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A Study of the Surface Heterogeneity of Nickel Oxide Catalysts by the Flash Desorption Method

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The flash desorption method was applied to the carbon dioxide - nickel oxide system in order to investigate the surface heterogeneity of nickel oxide catalysts. It was found that there were two peaks in flash desorption chromatograms. The Arrhenius plots for carbon monoxide oxidation on nickel oxide were found to be composed of two straight lines. It was shown that the inflection of the Arrhenius plots was due to the existence of two kinds of active sites which differ in activation energy for the oxidation reaction and in the strength of interaction with carbon dioxide. The numbers of active sites for carbon monoxide oxidation were determined by the measurement of the amounts of desorbed carbon dioxide.

Much work has been done in attempting to clarify the correlation between catalytic activities and the physical or chemical properties of catalysts. The oxidation of carbon monoxide on nickel oxide catalysts has been widely investigated as a test reaction. Various kinds of physico-chemical methods, *e. q.*, electronic semiconductivity¹⁾, infrared spectrometry,²⁾ microcalorimetry,³⁾ surface potential measurement⁴⁾ and tracer method,⁵⁾ as well as kinetical methods have been applied in attempting to elucidate the reaction mechanism of carbon monoxide oxidation. In a previous report⁶⁾ the ability of carbon dioxide adsorption on nickel oxide was shown to have a close correlation with the catalytic oxidation of carbon monoxide. From the study of the flash desorption of carbon dioxide on nickel oxide, much information is expected to be obtained concerning the nature of the active sites of nickel oxide for the catalytic oxidation of carbon monoxide.

Experimental

a) Materials. Black nickel oxide was prepared by the thermal decomposition, in air at 350°C for 4 hr, of basic nickel carbonate which had been precipitated from aqueous solution of nickel nitrate (G. R.) with ammonium carbonate (G. R.). Four samples of nickel oxide were prepared from the black nickel oxide by calcining them further in air under the conditions shown in Table 1.

Commercial gases of carbon monoxide, helium and oxygen were used after passing them through dry ice-ethanol traps in order to remove any water vapor. Carbon dioxide was obtained from dry ice and purified further through a silica-gel column.

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1) G. Parravano and M. Boudart, *Advances in Catalysis,* **7**, 47 (1955).

2) R. P. Eischens and W. A. Pliskin, *ibid.,* **9**, 662 (1957).

3) F. S. Stone, *ibid.,* **13**, 1 (1962).

4) D. Chee and Y. Yoneda, to be published.

5) E. R. S. Winter, *Advances in Catalysis,* **10**, 196 (1958).

6) J. Kondo, T. Uchijima and Y. Yoneda, This Bulletin, **37**, 2781 (1966).

TABLE 1. PARTICLE SIZE AND BET SURFACE AREA OF NICKEL OXIDE SAMPLES PREPARED UNDER DIFFERENT CONDITIONS FROM BLACK NICKEL OXIDE

Catalyst	Condition of sintering		Particle size mesh	BET surface area m^2/g
	Temp. °C	Time hr		
A	350	24	60—100	63
B	500	14	60—100	—
C	700	4	60—100	—
C′	700	4	<100	4

b) Apparatus. The usual assembly used for gas chromatography, modified by the addition of a stainless steel reactor, was used, as shown in Fig. 1. Helium was used as the carrier gas and Molecular Sieve 5A was packed in the analytical column.

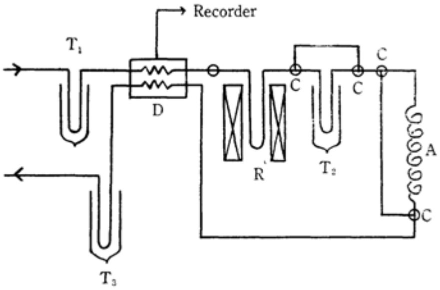

Fig. 1. Apparatus.

A: Analytical column
C: Three ways cock
D: Detector of gas chromatograph
R: Reactor
T_1, T_2: Dry ice - ethanol trap
T_3: Liquid nitrogen trap
T_2 and T_3 were used only in the case of flash desorption measurement.

c) Procedure. *i) Measurements of the Amounts of Flash-desorbed Carbon Dioxide.* The analytical column was removed for these measurements. The catalyst samples were pretreated in oxygen for 1 hr and then in helium gas for 1 hr at 300°C for NiO(A), and at 500°C for NiO(B) and NiO(C). Carbon dioxide of one atmospheric pressure was then made to flow through the reactor at 60°C for about 14 hr. After this treatment, the catalyst was evacuated for 30 min below −30°C and then exposed to a helium flow for about 2 hr at room temperature. After no carbon dioxide liberation could be recognized, the catalyst temperature was raised at a constant speed of 10°C/min under a helium flow, and the amount of desorbed carbon dioxide was recorded against the temperature.

ii) Measurements of the Oxidation Rate of Carbon Monoxide on Nickel Oxide. The rate of oxidation was measured by the pulse technique similar to one which had been reported previously.[6] Pretreatments of nickel oxide catalysts were carried out in the same way as in c-i). Furthermore, catalysts were treated with helium at 300°C for 15 min, intermittently between the pulses of a reactant gas mixture.*1

One milliliter of a stoichiometric gas mixture of reactants (0.5 m*l* of carbon monoxide, 0.25 m*l* of oxygen and 0.25 m*l* of helium) was injected at the top of the catalyst column. The conversion, x, of carbon monoxide to carbon dioxide was determined from the decrease in the carbon monoxide peak in the gas chromatogram. Since the kinetics of carbon monoxide oxidation is generally accepted to be nearly first order with respect to the total pressure, the rate constant was calculated according to the following equation:

$$k = F/W[\ln(1-x)^{-1}] \qquad (1)$$

where W(g) is the weight of the catalyst and F(m*l*/min) is the flow rate of the carrier gas. The values of $F/W\cdot[\ln(1-x)^{-1}]$ were confirmed to be constant for various sets of F/W values.

Results

Flash Desorption. A typical flash desorption chromatogram for NiO(A) is shown in Fig. 2. The chromatograms consisted of two peaks for all samples. However, the separation between the two peaks were not clear for NiO(B) and NiO(C); this lack of clarity might be ascribed to small surface areas. The peak maximum temperatures, T_{MI} and T_{MII}, for the first and second peak respectively are given in Table 2.

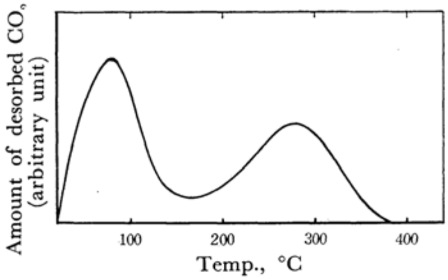

Fig. 2. Typical flash desorption chromatogram of carbon dioxide on NiO(A).

TABLE 2. TEMPERATURE OF MAXIMUM PEAK HEIGHT FOR PEAK I AND PEAK II

Rate of raising temperature, 10°C/min

Catalyst	T_{MI} °C	T_{MII} °C
A	80	300
B	100	—
C	—	—
C′	120	370

The activation energy of the desorption of carbon dioxide, E_d, was determined according to the following equation:[7]

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*1 Poisoning by carbon dioxide during the oxidation reaction of carbon monoxide over the sites for peak II may be negligible, because the activation energy was required experimentally for carbon dioxide to be adsorbed on them.

[7] Y. Amenomiya and R. J. Cvetanović, *J. Phys. Chem.*, **67**, 144 (1963).

$$2 \log T_M - \log \beta = C_1 E_d / T_M + C_2 \log E_d \qquad (2)$$

where β is designated as the temperature elevation speed and C_1 and C_2 are constants. The activation energy of desorption for NiO(A) was obtained as 8 kcal/mol for peak I and 25—27 kcal/mol for peak II.

The amounts of desorbed carbon dioxide for each peak was determined by collecting the gas with a liquid nitrogen trap, followed by volumetric measurements. The amounts of desorption are shown in Table 3. The reproducibility was fairly good.

Table 3. The amounts of desorbed carbon dioxide from peak I and peak II by flash desorption

Catalyst	Peak I m*l*/g	Peak II m*l*/g
A	1.51	1.36
B	1.01	0.49
C	0.51	—
C′	0.33	0.3*

* Reproducibility was rather poor.

Oxidation of Carbon Monoxide on Fresh Catalysts. In Figs. 3 and 4, log *k* is plotted as a function of 1/*T* for NiO(A) and NiO(B) respectively. Arrhenius plots for fresh catalysts give curved lines. The curved lines, however, seem to be composed of two straight lines, with an activation energy of about zero for the low temperature range and of 14—15 kcal/mol for high temperature range, these results are summarized in Table 4.

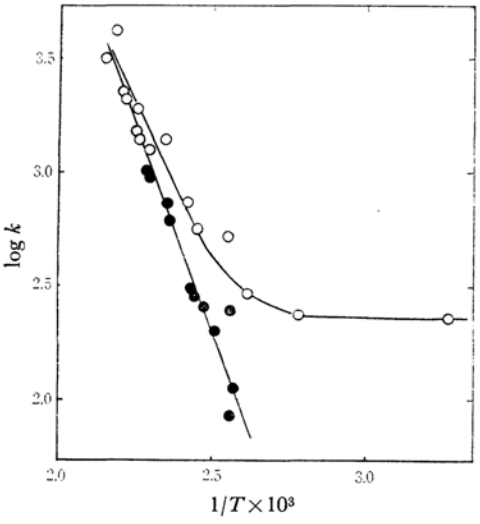

Fig. 3. Arrhenius plots of carbon monoxide oxidation or NiO(A).
○: Fresh catalyst
●: Catalyst poisoned with carbon dioxide for peak II

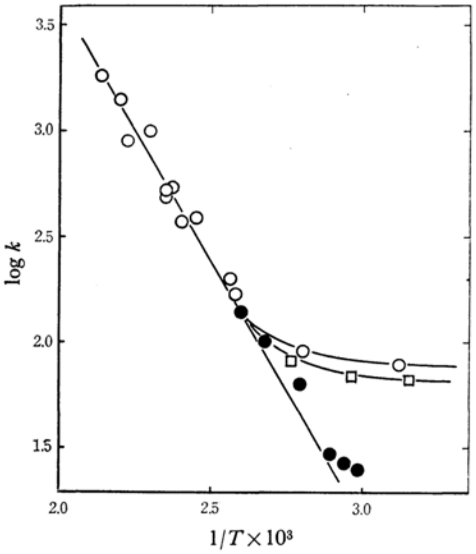

Fig. 4. Arrhenius plots of carbon monoxide oxidation on NiO(B).
○: Fresh catalyst
●: Catalyst poisoned with carbon dioxide for peak II
□: Reactivated catalyst

Table 4. Activation energy for high temperature range of carbon monoxide oxidation

Catalyst	Activation energy kcal/mol
A	14.2
B	14.6
C	15.6
C′	15

The transition temperature between the two straight lines was about 110°C for both NiO(A) and NiO(B) and about 160°C for NiO(C).

Carbon Monoxide Oxidation on Poisoned Catalysts. When the NiO(A) catalyst was exposed to carbon dioxide for about a week at room temperature and then to a helium flow for about 1 hr at 200°C, the Arrhenius plot of its catalytic activity in carbon monoxide oxidation gave a straight line with an activation energy of 15.2 kcal/mol, as shown in Fig. 3. It had already been ascertained that the adsorption sites for peak II of the catalyst were only poisoned with carbon dioxide under these conditions. Therefore, the adsorption sites for peak I were unposioned and were still available for the catalytic oxidation of carbon monoxide.

The NiO(B) catalyst was treated in a carbon dioxide atmosphere at 60°C for about 14 hr and then to a helium flow at 110°C for 1 hr so that carbon dioxide was thus desorbed from peak I sites, while peak II sites were still covered with carbon dioxide. The Arrhenius plot for this catalyst also gave a straight line, as shown in Fig. 4.

When partially-poisoned catalysts were treated in a helium flow at 300°C for 1 hr, the adsorption sites for peak II were regenerated and their catalytic activities were almost recovered up to the initial values, as Fig. 4 shows.

Discussion

The Arrhenius plots of carbon monoxide oxidation on nickel oxide catalysts were found to be composed of two straight lines. This behavior was not due to an inadequate application of the pulse technique, although the pulse technique cannot be used when either the reactants are separated in the catalyst bed or irreversible adsorption of reactants or products on the catalyst occurs. Firstly the retention volumes of both carbon monoxide and oxygen on nickel oxide were found to be the same as that of argon, indicating that no separation of the reactant gases occurred in the catalyst bed. Secondly, no irreversible adsorption of carbon monoxide was observed, while a certain amount of carbon dioxide was adsorbed irreversibly. Thus, the characteristic behavior concerning the Arrhenius plots was concluded to be intrinsic for the catalysts themselves.

When peak II adsorption sites of nickel oxide catalysts were poisoned with carbon dioxide, Arrhenius plots in one straight line and with large activation energies were obtained even for the low temperature range. When both peak I and peak II adsorption sites of nickel oxide catalysts were poisoned with carbon dioxide, the catalytic activity was so small that it could not be measured.

Therefore, it may be concluded that the nickel oxide surface has two kinds of active sites, one corresponding to the peak I adsorption sites and the other to the peak II adsorption sites. The activation energies of carbon monoxide oxidation for the two kinds of active sites were different. The active sites responsible for the peak I adsorption have higher activation energies than those for peak II.

A similar irregularity in Arrhenius plots has been pointed out by several authors. Parravano and Boudart[1] and Parravano[8] observed that the activation energy of carbon monoxide oxidation on green nickel oxide was 2.2 kcal/mol below 180°C and 13 kcal/mol above this temperature; they claimed that the reaction kinetics changed at this temperature. Kubokawa *et al.*[9] studied the same reaction on nickel oxide sintered at 1000°C and reported that the activation energy changed from 5.5 kcal/mol below 350°C to 16.2 kcal/mol above 350°C under a reduced pressure and to 18.4 kcal/mol above 350°C under a normal pressure. They ascribed the change in activation energies to different reaction mechanisms.

If the reactions proceeded on the same active sites in the low and high temperature ranges, the ratio of the reaction rates at a high temperature to those at a low temperature might be constant for all samples, since the activation energies are practically the same for the four nickel oxide catalysts used. In our study, however, the ratio of the reaction rate at 163°C to that at room temperature was 4.2 for NiO(A) and 7.6 for NiO(B). This shows that the number of active sites in the high temperature range must be different from that in the low temperature range.

The rate constants of the reaction in both temperature ranges were compared with the amounts of carbon dioxide desorbed from peak I and peak II. As shown in Fig. 5, a good correlation was obtained; this proves the existence of two kinds of active sites.

From infrared spectroscopic[2] and calorimetric[3] studies, it was ascertained that carbon dioxide was adsorbed on the surface oxygen of nickel oxide in the form of a "CO_3-complex". The heats of adsorption of carbon dioxide on nickel oxide were reported to be 28 kcal/mol on an evacuated surface and 37 kcal/mol on an oxidized one.[3] These facts seem to indicate that carbon dioxide

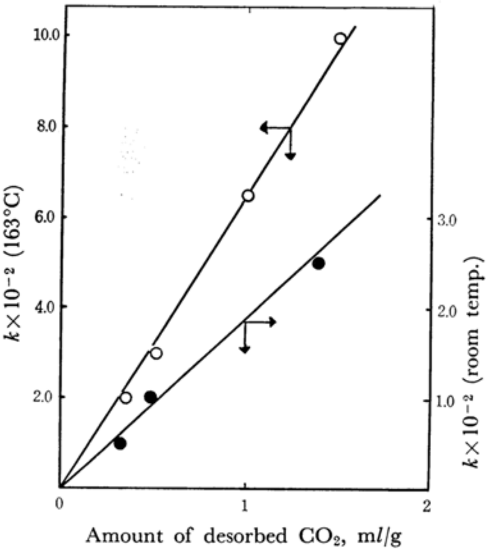

Fig. 5. The correlation between the amount of desorbed carbon dioxide and the oxidation rate constant of carbon monoxide.

- ●: Amount of desorbed carbon dioxide from peak II *vs.* the reaction rate constant at room temperature.
- ○: Amount of desorbed carbon dioxide from peak I *vs.* the reaction rate constant at 163°C.

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[8] G. Parravano, *J. Am. Chem. Soc.*, **75**, 1452 (1953).

[9] I. Matsuura, Y. Kubokawa and O. Toyama, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **81**, 1003 (1960).

adsorbed on the oxygen atoms and that the heat of adsorption is large on the labile oxygen.

On the other hand, the major role of the surface oxygen of the catalyst in the catalytic oxidation of carbon monoxide should be emphasized. In a previous paper,⁶⁾ the rate of the reduction of nickel oxide by carbon monoxide was reported to be parallel to the rate of the oxidation of carbon monoxide on nickel oxide. From the surface potential measurements of nickel oxide, Chee *et al.*⁴⁾ pointed out that the catalyst surface was always in an oxidized state during the oxidation of carbon monoxide, irrespective of pretreatment, and that the rate-determining step ought to be the step of the reaction between gaseous carbon monoxide and adsorbed oxygen. In view of the infrared absorption at 4.56 μ, the reaction intermediate of carbon monoxide oxidation was assumed to be $\mathrm{Ni\cdots O\overset{\cdots}{-}C\overset{\cdots}{=}O}$.²⁾

All these results would suggest that the active sites for carbon monoxide oxidation are to be regarded as surface oxygen, the amount of which is given by the amount of adsorbed carbon dioxide. The active sites responsible for the catalytic activity for carbon monoxide oxidation in a low temperature range with a low activation energy, corresponding to the peak II sites, are composed of relatively labile and weakly bound oxygen atoms. These oxygen atoms must have a strong interaction with carbon dioxide, since the carbon dioxide adsorbed on peak II sites cannot be removed at a low temperature. On the contrary, the active sites responsible for the activity mainly in a high temperature range with a high activation energy, corresponding to peak I sites, must be composed of relatively stable and strongly bound oxygen atoms, which should have only a weak interaction with carbon dioxide.

Previously Parravano⁸⁾ reported that the oxidation rate of carbon monoxide on nickel oxide calcined at 640°C was 1.25 mmHg/min·g at 222°C with a total pressure of 280 mmHg. This rate has now been recalculated to be $8.1\cdot10^{-4}$ m*l*/min·m^2·mmHg. In the present work the reaction rate was $8.8\cdot10^{-1}$ m*l*/min·m^2·mmHg at the same temperature on NiO(C′) sintered at 700°C. The difference of ten to the third power in the reaction rate between the two experimental data seems to reflect the degree of poisoning of the active sites of nickel oxide by carbon dioxide.

A substantial merit of this work is that it makes it possible to measure the reaction rate on refreshed surfaces at every pulse; thus two kinds of active sites on nickel oxides were found. The discrepancies among the former researchers mentioned above are understandable, if they conducted the reaction under more or less poisoned conditions.

Conclusions

The nickel oxide surface has two kinds of adsorption sites for carbon dioxide, *i. e.,* the weak adsorption sites (peak I) and the strong adsorption sites (peak II). The nickel oxide surface has two kinds of active sites for carbon monoxide oxidation, one corresponding to peak I adsorption sites and the other to the peak II adsorption sites.

The activation energies for carbon monoxide oxidation for two kinds of active sites are different. The active sites responsible for peak I gives a high activation energy, while those for peak II give a low one.

The discrepancies among the former researchers concerning the activation energy for carbon monoxide oxidation on nickel oxide are understandable, if their catalysts were poisoned by carbon dioxide in different degrees.

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