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SOLID–SOLID INTERACTIONS IN THE MoO_3–Al_2O_3 SYSTEM

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ABSTRACT

Molybdenum/aluminium mixed oxide solids were prepared by thermal decomposition of aluminium hydroxide pretreated with different proportions of ammonium molybdate. The proportions of molybdenum expressed as wt.%MoO_3 were 12.4, 22 and 41.4. The prepared mixed solid specimens were calcined in air at 500–1000 ° C and the solid–solid interactions between MoO_3 and Al_2O_3 were investigated using DTA, TG, DTG and XRD techniques.

The results obtained revealed that ammonium molybdate and aluminium hydroxide decomposed readily at 250 and 320 ° C yielding MoO_3 and an amorphous alumina respectively. The produced oxides underwent solid–solid interaction at 500–700 ° C, forming well crystallized orthorhombic $Al_2(MoO_4)_3$ phase. This compound remained thermally stable until about 850 ° C, then decomposed above this temperature giving very well crystallized α-Al_2O_3 (corrundum) and MoO_3. The latter oxide partly volatilized and the remaining portion dissolved in the alumina matrix forming MoO_3–Al_2O_3 solid solution. The amounts of MoO_3 dissolved in Al_2O_3 at 900 or 1000 ° C are 9.4, 12.2 and 16.4 wt.% for the solids containing 12.4, 22 and 41.4 wt.%MoO_3 respectively. The presence of MoO_3 greatly enhanced the crystallization of alumina into the kappa and alpha phases upon heating at 700 and 900 ° C respectively. This effect was attributed to the formation of some kind of MoO_3–Al_2O_3 solid solutions. Crystalline MoO_3, when mixed with Al_2O_3 and heated to 500 ° C, loses its crystallinity due to its dispersion on the alumina surface. The monolayer dispersion capacity of Al_2O_3 for MoO_3 was found to be 0.116 g per 100 m^2 of the alumina surface.

INTRODUCTION

Molybdenum oxides supported on alumina are technologically one of the most important classes of solid catalysts [1–7]. Molybdenum may exist as isolated Mo species, as well dispersed oxomolybdenum patches, and also as MoO_3 or $Al_2(MoO_4)_3$ compounds [5–9]. The identification of the different chemical states of molybdenum requires extensive studies using XRD, ESR, DRS, XPS and laser Raman spectroscopy techniques [1–7]. The supported

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catalysts are usually prepared by impregnation of an alumina support from an aqueous solution of ammonium heptamolybdate.

It has been reported that heating a mixture of crystalline MoO_3 and gamma alumina at 400 °C for about 24 h. resulted in the disappearance of all the diffraction lines of the MoO_3 phase [10–12]. The collapse of the crystallinity of MoO_3 was attributed to monolayer dispersion of this oxide on the surface of the Al_2O_3 support. The thermal treatment of supported catalysts at higher temperatures $\geqslant 600\,°C$ greatly increases the surface and bulk mobilities of the molybdenum species leading to the formation of well crystallized MoO_3 or $Al_2(MoO_4)_3$ compounds [5,10]. The formation of these compounds may be influenced by certain foreign cations such as Li^+, Zn^{2+}, Ga^{3+} and Ge^4 ions [1,4].

The present investigation reports on a study of the solid–solid interactions in the MoO_3–Al_2O_3 system. The techniques employed were DTA, TG, DTG and XRD. The mixed solid specimens were prepared by impregnation of solid $Al(OH)_3$ from an aqueous solution of ammonium molybdate followed by heating in air at temperatures ranging between 500 and 1000 °C.

EXPERIMENTAL

Materials

Aluminium hydroxide was prepared from hydrated aluminium nitrate $Al(NO_3)_3 \cdot 9H_2O$ using a saturated solution of ammonium carbonate. Precipitation was at pH 7.5 and 70 °C while stirring. The precipitate was washed with distilled water until free from ammonium and nitrate ions. The filter cake was dried at 120 °C for 4 days. A known mass of the obtained $Al(OH)_3$ was impregnated with ammonium molybdate solution containing different proportions of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The pH of the system was fixed at 7. The proportions of ammonium molybdate were 0.2/7, 0.4/7 and 1.0/7 mol per mol $Al(OH)_3$. The impregnated solids were dried at 120 °C then roasted in air at 500, 700, 900 and 1000 °C. The time of heating was fixed at 5 h. The prepared mixed solid specimens were designated AlMoI, AlMoII and AlMoIII. The molybdenum oxide contents of these solids, expressed as wt.%MoO_3 are 12.4, 22.0 and 41.4 respectively.

Techniques

DTA, TG and DTG analyses of various solids were carried out using a Netzsch-Gerätebau simultaneous thermal analysis apparatus (STA 409, type 6.223). The rate of heating was kept at 10 °C min^{-1}. A 100 mg sample of each solid specimen was employed in each case.

An X-ray investigation of the thermal products of the different mixed solids was performed with a Philips diffractometer (type PW 1390). The patterns were run with nickel-filtered copper radiation ($\lambda = 1.5405$ Å) at 36 kV and 16 mA with a scanning speed of 1° in $2\ \theta\ \mathrm{min}^{-1}$.

The specific surface area S_{BET} of the employed $Al(OH)_3$ precalcined in air at 500 °C for 5 h was determined from the N_2 adsorption isotherm at -196 °C and was found to be 234 $m^2\ g^{-1}$.

RESULTS AND DISCUSSION

Thermal decomposition of ammonium molybdate–aluminium hydroxide mixed solids

Figure 1 shows the DTA curves of AlMoI, AlMoII and AlMoIII solids. Seven endothermic peaks were observed in the DTA curves of different mixed solid specimens. The first peak is weak and broad located at about 100 °C, indicating the loss of physisorbed water. The second peak is relatively strong and sharp having its maximum at 210 °C; its area increases with increasing proportion of ammonium molybdate. This peak characterizes the removal of the four water of crystallization molecules bound to the ammonium molybdate molecule. The third peak is also sharp and strong with its maximum at 245 °C, indicating the thermal decomposition of ammonium molybdate into molybdenum oxides(s). The fourth endothermic peak is the most sharp and strong having its maximum at 325 °C, characterizing the thermal decomposition of $Al(OH)_3$ into Al_2O_3 [13,14]. The fifth peak, relatively sharp and strong, is at 550 °C and might correspond to removal of the OH groups bound to the alumina matrix [15]. In fact, it has been shown that the complete dehydroxylation of Al_2O_3 solid requires prolonged heating of the solid at temperatures $\geqslant 500$ °C [15,16]. The last two peaks are sharp and strong having their maxima at 950 and 1000 °C in the case of AlMoIII mixed solid sample, and relatively weak with their maxima located at 870 and 940 °C in the case of AlMoI and AlMoII solids. These two peaks might correspond to the thermal decomposition of a molybdenum–aluminium compound, that may be formed by a solid–solid interaction between the two oxides, and/or to sublimation of molybdenum oxide respectively [17].

Figure 2 shows the TG and DTG curves of aluminium hydroxide specimens pretreated with different proportions of ammonium molybdate. The percentage loss in weight corresponding to the loss of physisorbed water (100 °C) was about 2%, and the total weight loss resulting from the thermal treatment of various solids at temperatures ranging between 100 and 600 °C reached 32, 32 and 29.5% for AlMoI, AlMoII and AlMoIII mixed solids respectively. The calculated weight loss accompanying the thermal decom-

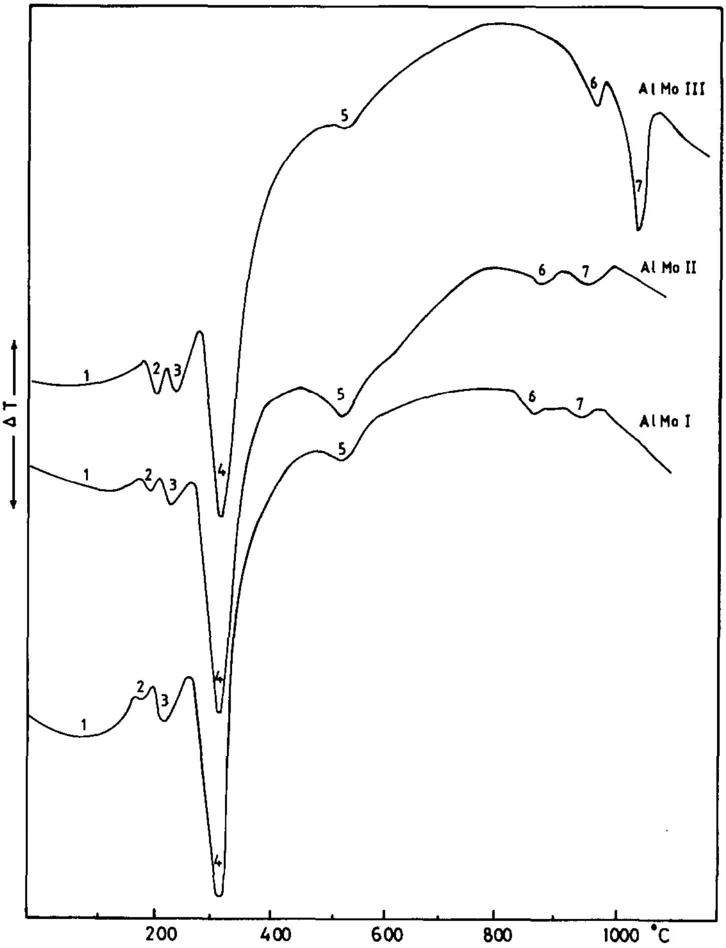

Fig. 1. DTA curves of aluminium hydroxide pretreated with different proportions of ammonium heptamolybdate.

position of $Al(OH)_3$–$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ mixed solids to the corresponding oxides (alumina and molybdenum trioxide) is 32.9, 31.6 and 28.8 for AlMoI, AlMoII and AlMoIII solids respectively. These values are very close to those found experimentally (Fig. 2), and so the following reaction can be written

$$(NH_4)_6Mo_7O_{24} \cdot 4H_2O + Al(OH)_3$$

$$\xrightarrow{210\text{–}550\,^\circ C} 7MoO_3 + \tfrac{1}{2}Al_2O_3 + 5H_2O(g) + 6NH_3(g) \qquad (1A)$$

It can also be shown from Fig. 2 that the total % loss in weight following the thermal treatment up to 1000 °C of the different mixed solids investigated is 38, 44.5 and 56 for AlMoI, AlMoII and AlMoIII mixed solid specimens respectively. Figure 2 also shows that there is no loss or gain in

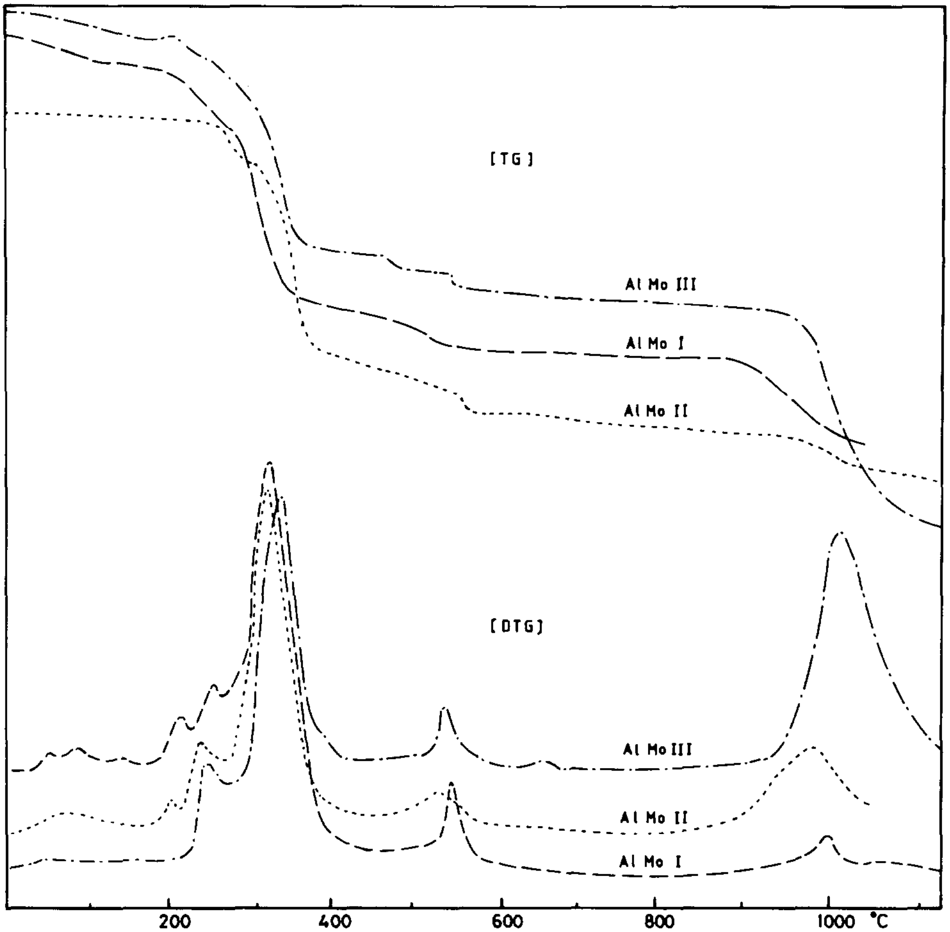

Fig. 2. TG and DTG of different aluminium/molybdenum mixed solids.

weight of the three investigated solid samples upon heating at temperatures varying between 600 and 800 ° C. The last endothermic peak (940, 1000 ° C) in the DTA curves of the different solids is accompanied by a weight loss of 4%, 10% and 25% for AlMoI, AlMoII and AlMoIII solids respectively. These values suggest a possible volatilization of MoO_3 solid. Preliminary experiments showed that the thermal treatment of ammonium molybdate in air at temperatures $\geqslant 800\,^\circ C$ resulted in a complete sublimation of the calcined solid. In fact, pure molybdenum trioxide undergoes sublimation upon heating at temperatures above its melting point (795 ° C) [17]. Assuming a complete volatilization of MoO_3 solid in the various mixed solids investigated, the corresponding loss in weight will be 12.4%, 22% and 41.4% for AlMoI, AlMoII and AlMoIII solids respectively. A comparison of these values with those found experimentally reveals that a fraction of the MoO_3 present was liable to escape into the gaseous phase and the remaining portion was retained in the solid state through the possible formation of a solid solution in the alumina matrix. Confirmation of this speculation can be readily achieved by an XRD investigation of various solids.

XRD investigation of the thermal products of pure and mixed aluminium hydroxide and ammonium molybdate solids

Pure solids

Figure 3 shows the XRD patterns of pure aluminium hydroxide and ammonium molybdate preheated in air at different temperatures. In the case of the molybdate sample, the calcination temperatures were only 500 and 700 ° C because of sublimation of the produced solid when heated above this limit. All the diffraction lines of well crystallized orthorhombic MoO_3 phase were detected in the patterns of ammonium molybdate precalcined at 500 and 700 ° C. On the other hand, the thermal products of $Al(OH)_3$ at 500 or 700 ° C are amorphous in nature while the solid fired at 1000 ° C consists of crystallized kappa alumina together with a minute amount of α-Al_2O_3 (corrundum) [13,15,16]. The complete transformation of the pure alumina specimen into the alpha form required a thermal treatment at elevated temperatures > 1200 ° C [13,15,16] or the presence of certain foreign oxides such as NiO [14], V_2O_5 [18], Co_3O_4 [19] and CuO [20]. These oxides much enhanced the crystallization process of Al_2O_3 into the alpha corrundum phase.

Mixed solids

The XRD patterns of the different mixed solids precalcined in air at 500, 700, 900 and 1000 ° C are given in Figs. 4, 5 and 6. Figure 4 shows the diffraction patterns of AlMoI, AlMoII and AlMoIII preheated in air at 500 ° C. Figure 4 shows that the first two mixed solids are amorphous while the AlMoIII specimen is a crystalline solid consisting of crystallized orthorhombic MoO_3 phase together with a very small amount of a different compound which has diffraction lines at 4.26, 4.0, 3.84, 3.79 and 3.4 Å. These lines correspond to an orthorhombic aluminium molybdate $Al_2(MoO_4)_3$ [21]. The amorphous nature of AlMoI and AlMoII mixed solids, containing 12.4 and 22 wt.% MoO_3 and precalcined at 500 ° C, clearly indicates the dispersing effect of the alumina support towards the MoO_3 phase. The appearance of the diffraction lines of MoO_3 phase in the patterns of AlMoIII solid sample indicates the limit of the dispersion capacity of Al_2O_3 for molybdenum trioxide solid. This limit is normally known as the monolayer dispersion capacity (MLDC) of a given oxide in certain support materials and is expressed as the weight of this oxide per 100 m^2 of the support. The value of the MLDC of the employed alumina support material towards MoO_3 can be readily calculated from the S_{BET} of Al_2O_3 at 500 ° C and the amount of molybdenum trioxide in AlMoII solid; the obtained

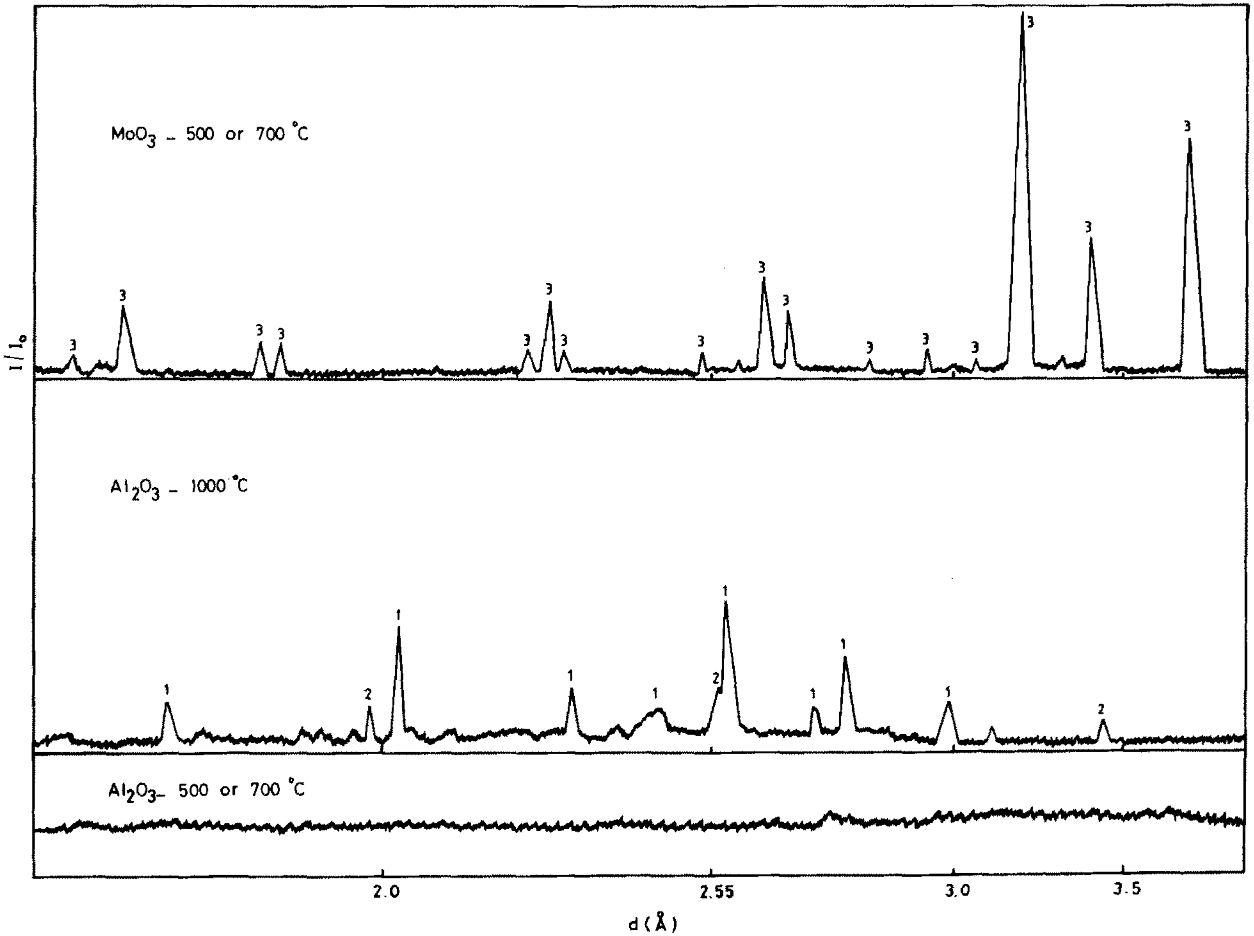

Fig. 3. XRD patterns of the calcination products of pure $Al(OH)_3$ and ammonium heptamolybdate, (1) κ-Al_2O_3 phase, (2) α-Al_2O_3 phase, (3) orthorhombic MoO_3 phase.

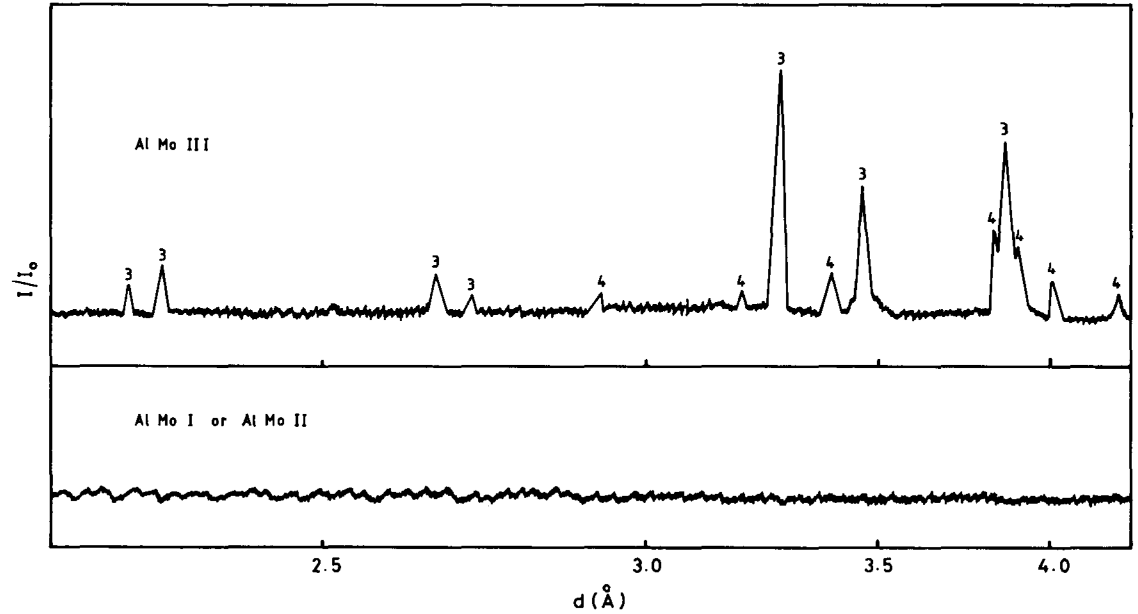

Fig. 4. XRD patterns of the thermal products of AlMoI, AlMoII and AlMoIII solids precalcined in air at 500 ° C, (3) orthorhombic MoO_3 phase, (4) $Al_2(MoO_4)_3$ phase.

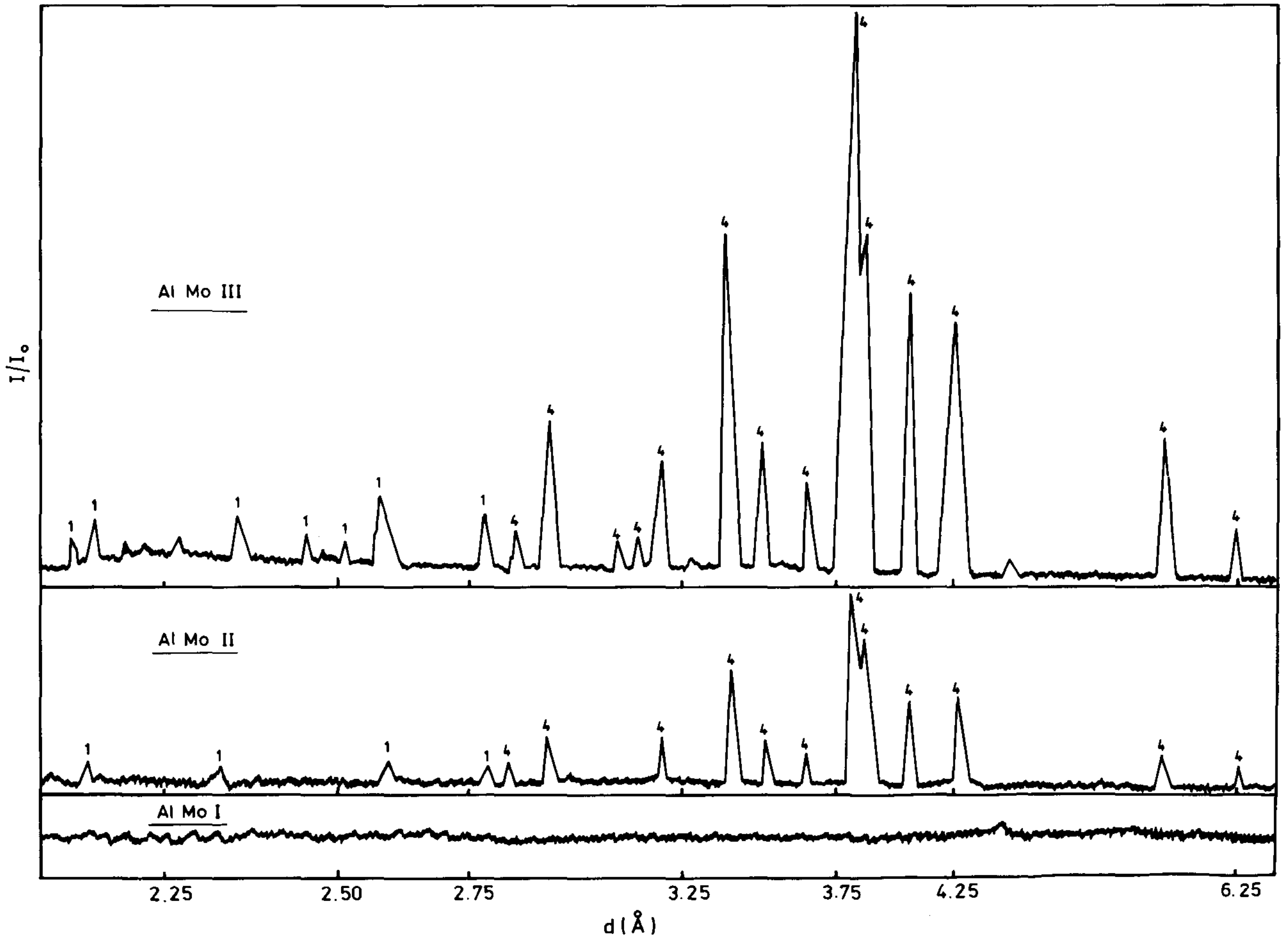

Fig. 5. XRD patterns of the thermal products of AlMoI, AlMoII and AlMoIII solids preheated in air at 700 °C, (1) κ-Al_2O_3 phase, (4) $Al_2(MoO_4)_3$ phase.

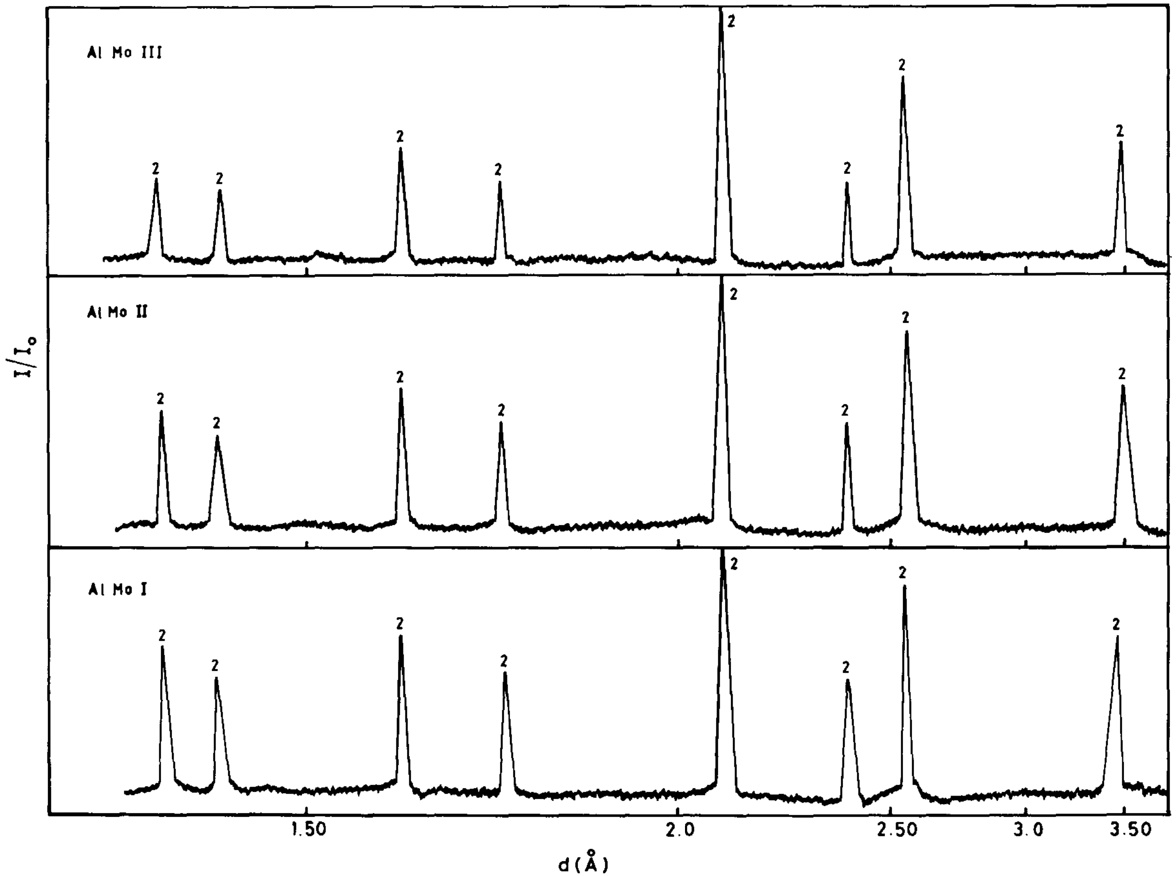

Fig. 6. XRD patterns of AlMoI, AlMoII and AlMoIII mixed solids preheated in air at 900 or 1000° C, (2) α-Al_2O_3 (corrundum phase).

value was found to be 0.116 g of MoO_3 per 100 m^2. This value is identical to that reported earlier [9]. Different mechanisms have been proposed to account for the dispersion power of some support materials for a large variety of oxides [12,22–24]. These mechanisms lie beyond the scope of the present investigation. The formation of $Al_2(MoO_4)_3$ in the case of the AlMoIII specimen preheated in air at 500 °C took place via the following solid–solid interaction

$$3MoO_3 + Al_2O_3 \xrightarrow{500\,^\circ C} Al_2(MoO_4)_3 \tag{1B}$$

This reaction is not followed by any change in weight and at 500 °C might take place at such an extremely slow rate that it cannot be detected by a normal DTA technique (Fig. 1) and so the amount of aluminium molybdate produced was very minute. The formation of appreciable amounts of this compound thus requires the thermal treatment of various mixed solids at higher temperatures.

Figure 5 shows the XRD patterns of the different mixed solid specimens preheated in air at 700 °C. Figure 5 indicates that the AlMoI solid is amorphous while the other two mixed solids are crystalline. All the diffraction lines of free MoO_3 phase have disappeared from the patterns of these solids. This indicates that the molybdenum trioxide present interacted completely with Al_2O_3 to produce well crystallized $Al_2(MoO_4)_3$ phase. It can be observed from Fig. 5 that some of the excess alumina present in AlMoII and AlMoIII solids, preheated to 700 °C, crystallizes into κ-Al_2O_3. The fact that pure alumina sample precalcined at 700 °C is an amorphous solid and is partly transformed into κ-Al_2O_3 in the presence of molybdenum trioxide indicates the role of this oxide in catalysing the crystallization process of the treated alumina. It is plausible to argue that the catalysing effect of MoO_3 might occur via the formation of some kind of solid solution in the alumina matrix. The reaction can be written as follows

$$Al_2O_3(\text{amorphous}) \xrightarrow[MoO_3]{700\,^\circ C} Al_2O_3(\kappa\text{-form}) \tag{2}$$

The fact that the phase transformation process represented by reaction 2 was not detected in the DTA curves (Fig. 1) indicates that at 700 °C this reaction proceeds at a very slow rate.

The aluminium molybdate compound formed in various mixed solids is liable to thermal decomposition by heating at relatively high temperatures. The thermal stability of this compound can be studied by the XRD investigation of the different mixed solids prefired at 900 or 1000 °C. This has been achieved and the results obtained are given in Fig. 6. It can be observed from Fig. 6 that the diffraction lines of $Al_2(MoO_4)_3$ phase have disappeared completely from the patterns of the mixed solids precalcined at 900 or 1000 °C. It can thus be concluded that aluminium molybdate decomposes readily by heating at these temperatures according to

$$Al_2(MoO_4)_3 \xrightarrow{900\,^\circ C} Al_2O_3 + MoO_3 \qquad (3)$$

This reaction is not followed by any change in weight, so the sixth endothermic peak observed in the DTA curves of the AlMoI, AlMoII and AlMoIII solids found at 870–950 °C (Fig. 1) corresponds to reaction 3. Figure 6 also shows that the diffraction lines of very well crystallized α-Al_2O_3 (corrundum) were only detected in the patterns of the mixed solids preheated in air at 900 or 1000 °C. The thermal decomposition of aluminium molybdate yields Al_2O_3 and MoO_3, the absence of the diffraction lines of the second oxide may indicate its sublimation and/or its dissolution in the Al_2O_3 matrix. The sublimation process is normally accompanied by a loss in weight while the formation of MoO_3–Al_2O_3 solid solution is not necessarily followed by a change in weight of the precalcined solids. Different weight losses were observed for the various mixed solids varying between 4 and 25% (c.f. Fig. 2). These values are, however, smaller than those corresponding to the complete volatilization of MoO_3 solid. Indeed, the mixed solids prefired at 900 or 1000 °C became light to dark grey (Al_2O_3 being white in colour) indicating the formation of MoO_3–Al_2O_3 solid solution. These results suggest that MoO_3 escapes, in part, into the gaseous phase and the portion remaining dissolves in Al_2O_3 solid. The proportions of molybdenum trioxide contributing to both processes (sublimation and formation of solid solution) can be calculated for each mixed solid specimen. The obtained results are as follows: (i) 32.3% of MoO_3 in AlMoI sample volatilized and 67.7% dissolved in Al_2O_3; (ii) 45.5% of MoO_3 in AlMoII escaped as a gas and 55.5% dissolved in the alumina solid; and (iii) 60.4% of MoO_3 in AlMoIII sublimed and 39.6% was included in the MoO_3–Al_2O_3 solid solution. In other words, the amounts of MoO_3 dissolved in alumina at 900 or 1000 °C are 9.4, 12.2 and 16.4 wt.%MoO_3 for AlMoI, AlMoII and AlMoIII solids respectively. A comparison of the XRD patterns of the pure alumina sample calcined at 1000 °C and those containing MoO_3 and heated at 900 or 1000 °C (Figs. 3 and 6) clearly indicates that molybdenum trioxide much enhanced the crystallization process of Al_2O_3 into α-corrundum. Such a phase transformation requires the thermal treatment of pure alumina at $\geqslant 1200\,^\circ C$ [13,15,16]. The presence of MoO_3 lowers this temperature to 900 °C. It seems that the formation of a stable MoO_3–Al_2O_3 solid solution can account for the observed catalysing effect of the MoO_3 in the phase transformation,

$$Al_2O_3 \xrightarrow[MoO_3]{900\,^\circ C} \alpha\text{-}Al_2O_3.$$

CONCLUSIONS

These are the main conclusions that can be derived from the obtained results:

1. Crystalline MoO_3 solid, when mixed with Al_2O_3 and heated in air at 500 ° C for 5 h, loses its crystallinity due to its dispersion on the alumina surface. The dispersion capacity of Al_2O_3 for MoO_3 was calculated and found to be 0.116 g per 100 m^2 of the support.
2. MoO_3 readily interacts with Al_2O_3 at 500–700 ° C yielding well crystallized orthorhombic $Al_2(MoO_4)_3$ phase. This compound remained thermally stable until about 850 ° C then decomposed above this temperature producing very well crystallized α-Al_2O_3 (corrundum) and MoO_3 solids. The produced MoO_3 partly volatilized and the remaining portion dissolved in the alumina solid forming MoO_3–Al_2O_3 solid solution.
3. Molybdenum trioxide was found to greatly enhance the crystallization processes of kappa and alpha corrundum phases at 700 and 900 ° C respectively. The catalysing effect of MoO_3 in promoting the production of crystalline κ- and α-Al_2O_3 phases was attributed to the formation of some kind of MoO_3–Al_2O_3 solid solutions.

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