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Studies on the Catalytic Decomposition of N_2O on Rare Earth Cuprates of the Type Ln_2CuO_4

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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 (Ln_2CuO_4) is described. The kinetics obeyed a rate expression corresponding to strong inhibition by oxygen at both the initial pressures, except on La_2CuO_4. 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 N_2O 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 K_2NiF_4 type of oxides, have received considerable attention in view of their potential applications in catalytic conversion reactions (*1–8*). K_2NiF_4, 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 NH_3 and oxidation of methanol to a limited extent (*4, 13*).

The present study of the kinetics of the decomposition of N_2O on a series of rare earth cuprates, with the general formula Ln_2CuO_4 (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 observed 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 Ln_2CuO_4 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 K_2NiF_4 structure was confirmed using X-ray diffraction and chemical analysis techniques. The surface areas of these powders were evaluated using BET method employing N_2 as adsorbate at liquid N_2 temperature. The electrical conduction properties were determined on sintered pellets of the cuprates in a conventional two proble cell in the temperature range 300–773 K. The magnetic susceptibility measurements were conducted in a Guoy balance.

The kinetics of N_2O decomposition was studied in an all-glass static recirculatory reactor of volume 210 ml. The decomposi-

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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 O_2 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 La_2CuO_4 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

$$t = \frac{r_A + r_0}{\sqrt{2}(r_B + r_0)}$$

for these series falls in the range prescribed for the K_2NiF_4 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 Cu^{2+}–O^{2-} bond Thus, it is clear that, across the series of La_2CuO_4, from La–Gd there is a shortening of Cu^{2+}–

TABLE 1

Structural Parameters for Rare Earth Cuprates

Compound	Symmetry	Lattice parameters (Å)			Volume of the unit cell ($Å^3$)	t	Surface area (m^2/g)
		a	b	c			
La_2CuO_4	O	5 362	5 409	13 169	381 8	0 863	0 5
Pr_2CuO_4	—	3 961	—	11 988	188 0	0 856	1 1
Nd_2CuO_4	—	3 949	—	11 951	186 4	0 851	0 3
Sm_2CuO_4	—	3 940	—	11 881	184 4	0 840	1 8
Gd_2CuO_4	—	3 932	—	11 856	183 3	0 832	2 1

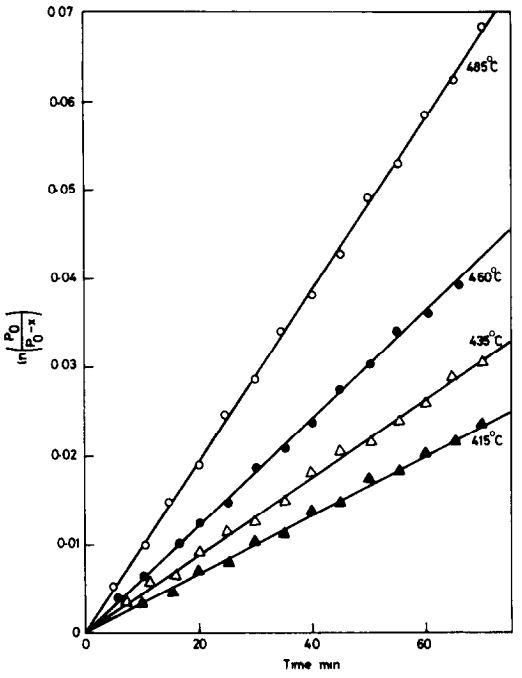

FIG 1 Kinetic plots for N_2O decomposition at an initial pressure of 50 Torr on La_2CuO_4

O^{2-} bond length, amounting to a higher degree of deformation of Cu–O octahedra The geometry of La_2CuO_4 (*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 Cu^{2+} has also been found to play a decisive role in the geometric orientation of these cuprates The single electron of Cu^{2+} in La_2CuO_4 occupies the $d_{x^2-y^2}$, thereby resulting in higher c/a value in that symmetry

The kinetics of decomposition of N_2O 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

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

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

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 Ln_2CuO_4 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 N_2O, only La_2CuO_4 and Pr_2CuO_4 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 La_2CuO_4 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

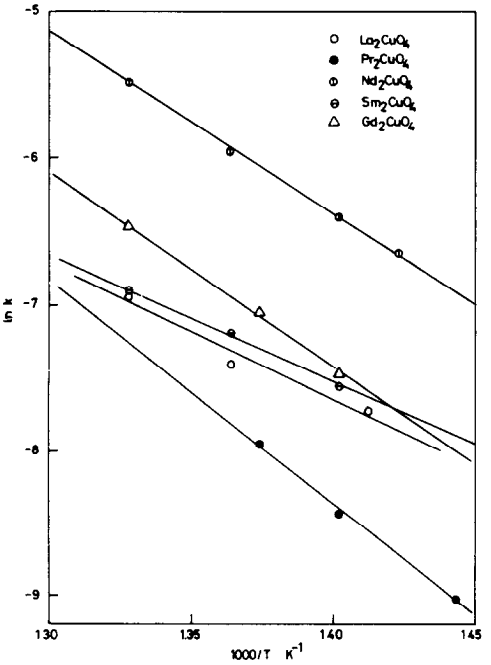

FIG 2 Arrhenius plots for the decomposition of N_2O on La_2CuO_4 oxides (50 Torr)

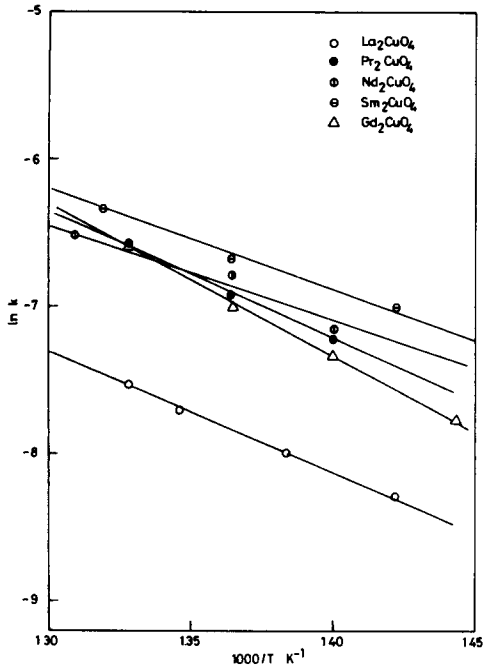

FIG 3 Arrhenius plots for the decomposition of N_2O on Ln_2CuO_4 at 200 Torr

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

$$N_2O_{(g)} \rightarrow N_2O_{(ads)} \quad (i)$$

$$N_2O_{(ads)} \rightarrow N_{2(g)} + O_{(ads)} \quad (ii)$$

$$2O_{(ads)} \rightarrow O_{2(g)} \quad (iii)$$

or

$$O_{(ads)} + N_2O_{(g)} \rightarrow N_{2(g)} + O_{2(g)} + e_{(s)} \quad (iv)$$

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, 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 N_2O Decomposition on Rare Earth Cuprates

Catalyst	Pressure (Torr)	Rate equation obeyed	Temperature (°C)	Rate constant[a] ($\times 10^{-4}$)	Activation energy (kcal/mol)	Frequency factor in A
La_2CuO_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
			450	2 90		
			470	4 26		
			480	5 33		
Pr_2CuO_4	50	1	420	1 02	34 50	15 90
			440	2 15		
			455	3 50		
	200	2	410	5 26	12 60	1 80
			440	7 76		
			460	11 20		
			490	14 50		
Nd_2CuO_4	50	2	430	9 82	28 60	13 61
			440	16 50		
			460	26 00		
			480	40 90		
	200	2	420	11 10	17 60	5 15
			440	17 60		
			460	20 90		
			480	27 80		
Sm_2CuO_4	50	2	440	4 68	19 61	6 24
			460	8 12		
			480	10 00		
	200	2	400	5 75	15 56	4 06
			430	8 75		
			460	12 50		
			482	17 80		
Gd_2CuO_4	50	2	440	5 25	35 47	17 30
			455	9 25		
			480	15 50		
	200	2	420	4 25	20 60	7 21
			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 N_2O molecule has been developed (*21*) to account for various observations mainly concluded in Ln_2CuO_4 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 K_2NiF_4 structure The molecular orbital scheme is given in Fig 4 The interaction of various molecular orbitals of N_2O with the Ln–O–Cu system is

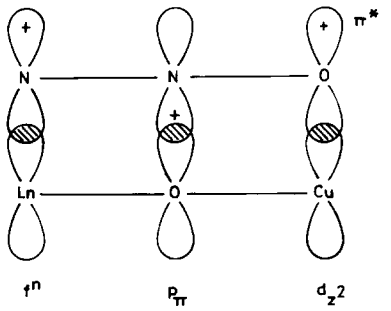

FIG 4 The interaction of various N_2O molecular orbitals with the Ln–O–Cu System

considered as follows The π^* orbitals of N_2O have an orbital throw 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 throw 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 kinetics 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 physicochemical 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 on 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

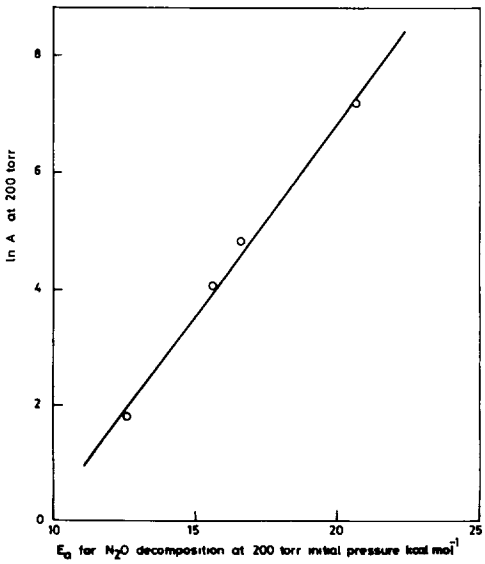

FIG 5 Compensation effect in the decomposition of N_2O on Ln_2CuO_4 oxides at 200 Torr initial pressure

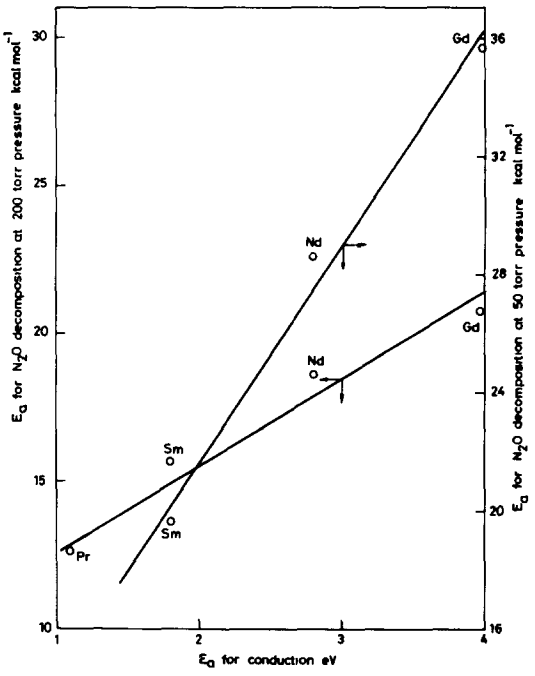

FIG 6 Correlation between E_a for conduction and E_a for reaction (at both initial pressures) in Ln_2CuO_4 oxides

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 3*d* 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 activity of the system in electron transfer reactions

In the sequence of the mechanism for the N_2O decomposition, the adsorption of N_2O molecule (step ii) in the reactive form of N_2O requires the presence of anion vacancies or F-centers in the catalyst On the other hand the desorption of O_2 will give rise to an R_2 center on the surface, which is subsequently destroyed by the oxygen adsorption or migration of lattice O^2 ions, thus creating the necessary F-centers for N_2O 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 Cu^{2+}–O^{2-} bond with an increase

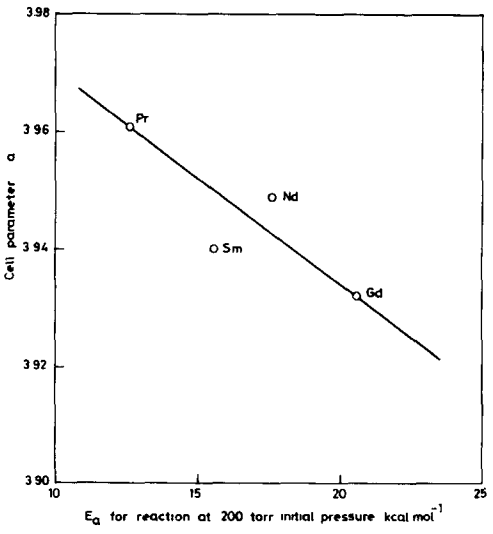

FIG 7 A plot of cell parameter, *a*, vs activation energy for the decomposition of N_2O on Ln_2CuO_4 oxides (at 200 Torr initial pressures)

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

REFERENCES

1 Nagasubramanian, G , Sastri, M V C , and Viswanathan, B , *Indian J Chem* **16A,** 242 (1978)
2 Muralidhar, G , Vijayakumar, K M , Swamy, C S , and Srinivasan, V , *Proc 7th Canadian Symp Catal* , Alberta, 1980 (in press)
3 Louis Raj, S , and Srinivasan, V , *J Catal* **65,** 121 (1980)
4 Arakawa, T , *Mat Res Bull* **14,** 507 (1979)
5 Voorhoeve, R J H , and Trible, L E , *Mat Res Bull* **9,** 655 (1974)
6 Parravanno, G , *J Amer Chem Soc* **83,** 2816 (1961)
7 Voorhoeve, R J H , Remika, J P , Freeland, P E , and Matthias, B T , *Science* **177,** 353 (1972)
8 Voorhoeve, R J H , Johnson, D W , Jr , Remeika, J P , and Gallaghar, P K , *Science* **195,** 827 (1977)
9 Foex, M , *Bull Soc Chim France* **109** (1961)
10 Muller-Buschbaum, Hk, and Wellschlager, W , *Z Anorg Allg Chem* **470,** 59 (1980)
11 Savehenko, I , *Vestdi Akad Navuk, SSSR, Khim Navuk* **6,** 44 (1969) *Chem Abst* **72** 940518
12 Muller-Buschbaum, Hk, *Z Anorg Allg Chem* **433,** 152 (1977)
13 Tetsuichi, K , Tersuo, G , and Kazuetsu, Y , *Environ Sci Technol* **12,** 185 (1978)
14 Ackerman, J F , *Mat Res Bull* **14,** 487 (1979)
15 Muller-Buschbaum, Hk , *Angew Chem Int Ed* (Engl) **16,** 674 (1977)
16 Muller-Buschbaum, Hk , and Wollschlager, W , *Z Anorg Allg Chem* **416,** 76 (1976)
17 Muller-Buschbaum, Hk , *Z Anorg Allg Chem* **428,** 120 (1977)
18 Tretyakov, Yu D , Kaul, A R , and Makukhim, N V , *J Solid State Chem* **17,** 183 (1976)
19 Fu, C M , Korchak, V N , and Hall, W K , *J Catal* **68,** 166 (1981)
20 Nagasubramanian, G , Viswanathan, B , and Sastri, M V C , *Indian J Chem* **14A,** 645 (1976)
21 Ramanujachary, K V , Vijayakumar, K M , and Swamy, C S , *J Bangladesh Acad Sci* **5,** 49 (1981)
22 Ramanujachary, K V , Vijayakumar, K M , and Swamy, C S , *React Kinet Katal Lett* **20,** 233 (1982)
23 Rienacker, G , and Scheve, J , *Z Anorg Allg Chem* **328,** 201 (1964)
24 Galwey, A K , *in* "Advances in Catalysis," Vol 26, p 247, Academic Press, New York, 1977