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The Paramagnetic Species Found on the Surface of Al_2O_3–MoO_3–CoO Particles

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The paramagnetic species on the surface of Al_2O_3–MoO_3–CoO catalysts were studied. The ESR spectra of unsupported oxides CoO, Co_2O_3, Co_3O_4, $CoAl_2O_4$, and $CoMoO_4$ were first studied. The ESR spectra of supported cobalt oxides were also studied. The spectra of supported oxides were different from those of the unsupported oxides, indicating that the supported cobalt ions are in a different state from those in unsupported oxides. The two-phase theory for the supported cobalt ions interprets the experimental results well. The Co^{2+} and Co^{3+} concentrations on the surface were estimated from ESR results. The desulfurization rate of Al_2O_3–MoO_3–CoO catalysts were measured together with the surface concentrations of Co^{2+}, Co^{3+}, Mo^{5+}, and thionaphthol$^{+}O^{*2-}$ surface cation complex when H_2 and thionaphthol were added to the surface. A simple correlation between the desulfurization rate and the concentrations of these paramagnetic species was found.

INTRODUCTION

Various studies have been made of the magnetic and other properties of Al_2O_3–MoO_3–CoO catalysts. Richardson studied the effects of the Co:Mo ratio on the surrounding environment of both ions and determined the optimum Co:Mo ratio at which activity is the highest (*1*). According to him the activity mainly belongs to MoO_3 promoted by nonreducible cobalt. Lipsch and Schuit studied the compounds formed on the surface of the catalyst and the stereochemical distribution of the negative ions around Mo and Co ions (*2*, *3*). They concluded that $CoMoO_4$ exists in two forms and that the Mo^{6+} ion exists in an octahedral site of alumina. According to ir data they concluded that cobalt exists as $CoAl_2O_4$, but the active role of cobalt was concluded to be unclear. Mitchell and Ashley, on the other hand, studied the incorporated states of Co and Mo ions onto an alumina surface by means of uv, visible and ir absorption spectroscopy, and magnetic susceptibility measurements (*4*, *5*). They showed that cobalt, when it is incorporated from a dilute solution, is adsorbed at tetrahedral sites, and if it is incorporated from a concentrated solution, is attached to the octahedral sites. It was also reported that in the 2.77% Co, 8.03% Mo, and 80.0% Al_2O_3 catalyst, 50% of Co is in the tetrahedral site and the remaining 50% is in the octahedral site. The present authors studied the mechanism for the desulfurization reaction by Al_2O_3–MoO_3–CoO catalyst after quantitatively analyzing the ESR intensities obtained (*6*). Compared to the Al_2O_3–MoO_3 system, few ESR studies of this catalyst have appeared because of the more complicated nature of ESR spectra caused by cobalt ions. As for the Al_2O_3–CoO system, Tomlinson has studied its magnetic susceptibilities (*7*). In the present work, the authors tried to find the correlation between the past results and the ESR data obtained in this study.

METHODS

Preparations. Commercially used alumina (Al_2O_3) from Shokubai Kasei Co. was used. Its ESR spectra are almost identical to those obtained from the one prepared from the decomposition of purified aluminum isopropoxide. $CoMoO_4$ was obtained by heating a mixture of $CoNO_36H_2O$ and MoO_3 to 1100°C. $CoAl_2O_4$ was obtained by heating a mixture of Al_2O_3 and CoO at 1000°C. CoO was obtained by decomposing $CoCO_3$ at 450°C in a vacuum. $CoCO_3$ was obtained by mixing a $CoNO_3$ solution and a CO_2-saturated $NaHCO_3$ solution. Co_2O_3 was a special reagent grade from Junsei Pure Chemicals and Co., Ltd. Co_3O_4 was reagent grade, Kishida Chemicals and Co., Ltd. For CoO supported on Al_2O_3, cobaltous salts, sulfate, nitrate, acetate, formate, bromide, and $CoSO_4(NH_4)_2SO_46H_2O$ were dissolved in water to the concentration of 6.87 mM/20 ml. Alumina particles, 10–20 mesh, were dipped in the solution and kept there for 2 hr. Then the alumina particles were removed from the solution and dried on filter papers, by soft pressing. Then they were dried and calcined, the details of which are described later. The CoO content in the sample thus prepared is about 2.0% in the case of $CoNO_3 \cdot 6H_2O$. The Al_2O_3–MoO_3–CoO catalyst was prepared thusly: Ammonium molybdate was first supported on alumina and then it was calcined at 550°C. Then $CoNO_3$ was supported on it and then the resulting catalyst was calcined at 550°C. The catalysts were powdered to 100 mesh to adsorb thio-β-naphthol more efficiently.

ESR measurements. A JES-3BX-type ESR spectrometer (x-band) was used. A quartz sample tube of 0.4-mm thickness and 5.0 mm o.d. was filled with the sample. The temperature of measurement was 20°C. The microwave frequency was read by a cavity wavemeter. The strength of the magnetic field was measured by a Hall-element type gaussmeter (Yokogawa type 3251), the output of which was recorded on the same chart paper as the ESR signal. The ESR intensity was calibrated with one of the lines (with the lowest resonant field) of Mn^{2+} ion dispersed in MgO, which is fixed inside the sample cavity, by sweeping the magnetic field at the rate of 0.16 gauss/sec. The microwave incident power to the sample cavity was approximately 15.0 mW.

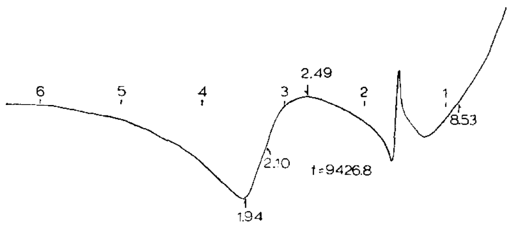

Fig. 1. ESR spectrum of alumina used. The numbers on the horizontal axis indicate the strength of the magnetic field, $\times 10^3$ G. f is the microwave frequency used. The figures with an arrow indicate $h\nu/\beta H$ values. The ref = 38.

Determination of the desulfurization rate. Catalysts were charged in an autoclave with Kafuji residue oil and the reaction was carried out at a hydrogen pressure of 200 atm and 400°C for 100 hr.

Results

The ESR of unsupported oxides. In Fig. 1, the ESR absorption of the alumina carrier used is shown. The sample was calcined at 550°C prior to use, but the same result was obtained when the same sample was evacuated to 10^{-4} mm Hg at 400°C. All the ESR spectra are shown in the form of the first derivative of the true resonance curve. The figures with an arrow pointing to the position on the curve are all in the unit of $h\nu/\beta H$ or in a g-factor unit. The values shown in the figure caption as ref = are the intensity of the Mn^{2+} reference line recorded together with the spectrum. In Fig. 2, ESR absorption of CoO, Co_2O_3 and Co_3O_4 when 40 mg of each was placed in the center of the resonance cavity is shown. In Fig. 3, the ESR spectra of $CoAl_2O_4$ and $CoMoO_4$ are shown.

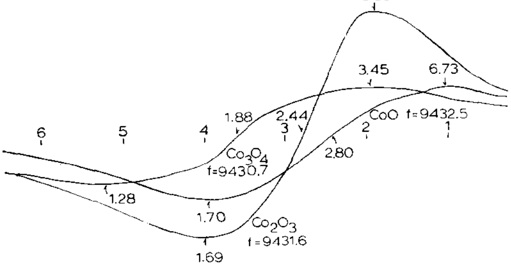

Fig. 2. ESR spectra of CoO, Co_2O_3, and Co_3O_4. The ref = 8(CoO), 17(Co_2O_3), and 70(Co_3O_4).

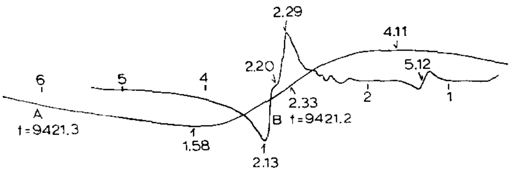

FIG. 3. ESR spectra of $CoAl_2O_4$(A) and $CoMo_4$(B). The ref = 34(A) and 25(B).

The ESR of supported oxides. When CoO is supported on alumina, the ESR spectra obtained greatly depends on the treatment of the sample such as drying and calcination. All of the 130 spectra observed by using different cobalt salts and after various ways of drying and calcination correspond to one of the spectra shown in Figs. 4–6. In this study the effect of drying and calcination on the ESR spectra were surveyed. Figure 4A was observed when $CoNO_3$ was supported on alumina, dried in a vacuum at 20°C, and then sealed in a glass ampoule at 10^{-4} mm Hg pressure, heated for 1 hr at 400°C. After cooling it was again dried in a vacuum at 200°C. Figure 4B was obtained when cobalt acetate was supported on alumina, dried in air or in a vacuum, partly decomposed at 100–300°C, immersed in the cobalt acetate solution again, then dried in a similar way, and finally heated at 700°C in air. The second contact with the acetate solution was necessary to cover all the alumina surface with cobalt ions. Figure 5B was obtained when cobalt was supported on alumina from $CoSO_4$ solution, and then dried and decomposed in air at 100, 200, 300, 400 and 500°C, having been kept at each temperature for 1 hr. The intensity of Fig. 5B is some 9 times as strong as that of Fig. 5A. Cobalt salts other than sulfate can also give an identical spectrum. Figure 6A was obtained when cobalt was supported on alumina from $Co(CH_3COO)_2$ solution or $CoNO_3$ solution. After drying in air, the alumina obtained was placed in a 550°C oven and was kept at 550°C for 1 hr. Other salts also gave an identical spectrum. Raising the temperature quickly to 550°C is necessary to obtain this spectrum. Figure 6B was obtained when the sample giving rise to Fig. 6A was reduced with H_2 (414 mm Hg, at 20°C) and then was kept at 450°C for 17 hr. Figure 6B is a very broad spectrum, and so it can be regarded as a mixture consisting of Figs. 4 and 5.

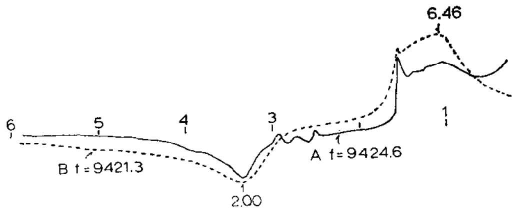

FIG. 4. ESR spectra of cobalt ion supported on alumina. A: treated at 400°C in an evacuated and sealed tube. B: treated at 700°C in air.

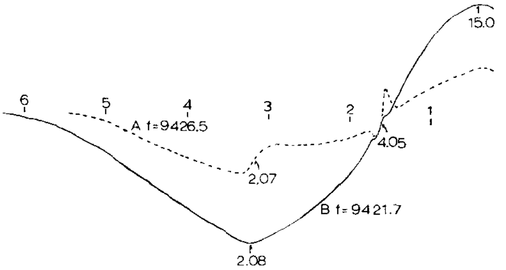

FIG. 5. ESR spectra of cobalt ion supported on alumina. A: treated at 250°C in an evacuated sealed tube. B: heating temperature gradually increased from 100 to 500°C in air. The ref = 37(A) and 8.5(B).

The ESR of catalysts. The ESR spectra of the powdered catalysts with thio-β-naphthol, which was adsorbed from benzene solutions, and H_2 (300 mm Hg) are shown in Fig. 7. Figure 7A is obtained from

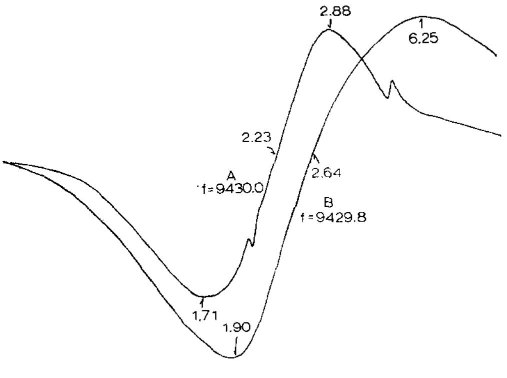

FIG. 6. ESR spectra of cobalt ion supported on alumina. A: $Co(CH_3COO)_2$ was supported on alumina and calcined at 550°C; B: after reduction in H_2. The ref = 18(A) and 34(B).

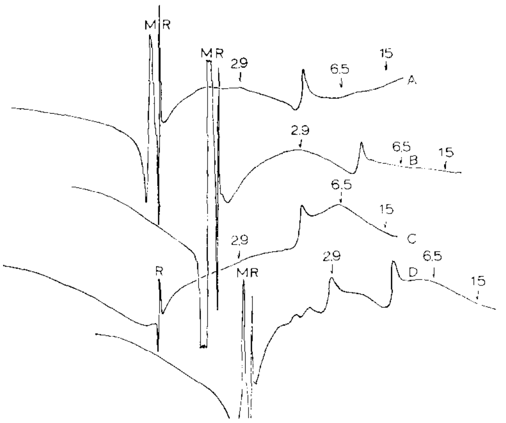

FIG. 7. ESR spectra of Al_2O_3–MoO_3–CoO catalyst with H_2 and thio-β-naphthol. The numbers indicate the positions of the expected peaks in g-factor units. M is for Mo^{5+} and R is for R^+O^{*2-} ions. Letters A–D are defined in the text.

sample No. 1 in Table 1, 7B from the sample No. 7, 7C from the sample No. 3, and 7D is from the sample No. 9.

Desulfurization rate. The results of the desulfurization rate measurements are shown in Table 1.

DISCUSSION

According to Selwood, pure CoO and Co_3O_4 are paramagnetic (*8*). Considering this fact and the intensity of the ESR signal obtained, it is concluded that the ESR signals obtained by supported cobalt oxides are due to the unpaired electrons distributed in the bulk. Though the cobalt ions supported on alumina exhibit several different ESR spectra, it is concluded that any of the ESR spectra of the pure oxides does not interpret the spectra of the supported cobalt oxides. The ESR spectrum of $CoAl_2O_4$ does not interpret them, either. The results in Figs. 1–6 indicate that supported cobalt ions are not in the type of environment which exists in CoO, Co_2O_3, Co_3O_4, $CoAl_2O_4$, or $CoMoO_4$.

The fact that ESR absorption of supported molybdenum ion, Mo^{5+}, has a g-factor of 1.93 is well known (*9–11*). Compared to it, almost no reports have appeared with cobalt ions. Selwood postulated the existence of two phases in which cobalt ions exist on the surface of an alumina carrier, though he later denied it (*12*). What he postulated is the existence of an infinitely diluted state and an infinitely concentrated state of the oxides which are supported. However, Tomlinson and his coworkers studied the magnetic susceptibilities of the supported cobalt oxides and showed that there are two phases, δ and β, in which the cobalt ion exists (*7*). The δ phase is the well dispersed phase and the β phase is the nondispersed phase. He also showed that in the case of the NiO–Al_2O_3 system the same phenomena can be observed, while the NiO–SiO_2 system has the β-phase only (*13*). Ashley and Mitchell, by means of absorption spectra and magnetic susceptibility measurements, studied the environment of Co and Mo ions in Al_2O_3–MoO_3–CoO catalysts, and showed that the cobalt ions occupied two sites on the surface (*4*, *5*). They also showed that octahedral Co^{2+} can be oxidized to Co^{3+}, while the tetrahedral Co^{2+} cannot be oxidized.

TABLE 1
DESULFURIZATION RATES OF THE CATALYSTS USED

Catalyst	CoO %	MoO_3 %	Co/Mo	Co^{2+}/Mo^{5+}	DS rate %
No. 1	0.38	6.50	0.112	0.050	57.4
No. 2	3.09	4.25	1.396	10.0	72.5
No. 3	5.74	5.17	2.132	26.5	72.6
No. 4	0.76	8.67	0.168	0.034	69.8
No. 5	2.50	8.62	0.557	0.191	80.3
No. 6	5.49	8.98	1.175	3.281	77.9
No. 7	1.09	12.90	0.162	0.022	65.0
No. 8	2.57	14.09	0.350	0.096	78.4
No. 9	4.03	11.99	0.645	0.213	78.9

From the above considerations, there are only three possible states of cobalt ions to be found on an alumina surface: $Co^{2+}(T)$, $Co^{2+}(O)$, and $Co^{3+}(O)$, where (O) indicates an octahedral and (T) indicates a tetrahedral environment. The cobalt ion which gives ESR spectra in Fig. 4 is concluded to be $Co^{2+}(T)$. As the specimen for this spectrum had been completely degassed before heating, no oxidation should have occurred and the oxidation state should be +2. The strong heating of the sample also gives an identical spectrum. This fact suggests that Co^{2+} has the more stable tetrahedral site. The ESR spectrum of the single crystals of Co^{2+} when diluted with either one of $K_2Zn(SO_4)_2 \cdot 6H_2O$ or $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ as a host crystal, indicates that the g-tensor has the principal values 6.4–6.5, 2.5–3.0, and 3.0–3.3, which are somehow similar to those in Fig. 4. The spectra in Fig. 5 were obtained when supported cobalt salt was decomposed in the absence of air at 250°C or supported cobalt salt was decomposed in air by slowly raising the heating temperature. This would have yielded Co^{2+} without accompanying the transfer of Co^{2+} ion from the occluded octahedral site to the tetrahedral site. Therefore, the cobalt ions in Fig. 5 are very likely $Co^{2+}(O)$. The spectra as shown in Fig. 6A can be obtained only when the supported cobalt salt is brought into a 550°C oven. A slow raising of the temperature yields the spectrum of either Fig. 4 or 5. The fact that cobalt ion which gives Fig. 6A yields Fig. 6B when reduced with H_2 would indicate that $Co^{3+}(O)$ is transformed to both $Co^{2+}(O)$ and $Co^{2+}(T)$ by H_2 reduction at 450°C. Actually Fig. 6B can be disintegrated into two component spectra, Figs. 4 and 5.

In the case of the ESR spectra of Al_2O_3–MoO_3–CoO catalysts, maximum values at 2.9 and 6.5 (in $h\nu/\beta H$ or g-factor units) are observed but no peak values at 15 (in the same units) are observed. This fact will indicate that when calcined in coexistence with molybdenum trioxide on alumina, no $Co^{2+}(O)$ is left and all is oxidized to $Co^{3+}(O)$, and therefore only $Co^{2+}(T)$ and $Co^{3+}(O)$ are found.

Thus it has become possible to estimate Co^{2+} and Mo^{5+} from ESR spectra. The ratios of Co^{2+}/Mo^{5+} were determined with the catalysts used and were plotted against an (added cobalt)/(added molybdenum) ratio, as shown in Fig. 8 and Table 1. This result indicates that $Co^{2+} + Mo^{6+} \rightleftharpoons Co^{3+} + Mo^{5+}$ is attained on the surface of the catalyst. The authors have presented the reaction scheme for the desulfurization re-

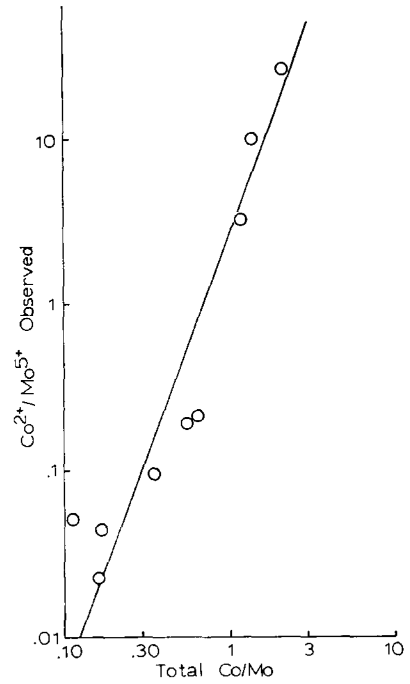

FIG. 8. The ratio, Co^{2+}/Mo^{5+}, found on the catalyst surface vs Co/Mo (added total) ratio.

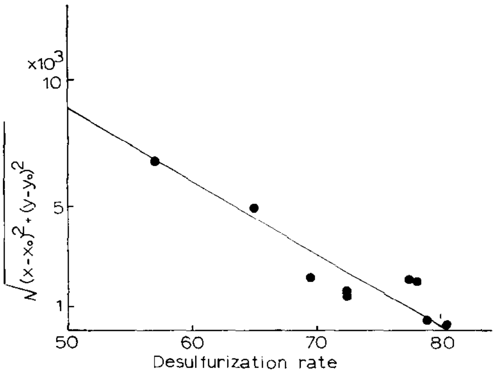

FIG. 9. The correlation between the desulfurization rate and the concentration of paramagnetic surface species. $x_0 = 1600$ and $y_0 = 3530$.

action with this catalyst (*6*). In that scheme, the abovementioned redox system plays an important role. It is therefore assumed that in a highly active catalyst surface there will be attained a good balance between the concentrations of the oxidized species, R^+O^{*2-}, where R signifies thio-β-naphthol and the reduced species, Co^{2+} and Mo^{5+}. If the concentration of R^+O^{*2-} is written as x and that of (Co^{2+} + Mo^{5+}) is written as y and experimentally obtained x and y values are plotted on an x–y plane, the observed points (x,y) are distributed around the central point (x_0, y_0). Since it is found that the catalyst whose (x, y) is closer to (x_0, y_0) has a higher desulfurization rate, then it is expected that there is a correlation between the desulfurization rate z and the value: $[(x - x_0)^2 + (y - y_0)^2]^{1/2}$. The correlation of z and $[(x - x_0)^2 + (y - y_0)^2]^{1/2}$ is shown in Fig. 9. It seems there exists a fairly well-defined correlation between these values, and it may be used as a diagnosis method for the catalyst.

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