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Total oxidation of Cl-containing VOCs over mixed heteropoly compounds derived catalysts

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Abstract

Catalysts derived from mixed PMoV and PWV heteropoly compounds with Keggin structure supported on titania were prepared. The samples were characterized by the S_{BET} method, Fourier transform infrared spectroscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The effect of the temperature pretreatment of the samples, the number of vanadium atoms in the starting heteropolyanions and the nature of the peripheral atom on the surface properties and catalytic behavior of the samples in total oxidation of Cl–benzene was studied. The results provided clear evidence for the Keggin unit preservation in the heteropolyanions for pretreatments at temperature not exceeding 723 K. It was shown that the high-temperature (723 K) pretreated catalysts and/or replacement of W or Mo in the heterepoly anions with V atoms lead to an increase in the catalytic activity due to the redox capability of vanadium centers.

Keywords: Mixed heteropoly catalysts; VOCs; XRD; FTIR; XPS

1. Introduction

The strict legislation for controlling the emission to the atmosphere of industrial volatile organic compounds (VOCs), which contribute to photochemical smog, ground level ozone and toxic emissions [1–4], has made the catalytic destruction of hydrocarbons a very important topic of research, aimed at developing new processes and catalysts for limiting air pollution by VOCs.

Among all the applied methods (thermal incineration at 1073–1273 K, hydrodechlorination, biological processes, steam reforming, photocatalytic degradation, etc.) [1–4], the catalytic destruction is the most economical and effective way for a destructive removal of chlorinated VOCs. It stands for a wide range of pollutant concentrations, and it exhibits an excellent selectivity toward formation of harmless products. Furthermore, catalytic processes operate at a relatively low reaction temperature [2,5].

Oxides of transition metals (Cu, Co, V, Mn, Fe, Cr, Ni oxides) [6–8], noble metals (Pt, Pd) [9,10], perovskites [11] and basic catalysts are the catalysts mainly studied for the catalytic combustion of VOCs (chlorinated or not). Noble metal catalysts have been claimed to be highly active in the destructive oxidation of chlorinated VOCs, but they often lead to polychlorinated-undesired molecules, and they often undergo an easy deactivation by HCl and Cl_2 produced along the reaction. The TiO_2-supported V_2O_5-MoO_3(WO_3) catalysts constitute one of the most largely used catalytic systems for the combustion of chlorinated VOCs [6,12–14].

It is well known that heteropoly acids (HPAs), such as 12-molybdophosphoric and 12-tungstophosphoric acids, possess purely Brönsted acidity and are stronger acids than many conventional solid acids such as SiO_2/Al_2O_3, H_3PO_4/SiO_2 and HY zeolite. They have been widely used in acid-catalyzed reactions as well as in oxidation reactions both in heterogeneous and homogeneous systems [15]. The acidic and redox properties of HPAs can be easily controlled by the substitution of the constituent elements without changing the fundamental structure [16]. The substitution of one or more molybdenum or tungsten atoms of the Keggin heteropoly anion by vanadium leads to a change in the acid strength and to an improvement of the catalytic performances in the redox reactions [17–22].

In the literature, there is practically no data reporting the use of heteropoly compounds (HPCs) as catalysts in the

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process of total oxidation of Cl-containing VOCs. In our work we attempted to develop new, active and stable catalysts on the basis of mixed PMoV and PWV heteropoly compounds supported on a TiO_2 carrier for total oxidation of chlorobenzene. The effect of the temperature treatment, the number of V atoms in the heteropoly anions and the nature of the peripheral atom (Mo or W) on the thermal stability, surface and catalytic properties of the mixed heteropoly catalysts, was studied.

2. Experimental

2.1. Sample preparation

Commercially available (Aldrich, reagent grade) 12-molybdophosphoric and 12-tungstophoshoric acids were used. Sodium metavanadate (Aldrich, reagent grade), sodium molybdate dihydrate or sodium tungstate dihydrate and anhydrous di-sodium hydrogen phosphate (Merck, reagent grade) were used for the preparation of mixed PMoV and PWV samples. The mixed MoV samples were synthesized as described by Tsigdinos and Hallada [23], while mixed WV samples were synthesized as described by Kuznetsova et al. [19]. Supported heteropoly catalysts were prepared by the wetness impregnation method using a mesoporous TiO_2 carrier (Degussa) and aqueous solutions of the mixed heteropoly compounds. The impregnation solutions were prepared by dissolving 3 g parent Mo-containing HPC and 2 g parent W-containing HPC in 10 and 7 ml H_2O, respectively. The impregnation solutions were used for 10 g of support. The resulting catalysts were dried at 343 K for 6 h and were calcined in the temperature range of 423–823 K in a muffle furnace at a rate of 2 K/min, for 2 h at each temperature under air at atmospheric pressure. The quantities of the used impregnation solutions were so that the theoretical amount of Mo (or W) was about 12 wt.%. The V/Mo or V/W ratio in the system was varied between 1/11 and 3/9. The prepared catalysts were denoted as follows: $HPMo_{12}/Ti$, $HPMo_{11}V_1/Ti$, $HPMo_9V_3/Ti$, HPW_{12}/Ti, $HPW_{11}V_1/Ti$, HPW_9V_3/Ti.

2.2. Physicochemical characterization

Nitrogen adsorption–desorption isotherms were recorded at 77 K in a TriStar 3000 equipment from Micromeritics. Prior to the experiments, the samples were degassed at 423 K for 5 h. The volume of adsorbed N_2 was normalized to standard temperature and pressure.

X-ray diffraction (XRD) analysis was carried out on a Siemens D5000 diffractometer using the Kα radiation of Cu ($\lambda = 1.5418$ Å). The diffraction patterns were taken over the range of 2θ between 5° and 75° at a rate of 0.02°/s. The identification of the phases was achieved by using the ICDD-JCPDS database.

Fourier transform infrared (FTIR) spectra were recorded using an Equinox IFS55 spectrometer (Brücker) equipped with a DTGS detector. The absorption spectra were obtained by recording 100 scans between 800 and 1200 cm^{-1} with a resolution of 4 cm^{-1}. Wafers were prepared after diluting the sample in KBr by a factor 100.

X-ray photoelectron spectra (XPS) were recorded on a SSI X-probe (SSX-100/206) spectrometer from Surface Science Instruments working with a monochromatic Al Kα (1486.6 eV) radiation (10 kV, 22 mA). The analysis chamber was operated under ultrahigh vacuum with a pressure close to 5×10^{-9} Torr. The binding energy (BE) values were referred to C 1s photopeak at 284.8 eV. The surface atomic concentrations were calculated by using a Shirley baseline and correcting the intensities with theoretical sensitivity factors based on Scofield cross sections [24].

2.3. Catalytic test

The catalytic activity of the samples was measured in the reaction of total oxidation of chlorobenzene at 473 K. The tests were performed in a metallic fixed-bed micro reactor operated at atmospheric pressure. The catalytic bed was composed of a layer of inert glass wool surmounted by 200 mg of catalyst powder selected within the granulometric fraction of 200–315 μm and diluted in 800 mg of inactive glass spheres with diameters in the range of 315–500 μm. Chlorobenzene was introduced in the feed at a concentration 100 ppm starting from a mixture of chlorobenzene in helium. He was used as diluting gas to obtain a total stream of 200 ml/min. The amount of catalyst and the total gaseous stream were chosen in order to reach a total feed rate of 37 000 h^{-1}, which corresponds to industrial conditions usually found at the outlet of chimneys of incineration units (before trapping and gas-washing units). The analysis of the reactants and products was continuously performed by on-line gas chromatography equipped with 4 columns, 1 methanizer, 2 FID and 1 TCD allowing to quantify benzene, chlorobenzene, O_2, CO, CO_2, N_2 and to detect other hydrocarbons and chlorinated hydrocarbons.

3. Results and discussion

3.1. Porosity characteristics

The textural parameters of the samples calcined at 523 and 723 K, such as BET surface area (S_{BET}) and pore volume (V_p), are listed in Table 1. The TiO_2 support has the highest S_{BET} (83 m^2/g). It is evident that the textural parameters of the samples decrease with the increasing calcination temperature and the number of vanadium atoms in the heteropoly anions. The BET surface area of Mo-containing samples treated at both temperatures is changed in the following order: $TiO_2 > HPMo_{12}/Ti > HPMo_{11}V_1/Ti > HPMo_9V_3/Ti$ (Table 1). The same trend in the change of the surface area is observed for W-containing samples at 523 K: $TiO_2 > HPW_{12}/Ti > HPW_{11}V_1/Ti > HPW_9V_3$, whereas at higher calcination temperatures the change is negligible (Table 1). The pore volume of the samples decreases in the same way. This can be attributed to a plugging of the pores of the support with molecules of heteropoly compounds. Since the TiO_2 carrier contains pores of 0.31 cm^3/g with a diameter of 135 Å, the Keggin units having a diameter of

Table 1
Textural characteristics of mixed MoV and WV heteropoly catalysts at different temperature treatment

Sample	Temperature (K)	S_{BET} (m^2/g)	V_p (cm^3/g)
TiO_2	723	83	0.31
$HPMo_{12}$/Ti	523	58	0.19
	723	61	0.23
$HPMo_{11}V_1$/Ti	523	53	0.19
	723	55	0.20
$HPMo_9V_3$/Ti	523	49	0.17
	723	48	0.18
HPW_{12}/Ti	523	73	0.26
	723	68	0.26
$HPW_{11}V_1$/Ti	523	71	0.25
	723	68	0.26
HPW_9V_3/Ti	523	65	0.23
	723	63	0.25

about 12 Å can indeed readily penetrate into them. W-containing samples have higher surface areas and pore volumes than those for Mo-containing samples, a fact which can be related to a better dispersion of supported tungstophosphates on titania or to a deeper penetration of the supported Mo-heteropoly compounds inside the pores.

3.2. XRD measurements

The XRD patterns of titania-supported mixed PMoV- and PWV samples heated at different temperatures (523–823 K) are shown in Figs. 1 and 2, respectively. A strong peak at $2\theta = 25.52^\circ$ of TiO_2 support is detected in all XRD diagrams. It corresponds to the anatase phase of the support. No diffraction peaks typical for heteropoly compounds with the Keggin structure are observed in the XRD diagrams of Mo-containing heteropoly catalysts heated up to 623 K. This means that supported heteropoly anions are amorphous and/or the particles are too small and not detectable by XRD. However, well-defined diffraction peaks assigned to the formation of orthorhombic α-MoO_3 phase ($2\theta = 23.4$ and 27.4°) [25] are detected for the $HPMo_{12}$/Ti sample heated at 723 K (Fig. 1, line b). The XRD patterns of mixed PMoV catalysts ($HPMo_{11}V_1$/Ti and $HPMo_9V_3$/Ti) calcined in the range 523–823 K (Fig. 1d–i) show behaviors different than those of the sample without vanadium. The α-MoO_3 pattern is clearly visible in the diagram of sample $HPMo_{11}V_1$/Ti after calcination at higher temperature (823 K) (Fig. 1f). No diffraction peak~~s~~ of α-MoO_3 phase are observed in the diffraction pattern of sample $HPMo_9V_3$/Ti at different temperature treatments. This means that the Keggin unit decomposition occurs at higher temperature after introduction of vanadium atoms into the molybdophosphate heteropoly anion.

It should be noted that the mechanism of the Keggin anion transformation into the corresponding oxides is modified by the precise nature of the peripheral atoms. In contrast to Mo-containing samples, no diffraction peaks of WO_3 phases are detected in the diagrams (not shown) of any W-containing catalysts, although they are heated in the same temperature region. This suggests that the HPW and mixed HPWV particles are too small and/or well dispersed on the TiO_2 surface and are undetectable by XRD. It was observed that the unsupported PWV hetreopoly compounds, heated in the same temperature region, kept the Keggin unit up to 923 K. It can be concluded that the tungstophosphate heteropoly anions are thermally more stable than molybdophosphate heteropoly anions.

3.3. Infrared spectra

The IR spectra of titania-supported mixed PMoV and PWV compounds heated at different temperatures are displayed in Fig. 2A and B, respectively. It should be noted that some of the bands of supported HPCs in the region 1200–800 cm^{-1} are partially or totally overlapped with the strong band of the titania carrier. Therefore, only the bands below 800 cm^{-1} will be discussed. A broadening of all the IR bands is observed after supporting the HPCs on titania. This can be a result of the interaction between the heteropoly anion and the carrier surface that leads to a weakening of the interaction between the bonds in the heteropoly anions and loss of the heteropoly anion symmetry [25]. Well-defined bands at 1065 cm^{-1}, 963 cm^{-1} and 865 cm^{-1} are observed in the IR spectra of all Mo-containing samples heated at 523 K (Fig. 2A, a, d and g). These bands can be assigned to stretching vibrations $\nu_{as}(P\text{–}O_a)$ $\nu_{as}(Mo\text{–}O_d)$ $\nu_{as}(Mo\text{–}O_b\text{–}Mo)$, respectively, characterizing the Kegin unit [25,26]. At higher temperature treatment a strong distortion of the molybdophosphate anion and formation of new species are evident in the IR spectra. A transformation of the

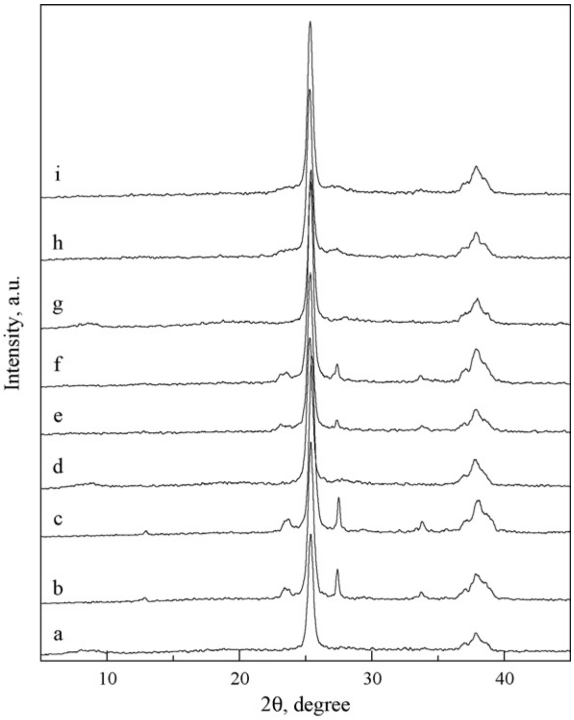

Fig. 1. XRD patterns of titania-supported PMoV HPCs after different temperature treatment: $HPMo_{12}$/Ti at 523, 723 and 823 K (a–c); $HPMo_{11}V_1$/Ti at 523, 723 and 823 K (d–f); $HPMo_9V_3$/Ti at 523, 723 and 823 K (g–i).

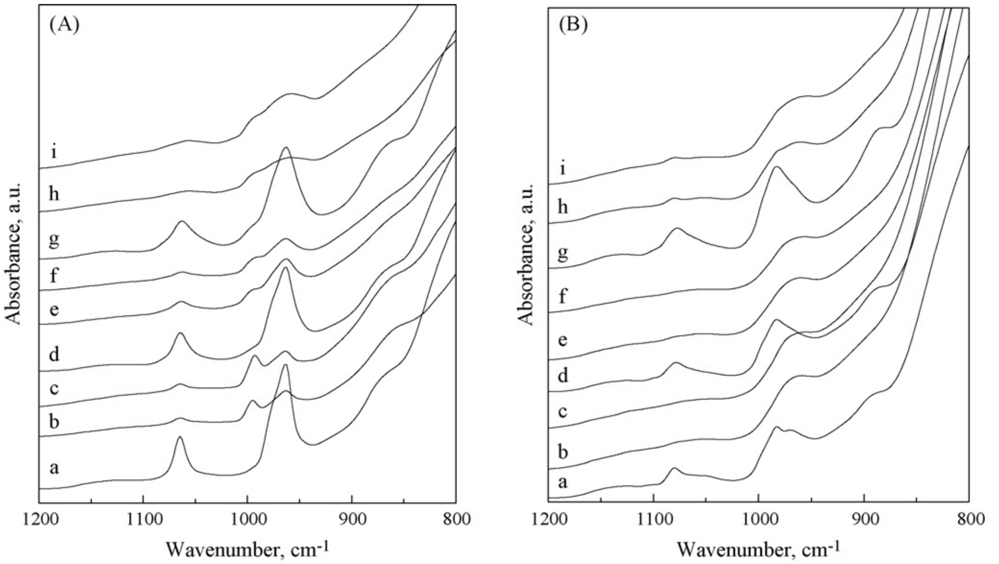

Fig. 2. (A and B) IR spectra of titania-supported PMoV (A) and PWV (B) HPCs after different temperature treatment: $HPMo_{12}/Ti$ at 523, 723 and 823 K (A (a–c)); $HPMo_{11}V_1/Ti$ at 523, 723 and 823 K (A (d–f)); $HPMo_9V_3/Ti$ at 523, 723 and 823 K (A (g–i)); HPW_{12}/Ti at 523, 723 and 823 K (B (a–c)); $HPW_{11}V_1/Ti$ at 523, 723 and 823 K (B (d–f)); and HPW_9V_3/Ti at 523, 723 and 823 K (B (g–i)).

heteropoly anion to MoO_3 (new band at 995 cm^{-1}) [25] at 723 K is observed for the $HPMo_{12}/Ti$ sample (Fig. 2A, b and c). The MoO_3 band is beginning to become visible in the IR spectrum of sample $HPMo_{11}V_1/Ti$ at 823 K (Fig. 2A, e and f), while that one for $HPMo_9V_3/Ti$ (Fig. 2A, lines h and i) is observed as a shoulder only. The band corresponding to the Mo–O_b–Mo bond vibration is still visible at 723 K in the spectra of V-containing samples. It means that V-containing molybdophosphate anions are more thermally stable compared to that without vanadium.

In the IR spectra of the W-containing samples (Fig. 2B, lines a–i) the band at 1075 cm^{-1} corresponds to the ν_{as}(P–O) stretching vibration. The bands at 975 and 890 cm^{-1} for sample HPW_{12}/Ti (Fig. 2B, a–c) and at 980 and 884 cm^{-1} for the $HPW_{11}V_1/Ti$ and HPW_9V_3/Ti samples (Fig. 2B, d–i) are associated to the stretching vibrations ν_{as}(W–O_t) and ν_{as}(W–O_b–W), respectively [25,27,28]. The intensities of the bands decrease with the increasing of the temperature treatment, but the main characteristic features of the tungstophosphate anion did not change upon heating at 723 K. A strong disorder of the Keggin heteropoly anions is observed at 823 K. Broad bands at 1149, 941 and 786 cm^{-1} assigned to formation of WO_3 are detected in the IR spectra of W-containing samples after treatment at 823 K. It means the presence of partially destroyed heteropoly anions, but the Keggin unit is preserved since the band due to the ν_{as}(P–O) vibration is well visible in the IR spectrum of the sample with the highest number of vanadium (Fig. 2B, i).

3.4. XPS measurements

The XPS spectra of Mo 3d and W 4d regions for Mo- and W-containing samples heated at 523 and 723 K are shown in Figs. 3 and 4, respectively. The binding energies of various core electron levels (P 2p, O 1s, Mo $3d_{5/2}$, W $4d_{5/2}$, Ti 2p, V $2p_{3/2}$) are summarized in Tables 2 and 3. The XPS of Mo samples treated at 523 K (Fig. 3A) consist of a single Mo 3d doublet with Mo $3d_{5/2}$ binding energy of 232.9–233.3 eV (Table 2). This value characterizes Mo^{6+} ions in polymolybdates [29]. After treatment of the samples at higher temperatures the XPS Mo 3d is broader (Fig. 3B), in agreement with the presence of

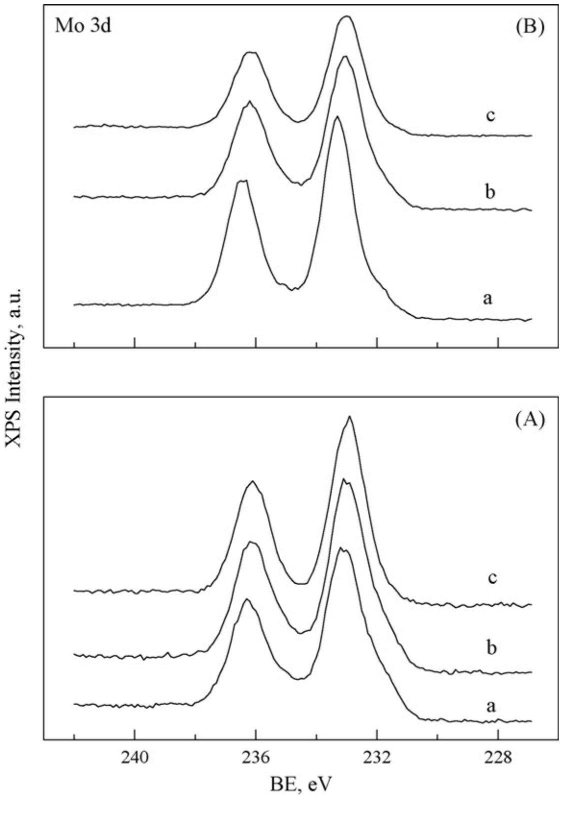

Fig. 3. (A and B) XPS of Mo 3d for titania-supported PMoV HPCs after temperature treatment at 523 (A) and 723 K (B): HPMo/Ti (a); $HPMoV_1/Ti$ (b); and $HPMoV_3/Ti$ (c).

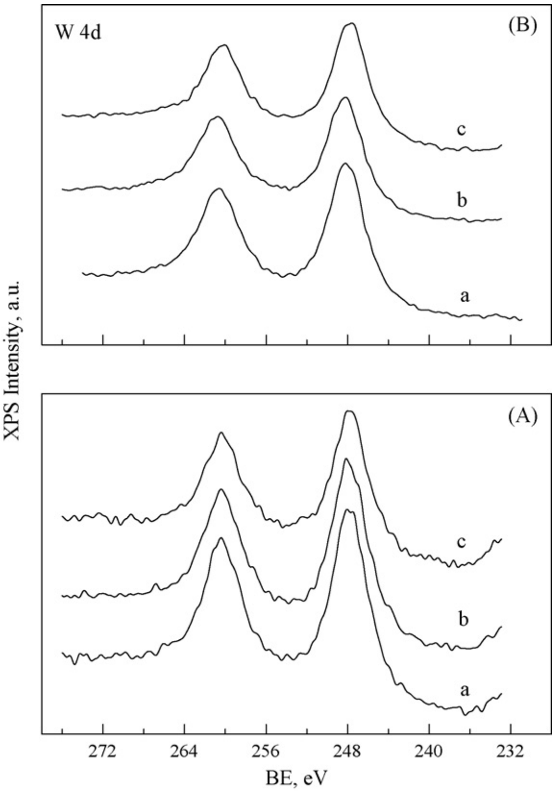

Fig. 4. (A and B) XPS of Mo 3d for titania-supported PWV HPCs after temperature treatment at 523 (A) and 723 K (B): HPW/Ti (a); HPWV$_1$/Ti (b) and HPWV$_3$/Ti (c).

different molybdenum species. This is an indication for the strong distortion of the molybdophosphate anions upon heating.

The XPS W 4d spectra for W-containing samples are changed after increasing the temperature treatment (Fig. 4), in a similar way to that for Mo 3d spectra. The values of BE of W 4d$_{3/2}$ core levels at 247.3–248.3 eV suggest the presence of W^{6+} in tungsten oxide species [30]. The slight change in the values of W 4d$_{3/2}$ for vanadium substituted HPW samples could be due to the change in the coordination number of the tungsten caused by the presence of vanadium atoms and/or the temperature treatment (Table 3).

A single broad phosphorus peak was detected in the XPS spectra of the samples. The values of BE of P 2p core levels in the region 133.9–134.3 eV are typical for phosphorus in heteropoly acids [29].

A strong O 1s photopeak at 530.3 ± 0.3 eV is observed for all Mo- and W-containing samples (Tables 2 and 3, respectively) accompanied by a high binding energy asymmetry at ca. 531.0 eV (Fig. 5). The first peak is assigned to oxygen of the TiO$_2$ support. The second one is due to oxygen of M–O–M (M = Mo or W) [31], M–O–P and/or M–O–H [32] in polymolybdate and polytungstenate structures.

The BE of Ti 2p core levels at 459.0 ± 0.3 eV remains unchanged after different temperature treatments given to the samples (Tables 2 and 3), confirming that the oxidation state of titanium is constant, namely Ti^{4+} [33]. A slight shift of the BE of Ti 2p to higher values is observed at 723 K for the vanadium substituted W-containing sample (Table 3), which can be related to some interaction between supported metal oxide species and the support.

The values of BE of V 2p$_{3/2}$ core levels for titania-supported samples characterize V^{5+} ions [18]. The slight shift of the BEs to lower value (from 517.1 to 516.3 eV, Table 2) with the treatment at decreasing temperatures and the number of introduced vanadium atoms demonstrates a corresponding decrease in the oxidation state of vanadium for HPMoV$_1$/Ti sample. It should be noted that the values of BE of V 2p$_{3/2}$ for W-containing samples containing three vanadium atoms (Table 3) are lower than those for Mo-containing ones (Tables 2 and 3). This means a lower oxidation state of vanadium ions, V$^{\delta+}$ ($4 < \delta^+ < 5$).

The surface atomic Mo/Ti, W/Ti and V/Ti ratios for Mo- and W-containing samples calculated from the XPS are listed in Tables 2 and 3, respectively. Well-dispersed molybdenum- and tungsten oxide species are observed for all samples after their treatment at high temperature (723 K). This is evident from the high values of the XPS Mo/Ti and W/Ti ratios in Tables 2 and 3, respectively. For all samples, with exception of HPMoV$_3$/Ti, the XPS Mo(W)/Ti ratios increase by a factor of approximately 1.5–2 when the temperature is increased from 523 to 723 K. It means that a destruction of the large heteropoly anion clusters into smaller ones takes place upon heating and the molybedum- and tungsten oxide species are well dispersed on the titania surface. It should be noted that the XPS Mo/Ti ratios for titania-supported PMoV catalysts treated at high temperature are lower if compared to that for the vanadium-free one, HPMo/Ti (Table 2). It means that the decomposition of the mixed PMoV heteropolyanion clusters into smaller ones with preserved Keggin unit on titania surface is in a lower stage.

Table 2
Binding energies and XPS atomic ratios for Mo-containing heteropoly catalysts at different temperature treatment

Sample	Temperature (K)	Binding energies (eV)					Mo/Ti	V/Ti
		P 2p	O 1s	Mo 3d$_{5/2}$	Ti 2p	V 2p$_{3/2}$		
HPMo$_{12}$/Ti	523	134.1	530.4, 531.8	233.1	459.1	–	0.15	–
	723	134.1	530.4, 531.5	233.3	459.1	–	0.31	–
HPMo$_{11}$V$_1$/Ti	523	133.6	530.0, 531.4	232.9	458.7	516.3	0.14	0.02
	723	133.9	530.3, 531.6	233.0	459.0	516.8	0.23	0.03
HPMo$_9$V$_3$/Ti	523	134.0	530.4, 531.9	232.9	459.1	517.0	0.12	0.05
	723	133.9	530.3, 531.6	232.9	459.0	517.1	0.17	0.09

Table 3
Binding energies of core electron levels and XPS atomic ratios for W-containing heteropoly catalysts at different temperature treatment

Sample	Temperature (K)	Binding energies (eV)					W/Ti	V/Ti
		P 2p	O 1s	W $4d_{5/2}$	Ti 2p	V 2p $_{3/2}$		
HPW_{12}/Ti	523	134.3	530.5, 532.0	247.7	459.3	–	0.14	–
	723	134.3	530.6, 532.0	248.2	459.3	–	0.24	–
$HPW_{11}V_1/Ti$	523	134.2	530.4, 531.9	247.7	459.1	517.1	0.12	0.01
	723	134.7	530.6, 532.0	248.2	459.8	516.4	0.24	0.02
HPW_9V_3/Ti	523	133.7	529.8, 531.4	247.7	458.6	515.6	0.08	0.02
	723	133.9	530.2, 531.6	247.6	458.9	516.5	0.21	0.04

Well-dispersed vanadium-oxide species on the catalyst surface are observed after increasing the temperature treatment of V-containing samples, as revealed by the higher values of the XPS V/Ti ratios at 723 K (Tables 2 and 3).

3.5. Catalytic test

Total oxidation of chlorobenzene over titania-supported heteropoly compounds was performed at 473 K. The chlorobenzene conversion curves as a function of time-on-stream for Mo- and W-containing catalysts pretreated at 523 and 723 K are shown in Figs. 6 and 7, respectively. All catalysts pretreated at low temperature of 523 K show very high initial activity, which decreases with time-on-stream, more evidently during the first 3–4 h on-stream. After that time the conversion is considered constant for HPW/Ti and $HPWV_3/Ti$ catalysts. It is surprising that the $HPWV_1/Ti$ catalyst is, practically, deactivated after 7 h on stream. The decrease in the initial activity of the catalysts could be assigned to some additional surface reduction of the heteropoly compounds occurring during catalytic reaction that increases the rate of surface decomposition. The catalysts treated at 723 K show higher and relatively more stable activity (Fig. 7) compared to those of the low-temperature treated ones.

From Figs. 6 and 7 it is clear that the mixed PMoV catalysts are more active in the reaction of oxidation of Cl–benzene than the PWV catalysts. On the other hand, the results show that introduction of vanadium atoms into the heteropoly anion leads to an increase in the catalytic activity of the catalysts. Heteropoly catalysts with higher number of vanadium atoms (three) are the most active ones. The change in the catalytic activity as a function of the kind of peripheral atom and the number of introduced vanadium atoms would be explained by the change in the oxidation potential of the heteropoly compounds, that decreases in the following order: HPC-V/Mo > HPC-Mo > HPC-W [34]. It can be concluded that vanadium-containing heteropoly compounds are the strongest

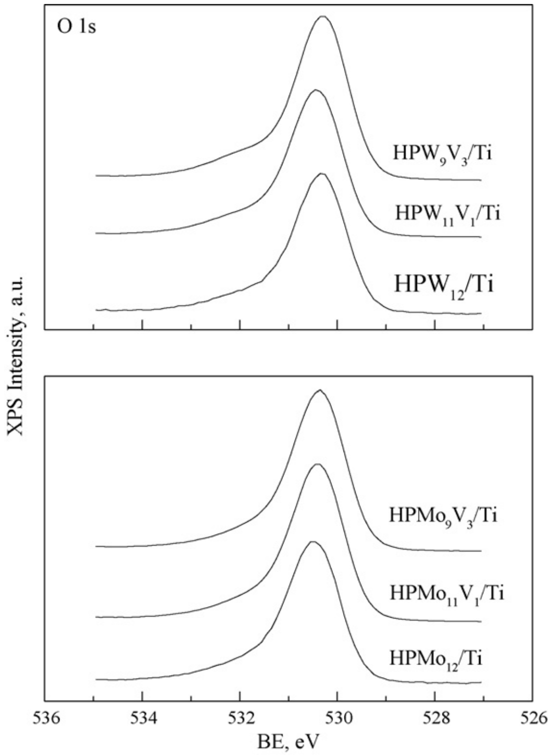

Fig. 5. XPS spectra of O 1s for titania-supported PMoV and PWV HPCs pretreated at 523 K.

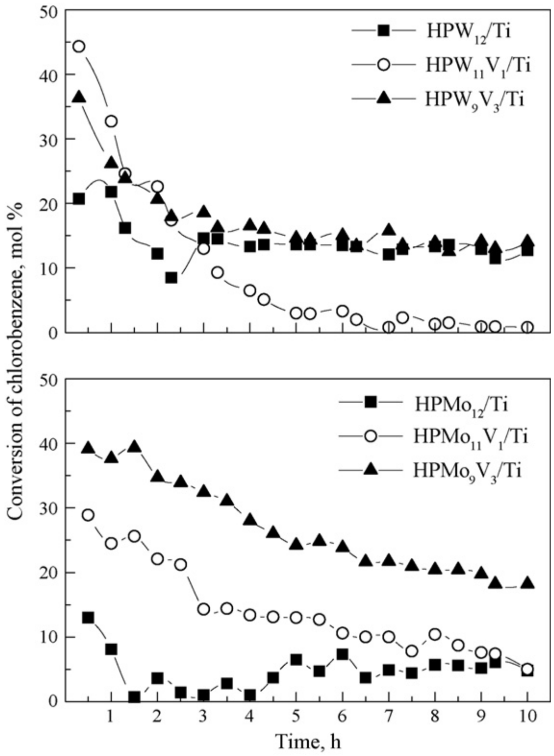

Fig. 6. Conversion of chlorobenzene over PMoV and PWV heteropoly catalysts pretreated at 523 K.

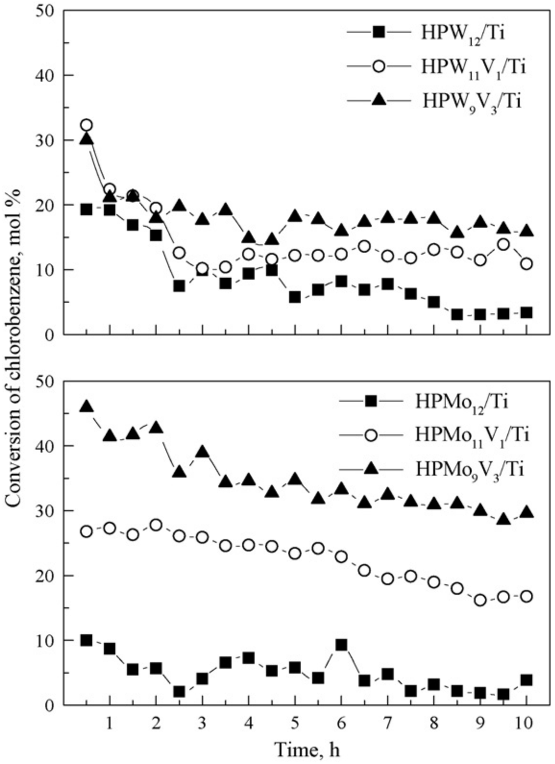

Fig. 7. Conversion of chlorobenzene over PMoV and PWV heteropoly catalysts pretreated at 723 K.

oxidants, which was related to the vanadium reducibility [34]. The catalyst system operates very efficiently, due to the redox properties of vanadium atoms when they are incorporated in the Keggin framework. According to Ressler et al. [35], the easy capability of vanadium centers to substitute Mo in the mixed MoV heteropoly acids was explained by the similar ion radii of V^{5+} (68 pm) and V^{4+} (72 pm) compared with Mo^{6+} (74 pm) in a six fold coordination. It has been shown [34] that the oxidation state of vanadium centers in molybdophosphate anion can be changed from V^{5+} to V^{4+} without a significant detectable destabilization of the Keggin unit, this change leading to an increase in the oxidation potential of HPC.

On other hand, vanadium may act as a structural promoter facilitating the formation of active Mo–O–V and W–O–V species [34,35] on the surface of the mixed PMoV and PWV catalysts, respectively. For all catalysts treated at high temperatures of 723 K, an increase in the chlorobenzene conversion is observed. It is quite reasonable that the catalytic activity depends on the surface concentration of the active sites. Probably, a maximum concentration of surface redox sites is obtained after pretreatment of the catalysts at 723 K. The higher values of the XPS atomic Mo(W)/Ti and V/Ti ratios for V containing catalysts (Tables 2 and 3) is an indication for the higher dispersion of the surface Mo–O–V and W–O–V species that is responsible for the increasing catalytic activity of the heteropoly catalysts.

The difference in the catalytic behavior of V-containing catalysts would be connected to a change of the redox properties of supported species. It has been shown that the increase in the surface concentration of redox sites for V_2O_5-MoO_3 and V_2O_5-WO_3 catalysts was attributed [35,36] to the formation of V^{4+} ions (V = O species) and the activation of the surface Mo = O and W = O species. Probably, the strong disorder of the heteropoly anions after high temperature treatment leads to a mixing of the surface vanadium and molybdenum (tungsten) ions that should be the most important factor for the increase in the surface redox sites and the activation of the Mo = O and W = O species.

It can be concluded that the mixed PMoV and PWV heteropoly compounds supported on a suitable carrier can be very promising catalyst precursors for obtaining effective catalysts for destructive oxidation of VOCs.

4. Conclusions

The difference in the surface and catalytic properties of titania-supported mixed PMoV and PWV heteropoly catalysts depends on the temperature treatment, the number of introduced vanadium atoms into the Keggin anion and the specific nature of the peripheral atom (Mo or W). An increase in the temperature of catalyst pretreatment leads to an increase in the dispersion of molybdenum-, tungsten- and vanadium-oxide species. Mixed PMoV catalysts show higher catalytic activity than that of PWV catalysts. The presence of vanadium centers appears to be responsible for the increased activity of the catalysts in the reaction of total oxidation of chlorobenzene by the activation of redox properties of the catalysts.

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