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Thermal and spectroscopic characterization of the products obtained from the reaction between Mn-Carbonate and Ammonium Dichromate at different temperatures

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Pure and mixed Mn-Cr oxides were prepared from the reaction between manganese carbonate and ammonium dichromate with molar ratios of 3:1, 1:1 and 1:3 with respect to Mn_2O_3:Cr_2O_3. Thermal decomposition for each of the mixture and the pure compound was studied using DTA and TG techniques. Pure and mixed salts were thermally treated at temperatures of 250°C, 500°, 750° and 1000°C and characterized by means of x-ray, diffraction analysis and IR absorption spectroscopy.

The results obtained revealed that the thermal treatment of mixtures at 250°C produced a well crystalline $MnCO_3$ and/or Cr-oxide phases depending on the composition of the mixture. At 500°C, poorly crystalline Mn_2O_3, Cr_2O_3 and amorphous manganese chromate intermediates were detected. Further increase in temperature of treatment was accompanied by the formation of $Mn_{3-x}Cr_xO_4$ compound in all mixtures. This compound decomposes at temperatures just lower than 700°C to form crystalline phase of Mn_3O_4 and Cr_2O_3.

Introduction

Many binary oxides are widely used in catalysis[1-4]. These binary systems were found to be more catalytically active than their separated oxide components[5,6]. In catalysis, it is well known that the activity of oxide catalysts depends on many factors, such as methods of preparation, calcination conditions and the interaction occurring between the different components of the catalyst, the latter is a very important factor and many investigations are cited in the literature concerning this subject[7-9].

In the present investigation, we studied the effect of temperature on the interaction between manganese and chromium salts in order to characterize the different products obtained at various temperatures of treatment. The techniques employed in this work were DTA, X-ray diffraction spectroscopy and IR absorption spectroscopy.

Experimental

The starting materials used in this investigation were pure ammonium dichromate and manganeses carbonate from BDH grade. Mixtures of molar ratios 3:1 (I), 1:1 (II) and 1:3 (III) with respect to Cr_2O_3:Mn_2O_3 were prepared by mixing and grinding the salts. Each one of the pure ammonium dichromate, manganese carbonate and their mixtures I, II and III was heated at temperatures of 250^o, 500^o, 750^o, or 1000^oC for 4 hours.

Thermal analysis for each of $(NH_4)_2Cr_2O_7$ and Mn-carbonate was carried out using DTA and TG unit of the NETZSCH Gertebau simultaneous thermal analysis system (STA 409, 6.223). The rate of heating was 10^oC min^{-1}.

The X-ray diffractograms of the samples were taken on a diffractometer Philips (Holland) with a scintillation counter and plus height analysis at 35Kv, 14 mA using Co-target radiation. The spectra were scanned at rate of 2^omin^{-1} in 2O.

IR spectra of the samples were recorded on a Beckman infrared spectrophotometric unit using the KBr disc technique.

Result and Discussion:

The thermal analysis diagrams for pure manganese carbonate, Fig. 1, show that the compound starts to decompose by losing the dehydration water at temperature range of 100-250°C. The weighing loss ≈ 29% occurring at temperature rang of 300-400°C refers to the decomposition of Manganese carbonate to MnO_2. This oxide dissociates to Mn_2O_3 (weight loss ≈ 9%) at a temperature range of about 450-500°C. The decomposition of $MnCO_3$ can be represented as follows:

$$MnCO_3.0.5H_2O \xrightarrow[\text{Loss} \approx 7\%]{< 300^oC} MnCO_3 + 0.5H_2O$$

$$MnCO_3 + 1/2\ O2 \xrightarrow[\text{Loss} \approx 22\%]{300\text{-}400^oC} MnO_2 + CO_2$$

$$2MnO_2 \xrightarrow[\text{Loss} \approx 9\%]{> 400^oC} Mn_2O_3 + 0.5O_2$$

The ammonium dichromate decomposes thermally in several steps, Fig. 2, with a total weighing loss of ≈ 65%.

The decomposition steps observed here agree with those reported by EZ-Eldin(10).

$$4(NH_4)_2Cr_2O_7 \xrightarrow{\approx 200^{o}C} 4Cr(OH)_3 + 2CrO_3 + 2CrOOH + 2NH_3 + 3N_2 + 6H_2O$$

$$2CrO_3 + 1/2CrOOH \xrightarrow{\approx 200^{o}C} 0.5CrO_2 + 0.25Cr_2(Cr_2O_7)_3 + 0.25H_2O + 0.25O_2$$

$$1.5CrOOH \xrightarrow{\approx 250^{o}C} 0.75Cr_2O_3 + 0.75\ H_2O$$

$$0.5CrO_2 \xrightarrow{> 350^{o}C} 0.25Cr_2O_3 + 0.125O_2$$

$$0.25Cr_2(Cr_2O_7)_3 \xrightarrow{> 350^{o}C} Cr_2O_3 + 1.125O_2$$

To identify the phases formed during the thermal treatment, the X-ray diffraction spectra for pure $MnCO_3$ heated at different temperatures 250°, 500°, 750° and 1000°C were recorded and summarized in Fig. (3,4 and 5).

For sample heated at 250°C, crystalline phase of $MnCO_3$ (d-values 1.76, 2.17, 2.84 and 3.66 A°)(11) was only detected. While the heated samples at temperatures of 500°, 750° and 1000°C showed crystalline tetragonal phase for Mn_2O_3 (d-values 2.49, 2.76, 3.08 and 4.22 A°)(12). The crystallinity of this phase increase with temperature. At temperature of 1000°C, crystalline phase of Mn_3O_4 (d-values 1.49, 2.10, 2.54 and 4.86 A°)(13) could be detected beside the phase of Mn_2O_3.

The X-ray diffraction pattern of heated ammonium dichromate sample at 500°C, Fig. 3, support the above thermal decomposition results which showed the formation of Cr_2O_3 at 500°C(14).

The degree of crystallinity of Cr_2O_3 increases with increasing the heating temperature, Figs. 4 and 5.

The X-ray diffraction patterns for the mixture samples (I, II, III) heated at 250°C showed the absence of any crystalline phases. The disappearance of the patterns of crystalline phases of $MnCO_3$, which was observed in case of pure sample can be attributed to the interaction occurring between $MnCO_3$ and the composition products of ammonium dichromate.

For all mixtures heated at 500°C, the X-ray diffraction patterns showed crystalline phases of Mn_2O_3(12) and Cr_2O_3(14).

At temperature 750°C, crystalline phases of Cr_2O_3 and Mn_3O_4 could be detected. The formation of Mn_3O_4 at 750°C could be explained as a result of certain reaction to form $Mn_{3-x}Cr_xO_4$, which is then dissociate to Cr_2O_3 and Mn_3O_4, (at $500^0<T<750^0$C).

$$\text{Mn-oxide} + \text{Cr-oxide} \xrightarrow{>500^0\text{C}} (Mn_{3-x}Cr_xO_7) \xrightarrow{750^0\text{C}} Cr_2O_3 + Mn_3O_4 + XO_2$$

The mixed oxides of $Mn_{3-x}Cr_xO_4$ was also detected as a result of the reaction between manganese carbonate and chromium nitrate at about 500^oC(15).

The x-ray diffraction patterns for the mixtures heated at 1000^oC showed an increase in the intensity of patterns for crystalline phases of Mn_3O_4 and Cr_2O_3.

Figs. 6,7,8 and 9 illustrate the IR spectra for pure and mixed manganese and chromium salts heated at different temperatures. Fig. 6 shows the IR spectra of the pure salts and their mixtures heated at 250^oC. The bands appeared at wave lengths of ≈1810, 1437, 1087, 870 and 728 cm^{-1} indicate the presence of carbonate group. The increase in the concentration of chromium in the mixtures led to decrease intensity of the manganese carbonate bands and at the same time an increase in the intensity of the corresponding bands of chromium oxide at 1100, 710, 650, 570, 555, 440 and 407 cm^{-1}. The IR-spectra for pure Mn-carbonate heated at 500^oC showed the disappearance of carbonate bands of pure Mn-carbonate and the appearance of new bands at 1150, 980, 845, 690, 610, 485 and 410 cm^{-1} which are characterized for Mn_2O_3.

For mixture samples heated at 500^oC, the IR spectrogram showed a broad band pointing to the presence of some sort of chromates, which formed as a result of solid state reactions between manganese carbonate and ammonium dichromate. The IR spectra of calcined mixtures at 750^oC showed

bands corresponding to Cr_2O_3 and Mn_3O_4. Further increase in temperature, 1000^oC increases the intensity of Cr_2O_3 and Mn_3O_4 bands, which confirmed the results obtained from X-ray.

Figure Captions

Fig. 1: DTA and TG of manganese carbonate.

Fig. 2: DTA and TG of ammonium dichromate.

Fig. 3: X-ray diffraction patterns of ammonium dichromate, manganese carbonate and their mixtures calcined at 500°C.

1- Cr_2O_3 2- Mn_2O_3

Fig. 4: X-ray diffraction patterns of ammonium dichromate, manganese carbonate and their mixtures calcined at 750°C.

1- Cr_2O_3 2- Mn_2O_3 3- Mn_3O_4

Fig. 5: X-ray diffraction patterns of ammonium dichromate, manganese carbonate and their mixtures calcined at 1000°C.

1- Cr_2O_3 2-Mn_2O_3 3- Mn_3O_4

Fig. 6: IR-spectra of ammonium dichromate, manganese carbonate and their mixtures calcined at 250°C.

Fig. 7: IR-spectra of ammonium dichromate, manganese carbonate and their mixtures calcined at 500°C.

Fig. 8: IR-spectra of ammonium dichromate, manganese carbonate and their mixtures calcined at 750°C.

Fig. 9: IR-spectra of ammonium dichromate, manganese carbonate and their mixtures calcined at 1000°C.

References

1. M.E. Dry and F.S. Stone Dicuss. Faraday. Soc., 28,192 (1955).

2. D. Dollimore and T.E. Jones J. Appl. Chem. Biolechnol., 23,29 (1973).

3. M.M. Selim, G.A. El-Shobaky and A.I.Kira, Surf. Technol., 10,73 (1980).

4. V. Mucka and K. Lang, Collect Czech. Chem. Commun. 53,1636 (1988).

5. A.M. Trunov and L.V. Moroz, Izv. Vyssh. Ucheb. Zoved., Khim. Khim. Technol, 14,709 (1971).

6. M.M. Selim and L.B. Khalil. AFINIDAD 433,167 (1991).

7. G.C. Naiti and S.K. Chosh Indian J. Chem. Sect. A, 24A (6), 513 (1985).

8. M.M. Selim and N.A. Youssef Thermochimica Acta 118, 57 (1987).

9. M.F.R. Fouda, R.S. Amine and M.M. Selim, Thermochimica Acta 141,277 (1989).

10. Wafaa EZ-Eldin, M.Sc. Thesis, Cairo University.

11. Dono's System of Mineralogy 7th. E.D. Vol. 2.

12. Bricker, Am. Mim. 50. 1296-1354 (1965).

13. Faulring, Zwicker and A.M. Forgeng Min. 45,947 (1960).

14. Swanson Et. Al., NES Ciroular 539 Vol. 7 (1959).

15. M.M. Selim, S.A. Hassan and H.S. Mazhar, Bull. NRC, Egypt, Vol. 17. No. 3, PP 129-139 (1992).

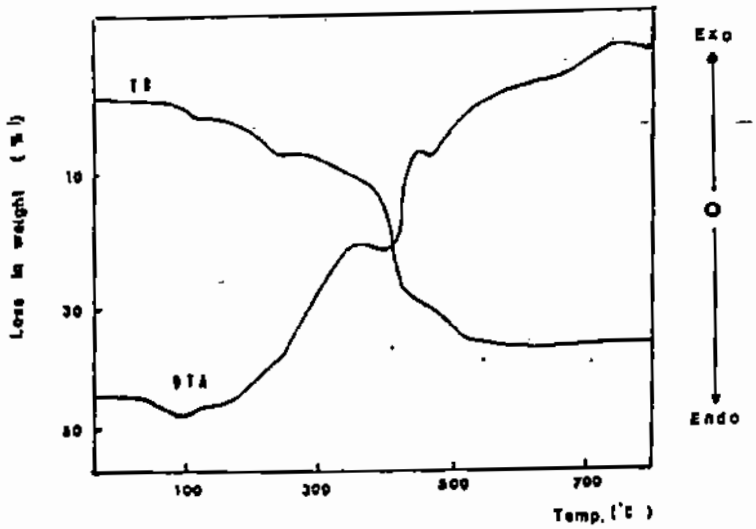
TG
DTA
Loss in weight (%)
10
30
50
100
300
500
700
Temp. (°C)
Exo
Endo

Fig 1

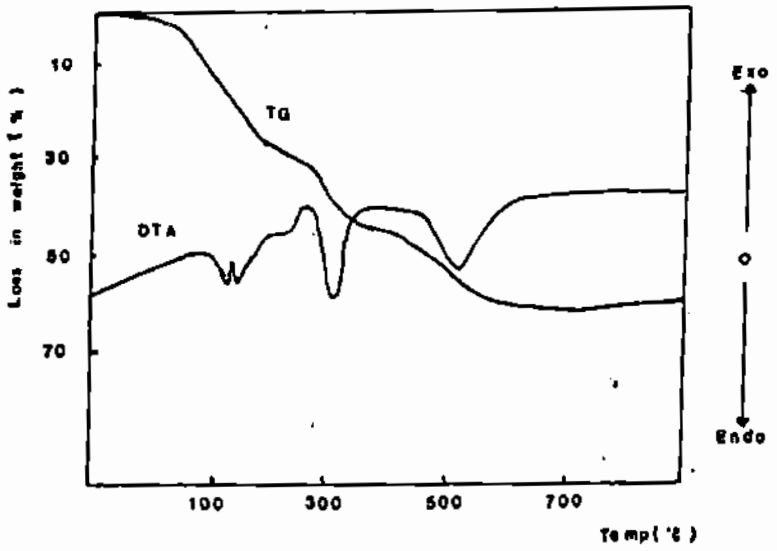
TG
DTA
Loss in weight (%)
10
30
50
70
100
300
500
700
Temp(°C)
Exo
Endo

Fig 2

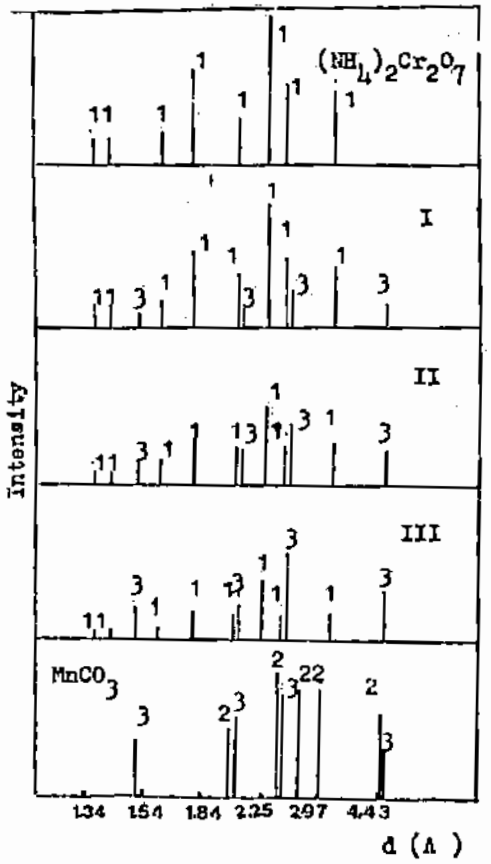

Fig 5

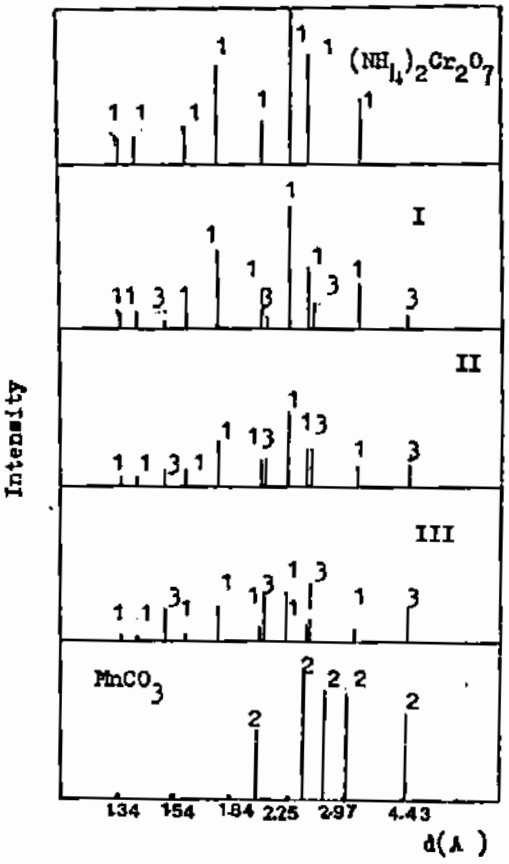

Fig 4

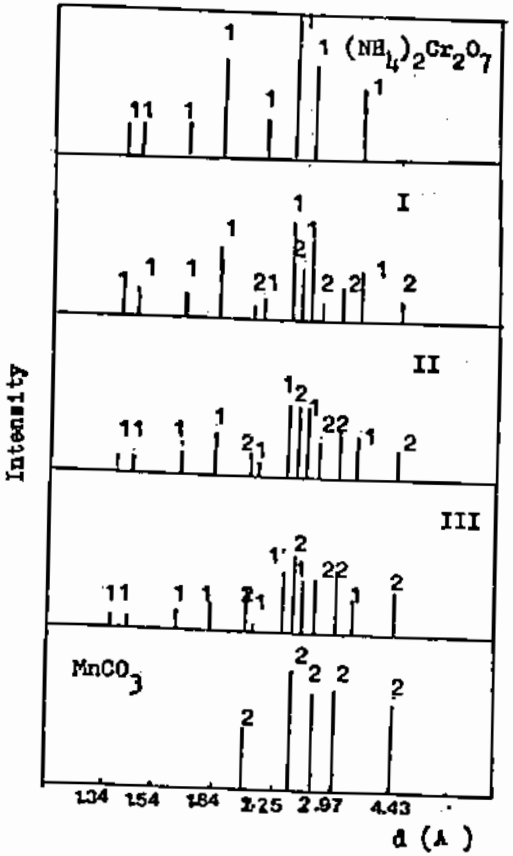

Fig 3

Fig 5

Fig 6

Fig 8

Fig 9