Effect of semiconducting metal oxide additives on the kinetics of thermal decomposition of sodium oxalate under isothermal conditions

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ABSTRACT

The effect of semiconducting metal oxide (CuO and TiO$_2$) additives on the kinetics of thermal decomposition of sodium oxalate (Na$_2$C$_2$O$_4$) to sodium carbonate has been studied at five different temperatures in the range 783–803 K under isothermal conditions by thermogravimetry (TG). Irrespective of whether p- or n-type, the metal oxides show an increase in the rates of both stages of decomposition up to an oxide concentration of 1 wt% and then decreases (at higher concentrations). The TG data were subjected to model fitting kinetic methods of analysis. The rate law for the decomposition of Na$_2$C$_2$O$_4$ (Prout–Tompkins and contracting cylinder models respectively for the acceleratory and decay stages) remained unaffected by the additives. Similar effects were observed with pre-compressed metal oxide additives on the thermal decomposition of Na$_2$C$_2$O$_4$. The results support the diffusion controlled mechanism proposed earlier for the isothermal decomposition of sodium oxalate.

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1. Introduction

Thermal decomposition of metal oxalates has been the subject of many researches, both from a practical and theoretical viewpoint [1–3]. Duval [4] has summarized the thermogravimetric data for the drying and ignition temperature of a large number of metal oxalates. Galwey and Brown [5] have identified and discussed the studies on the thermal decomposition of silver oxalate. A review on the literature of the thermal behavior of inorganic oxalates reveals that except yttrium oxalate, all undergo decomposition before melting and the decomposition kinetics are not complicated except in the case of a few. However, the kinetic models proposed vary from oxalate to oxalate and author to author. Górski and Kraśnicka [6] proposed that the decomposition in oxalates begins with the heterolytic dissociation of C—C bond forming CO_2 and CO_2^{2-}. The decomposition of oxalates involves the cleavage of the C—C bond, since the products are CO and CO_2 which contain only one carbon atom each. In many cases the C—C bond cleavage is the rate determining step [7]. The cleavage may be heterolytic to produce CO_2 and CO_2^{2-} [6] or hemolytic to produce two CO_2^- anions [8]. In silver oxalate [9], the transfer of an electron from the $C_2O_4^{2-}$ to the cation is the first stage of the decomposition which leads to the rupture of the C—C bond [10].

We have studied the effects of several pre-treatments on the kinetics and mechanism of the thermal decomposition of Na$_2$C$_2$O$_4$ [11–13]. We found that no single kinetic equation fitted the whole α versus t data of the thermal decomposition of sodium oxalate with a single rate constant throughout the reaction [11,12]; there are two stages in the thermal decomposition reaction, an acceleratory stage up to $\alpha = 0.5$ followed by the decay stage, which are respectively described by the Prout–Tompkins $\{\ln[\alpha/(1-\alpha)] = kt\}$ [13] and contracting cylinder model $[1-(1-\alpha)^{1/2} = kt]$ rate laws with separate rate constants, k_1 and k_2. Such a description of reaction kinetics using different rate laws for different ranges of conversion is not unusual in solid-state reactions. For instance Philips and Taylor used Prout–Tompkins equation to describe the acceleratory region of the decomposition of potassium metaperiodate (KIO$_4$) and the contracting sphere equation for the decay stage [14]. It has also been reported that under isothermal conditions KIO$_4$ decomposes via two stages; the Prout–Tompkins equation best describes the acceleratory stage and the deceleratory stage proceeds according to contracting cylinder law [15–17]. The acceleratory stage in the decomposition of lithium perchlorate followed Prout–Tompkins rates law whereas the decay stage followed the monomolecular model [18]. Similarly both the acceleratory and decay regions of the thermal decomposition of sodium perchlorate and of potassium bromate were well described by the Prout–Tompkins relation with separate rate constants [19].

In continuation of our investigations on the thermal behavior of oxalates of alkali metals [11–13] in this paper we report the effect of metal oxide, such as cupric oxide (CuO) and titanium dioxide (TiO$_2$), additives on the isothermal decomposition kinetics of

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$Na_2C_2O_4$ to Na_2CO_3 in the temperature range 783–803 K. Mechanical addition of foreign substances into inorganic salts is known to give rise to two different types of effects on the thermal behavior of salts: (i) by the formation of a stable compound between the salt and the additive [20] and (ii) by a catalytic action of the additive [21–24]. Algird [9,25] observed that electron donors when present along with $Ag_2C_2O_4$ accelerates the thermal decomposition rate and electron acceptors retards.

CuO is a black solid having molar mass of 79.545 with an ionic structure. It melts above 1474 K with some loss of oxygen. CuO has application as a p-type semiconductor, because it has a narrow band gap of 1.2 eV [26]. The effectiveness of the reagent depends on the method of preparation, a problem that is typical for other heterogeneous reagents where surface area, among other variables, is significant [27]. TiO_2 is a white solid having a molar mass of 79.870. It melts at 2143 K and boils at 3245 K. Titanium dioxide is the most widely used white pigment because of its brightness and very high refractive index ($\eta = 2.4$). It is also used as a semi-conductor [28].

2. Experimental

2.1. Materials

All the chemicals used in the present study were of AnalaR grade samples of E Merck. Mechanical mixtures of sodium oxalate and metal oxides, CuO and TiO_2, were prepared by mixing the oxalate and oxide of same particle size, viz., 106–125 μm. Different samples with oxide concentrations 0.5, 1, 2, 5 and 10 wt% were prepared by mixing 2 g sodium oxalate thoroughly, in an agate motar, with the required quantity of the oxide.

Pre-compressed oxides (CuO and TiO_2) were prepared by subjecting to compression to 0.5 g each of CuO and TiO_2 of particle size 106–125 μm in a hydraulic press at pressures of 2×10^3, 4×10^3 and 6×10^3 kg cm^{-2}. The pellets of metal oxides were taken out, powdered in an agate mortar and fixed the particle size in the range 106–125 μm. Required quantity of the pre-compressed oxide was thoroughly mixed with sodium oxalate (particle size: 106–125 μm), in an agate mortar, to get 1 wt% mixture.

2.2. Methods

2.2.1. Thermogravimetric analysis

Thermogravimetric measurements in static air were carried out on a custom-made thermobalance fabricated in this laboratory [15,29]. A major problem [30] of the isothermal experiment is that a sample requires some time to reach the experimental temperature. During this period of non-isothermal heating, the sample undergoes some transformations that are likely to affect the succeeding kinetics. The situation is especially aggravated by the fact that under isothermal conditions, a typical solid-state process has its maximum reaction rate at the beginning of the transformation. So we fabricated a thermobalance particularly for isothermal studies, in which loading of the sample is possible at any time after the furnace has attained the desired reaction temperature. The operational characteristics of the thermobalance are, balance sensitivity: $\pm 1 \times 10^{-5}$ g, temperature accuracy: ± 0.5 K, sample mass: 5×10^{-2} g, atmosphere: static air and crucible: platinum. Thermal decomposition of sodium oxalate was found to be very slow below 783 K and very fast above 803 K. The decomposition was thus studied in the range 783–803 K. The loss in mass of sodium oxalate was measured as a function of time (t) at five different temperatures (T), viz., 783, 788, 793, 798 and 803 K.

2.2.2. Kinetic analysis

Historically model-fitting methods were widely used because of their ability to directly determine the kinetic triplet. On the other

hand, isoconversional methods do not compute a frequency factor nor determine reaction models which are needed for a complete and accurate kinetic analysis. In solid state kinetics, mechanistic interpretations usually involve identifying a reasonable reaction model [31] because information about individual reaction steps is often difficult to obtain. A model can describe a particular reaction type and translate that mathematically into a rate equation. Many models have been proposed in solid-state kinetics and these models have been developed based on certain mechanistic assumptions. Solid-state kinetic reactions can be mechanistically classified as nucleation, geometrical contraction, diffusion and reaction order models [10]. The TG data were subjected to weighted least squares analysis by all kinetic models given in [10].

3. Results and discussion

The effects of semiconducting oxides such as CuO and TiO_2 on the thermal decomposition kinetics of $Na_2C_2O_4$ were examined using mechanical mixtures of compositions 0.5, 1, 2, 5 and 10 wt% of the oxide. The experimental mass loss data obtained from TG were transformed into α versus t data as reported earlier [32], in the range $\alpha = 0.05$–0.95 with an interval of 0.05, at all temperatures studied. The α versus t curves for the thermal decomposition of all oxide mixed samples are shown in Figs. 1 and 2. The effect of pre-compressed oxide (CuO and TiO_2) additives on the thermal decomposition of $Na_2C_2O_4$ was also examined at 783 K; the α versus t plots is shown in Fig. 3.

Weighted least squares analysis of the thermal decomposition of oxide mixed samples of $Na_2C_2O_4$ showed that, as with untreated sodium oxalate [11], there are two stages in the decomposition; an acceleratory stage up to $\alpha = 0.5$ followed by the decay stage, which are respectively described by the Prout–Tompkins $\{\ln[\alpha/(1-\alpha)] = kt\}$ and contracting cylinder model $[1 - (1 - \alpha)^{1/2} = kt]$ rate laws with separate rate constants, k_1 and k_2. The rate constants obtained for both stages of thermal decomposition are shown in Table 1. Both oxides cause an increase in the rates of both stages of decomposition up to an oxide concentration of 1 wt% and then decreases (see Fig. 4 and Table 1). The effect of mixing pre-compressed oxides on the thermal decomposition of $Na_2C_2O_4$ was also examined at 783 K (Table 2). The dependence of the rate constant of both acceleratory and decay stages of the thermal decomposition of pre-compressed oxide mixed sodium oxalate on the concentration of pre-compressed
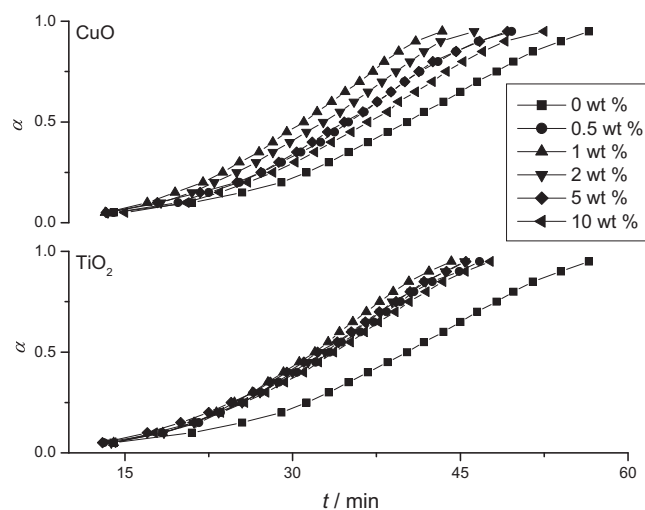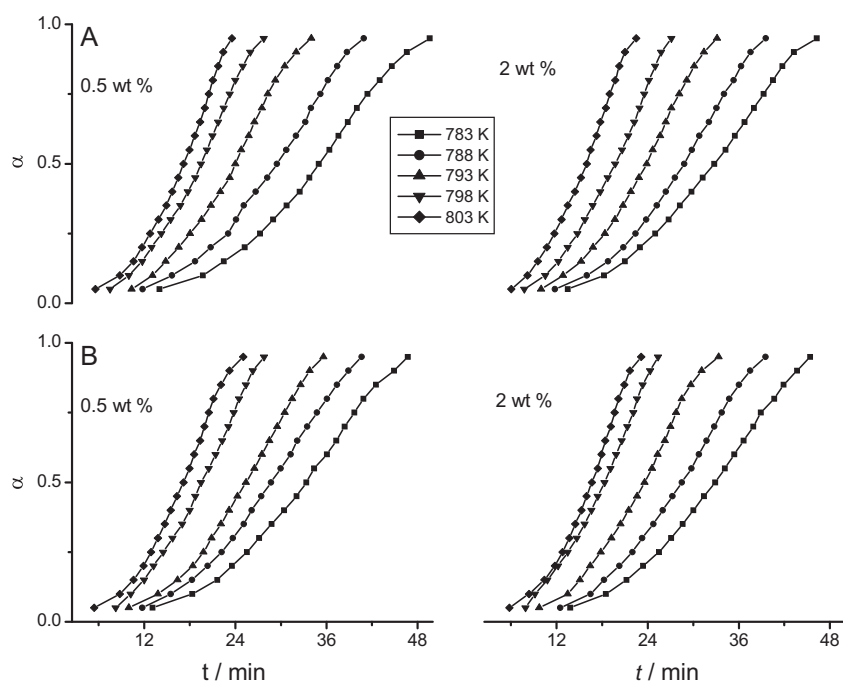

Fig. 1. α versus t plots for the thermal decomposition of oxide mixed sodium oxalate samples at different concentrations at 783 K.

Fig. 2. α versus t plots for the thermal decomposition of oxide (A: CuO, B: TiO$_2$) mixed (each at 0.5 and 2 wt% concentrations) sodium oxalate samples at different temperatures.

oxide additive is shown in Fig. 5. Pre-compression does not alter the effect of oxide additive on thermal decomposition, as is evident from the data from Table 2.

The activation energies of the thermal decomposition of CuO and TiO$_2$ (each at 0.5 and 2 wt% concentrations) mixed sodium oxalate were determined from Arrhenius plots. The Arrhenius plot for the acceleratory and deceleratory stages of the thermal decomposition of all oxide mixed samples of sodium oxalate under study are respectively shown in Figs. 6 and 7. The values of activation energy (E), standard deviation (SD), error and correlation coefficient (r) obtained from the Arrhenius plot for the acceleratory (I) and decelerator (II) stages of the thermal decomposition of oxide mixed sodium oxalate samples are given in Table 3.
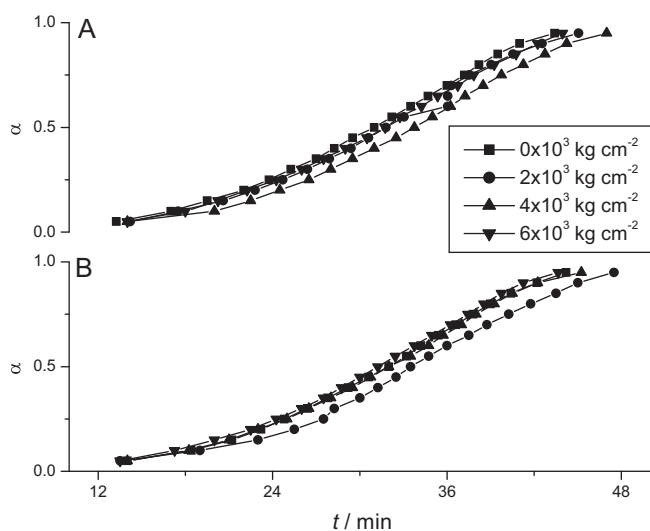
The effect of an oxide additive on solid state reaction involving electron transfer may be explained in terms of the contact potential

difference which depends on the work function of the solid reactant in contact [33]. An oxide with greater work function than that of the solid reactant acts as electron acceptor and enhances electron transfer process, whereas an oxide with smaller work function
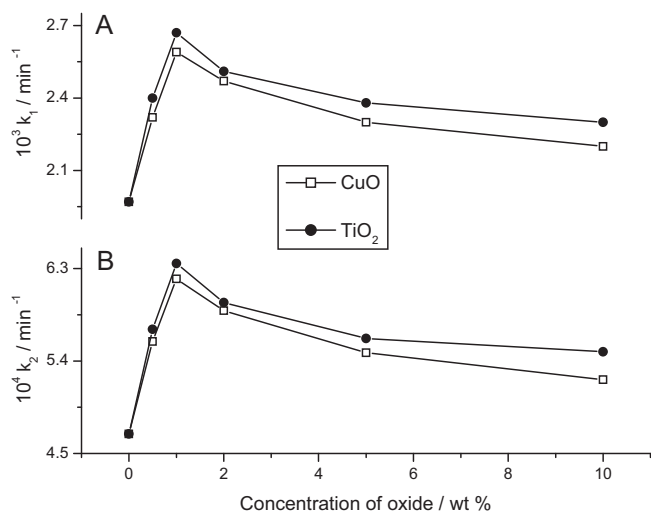
Table 1
Values of rate constants, k_1 and k_2, obtained from model fitting respectively to Prout–Tompkins model (acceleratory stage) and contracting cylinder model (deceleratory stage) for the thermal decomposition of pure and oxide mixed sodium oxalate samples at different temperatures.

Oxide	Concentration of oxide (wt%)	T (K)	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^4$ (min^{-1})
Nil	0	783	1.97	4.69
CuO	0.5	783	2.32	5.59
	1	783	2.59	6.20
	2	783	2.47	5.89
	5	783	2.30	5.48
	10	783	2.20	5.22
	0.5	783	2.32	5.59
	0.5	788	2.71	6.76
	0.5	793	3.15	8.15
	0.5	798	3.66	9.76
	0.5	803	4.24	11.8
	2	783	2.47	5.89
	2	788	2.88	7.06
	2	793	3.35	8.52
	2	798	3.87	10.2
	2	803	4.52	12.2
TiO$_2$	0.5	783	2.40	5.71
	1	783	2.67	6.35
	2	783	2.51	5.97
	5	783	2.38	5.62
	10	783	2.30	5.49
	0.5	783	2.40	5.71
	0.5	788	2.81	6.24
	0.5	793	3.23	7.47
	0.5	798	3.79	9.06
	0.5	803	4.36	10.8
	2	783	2.51	5.97
	2	788	2.90	7.17
	2	793	3.38	8.67
	2	798	3.93	10.5
	2	803	4.56	12.6

Fig. 3. α versus t plots for the thermal decomposition of pre-compressed oxide (A: CuO, B: TiO$_2$) mixed sodium oxalate samples at 783 K.
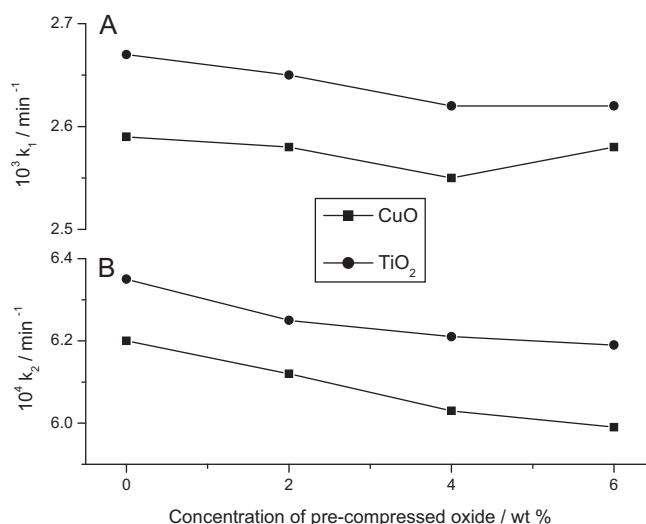
Fig. 4. Dependence of rate constant of the thermal decomposition of oxide mixed sodium oxalate on the concentration of oxide additive (A: acceleratory and B: decay stage).

Fig. 5. Dependence of rate constant of the thermal decomposition of pre-compressed oxide mixed sodium oxalate on the concentration of pre-compressed oxide additive (A: acceleratory and B: decay stage).

Table 2
Values of rate constants, k_1 and k_2, obtained from model fitting respectively to Prout–Tompkins model (acceleratory stage) and contracting cylinder model (deceleratory stage) for the thermal decomposition of sodium oxalate mixed with pre-compressed oxide at 783 K.

Oxide	Pressure applied $(10^{-3}/(\text{kg cm}^{-2}))$	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^4$ (min^{-1})
CuO	0	2.59	6.20
	2	2.58	6.12
	4	2.55	6.03
	6	2.58	5.99
TiO$_2$	0	2.67	6.35
	2	2.65	6.25
	4	2.62	6.21
	6	2.62	6.19

acts as an electron donor and desensitizes electron transfer. This was confirmed by the observation that CuO having a work function greater than that of Ag$_2$C$_2$O$_4$ accelerates its decomposition whereas Ag$_2$S with smaller work function decelerates [34].

With Na$_2$C$_2$O$_4$, we found that both oxides, CuO (p-type) and TiO$_2$ (n-type) enhance the rate of decomposition at lower oxide concentrations followed by a decrease at higher concentrations (Table 1 and Fig. 4). All oxide mixed samples have a decomposition rate higher than that of the pure sample. The change in the decomposition rate may not be due to a change in the mechanism, since the activation energy of the process remains unchanged (Table 3). Thus even in the presence of the oxide, diffusion of Na$^+$ determines the rate. Besides affecting the electronic steps, the additives may also influence the ionic steps by binding the ions of the host crystal, modifying the heat conductivity, etc. The presence of the additive
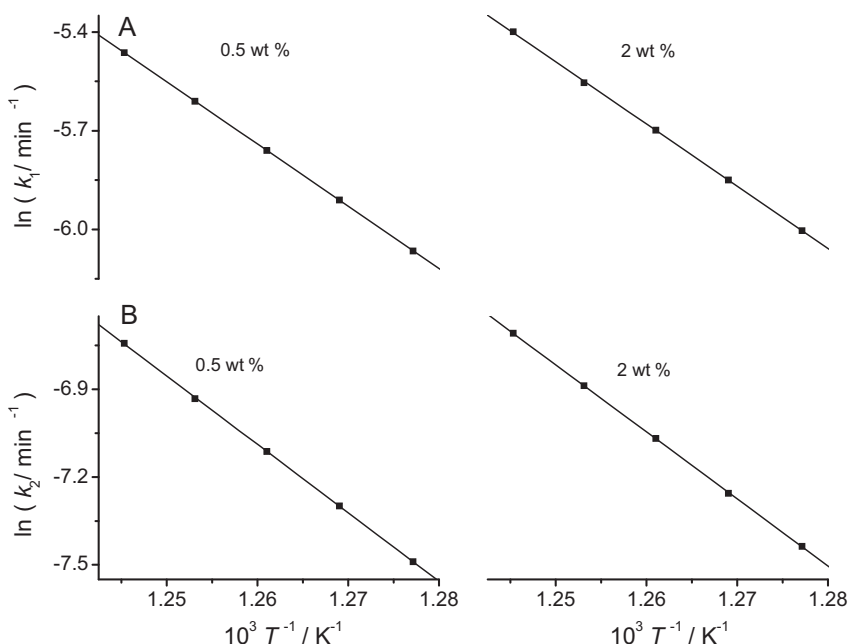
Fig. 6. Arrhenius plot for the aceleratory (A) and deceleratory (B) stages of the thermal decomposition of CuO mixed sodium oxalate at different concentrations.
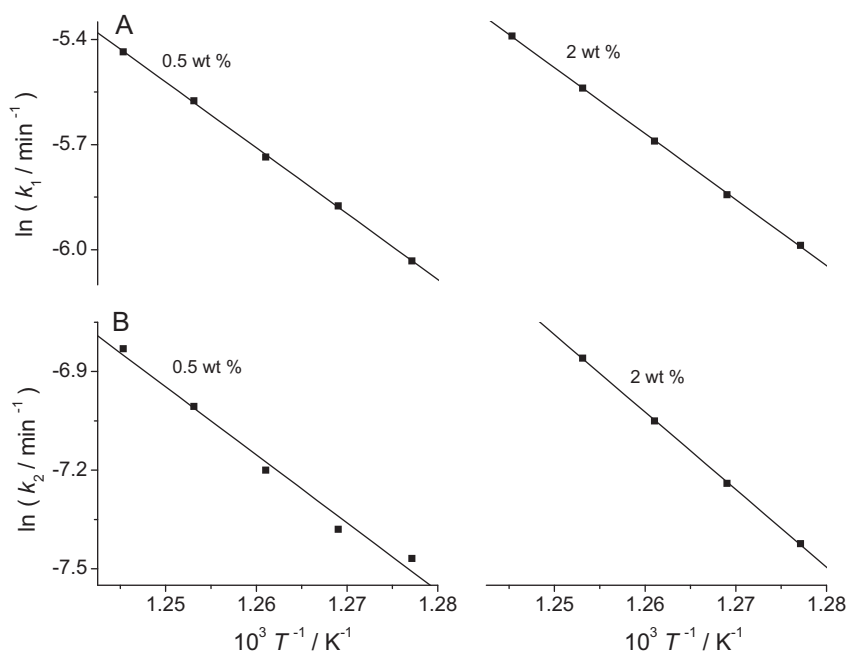
Fig. 7. Arrhenius plot for the aceleratory (A) and deceleratory (B) stages of the thermal decomposition of TiO_2 mixed sodium oxalate at different concentrations.

material can affect the heat flow within the solid matrix and hence can influence the course of the reaction.

The explanation cannot account for the decrease of decomposition rate above an oxide concentration of 1 wt%. We have examined the possibility of TiO_2 and CuO to adsorb the decomposition product CO, which can lead to a decrease in the rate. For this, we have done TG analysis of 50 mg of the oxide under static CO atmosphere in the temperature range 783–843 K. We found an initial weight loss which can be attributed to desorption of the adsorbed gases followed by a gain in weight, after 13–15 min, due to the adsorption of CO over the oxide. The possibility of adsorption of CO on the platinum bucket had been taken into account by running a blank experiment.

Thus the decrease in rate above an oxide concentration of 1 wt% seems to be due to the adsorption of one of the reaction products (CO) by the oxide, and thus suppressing the forward reaction. If this argument is true, the pre-compressed oxide should show such a suppressing effect more than the uncompressed. Though small, we found, as expected, a decrease in the decomposition rate with the increase in the pressure applied over the oxide (Fig. 4). Pressing of the oxide results in an increase of its surface area; this helps the oxide to adsorb the CO more effectively which results in a decrease of the decomposition rate. The effects of pre-compressed TiO_2 and CuO additives on the thermal decomposition of $Na_2C_2O_4$ are similar.

Table 3
Values of *E*, standard deviation (SD), error and correlation coefficient (*r*) obtained from the Arrhenius plot for the accelerator (I) and decelerator (II) stages of the thermal decomposition of oxide mixed sodium oxalate samples.

Oxide	Concentration (wt%)	Stage	E (kJ mol^{-1})	SD	Error	$-r$
CuO	0.5	I	157.5	0.0008	0.0328	1.0000
		II	194.6	0.0030	0.1201	1.0000
	2	I	157.2	0.0033	0.1291	0.9999
		II	190.7	0.0022	0.0857	1.0000
TiO$_2$	0.5	I	156.1	0.0055	0.2182	0.9998
		II	197.1	0.0370	1.4716	0.9925
	2	I	156.6	0.0037	0.1460	0.9999
		II	196.1	0.0039	0.1549	0.9999

4. Conclusion

The behavior of mechanical mixtures of sodium oxalate with n- and p-type semiconducting oxides suggests that the electron work functions of these oxides might be smaller than that of $Na_2C_2O_4$ so that they lack electron acceptor property with respect to $Na_2C_2O_4$. Both the metal oxides, CuO (p-type) and TiO_2 (n-type), enhance the rate of thermal decomposition of $Na_2C_2O_4$ at lower oxide concentrations followed by a decrease at higher concentrations due to the adsorption of one of the products of the reaction (CO) by the oxide, and thus suppressing the forward reaction. The results support the diffusion controlled mechanism proposed earlier for the isothermal decomposition of sodium oxalate.

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