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Mechanism of the Solid State Synthesis of Cobalt Molybdite

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The mechanism and kinetics of the solid state reaction $2CoO + 2MoO_3 + Mo = Co_2Mo_3O_8$ (1) was studied in the temperature range 500–1100°C by chemical and X-ray analysis. At three intergranular contacts existing in such a powder mixture, the following reactions proceed at comparable rates: $2MoO_3 + Mo = 3MoO_2$ (2), $MoO_3 + CoO = CoMoO_4$ (3), and $8CoO + 3Mo = Co_2Mo_3O_8 + 6Co$ (4). Subsequent reactions of their products may be described by the following equations: $3Co + 3MoO_3 = Co_2Mo_3O_8 + CoO$ (5), $2CoO + 3MoO_2 = Co_2Mo_3O_8$ (6), and $2CoMoO_4 + Mo = Co_2Mo_3O_8$ (7). Reaction (5) is very rapid whereas (6) and (7) are slow. The path (4) + (5) is thus responsible for the first rapid step of (1), the subsequent slow step being due to (2) + (6) and (3) + (7). No metallic cobalt is found in products of (1) because of its very rapid consumption in (5); its role as intermediate, however, was confirmed by magnetic measurements. Metallic cobalt is very reactive even at 300°C with $CoMoO_4$ and MoO_3. This suggests its important role in the reconstruction of the surface of cobalt molybdate catalysts in the course of the catalytic reaction.

Cobalt molybdate, $CoMoO_4$, is well known as an active and selective catalyst in the oxidation of hydrocarbons. It is now accepted that these reactions proceed via the redox mechanism, the hydrocarbon molecule being oxidized by an oxygen ion from the catalyst lattice, the latter being then reoxidized by oxygen from the gas phase. In the steady state a certain degree of reduction of the catalyst surface is thus established, depending on the redox potential of the reactants and the oxygen bond strength at the surface of the catalyst. The degree of reduction may have in turn a pronounced influence on the selectivity of the reaction. Studies of the reduction of $CoMoO_4$ by hydrogen and propylene have shown (*1–4*) that the products consist of cobalt molybdite $Co_2Mo_3O_8$, cobalt–molybdenum (IV)-spinel Co_2MoO_4 as well as Co, CoO, MoO_2 and Mo. Subsequent reactions between these products may result in the reconstruction of the catalyst surface.

An interesting question arises as to whether the reduced molybdenum compounds $Co_2Mo_3O_8$ and Co_2MoO_4 are formed directly on reduction, or result from the solid state reaction between such primary reduction products as MoO_2, CoO or Co.

Cobalt molybdite may be synthesized by the solid state reaction

$$2CoO + 2MoO_3 + Mo = Co_2Mo_3O_8 \quad (1)$$

It was first conducted by McCarrol et al. (*5*). Obviously, this reaction cannot proceed in one step. In the powder mixture of the reactants three types of intergranular contacts exist (Fig. 1) where intermediate products are formed, which then react further to form cobalt molybdite as the final product. The aim of the present research was to determine the types of these reactions, their kinetics and their sequence, in order to find the mechanism of the solid state synthesis of cobalt molybdite.

Experimental

MoO_3 was prepared by thermal decomposition of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and subse-

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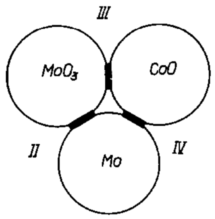

FIG. 1. Three types of intergranular contacts in the mixture of Mo + MoO_3 + CoO.

quent resublimation. Its specific surface area, as determined from the adsorption of krypton at liquid nitrogen temperature by the BET method, amounted to $S = 0.30\ m^2g^{-1}$.

CoO ($S = 0.30\ m^2 \cdot g^{-1}$) was obtained by thermal decomposition of Co_3O_4 in the stream of nitrogen at 1000°C. The resulting preparation contained 0.18 at % of excess oxygen as determined by the modified iodometric method (*6*).

Metallic powders of Mo and Co were the POCh preparations. Their surface areas amounted to 0.30 and 0.69 m^2g^{-1}, respectively.

a-$CoMoO_4$ (high temperature violet modification), $S = 20.0\ m^2\ g^{-1}$, was prepared by precipitation of hydrated molybdate from the solutions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$, washing, drying and heating at 400°C for 10 hr.

MoO_2, $S = 1.41\ m^2\ g^{-1}$, was obtained by solid state reaction of MoO_3 and Mo, carried out at 700°C in quartz tubes sealed under vacuum of 10^{-2} torr. All reagents were of anal. grade.

The investigation of the solid state reactions was carried out in quartz tubes sealed under vacuum of 10^{-2} torr. The phase composition of the reaction products was determined by X-ray analysis in the Rigaku–Denki diffractometer with CoK_α radiation. Identification of the different phases was based on the ASTM data and data quoted in (*7–9*).

In the case of a system as complex as the one investigated, composed of many phases characterized by low symmetry, where a continuous change of composition and grain size takes place resulting in the variation of the dispersion of X-ray radiation, and where superposition and screening of diffraction lines occurs, the intensity of the diffraction lines cannot be taken as the direct quantitative measure of the rate of solid state processes. The comparison of different series of lines, however, made possible phase identification and the approximate estimation of the reaction progress. The kinetics of the reaction was determined by chemical analysis. The degree of conversion into molybdite was calculated from the determination of the amount of cobalt, which could be dissolved in concentrated HCl, since under the experimental conditions, used molybdite does not pass into solution, as opposed to all other cobalt-containing components of the reacting mixture. Cobalt content was determined colorimetrically by means of the rhodanate method in 50% acetone solution. Molybdenum, which interferes in the determination, was first removed by precipitation in the form of $PbMoO_4$ from weakly acid solution. Relative error of the analysis did not exceed 5%.

In the case of some preparations, magnetic susceptibility was determined by use of the Gouy method at room temperature in the range of field 2–10 kÖe.

Results and Discussion

Preliminary experiments with mixtures of composition corresponding to the stoichiometry of reaction (1) showed that after heating at 500°C for several hours the products contain a–$CoMoO_4$, b–$CoMoO_4$, MoO_2 and traces of unreacted substrates, but no molybdite is formed even after 60 hr. This indicates that at 500°C, the following reactions proceed at intergranular contacts (II) and (III):

$$2MoO_3 + Mo = 3MoO_2 \qquad (2)$$

$$MoO_3 + CoO = CoMoO_4 \qquad (3)$$

In the X-ray diffraction pattern of products formed at 600°C, the diffraction lines of molybdite are clearly visible, but conversion does not exceed 20% after 20 hr of heating. The efficient synthesis of $Co_2Mo_3O_8$ proceeds only at 700°C, but even after 10 hr at 1100°C, total conversion is not attained. This may be due to the fact that in the later periods of the reaction, the grains of substrates or intermediate products are separated by thick layers

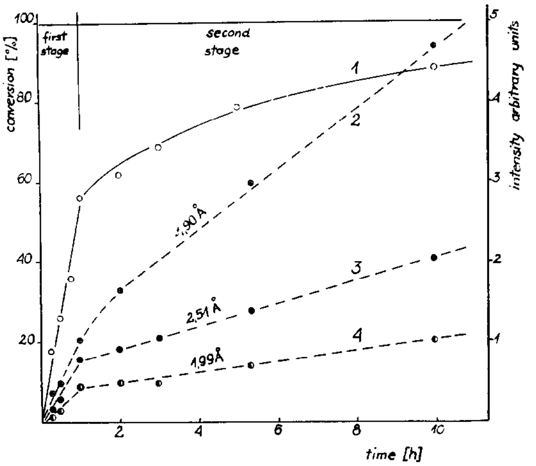

FIG. 2. Kinetics of reaction (1). Curve 1. Conversion to $Co_2Mo_3O_8$ as determined by chemical analysis. Curves 2, 3, 4. Intensities (in arbitrary units) of 4.90, 2.51 and 1.99 Å diffraction lines of $Co_2Mo_3O_8$ in the diffraction pattern of the products of reactions (1).

of $Co_2Mo_3O_8$ and the mass-transport is considerably hindered. Pure $Co_2Mo_3O_8$, however, can be obtained by washing out the unreacted substrates in concentrated HCl. On the basis of these experiments, a temperature of 700°C was chosen for kinetic investigations.

Figure 2, curve 1, shows the degree of conversion to $Co_2Mo_3O_8$ in the mixture of a composition corresponding to the stoichiometry of reaction (1) as determined by chemical analysis; curves 2, 3 and 4 illustrate the intensity of three diffraction lines of $Co_2Mo_3O_8$ (d = 4.90 Å, d = 2.51 Å and 1.99 Å) as a function of the time of heating. Two stages of the reaction may clearly be distinguished: the initial rapid period, when more than 50% of conversion is attained, and a subsequent slower one.

Reactions in two-component mixtures corresponding to intergranular contacts (II), (III) and (IV) were then investigated. In the first two mixtures, reactions (2) and (3) take place respectively. A 60–80% conversion of substrates after 30–60 min at 700°C could be estimated from the intensity of the diffraction lines. In the mixture of CoO and Mo, the reaction products were $Co_2Mo_3O_8$ and β-Co; the reaction can be described by the equation

$$8CoO + 3Mo = Co_2Mo_3O_8 + 6Co. \quad (4)$$

Progress of this reaction was followed analytically and the results are shown in Fig. 3. The rate of reaction (4) is comparable with that of reactions (2) and (3). Thus it may be concluded that in the first stage of reaction (1), three independent parallel processes, (2), (3) and (4), are taking place at comparable rates. Comparison with Fig. 2 shows that these rates are considerably higher than the rate of reaction (1). Thus the subsequent reactions, in

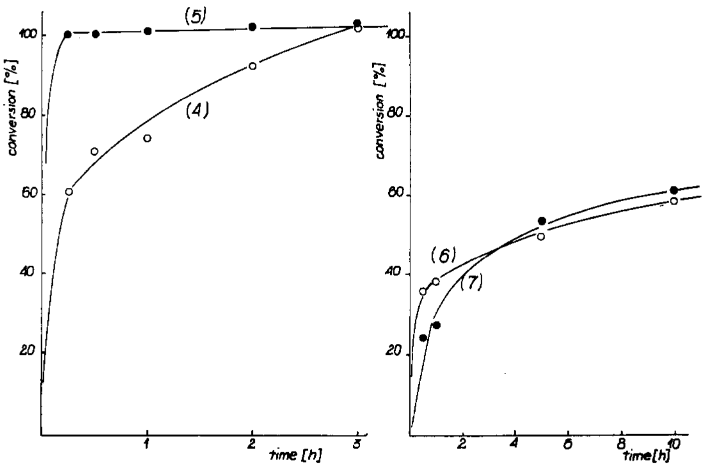

FIG. 3. Kinetics of reactions (4), (5), (6) and (7). The molar ratio of reagents were 2:1, 1:1, 2:3 and 2:1 respectively.

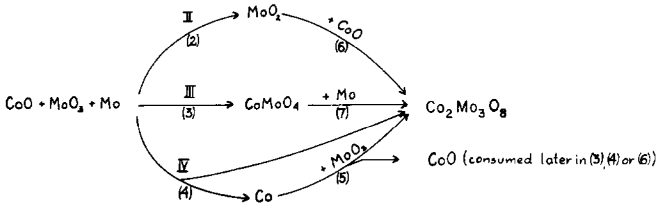

FIG. 4. Reaction scheme of the synthesis of cobalt molybdite, II, III, IV (see Fig. 1); numerical indexes of reactions—see text.

which the intermediate products react further to form $Co_2Mo_3O_8$ must be slower. X-ray data indicate that these reactions are

$$3Co + 3MoO_3 = Co_2Mo_3O_8 + CoO, \quad (5)$$

$$2CoO + 3MoO_2 = Co_2Mo_3O_8, \quad (6)$$

and

$$2CoMoO_4 + Mo = Co_2Mo_3O_8. \quad (7)$$

Results of kinetic measurements of these reactions are illustrated in Fig. 3. They indicate that reactions (6) and (7) are in fact slower than reactions (2) and (3), but reaction (5) proceeds at a much faster rate than reaction (4). Formation of CoO as result of reaction (5) was confirmed by X-ray analysis. It may then be consumed in rapid reactions (3) and (4) as well as in the slower reaction (6). All these reaction paths are summarized in Fig. 4.

As already mentioned, the complete quantitative X-ray analysis of the product composition in the course of reaction (1) could not be performed; it was possible, however, to estimate the phase composition of the reacting mixture as a function of time. Results are shown schematically in Fig. 5.

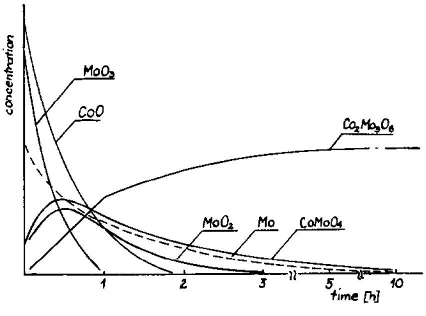

FIG. 5. Phase composition of the reacting mixture as a function of time.

We would like to emphasize the fact that no metallic cobalt was found in the products of reaction (1). On the other hand, results of the kinetic measurements show that reaction (4) must take place. However, since the rate of the consumption of cobalt by reaction (5) is much greater than the rate of its formation, cobalt may appear in the reacting mixture only in trace amounts. We have, in fact, confirmed this conclusion by the measurements of the magnetic susceptibility. Fig. 6 shows the magnetic susceptibility of the reacting mixture as measured at room temperature and the value of $c = dX/dH$ as a function of the time of reaction. In the period 15–45 min of the reaction, the susceptibility of the reacting mixture attains a maximum and shows a dependence on the field strength which points

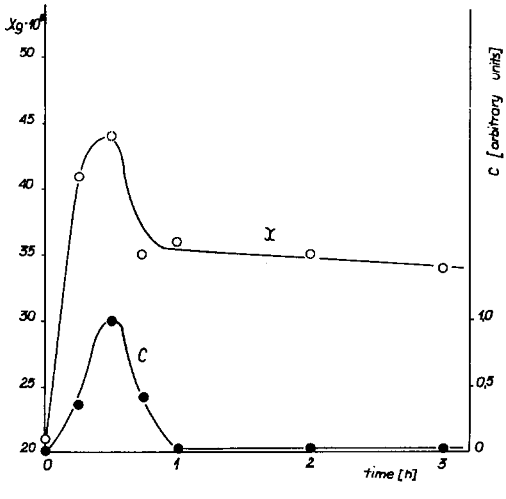

FIG. 6. Magnetic susceptibility X and the content of ferromagnetic components as a function of the time of reaction 1.

to the presence of trace amounts of a ferromagnetic substance, which in the investigated system can be only metallic cobalt.

The following mechanism of reaction (1) may be advanced to explain the described results. In the first 60 min, reactions (2), (3) and (4) proceed simultaneously and independently at comparable rates, which results in the total consumption of MoO_3 and almost total consumption of CoO. Reaction (4) leads directly to the formation of certain amount of $Co_2Mo_3O_8$ and its second product: β-Co reacts further almost immediately to give also $Co_2Mo_3O_8$ as the result of reaction (5). Branch (4) + (5) of reaction (1) thus proceeds at the highest rate, but stops after less than 1 hr because of the exhaustion of the substrates, also consumed in reactions (2) and (3). This branch is responsible for the first rapid stage of reaction (1) (see Fig. 2), although the other two branches also contribute at this stage, as the value of the conversion corresponding to the inflection point on the kinetic curve exceeds the conversion, which could be attained on path (4) + (5) only. Branch (2) + (6) is slower and participates in both the rapid and slow stages of reaction (1). Diffraction lines of its intermediate products disappear after 2 hr (CoO) or 3 hr (MoO_2) of the reaction. The smallest rate is shown by branch (3) + (7), which is responsible for the second slow stage of reaction (1). Diffraction lines of $CoMoO_4$ and Mo persist in the X-ray pattern even after 10 hr of reaction.

Results of our studies thus lead to the conclusion that in the reduced cobalt molybdate catalyst several secondary reactions may proceed at a considerable rate already at lower temperatures, thus changing the phase composition of the catalyst and reconstructing its surface. We would like to recall at this point that the most rapid path of the synthesis of cobalt molybdite is composed of reactions (4) and (5) for which the reducing atmosphere would be favorable.

Particularly interesting is the very high reactivity of metallic cobalt. Formed as a product of reaction (4), it reacts immediately so that its presence in the reacting mixture, of a composition corresponding to the stoichiometry of reaction (1), cannot be detected by X-ray analysis. Thus, it seems quite probable that metallic cobalt may be formed in the catalyst in the course of its performance as the result of the reduction of $CoMoO_4$ already at lower temperatures, and then rapidly react with other components of the reduced surface. In fact, on heating $CoMoO_4$ in propylene, it was found (*10*) that surface reduction takes place at about 160°C and the bulk reduction starts at about 400°C. Formation of metallic cobalt and its subsequent reaction could then constitute the most important contribution to the modification of the catalyst surface.

In order to check this hypothesis, the following mixtures of metallic cobalt with various components of the reduced catalyst were prepared, $Co + CoMoO_4$, $2Co + 3MoO_3$ and $2Co + 7MoO_2$, and the solid state reactions were carried out at 300, 400 and 500°C for 10 hr in quartz tubes sealed under vacuum, as described above. As an example, Fig. 7 shows the diffraction patterns of the products obtained at 300 and at 500°C.

In the case of the first mixture, the products $Co_2Mo_3O_8$ and CoO are already formed at 300°C, their amount increasing with rising temperature. This result indicates that in the two-component mixture Co interacts with $CoMoO_4$ already at low temperatures. However, as mentioned before, the X-ray lines of $CoMoO_4$ in products of reaction (1) persist even at 700°C. Apparently, the reaction between Co and MoO_3 is much faster than that with $CoMoO_4$, and in the case of reaction (1), Co is totally consumed in the first of these reactions as shown in Fig. 4.

In the second mixture, MoO_2 appears after the reaction at 300°C, whereas the presence of $Co_2Mo_3O_8$ could be detected only after the reaction at 500°C. Practically no reaction was observed in the temperature range 300–500°C in the case of the $Co + MoO_2$ mixture. Further experiments have shown that at higher temperatures they react to form $Co_2Mo_3O_8$ and Mo_2O_3. The presence of trace amounts of Mo_2O_3 in the products of reaction (1) cannot be ignored; this would mean that Mo_2O_3 would have to be rapidly consumed in some subsequent reactions resulting in the formation of the molybdite.

All diffraction patterns of the products

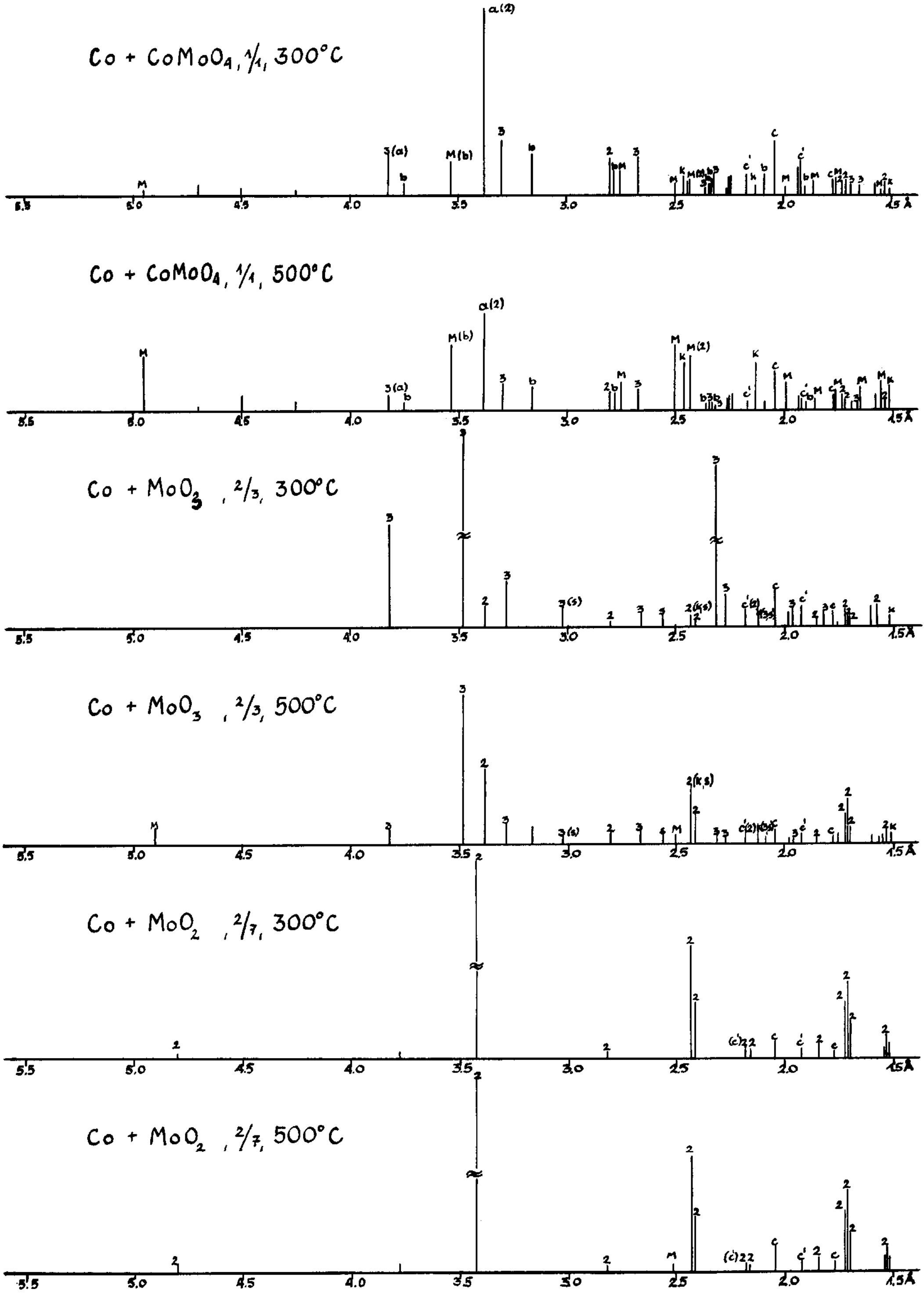

FIG. 7. Diffraction patterns of reaction products, M–$Co_2Mo_3O_8$, a–a-$CoMoO_4$, b–b-$CoMoO_4$, 2–MoO_2, 3–MoO_3, k–CoO, c–βCo, c′–αCo, s–spinel Co_2MoO_4.

(Fig. 7) showed the presence of several weak lines which could not be identified. However, no formation of the spinel Co_2MoO_4 could be detected. This is in agreement with the results of Janas (*4*) who found that Co_2MoO_4 is formed on reduction of $CoMoO_4$ in hydrogen or propylene, whereas all attempts to synthesize this compound by the solid state reactions failed.

Results of our studies thus indicate that solid state reactions involving metallic cobalt may play an important role in the reconstruction of the surface of the cobalt molybdate catalyst in the course of the catalytic reaction, which may strongly modify the catalytic properties.

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