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Kinetics of the Formation of MoO_{3-x} at Elevated Temperatures from a Mixture of MoO_3 and α-Al_2O_3

Yoshihide KOTERA and Akifumi UENO
National Chemical Laboratory for Industry, Mita, Meguro-ku, Tokyo 153

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The kinetics of the formation of MoO_{3-x} from a mixture of MoO_3 and α-Al_2O_3 was studied by means of high temperature X-ray diffraction. The species of MoO_{3-x} formed in the temperature range 600—700 °C were identified as $MoO_{2.88}(Mo_8O_{23})$, $MoO_{2.76}(Mo_{17}O_{47})$, and $MoO_{2.75}(Mo_4O_{11})$. The activation energies of their formation were estimated to be 18.4 kcal/mol for Mo_8O_{23}, 23.0 kcal/mol for $Mo_{17}O_{47}$ and 29.2 kcal/mol for Mo_4O_{11}. Other types of species of MoO_{3-x} observed above 800 °C were $MoO_{2.89}(Mo_9O_{26})$ and MoO_2. Little effect of water vapor, oxygen or nitrogen on the formation of the species was observed. No MoO_{3-x} was observed in the mixture of MoO_3 with SiO_2 or α-Fe_2O_3.

Detailed X-ray studies on the existence of the oxide intermediates between molybdenum dioxide and molybdenum trioxide have been made by Magneli *et al.*[1] by heating the mixture of molybdenum trioxide and molybdenum metal powder *in vacuo* in a glass tube at temperatures up to 700 °C. The following phases were identified by means of X-ray powder photography.

α-phase	MoO_3	orthorhombic
β-phase	Mo_9O_{26}	monoclinic
β'-phase	Mo_8O_{23}	monoclinic
γ-phase	Mo_4O_{11}	monoclinic
δ-phase	MoO_2	monoclinic

In later works other species such as $Mo_{17}O_{47}$, $Mo_{18}O_{52}$, and Mo_5O_{14} were shown to exist, their crystal structures being determined exactly.[2,3] The formation of these oxide intermediates was found, however, only in the case where a mixture of molybdenum trioxide and molybdenum metal powder or that of molybdenum trioxide and molybdenum dioxide was heated.

Recently a hydrodesulfurizing catalyst consisting of molybdenum trioxide, cobalt oxide and alumina was developed[4] and its active species studied extensively. Crystallographic[5] and spectroscopic[6] investigations on the mixture of molybdenum trioxide or alumina with cobalt oxide have been made to some extent. The reaction product between alumina and cobalt oxide was elucidated by structural and magnetic studies.[7] Formation of $CoAl_2O_4$ was observed when a mixture

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[1] A. Magneli. G. Anderson, B. Blomberg, and L. Kihlborg, *Anal. Chem.*, **24**, 1998 (1952).

[2] L. Kihlborg, *Arkiv Kemi.*, **21**. 357, 417 (1963).

[3] A. Magneli, *Acta Crystallogr.*, **6**, 495 (1953); L. A. Bursill, *ibid.*, **28**, 187 (1972).

[4] N. Todo, T. Kabe, K. Ogawa, M. Kurita, T. Sato, K. Shimada, Y. Kuriki, T. Oshima, T. Takematsu, and Y. Kotera, *Kogyo Kagaku Zasshi*, **74**, 563 (1971).

[5] G. W. Smith, *Acta Crystallogr.*, **19**, 269 (1965).

[6] J. M. J. Lipsch and G. C. A. Shuit, *J. Catal.*, **15**, 163, 173 (1969); J. H. Ashley and P. C. H. Mitchell, *J. Chem. Soc., A*, **1968**, 2821, 2730.

[7] J. T. Richardson and L. W. Vernon, *J. Phys. Chem.*, **62**, 1153 (1958).

of cobalt compound and alumina was heated above 850 °C, while at lower temperature only the oxidation or reduction of cobalt oxide would occur.[8] However, studies on the mixture of alumina and molybdenum trioxide have not been carried out thoroughly. A new compound containing molybdenum trioxide, alumina and silica was prepared and studied by the X-ray diffraction method.[9] The aim of the present work is to clarify the crystallographic changes of molybdenum trioxide mixed with α-alumina during the course of heating and to study the kinetics of the formation of MoO_{3-x} in the mixture.

Experimental

Molybdenum trioxide (Climax Molybdenum Co.) containing less than 0.05% of metallic impurities was employed. α-Alumina and α-ferric oxide were of guaranteed grade, while silica containing less than 0.01% of metallic impurities was converted into α-cristobalite by heating at 1100 °C before use.

Molybdenum trioxide and α-alumina were mixed well and the mixture was set in a platinum sample holder for the measurement of high temperature X-ray diffraction during the course of reaction. Temperature fluctuation did not exceed ± 2 °C during the measurement. The X-ray instrument was operated at 35 KV with a filament current of 15 mA, a nickel filter being employed for CuKα radiation to provide an incident wave length of 1.5405 Å. Reflection peaks at 2θ angles were recorded on the strip chart, and the "d" values corresponding to these angles were calculated from the Bragg diffraction law. Oxygen or nitrogen was obtained from cylinders. It was wetted by passing through water at 20 °C (water vapor pressure 17.5 mmHg), or dried by passing above calcium chloride. The flow rate was held constant by means of a Venturi type manometer.

Relative amounts of the species were estimated from the measurements of the peak heights recorded on the strip chart. In order to determine the relative amount of the formed MoO_{3-x} species during the course of reaction, the characteristic peaks of X-ray diffraction pattern were selected as follows, $2\theta = 12.7°$ for MoO_3, 14.4° for Mo_8O_{23}, 15.8° for $Mo_{17}O_{47}$ and 23.7° for Mo_4O_{11}. Reproducibility of the peak height was within $\pm 5\%$ error.

Results

A typical X-ray diffraction pattern is shown in Fig. 1, where the mixture of the oxide with a MoO_3/α-Al_2O_3 weight ratio of 2: 1 was heated at 650 °C for 2 hr in a stream of dry nitrogen gas. New species such as Mo_4O_{11}, Mo_8O_{23}, and $Mo_{17}O_{23}$ were identified by a comparison of their 'd' values with those in calibration graphs[10] (Fig. 1).

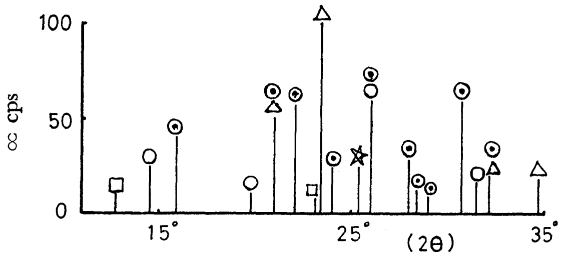

Fig. 1. The X-ray diffraction pattern for the mixture of the oxides with a MoO_3/α-Al_2O_3 ratio of 2: 1 after heated at 650 °C for 2 hr (□: MoO_3, △: Mo_4O_{11}, ○: Mo_8O_{23}, ⊙: $Mo_{17}O_{47}$, ☆: α-Al_2O_3).

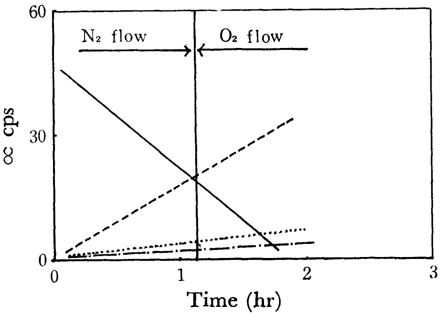

Fig. 2. The behaviors of MoO_{3-x} observed at 650 °C and the effect of the surrounding atmosphere on the reaction. ——: MoO_3, - - - -: Mo_4O_{11}, —·—·—: Mo_8O_{23}, ······: $Mo_{17}O_{47}$.

The changes of peak height for the respective MoO_{3-x} observed during the course of heating are shown in Fig. 2. We see that the effect of surrounding atmosphere on the reduction is not noticeable. Reduction of MoO_3 to MoO_{3-x} at 600, 650, or 700 °C was analyzed, the formation of Mo_8O_{23}, $Mo_{17}O_{47}$, and Mo_4O_{11} as well as the decrease of molybdenum trioxide being plotted in Figs. 3, 4, 5 and 6, respectively.

The rate of formation of respective MoO_{3-x} and that of the decomposition of MoO_3 were of zeroth order with respect to the molybdenum oxide concentrations (Fig. 2). The rate constant for the formation of MoO_{3-x} and that for the decomposition of molybdenum trioxide were calculated from the initial slopes of the

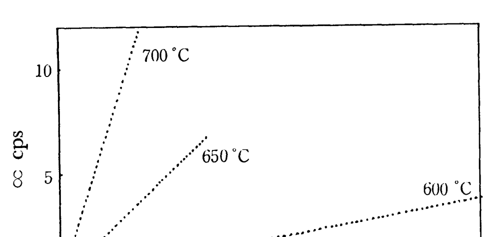

Fig. 3. Formation rate of Mo_8O_{23} at various temperatures.

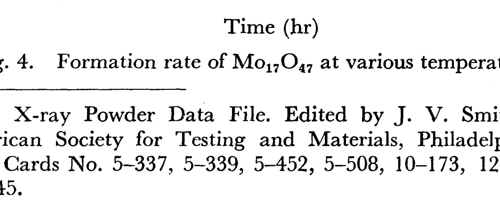

Fig. 4. Formation rate of $Mo_{17}O_{47}$ at various temperatures.

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[8] T. Nishina, M. Yonemura, and Y. Kotera, *J. Inorg. Nucl. Chem.*, **34**, 3279 (1972).

[9] A. Ueno and Y. Kotera, *Chem. Lett.*, **1973**, 21.

[10] X-ray Powder Data File. Edited by J. V. Smith, *et al.*, American Society for Testing and Materials, Philadelphia, Pa., 1968 Cards No. 5-337, 5-339, 5-452, 5-508, 10-173, 12-753 and 13-345.

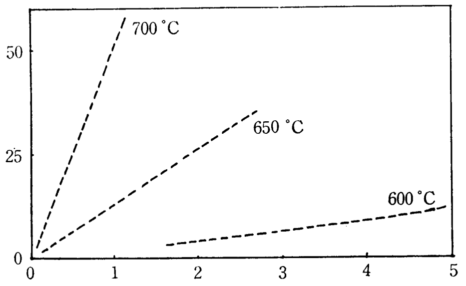

Fig. 5. Formation rate of Mo_4O_{11} at various temperatures.

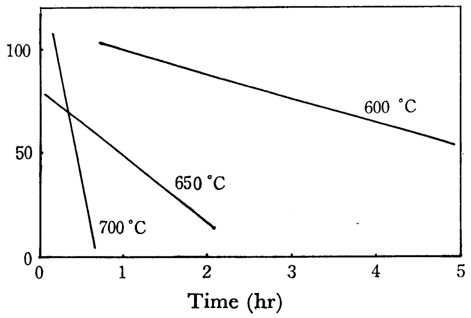

Fig. 6. Decomposition rate of MoO_3 at various temperatures.

curves in Figs. 3—6. The activation energies for the formation of MoO_{3-x} and the decomposition of molybdenum trioxide were estimated from the Arrhenius plot in Fig. 7. The deviation of each plot from the straight line is within ±5%. Values of the activation energies thus obtained were 18.4, 23.0, and 29.2 kcal/mol for the formation of Mo_8O_{23}, $Mo_{17}O_{47}$ and Mo_4O_{11} and 27.8 kcal/mol for the decomposition of MoO_3, respectively.

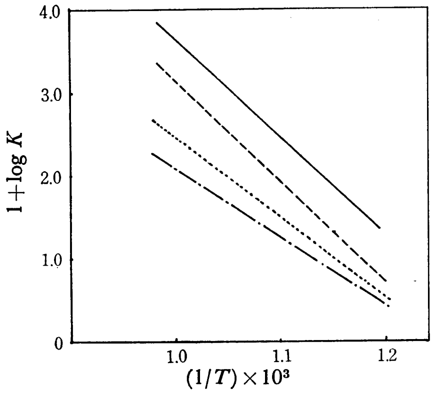

Fig. 7. The standard Arrhenius plot for the formation of MoO_{3-x} and the decomposition of MoO_3. ——: MoO_3, ----: Mo_4O_{11}, —·—·—: Mo_8O_{23}, ······: $Mo_{17}O_{47}$.

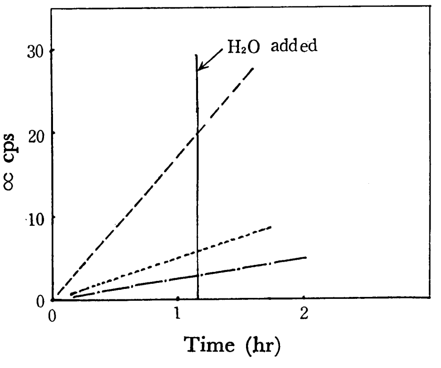

Fig. 8. The effect of the additional water vapor on the formation of MoO_{3-x} at 650 °C. ----: Mo_4O_{11}, —·—·—: Mo_8O_{23}, ······: $Mo_{17}O_{47}$.

Figure 8 shows that no change of reaction rate was observed when the wet nitrogen was introduced into the mixture with a $MoO_3/\alpha\text{-}Al_2O_3$ weight ratio of 2: 1 after being heated at 650 °C for 70 min in a stream of dry nitrogen. This indicates that no effect of the ambient water vapor is observed upon the rate of formation of MoO_{3-x}.

Dsicussion

A catalyst consisting of molybdenum and cobalt compounds and alumina was developed to hydrodesulfurize light or heavy oil[4] and was studied on its active species. A crystallographic investigation[5] on molybdenum and cobalt compounds showed that the formation of $CoMoO_4$ was observed by heating the mixture of cobalt oxide and molybdenum trioxide above 700 °C, and at lower temperature the other types of molybdenum cobalt oxides formed, while it was assumed from the spectroscopic investigation[6] that the octahedron of $[CoO_6]$ might be the active species of the catalyst consisting of molybdenum and cobalt compounds and alumina. However it is very difficult to clarify the active species. It seems important to assure the reaction between two oxides under the conditions for the preparation of the catalyst.

The behavior of the mixture of cobalt compound and alumina was studied during the calcination at temperatures where catalysts are prepared.[8] The formation of cobalt aluminate spinel above 850 °C was observed by means of high-temperature X-ray diffraction and chemical analysis. At lower temperature cobalt oxide behaves in the mixture with alumina in almost the same way as alone.

The behavior of the mixture of molybdenum compounds and alumina has not been so extensively studied. It was proposed[11] that three new compounds might be formed during the heating of the mixture of molybdenum trioxide and γ-alumina. The formation was assumed by the appearance of new X-ray lines. We reported[9] that the new compound is formed by heating the mixture of molybdenum trioxide and alumina when either oxide contains silica. The above postulate would be the case where molybdenum trioxide or γ-alumina is contaminated by silica. In the present study with the use of alumina or molybdenum trioxide free from silica, new X-ray lines were found, which are representative for MoO_{3-x}[1,2] as shown in Fig. 1.

The formation of the respective MoO_{3-x} species was spontaneously observed as shown in Figs. 2—5.

From the results it is assumed that the reduction of MoO_3 to MoO_{3-x} does not proceed in a successive reduction of molybdenum trioxide to dioxide through Mo_8O_{23}, $Mo_{17}O_{47}$, and Mo_4O_{11}, but by a parallel reduction from MoO_3 to respective MoO_{3-x}. The

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[11] T. Shirasaki, O. Shin, M. Kato, and K. Morikawa, *Shokubai*, **4**, 337 (1962).

TABLE 1. FORMATION OF MoO_{3-x} FROM THE MIXTURE OF MoO_3 AND α-Al_2O_3 DURING THE HEATING

TEMP (°C)	OBSERVED COMPOUND
500 600	MoO_3 Al_2O_3
700 800	MoO_3 Al_2O_3 Mo_4O_{11} Mo_8O_{23} $Mo_{17}O_{47}$
900 1000	MoO_2 Al_2O_3 Mo_9O_{26}
1100	Al_2O_3

activation energies estimated above are assumed to represent those for each step of the parallel reduction.

The decrease of molybdenum trioxide was observed as shown in Figs. 2 and 6. The activation energy estimated above would be the weighted mean of three parallel reactions. The amount of sublimation of molybdenum oxide is negligibly small since the measurement of high-temperature X-ray diffraction was carried out between 600 and 700 °C and molybdenum trioxide sublimes above 800 °C.[12]

In order to know whether molybdenum oxides form compounds with α-alumina or not, an aqueous solution of ammonia was poured into a mixture of MoO_3 and α-alumina which had been ignited at 650 °C for 2 hr. X-Ray analysis of the residue was carried out, the X-ray pattern being found to be that of only α-alumina. While molybdenum oxides are known to be soluble in aqueous ammonia,[13] it is deduced that molybdenum oxides did not form any compounds with α-alumina by heating under the conditions cited above.

The effect of alumina or silica upon the electron spin resonance spectrum of molybdenum was recently studied.[14] It was observed that the ESR spectrum due to molybdenum supported on alumina differed from that on silica but no reason was given. When silica was heated with molybdenum trioxide instead of α-alumina, no reduction of molybdenum trioxide was observed up to 800 °C.

R. Schenck *et al.*[15] observed the evolution of oxygen by heating the mixture of alumina and cupric oxide. This was explained by assuming that alumina promotes the reduction of cupric oxide by the formation of a spinel phase of $CuO\cdot Al_2O_3$. They also reported the reduction of cupric oxide by ferric oxide in a similar way to that by alumina. For molybdenum trioxide α-alumina similarly reduced MoO_3 to MoO_{3-x}, but no reduction of MoO_3 occurred by heating with α-ferric oxide up to 800 °C. The spinel formula $MoAl_2O_4$ does not seem to be a reaction intermediate during calcination of the mixture of molybdenum trioxide and alumina.

The authors express their thanks to Dr. S. Shin, Miss M. Yonemura and Mr. T. Sekine for their useful discussion and encouragement.

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12) R. Horbe, O. Knacke, and K. E. Prescher, *Z. Erzbergbau Metallhüttenw.*, **14**, 232 (1961); E. A. Gulbransen, K. F. Andrew, and F. A. Brassart, *J. Electrochem. Soc.*, **110**, 242 (1963).

13) "Gmelins Handbuch der Anorganischen Chemie," 8 Auflage System-Nummer 53 (1953).

14) M. Akimoto and E. Echigoya, *J. Catal.*, **29**, 191 (1973).

15) R. Schenck and F. Kurzes, *Z. Anorg. Allgem. Chem.*, **235**, 97 (1937).