On the Adsorption of Carbon Monoxide on Platinum Catalyst

By Takao KWAN

(Received November 11, 1949)

For elucidating the mechanism of contact catalysis it is necessary to have the information on the adsorbed state of the reactant. As regard to that of hydrogen on the metallic catalysts the conclusive evidence has been obtained by many workers for the existence of hydrogen atoms on the surface of catalyst. As to the adsorbed state of the other reactants, only a few data are available even with such simple molecule as carbon monoxide or carbon dioxide.

Among these, carbon monoxide might be one of the most interesting reactant both from the fundamental and industrial points of view, because it yields by hydrogenation, and, notwithstanding the simple structure, it has such a variety of product at various conditions of the reaction as those of Fischer-Tropsch synthesis for hydrogenation, methanol synthesis etc.

With regard to the former reaction Kodama and co-workers(1) proposed from the kinetic investigation that carbide was formed by the dissociation of carbon monoxide into carbon and oxygen atom in contradiction to Craxford.(2)

According to Beeck and co-workers(3) who observed the relative amount of adsorption of various gases to that of carbon monoxide on nickel film found that the latter is twice as large as that of hydrogen, suggesting that carbon monoxide molecule as well as the dissociated hydrogen atom occupies one adsorption site on the surface or that carbon monoxide is adsorbed without dissociation.

The present author has previously investigated the adsorption of hydrogen on reduced nickel, cobalt and platinum and concluded, having recourse to the statistical mechanical method, that each of metal atoms on the surface of catalyst is equally capable of adsorbing a dissociated hydrogen atom.(4) Extending the latter conclusion it may be assumed that every metal atom at the catalyst surface behaves physically identical even in the case of carbon monoxide adsorption.

On the basis of the assumption the adsorbed state of carbon monoxide on platinum catalyst is investigated in the present work by the similar method by determining the adsorption isotherm with special precaution for the thermodynamical equilibrium.

Materials and Experimental Procedure

Carbon monoxide.—Carbon monoxide was prepared by dropping formic acid from a dropping funnel into an evacuated flask containing concentrated sulfuric acid at 90°~100° and passed through a trap immersed in liquid air and then stored in a reservoir which was beforehand highly evacuated.

Platinum black.—0.93 gram of platinum black once used for the hydrogen adsorption was used here again.

The apparatus and the procedure for measurement of the adsorption was quite the same as those described in the foregoing paper.(4)

Experimental Result

Measured quantity of carbon monoxide was admitted into the reaction vessel containing the platinum catalyst and maintained at a desired temperature. Although the adsorption rate was fairly rapid as in the case of hydrogen, the equilibrium pressure was determined about 20 hours after admission by approaching both from desorption and adsorption sides similarly as in the previous case. Typical result is shown in Fig. 1 by the plots of the observed pressure against time elapsed along with occasionally varied temperature shown by annexed figures.

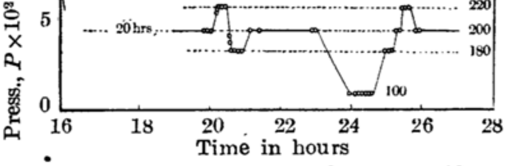

Fig. 1.—Reversibility of carbon monoxide adsorption on platinum catalyst.

After the equilibrium was thus attained and appropriate pressure read off additional portions of carbon monoxide were admitted successively into the reaction vessel and the corresponding equilibrium pressure were similarly determined in each case. The reversibility of the adsorption was assured over the whole range of adsorbed quantity although this was not the case with nickel or cobalt or iron at

---

(1) Matsumura, Kodama and Tarama, *J. Ind. Chem. Soc. Japan*, **42**, 42 (1940).

(2) Craxford, *Trans. Far. Soc.*, **35**, 946 (1939).

(3) Beeck, Smith and Wheelor, *Proc. Roy. Soc.*, **177**, 64 (1940).

(4) Kwan and Izu, "*Catalyst*", **4**, 22; 44 (1948). Kwan, *Jour. Res. Inst. Catalysis, Hokkaido Univ.*, Vol. 1, No. 2, 81 (1949).

a lower adsorbed quantity.(5)

Calculating now the adsorbed quantity from the equilibrium pressure and the known quantity of admitted gas, adsorption isotherms were worked out at 180°, 200°, 220°, 280° and 300° and at pressures lower than 1 mm. Hg. The result is shown in Fig. 2.

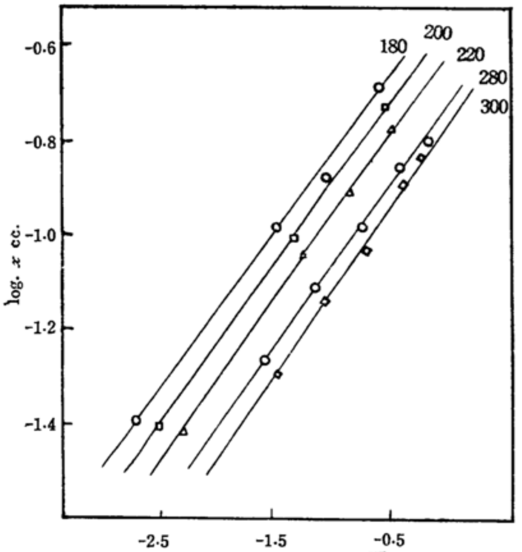

Fig. 2.—Adsorption isotherm of carbon monoxide on platinum black.

The observed isotherms were found to be expressed by the Freundlich's adsorption formulae as that,

$$x = CP^{1/n}, \qquad n = 2.7$$

where x is the adsorbed quantity and P the equilibrium pressure.

It was already reported that carbon monoxide decomposed readily into carbon and carbon dioxide in the presence of metallic catalysts,(5) but it has not taken place in the present case as shown by the following control experiment.

The U-tube connected directly to the reaction vessel and immersed into liquid air during the adsorption measurment was now dipped into an alcohol bath cooled at $-80°$. No pressure increase above that due to the relevant thermal expansion was observed, and it showed that the evolution of carbon dioxide and hence the appropriate decomposition may be practically ignored in the present case.

Differential heat of adsorption $\varDelta\mathcal{E}$ was derived from the usual expression,

$$\varDelta\mathcal{E} = RT^2\left(\frac{\partial \log P}{\partial T}\right)_x$$

separately from the isotherms at 280° and 300° on one hand and from those at 180°, 200° and 220° on the other hand inasmuch as the catalyst was treated with hydrogen at 350° between the observation of the former group of isotherms and that of the latter one and such procedure is known liable by experience to disturb the reproducibility of the catalyst's activity. The results are shown in Table 1.

Table 1

Heat of Adsorption of Carbon Monoxide on Platinum Catalyst (kcal./mole)

From isotherms at	x in cc.		
	0.039	0.063	0.100
200° and 300°	11	11	10
180°, 200° and 220°	11	11	10

As shown in Table 1 $\varDelta\mathcal{E}$ is affected neither by the temperature range at which it is determined nor by x within the experimental error.

Statistical Mechanical Treatment

Adsorption isotherm of diatomic molecule δ formed by atoms δ_1 and δ_2 is statistical mechanically derived introducing a set of function p, q and θ due to Horiuti(6) as follows:

$$\frac{\theta}{1-\theta} = \frac{q^{\delta(a)}}{p^{\delta(a)}} \qquad (1\cdot2)$$

$$\frac{\theta}{1-2\theta} = \frac{q^{\delta_1(a)}}{p^{\delta_1(a)}} = \frac{q^{\delta_2(a)}}{p^{\delta_2(a)}}{}^{(7)} \qquad (1\cdot2)$$

where $\delta(a)$ denotes the molecule δ, $\delta_1(a)$ and $\delta_2(a)$ dissociated atoms respectively at the adsorbed state.

At adsorption equilibrium we have that,

$$p^{\delta} = p^{\delta(a)} \qquad (2\cdot1)$$

or $$p^{\delta} = p^{\delta_1(a)}p^{\delta_2(a)} \qquad (2\cdot2)$$

respectively for the case when δ is undissociated at the adsorbed state. In the former case we have from Eqs. (1·1) and (2·1) as that,

$$\frac{\theta}{1-\theta} = \frac{q^{\delta(a)}}{p^{\delta}} \qquad (3\cdot1)$$

and in the latter as that,

$$\left(\frac{\theta}{1-2\theta}\right)^2 = \frac{q^{\delta_1(a)}q^{\delta_2(a)}}{p^{\delta}}. \qquad (3\cdot2)$$

Since p^{δ} is however denoted from its definition as that,

$$p = \frac{Q^{\delta}}{N^{\delta}} = \frac{kTQ^{\delta}}{P} \qquad (4)$$

where P is the pressure and Q the partition function, Eqs. (3·1) and (3·2) are now expressed respectively as that,

---

(5) Kwan and Izu, "Catalyst", 5, 43 (1949).

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

(7) The θ must be equal because of the stoichiometrical relation for δ_1 and δ_2.

$$\frac{\theta}{1-\theta}=\frac{q^{\delta(a)}P}{kTQ^{\delta}} \tag{5·1}$$

$$\left(\frac{\theta}{1-2\theta}\right)^2=\frac{q^{\delta_1(a)}q^{\delta_2(a)}P}{kTQ^{\delta}}. \tag{5·2}$$

Eqs. (5·1) and (5·2) are further transformed in a suitable form for calculation respectively as that,

$$\frac{\theta}{1-\theta}=q^{\delta(a)}\,e^{T\frac{\partial \log q^{\delta(a)}}{\partial T}}\,\frac{P}{Q_0{}^{\delta}}\,e^{\frac{\Delta\varepsilon}{RT}}{}^{(4)} \tag{6·1}$$

$$\left(\frac{\theta}{1-2\theta}\right)^2=q^{\delta_1(a)}q^{\delta_2(a)}\,e^{T\frac{\partial \log q^{\delta_1(a)}q^{\delta_2(a)}}{\partial T}}$$

$$\times\frac{P}{Q_0{}^{\delta}}\,e^{\frac{\Delta\varepsilon}{RT}} \tag{6·2}$$

where

$$Q_0{}^{\delta}=kT\frac{(2\pi mkT)^{\frac{3}{2}}}{h^3}\,\frac{8\pi^2IkT}{sh^2}\,(1-e^{\frac{-h\nu}{kT}})^{-1}e^{\frac{7}{2}}$$

h ; Planck constant,
k ; Boltzman constant,
s ; symmetry number,
m, I and ν ; mass, moment of inertia and fundamental frequency of gaseous molecule δ.
$q^{\delta(a)}$, $q^{\delta_1(a)}$ and $q^{\delta_2(a)}$; function particular to the adsorbed state of $\delta(a)$, $\delta_1(a)$ and $\delta_2(a)$ denoted as $q^{\delta_1(a)}=\prod^{i}(I-e^{-\frac{h\Sigma\nu_i}{kT}})^{-1}\times e^{-\frac{\varepsilon_0+\frac{1}{2}h\Sigma\nu_i}{kT}}$ etc. where $\nu_i's$ are frequency of normal vibration at the adsorbed state.

Taking now $\delta\equiv CO$ and assuming $h\nu\gg kT$ in $q's$ and hence

$$q^{\delta(a)}e^{T\frac{\partial \log q^{\delta(a)}}{\partial T}}=1,\quad q^{\delta_1(a)}q^{\delta_2(a)}e^{T\frac{\partial \log q^{\delta_1(a)}q^{\delta_2(a)}}{\partial T}}=1$$

the calculation of the covered fraction of the surface $\theta_{calc.}$ was carried out at 300° and at pressures 0.01 and 0.1 mm. Hg using the observed heat of adsorption 11 kcal. mole and the following molecular constants of carbon monoxide molecule respectively for Eqs. (6·1) and (6·2).

$$I=14.37\times10^{-40}\ \text{g. cm.}^{2\ (8)}$$

$$\nu=2168.89\ \text{cm.}^{-1(8)}$$

On the other hand the covered fraction of the surface $\theta_{obs.}$ was determined from the adsorbed quantity and the surface area of the catalyst, assuming that every platinum atom on the surface was equally capable of adsorbing carbon or oxygen atom.

The particle size of platinum black estimated by the observation of the diffuseness of the Debye-Scherrer pattern of the electron diffraction was found, as mentioned in the previous paper⁽⁴⁾, appreciably smaller than that given by B. E. T. method, although, in the case of nickel, the particle size estimated by either of the methods was found satisfactorily coincident with each other. Without inquiring into the above discrepancy $\theta_{obs.}$ was calculated on the basis of 280×10^4 cm.²/g. or the particle size 10 Å., due to the electron diffraction method as well as of 14×10^4 cm.²/g. due to B.E. T. method assuming that 10^{15} Pt atoms per square centimeter are capable of adsorbing each one carbon or oxygen atom. The results are shown together with those given by statistical mechanical calculation in Table 2.

Table 2

The Relation between the Equilibrium Pressure P and the Covered Fraction $\theta_{obs.}$ or $\theta_{calc.}$
$T=300°$ C., $\Delta\varepsilon=11$ kcal./mole.

θ	Remark	Equil. press. (mm.Hg)	
		0.01	0.1
$\theta_{calc.}$	$CO \rightleftarrows CO\ (a)$	10^{-12}	10^{-11}
	$CO \rightleftarrows C\ (a)+O(a)$	10^{-6}	3×10^{-6}
$\theta_{obs.}$	Electron diffraction	3×10^{-4}	7×10^{-4}
	B.E.T.	6×10^{-3}	10^{-2}

As seen from Table 2, the assumption of adsorbed state of CO(a) fails in accounting for the experimental result, whereas the assumption of the dissociated state into C(a) and O(a) gives the calculated values which are somewhat in accord with the observed values. In the case of undissociated adsorption, different values should be obtained for $\theta_{obs.}$, according as carbon monoxide occupies one or two Pt atoms, but the fact gives little modification to the above conclusion.

Conclusion is that carbon monoxide is adsorbed on platinum, being dissociated into carbon and oxygen atom.

The present author wishes to express his sincere thanks to the Director of the Institute, J. Horiuti, for his kind and valuable direction on this work. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

The Research Institute for Catalysis,
Hokkaido University,
Sapporo

---

(8) Sponer, "Molekulspektren", Berlin 1936.