Mixed Metal Oxides and Catalysis

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Mixed metal oxides particularly the perovskites have been found
to be excellent catalysts of great versatility and diversity. Analysis
of the kinetic results obtained for the thermal degradation of urea
using $GdCoO_3$ and $GdNiO_3$, as catalysts in terms of the basic
concept of thermodynamics has led to the observation of "a family
of catalysts" in close analogy to a family of reactions well defined
and explained in literature. However, much more results are needed
to corroborate this observation.

**Key Words: Catalytic degradation of urea, Catalytic activity
of mixed metal oxides.**

INTRODUCTION

Solid state chemists and material scientists have become interested in deciding
the role of solid state properties of mixed metal oxides as catalysts, the mixed
metal oxide of perovskite type, especially substituted with small amount of nobel
metals, have been chosen emphatically for the purpose. Recently, Bhagat[1] and
Kumar[2] made a comprehensive study on physico-chemical and catalytic proper-
ties of mixed oxides of transition metals having perovskite structures. Thus, it
appears that a lot of work regarding the electrical transport, magnetic measure-
ments, surface properties etc. has been carried out but due attention has not been
paid to the catalytic properties of the mixed metal oxides of the type $GdMO_3$. In
the present programme, mixed metal oxides of the type $GdMO_3$ (M = Co, Ni)
have been prepared and their catalytic activities for the thermal degradation of
urea have been determined.

The theoretical results on the thermodynamical prameters, *viz.*, ΔH_a°, enthalpy
of activation and ΔS_a°, entropy of activation, obtained by employing the Eyring
equation in its usual form for the kinetically first order degradation process of
urea have been computed[3]. In the light of isokinetic relationship it has been
observed that both ΔS_a° and ΔH_a° vary and the plot of ΔH_a° *vs.* ΔS_a° has been found
to be linear whose positive slope becomes equal to the isokinetic temperature,
T_{iso}. This observation has emboldened us to conclude what constitutes "a family
of catalysts" in close analogy to a family of reactions.

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EXPERIMENTAL

The mixed metal oxide catalysts were prepared by ceramic method followed by heat treatment in vacuum[4]. GdCoO$_3$ samples subjected to heat treatment at 700, 800, 900 and 1000°C were labelled as M$_1$, M$_2$, M$_3$ and M$_4$ and those of GdNiO$_3$ as N$_1$, N$_2$, N$_3$ and N$_4$ respectively.

The kinetic degradation of urea in solid state was studied following the process adopted by Rustamova[5]. The process of degradation was followed by the rate of evolution of ammonia. The experiments were carried out at 140, 150 and 160°C in a glycerol thermostatic bath with temperature control of ±1°C. The degradation of urea was found kinetically to be of the first order. The kinetic parameters such as specific rate constants, energy of activation, etc. were calculated adopting the usual procedure.

RESULTS AND DISCUSSION

Table-1 contains the calculated values of enthalpy of activation (ΔH_a°) and entropy of activation (ΔS_a°) for the degradation process of urea. The close examination of results reveals that the maximum value of enthalpy of activation is 47832.9 J mol^{-1} while the entropy of activation for the same process under the same conditions catalysed or uncatalysed varies from –190.34 to –261.07 J K^{-1} mol^{-1}. As regards to the simultaneous changes in the values of enthalpy of activation and entropy of activation for the catalysed process in question the minute analysis of the results has led to the observation of far reaching consequences. Fig. 1 represents the isokinetic plot showing the variation of ΔH_a° with the change in ΔS_a° for the degradation process catalysed by GdCoO$_3$ and GdNiO$_3$ at 140°C. Similar plots have also been obtained at two different

Fig. 1. Isokinetic plot (ΔH *vs.* ΔS) at 140°C
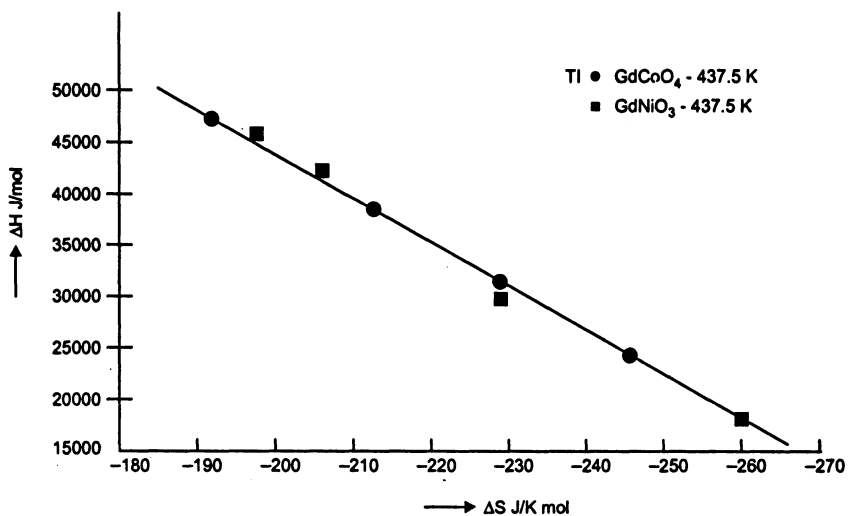
TABLE-1

THERMODYNAMIC PARAMETERS FOR DEGRADATION OF UREA

Sample	Degradation temp. (°C)	Activation temp. (°C)	Value of $K \times 10^{-2}$ (min^{-1})	E_A (kcal mol^{-1})	ΔH_a° (J mol^{-1})	ΔS_a° (J mol^{-1})
Carbamide alone	140	—	1.67	12.253	87832.90	–199.926
GdCoO$_3$		700	6.24	10.066	38682.50	–211.115
		800	8.25	6.655	24410.84	–243.343
		900	7.70	8.135	30603.20	–228.930
		1000	5.52	12.204	47627.86	–190.482
GdNiO$_3$		700	6.65	10.560	40749.40	–205.561
		800	8.79	4.880	16984.24	–260.811
		900	9.20	7.932	29753.80	–229.508
		1000	6.25	11.525	44786.90	–196.325
Carbamide alone	150	—	3.14	12.253	47749.80	–197.815
GdCoO$_3$		700	9.14	10.066	38599.30	–210.556
		800	9.72	6.655	24327.70	–243.779
		900	11.15	8.135	30520.00	–228.000
		1000	8.16	12.204	47544.70	–190.349
GdNiO$_3$		700	9.82	10.560	40666.20	–205.069
		800	11.00	4.880	16901.10	–260.308
		900	11.55	7.932	29670.70	–229.731
		1000	9.00	11.525	44703.80	–196.252
Carbamide alone	160	—	4.05	12.253	47666.60	–198.696
GdCoO$_3$		700	10.54	10.066	38516.20	–211.860
		800	11.35	6.665	24244.60	–244.205
		900	11.85	8.135	30436.90	–229.557
		1000	11.12	12.204	47461.60	–190.789
GdNiO$_3$		700	11.54	10.560	40583.10	–210.306
		800	11.75	4.880	16817.90	–261.077
		900	13.10	7.932	29587.50	–230.679
		1000	11.65	11.525	44620.60	–196.938

temperatures 150 and 160°C. These plots have been used to estimate the isokinetic temperature for the process. Analysis of the results recorded in Fig. 1 indicates the definite trend in the variation of values of enthalpy of activation and entropy of activation for the process catalyzed by various samples of GdCoO$_3$ and GdNiO$_3$. The values of enthalpy of activation decrease at first and then increase, whereas the values of entropy of activation increase at first and then decrease. However, the overall trend in both the cases considered in its own way is the same. It is of much interest to point out that the changes in the rate of the degradation process are due to the simultaneous changes in the enthalpy of activation and entropy of activation indicating the possibility of the existence of

"a family of catalysts" in the same way as "a family of reactions" already cited in literature[6]. In close analogy with that of a family of reactions the possibility of the existence of a family of catalysts is likely to be supported by the isokinetic relationship. It has been established that for a family of reactions if ΔH_a° is plotted *vs.* ΔS_a°, the isokinetic plot. a straight line with a positive slope equal to T_{iso} (isokinetic temperature), is obtained. For the degradation process in presence of various catalysts which we have marked now as a family of catalysts, the isokinetic plots exactly of the same nature, *i.e.*, a straight line (Fig. 1) reflecting the simultaneous variation in the values of enthalpy of activation and entropy of activation have been obtained. From the positive slopes T_{iso} has been calculated and presented in Table-2. The Arrhenius plots of log K *vs.* 1/T (the symbols have

TABLE-2
VALUES OF ISOKINETIC TEMPERATURE

Catalysts	Temperature (K)	T_{iso} (K) calcd. from isokinetic plots
GdCoO$_3$	413	437.8
	423	437.5
	433	437.6
GdNiO$_3$	413	437.5
	423	437.5
	433	437.8

usual meaning) for the reactions constituting a family of reactions will be a set of straight lines intersecting at a point corresponding to T_{iso}; all the reactions will have the same value of the rate constants at the point of intersection. Accordingly for this degradation process also catalysed by a set of catalysts of different activities the Arrhenius plot (Fig. 2) has been drawn. On examining these plots it has been found that these straight lines intersect at a point corresponding to $1/T_{iso}$ in close similarity with that of a family of reactions. From the Arrhenius plot the value of isokinetic temperature has been found to be 438.5 K in case of GdCoO$_3$ which is quite comparable with those in Table-2. This has been found to be the same in case of GdNiO$_3$. The relative contributions of enthalpy and entropy terms depend on temperature. At the isokinetic temperature it is interest-ing to note that the values of K, the reaction constant, for the degradation process of urea in presence of different catalysts are equal. In fact, the occurrence of isokinetic temperature provides a strong support to the observation of "a family of catalysts". To adduce adequate ground for the presence of isokinetic plots and our observation of a family of catalysts let us look at the problem in another way.
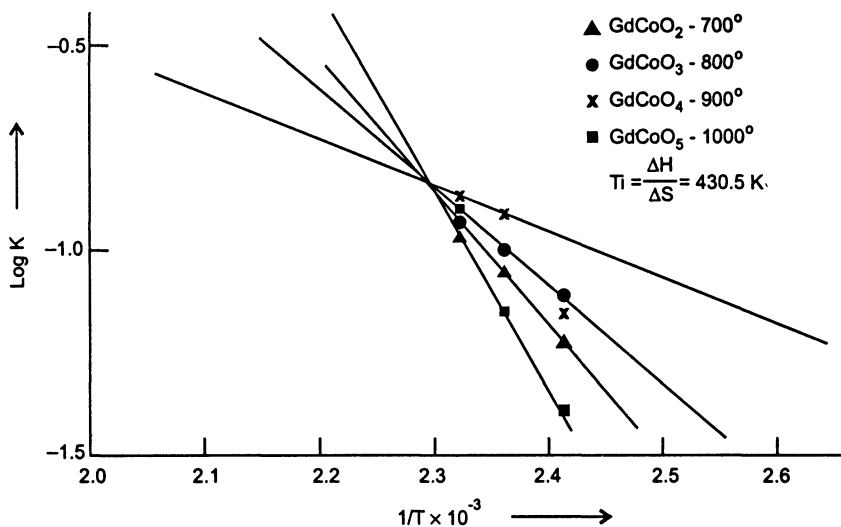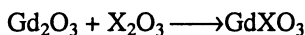
Fig. 2.   Arrhenius plot (log K $vs.$ 1/T)

During the process of synthesis the ultimate product of mixed metal oxides is supposed to be formed through the addition step as elaborated.

$$Gd_2O_3 + X_2O_3 \longrightarrow GdXO_3$$

where X = Co, Ni.

Thus, into the main oxide of Gd_2O_3 the subsidiary oxides Co_2O_3 and Ni_2O_3 are introduced leading to the formation of $GdCoO_3$ and $GdNiO_3$. These two mixed oxides are heated at different temperatures, $viz.$, 700, 800, 900 and 1000°C for definite periods yielding eight different samples of catalysts. Thus, these eight samples present a group of catalysts of different catalytic capabilities forming a family of catalysts. It is worth mentioning that Hammett[6] critically analyzed the results on a family of reactions and proposed the basic relation between the rate constants in the form of the equation,

$$\log K = \log K^0 + \sigma\rho$$

where K is the rate constant for a reaction involving substituted aromatic compound and K^0 is the rate constant for the parent compound. The parameter ρ is called reaction constant, which depends upon the nature of the reaction, and external conditions while the parameter σ is called a substituent constant.

It seems to be logical to identify the single oxide Gd_2O_3 as the parent catalyst and the derived mixed oxides containing Co and Ni constitute what we call a family of catalysts. However, to establish the relation between the rate constant for the degradation of urea in the presence of parent catalyst and derived mixed catalyst as demanded by the Hammett equation it needs a comprehensive programme to be accomplished.

In support of this observation the decarboxylation of phenylalanine in presence of these catalysts is being continued.

Conclusions

The kinetic results on the thermal degradation of urea when analyzed in the light of isokinetic relationship lead to the conclusion that there exists "a family of catalysts" similar to the occurrence of a family of reactions. However, this observation is to be corroborated by further investigations.

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