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Thermal and Spectroscopic Characterization of Reaction Products of Aluminium Nitrate-Chromium (III) Acetate Interaction at Different Temperatures

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A series of five mixtures of aluminium nitrate (AlN) and chromium (III) acetate (CrA) with molar ratios, 3 : 1(I), 2 : 1(II), 1 : 1(III), 1 : 2(IV) and 1 : 3(V) were prepared and subjected to thermal treatment at 350, 500 750 and 1000°C. The decomposition products of pure salts and their mixtures were characterized by means of chemical analysis, diffuse reflectance and X-ray diffraction.

INTRODUCTION

Even though a considerable amount of work has been reported on chromia-alumina systems in the field of catalysis[1-6] and other industrial purposes such as pigments[7] and refractory materials[8] but no detailed investigations on chemical reaction between chromium and aluminium salts in molten states and at elevated temperatures were carried out. In our previous work we studied the interaction between chromium nitrates and both aluminium nitrate[9] and aluminium hydroxyacetate.[10] The present investigation, which is considered as a continuation of our previous studies is aimed to investigate and characterize the reaction products between aluminium nitrate and chromium (III) acetate with different molar ratios over a wide range of temperatures using different techniques.

EXPERIMENTAL

The starting materials, aluminium nitrate and chromium (III) acetate were obtained from Merck and Riedel-de Haen AG Chemicals (FRG). Five mixtures of aluminium nitrate and chromium (III) acetate of molar ratios 3 : 1(I), 2 : 1(II), 1 : 1(III), 1 : 2(IV) and 1 : 3(V) with respect to Al_2O_3 and Cr_2O_3 were prepared according to the procedure described earlier[9]. The thermal analysis, X-ray diffraction and electronic absorption spectra were performed as mentioned previously[9].

The percentage of Al_2O_3 and Cr_2O_3 in aluminium nitrate and Chromium (III) acetate were determined by ignition of the sample at 1200°C and 1100°C, respectively, until constant weight was obtained. They amount to 13.72 and 41.42 respectively which are in accordance with their chemical formulae $Al(NO_3)_3.9H_2O$ and $Cr_2(CH_3COO)_6.2H_2O.Cr(OH)_3$.

Both aluminium and chromium perecentage in intermediates or solid solutions were determined according to the method described elsewhere.[9]

RESULTS AND DISCUSSION

The characterization of thermal products resulted from both salts is carried out in order to shed some light upon the probable interactions between these products at different temperatures.

(a) Aluminium Nitrate

The thermal decomposition of aluminium nitrate was described in detail elsewhere[9] where it was mentioned that at 285°C, nitric acid is liberated out in addition to hydrated aluminium hydroxide which is gradually dehydrated between 285° and 628°C leading to hydrated γ-Al_2O_3. The latter is transformed into crystalline species on raising the temperature up to 700°C.

Chromium (III) acetate

By inspection of the TG curve of chromium (III) acetate (Fig. 1) it can

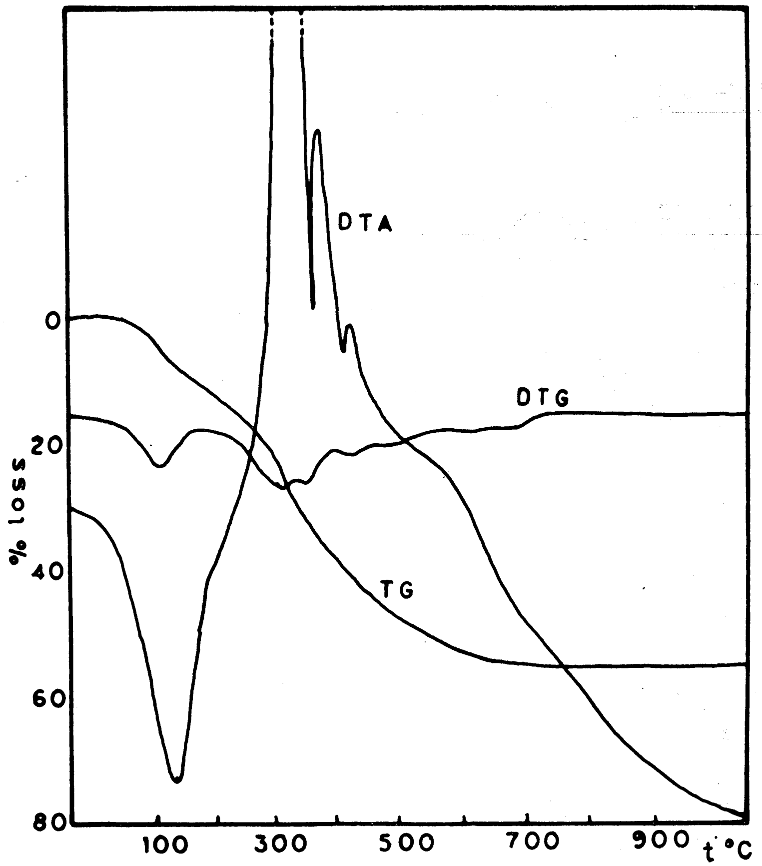
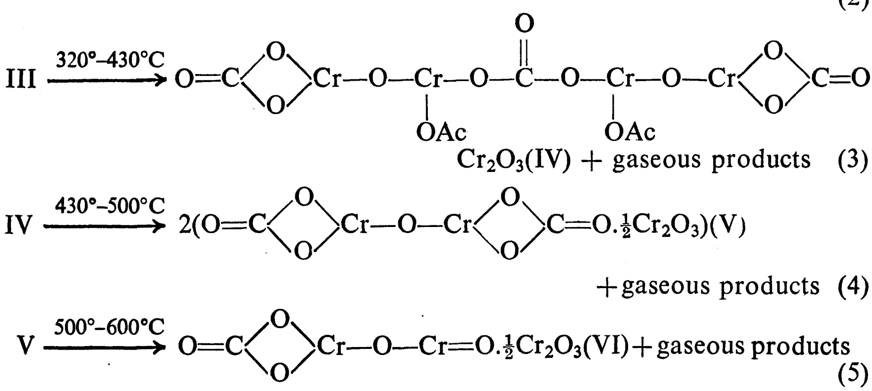


Fig. 1. Thermal analysis of Cr(III) acetate

be seen that the salt is stable up to 65°C. Moreover the observed weight losses above this temperature are not separated by a period of mass constancy. This indicates that the intermediate products formed are not stable over a certain range of temperatures. However, the TG curve show a number of discontinuities at different temperatures owing to the formation of thermodynamically unstable non-isolable intermediates. Based on weight losses calculated from TG curve (Fig. 1) the decomposition steps can be represented as follows:

$$Cr_2(OAc)_6 2H_2O.Cr(OH)_3(I) \xrightarrow{60°-160°C} Cr_2(OAc)_6 \tfrac{1}{2}Cr_2O_3(II) + 3.5H_2O \quad (1)$$

$$II \xrightarrow{160°-320°C} (AcO)_2—Cr—O—Cr(OAc)_2.\tfrac{1}{2}Cr_2O_3(III) + \text{gaseous products} \quad (2)$$



$$VI \xrightarrow{>660°C} 1.5\ Cr_2O_3\ (VII) + \text{gaseous products} \quad (6)$$

As can be seen from the suggested chemical equations (1-6) Cr_2O_3 is resulted from $Cr(OH)_3$ species over 160°C, whereas it is resulted from $Cr(OAc)_3$ species after several decomposition steps above 600°C. On other hand, it is obtained by heating the salt at 350°C statically for 4th due to the formation of thermodynamically unstable intermediates which lead to several successive unstable intermediates ending with production of Cr_2O_3 on such prolonged heating. The percentage of chromium in the resulted oxide is determined by chemical analysis and agree well with its theoretical value. X-ray diffraction pattern (Fig. 2) indicates that the oxide posses 'd' spacings similar to that of ASTM Index.

Chemical Interaction Between Aluminium Nitrate and Chromium (III) Acetate :

The interaction between aluminium nitrate and chromium (III) acetate for mixtures I-V at different temperatures up to 1000°C was investigated by means of different spectroscopic studies to establish the possible reaction which may take place between their decomposition products.

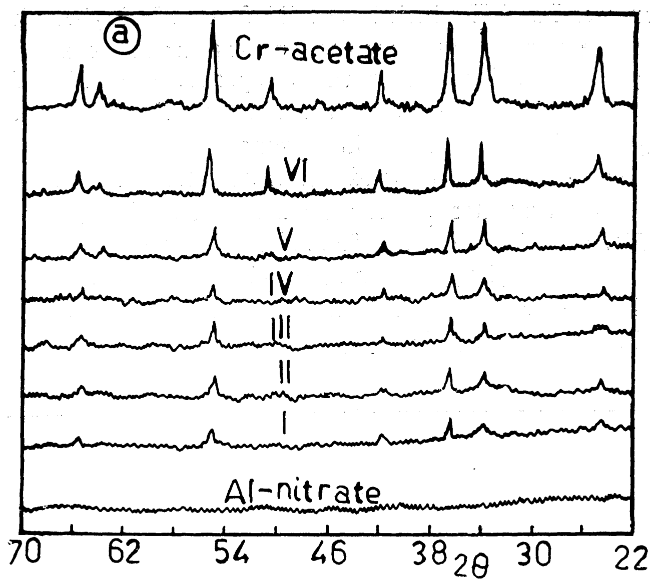


Fig. 2. X-ray diffraction patterns of aluminium nitrate-chromium acetate and their mixtures I, II, III, IV and V at 350°C.

TABLE 1
THE TG, DTG AND DTA DATA FOR DECOMPOSITION OF CHROMIUM (III) ACETATE BY THERMAL TREATMENT

Thermal step	Temp. range (°C)	DTG peak (°C)	Type of corresponding DTA peak	Loss %	
				Calcd.	Found
1	60–185	125	exothermic	10.56	10.0
2	185–345	325	exothermic	24.97	24.0
3	345–385	350	exothermic	39.56	40.50
4	385–450	435	exothermic	44.42	46.0
5	450–600	broad	exothermic	51.79	54.0
6	>600	broad	exothermic	59.16	58.0

It was found that the reaction products of mixtures heated at 350° or 500°C for 4 hrs. composed essentialy of crystalline Cr_2O_3 and amorphous aluminium hydroxychromates with different compositions depending on AlN/CrA ratio as will be seen later. The chromates are characterized by the presence of charge transfer band in the ultraviolet region at 270–295 nm.

The X-ray diffraction patterns of mixtures III-V heated at 750°C for 4 hrs. show new crystalline phases having the characteristic 'd' spacings of $(Al_{1-x}Cr_x)_2O_3$ solid solutions. On other hand the chromates formed in case of mixtures I and II which have AlN/CrA ratio higher than 1 show poor crystalline compounds having 'd' spacing similar to a certain extent to that of γ-alumina. By raising the temperature to 1000°C they well crystallized and show also the 'd' spacings which are characteristic for $(Al_{1-x}Cr_x)_2O_3$ solid solutions rich in alumina.

The chemical formulae of solid solutions were obtained from the plot of their lattice parameter values vs. composition of $(Al_{1-x}Cr_x)_2O_3$ mixed crystals (Fig. 3). The chemical formulae of these solid solutions are $(Al_{0.83}Cr_{0.17})_2O_3$, $(Al_{0.75}Cr_{0.25})_2O_3$ and $(Al_{0.67}Cr_{0.33})_2O_3$ for mixtures I, II and III respectively, whereas both mixtures IV and V produced the same solid solution with formula $(Al_{0.5}Cr_{0.5})_2O_3$.

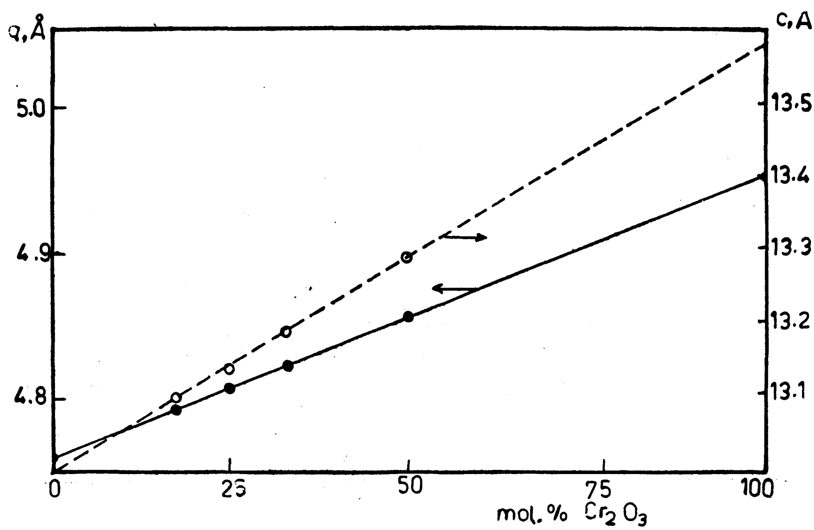


Fig. 3. Dependence of the lattice parameter on the chemical composition.

They showed two absorption bands in the visible region of spectra designated as $^4A_{2g} \rightarrow {}^4A_{2g}$ and $^4A_{2g} \rightarrow {}^1T_{1g}$ for low and high frequency bands respectively. The locations of them are shifted to shorter wavelengths in comparison to Cr_2O_3 (Fig. 3) which is a characteristic phenomenon of $(Al_{1-x}Cr_x)_2O_3$ mixed crystals.

It was reported[9-11] that aluminium hydroxychromates are transformed to $(Al_{1-x}Cr_x)_2O_3$ mixed crystals at relatively high temperature. The same phenomenon was also observed in the present investigation. Based on these findings the composition of aluminium hydroxychromates which are corresponding to the previous mentioned solid solutions can be represented as follows,

$Al_2O_3Al_3(OH)_7CrO_4$, $Al_2O_3Al(OH)CrO_4$, $Al_2(OH)_4CrO_4$ for mixtures I, II and III respectively, and $AlCrO_3Al(OH)CrO_4$ for both mixtures IV and V (Table 2).

TABLE 2

LATTICE PARAMETER OF $(Al_{1-x}Cr_x)_2O_3$ SOLID SOLUTIONS PRODUCED FROM HEATING OF CORRESPONDING CHROMATES AT 1000°C

Mixture	Chemical formula of Chromates	Corresponding Solid Solution	Lattice Parameter (A°)	
			a	C
I	$Al_2O_3Al_3(OH)_7CrO_4$	$(Al_{0.83}Cr_{0.17})_2O_3$	4.796	13.10
II	$Al_2O_3Al(OH)CrO_4$	$(Al_{0.75}Cr_{0.25})_2O_3$	4.80	13.14
III	$Al_2(OH)_4CrO_4$	$(Al_{0.67}Cr_{0.33})_2O_3$	4.82	13.18
IV	$AlCrO_3Al(OH)CrO_4$	$(Al_{0.5}Cr_{0.5})_2O_3$	4.84	13.28
V	$AlCrO_3Al(OH)CrO_4$	$(Al_{0.5}Cr_{0.5})_2O_3$	4.845	13.285

According to weight losses determined from heating the mixtures at 400°C till constant weight the chromates may be formed according to the following equations.

Mixture I

$$9Al(NO_3)_3.9H_2O + Cr_2(OAc)_6 2H_2O{\cdot}Cr(OH)_3 \xrightarrow[=79.50]{\%\text{Loss at } 400°C}$$

$$1.8Al_2O_3Al_3(OH)_7CrO_4 + 0.6Cr_2O_3 + \text{gaseous products.}$$

Mixture II

$$6Al(NO_3)_3.9H_2O + Cr_2(OAc)_6{\cdot}2H_2O{\cdot}Cr(OH)_3 \xrightarrow[=78.1]{\%\text{ Loss at } 400°C}$$

$$2Al_2O_3Al(OH)CrO_4 + 1/2Cr_2O_3 + \text{gaseous products}$$

Mixture III

$$3Al(NO_3)_3.9H_2O + Cr_2(OAC)_6 2H_2O{\cdot}Cr(OH)_3 \xrightarrow[72.6]{\%\text{ Loss at } 400°C}$$

$$1\tfrac{1}{2}Al_2(OH)_4CrO_4 + 0.75\ Cr_2O_3 + \text{gaseous products}$$

Mixture IV

$$Al(NO_3)_3.9H_2O + 2/3Cr_2(OAC)_6 2H_2O{\cdot}Cr(OH)_3 \xrightarrow[71.8]{\%\text{ Loss at } 400°C}$$

$$\tfrac{1}{2}AlCrO_3AlOHCrO_4 + \tfrac{1}{2}Cr_2O_3 + \text{gaseous products}$$

Mixture V

$$Al(NO_3)_3.9H_2O + Cr_2(OAC)_6 2H_2O{\cdot}Cr(OH)_3 \xrightarrow[65.5]{\%\text{ Loss at } 400°C}$$

$$\tfrac{1}{2}AlCrO_3AlOHCrO_4 + Cr_2O_3 + \text{gaseous products}$$

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1989 PERKIN-MEDAL

Dr. Frederick J. Karol, senior corporate fellow in the polyolefins Division of Union Carbide, U.S.A. has now the 1989 Perkin Medal for outstanding achievement in applied chemistry. The medal has been awarded to him in recognition of his technical accomplishments and readership in the field of catalysis, particularly his role developing linear low-density polyethylene (LLDPE).