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Effect of MgO-doping on solid–solid interactions in MoO_3/Al_2O_3 system

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Abstract

The effect of MgO-doping (2–10 mol%) on solid–solid interactions and phase transformation process in MoO_3/Al_2O_3 system were studied using thermogravimetry and X-ray diffraction (TG, DTG and XRD) techniques. The proportions of molybdena expressed as weight percent were 12.36, 22.01 and 41.37. The results obtained showed that the MgO-doping promoted the solid–solid interaction taking place at 500°C between Al_2O_3 and MoO_3 to produce $Al_2(MoO_4)_3$. However, MgO interacts readily with MoO_3 at temperatures starting from 500°C yielding $MgMoO_4$ which remains stable even when heating at 1000°C. The produced $Al_2(MoO_4)_3$ decomposed at temperatures starting from 800°C producing α-Al_2O_3 and MoO_3, a portion of which sublimed and the other portion dissolved in alumina matrix forming MoO_3–Al_2O_3 solid solution. MgO-doping decreased slightly the solubility of MoO_3 in Al_2O_3. The promotion of $Al_2(MoO_4)_3$ formation at 500°C and the decrease in the solubility of MoO_3 in Al_2O_3 by MgO have been attributed to dissolution of a small portion of MgO in the MoO_3 lattice with subsequent increase in the mobility of Mo^{6+} ions. The promotion effect of magnesia towards $Al_2(MoO_4)_3$ formation and dissolution of MoO_3 in Al_2O_3 solid are relatively small when compared to the observed effects reported in the case of Li_2O-doping of MoO_3/Al_2O_3 system. The limited effect of MgO-doping has been attributed to a limited solubility of MgO in MoO_3/Al_2O_3 system due to the formation of $MgMoO_4$.

Keywords: Solid–Solid interactions; MgO-doping MoO_3/Al_2O_3 system; TG; XRD

1. Introduction

Molybdenum oxides loaded on an active Al_2O_3 support are one of the most important solid catalysts [1–5]. The supported catalysts are usually prepared by impregnation of an alumina support from an aqueous solution of ammonium molybdate followed by thermal treatment at suitable temperatures.

The heating of physical mixture of crystalline MoO_3 and γ-Al_2O_3 at 400°C for about 24 h resulted in 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 surface of Al_2O_3 particles [6–8]. 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 well-crystallized $Al_2(MoO_4)_3$ phase [9,10].

The metal–support interactions in the MoO_3/Al_2O_3 system could be influenced by doping with certain foreign cations such as Zn^{2+}, Ga^{3+}, Ge^{4+}, Li^{+} and Na^{+} [3,4,11,12]. This influence may result from modification in the mobility of Mo^{6+} ions in the MoO_3

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lattice. It has been reported that doping of MoO_3/Al_2O_3 mixed solids either with Li_2O [11] or Na_2O [12] enhanced metal–support interactions producing $Al_2(MoO_4)_3$ phase.

The present investigation reports a study of MgO-doping on solid–solid interactions in the MoO_3–Al_2O_3 system using TG and X-ray diffraction techniques. These techniques permitted us to clarify the effect of MgO-doping in the thermal behaviour of MoO_3/Al_2O_3 mixed solids subjected to thermal treatment at temperatures up to 1000°C and to identify the different crystalline phases produced by heating the mixed solids at various temperatures.

2. Experimental

2.1. Materials

A known mass of $Al(OH)_3$, analytical grade supplied by BDH, was impregnated with ammonium paramolybdate (BDH) solutions containing three different proportions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. The proportions of ammonium molybdate were calculated so that the molar compositions of the calcined materials were $0.1MoO_3$:Al_2O_3, $0.2MoO_3$:Al_2O_3 and $0.5MoO_3$:Al_2O_3. The impregnated materials were dried at 120°C, then calcined at 500°C, 700°C, 900°C and 1000°C. The magnesium oxide doping was effected by treating the dried impregnated materials with an aqueous $Mg(NO_3)_2$ solution prior to the calcination. The time of heating of pure and doped materials was fixed for 5 h, and the amount of magnesium were 2, 4 and 10 mol% MgO, respectively, (with respect to the sum of Al_2O_3 and MoO_3). The prepared mixed solid specimens were designated as AlMo-I, AlMoI–2MgO, AlMo-I–4MgO, AlMO-I–10MgO, AlMo-II, AlMo-II–2MgO, AlMo-II–4MgO, AlMo-II–10MgO, AlMo-III, AlMo-III–4MgO and Al Mo-III–10MgO. The nominal molar compositions of the calcined mixed solids were $0.1MoO_3$:Al_2O_3 (I), $0.2MoO_3$:Al_2O_3 (II) and $0.5MoO_3$:Al_2O_3 (III) and contained 12.4, 22.01 and 41.37 wt% MoO_3, respectively. $Al(OH)_3$ was used as a starting support material due to its decomposition during the thermal transformation of molybdate (into molybdena) which may provide chances for solid–solid interactions that was not attainable on using Al_2O_3 as a support.

2.2. Techniques

TG and DTG analyses of various uncalcined materials were carried out using a Perkin-Elmer (DT-7 Unix system) thermal analyser. A 18 mg solid portion was taken in each TG measurement. The reference material was α-Al_2O_3 (corundum). The rate of heating was kept as 10°C min^{-1} and all the measurements were carried out in a current of N_2 flowing at 50 cm^3 min^{-1}.

The X-ray powder diffraction patterns of the various calcined samples were measured using Nippon denshi kagaku. The patterns were run with nickel-filtered Cu Kα radiation (λ=1.5405 Å) at 40 kV and 30 mA at a scanning rate of $2\theta=8^\circ$ min^{-1}.

3. Results and discussion

3.1. Thermal behaviour of pure and doped materials

TG and DTG curves of various pure and doped materials are summarized in Table 1. Representative TG and DTG curves are given in Figs. 1 and 2 for AlMo-II and AlMo-III doped with 10 mol% MgO. The recorded TG curves of the tested materials consist of seven successive mass loss processes. The first step extended between room temperature and 130°C and corresponds to departure of the physiosorbed water, while the second one extended between 130°C and 186°C indicates the removal of water of crystallization. The third and fourth steps were found between 186– 217°C and 217–283.9°C, respectively. These steps characterize the decomposition of $Al(OH)_3$, $(NH_4)_6Mo_7O_{24}$ and $Mg(NO_3)_2$ producing the corresponding oxides according to

$$\begin{aligned}&(NH_4)_6Mo_7O_{24} + Al(OH)_3 + Mg(NO_3)_2\\&\quad\to 7MoO_3 + 1/2\,Al_2O_3 + MgO + 2NO_2\\&\quad+6NH_3 + 4.5H_2O + 1/2\,O_2\ldots\end{aligned}\qquad(1)$$

Details of the mechanism of thermal decomposition of ammonium molybdate yielding MoO_3 have been given elsewhere [9]. The fifth and sixth steps extended were between 450–550°C and 550–800°C, respectively. These steps might correspond to the removal of strongly bound hydroxyl groups and the last traces of these groups from alumina matrix. The last step

Table 1
TG results of pure and doped materials

Solid	Weight loss (%)			MoO_3 (wt%)		
	100–800°C	100–800°C (calculated)	800–1000°C	Total	Reacted with MgO	Dissolved[a] in Al_2O_3
AlMo-II						
0.0-MgO	33	31.6	14.3	22.01	0	7.8
4-MgO	34.65	33.6	9.72	21.7	4.34	7.7
10-MgO	37.26	36.25	3.88	21.35	10.67	6.8
AlMo-III						
0.0-MgO	29.93	28.8	25.29	41.37	0	16.08
4-MgO	30.1	30.4	23.28	40.95	3.27	14.40
10-MgO	33.25	32.7	18.67	40.36	8.09	13.60

[a] The data of this column were computed by substracting the sum of the data of columns four and six from those of column five.

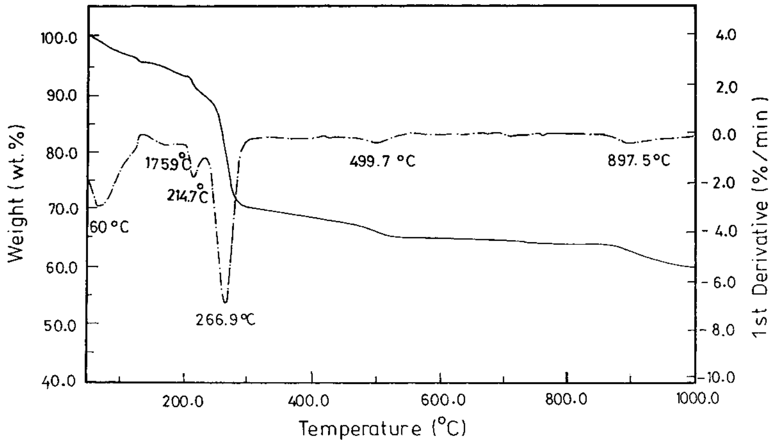

Fig. 1. TGA and DTG curves of uncalcined AlMo-II-10 MgO.

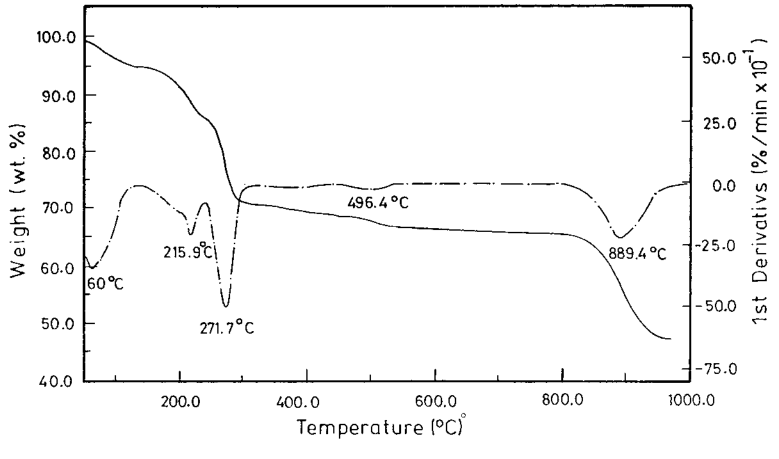

Fig. 2. TGA and DTG of uncalcined AlMo-III–10MgO sample.

extended between 800–1000°C characterize the sublimation of some of the molybdena produced.

The values of mass loss due to heating at the temperature range 100–800°C for the various samples were given in column two of Table 1. The theoretical mass loss accompanying the thermal decomposition of the tested materials producing the corresponding oxides according to Eq. (1) were calculated and given in column three of Table 1. The values given in the columns two and three are close to each other for the different investigated mixed solid samples which indicates the thermal stability of MoO_3 produced up to 800°C. The total weight loss accompanying the thermal treatment at 800–1000°C were calculated for each sample and the values obtained are given in column four of Table 1. It is seen from Table 1 (column four) that the weight loss decreases progressively as a function of the amount of MgO added. This might indicate that the MgO present hinders the sublimation of MoO_3 to an extent proportional to its amount present. This hinderance could be attributed to a possible decrease in the mobility of the molybdena species or formation of MgO–MoO_3 compounds which are thermally stable at 1000°C. The formation of such compounds will be identified by XRD investigation given in the next section of this paper.

3.2. XRD investigation of various solids

Preliminary experiments showed that 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 by heating at 800°C.

X-ray differactograms of pure and doped mixed solids preheated in air at 500°C, 700°C, 900°C and 1000°C and those of pure $Al(OH)_3$ calcined at 500–1000°C were determined. Table 2 lists the different phases present in various calcined solids. Representative differactograms of pure and doped AlMo-II and AlMo-III samples are given in Figs. 3 and 4.

It is seen from Table 2 that Al_2O_3 heated at 500–700°C is amorphous in nature. While that calcined at 800°C consists of poorly crystalline γ-Al_2O_3. The X-ray diffractograms of pure Al_2O_3 preheated at 900°C and 1000°C, not given, include the diffraction lines characteristic for κ-Al_2O_3 for the solids calcined at 900°C and κ-Al_2O_3 together with a minute amount of α-Al_2O_3 (corundum) phase for the solid sample preheated at 1000°C. These results are in agreement with those published before [13,14]. Table 2 reveals that the pure and MgO-doped mixed oxide solid samples calcined at 500°C are composed of γ-Al_2O_3 while that preheated at 700°C consists of κ-Al_2O_3 and that calcined at 900°C and 1000°C constitute of α-Al_2O_3 phase except the doped AlMo-I sample calcined at 900°C. This particular sample consists of a mixture of α-, γ- and θ-aluminas. From the above results it can be concluded that MoO_3 catalyses the crystallization process of Al_2O_3. In fact, the complete transformation of pure Al_2O_3 specimen into the α-form requires thermal treatment at elevated temperatures >1200°C [14–16], or the presence of certain foreign oxides such as NiO [17], V_2O_5 [18], Co_3O_4 [19] and CuO [20]. These oxides enhance the crystallization process of alumina into α-Al_2O_3 (corundum) phase. In the present work the role of MoO_3 in catalysing the crystallization of Al_2O_3 into α-alumina like the above oxides is clear.

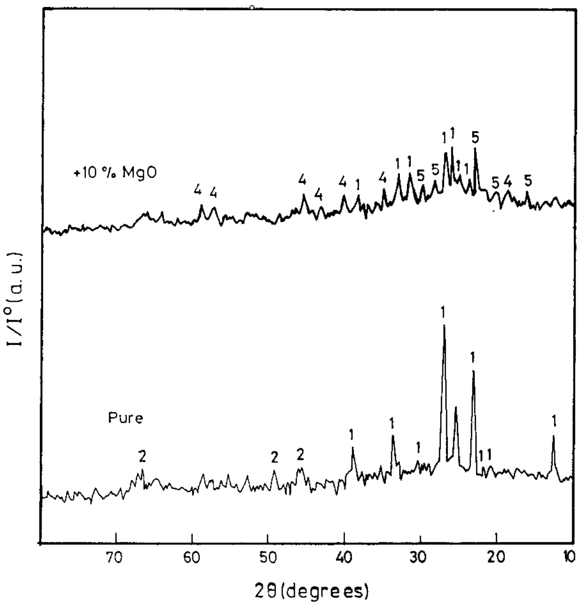

Fig. 3. X-ray diffractograms of pure and doped AlMo-III samples precalcined at 500°C: (1) MoO_3, (2) γ-Al_2O_3, (4) $MgMoO_4$, (5) $Al_2(MoO_4)_3$.

Inspection of the results obtained for pure and doped mixed oxide solids calcined at 500°C revealed that:

Table 2
Crystalline phase compositions of the calcined products detected by XRD

Solid	Calcination temperature °C	Crystalline phases present
Al_2O_3	500–700	Amorphous
Al_2O_3	800	Poorly crystalline γ-Al_2O_3
Al_2O_3	900	κ-Al_2O_3
Al_2O_3	1000	κ-Al_2O_3, minute amount of α-Al_2O_3
AlMo-I–0MgO	500	Poorly γ-Al_2O_3, poorly crystalline MoO_3
+10% MgO	500	$MgMoO_4$, poorly crystalline γ-Al_2O_3
AlMo-II–0MgO	500	Poorly crystalline γ-Al_2O_3 and MoO_3
+10% MgO	500	Poorly crystalline γ-Al_2O_3, $MgMoO_4$
AlMo-III–0MgO	500	MoO_3 well-crystallined, poorly crystalline γ-Al_2O_3
+10% MgO	500	Some diffraction lines of MoO_3, $MgMoO_4$ and $Al_2(MoO_4)_3$
AlMo-I–0MgO	700	γ-Al_2O_3, κ-Al_2O_3
+10% Mgo	700	Well crystalline $MgMoO_4$, γ-Al_2O_3
AlMo-II–0MgO	700	$Al_2(MoO_4)_3$, κ-Al_2O_3
+10% MgO	700	$MgMoO_4$, κ-Al_2O_3
AlMo-III–0MgO	700	Well crystalline $Al_2(MoO_4)_3$, κ-Al_2O_3
+10% MgO	700	Well ordered $MgMoO_4$, well crystalline $Al_2(MoO_4)_3$, κ-Al_2O_3.
AlMo-I–0MgO	900	Very well crystalline α-Al_2O_3, γ-Al_2O_3
+2% MgO	900	Drop in I/I^0 for α-, γ- and θ-Al_2O_3
+4% MgO	900	$MgMoO_4$ and mixture of α, γ, and θ-Al_2O_3
+10% MgO	900	$MgMoO_4$, γ-Al_2O_3
AlMo-II–0MgO	900	α-Al_2O_3 very well crystalline
+2% MgO	900	α-Al_2O_3, trace of $MgMoO_4$
+4% MgO	900	α-Al_2O_3, $MgMoO_4$
+10% MgO	900	α-Al_2O_3 $MgMoO_4$
AlMo-III–0MgO	900	α-Al_2O_3
+10% MgO	900	α-Al_2O_3, $MgMoO_4$
AlMo-I–0MgO	1000	α-Al_2O_3
+10% MgO	1000	α-Al_2O_3, $MgMoO_4$
AlMo-II–0MgO	1000	α-Al_2O_3
+10% MgO	1000	α-Al_2O_3, $MgMoO_4$
AlMo-III–0MgO	1000	α-Al_2O_3
+10% MgO	1000	α-Al_2O_3, $MgMoO_4$

1. All the tested pure and mixed oxide solids consisted of MoO_3 phase.
2. Doping of AlMo-I and AlMo-II with 10% MgO resulted in stimulating an interaction between MgO and MoO_3 yielding $MgMoO_4$ according to

$$MgO + MoO_3 \overset{500^\circ C}{\rightarrow} MgMoO_4 \ldots \qquad (2)$$

3. Doping of AlMo-III specimen with 10% MgO led to the formation of $MgMoO_4$ and aluminium molydate which takes place according to

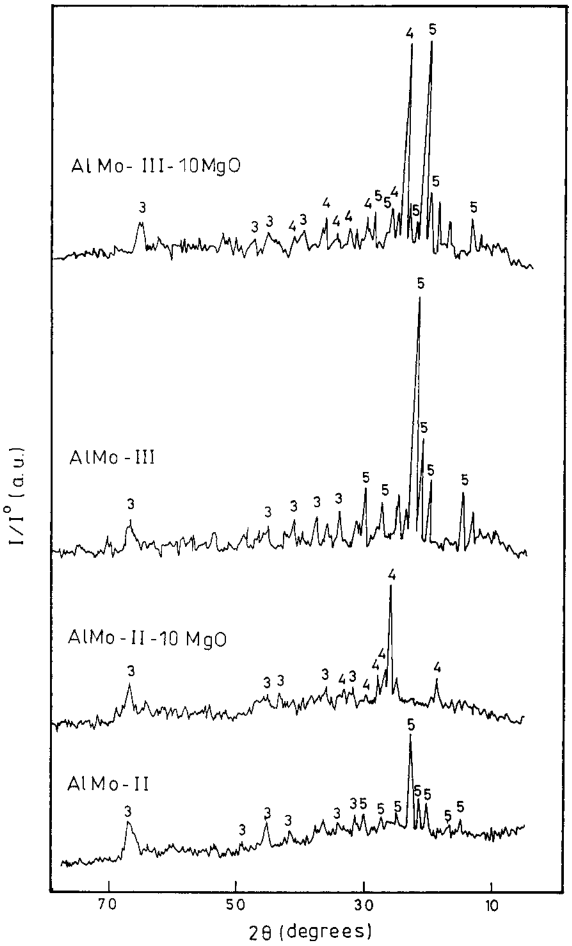

Fig. 4. X-ray diffractograms of pure and doped AlMo-II and AlMo-III samples precalcined at 700°C: (3) κ-Al_2O_3, (4) $MgMoO_4$, (5) $Al_2(MoO_4)_3$.

$$3MoO_3 + Al_2O_3 \underset{MgO}{\overset{500^\circ C}{\rightarrow}} Al_2(MoO_4)_3 \ldots \qquad (3)$$

The later reaction clarifies the role of MgO in enhancing the solid–solid interaction between Al_2O_3 and MoO_3.

It can be expected that this role arises from dissolution of a small portion of MgO in MoO_3 lattice leading to an increase in the mobility of molybdenum ions. The fact that $MgMoO_4$ was formed in the case of AlMo-I (containing 12.36 wt% MoO_3) and $Al_2(MoO_4)_3$ was observed in the case of AlMo-III (containing 41.37 wt% MoO_3) might indicate that MgO–MoO_3 interaction takes place prior to Al_2O_3–MoO_3 one. From the above results it can be concluded that a portion of MgO dissolved in MoO_3 lattice enhances the interaction between Al_2O_3 and MoO_3. The other portion of MgO reacts readily with MoO_3 and the MgO–MoO_3 interaction is easier than Al_2O_3–MoO_3 one.

Analyses of the results given in Table 2 for the pure and doped mixed oxide solids preheated in air at 700°C showed that:

1. For AlMo-I there are no diffraction lines characteristic for free MoO_3 or $Al_2(MoO_4)_3$ phases which might indicate that MoO_3 interacted with Al_2O_3 yielding an amorphous $Al_2(MoO_4)_3$.
2. Doping of AlMo-I with 10% MgO resulted in the formation of well-crystallized $MgMoO_4$. The formation of mangnesium molybdate must not be accompanied by any change in weight.
3. Pure AlMo-II consists of $Al_2(MoO_4)_3$, while AlMo-II-10MgO consists of $MgMoO_4$ only. The disappearance of the diffraction lines of $Al_2(MoO_4)_3$ in the case of the doped mixed oxide solid sample calcined at 700°C reveals that MgO–MoO_3 interaction is more favourable, easier and prior to Al_2O_3–MoO_3 interaction taking place at 700°C. These results are in agreement with those obtained in case of solids calcined at 500°C.
4. Pure AlMo-III mixed solid samples consisted of $Al_2(MoO_4)_3$ phase, while those doped with 10% MgO was composed of a mixture of $MgMoO_4$ and $Al_2(MoO_4)_3$.

These results showed that Mgo–MoO_3 interaction is more favourable than Al_2O_3–MoO_3 interaction and when takes place it goes to completion.

Inspection of results concerning the phases present in pure and doped solids calcined at 900°C and 1000°C showed that:

1. The diffraction patterns of all pure and mixed oxide solids reveal the absence of all diffraction lines characteristic for $Al_2(MoO_4)_3$ indicating its decomposition into alumina phase.
2. All doped mixed oxide solids (2–10 mol%) contain $MgMoO_4$ beside alumina phases. The obtained results indicate that $Al_2(MoO_4)_3$ decomposed at

temperature ≥800°C and $MgMoO_4$ is thermally stable even when heated up to 1000°C.

From the XRD results the role of MgO in the enhancement of $Al_2(MoO_4)_3$ formation at 500°C is evident. However, the amount of MgO dissolved in MoO_3 lattice might be small because of the chemical affinity towards interaction with MoO_3 yielding $MgMoO_4$. On this basis, the calculation of the amount of MoO_3 reacting with MgO is given in Table 1 (column six) neglecting the amount of MgO dissolved in MoO_3 lattice.

Finally, doping of MoO_3/Al_2O_3 system with MgO led to two solid–solid interactions, the first reaction takes place between MgO and MoO_3 and the second occurs between Al_2O_3 and MoO_3. The first reaction is more easier and takes place prior to the second one so, it can be assumed that MgO–MoO_3 interaction goes to completion. The amount of MoO_3 consumed in $MgMoO_4$ formation increases as a function of MgO content as shown in Table 1 (sixth column). Therefore, the amount of MoO_3 consumed in the formation of $Al_2(MoO_4)_3$ decreases by increasing the amount of dopant oxide present.

Aluminium molybdate decomposes at temperatures starting from 800°C yielding MoO_3, a portion of which sublimed (cf Table 1 column four) and the other one dissolved in Al_2O_3 matrix (cf. Table 1 column seven). It is seen from the last column of Table 1 that MgO-doping (10 mol%) of MoO_3/Al_2O_3 system brought about a small decrease in the amount of MoO_3 dissolved in Al_2O_3 lattice (it decreases from 7.8 to 6.8 wt% MoO_3 in the case of AlMo-II and from 16.08 to 13.6 wt% MoO_3 in the case of AlMo-III). This effect is much more pronounced in the case of Li_2O doping of the same system [11]. In fact, it has been reported by El-Shobaky et al. [11] that Li_2O (6 mol%) doping of MoO_3/Al_2O_3 system containing 22.01 wt% MoO_3 (which corresponds to AlMo-II) resulted in the decrease of amount of MoO_3 dissolved in Al_2O_3 matrix, forming solid solution, from 7.1 to 2.5 wt% MoO_3. The comparison of MgO doping with Li_2O doping of MoO_3/Al_2O_3 system reflects the limited role of MgO in enhancing the sublimation of MoO_3 dissolved in Al_2O_3 matrix. This limited role might be discussed in terms of the limited amount of MgO contributing in the formation of MgO–MoO_3 solid solution.

4. Conclusions

The main conclusions that can be derived from the obtained results are as follows:

1. Doping of MoO_3/Al_2O_3 mixed solids with MgO enhance solid–solid interaction at 500°C to form $Al_2(MoO_4)_3$.
2. MgO interact readily with MoO_3 at temperatures starting from 500°C producing $MgMoO_4$ which remain thermally stable even by heating at 1000°C.
3. Aluminium molybdate decomposed at temperature ≥800°C giving α-Al_2O_3 and MoO_3, a portion of which sublimed and the other portion dissolved in aluminium lattice forming MoO_3–Al_2O_3 solid solution.
4. MgO-doping decreased the solubility of MoO_3 in alumina support material to an extent proportional to its amount present.
5. MoO_3 enhanced the crystallization process of alumina into κ-Al_2O_3 at 700°C and α-Al_2O_3 phase at 900°C and 1000°C.

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