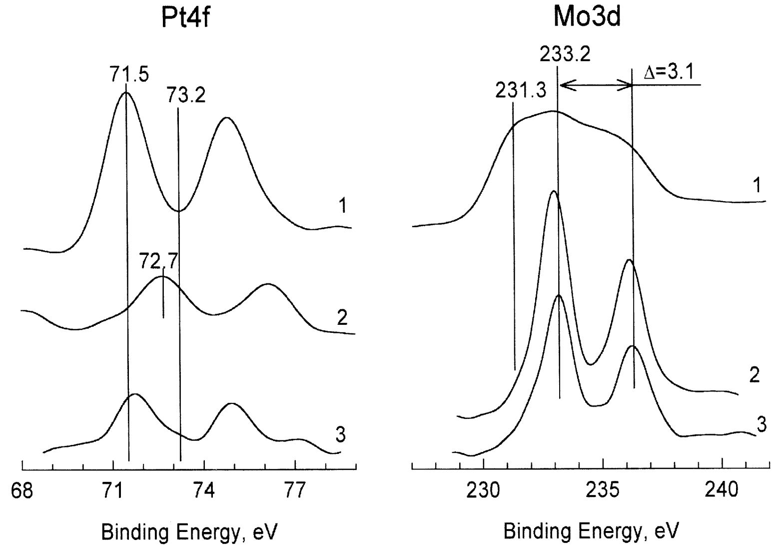


Figure 5. XPS spectra of the $[Pt(NH_3)_4][H_2PMo_{12}O_{40}]_2{\cdot}7H_2O$ salt calcined at 300 °C and reduced at 200 °C (spectrum 1), reduced at 115 °C (spectrum 2), reduced at 200 °C and treated with a wet air at 100 °C (spectrum 3).

components Pt and $PMo_{12}O_{40}^{3-}$ anions in both systems, the solid catalyst gave three times higher yield of the oxygenated products. It can be considered as an indication of the process taking place on the surface of the catalyst without the entry of intermediates into the reaction volume. Under reaction conditions the solid Pt–PMo_{12} sample was partially dissolved. Pt was kept in the solid state and was not detected in solution after reaction, whereas about 50% of HPC went into solution after 1 h. The time dependency of the products formed (figure 6) showed no acceleration but progressive slowing of the rate of product accumulation during 1 h from the start of the reaction. Quenching the process simultaneously with the catalyst dissolving gave further evidence that the oxidation did proceed on the surface of the solid. Otherwise, HPC transfer into the solution would accelerate oxidation. Partial loss of the catalytic activity may be directly concerned with destruction of the active catalyst surface under HPC dissolution.

Proceeding from the state of the active catalysts, the mechanism including intermediates of the radical character can be represented by scheme 1. Owing to the contact between Pt and HPC, reduction of the Pt adsorbed dioxygen with hydrogen resulted in formation

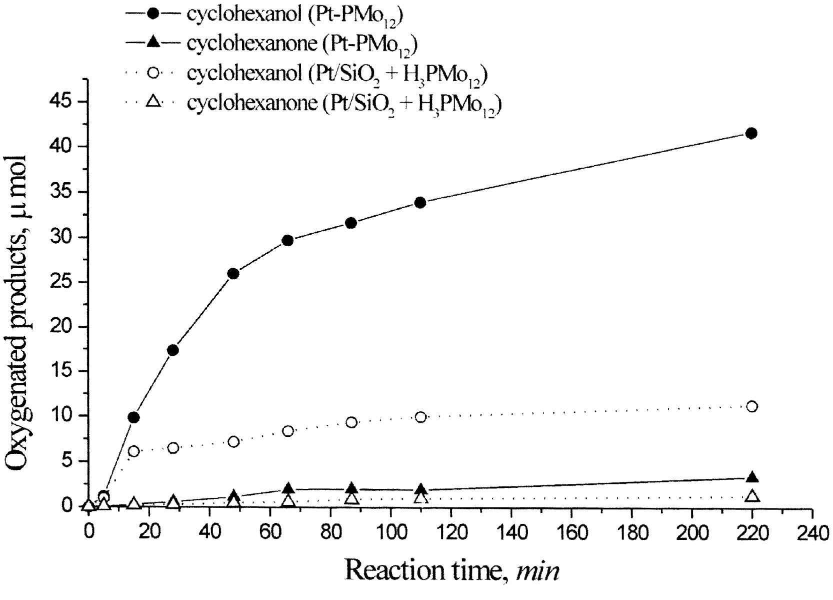
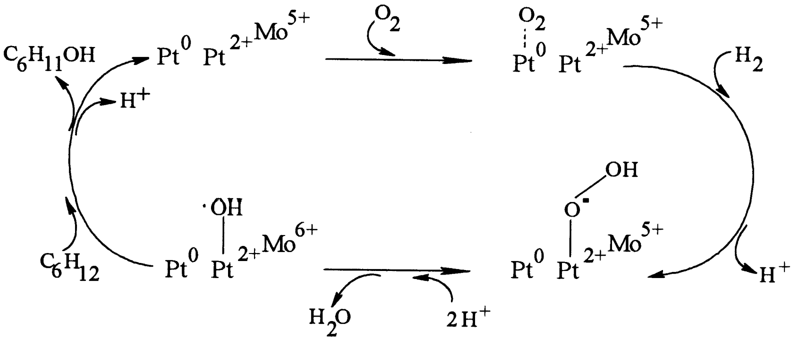


Figure 6. Time dependency of the oxygenated products. Conditions: 10 mg of the Pt–PMo_{12} or 10 mg of the 5%Pt/SiO_2(280) + 7 mg $H_3PMo_{12}O_{40}$, 1 ml CH_3CN, 0.1 ml C_6H_{12}, $T = 35$ °C, $O_2/H_2 = 1/2$, $t = 1$ h. The catalysts were stored in air for 3 months.



Scheme 1.

of peroxide species. Platinum peroxide interacted with Mo^{5+} ions included in the reduced form of HPC to generate hydroxyl radicals, which oxidized cyclohexane into oxygenated products.

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