

Characterization and Catalytic Properties of a Series of CuO-MoO₃ Mixed Oxides

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A SERIES of single and mixed oxides of CuO-MoO₃ system were prepared by thermal treatment of pure and mixed basic copper carbonate and ammonium molybdate tetrahydrate solids. The thermal behavior of the pure and binary salts has been studied using thermal analysis (TG-DTA) technique. The thermal products were characterized using the X-ray diffraction analysis. The results revealed that, pure solids decomposed to CuO, MoO₃ and Cu₂O phases at 250, 340 and 1000°C respectively. Solid-solid interaction takes place between single oxides forming different phases of copper molybdate depending on treatment temperature and mixture composition. The degree of crystallinity of detected phases affected by calcination temperature solids and composition. The catalytic activity of single and binary oxides was tested in decomposition of hydrogen peroxide as a model reaction. The catalytic activity of mixed oxides was found to be higher than that of single oxides at different treatment temperature. The mechanism of decomposition reaction over the prepared oxides was discussed.

Keywords: CuO-MoO₃, Thermal analysis, X-ray, Catalytic activity, H₂O₂.

Introduction

The decomposition reactions of various compounds are of major importance because of their frequent applications in calcination in metallurgy and in the production of large-surface materials for sorbents and catalysts [1-2]. The so-called mixed catalysts are often produced by thermal decomposition of mixed components of transition metals [3-4]. The thermal treatment of mixed solids may also lead to the formation of new compounds as a result of solid-solid interaction between the thermal products [5-6]. The compound formed may have new physicochemical and catalytic properties better than that of the pure components. Therefore, the catalytic activities of mixed catalysts were often much higher than the activities of mechanical mixtures of the same composition [7-8].

A great deal of fundamental research has been done on the mixed oxides in the field of heterogeneous catalysis. The results show that the combination of two oxides leads to new system with new physical and chemical properties [9-10].

The present work reports a study of the thermal behavior of pure and mixed solids of basic copper carbonate and ammonium molybdate tetrahydrate as well as the effect of chemical composition and calcination temperature on the course of solid-solid interactions between the thermal products. The pure and mixed solids were thermally treated at 500, 750 and 1000°C. The starting materials and the mixtures were characterized by means of thermal analyses (TG-DTA), and the thermal products of the starting materials and the mixtures were characterized by X-ray diffraction (XRD) techniques. The catalytic activity of pure and mixed CuO-MoO₃ prepared at different temperatures was measured by using hydrogen peroxide decomposition as a model reaction at 30, 40 and 50°C. The mechanism of decomposition reaction over the prepared oxides was discussed.

Experimental

Materials

The starting materials were solids of basic copper carbonate; CuCO₃.Cu(OH)₂

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and ammonium molybdate tetrahydrate; $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$. The chemicals employed were supplied by PROLABO Company.

Pure copper and molybdenum oxides were prepared by heating their solids separately at 250°C in air for 4 hr. The same heating process was performed at other temperatures namely, 500°, 750° and 1000°C.

The binary CuO-MoO_3 with molar ratios of the precursor of 3:1; 1:1; and 1:3 were prepared by mixing the materials, homogenizing and grinding. The produced powders were thermally treated by gradual increase of temperature to 250°C, and kept in air at that temperature for 4 hr. The same heating process was performed at other temperatures namely, 500°, 750° and 1000°C.

Techniques

Thermal analyses (TG-DTA) of pure and mixed solids were carried out using Shimadzu DTA-50H systems. The rate of heating was kept at 10°Cmin⁻¹. The analysis was followed up at temperatures between room temperature and 1000 °C with $\alpha\text{-Al}_2\text{O}_3$ as a reference material. A 40mg sample of each solid specimen was employed in each case. The measurements were carried out in a current of nitrogen flowing at a rate of 50 cm³ min⁻¹.

An X-ray investigation of pure and mixed solids preheated in air at 500, 750 and 1000°C was conducted using a Philips diffractometer (type PW 1390). The patterns were run with copper $\text{K}\alpha_1$ with secondly monochromator ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 40 mA.

The catalytic activity of individual and mixed solids obtained at different calcination temperatures was determined using H_2O_2 decomposition in aqueous solution at 30, 40 and 50°C using 0.5ml of H_2O_2 of known concentration diluted to be 20ml with distilled water. The

mass of catalyst sample taken in each kinetic experimental was fixed at 10mg for all samples. The reaction was followed up through a gasometric measurement of oxygen liberated at different time intervals till no further O_2 was liberated [10].

Results and Discussion

The thermal behavior of pure solids

Figure 1-a shows the process of thermal decomposition of pure basic copper carbonate. DTA-curve shows one strong and sharp endothermic peak, its minimum located at about 291.5°C [2].

TG represents one step for this process. This step is located in temperature range 220-305°C with percentage weight loss of 27.95%.

Figure 1-b illustrates thermal analyses curves of pure ammonium molybdate tetrahydrate. DTA- curve shows five endothermic peaks with their minima being located at 115°,160°,235°, 280°, and 790°C

TG- curve reveals five stages for the process of thermal decomposition of ammonium molybdate [11] which are located in the temperature ranges, 100-140°C, 175°-235°C, 275-298°C, 320°-340°C and $\geq 340^\circ\text{C}$ with percentage weight losses, 6.70, 11.10, 16.50, 17.20 and 18.50% , respectively.

Thermal behavior of mixed solids

Figures 1-c & 1-d represent thermal decomposition of the mixed solids of basic copper carbonate and ammonium molybdate tetrahydrate with molar ratios, 3:1 and 1:3, respectively. The peak of DTA-curves located at 303°C refers to decomposition of copper carbonate to copper oxide. The other peaks point to decomposition of ammonium molybdate to its different phases. The last peak (330°-350°C) refers to the formation of molybdenum oxide [11].

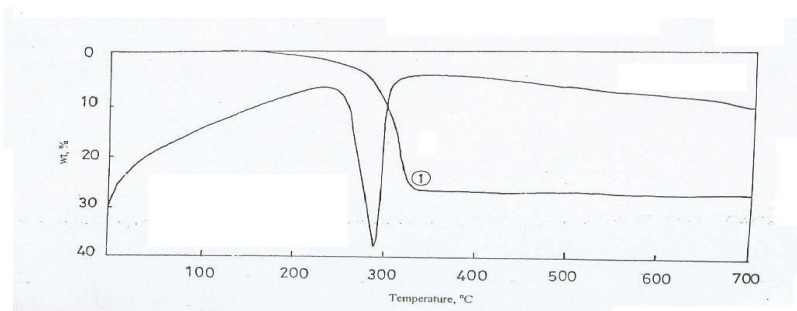


Fig. (1-a) Thermal analysis (DTA and TG) of pure basic copper carbonate.

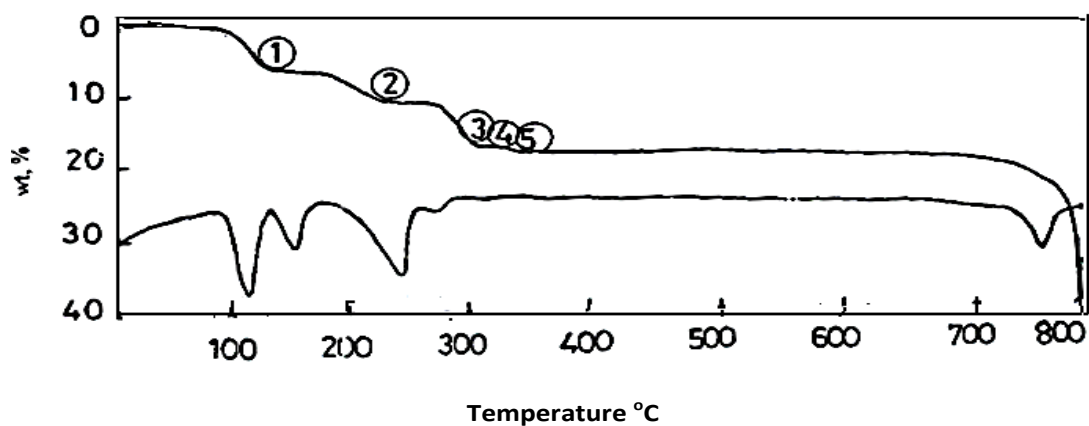


Fig.(1-b) Thermal analysis (DTA and TG) of pure ammonium molybdate tetrahydrate

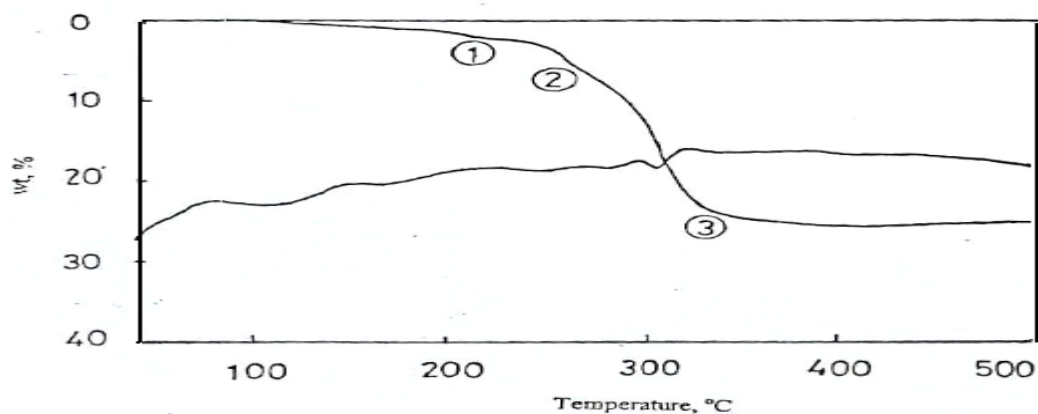


Fig.(1-c). Thermal analysis (DTA and TG) of mixed solids with molar formula $[3/2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 : 1/7(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$.

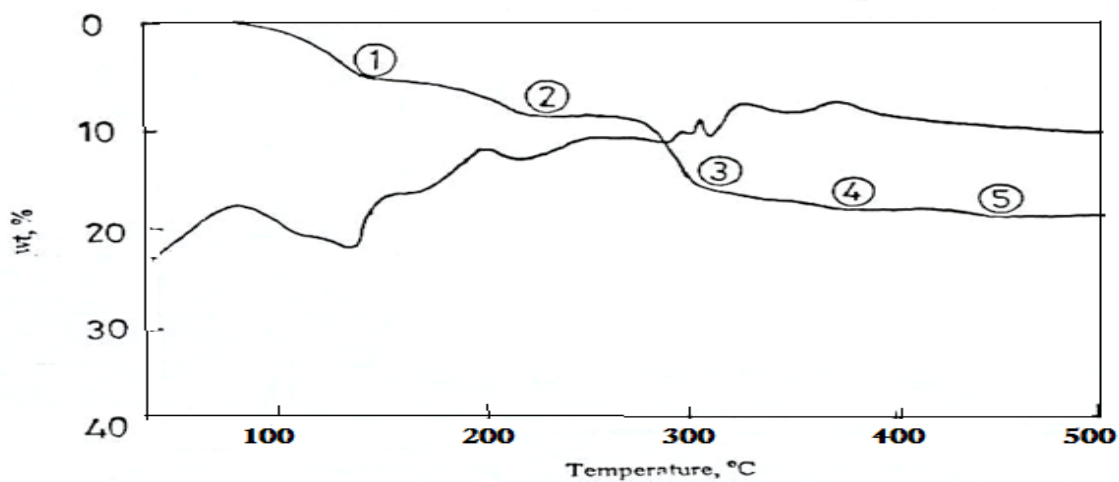


Fig.(1-d) Thermal analysis (DTA and TG) of mixed solids with molar formula $[1/2 \text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 : 3/7 (\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$

TG-curves of the mixed mixtures illustrate negligible loss above 400°C. This may be due to the formation of CuMoO_4 as detected in XR-diffractograms for the mixtures preheated at 500°C. The decrease in the area of endothermic peaks may be due to the evolved heat from solid-solid interaction between thermal products.

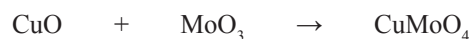
XRD investigation of pure solids calcined at 500-1000°C

Figure 2-a shows that the thermal treatment of basic copper carbonate heated at 500°, 750° and 1000 °C, yields crystalline phase of monoclinic CuO. The degree of crystallinity increases with increasing the temperature of treatment up to 750 °C. A slight decrease in the degree of crystallinity is observed when the calcination temperature is increased up to 1000°C. This may be due to the fact that, at this high temperature bivalent copper oxide reduces partially into amorphous monovalent cuprous oxide.

Figure 2-b represents the results of XRD-analysis of pure ammonium molybdate tetrahydrate thermally treated at both 500° and 750°C. It shows the formation of orthorhombic MoO_3 crystalline phase. The degree of crystallinity of molybdenum oxide significantly increased with increasing calcination temperature up to 750°C with preferred orientation process for lines with (hkl) {(020),(040),(021),(060)}. Molybdenum oxide (MoO_3) melts at 790°C and evaporates by increasing calcination temperature.

XRD investigation of mixed solids calcined at 500-1000°C

Figures 2c, 2d and 2e show the results of XRD-analysis of the mixtures, 3Cu:1Mo, 1Cu:1Mo and 1Cu:3Mo, preheated at 500°, 750°, and 1000°C. Figure 2-f represents the dependence of degree of crystallization of different phases detected at different calcination temperatures on the composition of the mixture. It can be seen from figures (2a-f) that: (i) mixtures preheated at 500°C show a gradual decrease in the intensities of the line of CuO with increasing molybdenum content. At the same time, a noticeable increase of the crystallinity of CuMoO_4 is observed reaching a maximum for the ratio, 1Cu:1Mo, then decreases with increasing molybdenum content after which a separate crystalline MoO_3 phase appears. This means, that the optimum condition for the formation of CuMoO_4 at 500°C is being attained with CuMoO_4 when the ratio is 1Cu:1Mo. (ii) Crystalline CuMoO_4 phase is formed as a result of solid-solid interaction according to the following equation:-



(iii) By increasing the treatment temperature up to 750°C, the optimum condition for the formation of CuMoO_4 is shifted towards the ratio, 1Cu:3Mo, producing maximum degree of crystallinity of phases of copper molybdate and MoO_3 . The amount of both crystalline CuMoO_4 and MoO_3 detected at 750°C decreased on increasing copper content in the mixture.

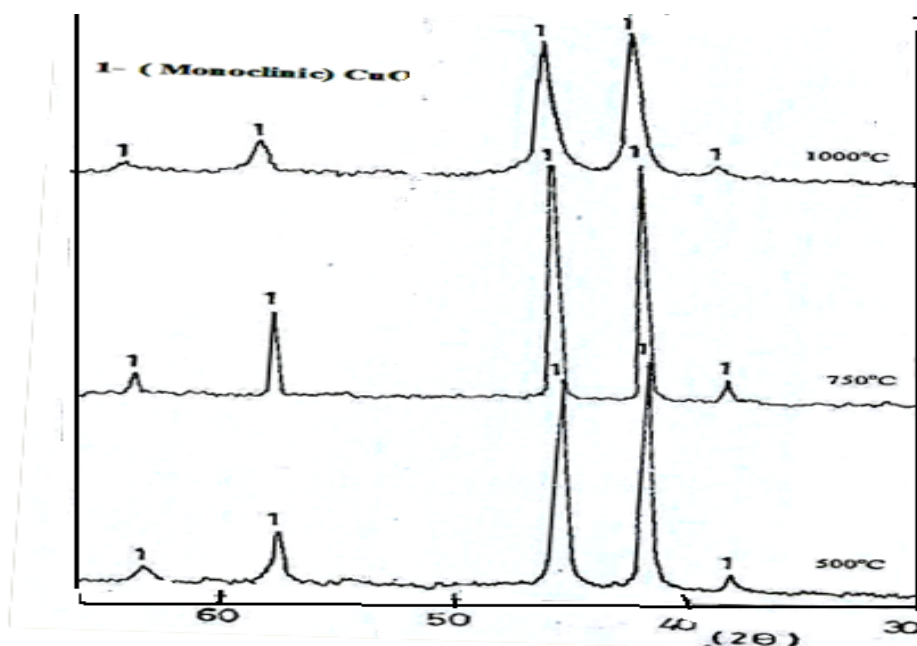


Fig. (2-a) XR-diffractograms of [pure $\text{CuCO}_3 \cdot \text{Cu(OH)}_2$] preheated in air at different temperatures, 500, 750 and 1000°C

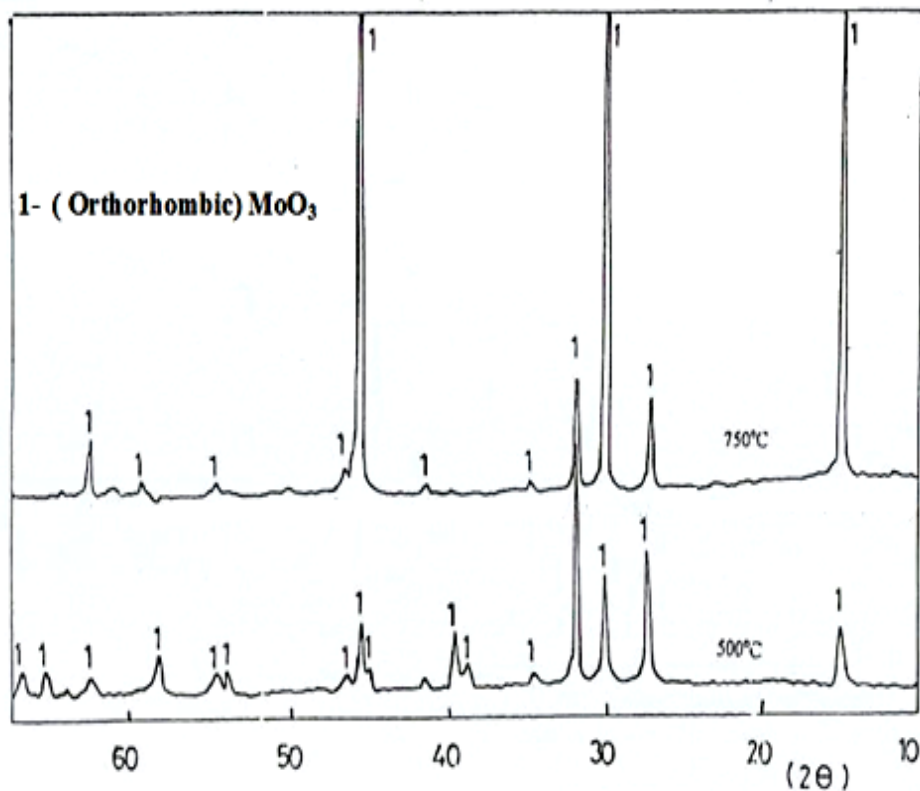


Fig.(2-b). XR-diffractogram of $[\text{pure}(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ preheated in air at different temperatures, 500 and 750°C.

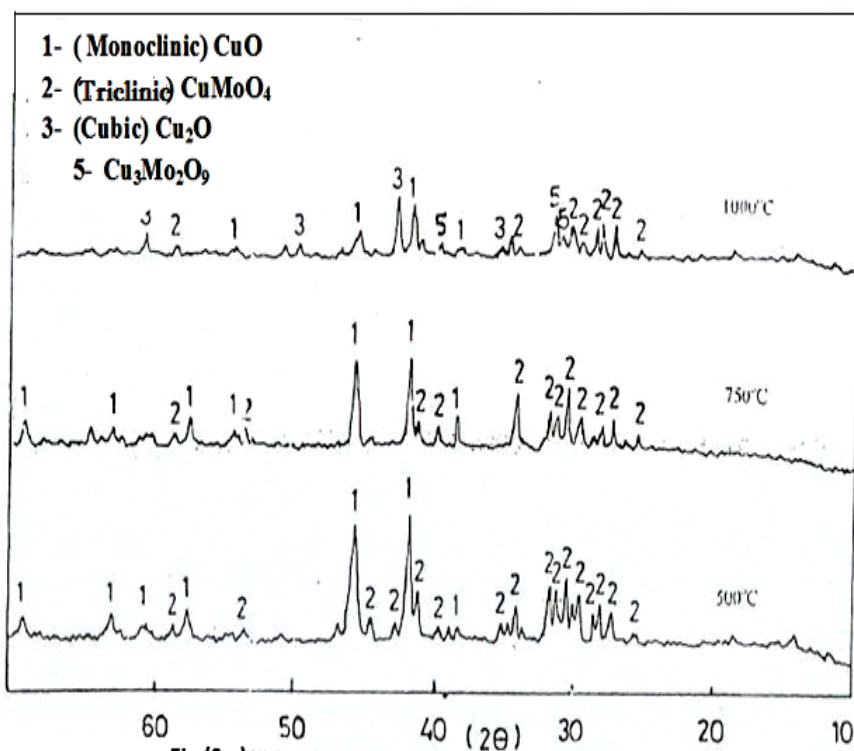


Fig.(2-c). XR-diffractograms of mixed solids with molar formula $[\frac{1}{2}\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 : \frac{1}{7}(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ preheated on air at different temperatures, 500, 750 and 1000°C

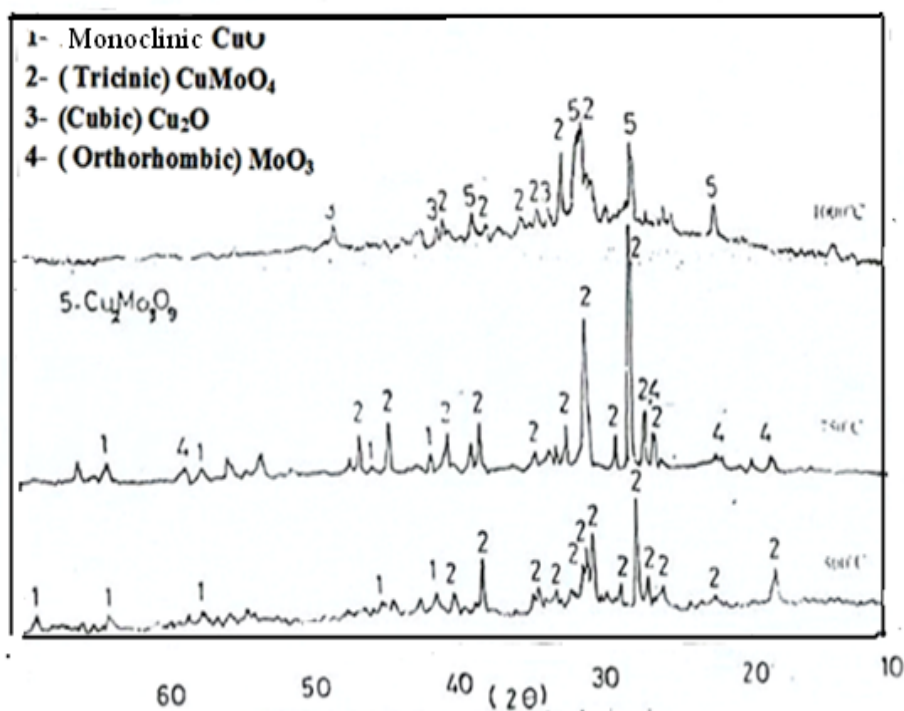


Fig.(2-d) XR diffractograms of mixed solids with molar formula $[1/2\text{CuCO}_3.\text{Cu}(\text{OH})_2:1/7(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}]$ preheated in air at different temperatures, 500,750 and 1000°C

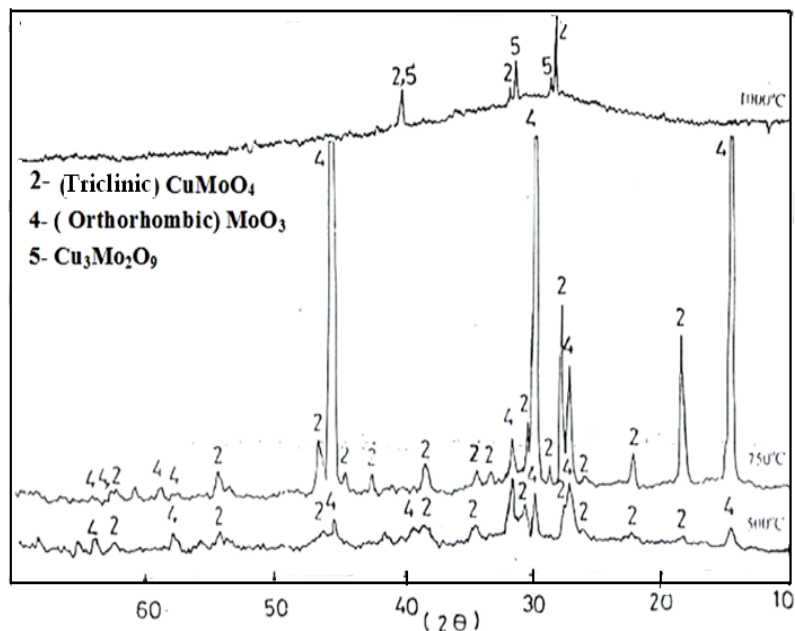


Fig.(2-e). XR diffractograms of mixed solids with molar formula $[1/2\text{CuCO}_3. \text{Cu}(\text{OH})_2 . 3/7(\text{NH}_4)_6.\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}]$ preheated I n air at different temperatures, 500, 750 and 1000°C.

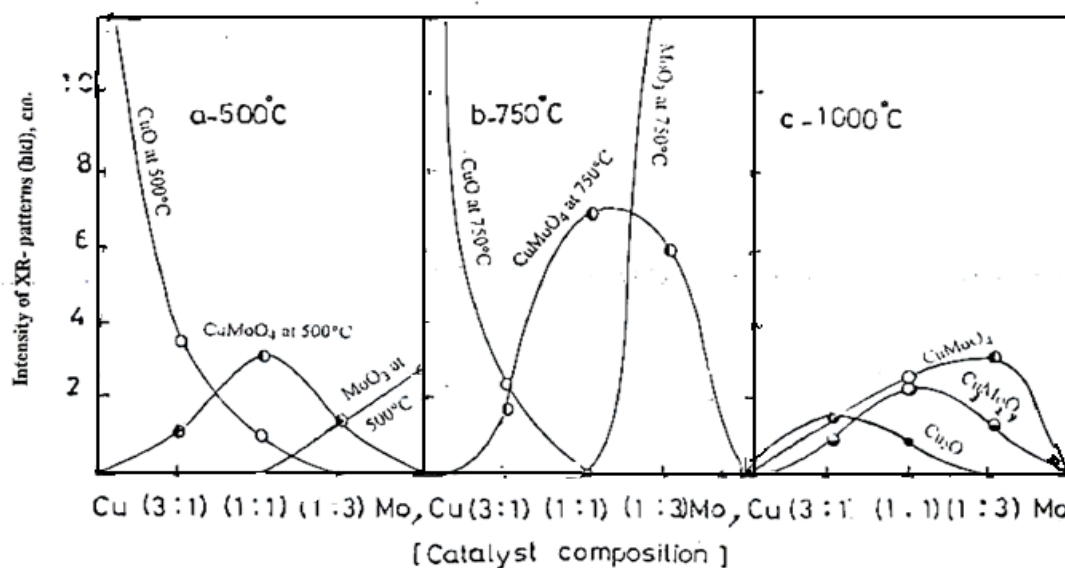


Fig.(2-f). The dependence of the degree of crystallization [intensity of patterns] on the composition of mixtures (Cu : Mo) preheated in air at different temperatures. 500, 750 and 1000°C.

(iv) Further increase of calcination temperature to 1000°C, leads to formation of different crystalline compounds depending on the composition of the mixture. For the mixture, 3Cu:1Mo, crystalline phases, CuO, Cu₂O, CuMoO₄ and Cu₃Mo₂O₉ are detected. The formation of cuprous oxide is attributed to reduction of copperic oxide at elevated temperature. Copper molybdate with different forms are formed as a result of solid-solid interaction between copper and molybdenum oxides.

The mixture of 1Cu:1Mo, preheated at 1000°C shows the formation of Cu₃Mo₂O₉ phase beside CuMoO₄ and Cu₂O phases. However, for the mixture, 1Cu:3Mo, preheated at 1000°C, only one crystalline phase appeared, namely, Cu₃Mo₂O₉.

Catalytic activity measurement of pure and mixed (CuO-MoO₃) oxides prepared at 500- 1000°C

The catalytic activity of all pure and mixed solids significantly decreased with increasing treatment temperature up to 750°C. Further increase in calcination temperature up to 1000°C no measurable activity was detected because of sintering process of active phases takes place.

Figures 3-a & 3-b represent curves of the decomposition of H₂O₂ over pure CuO and MoO₃ obtained by treatment of single salts at 250°, 500°, and 750°C. The experimental results

followed the first order kinetics as well as for the mixture; 3Cu:1Mo; preheated at 250°C.

Figures 3-d & 3e show the experimental results of H₂O₂ decomposition reaction over the other mixtures (Cu:Mo) preheated at 250°, 500°, and 750°C possess autocatalysis after certain induction period. It can also be seen that, the sample 1Cu:1Mo, preheated at 250° and 500°C and the sample, 1Cu:3Mo, preheated at 750°C are more active than the other mixtures preheated at the same temperatures.

Figure 4 shows the dependence of rate constant ($k \cdot \text{min}^{-1}$) on the catalyst composition of (Cu:Mo) thermally treated at different temperatures namely, 250°, 500°, 750°C. It can be seen from this figure that the catalytic activity significantly increased with reaction temperature and content of molybdenum in the mixture.

The departure of first order mechanism and the establishment of the autocatalysis and the higher catalytic activity of all the samples of Cu:Mo calcined at different temperatures; (except the mixture, 3Cu:1Mo, preheated at 250°C); than pure copper carbonate or ammonium molybdate preheated at the same temperatures can be attributed to the two oxides affecting each other and can be explained in terms of bivalent catalytic centers.

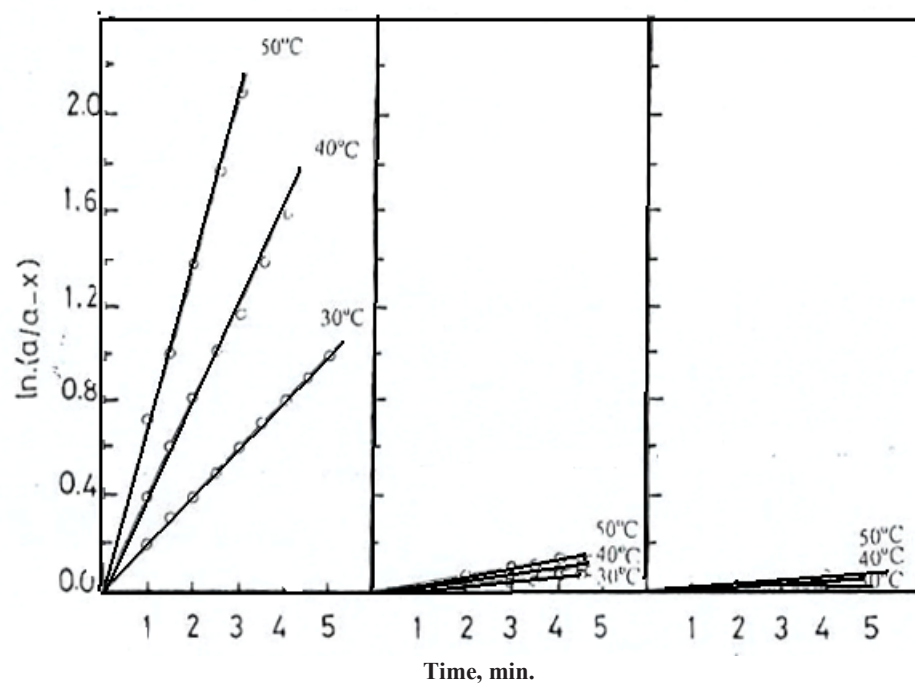


Fig.(3-a). Dependence of $\ln a/(a-x)$ Vs Time for catalyst $[\text{CuCO}_3.\text{Cu}(\text{OH})_2]$ preheated in air at different temperatures 250, 500 and 750°C

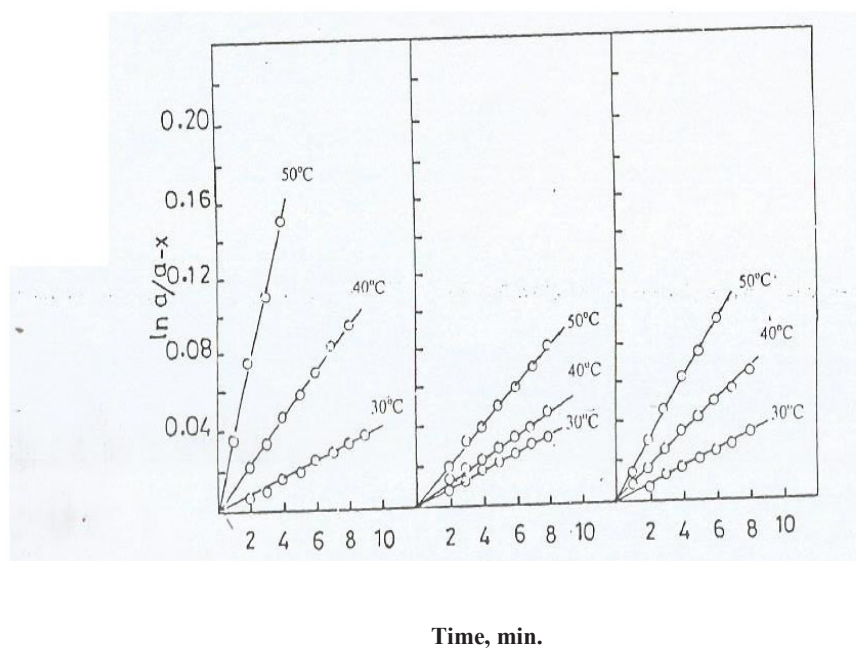


Fig.(3-b). Dependence of $\ln a/(a-x)$ Vs Time for catalyst $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}.4\text{H}_2\text{O}$ preheated at different temperatures 250°C, 500°C and 750°C.

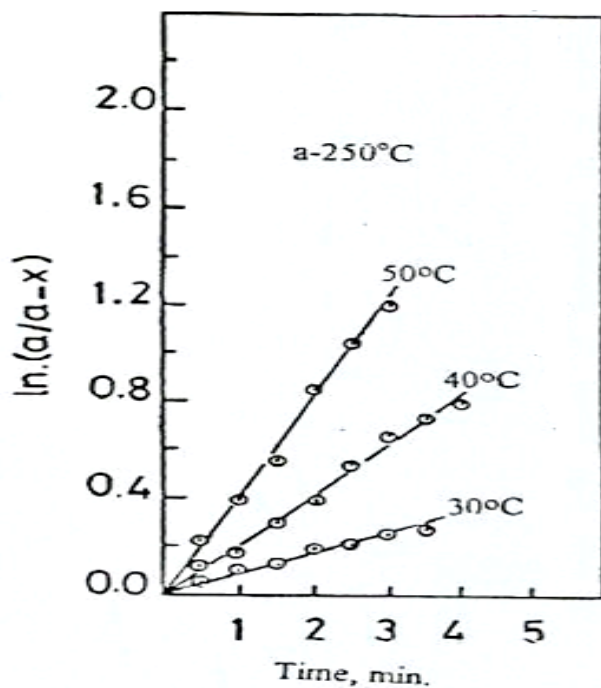


Fig.(3-c) Dependence of $\ln a/(a-x)$ Vs. Time for catalyst [3 Cu : Mo] preheated at different temperatures; a- 250°C

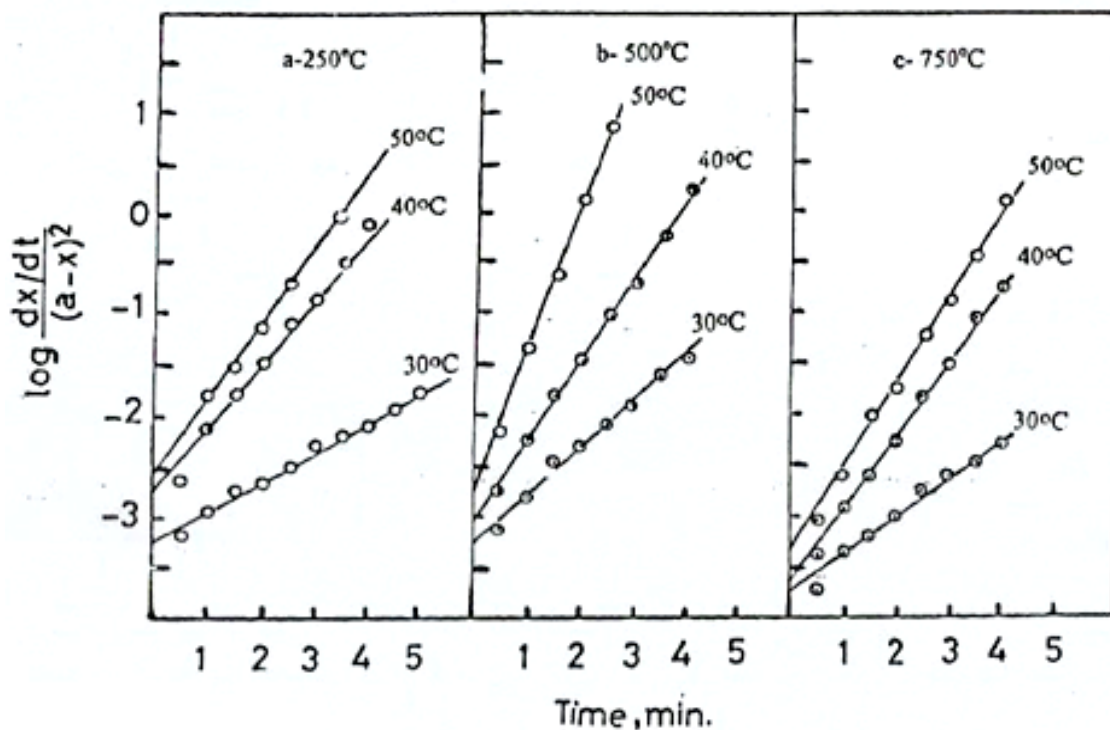


Fig.(3-e) The dependence of $\log (dx/dt)/(a-x)^2$ Vs time for catalyst [Cu : Mo] preheated at a- 250°C , b- 500°C and c- 750°C.

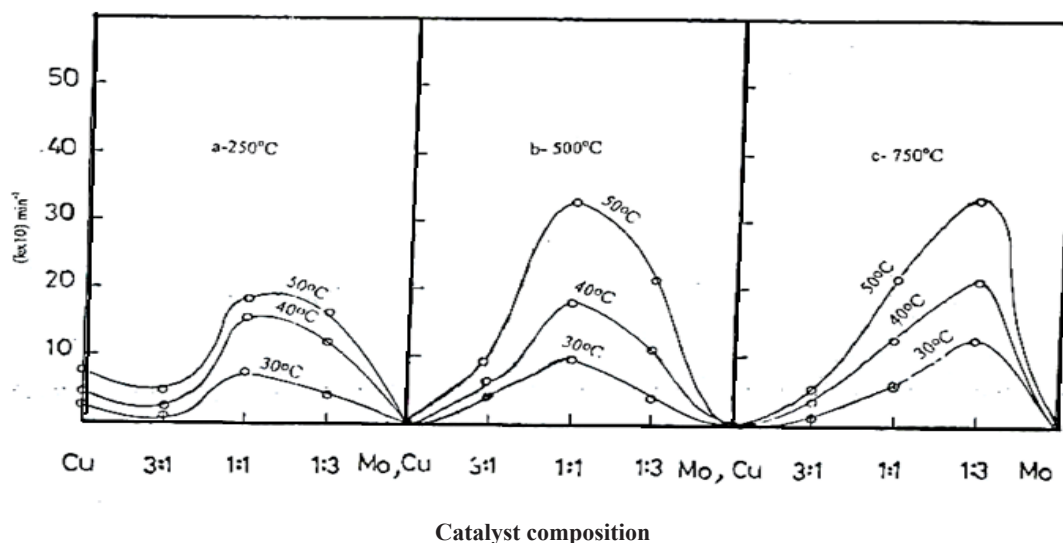
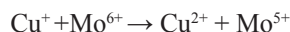


Fig. 4. The dependence of rate constant ($k \cdot \text{min}^{-1}$) on the catalyst composition [Cu:Mo]. Catalysts thermally treated at diff

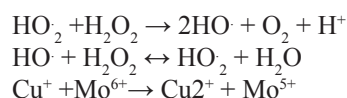
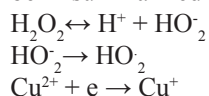
The presence of reduced copper in the system is able to reduce Mo^{6+} (major catalytic centers) to ions of lower oxidation state; i.e; Mo^{5+} or Mo^{4+} (minor centers) being more active [6]:



The increase of molybdenum content in the mixture increases the catalytic effect and also decreases the induction period. This indicates that the reduction of Mo^{6+} to Mo^{5+} ions proceeds faster with increasing MoO_3 content. This means that the observed changes of the catalytic activity are probably due to the changes of the valency state of the catalytically active molybdenum sites of the catalyst [12].

The results also indicate that the decomposition of hydrogen peroxide on these catalysts is promoted by a composite oxide on both compounds ($\text{CuO} + \text{MoO}_3$). The maximum catalytic activity for solids preheated at 500°C is found in the case of mixture, 1Cu:1Mo, with a maximum formation of composite copper molybdate. On the other hand, mixtures preheated at 750°C are active and the activity increases with increasing the molybdenum content.

From the above, the mechanism of H_2O_2 decomposition on $(\text{CuO}-\text{MoO}_3)$ catalysts can be summarized as follows [7,13]:



Conclusion

The main conclusions that may be drawn from the obtained results are:

- 1- $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ accelerates the decomposition of $(\text{NH}_4)_2\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in the initial steps. The latter retards the decomposition of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ to copper oxide.
- 2- Solid-solid interactions between thermal products in the binary mixtures preheated at 500°C up to 1000°C forming stable phase of copper molybdate, its intensities depend on composition and calcination temperature.
- 3- All mixtures (Cu-Mo) calcined at 1000°C shows patterns of Cu_2O .
- 4- Pure CuO and MoO_3 have catalytic activity in H_2O_2 decomposition reaction and followed first order kinetics. While mixed oxides of $(\text{CuO}-\text{MoO}_3)$ have catalytic activity; except sample excess in
- 5- copper preheated at 250°C ; higher than that detected for pure oxides possess autocatalysis behavior and deviation from the first order mechanism.
- 6- There is no measurable catalytic activity of solids preheated at 1000°C because of formation of inactive oxides and/or sintering process of active phases.

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توصيف والخواص الحفزية لسلسلة من أكاسيد النحاس والمولبيدوم المختلطة

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قسم الكيمياء الفيزيائية – معمل كيمياء السطوح والحفز – المركز القومي للبحوث

تم تحضير سلسلة من أكاسيد النحاس والمولبيدوم في الصورة المنفردة والمزدوجة بنسب مختلفة بواسطة الخلط الميكانيكي لأملح كربونات النحاس القاعدية ومولبيدات الأمونيوم المائية. تم دراسة السلوك الحراري للمواد باستخدام أجهزة التحليل الحراري وتم معالجة المواد المحضرة بالتسخين عند درجات حرارة مختلفة ٢٥٠ و ٥٠٠ و ٧٥٠ و ١٠٠٠م° وتم توصيف المواد الناتجة بجهاز حيود الأشعة السينية. وأظهرت النتائج أن المواد المنفردة تتحلل لأكسيد النحاس وأكسيد المولبيدوم وأكسيد النحاسوز عند ٢٥٠ و ٣٤٠ و ١٠٠٠م° على الترتيب. في المخاليط ظهرت صور مختلفة من مركبات مولبيدات النحاس كنتاج لتفاعل الصلب-صلب بين الأكاسيد المناظرة بداية من ٥٠٠م° وتكوين هذه الأطوار المختلفة يعتمد على مكونات المخلوطة ودرجة المعالجة الحرارية. وتم قياس الكفاءة الحفزية للأكسيد المنفردة والمزدوجة في تفاعل التكسير الحفزي لفرق أكسيد الهيدروجين كتفاعل نموذجي عند درجات حرارة مختلفة وتم دراسة ميكانيكية التفاعل لكل العينات.