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ORIGINAL ARTICLE

Physico–chemical properties of $CdO–Al_2O_3$ catalysts. I – Structural characteristics

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KEYWORDS

$CdO–Al_2O_3$ system;
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Abstract Alumina gels AN6 and AN7 were prepared by precipitation with NaOH from hydrated aluminum sulfate at pH 6 and 7, respectively. A third alumina gel AA7 was similarly prepared, but by precipitation with 30% ammonia. Pure cadmia C8 and C9 were precipitated from cadmium sulfate at pH 8 and 9 using NaOH. Five mechanically mixed gels ACM (1:0.25), ACM (1:0.5), ACM (1:1), ACM (0.5:1) and ACM (0.25:1) were prepared by thoroughly mixing the appropriate molar ratios of AN7 and C8. Also, five coprecipitated gels ACC (1:0.25), ACC (1:0.5), ACC (1:1), ACC (0.5:1) and ACC (0.25:1) were coprecipitated by dropping simultaneously the appropriate volumes of 1 M aluminum sulfate, 1 M cadmium sulfate and 3 M NaOH. Calcination products at 400, 500, 600, 800 and 1000 °C were obtained from each preparation.

TG–DTA patterns of uncalcined samples were analyzed and the XRD of all 1000 °C-products and some selected samples calcined at 400–800 °C were investigated. The thermal behaviors of pure and mixed gels depend on the precipitating agent, pH of precipitation, chemical composition and method of preparation. Generally, calcination at temperatures below 800 °C gave poorly crystalline phases. Well crystalline phases are obtained at 800 and 1000 °C. For pure alumina γ-Al_2O_3 was shown as 400 °C-calcination product that transforms into the δ form around 900 °C and later to θ-Al_2O_3 as a major phase and α-Al_2O_3 as a minor phase at 1000 °C. CdO was shown by 500 °C-calcined cadmia gel that showed color changes with rise of calcination temperature. The most stable black cadmium oxide phase (Monteponite) is obtained upon calcination at 1000 °C. Thousand degree celsius- calcined mixed oxides showed θ-Al_2O_3, α-Al_2O_3, $CdAl_2O_4$ and monteponite which dominate depending on the chemical composition.

1. Introduction

Mixed metal oxide catalysts often have catalytic properties which are superior to those of pure oxides (Reddy et al., 1999; Glinski and Kijenski, 2000). The catalytic properties of mixed metal oxides depend mainly on the method of prepara-

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tion (Leyrer et al., 1986; Youssef and Youssef, 1991), chemical composition (Castle and Wachs, 1988; Ruth et al., 1998) and calcination temperature (Abu et al., 2003; Manriqez et al., 2004). The catalytic behavior of mixed metal oxides may be described in terms of their acid–base properties and oxidation–reduction properties (Daniell et al., 2000; Miller and Ko, 1996). Mixed oxides are also prepared to have synergistic effects (Luo and Zheng, 1999). This synergistic effect may be ascribed to the formation of bifunctional catalysts (Faus et al., 1991), or to the formation of new active compound resulting from the interaction between the two oxides (Guerrero-Perez et al., 2007).

The oxides of the transition metals are more active than those of ion-transition metals because they have the ideal characteristics to be used in catalysis. They have pronounced but moderate directional binding and also because they are not strongly electropositive. So, they may not strongly attach to the reacting molecules if the latter are either electropositive or if they have a dipole. The supported transition metal oxides may exhibit different behavior when compared with the unsupported ones. Supported transition metal oxides often exist as isolated species at low loading levels. However, as loading increases, poly-aggregates or clusters form and crystalline domains can appear above the monolayer coverage (Youssef et al., 1993). Besides the use of alumina in many chemical and industrial fields, it is also used as a catalyst and more frequently as a catalyst support. Alumina exists in many phases which are different in their textural properties as well as in their surface functionalities (Mostafa et al., 1991). γ-Al$_2$O$_3$ is frequently used as a support for transition metals and transition metal oxides for reactions operating at relatively low temperatures i.e. lower than 700 °C. Other alumina phases, particularly α-Al$_2$O$_3$ are used as a support for catalysts operating at high temperatures.

Alumina supported transition metal oxides are bifunctional catalysts. The existence of Bronsted and Lewis acid sites on the surface of alumina on one hand and the partially filled *d* or *f* orbits of transition metals on the other hand, allow the enhancement of acid–base reactions and oxidation–reduction reactions, respectively. Extensive investigation has been devoted for the characterization of the textural properties, surface functionalities and catalytic activities of many alumina-supported metal oxides with the conversion of alcohol being the reaction which received the highest interest. Surprisingly, the system CdO/Al$_2$O$_3$ did not receive any attention. This stimulated a research trend in our laboratory to characterize this particular system.

The present investigation is devoted to determine the structural and textural properties of CdO/Al$_2$O$_3$ samples. These samples are prepared by mechanical mixing or coprecipitation. They are different in chemical composition and received a different thermal treatment. The changes in the textural properties and phase changes brought about by calcinations at different temperature are the main object of this study.

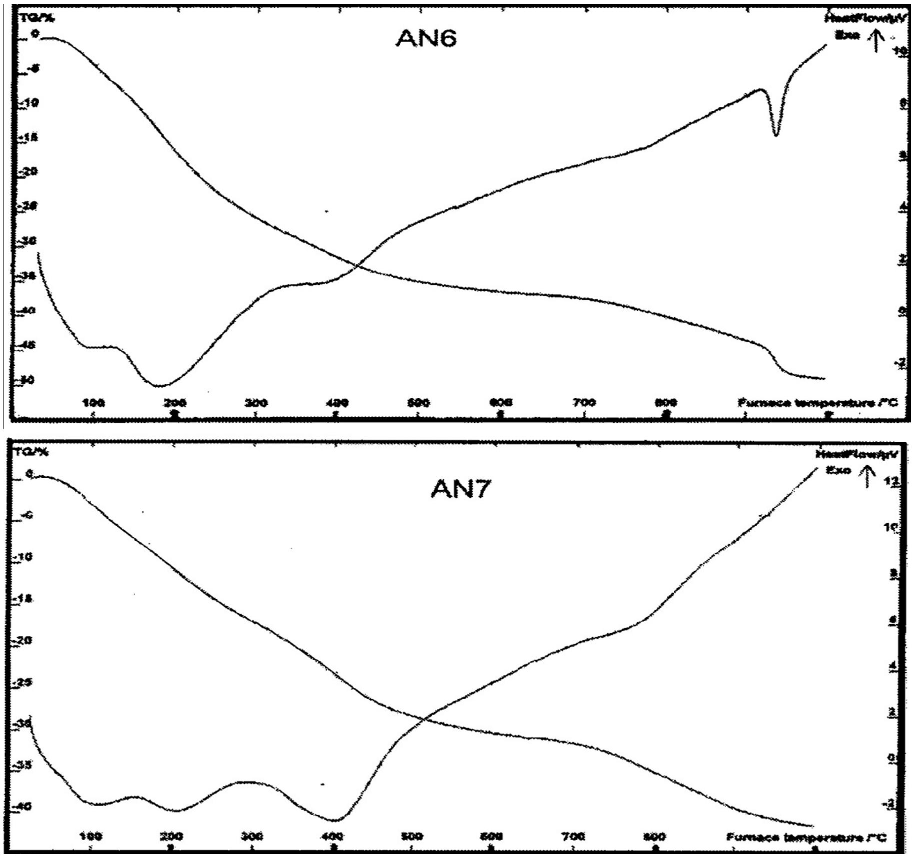

Figure 1 TG–DTA curves of AN6 and AN7 samples.

2. Experimental

2.1. Materials

Pure aluminum hydroxide was precipitated from 1 M $Al_2(SO_4)_3 \cdot 16H_2O$ (BDH) using 3 M NaOH (BDH) at room temperature and pH 6 with continuous mechanical stirring for 3 h. The gel was left to settle down for 24 h and then filtered using a Buchner funnel. The precipitate was washed several times with distilled water until it was free from SO_4^{-2} ions and then dried at 125 °C to a constant weight. The dried precipitate was ground and reserved in stoppered glass bottle and designated as AN6. A second sample (AN7) was prepared following the same procedure but at pH 7. A third sample (AA7) was prepared by precipitation from 1 M $Al_2(SO_4)_3 \cdot 16H_2O$ at pH 7 using 30% ammonium hydroxide.

Cadmium hydroxide was precipitated from 1 M $CdSO_4 \cdot 8/3H_2O$ (Merck) using 2 M NaOH at pH 8 during continuous stirring for 3 h. The gel was allowed to settle down over night, washed, dried to constant weight at 125 °C and then reserved and designated as C8. A second $Cd(OH)_2$ sample (C9) was similarly prepared but precipitation was made at constant pH 9.

Mechanically mixed gels were prepared using aluminum hydroxide gel attained by the addition of 3 M NaOH solution to 1 M aluminum sulfate at constant pH 7 and $Cd(OH)_2$ by the addition of 2 M NaOH to 1 M cadmium sulfate at constant pH 8 with continuous stirring. Five CdO/Al_2O_3 samples with Al_2O_3/CdO molar ratio = 1:0.25, 1:0.5, 1:1, 0.5:1 and 0.25:1, which contain weight% of alumina = 80, 66.7,50, 33.3 and 20, respectively, were prepared by mixing the appropriate amounts of alumina and $Cd(OH)_2$ for 3 h using a mechanical mixed gel followed by settling over night, washing with distilled water, drying at 125 °C until constant weight was obtained. ACM is the general designation of these mechanically mixed samples. The molar ratio following this designation determines the individual designation. Thus sample ACM (1:0.5) stands for a mechanically mixed oxide prepared by mixing 1.0 M of alumina gel with 0.5 M of CdO gel.

Five coprecipitated samples of varying composition were prepared by dropping simultaneously the appropriate amounts of 1 M aluminum sulfate, 1 M cadmium sulfate and 3 M NaOH from three separate funnels into a beaker containing 100 ml of distilled water with continuous stirring for 3 h at pH 8. The coprecipitates were allowed to settle down overnight and then washed till free from SO_4^{2-} ions and dried at 125 °C until constant weight was obtained and then reserved in stoppered bottles until used. The molar ratios were Al_2O_3/CdO = 1:0.25, 1:0.5, 1:1, 0.5:1 and 0.25:1. The general designation is ACC, which when followed by the molar ratio will give the respective sample. The sample ACC (0.5:1) stands for coprecipitated oxide containing 0.5 M Al_2O_3 and 1 M CdO.

Calcination was made at 400, 500, 600, 800 and 1000 °C with the rate of heating at 10°/min and soaking for 4 h at

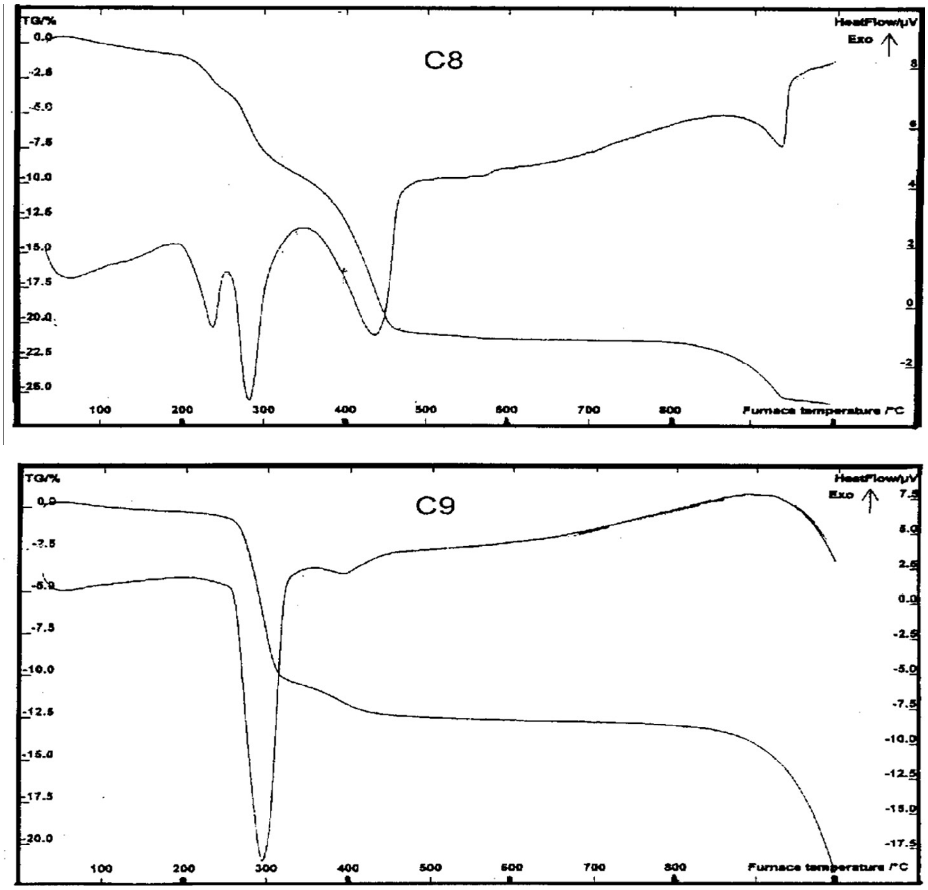

Figure 2 TG–DTA curves of C8 and C9 samples.

the maximum temperature. To refer to the thermal treatment temperature, the calcination temperature is added to the designation of the sample. Thus for example AN7-400 refers to alumina precipitated with NaOH at pH 7 and then calcined at 400 °C for 4 h.

2.2. Techniques

Thermogravimetric analysis TG and differential thermal analysis DTA of uncalcined samples was carried in argon atmosphere using a thermal analyzer model LABSYS^{TM} (TG–DTA) produced by SETARAM (France). A weight of 50–70 mg was placed in a crucible of 100 µL capacity. The run was followed between 25 and 1000 °C at a rate of heating 10°/min.

X-ray diffraction XRD was carried out for all the 1000 °C-calcination products and for ACM (1:0.25)-400, ACM (1:0.25)-600, ACM (1:1)-800, ACC (1:0.25)-400, ACC (1:0.25)-600 and ACC (1:1)-800. The apparatus was Philips Diffractometer Type PW (1830). The pattern was obtained with nickel filtered copper radiation ($\lambda = 15405$) at 40 kV and 30 mA with scanning speed of 1° in 2θ $\min^{-1}$. The spacing d corresponding to 2θ of the peaks were calculated and correlated with those of ASTM to determine the phases existing.

3. Results and discussion

3.1. Structural properties

TG–DTA was carried out for pure and mixed gels in an argon atmosphere in the temperature range of 20–1000 °C at a heating rate of 10°/min. The % of ignition loss (I.L. wt%) of all the samples was also determined via calcination in the temperature range of 400–1000 °C for 4 h. Representative TG–DTA curves are illustrated, but the analysis of all the TG–DTA patterns is considered.

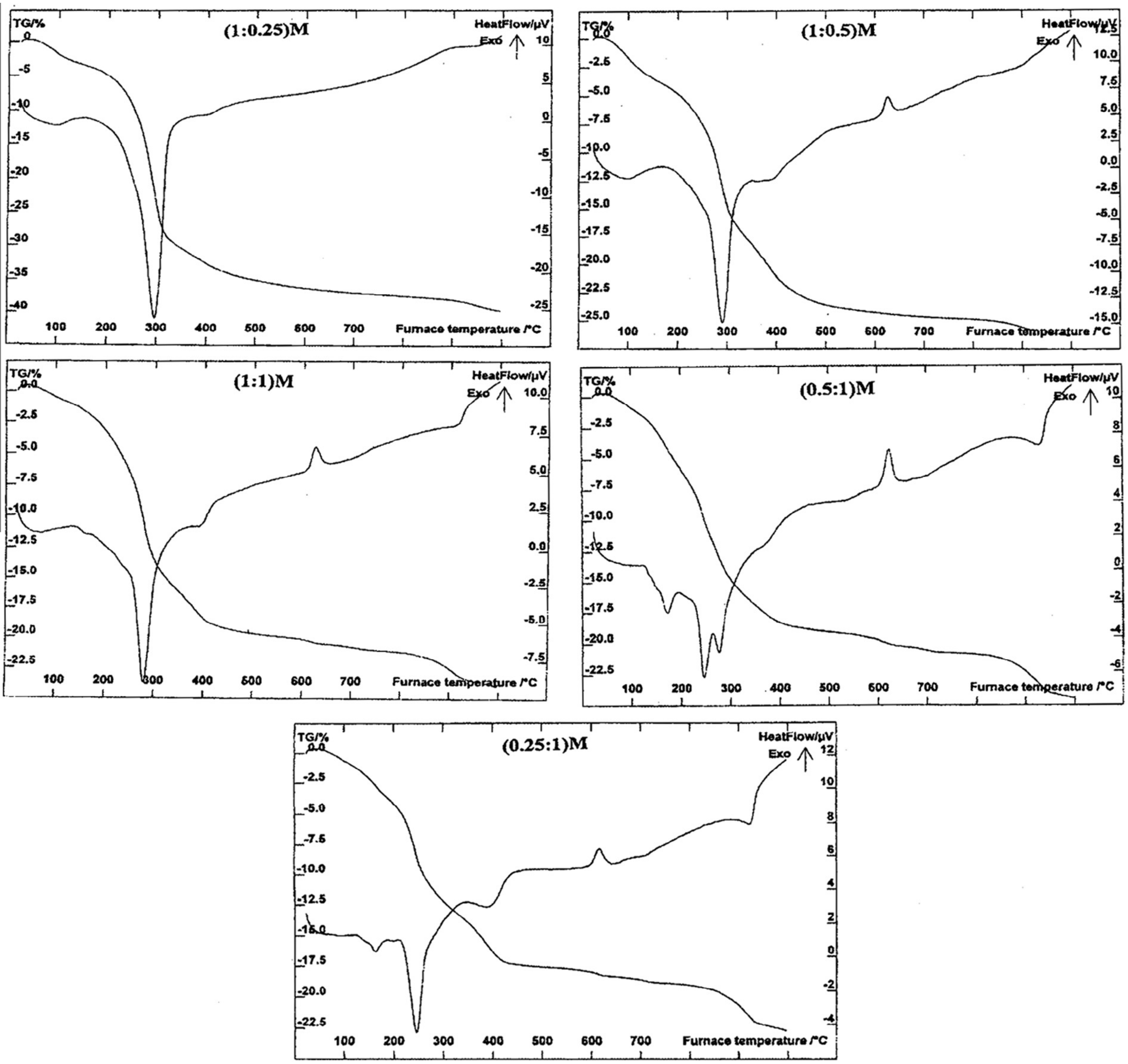

Figure 3 TG–DTA curves of mechanically CdO–Al_2O_3 gels.

TG–DTA curves of pure alumina gels AN6 and AN7 (Fig. 1) depict four endothermic effects with their location depending on the pH of the precipitation. The first endotherm covers the range 60–110 °C with the maximum located at 88 °C, this endotherm is associated with ~5 wt% loss ascribed to the loss of physisorbed water. The first endotherm is followed by a broad endotherm covering the range 130–300 °C with its maximum at 182 °C, the second endotherm is associated with 22 wt% loss attributed to the removal of chemically combined water and to the formation of γ-AlOOH. The 310–500 °C endotherm is broad with its maximum at 400 °C and is associated with ~9 wt% loss attributed to the loss of chemisorbed water and hydroxyl groups and to the complete transformation to γ-Al_2O_3. The TG curve of these three endotherms is smooth indicating the overlap of these endothermic effects. The fourth endotherm 920–970 °C is sharp and well developed with its maximum centered at 940 °C and is associated with ~6 wt% loss. This endotherm corresponds to the loss of the combined OH groups on alumina surface and the transformation of active alumina to θ-Al_2O_3 (Mackenzie and Berggren, 1970). The DTA curve of AN7 shows a shift of the first three endotherms to higher temperatures compared with their corresponding endotherms exhibited by AN6, the maxima of these effects are located at 103, 206 and 410 °C. Also, the fourth endotherm exhibited by AN7 is broad covering the temperature range 700–900 °C and its minimum is located at 800 °C. The TG curve of AN7 is also smooth and shows weight losses of 7, 10, 11 and 12 wt% for the first-four endotherms, respectively.

The DTA of AA7 precipitated with ammonia is different compared with that of AN7 precipitated at the same pH with NaOH. Thus, the DTA of AA7 (not illustrated) shows the first endotherm at 90 °C associated with ~5 wt% loss. This endotherm was followed by a broad endotherm covering the range 153–400 °C with its maximum at 237 °C and is associated with 21 wt% loss. The DTA of AA7 does not show any other endothermic effects up to 900 °C where two interfering endotherms are shown at 905–980 °C, these two endotherms are associated

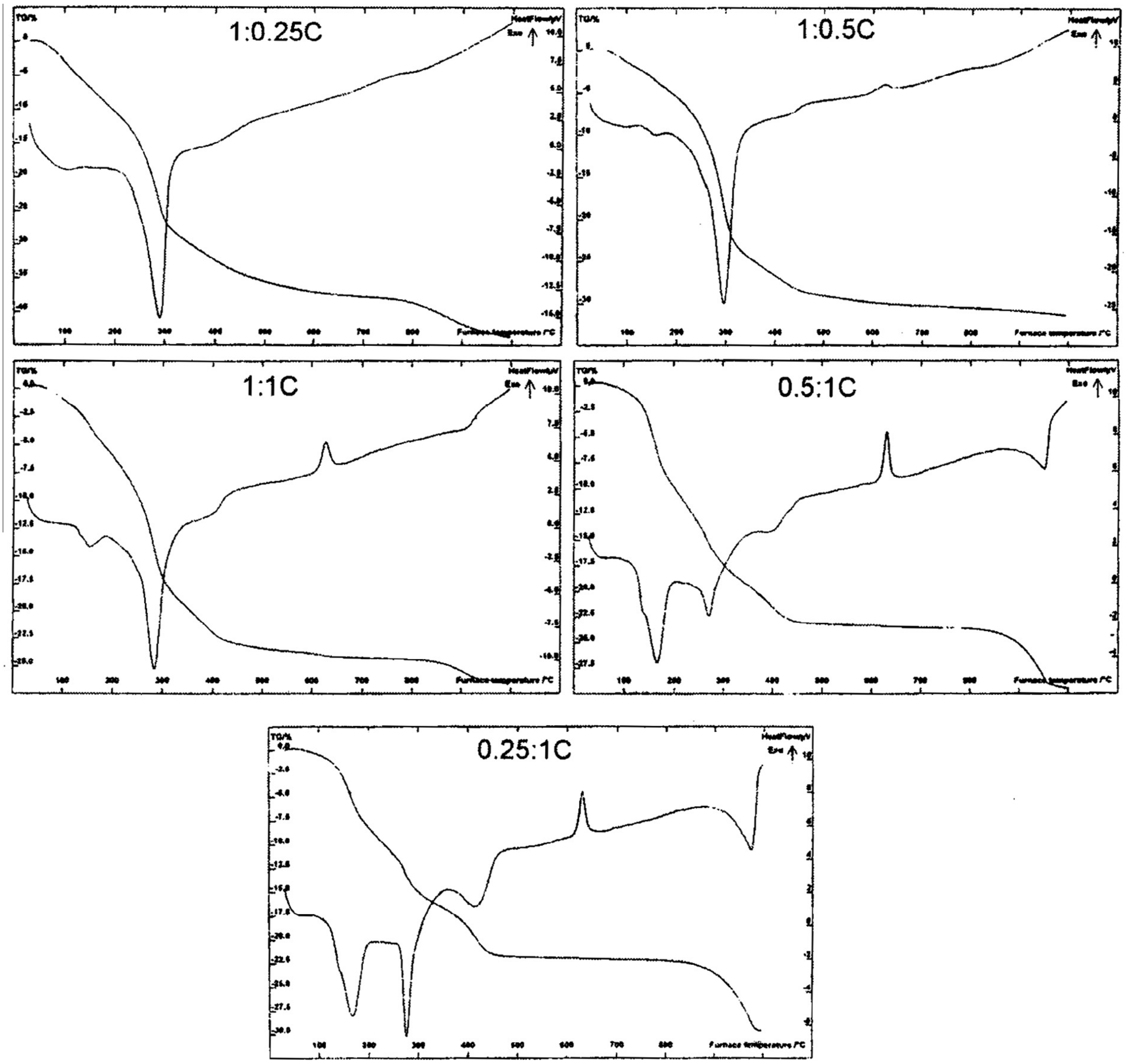

Figure 4 TG–DTA curves of coprecipitated CdO–Al_2O_3 gels.

with a sharp weight loss of 9% as depicted by the TG curve. Evidently, the DTA curve of alumina gels precipitated at pH = 8 following the same procedure are different compared with those precipitated at pH = 7. This refers to the importance of pH of precipitation of aluminas (El-Nabarawy et al, 1995; Alaya and Soubahy, 1993).

The TG–DTA curves of the two $Cd(OH)_2$ samples C8 and C9 (Fig. 2) are different. C8 exhibited five endothermic effects. The first covers the range 50–120 °C with the minimum centered at 96 °C. The second endotherm covers the range 139–255 °C with its minimum located at 235 °C. The second endotherm is directly followed by a sharp endotherm covering the range 255–330 °C with the minimum centered at 283 °C. The fourth endotherm is relatively broad covering the range 340–470 °C with its minimum at 456 °C. The fifth endotherm extends from 870 to 960 °C. These endotherms are associated with a gradual weight loss of 25.9 wt%. The TG curves indicate that a small weight loss of 1% is observed in the temperature range 450–850 °C. The weight loss is probably due to the removal of physisorbed water than chemically combined water followed by dehydroxylation and hydroxide–oxide transformation and finally to the removal of the OH groups on the oxide surface. The poorly developed exotherm at 400–850 °C may be ascribed to the transformation of the shapeless CdO to the cubic phase (Grge, 2009).

Sample C9 exhibits three endothermic effects. The first covers the range 40–100 °C and the second endothermic effect covers the range 255–340 °C as it appears in the DTA curve (Fig. 2) as a well developed sharp endotherm with a minimum at 294 °C and is associated with 9 wt% loss. The third endotherm covers the range 350–460 °C with a minimum centered at 394 °C. A fourth endotherm associated with 8 wt% loss starts to appear at 920 °C. The TG curve of the sample C9 shows a total gradual weight loss of 21.8%. The above-mentioned results indicate that the thermal behavior of pure gels depends on the pH of precipitation, the reagent of precipitation and the original salt used. This is agreeable with a previously reported suggestion (Mackenzie and Berggren, 1970).

Figs. 3 and 4 depict the TG–DTA curves of mechanically mixed and coprecipitated gels precipitated at pH 8 and mixed with a different percentage to contain between 20 and 80 mol% Al_2O_3. For samples containing 80 mol% Al_2O_3, i.e. samples 1:0.25 M and 1:0.25 C, endotherms with minima centered at 100 °C are observed and are associated with 4 wt% loss attributed to the removal of humidity and physisorbed water. These low temperature endotherms are followed by relatively sharp endotherms with minima located at 293 °C and associated with ~28 wt% loss as shown by their corresponding TG curves. The third endotherm at 370–430 °C is sharp with a minimum centered at 400 °C. These two samples also exhibited a weak endothermic effect in the range 860–960 °C with minima located at 895 °C for the sample 1:0.25 M and at 920 °C for the sample 1:0.25 C. No exothermic effects have been shown by DTA curves of 1:0.25 M and 1:0.25 C.

Table 1 The values of ignition loss (I.L. wt%) and TG% of prepared samples.

Sample	Calcination temperature (°C)					Theoretical value (wt%)
	400	500	600	800	1000	
AN6 I.L. wt%	28.0	29.8	30.8	37.2	42.0	34.6
TG%	31.2	35.1	36.4	40.1	49.1	
AN7 I.L. wt%	22.0	24.0	25.6	32.6	35.0	34.6
TG%	23.1	23.5	30.5	35.0	41.6	
AA7 I.L. wt%	26.0	28.8	29.0	37.0	45.6	34.6
TG%	29.0	32.0	33.2	36.8	53.2	
C8 I.L. wt%	18.0	18.6	19.2	19.6	23.0	12.3
TG%	18.5	20.8	21.3	21.4	25.9	
C9 I.L. wt%	10.1	11.2	11.6	12.0	22.4	12.3
TG%	11.8	12.5	12.8	13.1	21.9	
1:0.25 M I.L. wt%	29.4	30.8	31.4	32.3	34.0	30.2
TG%	32.5	35.2	36.5	37.3	39.9	
1:0.5 M I.L. wt%	19.0	19.9	20.0	20.8	21.2	27.2
TG%	20.8	23.7	24.2	24.7	26.4	
1:1 M I.L. wt%	16.8	17.7	18.4	18.8	20.2	23.5
TG%	18.5	19.1	20.2	21.1	24.0	
0.5:1 M I.L. wt%	16.2	16.6	17.6	17.8	21.4	19.7
TG%	18.3	19.1	19.7	21.3	24.4	
0.25:1 M I.L. wt%	15.8	16.7	17.2	17.4	20.8	16.7
TG%	16.3	17.1	18.0	19.1	22.8	
1:0.25 C I.L. wt%	28.8	30.4	31.4	35.4	37.0	30.2
TG%	32.5	35.4	37.2	38.4	44.1	
1:0.5 C I.L. wt%	24.2	25.2	25.4	26.0	26.2	27.2
TG%	26.7	29.2	29.8	30.5	31.3	
1:1 C I.L. wt%	20.0	20.6	20.8	21.1	22.8	23.5
TG%	21.1	23.5	24.0	24.5	26.6	
0.5:1C I.L. wt%	19.8	20.4	20.6	21.0	26.0	19.7
TG%	21.5	23.2	23.3	23.7	29.5	
0.25:1 C I.L. wt%	18.4	18.8	19.0	19.2	26.0	16.7
TG%	18.7	21.8	21.9	22.2	29.7	

For the samples 1:0.5 M and 1:0.5 C, the endotherms with minima at 100, 296 and 900 °C, which are attributed to the loss of humidity and physisorbed water, decomposition of hydroxides to oxides and the removal of the OH groups on the oxide surface respectively are shown in the DTA curves of these samples. Evidently, for these two samples an exotherm covering the range 610–650 °C and centered at 627 °C is shown for each sample and is attributed to cadmium aluminate. The DTA curve of the sample with composition 1:0.5 C shows an endothermic effect with its minimum located at 130 °C. Figs. 3 and 4 also show that the endotherms appearing at 150 and 900 °C become more pronounced with the increase of cadmium oxide content and the minima of the peaks also shift to higher temperature with the increase of CdO content. The exothermic effect centered at 627 °C increases also with the increase of CdO content.

The DTA curve of sample 0.5:1 M shows two interfering endothermic effects with minima at 245 and 276 °C, whereas the endothermic effect of the samples containing 20 mol% Al_2O_3 covers the range 230–310 °C with minimum at 245 °C for the sample 0.25:1 M and at 276 °C for 0.25:1 C. These endotherms are associated with stepwise TG curves.

Table 1 lists the weight loss due to ignition (I.L. wt%) and those determined from TG (TG%) of the prepared samples, at different temperatures together with theoretically calculated values. Table 1 reveals that (i) the values of weight loss determined from TG at a certain temperature are always higher than those determined on ignition at the same temperature, which may be attributed to the sorption of humidity. (ii) TG loss and ignition loss are both higher than theoretically calculated values as a result of the decomposition of corresponding hydroxides. This indicates that the water contents of the gels are higher than those of the hydroxides. The pores in the gels retain some water specifically held on their walls. (iii) The rise of the precipitation pH decreased the water content and consequently the water loss upon thermal treatment. (iv) The water content of ammonia-precipitated samples is higher than the water content of NaOH- precipitated equivalents. (v) Coprecipitated oxides exhibited higher weight loss compared to mechanically mixed oxides of the same chemical composition. (vi) The weight loss at the temperature range 400–800 °C is small in case of mixed oxides whereas the weight loss is more or less gradual in the case of alumina gel. (vii) The precipitation pH affects the course of water loss.

3.2. X-ray diffraction (XRD)

The XRD of 1000 °C calcination products of all the samples and of 400, 600 and 800-calcination products was carried

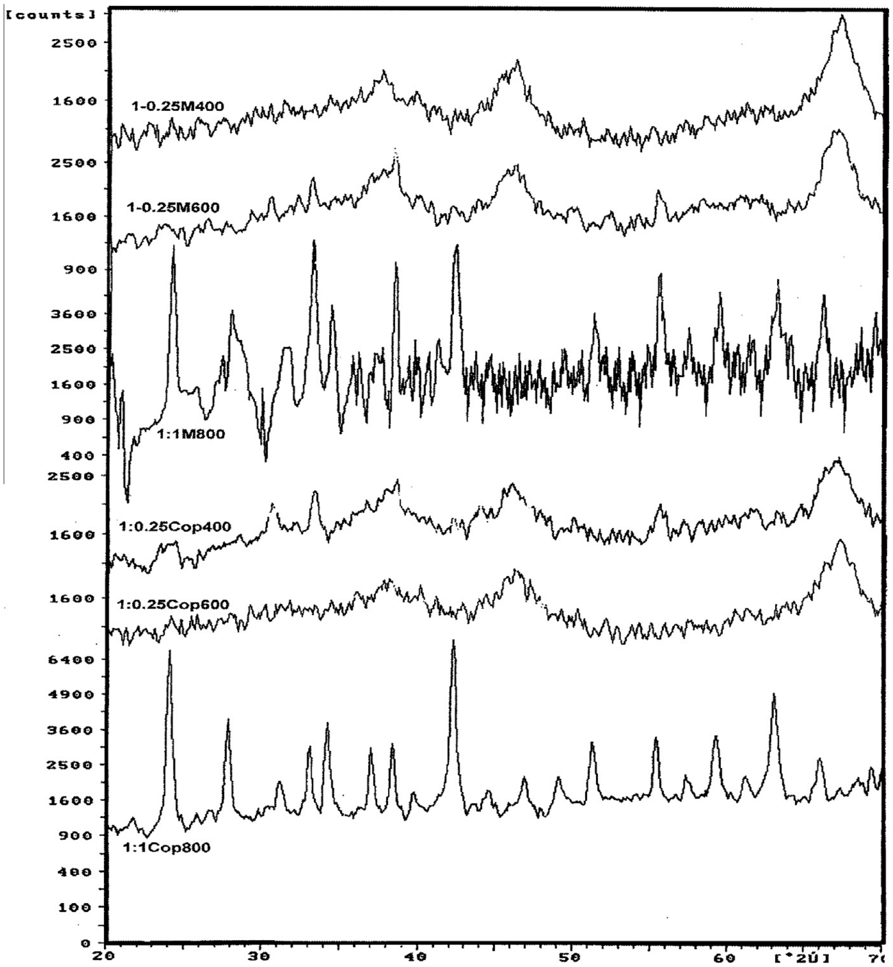

Figure 5 XRD patterns of some calcined products at 400,600 and 800 °C.

out. Fig. 5 shows the XRD pattern of 400, 600 and 800-calcination products. It is shown that the samples calcined at 400 and 600 °C are poorly crystalline whereas those calcined at 800 °C are well crystalline. Thus, for example the 800-calcination products of samples 1:1 C and 1:1 M are well crystalline showing the spectral lines and *d*-spacing characteristic of cadmium aluminate, $CdAl_2O_4$, (card no. 12252-16-3). This agrees with the DTA tracings of the samples, which showed exothermic effects at temperatures higher than 600 °C. The XRD studies indicated that heating of alumina gel at 400 °C led to the formation of the active γ-Al_2O_3 phase whereas the calcinations at about 900 °C gave the δ phase. Calcination at 1000 °C was found to be associated with the formation of θ-alumina as a major phase together with α-Al_2O_3 as a minor phase. Above 1000 °C, α-Al_2O_3 as the most stable phase predominates (Lippens and Steggerda, 1970).

Thermal treatment of cadmia gel at 500 °C results in the transformation to CdO. Further rise of the calcination temperature at $\geqslant$850 °C resulted in the dehydroxylation of the oxide and to the gradual change of the oxide color from pale brown to black at 1000 °C. These changes are in good agreement with the XRD of 800 and 1000 °C products, Fig. 6, which depict the crystalline characteristics of Monteponite (card no. 05-0640).

Figs. 6 and 7 show the XRD patterns of 1000 °C- calcination products of mechanically mixed and co-precipitated CdO/Al_2O_3 systems. It is shown that for the sample 1:0.25 M, the principal spectral lines of θ-Al_2O_3 predominate whereas those characteristic of $CdAl_2O_4$ are less predominating. On the other hand, the principal lines characteristic of corundum (card no. 42-1468) predominate in the XRD pattern of the sample 1:0.25 C. This refers to the role of the method of preparation of mixed oxide in determining its structural characteristics. The XRD of 1000 °C-samples containing 66.7 mol% Al_2O_3 whether they are mechanically mixed or coprecipitated was the same. Thus the patterns showed θ-Al_2O_3 and $CdAl_2O_4$ phases. For 1000 °C-samples containing 50 mol% Al_2O_3, only $CdAl_2O_4$ showed its existence. The decrease of Al_2O_3 content to 33.3 mol%, the XRD patterns of both $CdAl_2O_4$ θ-Al_2O_3 and montiponite were shown. Further decrease of Al_2O_3 content to 20 mol% in samples thermally treated at 1000 °C gave XRD patterns showing $CdAl_2O_4$ as a minor phase and monteponite as a major one.

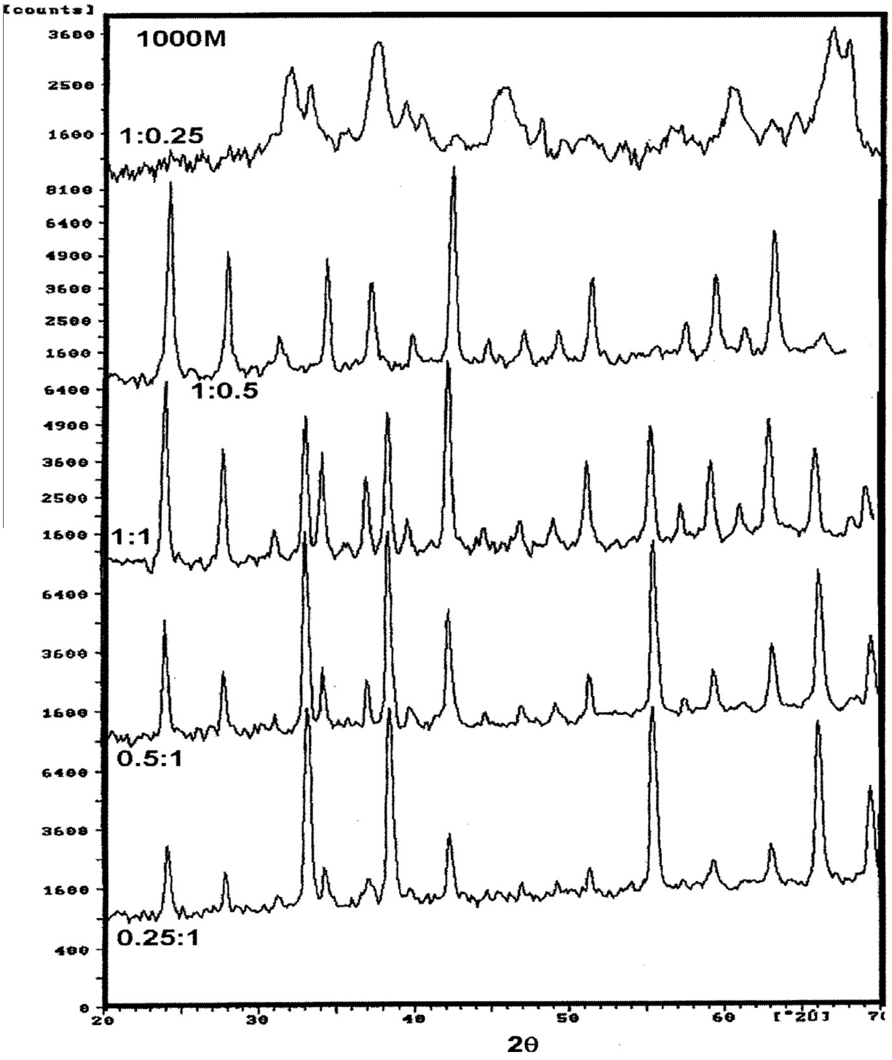

Figure 6 XRD patterns of the 1000 °C-products of ACM samples.

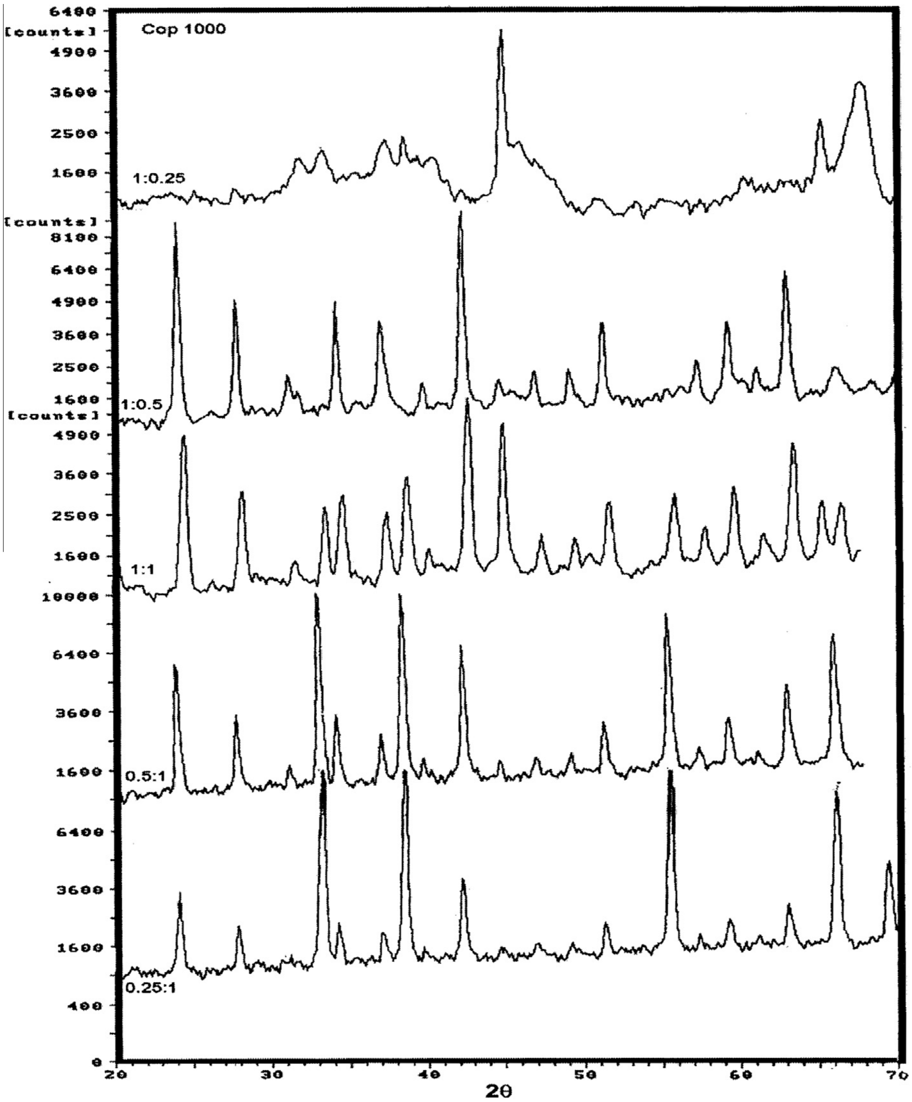

Figure 7 XRD patterns of the 1000 °C-products of ACC samples.

4. Conclusions

The thermal behaviors of metal oxide gels, such as alumina and cadmia and also of mixed oxide gels are related to the type of precipitating agent and the precipitation pH. The method of preparation and chemical composition are also determining factors. Cadmia and alumina and cadmia-alumina calcined at 400–600 °C are poorly crystalline. Well crystalline single oxides and solid–solid reaction may take place at ⩾800 °C. Well crystalline γ-Al_2O_3, CdO and $CdAl_2O_4$ were shown by mechanically and coprecipitated cadmia-alumina calcined at 800 °C. The most stable phases θ-Al_2O_3, α-Al_2O_3, black CdO (Montep-onite) together with $CdAl_2O_4$ were shown by the XRD patterns of CdO–Al_2O_3 calcined at 1000 °C with the most predominating phases depending on the chemical composition.

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