XPS study of polyaniline supported dodecatungstosilicic acid catalyst

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Abstract

The presence of hydrogenoheteropolyanions at the polyaniline surface supported $H_4SiW_{12}O_{40}$ catalyst playing most probably the role of catalytically active Brønsted acid centers in cumene cracking was confirmed by the XPS measurements. These centers are partially removed by heating at 573 K in the atmosphere of dry air but easily regenerated by the water vapor introduced into the reactor in the stream of helium carrier gas.

Keywords: Heteropolyacid; Keggin unit; Polymer; Polyaniline; Cumene cracking; XPS

1. Introduction

In the series of earlier papers of the present authors the properties of the catalytic systems containing dodecaheteropolyacids $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ (HPA) supported on conjugated polymers: polyacetylene, polypirrole and polyaniline were investigated [1–5]. In all cases electrically neutral and non-conducting polymer chains either by bonding protons or by the oxidation process acquired positive charge and became conductive. The positive charge of the polymer is neutralized by the negative charge of heteropolyanions penetrating into the bulk of the organic matrix and partially remaining also at the surface.

In the case of polyaniline supported dode-catungstosilicic acid $H_4SiW_{12}O_{40}$, conversion of ethanol was used as a catalytic test reaction [4]. Ethylene and diethylether were the products besides which only small amounts of acetaldehyde also appeared. The fact that the acid–base type catalytic activity of conjugated polymer supported heteropolyacid was quite appreciable, was interpreted by us as the indication that the heteropolyacid molecules at the catalyst surface were deprotonated only partially and were present in the form of hydrogenoanions such as e.g. $H_3SiW_{12}O_{40}^-$, $H_2SiW_{12}O_{40}^{2-}$ or $HSiW_{12}O_{40}^{3-}$. The aim of the present research was to confirm this conclusion by using XPS spectroscopy. It should be observed here that among the conjugated polymer supported heteropolyacid catalysts hitherto studied by us polyaniline is the strongest base (pK_b of aniline in water 9.4, pyrrole ~ 13.0).

The above mentioned experiments with pure and polymer supported heteropolyacids have indicated in ethanol conversion that the observed deactivation of the catalyst has to be ascribed to the formation of carbonaceous deposit, called here coke, the amount of which may be estimated from the mass balance of the substrate and the products. The deactivation can be — at least partially — removed by the regeneration in a current of air at temperatures as low as 573 K. Hence the second aim of the present work was to investigate how the postulated hydrogenoheteropolyanions behave during the coking and regeneration of our catalyst. Still stronger coking of unsupported $H_4SiW_{12}O_{40}$ than in the case of ethanol conversion was observed by us also in the case of cumene cracking carried out in a constant flow reactor [6]. This is why besides the XPS measurement on the pristine catalysts we carried out the XPS measurements also on the catalysts deactivated in the cumene cracking as well as subsequently regenerated.

2. Experimental

Samples of the catalyst were prepared by protonation of polyemeraldine base with 12-tungstosilicic acid (SiW) as described in [4]. Their composition corresponded to the formula $C_{24}H_{18}N_4 \cdot 0.06H_4SiW_{12}O_{40}$ and the physicochemical properties are described in [4].

XPS analyses of the pristine catalyst and catalyst samples after different treatments in the catalytic reactor were carried out in a VSW ESCA 100 spectrometer using Mg K_α radiation (1253.6 eV). All spectra were obtained with an analyzer pass energy of 44 eV in a fixed analyzer transmission mode. The operating pressure was below 10^{-6} Pa. The catalyst samples were mounted by pressing the powder onto a copper net. They were continuously cooled by liquid N_2 during the measurements. The necessary acquisition time to obtain N 1s, O 1s and W 4f

spectra was 2h, 15 min and 30 min, respectively.

Data acquisition and analysis were made using the EC V:7.02 software package supplied by VSW Manchester. The following routines were applied: The Shirley method for background subtraction and a standard method for deconvolution using a mixed Gaussian–Lorentzian line shape always in the same proportion, 25% Lorentzian and 75% Gaussian. The position of the partial peaks in the total envelope as well as the full width at half maximum were kept constant. An energy correction was made to account for sample charging based on the C 1s peak at 284.6 eV as the inert standard.

The following samples were taken for XPS investigation:

Sample a was pristine $H_4SiW_{12}O_{40}$–polyaniline catalyst.

Sample b before XPS investigation has been heated for 2 h in a constant flow catalytic microreactor at 333 K in the He stream saturated with water vapor. This was a standard treatment of the catalyst before the catalytic runs.

Sample c after an analogous standardization as sample b at 333 K was used as the catalyst in cumene cracking at temperature 573 K. A stream of helium saturated at room temperature with the vapors of cumene and water was introduced into the catalytic reactor and the products of catalytic reaction were analyzed using a Hewlett-Packard 5890 series II A gas chromatograph on line. The course of catalytic reaction is shown in Fig. 1. It is seen that the activity of the catalyst decreases rapidly in the initial 10–15 min but then after 60–80 min reaches an almost constant level. After 1.5 h the catalyst has been regenerated in the current of dry air at 573 K for 2 h. Reaction was then prolonged for 17 h and after the second regeneration for 2 h. It is seen that the initial activity after standardization as well as after regeneration was high but decreased fast to a relatively constant level.

In the gas chromatographic analysis three peaks of the catalytic reaction products were
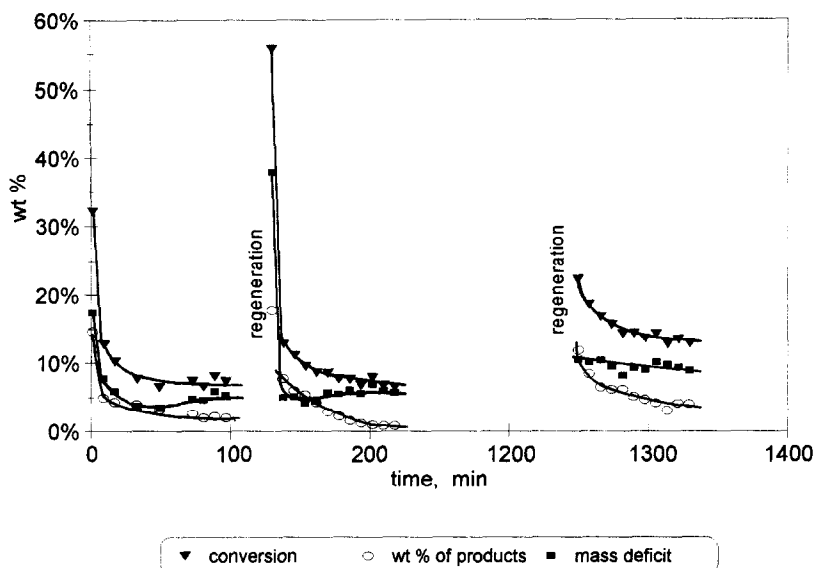
Fig. 1. Catalytic runs on $H_4SiW_{12}O_{40}$/polyaniline sample at 573 K, regeneration at 573 K in dry air. ▼ cumene conversion, ○ mass of products. ■ mass deficit.

registered. Additional mass spectrographic analysis has shown that they corresponded to propane, small amounts of benzene and iso-propenylbenzene. Moreover it has been stated that the peak of propane contained also a compound of the mass 40 corresponding to formulas $CH_2=C=CH_2$ (propadien) or $(CH_3)C\equiv CH$

(propyne), both compounds being characterized by the same mass spectra [7]. Mass spectrometric analysis did not show the presence of any other products.

The mass balance of all the products detected in the gas phase allowed to estimate a distinct mass deficit corresponding to the amount of
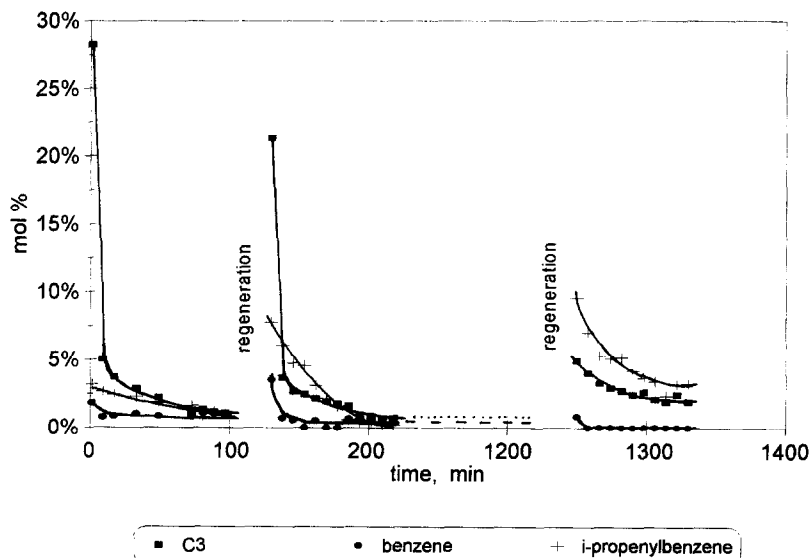

Fig. 2. Composition of gaseous products. ■ C_3 hydrocarbons, ● benzene, + i-propenylbenzene.

Table 1
Binding energies of tungsten W $4f_{7/2}$

Sample	Energy (eV)			Peak contribution (%)		
	W 1	W 2	W 3	W 1	W 2	W 3
(a) Pristine SiW/polyaniline		35.1	36.4		89	11
(b) Standardized as before catalytic test	34.3	35.2	36.2	26	34	40
(c) After few tests with cumene and few regenerations		35.1	36.3		85	15
(d) Standardized and few times regenerated in air		35.1	36.4		96	4
(e) After few tests with benzene and few regenerations		35.1	36.4		79	21

substrate and/or products remaining on the catalyst. It will be called here the coke. By integrating the curves representing the instantaneous mass deficit (Fig. 1) calculated from particular chromatographic analyses the total amount of coke forming during the particular reaction stages could be evaluated. The sum of all such coke increments gives only the upper limit of the total coke content. The real content of coke may be somewhat lower because of the fact that some oxidation of coke during the regenerations cannot be excluded. This amount of coke calculated for sample c was 28 mg in a 0.5 g sample. It was reached after a cycle of activation–deactivation periods lasting 20.5 h and corresponded to 2.9 wt% of cumene introduced into the apparatus. Fig. 2 shows the composition of gaseous products among which C_3 hydrocarbons predominate.

Sample d was prepared by exposing the pristine catalyst to several cycles comprising only standardization and regeneration treatment (without catalytic reaction) carried out as in the case of sample c.

Sample e has been treated at the same condi-

tions as sample c with the difference that instead of cumene, benzene saturated vapor was introduced into the catalyst in the helium stream. No gas products were registered but a distinct mass deficit was observed, indicating sorption of benzene by the catalyst. The amount of benzene sorbed in the course of 2 cycles was 60.8 mg in a 0.5 g sample, which corresponds to 4.8 wt% of benzene introduced.

In all cases the samples for XPS measurements after the treatment in the catalytic reactor were cooled in situ in the stream of helium and transferred into the sealed glass tubes thus rendering their contact with air as short as possible.

The samples are listed in Tables 1 and 2 where the positions of deconvoluted XPS peaks as well as the contributions (in %) of corresponding peak areas are given. Electron binding energies in various oxygen and tungsten containing species in the polyaniline samples protonated by several heteropolyacid have been determined in a previous investigation [8]. These values were also compared and appropriately discussed with the other data in available literature.

Table 2
Binding energies of oxygen

Sample	Energy (eV)				Peak contribution (%)			
	O^{2-}	OH^-	H_2O		O^{2-}	OH^-	H_2O	
(a) Pristine SiW/polyaniline	530.5	531.9	533.4		67	23	10	
(b) Standardized as before catalytic test	530.4	531.8	533.4		67	25	8	
(c) After few tests with cumene and few regenerations	530.3	531.9	533.4	535.0	43	18	20	19
(d) Standardized and few times regenerated in air	530.5	531.8	533.3		79	18	3	
(e) After few tests with benzene and few regenerations	530.2	531.9	533.3	534.8	47	23	17	13

3. Results and discussion

As already said the only products of cumene cracking on polymer supported $H_4SiW_{12}O_{40}$

catalyst were propane (as predominant one) as well as much smaller amounts of benzene and isopropenylbenzene. The presence of C_3 hydrocarbons and benzene indicates that cumene
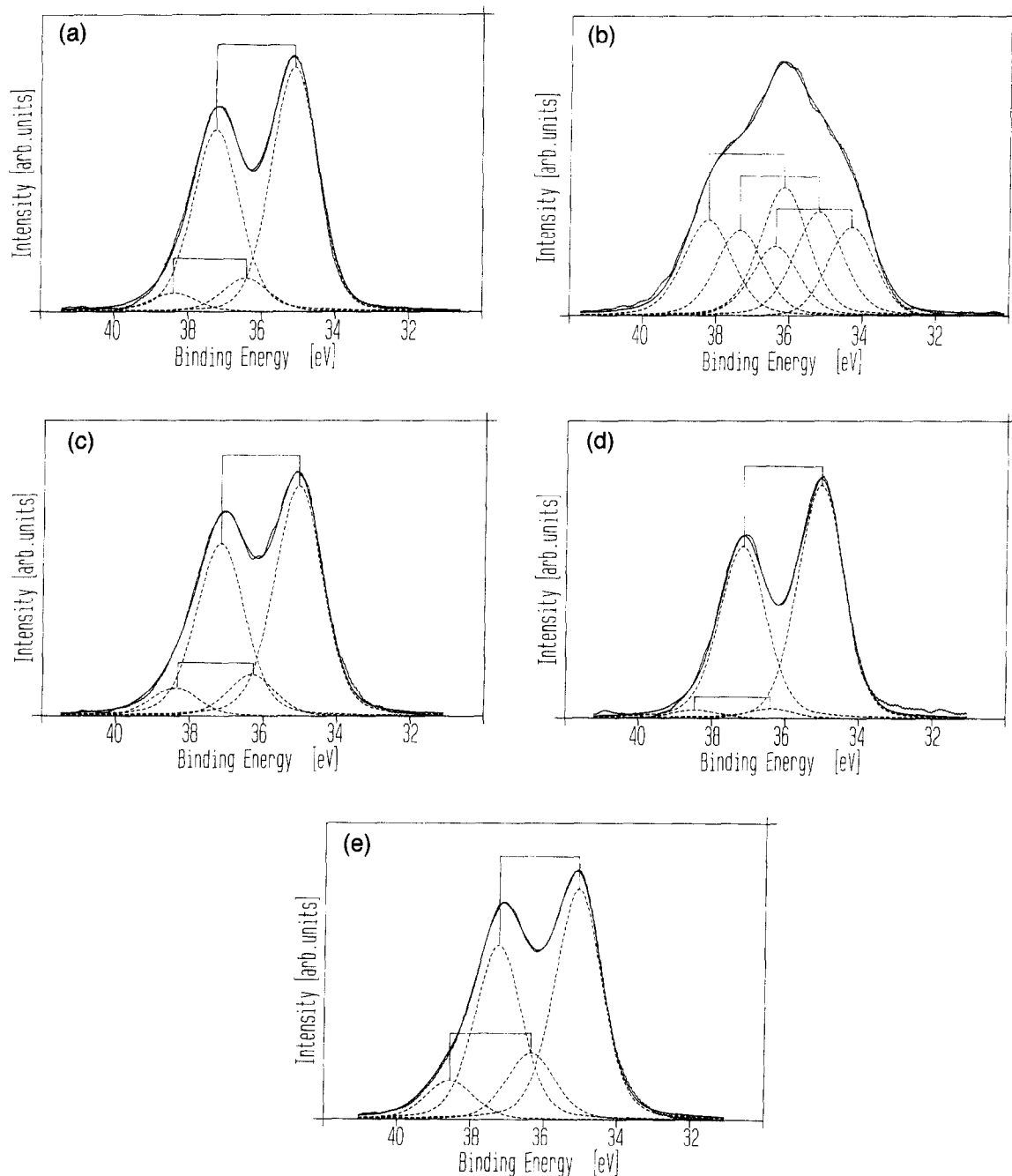

Fig. 3. W $4f_{7/2}$ spectra of polyaniline doped by $H_4SiW_{12}O_{40}$. Symbols of samples a–e the same as in Table 1. The peaks forming doublets of W(4f) are connected by a full line.

cracking into propylene and benzene was the primary catalytic reaction. However owing to the sorption of benzene by the catalyst confirmed in the separate experiments (sample e) the molar concentration of benzene in the gas phase was many times lower than that of C_3. The fact that the predominant C_3 hydrocarbon is not propylene but propane and simultaneously
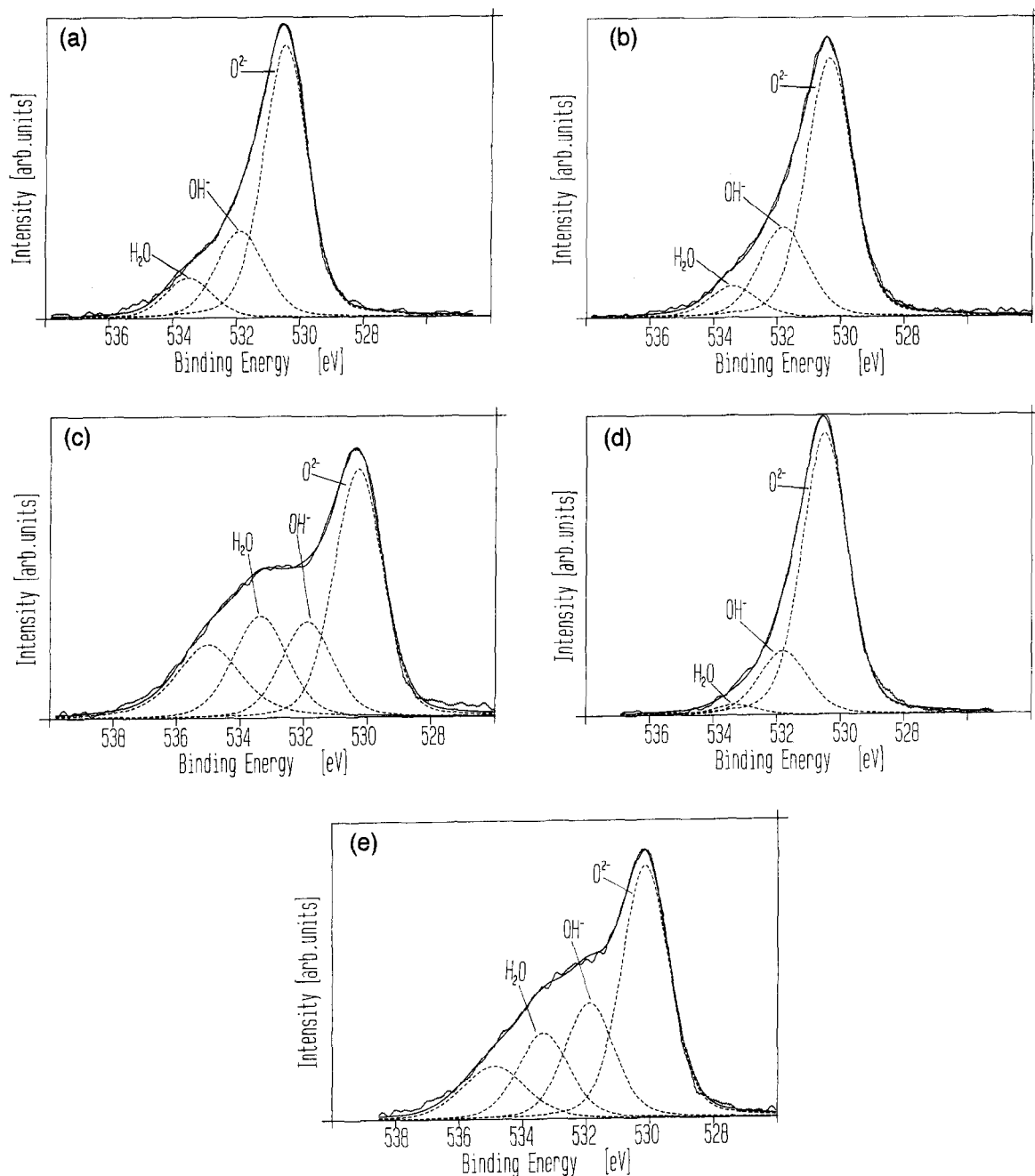

Fig. 4. O(1s) spectra of polyaniline doped by $H_4SiW_{12}O_{40}$. Symbols of the samples a–e are the same as in Table 2.

certain amounts of isopropenylbenzene and C_3H_4 hydrocarbons appear indicates that in the contact with the catalyst covered with coke complicated disproportionation processes do occur. The catalytic behavior of polyaniline supported $H_4SiW_{12}O_{40}$ is very different from that of unsupported $H_4SiW_{12}O_{40}$. In this latter case propylene and benzene were the predominant products and despite the formation of coke the deactivation of the catalyst was slower. Such differences clearly indicate that the interactions between the polymer support and heteropolyacid are appreciable. It should be here observed that in a separate series of experiments it has been confirmed that the polyaniline support (without HPA) protonated with HCl is catalytically not active although very weak sorption of cumene could be observed.

Let us now discuss the results of XPS investigations.

The W 4f spectra and the O 1s spectra of the samples are presented in Figs. 3 and 4.

The W 4f doublet consists (according to XPS standards [9]) of two peaks differing by 2.15 eV in the electron binding energies. In the case of pristine SiW/polyaniline catalyst partial peaks are asymmetric and wide (Fig. 3a). The further discussion is based on the chemical shift of W $4f_{7/2}$ only. The spectra deconvolution results in finding a second tungsten species at 36.4 eV besides the major species at 35.1 eV. The difference of 1.3 eV is too small to accept a change in the oxidation state of W atoms. Hence a partial substitution of oxygen anions by hydroxyl ones in the coordination sphere of W atoms must be assumed. This is in accordance with the expected presence of hydrogenoanion of HPA at the catalyst surface as the requirement for the presence of acid centers on the catalyst surface.

The standardization procedure resulted in quite serious changes in the W 4f spectrum: a new band appeared at 34.3 eV (Fig. 3b). The same value was found by Biloen and Pott [10] after reduction of WO_3/γ-Al_2O_3, resulting in the formation of $W_{18}O_{49}$ phase. It can be therefore supposed that during the activation procedure a partial reduction takes place, as a result of which ensembles of WO_6 octahedra similar to those present in $W_{18}O_{49}$ are formed on the catalyst surface. This might e.g. involve splitting of the oxygen atom from the Keggin unit and the rearrangement of its structure resulting in increasing the number of triply coordinated oxygen atoms. The 34.3 eV band vanishes in the spectra of catalysts treated in air as was done during the regeneration (Fig. 3d) and also in samples investigated after the catalytic test (Fig. 3c, e) (reoxidation during regeneration procedure). These facts indicate the reversibility of HPA anion partial destruction.

Another effect of catalyst regeneration in dry air is a distinct decrease of the concentration of hydroxylated W(VI) atoms (Table 1). However, as the spectra of catalyst taken after the catalytic test show, OH^- groups coordinated to W atoms are easily regenerated in the atmosphere of humid cumene vapor–helium mixture. In the catalyst examined after several consecutive catalytic tests and regenerations the ratio of 35.1 ± 0.1 and 36.3 ± 0.1 eV intensivities is very much similar to the same ratio in the case of pristine catalyst.

Table 2 and Fig. 4 show that three peaks of O 1s appear in the XPS spectra of the samples: 530.4 ± 0.2, 531.9 ± 0.1 and 533.4 ± 0.1 eV which can be ascribed to O^{2-}, OH^- and oxygen in H_2O molecules, respectively. This result is in good accordance with the results given in Table 1 indicating the presence of hydrogenoanions which evidently play the role of catalytically active Brønsted acid sites. Standardization in the stream of humid helium did not introduce appreciable changes in the intensity relations of the three peaks. However, heating in the air dramatically decreases the concentration of the adsorbed water vapor and also diminishes the concentration of OH^- groups (Fig. 4d).

In the sample investigated after the catalytic test a new O 1s peak appeared at 534.9 eV (Fig. 4c). It should be observed that the same peak appeared also in the case of our catalyst sample

which was exposed to the vapor of benzene at conditions analogous to the conditions of catalytic reaction (Fig. 4e). As was stated benzene is partially sorbed by the catalyst without giving any products to the gas phase.

As it was supposed the deactivation of the catalyst is related to the formation of coke on the catalyst surface. The O 1s spectra allow to postulate the presence of oxygen containing functionalities in the coke. The O 1s envelope must be deconvoluted into four peaks (Table 2). One of them, at 534.9 ± 0.1 eV, was observed by Yoshida et al. [11] during his study of activated carbon fibers. It was ascribed to the hydroxyl oxygen atoms in carboxyl or phenolic groups. The other possible oxygen containing functionalities are however non-recognizable by XPS method because the electron binding energy of O 1s in quinones, alcohols and aliphatic ketones are too close to that characteristic for H_2O molecules.

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