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EPR Study of S_2^- Species on the Surface of MoO_3/SiO_2 and $MoO_3/\gamma\text{-}Al_2O_2$ Catalysts

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The nature of paramagnetic species, which are responsible for the EPR signal with $g_1 = 2.048$, $g_2 = 2.029$, and $g_3 = 1.998$ observed after the treatment of MoO_3/SiO_2 and $MoO_3/\gamma\text{-}Al_2O_3$ catalysts in H_2S at 300°C, has been investigated using ^{33}S and ^{95}Mo isotopes. The hyperfine splittings $A_1 = 14$ Oe, $A_2 < 8$ Oe, and $A_3 = 43$ Oe from two equivalent sulfur nuclei and the super hyperfine splittings $a_1 = 3.3$ Oe, $a_2 = 2.2$ Oe, and $a_3 = 2.0$ Oe from one molybdenum nucleus is shown to be observed. The experimental data and quantum chemical calculations by CNDO/SP method allows us to conclude that the S_2^- anion-radicals adsorbed in the first coordination sphere of Mo^{6+} ions are formed on the surface of catalysts after their treatment in H_2S.

INTRODUCTION

Investigations of processes which take place during an interaction of sulfur containing molecules with oxide catalysts are of interest for the theory and practice of the heterogeneous catalysis. In recent years it was shown by EPR method that paramagnetic species can be observed after the exposure of some catalysts to the sulfur containing molecules (*1–4*). For the undoubted identification of these species the samples enriched with the ^{33}S isotope were used. In such a way the S_3^- anion-radicals were shown to appear upon the interaction of elemental sulfur with magnesium oxide (*1*). Biradicals of sulfur were also found in zeolites by using the same isotope of sulfur (*2*).

On the contrary, the interpretation of the EPR spectra obtained with the natural abundance of isotopes is not so apparent. Nevertheless, the EPR signal with the g-values of $g_1 = 2.048$, $g_2 = 2.029$, and $g_3 = 1.998$ which was observed for the supported MoO_3/SiO_2 catalysts after an interaction with H_2S was attributed to the S_3^- anion-radicals (*3*). Another signal which appeared after a high temperature treatment of the $MoO_3/\gamma\text{-}Al_2O_3$ catalysts with the mixture of H_2S and H_2 was tentatively attributed either to the chain radicals of sulfur or to the S_3^- anion-radicals (*4*). However, because of the lack of the hyperfine splittings in the EPR spectra (*3, 4*) the conclusions about the nature of the observed species, which were based only on the g-values, need better evidence. For this purpose in this work the study of the nature of the paramagnetic species, which are formed on the surface of the MoO_3/SiO_2 and $MoO_3/\gamma\text{-}Al_2O_3$ catalysts after their heating in H_2S or in a mixture of H_2S and H_2, was carried out by using the ^{33}S ($I = \frac{3}{2}$) and ^{95}Mo ($I = 5/2$) isotopes.

EXPERIMENTAL METHODS

The MoO_3/SiO_2 and $MoO_3/\gamma\text{-}Al_2O_3$ (2 wt% of molybdenum) were prepared by

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impregnation of silica gel (S = 300 m^2 g^{-1}) and γ-alumina (S = 340 m^2 g^{-1}) with aqueous solution of $(NH_4)_2Mo_2O_7$. The labeled samples containing 96 at.% of ^{95}Mo were prepared by impregnation of the same supports with solution of $^{95}MoO_3$ in NH_4OH. Then the samples were dried at 60–70°C and heated at 500°C for 2 hr in air. Before a treatment of the samples in H_2S or in the mixture of H_2S and H_2 they were heated in oxygen (200 Torr) for 30 min at 500°C and evacuated (10^{-5} Torr) for 1 hr at the same temperature.

EPR spectra were recorded mainly at liquid nitrogen temperature in *X*- and *K*-bands. *G*-values were determined to an accuracy of 0.001 with respect to a DPPH sample with $g = 2.0036$.

RESULTS

H_2S Labeled by ^{33}S Isotope

a. Molybdenum–silica gel catalysts. Earlier (*3*) it was shown that the intensive EPR signal with $g_1 = 2.0048$, $g_2 = 2.029$ and $g_3 = 1.998$ was observed for the MoO_3/SiO_2 catalysts after their treatment in H_2S (10–50 Torr) at 200–300°C for several minutes. It should be mentioned that after the treatment at more moderate temperature the signals attributed to Mo^{5+} ions with sulfur ions as ligands had been also seen simultaneously with the above signals (*3*) but we shall not consider them in the present paper.

Adsorption of the labeled H_2S (50 and 97 at.% of ^{33}S) at the same conditions gives rise to the spectra which are shown in Figs. 1 and 2. It is obvious from Figs. 1a and 2 that at the g-factor of 1.998 there is a hyperfine splitting caused by more than one nucleus of sulfur. At the same time it is clear from Fig. 1b that the paramagnetic species contain only two magnetic equivalent sulfur atoms. The hyperfine splitting for g-value of 1.998 is of 43 ± 1 Oe. The estimation from the widths of the lines gives the values of the hyperfine coupling constants less than 8 Oe for g-factor of 2.028 and not greater than 15 Oe for $g = 2.048$.

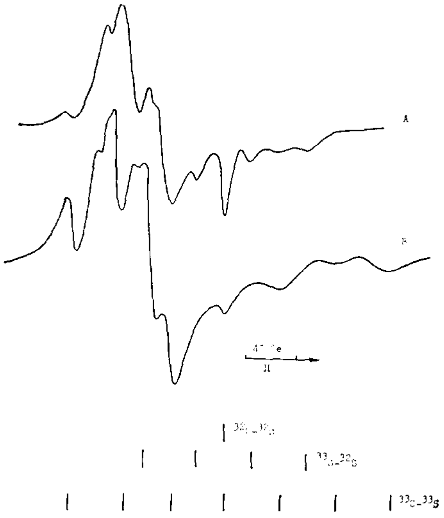


FIG. 1. *X*-Band ESR spectrum of MoO_3/SiO_2 catalyst after heating in H_2S at 300°C: (A) 50% ^{33}S; (B) 97% ^{33}S.

b. Molybdenum alumina catalysts. The treatment of the $MoO_3/\gamma\text{-}Al_2O_3$ catalysts in H_2S (10–50 Torr) at 300°C for several hours yields the spectrum with the same g-values and hyperfine coupling constant associated with 1.998 g-factor as those for the MoO_3/SiO_2 samples, Fig. 3. There is also a signal from Mo^{5+} ions

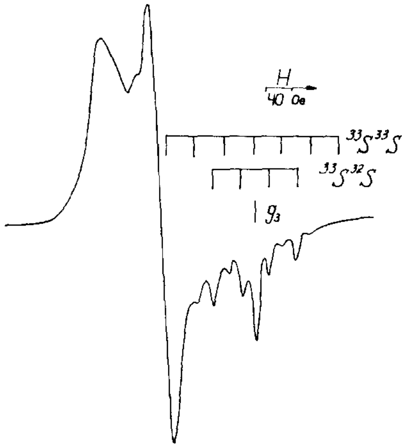


FIG. 2. *K*-Band ESR spectrum of MoO_3/SiO_2 catalyst after heating in H_2S at 300°C (50% ^{33}S).

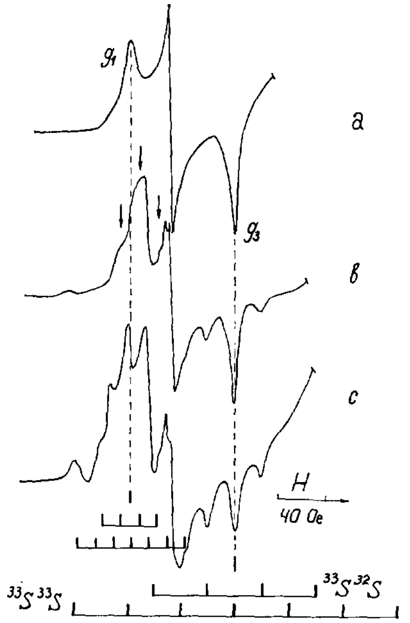


FIG. 3. X-Band ESR spectra of MoO_3/Al_2O_3 catalyst after heating in H_2S at 300°C: (a) Nonlabeled H_2S; (b) 25% ^{33}S; (c) 50% ^{33}S.

after the treatment which is not discussed in this paper.

Contrary to the signal for the MoO_3/SiO_2 catalysts in this case the resolution is better and it allows the hyperfine splitting constant (14 ± 1 Oe) for the g-factor of 2.048 to be determined as it is shown in Fig. 3 for the 50% abundance of ^{33}S. In order to obtain another evidence for the magnitude of 14 Oe we measured also the EPR spectrum of the species containing 25 at.% of ^{33}S. For this abundance the species with two sulfur atoms must contain 56.25% of species without labeled sulfur, 37.5% of species with the only labeled atom and 6.25% with two labeled atoms. Hence the splittings mainly from one nucleus of sulfur can be observed in the spectrum. As shown in Fig. 3b, the components of the hyperfine structure indeed appear on the positions (they are shown by arrows) where more intensive lines have to be expected, i.e., the components which are nearest to the g-factor of 2.048 and the distance between them is of 14 Oe.

Molybdenum Labeled by ^{95}Mo

The heating of $^{95}MoO_3/SiO_2$ and $^{95}MoO_3/\gamma\text{-}Al_2O_3$ catalysts with the nonlabeled H_2S at the same conditions as those above results in the spectra which show the hyperfine splittings from one nucleus of molybdenum with $a_1 = 3.3$ Oe, $a_2 = 2.2$ Oe, and $a_3 = 2.0$ Oe, Fig. 4.

Treatment in the H_2S–H_2 Mixture

Lojkono *et al.* (*4*) have reported that the EPR signal with $g_1 = 2.053$, $g_2 = 2.030$, and $g_3 = 2.000$ is observed after adsorption of oxygen on $MoO_3/\gamma\text{-}Al_2O_3$ samples which have been pretreated in a flow of H_2S–H_2 mixture. To understand the nature of this signal we carried out the treatment of $MoO_3/\gamma\text{-}Al_2O_3$ and MoO_3/SiO_2 samples in the mixture of H_2S (20 Torr) and H_2 (100 Torr) under static conditions at 200°C for 1 hr. After this treatment there were no EPR signals but only the

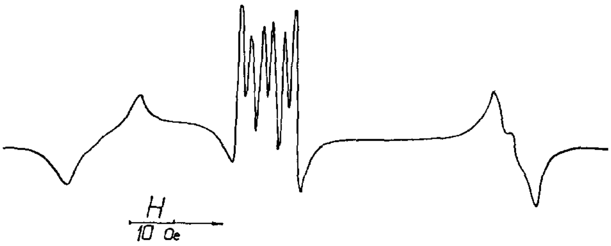


FIG. 4. X-band ESR spectrum (second derivative) of MoO_2/Al_2O_3 catalyst after the heating in H_2S at 300°C (nonlabeled H_2S, 96% ^{95}Mo).

broad line belonged to Mo^{5+} ions. The heating of such samples in oxygen (10 Torr, 200°C, 10 min) gives rise to the signal with the same g-values and hyperfine coupling constants like those for the signal appeared after the treatment in the pure H_2S. Since the deviations of the g-values of the signal obtained in Ref. (*4*) from ours are almost within the experimental errors we think that under the conditions of the work (*4*) the same paramagnetic species was formed.

Properties of the Paramagnetic Species with Respect to Adsorption of Molecules

Adsorption of oxygen at liquid nitrogen temperature results in the considerable broadening of the signal. After outgassing at room temperature the shape of the spectrum is returned to the original one. Adsorption of H_2, C_2H_4, C_4H_{10}, H_2O, CH_3OH, SO_2, and N_2O does not change the spectrum at room temperature, but at the same time the adsorption of NH_3 molecules yields the disappearance of the signal.

DISCUSSION

Nature of the Paramagnetic Species

Small values of hyperfine coupling constants for molybdenum nucleus show that the unpaired electron is localized not in a molybdenum atom but mainly in the paramagnetic species stabilized in the first coordination sphere of molybdenum ions. Taking into account the existence of the hyperfine splittings from two magnetic equivalent atoms of sulfur as well as the appearance of the spectrum after heating in oxygen of the samples prereduced by the H_2S–H_2 mixture it is clear that there are two opportunities for the nature of paramagnetic species, namely, species without oxygen, i.e., S_2^+ and S_2^- radicals and those involving oxygen, for example, S_2O^+ and S_2O^- radicals. We shall not consider the structures containing more than one oxygen atom because of the lack of data about the possibility of the existence of such structures at high temperatures.

From theoretical and experimental viewpoints it is likely that our spectrum could not be attributed to the S_2^+ or S_2O^+ species. For example, the components of the g-tensor of the S_2^+ species, which are isoelectronic to O_2^+ species, are determined by expressions:

$$g_1 = g_e - \frac{2\lambda}{\delta}, \quad g_2 = g_e + \frac{\lambda^2}{\Delta\delta} - \frac{\lambda^2}{\delta^2},$$

$$g_3 = g_e + \frac{2\lambda}{\Delta},$$

where $\lambda/\Delta < \lambda/\delta \ll 1$, λ is a spin–orbital coupling constant, δ and Δ are the corresponding differences in energies of the nonoccupied π_x^* orbital and below-lying half occupied π_y^* and doubly occupied σ orbitals of S_2^+, respectively (*5*). These equations show that for the S_2^+ radical the g_1-value must be substantially less than g_e while g_2 is close to g_e, but, nevertheless, less than g_e and only g_3 can exceed g_e. However, this conclusion contradicts the main features of our spectrum. Likewise, the S_2O^+ species is isoelectronic to the σ-radicals CO_2^-, CS_2^-, and COS^- which have been investigated (*6*, *7*). All components of g-tensor of these radicals are very close to g_e. The largest value of the hyperfine splitting corresponds to g_2. Both these conclusions are not valid for our spectrum.

The choice between the S_2^- and S_2O^- structures is not so evident. However, it seems that there are several reasons which enable the S_2O^- species to be rejected.

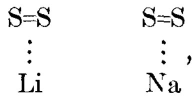
1. As was pointed out in the only available work on EPR of the S_2O^- radical (*8*), one should expect its structural formula to be of the form $[S–S–O]^-$ with the nonequivalent sulfur atoms, because the corresponding molecule S–S–O is stable while

symmetrical structure S–O–S is unknown. The results (*9*) of experimental and theoretical investigations of the isoelectronic S_2Cl radical also speak in favor of this conclusion. By contrast, two sulfur atoms in our paramagnetic species are magnetically equivalent. This observation is in contradiction to the hypothesis concerning the S_2O^-.

2. Even though one supposes that the S–O–S structure is realized on surface of the catalysts, then the tensor of hyperfine interactions for SOS^- radical, which is isoelectronic to the O_3^-, SO_2^- and S_3^- radicals, would be nearly axial, i.e., with two almost equal components, as it usually takes place for paramagnetic systems with the nondegenerate ground state (*1*, *10–14*). However, in our case there is a considerable deviation of the hyperfine coupling tensors from axial symmetry. At the same time, this result is in agreement with the theory (*15*) for degenerate systems similar to the S_2^- radical as well as with the experimental data, Table 1. This deviation is shown to be caused by interaction of the magnetic moment of the nuclei with the orbital magnetic moment (*15*).

3. The super hyperfine splitting from the cation of the adsorption center is shown to be observed for the diatomic O_2^- anion-radicals on MoO_3/SiO_2 (*20*), V_2O_6/SiO_2 (*21*), and other (*22*) catalysts. By contrast, in the case of the formation of the triatomic SO_2^- anion-radicals on the V_2O_5/SiO_2 catalysts containing the nuclei with the spin the superhyperfine splittings were not observed (*14*). We have carried out the SO_2 adsorption on the labeled MoO_3/SiO_2 samples containing the ^{95}Mo ions and obtained exactly the same signal of the SO_2^- radicals without the hyperfine splitting from the molybdenum like that was obtained earlier for the MoO_3/SiO_2 catalysts containing the natural abundance of molybdenum (*13*). Thus, the lack of the superhyperfine splittings in the case of the triatomic radicals SO_2^- and their existance in the our case give certain evidence for the formation of the S_2^- radicals.

The experimental proofs in favor of S_2^- are also supported by approximate quantum chemical calculations we have carried out for both the $[S–O–S]^-$ anion-radical and two model systems for S_2^- radical:



$$\begin{matrix} S{=}S \\ \vdots \\ Li \end{matrix} \qquad \begin{matrix} S{=}S \\ \vdots \\ Na \end{matrix},$$

where the influence of the solid surface was approximated by the interaction of the radical with the Li^+ and Na^+ ions.

Geometry of S_2O^- was assumed to be triangular with the chemical bond length $r_{SO} = 1.5$ Å and angle $\theta = 109°$ or $\theta = 120°$. In the case of the systems $S_2^- \ldots Li^+$ and

TABLE 1

Parameters of EPR Spectra of O_2^-, S_2^- and Se_2^- Anion-Radicals[a]

Radical	System	g_1	g_2	g_3	A_1	A_2	A_3	Ref.
O_2^-	KCl(bulk)	2.436	1.955	1.951	19.6	0 ± 3	67.7	(*5*, *15*)
O_2^-	MgO	2.077	2.007	2.001	15 ± 2	0 ± 4	77	(*16*)
O_2^-	ZnO	2.049	2.008	2.002	15 ± 4	0 ± 4	80	(*17*)
S_2^-	KCl(bulk)	3.4303	0.9500	0.9484	28	—	—	(*18*)
S_2^-	NaI(bulk)	2.2303	2.0178	1.9942	—	—	—	(*18*)
Se_2^-	NaI(bulk)	2.8015	1.9042	1.8148	67	15	125	(*19*)
S_2^-	MoO_3/SiO_2 MoO_3/Al_2O_3	2.047	2.028	1.998	14	<8	43	This work

[a] A_1, A_2, A_3 in Oe.

S_2^- . . . Na^+ there was used the value of bond length $r_{SO} = 2$ Å typical of sulfur compounds while the nuclei of the Li and Na atoms were located at the distances estimated from ionic radii.

Magnetic resonance parameters were evaluated within the scope of the CNDO/SP (complete neglect of differential overlap/spin polarization) method (*23*) which was extensively utilized previously in systematic calculations of g-tensors (*24*) as well as of isotropic hyperfine coupling (ihfc) constants a_{iso}^A (*25*) and anisotropic hyperfine coupling (ahfc) tensors T^A (*26*) of free radicals. The computations of ihfc and ahfc were performed with the use of the Hartree–Fock magnitudes of the atomic dipolar integrals (*27*).

The results of the CNDO/SP calculations are summarized in Table 2 (ihfc and ahfc in Oe). A general direction for the g_{11} and T_{11} principal values of all tensors is perpendicular to the plane of the triatomic paramagnetic systems. Comparing the entire set of the calculated magnetic resonance parameters for S_2O^- with our experimental data one can readily infer that the detected paramagnetic species may hardly be identified as the electronically nondegenerate S_2O^- radical. On the contrary, keeping in mind the roughness of the admitted models, which were mainly intended for qualitatively outlining the magnetic resonance parameters of the S_2^- species whose electronic degeneracy is somewhat lifted due to the influence of the surface ions, it should be recognized that the results of the CNDO/SP calculations fitted the above hypothesis concerning the S_2^- radical.

From the above experimental and theoretical reasons it seems quite reasonable to assign the signal to the S_2^- anion-radicals adsorbed on the surface in the first coordination sphere of Mo^{6+} ions.

TABLE 2

Magnetic Resonance Parameters Calculated by CNDO/SP Method

Paramagnetic species	S_2^-		S_2O^-	
	Li^+	Na^+	109°	120°
g_{11}	2.0357	2.0313	1.9883	2.0023
g_{22}	2.0023	2.0023	2.0234	2.0190
g_{33}	2.0542	2.0528	2.0394	2.0491
g_{iso}	2.0307	2.0288	2.0170	2.0235
a_{iso}^S	5.7	6.4	1.9	1.3
T_{11}^S	−13.7	−12.5	−13.0	−21.6
T_{22}^S	27.4	25.0	−12.4	−11.0
T_{33}^S	−13.7	−12.5	25.4	−10.6
a_{iso}^O			−1.0	−12.2
T_{11}^O			2.0	−17.7
T_{22}^O			2.0	9.4
T_{33}^O			−4.0	8.3

The experimental data on the adsorption of a number of molecules provide evidence that the S_2^- anion-radicals are stabilized on the surface of the catalysts (data on the broadening of the spectra by oxygen) and do not interact at room temperature with the variety of molecules (H_2, C_2H_4, C_4H_{10}, H_2O, CH_3OH, SO_2, N_2O) except the NH_3 molecules. The S_2^- anion-radicals have considerable stability at room temperature, but their spectrum disappeared after heating in vacuum at temperatures higher than 350°C.

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