

# **Surface chemistry of silica and related sorbents**

## **ELECTRON SPIN RESONANCE STUDY ON Mo-SiO<sub>2</sub> AND Mo-TiO<sub>2</sub> WITH ADSORBED BENZENE**

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### **Abstract**

The study is devoted to ESR-investigation of the primary processes upon chemisorption of benzene molecules onto the molybdenum supported on dispersed SiO<sub>2</sub> and TiO<sub>2</sub> samples. It has been confirmed that benzene chemisorption onto the Mo<sup>6+</sup> species results in one-electron transfer in the ground state and paramagnetic species formation, namely reduced molybdenum species (Mo<sup>5+</sup> species) and radicals of benzene. Computer treatment of ESR experimental data revealed that there are several types of Mo<sup>5+</sup> species and benzene radicals, the assignment of which is proposed.

### **Introduction**

During several decades molybdenum species (Mo-species) supported on different oxide carriers by various preparation methods are extensively studied by a multitude of the spectroscopic techniques because of prominent catalytic and photocatalytic properties of such materials [1-6]. Comprehensive investigations aimed at preparation and spectroscopic characterization have been reported by many research groups [7-10]. It is well documented that many efforts have already been made to prepare the samples with Mo-species - well-defined, highly dispersed, and of a certain local structure [3, 4, 7]. However, in the most cases in the materials obtained just several kinds of Mo-species of different oxidation, coordination and dispersion states coexist even at low Mo loadings [9, 11, 13]. ESP techniques was widely used and proved to be very informative for detailed characterization of reduced Mo-species, in particular, Mo<sup>5+</sup>-complexes [7-9, 12, 13].

This investigation have been stimulated by our previously performed studies on electron-transfer and charge-transfer complexes formation upon chemisorption of arene molecules – naphthalene (Nph), anthracene (An) and perylene (Py) onto silica or zeolites [14, 15]. It has been shown with by ESR and photoluminescence techniques that oxidation of Nph and An with cation radicals generation requested UV-irradiation. Only Py, which has the lowest ionization potential, is oxidized to cation radicals directly upon chemisorption. However, mere exposure of these molecules onto fully oxidized Mo<sup>6+</sup>-SiO<sub>2</sub> surfaces at room temperature resulted immediately in aromatic radicals and reduced Mo<sup>5+</sup>-species formation. Thus, one-electron redox process on the Mo-SiO<sub>2</sub> surfaces was confirmed and monitored directly by ESR [16].

The present paper is an attempt to study in more details the nature of radicals generated upon interaction of electron-donating molecules with supported Mo-species. Interaction of benzene (Bz) molecules with Mo-species supported on SiO<sub>2</sub> and TiO<sub>2</sub> was studied by ESR techniques complemented with computer treatment.

## Experimental

*Sample preparation and treatment.* Molybdenum-containing samples were prepared using two methods:

- i) conventional impregnation technique using an aqueous solution of ammonium heptamolybdate;
- ii) grafting of MoCl<sub>5</sub> (in CCl<sub>4</sub> solution) onto dehydrated at 873K supports under dry nitrogen conditions (as in [9]). For sample preparation highly dispersed fumed silica and titanium oxide have been used (with specific surface area 200 and 120 m<sup>2</sup>/g respectively). As-prepared impregnated samples were dried at 393K. Grafted samples were twice washed with CCl<sub>4</sub>, then hydrolyzed in the water vapor for 8 hours and dried in N<sub>2</sub> at 393K. Hydrolyzed samples had blue color.

All the samples were subsequently oxidized in O<sub>2</sub> flow for 6 hours at 673K. After this treatment both type of samples became almost white, evidencing that the most of Mo atoms were oxidized to Mo<sup>6+</sup>. The Mo-loading was in the range of 1-5 wt. %. As within this Mo concentration range the experimental results were basically the same, in the paper the samples will be regarded with 3.0 wt. % for impregnated and 3.6 wt. % for grafted specimens.

Hot oxidized samples were transferred for thermoevacuation and interaction with benzene to vacuum-spectral cell. This cell had attached ESR tubes and ampoule with benzene (Bz) previously deoxygenated by freeze-pump-thaw technique. After thermoevacuation (for 3 hours at 673K) one part of sample was transferred to ESR tube that was then sealed under vacuum. The sample remaining in the cell, after cooling to room temperature, was exposed for several minutes to Bz vapors (the excess of Bz vapor being then evacuated at room temperature) and also transferred to ESR tube. Thus, ESR spectra were taken of the samples kept in the sealed under vacuum ESR tubes.

*ESR measurement.* Spectra were recorded at 300 and 77K with SEX-2543 spectrometer (Radiopan). Experimental g-values were determined by direct measurements of the frequency and magnetic field. For computer simulation of ESR spectra the programs WINEPR and SIMFONIA (Bruker) were used.

## Results and discussion

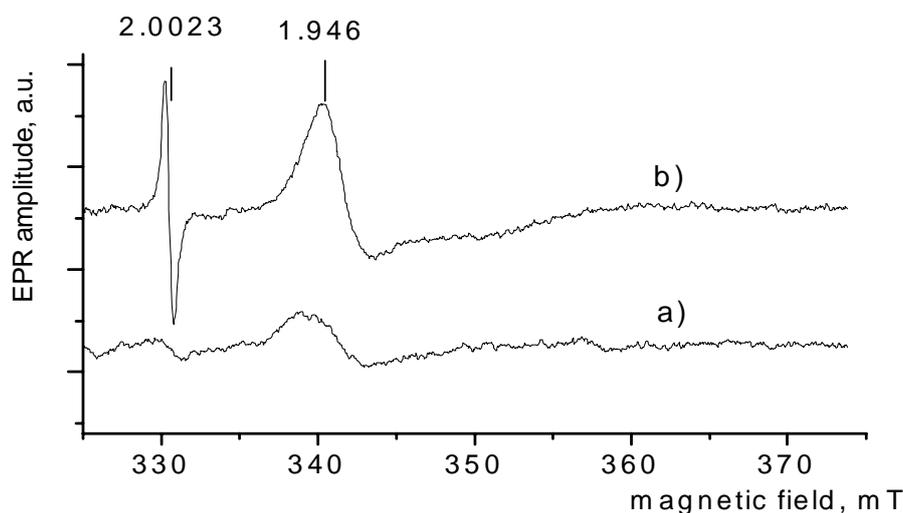
Figs. 1 and 2 represent respectively the typical experimental spectra of Mo-SiO<sub>2</sub> and Mo-TiO<sub>2</sub> samples. In the both cases the *a*-signals relate to thermoevacuated and *b*-signals - to the samples after Bz vapor sorption. It is important to note that in the blank experiment pure supports SiO<sub>2</sub> and TiO<sub>2</sub> have not exhibited ESR signals neither for thermoevacuated samples, nor for those ones after exposure with Bz. Thus, it is clear that ESR signals presented in the Figs. 1 and 2 should be related to Mo-species (spectra *a*) and their interaction with Bz (spectra *b*). Also it should be indicated that the receiver gain for recording of spectra in Fig. 1 is 10 times greater, than that in Fig. 2.

The temperature independence of line shape and the magnitude of g-values of 1a and 2a signals that arose upon thermoevacuation at 673K strongly pointed to the presence of reduced Mo<sup>5+</sup>-species. The local structure of Mo<sup>5+</sup>-species will be discussed in more details later, but now worthwhile pay an attention to different reducibility of Mo-species, supported on SiO<sub>2</sub> and

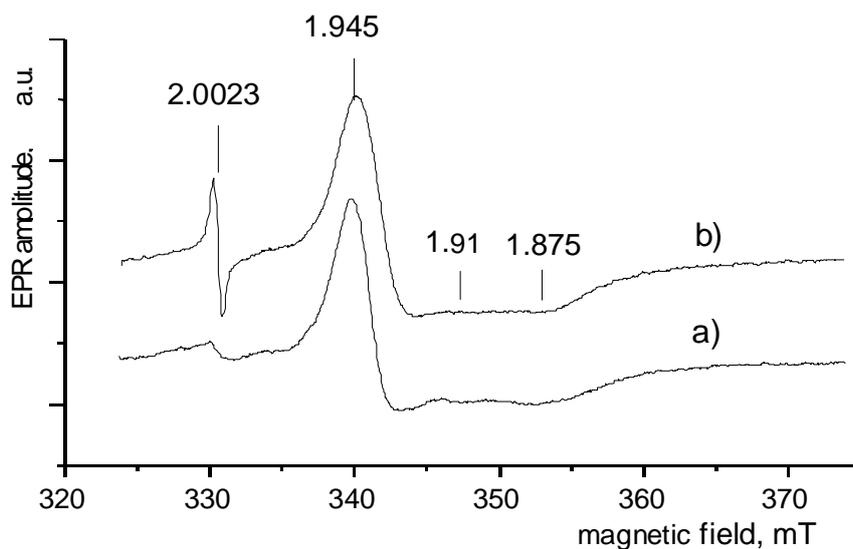
TiO<sub>2</sub>. Intensity of Mo<sup>5+</sup>-signal (see Fig. 2, *a*) is almost one order larger than signal (Fig. 1, *a*) at practically the same Mo-loading for Mo-SiO<sub>2</sub> and Mo-TiO<sub>2</sub> samples.

Exposure of thermoevacuated samples to Bz vapor resulted in the following:

- i) the appearance of new narrow singlet signal in the free-electron region that was similar for both samples (spectra 1b and 2b);
- ii) the remarkable increasing of Mo<sup>5+</sup> signal for Mo-SiO<sub>2</sub> samples.



**Fig. 1.** Experimental ESR spectra of Mo-SiO<sub>2</sub> samples registered at 77K:  
*a* - thermoevacuated sample; *b* - after exposure in benzene vapor.  
 The receiver gain for registration signals is  $0.5 \times 10^3$ .

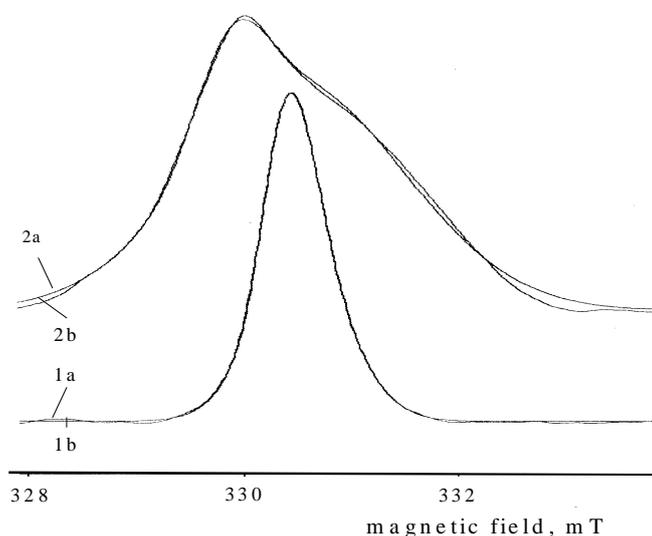


**Fig. 2.** Experimental ESR spectra of Mo-TiO<sub>2</sub> samples registered at 77K:  
*a* - thermoevacuated sample; *b* - after exposure in benzene vapor.  
 The receiver gain for registration signals is  $5 \times 10^3$ .

The appearance of new singlet ESR signals in the free-electron region is a quite common feature, observed in the numerous studies at interaction of organic electron-donating molecules with the solids, which possessed electron-accepting properties. It is usually assigned to cation radicals [17].

Previously we also observed very similar intensive narrow singlet signals with  $g=2.0025$  and  $g=2.0029$ , developed at interaction of Mo-SiO<sub>2</sub> samples with aromatic molecules - naphthalene and anthracene, respectively [14]. It is worth to note that the intensities of these singlets were significantly larger as compared with intensities developed upon Bz interaction, that is in good agreement with the ionization potentials of these molecules. Thus, it seems quite reasonable to assume one-electron oxidation of adsorbed Bz molecules leading to Bz radicals generation.

Fig. 3 demonstrates the line shape simulation of the experimental signals in free-electron region for Mo-SiO<sub>2</sub> sample, recorded at 300K (curves 1 and 1a) and at 77K (curves 2 and 2a).



**Fig. 3.** Integrated form of ESR spectra for Mo-SiO<sub>2</sub> sample in the free-electron region: 1 – registered at 300K; 2 – at 77K (1a and 2a are experimental spectra, 1b and 2b are approximations by Gauss singlets).

The asymmetric single signal recorded at 300K may be satisfactorily approximated by two Gaussian curves with such widths as 0.59 and 1.18 mT (Fig. 3, curves 1 and 1a). The line shape of the signal recorded at 77K is more complicated, *i.e.* experimental signal is approximated by three Gaussian curves with the following widths – 1.04, 1.42 and 3.1 mT (Fig. 3, curves 2 and 2a). It is important to note that each of them is broader than the corresponding curves recorded at 300K. Results concerning Mo-TiO<sub>2</sub> sample are rather similar as it is seen from data of Table. Line shape analysis of Bz-radicals experimental signal revealed the superposition of individual Gauss-shape singlets with slight difference of  $g$ -values but noticeable difference of width ( $\Delta H$ ). Results of line shape simulation of Bz-radicals signal are expressed as appropriate parameters of centers 1, 2, and 3 in the Table.

Thus, two types of Bz radicals (for Mo-TiO<sub>2</sub>) and three types of them (for Mo-SiO<sub>2</sub>) should be considered at benzene interaction, but further specification can not be done because resolved spectra with hyperfine structures are lacking. But it deserves to explain the possible

reasons of it. Available numerous data, discussed in the comprehensive review[17], give evidence that:

- i) singlet signals with  $g \sim 2.00$ , as a rule, were observed when benzene molecule (or other electron donors) were adsorbed from the vapor phase;*
- ii) resolved spectra with hyperfine structure of Bz or other aromatic radicals succeeded to detect after contact of diluted solution with microporous materials;*
- iii) the primary Bz radical  $C_6H_6^+$  very quickly undergoes the subsequent transformations and rearrangements that lead to biphenyl radical, then to more stable polyphenyl species, that displays the singlet signals.*

We can also speculate about other possible reasons such as:

- iv) anisotropic broadening;*

Preliminary we showed that the broadening (more than 0.4 mT) of individual components of 7-component primary cation Bz-radical spectrum causes unresolved singlet lineshape.

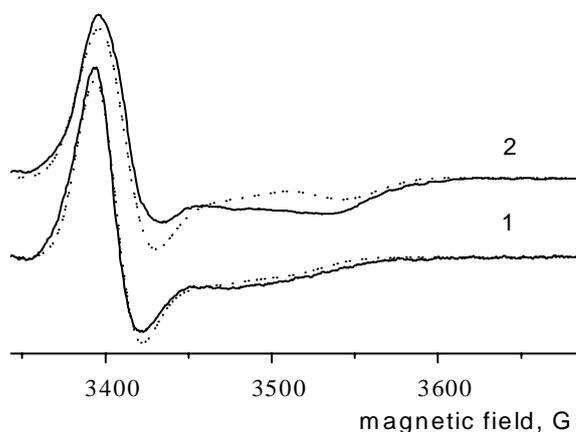
- v) restriction of motion due to adsorption on surface and interaction with neutral Bz molecules.*

Gaussian line shapes and the absence of hyperfine (HF) pattern suggest that the anisotropic HF interactions with the surface protons of  $SiO_2$  and  $TiO_2$  and magnetic dipole-dipole interaction between the primary Bz-radicals occur.

The narrowing of the line width of the signal at 300K in comparison with that at 77K (Fig. 3 and Table) confirms our suggestion about anisotropic HF interaction; as upon increasing the temperature the interaction of Bz-radical with the surface becomes more weak and anisotropic part of HF interaction is averaged, so ESR line is narrowed. Broadening of the signal of the type 2 Bz-center comparing to the type 1 can be explained also by dipole-dipole interaction between Bz-radicals of the type 2.

Now anisotropic signal of  $Mo^{5+}$ -species are to be considered. It is beyond doubt that the oxidation state of molybdenum is  $Mo^{5+}$ , so we will focus attention to local structure of  $Mo^{5+}$ -species. For discrimination of two most common site symmetry of  $Mo^{5+}$ -species distorted octahedral ( $O_h$ ) and tetrahedral ( $T_d$ ) should be regarded the following features of the ESR signal:

- i) the temperature dependence of the line shape;
- ii) relative magnitudes of  $g_{\perp}$ ,  $g_{\parallel}$  and  $\Delta g$ -degree of g-value anisotropy.



**Fig. 4.** Experimental and computer simulated spectra of  $Mo^{5+}$  species:  
1 – Mo- $SiO_2$ , 2 – Mo- $TiO_2$  samples.

Solid line – experimental spectra; dotted line - simulated ones.

**Table.** Parameters of paramagnetic centres of Mo-SiO<sub>2</sub> and Mo-TiO<sub>2</sub> samples.

Centre type	Sample	Temperature of measurement				Relative concentration *	
		300K		77K		300K	77K
		g-value	$\Delta H(\text{mT})$	g-value	$\Delta H(\text{mT})$		
1	Mo/SiO <sub>2</sub>	2.0023	0.59	2.0023	1.04	2.0	2.0
	Mo/TiO <sub>2</sub>	2.0023	0.76	2.0022	0.90		
2	Mo/SiO <sub>2</sub>	2.0019	1.18	2.0030	1.42	2.5	2.5
	Mo/TiO <sub>2</sub>	2.0003	1.74	1.9883	2.19		
3	Mo/SiO <sub>2</sub>	-	-	2.0021	3.1		3.0
4	Mo/SiO <sub>2</sub>	-	-	$g_{\perp}$ 1.946	2.5	95	250
				$g_{\parallel}$ 1.885	4.0		
5	Mo/SiO <sub>2</sub>	-	-	$g_{\perp}$ 1.946	2.5	95	250
				$g_{\parallel}$ 1.905	4.5		
6		-	-	1.95	15		
7	Mo/TiO <sub>2</sub>	-	-	$g_{\perp}$ 1.944	3.0	470	1600
				$g_{\parallel}$ 1.867	4.0		
8	Mo/TiO <sub>2</sub>	-	-	$g_{\perp}$ 1.944	3.0	470	1600
				$g_{\parallel}$ 1.900	4.0		
6		-	-	1.95	15		

- For correct comparison of relative concentrations for Mo<sup>5+</sup> species measured at 300 and 77K relative concentrations for Mo<sup>5+</sup> species measured at 300 K should be multiplied by 300/77 factor.

Registration of the Mo<sup>5+</sup> signal at 300K with the same line shape as at 77K clearly points on distorted O<sub>h</sub> coordination in our case. Besides, the intensities of Mo<sup>5+</sup> species signals recorded at 300 and 77K obeyed the Curie law. The relative concentration of Mo<sup>5+</sup> species (measured by double integration of spectra) revealed good coincidence between concentration of Mo<sup>5+</sup> species at 300 and 77K (Table). This is an important fact that confirms the absence of Mo<sup>5+</sup> species non-observable at room temperature but detectable at 77K. It is well known that just tetrahedrally coordinated Mo<sup>5+</sup> complexes can be detected only at 77K or lower because of fast spin-lattice relaxation [13]. The absence of T<sub>d</sub> Mo<sup>5+</sup> species has been shown for both Mo-SiO<sub>2</sub> and Mo-TiO<sub>2</sub> as for impregnated and grafted samples as well.

In order to obtain the additional information about the site symmetry of Mo<sup>5+</sup> species a computer simulation of the line shape was performed. The results are demonstrated in the Fig. 4 and Table. In the Fig. 4 the experimental spectra are compared Mo<sup>5+</sup> species with adsorbed Bz on SiO<sub>2</sub> (spectrum 1) and on TiO<sub>2</sub> (spectrum 2) with the simulated ones.

For Mo-SiO<sub>2</sub> sample, a good fitting was achieved by superposition of two signals with the following parameters: 1A  $g_{\perp} = 1.946$ ;  $g_{\parallel} = 1.885$ ; 1B  $g_{\perp} = 1.946$ ;  $g_{\parallel} = 1.905$ . Centers 1A and 1B are denoted in the Table as centers 4 and 5. The contribution of 1B signal is three times larger than that for 1A.

Similarly, for Mo-TiO<sub>2</sub> sample, to fit satisfactorily the experimental spectrum, two signals are also requested with such parameters: 2A  $g_{\perp} = 1.944$ ;  $g_{\parallel} = 1.867$ ; 2B  $g_{\perp} = 1.944$ ;  $g_{\parallel} = 1.900$ ; centers 2A and 2B are denoted in the Table as center 7 and 8. In this case the contributions of 2A and 2B signals into simulated spectrum are equal. It should be noted that the fitting for Mo-SiO<sub>2</sub> is better than that for Mo-TiO<sub>2</sub> sample, in particular, in the  $g_{\parallel}$  range. It is probable, that on TiO<sub>2</sub> there are more than two types of Mo<sup>5+</sup> species with the same  $g_{\perp}$  but with slightly different  $g_{\parallel}$ .

The parameters obtained by computer simulation permit to discuss in more details the local structures of Mo<sup>5+</sup> species, taking into account relative magnitude of  $g_{\perp}$  and  $g_{\parallel}$  and degree of  $\Delta g$  anisotropy.

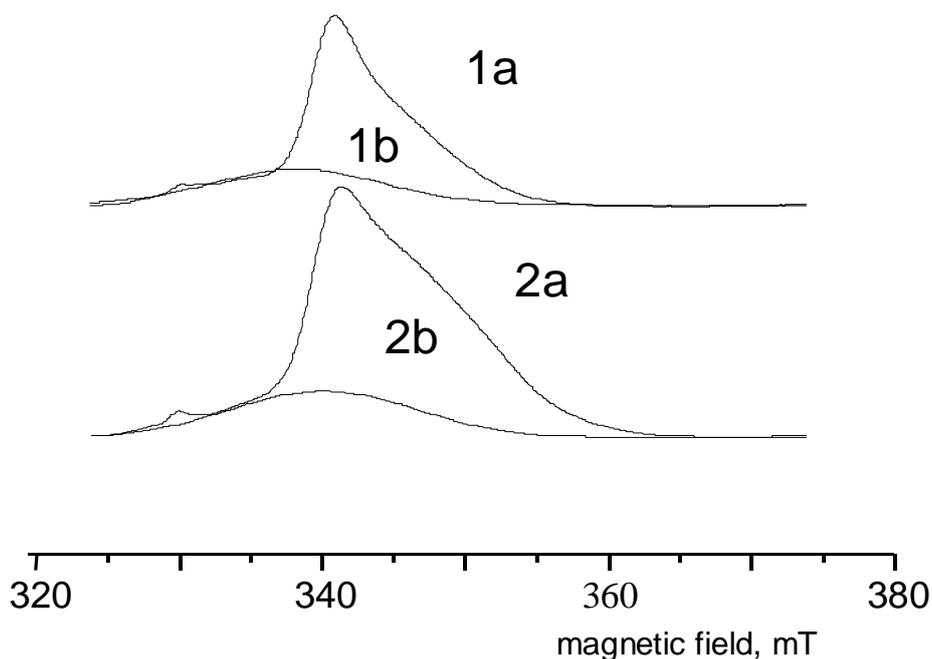
All four types of revealed Mo<sup>5+</sup> centers are characterized by  $g_{\perp} > g_{\parallel}$ , that gives clear evidence on the presence of octahedral distorted (compressed) Mo<sup>5+</sup> oxo-complexes with Mo=O double bond [18]. The elongated octahedral complexes exhibit reversal relation  $g_{\perp} < g_{\parallel}$  [13]. Distorted tetrahedral Mo<sup>5+</sup> complexes are characterized by essentially different g-values and significantly greater  $\Delta g$ . Besides it has been shown that tetrahedral Mo<sup>5+</sup> species are generated only by low temperature (77K) photoreduction and are irreversibly transformed into octahedral at room temperature [8].

Revealed two types of octahedral Mo<sup>5+</sup> species, as it seen in the Table, display different degree of  $\Delta g$  anisotropy; in accordance with [8] it reflects the different degree of symmetry distortion. *Tentatively we presume, that it may be connected with two different routes of reducing of supported Mo: the former is achieved during thermo-evacuation and is caused by O<sup>2-</sup> extraction, while the second - by electron donating from Bz molecule. In the first case more distorted penta-coordinated Mo<sup>5+</sup> species will be formed (centers 4 and 7), while the electron donating will result in less distorted six-coordinated Mo<sup>5+</sup> species generation (centers 5 and 8).*

Besides above-described types of Mo<sup>5+</sup> species, it was revealed also the presence of additional type (on both Mo-SiO<sub>2</sub> and Mo-TiO<sub>2</sub> samples). Computer simulation of experimental spectra 1b (Fig. 1) and 2b (Fig. 2) using the parameter for centers 1-3; 4-5 and 7-8 in the Table revealed the presence of additional center 6 with isotropic g-value  $g = 1.95$  and very large linewidth ( $\Delta H = 15$  mT). Fig. 5 demonstrates the presence of Mo<sup>5+</sup> centers of type 6 (1b curve - for Mo-SiO<sub>2</sub>; 2b curve - for Mo-TiO<sub>2</sub>). The contribution of type 6 center to total Mo<sup>5+</sup> spectrum is 1/5 for Mo-SiO<sub>2</sub> and 1/3 for Mo-TiO<sub>2</sub>. Obtained g-value of this center is in a good agreement for polymolybdate clusters like molybdenum "blues" or heteropolyanions, reported in the literature [19-20]. But a certain controversy should be noted concerning the line width and its temperature dependence. At present time we have no sufficient data to discuss this question.

An analysis of data concerning the total concentration of Bz radicals (centres 1-3) and Mo<sup>5+</sup>-species (centres 4-6) for Mo-SiO<sub>2</sub> sample revealed an important fact. It appeared, that the concentration of Bz radicals is more than 40 times less comparing to the total Mo<sup>5+</sup> species concentration. For this sample Mo<sup>5+</sup>-species are formed mainly during the redox process that can be schematically written as





**Fig. 5.** Integrated form of experimental spectra: 1 - Mo-SiO<sub>2</sub>, 2 - Mo-TiO<sub>2</sub> samples. Curve 1a is integrated form of experimental spectrum 1b (from Fig. 1); curve 2a is integrated form of experimental spectrum 2b (from Fig. 2); curves 1b and 2b are simulated ones for Mo<sup>5+</sup> species (6 type centers in the Table).

This oversimplified schematic representation (1) predicts that the concentration of Bz-radicals and Mo<sup>5+</sup>-species should be equal. So, observed discrepancy in these concentrations indicates that the significant part of Bz radicals is ESR-silent. We consider this fact as an independent confirmation of complicated secondary reactions of primary Bz-radicals already discussed in this paper.

## Conclusions

Direct experimental ESR evidence was obtained that the benzene chemisorption on the surface species of supported molybdenum results in one-electron redox processes and paramagnetic centres formation - reduced molybdenum (Mo<sup>5+</sup>-species) and benzene radicals (Bz-radicals). Computer treatment of ESR experimental data revealed the superposition of several types of Mo<sup>5+</sup>-species and Bz-radicals. There are three types of Bz-radicals on Mo-SiO<sub>2</sub> and two types on Mo-TiO<sub>2</sub> samples. All Bz-radicals showed singlet with Gauss line shape signals with slight difference in g-values and noticeable one in linewidths. Such features of Bz-radicals spectra are explained as a result of secondary transformations and rearrangements of the primary Bz-cation radicals that led to polyphenyl radical formation. Besides, the anisotropic hyperfine coupling of primary Bz-radicals and their dipole-dipole interactions are also considered to be responsible for unresolved singlet lineshape.

There are three types of Mo<sup>5+</sup>-species on both Mo-SiO<sub>2</sub> and Mo-TiO<sub>2</sub> samples. Two of Mo<sup>5+</sup>-species displayed the features, typical for localized Mo<sup>5+</sup> state with distorted octahedral coordination. The analysis of g-value magnitudes and degree of Δg anisotropy give evidence

for penta-coordinated and six-coordinated distorted octahedral  $\text{Mo}^{5+}$ -species. The assumption is advanced that different degree of octahedral  $\text{Mo}^{5+}$ -species distortion reflects two different routes of reduced  $\text{Mo}^{5+}$ -species formation: extraction of  $\text{O}^{2-}$  at thermoevacuation and electron donating at benzene interaction. Third type of  $\text{Mo}^{5+}$  species exhibited the characteristics of  $\text{Mo}^{5+}$  clusters.

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