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CATALYTIC DEHYDROGENATION OF ISOPROPANOL ON $La_{2-x}Sr_xNiO_{4\pm y}$

R. JEYALAKSHMI, B. JAGANNADHASWAMY, K. RENGARAJ and B. SIVASANKAR

Department of Chemical Engineering, A.C. College of Technology, Anna university, Madras 600 025, India

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The series of compounds $La_{2-x}Sr_xNiO_{4\pm y}$ $(0.0 \leqslant x \leqslant 1.0)$ crystallising in tetragonal K_2NiF_4 structure were prepared and catalytic activity have been investigated using isopropanol decomposition as model reaction. All the catalyst compositions catalyse only the dehydrogenation of isopropanol reaction. The composition $La_{1.5}Sr_{0.5}NiO_4$ showed high activity compared to other compositions in the series. The composition is unique not only in catalytic property but also in other physical properties like structural characteristics, electrical resistivity and metal to semiconductor transition.

Keywords: $La_{2-x}Sr_xNiO_{4\pm y}$, dehydrogenation of isopropanol

1. Introduction

Mixed oxides with K_2NiF_4 structure consist of alternating layers of ABO_3 perovskite and AO rock salt, exhibiting two-dimensional characteristics [1]. The systems with a variety of A and B site ions are characterised by good stability of the structure, simultaneous existence of multiple oxidation states and oxygen nonstoichiometry which have profound influence on the physico-chemical properties. These oxides are, therefore suitable model compounds for the study of the relationships between solid state properties and catalytic activity. Mixed oxide compounds with K_2NiF_4 structure have been reported as oxidation catalysts [2–4].

In the present study, the catalytic activity of $La_{2-x}Sr_xNiO_{4\pm y}$ $(0.0 \leqslant x \leqslant 1.0$, y = oxygen nonstoichiometry) has been determined by taking the isopropanol decomposition reaction as a model reaction in order to correlate the catalytic activity with their physicochemical properties.

2. Experimental

The catalyst compositions of the series $La_{2-x}Sr_xNiO_{4\pm y}$ $(0.0 \leqslant x \leqslant 1.0)$ were prepared from stoichiometric mixtures of La_2O_3, $NiCO_3$ and $SrCO_3$. Mixtures

were thoroughly ground and heated to 823 K for 6 hrs followed by heating at 1173 K for 12 hrs. The mixtures were then reground, pelletised and sintered in air at 1273 K for a further period of 12 hrs. The phase purity and crystal symmetry were checked by powder X-ray diffraction patterns. The surface area of the samples was determined by nitrogen adsorption at liquid nitrogen temperature by the BET method. The ratio of the concentration of Ni^{3+}/Ni^{2+} in the catalysts was determined by means of the iodometric method [5].

The catalytic decomposition of isopropanol was carried out in a steady state integral reactor (10 mm dia, 200 mm length containing 1 g of catalyst) provided with temperature controller. The kinetics of the reaction was quantitatively studied by varying the contact time, W/F where W is weight of the catalyst in g, and F is the flow rate of pure isopropanol in g · mole/h and temperature. The W/F was varied in the range 5–20 g · h/g · mole and temperature of the catalyst bed between 530–630 K. The products were analysed by a gas chromatograph using a carbowax 20M column (2 m length) maintained at a temperature of 353 K and connected to a TCD.

3. Results

All catalyst compositions in the series $La_{2-x}Sr_xNiO_{4\pm y}$ ($0.0 \leqslant x \leqslant 1.0$) crystallised in the tetragonal K_2NiF_4 structure. The lattice parameters of the compounds calculated in the present study corroborated with literature reports [6].

The average oxidation number of nickel ion at the B site increased monotonically from 2.07 ($x = 0.0$) to 2.93 ($x = 1.0$) with the increase of strontium concentration, x. The oxygen non-stoichiometry varied from an excess in the compositions $x = 0$ and 0.2 through a stoichiometric composition for compositions $x = 0.4$, 0.5 and 0.6 to oxygen deficient compositions for $x > 0.6$. The compositions and structural properties of the catalysts are tabulated in table 1. The product analysis confirmed the absence of propene for $La_{2-x}Sr_xNiO_{4\pm y}$

Table 1
Physico chemical and catalytic properties of the series $La_{2-x}Sr_xNiO_{4\pm y}$

Compositions	Lattice parameters		%Ni^{3+}	Kinetic parameters		Percentage conversion at 600 K	k_{600} (lr·atm/h·g)
	a(Å)	c(Å)		E_a (k·J/mole)	ln A		
$La_2NiO_{4.07}$	3.858	12.6720	7.0	41.59	7.1	7.4	0.264
$La_{1.8}Sr_{0.2}NiO_{4.005}$	3.869	12.7331	20.5	51.59	9.38	10.4	0.340
$La_{1.6}Sr_{0.04}NiO_4$	3.830	12.7600	40.0	58.00	10.52	9.8	0.335
$La_{1.5}Sr_{0.5}NiO_4$	3.816	12.7890	51.0	45.03	8.73	19.7	0.875
$La_{1.4}Sr_{0.6}NiO_4$	3.810	12.6511	59.0	46.04	8.82	15.0	0.607
$La_{1.2}Sr_{0.8}NiO_{3.99}$	3.818	12.6080	78.3	53.44	9.59	9.7	0.375
$LaSrNiO_{3.97}$	3.820	12.5821	93.3	86.34	16.44	10.2	0.410

($0.0 \leqslant x \leqslant 1.0$) catalysed decomposition of isopropanol in the temperature range 530–630 K. Thus the catalyst compositions catalyse the dehydrogenation reaction of isopropanol only under the experimental conditions employed in the present investigation. The percentage conversion of isopropanol to acetone was found to increase with increasing W/F and also with temperature for all catalyst compositions. The percentage conversion for the catalyst compositions $x = 0.5$ and $x = 0.6$ are much higher compared to other catalyst compositions at all temperatures.

The kinetics of the dehydrogenation reaction was studied by varying the contact time (W/F) and temperature of the catalyst bed. Experimental data were analysed on the basis of the integral method by using the equation [7]:

$$-x' - 2\ln(1 - x') = k\,P/RT(W/F) \tag{1}$$

where x' is the fractional conversion, k is the rate constant, P is the total pressure, R the gas constant and T the temperature.

The order of the reaction was confirmed to be one with respect to isopropanol concentration from the linear plot $-x' - 2\ln(1 - x')$ vs W/F for all temperatures and rate constants were evaluated from the slope of the plots. The energy of activation and frequency factor were calculated from the Arrhenius plots and values are given in table 1.

4. Discussion

A comparison of the kinetic parameters of the reaction catalysed by the isostructural compositions in $La_{2-x}Sr_xNiO_{4\pm y}$ has indicated three important features. These include (i) compensation effect (ii) variation of energy of activation and (iii) the variation of rate constant with strontium concentration x.

The linear relationship between ln A and E_a for all compositions within the series indicates the identical nature of the active sites for all the compositions. The introduction of divalent strontium at the lanthanum site of La_2NiO_4 apparently modifies the energy of the active site but does not alter the nature of the active site.

The activation energy of the dehydrogenation reaction catalysed by different compositions in these series shows a non-linear variation with strontium concentration, as shown in fig. 1. Initially it increases with x up to $x = 0.4$ followed by a decrease for $x = 0.5$, with further increase of strontium concentration E_a also increases rather steeply.

The first order rate constant for the reaction on $La_{2-x}Sr_xNiO_{4\pm y}$ does not vary uniformly with strontium concentration x. As can be seen from the fig. 2, the rate constant for all compositions except $La_{1.5}Sr_{0.5}NiO_4$ and $La_{1.4}Sr_{0.6}NiO_4$ are almost identical at any given temperature. The rate constant for $La_{1.5}Sr_{0.5}NiO_4$ alone is uniformly higher at all temperatures.

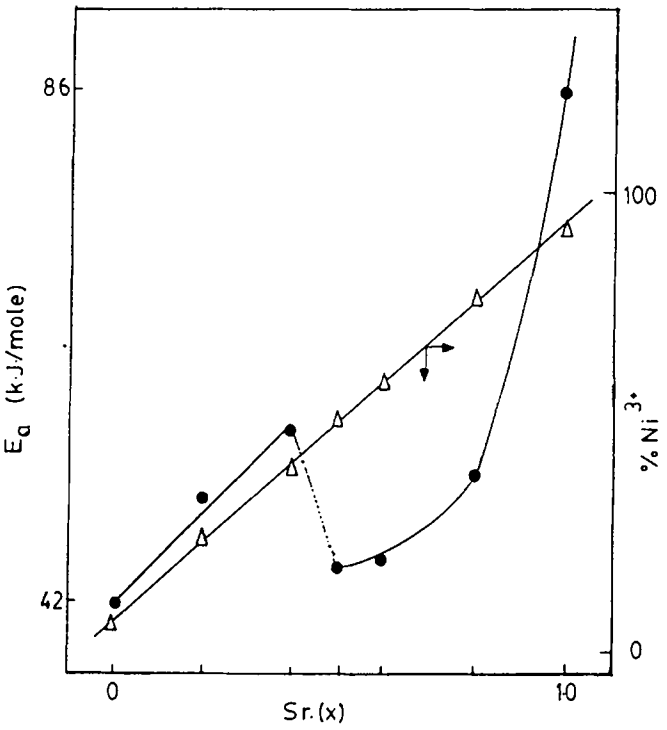

Fig. 1. Variation of E_a and $\%Ni^{3+}$ with strontium content.

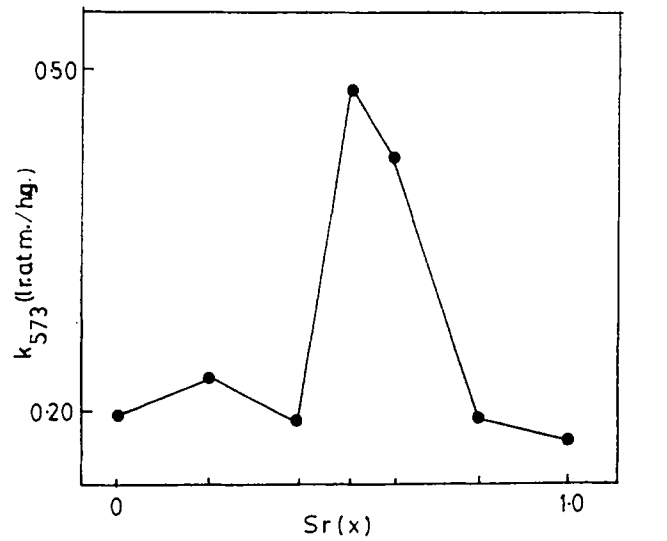

Fig. 2. Variation of rate constant with strontium content.

5. Structure–physicochemical property–catalytic activity correlation

The tetragonality ratio calculated for the series of a catalyst compositions in the $La_{2-x}Sr_xNiO_{4\pm y}$ system showed a maximum value of 3.345 for the composition $La_{1.5}Sr_{0.5}NiO_4$ and decreases with further increasing x. The variation has been attributed to the change of the electronic configuration of Ni^{3+} from $t_{2g}^6 d_{z^2}^1$ to $t_{2g}^6 d_{x^2-y^2}^1$ with consequent decrease of Ni-O distance along the c-axis.

The electrical properties of these compounds have already been reported in the literature [6]. All the compositions except $x = 0.5$ exhibited metal-semiconductor transitions. A parameter α, defined as the metallic to semiconductor ratio, for a given composition has been introduced to explain the fact that $La_{1.5}Sr_{0.5}NiO_4$ does not exhibit metal-semiconductor transition. It has been proposed that for a given composition, metal-semiconductor transition is observed only, if $\alpha = 0.3 \pm 0.1$. The composition $x = 0.5$ has been found to have a value greater than the critical value in the temperature range 100–600 K and hence does not show any metal-semiconductor transition in this temperature range, whereas all other compositions reach the critical value α. Thus $La_{1.5}Sr_{0.5}NiO_4$ has a unique behaviour.

The catalytic activity of the solid solution series towards CO oxidation has been reported in the literature [4]. The activity per surface Ni ion has been calculated and it was found that the oxidising power of the surface increased steeply from $x = 0.4$ to 0.8. The low catalytic activity observed for the composition $x = 0.0$ to 0.2 can be correlated to the oxygen excess compositions.

In the present study, the catalytic activity of the isomorphous compounds in the series $La_{2-x}Sr_xNiO_{4\pm y}$ ($0.0 \leqslant x \leqslant 1.0$) can be correlated either on the basis of energy of activation or rate constant. The variation of E_a vs x can be correlated to the Ni^{3+} concentration. The inactivity of Ni^{3+} compared to Ni^{2+} is known in the oxidation of CO, propene [4,8] and it has been reported that as the Ni^{3+} concentration increases, the catalytic activity is bound to decrease. In the present series the Ni^{3+} content increases uniformly with increase in the strontium substitution whereas the energy of activation does no show a similar trend. However, E_a increases from $x = 0.0$ to $x = 0.4$ linearly and then shows a sudden drop for the composition $x = 0.5$ which may be attributed to change in electronic configuration of Ni^{3+}. The energy of activation once again shows an increasing trend for compositions with $x = 0.6$. From the variation of the rate constant with x, it is clear that the composition $La_{1.5}Sr_{0.5}NiO_4$ has an abnormally high value for the rate constant at all temperatures.

The structure-physicochemical property, catalytic activity correlation within the series $La_{2-x}Sr_xNiO_{4\pm y}$ has shown an interesting feature for the composition $La_{1.5}Sr_{0.5}NiO_4$. This composition is unique in all physicochemical properties, namely the tetragonality ratio (c/a), electrical property (metal-semiconductor transition) and finally in catalytic activity. A comparison of the E_a's indicates

that $x = 0.6$ is very similar to $x = 0.5$. However the comparison does not hold well on the basis of comparison of the rate constant.

6. Conclusions

A series of catalysts $La_{2-x}Sr_xNiO_{4\pm y}$ $(0.0 \leqslant x \leqslant 1.0)$ with tetragonal K_2NiF_4 structure were prepared. All catalyst compositions catalyse only the dehydrogenation of isopropanol to acetone. The higher rate constant and low activation energy of the reaction shown by the composition $La_{1.5}Sr_{0.5}NiO_4$ can be correlated to the structural characteristics such as high-tetragonality ratio, change of electronic configuration and physical properties such as electrical properties.

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