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THERMAL DECOMPOSITION OF $KClO_4$ CATALYZED BY MnO_2-CuO MIXED OXIDES SYSTEMS

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ABSTRACT

The catalytic effect of a mixed oxides system, consisting of MnO_2-CuO in different atomic ratios ($Cu/(Cu+Mn) = x$, where $x = 0$-1), on the non-isothermal decomposition of $KClO_4$ has been studied. The results are discussed according to an electron transfer mechanism. The enhancement effect of trace Cu(II) added to the host oxide MnO_2 was attributed to an increase of the exchange capacity of manganese cations between the different oxidation states, while the retarding effect associated with Cu(II)-rich samples was attributed to the trapping of the electrons required to initiate the decomposition reaction by the holes created. On the basis of the applicability of a non-isothermal kinetic equation, it was demonstrated that two main stages are involved in the decomposition process.

INTRODUCTION

As catalysts, mixed metal oxides possess many advantages over the simple ones: combination of two transition metal oxides can contribute to modifications in their geometric and electronic properties that lead to changes in their catalytic functions. The catalyzed thermal decomposition of $KClO_4$ has been found to be remarkably sensitive to metal oxide additives [1-8]. Considerable research work has been undertaken with the aim of demonstrating a relationship between the possible sites required to catalyze this decomposition process and the nature of the oxide added, but discrepant results have been reported in this field [1-3,9].

In reports from our laboratory [3,9,10], we investigated the thermal decomposition of $KClO_4$ using simple oxides. In this study we aim to investigate such decomposition using a system consisting of MnO_2 mixed with CuO in different ratios. The results are discussed with special reference to the exchange capacity between the different oxidation states for both Mn(IV) and Cu(II) cations. We employed electrical conductivity measurements as well as the catalyzed decomposition of H_2O_2 over the various mixed oxide compositions to support our results.

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EXPERIMENTAL

Reagent grade chemicals were used. A series of MnO_2–CuO systems in 10 different atomic ratios ($Cu/(Cu + Mn) = x$, where $x = 0$–1) was used in this study. It was prepared by the impregnation method (a wet mixing of $MnCO_3$ with the appropriate volume of $Cu(NO_3)_2 \cdot 3\ H_2O$ solution) then drying at 110 °C for 24 h. The compounds produced were calcined at 500 °C for 4 h. Catalyzed thermal decomposition of $KClO_4$ was performed as described previously [9]. The total volume of oxygen that could theoretically be liberated was calculated from the known amount of $KClO_4$ and finally corrected for room temperature to correspond to $\alpha = 1$. The electrical conductivity measurements were carried out with a conductivity cell described by Chapman et al. [11]. The resistance was measured using a 610 C electrometer and a high voltage supply type 240 A (Keithley Instruments). The activation energy was calculated by applying the Arrhenius equation [12]. Decomposition of H_2O_2 was carried out using the gasometric technique [13]; the experiments were conducted for 30 min at 40 °C and the first-order rate constants were calculated from the good straight lines obtained.

RESULTS AND DISCUSSION

The TG curves for the catalytic thermal decomposition of $KClO_4$ by the system MnO_2–CuO in different ratios are presented in Fig. 1 as α–temperature relationship, where α is the decomposed fraction. As shown in the figure an enhancement of the decomposition process is obtained with addition of pure MnO_2 (curve b in Fig. 1). This enhancement effect increases when the catalyst consists of MnO_2 mixed with lower ratios of CuO (curves c–e in Fig. 1) and becomes lower for CuO rich samples (curves f–k in Fig. 1). In order to interpret these findings two factors must be considered. The first is the mechanism by which $KClO_4$ decomposes and the second is the nature of the catalyst added. Concerning the former, a series of consecutive reactions was proposed [14,15] to explain the decomposition of $KClO_4$; the rate-controlling step was reported to be the dissociation of ClO_4^- ions into ClO_3^- ions and oxygen [9]. In the presence of a catalyst a mechanism [16] involving both electron transfer and abstraction of atomic oxygen was proposed

$$\underset{\text{I}}{2e_{\text{oxide}} + ClO_4^-} \rightarrow \underset{\text{II}}{O^{2-} + ClO_3^-} \rightarrow \underset{\text{III}}{\tfrac{1}{2}O_2 + ClO_3^- + 2e_{\text{oxide}}} \qquad (1)$$

where e_{oxide} is an electron in the conduction band of the oxide and O^{2-}_{oxide} is an oxygen abstracted by the oxide.

Accordingly, one can explain the enhancement role of MnO_2 (as detected from the lowering in the decomposition temperature of $KClO_4$) as a result of

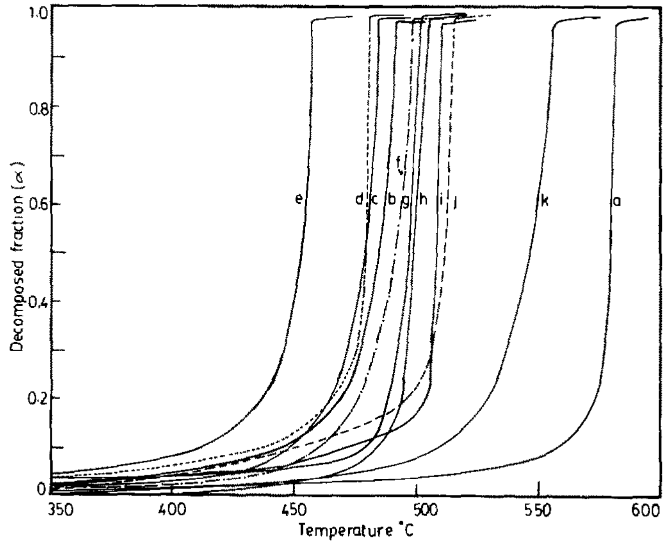

Fig. 1. TG curves of the thermal decomposition of $KClO_4$ (curve a) and of $KClO_4$ catalyzed with MnO_2–CuO mixed oxides systems in the atomic ratios [Cu/(Cu + Mn)] of 0 (pure MnO_2) 0.01, 0.05, 0.10, 0.50, 0.70, 0.90, 0.95, 0.99, and pure CuO (curves b–k, respectively).

its non-stoichiometry. It was known [17] that MnO_2 when calcined at 500 °C decomposes partially to Mn_2O_3. The coexistence of the resultant Mn(III) and Mn(IV) acts as a donor–acceptor pair; such a pair may initiate the decomposition reaction [through step I in eqn. (1)] by the electron donation from Mn(III) coupled with consumption of the electrons produced in step III by Mn(IV) which push the decomposition reaction forward.

Since the exchange capacity between the two oxidation states of manganese ions is responsible for the resultant catalytic activity of the non-stoichiometric MnO_2, we might expect that samples containing lower ratios of Cu(II) ions will have a more pronounced effect than Cu(II)-rich samples in enhancing this exchange capacity. This conclusion was shown by the sequence of lowering the decomposition temperature of $KClO_4$, and it was supported by the electrical conductivity measurements. Values of σ for the various samples as measured at steady state conditions at 200 °C, as well as the calculated activation energy (Fig. 2), using the Arrhenius equation, are shown in Table 1.

Examination of the data depicted in Table 1 revealed that introducing 1.0, 5.0 and 10% Cu(II) ions into the MnO_2 lattice caused an increase in the concentration of the charge carriers. However, this increase was associated with a parallel increase of the forbidden gap, as shown by the increasing activation energy values. On the other hand, addition of more than 10% Cu(II) ions raised the conduction but reduced the E_a values. It is obvious that the most active samples are those having higher E_a values, a situation most probably characteristic of a d^9s configuration of copper ions [18].

TABLE 1

Variation of σ at 200 ° C and the calculated activation energy (E_a) with the composition of MnO_2–CuO system calcined at 500 ° C for 4 h

	Cu/(Cu + Mn)									
	Pure MnO_2	0.01	0.05	0.10	0.50	0.70	0.90	0.95	0.99	Pure CuO
$\sigma \times 10^{-4}$ ($ohm^{-1} cm^{-1}$)	0.145	0.589	1.45	3.63	36.3	30.9	13.8	12.6	7.75	14.1
E_a (eV)	0.361	0.463	0.467	0.517	0.281	0.307	0.25	0.272	0.307	0.40

TABLE 2

Activation energy values for the two-stage decomposition of pure $KClO_4$ and mixed with the MnO_2–CuO system

E_a ($kcal\ mol^{-1}$)	Composition										
		Cu/(Cu + Mn) ratio of the catalyst mixed with $KClO_4$									
	Pure $KClO_4$	Pure MnO_2	0.01	0.05	0.10	0.50	0.70	0.90	0.95	0.99	Pure CuO
E_{a_1}	6.1	13.8	13.3	10.5	10.3	8.0	13.3	14.3	8.3	10.50	6.7
E_{a_2}	66.8	44.4	44.0	42.6	40.0	52.0	47.6	49.1	54.6	55.00	61.8
$E_{a_1} + E_{a_2}$	72.9	58.2	57.3	53.1	50.3	60.0	60.9	63.4	62.9	65.5	68.5

TABLE 3

Variation of the reaction rate constants (K) for the catalytic decomposition of H_2O_2 with the composition of the catalysts

	Cu/(Cu + Mn)									
	Pure MnO_2	0.01	0.05	0.10	0.50	0.70	0.90	0.95	0.99	Pure CuO
K ($10^{-3}\ min^{-1}$)	71.9	99.3	103.5	134.2	27.1	35.8	29.1	25.0	15.7	4.10

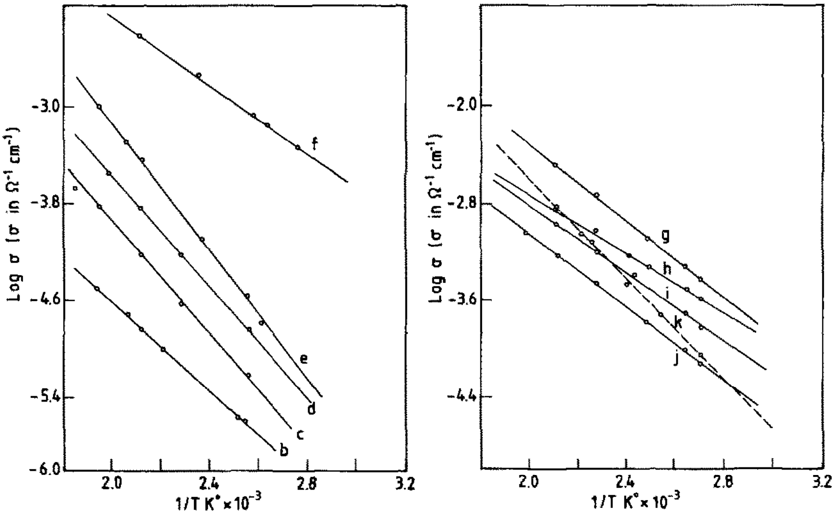

Fig. 2. Log σ vs. $1/T$ for the MnO_2–CuO mixed oxides systems in different atomic ratios. Symbols as in Fig. 1.

Our results could be interpreted in terms of the establishment of a $Cu^{2+} + e \leftrightharpoons Cu^{+}$ redox cycle [19] in which Cu(I) ions will have different electronic configurations, based on the electronegativity of their environment [18]. In a more electronegative environment, i.e. in samples with higher copper ions content, the d^{10} ion with a hole in the valence shell is the preferred one. Such configuration acts as an inhibitor for the decomposition process by the trapping of the electrons required to initiate the process by the holes in the valence shell. On the other hand, transferring the hole to the d shell in the second configuration (d^9s), in a low electronegative environment, will cancel this trapping effect, and then the Cu^{2+}–Cu^{+} redox cycle will work in the direction of promoting the decomposition process.

The applicability of the non-isothermal kinetic equation [20]

$$\ln \alpha - 2\ln T = A_0 - E/RT \tag{2}$$

was checked by plotting $\ln \alpha - 2\ln T$ (as obtained from TG curves) vs. $1/T$, as seen in Fig. 3, whereby a good linear correlation associated with breaking of the straight lines was obtained. Such breaking indicates a two-stage decomposition process. The first may be referred to as a reversible crystallographic transition of $KClO_4$ from the rhombic to the cubic form [21], with the second corresponding to the decomposition stage. The values of the activation energy for the two stages, denoted as E_{a_1} and E_{a_2}, are included in Table 2.

The variation of the values of E_{a_1} and E_{a_2} illustrates that both the decomposition stages are influenced by adding the catalyst. This means that the effect of the catalyst on the decomposition process affects both the

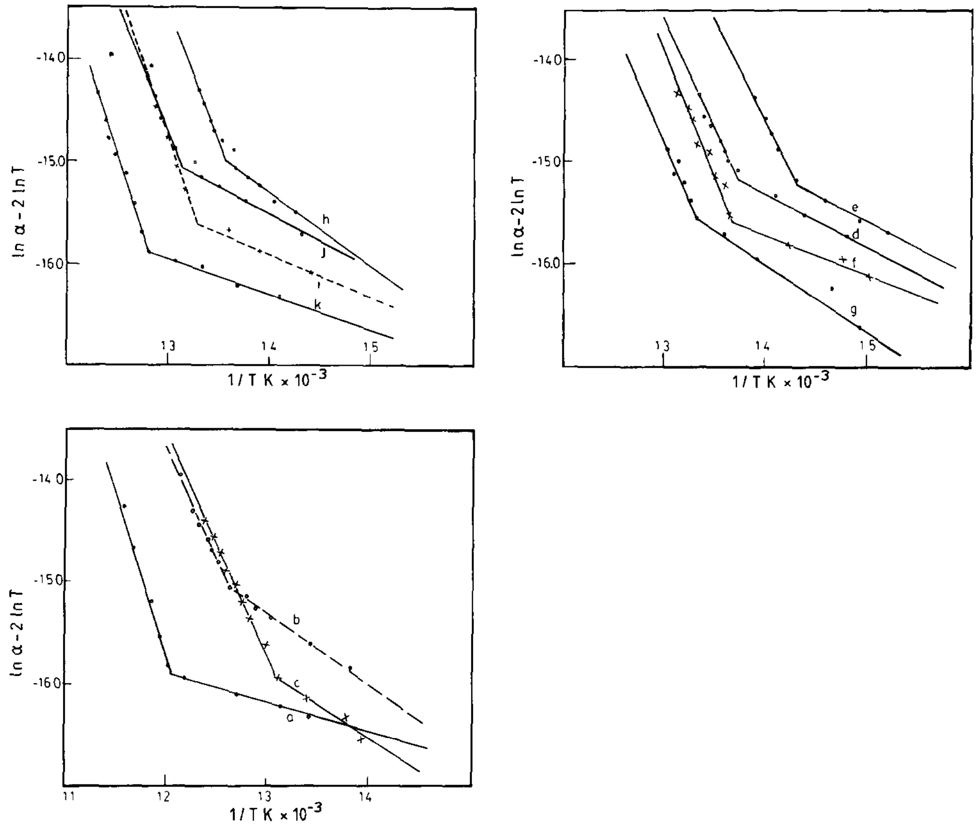

Fig. 3. Ln $\alpha - 2 \ln T$ as a function of $1/T$ plotted in terms of eqn. (2) for the thermal decomposition of pure $KClO_4$ and of $KClO_4$ catalyzed with MnO_2–CuO mixed oxides systems. Symbols as in Fig. 1.

electronic and the lattice parameters of $KClO_4$. It is of interest to note the direct proportional relationship between the enhancement effect of the catalyst and the decrease in the total activation energy ($E_{a_1} + E_{a_2}$), whereas a trial to set a similar relation between the enhancement and the activation energy for each individual stage was unsuccessful.

In order to continue our study on the changes in the electronic parameters associated with a combination of MnO_2 with different ratios of Cu(II) ions, the catalytic decomposition of H_2O_2 was tested over the various catalysts. The experimental data have been analyzed on the assumption that the decomposition of H_2O_2 is a first-order process [13]. The reaction rates are given in Table 3.

From the present experimental data for the catalytic decomposition of H_2O_2, and considering the decomposition mechanism to take place as follows [22]

$$O^-_{surface} + H_2O_2 \rightarrow OH^- + OH^\star + O \qquad (3)$$

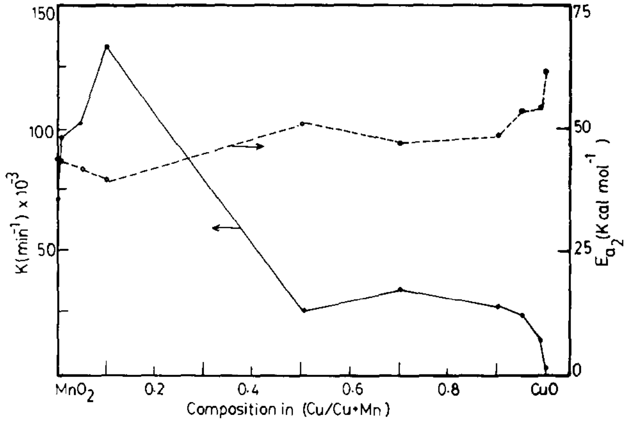

Fig. 4. Variation of specific rate constants of catalyzed decomposition of H_2O_2 and the E_{a_2} values for the catalyzed thermal decomposition of $KClO_4$ with the composition of the catalyst.

$$OH^{\star} + H_2O_2 \rightarrow H_2O + HO_2^{\star} \tag{4}$$

$$HO_2^{\star} + H_2O_2 \rightarrow O_2 + H_2O + OH^{\star} \tag{5}$$

the retarding effect of the Cu(II)-rich catalysts may be attributed to a decrease in the donating sites which are essential for the proceeding of the H_2O_2 decomposition reaction [step (3)]; on the other hand, lower ratios of Cu(II) ions added to MnO_2 increased the donating capacity of the catalysts as reflected from the higher K (min^{-1}) values. Finally, the correlation obtained between the specific rate constants of H_2O_2 decomposition and the calculated E_{a_2} value of the $KClO_4$ decomposition (as seen in Fig. 4 provides further support for our suggestion for the dependence of the main stage of the $KClO_4$ decomposition on electronic factors.

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