

## Interaction between the Active Components and Support in the Co-Mo-Al<sub>2</sub>O<sub>3</sub> System

### III. Magnetic and Electron Spin Resonance Spectroscopic Study of the Influence of Sodium on the Nature of Cobalt

A. V. RAMASWAMY, S. SIVASANKER, AND P. RATNASAMY

*Indian Institute of Petroleum, Dehradun 248 005, India*

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The influence of sodium on the magnetic and electron spin resonance properties of Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalysts both in the fresh state and after reduction at various temperatures in hydrogen, hydrogen-isooctene and hydrogen-isooctene-thiophene atmospheres has been investigated. In samples containing sodium, metallic cobalt is formed on reduction in hydrogen or hydrogen-isooctene at 500°C. In the presence of sulfur as well as in samples not containing sodium, reduction to the metal is suppressed. In addition to this influence on cobalt, sodium also enhances the reducibility of molybdenum ions in the support. These results lend additional support to the model of the catalyst surface proposed in part II of this series and highlight the importance of the alumina support in determining the structural characteristics of "cobalt-moly" catalysts.

#### INTRODUCTION

The influence of sodium on the valence and coordinative environment of cobalt in Co-Mo-Al<sub>2</sub>O<sub>3</sub> hydrodesulfurization catalysts continues to be an intriguing problem. During an investigation of the reducibility of Co-Mo-Al<sub>2</sub>O<sub>3</sub> in hydrogen using isothermal thermogravimetry (1), we had found that sodium ions present in alumina enhance the reducibility markedly. To account for this and other results, we had postulated that in the presence of sodium part of cobalt occurs in a form like CoO or Co<sub>3</sub>O<sub>4</sub> which on reduction forms the metal. Once formed, cobalt metal, facilitating the surface mobility of hydrogen, accelerates the reduction of supported MoO<sub>3</sub>. In the absence of sodium, cobalt, now occurring mostly as well dispersed Co<sup>2+</sup> ions which are not reduced during the reduction, strongly retains the water evolved during the process and

thereby suppresses the reduction of MoO<sub>3</sub>. It is the objective of the present study to test this postulate that metallic cobalt is present in Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalysts under reduction conditions only in the presence of sodium. For this purpose, magnetic susceptibility and ESR spectroscopic techniques have been used. Samples of Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalysts with and without sodium have been reduced at various temperatures in H<sub>2</sub>, H<sub>2</sub>-isooctene, and H<sub>2</sub>-isooctene-thiophene atmospheres and their magnetic and ESR properties were measured. The results have enabled us to confirm the presence of metallic cobalt in samples containing sodium and reduced in H<sub>2</sub> at elevated temperatures. The nature of the oxide precursor that gives rise to cobalt metal is also discussed.

#### EXPERIMENTAL METHODS

The preparation of MoAl (12.5% MoO<sub>3</sub> by wt impregnated on  $\gamma$ -alumina), CoMoAl

(containing 12.5% MoO<sub>3</sub> and 2.5% Co<sub>3</sub>O<sub>4</sub> by wt impregnated simultaneously on  $\gamma$ -alumina) and CoMoAlNa (containing 12.5% MoO<sub>3</sub>, 2.5% Co<sub>3</sub>O<sub>4</sub>, and 200 ppm sodium on  $\gamma$ -alumina) has been detailed in part II of this series (1). MoAl was prepared by impregnation of pure alumina (obtained from boehmite at 550°C; surface area, 240 m<sup>2</sup>/g) with an aqueous solution of ammonium paramolybdate, drying at 110°C and further calcining at 550°C for 24 hr. CoMoAl was prepared by simultaneously impregnating the pure alumina support with an aqueous solution containing a mixture of ammonium paramolybdate and cobalt nitrate. Drying and calcination were done at 110 and 550°C, respectively. The alumina support used for preparing CoMoAlNa was obtained from pure alumina (used for MoAl and CoMoAl) by impregnation with a solution of NaOH (0.02% of Na by wt). The cobalt and molybdenum salts were then impregnated on this support in a manner similar to that used for preparing the CoMoAl sample.

The magnetic susceptibility of the samples was measured by the Gouy method using an electromagnet (Andhra Scientific, India). NiCl<sub>2</sub> was used for calibration purposes (2). Since our electromagnet did not have a variable temperature attachment, all the measurements were carried out at 25°C. Gram susceptibilities of different packings of the same sample were reproducible to about 3%. Electron spin resonance spectra of the samples were recorded at 22°C by a Varian E 400 EPR spectrometer at 9.41 GHz. DPPH was used as the internal calibrant. Samples contained in quartz tubes (6 mm o.d.) were attached to a conventional adsorption system, given various pretreatments (like evacuation, reduction, etc.), sealed *in situ* and then transferred to the spectrometer for recording the spectra.

## RESULTS AND DISCUSSION

### *Magnetic Measurements*

In the Co-Mo-Al<sub>2</sub>O<sub>3</sub> system, the paramagnetic susceptibility is due mainly to cobalt. Both supported molybdenum oxide and alumina are diamagnetic (3). The magnetic moment of cobalt depends on its valence state (di- or trivalent) and its coordination number (tetrahedral or octahedral) in the oxide lattice. There is no evidence from ESCA studies for the presence of Co<sup>3+</sup> in our samples (4) and hence all the cobalt is present in the divalent state. In a tetrahedral environment of oxide ions, Co<sup>2+</sup> has a ground term <sup>4</sup>A<sub>2</sub> which is mixed with the higher levels <sup>4</sup>T<sub>1</sub> and <sup>4</sup>T<sub>2</sub> through spin-orbit coupling giving rise to observed magnetic moments  $\mu_{\text{eff}}$  in the range 4.2–4.7 BM. The orbital contribution is higher in the case of Co<sup>2+</sup> octahedrally surrounded by oxide ions (high spin). Values in the range  $\mu_{\text{eff}} = 4.7$ –5.3 BM are observed. Among the various compounds of cobalt identified or postulated to exist in Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalysts, the oxides of cobalt (like CoO), wherein cobalt occurs in an octahedral environment have the largest  $\mu_{\text{eff}}$  while CoAl<sub>2</sub>O<sub>4</sub> (tetrahedral coordination of O<sup>2-</sup> around Co<sup>2+</sup>) has the lowest value (3). Co<sup>2+</sup> occurs in an octahedral position in CoMoO<sub>4</sub> also (5).

The observed gram magnetic susceptibility values,  $\chi_g''$ , of the catalyst were corrected for the diamagnetic contribution of the Pyrex container, the alumina support and the molybdenum ions. For CoMoAl and CoMoAlNa the total diamagnetic contribution was  $-0.3 \times 10^{-6}$  cgs units. The corrected values,  $\chi_g'$ , were then plotted against the reciprocal magnetic field strength,  $H$  (four values in the range, 4–9 kG) and extrapolated to  $1/H = 0$  to eliminate the influence of ferromagnetism (6). The extrapolated value  $\chi_g$  was used to calculate the effective magnetic moment,  $\mu_{\text{eff}}$ , of cobalt in the sample using the

TABLE 1

Changes in the Magnetic moments of CoMoAl and CoMoAlNa under Various Pretreatments

No.	Pretreatment	$\mu_{eff}$ BM <sup>a</sup>	
		CoMoAl	CoMoAlNa
1.	Fresh	4.8	5.7
2.	Reduction in H <sub>2</sub> flow at 380°C for 3 hr	4.9 <sup>b</sup>	6.4
3.	Reduction in H <sub>2</sub> flow at 500°C for 3 hr	5.0	7.2
4.	Reduction in H <sub>2</sub> + iso-octene flow (10:1, atm press., LHSV = 3) at 380°C for 3 hr	4.8	6.0
5.	As in (4) above, but 1% S as thiophene was added to the feed		5.7
6.	As in (4) above, but carried out at 500°C		7.0
7.	As in (6) above, but 1% S as thiophene was added to the feed		4.9

<sup>a</sup> The values of  $\mu_{eff}$  are reproducible to  $\pm 0.1$ .<sup>b</sup> The reduction was carried out at 250°C.

equation (6),

$$\mu_{eff} = 2.84(\chi_A T)^{\frac{1}{2}} \text{ BM}, \quad (1)$$

where  $T$  is the absolute temperature and

$$\chi_A = \frac{58.94\chi_g}{f_{Co}}. \quad (2)$$

Here,  $f_{Co}$  is the fraction (by wt) of cobalt in the sample. Equation (1) is an approximation of Eq. (3).

$$\mu_{eff} = 2.84[(\chi_A - a)(T - \theta)]^{\frac{1}{2}}, \quad (3)$$

where  $a$  is the temperature independent paramagnetism and  $\theta$  is the Weiss constant. The amount of error involved in using Eq. (1) was estimated by measuring the magnetic moment of a sample of Ketjenfine 124 for which Lipsch and Schuit (5) had reported a value of 4.2 BM. Using our procedure we measured a value of 4.1 BM. The fairly satisfactory agreement is probably due to the small value of the Curie-Weiss constant,  $\theta = 22^\circ$  (5).

The magnetic moments  $\mu_{eff}$  of both CoMoAl and CoMoAlNa under various conditions of pretreatment are shown in Table 1. The pretreatments were carried out in a conventional down-flow integral type of reactor. After the pretreatments the catalysts were transferred to a Gouy tube (2) and their magnetic susceptibility was measured. Samples of MoAl, both in the fresh state and after the pretreatments shown in Table 1 had negligible values of  $\chi_g''$  and hence are not discussed further. Plots of  $\chi_g'$  against  $1/H$  are shown in Fig. 1. Except for samples of CoMoAlNa subjected to pretreatment nos. 3 and 6, there was no evidence of ferromagnetism in the samples.

For the fresh catalysts, the higher value of  $\mu_{eff}$  for CoMoAlNa (5.7 BM) compared to CoMoAl (4.8 BM) indicates that in the presence of preimpregnated Na<sup>+</sup> ions on the alumina surface more of cobalt occupies

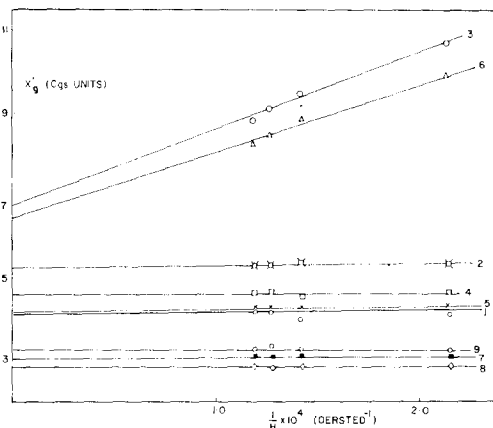


FIG. 1. Variation of magnetic susceptibility,  $\chi_g'$ , with the reciprocal of the magnetic field for various samples: (1) CoMoAlNa, fresh, oxide state; (2) CoMoAlNa reduced in a flow of H<sub>2</sub> at 380°C for 3 hr; (3) CoMoAlNa reduced in a flow of H<sub>2</sub> at 500°C for 3 hr; (4) CoMoAlNa reduced in a flow of H<sub>2</sub> + iso-octene at 380°C for 3 hr; (5) CoMoAlNa reduced in a flow of H<sub>2</sub> + iso-octene + thiophene at 380°C for 3 hr; (6) CoMoAlNa reduced in a flow of H<sub>2</sub> + iso-octene at 500°C for 3 hr; (7) CoMoAlNa reduced in a flow of H<sub>2</sub> + iso-octene + thiophene at 500°C for 3 hr; (8) CoMoAl, fresh, oxide state; (9) CoMoAl reduced in a flow of H<sub>2</sub> at 500°C for 3 hr.

positions in which they are octahedrally surrounded by oxide ions. Such positions are (a)  $\text{Co}^{2+}$  ions in octahedral  $\text{Al}^{3+}$  vacancies in the alumina support, (b)  $\text{Co}^{2+}$  ions in  $\text{CoO}$  and  $\text{Co}_3\text{O}_4$  and (c)  $\text{Co}^{2+}$  ions in  $\text{CoMoO}_4$ . The various possibilities are discussed below in more detail. On reduction in  $\text{H}_2$  (at 250 or 500°C) or in hydrogen-isooctene at 380°C, the value of  $\mu_{\text{eff}}$  for  $\text{CoMoAl}$  is not changed. On the other hand, for  $\text{CoMoAlNa}$  the value increases from 5.7 for the fresh catalyst to 6.4 BM on reduction in  $\text{H}_2$  at 380°C and increases further to 7.2 BM at 500°C. Moreover, the sample reduced at 500°C exhibits ferromagnetism (Fig. 1, curve 3) revealing the presence of metallic cobalt. The increase in  $\mu_{\text{eff}}$  observed for  $\text{CoMoAlNa}$  reduced at 380°C is also undoubtedly due to the reduction of  $\text{Co}^{2+}$  ions, but the absence of ferromagnetism (Fig. 1, curve 2) in the sample implies that the reduction is not complete and that the reduced species ( $\text{Co}^0$ , for example) is sufficiently well dispersed in the diamagnetic molybdena-alumina, thereby not constituting a condensed ferromagnetic phase.

Interesting changes in  $\mu_{\text{eff}}$  occur for  $\text{CoMoAlNa}$  when it is reduced in a mixture of hydrogen and isooctene (Table 1). At 380°C, the value (6.0 BM) is intermediate between those of the fresh (5.7) and  $\text{H}_2$ -reduced (6.4) samples. The same trend is observed at 500°C also. When, however, 1% sulfur (as thiophene) is present in the feed, it affects profoundly the reducibility of cobalt (Table 1, pretreatment nos. 5 and 7). At 380°C, the value of  $\mu_{\text{eff}}$  (5.7 BM) is not different from that of the fresh catalyst. At 500°C, there is actually a decrease in the  $\mu_{\text{eff}}$  value (4.9 BM). We attribute this decrease to the formation of the sulfides of cobalt in the presence of  $\text{H}_2\text{S}$  at 500°C (7). These sulfides have a low value of magnetic susceptibility. For example, the molar magnetic susceptibility of  $\text{CoS}$  at 20°C is only  $225.0 \times 10^{-6}$  cgs units while those of  $\text{CoO}$ ,  $\text{Co}_2\text{O}_3$  and  $\text{Co}_3\text{O}_4$ ,

are 4900, 4560 and  $7380 \times 10^{-6}$  cgs units, respectively (8). The formation of sulfides by  $\text{Co}^{2+}$  ions which were originally in an oxide environment should thus lead to a lowering of the  $\mu_{\text{eff}}$  values, as indeed observed experimentally.

An intriguing but interesting feature of Table 1 is the identical value of  $\mu_{\text{eff}}$  for the fresh  $\text{CoMoAlNa}$  and for the same sample reduced at 380°C in a flow of  $\text{H}_2$  and isooctene containing 1% sulfur as thiophene (pretreatments 1 and 5). This identity of values may arise from two possible alternatives: (a) the  $\text{Co}^{2+}$  ions in the fresh catalysts are neither reduced to lower valent state nor sulfided to  $\text{CoS}$ , or (b) the increase in  $\mu_{\text{eff}}$  caused by reduction of part of the  $\text{Co}^{2+}$  ions to  $\text{Co}^0$  is exactly compensated by the decrease due to formation of the sulfide. In this context, it may be mentioned that LoJacono *et al.* (9) found no evidence for the presence of metallic cobalt on reduction of  $\text{Co-Mo-Al}_2\text{O}_3$  catalyst in  $\text{H}_2\text{-H}_2\text{S}$  at 400°C. They further held that under the above conditions, the  $\text{Co}^{2+}$  ions are not affected by sulfidation or reduction. Our result, namely, the identity of  $\mu_{\text{eff}}$  values for both the fresh and sulfided samples of  $\text{CoMoAlNa}$ , supports this conclusion and extends its validity to the  $\text{H}_2$ -hydrocarbon-thiophene system also, at least at atmospheric pressure. Preliminary results at high pressures (20 kg) also reveal a similar picture (14). At 500°C, however, the  $\text{Co}^{2+}$  ions react with sulfur compounds to form the sulfide responsible for the observed lower value of  $\mu_{\text{eff}}$ . Identification of metallic cobalt in  $\text{CoMoAlNa}$  under reduction conditions in  $\text{H}_2$  at 500°C (Fig. 1, curve 3) and its absence in  $\text{CoMoAl}$  under similar conditions (Fig. 1, curve 9) lends excellent support to our earlier hypothesis (see Introduction).

#### ESR Measurements

The samples of  $\text{MoAl}$ ,  $\text{CoMoAl}$ , and  $\text{CoMoAlNa}$ , both after evacuation to  $10^{-4}$

TABLE 2  
*g* Values and Relative Concentrations of Mo<sup>5+</sup> Ions<sup>a</sup>

No.	Pretreatment	Sample		
		MoAl	CoMoAl	CoMoAlNa
1.	Evacuation to 10 <sup>-4</sup> cm at 25°C	1.96 (1.0) ( <i>g</i> <sub>I</sub> = 1.98, <i>g</i> <sub>II</sub> = 1.92)	1.95 (0.1) ( <i>g</i> <sub>I</sub> = 1.97, <i>g</i> <sub>II</sub> = 1.92)	2.04
2.	Reduction in a static atm of H <sub>2</sub> at 250°C	1.92 (7.5)	1.93 (3.5)	1.92 (0.2)
3.	Reduction in flowing H <sub>2</sub> at 250°C	1.93 (3.8)		1.93 (0.5)
4.	Reduction in a static atm of H <sub>2</sub> at 350°C		1.93 (15.6)	1.93 (8.4)
5.	Reduction in flowing H <sub>2</sub> at 350°C	1.93 (1.9)		1.92 (5.0)
6.	Reduction in a static atm of H <sub>2</sub> at 500°C		1.93 (26.3)	1.93 (3.5)
7.	Reduction in flowing H <sub>2</sub> at 500°C	1.93 (0.2)		1.94 (0.9)
8.	Sulfidation at 250°C with a mixture of H <sub>2</sub> + CS <sub>2</sub> (10:1)	1.92 (2.0)	1.92 (3.3)	1.92 (2.0)

<sup>a</sup> The *g* values are reproducible to ±0.01. The duration of the reduction as well as the reduction-cum-sulfidation runs was 3 hr. The values in parentheses refer to the relative concentration of Mo<sup>5+</sup> ions in arbitrary units.

cm at 25°C and after the pretreatments mentioned in Table 2, were subjected to ESR analysis. Particular mention should be made that the samples were not exposed to air after the various pretreatments. All the spectra were recorded as the first derivative of the absorption curve at 22°C. The formula,

$$I = KW^2H, \quad (4)$$

was used to calculate the intensity *I* of the resonance (10). In the above formula, *W*

is the peak-to-peak separation and *H*, the peak-to-peak height of the derivative curve. The constant *K* was fixed by letting the resonance intensity of a standard sample of MoAl equal unity. The *I* values were normalized using the appropriate values of the receiver gain. The *g* values were calculated using DPPH as a *g*-calibrant.

Representative ESR spectra of Mo<sup>5+</sup> ions are shown in Figs. 2-4. The *g* values together with the relative intensities (in

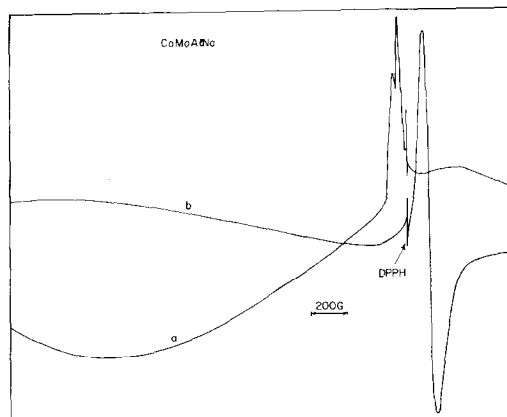


FIG. 2. ESR spectra of CoMoAlNa: (a) fresh, oxide state; (b) after reduction in H<sub>2</sub> (760 Torr) at 350°C.

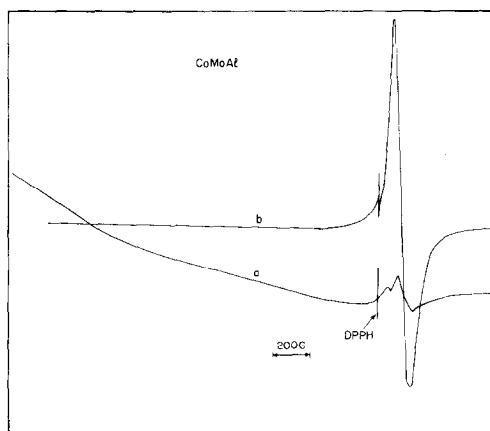


FIG. 3. ESR spectra of CoMoAl: (a) fresh, oxide state; (b) after reduction in H<sub>2</sub> (760 Torr) at 350°C.

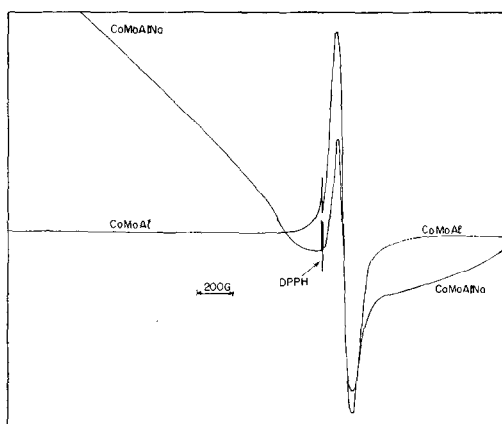


FIG. 4. ESR spectra of CoMoAl and CoMoAlNa after reduction in  $H_2$  (760 Torr) at  $500^\circ C$ .

arbitrary units) are compiled in Table 2. In Figs. 2-4, the sharp line-peak is due to DPPH ( $g = 2.0036$ ). All the  $g$  values reported in Table 2 correspond well with those reported in the literature (1.92-1.96) for  $Mo^{5+}$  ions in a tetragonal square arrangement on alumina (9, 11). For CoMoAlNa, in addition to the sharp peak with  $g = 2.04$  there is a broad resonance (peak-to-peak width, 960 G) centered around  $g = 2.5$  (Fig. 2, curve a). The latter peak is present in CoMoAl also ( $g = 2.9$ ) but is much broader (peak width,  $\approx 2280$  G). The species responsible for these peaks are cobalt ions, probably in an oxidic environment, in the alumina lattice. This broad peak is not affected by the various reduction treatments indicating that the cobalt ions in this environment are not affected by reduction or reduction-sulfidation. The signal at  $g = 2.04$  is similar to that observed by Galiasso and Menguy (12) ( $g_1 = 2.026$ ,  $g_2 = 2.035$ ,  $g_3 = 2.051$ ) and attributed by them to oxygen ion-radicals chemisorbed on  $Mo^{6+}$ . Its disappearance in  $H_2$  atmosphere is commensurate with the above assignment (Fig. 2, curve b).

On reduction in  $H_2$ , the resolution of the  $g_1$  and  $g_{11}$  components observed for the fresh catalysts disappears due to the in-

creased formation of  $Mo^{5+}$  from  $Mo^{6+}$  ions and the resultant dipole-dipole broadening of the resonance lines. The constant value of  $g$  ( $1.93 \pm 0.01$ ) observed for MoAl, CoMoAl, and CoMoAlNa under all the reduction and reduction-cum-sulfidation conditions mentioned in Table 2 means that the coordinative environment of  $Mo^{5+}$  ions is very similar in all these samples. The relative variation of the concentration of  $Mo^{5+}$  ions after different pretreatments is shown in Fig. 5. Now, during any reduction process  $Mo^{5+}$  ions are formed from  $Mo^{6+}$  and are in turn further reduced to lower oxidation states. The relative rates of these two consecutive processes determine the signal intensity of  $Mo^{5+}$  (12). At moderate conditions of reduction (for example, reduction at  $250^\circ C$  in a static atmosphere of  $H_2$ ) the former will predominate while the reduction of  $Mo^{5+}$  to  $Mo^{4+}$  is expected to be more rapid at more severe conditions (like reduction at  $500^\circ C$  in flowing  $H_2$ ). The ESR signal intensity is thus expected to pass through a maximum at conditions of intermediate severity. Both MoAl and CoMoAlNa exhibit this maximum, though at different conditions of severity (Fig. 5). For CoMoAl, however, the concentration of  $Mo^{5+}$  continues to increase even after reduction in flowing  $H_2$  at  $500^\circ C$  indicating

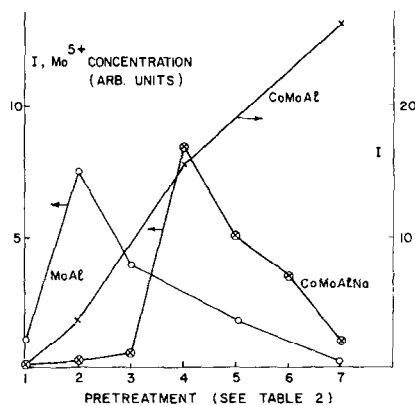


FIG. 5. Variation of  $Mo^{5+}$  concentration in MoAl, CoMoAl, and CoMoAlNa after the pretreatments given in Table 2.

that the conversion of Mo<sup>5+</sup> to Mo<sup>4+</sup> is relatively small even at 500°C. The relative reducibilities (Mo<sup>6+</sup> to Mo<sup>4+</sup>) of the three samples are thus, MoAl > CoMoAlNa > CoMoAl. An identical conclusion was derived by us earlier (1) from the rates of reduction of these samples in H<sub>2</sub> at 490°C using isothermal gravimetry. ESR spectroscopy, thus, confirms our earlier findings that the presence of sodium ions increases the reducibility of Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalysts.

Additional information from the ESR spectra of Fig. 4 is the presence of the broad and asymmetric band due to ferromagnetic resonance observed for CoMoAlNa after reduction in H<sub>2</sub> at 500°C and its absence in the spectra of CoMoAl under the same conditions. LoJacono *et al.* (9) had also observed this band for Co-Al<sub>2</sub>O<sub>3</sub> samples reduced in H<sub>2</sub> + H<sub>2</sub>S at 400°C and attributed it to metallic cobalt. We also ascribe this band to cobalt metal. Its presence in CoMoAlNa and absence in CoMoAl agrees very well with the magnetic data presented earlier, wherein, on reduction at 500°C in flowing H<sub>2</sub>, ferromagnetic cobalt was formed only in the case of samples containing sodium.

The following salient features emerge from the present studies: In the Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst system, sodium ions in the support influence strongly the structural nature of cobalt. For samples containing sodium (CoMoAlNa) reduction at elevated temperatures in H<sub>2</sub> or a mixture of H<sub>2</sub> and isooctene leads to the formation of Co<sup>0</sup>. In the presence of sulfur this reduction is suppressed. For catalysts without sodium (CoMoAl), however, reduction to Co<sup>0</sup> does not occur to a significant extent at 500°C even in a flow of H<sub>2</sub>. Obviously cobalt in the fresh CoMoAlNa is present in a form which is different from that in fresh CoMoAl, and which, in addition, is more susceptible to reduction by H<sub>2</sub> to the metallic state but which, at the same time, does not undergo this reduction if thiophene is present. Now, what is the cobalt species

which is the precursor of Co<sup>0</sup>? It is unlikely to be Co<sup>2+</sup> in tetrahedral positions in the alumina lattice because CoAl<sub>2</sub>O<sub>4</sub> (where Co<sup>2+</sup> occurs in such a position) is not reduced in H<sub>2</sub> (1, 3a). It is most probably either Co<sup>2+</sup> in a condensed oxide phase like Co<sub>3</sub>O<sub>4</sub>, CoO, or CoMoO<sub>4</sub> [the β phase (13)] or Co<sup>2+</sup> dispersed among the surface octahedral Al<sup>3+</sup> vacancies (the δ phase). (Of course, since the X-ray diffraction patterns of all these samples do not contain any line due to cobalt or molybdenum, the dimensions of even the condensed phase cannot exceed, say, 40 Å). There is no evidence for the presence of CoMoO<sub>4</sub> in Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalysts either from the studies of Ashley and Mitchell (3b) (spectroscopic and magnetic study) or from our ESCA measurements (4). The ESCA spectrum had revealed the presence of a peak at a binding energy value of 780.5 eV which was assigned to Co<sup>2+</sup> in an oxide phase, most probably CoO. The presence of such small patches (of dimension, 10–20 Å) of cobalt oxide on the surface of alumina can account for the observed changes in magnetic moments in Table 1. At 380°C in H<sub>2</sub>, the absence of ferromagnetism is due to the fact that the oxide patches are only partly reduced and the Co<sup>0</sup> atoms formed are not sufficiently mobile. At 500°C, the reduction being more complete, the cobalt atoms agglomerate to form larger crystallites which exhibit ferromagnetism. The larger observed value of μ<sub>eff</sub> for CoMoAlNa compared to CoMoAl (5.7 vs 4.8 BM, Table 1) revealing the preponderance of octahedral cobalt in the former also supports our conclusion that sodium ions on the surface of the alumina support favor the distribution of cobalt in the condensed β phase rather than in the dispersed δ phase. Sulfur compounds are either strongly adsorbed (380°C) or react to form the sulfide with the β phase cobalt (500°C) with the result that reduction to the metal is suppressed.

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