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# CHEMISORPTION OF $CO_2$ OVER OXIDE CATALYSTS OF SPINEL TYPE*

By

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## Introduction

One question of interest to the study of chemisorption of gases on solid catalysts is whether chemisorbed particle remains molecule or dissociates into atoms at the surface. Except for simple diatomic molecules, little work has so far been done in this direction, for example, with carbon dioxide, ethylene and others. Even with such simple molecule as carbon monoxide its state at a metallic surface is not settled enough: BEECK, SMITH and WHEELER[1] found that the relative adsorption ratio of CO to $H_2$ on evaporated nickel films is 2/1, concluding that one CO molecule occupies one nickel atom at the surface. A similar investigation by RIDEAL and TRAPNELL[2] for the adsorption of CO and $O_2$ on evaporated tungsten films led them to suggest that CO is chemisorbed without dissociation.

Recent work by EISCHEN and WEBB[3] who studied the chemisorption of a gaseous mixture of $CO^{18}$ and $C^{13}O$ on reduced iron showed, however, that significant oxygen exchange occurred between two samples of carbon monoxide, i. e., $C^{13}O^{18}$ was present in the desorbing gas at temperatures as low as $-33°C$. The occurrence of the exchange reaction might be interpreted by postulating the dissociation of C—O bond at the surface. The dissociative mechanism for CO chemisorption on platinum has been claimed by KWAN[4] on the basis of statistical mechanical consideration.

The chemisorption of carbon dioxide was also investigated on reduced nickel by KWAN and FUJITA[5] with particular reference to the

* Partly presented at the *Conference on Catalysis* of the Chemical Society of Japan, Sapporo, Sept. 6-8, (1951).

1) O. BEECK, A. E. SMITH & A. WHEELER, Proc. Roy. Soc., A **177**, 62 (1940).

2) E. K. RIDEAL & B. M. W. TRAPNELL, Proc. Roy. Soc., A, **205**, 409 (1951).

3) R. P. EISCHEN & A. N. WEBB, J. Chem. Phys., **20**, 1043 (1952).

4) T. KWAN, J. Res. Inst. Catalysis, Vol. I, No. 2, 110 (1949).

5) T. KWAN & Y. FUJITA, Bull. Chem. Soc. Japan, **24**, 46 (1951).

degree of dissociation at the surface and it was concluded that carbon dioxide molecule was completely dissociated into three atoms. This conclusion was drawn from the following fact. Using the chemisorption heat of carbon dioxide evaluated from the chemisorption isotherms for a sparcely covered surface the fraction of surface covered $\theta$ was calculated from the expression,

$$\theta^n = \frac{P}{P_0} e^{\Delta\varepsilon/RT} \qquad (1)$$

where $n$ is 1 when the substrate molecule is undissociated at the surface and 2 or 3 respectively for the case when dissociated into 2 or 3 parts, $\Delta\varepsilon$ the chemisorption heat, $P$ the equilibrium pressure and $P_0$ a constant, being given for the present case as,

$$P_0 = kT \frac{(2\pi mkT)^{\frac{3}{2}}}{h^3} \frac{4\pi^2 IkT}{h^2} \prod^{i} (1-e^{-\frac{h\nu_i}{kT}})^{-1} e^{\frac{7}{2}}$$

The fraction of surface covered was also derived from the chemisorbed quantity of carbon dioxide and the Brunauer-Emmett-Teller surface area of the adsorbent assuming that each metal atom on the surface is equally capable of chemisorbing a dissociated particle and compared with the coverage given by eq. (1) respectively for three different chemisorbed states. It was found that much better agreement can be attained when completely dissociative chemisorption, that is, $n=3$ is postulated.

The present work was undertaken to investigate the degree of dissociation of carbon dioxide over several oxide catalysts of spinel type on the basis of the method described above.

## Experimental

### *Materials.*

**Copper Ferrite:** 1 normal KOH solution was added to a boiling solution containing a mixture of copper sulphate and ferric sulphate (1 : 1 in molar ratio). The precipitate was filtered off, washed and dried. The oxide was then ignited at 500°C in vacuum for a few weeks.

**Copper Chromite, Zinc Chromite:** Copper chromite, (or zinc chromite) was prepared by the method of ADKINS-CONNOR[6], i.e., concentrated ammonium hydroxide was added to a solution containing ammonium

6) H. ADKINS & R. CONNOR, J. Am. Chem. Soc., 53, 1901 (1930).

bichromate and copper nitrate (or zinc nitrate) (1 : 2 in molar ratio). The yellow precipitate was washed, dried and ignited. The resultant black oxide was then washed repeatedly with hot hydrochloric acid in the manner after GRÖGER[7] and washed with distilled water until the solution was free of chloride ion. The oxide was then ignited in vacuum similarly as the case of copper ferrite.

**Magnetite:** A slight reddish iron oxide was obtained by drying the precipitate from ferrous sulphate and ferric sulphate solution (1 : 1 in molar ratio) with ammonium hydroxide. The stream of hydrogen-water vapor mixture was then passed over the oxide at 500°C. The resultant black oxide was ignited in vacuum likewise.

In each case of oxide catalysts prepared in the above manner chemical analysis was carried out after the chemisorption measurements were made and proved that the composition was in accord with that of the stoichiometric proportion $Me^{II}O$-$Me^{III}_2O_3$ within the limits of experimental error. The X ray analysis of the oxide was also carried out, showing that it was of spinel structure.

**Carbon Dioxide:** Carbon dioxide was prepared by igniting sodium bicarbonate in an evacuated tube and purified by repeated fractional distillation by means of liquid air.

**Nitrogen:** Nitrogen, used for the B.E.T. surface area determination, was prepared by thermal decomposition of sodium azide in vacuum.

### *Apparatus and Procedure.*

The apparatus and the general procedure for the measurement of chemisorption of carbon dioxide have been described elsewhere.[5)8)]

## Results

Carbon dioxide was admitted over oxide catalysts which were in advance evacuated with a mercury diffusion pump for several hours at 500°C and then kept at the desired temperature. The chemisorption rate or the decrease in carbon dioxide pressure was found in all measurements to be immeasurably fast at the initial stage and then slowing down. Although no perceptible change in carbon dioxide pressure was occurred after a few hours, the pressure was always read off as the equilibrium allowing to stand for about 20 hours. Carbon

7) M. GRÖGER, Z. anorg. Chem., 76, 30 (1912).
8) T. KWAN, J. Res. Inst. Catalysis, Vol. 1, No. 2, 81 (1949).

dioxide was then successively introduced and the relevant pressure was read off likewise. Several points were taken further from higher to lower side of equilibrium pressure, evacuating a definite quantity of carbon dioxide from the adsorption vessel and found to overlap those of ascending run. Chemisorption isotherms were thus determined at pressures ranging from $10^{-3}$ to *ca.* 1 mm Hg in all cases and at temperatures 400, 350, 300 and 250°C for copper ferrite, 200, 150 and 100°C for copper chromite, 100 and 50°C for zinc chromite and 20 and 0°C for magnetite.

Any of chemisorption isotherms established above was found to obey FREUNDLICH's type, i.e., the plot of log of chemisorbed quantity against log of equilibrium pressure was nearly linear. Chemisorption heats of carbon dioxide $\Delta\varepsilon$ were evaluated from isotherms as usual for various quantities chemisorbed. These values are shown in Table I.

TABLE I. Chemisorption Heats of $CO_2$ for a Lower Coverage.

| Adsorbent | Wt. (gm.) | B. E. T. area ($M^2$) | Chemisorbed quantities of $CO_2$ (mole) | $\Delta\varepsilon$ ($\pm$0.5 kcal/mole) |
|---|---|---|---|---|
| $CuFe_2O_4$ | 4,2 | 210 | $1\times10^{-6}$ | 31 |
| | | | $4\times10^{-6}$ | 29 |
| $CuCr_2O_4$ | 1,0 | 43 | $1\times10^{-7}$ | 21 |
| | | | $2\times10^{-7}$ | 21 |
| $ZnCr_2O_4$ | 3,5 | 103 | $1\times10^{-6}$ | 16 |
| | | | $4\times10^{-6}$ | 16 |
| $Fe_3O_4$ | 6,0 | 65 | $4\times10^{-8}$ | 11 |
| | | | $8\times10^{-8}$ | 11 |
| | | | $2\times10^{-7}$ | 10 |

The fraction of surface covered was now calculated by means of eq. (1) using the isothermal heat for a lower coverage respectively for each case when $n=1$, 2 and 3 (denoting "$\theta_{calc}$"). On the other hand "$\theta_{obs}$" was evaluated, in any of oxide catalysts, by assuming that $5\times10^{14}$ metal ions or average numbers of metal ions per sq. cm. of the B. E. T. surface of the oxide are equally capable of chemisorbing each dissociated particle, and compared with "$\theta_{calc}$". The results are shown in Fig. 1–4 where any $\theta$ is plotted against equilibrium pressure $P$.

As is seen from the figures the $\theta_{calc}$ only when $n=2$ fits in satisfactorily the $\theta_{obs}$ in all cases. The results are thus in distinct contrast

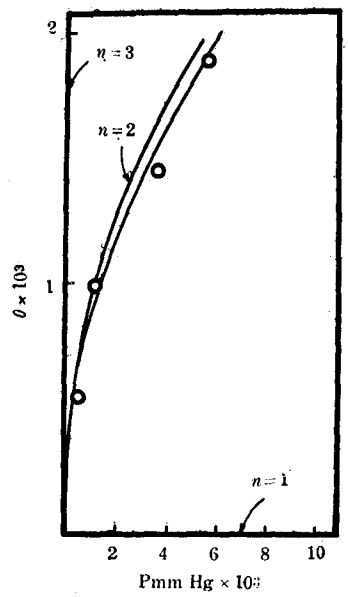


**Fig. 1.**
$CuFe_2O_4$–$CO_2$, T=300°C.
—— $\theta_{calc}$, -○- $\theta_{obs}$.

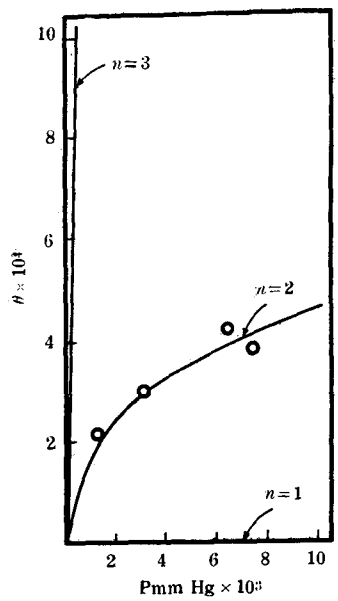


**Fig. 2.**
$CuCr_2O_4$–$CO_2$, T=200°C.

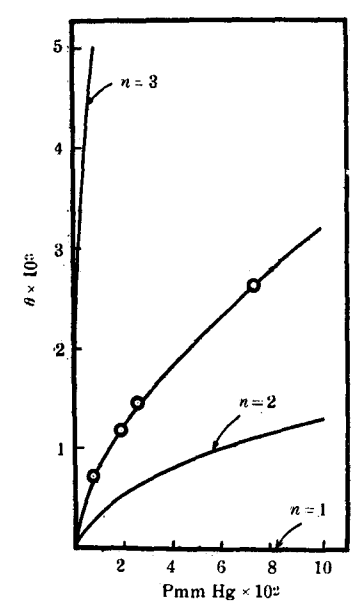


**Fig. 3.**
$ZnCr_2O_4$–$CO_2$, T=100°C.

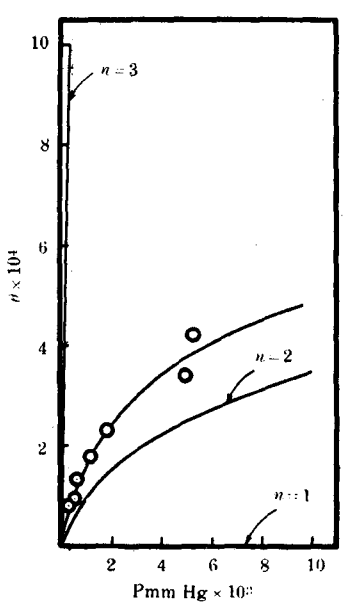


**Fig. 4.**
$Fe_3O_4$–$CO_2$, T=0°C.

to that for reduced nickel as previously reported. In Table II values of $\theta_{calc}$s and $\theta_{obs}$ are listed at a equilibrium pressure of 0,01 mm Hg and at a respectively given temperature.

TABLE II. $\theta_{calc}$ and $\theta_{obs}$ for $CO_2$ Chemisorption.
$P = 0{,}01$ mm Hg.

| Chemisorption on | $T$ °C | $\Delta\varepsilon$ kcal/mole | Number of chem. $CO_2$ molecules $cm^{-2}$ | Fraction of surface covered | | | |
|---|---|---|---|---|---|---|---|
| | | | | $\theta_{obs}$ | $\theta_{calc}$ | | |
| | | | | | $n=2$ | $n=1$ | $n=3$ |
| $CuFe_2O_4$ | 300 | 31 | $1{,}3\times10^{12}$ | $2{,}6\times10^{-3}$ | $2{,}8\times10^{-3}$ | $7{,}6\times10^{-6}$ | $1{,}9\times10^{-2}$ |
| $CuCr_2O_4$ | 200 | 21 | $2{,}3\times10^{11}$ | $4{,}6\times10^{-4}$ | $4{,}9\times10^{-4}$ | $2{,}4\times10^{-7}$ | $6{,}2\times10^{-3}$ |
| $ZnCr_2O_4$ | 100 | 16 | $4{,}5\times10^{11}$ | $9{,}0\times10^{-4}$ | $4{,}1\times10^{-4}$ | $1{,}7\times10^{-7}$ | $5{,}5\times10^{-3}$ |
| $Fe_3O_4$ | 0 | 11 | $2{,}5\times10^{11}$ | $5{,}0\times10^{-4}$ | $3{,}5\times10^{-4}$ | $1{,}2\times10^{-7}$ | $4{,}9\times10^{-3}$ |

From the data of Table II it goes that if we assume $n=1$ or 3 the $\theta_{calc}$ fails exclusively to account for the $\theta_{obs}$ in any catalyst whilst $\theta_{calc}$ corresponding to $n=2$ agrees with $\theta_{obs}$ within a factor of two which may arise from the uncertainty in magnitude of the isothermal heat ($\pm0.5$ kcal/mole) or in the number of adsorption sitesassumed.

## Conclusion

Quite apart from the numerical agreement between $\theta_{obs}$ and $\theta_{calc}$ for $n=2$, it seems very likely that carbon dioxide is chemisorbed with partial dissociation into two particles over oxide catalysts in interest, presumably into chemisorbed carbon monoxide and oxygen atom.

Acknowledgments.—We wish to thank Mr. T. MATSUI for obtaining X ray data referred to in this work, and our sincere thanks are also due to Prof. J. Horiuti, Director of Institute, for his valuable advice and suggestions.

## Summary

1. Chemisorption measurements have been made for carbon dioxide over several oxide catalysts with spinel structure.
2. The isothermal chemisorption heats of carbon dioxide for a sparcely covered surface were found to be 31, 21, 16 and $11\pm0.5$ kcal/mole respectively over $CuFe_2O_4$, $CuCr_2O_4$, $ZnCr_2O_4$ and $Fe_3O_4$.

3. By use of the chemisorption heat the fraction of surface covered was calculated statistical mechanically for each of completely dissociated, partially dissociated and undissociated chemisorption and compared with that given by the chemisorbed quantity and the B.E.T. surface area of the adsorbents.
4. Dissociative chemisorption of carbon dioxide into two parts was found to be in accord with the experiment in all cases.

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