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Adsorption of Carbon Dioxide on Metal Catalysts

By Takao KWAN and Yuzabro FUJITA

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One of the present authors recently investigated the adsorption of carbon monoxide on platinum catalyst[1] with special reference to its state on platinum, and concluded that it was dissociated into statistically independent atoms. Developing the method further, carbon dioxide adsorption was now investigated on reduced nickel, cobalt and iron respectively.

Adsorption isotherm of carbon dioxide is derived by introducing the functions p, q and θ due to Horiuti,[2] respectively for the undissociative adsorption $CO_2 \rightleftarrows CO_2(a)$, for the

(1) Kwan, *J. Res. Inst. Catalysis*, Vol. 1, No. 2, 110 (1949).

(2) Horiuti, *J. Res. Inst. Catalysis*, Vol. 1, No. 1, 8 (1948).

partially dissociative one, $CO_2 \rightleftarrows CO(a) + O(a)$, and for the completely dissociative one into three statistically independent atoms, $CO_2 \rightleftarrows C(a) + O(a) + O(a)$, as follows;

$$\frac{\theta}{1-\theta} = \frac{q^{CO_2(a)}}{p^{CO_2(a)}} \tag{1.1}$$

$$\frac{\theta}{1-2\theta} = \frac{q^{CO(a)}}{p^{CO(a)}} = \frac{q^{O(a)}}{p^{O(a)}} \tag{1.2}$$

$$\frac{\theta}{1-3\theta} = \frac{q^{C(a)}}{p^{C(a)}} = \frac{q^{O(a)}}{p^{O(a)}} = \frac{q^{O(a)}}{p^{O(a)}} \tag{1.3}$$

(3)

where θ is the covered fraction of the surface and $q^{CO_2(a)}$, $q^{CO(a)}$, $q^{C(a)}$ and $q^{O(a)}$ are the functions particular to the adsorbed states $CO_2(a)$, $CO(a)$, $C(a)$ and $O(a)$ expressed as,

$$q^{CO_2(a)} = \Pi (1 - e^{-\frac{h\nu_i}{kT}})^{-1} e^{-\frac{\varepsilon_0 + \frac{1}{2}h\Sigma\nu_i}{kT}}, \text{etc.} \tag{2.q}$$

and $p^{CO_2(a)}$, $p^{CO(a)}$, $p^{C(a)}$ and $p^{O(a)}$ are related with the chemical petentials $\mu^{CO_2(a)}$, $\mu^{CO(a)}$, $\mu^{C(a)}$ and $\mu^{O(a)}$ of $CO_2(a)$, $CO(a)$, $C(a)$ and $O(a)$ as,

$$\mu^{CO_2(a)} = -RT \log p^{CO_2(a)}, \text{ etc.} \tag{2.p(a)}$$

and p^{CO_2} with the chemical potential of gaseous carbon dioxide μ^{CO_2} and hence with the ordinary partition function Q and its concentration N as,

$$\mu^{CO_2} = -kT \log p^{CO_2} = -RT \log Q/N \tag{2.p}$$

At adsorption equilibrium we have

$$\mu^{CO_2} = \mu^{CO_2(a)} \tag{3.1}$$

$$\mu^{CO_2} = \mu^{CO(a)} + \mu^{O(a)} \tag{3.2}$$

$$\mu^{CO_2} = \mu^{C(a)} + \mu^{O(a)} + \mu^{O(a)} \tag{3.3}$$

respectively for the case when CO_2 molecule is undissociated, partially dissociated or completely dissociated at the adsorbed state. From Eqs. (1), (2) and (3) we have

$$\frac{\theta}{1-\theta} = \frac{N q^{CO_2(a)}}{Q} \tag{4.1}$$

$$\left(\frac{\theta}{1-2\theta}\right)^2 = \frac{N q^{CO(a)} q^{O(a)}}{Q} \tag{4.2}$$

$$\left(\frac{\theta}{1-3\theta}\right)^3 = \frac{N q^{C(a)} q^{O(a)} q^{O(a)}}{Q} \tag{4.3}$$

Eqs. (4.1), (4.2) and (4.3) are expressed further in terms of the measurable quantities such as the equilibrium pressure P and the differential heat of adsorption per mole $\Delta\varepsilon$ neglecting the contribution from the higher vibrational levels of gaseous carbon dioxide molecules and for the case $\theta \ll 1$ as[4]

$$\theta = \frac{q^{CO_2(a)} e^{T\frac{\partial \log q^{CO_2(a)}}{\partial T}}}{Q_0} Pe^{\frac{\Delta\varepsilon}{RT}} \tag{5.1}$$

$$\theta^2 = \frac{q^{CO(a)} q^{O(a)} e^{T\frac{\partial \log q^{CO(a)} q^{O(a)}}{\partial T}}}{Q_0} Pe^{\frac{\Delta\varepsilon}{RT}} \tag{5.2}$$

$$\theta^3 = \frac{q^{C(a)} q^{O(a)} q^{O(a)} e^{T\frac{\partial \log q^{C(a)} q^{O(a)} q^{O(a)}}{\partial T}}}{Q_0} Pe^{\frac{\Delta\varepsilon}{RT}} \tag{5.3}$$

where

$$Q_0 = kT \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{8\pi^2 IkT}{sh^2} e^{\frac{7}{2}}$$

The investigation of the factors

$$q^{CO_2(a)} e^{T\frac{\partial \log q^{CO_2(a)}}{\partial T}}, \text{ etc.}$$

in the above equations shows that every one of them is generally greater than 1 and approaches 1 as $h\nu_i \gg kT$. Assuming that the latter condition is fulfilled, we have

$$\left.\begin{matrix}\theta \\ \theta^2 \\ \theta^3\end{matrix}\right\} = P e^{\frac{\Delta\varepsilon}{RT}} / Q_0 \qquad \begin{matrix}(6.1) \\ (6.2) \\ (6.3)\end{matrix}$$

The above equations give relations between θ and P respectively appropriate to the three different adsorbed states affording a method of experimental determination of them.

Materials

Reduced Nickel.—1 g. of nickel oxide obtained by igniting the basic carbonate at 500° was thoroughly reduced at 350° similarly as described in the previous paper[4] under several cm. Hg hydrogen for several days keeping the catalyst from volatile matter which might be evolved from stop-cock grease by means of liquid air trap attached directly to the catalyst vessel. The reduced nickel powder thus prepared was then subjected to the adsorption experiment of carbon dioxide and thereafter to the determination of the surface area by B. E. T. method using nitrogen at liquid oxygen temperature and the surface area was found to be 20 m^2.

(3) The θ must be equal because of the stoichiometrical relation for CO(a) and O(a) or for C(a), O(a) and another O(a).

(4) *Cf.* Kwan, *J. Res. Inst. Catalysis*, Vol. 1, No. 2, 81 (1949).

Reduced Cobalt.—Reduced cobalt prepared by reducing 0.5 g. of cobalt oxide at 450° and once used for hydrogen adsorption was used again. The B. E. T. area of the catalyst was 7 m^2.

Reduced Iron.—Reduced iron prepared by reducing 2 g. of magnetite at 500° and once used for hydrogen adsorption and then for carbon monoxide adsorption as well was used again. The B. E. T. area of the catalyst was 4.2 m^2.

Carbon Dioxide.—Carbon dioxide was prepared by igniting sodium bicarbonte in an evacuated tube and traces of air and water vapors were removed by fractionation with liquid air.

Experimental Procedure

The apparatus and the general procedure for the measurement of adsorption equilibrium are identical with those of the previous paper.[4] After any of the reduced metal catalysts has been prepared, U-trap is surrounded by copper gauge filled with copper powder whose bottom being slightly dipped into liquid air, then the temperature of U-trap can be kept at about −60° avoiding the condensation of carbon dioxide inside the U-tube on one hand and freezing out traces of volatile matter from stop-cock grease on the other.

The catalyst is then evacuated by means of mercury diffusion pump for one hour at 350°, one hour at 400° and one hour at 500° for nickel, cobalt and iron respectively. The known quantity of carbon dioxide is then admitted into the reaction vessel, which is maintained at a desired temperature by the electric furnace through the U-trap and the decrease in pressure is followed by McLeod gauge. After letting it stand for about 20 hours the equilibrium pressure is determined both from adsorption and desorption side by lowering or raising the temperature of the furnace.

Adsorbed quantity x is given by

$$x = P_0V_0/RT - \alpha P,$$

where P_0V_0/RT is the quantity of carbon dioxide initially taken and P the equilibrium pressure. α is the constant depending on the temperature of the reaction vessel and is determined preliminarily keeping any part of the apparatus precisely the same but without a catalyst.

Additional portion of carbon dioxide is then succesively admitted and the corresponding equilibrium pressure is similarly determined in respective cases.

Results

Nickel.—The rate of adsorption and of desorption as well were found appreciably quick as was in the case of hydrogen adsoption on this catalyst, suggesting that adsorption equilibrium was instantaneously attained. Any of equilibrium pressures was however determined, after being left standing for about 20 hours, by approaching it both from adsorption and desorption side. Adsorption isotherms thus determined at 150° and 200° and at pressure ranging from 10^{-4} to 10^{-1} mm. Hg are shown by the plot of logarithm of the adsorbed quantities against logarithm of the equilibrium pressure in Fig. 1. As shown in

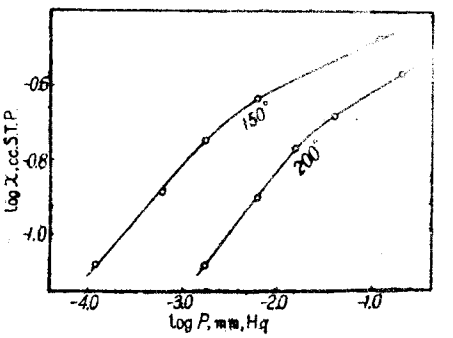

Fig. 1.—Adsorption isotherms of CO_2 on reduced nickel.

Fig. 1 the adsorbed quantity was found to be proportional to 1/3 power of the equilibrium pressure at the lower degree of adsorption, decreasing rapidly with increasing adsorption. It is apparent from the result that carbon dioxide adsorption takes place according to Eq. (6.3) viz. with completely dissociative adsorption at least in the lower pressure region.

Differential heat of adsorption $\Delta\varepsilon$ calculated from the isotherms according to the usual expression $\Delta\varepsilon = RT^2(\partial \log P/\partial T)_x$ was almost constant at 22 kcal./mole over the range of the smaller adsorption.

Using the heat of adsorption derived, the covered fraction θ_{calc} was now calculated at 200° according to Eqs. (6.1), (6.2) or (6.3) and compared in Fig. 2 with θ_{obs} derived from the adsorbed quantity and the B. E. T. area of the adsorbent assuming that 10^{15} nickel atoms per square centimeter were available and each atom was equally capable of adsorbing CO_2(a), CO(a), C(a) or O(a)[5].

It is obvious that θ_{obs} agrees fairly well with θ_{calc} derived from Eq. (6.3) and not with that from Eq. (6.1) or (6.2), hence showing that carbon dioxide molecule dissociates into three statistically independent atoms. Somewhat small value of θ_{calc} may be probably attributed to the simplification that $h\nu_i \gg kT$ in q's,

(5) In the case of undissociative or partially dissociative adsorption, θ_{obs} may be more or less different according as whether CO_2 (a) or CO (a) occupies how many atoms of nickel. But this would be rather ignored as far as three adsorbed states, mentioned above, concern whose θ_{calc} s in interest are much more differed with each other.

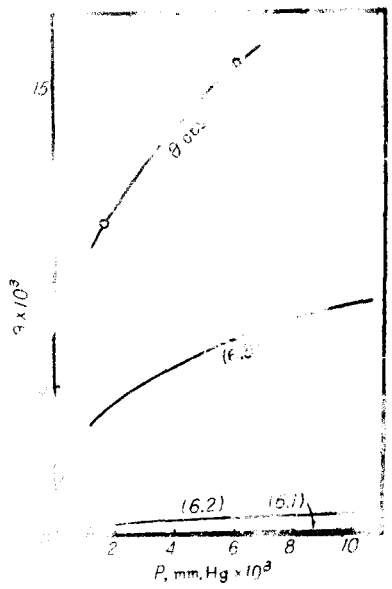

Fig. 2.—The relation between θ and P on reduced nickel, $T=200°C$.

although we have no available data with respect to ν_i's of C(a) or O(a).

In the case of the adsorbed hydrogen atom H(a) on reduced nickel, Horiuti and co-workers[6] obtained three vibrational frequencies by calculation as

$$417 \text{ cm.}^{-1} \quad 479 \text{ cm.}^{-1} \quad 1900 \text{ cm.}^{-1}$$

taking into consideration the potential of the surrounding nickel atoms upon the adsorbed hydrogen atom for the (110) plane.

On the basis of these values the calculation of the factor $q^{H(a)}e^{T\frac{\partial \log q^{H(a)}}{\partial T}}$ was carried out, affording 7, 5 and 2 at 300°, 200° and 20° respectively. The experimental facts on reduced nickel or cobalt[3] however revealed, as reported previously, that the above factor was approximately 1, giving no temperature effect below 300°. It seems likely that the assumption $h\nu_i \gg kT$ is not hold enough as far as the hydrogen adsorption on these catalysts concerns.

Reduced Cobalt.—Adsorption isotherms of carbon dioxide on reduced cobalt were determined similarly as those of reduced nickel at 0° and 40° and below 0.1 mm. Hg as shown in Fig. 3. The isotherms appear to obey nearly Freundlich's type in this case, probably missing such a lower degree of adsorption as proportional to 1/3 power of the equilibrium pressure.

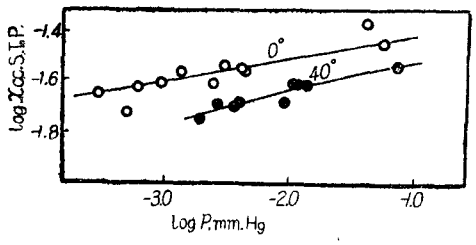

Fig. 3.—Adsorption isotherms of carbon dioxide on reduced cobalt.

Differential heat of adsorption calculated therefrom was found to be 14 kcal./mole. Using the heat of adsorption derived, θ_{calcs} were calculated at 0° similarly as in the case of nickel and were compared in Fig. 4 with θ_{obs} showing the satisfactory agreement of the latter with θ_{calc} derived from Eq. (6.3) at a very low degree of adsorption and θ_{obs} rapidly flattened with increasing adsorption.

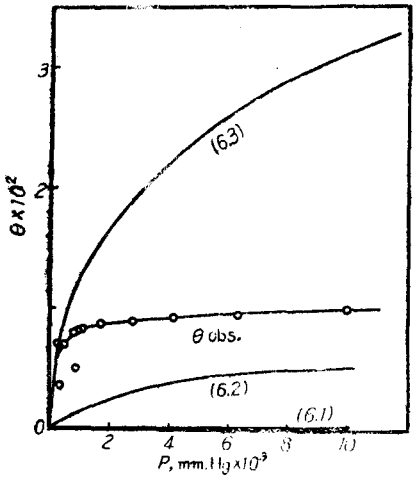

Fig. 4.—The relation between θ and P on reduced cobalt. $T=0°C$.

Reduced Iron.—The adsorption isotherms on reduced iron determined at 0° and 25° similarly as in the case of nickel or cobalt are shown in Fig. 5. Differential heat of adsorption calculated therefrom was found to be 15.5 kcal./mole at the lower degree of adsorption. The plot of the covered fraction θ_{obs} against the equilibrium pressure P in the present case lies without agreeing with any θ_{calc} given by Eqs. (6.1), (6.2), (6.3) as shown in Fig. 6, being more or less differed from the results given by the two catalysts cited above.

(6) Horiuti, Okamoto and Hirota, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **29**, 223 (1936).

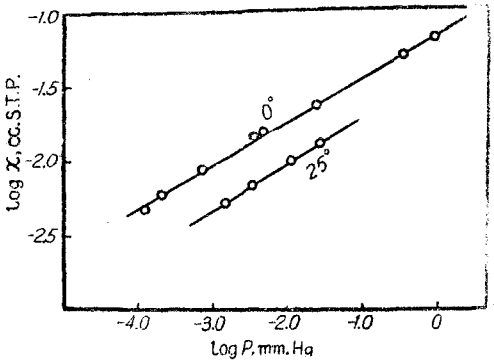

Fig. 5.—Adsorption isotherms of carbon dioxide on reduced iron.

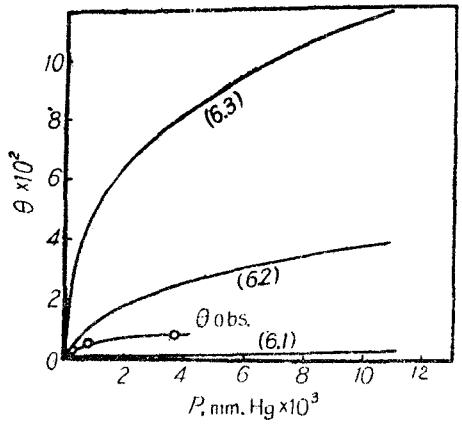

Fig. 6.—The relatien between θ and P on reduced iron. $T=0°C$.

It should be however remembered t' ·t the surface of the reduced iron is not homogeneous on the basis of the statistical mechanical investigation of hydrogen adsorption,[7] exposing at least two crystal planes. We hereby have to take into consideration quantitatively the extent of heterogeneity of the surface.

It is now assumed that two crystal planes 1 and 2 are exposed and every iron atom at the surface behaves physically identical even in the case of carbon dioxide adsorption, namely, the corresponding heats of adsorption of carbon dioxide $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ appear identically with those of hydrogen adsorption. The observed heat of adsorption of carbon dioxide $\Delta\varepsilon$ at a very low degree of adsorption would hence reveal $\Delta\varepsilon_1$ of the plane 1 provided that $\Delta\varepsilon_1 \gg \Delta\varepsilon_2$.

The ratio of $\theta_{obs.}$ to $\theta_{calc.}$ calculated statistical mechanically using the observed heat of adsorption $\Delta\varepsilon$ means the fraction of that "active" plane 1 as described in the previous paper, *i. e.*

$$\frac{\theta_{obs.}}{\theta_{calc.}} = \frac{N_1}{N_1+N_2}$$

where N_1 and N_2 are the numbers of iron atom respectively belong to the plane 1 and 2. N_1/N_1+N_2 is about 1/100 according to the previous investigation of this catalyst. Hence multiplying 100 to $\theta_{obs}/\theta_{calc}$ we find a better agreement between θ_{obs} and θ_{calc} derived from Eq. (6.3) with regard to the order of magnitude, leading to the same conclusion on the adsorbed state of carbon dioxide as in the case of nickel or cobalt.

Summary

Differential heat of adsorption of carbon dioxide on reduced nickel, cobalt or iron catalyst was determined by the indirect method at the lower degree of adsorption with particular precaution for securing thermodynamical equilibrium, being found at 22, 14 and 15,5 kcal. mole respectively. Using the heat of adsorption derived adsorption isotherms were investigated statistical mechanically with reference to the adsorbed state of carbon dioxide molecule, leading to the conclusion that the molecule dissociates into three statistically independent atoms in any case of the catalysts.

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(7) Kwan, *J. Res. Inst. Catalysis*, Vol. 1, No. 2, 100 (1949).