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The CoO–MoO_3–Al_2O_3 Catalyst

I. Cobalt Molybdate and the Cobalt Oxide Molybdenum Oxide System

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The present investigation deals with cobalt molybdate and the cobalt oxide molybdenum oxide system. It is a prelude to an investigation of the CoO–MoO_3–Al_2O_3 hydrodesulfurization catalyst. DTA and X-ray spectroscopy show that compound formation only occurs at the composition $CoMoO_4$. Two modifications of $CoMoO_4$ were prepared. DTA shows the existence of two transition temperatures of the modifications into each other. Infrared spectra indicate that the molybdenum is octahedrally surrounded by oxygen in both modifications. The surrounding of the cobalt remains undetermined from reflection spectra, but from measurements of the magnetic susceptibility it follows that the cobalt is octahedrally surrounded in both modifications.

INTRODUCTION

The present paper deals with the first part of an investigation (*1*) concerning the structure and the properties of the hydrodesulfurization catalyst "cobalt molybdate" on alumina. There are several structural possibilities. The catalyst may be composed of independent cobalt and molybdenum oxides or these oxides may form compounds, viz., cobalt molybdates. A third possibility is that one of these oxides, or both, react with the carrier aluminum oxide to form aluminum-containing compounds. Therefore, it has to be investigated first of all what compounds can be formed by cobalt oxide and molybdenum oxide.

Compound formation is only mentioned in the literature for the composition $CoO \cdot MoO_3$. A survey of the X-ray patterns of this compound published in the literature is given in Fig. 1. Corbet and Eyraud (*2*) obtained their samples by precipitation from a solution of cobalt nitrate and a solution of molybdenum oxide in ammonia. Type C was prepared by calcination at about 800°C and type D by calcination below 700°C. Colleuille (*3*) obtained $CoMoO_4$ by precipitation from solutions of ammonium paramolybdate and cobalt nitrate, followed by a heating of the precipitate to 950°C. The sample when removed from the furnace was a compact violet mass, which upon cooling, underwent a violent, explosionwise transition to a black powder. From this, Colleuille concluded that there should exist two modifications of cobalt molybdate. Ricol (*4*) prepared cobalt molybdate by exposing cleaned sheets of cobalt metal to a solution of molybdenum trioxide. He gave three X-ray patterns: (A) for a non-calcined powder, (B) for a powder 7 hr calcined at 650°C, and (C) for a powder calcined 7 hr at 650°C followed by a 3 hr calcination at 950°C.

Smith (*5*) obtained orthorombic and monoclinic crystals from a melt of sodium molybdate, cobalt chloride, and sodium chloride. He first published the cell dimensions for the orthorombic crystals. We calculated *d*-values from the cell dimensions

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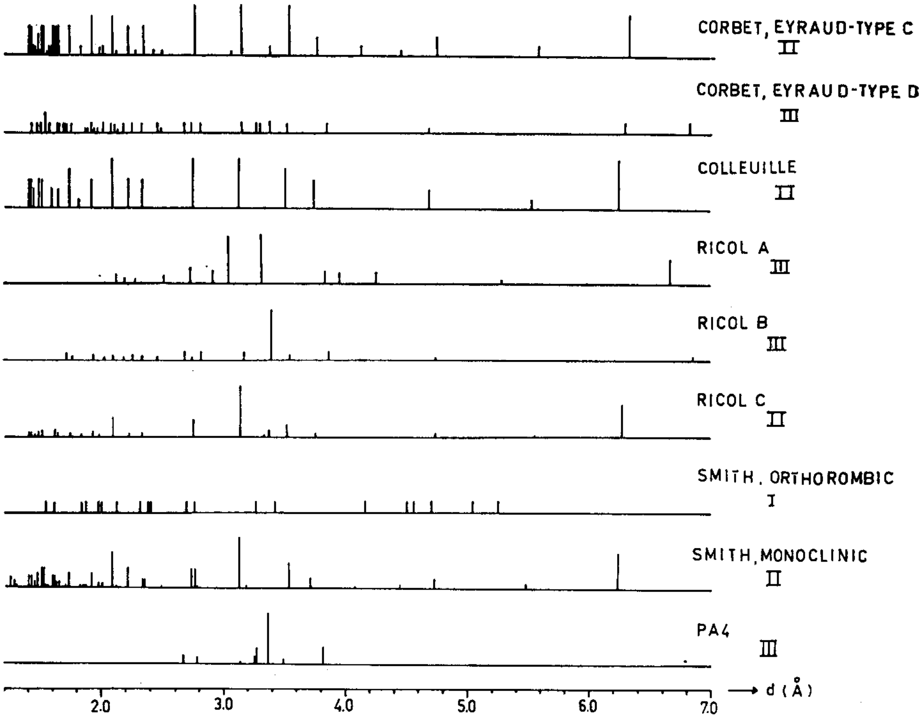

FIG. 1. Survey of X-ray patterns from the literature (relative intensities, except for I) (for references see text).

and they are quoted in Fig. 1. In a second publication (*6*) Smith gave data for the monoclinic crystals. He stated that this compound, having the formula $CoMoO_4$, could also be obtained by heating a precipitate from solutions of a cobalt salt and sodium molybdate to a temperature between 700–1100°C and by heating stoichiometric mixtures of cobalt chloride and sodium molybdate at 750–800°C. The compound consisted then of shiny black crystals, which when ground in a mortar, turned olive green. The *d*-values in Fig. 1 for the monoclinic compound have been calculated from $\sin^2\theta$ values, given by Smith (*6*). In a third publication (*7*) Smith and Ibers gave a complete structure determination of the monoclinic compound. It consists of cobalt and molybdenum atoms octahedrally surrounded by oxygen atoms. The octahedra, which are slightly distorted, share edges and form infinite chains parallel to the *c*-axis. Each chain is surrounded by four other chains and joined to them by corner sharing of oxygen atoms with a displacement, parallel to *c*, of one octahedron of the central chain relative to its four neighbors. Between the filled chains occur chains of "holes" formed by unfilled octahedra, and, viewed down the *c*-axis, the structure exhibits a pseudotetragonal symmetry.

In summary of the X-ray data from the literature, three modifications of cobalt molybdate can be distinguished: (I) orthorhombic cobalt molybdate: the pattern of Smith (*5*). (II) monoclinic cobalt molybdate: the diagrams of Smith (*6*), Colleuille (*3*), Corbet and Eyraud (*2*) type C, and Ricol (*4*) C. It has characteristic *d*-values of 2.09, 2.75, 3.13, 3.52, 4.7, and around 6.25 Å. All these patterns were obtained from samples heated during their preparation at a temperature above 700°C. (III) The patterns of Corbet and Eyraud (*2*) type D, and of Ricol (*4*) A and B. It has characteristic *d*-values of 2.67, 3.27, 3.37, and 3.83 Å. The calcination of these samples was below 700°C. Colleuille (*3*) and Trambouze *et al.* (*8*) found an endothermal peak at about 420°C, when they investigated cobalt molybdate by DTA.

Trambouze *et al.* (*8*) made high temperature X-ray measurements, but could not detect any changes in the crystalline state. Repeating the DTA measurements on the same sample, as used in the first run, they now failed to show the endothermal peak. However, after the sample was allowed to remain at room temperature for a few days, the peak reappeared again. The nature of this transition will be discussed later on.

Because X-ray spectroscopy fails for the determination of the $CoO-MoO_3-Al_2O_3$ catalyst structure, we have to resort to other methods like infrared and reflection spectroscopy and magnetic measurements. This, in its turn, makes it necessary to investigate the pure compound cobalt molybdate also with these methods.

METHODS

We prepared our samples by melting mixtures of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ and ammonium paramolybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in the desired Co/Mo ratio. They were then heated at 280°C to eliminate the ammonium nitrate and finally calcined at the desired temperature.

The X-ray patterns were obtained on a Philips diffractometer using Fe $K\alpha_1$ radiation, with wavelength 1.93597 Å, and Mn filter. The DTA investigation was carried out with the help of a Linseis apparatus with a heating rate of 10°C min^{-1}. The infrared spectra were taken with a Perkin-Elmer 137 Infracord spectrophotometer, a Perkin-Elmer 237 grating spectrophotometer and a Hitachi EPI-G2 spectrophotometer, using the potassium bromide wafer technique. For the reflection spectra we used the diffuse reflectance method and our apparatus consisted of a Zeiss PMQ II spectrophotometer with an RA2 reflectance attachment for the 11000–50000 cm^{-1} wavenumber range and an RA3 attachment for the 4000–12000 cm^{-1} range. With the RA2 attachment the light is reflected from a plane mirror on to the sample or reference surface at a 45° angle of incidence, while the reflected light at a 0° angle with the normal to surface is focused on to the cathode of a photomultiplier. The RA3 attachment is of the integrating sphere type. The sphere is coated with magnesium oxide, which serves also as standard. Therefore, if other references than magnesium oxide are used the extinction of the reference has to be measured also and has to be substracted from the extinction of the sample to fit the data obtained with the RA3 attachment to those obtained with the RA2 attachment. A review of the theory, instrumentation and applications of reflectance spectroscopy is given by Wendlandt and Hecht (*9*). We used gamma alumina—the same as the catalyst carrier—as reference. The samples were diluted with gamma alumina, so that they finally contained 16% cobalt molybdate. This value was chosen because the hydrodesulfurization catalyst at our disposal contained 12% MoO_3 and 4% CoO. Samples and references were ground during 20 min in a ball mill.

The magnetic susceptibilities were measured with the help of a Newport variable Temperature System which was modified to allow measurements according to the Faraday method. For a more detailed description and for the calibration see (*1*).

RESULTS AND DISCUSSION

The Cobalt Oxide Molybdenum Oxide System

This system was investigated to check if, besides $CoMoO_4$, other cobalt molybdates exist. The samples were calcined for 16 hr at 600°C. The X-ray patterns are shown in Fig. 2. The cobalt oxide, obtained by heating of cobalt nitrate, has an X-ray diagram, which is in good agreement with that of Co_3O_4 published in the ASTM file no. 9-418 (Fig. 3). This is in accordance with the fact that Co_3O_4 is the stable modification of cobalt oxide below 990°C, as mentioned by, for instance, De Bie and Doyen (*10*). Figure 3 also shows that ammonium molybdate, after heating, produces an X-ray diagram in fairly good agreement with that of MoO_3 ASTM 5-0508. The differences in intensities might be explained by an orientation in the sample. Figure 2 shows that compound formation occurs only at a Co/Mo ratio

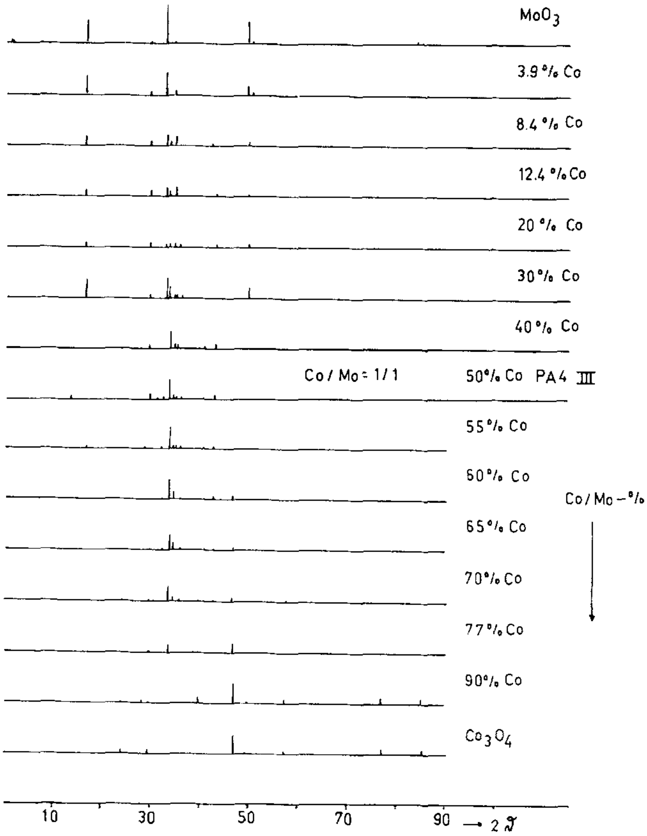

FIG. 2. X-ray patterns of the Co_3O_4–MoO_3 system.

of 1/1. This compound was analyzed and its composition corresponded with the formula $CoMoO_4$. It was a dark violet sample, the color of which changed to olive green, when ground in a mortar. Its X-ray pattern is also depicted—as PA4—in Fig. 1. As shown this pattern corresponds with those of modification III, as was expected because of the fact that the calcination temperature of PA4 was below 700°C.

A DTA investigation was carried out to determine the phase diagram. As the apparatus at our disposal did not allow

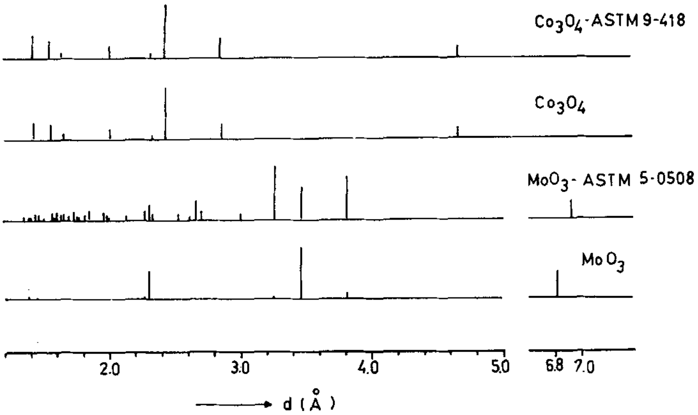

FIG. 3. X-ray patterns of cobalt oxide and molybdenum oxide.

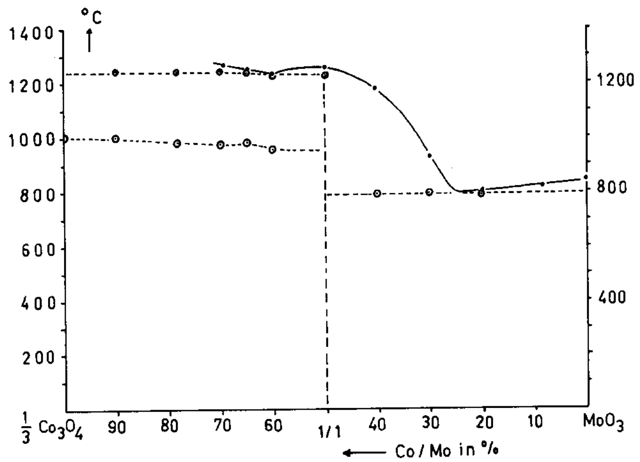

FIG. 4. Phase diagram of the Co$_3$O$_4$–MoO$_3$ system.

measurements above 1250°C, the complete diagram could not be obtained. The information is only complete in the range with Co/Mo ratio's equal to and smaller than 1. The diagram is represented in Fig. 4. There are eutectic lines at 1240 and 790°C. The line at 990°C corresponds to the transition $2Co_3O_4 \rightarrow 6CoO + O_2$ (*10*). The phase diagram supports the conclusion drawn from the X-ray measurements, that compound formation occurs only at the Co/Mo ratio 1/1.

It is, however, somewhat peculiar that these DTA measurements do not give any indication for the presence of several different modifications. Therefore, a more extensive search was made to clear up this problem.

The Phase Transitions of Cobalt Molybdate CoMoO$_4$

The DTA measurements discussed above were made by simply heating the samples until their melting point was reached. If however thermograms were taken of a sample that had already undergone a run in the apparatus, the following transitions were found:

(a) An exothermal transition at 35°C, only found when cooling a sample after it was heated to a temperature of at least 710–712°C. The form of the peak was rather strange; it is represented in Fig. 5. The only explanation for this form can be that the peak corresponds to the violent explosionwise transformation mentioned by Colleuille (*3*).

(b) An endothermal transition at 420°C, always found when heating up a sample that had undergone the exothermal 35°C transition. The endothermal transition is the same as mentioned in (*3*) and (*8*). No other transitions were found, in particular not at 710–712°C.

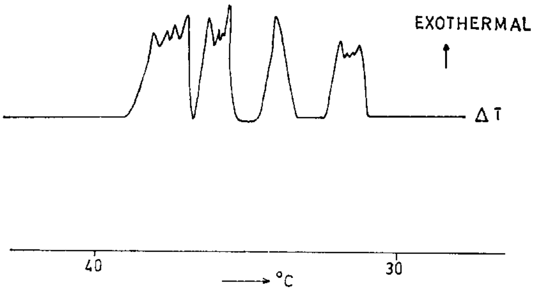

FIG. 5. Exothermal DTA peaks around 35°C.

To obtain different modifications of cobalt molybdate the following samples were prepared:

PB1, the sample was only calcined for 16 hr at 280°C.

PB2, a portion of PB1 was fired for 16 hr at 1000°C and then cooled. When the sample was removed from the furnace it was a compact violet mass. Upon reaching room temperature it underwent the violent explosionwise transformation to shiny black crystals. When the crystals were ground their color changed to olive green.

PB3, a portion of PB2 was heated for

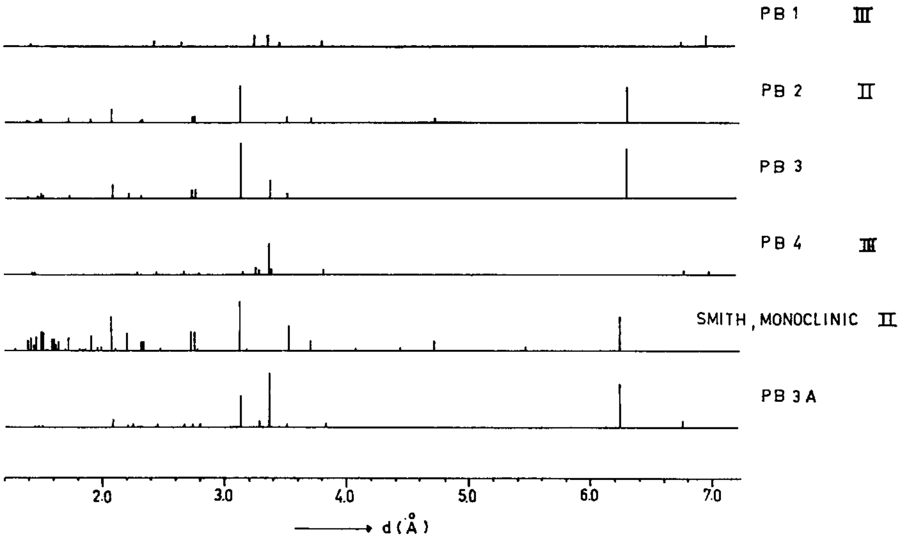

FIG. 6. X-ray patterns of PB samples together with modification II (Smith).

16 hr at 500°C and then cooled. The color was violet. When the sample was shaken, its color changed to dark grey violet, and when ground it became olive green.

PB4, as a comparison with the PA4 preparation, another portion of PB1 was calcined for 16 hr at 500°C. The color was violet and when rubbed, it changed also to olive green. PB4 had the same X-ray pattern as modification III, as represented as PA4 in Figs. 1 and 2.

A survey of the X-ray patterns of these samples is given in Fig. 6 together with the pattern for the monoclinic modification II (*6*). The X-ray patterns of PB2 and II are closely similar as show the lines at *d*-values of 2.09, 2.75, 3.13, 3.52, 4.7 and 6.25 Å. So by heating above 712°C—for instance 1000°C—and cooling to room temperature modification II is obtained. This was to be expected for Smith heated his sample during, its preparation, to a temperature of 1100°C. From the coincidence of the *d*-values 1.43, 2.44, 2.67, 3.25, 3.37, 3.81, and 6.75 Å we can conclude for PB1 and PB4 that they have the same form, viz., modification III. The crystalline state of PB4 is obviously better defined than that of PB1, giving a more pronounced X-ray diagram. That PB1 and PB4 have the same form was to be expected, for PB4 was made from PB1 by a calcination at 500°C, during which heating and subsequent cooling no peaks on the thermogram were observed.

The pattern of PB3 resembles very much

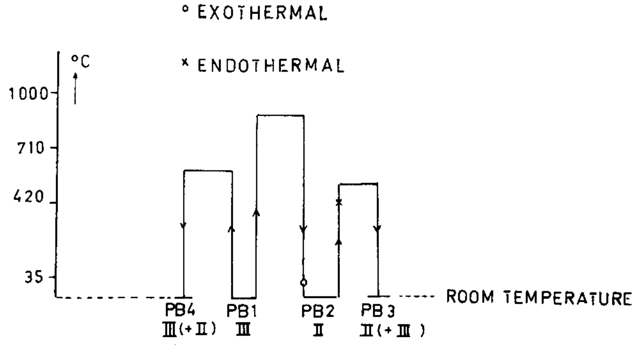

FIG. 7. Phase transitions of $CoMoO_4$.

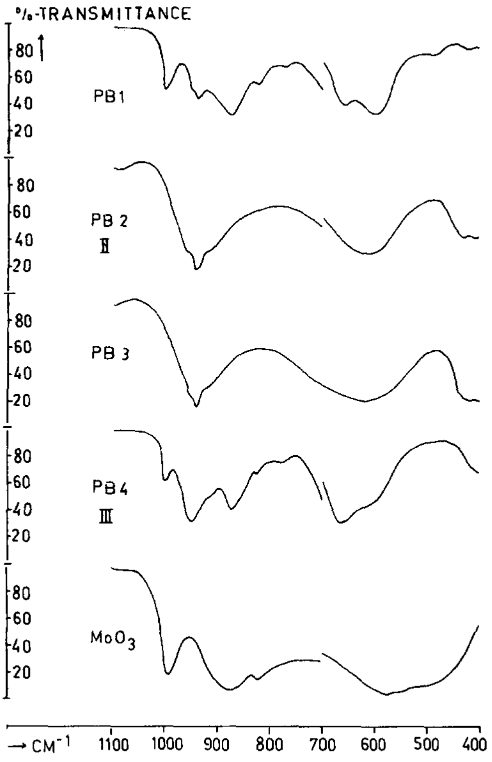

FIG. 8. Infrared spectra of PB samples.

that of modification II (see the lines at 2.09, 2.75, 3.13, 3.52, and 6.25 Å). This during which heating it underwent the was not expected because PB3 was made from PB2 (II) by heating it to 500°C, endothermal transition at 420°C, whereas upon cooling it did not undergo the exothermal transition at 35°C. Figure 6 also shows that a small amount of III is present in PB3 (3.27 Å). PB3 is a mixture of II and III. When we heated a sample of PB2 at 500°C, cooled it as quickly (PB3 A) as possible, the pattern had more and stronger lines, all belonging to modification III, viz., the lines at 2.44, 2.67, 3.29, 3.37, 3.81, and 6.75 Å.

We can conclude now that the endothermal peak at 420°C corresponds to a transition of II to III. This is not in agreement with the results of Trambouze *et al.* (*8*), who could find no differences in X-ray diagrams taken at room temperature and at 600°C. The exothermal peak at 35°C corresponds to the transition of III to II. This transition takes place in a sudden and violent way, during cooling from a temperature above 712°C, whereas during cooling from a temperature between 420–710°C it is so slow that it cannot be recorded on the thermogram. This may also explain the fact mentioned in (*3*) and (*8*) that no peaks were found by DTA if a sample was cooled, subsequent to heating it to about 600°C, that directly hereafter no peak at 420°C was observed either, but that this peak reappeared again after a few days. The modification III can be contained in a relatively stable state by avoiding any heating above 710°C during preparation. This explains why the X-ray diagrams of PB1 and PB4 (Fig. 6) and of A and B of Ricol and of PA4 (Fig. 1) are similar. All these samples contain however a certain amount of II as can be seen from the lines at 3.13 for PB4 (Fig. 6), at 3.13, and 3.52 for PA4 (Fig. 1) and at 3.52 for Ricol's sample B (Fig. 1). It appears, therefore, possible for modification III to change slowly to the monoclinic modification II.

To summarize we depict the ways of the transformations in Fig. 7. When cobalt nitrate and ammonium paramolybdate are melted together a stable compound with modification III is obtained. Its crystalline state becomes better defined by a calcination at higher temperature, as long as the temperature remains below 710°C. Calcination above 712°C, followed by cooling to room temperature, yields modification II. This transforms again at 420°C to III, but now it is not stable and changes at lower temperatures again to II.

Infrared Spectra

To get somewhat more insight in the structure of cobalt molybdate, especially modification III, infrared spectra were made. They give information about the surrounding of the molybdenum. A theoretical exposition of infrared spectra is given by Nakamoto (*11*). The spectra of PB1, PB2, PB3, and PB4 are shown in Fig. 8. The spectra of PB2 and PB3 are similar—as was expected from the X-ray data—with an adsorption maximum with two shoulders at 945, a maximum at 625 and

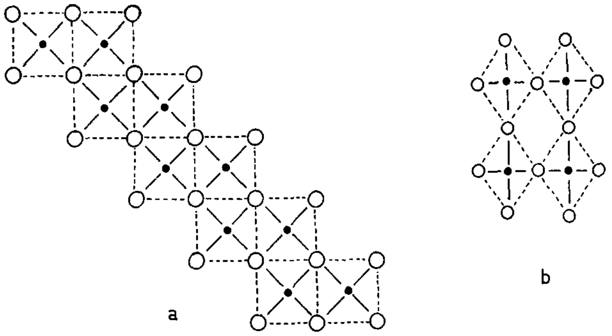

FIG. 9. MoO_3 structure: (a) the plane of the layer; (b) perpendicular to this plane.

a double maximum at 420 cm^{-1}. The spectra of PB1 and PB4 (III) are also very similar. Next to the peaks of II they have other peaks, namely two very sharp peaks at 995 and 820, two somewhat broader peaks at 875 and 775 cm^{-1} and a very broad peak, which brings about a shoulder in the 625 peak at 580 cm^{-1}. These extra peaks are, with the exception of the 775 peak, identical to those found in the MoO_3 spectrum, which is also shown in Fig. 8.

According to Smith and Ibers (7) molybdenum in modification II occurs in an octahedral oxygen surrounding. Two of the oxygens are corner shared, while the other four are edge-shared. The site symmetry therefore is low; nevertheless the number of infrared lines is small. The spectrum of III is richer in lines than that of II, which either points to a different co-ordination of the molybdenum, or to a more strongly distorted octahedron. In view of the fact that the extra lines closely resemble those of MoO_3, where Mo also occurs in an octahedral surrounding, (see Fig. 9), we tend to the belief that the latter is the case. Barraclough *et al.* (*12*) propose for Mo–O bonds in an octahedron that a strong band at 985 corresponds to an "independent" Mo–O bond, while bands at 870 and 813 correspond to two different types of continuous Mo–O bonds. This does not fit very well with the Smith and Ibers structure, where all bonds are continuous. The proposal, however, is in agreement with the MoO_3 structure and spectrum.

A tentative hypothesis for the identification of our infrared spectra is that the $(MoO_6)^{6-}$ octahedron in modification II differs not so much from the O_h symmetry, that the infrared allowed transitions of threefold degeneracy are already split, so that the 945 line corresponds to one of these transitions. The lowering of symmetry connected with the conversion of modification II to III is then reflected in the splitting of this line into three resonances, viz., 995, 875, and 820 cm^{-1}. Following Barraclough *et al.* the 995 line then appears to point to the presence of independent Mo–O bonds. This agrees with the fact that the disap-

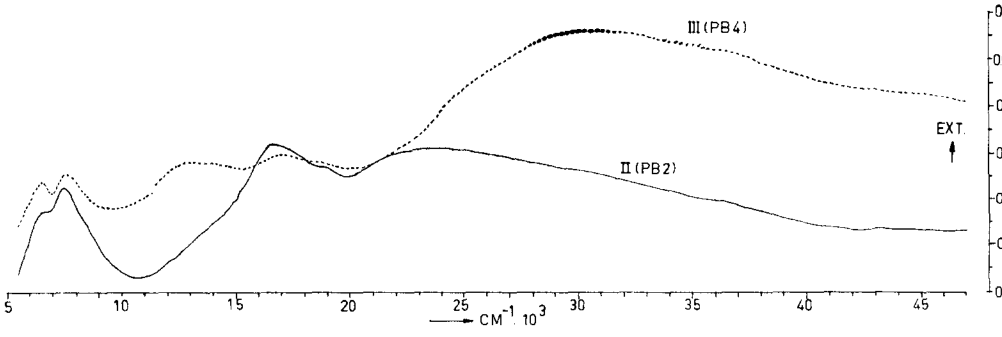

FIG. 10. Reflection spectra of the $CoMoO_4$ modifications.

pearance of the 945 line corresponds with the growth in intensity of the 995, 875, and 820 lines. As a conclusion we can say that the difference in structure between II and III lies in the manner in which the $(MoO_6)^{6-}$ octahedra are connected.

Reflection Spectra

In Fig. 10 the reflection spectra of PB2 (II) and PB4 (III) are shown. Modification II has sharp maxima at 6500, 7500, 16,500, and 19,000, a very broad band with a maximum at 24,000, and probably a shoulder at 13,500 cm^{-1}. Modification III has sharp maxima at 6500, 7500, 13,250, and 17,000, a very broad band with a maximum at 31,000 and probably a shoulder at 37,000 cm^{-1}. To identify the various bands, spectra of cobalt in MgO, ZnO, and Al_2O_3 were made. The samples contained respectively 9, 0.5, and 4% CoO. They were prepared by boiling to dryness solutions of the nitrates followed by a 2 hrs calcination at 600°C to expel the nitrous gases. The samples were then ground during 20 min in a ball mill and finally fired for 16 hr at 1100°C in a dry and oxygen free nitrogen atmosphere. MgO, ZnO or Al_2O_3, prepared in the same manner as the samples were used as references. According to, for instance, Cossee (*13*), cobalt occurs as Co^{2+} in an octahedral oxygen surrounding in MgO; in ZnO it occurs as Co^{2+} in a tetrahedral surrounding. In Al_2O_3 it also occurs as Co^{2+} in a tetrahedral surrounding, forming the blue compound $CoAl_2O_4$, according to Cossee (*13*) and Romeyn (*14*). The spectra are recorded in Fig. 11. Co^{2+} in ZnO is dark green and has a threefold split band with maxima at 15,500 and 16,500 and a shoulder at 17,750 cm^{-1}, a twofold split band with maxima at 6000 and 7000 cm^{-1} and a strong band with a maximum at 24,500 cm^{-1}. All these bands, with the exception of the 24,500 band, are also found for Co^{2+} in Al_2O_3 with a shift of 500 cm^{-1} to higher wavenumbers. A new maximum at 39,000 is observed. The Co^{2+} in MgO has a pink color; its spectrum is very weak with maxima at 8000, 20,000, 36,000, and 47,000 cm^{-1}.

If Figs. 10 and 11 are compared, the spectrum of modification II seems only interpretable in therms of a tetrahedral surrounding of Co^{2+}. This is in contradiction with the Smith and Ibers (7) structure, who found that cobalt is octahedrally surrounded. The spectrum of III corresponds reasonably well with octahedrally surrounded Co^{2+} ions, but in view of the weakness of the bands the evidence is not

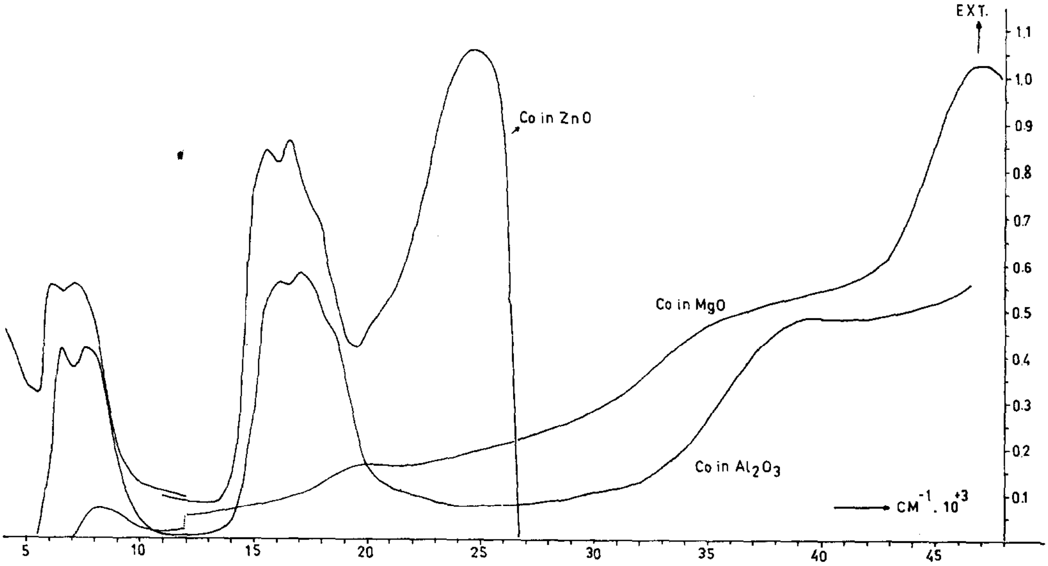

FIG. 11. Reflection spectra of Co^{2+} in MgO, ZnO, and Al_2O_3.

conclusive. In dealing with reflection spectra it should always be kept in mind that any information produced relates to surface layers, which might very well show a different orientation as encountered in the bulk situation. To make a definite determination about the surrounding of the cobalt we measured the paramagnetic susceptibility, as will be described next.

Magnetic Measurements

These measurements are extensively described in (*1*) and only a short description of the results is given here. The magnetic moment is calculated with the help of the method of the least squares from a plot of the reciprocal paramagnetic susceptibility ($1/\chi_p$) against the absolute temperature. The χ_p is related to 1 kg-atom of the cobalt ion and is obtained after a correction of the measured susceptibility for the diamagnetism. The diamagnetic contribution for $CoMoO_4$ is calculated from a table given by Selwood (*15*): $\chi_D = -84.20 \times 10^{-8}$ m^3 kgmole^{-1}. The plots of $1/\chi_p$ against T for II (PB2) and III (PB4) are shown in Fig. 12. The Curie–Weisz law is well obeyed. For modification II a magnetic moment of 5.4 Bohr magnetons and a Curie temperature of —4°K are found and for modification III a moment of 4.7 BM and a Curie temperature of —18°K.

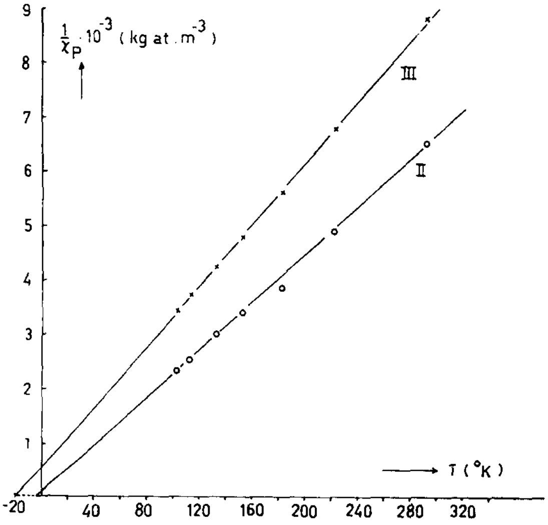

FIG. 12. Plots of the reciprocal paramagnetic susceptibility against the absolute temperature for the $CoMoO_4$ modifications.

Cossee (*13*) gives values of 4.0–4.1 BM for Co^{2+} in a tetrahedral oxygen surrounding, whereas he gives values of 4.7–5.1 BM for the octahedral interstice. A theoretical treatment is given by Griffith (*16*), who calculates for Co^{2+} a moment of 4.68 BM in an octahedral surrounding and of 3.87 BM in a tetrahedral surrounding. We can conclude that in both $CoMoO_4$ modifications the Co^{2+} ions are octahedrally surrounded. There exists a discrepancy between the magnetic and reflectance measurements for modification II; with the spectroscopic measurements a more tetrahedral character is found. The conclusion from the magnetic data, however, is in agreement with the Smith and Ibers (*7*) structure. The deviation of the spectroscopic measurements might be explained in two ways: first, the octahedra are slightly distorted, causing forbidden transitions to become less forbidden, and, secondly, some tetrahedrally surrounded Co^{2+} ions may be present at the surface of modification II.

CONCLUSIONS

In summary we can say that in the cobalt oxide molybdenum oxide system only the compound $CoMoO_4$ is found. This compound occurs in two modifications, that transform at 35 and 420°C into each other. The molybdenum and the cobalt are octahedrally surrounded in both modifications. The difference in structure between the two modifications is given by the manner in which the $(MoO_6)^{6-}$ octahedra are connected. Tetrahedrally surrounded cobalt ions may be present at the surface of modification II.

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REFERENCES

1. LIPSCH, J. M. J. G., thesis, University of Technology, Eindhoven, The Netherlands, 1968.
2. CORBET, F., AND EYRAUD, C., *Bull. Soc. Chim. France* **3**, 571 (1961).
3. COLLEUILLE, Y., thesis, Lyon 1955.
4. RICOL, P., *Compt. Rend.* **256**, 3125 (1963).
5. SMITH, G. W., Nature **118**, 306 (1960).
6. SMITH, G. W., *Acta Cryst.* **15**, 1054 (1962).
7. SMITH, G. W., AND IBERS, J. A. *Acta Cryst.* **19**, 269 (1965).
8. TRAMBOUZE, Y., COLLEUILLE, Y., AND THE, T. H., *Compt. Rend.* **242**, 497 (1956).
9. WENDLANDT, W. W., AND HECHT, H. G., "Reflectance Spectroscopy." Wiley (Interscience) New York, 1966.
10. DE BIE, E., AND DOYEN, P., *Cobalt* **15**, 3 (1962).
11. NAKAMOTO, K., "Infrared Spectra of Inorganic and Coordination Compounds." Wiley, New York, 1963.
12. BARRACLOUGH, C. G., LEWIS, J., AND NYHOLM, R. S., *J. Chem. Soc.* 3552 (1959).
13. COSSEE, P., thesis, Leiden, 1956.
14. ROMEYN, F. C., thesis, Leiden, 1953.
15. SELWOOD, P. W., "Magneto Chemistry," 2nd ed., p. 78. Wiley (Interscience) New York, 1956.
16. GRIFFITH, J. S., "The Theory of Transition Metal Ions," p. 273. Cambridge Univ. Press, London and New York, 1961.