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An ESR Study of an Al_2O_3-MoO_3-CoO Catalyst in a System with H_2 and Thio-β-naphthol

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This work was planned in order to determine the reaction mechanism of the catalytic, direct desulfurization of organic sulfur compounds on the surface of Al_2O_3-MoO_3-CoO particles. The experimental method consists of quantitative ESR measurements, by means of which the paramagnetic species on the surface of Al_2O_3, Al_2O_3-MoO_3, and Al_2O_3-MoO_3-CoO in the presence and in the absence of H_2 and thio-β-naphthol were studied. As it is expected that, in an ideal and fast-reacting catalytic reaction system, no reaction intermediate can be found because it will be immediately converted to the final product, several artificial reaction systems were investigated in which either one of the reactants, catalyst components, or reaction conditions (*e. g.*, temperature) was deficient. In such deficient systems, the reaction cycle is cut off and some intermediates are expected to accumulate. The paramagnetic species observed were Co^{3+}, Mo^{5+}, thio-β-naphthol^{+}–O^{*2-} or $RS^{+}H$–O^{*2-}, and some species formed on the surface of Al_2O_3, in the temperature region of 20°C—200°C. Mo^{6+} is concluded to be the electron trap to facilitate the formation of $RS^{+}H$–O^{*2-}, Co^{3+} is concluded to oxidize the Mo^{5+} thus formed to Mo^{6+}, and Co^{2+} is concluded to reduce the R–$S^{+}H_2$–O^{*2-} species. The latter then decomposes to H_2S and R·.

The catalytic desulfurization of organic sulfur compounds contained in residual oil using an Al_2O_3-MoO_3-CoO catalyst (to be abbreviated as "AMC catalyst") has been considered to be one of the most promising techniques for lessening the atmospheric pollution. Though several works have been done on the mechanism of the catalysis,[1-4] most of the results obtained are not conclusive. There has been, for example, no clear-cut explanation of the role of each component of the catalyst. One of the present authors previously obtained some information on the nature of the paramagnetic species formed on the surface of various oxides by the ESR method;[5] he found that the results obtained in that work would be useful in analysing the desulfurization reaction with an AMC catalyst.

As organic compounds are processed with the catalyst, the organic reaction intermediates as well as the inorganic reaction intermediates must be determined. Since it is said that a considerable portion of the sulfur compounds in petroleum are

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[1] J.T. Richardson, *Ind. Eng. Chem. Fundam.*, **3**, 154 (1964).

[2] J. H. Ashley and P. C. H. Mitchel, *J. Chem. Soc., A*, **1968**, 2861.

[3] J. M. Lipsch and G. C. A. Schuit, *J. Catal.*, **15**, 163 (1969).

[4] S. Namba, T. Aonuma and T. Shiba, *Kogyo Kagaku Zasshi*, **73**, 38 (1970).

[5] H. Ueda, This Bulletin, **43**, 319 (1970).

in the form of thiophenols and thioethers,[6] thio-β-naphthol (to be abbreviated as "TN") was chosen as the model compound to be added to the catalyst. The analysis of the catalytic reaction system consisting of TN, H_2, and the AMC catalyst has been carried out in the present work by a procedure based upon the results obtained in the previous paper.

The actual desulfurization reaction currently being engineered is at 400°C and at a hydrogen pressure of 200 atm. Industrial operation demands such conditions in order to get a reasonably fast reaction rate, thus securing a quick processing of the oil, mainly for economic reasons. In the present work, however, as the first and easiest possible approach to observe the actual reaction intermediates of the desulfurization reaction, a hydrogen pressure of lower than 1 atm and the highest observation temperature attainable with the attachment to our ESR equipment, 210°C, were used.

Experimental

The oxides and mixed oxides used in this study were all in the form of fine powder. Two different γ-alumina were used. One of them was prepared from aluminum isopropoxide (to be abbreviated as "Ai"), while the other was commercially-available (Shokubai Kasei Co., to be referred to as "Ac"). Al_2O_3-MoO_3 (the content of the latter being 5.44%; to be abbreviated as "AM") was prepared by precipitating ammonium molybdate on the surface of Ac, which was then oxidized in air. The AMC catalyst, consisting 91.38% of Al_2O_3, 5.44% of MoO_3, and 3.18% of CoO, was prepared by precipitating cobalt nitrate on the surface of AM, which was then oxidized in air. All of them were calcined at 500°C for one hour prior to use. The thio-β-naphthol was used after recrystallization. The H_2 used was 99.999% pure (Takachiho Co.) and was used at a pressure above 430 mmHg and at 20°C. Measurements of the ESR were made in the same way as in the previous paper,[5] except for the temperature of the measurements, which were here carried out in the temperature region between 20°C and 200°C. As quantitative ESR measurements are an essential part of this work, particular care had to be taken with them. Quartz tubes which gave almost no ESR signal in the D.C. magnetic field region of 300—5000 gauss and at *x*-band microwave frequencies, and which had almost identical dimensions, were used. As has been reported by Setaka *et al.*,[7] non-resonant microwave absorption by the specimen can affect the magnitude of the output of the microwave detector, which is due to the resonance absorption, even when the input power to the specimen is kept always constant. In the present specimens, all the samples have almost identical non-resonant absorptions, since all of them consist mostly of alumina (more than 90%). The resonant absorption is mostly due to the minor part of the sample components (less than 10%) existing on the surface. Therefore, the consideration of the non-resonant microwave absorption has been almost unnecessary in the present measurements. However, each of the intensities observed in the present work was calibrated by using the intensity of one of the lines from a Mn^{2+} ($g=2.1401$) sample which was placed inside the cavity, but not inside the sample section, which is inside a Dewar system. As this absorption line has a ralatively narrow line width compared to those of the absorption lines observed from the present specimens, a relatively slow sweeping rate of the magnetic field (0.16 gauss/sec) was necessary in order to record the intensity of this line accurately. The temperature variation of the sample also changes the non-resonant absorption of microwave. This, however, was the same value at 20°C and at 200°C under the present measuring conditions. The warming up of the 100 kHz lock-in amplifier was necessary to get a constant and stable amplification of the signal.

Results

As it is extremely difficult to measure ESR absorption under conditions identical with those actually employed in an engineering desulfurization reaction, it might be wise to start the research by examining the catalyst by conventional measurements. As will be discussed later, the quality of information obtained by conventional (meaning, at room temperature, and either in a vacuum or in atmospheric air) measurements are not as straightforward as might be expected. Figures 1a—1c illustrate the effects of the temperature of measurements, t_m, on the ESR intensities. In Fig. 1a, the intensity of the ESR line with $g=1.9328$ (for Mo^{5+}) of the sample consisting of AM and TN in a vacuum is shown. The sample which had not been subjected to any

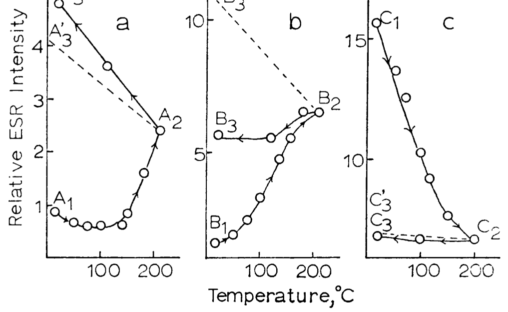

Fig. 1. Relative (the relative scale is not the same as that for the tables) ESR absorption intensities of Mo^{5+} and thio-β-naphthol$^+$-O^{2-} during a heating cycle. The temperature means t_m or the temperature at which measurements were made. a, Mo^{5+} in Al_2O_3-MoO_3 with thionaphthol and in vacuum. $g=1.9328$. b, thionaphthol$^+$-O^{2-} in the specimen same as a. $g=2.0036$. c, thionaphthol$^+$-O^{2-} in Al_2O_3-MoO_3-CoO with thionaphthol and in H_2, $g=2.0036$.

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6) B. T. Brooks in "The Chemistry of Petroleum Hydrocarbons," B. T. Brooks, C. E. Boord, S. S. Kartz, Jr., and L. Schmerling, eds., Vol. 1, Reinhold Publ. Co., New York, N. Y. (1954), p. 79.

7) M. Setaka, K. M. Sancier and T. Kwan, *J. Catal.*, **16**, 44 (1970).

thermal treatment before was measured at 20°C (point A_1), and then the t_m was elevated to as high as to 210°C (point A_2), after which the t_m was decreased to as much as to 20°C (point A_3). The A_3' point shows the value which is expected from the value for A_2 point by Curie's law. Figure 1b indicates the temperature variation in the intensity of the ESR line with $g=2.0036$ (for TN^+-O^{*2-}), for the specimen identical with that for Fig. 1a during one heating cycle. The B_1, B_2, B_3, and B_3' points correspond to A_1—A_3' in Fig. 1a. Figure 1c indicates the same quantity as does Fig. 1b for the specimen consisting of AMC, TN, and H_2. The C_1, C_2, C_3, and C_3' correspond to A_1—A_3' in Fig. 1a. These results indicate that the thermal history of the specimen, as well as the t_m value, strongly affects the concentration of these species on the surfaces of catalyst particles. In Fig. 2, the ESR spectra of alumina powder, Ai, are shown. The figure indicates that some unexplained paramagnetic species exist on the surface of the alumina specimen, which was supposed to be highly pure except for a small amount of organic contamination left when it was prepared from aluminum isopropoxide by decomposition. It is also shown that some new paramagnetic species are formed at higher temperatures, and that these species disappear when cooled to 20°C again. In Fig. 3, the ESR spectra of AM powder are shown. It will be seen that a new absorption appears at $g=2.1$ if the sample is observed at 200°C. In Fig. 4 the ESR spectra of AMC powder at 20°C are shown. In the spectra the broad absorption with $g=2.1$—2.2 which was found in Ai and AM at 20°C, is not found at all, or it is relatively very weak. In Fig. 4b and 4c, the part of the spectra where the absorption of R^+O^{*2-} is to be seen is not shown because the absorption in these parts is too strong to be shown together with the entire spectrum. It will be seen that the absorption with $g=2.2910$ appears if TN is added to the AMC powder in a vacuum, and that this species disappears when H_2 is introduced into the sample tube. In Fig. 5, the ESR spectra of AMC powder at 200°C are shown. a, b, and c correspond to those values in Fig. 4. The broad absorption with $g=2.1$—2.2, which was found in Fig. 2 and Fig. 3, but which was not found in Fig. 4, again appears in this figure. The absorption with $g=2.2910$, previously found only in Fig. 4b, is again found in Fig. 5b with a somehow decreased g-factor of 2.1428. The temperature dependence of the g-factor for this line is shown in Fig. 6. In Fig. 7, the effects of N_2O and NH_3 on the intensities of the line, the g-factor of which is shown in Fig. 6, are shown. The solid curves indicate those in N_2O, while the dotted curves indicate those in NH_3. It will be seen that N_2O intensifies this line at higher temperatures, while NH_3 cancels it. The amplitudes of the curves have been calibrated with one of the Mn^{2+} absorption lines. In Tables 1—4, the relative ESR intensities of the lines with $g=2.0036$ and $g=1.9328$, observed with the catalyst components of x, y, and z at 20°C and at 200°C, are shown. The relative intensities for the line with

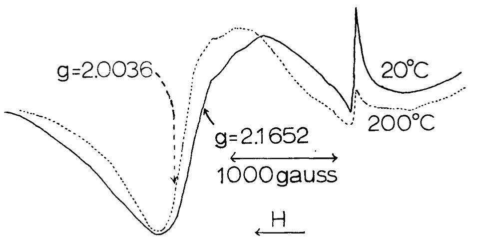

Fig. 2. ESR spectra of γ-alumina prepared from aluminum isopropoxide. Measurements were made at 20°C and at 200°C. Sample in vacuum.

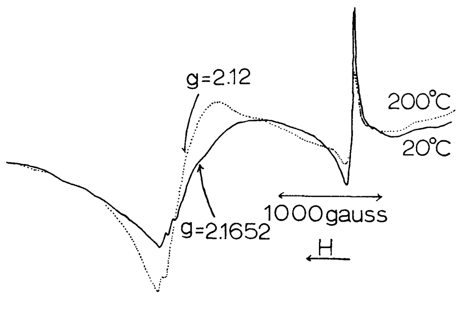

Fig. 3. ESR spectra of Al_2O_3-MoO_3. Measurements identical to Fig. 2.

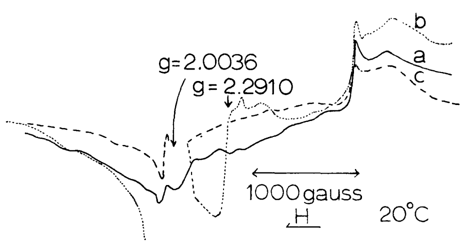

Fig. 4. ESR spectra of Al_2O_3-MoO_3-CoO with and without thio-β-naphthol at 20°C. a, with neither thionaphthol nor H_2. b, with thionaphtol and in vacuum. c, with thionaphthol in H_2.

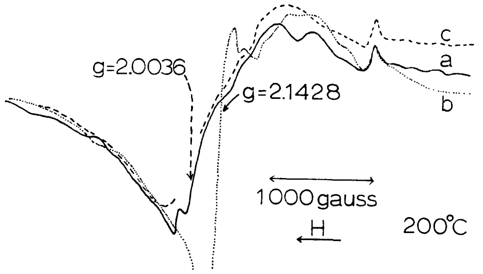

Fig. 5. ESR spectra of Al_2O_3-MoO_3-CoO with and without thio-β-naphthol at 200°C. a, b, and c are corresponding to those in Fig. 4.

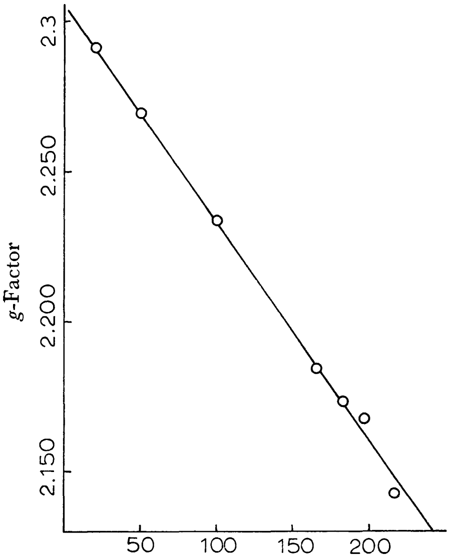

Fig. 6. The temperature dependence of the g-factor of the ESR absorption from Co^{3+} on the surface of a catalyst particle.

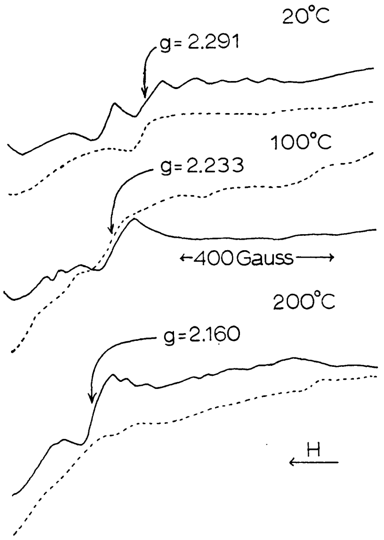

Fig. 7. ESR absorption from the sample consisting of AMC-TN in the region for g=2.0 to 3.0. The temperatures indicated are those of the measurements. The dotted curves are those in NH_3 while the solid curves are those in N_2O, both at 400 mmHg/20°C.

Table 1. Relative ESR Intensities[a)] of thionaphthol$^+$ —O^{2-} at 20°C.[b)]

Oxide components			Additive	Gas	Intensity	Data number
x	y	z				
Al_2O_3			Thio-β-naphthol		11700	1
Al_2O_3			Thio-β-naphthol	H_2	8900	2
Al_2O_3	MoO_3		Thio-β-naphthol		1500	3
Al_2O_3	MoO_3		Thio-β-naphthol	H_2	1183	4
Al_2O_3	MoO_3	CoO	Thio-β-naphthol		22500	5
Al_2O_3	MoO_3	CoO	Thio-β-naphthol	H_2	16766	6

Table 2. Relative ESR Intensities of thionaphthol$^+$ —O^{2-} at 200°C.

Oxide components			Additive	Gas	Intensity	Data number
x	y	z				
Al_2O_3			Thio-β-naphthol		5500	7
Al_2O_3			Thio-β-naphthol	H_2	5246	8
Al_2O_3	MoO_3		Thio-β-naphthol		6610	9
Al_2O_3	MoO_3		Thio-β-naphthol	H_2	5316	10
Al_2O_3	MoO_3	CoO	Thio-β-naphthol		2800	11
Al_2O_3	MoO_3	CoO	Thio-β-naphthol	H_2	6800	12

a) The relative scale used in the tables 1,2,3, and 4 is exactly the same and is consistent between Table 1 and Table 2, and between Table 3 and Table 4. It is also possible, if desired, to compare the values in Table 1 and Table 2 with the values in Table 3 and Table 4 provided that the line width difference is taken into account.

b) The values in Table 1 and Table 3 correspond to A_1, B_1, and C_1 in Fig. 1 and not to A_3, B_3, and C_3 in Fig. 1.

TABLE 3. RELATIVE ESR INTENSITIES OF MO^{5+} AT 20°C.

Oxide components x	y	z	Additive	Gas	Intensity	Data number
Al_2O_3	MoO_3				160	13
Al_2O_3	MoO_3			H_2	80	14
Al_2O_3	MoO_3		Thio-β-naphthol		9000	15
Al_2O_3	MoO_3		Thio-β-naphthol	H_2	17900	16
Al_2O_3	MoO_3	CoO			80	17
Al_2O_3	MoO_3	CoO		H_2	30	18
Al_2O_3	MoO_3	CoO	Thio-β-naphthol		570	19
Al_2O_3	MoO_3	CoO	Thio-β-naphthol	H_2	433	20

TABLE 4. RELATIVE ESR INTENSITIES OF MO^{5+} AT 200°C.

Oxide components x	y	z	Additive	Gas	Intensity	Data number
Al_2O_3	MoO_3				240	21
Al_2O_3	MoO_3		Thio-β-naphthol		10956	22
Al_2O_3	MoO_3		Thio-β-naphthol	H_2	13349	23
Al_2O_3	MoO_3	CoO			240	24
Al_2O_3	MoO_3	CoO	Thio-β-naphthol		10000	25
Al_2O_3	MoO_3	CoO	Thio-β-naphthol	H_2	6400	26

temperature-dependent g-factor have not been listed in the tables because of the irregular and temperature-dependent line shape.

Discussion

In the previous paper it was concluded that the species giving rise to the ESR absorption with $g=2.002$—2.004 was most properly written as R^+O^{*2-}, where R signifies the additive with a π-electron orbital and where O^{*2-} signifies some active surface oxygen anion at which the chemisorption of R takes place. The species for the ESR line with $g=1.9328$ has been concluded to be Mo^{5+}. The species for the ESR line, with a temperature-dependent g-factor as is shown in Fig. 6, has appeared in this study for the first time. It is most likely described to be Co^{3+} for the following reasons: (a) It is observed only in the specimen which has CoO as an oxide component. The unpaired electron may, therefore, be supposed to belong to the cobalt atom. (b) It is observed only when TN is added to the AMC powder. As TN forms TN^+-O^{*2-}, it may be concluded that the unknown species is a product of this reaction: $Co^{2+}+TN^+\text{-}O^{*2-}\rightarrow Co^{3+}+TN\text{-}O^{*2-}$. (c) It disappears if H_2 is introduced. (d) It disappears if NH_3 is introduced and the specimen is heated to above 100°C, but it is intensified if N_2O is added and the specimen is heated at above 100°C, as is shown in Fig. 7. As has previously been shown by one of the present authors,[5,8] NH_3 destroys a hole or an oxidized state, while N_2O eats a captured or solvated electron or an anion. The reactivity of this unknown species, as has been indicated above, is just like a hole. A hole formed in Co^{2+} should be a Co^{3+}. It can not be a free Co^{3+}; it would more properly be shown as $(Co\text{-}O_n)^{-(2n-3)}$ and so on, but in the present work the covalent bonds or molecular orbitals among the surface ions are neglected or are not discussed. For this reason, the "hole" found in some species which include at least a Co^{2+} ion is conveniently written as Co^{3+} in this paper. Therefore, it must be noted that the Co^{3+} postulated in this paper has not been obtained by the analysis of a single crystal spectrum, but has been concluded from the reactivity only; therefore, it must not be understood as having validity beyond the fact that it is a convenient nomenclature for a hole in a Co^{2+}. However, the fact that a surface species cannot be studied with a single crystal, or in an oriented state, and the fact that these surface species exhibit considerable anisotropy in their ESR spectra, both lead to the conclusion that an exact determination of the structures of these surface species by an analysis of the ESR spectra is impossible; therefore, the method employed in this report, reaching a conclusion after examining the reactivities of the species under investigation, is the only possible way to proceed.

Co^{3+}, $(3d)^6$, in an octahedral crystal field can be either paramagnetic or diamagnetic, depending on

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[8] H. Ueda, This Bulletin, **41**, 2578 (1968).

the strength of the field.[9,10] In the present AMC specimen, "Co^{3+}" must be formed from the Co^{2+} which is deposited on the surface of an Al_2O_3 particle, together with MoO_3; therefore, the crystal field surrounding "Co^{3+}" will not be a strong octahedral field, and will probably be of a C_{4v} or of C_{4d} symmetry. For this reason, paramagnetism can well be expected from the "Co^{3+}" in the present specimen. The temperature dependence of the *g*-factor in Fig. 6 would indicate a labile crystal field around this species; therefore, it is good evidence for rejecting the existence of a strong octahedral crystal field surrounding "Co^{3+}". A *g*-factor larger than 2.0 is to be expected from the $(3d)^6$ configuration. Generally speaking, the ESR spectrum from a d^6 ion in a symmetric crystal field is broadened or easily saturated, and is observed only at low temperatures and with a low microwave power. Only a few spectra, *e.g.*, that of Fe^{2+}, has been recorded. However, the effect of an asymmetric crystal field, such as that on a surface, on the ESR spectra of d^n metal ions has not been explored much; therefore, the experimental results obtained for "the ions in a symmetric crystal field or in a bulk state" are not always useful for analysing the spectra on the basis of the species on a surface.

It seems that cobalt affects the nature of the catalyst surface greatly. Evidence for this is the spectra in Fig. 4. The ESR absorption found in Fig. 2 and Fig. 3, which is due to some species on the alumina surface, has been almost totally cancelled by cobalt ions. The chemisorption of TN is greatly enhanced by cobalt ions. The datum No. 5, when compared to No. 3 in Table 1, shows that the ESR intensity at 20°C due to TN^+–O^{2-} is increased 15 times if cobalt ions are added to the surface of AM. These tendencies are not observed at 200°C; see the data No. 11 and No. 9, in Table 2, and B_1 and C_1 in the b and c of Fig. 1. These facts indicate that the cobalt ions are located on the catalyst surface so as to make it easy for foreign ligands to coordinate with them or to escape from them.

In the previous paper it has been established that Mo^{6+} ions act as electron acceptors on the surface, themselves being reduced to Mo^{5+}. By definition, the word "catalyst" signifies that, though it promotes a chemical reaction, there can be no overall change in the amount and structure of the catalyst itself during and after the reaction, if the circumstances are ideal. If so, it is quite hopeless to observe any reaction intermediate, at least on the side of the catalyst, if the catalytic reaction is proceeding in an ideal manner, except in a case where the catalyst itself is the intermediate. The accumulation of the intermediate is, then, to be expected only when some of the reaction components or some of the reaction conditions are lacking. The intensity of the ESR absorption is determined by the following formula:

$$\text{ESR intensity of a sample} = (x, y, z \text{ R and G})_{g, t_m}$$

if we ignore the history of the specimen. In this formula, *x*, *y*, and *z* are the oxide components (see Tables 1 to 4), R is an added compound such as TN, G is the gas added to the sample tube, and *g* is the *g*-factor of the line being measured. A sample have many absorption lines with varied *g*-factors and with different intensities. The effect of one of the variables, say, z_0, can be judged by comparing $(x, y, z=z_0, \text{R and G})_{g, t_m}$ with $(x, y, z=\text{O}, \text{R and G})_{g, t_m}$. For example, the datum No. 26 in Table 3 is for $x=91.38\%$ Al_2O_3, $y=5.44\%$ MoO_3, $z=3.18\%$ CoO, R=TN at the concentration of 0.2 mM/g of oxide, $G=H_2$ at 450 mmHg/20°C, $g=1.9328$ (the absorption by Mo^{5+}), and $t_m=200°C$, while the datum No. 23 is for the variables almost identical with those for the datum No. 26 except that no CoO was added to the system (accordingly, the value of $x=94.54\%$); in other words, $z=0$. The ratio of these two data, 6400/13349=0.48, can be accepted as indicating that Co^{2+} reduces the amount of Mo^{5+} at 200°C in the presence of H_2.

By similar arguments, it is possible to write the reaction cycle shown in Fig. 8. The equilibrium between charged species on the surface of oxide particles has been discussed in previous papers.[5,11] The process (1) in Fig. 8 has already been used to describe how "Mo^{6+} behaves as an electron trap in the formation of R^+O^{*2-} from RO^{*2-}." The process (2) is the reduction of Mo^{6+} by H_2, which is confirmed by comparing the datum No. 23, Table 4, with the datum No. 22. The process (3) can, in other words, be written as $Mo^{5+}+Co^{3+}\rightarrow Co^{2+}+Mo^{6+}$. Comparisons of the datum No. 25 with the datum No. 22, Table 4, and especially No. 19 with No. 15, Table 3, and No. 20 with No. 16, indicate that added cobalt oxide reduces the amount of Mo^{5+}. Such an effect of cobalt oxide can be explained only by the action of the Co^{3+} formed. Co^{3+} was observed only when TN was added in the absence of H_2 (see Fig. 4 and Fig. 5). Without H_2, the $H_2+Co^{3+}\rightarrow H^++H+Co^{2+}$ process does not occur, and so an observable amount of Co^{3+} is accumulated. It is also possible that, in a vacuum, the $Mo^{6+}+Co^{2+}\rightarrow Mo^{5+}+Co^{3+}$ equilibrium moves to the right, No. 25 and No. 26. The overall flow of electrons by the processes (1) and (3) can be seen in Table 1 and Table 3. The AM–TN system in a vacuum give the ESR intensity of 1500 at 20°C and for $g=2.0036$, the datum No. 3, which is increased to 22500 by the addition of cobalt to the above system, the datum No. 5. On the contrary, the AM–TN

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[9] J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, **53**, 601 (1957).

[10] C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill Book Co., New York, N. Y. (1962), p. 274.

[11] H. Ueda, *Can. J. Chem.*, **64**, 891 (1968).

system in a vacuum gives the ESR intensity of 9000 at 20°C and for $g=1.9328$, the datum No. 15, which is decreased to 570 by the addition of cobalt to the above system, the datum No. 19. The fact that, at lower temperatures, where the reactions of cobalt ions with H_2 and RS^+O^{*2-}–H are relatively slower, cobalt ions decrease the amount of Mo^{5+} and simultaneously increase the amount of TN^+–O^{*2-}, fits very well with the scheme. Though the electron-transfer reaction (5) can be postulated for the reason stated above, the products of the reaction (6) cannot be determined by the present results. As the species RS^+H–O^{*2-} has an unpaired electron, it is very likely that it will react with a hydrogen atom to yield RS^+H_2–O^{*2-}, which is then neutralized by the step (5) and decomposes to H_2S and R·. The R·, which may be $C_{10}H_7$· in the present case, will subsequently react with H_2 and/or with another R· to form some hydrocarbons.

The vast difference between the present conditions of ESR measurements, 200°C and 0.6 atm pressure of H_2, and the engineering conditions of the desulfurization reaction, 400°C and a 200 atm pressure of H_2, would lead one to suspect the suitability of the present ESR experiments for analyzing the reaction scheme in the engineering desulfurization. However, there is actually no reason to conclude that the reactions occurring under these two sets of conditions are contrary in nature, though the rates of reaction are enormously different. The present authors are planning to fill this gap by further studying this subject; the effect of the pre-treatments with H_2 and H_2S on ESR spectra is particularly interested.

In the engineering desulfurization, the oxide is pre-sulfurized. The actual desulfurization is, therefore, carried out by the sulfide catalyst. As the present ESR measurements are made with oxide powders, this difference must be considered. Since oxygen and sulfur belong to the same group in the periodic table of elements, the VIb group, and since both have the same number of *p*-electrons in the outermost shell, the species R^+O^{*2-} should have its sulfide version, R^+S^{*2-}, on the sulfide particles. Therefore, it is not likely that the difference between S^{2-} and O^{2-} essentially alters the reaction scheme on the surface of these particles. The fact, that, in the engineering operation, the pre-sulfurization is made with H_2 and the residual oil diluted with kerosene shows that desulfurization is actually going on with the oxide catalyst.

It may often happen that an intermediate or an intermediate-like species which is detected only after a lot of time and labor proves to be not the essential component of the reaction system under investigation, but one of the by-product of the reaction. The reaction cycle found, Fig. 8, might be one such off-route phenomenon. The first step of the reaction, the formation of the cation-like species, might be untrue; instead the formation of an anion might be the real first step. The discussion in the previous paper led to the conclusion that the formation of an anion is not likely on an oxide surface. The evidence of the succeding steps has already been discussed.

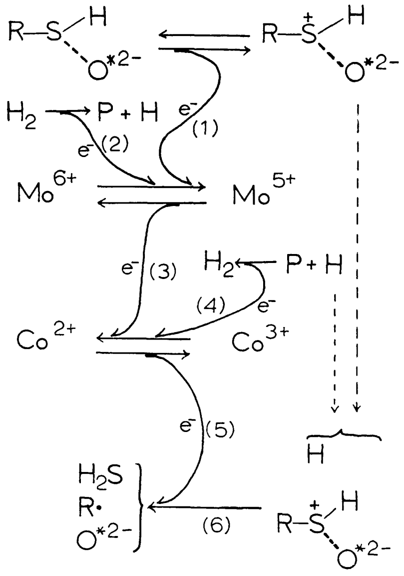

Fig. 8. The catalysis cycle of the desulfurization reaction of thio-β-naphthol with H_2 on the Al_2O_3-MoO_3-CoO catalyst particles. R signifies $C_{10}H_7$– group. S-O^{*2-} signifies the chemisorbed state. About O^{*2-}, see text and Ref. (5). P signifies a proton.

Another species which it might be necessary to consider as a component in the desulfurization cycle shown is Mo^{4+}. As Mo has the electronic configuration of (Krypton shell)$(4d)^5(5s)^1$, it can have four oxidation states, 3+, 4+, 5+, and 6+. Actually, MoS_2 is accumulated on the catalyst surface during desulfurization. Therefore, Mo^{5+}–Mo^{4+} might play some important role in the desulfurization cycle instead of Mo^{6+}–Mo^{5+}. The Mo^{4+} ion is paramagnetic in an octahedral crystal field, and it may or may not have paramagnetism in a field of lower symmetry.[10] In the present work, no ESR evidence for Mo^{4+} was found. This fact indicates that either the absence of the Mo^{4+} ions or the presence of the crystal field surrounding the Mo^{4+} ion, which makes the Mo^{4+} ion diamagnetic. However, the conclusions in the previous paper indicated the importance of Mo^{6+} as an electron trap on the surface of oxides. For this reason, it is unlikely that Mo^{4+} is an essential component of the catalysis cycle. If this is true, then it follows that the deactivation of the catalyst is due to the accumulation of Mo^{4+} on the catalyst surface.

Among the ingredients of the catalyst, the most important ingredient is alumina. The activity and the life of a catalyst is actually decided with it. In the reaction scheme (Fig. 8), this important role of alumina appears in the form of O^{*2-}, indicating the active oxygen anion where the chemisorption occurs. The difference between a good alumina and a bad one lies not in the quality of their properties, but in the quantity of their properties; some quantitative measurement of the ESR absorption by the alumina surface might, therefore, be helpful in explaining the difference between good and bad carriers.

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