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NOTES

The Activity of Mn^{3+} and Mn^{4+} in Lanthanum Strontium Manganite for the Decomposition of Nitrous Oxide

Transition metal ions that are capable of exhibiting variable valency are interesting systems in that by a controlled variation of the valence states and the study of their activity toward a chosen test reaction, it is possible to identify the active valence state. Substituted manganites have been found to be active catalysts in a number of reactions. The activity of $La_{0.65}Sr_{0.35}MnO_3$ has been studied for CO oxidation (*1*) and that of $La_{0.7}Pb_{0.3}MnO_3$ has been studied for CO oxidation and NO reduction (*2*). The system $La_{1-x}Sr_xMnO_3$ is interesting in that by the substitution of strontium in varying amounts, it is possible to vary the Mn^{3+}/Mn^{4+} concentrations in the samples. Hence this system has been chosen for the study of nitrous oxide decomposition.

In the system $La_{1-x}Sr_xMnO_3$, strontium could be substituted only upto $x = 0.7$ keeping the perovskite structure, in accordance with the limitations of Goldschmidt's tolerance factor (*3*). The catalysts with $x = 0$, 0.1, 0.3, 0.5, 0.6, and 0.65 were prepared by a coprecipitation method (*4*) from a mixture of the solutions of the nitrates of La, Sr, and Mn in proper stoichiometry using ammonium carbonate. For $x = 0$, the coprecipitated mixture of carbonates was fired in nitrogen atmosphere at 950°C. The coprecipitated carbonates of all other compositions were fired in oxygen atmosphere at 950°C, as this was found necessary in the preparation of compounds with higher Mn^{4+} content (*5*). The catalysts were characterised by X-ray diffraction using CuK_α radiation. The percentages of Mn^{3+}/Mn^{4+} in the catalysts were determined by a redox titration (*6*) with ferrous ammonium sulfate. The surface areas of the catalysts were determined by BET method using nitrogen as the adsorbate. Magnetic susceptibility measurements were carried out using a Cahn electrobalance by the Faraday method. The kinetics of the decomposition of nitrous oxide has been studied in a static recirculatory reactor described earlier (*7*).

It was observed that the amount of Mn^{4+} in any given sample was greater than the amount of strontium substituted (Table 1). This is because of the nonstoichiometry (*8*) exhibited by the catalysts, i.e, they take up more excess oxygen than that required for a stoichiometric phase. The presence of excess oxygen is compensated by the existence of corresponding amount of cation vacancies.

At an initial pressure of 200 Torr (1 Torr = 133 N m^{-2}) the kinetic data for N_2O decomposition obeyed the rate equation (*9*):

$$\frac{P_0^{1/2}}{2^{1/2}} \ln \frac{P_0^{1/2} + y^{1/2}}{P_0^{1/2} - y^{1/2}} - 2^{1/2} y^{1/2} = kt \quad (1)$$

where P_0 is the initial pressure of nitrous oxide and y is the pressure of nitrous oxide decomposed at time t. Plots of L.H.S. of Eq. (1) vs time were suitably corrected for

TABLE I

Activation Energies for N_2O Decomposition and Physicochemical Characteristics for the Series $La_{1-x}Sr_xMnO_3$

Catalyst (x)	Mn^{4+}%	Surface area (m^2 g^{-1})	T_C[a] (K)	E_a (kcal mol^{-1})
0	6.3	4.2	148	18.2
0.1	35.8	4.7	188	13.2
0.3	41.4	6.4	330	7.3
0.5	54.7	6.0	356	7.5
0.6	59.5	6.6	348	9.6
0.65	67.6	4.1	326	18.0

[a] T_C, Curie temperature.

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the temperature-dependent oxygen adsorption on the catalyst surface of part of the oxygen produced from the decomposition by a numerical least-squares regression method (*10*) and the derived activation energies are presented in Table 1.

Plots of activation energy for N_2O decomposition vs x (strontium substituted) and $Mn^{4+}\%$ vs x given in Fig. 1 indicate that there is a minimum in the activation energy at $x = 0.41$ corresponding to $Mn^{4+}\%$ of 50, i.e., the catalyst with 50% Mn^{4+} possesses the maximum catalytic activity. This observation suggests that Mn^{3+} and Mn^{4+} do not act as individual active ions but are part of a large cluster group which acts as an electron donor or as an electron acceptor. Since a 50% Mn^{4+} concentration represents a system with the distribution of Mn^{3+} and Mn^{4+} in the ratio 1 : 1, the couple Mn^{3+}/Mn^{4+} seems to be the active cluster site for the decomposition. It can therefore be postulated that in the decomposition reaction, initially N_2O can be expected to be adsorbed as an anionic species preferentially on the Mn^{3+} sites. This will be followed by the surface reaction and the O^- species produced can be expected to migrate to adjacent Mn^{4+} site from which it can desorb as molecular oxygen after electron transfer to the surface site. The redox electron transfer steps discussed above cannot effectively change the concentrations of Mn^{3+} or Mn^{4+} as the Mn^{3+}/Mn^{4+} contents in the samples were found to be the same before and after use in the reaction.

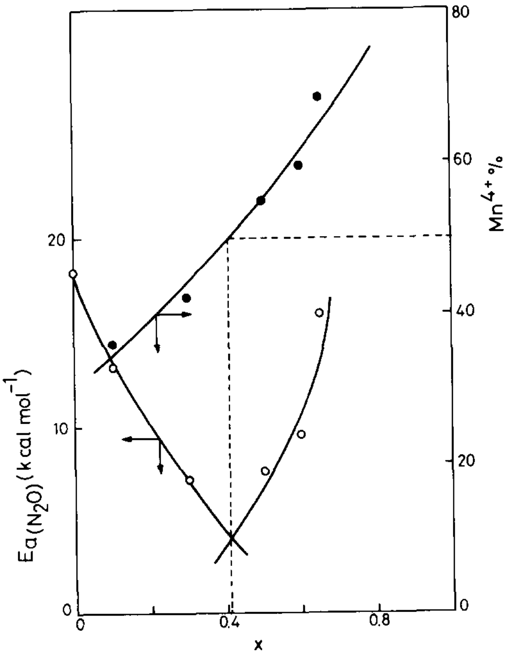

FIG. 1. Activation energy for N_2O decomposition or $Mn^{4+}\%$ versus x plots for the series $La_{1-x}Sr_xMnO_3$.

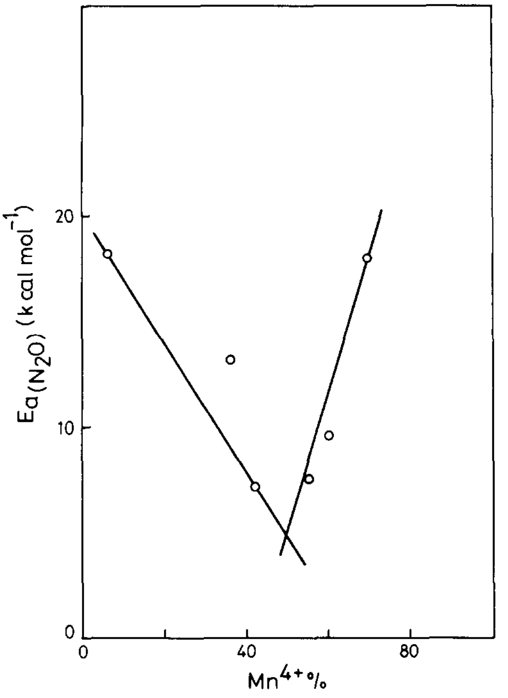

FIG. 2. Activation energy for N_2O decomposition versus Mn^{4+} for the series $La_{1-x}Sr_xMnO_3$.

Among the solid solutions, it will be seen that in the case of $La_{0.9}Sr_{0.1}MnO_3$, which has 10% strontium substitution, Mn^{4+} concentration is 36%, indicating the presence of 8–9% cation vacancies, the concentration of cation vacancies being the highest among the members of the solid solution series. A plot of energy of activation for N_2O decomposition vs $Mn^{4+}\%$ reveals that the observed value of energy of activation (Fig. 2) for $La_{0.9}Sr_{0.1}MnO_3$ is considerably higher. It is clear that the cation vacancies contribute toward the lowering of catalytic activity due to the reduction of Mn^{3+}/Mn^{4+} cluster sites.

Studies of N_2O decomposition on Mn^{3+}/Mn^{4+} ions in very dilute concentrations of these ions dispersed in MgO have revealed (*11*) that Mn^{3+} ions are more active than Mn^{4+} ions. The catalysts reported in the present study contain the active transition metal ions at high concentrations where the neighboring ion participation becomes an important factor.

Recent studies (*12*) on the catalytic activity of $La_{1-x}Sr_xMnO_3$ supported on α-Al_2O_3 for CO oxidation have shown that the catalysts in the region $x = 0.3-0.5$ exhibit maximum catalytic activity. Oxidation of NH_3 on $La_{1-x}Ca_xMnO_3$ studied by Vrieland (*13*) has revealed that the selectivity toward N_2O decreases at $x = 0.4$. These two observations are consistent with the present results. Magnetic susceptibility measurements on these catalysts have shown that the catalyst with 50% Mn^{4+} is the one that possesses the maximum Curie temperature (Table 1) in view of the positive Mn^{3+}–Mn^{4+} exchange interactions which could be maximum for this concentration with the distribution of Mn^{3+} and Mn^{4+} in the ratio 1 : 1. The redox couple Mn^{3+}/Mn^{4+}, by its capacity to facilitate easy charge transfers in the decomposition reaction, thus exhibits the maximum catalytic activity at this optimum concentration.

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