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Title	STUDIES ON COMOX CATALYST-PART 1 : A study on fresh $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -CoO, $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -MoO <sub>3</sub> and $\gamma$ -Al <sub>2</sub> O <sub>3</sub> -CoO-MoO <sub>3</sub> systems by ESR technique
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## STUDIES ON COMOX CATALYST-PART 1

### A study on fresh $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-CoO, $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub> and $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-CoO-MoO<sub>3</sub> systems by ESR technique

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#### Abstract

It is found that cobalt doped  $\gamma$ -alumina tends to incorporate the cobalt ions in the bulk forming cobalt aluminate spinel. Molybdenum doped  $\gamma$ -alumina contains molybdenum on the surface only and shows the presence of Mo(V) in small concentrations. Interaction between support and molybdenum starts at 300°C. In doubly doped (cobalt and molybdenum) samples two competitive processes occur. Previously present surface layer of molybdenum favours cobalt molybdate formation, otherwise cobalt diffuses in the bulk forming spinel. Magnetic susceptibility data are also reported.

#### Introduction

Comox is used extensively in industry for hydrofining purposes. In general, it contains cobalt and molybdenum oxides, which are the active constituents, supported on a refractory base. Although the use of this catalyst is very common but the roles played by individual constituents in the catalytic composition, structure *etc.*, as reported by various workers, are not consistent.

The optimum atomic ratio of cobalt and molybdenum from activity point of view reported in literature<sup>1-3)</sup> ranges from 0.2 to 1. Even the nature of distribution of cobalt and molybdenum and their different compounds detected by various workers differ considerably. Mitchel *et al*<sup>4,5)</sup> found that cobalt is present as Co(II) with 50% in octahedral and 50% in tetrahedral coordination in well dispersed state and with very little magnetic interaction. Molybdenum has been found in hexavalent state and tetrahedral coordination. None of well defined compounds of Al, Co and Mo could be detected. On

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P. K. GOUR *et al.*

the other hand SCHÜIT *et al.*<sup>6,7</sup> have reported that Co is distributed throughout the bulk as spinel  $\text{CoAl}_2\text{O}_4$  and Mo is present in hexavalent state as a monolayer covering about 20% of the carrier surface.

RICHARDSON<sup>8</sup> found that of the samples having Co : Mo ratio higher than 0.3, the final composition depended on the cobalt concentration and the curing temperature. The extent of  $\text{CoAl}_2\text{O}_4$  formation increased with increase in temperature up to 650°C at the expense of CoO and active cobalt. Above 650°C, the formation of  $\text{CoMoO}_4$  starts at the expense of  $\text{CoAl}_2\text{O}_4$ . DUFAUX *et al.*<sup>9</sup> detected the presence of Mo(V) in  $\gamma\text{-Al}_2\text{O}_3$ -Molybdenum system cured at 477°C but they also concluded that Mo stabilises only in hexavalent state.

Keeping above facts in view a detailed investigation on Comox catalyst and its constituents with special reference to mechanism of hydrodesulphurisation has been undertaken. The present paper deals with study on the state of combination of  $\gamma\text{-Al}_2\text{O}_3\text{-CoO}$ ,  $\gamma\text{-Al}_2\text{O}_3\text{-MoO}_3$  and  $\gamma\text{-Al}_2\text{O}_3\text{-CoO-MoO}_3$  systems by ESR technique.

## Experimental

### Preparation :

(a)  $\gamma\text{-Al}_2\text{O}_3$ : Aluminium hydroxide was precipitated from  $\text{Al}(\text{NO}_3)_3$  solution by  $\text{NH}_4\text{OH}$  at pH 8~9. The precipitate was filtered, washed free from  $\text{NO}_3^-$  and dried at 120°C. Dried mass was cured at 500°C for 8 hrs. Alumina so prepared was used for all sample preparations.

(b)  $\gamma\text{-Al}_2\text{O}_3\text{-CoO}$ :  $\text{Al}_2\text{O}_3$  grits prepared as mentioned above were soaked in  $\text{Co}(\text{NO}_3)_2$  solution to build up 6~7% cobalt concentration as CoO by weight. After soaking the alumina grits were separated, dried at 120°C and finally cured at 500°C in the air for 8 hrs. Mechanical mixture containing 5% CoO by weight was prepared for detection and confirmation of interaction between CoO and  $\text{Al}_2\text{O}_3$ . Cobalt oxide for preparing mechanical mixture was obtained by thermal decomposition of  $\text{Co}(\text{NO}_3)_2$  at 500°C for 8 hrs in air.

(c)  $\gamma\text{-Al}_2\text{O}_3\text{-MoO}_3$ : Alumina grits were soaked in ammonium paramolybdate solution to build up the requisite concentration of molybdenum. Later on grits were separated, dried and cured at 500°C for 8 hrs. Since in single soaking the molybdenum concentration of the order of 19~20% could not be attained so the process of soaking and curing was repeated. To investigate the effect of heat treatment on interaction between  $\text{Al}_2\text{O}_3$  and molybdenum, samples were prepared by single soaking and curing in the temperature range of 250 to 500°C in steps of 50°C.

*Studies on Comox Catalyst. I.*

(d)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-CoO-MoO<sub>3</sub>: Samples containing approximately 6 to 7% CoO and 19 to 20% MoO<sub>3</sub> by weight were prepared by soaking in Co(NO<sub>3</sub>)<sub>2</sub> and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4 H<sub>2</sub>O solutions respectively. Process employed for CoO and MoO<sub>3</sub> incorporation in  $\gamma$ -Alumina was same as mentioned earlier. Since incorporation of MoO<sub>3</sub> required two soakings, so three samples with different combination were prepared to investigate the effect of different sequence of incorporation. The sequence observed for incorporation was (1) CoO followed by two successive soaking and curing in air of MoO<sub>3</sub> (2) MoO<sub>3</sub> followed by cobalt and finally again MoO<sub>3</sub> and (3) two MoO<sub>3</sub> soaking and curing and finally followed by CoO. The samples so prepared were termed as sample No. 1, 2 and 3 respectively.

The electron spin resonance spectra were recorded on a BRÜKER-Physik, Model B-ER 402, X-band ESR spectrometer operating at 9.6 GHz and fitted with a TE<sub>102</sub> mode rectangular cavity. The magnetic field was modulated at 100 kHz. Thin walled silica tube was utilised for keeping samples in the cavity and the first derivative of the spectra was recorded. The magnetic field was measured by a proton resonance gaussmeter and the  $g$  values measured using polycrystalline DPPH as reference ( $g=2.0036$ ). Quantitative measurements of Mo(V) in different samples were done by comparing the areas under the adsorption curves obtained by integrating the recorded signals for the different samples with those of standards supplied by the instrument manufacturers.

The magnetic susceptibility of the samples at the room temperature were determined by a Faraday type magnetic balance where pure CuSO<sub>4</sub>·5H<sub>2</sub>O was used as standard.

All the chemicals and reagents used were of A. R. grade. For estimation of molybdenum and cobalt the sample was digested in *conc.* H<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. Subsequently the dried-up mass was dissolved in *dil.* HCl. Molybdenum was estimated gravimetrically by precipitating it as PbMoO<sub>4</sub>.<sup>10,11</sup> Cobalt was estimated volumetrically by EDTA using murexide as indicator.<sup>12</sup> In mixtures containing molybdenum and cobalt, the molybdenum was separated out as PbMoO<sub>4</sub> by lead acetate. After separation of molybdenum the excess lead was removed by *dil.* H<sub>2</sub>SO<sub>4</sub> and subsequently the cobalt was estimated as mentioned above.

### Results and Discussion

The ESR spectra of pure MoO<sub>3</sub> produced no signal. The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> used as support gave a very weak signal at high  $g$ -value. This is probably due to presence of some impurity in the sample. Similar signal in Al<sub>2</sub>O<sub>3</sub> support

was observed by UEDA and TODO *et al.*<sup>13)</sup> Cobalt oxide exhibited a broad signal at  $g=2.24$  with peak to peak width of 2400 gauss. Its magnetic susceptibility at 30°C and 6 k gauss magnetic field was  $26.7 \times 10^{-6}$  CGS units. Although pure alumina and MoO<sub>3</sub> did not exhibit any signal but MoO<sub>3</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> system cured at 500°C exhibited signal at  $g=1.9318$  indicating presence of Mo(V) in the sample and interaction between support and molybdenum. The interaction between support and molybdenum oxide started at 300°C (Fig. 1). Formation of Mo(V) increased with temperature up to 400°C and thereafter the concentration of Mo(V) started decreasing (Table 1). Probably at higher temperature the Mo(V) formed due to interaction of support and molybdenum is oxidised to hexavalent state. At present the mechanism of interaction between support and molybdenum

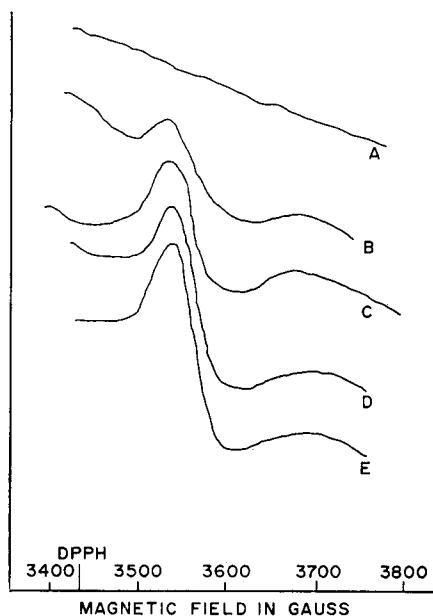


Fig. 1. Mo(V) signal of ESR spectra for Al<sub>2</sub>O<sub>3</sub>+MoO<sub>3</sub> system cured at temperature 250(A), 300(B), 350(C), 400(D) and 500°C(E), respectively.

TABLE 1.

No.	Details of samples	Magnetic susceptibility at 30°C, 6k Gauss CGS Unit.	No. of ESR lines.	$g$ -values	Peak to peak width (Gauss)	%MoO <sub>3</sub> by weight	Concentration of Mo(V) (Spins/gm)	$\frac{\text{Mo(V)}}{\text{Mo(VI)}} \times 10^6$
1.	Al <sub>2</sub> O <sub>3</sub> +MoO <sub>3</sub> cured at 250°C	Diamagnetic	—	—	—	15.31	—	—
2.	Al <sub>2</sub> O <sub>3</sub> +MoO <sub>3</sub> cured at 300°C	<i>do.</i>	One	$g_c=1.9318$ $g_1=1.9423$ $g_2=1.9111$	62.47	15.31	$191 \times 10^{14}$	29.9
3.	Al <sub>2</sub> O <sub>3</sub> +MoO <sub>3</sub> cured at 350°C	<i>do.</i>	One	<i>do.</i>	<i>do.</i>	15.31	$235 \times 10^{14}$	36.7
4.	Al <sub>2</sub> O <sub>3</sub> +MoO <sub>3</sub> cured at 400°C	<i>do.</i>	One	<i>do.</i>	<i>do.</i>	15.31	$453 \times 10^{14}$	80.8
5.	Al <sub>2</sub> O <sub>3</sub> +MoO <sub>3</sub> cured at 500°C	$-0.25 \times 10^{-16}$	One	<i>do.</i>	<i>do.</i>	17.89	$360 \times 10^{14}$	47.9

Colour of all the samples was whitish.

TABLE 2.

No.	Details of sample	Colour	Magnetic susceptibility at 30°C, 6k gauss CGS unit.	No. of ESR lines	<i>g</i> -values	Peak to peak width (gauss)	%CoO by weight.
1.	Al <sub>2</sub> O <sub>3</sub>	White	Diamagnetic	Nil	—	—	—
2.	CoO	Black	26.7 × 10 <sup>-6</sup>	One	2.24	2400	100
3.	Al <sub>2</sub> O <sub>3</sub> +CoO cured at 250°C	Blackish	Zero	Nil	—	—	5.01
4.	Al <sub>2</sub> O <sub>3</sub> +CoO cured at 500°C	Greenish black	1.31 × 10 <sup>-6</sup>	Nil	—	—	5.01
5.	Al <sub>2</sub> O <sub>3</sub> +CoO (5%) mechanically mixed.	Grey	2.08 × 10 <sup>-6</sup>	Nil	—	—	5.00

TABLE 3.

No.	Details of sample	Colour	Magnetic susceptibility at 30°C, 6k gauss CGS unit.	No. of ESR lines	<i>g</i> -values	Peak to peak width (Gauss)	%CoO by weight	%MoO <sub>3</sub> by weight	Concentration of Mo(V) (spins/gm)	$\frac{\text{Mo(V)}}{\text{Mo(VI)}} \times 10^6$
1.	Al <sub>2</sub> O <sub>3</sub> +CoO+MoO <sub>3</sub> +MoO <sub>3</sub> cured at 500°C	Greenish	0.789 × 10 <sup>-6</sup>	One	<i>g</i> <sub>c</sub> =1.9318 <i>g</i> <sub>1</sub> =1.9423 <i>g</i> <sub>2</sub> =1.9111	62.47	6.31	19.93	420 × 10 <sup>14</sup>	50.3
2.	Al <sub>2</sub> O <sub>3</sub> +MoO+CoO+MoO <sub>3</sub> cured at 500°C	Dull Blue	1.07 × 10 <sup>-6</sup>	One	<i>do.</i>	<i>do.</i>	6.00	20.2	145 × 10 <sup>14</sup>	17.2
3.	Al <sub>2</sub> O <sub>3</sub> +MoO <sub>3</sub> +MoO <sub>3</sub> +CoO cured at 500°C	Blue	2.35 × 10 <sup>-6</sup>	Nil	Nil	Nil	5.92	22.04	Nil	Nil

leading to Mo(V) formation is difficult to explain and needs further investigations. DUFAUX *et al.*<sup>9</sup> also observed a weak signal at  $g=1.93$  for  $\text{Al}_2\text{O}_3$ - $\text{MoO}_3$  system cured at  $477^\circ\text{C}$  containing more than 10% by *wt* molybdenum. They also attributed it due to some interaction between molybdenum and support. The decrease in the Mo(V) signal intensity at the higher temperatures is consistent with their finding that molybdenum stabilises in the hexavalent state.

For comparison, a mechanical mixture of 5% CoO by weight with the  $\gamma$ -Alumina support was studied by ESR, as well as by magnetic balance. The signal to noise ratio was too poor to give any ESR signal. The magnetic susceptibility has the expected value (Table 2). In case of cobalt distributed over  $\gamma$ - $\text{Al}_2\text{O}_3$  and cured at  $250^\circ\text{C}$ , the magnetic susceptibility turned out to be zero. This result obviously shows that an antiferromagnetic compound of Co, Al and O has formed, where the spin moments of the Co(II) ions have cancelled one another out. SCHÜT *et al.*<sup>6,7</sup> have reported the formation of the spinel  $\text{CoAl}_2\text{O}_4$ , evenly over the bulk. Presumably, it is same phase, with the Co(II) ions distributed equally between the tetrahedral and octahedral sites. For the sample cured at  $500^\circ\text{C}$  however the magnetic susceptibility has shown some increase, indicating thereby that the spinel structure has been disturbed either through migration of Co(II) ions from one type site to another, or through partial oxidation of Co(II) to Co(III) state.

It was seen in the case of  $\gamma$ -Alumina doped with molybdenum, there is interaction between support and molybdenum, giving rise to a Mo(V) species, which may serve as an index to the extent of the interaction. In case of the doubly doped samples, there are two competing processes. Cobalt may be incorporated in the system in the form of a spinel or it may form a compound with Mo, which according to LIPSCH and SCHÜT could only be  $\text{CoMoO}_4$ , involving Mo(VI). The observations on the doubly doped samples find a ready explanation in this light. In the sample No. 1 where Co was first incorporated in the  $\gamma$ -Alumina, fol-

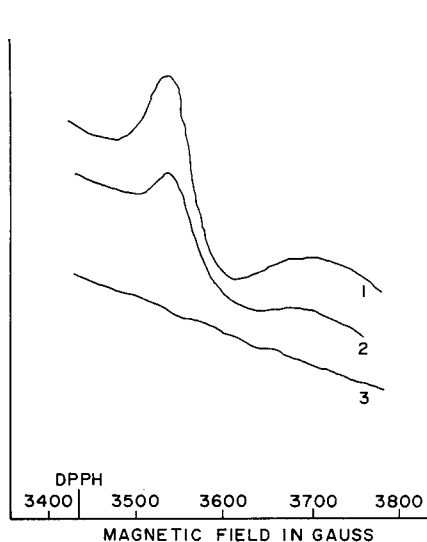


Fig. 2. Mo(V) signal of ESR for samples No. 1, 2 and 3, respectively.

*Studies on Comox Catalyst. I.*

lowed by two successive Mo soakings, spinel formation had already taken place and little Co was available for interacting with Mo. Formation of spinel is concluded from observed low magnetic susceptibility exhibited by the sample and strong ESR signal for Mo(V) confirms the interaction between molybdenum and the support (Table 3, Fig. 2).

In the sample No. 2 where an initial soaking with Mo was followed by Co treatment and finally another Mo soaking, the magnetic susceptibility is enhanced and at the same time the Mo(V) ESR signal intensity is reduced considerably showing the presence of Co in a state other than an antiferromagnetic one, as might be expected with  $\text{CoMoO}_4$ . Probably the chances of  $\text{CoAl}_2\text{O}_4$  formation are reduced due to barrier formed by molybdenum layer initially present there, which reacts preferentially with cobalt leading to  $\text{CoMoO}_4$  formation involving Mo(V) also. Weak signal for Mo(V) as exhibited by sample No. 2, probably results from fresh interaction between support and molybdenum due to final molybdenum treatment.

Finally, in conformity with the above, the magnetic susceptibility is the maximum and Mo(V) signal is the minimum (in fact zero) for sample No. 3, where Co soaking followed two initial soakings with Mo. Here Co reacted mainly with Mo, very little if at all being available for spinel formation. It also shows that molybdenum is confined to surface layer of the alumina support. Because had it been possible to incorporate it in the bulk, it should have been equally competitive in all the three samples in forming a compound with Co. The Mo surface layer hypothesis also finds support in the fact that in the first sample, where Co had formed spinel initially, the surface Mo layer had resulted in a lower magnetic susceptibility after curing at  $500^\circ\text{C}$  than in the corresponding sample with Co alone. It appears that the surface layer of molybdenum obstructs the oxidation of Co (II) to Co (III) state.

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P. K. GOUR *et al.*

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