

SHORT COMMUNICATIONS

DECOMPOSITION OF NITROUS OXIDE ON $\text{La}_2\text{Ni}_{1.5}\text{M}_{0.5}\text{O}_6$ (M = Mo, W and Re)

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THE double perovskites with their highly adaptable and stable structures¹ are suitable in the study of model catalytic reactions on solid state catalysts for a clearer understanding of the role of solid state chemistry in catalysis. Subramanian *et al*² studied the structural and conductivity properties of the compounds $\text{La}_2\text{Ni}_{1.5}\text{M}_{0.5}\text{O}_6$ [M = Mo^{6+} , W^{6+} and Re^{6+} and denoted henceforth as LNMO, LNWO and LNRO respectively] and the values of lattice parameter (Å) and E_a for conduction (eV) reported for these compounds in the same order are (7.868, 0.11); (7.884, 0.40) and (7.870, 0.23) respectively. All the compounds are reported to be *p*-type semiconductors. We have attempted the catalytic decomposition of N_2O on these compounds to establish the reactivity of the active Ni^{2+} ion in various matrices.

The experimental procedures were the same as those used earlier³. The reaction was studied in the temperature range of 390–490°C and at initial pressures of 50 and 200 torr of N_2O . The kinetic data were analysed using the rate equations,

$$-d P_{\text{N}_2\text{O}}/dt = k_1 P_{\text{N}_2\text{O}}, \quad (1)$$

and

$$-d P_{\text{N}_2\text{O}}/dt = k_2 P_{\text{N}_2\text{O}}/(P_{\text{O}_2})^{1/2}, \quad (2)$$

corresponding to no inhibition and strong inhibition by oxygen respectively. The magnetic moments of the compounds were measured on a Gouy balance at room temperature.

Strong inhibition by oxygen controlled the rate on LNWO and adsorption of N_2O on LNMO at both the pressures. However, LNRO exhibited no inhibition by oxygen at 50 torr and strong inhibition by oxygen at 200 torr of N_2O . The values of activation energy for the reaction at 50 and 200 torr of N_2O respectively are LNMO (20.1, 19.1); LNWO (15.8, 21.0) and LNRO (7.4, 9.0) and $\ln A$ for reaction at 50 and 200 torr are LNMO (4.9, 8.7), LNWO (7.1, 6.2) and LNRO (-0.9, 1.3). It is thus seen that no single rate equation obeyed all the three catalysts at any single pressure, confirming the matrix contributions to reactivity.

In the catalytic decomposition of nitrous oxide, adsorption of N_2O and desorption of oxygen are the important rate-limiting steps⁴. The desorption of oxygen which involves the decoupling of the spins of O^- ions would be facilitated on a catalyst with high magnetic moment (BM) (LNMO, 0.306; LNRO, 0.273 and LNWO, 0.238). The diffusion of O^- ions on the surface leading to desorption of oxygen is inhibited by increasing lattice parameter values⁵ and also with increasing localization of charge carriers. Thus the increasing inhibition by oxygen as we go along the series, LNMO < LNRO < LNWO can be well understood.

The comparison of activities was based on percentage conversion within the experimental temperature region⁶ at 50 torr and the order of activities is LNRO > LNWO > LNMO.

In LNMO, a small amount of Mo^{6+} goes to Mo^{5+} state with corresponding shift of Ni^{2+} to the Ni^{3+} state². Owing to the greater difficulty with which Ni^{3+} can donate electrons to the N_2O molecules (as compared to Ni^{2+}) in the rate-limiting step (adsorption of N_2O), the activity is lessened. The highest activity observed for LNRO may be attributed to the possible multipoint adsorption³ on Re-O-Ni clusters because of the availability of d^1 electrons on Re. The very low values of E_a and $\ln A$ for the reaction on LNRO support this view.

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