[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY]

The Catalytic Oxidation of Carbon Monoxide on Nickel Oxide. II. Nickel Oxide Containing Foreign Ions

BY G. PARRAVANO

RECEIVED JUNE 20, 1952

The activation energy for the carbon monoxide oxidation reaction on nickel oxide is not affected at low temperature (100–180°) by the addition of foreign ions to the nickel oxide lattice. At higher temperatures, however, the activation energy of the catalytic reaction is dependent upon the type of addition. This effect is related to the kinetic mechanism of the reaction and to the changes in electronic properties of nickel oxide brought about by the introduction in its lattice of foreign ions.

Present knowledge on the typical behavior of electron transfer processes involved in chemical reactions catalyzed by oxide semiconductors have been mainly obtained through the pioneering studies of Wagner and Hauffe[1] and Garner and associates.[2] These authors showed that in the course of the catalytic oxidation of carbon monoxide on nickel oxide and cuprous oxide surfaces electron transfer processes occur between the gas and the solid phase, as evidenced by measurements of the semi-conductivity of the solid phase during the reaction. Thus it became apparent that the defective structure of the catalytic surface, which controls its semi-conductivity, would affect the chemical reaction occurring on it. A study on the relation between the defective structure of the surface and its catalytic activity can therefore be instrumental in deciding how far a correlation between electronic structure of surfaces and their activity to catalyze chemical changes can be established. The present communication refers to the oxidation of carbon monoxide on nickel oxide samples, whose electronic characteristics have been modified following the method of controlled valency semi-conductors, recently developed by Verwey and associates.[3]

Experimental

Nickel oxide samples, containing foreign ions, were prepared under strictly controlled conditions, as previously described.[4] The purification of gases and the apparatus used in the determination of oxidation rates were similar to those already described.[5]

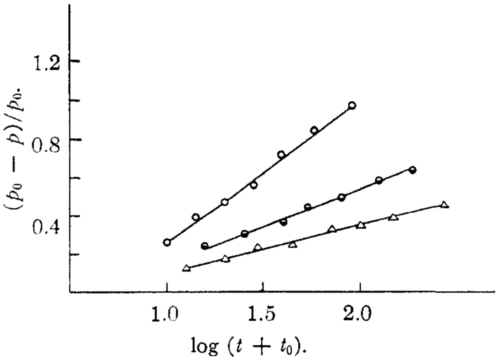

Fig. 1.—Initial rate of carbon monoxide oxidation on NiO + 1 mole % Ag_2O (0.483 g.), p_{CO} = 186 mm., p_{O_2} = 94 mm., t_0 = 10: Δ, 162°; ◒, 177°; O, 203°.

Results

As in the case of pure nickel oxide,[5] the initial rate of carbon monoxide oxidation was found to obey the exponential relation: $dg/dt = ae^{-\alpha g}$, where g is the amount of conversion a, α = constants. Some results for the catalyst NiO + 1 mole % Ag_2O are presented in Fig. 1. No other data were taken on the effect of additions to nickel oxide on the initial rate a. After the catalyst had been in use for some time, the data were found to fit quite well a first-order equation for the low temperature interval and a 1.25-order equation for the high temperature region (Figs. 2 and 3) giving

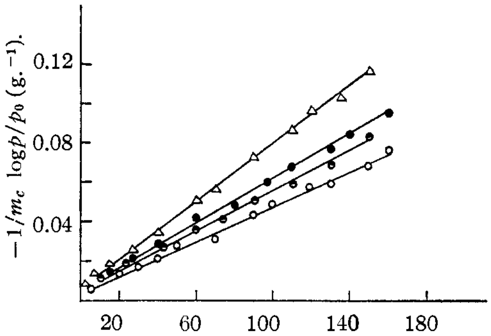

Fig. 2.—Carbon monoxide oxidation on NiO + 1 mole % Ag_2O, p_{CO} = 186 mm., p_{O_2} = 94 mm. Low temperature range: O; 106°; ◒; 125°; ●; 147°; Δ; 162°; m_c = weight of catalyst in g.

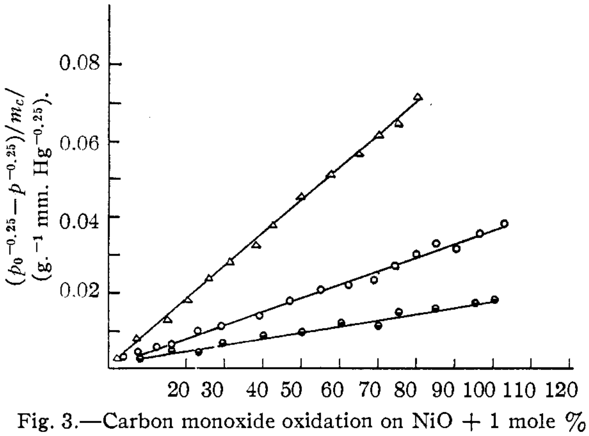

Fig. 3.—Carbon monoxide oxidation on NiO + 1 mole % Ag_2O, p_{CO} = 186 mm., p_{O_2} = 94 mm. High temperature range: ◒, 180°; O, 207°; Δ, 225°.

---

[1] C. Wagner and K. Hauffe, *Z. Elektrochem.*, **44**, 172 (1938).

[2] W. E. Garner, T. J. Gray, F. S. Stone, *Proc. Roy. Soc.* (*London*), **A177**, 314 (1949); *Disc. Faraday Soc.*, No. 8, 246 (1950).

[3] E. J. Verwey, P. W. Haaijman, P. C. Roweijn and G. W. Osterhout, *Philips Res. Reports*, **5**, 173 (1950).

[4] G. Parravano, THIS JOURNAL, **74**, 1194 (1952).

[5] G. Parravano, *ibid.*, **75**, 1448 (1953).

for the sample NiO + 1 mole % Ag_2O an over-all activation energy of 3.0 and 17 kcal./mole for the low and the high temperature interval, respectively. In order to obtain a rapid determination of the activation energies non-isothermal runs were performed by submitting the catalyst to a heating rate, which was linearly increasing with time and correcting the data for the thermal expansion of the gases. If $T = T_0 + \gamma t$, where T = temperature, t = time, γ = constant and $-\mathrm{d}p/\mathrm{d}t = kp$ is the rate law, then

$$-\mathrm{d}p/\mathrm{d}T = (k/\gamma)p \qquad (1)$$

For sufficiently small temperature intervals it is possible to approximate $-\mathrm{d}p/\mathrm{d}t \cong -\Delta p_i/\Delta T_i$, where $\Delta p_i = p_i - p_{i-1}$, $\Delta T_i = T_i - T_{i-1}$, p_i, p_{i-1} being successive pressure readings at temperatures T_{i-1} and T_i, respectively. Equation (1) then becomes

$$\Delta p_i/p_i\Delta T_i = \frac{k_0}{\gamma}\, e^{-E/RT}$$

A plot of log $(\Delta p_i/\Delta T)$ *vs.* $1/T$ should give a straight line, whose slope is proportional to the activation energy E. In order to test the correctness of this method a comparison was made among E values obtained from isothermal and non-isothermal runs. The data are summarized in Table I.

TABLE I

ACTIVATION ENERGIES FOR CARBON MONOXIDE OXIDATION CALCULATED FROM ISOTHERMAL AND NON-ISOTHERMAL RUNS

Catalyst	Temp. range, °C.	Activation energy, kacl./mole Isothermal	Non-isothermal
NiO	100–180	2.2	3.2
NiO	180–250	13.0	13.7
NiO + 1 mole % Ag_2O	180–225	3	1.9
NiO + 1 mole % Ag_2O	225–260	17.0	17.5

Different heating speeds were tried on the same sample and the values of E obtained did not differ appreciably. The non-isothermal method however suffers from the disadvantage that the experimental error in p_i is built up through the determination of Δp_i. Therefore when rate data for the calculation of the pre-exponential factor are needed, they are best obtained through isothermal runs. All the data obtained on nickel oxide samples containing foreign ions are collected in Figs. 4 and 5 and in Table II.

TABLE II

ACTIVATION ENERGIES FOR CARBON MONOXIDE OXIDATION ON NICKEL OXIDE CONTAINING FOREIGN IONS

Catalyst	Temp. range. °C.	E. kcal./mole
NiO	180–250	13.7
NiO + 0.01 mole % Ag_2O	180–250	14.9
NiO + 1 mole % Ag_2O	225–260	17.5
NiO + 0.01 mole % Li_2O	230–280	18.0
NiO + 0.01 mole % Cr_2O_3	160–220	7.9
NiO + 0.01 mole % Ce_2O_2	160–220	8.9
NiO + 1 mole % $NiCl_2$	160–220	8.2
NiO + 0.01 mole % WO_3	180–220	6.5

Discussion

The data reported show that the kinetic equations which were found to describe the reaction on pure nickel oxide, are also operative in the case of nickel oxide samples, containing foreign ions. In the low temperature region all catalysts operate practically with the same value of the activation energy. This indicates that in this temperature interval the added ions do not affect directly the catalytic process. They however modify the excess oxygen content of nickel oxide and therefore would probably influence the initial rate of oxidation. On the other hand at high temperature the data show an interesting phenomenon, inasmuch as the impurity affects directly the oxidation reaction, by changing its over-all activation energy. The values of the activation energy show a trend which is a function of the type of added ion (Table II). Introduction of monovalent cations increases, while cations with a valency higher than two decrease the activation energy of the process. The reverse effect is obtained by introducing foreign anions into the nickel oxide lattice.

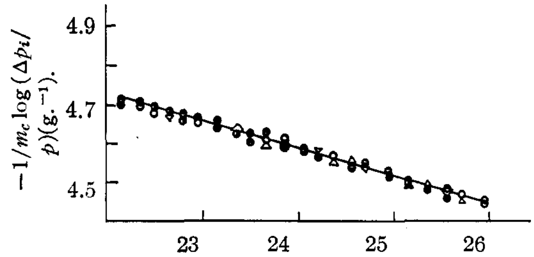

Fig. 4.—Arrhenius plot for the carbon monoxide oxidation on nickel oxide containing foreign ions. Low temperature range; ΔT_i = 3°; heating rate 1.25° min.$^{-1}$.: ◒, NiO + 1 mole % Li_2O; ●, NiO + 1 mole % Ag_2O; ⊕, NiO + 0.01 mole % Ag_2O; ▽, NiO + 0.01 mole % WO_3; △, NiO; ◐, NiO + 1 mole % $NiCl_2$; ◓, NiO + 0.01 mole % Cr_2O_3; ○, NiO + 0.01 mole % CeO_2.

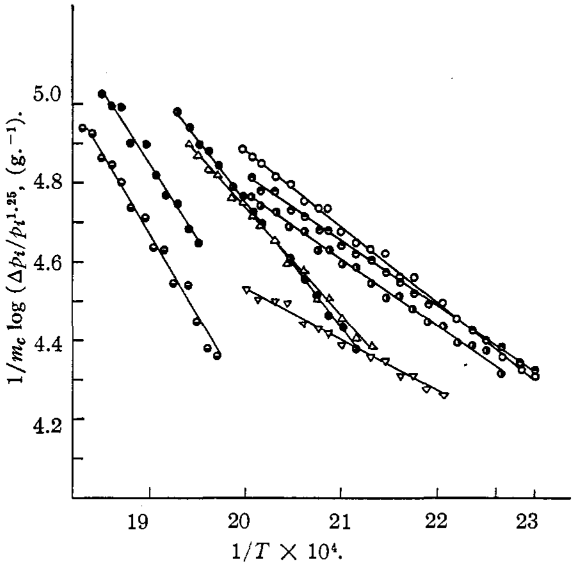

Fig. 5.—Arrhenius plot for the carbon monoxide oxidation on nickel oxide containing foreign ions. High temperature range: ΔT_i = 3° heating rate = 1.25° min.$^{-1}$: ◒ NiO + 1 mole % Li_2O; ●, NiO + 1 mole % Ag_2O; ▽, NiO + 0.01 mole % WO_3; △, NiO; ⊕, NiO + 0.01 mole % Ag_2O; ◐, NiO + 1 mole % $NiCl_2$; ◓, NiO + 0.01 mole % Cr_2O_3; ○, NiO + 0.01 mole % CeO_2.

A similar effect was already found in the reduction of nickel oxide with hydrogen.[4] Since in that case it was concluded that the over-all process is determined by hydrogen chemisorption and since it is known from semi-conductivity data[1,2] that on *p*-type oxides carbon monoxide behaves essentially as an electron donor, it is possible to conclude from the effect of impurities on the activation energy of the oxidation reaction that the interaction of carbon monoxide with the oxide surface is the controlling step in the high temperature interval of the reaction.

A similar conclusion was previously reached on kinetic grounds.[5] This agreement is regarded as supporting evidence for the kinetic scheme proposed. The addition of foreign ions into the nickel oxide lattice might modify the concentration and distribution of holes and electrons by suitable changes of the Fermi level of the semi-conductor. This can be related to the experimentally observed effect of additions on the activation energy of heterogeneous processes involving formation and/or destruction of acceptor and donor levels in semiconductors. Although the effect has been observed so far on the over-all activation energy, it may lead, if substantiated by further experimental work, to a method for controlling, at least qualitatively, the activation energies of heterogeneous processes occurring on semi-conducting materials.

PRINCETON, N. J.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Effect of Water on the Burning Velocities of Cyanogen–Oxygen–Argon Mixtures[1]

BY RICHARD S. BROKAW AND ROBERT N. PEASE

RECEIVED NOVEMBER 3, 1952

Burning velocities have been determined for cyanogen–oxygen–argon mixtures containing varying amounts of moisture. The effect of water is explainable on the basis of the Tanford–Pease theory of flame speeds. Experiments with heavy water suggest that the hydroxyl radical is more important than the hydrogen atom in determining the rate of flame propagation.

Tanford and Pease[2] have put forward a theory of burning velocity which assumes that the rate of flame propagation is determined by the rate at which atoms and radicals from the burned gas diffuse into and react with the unburned fuel. In particular they applied their theory to the measurements of Jahn[3] on moist carbon monoxide. In these calculations hydrogen atoms and hydroxyl radicals were the active species considered. Hoare and Linnett[4] have pointed out that it is possible to explain the effect of water or hydrogen on carbon monoxide flame velocities by a thermal theory of flame propagation.

In view of the above, it was felt that it would be desirable to determine the effect of added water on the burning velocity of another hydrogen-free fuel. Cyanogen was selected for these studies, since it is easily prepared, and as it is composed of carbon and nitrogen alone, equilibrium flame temperature calculations are not unduly complicated. Furthermore, the work of Hadow and Hinshelwood[5] shows that water has no effect on the rate of the slow oxidation of cyanogen (apparently a surface reaction).

Experimental

Flame velocities have been determined on a bunsen burner apparatus. Capillary flow meters were used to measure the rates of oxygen and argon flow. In order to conserve cyanogen, this gas was added to the gas stream by mercury displacement from a cylindrical reservoir flask of about 300-cc. capacity. A hydraulic cylinder was used to raise a cylindrical leveling bulb at a uniform rate, controlled by a needle valve on the water line. The travel of the hydraulic cylinder also closed and opened a switch on a Gralab Model No. 201 microtimer which measured the time required to displace a standard volume of gas, and thereby the cyanogen flow rate.

The flames were ignited by means of an induction spark and were stabilized on a 0.806 cm. i.d. Pyrex burner enclosed in a 4-cm. mantle. A flow of dry nitrogen approximately equal to the flow rate through the burner was introduced into the annular space. This helped to sweep out combustion products and aided in stabilizing the flame. Photographs were taken with a Leica camera equipped with a 5-cm. extension tube. The flames are highly luminous so that exposures as fast as $^1/_{500}$ second at f25 on Kodak plus-X film were in some instances used. Burning velocities were determined by considering the flow through a frustum of the cone between the diameters of 0.2 to 0.7 cm. This method, proposed by Dery,[6] eliminates the disturbed areas at the base and tip of the cone. Frustum areas were obtained from enlarged tracings of the flame photographs.

Cyanogen was prepared by thermal decomposition of mercuric cyanide which was first mildly heated *in vacuo* to drive off any moisture which might be present. The cyanogen was passed over magnesium perchlorate and frozen out by liquid nitrogen. It was stored in 3- and 5-liter glass flasks, and could be introduced into the cylindrical reservoir flask by means of a Toepler pump. A sample of cyanogen was analyzed for hydrogen cyanide by the method of Rhodes,[7] and no trace of the latter was found. In addition, vapor pressures at −78, −45 and −39° checked with the values of Perry and Bardwell.[8]

---

[1] The work described in this paper was carried out at Princeton University in connection with Contract NOrd 7920 with the United States Naval Bureau of Ordnance, as coördinated by the Applied Physics Laboratory, The Johns Hopkins University, and Contract N6-ori-105 with the Office of Naval Research and Office of Air Research as coördinated by Project Squid, Princeton University. Reproduction in whole or in part permitted for any purpose of the United States Government. We wish to acknowledge the assistance of Dean H. S. Taylor, who has general supervision of this project.

[2] C. Tanford and R. N. Pease, *J. Chem. Phys.*, **15**, 861 (1947).

[3] G. Jahn, "Der Zündvorgang in Gasgemischen," Oldenbourg, Berlin, 1942.

[4] M. F. Hoare and J. W. Linnett, *J. Chem. Phys.*, **16**, 747 (1948).

[5] H. J. Hadow and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A132**, 375 (1931).

[6] R. J. Dery, see M. E. Harris, J. Grumer, G. von Elbe and B. Lewis, "Third Symposium on Combustion and Flame and Explosion Phenomena," Williams & Wilkins Co., Baltimore, Md., 1949, p. 88.

[7] F. H. Rhodes, *J. Ind. Eng. Chem.*, **4**, 652 (1912).

[8] J. H. Perry and D. C. Bardwell, THIS JOURNAL, **47**, 2629 (1925).