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Research Article: Studies on Synthesis and Physico-Chemical Properties of Mixed Oxide of Rare-Earth Transition Metals of the type $LnMO_3$

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Abstract

Mixed metal oxides particularly of the type $LnMO_3$ (Ln = Yttrium, B = Cobalt, Nickel) have been prepared and their catalytic behavior for the thermal decomposition of Urea (Carbamide) has been studied. Surface acidity and excess surface oxygen (ESO) of the samples obtained from solid state decomposition of nitrates of yttrium, cobalt and nickel have been measured. it has been observed that the values of excess surface oxygen decreases as the decomposition temperature increases. The same observation was found in the case of acidity measurements. The nature of defects as well as other surface properties in many systems are yet to be studied. For example, not much is known about the catalytic properties of perovskite oxides. Presently we report the catalytic properties of $LnMO_3$ (Ln = Y, and M = Co, Ni) activated at different temperatures for the solid-state degradation of carbamide.

Abbreviation : ESO (Excess Surface Oxygen)

KEYWORDS: Mixed metal oxides; Solid State Mixing, Urea decomposition, Acidity, Catalytic activity.

Introduction

Rare-Earth oxides, simple or, mixed, stoichiometric or, non-stoichiometric have been the subject of intensive exploration and results recently obtained so far have proved fruitful in efforts to correlate solid state chemistry and catalysis.[1] Thus, it is to be concluded that the subject of mixed metal oxides and their properties have the great relevance to the chemistry.

The ideal perovskite structure of the type $LnMO_3$ (Ln = Yttrium (Y), B = Cobalt (Co), Nickel (Ni)) is cubic, which shows high structural stability because the position of Cation Ln/M can be replaced by different types of rare-earth transition metals. And it changes into different oxides with special chemical and physical properties.[2]

For the last twenty years, extensive work on catalytic activities of oxides of different nature viz. stoichiometric or, non- stoichiometric, single or, mixed have been carried out. Nutshell of the findings is worth mentioning and forms the basis for the growth of new ideas. It has been observed that catalytic activities depend upon various parameters such as atomic number, oxygen content, degree of non-stoichiometry, role of d and f-electrons, surface acidity and basicity and structural features. R. Kumar et.al. did considerable works on catalytic activities of the mixed oxides of type Ln_2MO_4 and $LnMO_3$ and concluded that there is no significant relationship between basicity and variation of excess surface oxygen.[3]

Scope of the article: Material Science Catalysis

Materials and Methods

The mixed metal oxide catalysts were prepared by ceramic method followed by heat treatment in vacuum.[4,5] $YCoO_3$ samples subjected to heat treatment at 700°C, 800°C, 900°C and1000°C were labelled as YC_1, YC_2, YC_3 and YC_4 and those of $YNiO_3$ as YN_1, YN_2, YN_3 and YN_4 respectively. The kinetic degradation of urea in solid state was studied by the following process adopted by Rustamova.[6] The process of degradation was followed by the rate of evolution of ammonia. The experiments were carried out at 140°C,150°C and160°C in glycerol thermostatic bath with temperature control of ±1°C. The degradation of urea was found kinetically to be of first order. The kinetic parameters such as specific rate constant, energy of activation etc. were calculated adopting the usual procedure.

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°C, 150°C and 160°C. 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 the case of sample $YNiO_3$ is shown in fig.-1. Similar curves have been obtained in the case of other samples too. Kinetic data for the solid-state decomposition of urea with and without mixed oxide samples. The values of rate constants, energy of activation and frequency factors are given in Table 2.

As is obvious from fig. 2, the mixed oxides samples $YNiO_3$ which is found to be catalytically active for solid state decomposition of carbamide. Similar graphs have been obtained in the case of other samples showing that all other samples are also catalytically active. Table-2 reveals that the mixed oxides samples of yttrium (Y) and nickel (Ni) heated at 700, 800°C, 900°C and 1000°C follow the activity sequence as $YN_3 > YN_4 > YN_1 > YN_2$. However, the mixed oxides samples containing yttrium (Y) and cobalt (Co) follow the different activity sequence i.e., $YC_1 > YC_3 > YC_2 > YC_4$.

It is clear from the data in the Table 2. all the samples activated at different temperatures catalyze the degradation of carbamide through their degree of catalytic activities for the thermal decomposition of urea seen to be different, taking the values of specific rate constants in consideration it is to be concluded that there is no regular pattern between the catalytic activities of the samples and temperature of activation. This is also reflected from the values of energy of activation.

However, the samples of $YCoO_3$ activated at 700 °C and 1000°C found to be more active than the samples activated at 800 °C and 900°C. Similar observation with respect to catalytic activity is also recorded in Table 2. in the case of $YNiO_3$.

As reported in the literature,[7] the degraded product of carbamide decomposition at low temperature which occurs in two steps are biuret and ammonia. Our experimental data also supports the same scheme. It is to be noted that all the samples activate the degradation of carbamide although the degree of activation differs. From the plots, volume of ammonia (NH_3) Vs time (t) the sample calculation yields 8.8cm^3, 13.9cm^3, 18.0 cm^3 of ammonia at 140 °C, 150 °C and 160°C respectively in 10 min. However, with the sample of $YNiO_3$ activated at 1000°C, 13.1cm^3, 16.7cm^3 and 21.7 cm^3 of ammonia obtained at corresponding temperature in the same specified time from the same quantity of urea. These observations conclude that the sample of perovskite type oxide containing nickel appear catalytically more active in comparison to that containing cobalt. This is also obvious from the rate constant data depicted in Table 2.

Table 1. also contains data on excess surface oxygen and acidity of our sample. These values decrease regularly with rise in temperature of activation of the samples. Similarly, variation in values of ESO (Excess Surface Oxygen) of $YCoO_3$ with rise in calcination temperature has been reported by Madhok.[8] However, from the analysis of our experimental data, we conclude that excess surface oxygen and activity seem to play no significant role towards the catalytic activity of samples.

The plots of log A Vs E_A values show linear relationship. It indicates that the active centers are transition metal ion, i.e., Ni^{2+} in $YNiO_3$. Thus, the variation in activity of the samples might attributed to the different amount of transition metal ionic species distributed on the surface. Similar type of observation has been reported by Johnson, Jr et.al.[9,10] for the catalytic activity of $LaMeO_3$ (Me = Fe, Co, Mn) for the oxidation of Co.

Table 1: Data For ESO, Acidity and Surface Area.

Samples	Decomposition temperature (°C)	ESO per 100g ($\times 10^{-3}$)	Acidity (meq/g)	Surface area (m^2/g)
YC_1	700	8	160.6	7.102
YC_2	800	5.04	156.585	—
YC_3	900	4.24	128.48	—
YC_4	1000	4	105.12	1.205
YN_1	700	4	173.448	2.176
YN_2	800	3.44	158.672	—
YN_3	900	3.2	146.788	—
YN_4	1000	2.08	128.48	2.176

Table 2: Kinetic data for the solid-state decomposition of urea with and without samples.

Samples	Decomposition Temperature	Specific rate ($\times 10^{-2}$)			Activation Energy (E_A) kcal mol^{-1}	log A
		140°C	150°C	160°C		
Urea Only	—	1.41	3.30	4.0	18.630	8.048
YC_1	700°C	7.88	16.95	16.08	13.297	5.978
YC_2	800°C	7.79	9.86	10.49	5.456	1.786
YC_3	900°C	7.39	10.58	11.73	8.463	3.358
YC_4	1000°C	4.88	7.70	10.09	14.436	6.304
YN_1	700°C	6.35	9.23	10.73	9.573	3.877
YN_2	800°C	8.42	10.39	10.08	3.373	0.724
YN_3	900°C	8.34	11.18	11.87	6.486	2.364
YN_4	1000°C	6.23	8.73	10.83	10.029	4.102

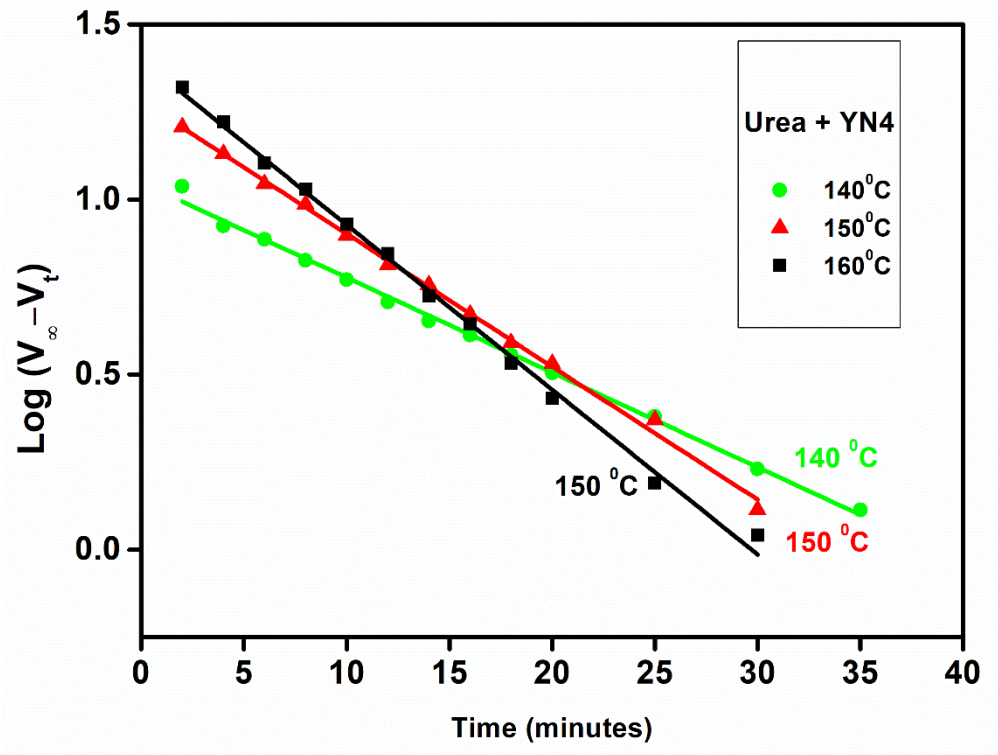

Fig. 1. First order kinetic plot for the solid-state degradation of urea with $YNiO_3$ (YN_4).

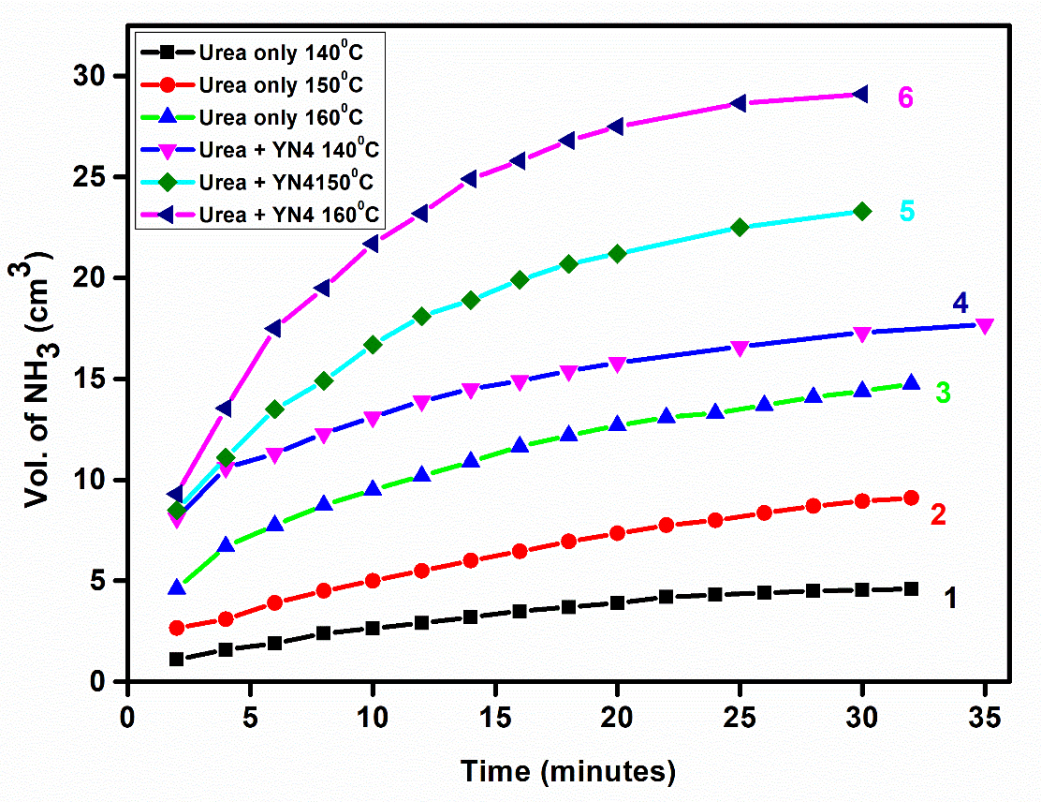

Fig. 2. Kinetics of degradation of carbamide: (1), (2), (3): Urea only; (4), (5), (6): Urea + $YNiO_3$ (YN_4) at 140°C, 150°C and 160°C respectively.

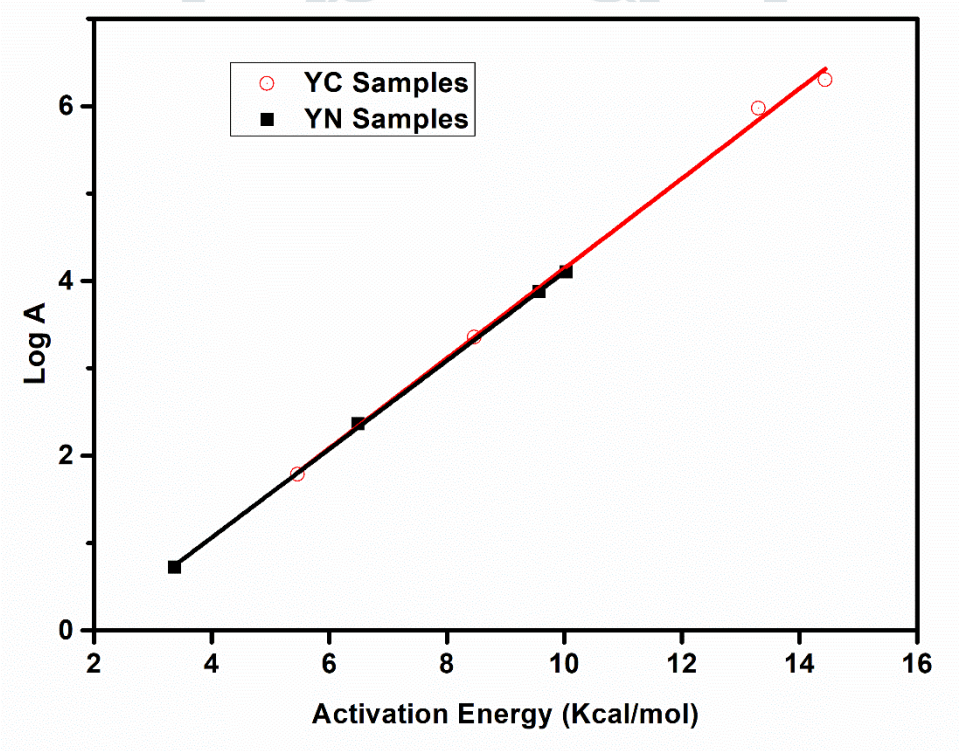

Fig. 3. Plot of log A *vs.* E_A for the solid-state degradation of urea with YC ($YCoO_3$) and YN ($YNiO_3$).

Conclusion

Thus, it is concluded that the transition metal ions are responsible for the activity of $LnMO_3$ type oxides and rare-earth ions moderate the catalytic activity of the transition metal ions.

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This research did not involve human participants, animal subjects, or any material that requires ethical approval.

Informed Consent Statement

This study did not involve human participants, and therefore, informed consent was not required.

Clinical Trial Registration

This research does not involve any clinical trials.

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Not Applicable.

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