Indian Journal of Chemistry
Vol. 21A, April 1982, pp. 350-352

Oxidation of Carbon Monoxide on Doped Nickel Oxide Catalysts

V. BHEEMA RAJU, D. Y. RAO & D. K. CHAKRABARTY*
Solid State Laboratory, Chemistry Department, Indian Institute of Technology, Bombay 400 076

Received 12 *August* 1981; *revised and accepted* 16 *September* 1981

Oxidation of carbon monoxide has been studied on nickel oxide doped with lithium and indium after carefully working out the preparative conditions and ascertaining the composition of the catalysts. The rate of the reaction increases with hole concentration in nickel oxide. The reaction rate decreases on γ-irradiation, but it is restored once the γ-ray source is withdrawn. The results are discussed in terms of electronic defects in the solids.

IN earlier papers from our laboratory[1,2] a good correlation was observed between the electrical conductivity of lithium and indium doped nickel oxide and their catalytic activities towards the dehydrogenation of 2-propanol. The results of carbon monoxide oxidation on the same catalysts are reported in this paper.

Materials and Methods

Nickel oxide was prepared by the decomposition of nickel oxalate dihydrate at 800°C for 10 hours. The lithium and indium doped catalysts were prepared by thoroughly mixing appropriate quantities of nickle oxide and lithium carbonate (or indium nitrate) on an agate mortar, pelletising and firing at 800°C for 10 hr as described earlier[1,2].

The products were checked by X-ray diffraction patterns. Electrical conductivity of the pellets was measured by using two platinum disc probes in a set up described earlier[3].

Carbon monoxide was prepared by heating formic acid with sulphuric acid (both AR grade) and its purity (99.9%) was checked by gas chromatography. Oxidation of CO was studied in a flow reactor using 5% CO, 5% O_2 mixed with nitrogen gas at flow rates 7,500, 10,000 and 12,000 ml/hr. The reaction mixture as well as the products were analysed by an on-line gas chromatograph using molecular sieve 13X column at 50°C, hydrogen as carrier gas and thermal conductivity detectors after removing CO_2 from the product by passing through a KOH bubbler. Irradiation of the reaction chamber when desired, was carried out using ^{60}Co γ-rays (dose rate 0.32 MR/hr).

Results

The surface area and the excess oxygen of the various catalysts are given in Table 1. The conversion of CO against residence time plots were found linear. The rate of the reaction was calculated as

$$r_s = \frac{FX}{WS}$$

where r_s is the rate (mole of CO converted per m^2 of the catalyst per second), F is the feed rate (mole of CO per second), X is the fraction of CO converted, W is the weight of the catalyst in gram and S is the specific surface of the catalyst (m^2/g). The Arrhenius plots are shown in Fig. 1 and the kinetic parameters are given in Table 1.

TABLE 1 — KINETIC PARAMETERS OF CARBON MONOXIDE OXIDATION ON DOPED NICKEL OXIDE CATALYSTS

Impurity content (at %)	Excess oxygen content (at %)	Surface area (m^2/g)	Activation energy (k cal/mol)	Pre-exponential factor, K_0 (sec^{-1} m^{-2})	Ni^{3+} content (at %)
0.00	0.03	2.65	10.1	0.144	0.05
0.03(Li)	0.06	2.51	8.9	0.075	0.12
0.80(Li)	0.32	1.62	9.9	0.443	0.64
1.90(Li)	0.35	0.88	10.0	1.059	0.7
1.00(In)	—	1.90	10.1	0.096	—
0.00 (irradiated)	0.03	2.65	12.5	0.915	0.05
0.03(Li) (irradiated)	0.06	2.51	10.6	0.284	0.12

It can be seen from Fig. 1 that the catalytic activity increases with lithium concentration but decreases in the indium doped compound. The activation energy (E_a) does not vary appreciably. The effect of partial pressures of CO (p_{CO}) and O_2 (p_{O_2}) on the rate is shown in Fig. 2, indicating the reaction to be of zero order and first order with respect to oxygen and carbon monoxide respectively. This was found to be same for all the catalysts studied in the present work. The product CO_2 had little effect on the rate.

The changes in the electrical resistivity of the nickel oxide catalyst as a function of time in different atmospheres are shown Fig. 3. It shows a rapid decrease in the resistivity in oxygen and a slow rise in carbon monoxide.

Discussion

It is observed that the rate of CO oxidation on various catalysts and the Ni^{3+} concentration in them change in the same direction although the change is not a linear one.

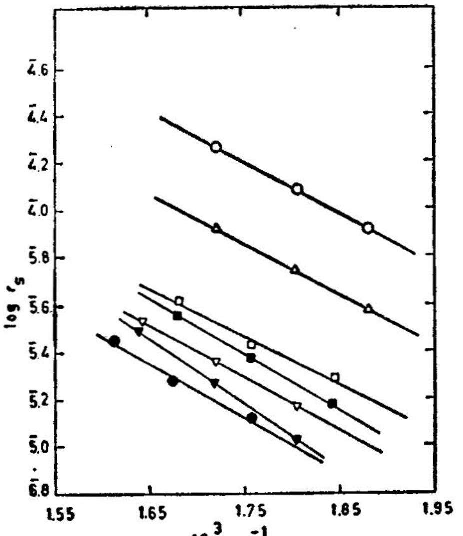

Fig. 1 — Arrhenius plots for CO oxidation on lithium and indium doped nickel oxide catalysts (—○—1.90 Li; —△— 0.80 Li; —□—0.08 Li; —■— 0.08 Li, irradiated; —▽—pure NiO; —▼— pure NiO, irradiated ; —● — 1.00 In)

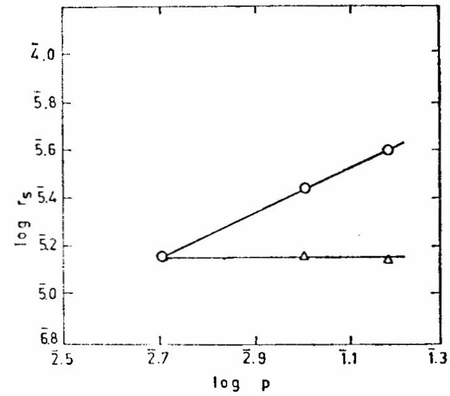

Fig. 2 — Effect of p_{CO} and p_{O_2} on CO oxidation rate on nickel oxide catalysts at 554 K (—○—p_{CO} ; — △ p_{O_2})

Schwab and Block[4] noticed that lithium doping increases the rate of CO oxidation on nickel oxide while doping the nickel oxide with chromium decreases the rate in the temperature range 300–400°C. Parravano[5] had earlier reported just the opposite in the temperature range 230–280°C. However, these workers used quite different temperature for catalyst preparation as well as different concentrations of lithium. Dry and Stone[6] later confirmed the results of Schwab and Block whereas Cimino *et al.*[7] confirmed Parravano's findings.

The temperature range of our study overlaps those used by the earlier workers[4,5]. We have presently found an increase in the rate of CO oxidation with lithium doping and a decrease in the rate for the indium doped sample over the entire temperature range. Thus, it appears that the preparative conditions and the composition of the catalyst, which is not very certain in all the cases, has important bearing on their catalytic activity.

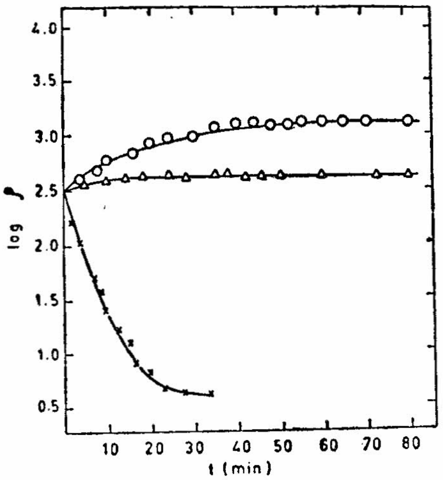

Fig. 3 – Resistivity of pure nickel oxide as a function of time in different atmospheres at 581 K (—○— in CO; —×— in O_2; —△— in $CO+O_2$).

Since we have observed an increase in catalytic activity with Ni^{3+} hole concentration, it is tempting to relate the activity with electronic property of the solid. It is to be noted that all the compounds are *p*-type semiconductors, conductivity increases with lithium concentration and decreases in the indium doped sample. Electrical properties of the solids in air have been reported elsewhere[1,2]. Resistivity of the pellets is found to increase with time in carbon monoxide (Fig. 3), suggesting electron transfer from CO to the solid during adsorption. The gradual change in resistivity also indicates that CO adsorption is slow process. The rapid decrease of resistivity in oxygen suggests that oxygen adsorption is a fast process. These conclusions are supported by the orders of the reaction with respect to CO and O_2.

The following mechanism may be suggested for the reaction :

$$CO + h \rightarrow CO^{+}_{ads.} \qquad \text{(slow)}$$

$$\tfrac{1}{2}\, O_2 \rightarrow O^{-}_{ads.} + h \qquad \text{(fast)}$$

$$CO^{+}_{ads.} + O^{-}_{ads.} \rightarrow CO_2 \qquad \text{(fast)}$$

Addition of lithium increases the hole concentration in nickel oxide[1], which in turn increases the rate of the slowest step. The reverse occurs with the addition of indium.

In order to check if lattice oxygen takes part in CO oxidation, carbon monoxide diluted with nitrogen was passed over the catalysts under the reaction conditions. Only traces of CO_2 were formed initially and the reaction did not proceed further. The small amount of CO_2 could be formed due to the pre-adsorbed oxygen on the catalyst surface. Thus, the participation of lattice oxygen can be ruled out.

When the reaction chamber was irradiated by ^{60}Co γ-ray, the rate of the reaction was found to decrease with increase in the energy of activation. The original activity, however, was restored once the γ-ray source was withdrawn. The order of the reaction remained unchanged throughout. γ-Ray is likely to produce short-lived electronic defects that may affect the rate. The results can be rationalised if one assumes that these defects are V-centres, i.e. holes trapped at cation vacancies. These will reduce the availability of holes at nickel sites that participate in the rate-determining step of the reaction. These short-lived defects will decay rapidly once the source is withdrawn restoring the original catalytic activity.

References

1. Bheema Raju, V., Chakrabarty, D. K. & Biswas, A. B., *React. Kinet. Catal. Lett.*, **11** (1979), 63.
2. Bheema Raju, V. & Chakrabarty, D. K., *Proc. Indian Acad. Sci.* (*Chem. Sci.*), **87** (1978), 133.
3. Rane, K. S., Chakrabarty, D. K. & Biswas, A. B., *Indian J. Chem.*, **15** (1977), 669.
4. Schwab, G. M. & Block, J., *Z. phys. Chem.* (*Frankfurt*), **1** (1954), 42.
5. Parravano, G., *J. Am. chem. Soc.*, **75** (1953), 1452.
6. Dry, M. E. & Stone, F. S., *Discuss. Faraday Soc.*, **28** (1959), 192.
7. Cimino, A., Mollinari, E.& Romeo, G., *Z. phys. Chem.* (*N. F.*), **16** (1958), 101.