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EPR Study of S_3^- Anion Radicals on the Surface of Supported MoO_3/MgO, WO_3/MgO, and CrO_3/MgO Catalysts

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The formation of S_3^- anion radicals has been observed by the EPR method on the surface of supported MoO_3/MgO, CrO_3/MgO, and WO_3/MgO catalysts upon their interaction with H_2S. Properties of S_3^- with respect to adsorption of different molecules such as O_2, H_2O, NH_3, SO_2, C_3H_6, and H_2S were also investigated. In the case of H_2S a complex is shown to be formed between S_3^- and H_2S. The nature of this complex and its structure is considered on the basis of experimental data and the results of quantum chemical calculations.

INTRODUCTION

In recent years the formation and properties of sulfur-containing radicals on the surface of catalysts have been widely studied by EPR in connection with their tentative role in various catalytic reactions (*1–5*). In particular, S_2^- anion radicals were shown to be formed on the surface of supported molybdenum–silica gel and molybdenum–alumina catalysts after their interaction with hydrogen sulfide (*5*). It is interesting to understand the role of the supports and supported transition metal ions for the formation of sulfur-containing radicals in such processes. For this purpose the present paper investigates the interaction of H_2S with supported magnesium oxide catalysts containing molybdenum, chromium, and tungsten ions. It is necessary to note that Lunsford *et al.* (*4*) have shown that the interaction of H_2S with MgO without transition metal ions does not yield any sulfur radicals, but exposure of MgO to elemental sulfur gives rise to S_3^- anion radicals.

EXPERIMENTAL

The MoO_3/MgO, CrO_3/MgO, and WO_3/MgO (~ 1 wt% of metal) were prepared by impregnation of magnesium oxide ($S \approx 30$ m^2 g^{-1}) with aqueous solutions of $(NH_4)_2Mo_2O_7$, CrO_3, and $(NH_4)_4W_5O_{17} \cdot 1.5H_2O$, respectively. Isotopically labeled samples containing 97 at% of ^{95}Mo were prepared by impregnation of the same support with solution of $^{95}MoO_3$ in NH_4OH. Labeled hydrogen sulfide (50 at% of ^{33}S) was prepared by reaction of labeled elemental sulfur with hydrogen and trap to trap distillation.

After impregnation the samples were dried at 60 to 70°C and heated at 600°C for 2 hr in air. Before treatment of the samples in H_2S, they were evacuated (10^{-5} Torr)[1] for 2 hr and then oxidized in oxygen (200–300 Torr) for 1 hr and outgassed for 5 to 10 min, all at 500°C. In some cases the reduced samples were investigated (H_2, 100–200 Torr, 500°C, 20–30 min).

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[1] 1 Torr = 133.3 N m^{-2}.

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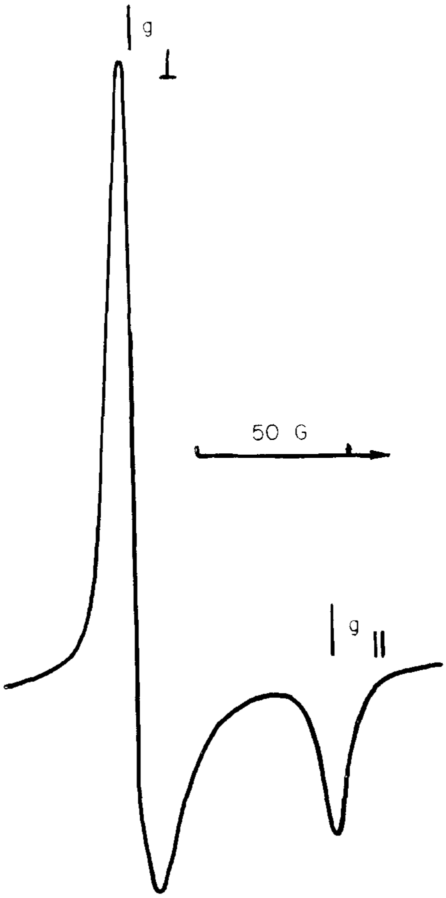

FIG. 1. EPR spectrum of the S_3^- anion radicals.

EPR spectra were recorded at room and liquid nitrogen temperatures in the X-band. G values were determined to an accuracy of 0.001 with respect to a DPPH sample with $g = 2.0036$. Optical reflection spectra were measured in diffused scattered light at room temperature with a Unicam-700 spectrometer. The MgO used for the preparation of the samples was also used as the reference standard for the optical spectra.

RESULTS

Molybdenum–magnesium oxide catalysts. The EPR spectrum of the magnesium oxide used for the preparation of the catalysts exhibits six lines from impurities of Mn^{2+} ions (*6*). Exposure of such magnesium oxide to H_2S does not give any new spectra at room or higher temperatures. In the EPR spectra of the oxidized MoO_3/MgO samples a broad line with an average g factor of about 1.92 is observed simultaneously with the six-line spectrum from Mn^{2+}. The same line is also observed for reduced samples, but in this case its intensity is several times greater. It has been shown (*7*) that Mo^{5+} ions are responsible for this broad line. In the present paper changes in the spectra of Mo^{5+} and Mn^{2+} ions are not considered in detail.

Exposure of the oxidized MoO_3/MgO catalysts to H_2S (10–50 Torr) for several minutes at 300°C and subsequent outgassing at room temperature (10^{-5} Torr, 15 min) gives rise to a new EPR spectrum with $g_{\parallel} = 2.004$ and $g_{\perp} = 2.042$ (Fig. 1). The intensity of the spectrum from the Mo^{5+} ions increases several times and the color of the samples changes from white to bright blue. The shape of the new spectrum depends on the temperature of the measurements rather strongly. Therefore, an atmosphere of helium was used to guarantee thermal equilibrium at liquid nitrogen temperature. At room temperature the spectrum becomes isotropic with $g = 2.029$ and $\Delta H = 60$ G. Integration of the spectra at liquid nitrogen temperature shows that the amount of the paramagnetic species is about 10^{19} per gram.

Exposure of the labeled $^{95}MoO_3/MgO$ samples (97 at% of ^{95}Mo) to H_2S results in a spectrum with the same shape and parameters as in the case of the unlabeled samples. Exposure of the unlabeled samples to labeled hydrogen sulfide (50 at% of ^{33}S) gives rise to the spectrum shown in Fig. 2 with hyperfine splittings of $A^{I} = 20.6$ G and $A^{II} = 39.4$ G centered on $g_{\parallel} = 2.004$.

The values of the g factors and the hyperfine constants of the spectra coincide with those for the S_3^- anion radical, $(S_I S_{II} S_I)^-$, which forms on the surface of pure magnesium oxide after its treatment by elemental sulfur (*4*). The temperature behavior of the spectrum for MoO_3/MgO and MgO samples is also similar. Lunsford *et al.* (*4*) conclude that the anisotropic interactions are averaged at 20°C due to rotations of the S_3^- species. The above data strongly suggest that the spectra observed after the interaction of MoO_3/MgO with H_2S belongs to the S_3^- anion radicals.

Chromium– and tungsten–magnesium oxide catalysts. Exposure of the oxidized CrO_3/MgO and WO_3/MgO samples to H_2S (10–50 Torr) for several minutes at 300°C and subsequent outgassing at room temperature (10^{-5} Torr, 15 min) also results in the EPR spectra of S_3^-. For CrO_3/MgO samples the appearance of EPR spectra of Cr^{3+} ions are observed simultaneously. The values of the g factors and the hyperfine splittings are the same as in the case of MoO_3/MgO samples. A change in the color of the samples accompanies this treatment. CrO_3/MgO samples blacken and WO_3/MgO change in color from white to blue. In the last case the optical diffusion reflectance spectra were measured (Fig. 3).

Reduced samples. The intensities of the S_3^- EPR spectra decrease strongly if the MoO_3/MgO and WO_3/MgO samples are first reduced in hydrogen and then exposed to hydrogen sulfide under the same experimental conditions as for the oxidized samples. In the case of CrO_3/MgO, preliminary reduction results in the complete disappearance of S_3^-.

Interaction of S_3^- with adsorbed molecules. Adsorption of O_2, H_2O, NH_3, SO_2, and C_3H_6 (10–20 Torr) at room temperature neither decreases the intensity nor changes the shape of the EPR spectrum of S_3^-. It is worth noting that in the case of pure MgO samples (*4*) the S_3^- spectrum disappears irreversibly in oxygen at room temperature. At liquid nitrogen temperature the EPR spectrum of S_3^- disappears in the presence of a large amount of oxygen but it appears again after outgassing the samples.

In contrast with the above molecules the adsorption of H_2S ($\sim$10 Torr) at room temperature leads to the reversible disappearance of the EPR spectrum measured both at room and at liquid nitrogen tem-

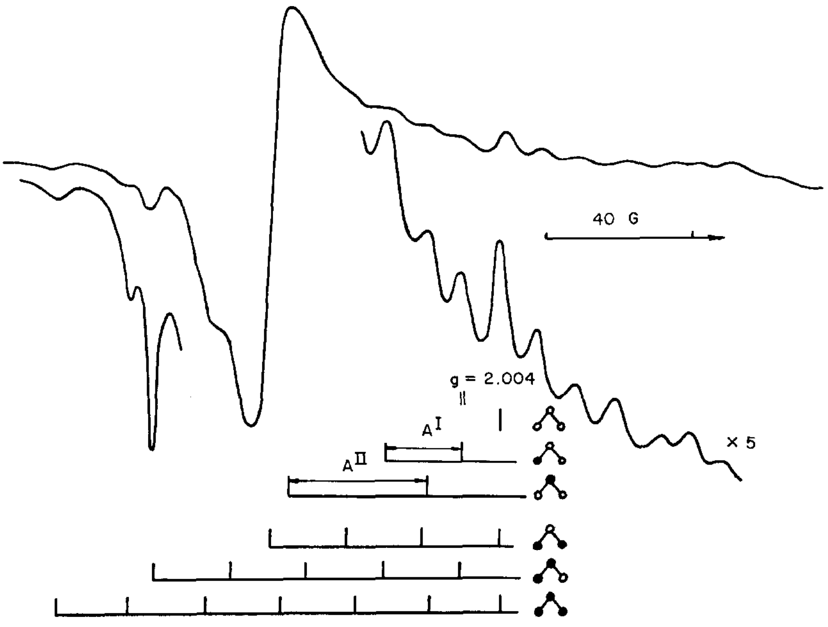

FIG. 2. EPR spectrum of the S_3^- anion radicals labeled with the ^{33}S isotope (50 at%).

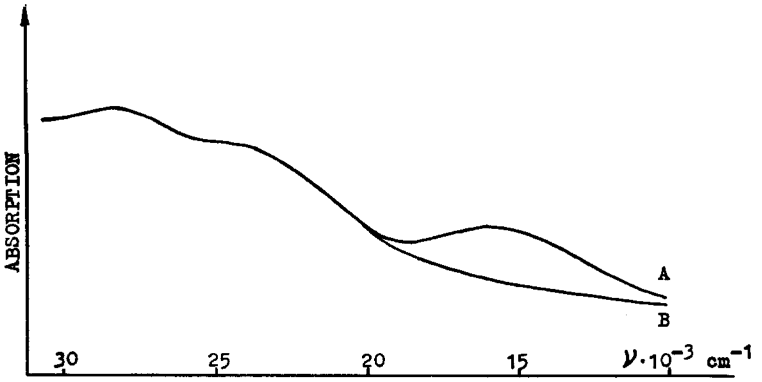

FIG. 3. Optical spectra of the WO_3/MgO samples: (A) after exposure to H_2S at 300°C and outgassing; (B) after subsequent H_2S adsorption at 20°C.

peratures. Outgassing of the samples for 30 min at room temperature restores their initial intensity and shape. The optical spectra of WO_3/MgO samples also show the reversible disappearance of the band at 610 nm after H_2S adsorption (Fig. 3B). Outgassing of the samples restores the initial optical spectrum (Fig. 3A). It is known (*8*) that the blue color of ultramarine is caused by the band at 610 nm belonging to the $^2B_1 \rightarrow {}^2A_1$ transition of S_3^-. Thus, the presence of this band in the optical spectra of the catalysts, only in the case when the EPR spectrum of S_3^- is observed, is evidence that the band at 610 nm belongs to the S_3^- anion radicals adsorbed on the surface. Reasons for its disappearance after H_2S adsorption is considered below.

Adsorption of the labeled H_2S (50 at% of ^{33}S) at room temperature on the samples containing the S_3^- anion radicals and subsequent desorption after several minutes leads to an EPR spectrum in which the hyperfine splittings from sulfur both in the middle and terminal positions of $S_IS_{II}S_I$ structure are observed. This indicates that rapid isotope exchange takes place.

As has been shown above, the oxygen adsorption does not change the EPR spectrum of S_3^-. But if samples containing S_3^- and H_2S are also exposed to oxygen, then an EPR spectrum which is reminiscent of that observed for polynuclear sulfur radicals is observed (*4*). Outgassing of these samples does not change their EPR spectra and does not restore the original S_3^- spectrum.

DISCUSSION

Mechanism of S_3^- formation. The above experimental data show that the interaction of the molybdenum-, chromium-, and tungsten-containing magnesium oxide catalysts with hydrogen sulfide leads to the formation of surface S_3^- anion radicals. Experiments using a thermocouple pressure detector show that hydrogen gas is not evolved in the reaction ampoules when the samples are heated in the presence of H_2S. Therefore, the hydrogen atoms of H_2S form surface hydroxyl groups or molecules of water:

$$3H_2S + 3O^{2-} \rightarrow S_3^- + 3H_2O + 5e^-$$

and

$$3H_2S + 6O^{2-} \rightarrow S_3^- + 6OH^- + 5e^-.$$

These reactions, of course, are not elementary steps. Formation of S_3^- may proceed via the recombination of monoatomic sulfur species produced in the course of the interaction of H_2S with the catalysts. The electrons released in the above reactions reduce the transition metal ions.

Additional evidence for this reaction

scheme comes from three sources. First, EPR spectra from the reduced species Mo^{5+} and Cr^{5+} appear simultaneously with the spectrum from the S_3^- anion radical. Second, prereduction of the catalysts results in a large decrease in the intensities of the S_3^- EPR spectra from MoO_3/MgO and WO_3/MgO and a complete disappearance of the S_3^- spectrum in the case of CrO_3/MgO. Finally, the interaction of H_2S with MgO in the absence of reducible transition metal ions produces no S_3^-.

Earlier (*5*), it was shown that the exposure of the molybdenum and chromium ions supported on silica gel or alumina to H_2S yields the formation of adsorbed S_2^- and not S_3^- anion radicals. This gives some evidence that the nature of the support used to prepare the catalyst is the preferable factor for the formation of one or another sulfur containing anion radical.

It is interesting to note that the nature of the support does not play such a dominant role for the formation of oxygen anion radicals. In this case the O_2^- anion radicals are formed after oxygen adsorption independently of the support (*9–11*).

Properties of S_3^-. The S_3^- anion radicals are formed on the surface of the catalysts and can be reached by adsorbed molecules. This is shown by the broadening of the EPR spectrum of S_3^- with oxygen at liquid nitrogen temperature. The EPR spectra of S_3^- described here are identical to those for S_3^- formed by the interaction of pure MgO with elemental sulfur. Isotopic labeling with ^{95}Mo shows that the unpaired electron of S_3^- is not delocalized on the transition metal ions. Therefore, it is difficult to decide whether the S_3^- is adsorbed only on the MgO support or whether it also contacts the transition metal ions.[2]

The S_3^- anion radicals are stable in atmospheres of O_2, H_2, H_2O, NH_3, SO_2, and C_3H_6 at room temperature. However, H_2S adsorption at room temperature leads to the reversible disappearance of the S_3^- EPR spectrum and optical band at 610 nm. The use of the labeled hydrogen sulfide shows that rapid isotope exchange takes place in this case:

$$^{32}S_3^- \xrightarrow[20°C]{H_2{}^{33}S} {}^{33}S_3^-,\ {}^{33}S\,{}^{32}S\,{}^{33}S^-,\ {}^{33}S\,{}^{33}S\,{}^{32}S^-,\ {}^{33}S\,{}^{32}S\,{}^{32}S^-,\ {}^{32}S\,{}^{33}S\,{}^{32}S^-.$$

All of these experimental data provide evidence for the formation of a complex between S_3^- and H_2S. The energy of formation of the complex is rather small since it can be easily destroyed by outgassing at room temperature. At the same time the disappearance of the EPR spectrum of S_3^- and optical band at 610 nm shows that a remarkable perturbation of the electronic structure of S_3^- occurs when this complex is formed. The ground electronic state of the complex between S_3^- and H_2S is likely to be degenerate or nearly degenerate since in this case the EPR spectrum would be very broad and might be unobservable as a result of the large anisotropy of the g tensor and short relaxation time.

Feasible structure of the $H_2S_4^-$ complex. Quantum chemical calculations were carried out within the scope of the extended Hückel theory (EHT) (*12*) for the purpose of a more profound insight into the mechanism of the isotopic exchange reaction accompanied by the disappearance of the EPR spectrum of the S_3^- radical. The H_2S and S_3^- initial reactants both had a C_{2v} geometry with a bond angle of 90° and bond lengths $r_{SH} = 1.34$ Å (*13*) and $r_{SS} = 2.0$ Å (*14, 15*), respectively.[3] The square

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[2] In both cases the stabilization of S_3^- on the surface is expected to be almost completely due to the electrostatic interactions with the terminated sulfur atoms, wherein the negative charge concentration appeared to be nearly 95% (*14*).

[3] Such geometry for S_3^- was chosen taking into account that the chemically significant semiquantitative results of calculation are not sensitive to small variations in the bond length and angle (*14, 20*).

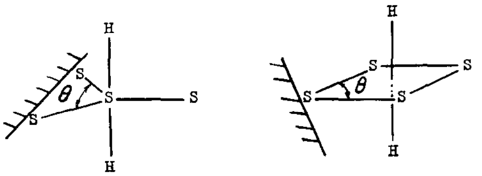

FIG. 4. The analyzed Y-shape and square structures of the $H_2S_4^-$ complex.

and rhombic as well as a planar Y-shape patterns of the S nuclei were assumed for the $H_2S_4^-$ intermediate complex (Fig. 4). The adsorbed S_3^- radical was assumed to be connected with the catalyst surface by either one or two S atoms. In the calculations the vacant $3d$-AO's of sulfur atoms were neglected, as it has been indicated that chemically significant qualitative results for similar systems were not sensitive to the inclusion of these AO's (*15, 16*).

The occupied and empty energy levels, obtained within the framework of EHT for the above $H_2S_4^-$ structures, are shown in Fig. 5 on the same vertical scale. In addition, the calculated values of the net atomic charges Q^A and the energies of the $H_2S_4^-$ complex formation, ΔE_c, from the H_2S molecule and the S_3^- free radical are presented in Table 1. When estimating the Q^A magnitudes, use was made of conventional Mulliken population analysis (*17*). The ΔE_c quantities were evaluated as differences in the corresponding total energies determined by the expression suggested by Ruedenberg (*18*):

$$E_t = \tfrac{3}{2} \sum^{\text{occ}} n_i \epsilon_i. \qquad (1)$$

Summation in Eq. (1) is over all doubly and singly occupied MO's with the orbital energies ϵ_i.

As is readily seen from Fig. 5, the degeneracy or small spacing of the upper MO's available to the unpaired electron can make difficult the observation of EPR spectra for the $H_2S_4^-$ paramagnetic species both with the square and Y-shape pattern of the S nuclei (e.g., due to large anisotropy of the g tensors or very short relaxation times).

However, according to the calculated energy of complex formation, the square structure is extremely unfavorable (1230 kcal/mol). This may reflect a large coulombic repulsion among the equally charged sulfur atoms (see Table 1). Although the energy loss upon complex formation decreases by 370 kcal/mol through rhombic distortion of the $H_2S_4^-$ square form, nevertheless, the value of $\Delta E_c^R \approx 860$ kcal/mol, as before, is much too high to be reasonable. Furthermore, the level scheme (Fig. 5) in this case is not consistent with the spectroscopic evidence for the formation of a weak complex unobservable by EPR. The gaps between the unpaired electron MO and the nearest doubly occupied or vacant MO's are no longer small. Therefore, it will not be suggested that the isotopic exchange reaction proceeds via the $H_2S_4^-$ intermediates with the square and rhombic patterns of the S nuclei.

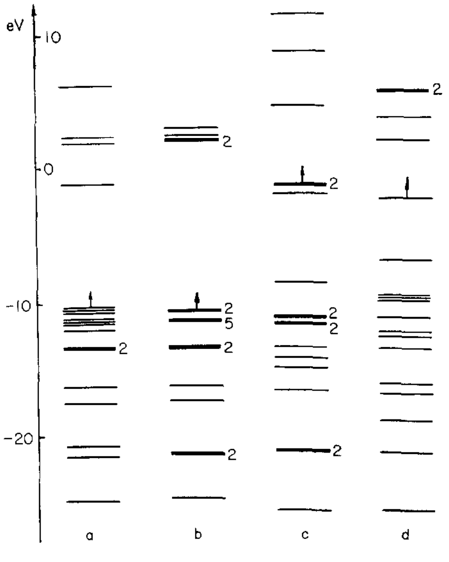

FIG. 5. The occupied and empty energy levels for the different $H_2S_4^-$ structures: (a) Y-shape, $\theta = 90°$; (b) Y-shape, $\theta = 120°$; (c) square structure, $\theta = 90°$; (d) rhombic structure, $\theta = 60°$. Figures show the degeneracy of the levels.

TABLE 1

Net Atomic Charges, Q, and Energies of Complex Formation, ΔE_c, (kcal/mol), for the Different Structures of the $H_2S_4^-$ Complex

Structure	S_3^- $\theta = 90°$	H_2S $\theta = 90°$	Y-shape $\theta = 90°$	Y-shape $\theta = 120°$	Square $\theta = 90°$	Rhombic $\theta = 60°$
Q^H		0.04	−0.41	−0.09	0.46	−0.20
Q_1^s	0.60	−0.08	2.22	2.24	−0.48	0.57
Q_2^s	−0.80		−0.65	−1.02	−0.48	−0.87
Q_3^s	−0.80		−0.65	−1.02	−0.48	0.57
Q_4^s			−1.10	−1.02	−0.48	−0.87
ΔE_c			140	110	1230	865

At the same time, the Y-shape geometries of the $H_2S_4^-$ intermediate complex are well suited for realizing the isotopic exchange reaction. Indeed, the energy loss in forming the Y-shape structures from the H_2S molecule and the S_3^- radical is no longer prohibitively large ($\Delta E_c^Y \approx 110$–140 kcal/mol) and can be entirely offset by stabilization of this structure in the electric field of the surface ions. Note that the Coulomb interaction energy of two point charges $|q| = 1$ at 1 Å distance exceeds 300 kcal/mol. A strong decrease in the ΔE_c^Y energy is possible because the chemical bonds are more ionic in the Y-shape complexes than in the H_2S and S_3^- starting reactants (cf. Q^A in Table 1; see also (*19*)). By virtue of the specific distribution of charges in the S_3^- anion radical its bonding with the catalyst surface by two but not one sulfur atoms should be preferred for energetic reasons. This attachment is also favorable for the formation of the $H_2S_4^-$ intermediate complex with the Y-shape pattern of the S nuclei.

CONCLUSION

The reactivity of the $H_2S_4^-$ complex is higher than the reactivity of S_3^- and H_2S separately. For example, the S_3^- anion radical is stable at room temperature in oxygen but the $H_2S_4^-$ complex reacts with oxygen at this temperature with the formation of sulfur-containing radicals. The possible role of the complexes between S_3^- and H_2S for the activation of hydrogen sulfide and elemental sulfur is quite intriguing.

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