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Semiconductivity and Catalytic Behavior of Doped Nickel Oxides in the Low-Temperature Oxidation of Ammonia

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The catalytic oxidation of NH_3 by air over NiO promoted with monovalent (Li, Na, K) and trivalent (Cr, Fe, Al) ions was investigated in a microreactor combined with a chromatographic unit. In the temperature range between 300° and 450°C, the reaction proceeds mainly to N_2 and N_2O. Among the monovalents, Li and Na exert the greatest influence. As more promoter is added, both activity and selectivity to N_2O increase sharply, with respect to the undoped samples. K, which does not penetrate into the lattice, has no catalytic influence. Doping with trivalent ions (with the exception of Cr), oppositely, depresses both activity and selectivity, although variations are well below those (in the opposite direction) induced by monovalent dopents. The degree of p-typeness, hence the relative abundance of extralattice oxygen, is likely to be the prevailing factor governing the catalytic behavior of NiO catalysts. To explain the results on the Cr-doped samples, the intervention of loosely bound oxygen is suggested.

1. INTRODUCTION

The study of correlations between the electronic structure of solid oxides and their catalytic activity has been the object of extensive investigations by various schools and very comprehensive reviews have been published on this topic (*1, 2, 3*).

The most widely studied reactions on electronically controlled oxides have been the N_2O decomposition and the CO oxidation, for which a definite order of activity for many oxides, depending on their electronic character, has already been established (*4, 5*).

A few studies have been made covering more complex reactions such as the NH_3 oxidation, in which case, not only the activity, but the selectivity also, could change when the electronic character of the catalyst is varied by doping. In a previous paper (*6*) we reported that the order of increasing catalytic activity for NH_3 oxidation on various oxide catalysts was as follows:

$$p\text{-type} > n\text{-type} > \text{insulators}$$

The results obtained by Johnstone (*7*), although confined to a few catalytic systems, fit nicely into the above sequence (*6*), which was found also to be in agreement with the general rule set up for typical oxidation reactions (*4, 5*). In addition, in the same paper (*6*), we reported that the selectivity of the reaction, in terms of N_2O yield, increases with increasing p-typeness of the catalyst, the semiconducting character of each oxide having been assigned at that time on the basis of literature sources only.

In order to confirm the soundness of the above conclusions, the NH_3 oxidation was reinvestigated on catalysts having controlled p-type character. NiO, whose p-type character has been definitely established, was chosen as a basic semiconducting oxide. Its electronic character was made to vary by doping with monovalent metal oxides (Li, Na, K) which would increase, and trivalent metal oxides (Cr, Fe, Al) which would decrease its p-typeness. Modifications of NiO by doping have been checked by electrical conductivity measurements.

2. EXPERIMENTAL

a. Preparation of catalysts. To prepare samples of catalysts, CP nickel nitrate was dissolved in distilled water. Doped catalysts were prepared by addition of calculated amounts of the parent nitrate solution to the nickel nitrate solution. The solutions were evaporated at 110°C to dryness, then the nitrates were decomposed by slowly raising the temperature to 400°C for 4 hr.

The samples were treated for 3 hr at 640°C, and then for 5 hr at 900°C in air. The catalysts prepared and tested are listed in Table 1 together with their surface areas.

TABLE 1
SURFACE AREA[a]

Atom % of dopant:	None	0.2%	0.5%	1%	2%	5%
Samples						
NiO + Fe	—	1.4	—	—	1.8	—
NiO + Cr	—	1.2	1.3	1.5	1.2	1.5
NiO + Al	—	—	2.8	2.8	5	—
NiO	1.4	—	—	—	—	—
NiO + Li[b]	—	1.2	1.9	0.9	1.2	0.9
NiO + Na	—	—	—	1.6	—	—
NiO + K	—	—	—	1.3	—	—

[a] In m^2g^{-1}.

[b] For Li, the actual concentrations were found to be 0.15, 0.40, 0.85, 1.30, 3.2 at. %, respectively. In Figs. 1, 2, 3, activity and selectivity refer to the actual concentrations.

Lithium-doped catalysts were analyzed for Li after firing. Li concentration had fallen to 0.15, 0.4, 0.85, 1.30, 3.2 at. %, respectively, from the initial values listed in Table 1: this was attributed to loss of Li_2O by evaporation from the sample during annealing. Undoped NiO samples were pale green in color, whereas those containing Cr, Fe, and Al were yellow-green or light brown. Li- and Na-containing samples varied from gray to black, depending on the amount of the additive. The K-containing sample was indistinguishable from pure NiO. Catalysts were obtained in the form of powder. They were pressed to pellets having some mechanical strength, then crushed to 42–65 mesh. In this particle size the samples were submitted to the catalytic tests.

b. Surface area measurements. Activity was always referred to the unit surface area of the catalyst. Owing to low surface areas of all catalysts investigated, the extension of the surface has been calculated from the amount of nitrogen adsorbed from a nitrogen-helium stream at liquid nitrogen temperature (*8*).

Table 1 shows the results of surface area measurements.

c. Catalytic activity measurements. Mixtures of ammonia and air (ratio 1:9) were passed over the catalyst at measured rate of 110 cm^3/min. A flow microreactor apparatus described elsewhere (*6*) was used. Reaction conditions (NH_3/air ratio, contact time) were kept constant for all catalysts investigated. The catalyst volume was 0.5 cm^3 of the 42–65 mesh fraction (0.85 g of catalyst). Runs were performed at rising temperatures from 300° to 450°C. Gases leaving the reactor were passed through an adsorber containing magnesium perchlorate to selectively remove NH_3 and water (*7*). The unadsorbed gas mixture was analyzed for O_2, N_2, and N_2O by a chromatographic unit. NO and NO_2 were seldom found in more than trace concentrations. The analytical procedure has been described elsewhere (*6*). Activity and selectivity of catalysts have been expressed in terms of NH_3 overall conversion and N_2O net yield, respectively. The results of catalytic tests are collected in Figs. 1, 2, 3 for three temperatures.

d. Electrical conductivity measurements. In order to check on whether the introduction of altervalent ions in NiO lattice has been effective for modifying in the expected direction the electronic properties of nickel oxide, some catalysts were submitted to electrical conductivity measurements.

Catalyst powders were pressed at 2.000 kg/cm^2 into pellets (12.5 × 9 mm) which were heated at 500°C under vacuum. Measurements were performed in air in the temperature range from 100° to 450°C. An impedance bridge, operated with DC, manufactured and marketed by Electro-

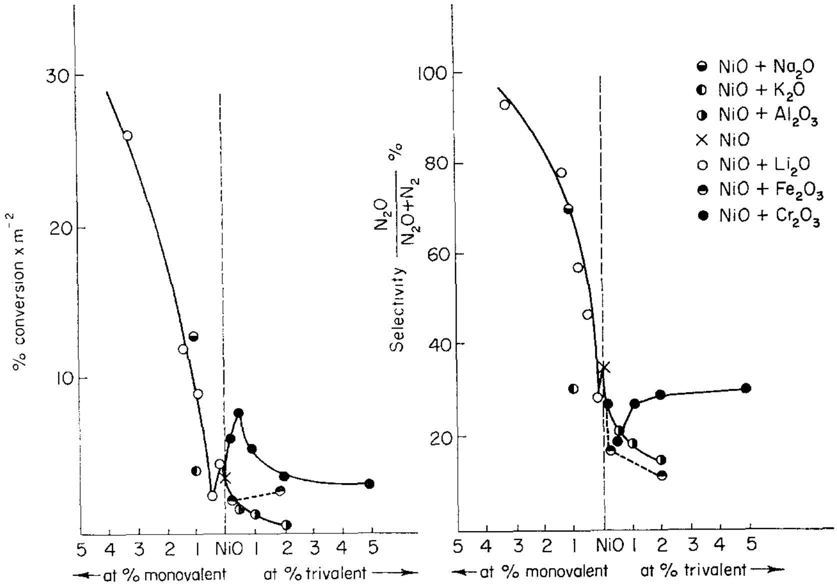

Fig. 1. Overall conversion of NH_3 and N_2O selectivity over doped NiO samples at 352°C.

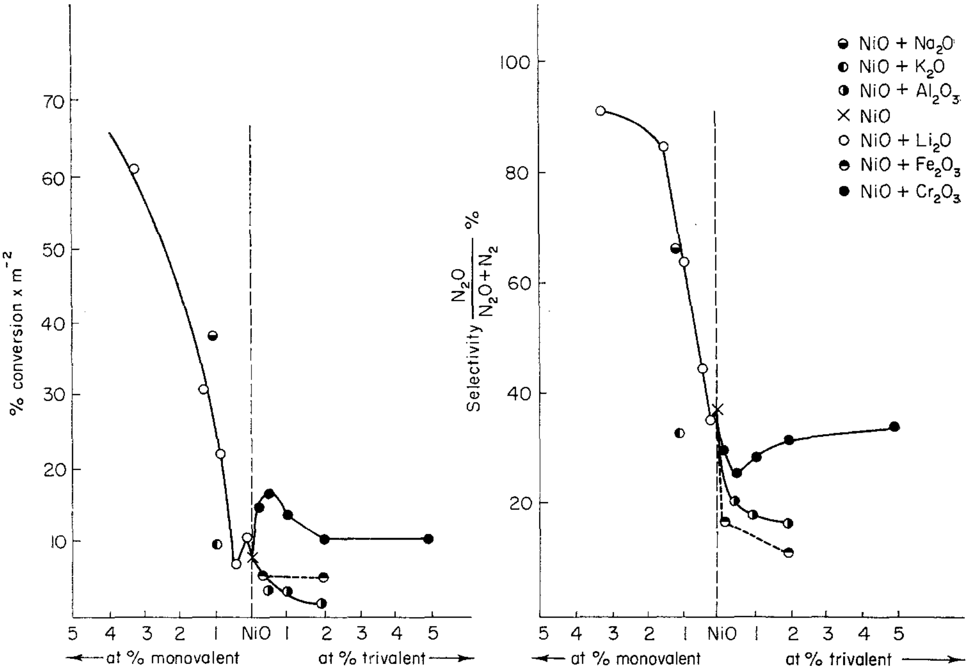

Fig. 2. Overall conversion of NH_3 and N_2O selectivity over doped NiO samples at 393°C.

Scientific Industries as Model 250 DA, was used.

Table 2 shows the values of specific electrical conductivities for some specimens at three selected temperatures. Activation energies for conduction were calculated from the equation $\sigma = \sigma_0 \exp(-E/2kT)$ and listed in Table 2. For all samples, both

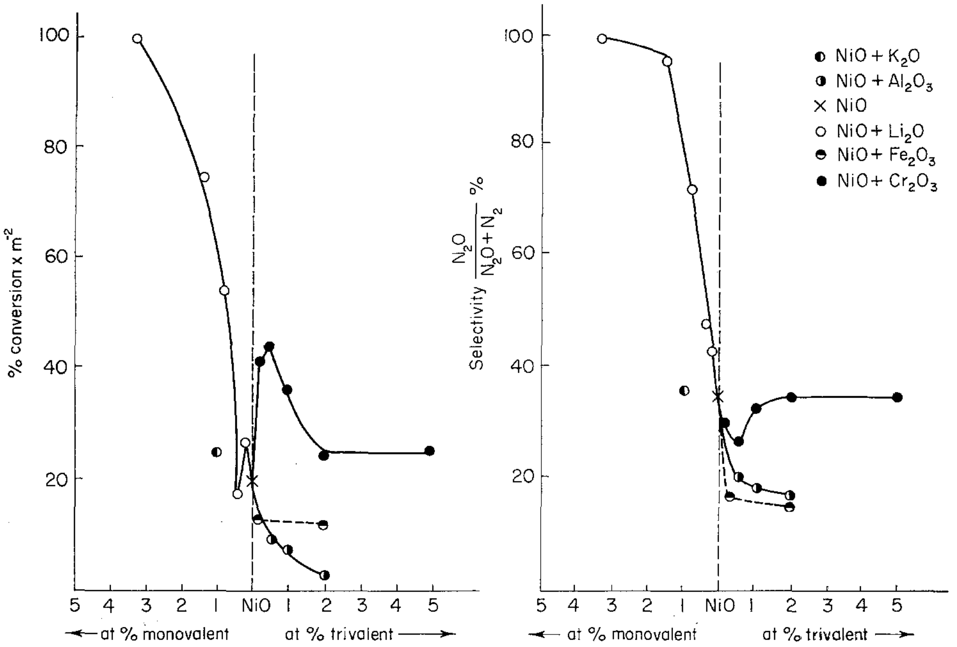

FIG. 3. Overall conversion of NH_3 and N_2O selectivity over doped NiO samples at 441°C.

TABLE 2
ELECTRICAL CONDUCTIVITIES AND ACTIVATION ENERGIES OF NiO- AND NiO-DOPED SAMPLES[a]

Samples	Electrical conductivities σ (ohm^{-1} cm^{-1}) measured at 100°C	300°C	450°C	E_σ, activation energies (eV)
NiO + 1 at. % Cr	5.5×10^{-9}	3.8×10^{-7}	1.5×10^{-5}	1.63
NiO + 1 at. % Al	4×10^{-6}	1.4×10^{-4}	7.0×10^{-4}	0.70
NiO	1.5×10^{-4}	4×10^{-3}	7.0×10^{-3}	0.66
NiO + 1 at. % Li	1.2×10^{-2}	8.3×10^{-2}	1.6×10^{-1}	0.37

[a] Measurements in air.

electrical conductivities and activation energies showed the expected changes.

3. RESULTS

As no specific attempts were made to determine the rate law for the reaction, the catalytic performance of various catalysts has to be compared in terms of experimental reaction rates. Since reaction conditions were kept constant for all the catalysts, comparison can be made on the basis of NH_3 overall conversion, referred to the unit surface area of the catalysts. For sake of convenience, results are divided according to the foreign oxide introduced into the NiO lattice and reported hereinafter.

a. Lithium oxide. There is an eightfold increase in the activity between the two ends of the scale, i.e., from pure NiO to NiO + 3.2 at. % of Li, over the whole range of temperatures (Figs. 1, 2, 3). Selectivity to N_2O also increases with increasing % of dopant, from a 35% value for pure NiO up to 90–100% for NiO + 3.2 at. % of Li (Figs. 1, 2, 3). In the neighborhood of 0.1 at. % Li there is an inversion point both in activity and selectivity, which is thought to be evidence of an inversion in physical properties of the catalyst as shown earlier by Parravano (*9*).

b. Sodium oxide. The behavior of the Na-doped sample is very close to that of the corresponding Li-doped sample (Figs. 1, 2). Selectivity is higher by a factor of 2 than in the undoped sample.

c. Potassium oxide. Activity for the K-doped catalyst is very slightly over that of NiO. Selectivity is almost indistinguishable from that of pure NiO, over the whole range of temperatures (Figs. 1, 2, 3).

d. Aluminum and iron oxides. Both the Al- and Fe-doped samples show quite a similar behavior both in activity and selectivity. Doping with these ions results in less active and selective catalysts than pure NiO (Figs. 1, 2, 3). With increasing percentage of dopant, selectivity levels off at values as low as one-third of that in pure oxide.

It should be noted here that the influence of these higher valent ions on catalytic performance of NiO is less striking than the corresponding (in the opposite direction) influence of less-valent ions.

e. Chromium oxide. Exploratory runs on Cr-doped samples revealed an anomalous behavior. A self-heating of as much as 80°C was observed in the reacting mixture being catalyzed at 370°C.

Pretreatment of the catalyst at 300°C with air for 2 hr before catalytic runs eliminates the self-heating. Cr-doped catalysts exhibit a different behavior with respect to the Al- and Fe-doped samples. The activity first rises up to a maximum (at 0.5 at. % of dopant), then falls down (Figs. 1, 2, 3) to values close to those of NiO.

Selectivity also shows an anomalous pattern (Figs. 1, 2, 3). It first decreases (up to 0.5 at. % of dopant) as in the case of the Al- and Fe-doped samples; then it raises and levels off at values close to those of the pure NiO.

4. Discussion

Summing up all the foregoing results, some relevant features emerge from the catalytic behavior of electronically modified oxide catalysts for NH_3 oxidation.

NiO is a true *p*-type semiconductor (*10*). The introduction of monovalent ions into its lattice leads to a semiconductor having a higher degree of *p*-typeness, while the opposite is true for doping with higher valent ions. This situation is accordingly described in the literature by the following symbolism (*1*):

$$1/2O_2(g) + M_2O \rightleftharpoons 2M_{\bullet}'(Ni) + 2\oplus + 2NiO \quad (1)$$

$$M_2O_3 + 2\oplus \rightleftharpoons 2M_{\bullet}^{\bullet}(Ni) + 2NiO + 1/2O_2(g) \quad (2)$$

To be so, homogeneous solution of the foreign ions into the host lattice is required. This condition is met if a not too great difference exists between ionic radii of the two metals and if a high firing temperature is chosen in order to speed up the diffusion of the dopant into the host lattice. Among monovalent ions, Li and Na have proper values of ionic radius for entering into NiO lattice; K ion is too large and it does not penetrate into, hence K doping is uneffective in modifying the semiconducting properties of NiO.

The results of Figs. 1, 2, 3 strongly indicate that activity and selectivity on "promoted" NiO catalysts are dependent upon the degree of *p*-typeness. To an increase of it, induced by doping with increasing amounts of Li and Na ions, corresponds an increase of both activity and selectivity. Doping with K ion, which leaves unchanged the degree of *p*-typeness of NiO, does not produce appreciable changes in the activity and selectivity of the catalysts. This correlation is supported also on the other side, by the catalytic behavior of the Fe- and Al-doped catalysts, in which case an electronically effective doping decreases the *p*-typeness of NiO and should give, as in fact it gives, less active and selective catalysts.

As we pointed out previously, doping with higher valent Fe and Al ions is less effective in modifying the catalytic performance of NiO than doping with monovalent ions. This feature and moreover the completely anomalous behavior of Cr-doped catalysts suggest that our picture needs to be worked out in more details.

Previous investigations by Krauss (*12*) on NH_3 oxidation over oxide catalysts led to the observation that extralattice oxygen containing oxides were the most active catalysts for the reaction. In addition, a linear relationship was found between N_2O yield and the extralattice oxygen content of catalysts as determined by a titration procedure (*12*). Here it must be noticed that extralattice oxygen really means Ni^{2+} vacancies, that is, Ni^{3+} ions in the lattice of the oxide, in order to satisfy the electroneutrality requirements (*9*). For the sake of simplicity we will retain hereinafter for description of this defective situation in the oxide, the extralattice oxygen equivalent formalism which has been more largely adopted in the catalytic terminology. If one now considers that the degree of *p*-typeness in some way reflects the extralattice oxygen content of the oxide, the catalytic behavior of less-valent doped catalysts is conceivable also in this context. In the same context the behavior of Al- and Fe-doped catalysts also becomes understandable. Higher valent ion doping decreases the already low extralattice oxygen content of NiO and correspondingly the activity and selectivity of catalysts. Doping is catalitically effective as long as it can consume extralattice oxygen of NiO, thereafter it becomes uneffective. So, while in doping with less-valent ions the limiting factor is the solubility of the dopent into the host lattice, in doping with higher valent ions the limiting factor is the low degree of *p*-typeness (or extralattice oxygen content) of NiO. Even so the catalytic behavior of Cr-doped catalysts, which should be the same as that of Al- and Fe-doped catalysts, cannot be explained.

Hence, one must recognize that the basic assumption of the extralattice oxygen as the essential partner in the catalytic NH_3 oxidation could be a too drastic one.

From oxygen adsorption experiments on doped NiO catalysts, the existence of at least two types of chemisorbed oxygen has been well established by various authors (*3*, *11*, *13*). Accordingly, the oxygen taken up by the catalyst during the annealing is partly a tightly bound oxygen adsorbed by electron exchange with the catalyst (extralattice oxygen) and partly a loosely bound oxygen chemisorbed without electron exchange (mobile oxygen). The intervention of mobile oxygen also in oxidation reactions has not been excluded as yet. In fact, this intervention has been claimed for the CO oxidation to explain some contradictory results obtained by different authors (*9*). However, while the accommodation of extralattice oxygen into the oxide has been related to its electronic properties, rules for correlating loosely bound oxygen with some characteristics of the oxide are still lacking. It has been observed only that, while in the less-valent-ion-doped NiO catalysts extralattice oxygen is prevailing with respect to the loosely bound oxygen species, a completely opposite situation occurs in the higher valent ions doped catalysts (*11*, *13*).

In this context, the catalytic behavior of Cr-doped NiO catalysts can be explained only by admitting that, in these catalysts, NH_3 oxidation is carried out by loosely bound oxygen also, while the role of extralattice oxygen is prevailing in the otherwise doped catalysts.

In order to explain the dependence of N_2O selectivity on the amount and the electronic nature of the dopant oxides in NiO, some reaction mechanisms must be formulated. Owing to the lack of detailed kinetic investigation on the reaction no more than a tentative kinetic mechanism, based on previous formulations (*5*), can be proposed

$$(NH_3)_{ads} + O^- \rightarrow (NH_3O)_{ads} + e \quad (3)$$

$$(NH_3O)_{ads} + O^- \rightarrow (HNO)_{ads} + H_2O + e \quad (4)$$

$$(NH_3O)_{ads} + (HNO)_{ads} \rightarrow N_2 + 2H_2O \quad (5)$$

$$(HNO)_{ads} + (HNO)_{ads} \rightarrow N_2O + H_2O \quad (6)$$

According to this reaction scheme, a prevailing NH_3 conversion to N_2O could be expected when reaction step (6) prevails over reaction step (5), that is, when adsorbed HNO species concentration is much higher than NH_3O species concentration on the catalyst surface. Such a situation is favored, by effect of reaction (4), by a high surface population of chemisorbed oxygen species such as that occurring, according to previous conclusions, on less-valent-ion-doped catalysts. Admittedly, all foregoing conclusions do not pretend to constitute an exclusive explanation of the catalytic behavior of oxide catalysts in the NH_3 oxidation. But the results seem to be consistent with the view that the electronic or semiconducting characteristics of the oxide catalysts are prevailing on the other ones.

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