Asian Journal of Chemistry Vol. 18, No. 2 (2006), 1025–1031

Catalytic Behaviour of Mixed Metal Oxides of Ln_2MO_4 for the Thermal Decomposition of Carbamide

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Mixed metal oxides of the type Ln_2MO_4 (Ln = Dy, Di; M = Cu, Zn, Cd) have been prepared and their catalytic behaviour for the thermal decomposition of carbamide has been studied.The mixed metal oxide samples follow the activity sequence as $Dy_2ZnO_4 > Dy_2CdO_4 > Dy_2CuO_4$. However, the oxide samples containing didymium follow the different sequences, *i.e.*, $Di_2CuO_4 > Di_2ZnO_4 > Di_2CdO_4$. Surface area seems to be the potential factor to account for the activity The possible mechanism for the decomposition process has been suggested.

Key Words: Catalytic, Behaviour, Ln_2MO_4, Thermal Decomposition, Carbamide.

INTRODUCTION

Considerable work has been done on the solid state degradation of carbamide in the presence of various metallic oxides of different origins and structures[1–4]. Catalytic activity has been observed to be the function of different factors like heat treatment, oxygen content, degree of non-stoichiometry, excess surface oxygen, acidity or basicity of the surface, structural change and surface area. It has been concluded that in the degradation process activated by certain oxide catalysts one or two factors predominate and account for the catalytic activity. The degradation of carbamide in the presence of mixed metal oxides of perovskite structure has been the subject of recent study[5]. Samples containing Ni appear catalytically more active in comparison to that containing Co.

The present investigation was undertaken with the following objectives:

(i) to study the catalytic activity of the mixed oxides of Ln_2MO_4 type;
(ii) to identify the factors responsible for the activity;
(iii) to suggest the mechanism for the process.

EXPERIMENTAL

Nitrates of dysprosium and didymium of 99.9% purity (Indian Rare Earth Ltd.) were used as such. [*Dymium (Di) is a mixture of praseodymium (Pr) and*

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neodymium (Nd) and regarded as an element and it behaves like the twin brother of lanthanum.]

Catalyst Preparation, Characterization and Measurements: The mixed metal oxide catalysts of two series: (a) Dysprosium with copper, zinc and cadmium, and (b) Didymium with copper, zinc and cadmium, were prepared by ceramic method[6, 7]. Usual procedures for the estimation of metals in the samples were adopted and the general formula assigned to the mixed metal oxides is Ln_2MO_4, where Ln = Dy, Di and M = Cu, Zn, Cd. Measurement of excess surface oxygen was done by the method described previously[8]. The acidity measurement was performed by the method of Arora *et al.*[9] Phenol adsorption method was employed for the measurement of surface basicity. B.E.T surface area was estimated in P.D.I.L Sindri (Bihar). The results are given in Table-1.

TABLE-1
ACIDITY, BASICITY, EXCESS SURFACE OXYGEN AND SURFACE AREA DATA OF THE SAMPLES

Samples	Excess surface oxygen per 100 g of the sample $\times 10^{-2}$	Acidity (meq/g)	Basicity (meq/g)	Surface area (m^2/g)
Dy_2ZnO_4	7.65	—	0.732×10^{-1}	14.40
Dy_2CdO_4	7.20	89.79	—	15.34
Dy_2CuO_4	4.48	67.52	—	12.86
Di_2ZnO_4	14.40	—	1.057×10^{-1}	17.04
Di_2CdO_4	9.12	—	2.850×10^{-1}	14.40
Di_2CuO_4	17.12	—	1.057×10^{-1}	18.96

Decomposition Study: Kinetic study of the thermal decomposition of carbamide was performed with and without the catalyst at 140, 150, 160°C following the method adopted by Rustamove[10]. The mixture of carbamide and catalyst (20 : 1) was ground intimately and the mixture (0.3 g) was taken in the reaction vessel dipped in a glycerine thermostat maintained at the desired temperature. The volume of the ensuing gas was recorded at regular intervals of time by noting the difference in the levels of the fluid in the manometer. The static state of the level showed the completion of the reaction. A plot between log ($V_\infty - V_t$) and time was drawn.

RESULTS AND DISCUSSION

The solid state thermal degradation of urea both in presence and in absence of catalysts was studied at three different temperatures, *viz.*, 140,150 and 160°C. The decomposition is found to follow the first order kinetics.The plots of log ($V_\infty - V_t$) *vs.* T were drawn, V_∞ and V_t being the volumes of NH_3 evolved at infinity and at definite time interval. One such graph in case of sample Dy_2CdO_4 is shown in Fig. 1. Similar curves have been obtained in case of other samples too. Fig. 2 shows the plot of volume of NH_3 evolved *vs.* time for the thermal decomposition of carbamide with and without the sample Dy_2ZnO_4. The values for rate constants, energy of activation and frequency factor are given in Table-2.

TABLE-2
KINETIC DATA FOR THE SOLID STATE DECOMPOSITION OF UREA WITH AND WITHOUT MIXED OXIDES

Samples	Specific rate at (t °C)			Activation energy (E_A) (cal mol^{-1})	log A
	140	150	160		
Urea only	1.65×10^{-2}	3.34×10^{-2}	4.48×10^{-2}	16.416×10^3	8.64
Dy_2ZnO_4 + urea	6.03×10^{-2}	7.37×10^{-2}	13.40×10^{-2}	8.549×10^3	4.55
Dy_2CdO_4 + urea	4.37×10^{-2}	7.08×10^{-2}	12.70×10^{-2}	18.810×10^3	10.02
Dy_2CuO_4 + urea	4.38×10^{-2}	5.64×10^{-2}	7.47×10^{-2}	9.660×10^3	5.16
Di_2ZnO_4 + urea	21.88×10^{-2}	25.91×10^{-2}	29.61×10^{-2}	5.470×10^3	3.06
Di_2CdO_4 + urea	12.28×10^{-2}	14.39×10^{-2}	11.52×10^{-2}	5.470×10^3	2.94
Di_2CuO_4 + urea	11.52×10^{-2}	21.32×10^{-2}	36.85×10^{-2}	20.670×10^3	10.88

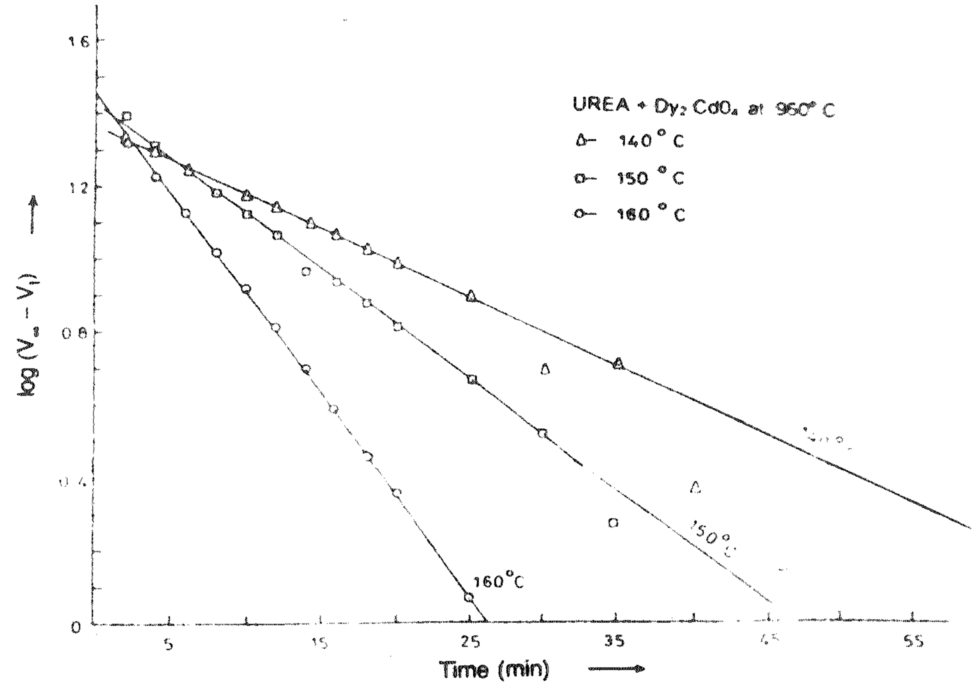


Fig. 1. First order kinetic plot for the solid state degradation of urea with Dy_2CdO_4

As is obvious from Fig. 2, the mixed oxide sample Dy_2ZnO_4 is found to be catalytically active for the solid state decomposition of carbamide. Similar graphs have been obtained in case of other samples showing that all other samples are also active catalytically. Table-2 reveals that the mixed oxide samples of dysprosium with copper, zinc and cadmium follow the activity sequence as $Dy_2ZnO_4 > Dy_2CdO_4 > Dy_2CuO_4$. However, the mixed oxide samples containing didymium as common element follow the different activity sequence, *i.e.*, $Di_2CuO_4 > Di_2ZnO_4 > Di_2CdO_4$. The oxide samples of didymium with copper,

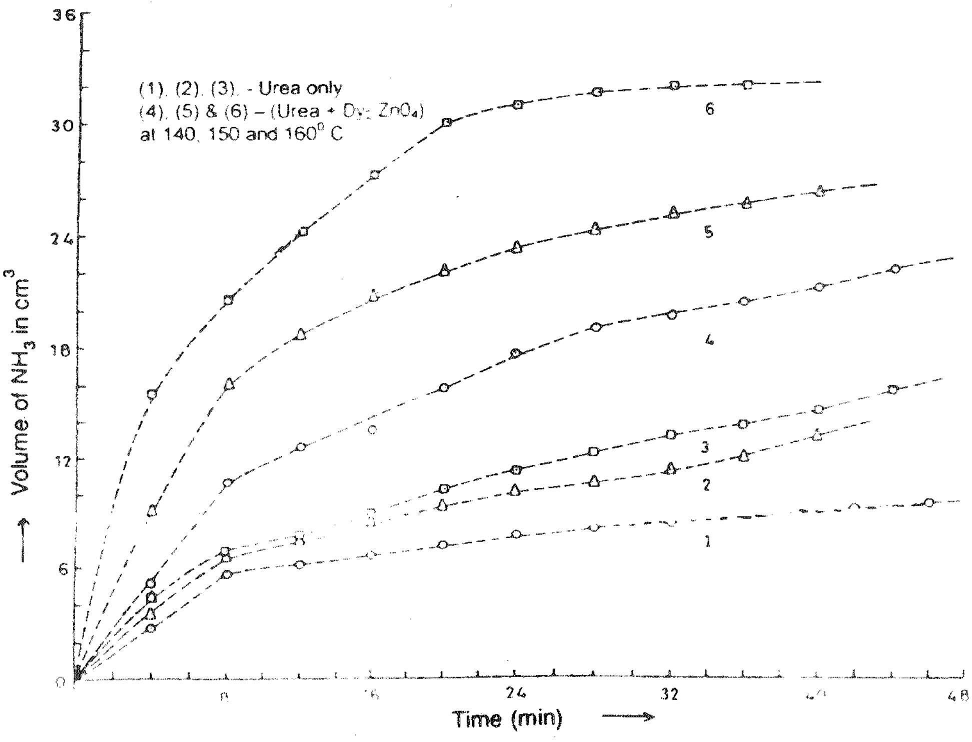


Fig. 2. Kinetics of degradation of carbamide: (1), (2), (3): Urea only; (4), (5), (6): (Urea + Dy_2ZnO_4) at 140, 150 and 160°C respectively

zinc and cadmium are observed to be more active than the samples of dysprosium with copper, cadmium and zinc. The mixed oxide sample Dy_2CuO_4 has the least catalytic activity whereas Di_2CuO_4 shows the maximum catalytic activity. Let the results be discussed in the light of the measured surface properties of the oxide samples. Table-1 shows that the surface natures of these oxides are different. The sample Dy_2ZnO_4 has the basic surface whereas samples Dy_2CdO_4 and Dy_2CuO_4 have acidic surfaces. If surface acidity is involved in the catalytic activity in some way then the samples Dy_2CdO_4 and Dy_2CuO_4 would have acted differently. It seems that it is not the acidity of the surface but basicity which plays the key role in activating the catalysts. Hence, the sample Dy_2ZnO_4 should be more active. It is to be the case (Table-2). However, our observation does not support the conclusion of the earlier workers[11] who have studied the degradation of carbamide in presence of non-stoichiometric oxides of yttrium. The activity sequence of the catalaysts observed is not explainable only on the basis data of basicity of surface. It is worth mentioning that some other surface property, probably excess surface oxygen, may determine the activity of the oxide samples. When we analyze the values of the excess surface oxygen depicted in Table-1, nothing very definite regarding its contribution towards the activity is ascertained, since the sample Dy_2ZnO_4 having the maximum activity in the series has not shown the highest value of excess surface oxygen . Again the sample Dy_2CdO_4 has been found to be comparatively less active in the series but its excess surface oxygen value is maximum (Table-1). Obviously, when the basicity of the surface and the excess surface oxygen are considered together, the former predominates in making the oxide samples active. The contribution of excess surface oxygen would always be positive however small it may be. This observation has gone against the finding of the earlier workers[11] who have found the surface excess oxygen to control the activity and selectivity of the catalysts. Now let us explain the catalytic activity in terms of surface area which as we know does play a vital role in adding to the catalytic action of the compounds. A close persual of the surface area values depicted in Table-1 shows that the oxide sample Dy_2ZnO_4 has quite a high value of surface area which in fact justifies the reflection of maximum catalytic activity of the oxide sample Dy_2ZnO_4 in unison with the excess surface oxygen. Thus, surface area has become a potential factor to account for the catalytic activities of mixed oxide samples. Our observation is quite in agreement with that of earlier workers[5] who have studied the catalytic activity of the mixed oxides of perovskite type strucures.

Let us now discuss the results of the decomposition of carbamide in presence of mixed oxide containing didymium. Table-2 shows the experimental data.

The decomposition follows the first order kinetics. The specific rate constant values are higher in comparison to that recorded in presence of mixed oxides containing dysprosium. The activation energy values vary but no regular trend in the variation is observed.The analysis of the specific rate constants indicates that the mixed oxide sample Di_2CuO_4 is the one possessing the highest catalytic activity for the process whereas the sample Di_2CdO_4 shows the least catalytic activity. It is known that catalytic activity is a function of a number of factors. Any factor responsible for activity in a certain process may be less active or inactive in another process. If we examine Tables 1 and 2, it is obvious that the sample Di_2CuO_4 with the highest activity in the series has got the maximum value of excess surface oxygen. In fact, if the surface excess oxygen is one of the factors responsible for activity, the sample Di_2CuO_4 should be the most active. The maximum catalytic activity of the sample Di_2CuO_4 is explained. Further, the values of excess surface oxygen follow the same sequence as that of the activities of the samples supporting the aforesaid conclusion. On the basis of the analysis of the values of surface basicity *vis-a-vis* activity (Tables 1 and 2), it is to be concluded that the activity is certainly favoured by the basicity of the surface in the process. Table-1 also contains the values of surface area of the samples. The surface area which has been held undoubtedly to be a potential factor in making the catalyst efficient. On account of this the sample Di_2ZnO_4 becomes more active than the sample Di_2CdO_4 though its surface is found to be more basic than the sample Di_2ZnO_4. It is worth while to conclude that the catalytic activity is certainly the resultant of all these surface properties.

Compensation Effect

Compensation effect is the variation of the pre-exponential factor 'A' with respect to the energy of activation 'E_A'. For a series of catalysts and for a given reaction, the relation between A and E_A takes the form

$$\log A = aE_A + b \qquad (i)$$

where a and b are constants. Fig. 3 shows the variation of log A with E_A.From Fig. 3 it is clear that log A varies linearly with E_A. Thus in the solid state decomposition of carbamide on oxide surface, the compensation effect is observed. The occurrence of compensation effect relates to the number of active sides on the surface of the catalysts.

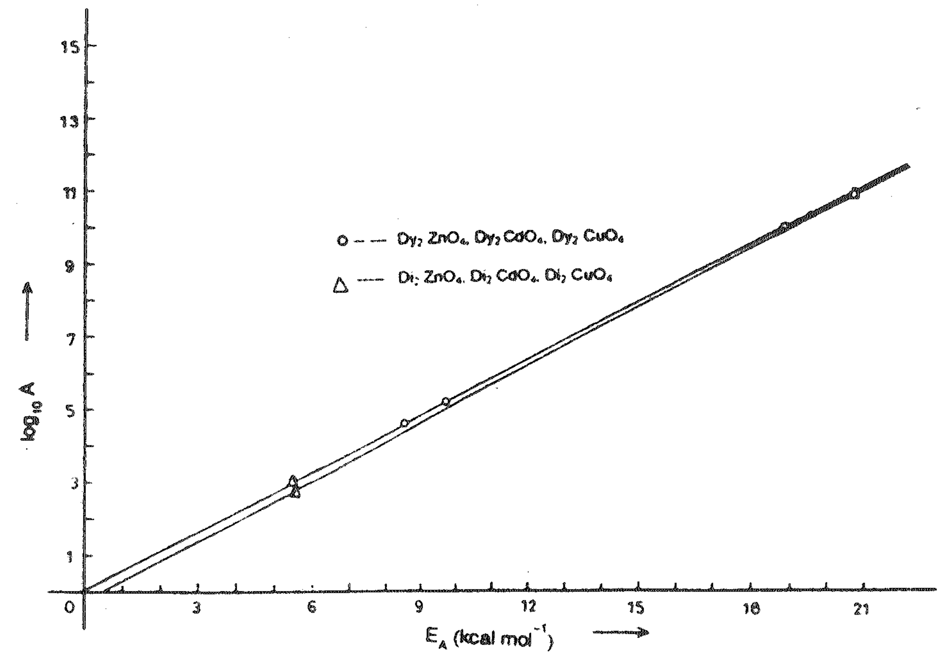
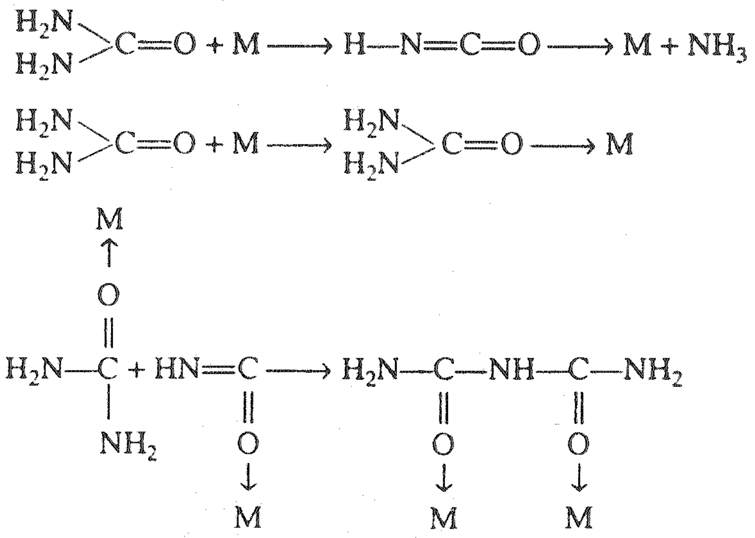


Fig. 3. Plot of $\log_{10}$ A *vs.* E_A for the solid state degradation of urea with Dy_2ZnO_4, Dy_2CdO_4, Dy_2CuO_4 and Di_2ZnO4, Di_2CdO_4, Di_2CuO_4

Mechanism of Decomposition

In the light of all facts and figures accumulated during the study, a possible mechanism of the decomposition of carbamide in the presence of these oxide samples has been suggested. Three possible steps are involved in the decomposition process. Carbamide itself is such a compound which has been shown to possess a remarkable complex formation capacity. Coming in contact with the catalyst, carbamide forms the hypocyanic acid-metal complex and loses a molecule of ammonia. Further, it is just possible that carbamide may form the carbamide-metal oxide complex owing to the presence of active oxygen site. The above two complexes condense to form the biuret metal oxide complex.



$$\text{(i)}\quad \begin{matrix}H_2N\\H_2N\end{matrix}\!\!>C{=}O + M \longrightarrow H{-}N{=}C{=}O \longrightarrow M + NH_3$$

$$\text{(ii)}\quad \begin{matrix}H_2N\\H_2N\end{matrix}\!\!>C{=}O + M \longrightarrow \begin{matrix}H_2N\\H_2N\end{matrix}\!\!>C{=}O \longrightarrow M$$

$$\text{(iii)}\quad H_2N{-}\underset{\substack{|\\NH_2}}{\overset{\substack{M\\\uparrow\\O\\\|}}{C}} + HN{=}\underset{\substack{\|\\O\\\downarrow\\M}}{C} \longrightarrow H_2N{-}\underset{\substack{\|\\O\\\downarrow\\M}}{C}{-}NH{-}\underset{\substack{\|\\O\\\downarrow\\M}}{C}{-}NH_2$$

Thus it is concluded that although carbamide is itself capable to liberate ammonia on solid state decomposition, the presence of metal/metal oxide destabilizes carbamide leading to the formation of biuret metal oxide complex and the evolution of ammonia gas in a greater speed. However, it needs a comprehensive study to corroborate the results.

ACKNOWLEDGEMENTS

The authors are grateful to Prof. R.P. Sahai, Head of Chemistry for providing facilities. One of us (BLB) is grateful to UGC, New Delhi for granting a Junior Research Fellowship.

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(*Received*: 2 April 2005; *Accepted*: 12 December 2005) AJC-4526