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ESR Studies of SO_2 and H_2S Adsorption on Alumina and Alumina-Supported Mo and Mo–Co

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When SO_2-treated γ-alumina or alumina-supported Mo or Mo–Co-oxide was heated at 450°C, SO_2^- species were formed. It seems that the SO_2^- ion plays an intermediate role in $H_2S + SO_2 \rightarrow S + H_2O$ reaction. While H_2S did not give any ESR signal with pure alumina at 450°C, weak signals of sulfur species were observed on Mo or Mo–Co–alumina. It was observed that O_2 did not effect the ESR signal for SO_2^- on alumina, but it decreased drastically over Mo–alumina and over Mo–Co–alumina. However, the O_2 effect on alumina-supported oxides was reversible. The sequence for the concentration of SO_2^- species under similar conditions on these catalysts was in the following sequence:

$$\text{Mo–alumina} > \text{alumina} \geqslant \text{Co–Mo–alumina}.$$

A possible mechanism for the formation of SO_2^- species has been discussed.

INTRODUCTION

Alumina and alumina-supported metal catalysts have been widely used for oxidation (*1*), desulfurization (*2*), and other hydrocarbon reactions (*3*, *4*). The formation of SO_2^- ions and other sulfur radicals on the surface of oxides (*5–7*) and on partially reduced metal oxides (*8*, *9*) are widely reported in the literature. The reaction involving SO_2^- ion and other paramagnetic species of sulfur has been studied by ESR in an effort to determine the importance of these species in the catalytic reactions, i.e., oxidation and reduction of SO_2 and H_2S. In the present paper we are reporting the formation of SO_2^- ions and other sulfur radicals on the unreduced surface of alumina and alumina-supported Mo and Mo–Co. The effect of oxygen on these species and the formation of sulfur species by H_2S at 450°C over studied catalyst is also reported.

EXPERIMENTAL

The techniques for ESR measurements are described elsewhere (*10*). Linde's 99.99% oxygen was used. Hydrogen, sulfur dioxide, hydrogen sulfide, and carbon dioxide were obtained from Matheson, Coleman and Bell.

The catalysts used in this work were the same as used by Parsons and Ternan (*2*). They were prepared by spraying aqueous solutions of the appropriate metal salts onto 500 g of γ-alumina monohydrate powder (Continental Oil Co., Catapal SB) which were mulled in a mix-muller. Initially a solution consisting of 14 ml of concentrated HNO_3 (70 wt%) and 1000 ml of distilled water was added to the powder. The ammonium paramolybdate or cobalt nitrate solution was added next. The impregnated mixtures were dried at 120°C for 3 hr and calcined at 500°C for 3 hr. The calcined powder was mixed with

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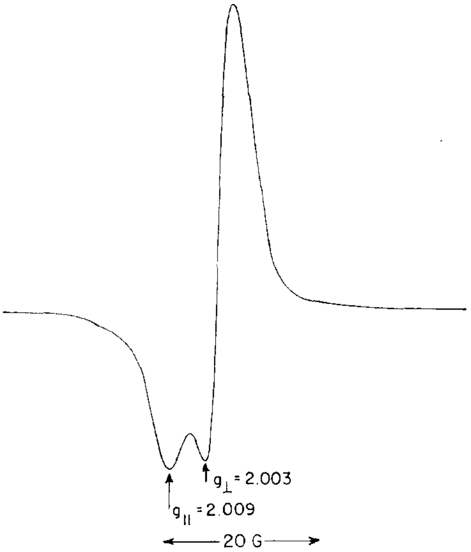


FIG. 1. ESR spectrum of SO_2^- ion on γ-alumina.

2 wt% stearic acid and pressed into cylindrical pellets ($L = D = \frac{3}{8}$ mm) in a continuous pellet press. The stearic acid acted as a binder and lubricant during pelleting. The pellets were recalcined at 500°C for 6 hr to remove the stearic acid and then were ground for ESR studies (40- to 60-mesh size).

RESULTS

γ-*Alumina Catalyst*

γ-Alumina, when evacuated and heated for 10 hr at 450°C in an ESR tube, did not give any ESR line under experimental conditions. When SO_2 was admitted into the ESR tube containing evacuated and heated alumina at room temperature, a large amount of SO_2 was adsorbed, as observed by the mercury manometer attached to the high-vacuum apparatus. No ESR spectra were observed in the presence of either SO_2 or evacuated SO_2-treated alumina at room temperature. Similar results were reported by Vorotyntsev *et al.* (*8*), and Maschenko *et al.* (*9*) on the surface of partially reduced supported molybdenum oxide. On heating the SO_2–alumina system for 5 min at 450°C, after cooling at room temperature, an ESR spectrum with two peaks was observed at $g = \sim 2.00$ (Fig. 1). This spectrum was assigned to the SO_2^- species (*7–9*). The color of the alumina changed from white to gray. Similar SO_2 ion spectra were observed by Schoonheydt and Lunsford (*7*), Vorotyntsev *et al.* (*8*), and Maschenko *et al.* (*9*). Table 1 shows the $g_\parallel$ and $g_\perp$ for $SO_2^{-\cdot}$ in the present study and the values which are reported in the literature. Further heating and evacuation of the SO_2–alumina system for several hours at 450°C did not affect the SO_2^- spectrum noticeably.

TABLE 1

A Comparison of the Results Obtained for SO_2^-

Reference	$g_\perp$	$g_\parallel$
Vorotyntsev *et al.* (*8*)	2.003	2.011
Present paper	2.003	2.009

When SO_2 or CO (400 mm Hg) was admitted into the ESR tube containing heated and evacuated alumina at room temperature, the ESR spectrum changed slightly and one broad line appeared. However the g value of the line did not change, i.e., ~ 2.003, and no appreciable change in the peak height was observed (Fig. 2). On evacuating SO_2 or CO at room temperature, the original spectrum of SO_2^- ions reappeared (Fig. 1) with almost original shape and intensity. In the presence of oxygen (5–400 mm Hg) though the two peaks in the spectrum of the SO_2^- ions could be distinguished sharply; there was no appreciable change in the intensity of the spectrum. It may be possible that O_2 makes the species, which are near to the surface, more axial symmetric. This behavior of oxygen was opposite to that observed in the case of acetylenic species over alumina-supported copper oxide catalyst (*10*), where, as oxygen drastically decreased the intensity of the ESR line assigned to acetylenic species,

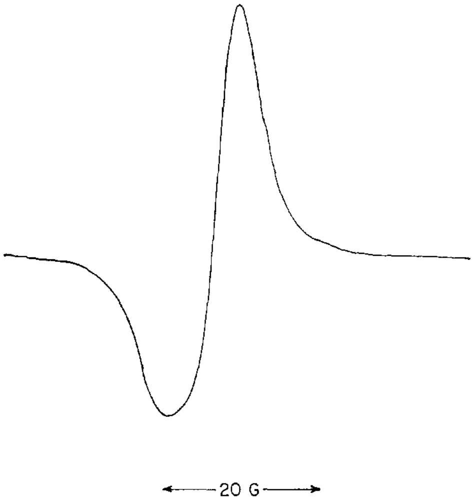


FIG. 2. Effect of CO on the ESR spectrum of SO_2^- ion on γ-alumina.

the original spectrum reappeared on evacuating the oxygen at room temperature.

On admitting H_2S (400 mm Hg) to the heated SO_2–alumina system at room temperature, though, the intensity of the spectrum of SO_2^- ions decreased, yet no appreciable change was observed in the g value and the shape of the line. The intensity of the spectrum did not return to its original level upon evacuating H_2S at room temperature. It seems that H_2S formed a nonparamagnetic species with SO_2^- ion. On heating the evacuated H_2S–SO_2–alumina system for 15 min at 450°C, the color of the system changed from gray to yellow (decomposed product S) and sulfur deposited on the colder parts of the tube. Some drops of a liquid which would be water were seen deposited at the top of the tube (colder parts). The ESR spectrum of SO_2^- ions was reduced drastically and a broad line was observed. However, after further heating the system for 70 hr at 450°C, the ESR spectrum of SO_2^- ions reappeared having a shape almost similar to that of the original spectrum (Fig. 1), but with less intensity (before admitting H_2S).

It seems that SO_2 ions played an intermediate role in the decomposition of H_2S and the $H_2S + SO_2 \rightarrow H_2O + S$ reaction. However when an excess of H_2S was used, the signal due to SO_2^- ions did not reappear on heating.

When evacuated and heated alumina was heated in the presence of H_2S (400 mm Hg) for 30 min at 450°C, no sulfur deposition or ESR signal was observed.

Mo- and Co–Mo–Alumina Catalysts

When calcined (at 500°C) alumina-supported molybdenum and molybdenum–cobalt were heated and evacuated at 450°C for 10 hr, an ESR line around $g = 1.923$ was observed. This ESR spectrum was due to Mo^{5+} ions (*11*). In the case of Co–Mo–

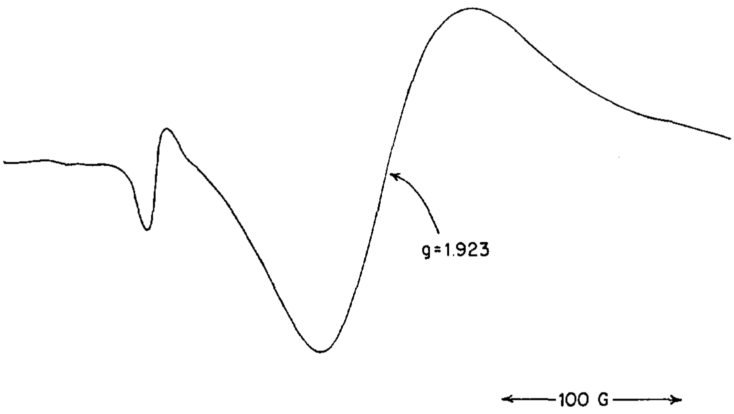


FIG. 3. ESR spectrum of SO_2^- ion on 18 wt% Mo–alumina.

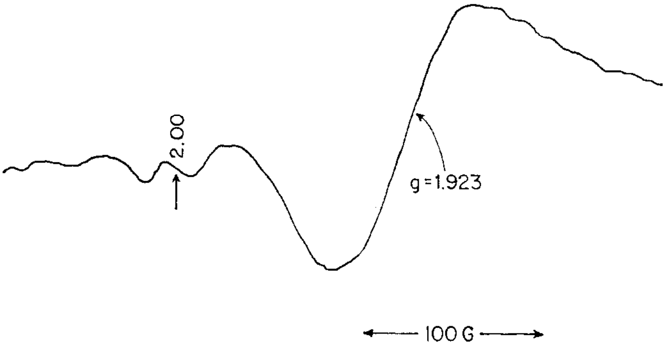


FIG. 4. ESR spectrum of sulfur species on Mo–Co–alumina (Mo/Co = 1) formed by H_2S at 450°C.

alumina, the intensity of the Mo^{5+} line was less than the intensity of the Mo^{5+} line obtained with Mo–alumina. On evacuating SO_2-treated catalyst at room temperature, no appreciable effect in the intensity of the Mo^{5+} line was observed. On heating the evacuated SO_2 catalyst system for 5 min at 450°C, a new ESR line at $g = \sim 2.003$ was observed (Fig. 3) which was assigned to SO_2^- species. The shape of this line was similar to that observed over pure alumina (Fig. 1). The color of the catalysts changed to dark black in both cases. On increasing the heating time to 5 hr, the concentration of Mo^{5+} ions increased slightly, but no change was observed in the SO_2^- line. On prolonged heating (70 hr) the intensity of both lines, i.e., SO_2^- and Mo^{5+}, decreased slightly. It seems that Mo^{5+} ions do not play a role in the formation of SO_2^- ions. However other possibilities could not be eliminated. The concentrations of SO_2^- species under similar conditions on these catalysts were in the following sequence:

Mo–alumina > alumina $\geqslant$ Co–Mo–alumina.

The number of spins on the catalysts are shown in Table 2.

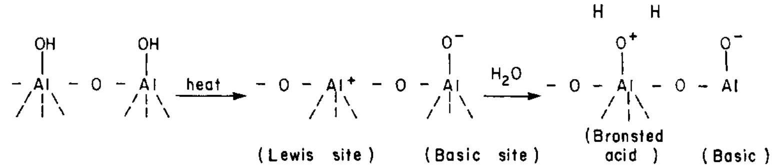
The effects of the excess of H_2S, SO_2, and CO on the SO_2^- ions over these catalysts were the same as observed over pure alumina. On heating the H_2S–SO_2–catalyst system, the color of the catalyst changed from dark black to the original color.

In the presence of oxygen, the intensity of the ESR spectrum of SO_2^- ions decreased, and the spectrum returned to its original shape and intensity on evacuating the oxygen. This behavior was the same as with acetylene–copper oxide–alumina (*10*). However, it was different from that observed with SO_2–alumina.

When H_2S was admitted into the evacuated and heated Mo–alumina or Mo–Co–alumina catalyst, the catalyst changed from its original color to dark brown. On heating the H_2S-treated catalyst for 20 min at 450°C, few new weak ESR lines were observed at $g = \sim 2.00$, including the Mo^{5+} line (Fig. 4). These new lines were assigned to sulfur species (*12*). The concentration of Mo^{5+} ions also increased slightly on heating. Though the concentration of Mo^{5+} ions increased considerably when the sample was further heated for 10 hr at 450°C, no appreciable change was observed in the ESR lines assigned to S species.

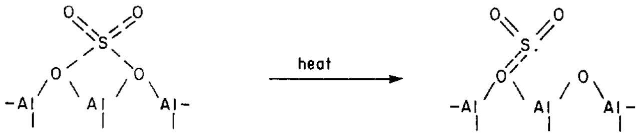
DISCUSSION

Alumina and alumina-supported metal catalysts are widely used for desulfurization (*2*), oxidation of hydrocarbons (*1*), and other catalytic reactions (*3*, *13*, *14*). The structure of γ-alumina is very complex. The nature of the acidic and basic sites of alumina can be represented as follows (*15*).



The Lewis acid is a positively charged aluminum ion, and the basic site is a negatively charged oxygen ion, O^-. It is also evident that different kinds of catalytically active sites are present on alumina depending on the preparation and pretreatment. When SO_2 was heated with γ-alumina, SO_2^- species were formed. The concentration or formation of SO_2^- species on different samples of alumina depends on the quality of the alumina used. Schoonheydt and Lunsford (*7*), and Vorotyntsev *et al.* (*8*) studied SO_2^- ion on partially reduced MgO, TiO_2, etc. Rao and Lunsford (*6*) also reported two types of SO_2 species (i.e., A and B). The present investigations indicate that the spectrum (Fig. 1) is due to only one species. The SO_2^- spectrum (Fig. 1) is slightly different from the SO_2^- spectrum observed by Rao and Lunsford (*6*) on vanadium oxide catalyst at room temperature. This difference may be due to different environments on the surface. The intense resonance obtained almost immediately on heating was an equilibrium value. These radicals were very stable and could not be destroyed by either heating or evacuating continuously at 450°C for several hours. The *g* values are approximately the same as obtained by Vorotyntsev *et al.* (*8*).

It has been reported that SO_2 adsorption on alumina takes place on basic sites and is a considerably irreversible adsorption (*16*, *17*). Thus the formation of the SO_2^- radical on the catalyst surface can be visualized in the following way.



On admitting the oxygen to the heated SO_2–alumina system at room temperature, no considerable change in the ESR spectrum of SO_2^- ions was observed. This was unlikely to be due to the oxygen effect on the sulfur radicals (*18*) and acetylenic species (*10*). Dudzik and Cvetanovic (*19*) reported that, when oxygen was admitted at room temperature to zeolite impregnated at 400°C with sulfur, the intensity of the signal assigned to sulfur radicals did not change. This will be caused by the fact that there is no net of interconnecting sulfur in the small-pore (3 Å in diameter) zeolite and hence no movement of free electron to the surface. It is possible that this phenomenon may be true for the present case as well. The broadening of the SO_2^- spectrum in the presence of CO or SO_2 (Fig. 2) may be due to the

TABLE 2

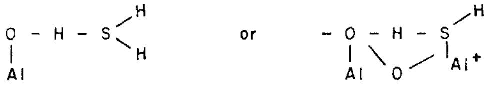
Number of Spins on the Catalyst under Same Condition

Catalyst	Number of Spins
Alumina	8.8×10^{16}
Mo–alumina	16×10^{17}
Co–Mo–alumina	8.4×10^{16}

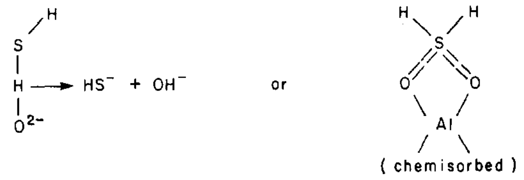
change in the environment of the radical. It may be possible that the presence of CO or SO_2 makes the species structure more rhombic.

On admitting H_2S into the evacuated and heated SO_2–alumina system, the intensity of the SO_2 ion spectrum decreased drastically. On evacuating H_2S the intensity of the ESR signal assigned to SO_2^- species did not change. It is possible that H_2S reacts with SO_2^- ions and forms nonparamagnetic species which are bound strongly. However some of the species of SO_2^- which give the ESR spectra in the presence of H_2S may be of a slightly different structure or may be located in a position where H_2S cannot react with these species at room temperature. The reasons for the reappearance of the SO_2^- ion signal after heating (72 hr) the evacuated H_2S–SO_2–alumina system are not very clear at present.

No ESR signal assigned for sulfur radical was obtained under experimental conditions when H_2S was heated with alumina. The infrared studies of H_2S adsorption (*17*, *20*) suggest that hydrogen bonding produces the following structure.



Irreversible adsorption of H_2S has been reported (*16*, *20*). It is also reported that H_2S adsorption may also take place via O^{2-} sites.



(20)

It is possible that the chemisorbed species are not affected by heating under experimental conditions.

Various investigators have studied both pure and deposited, partially reduced MoO_3 with ESR. It was shown that a signal from pentavalent molybdenum ions is observed in the ESR sample after reduction. In the present case the evacuated and heated supported Mo-oxide or Co–Mo-oxide gave the Mo^{5+} signal even in the absence of hydrogen. Mo^{6+} may be dissociating to Mo^{5+}, and Mo^{5+} to Mo^{4+} on heating as follows.

$$Mo^{+6} \longrightarrow Mo^{+5} + \square_{+}$$

$$Mo^{+5} \longrightarrow Mo^{+4} + \square_{+}$$

where $\square_{+}$ describe a hole with a positive charge. The hole is not seen in ESR (*22*) spectra.

Vorotyntsev *et al.* (*8*) and Maschenko *et al.* (*9*) observed SO_2^- ion species at room temperature when SO_2 was treated with reduced molybdenum–silicate catalyst. They explained that, during adsorption, SO_2 molecules, at room temperature, enter into the first coordination sphere of tetrahedrally coordinate pentavalent Mo ions, as a result of which the unpaired electron is transferred from the Mo^{5+} into the SO_2 molecules, with formation of the corresponding anion radical. In the present case, however, there was no appreciable decrease in the concentration of Mo^{5+} ions at room temperature. On the other hand a large amount of SO_2 was adsorbed in the alumina-supported catalysts. In the case of evacuated and heated alumina-supported catalysts, there could be no trapped electrons, since otherwise SO_2 would react at room temperature to form the stable SO_2^- ions. Not all of the adsorbed SO_2 was converted to SO_2^- on heating. Analogous to the results with TiO_2 (*9*) the majority of the SO_2 molecules are adsorbed in the nonparamagnetic form. On heating for 5 min at 450°C, initially the Mo^{5+} ion concentration decreased slightly after which it increased considerably and then remained constant. The concentration of SO_2^- ions also remained constant. It is possible that Mo^{5+} ions did not play a role in the formation of SO_2^- ions in the supported catalysts.

On admitting O_2 into SO_2–M-alumina system (M = Mo or Mo + Co), the intensity of the SO_2 ions decreased sharply, but, on evacuating O_2, the ESR spectrum of SO_2^- ions reappeared with almost original shape and intensity. Thus the effect of O_2 on the SO_2^- species was reversible. This phenomenon was similar to that observed earlier for the acetylene–copper oxide–alumina system (*10*). It seems that oxygen either formed a nonparamagnetic species with SO_2^- species or was involved in an equilibrium shift between paramagnetic and nonparamagnetic species (*10*). Other possibilities have not been eliminated. The effect of H_2S on the SO_2–M-alumina system was similar to that observed on the SO_2–alumina system. However in this case the concentration of Mo^{5+} ions increased considerably on heating the H_2S–SO_2–M-alumina system. Also, even when excess H_2S was used, no sulfur species were observed or detected.

When H_2S was admitted into the ESR tube containing evacuated and heated molybdenum alumina or Co–Mo–alumina, no appreciable effect on the signal of Mo^{5+} ions was observed. However, the color of the catalysts changed to dark brown. On heating weak signals of paramagnetic sulfur radicals were observed at $g = 2.003$. The concentration of Mo^{5+} ions slightly decreased in the early stages, but on prolonged heating it increased. No appreciable change was observed in the concentration of the paramagnetic sulfur radicals. Sheshadri *et al.* (*12*) favored the formation of tetravalent molybdenum, in sulfiding the Mo–alumina catalyst by H_2S–H_2 mixture, at the expense of Mo^{5+}, and suggested that the principle components of the system were Mo^{4+} and Mo^{5+}. In the present case the technique used for sulfiding was quite different from that used by Sheshadri *et al.* (*12*). Though Mo^{5+} concentration increased considerably on heating the catalyst with H_2S, yet no considerable increase in the intensity of the sulfur radicals was observed. It is doubtful that Mo^{5+} plays any role in the formation of paramagnetic sulfur compounds when the catalyst is heated in H_2S.

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