Formation and Phase Transition of Cobalt Molybdate in Cobalt Oxide–Molybdenum Trioxide–Alumina System

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In the cobalt oxide–molybdenum trioxide–alumina system with a molar ratio of 1 : 1 : 1, the amounts of the high-temperature modification (a) of $CoMoO_4$ formed during heating from 500 to 800°C and the low-temperature modification (b) formed by phase transition during the subsequent cooling to room temperature are influenced by the kinds of alumina used, such as α-, γ- and calcined γ-aluminas. Powder X-ray diffraction analysis revealed that in an α-alumina system formation of a-$CoMoO_4$ is most favorable at a calcination temperature of 500°C and phase transition from a- to b-$CoMoO_4$ during cooling is enhanced by higher calcination temperatures. In the γ-alumina system, formation of a-$CoMoO_4$ is slight at 500°C but increases with increase in the calcination temperature, as does slightly the degree of phase transition from a- to b-$CoMoO_4$ upon cooling. In a system containing calcined γ-alumina, formation of a-$CoMoO_4$ similar to α- and γ-alumina systems was observed to occur at 500°C and 800°C, respectively, together with phase transition to b-$CoMoO_4$ during cooling. The degree of dispersion in the CoO–MoO_3 coexistent system is affected by the particle size of aluminas, such as coarse α-, fine amorphous γ- and calcined γ-alumina consisting of both sizes, as observed with electron microscopy. Presence of finer γ-alumina is considered to suppress or retard the solid state reaction and phase transition.

Introduction

Extensive studies have been made of the physicochemical properties relevant to catalytic performance of the cobalt oxide–molybdenum trioxide–alumina system which constitutes catalytic systems usually used in catalytic hydrogenation, desulfurization, oxidation and other processes (1).

Numerous detailed investigations have also been reported on synthesis and polymorphic modifications of cobalt molybdate (2, 3). Cobalt molybdate has three major phases, that is, solvated $CoMoO_4$ prepared by coprecipitation, high-temperature

modification (a) on heating and low-temperature modification (b) on cooling and/or by grinding. It is recognized that mutual polymorphic transformations between these modifications can occur (2, 3).

In the cobalt oxide–molybdenum trioxide catalyst system, carriers or dispersants such as alumina are usually used. The effect of the additives on the behavior of catalytically active components, CoO and MoO_3, has also been investigated from the standpoint of the catalytic performance (4). In the catalytic systems, the active species are involved at relatively low levels: 1–4 wt% for CoO and 10–12 wt% for MoO_3. The behavior of these components in the solid phase changes, however, has not been clarified. In this study, the effects of the addition of three kinds of

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alumina on the solid phase formation of compounds at high temperatures and the phase transitions during subsequent cooling were investigated by room-temperature and high-temperature powder X-ray diffraction methods, along with electron microscopic observation.

Experimental

The commercial α- and γ-alumina used, both from Sumitomo Chemical Industry Co., contained minor impurities such as Fe_2O_3: 0.03 and 0.02; SiO_2: 0.03 and 0.02; Na_2O: 0.06 and 0.02 wt%, respectively. The calcined γ-alumina[1] was prepared by heating the commercial γ-alumina at 1200 °C for 6 hrs. The molybdenum trioxide and cobalt oxide were of special reagent grade from Kokusan Chemical Co.

A mixture of CoO, MoO_3 and Al_2O_3 with a molar ratio of $1:1:1$ was thoroughly mixed using a kneading machine, transferred to a flat-bottom crucible, which was then placed in the central part of a precision-controlled vertical tubular furnace. The mixture was held in the atmosphere of dry nitrogen (5) at the required temperature for two-and-a-half hours and then forced to cool to room temperature by an air blast outside the furnace. The estimated cooling rate was approximately 200 °C/hr. The sample was subjected to powder X-ray diffraction analysis with a diffractometer, "Rigaku" Rotaflex RU-200. In the case of high-temperature measurement, X-ray diffraction patterns were obtained by heating uncalcined mixtures at a heating rate of 50 °C/min to indicated temperatures in the same atmosphere. The sample was set in a platinum sample holder fixed to an attachment for the programmed high-temperature measurement. The X-ray diffraction

instrument was operated at 30 kV with a filament current of 10 mA using Mn-filtered Fe-K_α radiation to provide an incident wavelength of 1.9360 Å. The relative amounts of the species formed were estimated from measurement of the heights of the characteristic peaks, selected as follows; $2\theta = 33.4°(d = 3.37$ Å) for a-$CoMoO_4$ and $2\theta = 17.7°$ ($d = 6.29$ Å) for b-$CoMoO_4$. The samples were observed with a "Hitachi" HU-12 model electron microscope using an acceleration voltage of 75 kV and a filament current of 35 μA and at magnification ranging from 6 000 to 150 000.

Results

When a mixture of cobalt oxide, molybdenum trioxide and α- or γ-alumina is heated in the temperature range of 400–800°C, the high-temperature modification, a-$CoMoO_4$, begins to form at about 450°C and substantially increases above 500°C.

Figures 1a and b exemplify the high-temperature X-ray diffraction patterns of the mixtures with the above molar ratio of $0.1:1:1$ for both aluminas, heated at indicated temperatures. Besides Co_3O_4, some unreacted components and by-products, MoO_3-x, can be observed. For either nonstoichiometric mixtures or partially reacted mixtures, changes similar to the phase transitions in the CoO-α-Al_2O_3 system (5) and the formation of Mo_4O_{11}, Mo_8O_{23} and $Mo_{17}O_{47}$ in the MoO_3-α-Al_2O_3 system (6) are observed in the corresponding temperature ranges.

Figure 2 shows powder X-ray diffraction patterns of the mixtures with the molar ratio of $1:1:1$ for α- and γ-aluminas, which were calcined at 800°C and then cooled to room temperature. The low-temperature modification, b-$CoMoO_4$, appears when the mixtures are cooled to the vicinity of room temperature.

Figure 3 shows the relative amounts of a- and b-$CoMoO_4$, estimated from diffraction

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[1] The X-ray diffraction pattern indicated complete transition to α-alumina. This alumina will be designated hereinafter as calcined α-alumina.
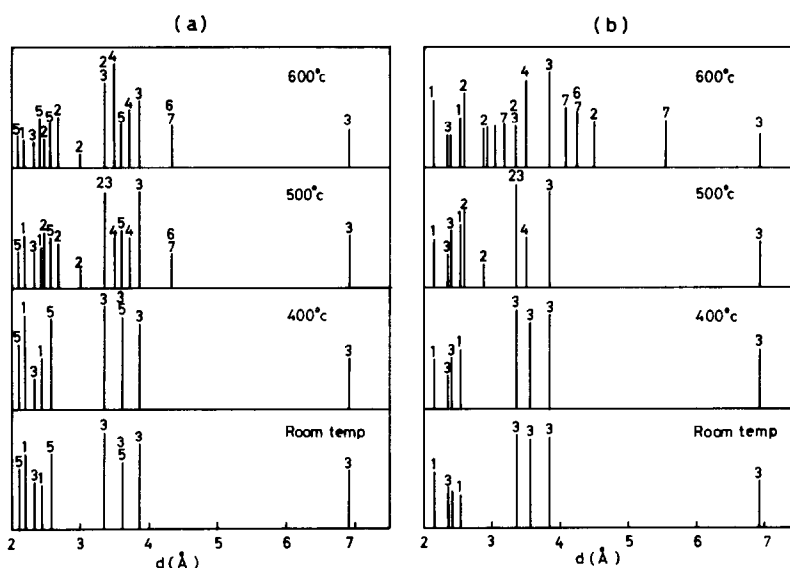
FIG. 1. High temperature X-ray diffraction patterns of the mixture at a $CoO:MoO_3:Al_2O_3$ molar ratio of $0.1:1:1$ with α-Al_2O_3 (a) and γ-Al_2O_3 (b), 20 min after indicated temperatures were reached. 1, CoO; 2, Co_3O_4; 3, MoO_3; 4, a-$CoMoO_4$; 5, α-Al_2O_3; 6, Mo_4O_{11}; 7, $Mo_{17}O_{47}$.

intensities observed by the powder X-ray method, which were formed when the systems containing α-, γ- of calcined α-alumina were heated for 2.5 hr at 400–800°C and forced to cool as indicated above. In the systems containing α-alumina, a-$CoMoO_4$

is predominant after calcination at 500–600°C and subsequent cooling, while a-$CoMoO_4$ decreases and b-$CoMoO_4$ increases after heating beyond 600°C, followed by cooling. In the γ-alumina-containing systems which are heated at
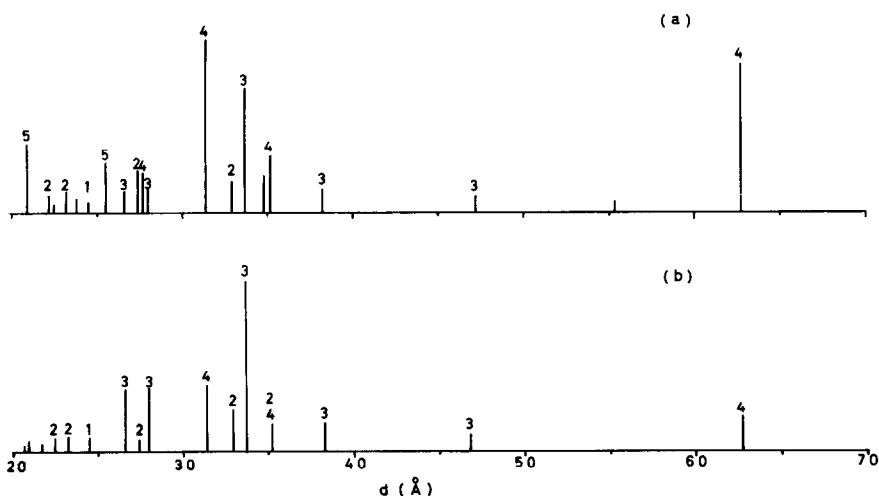

FIG. 2. Powder x-ray diffraction patterns of the mixture at a $CoO:MoO_3:Al_2O_3$ molar ratio of $1:1:1$ with α-Al_2O_3 (a) and γ-Al_2O_3 (b), after cooling preceded by heating at 800°C. 1, Co_3O_4; 2, MoO_3; 3, a-$CoMoO_4$; 4, b-$CoMoO_4$; 5, α-Al_2O_3.

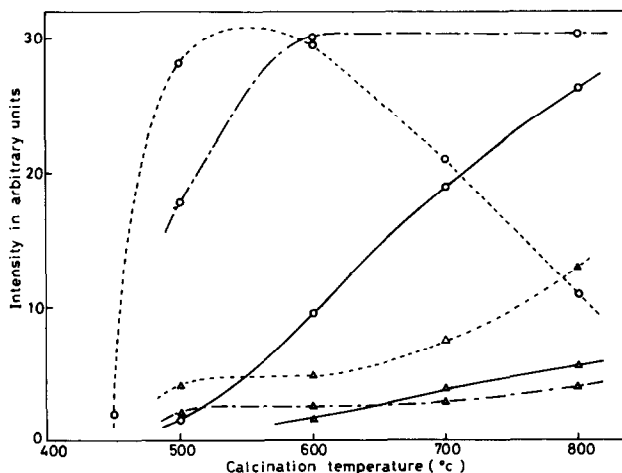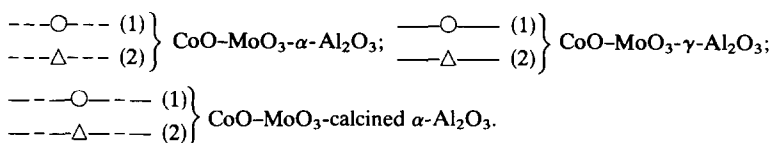FIG. 3. Relative amounts of a-$CoMoO_4$ (1) and b-$CoMoO_4$ (2) formed at a $CoO : MoO_3 : Al_2O_3$ molar ratio of $1:1:1$ with various kinds of alumina dependent on the calcination temperature followed by cooling.

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---O--- (1)]
            } CoO–MoO3-α-Al2O3;
---△--- (2)]

——O—— (1)]
            } CoO–MoO3-γ-Al2O3;
——△—— (2)]

————O———— (1)]
              } CoO–MoO3-calcined α-Al2O3.
————△———— (2)]
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various temperatures and then cooled, both a- and b-$CoMoO_4$ are minor components for lower temperature calcination. The amount of a-$CoMoO_4$ increases significantly as the calcination temperature increases beyond 600°C but the amount of b-$CoMoO_4$ is only slightly increased. For the calcined α-alumina systems, the behavior is similar to the α-alumina system in that a-$CoMoO_4$ dominates at all temperatures and to the γ-alumina system in that little phase transition to b-$CoMoO_4$ is observed over the entire calcination temperature followed by cooling. The calcined α-alumina system, thus, exhibits a composite effect.

Figure 4 indicates the case of CoO–MoO_3 systems without any kind of alumina. The phase transition to b-$CoMoO_4$ on cooling is more significant than in the α-alumina-containing system, as compared with the preceding figure. Thus, the presence of α-alumina is found to suppress the phase transition to b-$CoMoO_4$ due to cooling. The γ-alumina suppresses substantially both the

formation of a-$CoMoO_4$ for lower temperature heating and the phase transition on cooling to b-$CoMoO_4$ from a-$CoMoO_4$, although the latter is increasingly formed at higher temperatures.

Figure 5 shows the amounts of a-$CoMoO_4$ formed when CoO–MoO_3–Al_2O_3 systems are held for 2 hr at various temperatures. The amounts are expressed in terms of diffraction intensities obtained by the high-temperature X-ray measurement. The amount of a-$CoMoO_4$ is affected by the kind of alumina at 500°C, while it is little influenced at 800°C. Over the entire temperature range investigated, in the systems with α-alumina almost the same amounts of a-$CoMoO_4$ are found as that in the systems without alumina. Therefore, the difference between the large amount of a-$CoMoO_4$ in the α-alumina systems (Fig. 3) and the small amount of that in the alumina-free systems (Fig. 4) corresponds to the amount of the phase transition to b-$CoMoO_4$ and, in other words, indicates the action of α-alumina in
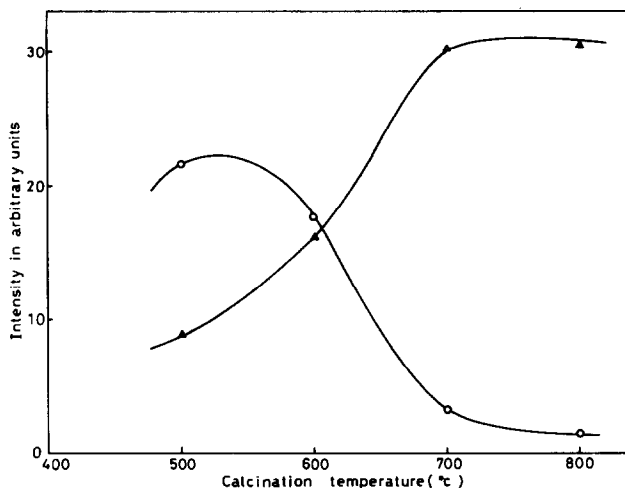
FIG. 4. Relative amounts of a-CoMoO$_4$ (1) and b-CoMoO$_4$ (2) formed at a CoO : MoO$_3$ molar ratio of 1 : 1 without alumina dependent on the calcination temperature followed by cooling. ——O—— (1); ——△—— (2)

suppressing the phase transition. This tendency is more marked at lower temperatures.

Figure 6 shows electron micrographs of these aluminas. The upper micrograph indicates commercial α-alumina, the lower, γ-alumina and the middle, α-alumina prepared by calcination of the γ-alumina. From these, it is found that the γ-alumina is made up of fine particles with diameters of about 0.01 μm while the α-alumina particles with

diameters of 5–10 μm. The calcined α-alumina is mostly made up of particles several times smaller than commercial α-alumina but does include a significant number of particles in well excess of 5 μm.

The particle size distributions (in terms of weight percent, particle number percent, surface area percent) estimated the light transmission method revealed that α-alumina has a maximum size distribution in the range of 5–10 μm, similar to the above
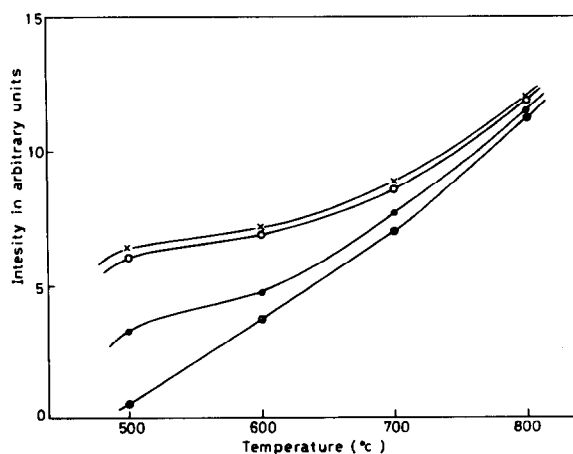

FIG. 5. Relative amounts of a-CoMoO$_4$ formed at a CoO : MoO$_3$: Al$_2$O$_3$ molar ratio of 1 : 1 : 1 with or without alumina dependent on the temperature by high temperature X-ray diffraction analysis. ——O—— α-Al$_2$O$_3$; ——●—— calcined α-Al$_2$O$_3$; ——⊙—— γ-Al$_2$O$_3$; ——×—— without alumina.

(a)

2.5 μm

(b)

0.5 μm

(c)

0.2 μm
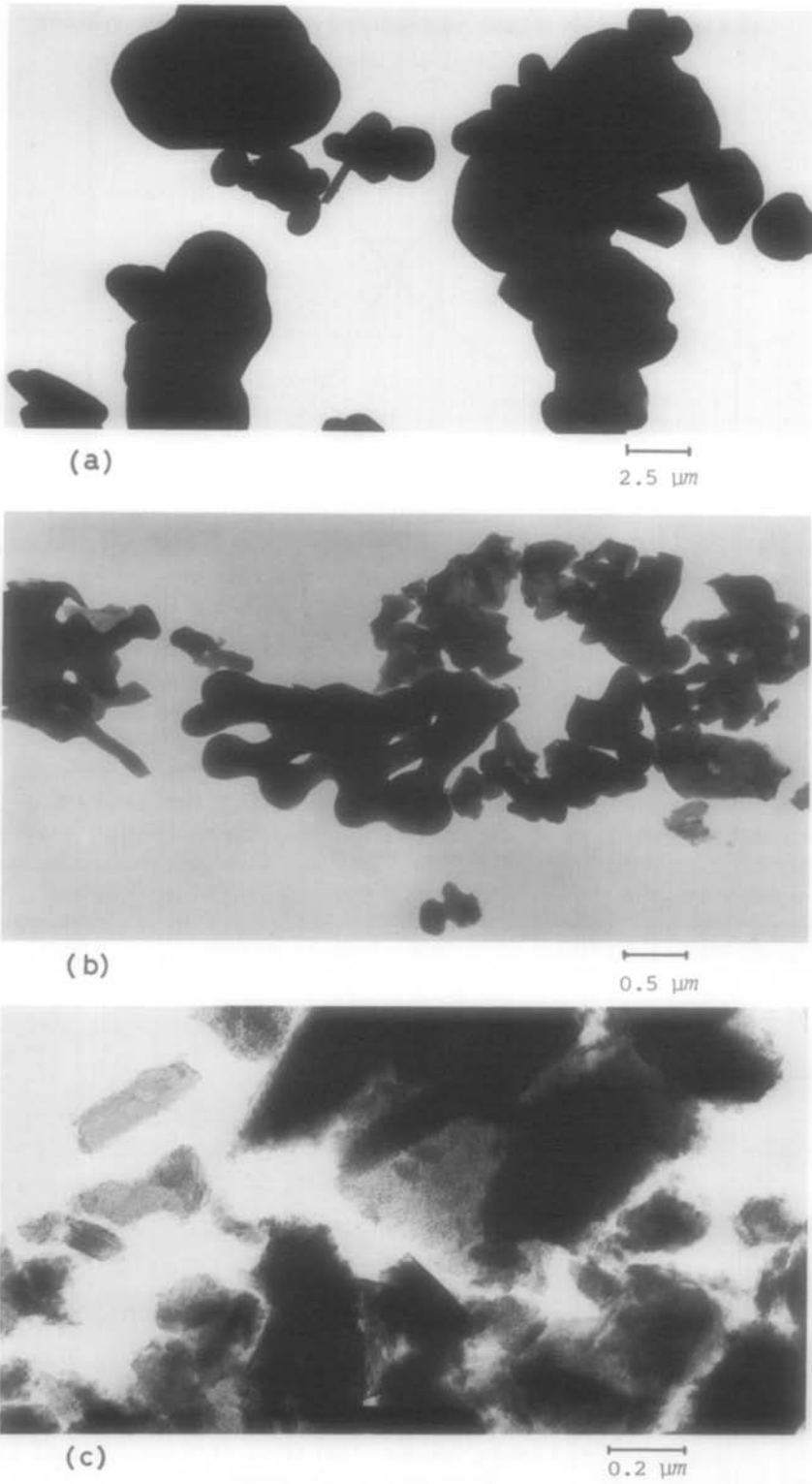
FIG. 6. Electron micrographs of aluminas after calcination. (a) α-Al_2O_3; (b) calcined α-Al_2O_3; (c) γ-Al_2O_3.

results, but γ-alumina has its maximum in the range of 20–40 μm, different from the above results. The calcined α-alumina has another peak in the range of 2–5 μm, in addition to a peak in the range of 20–40 μm. These observations suggest that γ- and calcined α-alumina particles are the agglomerates of finer particles observed with the electron microscope.

Figure 7 shows electron micrographs of cobalt molybdate formed from three component systems involving each of these aluminas. The α-alumina provides coarse particles of cobalt molybdate but the γ-alumina gives fine particles, as shown by the upper and lower micrographs, respectively. The calcined α-alumina furnishes a mixture of fine particles with coarse ones, as indicated by the middle micrograph.
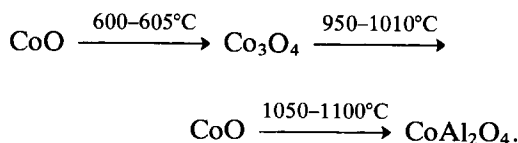
Discussion

The effect of the different aluminas on the formation of a-CoMoO$_4$ and its phase transition to b-CoMoO$_4$ on cooling to room temperature can be considered to be due to the difference in the particle size of aluminas, which causes difference in the degree of dispersion of the components, CoO and MoO$_3$. Very fine γ-alumina particles suppress the solid state reaction and phase transition through high degree of dispersion of these oxides, while larger α-alumina particles exert a smaller suppression effect.

Figure 8 shows the relative amounts of a- and b-CoMoO$_4$ formed in the system of CoO and MoO$_3$ with silica gel, which was used in place of alumina. With decreasing particle size of the silica gel, higher degree of suppression is observed mainly in the phase transition from a- to b-CoMoO$_4$. The particle size appears also to influence slightly the formation of a-CoMoO$_4$ in the low-temperature range. These observations may be considered to give an indirect support for the effect of the alumina particle size, as described above.

Figure 9 shows typical curves of thermogravimetric analysis of the CoO–MoO$_3$ systems containing γ-alumina (a), α-alumina (b) and no alumina (c). The difference in weight reduction between these systems is within 1–2% over the entire temperature range investigated. Similar changes to each other are observed in the lower temperature range corresponding to the dehydration process. From these results, it may be considered that the amount of water involved or absorbed in alumina has little influence on the difference in the effect of the alumina addition. Except slightly marked weight losses in the range of 500–600°C in (b) and (c), a similar weight reduction was observed for all three systems.

In the system of CoO-α- or γ-alumina, the following phase changes were reported (5),

$$CoO \xrightarrow{600\text{–}605°C} Co_3O_4 \xrightarrow{950\text{–}1010°C}$$

$$CoO \xrightarrow{1050\text{–}1100°C} CoAl_2O_4.$$

In the system involving Al$_2$O$_3$·3H$_2$O, depression of the oxidation temperature to 425°C for CoO→Co$_3$O$_4$ was also recognized therein.

In the present study, the presence of Co$_3$O$_4$ was detected from the X-ray diffraction patterns for temperatures above 500°C, shown as relative intensities in Fig. 1. The marked weight losses around 500°C in (b) and (c) may correspond to the more rapid formation of a-CoMoO$_4$ which occurs in this temperature range. The observation of the weight losses supports the results (3) that the following solid state reaction proceeds around 500°C or above,

$$Co_3O_4 + 3MoO_3 = 3CoMoO_4 + 1/2O_2.$$
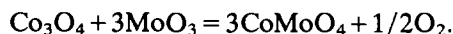
A smooth weight reduction is observed only in the system (a) where formation of a-CoMoO$_4$ is gradually increased over the whole temperature range studied.
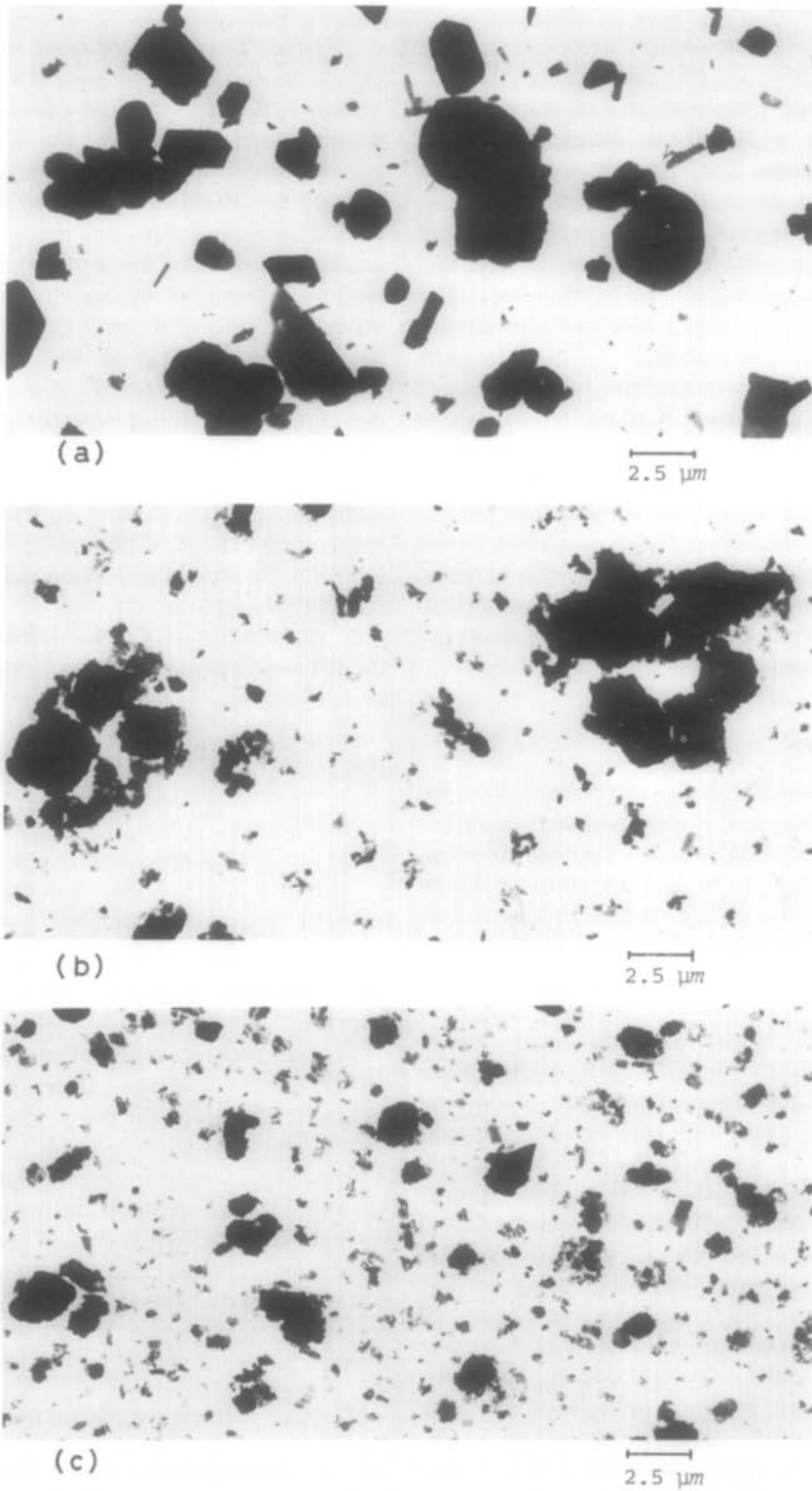
FIG. 7. Electron micrographs of the mixture at a $CoO:MoO_3:Al_2O_3$ molar ratio of $1:1:1$ after calcination. (a) $CoO:MoO_3:\alpha\text{-}Al_2O_3$ (800°C); (b) $CoO:MoO_3:$calcined $\alpha\text{-}Al_2O_3$ (500°C); (c) $CoO:MoO_3:\gamma_7Al_2O_3$ (800°C).
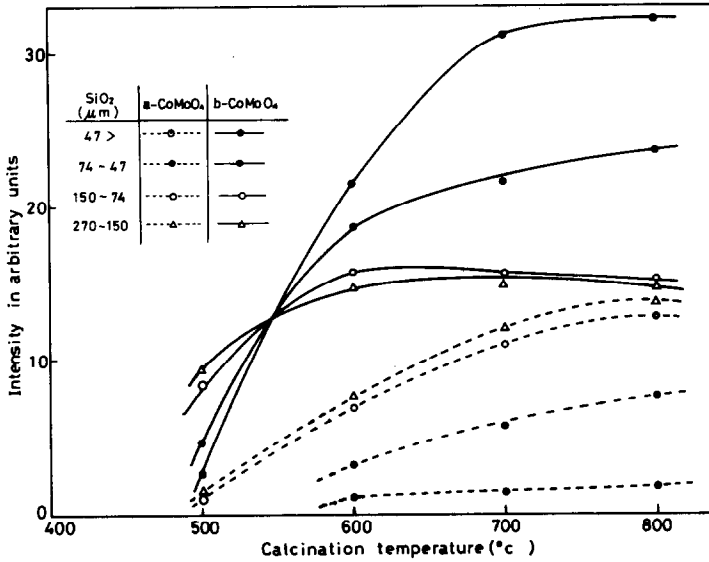
FIG. 8. Amounts of a-CoMoO$_4$ and b-CoMoO$_4$ formed at a CoO : MoO$_3$: SiO$_2$ molar ratio of 1 : 1 : 1 with SiO$_2$ of various particle sizes dependent on the calcination temperature followed by cooling.

In all cases, the DTA analysis showed continuously increasing endothermic curves above 200–300°C, on which a small endothermic peak appeared around 550°C in either (b) or (c).

In the system of MoO$_3$–α-Al$_2$O$_3$, simultaneous reactions of reduction to form various MoO$_{3-x}$ species are observed to begin around 600°C (6). However, in the three component systems, occurrence of these reactions and the effect thereof in the formation of a-CoMoO$_4$ have not yet been ascertained.

The thermogravimetric curves in Fig. 9 are considered to be complex results of various reactions in respective temperature ranges, as described above.

The table presents the sizes of crystallites of a- and b-CoMoO$_4$ obtained after calcination at respective temperatures and subsequent cooling to room temperature. The sizes were calculated by the Scherrer

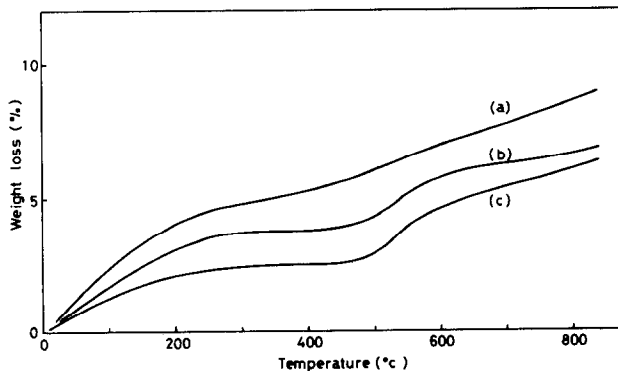FIG. 9. Thermogravimetric curves of the mixture at a CoO : MoO$_3$: Al$_2$O$_3$ molar ratio 1 : 1 : 1 with or without alumina at the heating rate of 10°C/min. (a) CoO : MoO$_3$: γ-Al$_2$O$_3$; (b) CoO : MoO$_3$: α-Al$_2$O$_3$; (c) CoO : MoO$_3$.

TABLE I

CRYSTALLITE SIZES OF a- AND b-CoMoO$_4$
FORMED IN USE OF INDICATED ALUMINAS
AFTER CALCINATION (Å)

Temp (°C)	CoMoO$_4$	α-Al$_2$O$_3$	γ-Al$_2$O$_3$	Calcined α-Al$_2$O$_3$	None
500	a	560	540	520	560
	b	480	—	505	530
600	a	610	540	600	600
	b	550	520	550	530
700	a	615	580	590	630
	b	560	550	560	560
800	a	620	650	620	680
	b	580	630	600	555

method for the intensities obtained by powder X-ray diffraction analysis. The table suggests that the crystal growth proceeds depending on degrees of rapid or gradual formation of a-CoMoO$_4$ and subsequent phase transition to b-CoMoO$_4$. In the systems which formed significant amounts of a-CoMoO$_4$ at lower temperatures, an increase in the crystallite size for the calcination temperature of 600–800°C was insignificant and the effect of the crystallite size change on the diffraction intensity from which relative amounts of cobalt molybdate were estimated, is considered to be little, except possibly a slight overestimation of the amount of a-CoMoO$_4$ formed in the γ-alumina system.

No consideration is made here of the physicochemical parameters controlling the effect of the particle size of alumina and the mechanism of the solid state reaction which is affected by the size. However, from the viewpoint of preparation of CoO–MoO$_3$–Al$_2$O$_3$ catalysts, studies should be made of the possibilities of the presence and variations of the mixed solid phase consisting of these starting or intermediate oxides and cobalt molybdate, the formation of which is influenced by the alumina carrier.

The low-temperature modification is of no direct significance for the catalytic reactions or the catalytic activities at elevated temperatures. The difference in the degree of formation of the high-temperature modification in the presence of α- or γ-alumina is thought to be taken into consideration in pretreatment of the catalysts and in the temperature range of catalytic reactions. In comparison with other carriers such as SiO$_2$ and activated carbon, alumina has the functions of stabilizing and dispersing the active components, in addition to those of providing the bifunctional catalytic activity and catalytic sites insusceptible to sulfur poisoning. It also plays a role to inhibit the formation of CoMoO$_4$, a precursor of such compounds as CoMoS$_2$ and CoMo$_2$S$_4$ which exhibit lower catalytic activity in the case of hydrodesulfurization process (4, 7).

From the results obtained in the present study, it is considered to be important to select appropriate alumina with suitable physicochemical properties, in due consideration of the catalyst preparation methods such as impregnation and kneading, subsequent pretreatment and reaction conditions.

The difficulty in detecting clear peaks in the X-ray diffraction patterns of the conventional desulfurization catalysts (8) seems to be due to amorphous or very fine particles of the alumina, together with the low concentration of active components in the systems.

References

1. "Molybdenum Catalyst Bilbiography" No. 1 (1964–1967), No. 2 (1968–1969), No. 3 (1970–1972), No. 4 (1973–1974), No. 5; (1975–1976), Climax Molybdenum Company of Michigan (Incorporated).

2. J. CHOJNACKI, R. KOZŁOWSKI, AND J. HABER, *J. Solid State Chem.* **11** 106 (1974) and the references cited therein.

3. J. HABER, in "Molybdenum," (P. C. H. Mitchell, eds.), University of Reading, England, September 1973, Climax Molybdenum Co. Ltd., London, 1974.

4. V. H. J. DE BEER AND G. C. A. SCHUIT, in "Preparation of Catalysts," (B. Delmon, P. A. Jacobs and G. Poncelet, Eds.), pp. 343–370, Elsevier, Amsterdam, 1976, and the references cited therein; V. H. J. DE BEER, M. J. M. VAN DER AALST, C. J. MACHIELS, AND G. C. A. SCHUIT, *J. Catal.* **43**, 78 (1976).

5. T. NISHINA, M. YONEMURA, AND Y. KOTERA, *J. Inorg. Nucl. Chem.* **34**, 3279 (1972); *J. Nat. Chem. Lab. for Industry, Tokyo* **68** 127 (1973).

6. Y. KOTERA AND A. UENO, *Bull. Chem. Soc. Japan* **46**, 3431 (1973).

7. F. E. MASSOTH, *J. Catal.* **50**, 190 (1977).

8. For example; P. L. VILLA, F. TRIFIRÒ, AND I. PASQUON, *Reaction Kinetics and Catalysis Letters* **1**, 341 (1974).