

Surface Area Changes of Nickel Oxide Catalysts

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Substantial changes in the BET areas of nickel oxide and of lithium-doped nickel oxide catalysts are recorded. These changes occurred during studies of the CO-O₂ reaction between 2 and 20 cm pressure and the adsorption of CO, O₂, and CO₂ at 10⁻¹ mm.

The catalytic activity also changed but not in a parallel fashion to the surface area. By correlation with earlier O¹⁸-exchange work the observations are interpreted as probably due to an unlocking of built-in lattice strain by exchange of oxygen between the surface layers of the solid and the gas molecules. Another possible reason for the release of strain is the large number of times the catalysts were taken through the Néel point (about 250°C) during the course of the work.

There are relatively few records in the literature of permanent changes in surface area of finely divided solids as a result of adsorption or as a result of their use as catalysts. In particular in studies of catalysis it is often stated that it was necessary to age or stabilize the catalyst by some preliminary runs and the surface area of the catalyst, if quoted, is determined either before the preliminary runs or after the whole series of reactions forming the main body of the work.

For several years we have been engaged upon a detailed study of the catalytic properties in the CO/O₂ reaction of nickel oxide and of nickel oxide doped with lithium oxide; the work has also included studies of the adsorption of the gases O₂, CO, and CO₂. Each series of experiments has extended over many days—from a month to nearly a year—and despite rigorous precautions against poisoning, and careful purification of gases we have been troubled with random drifts and sometimes abrupt changes in the activity of our catalysts. The general pattern has been that after a few days of erratic results meaningful results and satisfactory reproducibility would be obtained for a period varying from several days to many weeks. There was then a drift or a sudden rise to higher activity. Sometimes the

catalyst would settle down at the new level and sometimes the drift upwards would continue at a rate sufficiently slow to enable correction to a standard rate to be made for short series of experiments. The behavior of samples taken from the same preparation batch was not always the same in detail although the general trend was similar.

The kinetic experiments were conducted in a fixed volume using the gas circulating pump described elsewhere (1) at pressures mostly between 2 and 20 cm; the adsorptions were almost all performed at 10⁻¹ mm using a constant-pressure device which records the rate of adsorption (2). All samples were at all times protected from contamination by spiral cold traps cooled to -78°C; connection of the sample vessel to the rest of the apparatus was by a glass seal or a silica-Pyrex graded seal. Drikold was used as a refrigerant for convenience, extensive trials having shown that liquid nitrogen offered no advantages in the form of improved reproducibility of results. Most of our observations are collected in Table 1. The final column gives some idea of the time involved in each case since roughly 10 runs were performed per week with Samples 1-7 and half that number for the remainder. The samples were all prepared by igniting the nitrate, mixed with the requisite quantity of lithium

nitrate, to 650°C for 3 hr. Samples 1-7 inclusive were then ignited to 1000°C for a further 3 hr, and were used in studies of the CO-O₂ reaction; a stoichiometric mixture of the reactants was used in all except a very few cases. Samples 8-10 were used for measurements of rates of adsorption of CO, O₂, and CO₂. The treatment between runs

TABLE 1
BET SURFACE AREA CHANGES

Sample No.	Material	BET (m ² g ⁻¹)		No. of runs
		Original	Final	
1	NiO	0.78	29.5	200
2	NiO	0.78	73.6	70
3	NiO	0.78	1.65	50
4	NiO + 0.01% Li ₂ O	4.32	5.65	25
5	NiO + 0.01% Li ₂ O	4.32	8.08	13
6	NiO + 1.0% Li ₂ O	1.47	58.3	250
7	NiO + 5.0% Li ₂ O	0.95	14.3	220
8	NiO	3.44	6.30	40
9	NiO + 0.01% Li ₂ O	8.96	12.1	90
10	NiO + 1.0% Li ₂ O	2.42	16.6	60

for all except No. 1 was to outgas briefly while adjusting the temperature to 400°C, then to expose the sample for 10 min at this temperature to pure O₂ at 1 cm pressure. The brief pumping and exposure to O₂ was repeated and the sample was finally outgassed at 500°C. Sample 1 had no O₂ treatment between runs. The time of outgassing was 1 hr for No's 1-7 and 18 hr for No's 8-10.

Although these changes in area are not very reproducible it seems reasonable to draw some inferences from these observations. Sample 2 was used mainly for runs carried out above 250°C and Sample 1 mainly below this temperature: Comparison shows the much larger changes induced at the higher temperature. Similarly, comparison of 1 and 3 indicates the possible influence of exposure to O₂ at 400°C, as 3 was also used mainly for runs below 250°C. The rate of reaction did not always change in a parallel fashion to the change of area. For several of these samples it was possible to compare the rate under standard conditions towards the beginning of the series with the rate towards the end: For No's 1, 2, 6, and 7 these ratios were, respectively,

8, 1.2, 12, and 1.2 while from the Table the corresponding surface area ratios are 36, 90, 40, and 15. In general the three samples used for the adsorption work at low pressures show less change in surface area than the first seven; this might be due to the experimental conditions but could be because the last three materials were not fired to so high a temperature. That the latter is probably the case is shown by the following experiment.

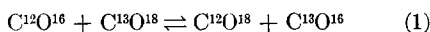
Samples of NiO and of NiO + 1.0% Li₂O, both prepared by ignition for 3 hr at 650°C, were given the following treatments, each of some 2 hr duration, each treatment being interposed with exposure to 1 cm O₂ at 400°C and outgassing for 1 hr at 500°C as for Samples 2-10: 10⁻¹ mm of CO₂ (10 times); 10⁻¹ mm CO (10 times) both at 110°C; 5 cm CO + ½O₂ mixture at 350°C (10 times). After each treatment the areas were measured and compared with the original sample; no significant change was recorded. The samples were then ignited at 1000°C for 24 hr, which reduced the areas from 5.8 to 0.45 m²g⁻¹ (NiO) and from 2.6 to 0.27 m²g⁻¹, and given another 10 treatments with 5 cm CO + ½O₂ mixture with the standard O₂ and outgassing procedure. The final areas were 0.87 m²g⁻¹ and 0.33 m²g⁻¹.

Taken as a whole these observations demonstrate a continuous and progressive modification of the catalyst surface with use: Samples 2 and 7 show that it is possible for profound changes in the surface to occur while the catalytic reactivity, as measured by one reaction under an arbitrarily chosen set of standard conditions, remains sensibly constant. Proper kinetic studies of the CO-oxidation reaction on these catalysts, or of the effect of lithium additions on the intrinsic activity of the solids are in these circumstances very difficult to make and will be of doubtful validity unless carried out with careful and frequent checks of the state of the catalyst. It is likely that such studies will be best carried out by a succession of short series of runs, each series upon a fresh specimen from a large master batch of catalyst.

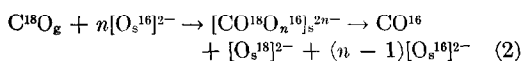
We believe that these changes are to be

attributed to the lability possessed by the surface oxide ion lattice of these and many other oxides. Thus, one of us has shown by isotopic experiments that at temperatures above say 300°C the whole surface layer of oxide ions will exchange with gaseous O₂; long exposure produces a much slower subsequent exchange with underlying layers (3). These observations have recently been confirmed and extended by Boreskov (4). In addition we have demonstrated by similar means that the CO/O₂ reaction on NiO at temperatures as low as 49°C involves the oxygen of the lattice (5). Only a small fraction of the surface ions is involved (<0.5%) but the proportion rises to 2% or 3% as the reaction temperature is raised to 200°C or so; similar observations were recorded with Cu/Cu₂O and Cr₂O₃, and for the N₂O decomposition reaction on doped NiO (6).

It has recently been shown (7) that the reaction



occurs readily around room temperature on the oxides of at least 30 metals. The general mechanism is



where n is a small number, probably 3 or less, governed by the geometry at the catalytic site, and $[\text{O}_s^{16}]^{2-}$ is a surface oxygen lattice ion. Reaction (2) occurs at a very small fraction ($\ll 1\%$ of the surface generally) of fixed sites and by its repetition leads to reaction (1) with only a very slight reduction in the O¹⁸ content of the CO. No CO₂ is produced. Exchange of the oxygen of CO and of CO₂ with larger fractions of the surface has been found to occur on some oxides at higher temperatures (3), and is probably a general phenomenon.

We suggest that exchange of oxygen between particularly active sets of surface sites and the oxygen-containing gases will, if many times repeated as in the long sets of experiments summarized in the Table, produce a gradual rearrangement of the surface which will be influenced by, and will itself influence, underlying defects. An array of a large number of subsurface lattice defects,

such as will occur along the borders of microdomains, or at slip planes or screw dislocations, etc., might by this means be "unlocked" leading to a considerable increase in the surface area available to gas molecules (and so to an increased BET area). It will clearly be a matter of chance whether the catalytic activity changes in a parallel fashion to the change in surface area. If the "unlocking" concept is correct it is likely that the change of surface area will be abrupt owing to the sudden release of strain throughout extensive sections of the lattice: It may also be somewhat irreproducible, as we have found. It is also likely that the oxide samples heated to 1000°C for some hours, being by this means partly sintered, would possess much more built-in strain than the materials which were heated only to 650°C. When the strain is released one might then expect much greater changes to occur in the former materials, and this is to a large extent borne out by our observations.

Another factor which is of importance in assisting to release some of the strain in the powder is that these long series of experiments in most cases involved many passes through the Néel point of the solid. For pure NiO this is about 247°C and by analogy with the Co/Li/O system is expected to fall with increasing Li content (10). Recent elegant studies by Slack (11) and Roth (12), using optical, X-ray, and neutron-diffraction techniques have demonstrated the presence of large numbers of antiferromagnetic domains, even in carefully prepared single crystals of NiO, unless they are annealed at about 1500°C. The domains are bounded by either T (twin) or S (spin-rotation) walls, both of which are associated with defects or imperfections in the crystal. The multiple twinning is due to the slightly distorted cubic (rhombohedral) structure of NiO below 247°C; reversion to the simple cubic form occurs above this temperature. The elastic properties also change markedly, Young's modulus being about 5.5×10^{11} dynes cm⁻² at 220°C and 8.7×10^{11} at 250°C (13).

Slack (ref. 11, Fig. 7) shows that the strain between two particular domains could be relieved by separating the two regions along one of the crystallographic axes. This would

give rise to a fissure in the solid surface of an angle equal to the degree of mismatch between the two regions—in this case $12'$ of arc. Relief of strain by this means could well account for our observations.

There have been a number of attempts to relate the catalytic activity of NiO doped with lithium and chromium with the type and amount of dopant but so far no agreement has been reached (8, 9). We believe that our present observations provide one of the reasons for this. It is also possible that the change in the mechanism of the CO-O₂ reaction which is thought to occur around 250°C on NiO (8, 9) is due to a change in the nature of the chemisorbed oxygen from mainly O₂⁻ at low temperatures to O⁻ above 250°C; this is in part confirmed by a change in the kinetics of O₂ adsorption at this temperature (14).

A recent study by one of us (6) on the N₂O decomposition reaction on these catalysts was completed before the possibility of the occurrence of surface area changes was realized. Unfortunately, most of the catalyst samples employed in that work were destroyed but we have confirmed that substantial surface area changes are induced under the conditions used in that study. This in no way alters the kinetic analysis nor the general conclusions of that paper since at all stages tests were carried out to ensure good reproducibility of kinetic rates but it does mean that the reduction of the velocity equations to rates per cm² is bound to be incorrect in at least some cases. Similarly

the attempt to calculate the accommodation coefficient of O₂ for the various catalysts should be ignored.

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