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STUDIES ON THE HETEROGENEOUS REACTION BETWEEN ZnO-$(NH_4)_2O.4MoO_3$

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ABSTRACT

The formation of $ZnMoO_4$ and $Zn_3Mo_2O_9$ were studied using x-ray diffraction analysis, IR, DTA-TG, electrical conductivity, elemental analysis and surface acidity measurements. The concentration of acidic sites on the surface of MoO_3-ZnO system was studied and the results illustrated a maxima at ZnO – MoO_3 (20-80%) at a calcination temperature of 600^0C.

The stability of the $ZnMoO_4$ and $Zn_3Mo_2O_9$ phases were studied at 600 and 750^0C. The $Zn_3Mo_2O_9$ phase is stable at lower temperature and disappears at temperatures above – 700^0C

1. INTRODUCTION

The intrusion of ZnO in the mixed MoO_3 – ZnO systems changes the physical and chemical characteristics of the system especially the acidity and the electrical conductivity. In fact, all actual crystalline materials are not perfect, mistakes produced in the structure, called defects, have a strong influence upon many properties of these crystals with regard to their electrical conductivity and reactivity(1-7)

Many types of defects can be present in the texture of the crystal lattice of solids. In surface defects, the external surface of the solid has an energy and the structure differs than that of the bulk of the solid. These effects indicate that the material gains certain physical properties such as catalytic activity due to the defects present on the surface(8) .

Many investigations have been devoted to the study of the solid state reaction, crystal structure, surface acidity and electrical conductivity of various mixed oxides(9-10). Magneli et al. (11) studied the $V_2O_5.MoO_3$ system. They noted that all of the intermediate preparations have a grayish black colour, contrarily to the colours of the pure oxides. The change in the colour might be due to the existence of a state of resonance among the vanadium and molybdenum atoms.

In the present work, we have studied the change in the physical properties by the formation of a new compound from the mixed oxides of ZnO and MoO_3.

Experimental:

The binary oxides MoO_3-ZnO were prepared by the impregnation technique in the composition 15:85, 50:50 and 85:15 mol.% of $(NH_4)_2O.4MoO_3$-ZnO respectively, from BDH chemical quality. The samples are designated as sample I, II and III respectively. The impregnated oxides were dried at 115^{0}C for 5 hours. The samples were then ground and only the samples which were collected between 100-200 mesh series were used. The powdered samples thus obtained were calcined at 600 and 750^{0}C for 5 hours at each temperature.

After the calcination, the samples were cooled in a dessicator and kept in a covered glass tube under vacuum. X-ray diffraction patterns of the samples were taken by the aid of Philips Unit, Type PW 2103/00 using a copper target and a nickel filter, and were investigated. IR spectra of the samples were recorded using a Beckman infrared spectrophotometric unit. The KBr disc technique was used in this study. DTA and TGA experiments were conducted using the DTA Schimadzu model 30 at a heating rate of 10^{0}C. min^{-1} in atmospheric air, using a 20mg sample.

The acidity measurement was realised by the amine titration method developed by Johnson(12). Benzol acetophenone (pK_a=-5.6),Dicinimal acetone (pK_a=-3.0), Benzene azodiphenylamine (pK_a=3.3) p-dimethylamino azo benzene (pK_a=3.3) were used as indicators. The electrical conductivity has been measured by a method reported elsewhere(13). The elemental analysis results and the symbols given for the investigated compounds are listed in Table (1).

Table (1): The analytical data of the investigated compounds

Molecular Formula	Calculated			Theoretical		
	Zn%	Mo%	O%	Zn%	Mo%	O%
$ZnMoO_4$	29.0	42.55	28.39	29.01	42.58	28.41
$Zn_3Mo_2O_9$	365.80	37.24	71.98	36.86	37.36	72.01

Results and Discussion:

Fig. (1) shows the x-ray diffraction patterns of the pure $(NH_4)_2O.4MoO_3$ and ZnO and their products of thermal treatment at 600 and 750^{0}C. The x-ray diffraction patterns of $(NH_4)_2O$. $4MoO_3$ which were calcined at 600^0C showed that, there were 2 phases presents at 600^0C MoO_3 (14) and Mo_9 O_{26}(15) . It can be seen that at a calcination temperature of 750^0C only the intensive line of MoO_3 (d-values of 4.56, 3.45, 2.53, 1.99 and 1.86nm), could be detected(14).

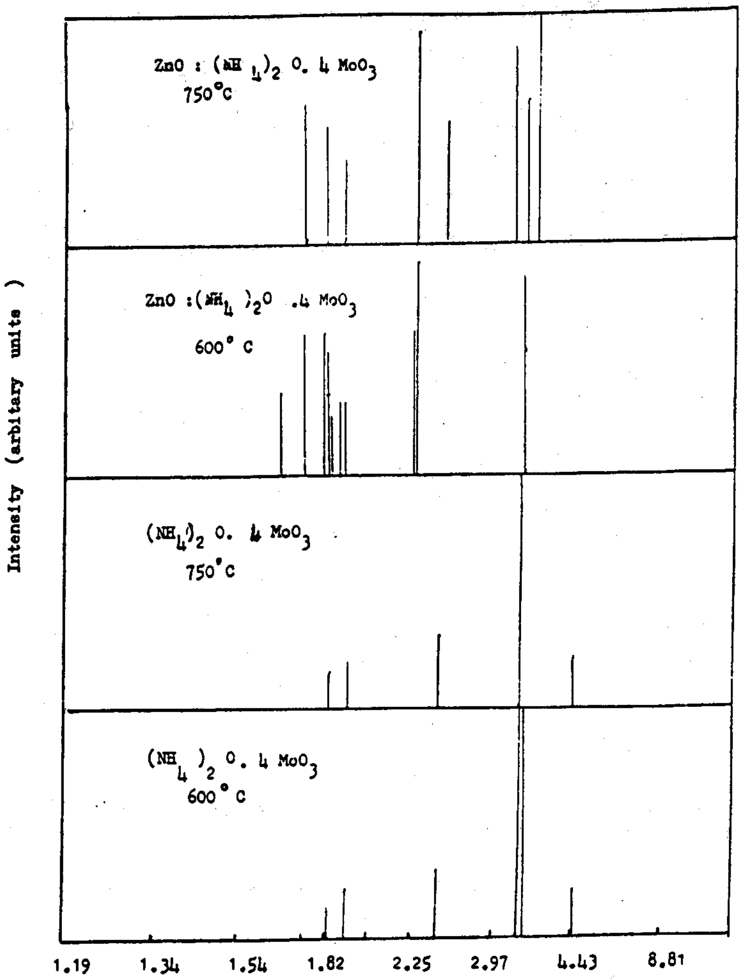

Fig.1: X-ray diffraction patterns of $(NH_4)_2.4MoO_3$ and $(NH_4)_2.4MoO_3$ and ZnO (1:1 molar ratio).

X-ray analysis of the ZnO-MoO_3 (1:1 molar ratio) showed that in the oxide mixture calcined at 600^0C, 4 phases were present as a result of the starting materials and the $Zn_3Mo_2O_9$(16), $Zn_3Mo_2O_9$(16) and $ZnMoO_4$(17) structures were formed. On the other hand, for the samples which were calcined at 750^0C, the X-ray analysis showed that only 3 phases were present as a result of the starting materials and the $ZnMoO_4$ structure (d-values 3.89, 3.6, 3.35, 2.68, 2.31, 1.98, 1.86 and 1.77 nm) could be detected, which is referred to the formation of the $ZnMoO_4$ at 600^0C. The $Zn_3Mo_2O_9$(16) structure which was changed to Zn Mo O_4(17) was the stable one at temperatures higher than 750^0C.

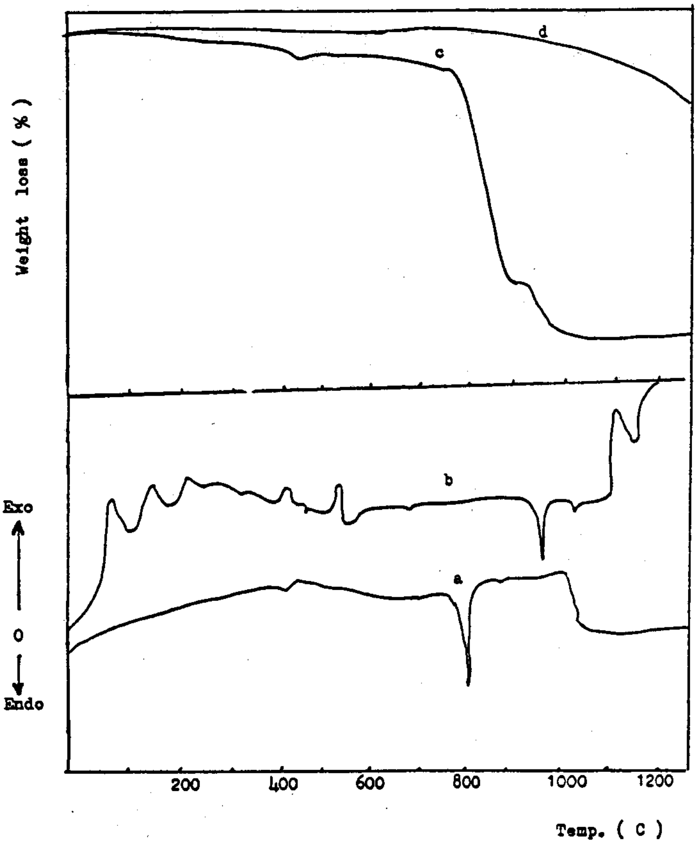

Fig. 2: DTA and TG of $(NH_4)_2.4MoO_3$ and $(NH_4)_2.4MoO_3$ –ZnO system.
a-DTA for $(NH_4)_2.4MoO_3$.
b-DTA for $(NH_4)_2.4MoO_3$-ZnO(1:1 molar ratio)
c-TG for $(NH_4)_2.4MoO_3$.

Fig. (2) represents the DTA-TG diagrams for pure $\{(NH_4)_2O\cdot 4MoO_3\}$ and $\{(NH_4)_2O.4MoO_3 - ZnO\}$ system. The DTA diagram (a) in fig. (2) shows that for $(NH_4)_2.4MoO_3$ there are three peaks at 450, 810 and 1000^{0}C. The first endothermic peak is due to the elimination of water and ammonia molecules, while the second endothermic peak corresponds to the melting of MoO_3(18). The last endothermic peak around 1000^{0}C is due to the evaporation process of the melted MoO_3(18).

For $\{(NH_4)_2O.4MoO_3 - ZnO\}$ system, DTA diagram (b) in Fig. (2) shows an exothermic peak corresponding to the first exothermic peak in the DTA diagram for $(NH_4)_2O.4MoO_3$. This peak is followed by a small sharp exothermic peak at 540^{0}C which is mainly due to the oxidation of Mo^{5+} to Mo^{6+} (i.e. Mo_9O_{25} to MoO_3). There is a small broad exothermic peak around 750^{0}C corresponding to the formation of $Zn_3Mo_2O_9$ followed by a small endothermic peak 690^{0}C which is mainly due to the formation of $ZnMoO_4$. The large endothermic peak around 980^{0}C is mainly due to the melting of the unreacted MoO_3(18). This is followed by a small endothermic peak at 1040^{0}C due to the evaporation of the melted MoO_3(18).

The thermogravimetry curve (c) in Fig. (2) for pure $(NH_4)_2O.4MoO_3$ shows a first step for the elimination of water and ammonia molecules in the temperature range between 400-450^{0}C, with an observed weight loss of 8% which is in good agreement with the theoretical value. The second step in the TG curve (c) is attributed to the melting of MoO_3(18), followed by the third and fourth step of losses which may be due to the boiling and evaporation of melted MoO_3.

The examination of the IR spectra (Fig. 3 and 4) of $(NH_4)_2O.4MoO_3$ and its mixtures with ZnO: There are two bands representing the Mo_9O_{25} and MoO_3 arising from the calcination of the $(NH_4)_2$ $O.4MoO_3$ at 600^{0}C. One of these bands reflecs a sharp absorption at 960 cm^{-1} and a broad band at 910 cm^{-1} .

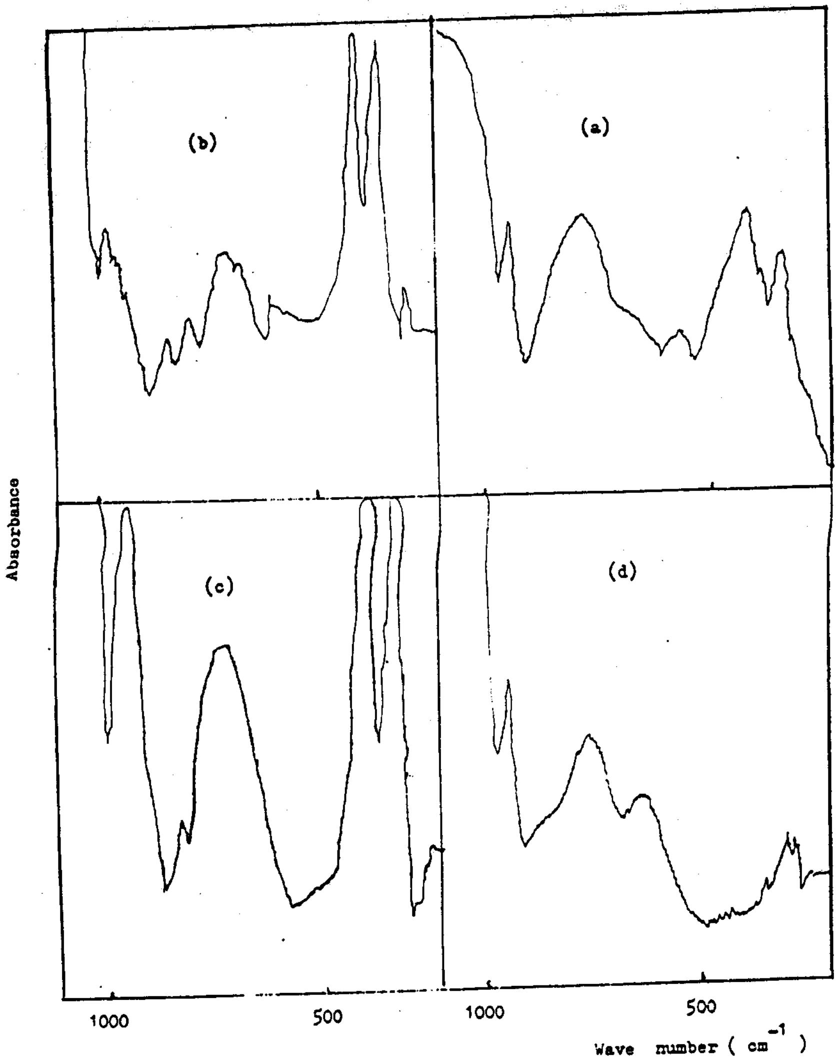

Fig. 3: IR-spectra of $(NH_4)_2.4MoO_3$ and its mixtures with ZnO at 600^0C
a-$(NH_4)_2.4MoO_3$.
b-$(NH_4)_2.4MoO_3$:ZnO (1:1 molar ratio).
c-$(NH_4)_2.4MoO_3$:(1:5 molar ratio).
d-$(NH_4)_2.4MoO_3$:ZnO (5:1 molar ratio).

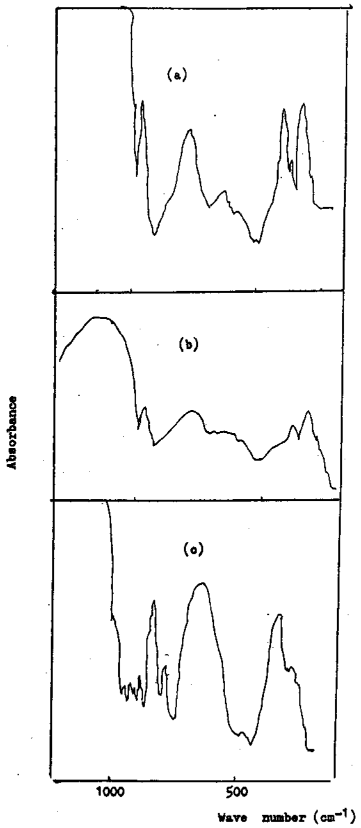

Fig. 4: IR-spectra of $(NH_4)_2.4MoO_3$-ZnO mixture at 750^{0}C.
a-$(NH_4)_2.4MoO_3$:ZnO (5:1 molar ratio).
b-$(NH_4)_2.4MoO_3$:ZnO (1:1molar ratio).
c- $(NH_4)_2.4MoO_3$:ZnO (5:1molar ratio).

The addition of 20, 50 and 80 mole % of ZnO to $(NH_4)_2O.4MoO_3$ heated to 600^{0}C causes a shift of the sharp absorption band from 960 cm^{-1} to 980, 970 and 985 cm^{-1} respectively, the broad bands are shifted to 920, 915 cm^{-1}. Increasing the calcination temperature to 750^{0}C with the same ratios of ZnO which were added to $(NH_4)_2O.4MoO_3$ causes a large shift of the sharp absorption band at 960 to 990, 980 cm^{-1} and splitting of the third band for the ratio (80 mole % ZnO) into 3 sharp bands due to the formation of a new compound between MoO_3 and ZnO catalysts, arised mainly from the transformation of ($Zn_3Mo_2O_9$) into the more stable compound ($ZnMoO_4$).

Acid amounts of various acid strengths of $(NH_4)_2O.4MoO_3$ –ZnO and samples I,II and III calcined at various temperatures are given in Fig.(5), $(NH_4)_2O.4MoO_3$ and ZnO oxides calcined at 600°C showed an acid strength of Ho ≤ -3.3 which is larger than that of $(NH_4)_2O.4MoO_3$ and ZnO products calcined at any other temperatures. The effects of ZnO content on the acidity of $(NH_4)_2O.4MoO_3$.calcined at 600°C are shown in Fig. (5). The maximum acidity sites were observed at 20 mol % ZnO. This could be a result of the substitution of Zn^{2+} instead of Mo^{6+}. The acidities of the mixed oxides containing 50 and 80 % ZnO molar ratios were smaller due to the formation of the new compounds $Zn_3Mo_2O_9$ and $ZnMoO_4$. For all the samples investigated the acidity was found to decrease with increasing calcination temperature up to 750° C.

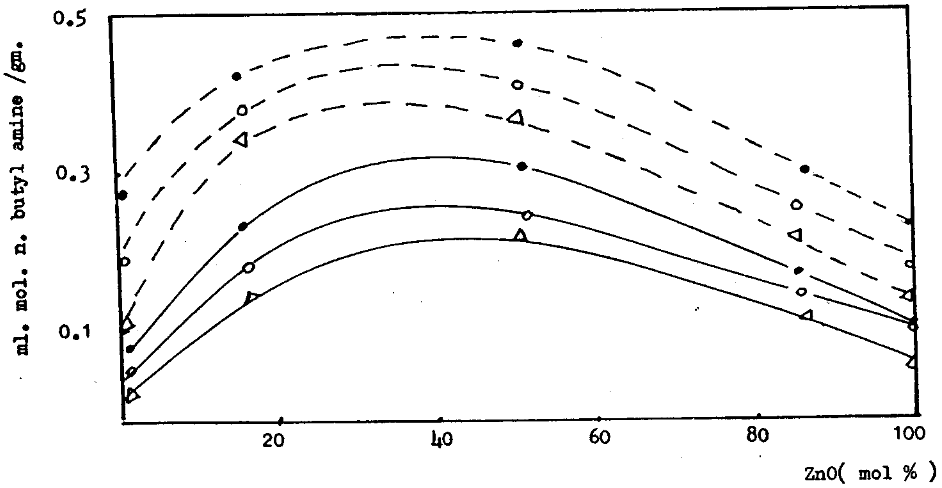

Fig. 5: Effect of composition on acidic properties of $(NH_4)_2.4MoO_3$-ZnO system at 600°C (......) and 750°C (----).

- $pK_a = +1$, (o) $pK_a = -3$( ) $pK_a = -5.3$

When, a certain ZnO concentration, corresponding to a maximum Zn^{2+} is reached, the ZnO will become apart from the MoO_3-ZnO surface, while the excess will precipitate as ZnO in the form of an independent layer with a lower acidic character than that of MoO_3-ZnO.

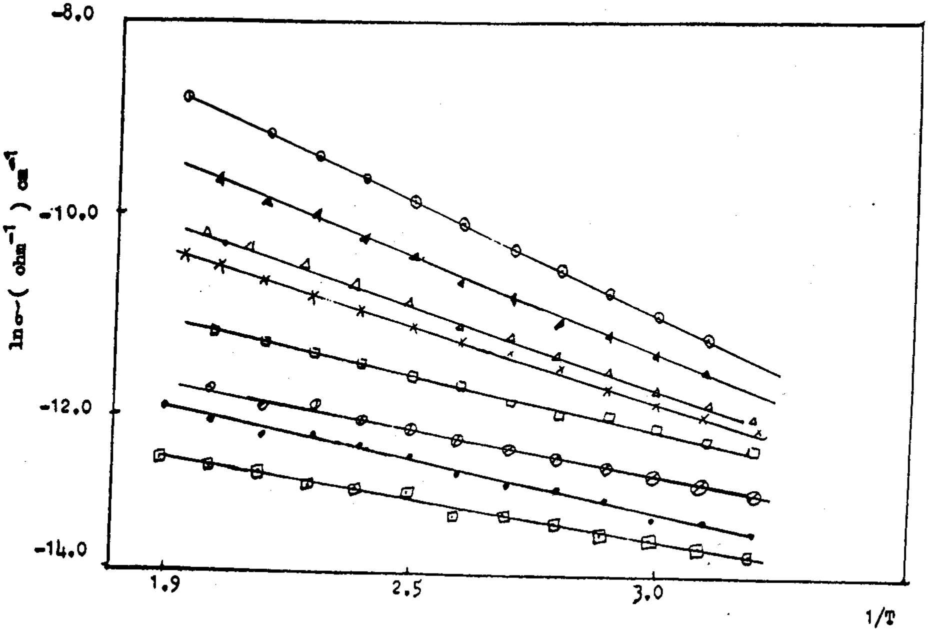

Fig. 6: Effect of temperature on the electrical conductivity of $(NH_4)_2.4MoO_3$ and its mixtures with ZnO.

The electrical conductivity of $NH_4O.4MoO_3$-ZnO and their mixtures give a good information about the type of charge carriers and the phases formed at different calcination temperatures. The results obtained are represented by plotting σ against 1/T, a typical plot is shown in fig. (6). The plots of all of the calcined samples investigated, showed straight lines with different slopes. The electrical conductivity increases with increasing temperature in an exponential manner, which are shown in the semiconducting behavior. The electrical conductivity for $(NH_4)_2O.4MoO_3$ increases by adding a 20% molar ratio of ZnO calcined at 600^0 due to the n-type semiconducting. The nature of ZnO, the quasi-free electron concentration can be increased by the addition of $Zn^{2+}O^{2-}$to Mo^{6+} ion which may change to Mo^{5+} ion: In the same way, the addition of relatively small quantities of MoO_3 of 20% molar ratio to ZnO will effect its activity by acting on the electron mobility. The electrical conductivity decreases by increasing calcination temperature due to the decrease in the number of quasi-free electrons by the formation of a more stable $ZnMoO_4$ compound at a higher temperature.

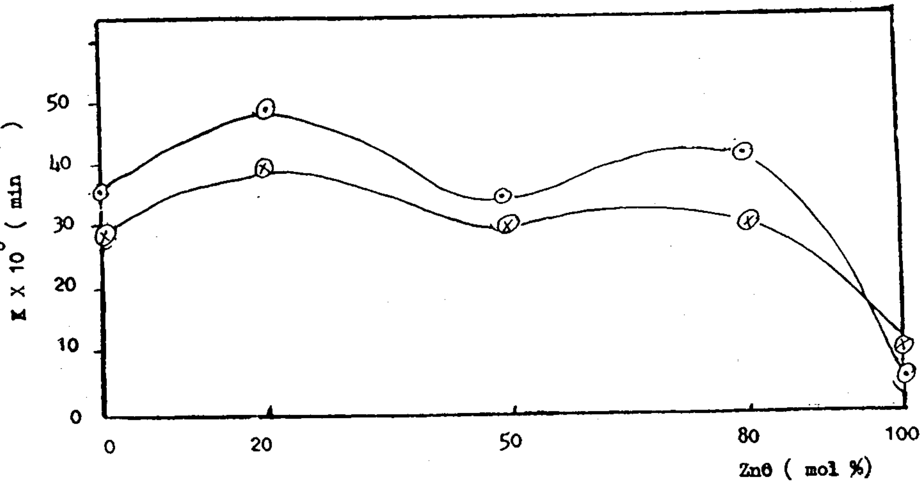

Fig.7: Effect of composition and calcination temperature on the decomposition rate of H_2O_2 $\{(O)750^0C, (x)600^0C\}$

The results of the decomposition of H_2O_2 over $(NH_4)_2O.4MoO_3$-ZnO are shown in fig. (7). The results show that the ZnO is less active than the pure $(NH_4)_2O.4MoO_3$. The rate of H_2O_2 decomposition has a maximum value at 20% ZnO due to the biggest number of electrons trapped. The presence of vacant Oxygen ion site by n-type semiconductor for ZnO and an impurity of higher oxidation state cation Mo^{6+}.

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