

Solid state properties of lithium doped nickel oxide and its catalytic activity towards dehydrogenation of isopropanol

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Abstract. Solid state properties of lithium doped nickel oxide samples and their catalytic activity towards isopropanol (IPA) decomposition have been studied. Electrical resistivity, surface area and lattice parameter decrease with doping which is due to substitutional incorporation of Li into the nickel oxide lattice. IPA undergoes only dehydrogenation on all the samples, dehydrogenation activity increasing with increased doping. There is a small but regular decrease in the Arrhenius activation energy with doping. The increase in catalytic activity on doping is attributed to the increase in hole concentration which is likely to favour the desorption of acetone, the rate determining step of the reaction.

Keywords. Nickel oxide-lithium doped; catalytic activity; dehydrogenation of isopropanol on NiO.

1. Introduction

Addition of altrivalent ions as impurities to semiconducting solids has been used by many workers to test the electronic theory of catalysis. Doping of nickel oxide with Li was tried because of the similarity of their ionic radii ($r_{Ni^{2+}} = 0.69 \text{ \AA}$; $r_{Li^+} = 0.68 \text{ \AA}$). The results obtained by various workers on these catalysts have been reviewed (Bickley and Stone 1968; Bielanskii and Deren 1968). Most of the studies have been carried out on the oxidation of carbon monoxide and the results are contradictory. One cause of such variation in the results seems to be the difference in the temperature of catalyst preparation. Iida *et al* (1960) have shown that at temperature lower than 800°C , Li remains mostly as Li_2O and if sintered above 1000°C , most of it volatilises. It has also been shown (Marshneva *et al* 1972) that CO oxidation on NiO is controlled partly by the surface reaction of the adsorbed species and partly by the reaction with lattice oxygen, the latter predominating at higher temperature. Since the temperature range in which various workers studied this reaction varied widely, their experimental observations on the effect of Li doping of nickel oxide on CO oxidation are not likely to be consistent. Besides, CO is known to reduce nickel oxide and getting reproducible rate data is difficult. This prompted us to choose decomposition of isopropanol (IPA) as the model reaction. Preliminary studies revealed that the nickel oxide catalysts do not undergo any noticeable structural change after their use as catalysts in this reaction.

Some interesting effects of Li doping of vanadium pentoxide on its solid state properties and on catalytic dehydration of IPA was reported by us (Chakrabarty *et al* 1976 and 1977). In this paper, we report the effect of Li doping on the properties of nickel oxide and its behaviour as a catalyst for IPA decomposition.

2. Experimental methods

Nickel oxide was prepared by heating nickel oxalate at 800°C. The solid solutions $\text{Li}_x\text{Ni}_{1-x}\text{O}$ were prepared by mixing thoroughly nickel oxide and lithium carbonate, pelletising at 8 tons/in² and sintering at 800°C for 10 hr. The pellets were then powdered, washed repeatedly with hot water, dried, pelletised again and sintered for electrical measurements. Powdered samples were used for surface area measurement and catalytic studies. The pellets of 8 mm thickness were used for measuring electrical resistivity (ρ) and Seebeck coefficient (α). The sintering temperature was chosen based on the report by Iida *et al* (1960) that very little Li_2O dissolves in NiO below 800°C and most of it are lost by evaporation above 1000°C. The Li content in the samples were analysed by flame photometry as follows: The sample was dissolved in concentrated hydrochloric acid, evaporated to dryness, extracted with water and nickel was precipitated out as NiS. It was then filtered and the filtrate was analysed for Li. For example, when 0.1 at % of Li in the form of Li_2CO_3 was taken for sample preparation, analysis showed 0.08 at % of Li.

X-ray diffraction patterns were recorded on a Philips PW 1057 diffractometer using $\text{CuK}\alpha$ radiation filtered through a nickel foil.

The apparatus used for the measurement of resistivity and Seebeck coefficient have been described by Chakrabarty *et al* (1976). The surface area of the samples was measured by nitrogen adsorption (BET) using a volumetric apparatus.

Catalytic decomposition of isopropanol (IPA) was studied in the temperature range 550–600°K on a flow reactor. Total conversion was kept around 5%. In this region, conversion vs contact time plots were found to be linear and initial rate (r_i) was obtained from the slope. Before every run, the catalyst was activated by heating at 400°C in the reactor in a slow current of air for 3 hr. The products and unreacted IPA were collected after allowing sufficient time for the steady state to attain. The liquid products were collected in a cold trap and analysed by gas chromatography using carbowax 20M on chromosorb column and hydrogen carrier gas. The gaseous product contained only hydrogen besides nitrogen that was added as a diluent.

The amount of Ni^{3+} in the catalysts were determined by iodometric method (Weller and Voltz 1954).

3. Results

Logarithmic plots of resistivity (ρ) against reciprocal temperature for all the samples are shown in figure 1. The slope changes at temperatures very near to the antiferromagnetic to paramagnetic transition of nickel oxide ($T_N = 520^\circ\text{K}$). Various physical properties of the samples are summarised in table 1. It can be seen that lattice parameter (a_0), specific surface area (S) and electrical resistivity (ρ) decreases whereas Ni^{3+} concentration increases with increased doping.

Results of IPA decomposition show that it undergoes only dehydrogenation to acetone. The Arrhenius plots are shown in figure 2. The kinetic data are presented in table 2.

Measurements of ρ at various temperature in the presence of IPA vapour were carried out on nickel oxide pellets. The results are shown in figure 3 which shows

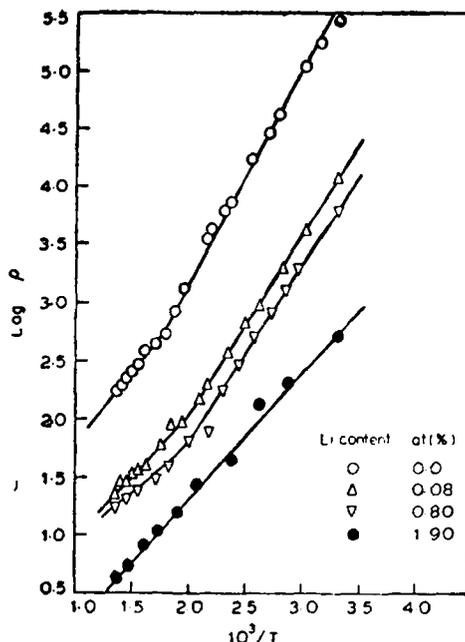


Figure 1. $\log \rho$ vs $10^3/T$ K^{-1} plots for nickel oxide containing various quantities of lithium ion.

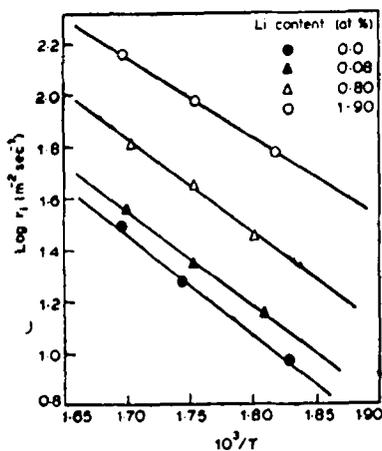


Figure 2. Arrhenius plots for the dehydrogenation of isopropanol on the various catalysts.

Table 1. Some properties of nickel oxide and lithium doped nickel oxide catalysts.

Lithium content (at %)	Lattice parameter (a_0) Å	Surface area (S) (m^2/g)	Ni^{2+} (at %)	Electrical resistivity (ohm cm)		Activation energy of conduction (eV)	
				300°K	600°K	$T < 520^\circ K$	$T > 520^\circ K$
0.00	4.179	2.65	0.03	0.30×10^6	0.41×10^2	0.36	0.23
0.08	4.177	2.51	0.06	0.12×10^6	0.43×10^2	0.29	0.19
0.8	4.173	1.62	0.32	0.63×10^4	0.31×10^2	0.27	0.15
1.9	4.173	0.88	0.35	0.53×10^3	0.10×10^2	0.20	0.20

that resistivity increases and after some time attains a constant steady state value. The activation energy of conduction in NiO remains unchanged by introducing IPA vapour.

The effect of partial pressure of acetone on dehydrogenation of IPA has been shown in figure 4. It can be seen that rate decreases with increase in partial pressure of acetone (p_{ac}).

Table 2. Kinetic data for isopropanol dehydrogenation on nickel oxide and lithium doped nickel oxide.

Lithium content (at %)	Surface area (S) (m^2/g)	Arrhenius activation energy, E_a , Kcal/mole	Pre-exponential factor (k_0) $sec^{-1} m^{-2}$
0.00	2.65	17.99	1.36×10^8
0.08	2.51	17.16	0.84×10^8
0.8	1.62	16.75	1.14×10^8
1.9	0.88	14.30	0.30×10^8

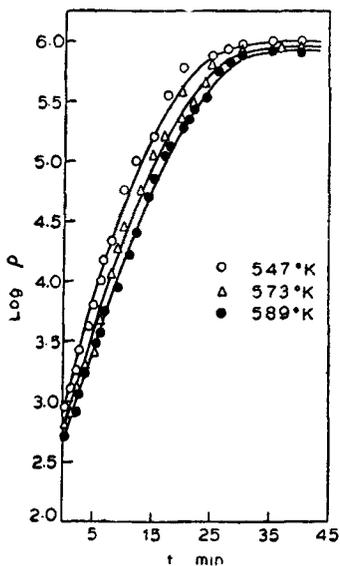


Figure 3. Change in resistivity of nickel oxide in the presence of isopropanol vapour.

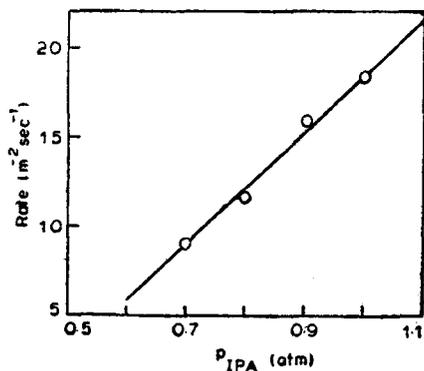


Figure 4. Effect of the partial pressure of acetone (P_{ac}) on the rate of dehydrogenation of isopropanol on nickel oxide. (temp. = 573°K; contact time = 0.078 sec; $P_{ac} + P_{IPA}$ = one atmosphere).

X-ray diffraction pattern of the samples recorded after their use as catalysts did not show any change in their crystal structure.

4. Discussion

4.1. Electrical properties

Electrical transport properties of nickel oxide has been a subject of controversy. It was generally held that the *p*-type conductivity of NiO is due to thermally activated jump of holes from a Ni³⁺ to a neighbouring Ni²⁺ site until Bosman and Crevecoeur (1966) reported a drift mobility 0.25 cm²/V.sec from Seebeck coefficient data. This value is higher than what the hopping model predicts and they proposed band conduction in nickel oxide. The situation was reviewed by Bosman and van Daal (1970), but the controversy on this point is still alive (Bransky and Tallen 1971). A change in the sign of Hall coefficient (R_H) near Neel temperature (N_T) has not been adequately explained (Daal and Bosman 1967).

Our results on resistivity are qualitatively in agreement with the literature. Our purpose in this paper is not to join the controversy on the transport mechanism in NiO, but to see if a relationship between the electrical properties and catalytic activity can be obtained. With this view in mind, we used samples sintered only at 800°C attaining only 80% of x-ray density for reasons already stated. The decrease in activation energy of conduction near Neel temperature is ascribed to the fact that in the antiferromagnetic region, the spin in the opposite sub-lattices are in opposite directions, and hence a greater energy is necessary for the carriers to migrate (Hass 1968).

4.2. Incorporation of Li ions in NiO lattice

It is seen from table 1 that lattice parameter (a_0) decreases by addition of Li ion. Bielanski *et al* (1965) noticed an initial increase in a_0 when Li content was very small, which they attributed to interstitial Li ions. We reject this interpretation as this is incompatible with the observation by other workers so far that addition of Li to NiO always reduces its resistivity. The results of Bielanski *et al* (1965) may be due to experimental error, as the lattice parameter reported by them for pure nickel oxide (4.169Å) is lower than that observed by precise measurements (4.177Å). Our results ($a_0=4.179\text{Å}$) are in good agreement with the literature. Bickley and Stone (1968) suggested that incorporation of Li into the NiO lattice takes place in two steps: first Li goes into the lattice substitutionally creating oxygen vacancies and then the lattice takes up oxygen from the surroundings. In the presence of oxygen, these two steps should occur simultaneously which amounts to substitutional incorporation of Li in the nickel oxide lattice. All workers agree that at higher concentration of Li, it always enters into the NiO lattice substitutionally. The changes in electrical resistivity and lattice parameter suggest that this happens even at very small Li doping. The smaller size of Ni³⁺ is then responsible for the shrinkage in the lattice.

4.3. Specific surface area

The decrease in specific surface area (S) with lithium doping is due to rapid sintering affected by the diffusion of the more mobile lithium ions. Bielanski and Deren (1968) reported an initial increase in S with small dopant concentration, which is difficult to understand. However, the change reported by them falls well within the experimental error that is possible in the BET method.

4.4. Dehydrogenation of isopropanol

We have seen that dehydrogenation activity of nickel oxide catalyst increases with the increase of Li concentration and no dehydration of IPA was observed in any of the catalysts. A mechanism for catalytic decomposition of alcohol was proposed by Wolkenstein (1960) according to which an alcohol molecule may undergo dissociative chemisorption either by breaking the O—H or the C—OH bond. In the former case, a negatively charged alcoholate species will be adsorbed as an electron donor and also a H^+ ion. The adsorbed proton will take up a surface electron and combine with a hydrogen atom of the alcoholate group and desorb as H_2 . The residual group will then leave an electron to the surface and desorb as a ketone (or aldehyde in the case of C_2H_5OH). Wolkenstein assumed that alcohol adsorption is the rate determining step and concluded that dehydrogenation will be favoured by an electron rich (n -type) surface. Most of the experimental observations, however, show that n -type oxides generally favour dehydration and p -type oxides favour dehydrogenation. This discrepancy may be due to wrong assumption of the rate determining step. It was shown that the dehydration of IPA on $Na_xV_2O_5$ (α -phase, x 0.06), a n -type oxide, increases with x as long as desorption of propene is the rate determining step (Chakrabarty *et al* 1977). When $x=0.33$, conductivity increases by a few orders and desorption of propene gives way to adsorption of IPA as the slowest step and dehydration activity falls despite an increase in conductivity. This shows the importance of understanding correctly the rate determining step of a reaction while correlating it with the semiconducting property of the catalyst.

In the present case, the strong retarding influence of P_{ac} on the dehydrogenation rate suggests acetone desorption as the rate determining step (figure 4). Increase in x also increases the hole concentration of Ni^{3+} . If the slowest step, i.e. desorption of acetone is an electron donor (to the surface) process as suggested by Wolkenstein, the increase in hole concentration will give rise to increased dehydrogenation, as has been observed experimentally by us.

Arrhenius activation energy decreases regularly with the increase of lithium content, but no such systematic change has been observed in the preexponential factor (k_0).

The electrical resistivity of nickel oxide increases in the presence of IPA vapour under reaction conditions attaining a steady value. This increase in the steady state resistivity of nickel oxide under reaction conditions as compared to the equilibrium resistivity in air indicate that electrons are donated to the surface in the slowest step of the reaction. This supports the view that increase in dehydrogenation rate is due to increase in hole concentration in the solid.

5. Conclusions

Decrease in electrical resistivity and lattice parameter of nickel oxide catalysts on Li doping suggest that Li always enters into the lattice substitutionally. Catalytic dehydrogenation of IPA increases with doping. Desorption of acetone is the rate determining step. The increase in activity is related to the increase in hole concentration in the solid.

Acknowledgement

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