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Synthesis of 3d Transition Metal Oxides and Correlation of Their Electrical and Catalytic Properties in Decomposition of Hydrogen Peroxide

CHETAN B. MEHER, ANAND VARADARAJAN, SUHAS P. TANDEL
and SHEELA P. MALVE*
Department of Chemistry
Institute of Science, 15, Madam Cama Road, Mumbai 400 032, India

Catalytic decomposition of hydrogen peroxide has been carried out employing some 3d transition metal oxides, synthesised mostly by the precipitation technique. Kinetic and thermodynamic activation energies have been calculated, making use of the Arrhenius plots in the latter case. The Seebeck coefficient measurement is used for the determination of the nature of charge carriers. An attempt has been made to correlate the thermodynamic and electronic activation energies of the synthesised oxides, calculated for the catalytic decomposition of hydrogen peroxide. It has been found that the electronic activation energy plays an important role in understanding the catalytic activity of these transition metal oxides.

INTRODUCTION

Oxides of 3d transition series have attracted the attention of various researchers in the field of catalysis. These oxides are extensively used in a number of oxidation-reduction reactions such as oxidation of carbon monoxide[1], decomposition of nitrous oxide, dehydration-dehydrogenation of alcohols[2] and decomposition of hydrogen peroxide.[3] Even though a lot of work has been carried out on the catalytic decomposition of hydrogen peroxide employing oxides and mixed oxides of 3d transition metals,[4–6] there is still a lot of scope for further investigations.

In the present investigation, we have prepared about nine oxides of 3d transition series and used them as catalysts for the decomposition of hydrogen peroxide. Also, an attempt has been made to correlate the electronic and thermodynamic activation energies, calculated for each metal oxide employed for the catalytic decomposition of hydrogen peroxide.

EXPERIMENTAL

Most of the oxides, except vanadium pentoxide and cuprous oxide, were prepared by precipitation technique. As per this technique, the respective metal ions were dissolved in distilled water. The hydroxides were precipitated using 10% NaOH solution, by maintaining proper pH (pH 9.0 to 9.5). The hydroxides were then digested on a water bath for 2 h followed by their oxidation on addition of a calculated amount of 30% hydrogen peroxide (100 vol.) with constant stirring at 363 K. The oxidised precipitate was then filtered, washed and dried. The dried precipitate was then powdered and heated to 1073 K for 6 to 8 h in a muffle furnace. Vanadium pentoxide was prepared by the decomposition of ammonium metavanadate[2] at 873 K and cuprous oxide was prepared by the reduction of Fehling's solution with glucose[7].

Measurement of Transport Properties

The DC electrical resistivity and thermoelectric power measurements of all the samples were carried out by the two-probe technique.[8, 9] As per this technique, a well-sintered pellet was coated with silver paste in xylene on both the sides in order to make the surface conducting. The pellet was placed in a ceramic sample holder. A calibrated Cr/Al thermocouple was used for the temperature measurement. The resistance of the sample was measured by using an LCR digital bridge and the plots of log ρ against $10^3/T$. The electronic activation energy E_e for all the oxides were calculated.

Thermoelectric power measurements were carried out by placing the pellet between two copper rods, maintaining a constant temperature difference. The potential developed was measured using a digital panel meter in the temperature range of 300–450 K.

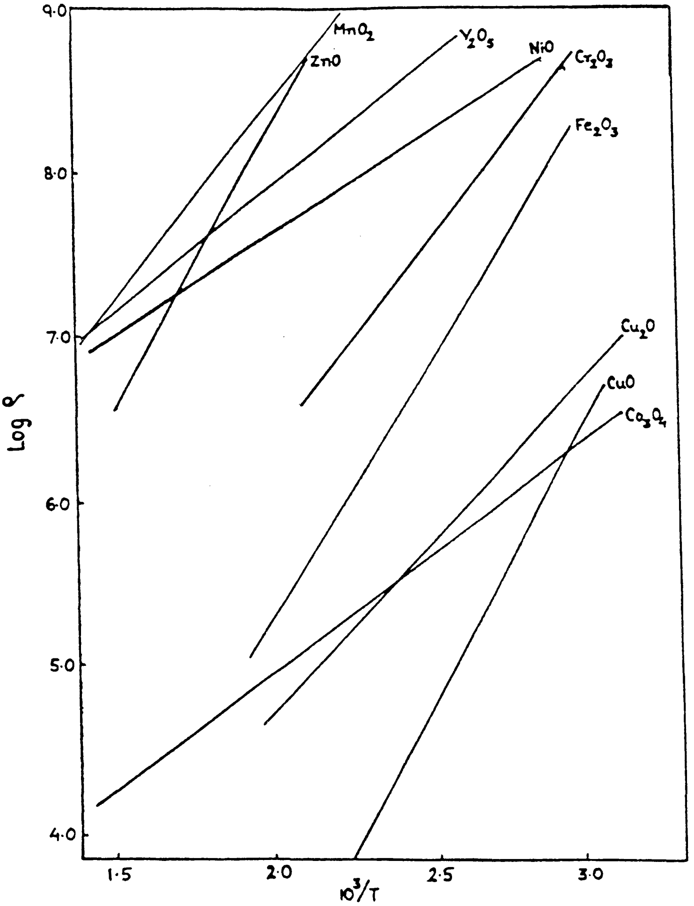

Fig. 1 Plot of log ρ against $10^3/T$ for different 3d transition metal oxide catalysts.

Study of Catalytic Measurements

Catalytic measurements were carried out by using the conventional gasometric technique.[10]

About 50 mg of the catalyst was added to a known amount of hydrogen peroxide (5 mL, 10 vol.) taken in a closed reaction vessel and the contents were stirred at 313 K. The volume of oxygen evolved was measured at regular time intervals, before and after the complete decomposition of hydrogen peroxide. The experiments were repeated at 323 K and 333 K. The values of the reaction rate k were calculated. Using the Arrhenius plots, the thermodynamic activation energy of the reaction was also calculated.

RESULTS AND DISCUSSION

DC resistivity of all the oxides measured as a function of temperature varied between 10^3 to 10^9 ohms/cm. The plot of log ρ *vs.* $10^3/T$ showed a linear nature obeying Wilson's law as shown in Fig. 1. The electronic activation energy values obtained from these plots varied between 0.26 eV to 0.77 eV (Table-1). The nature of the charge carriers were determined by using the Seebeck coefficient measurements. It indicates the *p*-type nature for NiO, CuO, Cu_2O, Cr_2O_3 and Co_3O_4 while the *n*-type semiconducting nature was observed for V_2O_5, Fe_2O_3, ZnO and

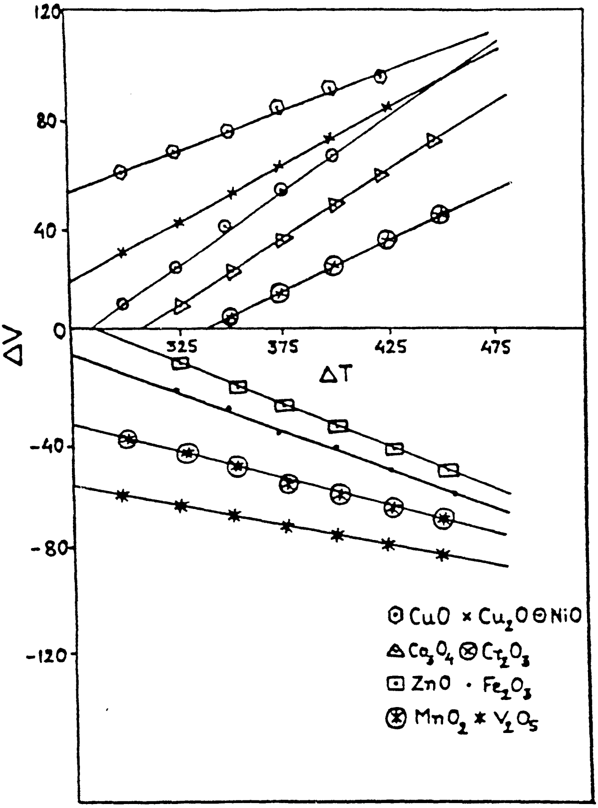

Fig. 2 Plot of ΔV against ΔT for different 3d transition metal oxide catalysts.

MnO_2 which is shown in the plots of ΔV against ΔT (Fig. 2). Further from Table-1, it is observed that the Seebeck coefficient values for the different oxides of the system varied between −160 μV/K to +570 μV/K.

Catalytic Measurements

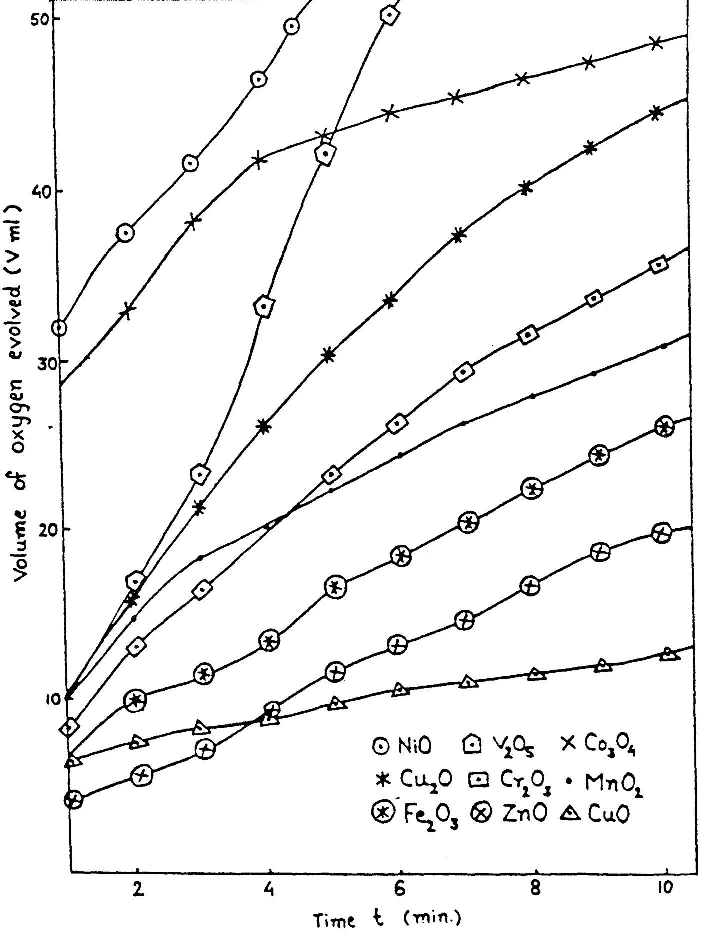

Fig. 3 Plot of Volume of oxygen evolved (V mL) against time (t) for different 3d transition metal oxide catalysts

Decomposition of hydrgen peroxide proceeds at sufficiently rapid rates on NiO, Co_3O_4 and V_2O_5 at 333 K. Moderate activity was seen on Cu_2O, Cr_2O_3 and MnO_2 while Fe_2O_3. ZnO and CuO showed less activity. Similar trends were observed at 323 K and 333 K. Fig. 3 shows a plot of volume of oxygen evolved (V mL) *vs.* time (t) at 333 K. Reaction rates were calculated from the plots of log (a − x) *vs.* t. The linear nature of the graphs indicates the first order kinetics for the reactions. The thermodynamic energy of activation values were calculated from the Arrhenius plots as shown in Table-1.

Correlation of the Thermodynamic (E_a) and Electronic (E_e) Activation Energies

Fig. 4 represents the total correlation between E_a and E_e. From Table-1, it is evident that the oxides with lower E_e values show lower thermodynamic energy of activation (E_a) for the decomposition of hydrogen peroxide, indicating that they are efficient catalysts. Thus, NiO with an electronic activation energy of 0.26 eV has a thermodynamic activation energy of 20.21 kJ/mol while Cr_2O_3 with an electronic activation energy of 0.46 eV has a thermodynamic activation energy of 42.54 kJ/mol. It is maximum for CuO having an electronic activation energy of 0.77 eV and a thermodynamic activation energy of 74.33 kJ/mol. It was reported that the *p*-type catalysts are the most active catalysts[11] for the decomposition of hydrogen peroxide. In our present investigation, we have obtained similar results with V_2O_5 being an exception that has been discussed separately.

TABLE-1
THERMODYNAMIC ACTIVATION ENERGY, ELECTRONIC ACTIVATION ENERGY AND SEEBECK COFFICIENT VALUES FOR DIFFERENT 3d TRANSITION METAL OXIDE CATALYSTS

S. No.	Oxides	Thermodynamic activation energy (E_a)	Electronic activation energy (E_e)	Seebeck coefficient (μV/K)
1.	CuO	74.33	0.77	+ 320
2.	ZnO	63.82	0.66	–360
3.	Fe_2O_3	61.69	0.61	–240
4.	MnO_2	46.80	0.52	–205
5.	Cr_2O_3	42.54	0.46	+ 369
6.	Cu_2O	37.23	0.38	+ 400
7.	V_2O_5	31.91	0.32	–160
8.	Co_3O_4	24.40	0.29	+ 480
9.	NiO	20.21	0.26	+ 570

From the above correlations, one may conclude that catalysis is a phenomenon involving the transfer of electrons or holes from the catalyst to the substrate. Lower the activation energy, lower is the distance between the conduction band and the valence band. In the mixed oxide system[12], Cu_2TiO_4-Zn_2TiO_4, Cu_2TiO_4 with the lowest activation energy proved to be an efficient catalyst for the decomposition of hydrogen peroxide while Zn_2TiO_4 having a higher activation energy value was not an efficient catalyst.

Exceptional Behaviour of Vanadium Pentoxide

V_2O_5 as a catalyst shows higher efficiency for the decomposition of hydrogen peroxide as compared to other oxides even though they possess a positive thermoelectric power coefficient. This is because V_2O_5 reacts with hydrogen peroxide in the solution phase that gives rise to the formation of peroxovanadic acid, $[H_3V(O_2)O_3]$.

It is soluble in the aqueous phase[13] and decomposes more rapidly. It proves to be an efficient homogeneous catalyst for the catalytic decomposition of hydrogen peroxide.

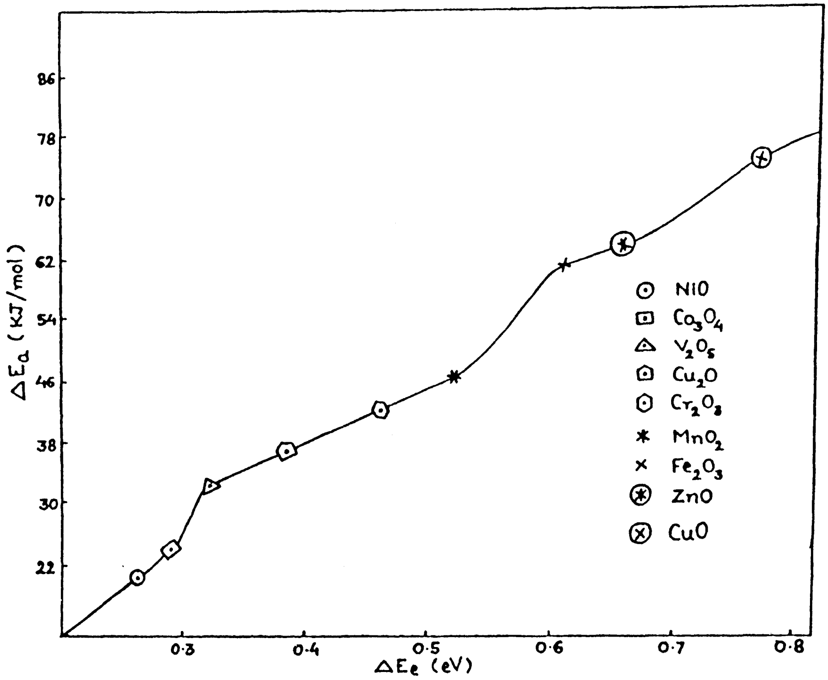

Fig. 4 Plot of thermodynamic activation energy (E_a) against the electronic activation energy (E_e) for different 3d transition metal oxide catalysts.

Conclusion

The catalytic activity of an oxide of a transition metal is influenced by its electronic behaviour. Lower the electronic activation energy, greater is the catalytic activity. Hence, electronic activation energy is of greater significance in understanding the catalytic activity of the transition metal oxides.

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