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Solid–solid interactions in pure and Na_2O-doped MoO_3/Al_2O_3 system

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Abstract

The effects of sodium oxide doping (2–10 mol%) on solid–solid interactions and phase transformation in MoO_3/Al_2O_3 system were investigated using X-ray diffraction technique. The proportions of molybdena were 12.4, 22 and 41.4 wt.% MoO_3 and the various mixed solids were calcined in air in the 500–900°C temperature range. The results obtained revealed that MoO_3 interacts with Al_2O_3 at temperatures starting from 500°C to produce orthorhombic $Al_2(MoO_4)_3$, and the completion of this reaction requires the heating of mixed oxide solids at temperatures >500°C or doping with suitable amount of sodium oxide, followed by heating at 500°C. The stimulation effect of Na_2O in aluminium molybdate formation was attributed to a possible increase in the mobility of hexavalent molybdenum ions in MoO_3 lattice. The heating of different pure and doped mixed solids (2 mol% Na_2O) at 700°C resulted in a complete conversion of MoO_3 into aluminium molybdate and a mixture of γ-, θ- and κ-aluminas. The increase in the amount of dopant to 4–10 mol% brought about the conversion of aluminium molybdate into sodium molybdate, having the formulae $Na_2Mo_3O_8$, $Na_2Mo_2O_7$, $Na_2Mo_4O_{13}$, $Na_2Mo_3O_4$ and Na_2MoO_4. The abundance of each compound depends, mainly, on the dopant concentration and MoO_3 content present in each mixed solids specimen. Heating of pure and mixed solid sample doped with 2 mol% Na_2O at 900°C led to a complete thermal decomposition of $Al_2(MoO_4)_3$ into α-Al_2O_3 (corundum) and MoO_3, a portion of which sublimes and the other portion dissolves in the alumina matrix forming MoO_3–Al_2O_3 solid solution. MoO_3 much enhances the crystallization of alumina into the α-phase by heating at 900°C instead of 1400°C in the case of pure Al_2O_3. The doping of different MoO_3/Al_2O_3 specimens with 4 or 10 mol% Na_2O and heating at 900°C increases the thermal stability of MoO_3 and aluminium molybdate even by heating at 900°C. © 1998 Elsevier Science B.V.

Keywords: Aluminium molybdate mobility; Doping; Sodium molybdates; Solid–solid interactions; Thermal stability

1. Introduction

The heating of a physical mixture of crystalline MoO_3 and γ-Al_2O_3 at 400°C for ca. 24 h brought about the disappearance of all X-ray diffraction lines of MoO_3 due to the formation of two-dimensional $Al_2(MoO_4)_3$ film covering the surfaces of Al_2O_3 particles [1–3]. The reported monolayer dispersion capacity (MLDC) of γ-Al_2O_3 towards MoO_3 is 0.116 g/100 m^2 of the alumina surface [1,4]. This value suggests a cross-sectional area of 20.6 $Å^2$ per each molybdate species [5]. The increase in calcination temperature of MoO_3/Al_2O_3 to $\geq$500°C enhances the surface and bulk mobilities of MoO_3, leading to the formation of well-crystallized $Al_2(MoO_4)_3$ phase [4,6].

The metal–support interactions in the MoO_3/Al_2O_3 system could be influenced by doping with certain

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foreign cations such as Li^+, Zn^{2+},Ga^{3+} and Ge^{4+} [5,7,8]. This influence may result from modification in the mobility of Mo^{6+} ions in MoO_3 lattice. The possible induced increase in the mobility of Mo^{6+} ions due to doping with Li_2O enhances metal–support interactions producing $Al_2(MoO_4)_3$ phase. MoO_3 dissolves in Al_2O_3 matrix forming MoO_3-Al_2O_3 solid solution which remains thermally stable even on heating at 800–900°C. The doping of MoO_3/Al_2O_3 with Li_2O has been found to increase the mobility of Mo^{6+} ions and decrease the solubility of MoO_3 in the alumina matrix [4,5].

The present work reports a study on the effect of Na_2O-doping on solid–solid interactions using X-ray powder diffractometry technique. This technique enabled us to identify the different crystalline phases present in the calcination products of pure and doped mixed solids, precalcined in air at temperatures between 500 and 900°C.

2. Experimental

2.1. Materials

A known mass of $Al(OH)_3$, analytical grade supplied by Prolabo, was impregnated with ammonium paramolybdate (BDH) solutions containing different proportions of $(NH_4)_6MoO_7O_{24}\cdot 4H_2O$. The proportions of ammonium molybdate were calculated so that the molar compositions of the calcined materials were 0.1 $MoO_3 : Al_2O_3$, 0.2 $MoO_3 : Al_2O_3$ and 0.5 $MoO_3 : Al_2O_3$. The impregnated materials were dried at 120°C, then calcined at 500°, 700° and 900°C. These mixed solid samples are designated below as AlMo-I, AlMo-II and AlMo-III and contain 12.4, 22 and 41.4 wt% MoO_3, respectively. The sodium-oxide doping was effected by treating the dried impregnated materials with an aqueous $NaNO_3$ solution prior to calcination. The time of heating of pure and doped materials was fixed at 5 h; and the amounts of sodium were 2, 4 and 10 mol% Na_2O (with respect to the sum of Al_2O_3 and MoO_3). The prepared doped mixed solid specimens are designated AlMo-I-2Na, AlMo-I-4Na, AlMo-I-10Na, AlMo-II-2Na, AlMo-II-4Na, AlMo-II-10Na, AlMo-III-2Na, AlMo-III-4Na and AlMo-III-10Na. $Al(OH)_3$ was used as a starting support material due to its decomposition during the thermal transformation of ammonium molybdate into molybdena, which may provide chances for solid–solid interactions that may not be attainable on using Al_2O_3 as a support.

2.2. Technique

An X-ray investigation of the thermal products of the different pure and doped mixed solids was carried out using a Philips diffractometer (type PW 1390). The patterns were run with Ni filtered CuK_α radiation (λ=1.5405 Å) at 36 kV and 16 mA with a scanning speed of 2° min^{-1}.

3. Results and discussion

3.1. XRD analysis of calcination products of aluminium hydroxide and ammonium molybdate

Preliminary experiments showed that the calcination of $Al(OH)_3$ at 500–700°C was amorphous in nature, and consisted of a mixture of κ, θ and γ-aluminas when calcined at 900°C. The thermal decomposition of ammonium molybdate in air at 500–700°C resulted in the formation of well-crystallized orthorhombic MoO_3 which sublimes completely on heating at 800°C.

3.2. XRD analysis of calcination products of pure and doped mixed solids

XR diffractograms of pure and doped mixed solids preheated in air at 500°, 700° and 900°C were measured. Table 1 lists the different phases identified in pure and sodium oxide-doped mixed solids precalcined in air at 500–900°C. The results obtained showed that pure and doped AlMo-I mixed solids preheated at 500°C were amorphous in nature. Fig. 1 shows the X-ray diffractograms of pure and doped AlMo-II and AlMo-III mixed solids preheated at 500°C. It is seen from Fig. 1 that pure mixed solid, (AlMo-II and AlMo-III) consist of a mixture of mostly MoO_3 and $Al_2(MoO_4)_3$ phase. The presence of 4 or 10 mol% Na_2O in AlMo-II resulted in a complete transformation of MoO_3 into $Al_2(MoO_4)_3$. These results clearly indicate the role of Na_2O-doping in stimulating the solid–solid interaction between MoO_3

Table 1
Crystalline phase compositions of the calcined products detected by XRD

Solid	Calcination Temp/°C	Crystalline composition
AlMo-I	500	Amorphous
AlMo-I-2%Na_2O	500	Amorphous
AlMo-I-4%Na_2O	500	Amorphous
AlMo-I-10%Na_2O	500	Amorphous
AlMo-II	500	MoO_3, $Al_2(MoO_4)_3$ and poorly crystalline κ-Al_2O_3
AlMo-II-2%Na_2O	500	$Al_2(MoO_4)_3$ and poorly crystalline κ-Al_2O_3
AlMo-II-4%Na_2O	500	$Al_2(MoO_4)_3$
AlMo-II-10%Na_2O	500	$Na_2Mo_2O_7$, $Al_2(MoO_4)_3$ and poorly crystalline κ-Al_2O_3
AlMo-III	500	MoO_3, $Al_2(MoO_4)_3$ and poorly crystalline κ-Al_2O_3
AlMo-III-2%Na_2O	500	$Al_2(MoO_4)_3$ (major phase) MoO_3 and poorly crystalline κ-Al_2O_3
AlMo-III-4%Na_2O	500	$Al_2(MoO_4)_3$ and MoO_3
AlMo-III-10%Na_2O	500	$Al_2(MoO_4)_3$ (major phase) MoO_3 and α-Al_2O_3
AlMo-I	700	$Al_2(MoO_4)_3$, poorly crystalline κ-, θ- and γ-Al_2O_3
AlMo-I-2%Na_2O	700	$Al_2(MoO_4)_3$, poorly crystalline κ-, θ- and γ-Al_2O_3
AlMo-I-4%Na_2O	700	$Na_2Mo_3O_8$
AlMo-I-10%Na_2O	700	Na_2MoO_4 and $Na_2Mo_3O_8$
AlMo-II	700	$Al_2(MoO_4)_3$ and κ-Al_2O_3
AlMo-II-2%Na_2O	700	$Al_2(MoO_4)_3$ and κ-Al_2O_3
AlMo-II-4%Na_2O	700	$Al_2(MoO_4)_3$, Na_2MoO_4 and κ-Al_2O_3
AlMo-II-10%Na_2O	700	$Na_2Mo_4O_{13}$, $Na_2Mo_2O_7$ and poorly crystalline κ-Al_2O_3
AlMo-III	700	$Al_2(MoO_4)_3$ and poorly crystalline κ-Al_2O_3
AlMo-III-2%Na_2O	700	$Al_2(MoO_4)_3$ and poorly crystalline κ-Al_2O_3
AlMo-III-4%Na_2O	700	$Al_2(MoO_4)_3$, poorly crystalline κ-, θ- and γ-Al_2O_3
AlMo-III-10%Na_2O	700	$Al_2(MoO_4)_3$, $Na_2Mo_2O_7$, $Na_2Mo_3O_8$ and δ-Al_2O_3
AlMo-I-7.5AlMo-I-2%Na_2O	900	α-Al_2O_3 (very well crystallized)
AlMo-I-4%Na_2O	900	α-Al_2O_3, $Na_2Mo_2O_7$, $Na_2Mo_3O_8$ and $Na_2Mo_4O_{13}$
AlMo-I-10%Na_2O	900	α-Al_2O_3 and Na_2MoO_4
AlMo-II-AlMo-II-2%Na_2O	900	α-Al_2O_3
AlMo-II-10%Na_2O	900	α-Al_2O_3, $Na_2Mo_4O_{13}$ and $Na_2Mo_2O_7$
AlMo-III-AlMo-III-2% Na_2O	900	α-Al_2O_3
AlMo-III-4%Na_2O	900	α-Al_2O_3, $Na_2Mo_2O_7$, MoO_3 and $Al_2(MoO_4)_3$
AlMo-III-10%Na_2O	900	α-Al_2O_3, $Na_2Mo_4O_{13}$, MoO_3 and $Al_2(MoO_4)_3$

and Al_2O_3 yielding aluminium molybdate according to

$$3MoO_3 + Al_2O_3 \overset{500^\circ C}{\rightarrow} Al_2(MoO_4)_3.$$

A complete conversion of MoO_3 into aluminium molybdate in the mixed oxide sample containing (22 wt% MoO_3) was achieved by the addition of a small amount of sodium oxide (4–10 mol%) and heating in air at 500°C for 5 h.

The stimulative effect of $Al_2(MoO_4)_3$ formation due to doping with sodium oxide at 500°C may reflect the role of Na_2O in increasing the mobility of molybdenum species (Mo^{6+}) through the lattices of MoO_3 and Al_2O_3. Similar results have been reported in the case of doping of MoO_3/Al_2O_3 with Li_2O [5]. The addition of 10 mol% Na_2O to AlMo-II and AlMo-III mixed solid samples and subsequent heating at 500°C resulted in the formation of $Na_2Mo_2O_7$, θ- and δ-aluminas, besides the formation of $Al_2(MoO_4)_3$. The formation of sodium molybdate took place by solid–solid interaction between Na_2O and MoO_3 according to

$$2MoO_3 + Na_2O \overset{500^\circ C}{\rightarrow} Na_2Mo_2O_7.$$

This indicates that a portion of sodium oxide dissolves in MoO_3 lattice and increases the mobility of its molybdenum ions and the other portion undergoes a solid–solid interaction with MoO_3 to produce sodium

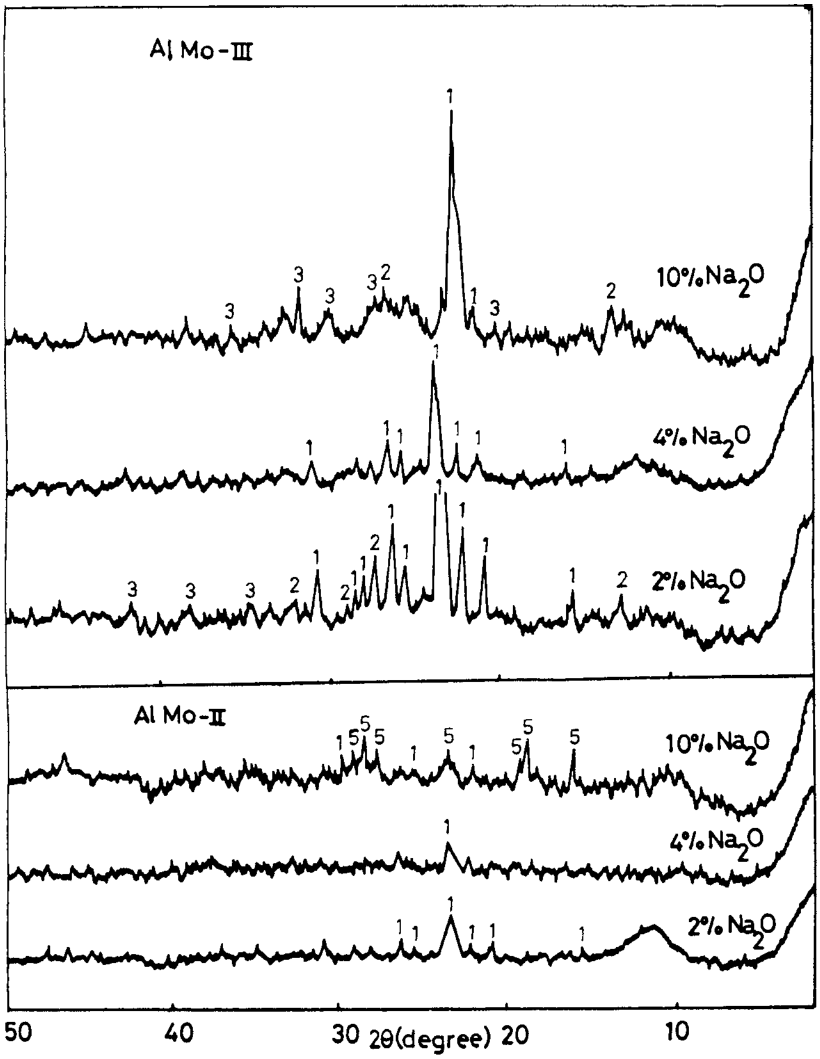

Fig. 1. XR-diffractograms of pure and doped mixed solids heated at 500°C. Peaks (1) refer to $Al_2(MoO_4)_3$; peaks (2) to MoO_3; peaks (3) to k-Al_2O_3; peaks (4) to δ-Al_2O_3; and peaks (5) to $Na_2Mo_2O_7$.

molybdate compound. Hence, the solubility of sodium oxide in MoO_3 lattice is limited and controlled by the chemical affinity towards formation of $Na_2Mo_2O_7$.

The crystallization of alumina into θ and δ phases in AlMo-III-10Na mixed solid sample preheated at 500°C indicates the role of both MoO_3 and Na_2O in catalyzing the phase transformation

$$2Al_2O_3(\text{amorphous}) \xrightarrow[Na_2O,MoO_3]{500^\circ C} \theta - Al_2O_3 + \gamma - Al_2O_3.$$

Fig. 2 shows XR diffractograms of pure and doped AlMo-I, AlMo-II and AlMo-III mixed solids preheated in air at 700°C. Pure and 2 mol% doped Na_2O-AlMo-I consist of $Al_2(MoO_4)_2$ having an excellent crystallinity and a mixture of γ-, θ- and κ-aluminas of weak crystallinity. The increase of the amount of Na_2O to 4 mol% resulted in a complete disappearance of all diffraction lines of $Al_2(MoO_4)_3$ and led to the appearance of some diffraction lines of $Na_2Mo_3O_8$ of weak crystallinity. The disappearance of the diffraction lines of aluminium molybdate due to doping with 4 mol% Na_2O may be attributed to its conversion

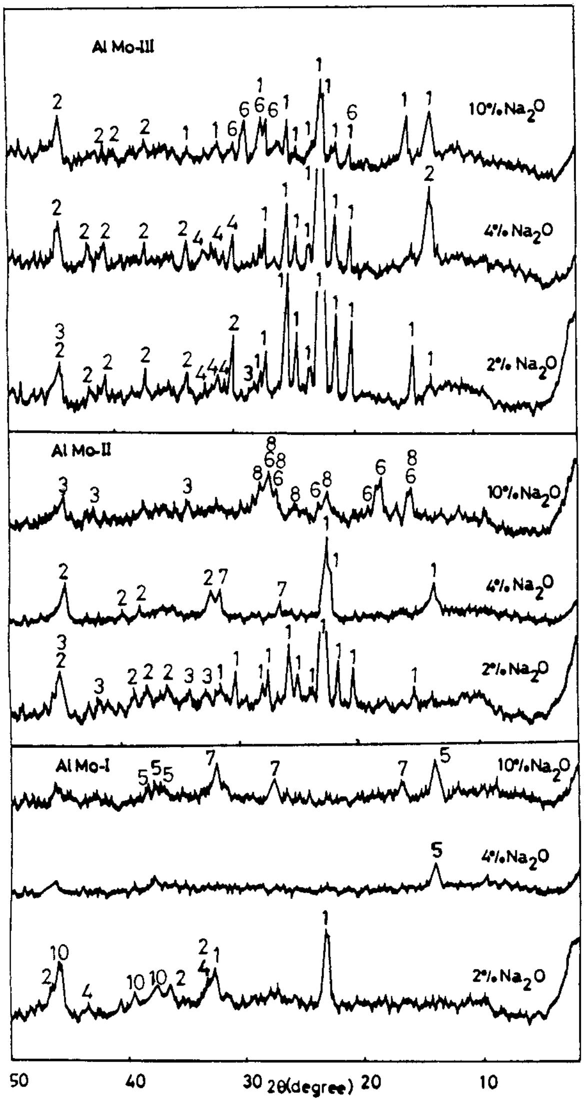

Fig. 2. XR-diffractograms of pure and doped mixed solids precalcined at 700°C. Peaks (1) refer to $Al_2(MoO_4)_3$; peaks (2) to k-Al_2O_3; peaks (3) to δ-Al_2O_3; peaks (4) to Θ-Al_2O_3; peaks (5) to $Na_2Mo_3O_8$; peaks (6) to $Na_2Mo_2O_7$; peaks (7) to Na_2MoO_4; peaks (8) to $Na_2Mo_4O_{13}$; peaks (9) to $Na_2Mo_2O_7$; and peaks (10) to Al_2O_3.

into an amorphous solid and/or its transformation into sodium molybdate according to:

$$Al_2(MoO_4)_3 + 2Na_2O \overset{700^\circ C}{\rightarrow} 3/2Na_2MoO_4$$
$$+1/2Na_2Mo_3O_8 + Al_2O_3 + 1/2O_2.$$

The treatment of Mo-II mixed solids with 2 mol% Na_2O and heating in air at 700°C did not modify the XRD patterns of mixed solids which show the presence of a well-crystallized $Al_2(MoO_4)_2$ together with a mixture of κ- and δ-aluminas with relatively weak crystallinity. The rise in the amount of dopant to 4 mol% Na_2O resulted in a considerable decrease in the intensity of all diffraction lines of $Na_2Mo_3O_8$. The further increase in the amount of Na_2O to 10 mol% resulted in a complete disappearance of all diffraction lines of aluminium molybdate with subsequent formation of sodium molybdate compounds in the form of $Na_2Mo_4O_{13}$ and $Na_2Mo_2O_7$. These compounds may result from solid–solid interaction between the dopant material and aluminium molybdate according to:

$$2Al_2(MoO_4)_3 + 2Na_2O \overset{700^\circ C}{\rightarrow} Na_2Mo_2O_7$$
$$+Na_2Mo_4O_{13} + Al_2O_3 + 3/2\,O_2.$$

Sodium oxide doping (2–10 mol%) of AlMo-III mixed solid specimen at 700°C led to a complete conversion of MoO_3 into a well-crystallized $Al_2(MoO_4)_3$ besides the formation of κ- and δ-aluminas. However, the intensity of the diffraction lines of $Al_2(MoO_4)_3$ phase decreases regularly by increasing the amount of Na_2O in the 2–10 mol% range. This finding might reflect a possible decrease in the degree of ordering of aluminium molybdate phase due to sodium oxide doping and/or a possible formation of amorphous sodium molybdate compounds via solid–solid interaction between $Al_2(MoO_4)_3$ and Na_2O.

Fig. 3 shows XR diffractograms of pure and doped mixed solids preheated in air at 900°C. It is seen from Fig. 3 that the heating of pure mixed solids and those doped with 2 mol% Na_2O are composed of well-crystallized α-Al_2O_3 (corundum) which indicates the decomposition of $Al_2(MoO_4)_3$ into α-alumina and MoO_3, a portion of which dissolves in the α-alumina matrix forming MoO_3–Al_2O_3 solid solution [5] and the other portion volatilizes. The thermal decomposition of aluminium molybdate takes place according to:

$$Al_2(MoO_4)_3 \overset{900^\circ C}{\rightarrow} MoO_3 + Al_2O_3\ (\alpha\text{-phase}).$$

The presence of well-crystallized α-Al_2O_3 (corundum) in the different investigated mixed solids (pure

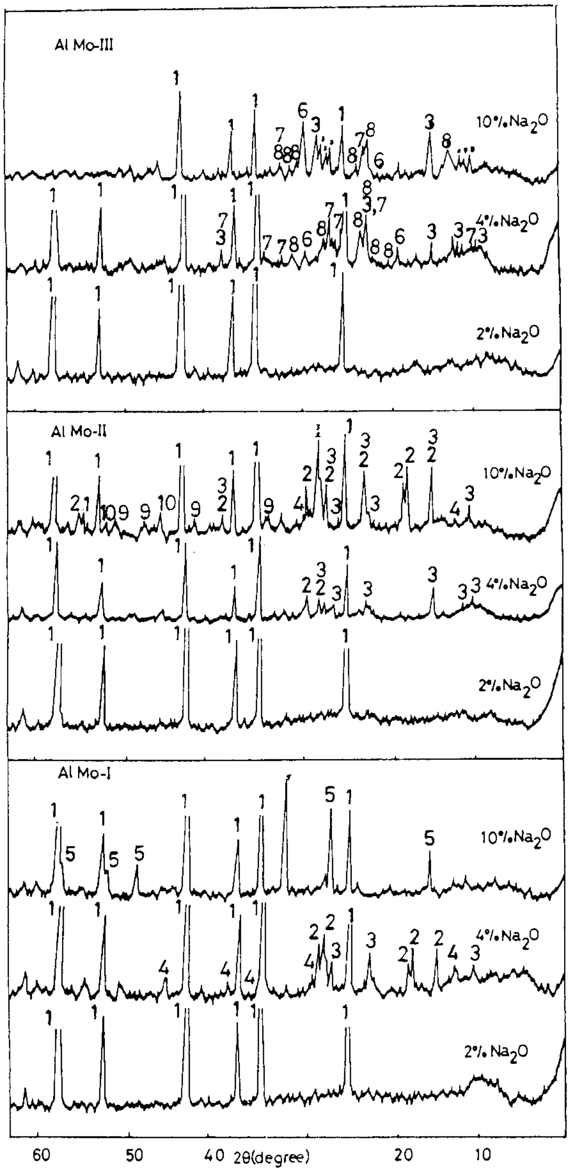

Fig. 3. XR-diffractograms of pure and doped mixed solids precalcined at 900°C. Peaks (1) refer to α-Al_2O_3; peaks (2) to $Na_2Mo_2O_7$; peaks (3) to $Na_2Mo_4O_{13}$; peaks (4) to $Na_2Mo_3O_8$ peaks (5) to Na_2MoO_4; peaks (6) to $NaAlO_2$; peaks (7) to MoO_3; and peaks (8) refer to $Al_2(MoO_4)_3$.

and doped) preheated in air at 900°C clearly indicates the role of MoO_3 in enhancing the crystallization process of alumina in the α-phase. The crystallization of α-Al_2O_3 in the absence of MoO_3 requires a prolonged heating of Al_2O_3 at temperatures $\geq$1400°C [9]. A similar effect had been reported in the case of NiO/Al_2O_3 [10], CuO/Al_2O_3 [11] and V_2O_5/Al_2O_3 [12].

The doping of AlMo-I mixed solid sample with 4 mol% Na_2O at 900°C resulted in the formation of $Na_2Mo_2O_7$, $Na_2Mo_4O_{13}$ and $Na_2Mo_3O_8$ phases of relatively high degree of crystallinity. These compounds were produced via direct solid–solid interaction between $Al_2(MoO_4)_3$ and sodium oxide. These sodium molybdate compounds were entirely converted into Na_2MoO_4 in the presence of 10 mol% Na_2O. It seems that Na_2O, in the heavily doped solids, facilitates the phase transformation via interacting with different sodium molybdate compounds according to:

$$Na_2Mo_2O_7 + Na_2Mo_4O_{13} + Na_2Mo_3O_8$$
$$+6Na_2O + O_2 \overset{900^\circ C}{\rightarrow} 9Na_2MoO_4.$$

The treatment of AlMo-II mixed solid samples with 4 or 10 mol% Na_2O followed by heating in air at 900°C resulted in a complete disappearance of aluminium molybdate a portion of which decomposes into α-Al_2O_3 and minute amounts of γ-, δ-Al_2O_3 and MoO_3 while the other portion interacts readily with Na_2O producing $Na_2Mo_4O_{13}$, $Na_2Mo_2O_7$ and $Na_2Mo_3O_8$ phases.

The doping of AlMo-III mixed solid specimens with 4 or 10 mol% Na_2O and heating at 900°C brought about a partial decomposition of $Al_2(MoO_4)_3$ into MoO_3 and α-Al_2O_3, besides the formation of $Na_2Mo_4O_{13}$ and $NaAlO_2$. The coexistence of free MoO_3 and $Al_2(MoO_4)_3$ in the mixed solid specimens containing 41.4 wt.% MoO_3, doped with 4 or 10 mol% Na_2O and preheated in air at 900°C clearly indicates the role of soda in stabilizing MoO_3 which otherwise undergoes volatilization at 800-850°C and also shows the thermal stability of $Al_2(MoO_4)_3$ by suppressing its thermal decomposition. The mechanism of the observed induced increase in the thermal stability of MoO_3 and aluminium molybdate compounds due to doping with Na_2O needs further investigation. However, some kinds of solid solution of sodium oxide in the matrices of MoO_3 and $Al_2(MoO_4)_3$ might play a role in the observed increase in the thermal stability of molybdenum trioxide and aluminium molybdate. The fact that different phases of sodium molybdates were formed in different mixed solids doped with Na_2O and preheated in air at 900°C suggests that the portion of sodium oxide involved in solid solutions is relatively small. So, other parameters may be responsible for increasing the thermal stability of MoO_3 and aluminium molybdate. The fact that the diffraction lines of Na–β-alumina ($NaAl_{11}O_{17}$) were not detected in the pattern of Na_2O-treated MoO_3/Al_2O_3 [13] preheated at 900°C might be attributed to favourable interactions between Na_2O and molybdenum species producing sodium molybdates and/or possible formation of very poorly crystalline Na–β-alumina.

4. Conclusions

The main conclusions that may be derived from the results are summarized as follows:

1. Solid–solid interactions between MoO_3 and its Al_2O_3 support yielding aluminium molybdate takes place at temperatures starting from 500°C, the complete conversion of MoO_3 into $Al_2(MoO_4)_3$ requires heating of MoO_3/Al_2O_3 mixed solids at temperatures >500°C or doping with suitable amount of Na_2O. The promotional effect of Na_2O in aluminium molybdate formation was tentatively attributed to an induced increase in the mobility of hexavalent molybdenum ions in MoO_3 lattice.
2. The heating of different pure MoO_3/Al_2O_3 mixed solids in air at 700°C brought about a complete conversion of molybdenum trioxide into aluminium molybdate and a mixture of γ-, θ-, and κ-aluminas. Doping with Na_2O followed by heating in air at 700°C led to transformation of aluminium molybdate into some sodium molybdate compounds in the form of $Na_2Mo_3O_8$, $Na_2Mo_2O_7$, $Na_2Mo_4O_{13}$, $Na_2Mo_3O_4$ and Na_2MoO_4. The abundance of each sodium molybdate phase depends, mainly, on the dopant concentration and MoO_3 content in each MoO_3/Al_2O_3 mixed solid sample.
3. Heating of pure and 2% Na_2O-doped MoO_3/Al_2O_3 mixed solids in air at 900°C resulted in a complete thermal decomposition of $Al_2(MoO_4)_3$ into α-Al_2O_3 (corundum) and MoO_3 a portion of which sublimes and the other dissolves in the produced α-alumina matrix forming MoO_3–Al_2O_3 solid solutions. The transformation of different types of alumina into the α-form otherwise requires a prolonged heating of pure alumina specimen at temperatures ≥1400°C.
4. Doping of different MoO_3/Al_2O_3 mixed solids with 4 or 10 mol% and heating at 900°C resulted in effecting a significant increase in the thermal stability of each of MoO_3 and $Al_2(MoO_4)_3$ even by heating at 900°C.

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