# A Correlation of Catalytic Activity for the Oxidation of Carbon Monoxide and the Adsorption of Carbon Dioxide on Nickel Oxide

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Various kinds of physical or chemical properties of oxides have previously been discussed, e. g., semiconductivity,1) the decomposition pressure of oxides,2) reducibility,3) the heat of the formation of oxides,4) and the rate of isotopic exchange reaction in molecular oxygen,5) in attempts to find a parameter which is capable of accounting for the oxidation activity of nickel oxide catalysts.

It is generally accepted that carbon dioxide is adsorbed on the oxygen atom of the nickel oxide surface in the form of the "$CO_3$-complex," the existence of which was ascertained by both infrared spectroscopic6) and micro-calorimetric7) studies. The nature of the surface oxygen would be made clear by the measurement of the interaction between carbon dioxide and the catalyst surface. The adsorption of carbon dioxide will be examined in this study by means of the gas chromatographic technique for the puropse of obtaining the parameter for the catalytic activity of the oxidation of carbon monoxide.

The apparatus was a conventional assembly used for gas chromatography, modified by an additional small reactor. The oxidation of carbon monoxide with oxygen, diluted with helium as a carrier gas, was performed on grayish-green nickel oxide, which had been prepared by calcining basic nickel carbonate in air at 700°C for 8 hr. Molecular Sieve 5A was packed in the analytical column.

In order to observe the behavior of the adsorbed carbon dioxide, a gas sample (0.1 ml.) of carbon dioxide, mixed with a small amount of argon, was injected at the top of the nickel oxide catalyst column and the values of the retention times of carbon dioxide and argon were measured. The true retention volume of carbon dioxide was calculated from the flow rate and the retention time of argon.

The extent of the oxidation of carbon monoxide by gaseous oxygen on nickel oxide was determined first, and then that by nickel oxide itself, that is, reduction rate of nickel oxide by carbon monoxide. The rate constant of the oxidation of carbon monoxide by gaseous oxygen, $k_o$, was obtained by injecting the stoichiometric reaction mixture of carbon monoxide (0.5 ml.), oxygen (0.25 ml.) and helium (0.25 ml.) as a pulse. The reduction rate constant of nickel oxide by carbon monoxide, $k_r$, was derived in the same way using a mixture of carbon monoxide (0.5 ml.) and helium (0.5 ml.). The conversion of carbon monoxide to carbon dioxide both by gaseous oxygen, $x_o$, and by nickel oxide, $x_r$, was obtained from the decrease in the gas chromatographic peak height of carbon monoxide. The reaction kinetics being assumed to be first order with respect to the total pressure, the rate constants, $k_o$ and $k_r$, were calculated as

$$k_o = F/W\,[\ln\,(1-x_o)^{-1}] \tag{1}$$

and

$$k_r = F/W\,[\ln\,(1-x_r)^{-1}] \tag{2}$$

respectively, where $F$ (ml./min.) is the flow rate of the carrier gas and $W$ (g.) is the weight of the catalyst.

The relationship between $x_r$ and the retention volume of carbon dioxide, $V(CO_2)$, is shown in Table I. Both the true retention volume and the reduction rate constant are large under oxidized conditions and small under reduced conditions.

TABLE I. RELATIONSHIP BETWEEN RETENTION VOLUME OF $CO_2$ ON NICKEL OXIDE COLUMN AND AMOUNT OF REDUCTION OF NICKEL OXIDE BY CO

Amount of catalyst, 4 g. Temperature, 140°C

| Pretreatment | $V(CO_2)$, ml. | $x_r$, % |
|---|---|---|
| Oxidation | 14.9 | 31 |
| Reduction | 8.0 | 16 |
| Reoxidation | 10.8 | 26 |

As to the retention volume, this may coincide with the schematic model of the adsorption of carbon dioxide on the surface oxygen proposed by Stone.7)

Correlation of the oxidation rate of carbon monoxide or the reduction rate of nickel oxide

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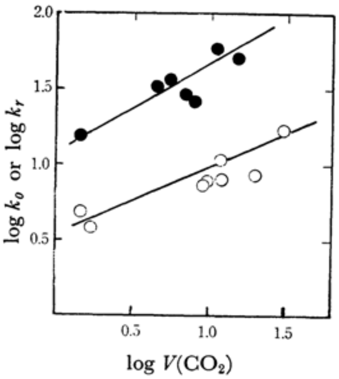

Fig. 1. Correlation between reaction rate constants and retention volume of $CO_2$ on nickel oxide at 120°C.

● Oxidation rate constant of carbon monoxide, $k_o$, in Eq. 1.
○ Reduction rate constant of nickel oxide, $k_r$, in Eq. 2.

with the retention volume of carbon dioxide over a nickel oxide catalyst is plotted in Fig. 1 for various conditions, such as oxidized or reduced, and fresh or poisoned. The oxidation rate of carbon monoxide by oxygen gas on nickel oxide is parallel to the reduction rate of nickel oxide by carbon monoxide. This correlation may reflect the fact that the more reactive surface oxygen for carbon monoxide the catalyst has, the more active is the catalyst for the catalytic oxidation of carbon monoxide.

By means of surface potential measurements, Chee and Yoneda[8] revealed recently that the surface state of nickel oxide during the oxidation of carbon monoxide is the oxidized one, irrespective of pretreatment and that the rate-determining step of this reaction is the process of the reaction between gaseous carbon monoxide and adsorbed oxygen.

A parallel correlation between the two kinds of rate constants and the retention volume of carbon dioxide seems to be reasonable, since the same surface oxygen may interact with carbon dioxide in both cases, and it may determine the catalytic activity as well.

On the basis of the above results and discussion, it may be concluded that the surface oxygen on which carbon dioxide is adsorbed can control the oxidation rate of carbon monoxide, and that the ability of carbon dioxide adsorption on nickel oxide is an important parameter for the catalytic activity of the oxidation of carbon monoxide. The value of the retention volume of carbon dioxide is the product of the number of adsorption sites and the equilibrium constant of the adsorption. In order to clarify the nature of the active center for the oxidation reaction of carbon monoxide on nickel oxide, it will be necessary to distinguish the amount of the adsorption of carbon dioxide from the adsorption strength. This problem will be dealt in another paper.

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