Catalytic Activity of Nickel Ions in a Spinel Matrix for N_2O Decomposition

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The catalytic decomposition of N_2O has been studied on spinel catalysts of composition $Ni_xMg_{1-x}Al_2O_4$, with $x = 0$; 0.002; 0.01; 0.03; 0.06; 0.10; 0.25; 0.50; 1. In the bulk of these solid solutions, nickel ions are predominantly distributed on octahedral sites, with a fraction of Ni^{2+} on tetrahedral sites. It is shown that the catalytic activity of surface Ni^{2+} ions which are exposed from octahedral sites is larger than the activity of surface Ni^{2+} ions exposed from tetrahedral sites. The catalytic activity is accordingly influenced by the extent of inversion. The results also point to a distribution of nickel ions in the surface layers different from that found in the bulk, the external layers being richer in tetrahedral nickel. Adsorption measurements have shown that oxygen chemisorption is strong, and amounts to 2–5% of monolayer coverage: this is larger than on $Ni_xMg_{1-x}O$. The results are discussed in terms of possible environment effects on the oxygen surface complex.

INTRODUCTION

The results of investigations devoted to the study of the effect of dispersion of nickel ions in MgO on the catalytic activity for the N_2O decomposition have been reported in earlier papers (1–3). In these studies it was shown that the catalytic activity per nickel ion increased with a decrease of the concentration of Ni^{2+} in the solid solution. Other transition metal ions dispersed in MgO have been investigated, and similar conclusions have been drawn also for the dispersion of chromium (4) and manganese (5) ions. The catalytic behavior was correlated with the oxygen adsorption properties and with the nature of the oxygen surface-complex. The results obtained on MgO-based solid solutions have given support to the idea that the oxygen surface-complex responsible for the catalytic behavior could be treated along lines similar to those successfully followed in inorganic chemistry (6, 7).

Following this work, it was of considerable importance to study the influence of the oxide matrix on the intrinsic catalytic activity of the nickel ions. Nickel ions having a coordination different from octahedral (as present in MgO–NiO solid solutions) could thus be tested. Furthermore a change of matrix allows one to explore the influence on the catalytic process of the surface properties of the matrix itself, such as surface disorder and ability to chemisorb oxygen. Among other oxide matrices, the spinels $M^{II} M_2^{III} O_4$ (M^{II}, M^{III} are divalent and trivalent cations, respectively), have the advantage of offering cationic sites of both octahedral and tetrahedral symmetry. It is interesting to recall that Schwab and coworkers (8) have explored the influence of the coordination of Fe^{3+} ions present in a spinel on catalytic activity (CO oxidation and N_2O decomposition).

Spinels have been the object of numerous studies (9–11) in which their structures and physical properties have been elucidated. Particularly attractive for the present work was the choice of $MgAl_2O_4$–$NiAl_2O_4$

solid solutions, in view of the recent studies devoted to these systems (12–14). The detailed investigation of the solid solutions $Ni_xMg_{1-x}Al_2O_4$, recently made by Porta, Stone and Turner (14) enabled us to use specimens of well-characterized properties (homogeneity, degree of inversion, i.e., fraction of Ni²⁺ in octahedral position). A study of the decomposition of N_2O and of oxygen chemisorption was thus carried out on specimens having nickel ions in both octahedral and tetrahedral positions. Furthermore, since the fraction of divalent Ni²⁺ ions in tetrahedral sites, α, varies slightly with temperature, it was decided to explore whether the catalytic activity of a catalyst of fixed composition was sensitive to the temperature of quenching. It will be shown that the results give a definite indication for a higher activity of Ni²⁺ ions exposed from octahedral sites with respect to the same ions exposed from tetrahedral sites. The participation of the matrix surface in the catalytic process also emerges from the present study. It will be shown that the results have a bearing on the problem of activity of supported nickel catalysts, and this will be further developed in subsequent articles.

EXPERIMENTAL

Catalysts: Preparation and Properties

Catalysts of composition $Ni_xMg_{1-x}Al_2O_4$ $(0 \leqslant x \leqslant 1)$ were portions of those prepared by Porta, Stone and Turner (14) for their work on cation distribution, except one specimen, having $x = 0.002$. Preparation of the solid solutions was made using "Specpure" MgO and NiO (Johnson and Matthey, London) and a specially supplied pure grade of Al_2O_3 (P. Spence, Widnes.). The appropriate amounts of the component oxides were mixed into a paste with a small amount of water, dried, pelleted and fired in air at 1400°C for 100 hr. For each composition, one batch of pellets was directly quenched in water from 1400°C, and a second batch was cooled to 1000°C, kept at this temperature for 50 hr and finally quenched in water from 1000°C. Some essential properties of the specimens are

listed in Table 1, while details of the chemical and of the physical (X-ray, magnetic, reflectance spectroscopy) analyses on the same specimens are reported by Porta, Stone and Turner (14). For the main part of the work these spinel specimens were used as catalysts as such (i.e., taken after the water-quench, ground, and subjected to the normal vacuum conditioning in the catalytic reactor, as specified below). However, some specimens, prior to their use as catalysts, were submitted to a further equilibration treatment in air, followed by a quenching in air, in order to check on any possible effect of the quench in water. In order to accomplish this further treatment, small amounts (∼200 mg) of powdered specimens were heated in air at 1000°C for 50 hr (except when stated) and the quenching operation was carried out by quick transfer of the powder into a cold platinum crucible.

Composition and history of the specimens are specified by the symbols designating the different catalysts. SAMN indicates $Ni_xMg_{1-x}Al_2O_4$, and the figure which follows the symbols is the nominal value of x. The symbols SAN and SAM stand for pure $NiAl_2O_4$, and pure $MgAl_2O_4$, respectively. The figure of 1000 or 1400 in brackets after the value of x indicates the temperature from which the specimens were quenched into water. The further equilibration in air at 1000°C, followed by quenching in air from 1000°C, is specified by the letter R. Thus the symbolism SANM 50 (1000) designates a sample of composition $Ni_{0.50}Mg_{0.50}Al_2O_4$, water-quenched from 1000°C, while SAMN 50 (1400) R designates a sample of the same composition, first water-quenched from 1400°C, subsequently annealed at 1000°C for 50 hr and air quenched from this temperature.

Apparatus and Procedure

The N_2O decomposition was studied in the temperature range 380–480°C in a circulating system (441.5 cm³), having a silica reactor vessel. The gas was forced (at about 100 cm³/min) through the catalyst (∼200 mg) spread over silica wool. Further details are reported elsewhere (5).

TABLE 1
CATALYSTS AND THEIR PROPERTIES

	x_{Ni} (Ni experimental mole fraction)	α (Percentage of Ni^{2+} in tetrahedral site)	Surface area m^2/g	E_a kcal/mole
SAM (1000)[a]	—	—	0.90	31
SAMN 0.2 (1000)	—	—	2.3	32
SAMN 1 (1000)	0.00366	—	1.3	28, 28[b]
SAMN 1 (1400)	0.00366	—	2.1	28
SAMN 3 (1000)	0.0117	—	1.2	23, 23
SAMN 3 (1400)	0.0117	—	1.9	26.5, 27
SAMN 3 (1400) R	0.0117	—	1.4	23
SAMN 6 (1000)	0.0232	22	1.6	26
SAMN 10 (1000)	0.034	19	1.4	26
SAMN 10 (1000) R	0.034	—	1.2	26
SAMN 10 (1400)	0.034	22	1.7	26
SAMN 10 (1400) R	0.034	—	1.4	27
SAMN 25 (1000)	0.090	11	1.0	26.5
SAMN 25 (1400)	0.090	14	1.1	25
SAMN 50 (1000)	0.185	12	1.3	26
SAMN 50 (1000) R	0.185	—	1.1	26
SAMN 50 (1400)	0.185	15	2.0	26
SAMN 50 (1400) R (12 hr)	0.185	—	1.8	26
SAMN 50 (1400) R	0.185	—	1.6	26
SAN (1000)	0.333	22	2.2	32, 32
SAN (1000) R	0.333	—	1.8	29
SAN (1400)	0.333	21	2.0	30, 31
SAN (1400) R	0.333	—	1.8	30

[a] For key to the symbols see text.
[b] The two values refer to determinations on two different specimens of the same batch.

Prior to each series of catalysis experiments, the catalyst was outgassed at 480°C for 4 hr at a pressure $<10^{-5}$ Torr. Between runs, evacuation at 480°C for 30 min was made. Particular attention was paid to the reproducibility, and temperatures were chosen in a random sequence. An initial N_2O pressure of about 60 Torr was used, and the reaction was followed until 0.3% or less had decomposed. The course of the reaction was followed by withdrawal of a small gas sample (5.3 cm³), condensation of N_2O in liquid nitrogen, and measurement of the pressure of incondensible gas by means of a Pirani gauge. The treatment of the experimental data has been specified elsewhere (1). All kinetic data are reported as absolute velocity constants (k_{abs}), with units of cm min⁻¹. Occasionally, for the purpose of checking the N_2/O_2 ratio and hence of determining the extent of chemisorption of oxygen on the

catalyst, analyses of the gaseous mixture were performed by mass spectrometry. At the end of the selected run, all the gas was contacted with a cold ($-196°C$) trap, and the last traces of N_2O were condensed by circulating the gas through the trap, but bypassing the reactor, for 15 min. The gas pressure was then read, and a sample transferred for analysis.

The direct oxygen adsorption measurements were carried out in the apparatus previously described (5). The initial surface conditioning of the catalyst was the same as in the catalysis experiments. Oxygen pressures of about 0.050 Torr, i.e., comparable to those built up in the N_2O decomposition experiments, were used. The oxygen uptake was essentially complete in 60 min, but the process was followed for 120–180 min. At the end of the time, a measurement of the more loosely bound oxygen, "reversible oxygen," was made by

outgassing the catalyst for ½ hr without changing the temperature, and then measuring the amount of oxygen which could be readsorbed, always at constant temperature. Due to the low surface area and to the low pressures, the adsorption measurements are affected by a large error (20–30%), and the measurement of "reversible oxygen" is only indicative (error of 50% or more) of it. It should be noted that all the direct adsorption measurements have been carried out on catalysts of series R (quenched in air).

Surface areas were determined by the BET method at $-196°C$, using spectroscopically pure krypton ($P_0 = 2.72$ Torr, and $\sigma = 19.4$ Å^2).

EXPERIMENTAL RESULTS

A large number of runs has been carried out on all catalysts, and reproducibility has always been found to be very satisfactory. The results will be presented in the form of Arrhenius plots (log k_{abs} vs $1/T$). For the sake of clarity, and due to the large number of experimental points pertaining to the same $1/T$ value, the average of several determinations of log k_{abs} at each temperature is reported as a single point. In general, the average deviation is less than $\pm10\%$ on k_{abs}, or ±0.04 on log k_{abs}.

Pure MgAl₂O₄. Pure magnesium aluminate (SAM) was found to show very little activity for the catalytic decomposition of nitrous oxide (Fig. 1). The apparent activation energy for the reaction is 31 kcal/mole. Figure 1 also reports (dashed line) the activity of pure magnesium oxide (5), determined on the same apparatus and with the same technique. It can be seen that MgAl₂O₄ is less active than MgO.

Pure NiAl₂O₄. For catalysts of this composition, the following four series have been studied: (i) SAN (1000), i.e., NiAl₂O₄ water-quenched from 1000°C (two specimens); (ii) SAN (1400), i.e., NiAl₂O₄
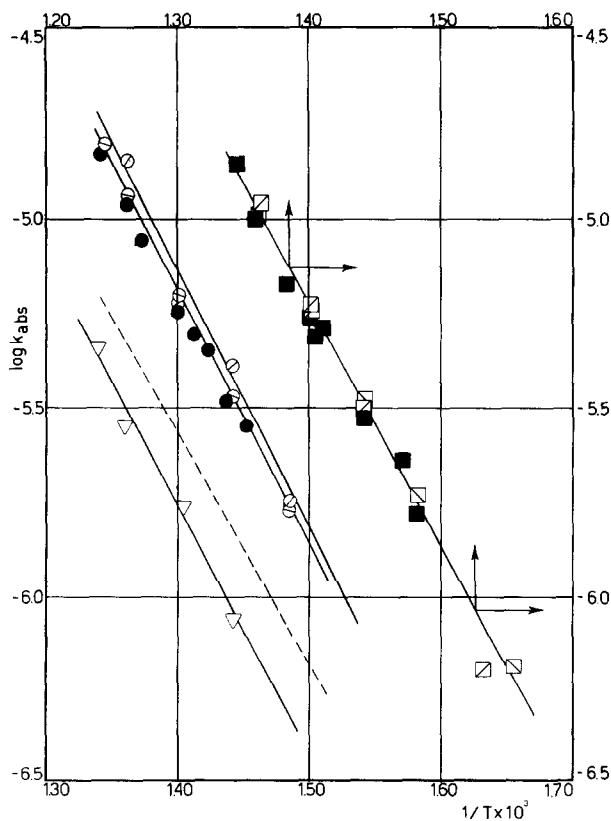

FIG. 1. A plot of log k_{abs} vs $1/T$; ▽, SAM (1000); -------- MgO, Ref. (5); ⊘, ⊘, SAN (1000) (different specimens); ●, SAN (1000) R; ◹, ◿, SAN (1400) (different specimens); ■, SAN (1400) R.

water-quenched from 1400° (two specimens); (iii) SAN (1000) R, [SAN (1000), fired in air, and quenched in air from 1000°C]; (iv) SAN (1400) R, [SAN (1400), quenched in air from 1000°]. The four types of catalyst do not show any appreciable difference, as Fig. 1 reports. It should be noted that the abscissae of points referring to SAN (1400) and SAN (1400) R have been shifted for the sake of clarity. The activity of all the SAN specimens is appreciably (factor of 3) higher than on MgAl$_2$O$_4$. The activation energy is 32 kcal/mole. A notable result is the lack of influence of the temperature of quenching [series (1000) and (1400)].

Water-Quench and Air Quench

The study of NiAl$_2$O$_4$ shows that specimens quenched in air [(1000) R and (1400) R] exhibit the same activity as those quenched in water, thus indicating that the water-quench did not effect the surface of the catalyst to such a degree that it could not be uniformly conditioned by the preliminary outgassing, at least in its initial (first 15 runs) state. The same correspondence between air-quenched and water-

quenched material has been found for catalysts of other compositions (see below). Accordingly, the air treatment and air-quench has not been carried out on all specimens. A secondary phenomenon, however, was observed to develop for pure NiAl$_2$O$_4$ after 15 runs, differentiating series (1000) and (1400) from (1000) R and (1400) R. The phenomenon will be briefly discussed in a separate section.

Solid Solution $Ni_xMg_{1-x}Al_2O_4$

Concentrated solid solutions. Figure 2 reports the data for specimens SAMN 10 (1000), 10 (1000) R, 10 (1400) and 10 (1400) R. Figure 3 reports the results for specimens SAMN 25 (1000) and 25 (1400). Figure 4 reports the results for SAMN 50 (1000), 50 (1000) R, 50 (1400), 50 (1400) R (12 hr), and 50 (1400) R (50 hr). These three figures show that the catalysts (1000) quenched from the lower temperature are
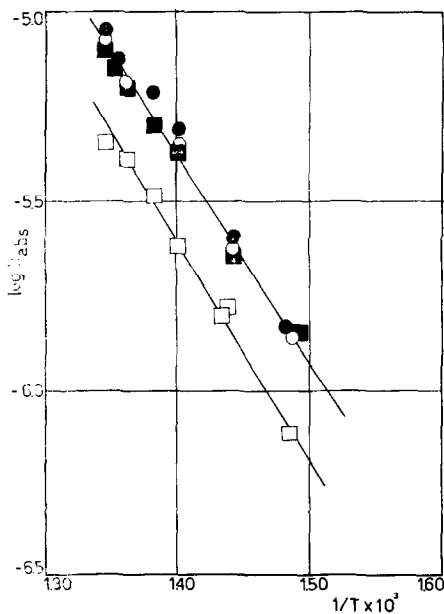
FIG. 2. A plot of log k_{abs} vs $1/T$; ○ SAMN 10 (1000); ●, SAMN 10 (1000) R; □, SAMN 10 (1400); ■ SAMN 10 (1400) R.
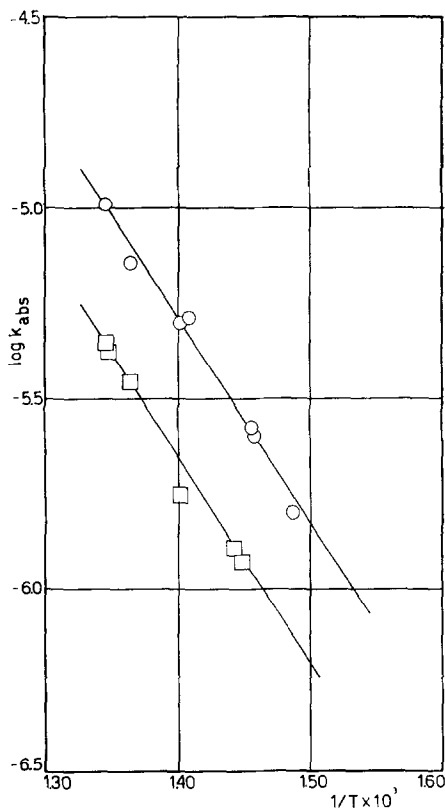
FIG. 3. A plot of log k_{abs} vs $1/T$; ○, SAMN 25 (1000); □, SAMN 25 (1400).
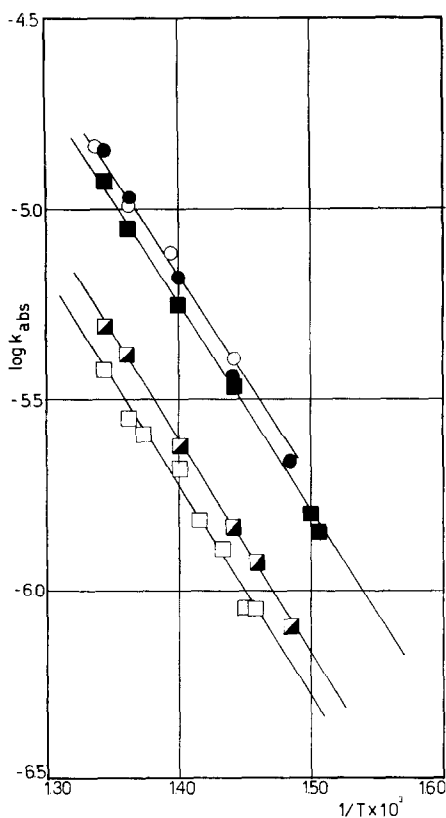
FIG. 4. A plot of log k_{abs} vs $1/T$; ○, SAMN 50 (1000); ●, SAMN 50 (1000) R; □, SAMN 50 (1400); ◩, SAMN 50 (1400) R (12 hr); ■, SAMN 50 (1400) R.

more active than those (1400) quenched from the higher temperature. The difference of activity between series (1000) and (1400) decreases from SAMN 50 to SAMN 10. The effect of the R treatment, by which catalysts of different history are equilibrated at 1000°C, and quenched in air from this temperature, clearly shows that the difference between series (1000) and (1400) is real. In fact, first a comparison between SAMN (1000) and SAMN (1000) R, such as between SAMN 10 (1000) and 10 (1000) R or between SAMN 50 (1000) and 50 (1000) R, shows that the air-quench is equivalent to the water-quench, as observed for pure NiAl₂O₄. Secondly, it can be considered that the R treatment (quenching from 1000°) performed on a (1400) specimen tends to equilibrate it to the state of an (1000) specimen. Accord-

ingly, a 12 hr equilibration—SAMN 50 (1400) R (12 hr)—tends to move the activity level of SAMN 50 (1400) towards that of SAMN 50 (1000). The equilibration time is, however, insufficient for attaining the same level. A longer (50 hr) time renders the catalyst equal to SAMN 50 (1000). It is clear, therefore, that the difference between an (1000) and (1400) catalyst is real, and solely due to the different temperature of quenching.

Dilute solid solutions. Catalyst SAMN 3 shows no significant difference in activity between series (1000) and (1400). The similarity between the specimens studied renders a shift of abscissae necessary in the Årrhenius plot (Fig. 5). The equivalence of activity is confirmed by the coincidence of SAMN 3 (1400) R with the (1000) and (1400) specimens. Only a small difference is observed in their apparent activation energies E_a, namely 23 kcal/mole for (1000) and for (1400) R, and 26 kcal/mole for (1400). The activity of catalysts SAMN 1 (1000) and (1400) are also practically coincident (Fig. 6).

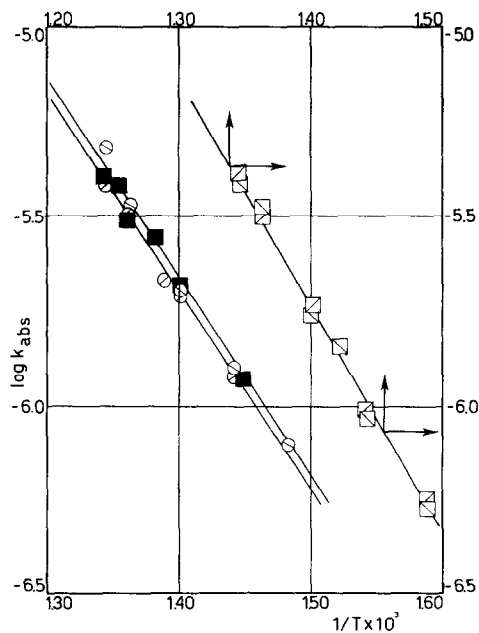A remarkable result is the fact that the

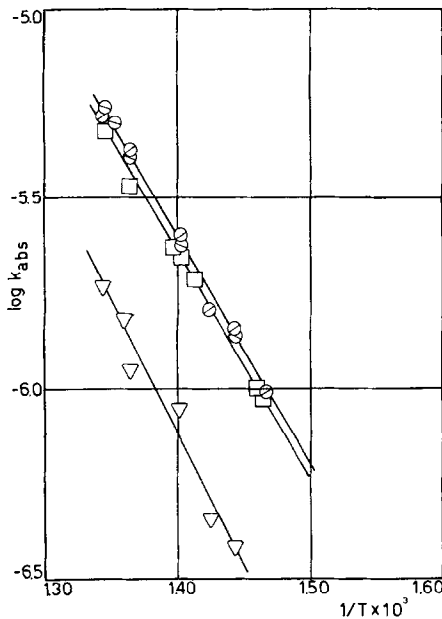FIG. 5. A plot of log k_{abs} vs $1/T$; ⊘, ⊘, SAMN 3 (1000) (different specimens); ◲, ▨, SAMN 3 (1400) (different specimens); ■, SAMN 3 (1400) R.

FIG. 6. A plot of $\log k_{abs}$ vs $1/T$; ⊘, ⊘, SAMN
1 (1000) (different specimens); □, SAMN 1 (1400);
▽, SAMN 0.2 (1000).

most dilute specimen, SAMN 0.2 (1000),
is less active than pure $MgAl_2O_4$ (Fig. 6).
Its E_a value (32 kcal/mole) is equal to
that of $MgAl_2O_4$ (31 kcal/mole), within
experimental errors.

Activation Energy and Composition

As summarized in Table 1, there is no
significant trend in E_a value vs composi-
tion: E_a is practically constant (26 kcal/
mole) for all (1400) solid solutions. The
lower value found for SAMN 3 (1000) and
SAMN 3 (1400) may be significant since
it is duplicated, but it does not suffice to
substantiate a minimum. A trend towards
a rise of E_a with dilution is however con-
firmed by both (1000) and (1400)
specimens.

Catalytic Activity per Nickel Ion

The absolute activity of SAMN speci-
mens, though decreasing with increasing
nickel content, does not vary as much as
the wide range covered by the nickel con-
centration. As a result, when the catalytic
activity per nickel ion is considered (as
may be done by dividing k_{abs} by the ex-
perimental nickel mole fraction x_{Ni} of ca-
tions), an increase of the catalytic activity
of each nickel ion is seen to occur as dilu-
tion increases. This important point is
illustrated in Fig. 7, where $\log(k_{abs}/x_{Ni}) =$
$\log k_{abs}^{Ni}$ is plotted against $1/T$ for the
different catalysts. The k_{abs}^{Ni} reported in
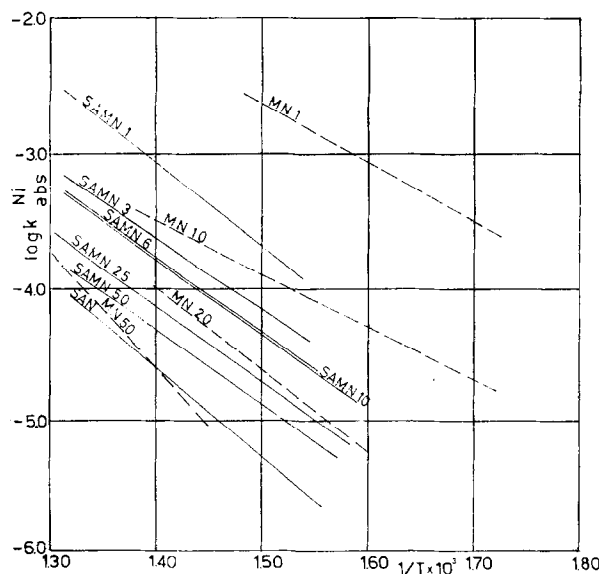Fig. 7 refer to the catalysts of the series

FIG. 7. Absolute activity referred to unit nickel concentration; ------------ Ref. (3).

(1000). For series (1400) the picture is the same for SAMN 1, SAMN 3, SAN; the position of SAMN 50, SAMN 25, SAMN 10 is lower when compared to the series (1000). Figure 7 also reports (dashed lines) corresponding plots obtained for the activity of nickel ions in the MgO matrix (*3*).

The Adsorption of Water and Catalytic Activity

When reporting the results for NiAl₂O₄, it has been specified that the activities of water-quenched and of air-quenched specimens were the same, for the first 15 runs. On continuing the use of the water-quenched catalysts SAN (1000) and (1400), beyond the 15th run, a systematic variation of activity took place, eventually leading to a higher activity level and to a lower E_a value ($\sim$17 kcal/mole). The effect, which was duplicated on different portions of the same batch, was observed on SAN (1000) and (1400), and to a much lesser extent on SAMN 50 (1000) and SAMN 50 (1400). It was not observed, in spite of very prolonged use, on the more dilute members of the solid solutions series. The results are illustrated in Fig.

8 where the first level (dashed line) and the final level of activity of the catalysts SAN (1000) are reported. At the end of the catalysis experiments, the catalyst SAN (1000) was checked by optical reflectance spectroscopy in the range 250–2600 mμ (Beckman DK 1 A) and three bands attributable to surface hydroxyls (1420, 1950, and 2400 mμ) (*15*a,b), not previously present in the freshly outgassed specimens, were found. The phenomenon can be attributed to the presence of water which entered into the particulate pellet because of the quenching process in water, and which subsequently diffused on to the surface. According to this hypothesis, the reason why the first runs were not altered is that the preliminary outgassing at 480°C had "cleared" the outer layers and the behavior would then reflect the property of a normal air-treated surface. This outgassing was not sufficient to remove all the water initially present. A more drastic outgassing was then carried out on a SAN (1400) specimen (650°C, 30 min), after which the usual conditioning was performed at 480°C; no increase of activity level was observed even after 35 runs. A further sup-
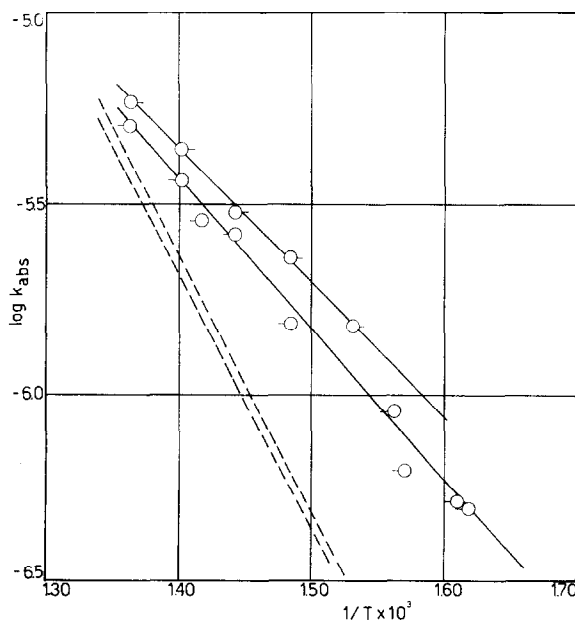

Fɪɢ. 8. Final level of activity for SAN (1000) catalysts; a plot of log k_{abs} vs $1/T$; -O, O-, SAN (1000) (different specimens); ------------ from Fig. 1.

port to the role of water is given by the failure of the R specimens to show this phenomenon, even after 33 runs. The beneficial effect of hydroxylation of the surface was confirmed in a series of experiments carried out on catalyst SAN (1400) which had not shown the rise of activity. The catalyst, in its stationary activity level, had a log k_{abs} value of -5.27 at 440°C. Water vapor at about 20 Torr was allowed into contact with the catalyst at 450°C, for 3 hr. After this, the normal conditioning procedure (vacuum, 480°C, 4 hr) was made. The log k_{abs} value at 440°C rose to -4.74. This higher activity level decayed after 3 runs. A second water treatment had a much smaller beneficial effect (log k_{abs} = -5.09, also at 440°C). It should be stressed that the development of this phenomenon does not interfere with the definition of catalytic activity of the specimens if the first 10–15 runs are considered. Furthermore, as already stated, it was only shown by $NiAl_2O_4$ and to a much lesser extent by SAMN 50 (1000) but was not shown by other solid solution specimens. The phenomenon can therefore be considered a secondary one with respect to the comparison of activity of different catalysts but it points to the possible influence of a hydroxylated surface in the catalytic process.

Oxygen Chemisorption during Catalysis

Several samples of the gaseous mixture have been analyzed by mass spectrometer and oxygen coverages estimated from the N_2/O_2 ratio, for a number of different catalysts of different composition and over the temperature range 340–460°C. Because of the large error in estimation of oxygen coverages, it is impossible to draw any firm conclusion about the temperature or composition dependence. The experimental values of oxygen surface coverages, however, allow an estimation of the extent of the chemisorption during catalysis to be made. In this connection, it may be noted that 40 determinations were carried out, and the surface coverages evaluated. For easier comparison with the rock salt structure, coverages in atoms of oxygen are de-

fined on the basis of anions rather than of cations; that is, they refer to the voids (not all filled by cations in the spinel structure) left by the anions. They ranged from a minimum of 2% to a maximum of 9%; in only 7 cases out of 40 were coverages higher than 5% observed, and in only 5 lower than 2.8%. It should be noted that the average value of about 4% coverage is definitely higher than coverages observed over MgO–NiO solid solutions (1, 2). For instance, for a sample MgO–NiO (1 atom % Ni) the percentage coverages of adsorbed oxygen at 350 and 400°C were 0.41 and 0.51, respectively.

Direct Studies of Oxygen Adsorption

In order to compare coverages attained during catalysis with those attained by adsorption from molecular oxygen, a few direct measurements of oxygen adsorption were made. Some indication of the ease with which oxygen could be desorbed was also sought. Because of the large error involved, these measurements could only show that coverages range 2–4% and that they increase as the temperature increases. These coverages, and also the reversible ones, are higher than those found for the MgO–NiO catalysts (2). This point is seen in Table 2, where oxygen coverages are reported for some $Ni_xMg_{1-x}O$ and $Ni_xMg_{1-x}Al_2O_4$ specimens.

It is to be recalled that the initial conditioning of the MgO–NiO catalysts was made at 850°C and the O_2 pressure was

TABLE 2
Oxygen Coverage Comparison Between $Ni_xMg_{1-x}O$ and $Ni_xMg_{1-x}Al_2O_4$ Catalysts

Catalyst	200°C	500°C
MgO	0.28 (0.06)[a]	0.42
MgO–NiO 1% at.	0.57 (0.27)	0.65 (0.28)
MgO–NiO 10% at.	0.37 (0.18)	0.96 (0.25)
	430°C	470°C
SAM (1000)	3.4 (1)	5.2 (1)
SAMN 3 (1400) R	1.3 (0.6)	2.9 (1.1)
SAMN 10 (1400) R	2 (1)	3.7 (1.4)
SAN (1400) R	1.6 (0.3)	3.4 (1.4)

[a] Reversible coverage in parentheses.

0.4 Torr. The discrepancy is therefore even higher than shown by Table 2, since a smaller coverage is attained when the outgassing temperature is limited to 480°C.

The percentages of reversible adsorption for $Ni_xMg_{1-x}Al_2O_4$ vary 20–50% and they increase as the temperature increases, except for SAN (1000) R. Another interesting point is that the adsorption on $MgAl_2O_4$ is higher than on pure $NiAl_2O_4$ and on SAMN specimens.

DISCUSSION

The results obtained in the present study are best discussed from separate, though interconnected, points of view: (1) activity of Ni^{2+} ions in octahedral vs tetrahedral symmetry, (2) the influence of the spinel matrix vs the MgO matrix, (3) the role of the cation interactions.

Activity of Nickel Ions in Octahedral and Tetrahedral Sites

It has been noted that solid solutions of intermediate composition $(0.03 < x \leqslant 0.050)$ always show a higher catalytic activity when quenched from 1000°C [series (1000)] with respect to those quenched from 1400°C [series (1400)]. The distribution of nickel among octahedral and tetrahedral sites in the spinel structure of $Ni_xMg_{1-x}Al_2O_4$ solid solutions varies with temperature, the fraction of Ni^{2+} in tetrahedral sites increasing with increasing temperature (12–14). Therefore, catalysts (1000) have a higher percentage of nickel occupying octahedral sites (α parameter lower). The observation that it was possible to raise the activity of a (1400) specimen exactly to that of an (1000) specimen by an equilibration at 1000°C, followed by a quenching from 1000°C, shows that the difference is real and due to the temperature of quenching. It is logical to infer that the catalytic activity of nickel ions in octahedral sites is higher than that of the ions in tetrahedral sites. This conclusion is supported by data obtained in this laboratory (16) which indicate that Ni^{2+} ions dispersed in ZnO (tetrahedral coordination) are very poor catalysts for the N_2O

decomposition, in contrast to Ni^{2+} dispersed in MgO (octahedral coordination).

One explanation for rationalizing the different catalytic activity of Ni^{2+}_{tet} and Ni^{2+}_{oct} can be sought in the difference of the nickel–oxygen bond strength. The $Ni^{2+}_{tet}–O^{2-}$ separation is $0.207\,a = 1.72\,\text{Å}$, while the $Ni^{2+}_{oct}–O^{2-}$ distance is $0.250\,a = 2.08\,\text{Å}$ (a, lattice parameter of the spinel), thus pointing to a larger strength in the former case. In the catalytic process, the metal–oxygen bond must be repeatedly formed and broken, and the last step (oxygen release) would be easier when an octahedral nickel is involved. It may be noted that the argument would still hold even if the formal charge of the oxygen where not $2-$, but a fraction of it.

Surface Effects on the Distribution of Nickel Ions among Tetrahedral and Octahedral Sites

The attribution of the higher activity of (1000) specimens to the higher percentage of octahedral nickel has some implications regarding the distribution of nickel ions in the layers. Indeed, as a first consideration, it can be observed that the difference of activity between (1000) and (1400) specimens (Figs. 2–4) is higher than expected on the basis of the variation of α with temperature (Fig. 9). After all, the occupancy of octahedral sites, as determined *in the bulk*, does not vary widely, since it stays around 80–90%. If the catalytic activity were proportional to the concentration of nickel ions present in octahedral sites, neglecting the activity due to tetrahedral nickel, only a small variation would have been observed. A second difficulty arises from the lack of difference of catalytic activity between (1000) and (1400) specimens of pure $NiAl_2O_4$ and $Ni_xMg_{1-x}Al_2O_4$ specimens with $x \leqslant 0.03$. It is interesting to note that although Fig. 9 hints at a higher temperature dependence of α for catalysts of intermediate composition, the variation of $\Delta\alpha$ with x is within the experimental errors, and $NiAl_2O_4$ does show a temperature dependence of α (12).
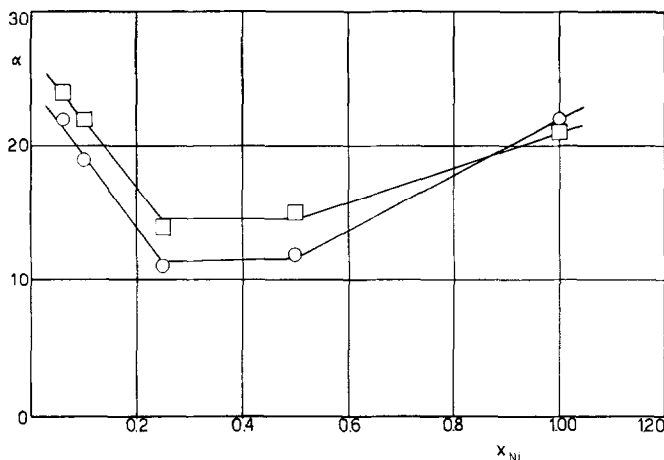
FIG. 9. Inversion parameter α vs nickel fraction x in $Ni_xMg_{1-x}Al_2O_4$; $\bigcirc$ series (1000); $\square$, series (1400), Ref. (14).

In order to overcome these difficulties, we are led to the conclusion that occupancy of tetrahedral sites in the outer layer which come into contact with the gas phase, *does not* correspond to that found in the bulk. The distribution of cations in the bulk can be rationalized on the basis of the lattice energy of the spinel structure. The lattice energy of a spinel structure, however, is a complex function of several parameters: cation charges, ionic radii, lattice parameter, cation distribution, oxygen position in the cell (u parameter), polarizabilities, and ligand field effects. Many of these parameters are strongly dependent on each other (9). It is then impossible to evaluate the effect of the discontinuity represented by the surface on the energy of the crystal, and hence to assess the most favorable distribution of cations when layers close to the surface are considered. The following remarks, however, tend to show that in the surface a distribution among cation sites different from that in the bulk can indeed be justified. Two fundamental points underly our reasoning: (a) the likelihood that under an oxidizing atmosphere (O_2, N_2O), the external faces will tend to expose anions rather than cations; and (b) the possibility of atomic movements in the outer layer, i.e., the existence of dynamic process involving surface atoms of the adsorbent, accompanying the adsorption–de-sorption processes, and tending all together to realize the most favorable arrangement of surface atoms.

Of the three surface planes (100), (110) and (111) which are most commonly present, let us consider the (100) plane first. There are two different and alternate atomic (100) planes, as outlined in Fig. 10.* The two planes are not electrically neutral, one including only cations of tetrahedral symmetry (A-sites), the other including cations of octahedral symmetry (B-sites) and anions. From the preceding considerations, it appears that in the first plane, the cation will have to be saturated with oxygen from the gas phase, and the crystal face (100) will then expose A-site cations immediately below the anions. In the second case (where a plane carrying an overall negative charge is present) it should be considered that due to the unsaturation

* Notice, however, that the spinel structure is not built up by simple superposition of the two planes. We simply draw attention to the pattern of tetrahedral and octahedral positions filled in different planes. In order to build up the spinel structure a set of four planes of each type (eight in all) must be taken, appropriately shifted one with respect to one another. The pattern found in the eight planes, however, always conforms to one of the two represented in Fig. 10. A similar qualification applies to the description of the other families (110) and (111).
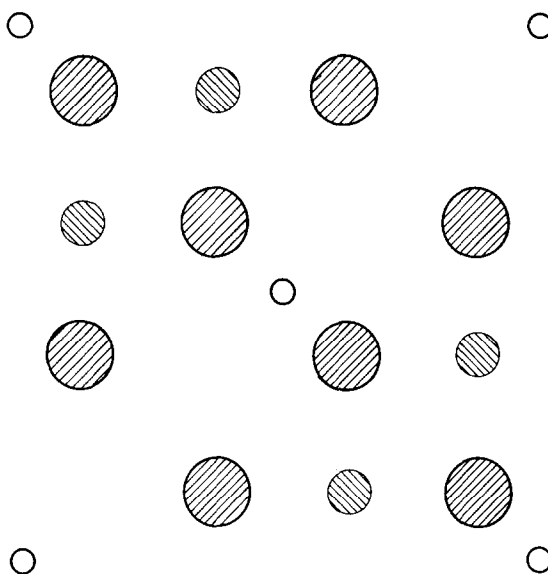
FIG. 10. Plane (100). Open symbols belong to the plane of the paper, hatched symbols are below it.

of the B-site cations, and to the different ease of movements between cations and anions, the B-site cations will tend to move below the plane, thus becoming more shielded from the anions. This process will result in a substantial increase of the Madelung energy.

The polarization energy assists a change of distribution towards a greater number of tetrahedrally coordinated Ni^{2+} cations, as pointed out by Blasse (9). Surface oxygen anions are more polarized than bulk oxygen ions, and the effect will therefore be more strongly felt. The external layer can therefore offer an occupancy different from the one found in the bulk, namely more tetrahedral Ni^{2+} than expected from bulk measurements.

The surface plane (110) is now considered. Here again there are two atomic planes, neither of which is electrically neutral, as shown in Fig. 11. The plane which carries an excess of positive charge (shown as the 1st layer in the drawing) has both A- and B-sites and also anions. From the preceding considerations, this plane will tend to adsorb oxygen. An initially outgassed surface, sparsely covered with oxygen, will tend to have more A-sites oc-

cupied than B-sites, since the coordination of the former can be completed with a more limited amount of excess (chemisorbed) oxygen. The alternate plane, which carries an excess negative charge, shows only B-sites and anions. A reasoning similar to that given for the (100) plane shows that recession of the five-coordinated B-cations into an unoccupied tetrahedral hole will tend to occur in order to achieve a less unsaturated situation, thus exposing anions to the gas phase. As a result, there are reasons to believe that occupancy of A- and B-sites does not correspond to that found in the bulk also for the face exposing (110) planes.

Finally, let us consider the plane (111). In a cubic close-packed arrangement of anions we can distinguish three distinct layers of anions, which correspond to the sequence $abcabc$. . . . Octahedral holes can be found midway between two such layers and tetrahedral holes can be found at 1/4 of the distance between layers of anions. The actual filling of holes with cations is accomplished in the spinel structure in the manner outlined in Fig. 12, taken from Hornstra (17), without specification of the elevation of each atom on the plane of the
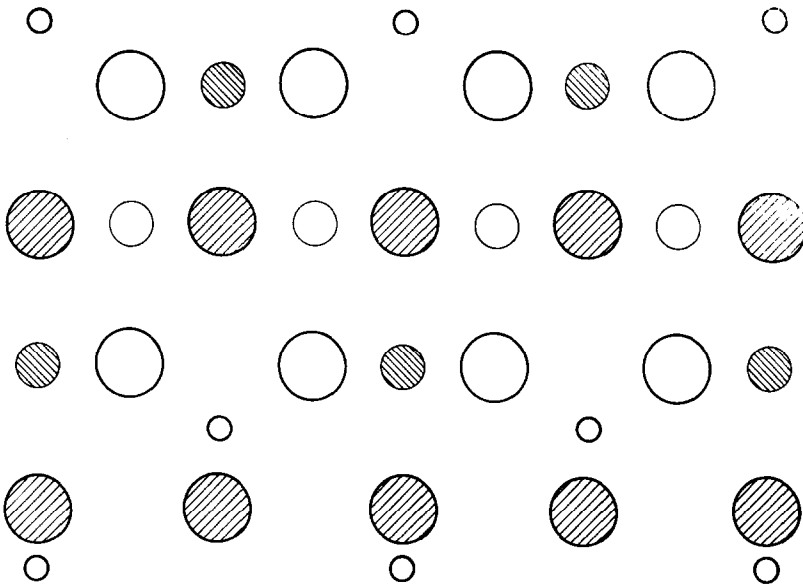
FIG. 11. Plane (110). Open symbols belong to the plane of the paper, hatched symbols are below it.

paper. It can be seen that if the crystal surface terminates with an anion layer, as required by our initial considerations, we can have either a layer *a* or *b* or *c*. If *a* is the terminating anion layer, the cation sites exposed immediately below the surface are tetrahedral *A*-sites. If the crystal terminates with a layer *b*, it is conceivable that cations from *B*-sites will tend to move outwards, into an *A*-site, thus allowing a stronger interaction with the approaching gas molecule. Thus, a cation in tetrahedral position is the interacting species.

The outlook to the situation offered by the three families of planes can then be summarized as follows. A vacuum conditioned surface, sparsely covered with oxygen, will tend to expose nickel ions in tetrahedral sites, which can achieve a shielding by oxygen ions which is more effective than the shielding achieved by cations in octahedral sites. With respect to the bulk distribution there is therefore a larger fraction of Ni^{2+} ions present in tetrahedrally coordinated positions, the same kind of effect as if an arbitrarily defined parameter α_s, referring to tetrahedral coordination in the surface layer, can be considerably larger than α, the true inversion parameter of the bulk.
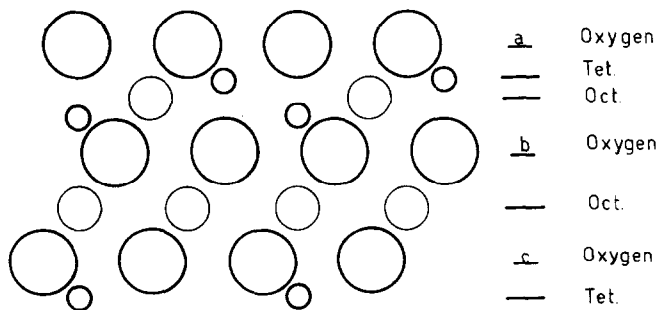

FIG. 12. Plane (111). A projection of the idealized spinel lattice on the ($1\bar{1}0$) plane [from Ref. (17)] without specification of elevation of individual atoms. The succession of planes (111) perpendicular to the plane of paper is indicated on the right, with the specification of sites involved. Layers *a*, *b*, *c*, are oxygen layers.

Temperature Effects of the Quenching Process on the Catalytic Activity

Turning now to temperature effects, in the same way as α is increased by an increase of T, so α_s will increase with T. However, as α_s is larger than α, the effect of temperature is more pronounced than predicted by a variation of α with T, since the variation of B-site occupation is larger by percent. A larger effect of temperature of quenching on the catalytic activity of solid solution specimens would thereby be expected, as is observed.

In order to explain the second point raised before, namely the equality of catalytic activity of (1000) and (1400) specimens of $NiAl_2O_4$ (and of specimens with $x \leqslant 0.03$), the variation of α with x shown by Porta, Stone and Turner (14) should be considered. The minimum of α found for $x = 0.25$ to 0.50 is a clear sign that the octahedral preference energy for Ni^{2+} in B-sites at $x = 0.25$ is greater than the same energy at $x = 1.00$ or at $x \to 0$, and indeed the Dq value at $x = 0.25$ is larger. Then the enthalpy change for the process

$$Ni_A{}^{2+} + (Al^{3+})_B \to Al_A{}^{3+} + (Ni^{2+})_B$$
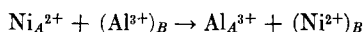
("interchange enthalpy" (18), where the subscripts A and B refer to ions in A- and B-sites, respectively) is greater for Ni^{2+} ions dispersed in $MgAl_2O_4$ than for pure $NiAl_2O_4$. As a consequence, the Ni^{2+} distribution is more temperature dependent around the minimum of α, i.e., around $x = 0.25$–0.50. It is interesting to note that an indication in this direction comes from Fig. 9, although as already noted the difference between values at 1400 and at 1000°C are small, and their variation with x cannot be measured accurately. It is in the right direction, therefore, to see that the largest difference of catalytic activity between (1000) and (1400) specimens is found at $x = 0.50$.

Comparison between $Ni_xMg_{1-x}O$ and $Ni_xMg_{1-x}Al_2O_4$

A comparison of $Ni_xMg_{1-x}O$ and $Ni_xMg_{1-x}Al_2O_4$ is now instructive. Dilute spinel solid solutions are less active than magnesium oxide–nickel oxide solid solu-

tions having the same cation mole fraction (see Table 1.) The presence of Ni^{2+} ions in tetrahedrally coordinated sites in the spinels is thought to be the main reason for the lower activity of the dilute $Ni_xMg_{1-x}Al_2O_4$ specimens compared to the activity of the dilute $Ni_xMg_{1-x}O$ specimens. Other effects, however, may well come in to differentiate the two matrices. It is indeed to be recalled that MgO is an oxide which can catalyze homomolecular exchange of oxygen rather efficiently (19) and it is also able to exchange its surface lattice oxygen with the gas phase. By contrast, for $MgAl_2O_4$, it may be inferred that the oxygen exchange is difficult (20). In other words, the oxygen surface mobility is greater on MgO than on $MgAl_2O_4$. The influence of the two matrices on the catalytic activity may then be sought also in the different mobility of oxygen, a process which can follow the primary step of rupture of the N_2–O bond, and which can precede the oxygen desorption, via a peroxide ion (21, 22). It is interesting to note that the oxygen chemisorption on $MgAl_2O_4$ is larger than on MgO. This fact tends to indicate a stronger oxygen surface bond, responsible for a higher coverage at comparable temperatures.

Effect of Dilution of Ni^{2+} Ions on their Specific Catalytic Activity

As seen from Fig. 7, the positive effect of dilution on the catalytic activity of each nickel ion is present for spinel solid solution specimens, although less pronounced than previously found for magnesium oxide solid solutions (1–3). In the spinel matrix the nickel ions are present partly in tetrahedral sites, and therefore the beneficial effect of the dilution is partially counterbalanced by the lesser activity shown by ions in tetrahedral symmetry. However, the trend for an increase of activity per nickel ion as dilution increases is still observed, as generally found for other transition metal oxide solutions (4, 5).

Surface Hydroxylation and Catalytic Activity

It remains now to discuss briefly the positive effect of the water on the catalytic

activity. The reflectance spectra performed on the catalyst (SAN) which had shown an increase of activity after about the 15th run, point to the presence of OH groups on the surface. Moreover the experiments where a water vapor treatment was made to the catalyst in the reactor have shown that there is a tendency for an enhancement of activity. Although erratic in extent, the effect is always in the same direction. The enhancement points to the role of OH groups initially present in determining the catalytic activity after a vacuum treatment. The effect could be speculatively explained by the assumption that during the outgassing at 480°C water molecules are released, each water molecule being released from two adjacent OH groups. An oxygen ion bridged to two sites is thus left behind. This arrangement can constitute an active surface site, since the two metallic ions are not completely saturated, and is therefore potentially capable of chemisorbing oxygen. The succeeding chemisorption step can be either an oxygen chemisorption, after which oxygen migrates, leaving the original site available, or more likely the transformation from the unshielded and bridged form to a fully oxygen-covered pair of metal ions (strong bond), leading to a loss of activity. It is in any case interesting to see that with this oxide system, the presence of some water on the surface in its initial state can be beneficial for a dynamic process involving oxygen.

ACKNOWLEDGMENTS

REFERENCES

1. CIMINO, A., BOSCO, R., INDOVINA, V., AND SCHIAVELLO, M., J. Catal. 5, 271 (1966).

2. CIMINO, A., SCHIAVELLO, M., AND STONE, F. S., Disc. Faraday Soc. 41, 350 (1966).

3. CIMINO, A., INDOVINA, V., PEPE, F., AND SCHIAVELLO, M., J. Catal. 14, 49 (1969).

4. CIMINO, A., INDOVINA, V., PEPE, F., AND SCHIAVELLO, M., Proc. Int. Congr. Catal. 4th 12, 1938.

5. CIMINO, A., AND INDOVINA, V., J. Catal. 17, 54 (1970).

6. DOWDEN, D. A., AND WELLS, D., Actes Deuxième Congr. Int. Catal. 2, 1499 (1961).

7. HABER, J., AND STONE, F. S., Trans. Faraday Soc. 59, 192 (1963).

8. SCHWAB, G. M., ROTH, E., GRINTZOS, CH., AND MAVRAKIS, N., in "Structure and Properties of Solid Surfaces," (R. Gomer and C. S. Smith, ed.), p. 464. The University of Chicago Press, 1953.

9. PLASSE, G., Philips Res. Rep. Suppl. No. 3 (1964).

10. KRÖGER, F. A., "Chemistry of Imperfect Crystals," p. 728, North Holland Publ. Co., Amsterdam, 1964.

11. GOODENOUGH, J. B., "Magnetism and the Chemical Bond," p. 193, Interscience, New York/London, 1963.

12. DATTA, R. K., AND ROY, R., J. Amer. Ceram. Soc. 50, 578 (1967).

13. DATTA, R. K., AND ROY, R., Amer. Mineral. 53, 1456 (1968).

14. PORTA, P., STONE, F. S., AND TURNER, R. G., to be published.

15. KLIER, K., AND RÁLEK, M., J. Phys. Chem. Solids 29, 951 (1968); CURCIO, J. A., AND PETTY, C. C., J. Opt. Soc. Amer. 41, 302 (1951).

16. SCHIAVELLO, M., CIMINO, A., AND CRIADO, J. M., to be published.

17. HORNSTRA, J. J. Phys. Chem. Solids 15, 311 (1960).

18. NAVROTSKY, A., AND KLEPPA, O. J., J. Inorg. Nucl. Chem. 29, 2701 (1967).

19. WINTER, E. R. S., Advan. Catal. Rel. Subj. 196 (1958).

20. YONEDA, Y., FUJIMOTO, A., MAKISHIMA, S., J. Phys. Chem. 63, 1987 (1959).

21. BICKLEY, R. I., AND STONE, F. S., Trans. Faraday Soc. 64, 3393 (1968).

22. DOWDEN, D. A., Lecture presented at the 4th Int. Congr. Catal. Moscow, 1968.