BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(4), 1146—1151 (1975)

An ESR study of the Role of CoO and NiO in Al_2O_3–MoO_3–CoO (or NiO) Desulfurization Catalysts

Hisashi UEDA and Naoyuki TODO

National Chemical Laboratory for Industry, Mita, Meguro-ku, Tokyo 153

(Received July 25, 1974)

The ESR spectra from the catalyst/perylene/purified-benzene system were studied. The surface equilibria, $Co^{3+}+P \rightleftharpoons Co^{2+}+P^+$, $Ni^{3+}+P \rightleftharpoons Ni^{2+}+P^+$, and $Mo^{6+}+P \rightleftharpoons Mo^{5+}+P^+$, have been established, with the equilibrium constants at 20°C, 3.3×10^{15}, 3.0×10^{14}, and 6.8×10^{9} respectively. In Al_2O_3–MoO_3–CoO, $Mo^{6+}+Co^{2+} \rightleftharpoons Mo^{5+}+Co^{3+}$, is attained; the equilibrium constant obtained was 2.0×10^{-6}, and the corresponding value for $Mo^{6+}+Ni^{2+} \rightleftharpoons Mo^{5+}+Ni^{3+}$ was 2.3×10^{-5}. These results indicate that the roles of NiO and CoO in these catalysts are essentially the same. It has been found that the supporting order was important when CoO and MoO_3 were supported together, but unimportant when NiO and MoO_3 were supported together. Considering the known fact that CoO is a more efficient Co-catalyst of MoO_3 than NiO at lower supported concentrations (less than 2%), it has been concluded that CoO is incorporated in the alumina-carrier surface less stereospecifically, but more effectively, than NiO.

Numerous papers have been written on Al_2O_3–MoO_3–CoO–type catalysts, including several reviews.[1] In only a few papers, however, have the catalytic roles of MoO_3, CoO, and alumina as the carrier been cosidered, particularly in the form of a discussion of the reaction mechanism.[2] This is probably because of the fact that, when handling this type of catalyst, the researchers are more concerned with the practical usefulness, high activity, or long life of the catalyst. The present authors have been studying this catalyst by means of the ESR method in an attempt to get some knowledge about the catalytic reaction mechanism. As one way of approaching this problem, the surface concentrations of the paramagnetic species have been observed.[3]

In the present paper, the surface concentrations of the paramagnetic species formed in the oxide catalysts, if they are in contact with a dehydrated and degassed perylene/benzene solution, were measured by a quantitative ESR method.[4] Particular attention had been paid to the roles which CoO and NiO play in the catalysis reaction.

The present authors have always thought it most desirable to make measurements of the properties of a catalyst under the circumstances in which the catalyst is actually used. In some of our past papers, a few such efforts have been described.[3] Comparisons of the concentrations of the paramagnetic species to be formed in the catalyst studied in the present work at, say, 400 °C and 100 atm of H_2 are very desirable, too. However, before trying such rather difficult experiments, it will be helpful to try some less difficult experiments and to find a few of the essential differences between the effects of cobalt and nickel, if possible. For this reason, the following experiments were carried out.

Experimental

Purity of the Carrier. It is often advisable to use as simple a system as possible to find the mutual interactions between the components being considered in the system. Accordingly it is better to use the purest available γ-alumina carrier in order to study the roles of the supported transition metal ions than to use a commercial-grade one. However, when some time-consuming experimental data, such as those of catalyst-activity measurements, have already been obtained using a certain commercially available carrier, a comparison between those data and the ESR results is possible by using the same commercial carrier in the sample preparation for the ESR measurements. It is for this reason that a commercial γ-alumina carrier (Shokubai Kasei Co.) was used in the experiments in this work. The ESR spectrum of the carrier used and of a relatively pure one (Baikowski A 125 AS–2; Fe 20 ppm, Si 18 ppm, Cr 8 ppm, V and Mn 3 ppm, *etc.*) are both shown in Fig. 1. It should be noted that some "built-in acid points" due to impurities already exist on the carrier surface, even when nothing is supported. The surface area of the carrier used was 200 m^2/g.

Supporting Method and Analysis. MoO_3 was supported on alumina by immersing the carrier in a solution of ammonium molybdate (impregnation method). It was then

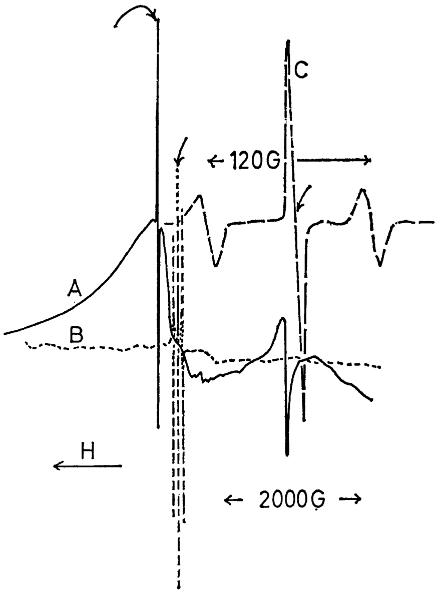

Fig. 1. ESR of the alumina carrier used. The right end of each spectrum is for 500 G, and the left end is for 5500 G of static magnetic field. The pointed arrows indicate $g=2.003$.
The modulation width used was 10 G. A: the γ-alumina used (Shokubai Kasei Co.). B: γ-alumina of Baikowski (France). The amplification of signal is 10 times of A. C: The central part of B, the amplication 1.6 times of A.

agitated for one hour at 40 °C, dried by means of a centrifuge, heated at 100 °C in an air bath, and then calcined at 550 °C for one hour. The mixed oxide thus prepared was denoted Al_2O_3–MoO_3. If a second ingredient (CoO or NiO) was supported, Al_2O_3–MoO_3 was then immersed in a solution of cobalt (or nickel) nitrate, dried, and calcined in the same way. This mixed oxide was denoted Al_2O_3–MoO_3–CoO (or NiO). If only CoO (or NiO) was supported, the supporting process for MoO_3 in the above processes was omitted. This was denoted Al_2O_3–CoO (or NiO). In the past works, the supporting order was always from MoO_3 to CoO (or NiO). In the present work, the reverse supporting order was also attempted. In this preparation, MoO_3 was supported on Al_2O_3–CoO or Al_2O_3–NiO. This was denoted Al_2O_3–CoO–MoO_3 (or Al_2O_3–NiO–MoO_3).

The analysis of the mixed oxides was done as follows: 1 g of the mixed oxide sample was heated to 130 °C with 10 ml of 1 : 1 H_2SO_4. After dissolution has been completed, it was cooled and diluted to 100 ml. The Co and Ni were analysed by means of an X-ray fluorescence analyser. The Mo was analysed by reducing all the Mo ions to Mo^{3+} and was then titrated with a $KMnO_4$ solution.

Preparation of the Sample and Measurements of ESR. By the same procedure as in a previous paper,[4] sample systems composed of oxide/perylene/purified-benzene were prepared and measurements were made after 10 min. The benzene pretreatment of the oxide was included.

Results

Figure 2 shows the concentrations of the perylene cation with the 9-line hyperfine structure, denoted as Pn^+, and those of the perylene cation without a hyperfine structure, denoted as Ps^+ (which has been denoted as P^+O^{*2-} in previous papers)[4,5] obtained by the use of Al_2O_3–CoO. The same values for Al_2O_3–NiO are shown in Fig. 3. In Fig. 3, the concentrations of Pn^+ and Ps^+ decrease when a relatively small amount of NiO is supported, probably because of some surface reactions between Ni^{3+} and the impurities. In Fig. 4, the concentrations of Pn^+, Ps^+, and Mo^{5+} obtained by Al_2O_3–MoO_3 are shown. In Figs. 2 and 4, the concenrations of Pn^+ and Ps^+ formed on the unsupported carrier have been subtracted from the concentrations observed by supported catalysts; therefore, the curves pass the original point. In Table 1, the concentrations of Pn^+, Ps^+, and Mo^{5+} obtained by the use of Al_2O_3–MoO_3–CoO are shown. Table 2 is for Al_2O_3–MoO_3–NiO. In Fig. 5 the decay curves of the Pn^+ concentration obtained by the carrier and singly supported catalysts are shown. In Fig. 6, the decay curves of Pn^+ concentrations obtained by doubly supported catalysts are shown. In Fig. 7 the formation curves of the Mo^{5+} concentration obtained by doubly supported catalysts are shown.

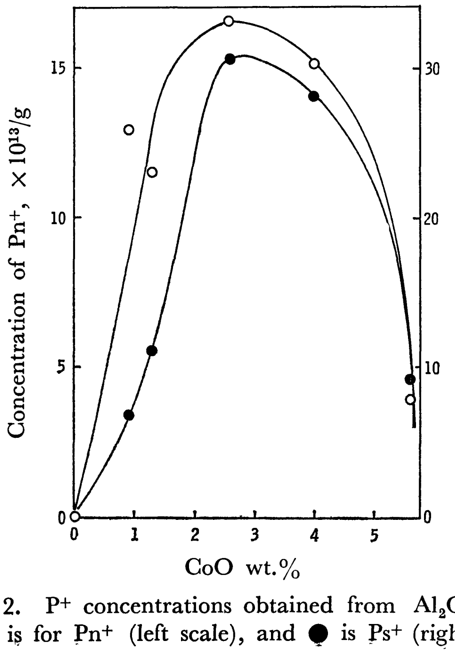

Fig. 2. P^+ concentrations obtained from Al_2O_3–CoO. ○ is for Pn^+ (left scale), and ● is Ps^+ (right scale).

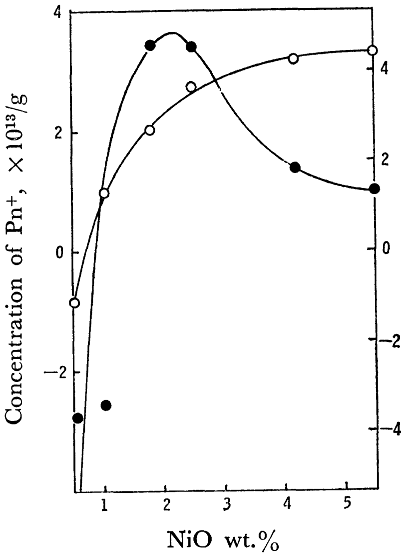

Fig. 3. P^+ concentions obtained from Al_2O_3–NiO. ○ is for Pn^+ (left scale), and ● is for Ps^+ (right scale).

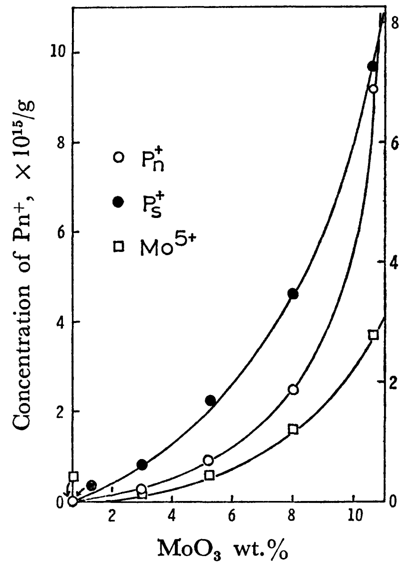

Fig. 4. P^+ and Mo^{5+} concentrations from Al_2O–MoO_3. ○ is for Pn^+ (left scale), ● is Ps^+ (right scale), and □ is for Mo^{5+} (right scale).

Discussion

Surface Reaction Constants and the Role of CoO and NiO

TABLE 1. CONCENTRATION OF Pn^+, Ps^+, AND Mo^{5+} IN Al_2O_3-MoO_3-CoO ($\times 10^{13}$/g)

CoO%		0.4—0.9	1.5—2.5	3.6—5.6
MoO%	Species			
0.7	Pn^+	6.1[a)]	10.2[d)]	13.4[g)]
	Ps^+	109	277	236
	Mo^{5+}	20	5.9	5.0
5.2	Pn^+	120[b)]	153[e)]	263[h)]
	Ps^+	1,570	2,940	3,480
	Mo^{5+}	283	61.4	10.0
10.6	Pn^+	1,020[c)]	1,070[f)]	675[i)]
	Ps^+	9,210	11,400	6,740
	Mo^{5+}	2,180	1,570	600

(MoO_3%)/(CoO%): a) 0.66/0.85. b) 5.18/0.60. c) 10.60/0.39. d) 0.65/2.47. e) 5.12/1.95. f) 10.48/1.54. g) 0.64/4.26. h) 5.01/4.19. i) 10.27/3.63.

TABLE 2. CONCENTRATION OF Pn^+, Ps^+, AND Mo^{5+} IN Al_2O_3-MoO_3-NiO ($\times 10^{13}$/g)

NiO%		0.2—0.6	1.0—1.8	2.6—4.2
MoO_3%	Species			
0.67	Pn^+	2.8[a)]	2.1[d)]	5.7[g)]
	Ps^+	69.8	123	226
	Mo^{5+}	18.2	15.5	4.5
5.22	Pn^+	73.9[b)]	39.4[e)]	40.5[h)]
	Ps^+	1,220	1,420	1,050
	Mo^{5+}	251	188	6.5
10.65	Pn^+	1,170[c)]	378[f)]	85.6[i)]
	Ps^+	13,900	5,400	2,870
	Mo^{5+}	3,870	2,510	361

(MoO_3%)/(NiO%): a) 0.66/0.50. b) 5.20/0.34. c) 10.62/0.20. d) 0.66/1.47. e) 5.15/1.26. f) 10.54/1.01. g) 0.65/3.22. h) 5.06/3.00. i) 10.37/2.62.

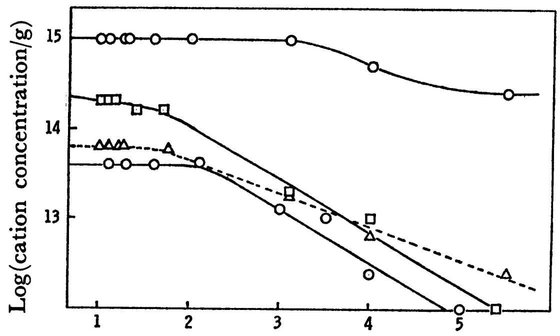

Fig. 5. Decay curves of Pn^+. ○ (bottom ones) are for Al_2O_3. △ (dotted line) are for Al_2O_3-NiO (98.2—1.8%), □ are for Al_2O_3-CoO (97.4—2.6%), and ○ (top ones) are for Al_2O_3-MoO_3 (94.8—5.2%).

As has already been discussed in previous papers, surface concentration equilibria are attained among surface redox species on an oxide surface;[5)]

$$Co^{3+} + P \rightleftharpoons Co^{2+} + P^+ \tag{1}$$

$$Ni^{3+} + P \rightleftharpoons Ni^{2+} + P^+ \tag{2}$$

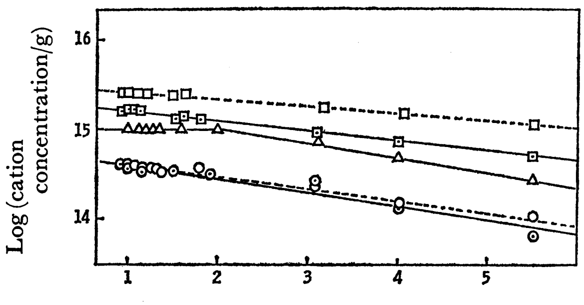

Fig. 6. Decay curves of Pn^+. △ are for Al_2O_3-MoO_3 (94.8—5.2%). ⊡ are for Al_2O_3-MoO_3-CoO (92.9—5.1—2.0%), □ are for Al_2O_3-CoO-MoO_3 (92.8—1.9—5.3%), ⊙ are for Al_2O_3-MoO_3-NiO (93.5—5.2—1.3%), and ○ are for Al_2O_3-NiO-MoO_3 (92.3—2.0—5.7%).

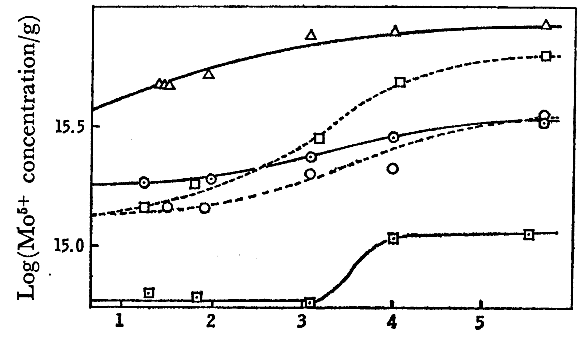

Fig. 7. Formation of Mo^{5+}. Symbols are the same as in Fig. 6.

The formation of P^+ (here, P^+ denotes both Pn^+ and Ps^+; therefore, $[P^+]=[Ps^+]+[Pn^+]$), as is shown in Figs. 2, 3, and 5, proves the existence of Co^{3+} and Ni^{3+} on the oxide surface. It is reasonable to use the activity coefficients, f_c, f_n, and f_m, for Co^{2+}, Ni^{2+}, and Mo^{6+} because it can easily be assumed that not all the metal ions supported on the oxide surface are actively working in the surface reactions. Actually, the activity of a catalyst depends not only on the amount of supported salts, but also on the method of preparation. Therefore, f_c = (concentration of active Co^{2+})/(concentration of total Co^{2+} supported). In an extreme case, in which only one Co^{2+} ion is supported on a 200 m^2 surface area (*i.e.*, one gram carrier), the Co^{2+} ion should be 100% active; in other words, $f_c=1.0$. Therefore,

$$\frac{f_c\cdot[Co^{2+}]\cdot[P^+]}{[Co^{3+}]\cdot[P]} = K_1 \tag{3}$$

Let K be equal to the following value;

$$K = \frac{[Co^{2+}]\cdot[P^+]}{[P]} = \frac{K_1\cdot[Co^{3+}]}{f_c} \tag{4}$$

If $[Co^{3+}]\rightarrow 1$ (ion/g catalyst) is considered, $[Co^{2+}]$ should also be close to 1 (ion/g catalyst), or $f_c\rightarrow 1.0$. Therefore, the limiting value of K_1 is K. The values of K are plotted against $[Co^{2+}]$ in Fig. 8–A. The value of K for $[Co^{2+}]\rightarrow 0$ gives $K_1=3.3\times 10^{15}$ for CoO. For NiO, K_1 of 3.0×10^{14} is obtained from Fig. 8–B.

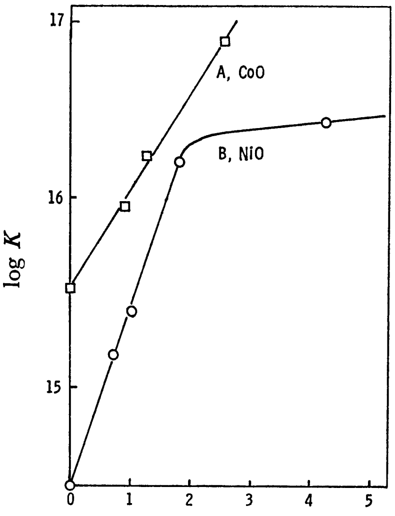

Fig. 8. Log K plotted against CoO (A) or NiO (B) concentration.

In the mixed oxide, Al_2O_3–MoO_3–CoO, there are those equilibria:

$$Mo^{6+} + Co^{2+} \rightleftharpoons Mo^{5+} + Co^{3+}\ ;\ K_r \tag{5}$$

$$Mo^{6+} + P \rightleftharpoons Mo^{5+} + P^{+}\ ;\ K_f \tag{6}$$

The constants are:

$$K_r = \frac{[Co^{3+}]\cdot[Mo^{5+}]}{f_c\cdot[Co^{2+}]\cdot f_m\cdot[Mo^{6+}]},\quad K_f = \frac{[Mo^{5+}]\cdot[P^{+}]}{f_m\cdot[Mo^{6+}]\cdot[P]}\ .$$

Then, $K_f=K_i\cdot K_r$. At the limit of $[Mo^{6+}]\to 1$ (ion/g catalyst), $f_m\to 1.0$. Then, in the same way as in (4), the value of K_f is obtained as the limiting value of K' at $[Mo^{6+}]\to 0$:

$$K' = \frac{[Mo^{5+}]\cdot[P^{+}]}{[P]} \to K_f \text{ (when } [Mo^{6+}] \to 1).$$

From Fig. 9, 9.93×10^{9} (for Al_2O_3–MoO_3–CoO), 5.62×10^{9} (for Al_2O_3–MoO_3–NiO), and 6.31×10^{9} (for Al_2O_3–MoO_3) are obtained as the K_f values. The average value of these three values is 6.82×10^{9}. The K_r values calculated from K_f and K_i are 2.06×10^{-6} for Al_2O_3–MoO_3–CoO, and 2.27×10^{-5} for Al_2O_3–MoO_3–NiO.

From (4), $f_c=(K/K_i)\cdot[Co^{3+}]$. Under the condition $[Co^{3+}]\simeq 1$, meaning that Co^{3+} has almost completely reacted, f_c values of 0.37,0.20,0.05, and 0.05 are obtained for 0.88, 1.27, 2.58, and 5.61% of CoO supported in Al_2O_3–CoO. In the same way, f_n values of 0.20, 0.12, 0.02, and 0.01 are obtained for 0.67, 1.02, 1.87, and 4.16% of NiO supported in Al_2O_3–NiO. f_m is obtained as $[P^{+}]$/(total $[Mo^{6+}]$ supported); the values are 2.8×10^{-5}, 8.4×10^{-5}, and 1.8×10^{-4} for 0.67, 5.22, and 10.65% of MoO_3 supported in Al_2O_3–MoO_3. The effective Mo^{6+} concentrations, $f_m\cdot[Mo^{6+}]$, are 7.8×10^{14}, 1.8×10^{16}, and 8.0×10^{16} (ion/g oxide). The $[Co^{3+}]$ value in Al_2O_3–MoO_3–CoO (CoO 1.5%, MoO_3 10.5%) was estimated by these values; it is 2.5×10^{14} (ion/g oxide), some 1 ppm of the total Co^{2+} supported concentration.

In the present catalyst, it has been established that MoO_3 plays the main role, while CoO plays the auxiliary part. The following three results obtained by our study make possible a theoretical interpretation for those facts: (1) In the Mo^{6+}–Mo^{5+} equilibrium, the higher oxidation state is relatively more stable than the lower oxidation state; therefore, it is more suitable to activate the hydrocarbon substrate. In the Co^{2+}–Co^{3+} equilibrium, the lower oxidation state is more stable than the higher oxidation state; therefore, it does not activate the hydrocarbon. However, it oxidizes Mo^{5+} to Mo^{6+}. (2) The K_i values are far larger than K_f; therefore, the recovery of the lower oxidation state (*e.g.*, the reversely directed reaction (5) with respect to the Mo ions) after the activation reactions, (1), (2) or (6), proceeds more easily with $Mo^{5+}\to Mo^{6+}$ than with $Co^{2+}\to Co^{3+}$. (3) There is another point which should be considered for a complete understanding of this problem — the rate constants of the following reactions:[3] $H^{+}+Co^{2+}\to H+Co^{3+}$ and $H^{+}+Mo^{5+}\to H+Mo^{6+}$. These constants must be compared in future studies.

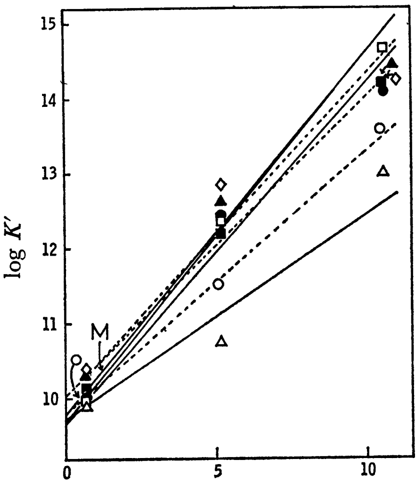

Fig. 9. Log K' plotted against MoO_3 concentration. The seven lines were obtained by, from top to bottom (viewed at 10% position), ◇, (marked M at left) Al_2O_3–MoO_3. □, NiO (0.2—0.6%). ▲, CoO (0.4—0.9%). ●, NiO (1.0—1.8%). ■, CoO (1.5—2.5%). ○, CoO (3.6—5.6%), and △, NiO (2.6—4.2%).

The carrier effects have been studied with the desulfurization catalysts, and it has shown that the γ-alumina carrier used in this type of catalyst stabilizes the metal ions supported on it.[3] For this reason, it is not unreasonable to assume the existence of the higher oxidation state of Co and Ni ions at elevated temperatures and under high pressures of H_2, though this point, too, must be confirmed by future studies.

Some Results Related to the Stereochemistry of the Catalysts.

In Eq. (1) through (5), the sum of $[Pn^{+}]$ and $[Ps^{+}]$, or $[P^{+}]$, have been used instead of any one of these two components. This has been done because both species are to be counted as cations.[3,5,6] If the $[Pn^{+}]/[Ps^{+}]$ ratio is written as r, this value depends on the solvent used.[4] In Table 3 the r values are shown. It will be found that, in Al_2O_3–CoO and Al_2O_3–NiO,

Table 3. $[Pn^+]/[Ps^+]$, or r-value

$MoO_3\%$ =0		$MoO_3\%$ =0.67		$MoO_3\%$ =5.22		$MoO_3\%$ =10.65	
CoO%	r	CoO%	r	CoO%	r	CoO%	r
0.00	0.061	0.00	0.055	0.00	0.053	0.00	0.125
0.88	0.126	0.85	0.056	0.60	0.076	0.39	0.111
1.27	0.088					1.54	0.094
2.58	0.055	2.47	0.037	1.95	0.052		
5.61	0.050	4.26	0.057	4.19	0.076	3.63	0.100
NiO%	r	NiO%	r	NiO%	r	NiO%	r
0.60	0.106	0.50	0.040	0.34	0.061	0.20	0.084
1.02	0.155			1.26	0.028	1.01	0.070
1.80	0.050	1.47	0.027				
4.16	0.086	3.22	0.025	3.00	0.038	2.62	0.030

the less the amount of the support, the higher the r value. In contrast, in Al_2O_3–MoO_3, the more the amount of the support, the higher the r value. In doubly supported Al_2O_3–MoO_3–CoO and Al_2O_3–MoO_3–NiO, no clear-cut tendency is found. However, the general tendency is the same as that in singly supported cases. These results can be understood if it is assumed that the supporting sites of Co^{2+} (or Ni^{2+}) and of Mo^{6+} are different. The assumption here agrees quite well with the conclusions of past literature that effective CoO and NiO are supported at the octahedral sites in the β-phase, while MoO_3 is supported at the tetrahedral sites in the δ-phase.[7,8] It has been shown that an analysis of the P^+ spectrum may give some knowledge about the stereochemistry of the catalyst surface.

Since the effective MoO_3 and the effective CoO (or NiO) seem to be occupying different surface sites, the catalyst prepared by the use of the reverse supporting order may have a different nature compared with the one made by the use of a normal supporting order. Such differences will be found in Figs. 6 (Pn^+ concentrations) and 7 (Mo^{5+} concentrations). In Fig. 7, the rates of the formation of Mo^{5+} before and after approximately 3×10^3 min. (the middle points of the curves) are different. Though each catalyst surface should be handled as one integrated system of Al^{3+}–Mo^{6+}–Co^{2+}–O^{2-}–*etc.* in the equilibrium state ($t=10^5$ min or more), in the initial period (t, less than 10^3 min.) the more reactive Co^{3+} may be receiving an electron from a perylene molecule faster than Mo^{6+}, thus making the initial part of the lowest curve (⊡) parallel to the time axis. It seems that this reactivity of Co^{3+} is faster for Al_2O_3–MoO_3–CoO than for Al_2O_3–CoO–MoO_3 (□). However, the equilibrium Mo^{5+} concentration must be estimated by the use of Eq. (5), not Eq. (6). The K_r value in (5) for Al_2O_3–CoO–MoO_3 is some 10 times larger than that for Al_2O_3–MoO_3–CoO. This difference may be explained as follows. If Mo^{5+} in the tetrahedral coordination is more efficiently oxidized by Co^{3+} than that in the octahedral coordination, and if a relatively larger portion of Co^{2+} ions is distributed to tetrahedral sites when CoO is supported prior to MoO_3 (Al_2O_3–CoO–MoO_3), and if, therefore, a relatively larger portion of Mo^{6+} is in this case coordinated to octahedral sites, the rsults in Fig. 7 may be interpreted by saying that the number of the combination sites, Mo^{6+} (tetrahedral)–Co^{2+}(octahedral), is smaller in Al_2O_3–CoO–MoO_3 than in Al_2O_3–MoO_3–CoO, although the overall compositions of the oxides are almost equal.

In the cases of Al_2O_3–MoO_3–NiO and Al_2O_3–NiO–MoO_3, the curves in Figs. 6 and 7 are quite similar. This may be interpreted by means of a hypothesis that Ni^{2+} is incorporated into the carrier more stereospecifically, but less effectively (for example, the number of Ni^{2+} ions in one NiO colony on the carrier surface is different from the number of Co^{2+} ions in one CoO colony), than Co^{2+} is. The ratios of the catalyst activity *vs.* the CoO and NiO content in the Al_2O_3–MoO_3–CoO (or NiO) curves are different.[9] CoO is quite efficient at 1%, and the activity reaches its maximum value at 2%, while NiO is quite inefficient at 1%, but the activity increases until the NiO content reaches 4% or more. These results show that the supporting order can be used to get information on the stereochemical interactions between the support and the carrier surface.

ESR as an Analysing Method of a Solid Catalytic Reaction System.

There are several advantages of the ESR method when it is used to analyse catalytic reaction systems. In this section, only its sensitivity will be considered as an advantage. If only 1% of CoO is supported on Al_2O_3, some 4×10^{13}/g of Pn^+ and 2×10^{15}/g of Ps^+ are formed. If all the Co^{3+} had been converted to either Pn^+ or Ps^+, $[Co^{3+}]$ should have been 2×10^{15}/g. As the $[Co^{2+}]$ supported is 8×10^{19}/g, the abundance of Co^{3+} ions in the supported cobalt salt is only 25 ppm. If only those Co^{3+} ions which produce Pn^+ are considered, their abundance is only 0.5 ppm in supported cobalt salt. No method other than ESR can detect such a very small quantity. For example, by magnetic susceptibility measurements, the contribution of $\mu(Co^{3+})$ to the observed average μ value at 25 ppm is completely negligible; this then leads to the wrong conclusion that Co^{3+} does not participate in the catalytic reactions.[10] Though their concentrations are quite small, Co^{3+} and Ni^{3+} play important roles in the dynamic reaction process of desulfurization. The detection of such dilute but reactive species can be done only either by a fast detection of a created transient state or by a trapping method. In the present application, those transient species have been transformed to Pn^+ and Ps^+ and have been measured as semistable paramagnetic species.

The authors wish to thank Mr. K. Ogawa of their Institute and Mr. K. Fujita of Kanagawa University for their cooperation in the preparation and analysis of the oxide catalysts.

References

1) P. C. H. Mitchell, "The Chemistry of Some Hydrocarbon Desulfurization Catalysts Containing Molybdenum," Climax Molybdenum Company, 1967. G.C.A. Schuit and

B. C. Gates, *A. I. Ch. E. Journal*, **19**, 417 (1973). K. Wakabayashi, *Nenryo Kyokaishi*, **49**, 825 (1970).

2) J. M. J. G. Lipsch and G. C. A. Schuit, *J. Catal.*, **15**, 179 (1969).

3) H. Ueda and N. Todo, This Bulletin, **43**, 3698 (1970). H. Ueda and N. Todo, *J. Catal.*, **27**, 281 (1972). H. Ueda, N. Todo, and M. Kurita, *J. Less-Common Metals*, **36**, 387 (1974).

4) H. Ueda, This Bulletin, **47**, 1338 (1974).

5) H. Ueda, *ibid.*, **43**, 319 (1970).

6) H. Ueda, *Can. J. Chem.*, **46**, 891 (1968).

7) J. H. Ashley and P. C. H. Mitchell, *J. Chem. Soc., A*, **1968**, 2821, **1969**, 2730.

8) P. E. Jacobson and P. W. Selwood, *J. Amer. Chem. Soc.*, **76**, 2641 (1954), G. T. Rymer, J. M. Bridges, and J. R. Tomlinson, *J. Phys. Chem.*, **65**, 2152 (1961).

9) N. Todo, K. Muramatsu, M. Kurita, K. Ogawa, T. Sato, M. Ogawa, and Y. Kotera, *Bull. Japan Pet. Inst.*, **14**, 89 (1972).

10) J. T. Richardson, *I. E. C. Fundamentals*, **3**, 154 (1964).