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Influence of Gas Phase on the Polymorphic Transformations in $CoMoO_4$

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Polymorphic transformation b-$CoMoO_4 \rightarrow a$-$CoMoO_4$ at 400°C was studied in the high-temperature X-ray camera in nitrogen, propylene, and hydrogen. It was found that the transformation is inhibited in the reducing atmosphere due to the interaction of the reducing agent from the gas phase with crystal nuclei of the new phase. Being very reactive, they are rapidly reduced, their elimination from the surface of crystallites inhibiting the transformation.

In papers (*1–3*) we have described investigations of the phase transformations of cobalt molybdate and the structure of its polymorphic modifications. The low temperature modification b-$CoMoO_4$, described in detail by Smith and Ibers (*4*, *5*) as consisting of blocks of edge-sharing CoO_6 and MoO_6 octahedra, on heating transforms at 400–450°C into phase a-$CoMoO_4$, composed of blocks of CoO_6 octahedra linked by MoO_4 tetrahedra (*3*). The reverse transformation is hindered and takes place at much lower temperatures, depending on the conditions of the experiment. Consequently, modification a can exist at room temperature as a metastable phase, and only when ground does it undergo a transformation into phase b. We have shown (*1*) that when modification b has been flashed in the high temperature X-ray camera to 600°C and quenched quickly to 380°C, a continuous increase of the intensity of diffraction lines of modification a is observed. Thus, we could conclude that nucleation of the new phase is the rate-determining step of the $b \rightarrow a$ transformation. However, we have noticed that when the sample was heated in hydrogen the transformation $b \rightarrow a$ did not occur. It therefore seemed interesting to investigate the influence of the gas phase on this transformation in more detail. The problem has a more general significance, as the dependence of the polymorphic transformation on the composition of the gas phase has been observed in many systems, but is far from being understood.

Experimental

Materials

Cobalt molybdate was obtained by adding the solution of ammonium paramolybdate at 60°C to the stirred solution of cobalt nitrate (*6*). The pH was maintained throughout the precipitation at a constant value of 5.5 by simultaneously adding aqueous ammonia. The precipitate (solvated cobalt molybdate) was washed by decantation until no nitrate ions were present in the solution, filtered, dried at 105°C, and then annealed at 500°C for 5 hr. After cooling the preparation consisted of violet modification a-$CoMoO_4$. To obtain black modification b-$CoMoO_4$, the precursor was annealed at 1200°C for 10 hr and carefully ground after cooling. X-ray analysis showed that the preparation contains pure b-$CoMoO_4$.

The composition was controlled by chemical analysis. The samples were dissolved in concentrated HCl on the water bath and the content of cobalt was determined colori-

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metrically by means of the rhodanate method in the 50% acetone solution. As it was found that the presence of molybdenum interferes with the analysis, it was removed by precipitating in form of $PbMoO_4$ in acetic acid. Molybdenum was determined based on the formation of a colored complex with phenylhydrazine in the acidic medium. The preparation of *b*-$CoMoO_4$ had the composition, $CoMo_{1.015}O_{4.07}$. Its surface area was 2.7 m^2/g.

Apparatus

All experiments were carried out in a high-temperature chamber of the X-ray diffractometer Japanese production (Rigaku Denki Model D-3F) using Cu lamp and Ni filter. The studied sample (about 0.4 g) was placed in a platinum holder as a layer 1 mm thick with a 2-cm^2 surface area. The temperature was measured with a PtRh–Pt thermocouple fixed directly in the neighborhood of the sample. The flow rate of the gas mixture was about 200 ml/min.

Results and Discussion

Figure 1 shows the changes of the diffraction pattern (the section corresponding to the interplanar spacings $d = 3.10$–3.60 Å, comprising the strongest line of phase *b*-$CoMoO_4$ at $d = 3.15$ Å and that of phase *a*-$CoMoO_4$ at $d = 3.38$ Å) observed on heating *b*-$CoMoO_4$ in the high temperature X-ray camera in different atmospheres. When the sample is heated in nitrogen, the *b* → *a* transformation is clearly seen to proceed in the temperature range 400–450°C. A similar picture is observed when propylene is present in the gas phase in the

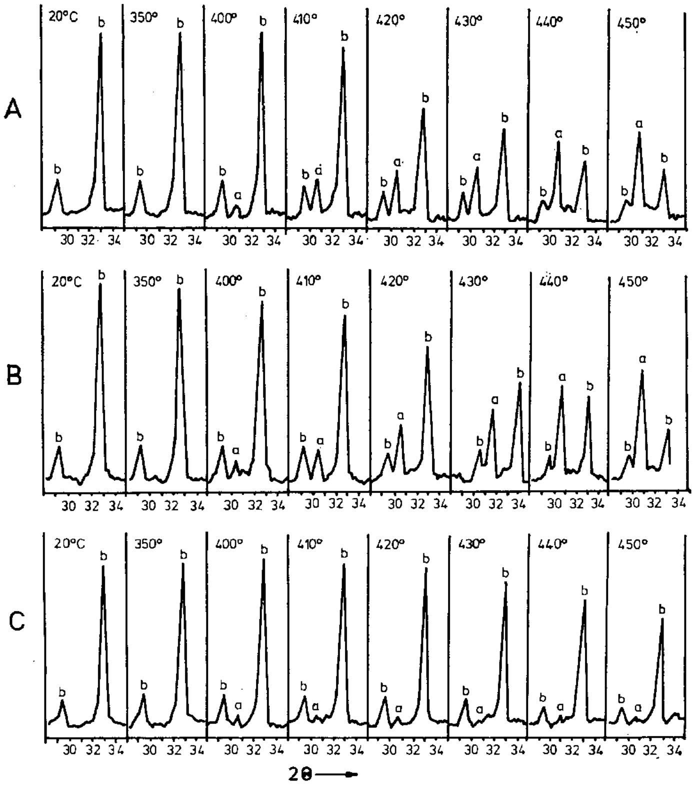

FIG. 1. Changes in X-ray diffraction pattern of *b*-$CoMoO_4$ phase during heating in different atmospheres. (A) Heating in nitrogen; (B) heating in the nitrogen–propylene mixture (1:1); (C) heating in the nitrogen–hydrogen mixture (1:1).

1:1 mixture with nitrogen. However, when the sample is heated in the 1:1 mixture of nitrogen with hydrogen, no lines of phase a appear in the X-ray diagram even at 450°C, which indicates that the $b \rightarrow a$ transformation does not occur. Despite the fact that the lines of phase *a* do not appear, a distinct decrease in the intensity of the lines of phase *b* is observed on heating the sample in hydrogen. The gravimetric measurements carried out in the vacuum ultramicrobalance showed that under the same conditions, the reduction of the sample takes place under the influence of hydrogen (7). The decrease of intensity in the lines of phase *b* thus may be explained as being due to the progress of reduction of this modification in hydrogen. Curve 4 in Fig. 3 shows the degree of reduction calculated on the basis of X-ray data from the high temperature camera as well as that determined gravimetrically. Excellent agreement of the data confirms the interpretation of the high temperature X-ray camera experiments.

Figure 2 shows the degree of the transformation of modification *b* into modification *a* observed in the course of isothermal heating in the high-temperature camera in the nitrogen atmosphere. Curve 1 was calculated on the basis of the decrease of intensity of the strongest line of modification *b* (3.15 Å) and curve 2 was determined from the increase of the intensity of the strongest line of modification *a* (3.38 Å); the agreement is satisfactory.

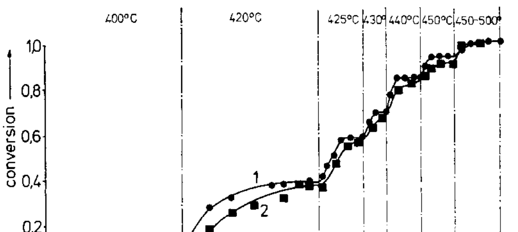

FIG. 2. Kinetics of polymorphic transformation b-$CoMoO_4 \rightarrow a$-$CoMoO_4$ in the atmosphere of nitrogen in isothermal conditions. (1) Conversion calculated on the basis of intensity of X-ray line of phase *b* (3.15 Å); (2) conversion calculated on the basis of intensity of X-ray line of phase *a* (3.38 Å).

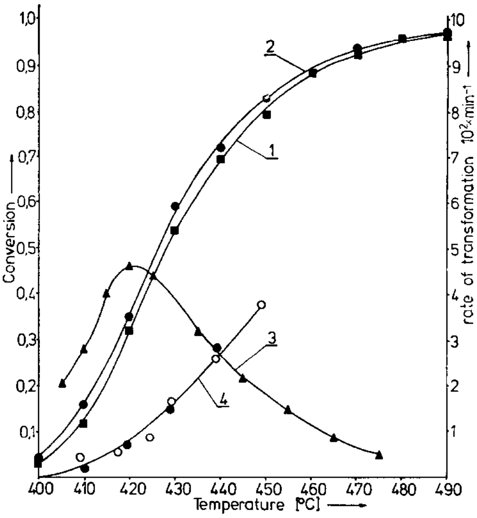

FIG. 3. Kinetics of polymorphic transformation b-$CoMoO_4 \rightarrow a$-$CoMoO_4$ at different gas atmospheres in polythermal conditions (the rate of heating, 2°/min). (1) Changes in conversion of b-$CoMoO_4$ during heating in the atmosphere of nitrogen; (2) changes in conversion of b-$CoMoO_4$ during heating in the nitrogen–propylene mixture (1:1); (3) the dependence of rate of polymorphic transformation $b \rightarrow a$ in nitrogen on temperature; (4) comparison of changes in conversion of phase *b* in nitrogen–hydrogen mixture (1:1) observed in high-temperature X-ray chamber (○) with the changes in conversion during reduction of phase *b* with hydrogen/vacuum microbalance data (●).

The results presented in Fig. 2 indicate that the transformation comes quickly to a standstill when the temperature is kept constant. The process starts again only when the temperature is raised. It may be concluded that the nucleation of the new phase is not taking place in the bulk of the crystallites as a result of statistical fluctuations, but requires the presence of some nucleation centers. At a given temperature, the centers appear on certain number of crystallites, which are then rapidly transformed into new phase. The fact that new centers on the next crystallites are formed only after raising the temperature indicates that they are energetically unequivalent. The influence of the gas phase on the kinetics of the transformation, described below, leads to the conclusion that they are present at the surface of crystallites.

Thus, we may assume that the rate of the phase transformation is proportional to the concentration n of nucleation centers at the surface of crystallites and to the number N_t of unreacted crystallites, which can be expressed in terms of the degree of conversion α, $N_t \sim (1 - \alpha)$. The rate is then given by

$$d\alpha/dt = k \cdot n \cdot (1 - \alpha). \qquad (1)$$

Figure 3 illustrates the changes of the degree of transformation of b-$CoMoO_4$ observed in the course of heating the sample at a constant rate of 2°/min in the nitrogen atmosphere (curve 1) and the 1:1 mixture of nitrogen and propylene (curve 2). On that basis, the rate of the phase transformation as function of temperature was calculated (curve 3). Its shape may be explained in terms of Eq. (1); as in the polythermic experiment illustrated in Fig. 3, the value of k increases with increasing temperature, whereas the value of $(1 - \alpha)$ decreases. On raising the temperature above the transformation point, at first the conversion increases slowly. The corresponding first raising portion of curve 3 thus may be interpreted as being due almost exclusively to the temperature dependence of k and can be approximated well by the Arrhenius plot. The activation energy evaluated from this plot amounts to 64 kcal/mole. The calculations of the dependence of rate on the conversion show that the second portion of curve 3 decreases much more rapidly than would be expected only on the basis of the changes of the term $(1 - \alpha)$. Thus, it may be concluded that the number n of nucleation centers decreases with rising temperature, implying their distribution in respect to the energy required for their formation.

The influence of the reducing gas atmosphere on the behavior of b-$CoMoO_4$ is illustrated in Fig. 4, which shows results of the experiment carried out in the high temperature X-ray camera in the 1:1 mixture of nitrogen with hydrogen. Curve 1 represents the conversion of phase b calculated on the basis of the decrease of the intensity of its lines, curve 2 represents the amount of phase a formed, calculated from the increase of the intensity of its line at $d = 3.38$ Å. As seen from this figure, the polymorphic transformation starts at 420° and at first the decrease of the amount of phase b is due entirely to its transformation into phase a. On further heating, however, the amount of phase a decreases and this phase disappears completely at 440°. At this point the flow of hydrogen was cut off and the sample was heated further in nitrogen. The amount of phase b remained at first constant and only at 550°C did its decrease start again, accompanied

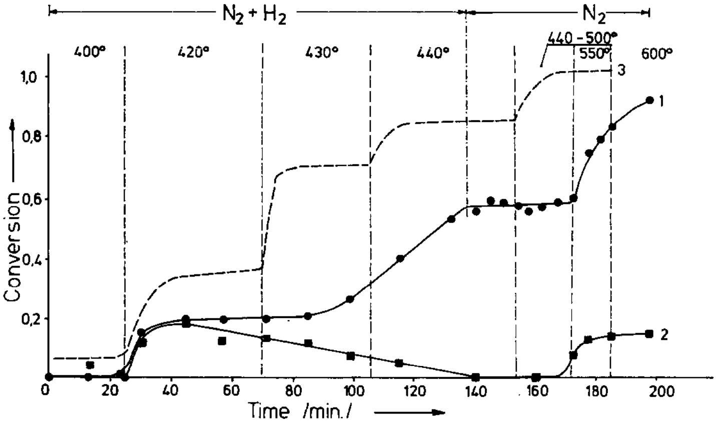

FIG. 4. The effect of the reducing atmosphere ($N_2 + H_2$ mixture) on kinetics of polymorphic transformation $b \rightarrow a$. (1) Conversion calculated from intensity of X-ray line of phase b (3.15 Å); (2) conversion calculated from intensity of X-ray line of phase a (3.38 Å). The broken line (3) denotes the changes in conversion observed in nitrogen (after Fig. 2).

by the appearance of phase *a*, the product being now fine crystalline.

Results of our experiments may be interpreted in terms of a model of consecutive parallel reactions:

$$\begin{tikzcd} & & a \\ b \arrow[r, "1"] & a^* \arrow[ur, "2"] \arrow[dr, "3"'] & \\ & & \text{products of reduction} \end{tikzcd}$$

where a^* denotes the nuclei of phase *a*. In an inert atmosphere, only the polymorphic transformation is observed, the nucleation (step 1) being rate determining. The pronounced effect of the atmosphere on this transformation indicates that the nuclei are present mainly at the surface of crystallites. The nuclei are characterized by a high reactivity and may undergo reduction at temperatures much lower than those at which the reduction of phase *b* is usually observed. In hydrogen, the rate of the reduction of these nuclei is so great that all nuclei initially formed are completely reduced and the process proceeds by steps 2 and 3. Under such conditions, in which $r_3 > r_1$, $r_3 > r_2$, and no polymorphic transformation of phase *b* into *a* takes place, only the reduction of the former is observed. Conversely, on heating in nitrogen only steps 1 and 2 are realized. Conversion of phase *b* attained on heating in hydrogen is thus much lower than that observed in the same temperature range in nitrogen (cf. curves 1 and 3, Fig. 4). When, in the experiment illustrated in Fig. 4, the flow of hydrogen was cut off at 440°C, no transformation of phase *b* took place on further heating because all crystal nuclei of phase *a* were removed from the surface of the crystallites. It was necessary to heat the sample to 550°C, at which the bulk nucleation had probably started already, in order to observe the transformation again.

In the mixture of propylene and nitrogen the reduction of nuclei is much slower than in hydrogen and only their small fraction is reduced, the majority growing slowly into crystallites of phase *a*. The total conversion of phase *b* is thus slightly higher than in nitrogen in which only the $b \rightarrow a$ transformation takes place (cf. curves 1 and 2, Fig. 3).

Experiments described in this paper thus lead to the conclusion that the influence of the gas phase on the polymorphic transformation $b\text{-CoMoO}_4 \rightarrow a\text{-CoMoO}_4$ consists in the interaction of the reducing agent from the gas phase with the crystal nuclei of the new phase. Being very reactive, they are rapidly reduced, their elimination from the surface of crystallites inhibiting the transformation.

References

1. J. Haber, J. Nowak, and J. Ziółkowski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **21**, 479 (1973).
2. J. Haber, *in* "Proc. 1st Climax Intern. Conf. on Chemistry and Uses of Molybdenum," p. 146, Reading, England, (1973).
3. J. Chojnacki, J. Haber, and R. Kozłowski, *J. Solid State Chem.* **11**, 106 (1974).
4. G. W. Smith, *Acta Crystallogr.* **15**, 1054 (1962).
5. G. W. Smith and I. A. Ibers, *Acta Crystallogr.* **19**, 269 (1965).
6. J. Haber and W. Szelejewski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **19**, 497 (1971).
7. J. Haber, A. Kozłowska, and J. Słoczyński, to appear.