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Catalytic Activity of Nickel Ions in Magnesium Oxide for the Decomposition of Nitrous Oxide

A. CIMINO,* V. INDOVINA, F. PEPE, AND M. SCHIAVELLO

From the Istituto di Chimica Generale ed Inorganica, Università di Perugia, Perugia, Italy

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The catalytic activity of several MgO-NiO catalysts has been tested for the decomposition of N_2O. The atomic nickel content ranges from 0.15% to 50%. It has been clearly shown that the activity per nickel ion is enhanced by the dilution. The occurrence of a minimum in the apparent activation energy in the region 1 to 10 at. % nickel is observed.

The results are discussed in terms of the different ionic and electronic interactions which develop according to the nickel content. The determination of the catalytic activity on a lithium-containing catalyst confirms the results already established that the presence of lithium increases the apparent activation energy.

INTRODUCTION

The results obtained in a recent study of the catalytic activity of nickel oxide–magnesium oxide solid solutions (*1*) prompted an investigation of oxygen adsorption on these solids, and also an extension of the catalytic work to MgO–NiO solid solutions having different compositions. The adsorption study, together with a discussion of a relationship between catalysis and chemisorption, has recently appeared (*2*). The present paper gives a complete account of the new catalytic data and discusses the question of the influence of the ionic and electronic interactions on the catalytic activity.

EXPERIMENTAL PROCEDURE

Apparatus and procedure. The progress of the reaction with time was followed by condensing a small sample of the reacting gas mixture in liquid nitrogen and measuring the pressure of incondensable gas with a Pirani gauge. The procedure was the same as that described in detail in an earlier paper (*1*). In particular, attention was given to studying the reaction at small decomposition percentages ($\leqslant 1\%$).

Materials. Samples of MgO, impregnated with a nickel nitrate solution and subsequently fired to produce MgO–NiO solid solutions, were prepared according to the procedure previously described (*1*). Samples are designated according to the system given earlier (*1*): MN and MNL indicate MgO–NiO and MgO–NiO–Li_2O specimens, respectively. The figure after the letter gives the nominal nickel (and lithium) atomic concentration referred to 100 magnesium atoms. Thus, MN 20 indicates a sample containing 20 Ni atoms per 100 Mg atoms. A, B, and P indicate different preparations.

Table 1 gives a summary of the catalysts used, together with some of their features. Particular care was paid in the preparation of the samples with high Ni content to ensure complete formation of solid solution. This was checked by X-ray diffraction analysis in two ways: (i) by establishing that no lines attributable to NiO were present at high θ values where reflections arising from MgO–NiO solid solutions do not superimpose on reflections from NiO, a

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* Present address: Istituto Chimico, Università di Roma, Roma, Italy.

TABLE 1

Catalysts and Their Properties

Catalyst	MgO source	Firing temperature (°C)	Surface area (m^2/g)
MN 0.15 B	Johnson Matthey	1200°	14.1
MN 0.5 A	From carbonate	1200°	15.6
MN 20 A	From carbonate	1200°	13.8
MN 50 P	From carbonate	1200°	2.3
MNL[a] 10:1 A	From carbonate	1200°	1.4

[a] Actual Li content after firing, 0.28 Li atoms/100 Mg atoms.

method which renders even small amounts of the latter detectable; (ii) by measuring the lattice parameter *a*, and comparing the experimental values with those theoretically expected on the basis of a linear variation of *a* with NiO concentration ($a_{\mathrm{NiO}} = 4.1800$ Å, $a_{\mathrm{MgO}} = 4.2116$ Å) (*3*a,b).

The following table shows the close correspondence obtained:

Sample	*a*(expt.) (Å)	*a*(theor.) (Å)
MN 20 A	4.2045 ± 2	4.2049
MN 50 P	4.1985 ± 2	4.1983

Other experimental procedures (surface area determination, purification of gases) were as described earlier (*1*).

Experimental Results

The experimental results are collected in Table 2, which reports the "absolute velocity constants" in units of cm/min as in ref. (*1*), determined from the initial decomposition rates, and the apparent activation energies. The data are also reported in Fig. 1 as an Arrhenius plot, together with the results for MOJM (pure MgO from Johnson & Matthey), MN 1, and MN 10 previously published (dashed lines) (*1*).

The new results make possible a comparison of activities and of activation energies for samples of widely different nickel content. Figure 2 shows the variation of the apparent activation energy with the logarithm of the nickel molar fraction. There is very clear evidence of a minimum in the region of 1 to 10 at. %.

TABLE 2

Absolute Velocity Constants and Apparent Activation Energy for Different Specimens

Catalyst[a]	log K_{abs}	T (°C)	E_{app}
MN 0.15 Bc			
3	−6.04	370°	31
7	−6.09	370°	
5	−5.59	400°	
4	−4.98	440°	
8	−5.04	440°	
6	−4.69	470°	
MN 0.5 Aa			
7	−5.93	310°	20.2
4	−5.40	350°	
3	−5.17	370°	
5	−5.15	370°	
6	−4.93	400°	
MNL 10:1 Aa			
7	−5.09	380°	30
9	−5.07	380°	
5	−4.90	400°	
11	−4.89	400°	
6	−4.17	450°	
8	−4.16	450°	
4	−3.91	470°	
10	−3.91	470°	
MN 20 Aa			
4	−6.0	350°	25.4
6	−5.63	350°	
5	−5.13	420°	
7	−4.84	440°	
MN 50 Pb			
7	−5.21	430°	37.0
4	−5.09	440°	
3	−4.72	470°	
6	−4.43	480°	
5	−4.19	500°	

[a] For definition of catalyst, see text. Small letters a, b, c refer to different portions of a single preparation; the numbers refer to each run.

A more significant comparison is that of the catalytic activity per nickel atom in the various solid solutions. To illustrate this, it is assumed that the surface molar fraction of nickel is the same as the bulk molar fraction. This assumption is based on the observation of the uniform lattice parameter decrease with nickel addition, which points to regular solid solutions between MgO and NiO having formed as expected from the thermodynamic behavior of the system (*4*). It is unlikely that gross devia-

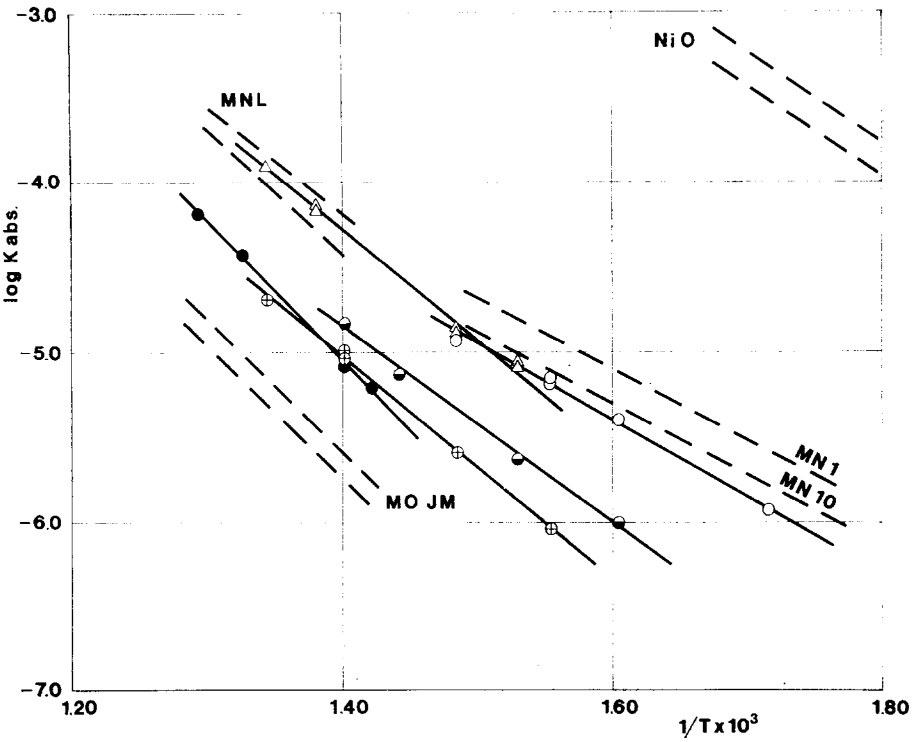

FIG. 1. A plot of log K_{abs} vs. $1/T$; ⊕, MgO + 0.15 at. % NiO (MN 0.15); ○, MgO + 0.5 at. % NiO (MN 0.5); ◒, MgO + 20 at. % NiO (MN 20); ●, MgO + 50 at. % NiO (MN 50); △, MgO + 10 at. % NiO + 1 at. % (nominal) Li_2O (effective Li concentration 0.28).

tions are then found in the surface. To show how the absolute activities of different catalysts compare when referred to unit nickel content, Fig. 3 illustrates a "normalized" Arrhenius plot in which the ordinates are log k_{Ni}, where k_{Ni} is obtained by dividing the K_{abs} of Fig. 1 by the nickel molar fraction. In this graph, catalyst MN 0.15 should be given less emphasis and is shown accordingly as a dotted line since the contribution from centers present in the MgO matrix is no longer negligible. This is shown by the higher E_{app} value and by the different kinetics obeyed by the reaction when high decomposition percentages are studied (*5*).

It follows that in Fig. 3 the rate constants of different catalysts are always referred to an equal number of nickel atoms, so that differences between various catalysts must arise from the different degree of interaction between the nickel ions. It should be noted that MN 1 and MN 0.5 practically coincide, but MN 10, MN 20, and MN 50 are progressively less active. The activity of pure NiO (*1*) is defined with some difficulty in view of the sensitivity to outgassing conditions in this case and the less satisfactory reproducibility. However, if the *maximum* activity values are chosen, a line lying approximately in the vicinity of MN 1 (dashed line in Fig. 3) is obtained.

DISCUSSION

The results obtained in the present work confirm and extend the observations outlined in the earlier study (*1*) regarding the effect of dilution on the catalytic activity of nickel ions. As shown by Fig. 3, diluted ions are markedly more active than ions present in concentrated solid solutions, with the possible exception of pure NiO.

It was shown earlier (*2*) that a variation of adsorption characteristics takes place in passing from a catalyst with 10 at. % Ni to one with 1 at. % Ni, a larger fraction of

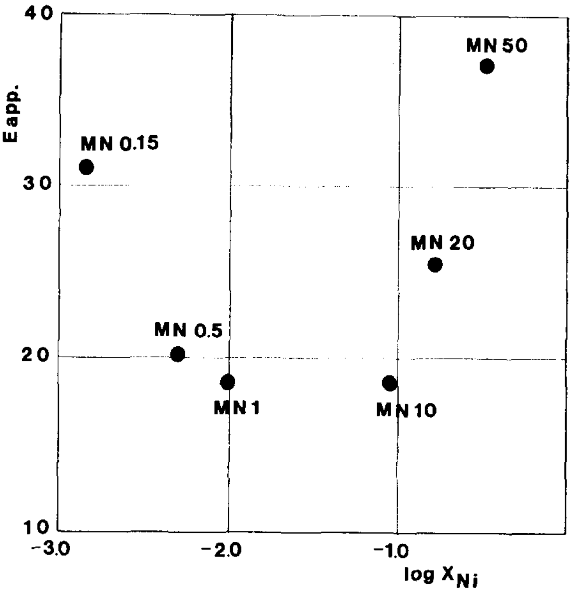

FIG. 2. Variation of the apparent activation energy as a function of the nickel content.

reversible, more weakly held, oxygen being present in the case of the more dilute sample. The larger activity per nickel ion shown in dilute (~1%) MgO–NiO solid solutions was attributed to the predominance of the weaker form of chemisorbed oxygen. The role of ionic interactions would thus be that of controlling the nature of the surface complex, which, in its turn, is of paramount importance in determining the overall rate in catalysis. The present results give a further proof of the marked difference encountered in dilute as opposed to concentrated solid solutions. Let us consider, for example, the two catalysts MN 0.5 and MN 50, where the nickel molar fractions are in the ratio 1:66. The variation of the apparent activation energies from 18.5 to 37 kcal/mole points to a marked variation of the heat of oxygen desorption, and consequently, to a variation of the nature of the predominant species of the oxygen–surface complex.

An understanding of the reason why this variation occurs must for the present be of a speculative nature, but it is possible to offer a picture consistent with the knowledge of the MgO–NiO system in the following way. In a dilute MgO–NiO solid solution, such as MN 0.5 or MN 1 (MN 0.15 is not considered, since the contribution from the MgO cannot be neglected), there will be a high probability of finding *isolated* Ni^{2+} ions, or pairs, but not continuous Ni^{2+}–Ni^{2+}–Ni^{2+} "chains" (anions being omitted for brevity, although they are obviously present in certain crystallographic directions). In saying this, a random or approximately random distribution of nickel ions is assumed, as is suggested from physical studies of lattice parameters and of magnetic susceptibility (*3*). The situation present in the dilute solution will differ from that in the concentrated solution in the ease with which electrons can be withdrawn from the interior of the crystals, the concentrated solid solution being more able to provide electron transfer to the surface. It follows that the two cases will be characterized by different equilibrium concentrations of the more charged species, such as O^{2-}. These species, which by virtue of their charge are held by more ionic bonds, will presumably be desorbed with greater difficulty, thus inhibiting the catalytic reaction. The inhibiting effect is therefore attributed to the more ionic forms of chemisorbed species, which are present in higher percentage on the surface of the more concentrated NiO–MgO solid solutions.

To sum up, the centers active for the decomposition of N_2O can be thought of as the nickel ions. According to the environment of the latter, a different oxygen–surface complex is created after decomposition of the N_2O molecule with correspondingly different inhibiting power on the progress of the reaction. The concentrated samples such as MN 20 and MN 50 will exhibit a large apparent activation energy, and a reduced activity per nickel ion, on account of the strong oxygen–surface complex deriving from the decomposition of the N_2O molecule.

Any explanation for the high activity per nickel ion found for pure NiO meets the difficulty of defining the state of the surface, which is obviously more rapidly changing than in MgO–NiO solid solutions. It is apparent from the experimental data that even though a rapid drop of activity can occur, well-outgassed samples of pure NiO with a clean surface (i.e., "fresh" catalysts in their first runs) exhibit a high catalytic activity. With NiO the defective surface structure can play an important role in provoking electron transfer to surface defects. These may be anion vacancies produced by outgassing the sample: $O^{2-}(\text{ads}) + \text{O-vacancy} \rightarrow O^- + (e)\text{-vacancy}$. The importance of the defective structure of the pure oxide has been clearly brought out in several studies. For example, it may be recalled that strikingly

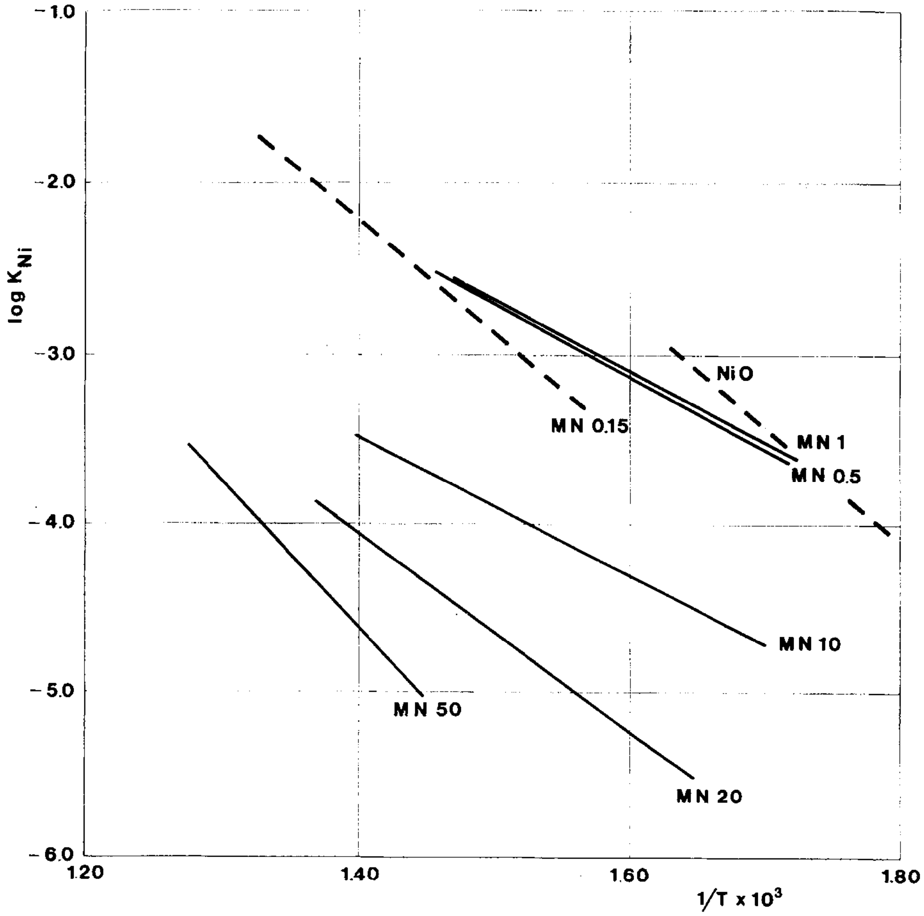

FIG. 3. Absolute activity referred to unit nickel concentration.

different properties of NiO have been reported by Teichner and Samaha (*6*) for oxide with high surface area prepared by low-temperature decomposition of $Ni(OH)_2$. The MgO–NiO solid solutions are less liable to undergo a marked disordering of the surface, and the participation of surface atomic defects such as vacancies will be more limited. The difference between pure oxides and solid solutions also is shown by the recent work of Volpe and Reddy (*7*). These authors showed that the activity for N_2O decomposition of a MgO–CoO single crystal (60 at. % CoO, in the surface) was considerably less than that shown by a pure CoO crystal, in agreement with a comparison between NiO and, for example, MN 50. Irrespective of the explanation offered, however, it should be stressed that in order to find the role of interactions between transition metal ions in an oxide matrix it is essential to study and compare *dilute* solid solutions, where the interactions can in fact be minimized. A comparison between pure oxides and *concentrated* solid solutions, such as our MN 50, or Volpe and Reddy's specimen, can offer a misleading pattern, since interactions are still present in the concentrated solutions, yet the defective structure of the surface is deeply affected in such a way to decrease the overall activity of the concentrated solid solution.

It is interesting to recall the data reported by Selwood and Vrieland (*8*), who found no difference between the catalytic activities of MnO and MnO–MgO solid solutions up to 50% MgO for the ammonia decomposition reaction. The conclusions drawn by the authors that the ionic interaction plays no role in the catalytic activity should be accepted with caution, since the catalyst compositions are such as still to give a very strong interaction between manganese ions. It would be desirable to extend the study to dilute solid solutions of MnO in MgO, in order to discover whether a change occurs when a marked decrease of interaction takes place.

In addition to pure MgO–NiO solid solutions, one further sample, with lithium doping, was studied in order to check the results previously presented (*1*). As shown in Fig. 1 and Table 2, the catalyst fully confirmed the existence of a higher activation energy on this type of specimen. In view of the high concentration of Ni^{3+} present in lithium-doped samples, surface complexes involving more highly charged ions (such as O^-–Ni^{3+} vs. O^-–Ni^{2+}; O^{2-}–Ni^{3+} vs. O^{2-}–Ni^{2+}), can be created, thus shifting the equilibrium in favor of the more strongly chemisorbed species. In contrast to this, it may be recalled that the addition of the lithium ions to *pure* NiO enhanced the catalytic activity, as shown by Hauffe and co-workers (*9*).

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