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LETTER TO THE EDITOR

The Catalytic Decomposition of Hydrogen Peroxide Vapor by Nickel Oxides and Promoted Nickel Oxides

In previous papers studies of the decomposition of hydrogen peroxide vapor on metallic oxides (*1*) and mixed metallic oxides (*2*) have been reported. It was shown that the order of catalytic efficiency of a range of metallic oxides could be given as follows:

$$Mn_2O_3 > PbO > Ag_2O > CoO > Cu_2O > NiO > Fe_2O_3 > CdO \gg ZnO = MgO > \alpha\text{-}Al_2O$$

Nickel oxide, an oxide of lower efficiency, seemed to be a convenient catalyst for further study. Since, nickel oxide has been examined in the pure state and with controlled impurity additions as a catalyst for nitrous oxide decomposition (*3*) and for the carbon monoxide/oxygen reaction (*4*). The present work describes the catalytic behavior of this oxide in various states of preparation—as films on glass and on nickel metal as well as the highly compressed bulk oxide, prepared pure or with addition of lithium oxide or gallium oxide as impurities.

The flow system already described (*1*) was used without modification.

Laporte's stabilizer-free hydrogen peroxide (86–90% w/w) was used after concentration to 99.9% ($n_D^{25} = 1.4066$) at 55–65° and 50–70 mm Hg pressure. Nickel oxide was prepared by igniting A.R. nickel nitrate in air at 400°, grinding to pass 300 mesh B.S. sieve, then further igniting at the same temperature for several hours. This gave a black oxide of composition $NiO_{1.16}$. Firing this for 24 hours in air gave a pale-green oxide of composition $NiO_{1.00}$. However this material (*5*) may still contain 0.02 to 0.2% excess oxygen.

The black oxide showed a marked dependence of paramagnetic susceptibility on field strength at room temperature ($\psi = 18.0 \times 10^{-6}$ c.g.s. units at 1,500 öersteds: 12.7×10^{-6} c.g.s. units at 10,600 öersteds). The green oxide gave negligible dependency, $\psi = 9.63 \times 10^{-6}$ and 10.05×10^{-6} c.g.s. units at the above field strengths. X-ray analysis showed no nickel metal lines but the black oxide unit cell was slightly smaller (4.160Å) than for the green material [4.183Å, c.f. Fensham (*6*) 4.181Å].

Gallium oxide was prepared by decomposition of the "Specpure" nitrate at 800° and lithium oxide by heating the A.R. carbonate at 800° in a stream of nitrogen.

Mixed oxides were prepared by intimately grinding the required amounts for 4 hr and annealing at 650° for 6 hr. After firing, NiO/Ga_2O_3 mixtures remained apple-green in color, while Li_2O additions gave black oxides. Oxide samples were pressed to $10 \times 25 \times 2$ mm slips in a highly polished chrome steel die at 17.5 tons/sq. inch (giving 90% of crystal density).

Glass-supported nickel oxide films were prepared by evaporating nickel at 10^{-5} mm and −183° from a "Specpure" wire. The deposits were 5–12 μ thick before oxidation in air at room temperature. For films on metal, "Specpure" nickel was cut to the same size as the oxide slips, degreased, and allowed to oxidize in air at the working temperatures. The metal was bright and the oxide films 100–500 Å thick as determined by coulometric reduction on parallel samples.

All the nickel oxide preparations gave a steady efficiency after about one hour of exposure to H_2O_2 vapor. Black nickel oxide on first exposure gave a high decomposition rate but over the course of runs at 100° and 38° the color changed, in time, to a murky green and the efficiency level tended to that of the stoichiometric bulk oxide. This deterioration in activity is probably due to a reduction of oxygen content on exposure to H_2O_2 which superficially reduces reaction initiation sites such as O^- and O_2^-. The Ga_2O_3- and Li_2O-containing oxides gave steady, stable activities almost immediately and there was no tendency for the Li_2O-doped samples to change from black to green.

The temperature dependence of the reaction rate with nickel oxide on flashed films was examined in the region 60°–160° with an H_2O_2 partial pressure of 0.88 mm Hg. An Arrhenius plot of these results is shown in Fig. 1 for a nickel flashed film 5.7 μ thick. The slope of this line corresponds to an activation energy of 11.0 ± 0.5 kcal/mole. In the same temperature range the nickel oxide on metal slip gave an experimental $E_A = 13.0 \pm 0.5$ kcal/mole.

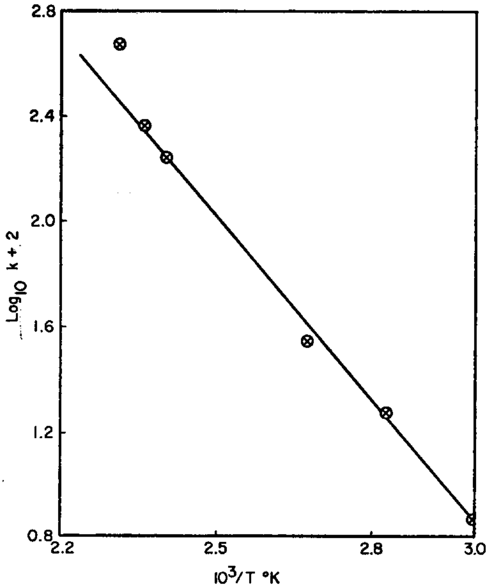

FIG. 1. Arrhenius plot, flashed nickel film.

In terms of steady decomposition values, the bulk NiO samples containing 0.004 to 2.1 mole % Ga_2O_3 were less active catalysts than those containing corresponding amounts of Li_2O. The effect of adding Li^+ ions to the stoichiometric oxide was to increase the decomposition as the Li^+ content increased, while adding more than 0.004 mole % Ga_2O_3 gave, at each temperature, a slightly improved activity which was independent of the amount of Ga_2O_3 added. Table 1 shows the steady activity levels obtained with pure and doped NiO samples along with their surface areas [BET: C_2H_4: —183° (7)] determined after exposure to H_2O_2.

TABLE 1

CATALYTIC ACTIVITIES FROM 38° TO 136° OF NICKEL OXIDE AND DOPED NICKEL OXIDES IN H_2O_2 DECOMPOSITION[a]

Catalyst	Percentage decomposition				Surface area (cm²)
	38°	60°	100°	136°	
NiO	8.0	21.0	50.0	65.0	184
NiO + 2.4 mole% Li_2O	31.5	43.5	77.5	97.0	166
NiO + 2.1 mole% Ga_2O_3	—	30.0	60.6	78.0	157

[a] Partial pressure H_2O_2 = 0.96 mm Hg.

The kinetics of the decomposition were studied on the 2.4 mole % Li_2O and 2.1 mole % Ga_2O_3 mixtures with an initial H_2O_2 partial pressure of 0.96 mm Hg. The two catalysts behaved similarly on making fast concentration decrease, in that the same fraction of H_2O_2 vapor was decomposed at 0.96, 1.64, and 0.32 mm, apart from a quickly damped cyclic variation on making the initial changes. The reversal from 0.32 mm to 0.96 mm was accompanied by a minor efficiency drop which was slightly more pronounced with Ga^{3+} as the impurity.

The influence of oxygen and water partial pressures, was determined, as described earlier (*1*), for nickel oxide on metal slip, green nickel oxide, and for 2.4 mole % Li_2O and 2.1 mole % Ga_2O_3 additions. These kinetic studies gave the following rate expression:

$$r = k(p_{H_2O_2}) \cdot (p_{O_2})^{1/8} \cdot (p_{H_2O})^{-1/2}$$

The kinetic results, together with the activity figures for the doped nickel oxides, are in harmony with earlier proposals (*1*) for the classification of inorganic oxide catalysts, in H_2O_2 decomposition, into activity groups which are related by the nature of the defect solid lattice.

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