Vol. 18 (1993).

Physicochemical studies on ZnO- Silica gel system

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Abstract:

Several mixed ZnO-Silica gel systems were prepared by the impregnation method and calcined for 5 h at 115, 300, 600 and 1000°C. The crystal structure, surface acidity, surface basicity, surface area, catalytic decomposition of H_2O_2 and the electrical conductivity of the samples prepared were studied. It was found that the decomposition of H_2O_2 is catalysed by each of the acidic and basic sites formed on the catalyst surface.

$ZnSiO_4$ spinel was found to be formed at temperatures $\geq$ 760°C. The results obtained were correlated together and the effect of composition on the physical properties of oxides investigated have been discussed.

Introduction:

The binary oxides are widely used in catalysis[1,2]. The main class of reactions that lead to the formation of active oxide catalysts is essentially thermal reactions of suitable compounds. The chemical composition of the

starting materials and the methods of preparation play an effective role in altering the properties of the final products.

Several studies[3-7] on the catalytic and the acidic properties of some inorganic solids showed the presence of a correlation between the acidic and catalytic properties of many inorganic solids. Also, the acid and the basic properties of solid surfaces are interesting aspects of surface structure and important in the fields of ion exchange.

The present work was designed to measure the acidity and the basicity of binary oxides, Zinc oxide and silica gel, in order to test how the catalytic activity correlates with the acid strength of the catalyst. The catalytic decomposition of H_2O_2 by the pure and mixed oxides as well as the electrical conductivity of these oxides have been also studied.

Experimental:

The binary oxides $ZnO-SiO_2$ were prepared in the composition 0,15,30,50,70,85 and 100 mol % ZnO from BDH quality chemical by impregnation technique. The impregnated oxides were dried at 115°C for 5 h. The samples thus obtained were powdered and only such samples were collected

between 100 and 150 mesh sieves were used. The powders thus obtained were calcined at 115, 300, 600 and 1000°C for 5 h. at each one of these temperatures. The samples after calcination were cooled in a desicator and preserved in covered glass tubes under vacuum.

DTA and TGA studies for pure and mixed oxides were carried out using Shimadzu model-30, at a heating rate of 10°K mim^{-1} in air atmosphere, using a 20 mg sample. The surface area of the binary mixed was determined with a surface area measurer B.E.T. micrometer p 2200.

I.R. spectra of the samples were recorded in the range of 200-4000 Cm^{-1} using a Beckman infrared spectra-photometric unit. The KBr disc technique was used in this study. X-ray diffraction patterns of the samples were obtained by using Shimadzu X-ray Diffraction Unit with the aid of Phillips unit type PW2103/00, using copper target and nickel filter. The acidity of the oxides investigated were measured by using the amine titration method developed by Johnson[8]. So 0.2g. of the mixed oxides suspended in benzene was titrated with a solution of 0.1N n-butylamine in benzene using Benzene-azodiphenylamine (pK_a = 1.5), P-dimethylamineazo-benzene (pK_a = 3.3). Benzalnaphthylamine (pK_a = 4.0) and neutral red (pK_a = 6.8) as indicators. The surface acidity of

n-butylamine used in the titration of 1 gm of the oxides investigated is expressed as m-mol.

The surface basicities of oxides were determined by titration method using 0.1N benzoic acid in benzene and bromothymol blue of (pK_a = 7.1) and phenolphthaline of (pK_a = 9.3) as indicators. The value given for each of the surface acidity and basicity is the mean of three experiments.

The decomposition of H_2O_2 was selected for the study on the catalytic reactivity of the catalysts and was conducted as described by Keating[9] in a temperature range of 45 to 65°C.

The electric conductivity of the oxides investigated has been measured by a method was reported elsewhere[10].

Results and discussion:

The DTA and TGA diagrams of ZnO and silica gel SiO_2xH_2O are given in fig.(1). The TGA diagrams for $SiO_2.H_2O$ showed a decrease in the weight at a temperature range of 30-1200°C for all calcined samples. Two endothermic peaks could be characterized by DTA for the silica gel samples. The first small one at about 70°C is attributed to the elimination of water molecules adsorbed on the surface,

while the second peak at ~600°C can be explained on the basis of the transformation of silica gel to SiO_2. This transformation was also observed by others[11,12].

The DTA and TGA diagrams of ZnO fig.(1), show an endothermic peak at 200 to 300°C with a decreasing in the weight (~10%) due to the elimination of water molecules adsorbed on the surface. This loss in the weight decreases with increasing the calcination temperature.

The diagram of $ZnO-SiO_2.xH_2O$ (~1:1 molar ratio) mixtures shows in addition to the peaks obtained in each of ZnO and silica gel a new endothermic peaks at 760°C. This new peak is attributed to a solid state reaction occuring between ZnO and SiO_2 to form Zn_2SiO_4 spinl. However Wolf[13] reported that Zn_2SiO_4 is formed at higher temperature than that found here.

Fig.2. illustrates the X-ray diffraction patterns of the pure and the product of thermal treatment of ZnO and silica gel at different calcination temperatures. It can be seen an amorphous nature for silica gel at all calcined temperatures. Also, the intensive lines of Zn_2SiO_4 spinel (d-values of 3.52, 2.82, and 2.67) could only be dectected for calcined mixtures at 1000°C. This confirm the formation of the spinel at 1000°C.

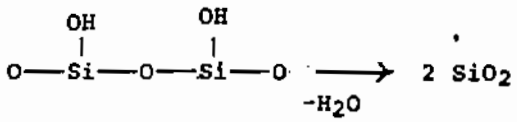
Fig.(3) shows the IR spectra of ZnO, $SiO_2.xH_2O$ and their mixtures ($\sim$1:1 molar ratio) calcined at different temperatures. The figure shows for each sample a band at $\sim$3410 cm^{-1} whose intensity decrease with increasing the calcination temperature. This band was assigned to -OH group[14] present in each of the hydrated ZnO, $SiO_2.xH_2O$ and their mixture. While IR spectra of calcined mixtures (at temperature 125, 300 and 600°C) show the same peaks appeared for each of the individual compounds, the spectra of calcined mixed oxides at 1000°C show new bands in the range 850-950 cm^{-1}. This new bands confirm also the formation of Zn_2SiO_4 at 1000°C as obtained from X-ray results.

The results of surface acidity are shown in fig.(4). It shows a non linear behaviour between the acidity and the composition of the oxides with maxima at 30 and 85 mol % ZnO.

The acidity was found to be increasing with increasing the calcination temperature and reaches a maximum at 600°C before its decreasing again. The decrease in the acidity surface at 1000°C is due to the decrease in the number of SiOH groups present on the surface at 1000°C and/or due to the formation of Zn_2SiO_4 at this temperature as revealed by X-ray analysis.

The surface basicities of $ZnO-SiO_2$ at various compositions are given in fig.(5). It shows a maximum basicities sites at 85 mol. % ZnO. The number of basicities sites increases in the manner observed for acidities i.e. at 600>300>1000°C.

The acidic and basic sites on the surface of SiO_2 can be explained according to the assumption that the acid sites of silica gel which has been dehydrated at high temperatures may be formed by lattice distortions.



As the calcination temperature is raised, a water molecule is removed from two hydroxyl groups attached to silicon atoms at the Si-O-Si link. The Si-O-Si link is readily formed between neighbouring Si-OH groups in the early stages of dehydration, but the distortion between them becomes progressively greater with further dehydration of Si-O-Si link (which is responsible for the acid strength). The increase in the acidic and basic sites by adding ZnO to silica gel is due to substitution of divalent zinc for tetravalent silicon in the silicon lattice. This creates a negative charge at the substituted silicon point on the solid surface -Si-O-Zn-O-Si, which causes an increase in the basicity. On the other hand

due to electrical neutrality, vacancy in oxygen sites may be formed which acts here as acidic sites. This causes also an increase in the acidity which is the case in our results.

The results of surface area measurements are given in table (1). It shows a change in the surface area with changing the oxide composition in a manner similar to that obtained in the results of surface acidity and basicity (except in pure silica gel.).

The results of decomposition of H_2O_2 over $ZnO-SiO_2.xH_2O$ system are shown in fig.(6) and summarized in table (2). The decomposition rate varies with each of the change in the composition and the calcination temperature, higher reactivity is found at 30 and 85 moles % ZnO (which showed also maximum acidity and basicity). It means that the rate of H_2O_2 decomposition depends to a large extent on the number of acidic and basic sites present on the surface of the solid. According to this concept the following mechanism is proposed.

For acidic sites:-

$$A^+ + H_2O_2 \longrightarrow A^+HO_2^- + H^+$$

$$A^+HO_2^- + H_2O_2 \longrightarrow H_2O + O_2 + A^+OH$$

For basic sites:-

$$B^- + H_2O_2 \longrightarrow B^-H^+ + HO_2^-$$

$$HO_2^- + H_2O_2 \longrightarrow H_2O + O_2 + OH^-$$

Where A^+ is acidic site and B^- is basic site, present on the surface. It can be seen that the mechanisms are similar in both cases. HO_2^- formed being responsible for the decomposition ion of H_2O_2.

Electrical conductivity measurements may give us information about the type of charge carriers and the phases formed for the different calcination temperatures. Therefore, the electrical conductivity, σ, of calcined samples ZnO, silica gel and their mixtures was measured as a function of temperature in the range 25 to 600°C. The results obtained are represented by plotting ln σ against $\frac{1}{T}$, a typical plot is shown in Fig.(7). The plots of all calcined samples investigated show the same trend. They show minima and maxima in σ-values for pure silica gel and each one of the mixed oxides, while the plots of the pure ZnO show only a minimum in σ-values. The maxima in σ-values appearing at all samples investigated, except pure ZnO, at $\sim$ 370°C should be attributed to the presence of silica gel in the sample.

The observed decrease in σ-values with increasing the temperature, in the lower temperature range can be attributed to the elimination of adsorbed water molecules present in the samples investigated. The conductivity data of the pure oxides calcined at 1000°C was found to be good coincide with those reported in the literature[14,15,16].

Since the samples investigated are heterogeneous many non linear plots for the relation $\ln \sigma$ vs. $\frac{1}{T}$ are obtained. The activation energies are calculated using Arrhenius equation from the linear parts in these plots. The conductivity results are summarized and given in table (3). From which it can be seen a decrease in E_a-values with increasing SiO_2 contents in the samples calcined at 1000°C. This may be attributed to the formation of Zn_2SiO_4 in these samples at 1000°C.

References

1- D. Dollimore and T.E. Jones, J. Appl. Chem. Biotechnol, 23 (1973) 29.

2- M.E. Dry and F.S. Stone. Discuss. Faraday Soc., 28 (1955) 192.

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

4- B. Bracconic and I.C. Dufour, J. Phys. Chem. 79 (1975) 2395.

5- K. Tanabe, "Solid Acids and Bases", Academic press, New York, (1970).

6- S.P. Walker and A.B. Halgeri, J. Ind. Chem. Soc., 50 (1973) 387.

7- M.A. Mousa, E.M. Diefallah. A.A. Abdel Fattah, Z.A. Omran, Journal of Materials Science, 25, (1990) 367.

8- O. Johnson, J. Phys. Chem., 59 (1955) 827.

9- K.B. Keating, M. Matsumoto and Koboyashi, J. Catal., 21 (1971) 48.

10- M.A. Mousa, E.A. Gomaa, A.A. El-Khouly, Mater. Chem. Phys., 11 (1984) 433.

11- G.J. Young., J. Collid. Sci., 13 (1958)) 67.

12- E.Naruko and H. Kogyo, J. Phys. Chem. 67 (1964)2019.

13- H.J. Emeleus and A. Wolf, J. Chem. Soc.,164 (1950).

14- A.R. Hulzon, J. Chem. Solids, 8, 467 (1959).

15- A.M.Miller, Phys. Rev. 60, 890 (1941).

16- J. Corella, J. Bilbao and M. Pilar, J. Indian Soc., 518, (1981).

Table (1): Surface area (m^2/g) of ZnO-SiO_2.

Calc. Temp.	100% ZnO	85% ZnO	70% ZnO	50% ZnO	30% ZnO	15% ZnO	100% SiO_2
600	2.2	122	80.9	87	153	132	230

Table (2): Rate constants of H_2O_2 decomposition over ZnO - SiO_2 system at different calcination temperatures.

Calc. temp. °C	300°C						600°C						1000°C					
	45°C		55°C		65°C		45°C		55°C		65°C		45°C		55°C		65°C	
Composition	$k\times10^4$ min^{-1}	r	$k\times10^4$ min^{-1}	r	$k\times10^4$ min^{-1}	r	$k\times10^4$ min^{-1}	r	$k\times10^4$ min^{-1}	r	$k\times10^4$ min^{-1}	r	$k\times10^4$ min^{-1}	r	$k\times10^4$ min^{-1}	r	$k\times10^4$ min^{-1}	r
0% ZnO	1.954	0.999	2.521	0.999	3.299	0.995	1.753	0.999	2.682	0.997	3.367	0.997	1.446	0.991	1.741	0.991	2.187	0.9
15% ZnO	3.519	0.996	4.139	0.970	4.993	0.999	4.648	0.999	5.002	0.997	7.436	0.999	2.889	0.991	3.851	0.991	5.539	0.9
30% ZnO	6.281	0.994	7.429	0.999	8.019	0.996	7.491	0.989	8.541	0.995	10.458	0.995	4.591	0.946	5.216	0.996	6.389	0.9
50% ZnO	3.853	0.893	4.599	0.996	5.393	0.996	4.872	0.994	6.193	0.993	7.999	0.964	3.654	0.992	3.829	0.991	4.838	0.9
70% ZnO	5.281	0.989	7.276	0.999	8.922	0.996	5.921	0.991	8.329	0.996	8.529	0.998	5.147	0.996	6.415	0.996	8.769	0.9
85% ZnO	6.918	0.996	8.459	0.992	10.765	0.992	6.886	0.955	10.078	0.986	11.909	0.998	6.174	0.989	7.056	0.996	10.057	0.9
100% ZnO	3.749	0.995	4.182	0.989	5.003	0.985	3.496	0.998	3.569	0.988	4.583	0.989	3.416	0.994	3.735	0.997	4.598	0.9

r Regression coefficient.

Table (3): Electrical conductivity Data of ZnO - SiO_2-xH_2O system.

Calc. temp.	600°C					1000°C				
	T_b	before T_b		after T_b		T_b	before T_b		after T_b	
Comp.		E_{a_1} $kJ.mol^{-1}$	r	E_{a_2} $kJ.mol^{-1}$	r		E_{a_1} $kJ.mol^{-1}$	r	E_{a_2} $kJ.mol^{-1}$	r
100% ZnO	190	55.249	0.9759	104.990	0.9967	120	22.586	0.9702	67.783	0.9988
85% ZnO	140	26.884	0.8328	155.933	0.9835	140	9.897	0.9058	118.344	0.9203
70% ZnO	100	30.402	0.9805	101.144	0.9806	100	34.715	0.9292	117.072	0.9898
50% ZnO	180	34.926	0.9197	122.888	0.9679	200	48.000	0.8480	73.115	0.9905
30% ZnO	200	32.684	0.8626	42.887	0.9453	200	55.023	0.9561	66.039	0.9469
15% ZnO	140	25.357	0.9277	48.357	0.9910	200	32.255	0.8686	68.106	0.9883
0% ZnO	260	32.887	0.9280	76.636	0.9492	120	36.466	0.9877	43.150	0.9498

T_b break temp.

r regression coefficient.

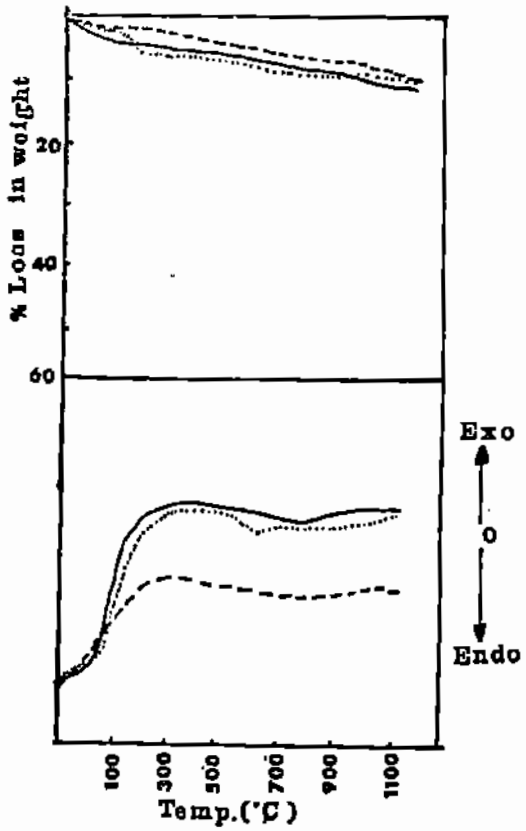


Fig.(1): DTA—TGA of $ZnO-SiO_2$ system calcined at 300°C
ZnO(— — —), $ZnO-SiO_2$(——), SiO_2(····)

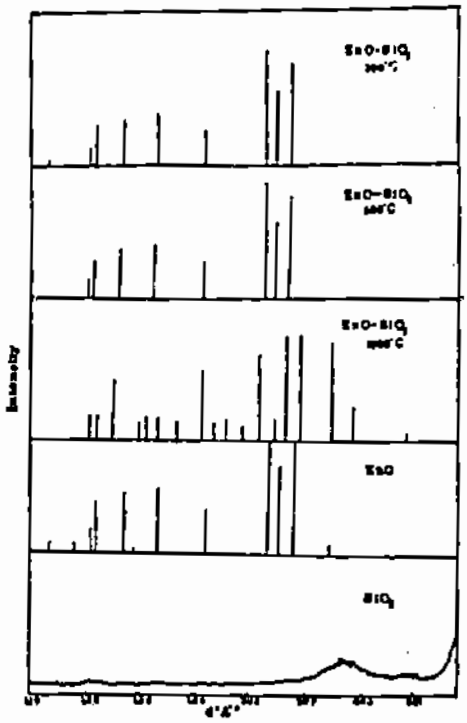


Fig.(2): X-ray diffraction patterns for ZnO-SiO system calcined at different temperatures.

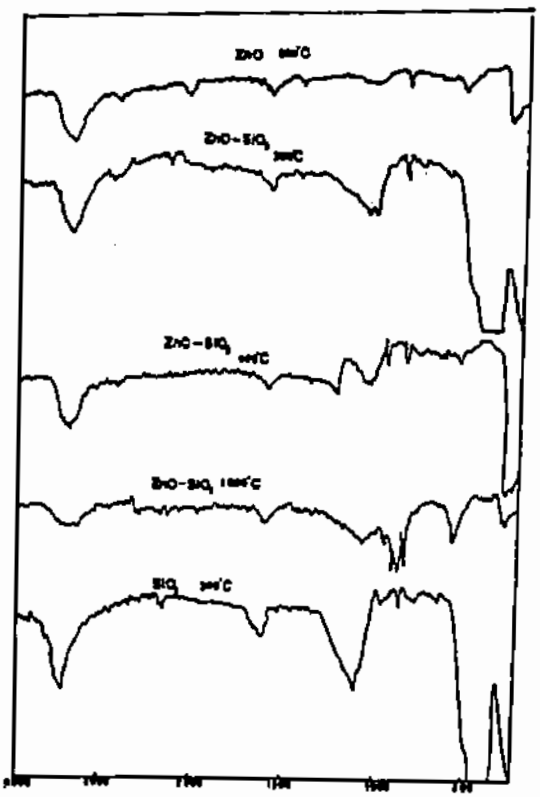


Fig.(3): I.R of $ZnO-SiO_2$ system calcined at different temperature.

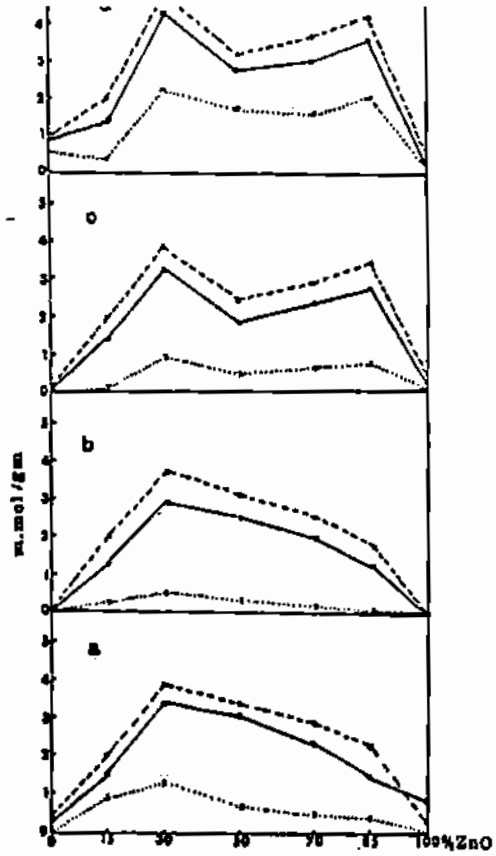


Fig.(4): Effect of composition on acidic properties of ZnO–SiO_2 for a – $pK_a = 1.5$ b – $pK_a = 3.3$ c – $pK_a = 4.0$ d – $pK_a = 6.8$ (• 300°C, ▪ 500°C, ▲ 1000°C)

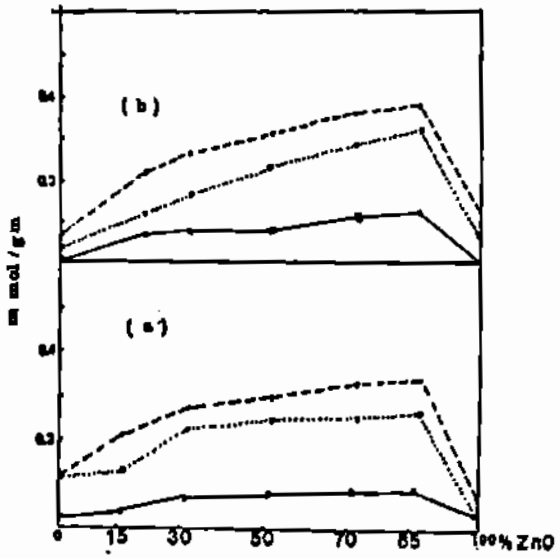


Fig.(5) The variation of basicity with the composition and calcination temperature. (a) $pK_a = 7.1$, (b) $pK_a = 9.3$ (• 1000°C, ▪ 500°C, ▲ 300°C.)

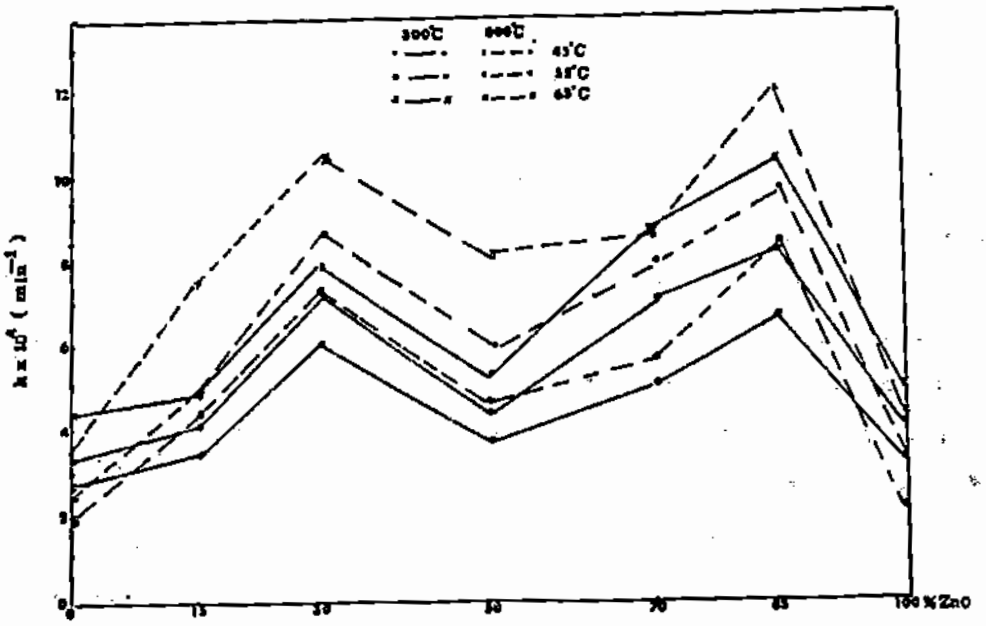


Fig.(6): Variation of rate constant of H_2O_2 decomposition on $ZnO-SiO_2$ system calcined at different temperature.

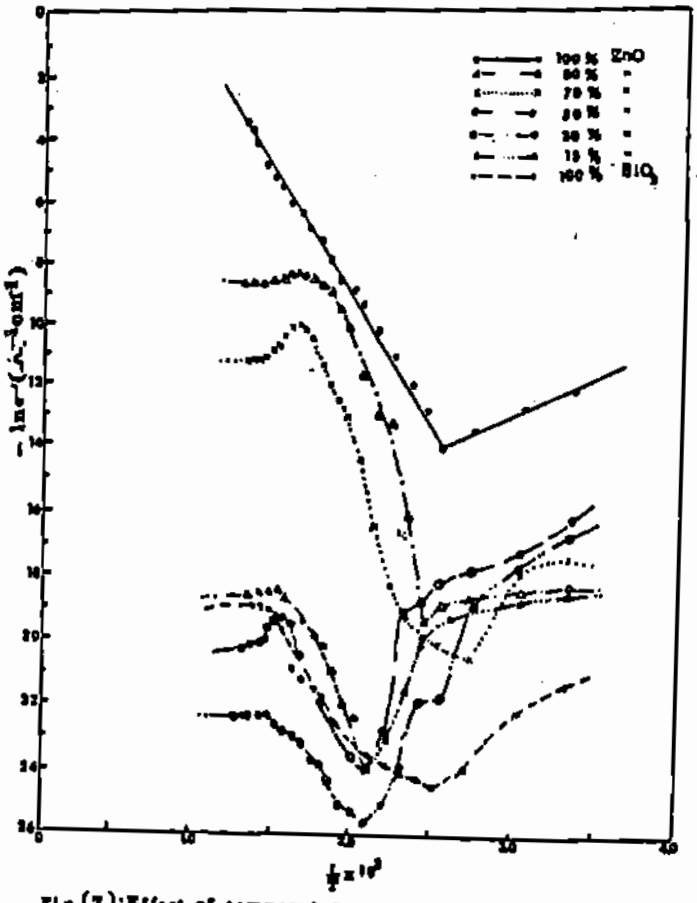


Fig.(7): Effect of temperature on the electrical conductivity of $ZnO-SiO_2$ x H_2O system calcined at 1000°C .

Women's coll. Ann.Rev.
Vol. 18 (1993).

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 $2^o min^{-1}$ 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).

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

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

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

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

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

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

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

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

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°C(15).

The x-ray diffraction patterns for the mixtures heated at 1000°C 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°C. 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°C 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°C, 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°C 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. Biotechnol., 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).

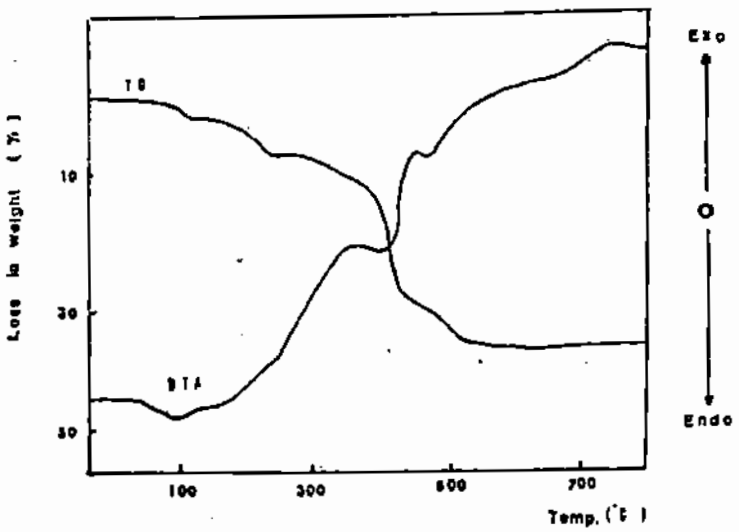
TG
DTA
Loss in weight (%)
10
30
50
100
300
500
700
Temp. (°C)
Exo
O
Endo

Fig 1

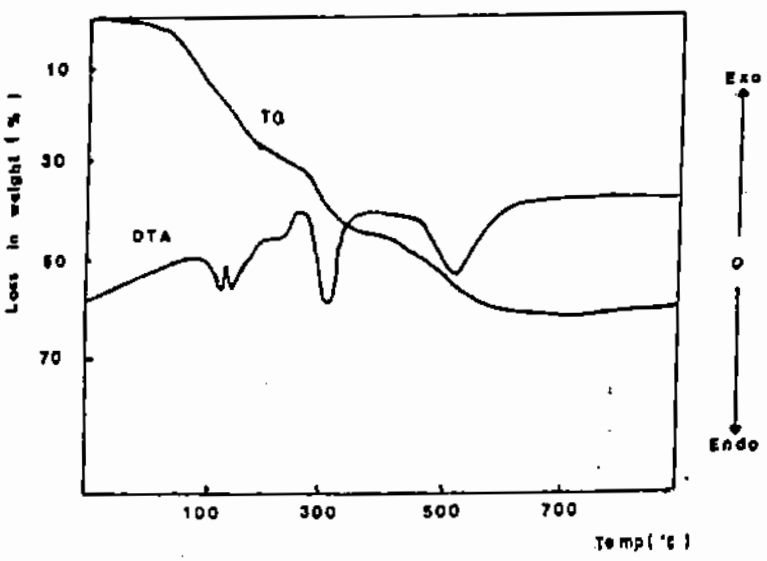
TG
DTA
Loss in weight (%)
10
30
50
70
100
300
500
700
Temp (°C)
Exo
O
Endo

Fig 2

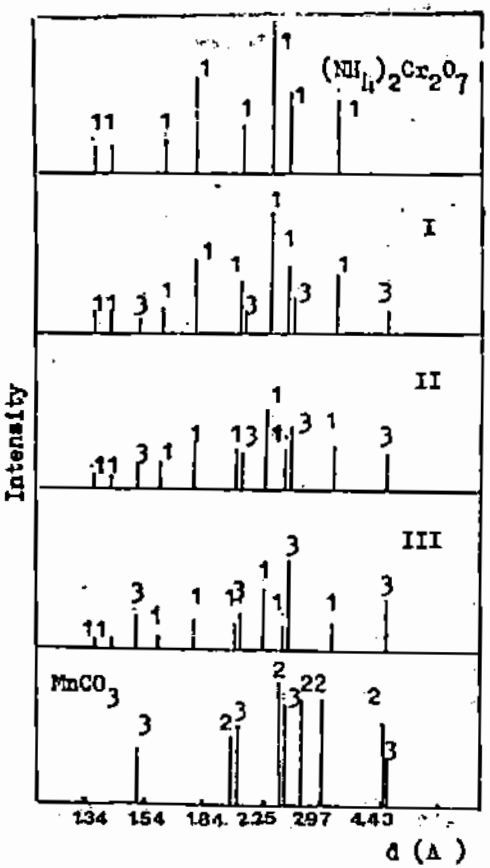

Fig 5

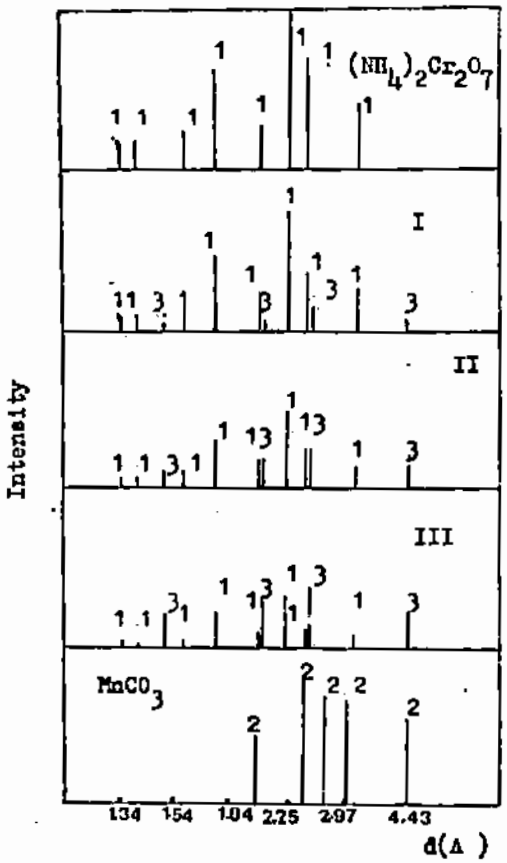

Fig 4

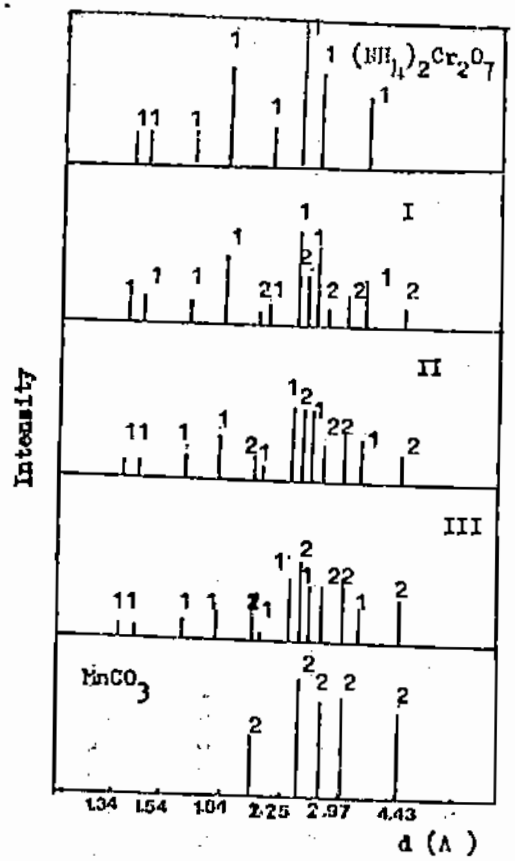

Fig 3

Absorbance
3000
2000
1500
500
Wave number(Cm⁻¹)
$(NH_4)_2Cr_2O_7$
I
II
III
$MnCO_3$
0

Absorbance
3000
2000
1500
500
Wave number(Cm⁻¹)
$(NH_4)_2Cr_2O_7$
I
II
III
$MnCO_3$

Fig 9

Absorbance
3000
2000
1500
500
Wave number(Cm⁻¹)
$(NH_4)_2Cr_2O_7$
I
II
III
$MnCO_3$

Absorbance
3000
2000
1500
500
Wave number(Cm⁻¹)
$(NH_4)_2Cr_2O_7$
I
II
III
$MnCO_3$

Fig 8