Oxidation of hydrocarbons by dioxygen reductively activated on platinum and heteropoly compounds

N.I. Kuznetsova*, N.V. Kirillova, L.I. Kuznetsova, V.A. Likholobov

Boreskov Institute of Catalysis, Novosibirsk 630090, Russia

Dedicated to Professor Renato Ugo on the occasion of his 65th birthday

Abstract

Based on Pt and heteropoly compounds (HPC), catalysts are applied to liquid-phase oxidation of cyclohexane and cyclohexene with a mixture of O_2 and H_2 gases. Platinum catalyst in the presence of PW_{11} and $PW_{11}Fe$ HPC represent the most active catalytic systems for alkene oxidation, whereas highest reactivity of cyclohexane was exhibited in the presence of PMo_{12} HPC.

Activity of the catalytic systems and composition of the oxygenated products are controlled by the nature of active intermediates generated under the action of the different HPC.
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1. Introduction

Application of hydrogen along with molecular oxygen is considered the most economical and ecologically sound approach to oxygenated compounds. A number of liquid-phase catalytic systems are known for O_2/H_2 oxidation of hydrocarbons [1], including benzene [2–5], alkanes [6–8], propene [9,10], and is now an active research in progress in this field of oxidation. Formation of hydrogen peroxide via incomplete reduction of molecular oxygen with hydrogen is considered the key feature, however, a detail mechanism of the oxidation is not discussed.

In our previous studies, some Pt and Pd containing systems were applied to hydrocarbon oxidation with the O_2/H_2 gases [11–14]. It was revealed that

the active catalytic systems for liquid-phase oxidation could be designed using heteropoly compounds (HPC). Our attention was focussed on relationships between the activity of the catalytic systems, and the composition and state of components. Investigation of the Pt- and HPC-based catalytic systems is continued in the study represented. The aim is to relate the catalytic properties of the liquid-phase systems to chemical properties of the HPC to gain understanding of the question how HPC participate in the oxidation process.

Cyclohexane and cyclohexene are chosen as substrates to be oxidized. In the classical works by Fusi et al. [15] and Lyons [16], the composition of oxygenates produced from hydrocarbons provided information for suggestion of the mechanism of oxidation. For example, oxyfunctionalization of cyclohexene at allylic position to form cyclohexenol and cyclohexenone argued for homolytic process, whereas

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* Corresponding author. Fax: +7-383-2355756.
E-mail address: kuznina@catalysis.nsk.su (N.I. Kuznetsova).

epoxide was produced via electrophilic attack of oxygen at a double bond. Radical reactants formed from peroxides produced alcohol and ketone from cyclohexane. In our study, the reactions with saturated and unsaturated hydrocarbons are used as some test for the nature of active oxidants.

2. Experimental

2.1. Preparation of catalysts

Commercial reagents of $H_3PW_{12}O_{40} \cdot 11H_2O$ (PW_{12}) and $H_3PMo_{12}O_{40} \cdot 14H_2O$ (PMo_{12}), the latter purified by ether extraction, were used. Abbreviation in parentheses are given here and hereinafter for HPC.

$H_4PMo_{11}VO_{40} \cdot 13H_2O$ ($PMo_{11}V$), $H_5PMo_{10}V_2O_{40} \cdot 9H_2O$ ($PMo_{10}V_2$), $H_6PMo_9V_3O_{40} \cdot 12H_2O$ (PMo_9V_3) were prepared according to the method described elsewhere [17].

Procedures for preparation of $H_4PW_{11}VO_{40} \cdot 10H_2O$ ($PW_{11}V$), $H_6PW_9V_3O_{40} \cdot 10H_2O$ (PW_9V_3) are given in [18].

$H_3PMo_6W_6O_{40} \cdot 13H_2O$ (PMo_6W_6) were prepared by boiling the water solution containing $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ in equimolar amounts for 1 h. Crystalline material was obtained after evaporation of the solution.

$H_5PW_{11}TiO_{40} \cdot 6H_2O$ ($PW_{11}Ti$) was prepared by ether extraction of a solution of the Na-salt in 5N H_2SO_4 [19].

$H_5PW_{11}ZrO_{40} \cdot 7H_2O$ ($PW_{11}Zr$) was prepared by the method described in [20].

Tetrabutylammonium (TBA) salts $TBA_3PW_{12}O_{40}$ (TBA-PW_{12}), $TBA_5H_2PW_{11}O_{39}$ (TBA-PW_{11}), TBA_4 $HPW_{11}Fe(OH)O_{39}$ (TBA-$PW_{11}Fe$), TBA_4HPW_{11} $Mn(H_2O)O_{39}$ (TBA-$PW_{11}Mn$), $TBA_4PW_{11}Cr(H_2O)$ O_{39} (TBA-$PW_{11}Cr$), $TBA_4HPW_{11}Co(H_2O)O_{39}$ (TBA-$PW_{11}Co$), $TBA_4HPW_{11}Cu(H_2O)O_{39}$ (TBA-$PW_{11}Cu$) were prepared as described in [21]. Identical procedure was performed for preparation of TBA_3 $PMo_{12}O_{40}$ (TBA-PMo_{12}), $TBA_4PMo_{11}VO_{40}$ (TBA-$PMo_{11}V$), $TBA_5PMo_{10}V_2O_{40}$ (TBA-$PMo_{10}V_2$).

A sample of 5% Pt/C was prepared according to modification of the procedure described by Gallezot et al. [22] through alkaline hydrolysis of H_2PtCl_6 on Sibunit (mesoporous pyrocarbon, $S = 300 \, m^2 \, g^{-1}$), and following reduction with sodium formate. According to CO adsorption measurement, Pt dispersion was around 0.5.

2.2. Catalytic experiments: oxidation of cyclohexane

Liquid-phase oxidation of cyclohexane (chemical purity grade) was conducted at $35\,°C$ at atmospheric pressure of a gas mixture of $O_2/H_2 = 1/2$. A powdered sample of platinum catalyst 5% Pt/C was suspended in a CH_3CN solution containing C_6H_{12} tetrahexylammonium chloride (THACl) or HPC. Organic products were analyzed by gas chromatography (GC) using a capillary column DB-1701 $30 \times 0.00055\,m$ and a flame ionization detector (a Crystal 2000 instrument). Cyclohexanol and cyclohexanone in a molar ratio of 10:1 to 50:1 were the main products, whose amount was determined by the presence of THACl or HPC of different composition (Table 1). In all experiments, the molar amount of oxidation products was 1–5% of ($O_2 + H_2$) gases consumed [14].

2.3. Oxidation of cyclohexene

The above described conditions were applied to oxidation of cyclohexene (Aldrich, stored under Ar), except for temperature, that was chosen lower, because cyclohexene underwent more readily oxidative transformations. The catalytic systems comprised THACl or HPC in the form of acids or TBA-salts.

Oxidation of cyclohexene produced cyclohexenol, cyclohexenone, cyclohexanol, cyclohexanone, epox-

Table 1
Products of cyclohexane oxidation in the presence of various HPC

No.	Additive	Cyclohexanol (μmol)	Cyclohexanone (μmol)
1	THACl	11.5	3.5
2	TBA-PW_{11}	38.7	9.3
3	TBA-$PW_{11}Fe$	39.6	17.3
4	TBA-$PW_{11}Mn$	13.4	1.4
5	TBA-$PW_{11}Cr$	12.6	1.6
6	TBA-$PW_{11}Co$	6.3	1.3
7	TBA-$PW_{11}Cu$	0	0
8	PMo_{12}	64.8	16.9
9	TBA-PMo_{12}	22.0	13.1

Composition of liquid mixture: 10 mg 5% Pt/C, 10 mg HPC, 1 ml CH_3CN, 950 μmol C_6H_{12}. Gas composition: $H_2/O_2 = 2/1$; $T = 35\,°C$; 1 h.

Table 2
Oxygenated compounds produced from cyclohexene

No.	Additive	Products (μmol)					
		Epoxide	Cyclohexanol	Cyclohexanone	Cyclohexenol	Cyclohexenone	Bifunctional
1	THACl	0.5	6.5	2.5	16.1	8.7	11
2	TBA-PW$_{11}$	5.6	10.2	3.5	46.5	22.5	17
3	TBA-PW$_{12}$	0	1.0	0	1.3	0.5	2.0
4	PW$_{11}$Zr	28	6	3	30	28	3.4
5	PW$_{11}$Ti	12	13	10	12	5.1	4.2
6	TBA-PW$_{11}$Fe	13	14	10	80	30	22
7	TBA-PW$_{11}$Mn	1.9	7.9	2.0	23	9.5	12
8	TBA-PW$_{11}$Cr	1.5	8	0	12	7.2	5.0
9	TBA-PW$_{11}$Co	1.4	3.0	0	20	7.5	3.0
10	PMo$_{12}$	0.1	1.0	0	9.7	3.6	6.0
11	PMo$_{11}$V	0.1	5.6	1.0	25	5.0	12
12	PMo$_{10}$V$_2$	0	1.6	0	10	1.7	7.2
13	PMo$_9$V$_3$	0	0.5	0	8	2.0	2.5
14	TBA-PMo$_{12}$	0.4	2.2	0	8.6	2.1	4.2
15	TBA-PMo$_{11}$V	0.4	2.6	0	29	8.4	12
16	TBA-PMo$_{10}$V$_2$	0.4	1.7	0	7.8	2	3.3

Composition of liquid mixture: 10 mg 5% Pt/C, 4 mg HPC or THACl, 1 ml CH$_3$CN, 970 μmol C$_6$H$_{12}$. Gas composition: H$_2$/O$_2$ = 2/1; T = 25 °C; 1 h.

ide, and compounds with two oxygen-containing functional groups which comprised diols and keto-alcohols, and attained 25% of the total products (Table 2). Apart from oxygen-containing compounds, cyclohexane was produced from ca. 1% of cyclohexene.

Reference experiments were performed with both the substrates, cyclohexane and cyclohexene, when conventional mixture of the solvent, catalyst, and hydrocarbon was exposed to pure dioxygen in the absence of hydrogen. No products were detected after 1 h.

3. Results and discussion

Bi-component transition metal catalysts are used for synthesis of hydrogen peroxide from O$_2$ and H$_2$, and oxidation of organics by the O$_2$/H$_2$ mixture, as well. Two electron transfer is considered as a key moment of both the processes.

$$[M^0] + O_2 \rightarrow [M^{2+}(O_2)^{2-}]$$
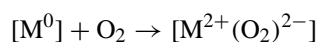
In our experiments, THACl, when added to the suspension of a platinum catalyst, initiated formation of oxygenated products from cyclohexane (No. 1 in Table 1) and cyclohexene (No. 1 in Table 2). Conversion of cyclohexane into a mixture of cyclohexanol and cyclohexanone is typical for peroxide oxidation. Cyclohexene produced a mixture of oxygenates including epoxide resulted from heterolytic oxygen transfer to the double bond, and cyclohexenol and cyclohexenone as primary products of allylic oxygenation. Cyclohexanol and cyclohexanone originated from hydrogenation of cyclohexenol and cyclohexenone, respectively, could refer to the products of allylic oxidation, too. No clear idea is available concerning origination of compounds with two oxygen-containing functions. They could be suggested to arise from secondary oxidation of the primary products. However, oxidation of cyclohexenol, cyclohexenone, and epoxide was determined to proceed very slowly under reaction conditions, that indicated formation of the two oxygen containing derivatives from cyclohexene in parallel with primary products. As these products amounted no more than 25% of total, we believed it most correct to ignore them and compare only the amounts of allylic products (cyclohexenol + cyclohexanol + cyclohexenone + cyclohexanone) and epoxide. The percentage of epoxide in the THACl-containing system was no more than 1% of the total molar amount of oxidation products.
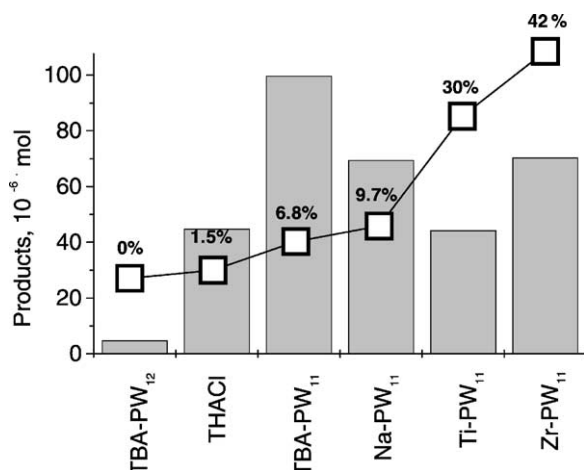
Fig. 1. Total yield of the products of cyclohexene oxidation (columns in the diagram) and the ratio of epoxide to total products resulted from allylic oxidation (cyclohexenol + cyclohexenone + cyclohexanol + cyclohexanone, the values over the curve). See Table 2 for conditions.

In combination with the platinum catalyst, some HPC were more effective than THACl, for example, TBA-PW$_{11}$. In the presence of TBA-PW$_{11}$ the yield of oxygenated products was 3–4 times higher than that obtained in THACl containing mixtures (No. 2 in Tables 1 and 2, Fig. 1).

By contrast to PW$_{11}$, coordinatively saturated PW$_{12}$ anion behaved another way (No. 3 in Table 2). Similarly, low efficiency of PW$_{12}$ anion was observed before in oxidation of cyclohexane [14]. Again, PW$_{11}$ and PW$_{12}$ anions behaved differently in epoxidation of cyclohexene with hydrogen peroxide: PW$_{11}$ was 25 times as active as PW$_{12}$ [21].

The positive properties of the PW$_{11}$ anion was believed to be an effect of vacancy in its molecular structure. It is commonly known, that localized nearby the vacancy of O^{2-} ions are responsible for ligation property of the heteropoly anion in transition metal complexes, in particular, in Pd^{II} and Pt^{II} complexes. Formation of the complexes with heteropoly anions stabilized ionic state of Pd^{II} in the presence of as strong reducer as H$_2$. The Pd^{II} complexes with P-W heteropoly anions were stable during several hours of the catalytic reaction, while palladium(II) sulfate was readily reduced to metal under the identical conditions [12].

In the reaction under study, interaction of platinum with PW$_{11}$ analogous to coordinate bond was realized under adsorption of the anions on the solid Pt catalyst. The interaction facilitated two electron transfer from the metal to dioxygen to form a peroxo complex. Localization of the peroxo species on Pt^{II} ions impeded their further reduction into water, thus allowing the peroxo species to participate oxidation of organic substrates. Scheme 1 illustrates oxygenation of hydrocarbons with the O$_2$/H$_2$ mixture in terms of this concept.

Hereinafter, platinum containing systems were examined with different HPC. Analyzing the data obtained, we revealed that the role of the HPC was not always limited to supporting the favorable catalysis for metal oxidation state. Along with the ligation properties, we should take into account the other features of the HPC. Of primary importance is interaction of some HPC with peroxides.

Oxidation with the O$_2$/H$_2$ gases proceeds through generation of hydrogen peroxide as more active oxidant than dioxygen. Interaction of the HPC with

Scheme 1.

$$[PW_{11}Ti^{IV}\text{-}Pt^{II}(O_2)^{2-}] \xrightarrow{H^+} [\ PW_{11}Ti^{IV}\text{-}Pt^{II}\ ]$$
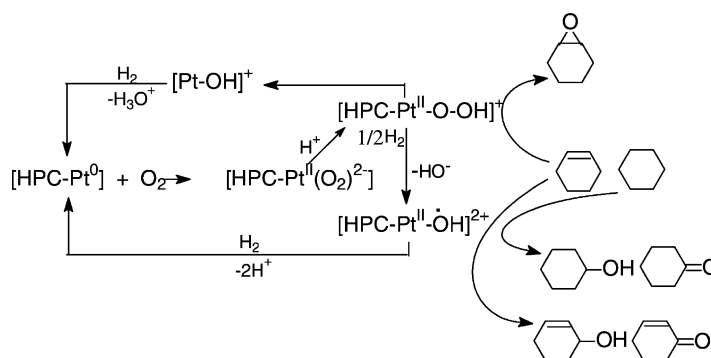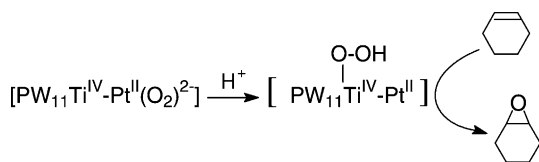
Scheme 2.

hydrogen peroxide may produce even more active oxidants, such as peroxo compounds, peracids or •OH radicals formed via hydrogen peroxide decomposition. From our data, we tried to determine a nature of interaction between HPC and peroxide species, which enclosed into catalysis.

The above mentioned reaction of cyclohexene with hydrogen peroxide [21] in the presence of TBA-PW$_{11}$ gave epoxide as the only oxidation product. The epoxide was formed selectively via intermediate peroxo complex, which attacked at alkene double bond. In our case, the peroxo complex pathway made, probably, minor contribution into total reaction, because epoxide comprised only 7–10% in total of products of cyclohexene oxidation (epoxide + cyclohexenol + cyclohexenone + cyclohexanol + cyclohexanone; the curve in Fig. 1). The probable reason was the Pt bounded peroxo species [HPC–Pt^{II}–O–OH]$^+$ to participate transformations without generation of free hydrogen peroxide and peroxo complex of W^{VI}.

When Ti^{IV} and Zr^{IV} ions were incorporated into heteropoly anion, the reaction with cyclohexene yielded epoxide in much higher amount (30 and 42% of the total product, respectively, see Nos. 4 and 5 in Table 2 and Fig. 1). Ti^{IV} and Zr^{IV} ions were, probably, involved into alkene epoxidation to form peroxo or hydroperoxo intermediate species, which contain strongly electrophilic oxygen (Scheme 2).

Formation of allylic products were not participated by Ti^{IV} and Zr^{IV} compounds.

The P-W HPC could not be characterized as redox labile. The redox properties may be introduced together with transition metal ions, such as Fe^{III}, Cr^{III},
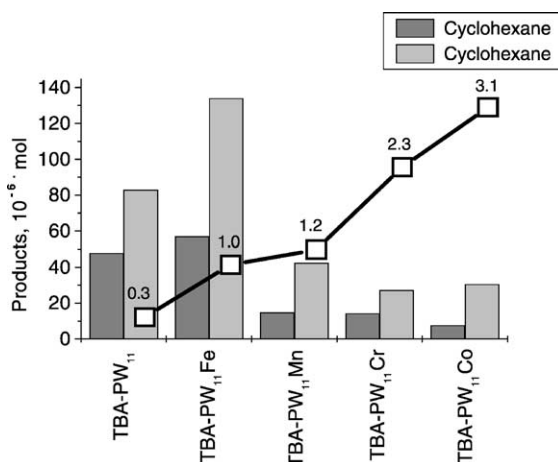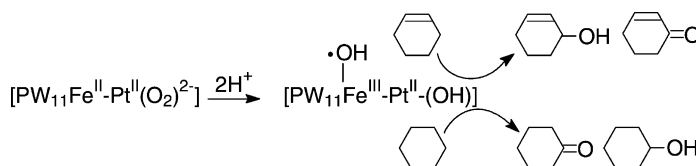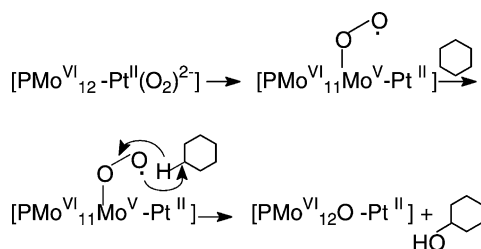

Fig. 2. Products of cyclohexane and cyclohexene oxidation in the systems containing metal-substituted heteropoly tungstates. See Tables 1 and 2 for conditions. The curve shows relative activity of HPC in decomposition of hydrogen peroxide (data are cited from [21]).

Mn^{II}, Co^{II}, and Cu^{II}. One electron transfer is typical for these ions, while the reaction conditions and catalytic action of platinum favors redox processes.

In fact, the ions performed their typical function catalyzing peroxide decomposition. The activity of the heteropoly tungstates in H$_2$O$_2$ decomposition grew in the series: PW$_{11}$ < PW$_{11}$Fe < PW$_{11}$Mn < PW$_{11}$Cr < PW$_{11}$Co ≈ PW$_{11}$Cu [21]. Incorporating Fe ions into heteropoly tungstate PW$_{11}$ anion produced higher activity of the system in oxidation of cyclohexane (No. 3 in Table 1) and cyclohexene (No. 6 in Table 2 and Fig. 2). The observed phenomenon was accounted for by more intense decomposition of the Pt^{II} peroxide [HPC–Pt^{II}–O–OH]$^+$ or peroxo complex [HPC–Pt^{II}(O$_2$)$^{2-}$] under the action of Fe^{II}. Decomposition of the peroxide gave •OH radicals which were highly active to both alkanes and alkenes, oxygenation at allylic position being preferable with the latter (Scheme 3).

$$[PW_{11}Fe^{II}\text{-}Pt^{II}(O_2)^{2-}] \xrightarrow{2H^+} [PW_{11}Fe^{III}\text{-}Pt^{II}\text{-}(OH)]$$
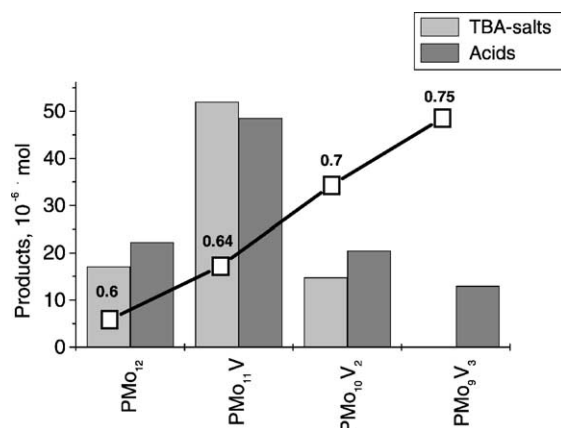
Scheme 3.

Scheme 4.

Fig. 3. Products of cyclohexene oxygenation at allylic position in the presence of P-Mo and P-Mo-V HPC. See Table 2 for reaction conditions. Points on the curve indicate redox potentials of heteropoly anions (reproduced from [24]).

Experimentally observed proportion of epoxide among the products of cyclohexene oxidation became lower in the presence of PW_{11}Fe than PW_{11} HPC, and further lessening proceeded when Fe was replaced by Mn, Cr, and Co which decomposed hydrogen peroxide more actively (Nos. 7–9 in Table 2). At the same time, the typical for Mn-, Cr-, Co-containing heteropoly tungstates high activity to peroxide decomposition made lower the total yield of oxygenated products with the both hydrocarbons (Fig. 2).

A special effect was represented by PW_{11}Cu HPC. The Cu^{II} ions were strong enough oxidant, to cause oxidation of the platinum surface and resulting deactivation to O_2 reduction. Neither formation of organic products (No. 7 in Table 1 for cyclohexane) nor reduction of dioxygen into water was observed in the presence of the Cu-containing heteropoly tungstate.

The P-Mo and P-Mo-V HPC are known to catalyze peroxide oxidation through peracid type intermediates. At the same time, the Mo^{VI} and V^V ions behave as reversible oxidants under the reaction conditions due to one-electron V^V/V^{IV} and Mo^{VI}/Mo^V transfer. Interaction of peroxide with oxidized state of HPC formed intermediate species of radical nature (Scheme 4) which were very reactive to hydrocarbons [23].

P-Mo and P-Mo-V HPC were revealed to be especially active in reaction with cyclohexane (Nos. 8 and 9 in Table 1). These systems were not the best, but active enough to oxidation of cyclohexene (Nos. 10–16 in Table 2).

Substitution of V for one Mo atom in HPC resulted in an increase in the oxidative potential of the heteropoly anion [24] to generate more actively the radical intermediate and, therefore, in a higher activity of the catalytic system. Substitution of the PMo_{11}V for PMo_{12} HPC had been observed to give a higher yield of cyclohexanol in oxidation of cyclohexane [14]. For oxidation of cyclohexene, an increase in the yield of cyclohexenol and cyclohexenone, but epoxide, was observed (Nos. 11 and 15 in Table 2 and Fig. 3). Further increase of potential was caused by introduction of the second and more V atoms, however, that was accompanied by negative changes in catalysis. The highest activity of the systems was observed at some optimal oxidative potential (Fig. 3).

4. Conclusion

The nature of active intermediates in O_2/H_2 oxidation of hydrocarbons is substantially determined by the chemistry of HPC. In the presence of PW_{11} oxidation is mediated by Pt^{II} peroxide capable of electrophilic attack at alkene double bond or oxygenation at allylic position. Pt^{II} peroxide is decomposed to generate $^\bullet$OH radical. Decomposition is more intense when the heteropoly tungstate contains Fe^{II}, Mn^{II}, Cr^{III} and Co^{II} ions. The radicals are active in oxidation of cyclohexane and allylic position of cyclohexene. The peroxide group can transfer from Pt^{II} to Ti^{IV} and Zr^{IV} ions. The corresponding peroxides behave as strong electrophilic agents with respect to the double bond and, therefore, are especially active in epoxidation of cyclohexene. PMo_{12} and PMo_{12}V HPC form active intermediates of radical nature that reveal high activity

with respect to allyl position of cyclohexene and especially to cyclohexane.

Acknowledgements

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