

Studies on the Catalytic Decomposition of N₂O on Rare Earth Cuprates of the Type Ln₂CuO₄

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The kinetics of nitrous oxide decomposition between 400 and 480°C at two different initial pressures namely, 50 and 200 Torr over a series of isostructural rare earth cuprates (Ln₂CuO₄) is described. The kinetics obeyed a rate expression corresponding to strong inhibition by oxygen at both the initial pressures, except on La₂CuO₄. The observed higher activation energy values at 50 Torr initial pressure as compared to 200 Torr has been understood in terms of the importance of O_(ads) species migration on the surface. A multicenter type of adsorption of N₂O over a cluster of Ln-O-Cu on these surfaces could account for the various observations made in the present investigation. The operation of compensation effect and correlation between the activation energy for the reaction and (i) E_a for conduction, (ii) lattice parameter suggested the importance of the electron transfer step in the kinetics of decomposition reaction.

INTRODUCTION

In recent years materials crystallizing in perovskite and perovskite-related structures, viz., double perovskites and K₂NiF₄ type of oxides, have received considerable attention in view of their potential applications in catalytic conversion reactions (1-8). K₂NiF₄, a structure derived from perovskite unit cell, possesses the same octahedral environment around the transition metal ion as that contained in the parent perovskite cell, but the coordination around rare earth/alkaline earth ion is nine as compared to that of a dodecahedral environment in perovskites (9). Many of the rare earth cuprates and nickelates have been found to crystallize in this structure (9-12). The catalytic activity of these materials has been tested toward the reduction of NO with NH₃ and oxidation of methanol to a limited extent (4, 13).

The present study of the kinetics of the decomposition of N₂O on a series of rare earth cuprates, with the general formula Ln₂CuO₄ (Ln = La, Pr, Nd, Sm and Gd), has the following aims: (a) to evaluate the efficiency of these catalysts towards oxidation reactions, and (b) to correlate the ob-

served catalytic activity with the predetermined physicochemical properties like lattice parameter, E_a for electrical conduction, and magnetic moment of the rare earth ion.

The active transition metal ion in this isostructural series is the Cu ion framed within the network of a coordinated Ln-O bond.

MATERIALS AND METHODS

The rare earth cuprates Ln₂CuO₄ were synthesized by firing the stoichiometric mixture of the component oxalates at 960°C for 24 hr in a Pt crucible in air. The formation and presence of the K₂NiF₄ structure was confirmed using X-ray diffraction and chemical analysis techniques. The surface areas of these powders were evaluated using BET method employing N₂ as adsorbate at liquid N₂ temperature. The electrical conduction properties were determined on sintered pellets of the cuprates in a conventional two probe cell in the temperature range 300-773 K. The magnetic susceptibility measurements were conducted in a Guoy balance.

The kinetics of N₂O decomposition was studied in an all-glass static recirculatory reactor of volume 210 ml. The decomposi-

tion reaction was carried out at two different initial pressures namely, 50 and 200 Torr (1 Torr = 133 N m⁻²) and at various temperatures. Activity measurements at various recirculation speeds of the gas indicated no influence of mass transfer on the rate of decomposition. The increase in the total pressure of the system was monitored in a Hg-manometer, attached to the system and this was employed in deriving the decomposition rates at any temperature. The following pretreatment has been given to the catalyst between the kinetic runs in that order: (a) Out gassing at 500°C and at a final pressure of 10⁻⁶ Torr for 6 hr; (b) Soaking of the catalyst with 100 Torr of O₂ for 12 hr at reaction temperatures; (c) Evaluation of gas phase and weakly adsorbed oxygen species for 2 min.

The above pretreatment was found to be indispensable to obtain reproducibility in the kinetic measurements.

RESULTS AND DISCUSSION

From the knowledge of the intensities and Miller indices of various interplanar spacings obtained by a detailed study of X-ray diffractogram, the cell parameters were evaluated. The observation that La₂CuO₄ alone crystallizes in orthorhombic symmetry, while the other cuprates in tetragonal lattice, is in perfect agreement with the literature reports on the same system (9). The tolerance factor, defined by Goldschmidt as

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

for these series falls in the range prescribed for the K₂NiF₄ compounds by Ackermann (14).

Table 1 contains the information pertaining to surface area, cell parameter, volume of the unit cell, and tolerance factor of the catalysts. The low values for the observed surface areas of these oxides are not surprising, in view of the high calcination temperatures employed in the synthesis. A decrease in the volume of the unit cell, with the increase in the atomic number of the rare earth ion, is due to the lanthanids contraction.

Muller-Buschbaum (15-17) reported a discrepancy in the coordination around the Cu atom in all these compounds and attributed it to Jahn-Teller distortions. This observation has also been supported in the present investigation, when the X-ray diffraction profiles of all the oxides exhibited a split in each of its peaks.

The structural stability along the series of these materials in relation to their component oxides has been evaluated by Tretyakov *et al.* (18) by means of electrochemical techniques. These studies have revealed that the Jahn-Teller distortions are prominent more in compounds with relatively stronger Cu²⁺-O²⁻ bond. Thus, it is clear that, across the series of La₂CuO₄, from La-Gd there is a shortening of Cu²⁺-

TABLE I
Structural Parameters for Rare Earth Cuprates

Compound	Symmetry	Lattice parameters (Å)			Volume of the unit cell (Å ³)	<i>t</i>	Surface area (m ² /g)
		a	b	c			
La ₂ CuO ₄	O	5.362	5.409	13.169	381.8	0.863	0.5
Pr ₂ CuO ₄	—	3.961	—	11.988	188.0	0.856	1.1
Nd ₂ CuO ₄	—	3.949	—	11.951	186.4	0.851	0.3
Sm ₂ CuO ₄	—	3.940	—	11.881	184.4	0.840	1.8
Gd ₂ CuO ₄	—	3.932	—	11.856	183.3	0.832	2.1

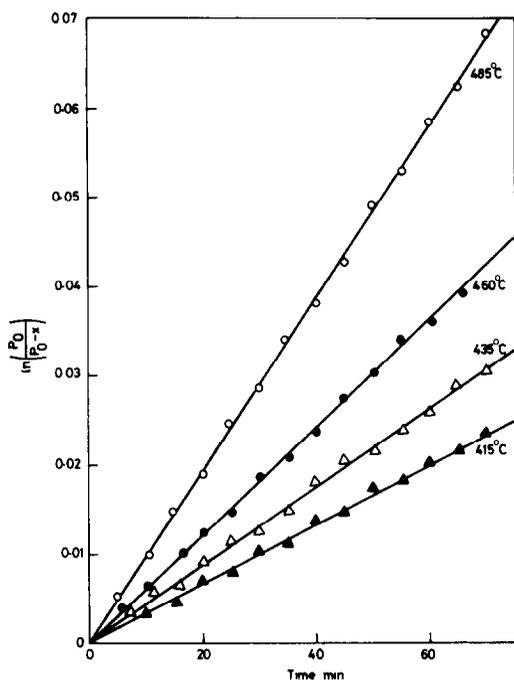


FIG 1 Kinetic plots for N₂O decomposition at an initial pressure of 50 Torr on La₂CuO₄

O²⁻ bond length, amounting to a higher degree of deformation of Cu-O octahedra. The geometry of La₂CuO₄ (17) indicates that there are two long (2.00 Å) and four short (1.90 Å) Cu-O bonds. On the other hand, in the case of other cuprates there are four long and two short Cu-O bonds. The position of the unpaired electron of Cu²⁺ has also been found to play a decisive role in the geometric orientation of these cuprates. The single electron of Cu²⁺ in La₂CuO₄ occupies the d_{x²-y²}, thereby resulting in higher c/a value in that symmetry.

The kinetics of decomposition of N₂O was studied at two different initial pressures. The kinetic data were analyzed using either of the following two equations corresponding to negligible and strong inhibition by oxygen, respectively

$$\frac{-dP_{N_2O}}{dt} = k_1 P_{N_2O} \quad (1)$$

$$\frac{-dP_{N_2O}}{dt} = \frac{k_2 P_{N_2O}}{(P_{O_2})^{1/2}} \quad (2)$$

The observed rate data for the title decomposition reaction could be accommodated in one of the integrated forms of the above equations. Typical kinetic plots obtained with La₂CuO₄ are shown in Fig 1. The Arrhenius plots were constructed using these rate data and are shown in Figs 2 and 3 for 50 and 200 Torr initial pressures, respectively.

It has been noticed that at 50 Torr initial pressure of N₂O, only La₂CuO₄ and Pr₂CuO₄ obeyed an equation corresponding to no inhibition by oxygen [Eq (1)] while on all other cuprates, one corresponding to strong inhibition [Eq (2)] was the kinetic expression. However, at an initial pressure of 200 Torr the rate data on all cuprates followed the equation corresponding to strong inhibition by oxygen, except on La₂CuO₄. In the latter case, there was no influence of oxygen on the kinetics even at the initial pressure of 200 Torr.

The observed rate constants at various temperatures, the activation energy for the decomposition reaction, and the frequency

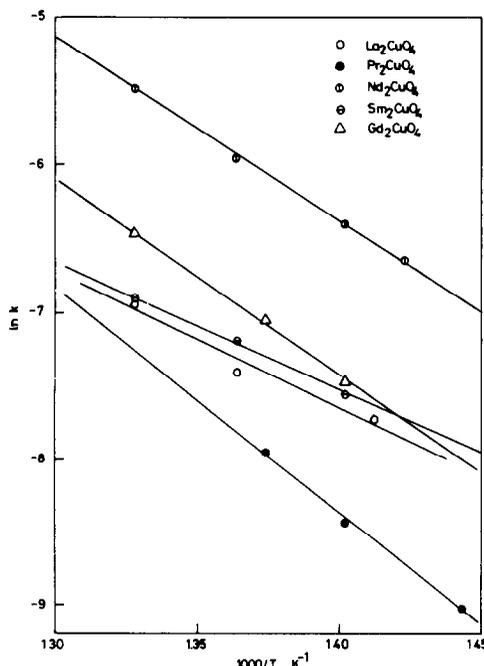


FIG 2 Arrhenius plots for the decomposition of N₂O on La₂CuO₄ oxides (50 Torr)

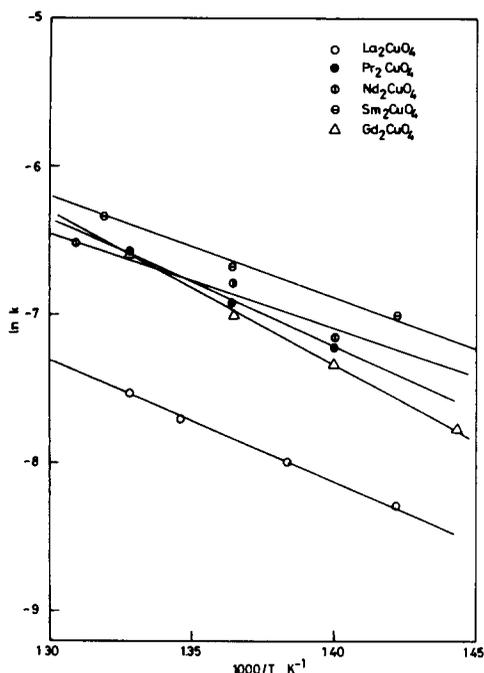
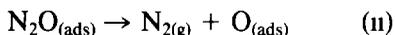
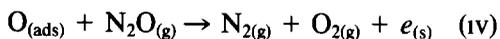


FIG 3 Arrhenius plots for the decomposition of N_2O on Ln_2CuO_4 at 200 Torr

factor are listed in Table 2. The general mechanism proposed for the decomposition of nitrous oxide on oxides has the following steps (19)



or



The above scheme involves the activation of a N_2O molecule by the donation of an electron from the surface. The surface decomposition of $N_2O_{(ads)}$ seldom is featured in the rate limiting step, owing to its quantum-mechanical instability caused by the presence of a 23 electron-linear system. Steps (iii) and (iv) indicate the desorption path of oxygen, by donation of a pair of electrons back to the surface.

The observation that at 200 Torr initial pressure of the reactant gas and in few

cases ($Ln = Nd, Sm, \text{ and } Gd$) even at 50 Torr initial pressure of N_2O , the kinetic expression corresponding to strong inhibition by O_2 [Eq (2)] fits the kinetic data indicates the following

(a) On all the cuprates the desorption of oxygen is not a facile process as that of adsorption of N_2O or the surface decomposition of $N_2O_{(ads)}$.

(b) On systems for which the kinetic data obey the same kinetic expression at both the initial pressures of N_2O (e.g., Nd_2CuO_4), approximately the same rate of decomposition is observed as revealed from the order of the rate constant (Table 2). This means that the surface is saturated with adsorbed N_2O at both the initial pressures and the decomposition is controlled mainly by the surface concentration and facility of the desorption of the adsorbed oxygen.

(c) On La_2CuO_4 and Pr_2CuO_4 the kinetic data at 50 Torr initial pressure obeys a first order kinetic equation indicating that on these systems the surface saturation by adsorbed N_2O is not reached at this initial pressure. This perhaps could be associated with the nature of the rare earth ion involved in these systems. The fact that there are no outermost 'f' electrons in La^{3+} and only one electron in Pr^{3+} makes the net availability of charge for transfer to the adsorbed N_2O molecule less and, hence, in these systems the adsorption of N_2O itself appears to be the rate-controlling step.

From the kinetic results presented in Table 2, it can be seen that the activation energy values corresponding to 50 Torr initial pressure are always higher than those noticed at 200 Torr initial pressure. This suggests that the migration of $O_{(ads)}$ on the surface plays an important role in the decomposition of N_2O .

The suprafacial nature of the decomposition of N_2O has been well documented in the literature (20). In a typical suprafacial reaction the catalyst acts as a template providing a collection of atomic and molecular orbitals [lowest unoccupied (LUMO) and

TABLE 2
 Kinetic Parameters for N₂O Decomposition on Rare Earth Cuprates

Catalyst	Pressure (Torr)	Rate equation obeyed	Temperature (°C)	Rate constant ^a (× 10 ⁻⁴)	Activation energy (kcal/mol)	Frequency factor in A
La ₂ CuO ₄	50	1	415	3.33	17.09	4.43
			435	4.40		
			460	6.02		
			482	9.64		
	200	1	432	2.67	10.83	-0.52
Pr ₂ CuO ₄	50	1	450	2.90	34.50	15.90
			470	4.26		
			480	5.33		
	200	2	410	5.26	12.60	1.80
			440	7.76		
460			11.20			
Nd ₂ CuO ₄	50	2	490	14.50	28.60	13.61
			430	9.82		
			440	16.50		
			460	26.00		
	200	2	480	40.90	17.60	5.15
			420	11.10		
			440	17.60		
			460	20.90		
Sm ₂ CuO ₄	50	2	480	27.80	19.61	6.24
			440	4.68		
			460	8.12		
	200	2	480	10.00	15.56	4.06
			400	5.75		
			430	8.75		
Gd ₂ CuO ₄	50	2	460	12.50	35.47	17.30
			482	17.80		
			440	5.25		
			455	9.25		
	200	2	480	15.50	20.60	7.21
			420	4.25		
			438	6.50		
			460	9.00		
			480	13.70		

^a sec⁻¹ for Eq. (1), mm^{1/2} sec⁻¹ for Eq. (2)

highest occupied molecular orbitals (HOMO)] of suitable symmetry for overlap with the adsorbate and the availability of orbitals of relevant symmetry and energy alone can control the overall rate of the reaction. A multicenter type of adsorption of N₂O molecule has been developed (21) to account for various observations mainly

concluded in Ln₂CuO₄ systems in these lines. Further, the validity of such a model of adsorption has been (22) substantiated in the case of rare earth nickelates with perovskite and K₂NiF₄ structure. The molecular orbital scheme is given in Fig. 4. The interaction of various molecular orbitals of N₂O with the Ln-O-Cu system is

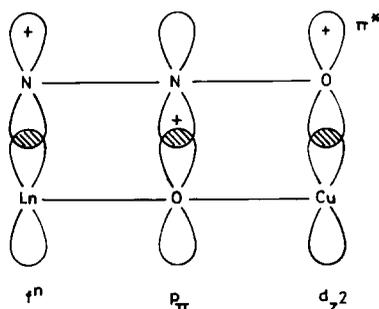


FIG 4 The interaction of various N_2O molecular orbitals with the Ln-O-Cu System

considered as follows. The π^* orbitals of N_2O have an orbital lobe in a direction similar to d_{z^2} orbital of Cu^{2+} . The π orbital of nitrogen can interact with the P_z orbital of the lattice oxide ion and the π orbitals of the terminal nitrogen can enter into interaction with the ' f ' orbitals of rare earth ion, having a maximum lobe in the axial direction leading to a multicenter adsorption of N_2O . The interaction between the axial ' f ' orbitals of the rare earth ion and d_{z^2} of Cu with P_z of the oxide ion is dependent on the electron density of ' f ' orbital of the rare earth ion. In this mode of adsorption of N_2O , a redistribution of charge density is possible due to the interactions between f , P_z , and d_{z^2} type of orbitals of Cu, N_2O , as well as Ln ions.

When lanthanum (with no outermost ' f ' electrons) is the rare earth ion the orbital interaction will bring a decrease in the net electron bond density around the Cu ion. Consequently, the desorption of $O_{(ads)}$, involving donation of electrons to the transition metal ion, will become facile and thus the desorption of oxygen can no longer be the rate-controlling step.

On similar lines, in the case of rare earth ions (f^n) with $n \geq 1$, the enhanced charge density at the transition metal ion retards the net electron flow from the adsorbed O species to the lattice and hence the rate-limiting step turns out to be the desorption of oxygen. This is also experimentally observed on all other cuprates, where the ki-

netics of N_2O decomposition obeys a rate equation involving strong inhibition by oxygen.

The catalytic reaction studies on isostructural, isocompositional systems have the prime motive of establishing physico-chemical correlations for a priori catalyst selection. For a typical suprafacial reaction like N_2O decomposition, wherein the orbitals of suitable symmetry and energy act as an electron relay switch to transform the species to a decomposable mode, the parameters of relevance are the activation energy for the reaction, frequency factor, lattice parameters of the systems studied, and electrical properties of the materials (23).

The operation of compensation effect (24) has been visualized in the system Ln_2CuO_4 as the values of energy of activation at both the initial pressures of N_2O vary linearly with logarithm of frequency factor and the plot in the case of 200 Torr initial pressure is shown in Fig 5. This implies that the sites responsible for the decomposition reaction are energetically different on different samples.

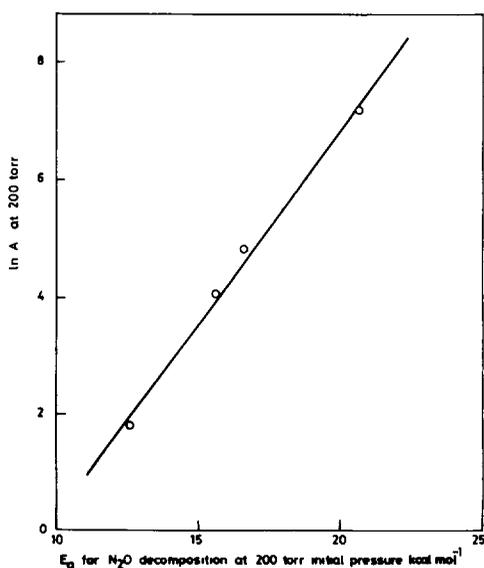


FIG 5 Compensation effect in the decomposition of N_2O on Ln_2CuO_4 oxides at 200 Torr initial pressure

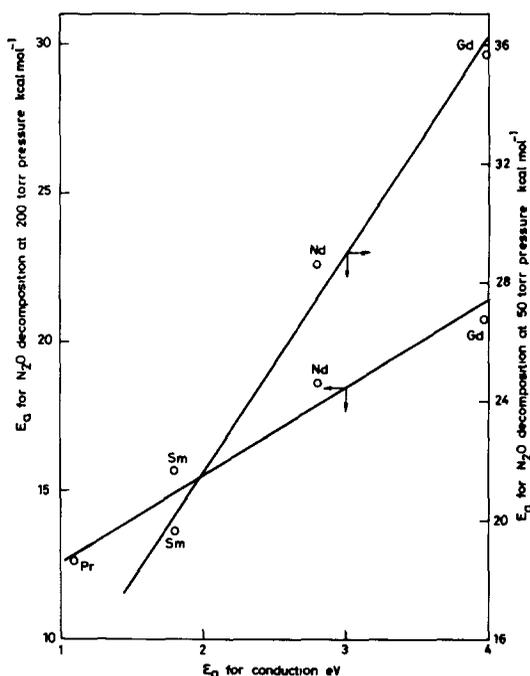


FIG 6 Correlation between E_a for conduction and E_a for reaction (at both initial pressures) in Ln_2CuO_4 oxides

Second, there is a linear correlation between the E_a for electrical conduction and E_a for catalytic reaction (Fig 6) This is expected on the basis of the suprafacial nature of the reaction studied In seeking a relationship between the electronic properties of the catalyst and the catalytic activity, the relevant energy levels are those around the Fermi level, namely, the lowest unoccupied and highest occupied levels In the case of ternary and quaternary oxides, the electronic structure is mainly determined by the 3d orbitals of the cations and p orbitals of the oxygen Accordingly, the interaction between these two states would give rise to various bonding and antibonding levels The antibonding levels appear to be of d character if the cations involved are transition metal ions and they suffer the usual crystal field splitting depending upon the nature and geometry of the coordination The position of the Fermi level appears between these levels, and this governs the ac-

tivity of the system in electron transfer reactions

In the sequence of the mechanism for the N₂O decomposition, the adsorption of N₂O molecule (step ii) in the reactive form of N₂O requires the presence of anion vacancies or F-centers in the catalyst On the other hand the desorption of O₂ will give rise to an R₂ center on the surface, which is subsequently destroyed by the oxygen adsorption or migration of lattice O²⁻ ions, thus creating the necessary F-centers for N₂O adsorption

If the electron release to the catalyst is the rate-limiting step then the mobility and number of electrons govern the transfer rather than their energy levels and accordingly there will be a correlation between the activation energy for electrical conduction and activity This has been experimentally realised in the present investigation

Finally, a plot of cell parameter (*a*) vs activation energy for the decomposition reaction is shown in Fig 7 An inverse linear correlation is indicated between the cell parameter and E_a for the reaction As has already been argued earlier there is a shortening of the Cu²⁺-O²⁻ bond with an increase

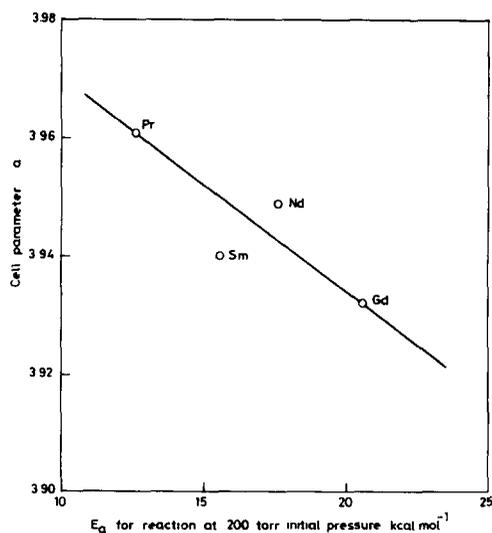


FIG 7 A plot of cell parameter, *a*, vs activation energy for the decomposition of N₂O on Ln_2CuO_4 oxides (at 200 Torr initial pressures)

in the lattice parameter. This would result in a weak interaction between the Cu^{2+} atom and the adsorbed oxygen. Consequently, it is evident that desorption of oxygen is facilitated on oxides having higher cell parameter values.

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