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The CoO–MoO_3–Al_2O_3 Catalyst

II. The Structure of the Catalyst

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The present paper deals with the structure determination of the "cobalt molybdate on alumina" catalyst. Infrared spectra show that the molybdenum is present as MoO_3. Reflection spectra lead to the conclusion that the cobalt is distributed throughout the bulk of the alumina as $CoAl_2O_4$, whereas the MoO_3 is spread over the carrier surface, probably as a monomolecular layer. Magnetic measurements confirm the conclusion that the cobalt is present as $CoAl_2O_4$.

INTRODUCTION

The present paper deals with a part of an investigation concerning the structure and the properties of the CoO–MoO_3–Al_2O_3 hydrodesulfurization catalyst (*1*). In a former paper (*2*) we reported on the cobalt oxide–molybdenum oxide system. This served as a prelude to the investigation of the catalyst structure. We are able now to check if the cobalt molybdates found in (*2*) are present in the catalyst or that it consists of other compounds, viz., the separate cobalt and molybdenum oxides or aluminium-containing compounds.

METHODS

We had at our disposal a commercially manufactured catalyst Ketjenfine 124 containing 4% CoO and 12% MoO_3 (wt % dry base). Its surface area amounts 250 m^2 g^{-1}. This catalyst was investigated with the help of infrared and reflection spectroscopy and magnetic measurements. The spectra and susceptibility were compared with those reported for $CoMoO_4$ in (*2*). For a detailed description of the experimental techniques see (*1*). The X-ray spectroscopy failed because the concentrations of cobalt and molybdenum are too low.

RESULTS AND DISCUSSION

Infrared Spectra

The spectra of the $CoMoO_4$ modifications II (PB2) and III (PB4), PK, PK500, PSM, and Ketjenfine are shown in Fig. 1. The samples PB2 and PB4 are described in (*2*). PK is a mixture of alumina—the catalyst carrier—and MoO_3, containing 12% MoO_3. PK500 was obtained by calcination of PK during 16 hr at 500°C. PSM is a sample placed at our disposal by Ketjen and prepared in the same way as Ketjenfine, but now containing only 12% MoO_3 and no CoO. Alumina has a broad and strong adsorption band in the wavenumber range, which is of interest for our measurements. For spectra of PK, PK500, PSM, and Ketjenfine, a postassium bromide wafer was used as reference, containing so much alumina that the alumina absorption was compensated. The absorption bands are rather weak owing to the small Mo content of the samples. Hence, the transmission scale is expanded by a factor 5 for PK500, PSM, and Ketjenfine, indicated as T 5× in Fig. 1.

The infrared spectra of $CoMoO_4$ (II and III) were already discussed in (*2*). The spectrum of PK is exactly the same as that of MoO_3 (*2*), as can be seen from the bands at 995, 875, 820, and around 600 cm^{-1}. This was to be expected, because PK is

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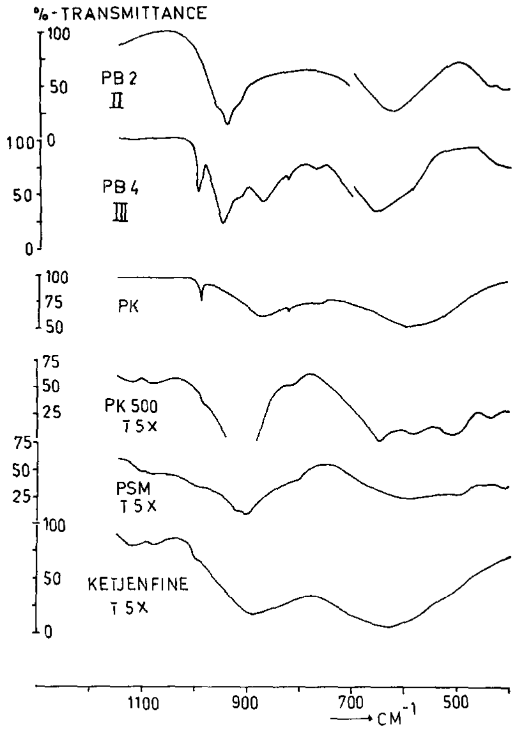

FIG. 1. Infrared spectra of various samples.

simply a mixture of MoO_3 and alumina. All MoO_3 bands are also found in the spectra of PK500 and PSM. However, they are now weaker and broader, possibly as a consequence of a more amorphous structure. The 600 band seems to be split into a number of separate bands, which might be due to the existence of Mo–O–Al continuous bonds and a consequent lowering of the symmetry. Two weak bands around 1100 cm^{-1} are observed in the spectra of PK500 and PSM, which were also found by Clark and Doyle (*3*) for calcium, barium, and lithium molybdate, in which the molybdenum is tetrahedrally coordinated. The strong band at 820–830 cm^{-1}, typical of tetrahedrally surrounded Mo coincides with the 820 band of MoO_3, which confuses the evidence, but the possibility remains that some molybdenum ions are tetrahedrally surrounded. The conclusion can be made that MoO_3 maintains its structure, in general, on alumina; it is somewhat more amorphous and some ions might occur in a tetrahedral surrounding.

If we now pass on to the spectrum of Ketjenfine, we do not find the resonances of the $CoMoO_4$ modifications II and III but those of PK500 and PSM. The bands of Ketjenfine are even broader and weaker, it is true, and there is no 820 band, but yet they are similar to those of PK500 and PSM. The two bands around 1100 cm^{-1} are also present and the 995 band is still present as a small shoulder. So we may conclude that the molybdenum is present as MoO_3 in Ketjenfine in the same form as in PK500 and PSM. The presence of cobalt has no significant influence on the spectrum. The absence of the resonances of II and III means that no cobalt molybdate is present in what is frequently called the "cobalt molybdate" catalyst, but that it is composed of MoO_3 and some other independent cobalt compound; the nature of the latter is investigated by reflectance and magnetic measurements.

Reflection Spectra

The reflection spectrum of Ketjenfine is shown in Fig. 2. It has a double maximum around 7000, a threefold split band with maxima at 16,000 and 17,000 and a shoulder at 18,500, and a strong and broad band beginning at 22,000 cm^{-1}. Figure 3 shows the spectra of PK, PK500 (both described above), and PL. The sample PL was prepared by impregnating alumina—the catalyst carrier—with a solution of cobalt nitrate in water and then calcining it for 12 hr at 750°C. The sample PL contained 4% CoO and its color was blue. PK has a weak band beginning at 22,500 cm^{-1}, whereas this band has much higher extinction values for PK500. We will later return to a discussion of this phenomenon. The double maximum at 7000 and the threefold split band around 17,000, found for Ketjenfine, are exactly the same as those found for PL; and the broad band beginning at 22,500 of Ketjenfine is very similar to the band found for PK500. A comparison of Figs. 2 and 3 reveals clearly that the spectrum of Ketjenfine is simply the superposition of the spectra of PL and PK500. Again it is found that cobalt oxide and molybdenum oxide have no influence on each other in the spectrum of Ketjenfine. They are, therefore, present as two independent compounds, viz., MoO_3 causing the broad band beginning at 22,500, and a cobalt compound causing the bands around 7000 and 17,000. A comparison of these last two bands, found for Ketjenfine and PL, with those of the $CoMoO_4$ modifications II and III [see Ref. (*2*)] and on the other hand the spectrum of Co^{2+} in Al_2O_3 ($CoAl_2O_4$) [see Ref. (*2*)], which has exactly the same bands around 7000 and 17,000, leads to the conclusion that the cobalt is not present as cobalt molybdate in the hydrodesulfurization catalyst, but as cobalt aluminate. Support for this conclusion will be found in the magnetic measurements.

The increase in intensity of the MoO_3 band mentioned above for PK500 is, we believe, a very significant detail, the more so since the infrared evidence suggest that there is no important change in the Mo–O configuration. Therefore, it appears as if we have to do with a form of MoO_3 possessing an abnormally high surface area, in view of the fact that reflectance measurements relate to the surface of a sample. An obvious explanation for the increase in intensity is that the MoO_3 is spread over the alumina surface. This is then even more true for Ketjenfine, since the extinction values of its MoO_3 band are somewhat higher than those found for PK500. The question arises whether this is physically possible. Assuming for MoO_3 a monomolecular layer with a thickness of 5 Å and a density of 4.5 g · cm^{-3}, the surface area of 0.12 g of MoO_3 would be 54 m^2. According to the specification, the catalyst has a specific surface area of 250 m^2 g^{-1}. From this we may conclude that it is indeed possible that the MoO_3 is present as a monomolecular layer: even then it would cover only 20% of the alumina surface.

In contrast to this, the extinction values of the $CoAl_2O_4$ bands of Ketjenfine are certainly not higher than those found for Co^{2+} in Al_2O_3 (*2*), which means that the cobalt ions are not spread over the alumina surface, but that they are distributed throughout the bulk; otherwise we would have found much higher extinctions in analogy with the MoO_3 band. These features are, of course, important with respect to the catalytic properties.

Magnetic Measurements

To confirm the conclusion that the cobalt in Ketjenfine is present as $CoAl_2O_4$, the

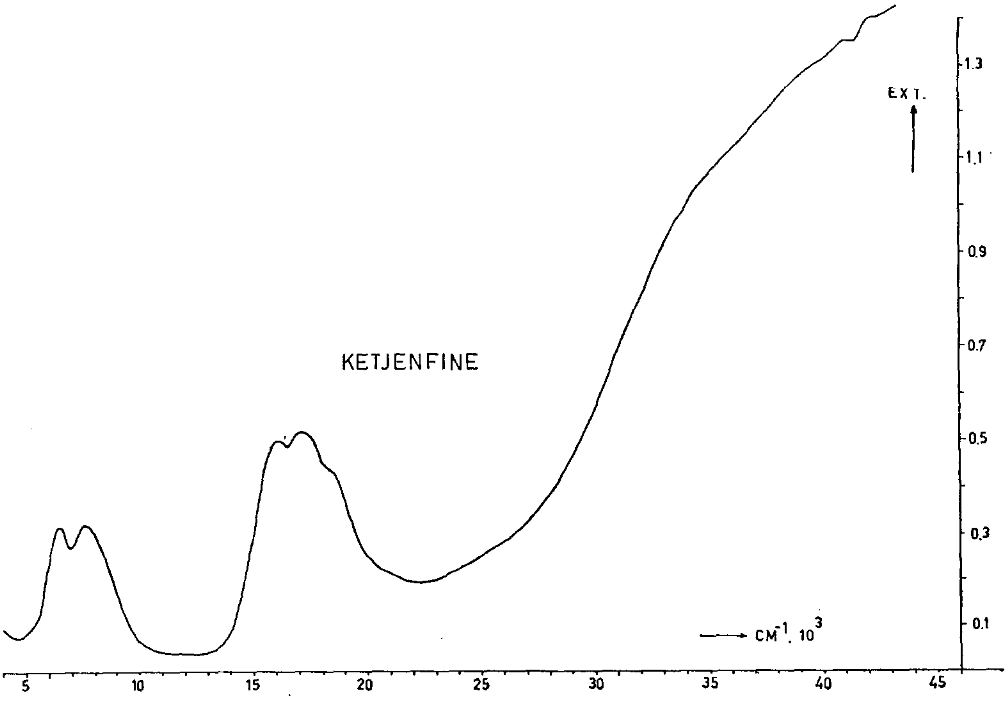

FIG. 2. Reflection spectrum of commercial catalyst.

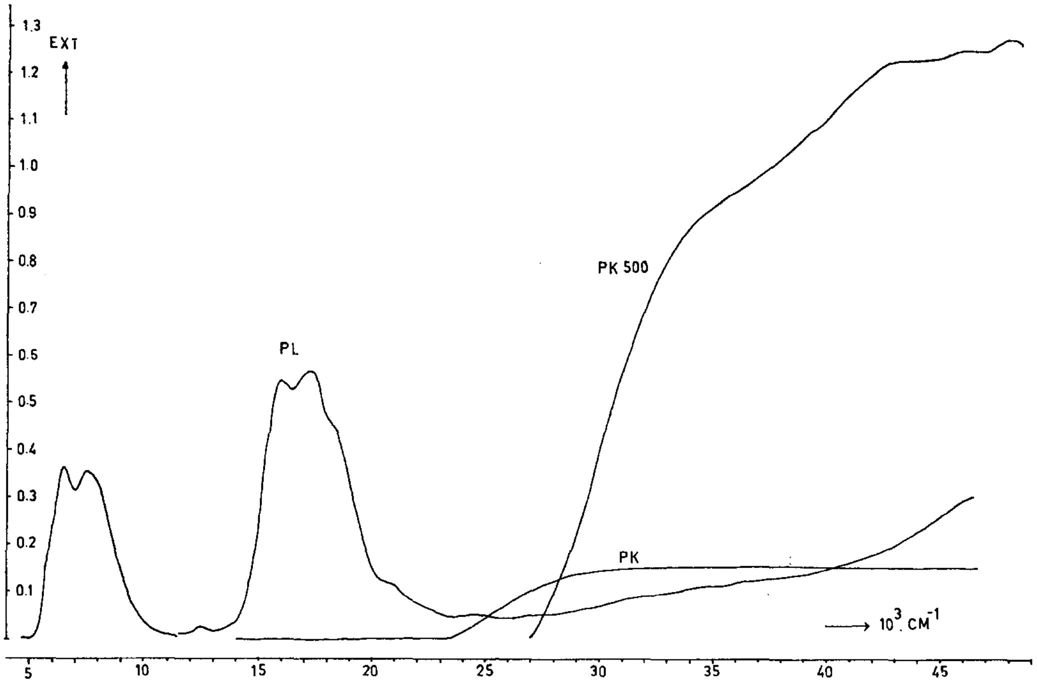

FIG. 3. Reflection spectra of various samples.

dependence of the paramagnetic susceptibility χ_P on the temperature was measured. For a detailed description of the measurements see (*1*).

The following formula is used:

$$\chi_P = (\chi - \chi_d)25M$$

in which χ_P = susceptibility related to 1 kg-atom of Co, corrected for the diamagnetic susceptibility (m^3 kg-atom^{-1}); χ = measured susceptibility (m^3 kg^{-1}); χ_d = diamagnetic contribution (m^3 kg^{-1}); and M = molecular weight of CoO, being 74.93. The factor 25 is used because of the fact that Ketjenfine contains 4% CoO. The diamagnetic contribution is equal to:

$$\chi_d = 0.04\chi_d(\mathrm{CoO}) + 0.12\chi(\mathrm{MoO_3}) + 0.84\chi(\mathrm{Al_2O_3})$$

$\chi_d(\mathrm{CoO})$ is calculated from a table given by Selwood (*4*), while $\chi(\mathrm{MoO_3})$ and $\chi(\mathrm{Al_2O_3})$ are taken from the Handbook (*5*). We obtain now: $\chi_d = -0.396 \times 10^{-8}$ m^3 kg^{-1}.

The plot of $1/\chi_P$ against the absolute temperature is given in Fig. 4. The Curie–Weisz law is well obeyed. A magnetic moment of 4.2 BM and a Curie temperature of +22°K are then calculated. The value of the magnetic moment agrees reasonably well with the value of 4.02 BM given by Cossee (*6*) for $CoAl_2O_4$. For the Curie temperature, however, he gives −35°K. He found a dependence of the magnetic moment and of the Curie temperature on the concentration

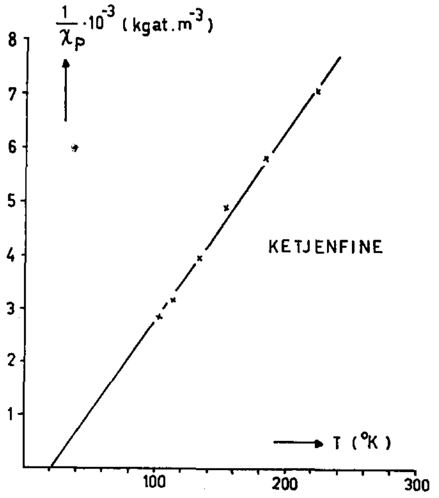

FIG. 4. Plot of the reciprocal paramagnetic susceptibility against the absolute temperature for commercial catalyst.

of cobalt. For $Co_{0.100}Zn_{0.900}Al_2O_4$, corresponding to 4% CoO, he found a magnetic moment of 4.06 BM and a Curie temperature of +15°K, both of which are in better agreement with our measurements. Another explanation for the differences between our values and those of Cossee may be found in the fact that only a small amount of paramagnetic material is present in the catalyst. An error in the diamagnetic correction plays now a rather important part.

The magnetic measurements are a strong support for the conclusion that in Ketjenfine the cobalt is present as cobalt aluminate; for $CoMoO_4$ we found magnetic moments of 5.4 BM (for II) and of 4.7 BM (for III) (*2*).

CONCLUSIONS

Summarizing we can say that infrared and reflection spectra show that no cobalt molybdate is present in the commercial hydrodesulfurization catalyst. The infrared spectra reveal that the molybdenum is present as MoO_3. The reflection spectra prove that the cobalt is distributed throughout the bulk of the alumina as cobalt aluminate, whereas they show that the MoO_3 is spread probably as a monomolecular layer covering about 20% of the carrier surface. Magnetic measurements confirm the conclusion that the cobalt occurs as $CoAl_2O_4$.

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Note added after completion of the manuscript

Recently, Ashley and Mitchell (*7*) described experiments similar to those in the present paper. The main conclusions of the two reports are in substantial agreement although there are differences in opinion as to details such as the amount of Co^{2+} in tetrahedral or octahedral environment and the surrounding of Mo(VI) which they believe to be tetrahedral. They also mention the strong reflection band at wavenumbers exceeding 22,000 cm^{-1} and ascribe it—first as we do—to MoO_3. However, there is no mention in their report of the fact that this band is far more intense than would result from a mixture of Al_2O_3 and MoO_3, a detail which we consider as very important in connection with the state in which this compound exists.

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