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Decomposition of Nitrous Oxide upon Nickel Oxide–Magnesium Oxide Solid Solutions

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The decomposition of N_2O has been studied over MgO catalysts, doped with NiO and NiO + Li_2O from 1 to 10% (atomic).

For pure MgO, activity is low, but is enhanced by addition of Ni^{2+} ions. The apparent activation energy is reduced from 35 kcal/mole for pure MgO, to about 18 kcal/mole. Oxygen acts as a poison, and it is chemisorbed on the catalyst.

The presence of lithium greatly increases the apparent activation energy. The results are interpreted in terms of oxygen chemisorption and of its influence on the course of the reaction.

The emphasis laid upon the physics of the solid state as a theoretical basis for the description of adsorption and catalysis has tended to obscure the chemical aspects of these processes. Indeed, in the reaction of a gaseous molecule with a surface, it should be considered that a surface complex is formed between the interacting species and one or more surface atoms. The nature and the stability of the surface complexes are of direct importance in the catalytic process, and they will depend on the structural and electronic properties of the adsorbent atoms, affected by the surface ligand field. This chemical standpoint is not in contradiction to, but rather complementary to the physical one, and it has recently received new attention (*1*, *2*). It is within this framework that we have begun a study on the catalytic activities of dilute solid solutions of transition metal ions in inert oxides. These systems offer in principle the advantage of allowing the investigation of the catalytic properties of the ions free from strong interference between themselves.

In this paper we report on the results obtained in a study of the catalytic decomposition of nitrous oxide on nickel oxide–magnesium oxide solid solutions, with particular regard to a comparison of catalysts of different composition.

EXPERIMENTAL PROCEDURE

Materials. Solid solutions of NiO in MgO, with or without addition of lithia, have been studied. As a starting material, magnesium oxide from two sources has been used: (i) Spec-pure MgO obtained from Johnson and Matthey (London) (stated impurities in ppm: Cr, 5; Ni, 2; Ca and Ag, 1; Cu and Si < 1); (ii) MgO prepared by thermal decomposition of the carbonate (Erba R.P.) (stated impurities, in per cent: Ca, 0.5; Fe and Ba, 0.002; $SO_4^{2-}Cl^-$ and NO_3^-, 0.002 to 0.003.)

A small sample of the oxide was impregnated with a comparable volume of a solution containing the calculated amount of the foreign ions (as nitrate, for nickel, and carbonate in acetic acid for lithium). The sample was dried, thoroughly mixed, heated at 600°C for 2 hr, mixed again and finally fired at the appropriate temperature, usually 1200°C, for 5 hr. This procedure was found to yield samples more homogeneous than those obtained by different methods.

Some experiments have also been carried out over pure NiO, prepared by ignition of nickel nitrate in air at 1000°C.

Table 1 gives a summary of the catalysts used, together with some of their features.

TABLE 1
Catalysts and Their Properties

Catalyst	Source	Firing temperature (°C)	Surface area (m^2/g)	Li (atoms/100 Mg atoms)
MO A	J.M.	1200°	20.4	—
MO D	Ex-carbonate	1200°	17.5	—
MO F	Ex-carbonate	1200°	17.5	—
MN1 D	J.M.	1200°	14.0	—
MN1 E	J.M.	1200°	14.0	—
MN10 R	J.M.	1000°	18.5	—
MNL 1:1B	J.M.	1200°	0.22	0.05
MNL 1:1D	Ex-carbonate	1050°	1.1	0.10

Pure MgO samples are designated as MO (MO—JM=MgO from Johnson and Matthey); Ni-containing ones as MN, followed by a figure indicating the percentage of nickel; Ni and Li-containing samples are designated as MNL, followed by two figures, indicating the Ni and Li percentage, respectively. Percentages are given as (atoms)/(100 Mg atoms) and are the nominal ones. While analysis of nickel confirmed the presence, within experimental error, of the amount initially added, the final lithium content was considerably lower. Table 1 also gives the actual amount as determined by flame photometric analysis, using a Beckman DK-2 spectrophotometer.

Particular attention was paid to the characterization of the solid catalysts. Precise X-ray determination of the lattice parameter, optical reflectance spectra, and magnetic susceptibility measurements were carried out. The results, which will be presented and discussed in detail elsewhere, confirm the presence of homogeneous solid solutions in the NiO–MgO system and indicate that the addition of lithium markedly influences the specimen properties. Li-containing samples are ochre-colored, in contrast to the pale green or white color of samples without lithium. A definition of the nature of the modification induced by the introduction of lithium would require a lengthy discussion which would be outside the scope of this paper. It should only be recalled that in pure NiO, the presence of lithium induces the formation of Ni^{3+} (*2*). The same process could take place in the case of the solid solutions in MgO.

Surface areas. Surface areas were measured by the BET method either with N_2 or with Kr at −196°C. For Kr, the following parameters were adopted: $G = 19.4$ Å^2, $p_0 = 2.63$ Torr (*3*). It should be mentioned that surface area values derived from adsorption of nitrogen were about 20% smaller than those based on Kr adsorption, as constantly observed when the two procedures were adopted on the same material. Surface area values for small area samples, where only krypton was employed, were accordingly reduced by 20%.

Gases. Cylinder N_2O was purified by double distillation from a −196°C trap into a −78°C trap, only the middle fraction being collected. Cylinder nitrogen was purified through hot copper turnings, magnesium perchlorate, and a liquid nitrogen trap. Spec-pure helium and krypton were used in the surface area measurements.

Apparatus and procedures. A conventional Pyrex static system (256 cm^3) was used. It was checked that in the absence of a catalyst no decomposition could be detected. The catalyst (~150 mg) was spread on the bottom of a small silica boat suspended on the thermocouple well. The fresh catalyst was subjected to a 7-hr high-vacuum (10^{-5} Torr) pretreatment at 480°C before beginning the experiments. Between runs, a half an hour evacuation at 480° was adopted for surface conditioning. This procedure led in general to reproducible activity. Occasionally, a marked fall in activity was observed and the catalyst was discarded. Prolonged high-vacuum treatment in these cases would tend to improve the activity of the catalyst, without, however, restoring its initial state. Accidental rise in the pressure (5×10^{-5} Torr) in the outgassing intervals appreciably decreased the activity of catalysts of the MNL series.

After introduction of the nitrous oxide, whose pressure, generally around 60 Torr, was read in a mercury manometer with the aid of a cathetometer, a small volume of gas (4.5 cm^3) was withdrawn at appropriate intervals and subsequently expanded in a small, closeby trap cooled at −196°C.

TABLE 2

Absolute Velocity Constants and Apparent Activation Energies for Different Specimens

Catalyst	log k abs.	T(°C)	E_{app}
MOA a			
8	−5.587	450°	
7	−5.332	470°	
5	−5.014	490°	36
6	−5.021	490°	
9	−5.008	490°	
MOA b			
10	−5.742	430°	
9	−5.433	450°	35
8	−5.120	470°	
6	−4.886	490°	
MOD a			
5	−5.900	400°	35
3	−5.099	450°	
MOF a			
3	−5.839	400°	
5	−5.917	400°	35
2	−5.124	450°	
MN 1 D b			
8	−5.553	310°	
14	−5.333	330°	
15	−5.339	330°	19.0
10	−5.124	350°	
12	−4.850	370°	
MN 1 D c			
11	−5.585	310°	
9	−5.366	330°	18.5
12	−5.356	330°	
15	−5.387	330°	
10	−4.854	370°	
14	−4.745	390°	
MN 1 E a			
9	−5.585	310°	
6	−5.328	330°	
7	−5.187	350°	18.2
10	−4.959	370°	
8	−4.745	390°	
MN 10R c			
22	−5.638	320°	
25	−5.409	340°	
12	−5.113	370°	
23	−4.854	400°	18.5
29	−4.824	400°	
16	−4.658	420°	
20	−4.658	420°	
21	−4.638	420°	
MNL 11B a			
7	−4.327	450°	
1	−3.991	470°	
5	−3.963	470°	
3	−3.730	490°	31.5
4	−3.738	490°	
6	−3.735	490°	
8	−3.735	490°	
MNL 11B b			
6	−4.060	450°	
7	−3.836	470°	29
3	−3.618	490°	
9	−3.585	490°	
MNL 11D a			
15	−4.592	470°	
17	−4.502	470°	
12	−4.407	480°	
18	−4.403	480°	42
27	−4.243	490°	
29	−4.259	490°	
11	−4.151	500°	

The ensuing small but significant drop in pressure in the reactor due to sample withdrawal was accounted for in the calculation. After a few minutes the incondensable gas expanded into a Pirani gauge, and the residual pressure was read. Particular attention has been paid to the accuracy of the sampling procedure. Mass spectrometric analyses of the collected gas were performed and confirmed that practically all N_2O ($>97\%$) had condensed. This would not have occurred if the gas had been directly expanded in the Pirani and subsequently condensed, thus involving larger volumes and longer paths for the gas. The amount of uncondensed N_2O was also not negligible if high decomposition percentages ($>10\%$) were attained. In the majority of the experiments, the total decomposition was kept below 1%. Only in a few cases were high percentages attained in order to investigate the kinetics of the reaction. The progress of the reaction was then followed directly on the manometer by reading the increase of pressure by means of a cathetometer.

The influence of the mass of catalyst has also been explored. Only if the mass was considerably larger (>300 mg) than that used in the present investigation (~ 150 mg) could a mass effect be found (apparent decrease of activity per unit area).

Mass spectrometric analyses. A sample of about 80 cm^3 was withdrawn for analysis* (Italelettronica mass spectrometer), after condensation of the N_2O. The mass 28 contribution due to the presence of small amounts of uncondensed N_2O (of the order of a few per cent) was taken into account. The instrument had been calibrated for sensitivity towards all of the above-mentioned gases. The error on the N_2/O_2 ratio depended upon the total pressure of sample, and it ranged from 1 to 5%.

EXPERIMENTAL RESULTS

Within the first 1%, the progress of the reaction was sufficiently linear with the time to allow a calculation of the initial rates. Lithium-doped catalysts showed an appreciable deviation from linearity and for this reason the initial rate could only be determined with a large error. It should be mentioned that for MN and MNL catalysts the kinetics did not conform to any simple law which could account for the progress of the reaction if studied up to high decomposition percentages.

From the initial rates, the kinetic constants were derived, and following the recommendation by Laidler (*4*), they are given as "absolute velocity constants." The results are presented in Table 2 and in Fig. 1, as an Arrhenius plot. The following observations refer more specifically to each group of catalysts, and to the result of the N_2/O_2 ratio.

Catalytic Activity

Pure magnesium oxide. Spec-pure magnesium oxide was found to show very little activity for the catalytic decomposition of nitrous oxide. Magnesium oxide of standard reagent grade purity was significantly more active than high-purity material. The activation energies for both types of catalysts are around 36 kcal/mole. This value is in excellent agreement with the value of 35.6 kcal/mole given by Dell, Hess, and Weller (*5*) for a catalyst (614 B) of the same origin, comparable area, but somewhat different surface conditioning. The value is also in fair agreement with that given by the same authors (30.4) for two catalysts (604 and 606) of different origin but similar area and pretreatment.

Particularly significant is the excellent agreement between the values of the absolute velocity constants found by us and those given by Dell, Hess, and Weller (who employed a circulating system) as illustrated in Fig. 1. The agreement also shows that the static system employed does not introduce any spurious effects due to diffusion. This result is in line with a low value of the parameter ϕ (*6*), as indeed would be expected from the low activity and from the low surface area and porosity of the catalyst.

A final remark is relevant to the low activity shown by pure MgO. From our data, a rough estimate can be made for the "reaction temperature" obtainable in a flow system under conditions similar to those adopted by Hauffe, Glang, and Engell (*7*). The reaction temperature would be of the order of 700°C or more, that is, much higher than usually reported.

Ni-doped oxides. The reaction could be studied conveniently at 300–400°C with these catalysts. The main features which have been found are: (i) The addition of NiO to MgO considerably enhances the activity of the catalysts. (ii) The activation energy is reduced to 18.5 kcal/mole for MN 1 and for MN 10. (iii) If the initial N_2O pressure is increased, the decomposition rate increases in the case of MN 1, but it decreases in the case of MN 10. (iv) Saturation of the surface with oxygen at 470°C and outgassing at the reaction temperature for only ½ hr greatly increased the apparent activation energy.

Ni- and Li-doped oxides. A striking decrease of surface area was caused by lithium addition. The reproducibility of the catalytic activity was less satisfactory than for specimens not containing lithium. The activity of freshly outgassed catalysts was higher than that observed after two or three runs. If the outgassing conditioning between runs was carefully under control, a constant behavior could be reached. The

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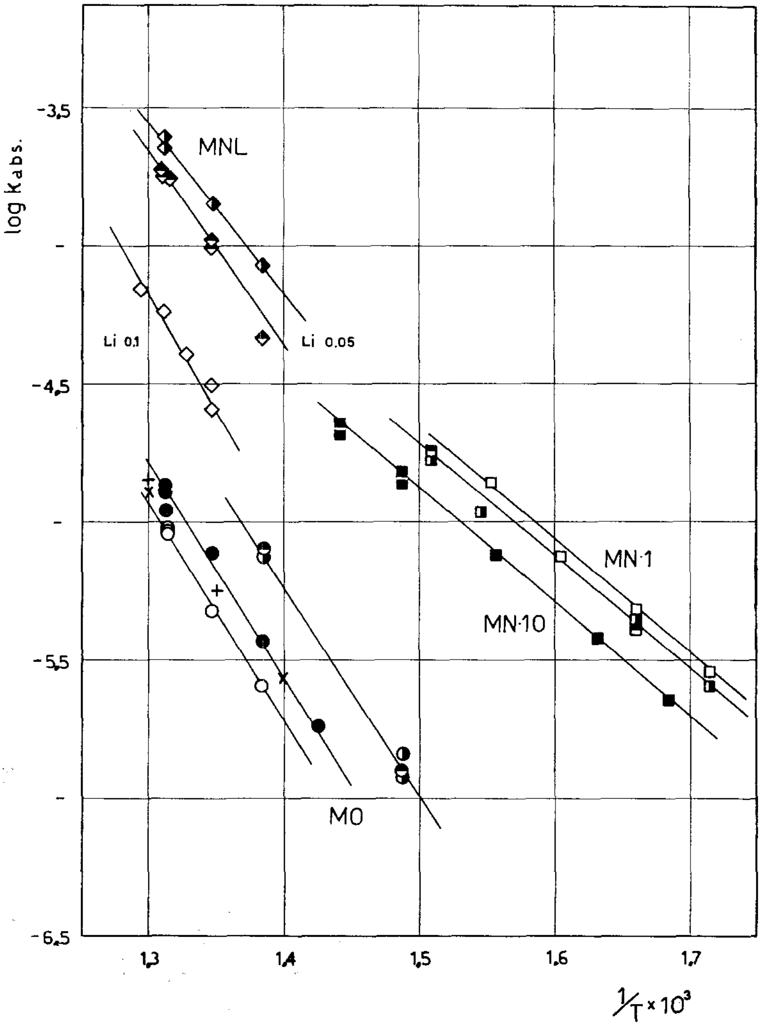

FIG. 1. A plot of log k_{abs} vs. $1/T$: ○, ●, Specpure MgO; ◑, ◓, MgO from reagent grade magnesium carbonate; □, ◨, ⬒, MgO + 1% (atomic) NiO (MN 1); ■, MgO + 10% (atomic) NiO (MN 10); ◈, ⬖, MgO + 1% NiO + 1% (nominal, atomic) Li$_2$O (effective Li concentration 0.05); ◇, MgO + 1% NiO + 1% (nominal atomic) Li$_2$O (effective Li concentration 0,10); +, × data reported by Dell, Hess, and Weller (ref. *5*) for pure MgO.

data reported refer to a catalyst which reached this constant condition. Owing to the low surface area the activity was too low to enable the reaction to be studied over the same temperature range as used for MN. It was necessary to go to 450°C before activity could be conveniently studied. It was then found that the activation energy was greatly increased by Li addition. The values are: 30 kcal/mole, for an effective lithium concentration of 0.05%, and 42 for a Li concentration of 0.1%. It should be added that when the activity of fresh catalysts was examined, a lower apparent activation energy (~25 kcal/mole) was obtained for the latter catalyst. Finally, the behavior of MNL catalysts shows that they are more sensitive towards oxygen.

Pure nickel oxide. Results obtained on pure NiO, under the same experimental conditions as for the magnesium oxide base catalysts, showed a strong inhibiting effect by reaction products. The apparent activation energy varied between 23 and 36 kcal/mole, according to outgassing conditions. A more marked influence of the latter appeared to be present for these catalysts.

The N_2/O_2 Ratio and Oxygen Adsorption

The theoretical ratio of 2 was found either when large decomposition was attained, since the unbalance due to the adsorption of small amounts of oxygen becomes undetectable, or at high temperatures. If the decomposition was kept below 1%, the ratio was found to be larger than 2. Table 3 gives the results obtained for different catalysts and conditions. The N_2/O_2 ratio, the final pressure of uncondensed gas, the calibrated volumes of the apparatus, and the initial number of N_2O molecules enable a calculation to be made of the deficit of oxygen molecules (Table 3, column 6). Also, the surface coverage [as number of oxygen atoms per numbers of cations in a (100) plane] can be given (Table 3, column 7).

It is evident from Table 3 that there is oxygen adsorption during the decomposition reaction. It can be seen that the unbalance of the N_2/O_2 ratio and the deficit of oxygen molecules tend to decrease with increasing reaction temperature. It is noteworthy that these types of catalyst show the same phenomenon of oxygen adsorption coverage during the N_2O decomposition as shown by NiO and doped NiO catalysts.

Also a remarkable result is the occurrence of oxygen chemisorption on "pure" MgO. The calculated coverage is close to that reported by Winter (*8*) (0.6% at 460°C).

The occurrence of oxygen chemisorption on MO catalysts makes it impossible to give a reliable estimate of oxygen coverage per nickel ion for MN 1. Indeed, the deficit of oxygen molecules for MN 1 is comparable to that calculated for MO. Accordingly, the error on the increment of oxygen adsorption due to introduction of nickel is very large. Since 1.14×10^{15} cations/cm^2 are present on the (100) plane of MgO, a complete monolayer of oxygen atoms on Ni ions in MN 1 would only require 6×10^{12} oxygen molecules. An error of 1×10^{12} oxygen molecules, which can arise from the experimental error on the N_2/O_2 ratio, corresponds to a coverage of about 15%.

A more favorable situation is met with MN 10. Here the number of oxygen molecules in deficit is definitely larger than those observed for MO. A surface coverage per Ni ions of the order 5% can be calculated.

Due to the small surface area of MNL, the minimum detectable number of oxygen molecules per unit area is very large. In spite of this handicap and the experimental error of the N_2/O_2 ratio, the large number of oxygen molecules in deficit per unit area points to the occurrence of extensive chemisorption. The data would even indicate that some incorporation (more than one monolayer of chemisorbed oxygen) occurs.

DISCUSSION

The N_2O decomposition has been used by several authors as a test reaction for the investigation of the relation between the catalytic activity of a solid and its electronic structure (*9*). These studies gave a valid contribution for taking solid state theories as a basis for the description and interpretation of catalytic phenomena. It had indeed been found that *p*-type oxide conductors are much better catalysts than *n*-type oxides. The grouping of different oxides according to their semiconductor behavior strongly pointed to the importance of the collective electronic properties of the solid. In order to explain the high activity of *p*-type oxides, it was assumed (*7*) that the oxygen desorption was the rate-determining step. Desorption of the negatively charged oxygen requires, in fact, participation of electronic holes and it is therefore easier on *p*-type semiconductors. It should be pointed out, however, that the existence of an inhibiting effect on the reaction by the oxygen formed does not necessarily require that desorption is rate-determining (*10, 11*). This point will be further discussed below. It is nevertheless clear that the occurrence of oxygen chemisorption is an important factor in controlling the course of the reaction and determining the over-all activity of the catalyst.

Clear evidence has been given by Winter

(*11*) that the apparent activation energy for N_2O decomposition over NiO contains a large term due to oxygen desorption. According to Winter the true activation energy is of the order of a few (from 0 to 4) kcal/mole. The variable extent of oxygen adsorption according to its partial pressure and to surface conditioning explains the different values found for the apparent activation energies over NiO: 4.5 (*11*); 7.5 (*12*); 14 (*13*); 18 (*11, 14*); 25 (*11, 13*); 32 (*7*); 37 (*15*).

It is interesting to see the effect of dilution of nickel ions in the inert matrix MgO, where Ni^{2+} ions are maintained in an octahedral surrounding. In spite of the dispersion of the nickel ions, oxygen chemisorption does occur and it has an inhibiting effect on the reaction. However, the trend shown by the sequence pure NiO, MN 10, MN 1 points to a decrease of the inhibiting effect with increasing dispersion, as reflected in the decrease of the apparent activation energy from $36 \div 23$ to 23 (NiO) to 18.5 (MN 10 and MN 1) kcal/mole. The respective values of k_{abs} for MN 1 and MN 10 (Fig. 1) confirm that the activity *per nickel ion* is higher when dilution is greater. This observation deserves further investigation.

This work thus points to two results: (i) An isolated Ni^{2+} is active for the decomposition of N_2O, probably through the formation of a surface complex such as N_2O^-. (ii) Isolation of Ni^{2+} weakens the oxygen adsorption and leads to an increase of catalytic activity.

These results do not support the view that the *p*-type semiconductors have high activity through their high positive hole concentration facilitating a rate-determining desorption of oxygen. If this were so, the isolation of Ni^{2+} ions, which reduces the mobility of the positive holes, would be expected to lead to a blockage of nickel ion sites by adsorbed oxygen, and to the inhibition of the reaction. In fact the reverse is observed. The results are more consistent with the concept of the reaction leading to the oxygen adsorption

$$N_2O^-_{ads} = N_2 + O^-_{ads}$$

being the rate-determining step. The correlation with the semiconducting type may then be explained along the lines already indicated by Dell, Stone, and Tiley (*16*), who discussed reasons why the above reaction should be easier on *p*-type semiconductors.

The increase of the apparent activation energy E upon addition of lithium points to a larger heat of oxygen adsorption.* The results obtained for MNL catalysts can be compared with those obtained by Winter (*11*) for lithium-doped nickel oxide. Winter found that an increase of E occurs upon first additions of lithium (0.01%) and the effect is more pronounced for specimens outgassed at high temperature (E increases from 18 to 30 kcal/mole). Further addition of lithium resulted in a decrease of E, which is thereby brought back to the initial values. The parallelism between increase of the apparent activation energy in MNL samples when compared with MN ones, and extent of oxygen adsorption (Table 3), also reflected in the kinetics (p. 275) indicates that on these catalysts there seems to be a more pronounced blocking by the oxygen. This result is supported by the findings of Keier (*17*), who showed that faster and stronger oxygen chemisorption occurs on Li-doped NiO. It should also be recalled that it has been found that the presence of lithium provokes the desorption (*18*) and the photodesorption (*19*) of larger amounts of oxygen. The data obtained by Winter (*8*) on the number of isotopically exchangeable sites are also relevant. The number n_s is compared with the number of surface sites as determined by BET methods n_{BET}, for pure and Li-doped NiO. The n_s/n_{BET} ratio is as follows: NiO ex-nitrate, 0.9; NiO ex-carbonate, 0.9; NiO + 0.1% Li_2O, 0.6; NiO + 0.1% Li_2O, 0.6. This result shows that the presence of Li diminishes the number of exchangeable sites, that is Li addition leads to an increase in the blocking effect. Winter (*8*) also studied the number of iodine equivalents liberated by

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* An experimental confirmation of this hypothesis has been obtained by S. J. Teichner and co-workers (Conference on "Chemisorption and Catalysis," Bristol, April, 1965).

TABLE 3
OXYGEN DEFICIT IN THE REACTION PRODUCTS

Run	T (°C)	N_2/O_2	Decomposition (%)	O_2 produced (molecules/cm²) $\times 10^{-13}$	O_2 in deficit (molecules/cm²) $\times 10^{-12}$	Coverage[a] (%)
MOF a6	400°	2.32	0.29	1.7	2.3	0.41
MOF a4	450°	2.085	0.66	3.1	1.3	0.22
MN 1D e5	350°	3.00	0.14	0.70	2.3	0.41
MN 1D e3	400°	3.06	0.17	0.84	2.9	0.51
MN 10B a35	300°	29.8	0.15	0.64	6.0	1.0
36	400°	2.25	0.89	4.1	4.1	0.7
37	500°	1.97	0.27	1.1	≤ 0.8	≤ 0.14
MNLD d8	450°	2.16	0.27	21	16	2.7
d5	490°	2.00	0.82	57	≤ 5.7	≤ 0.9

[a] Calculated for oxygen atoms per total number of cations in a (100) plane.

NiO with or without Li, before and after pumping. It can thus be derived that in pure NiO, the number of exchangeable sites n_s is larger than the number of oxygen atoms in excess in a ratio of 9:1; addition of Li, however, decreases this ratio to 5:1. Once more, it is apparent that the presence of lithium decreases the mobility of surface oxygen. This is probably due to an increase of the heat of adsorption. Direct measurements, however, are necessary in order to confirm this point, which is of particular interest due to its links with the problem of the nature and influence of surface defects, and with the possible role of Ni^{3+} ions.

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