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ON THE NONUNIFORM SURFACE NATURE OF ZINC CHROMIUM OXIDE CATALYST

By

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Introduction

Catalysts composed of zinc and chromium oxides, as have been well known, reveal a variety of catalytic activities sensibly depending on the mode of preparations and in particular on the proportions of the two constituents.¹⁾ According to SATO²⁾ the specific activities, *i. e.*, the activities per unit of surface area of the catalysts reach a maximum at 75 atomic % zinc toward the decomposition of methanol. A similar trend was also obtained by one of the present investigators³⁾; the specific rate of water-gas reaction, $H_2O + CO = H_2 + CO_2$, over the catalyst containing 50 atomic % zinc was far more active than those of 33 atomic % zinc or zinc oxide alone.

With a binary oxide catalyst it would be sometimes expected that two constituents react to form solid solution or some mixed crystals. In a previous paper⁴⁾ dealing with binary oxides KWAN and FUJITA led to the result, however, that the surface of zinc chromium oxide catalyst containing $1ZnO + 1Cr_2O_3$, which was prepared by co-precipitation and found to form a spinel structure, is uniform for the chemisorption of carbon dioxide. This was due to the fact that the fraction of surface covered, " θ_{cat} ", derived from the expression*

$$\theta^2 = P/P_0 \exp(\Delta\varepsilon/RT) \quad (1)$$

well fits " $\theta_{o.s.}$ " obtained from the chemisorbed quantities of carbon dioxide and the B. E. T. surface area of the catalyst. Here, $\Delta\varepsilon$ is the

1) J. R. HUFFMAN, B. F. DODGE, *Ind. Eng. Chem.*, **21**, 1056 (1929).

D. S. CRYDER, P. K. FROLICH, *ibid.*, **21**, 867 (1929).

2) T. SATO, Presented at the Japan Chem. Soc. Meeting (1951).

3) T. KWAN, Unpublished.

4) T. KWAN, Y. FUJITA, *J. Res. Inst. Catalysis*, **2**, 110 (1953).

*) As regards the derivation of the eq. (1) and its use, see T. KWAN, Y. FUJITA, *Bull. Chem. Soc. Japan*, **24**, 46 (1951).

heat of chemisorption of carbon dioxide, P the pressure and P_0 a constant.

In conjunction with these studies the chemisorption of carbon dioxide was investigated further over a binary oxide catalyst in the composition of $2ZnO+1Cr_2O_3$ and also over zinc oxide alone. Thus, an information relating to nonuniform surface nature of the binary oxide catalyst has been obtained, the results of which are here reported.

Experimental

$2ZnO + 1Cr_2O_3$.—The binary oxide in the composition of $2ZnO+1Cr_2O_3$ was prepared by the method of ADKINS-CONNOR⁵⁾; concentrated ammonium hydroxide was added to a solution containing ammonium bichromate and zinc nitrate (1:2 in molar ratio). The yellow precipitate was washed, dried and finely ground. This was carefully calcined in a casserole. The resultant black oxide was then ignited at 500°C in vacuum for a few weeks. Chemical analysis proved the sample to contain about 50 atomic % zinc. The B. E. T. surface area was 32 m² per g.

$1ZnO + 1Cr_2O_3$.—To obtain the binary oxide catalyst in the composition of $1ZnO+1Cr_2O_3$ the above oxide was washed repeatedly with 6*N* hot hydrochloric acid in the manner substantially the same as that used by GRÖGER.⁶⁾ This was zinc chromite catalyst with which chemisorption works for carbon dioxide have been published elsewhere⁷⁾.

ZnO .—Ammonium carbonate solution was added to a dilute solution of zinc nitrate (commercial sample in the highest grade). The precipitate was filtered off and calcined at 500°C in an atmospheric air for about 10 hours. The resultant oxide was then degassed by means of an oil diffusion pump at 500°C for several days until reproducible results for the chemisorption of carbon dioxide were reached. A spectroscopic analysis indicated a purity of 99.9%, with the principal impurities being *Fe*. The B. E. T. surface area was 6.2 m² per g. The apparatus and technique used in carrying out the measurement of carbon dioxide chemisorption was quite the same as that described previously.⁷⁾

5) H. ADKINS, R. CONNOR, *J. Am. Chem. Soc.*, **53**, 1901 (1930).

6) M. GRÖGER, *Z. anorg. Chem.*, **76**, 30 (1912).

7) T. KWAN, *J. Res. Inst. Catalysis*, **1**, 81 (1949).

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

Chemisorption of Carbon Dioxide on the Binary
Oxide $2ZnO + 1Cr_2O_3$

Chemisorption isotherms of carbon dioxide on the binary oxide catalyst in the composition of $2ZnO + 1Cr_2O_3$ were determined in the temperature range 300–400°C and at pressures from 0.0001 to ca. 0.1 mm. mercury. These isotherms are shown in terms of logarithm of chemisorbed quantities against logarithm of equilibrium pressures in Fig. 1. The differential heat of chemisorption of carbon dioxide derived usually from the isotherms was found to be almost constant at 43 ± 1 kcal./mole in the region of chemisorption investigated.

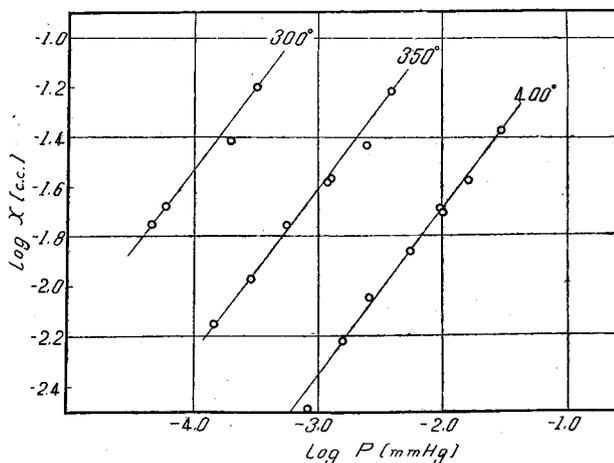


Fig. 1.

Chemisorption isotherms of carbon dioxide on zinc chromium oxide. ($2ZnO + Cr_2O_3$) (4.0 g., 129 M²).

Substituting this value of chemisorption heat for $\Delta\epsilon$ in eq. (1), the fraction of surface covered or θ_{calc} was calculated at 400°C and compared with θ_{obs} given by the chemisorbed quantities of carbon dioxide and the B. E. T. surface area of the adsorbent at pressures 0.01 and 0.001 mm. mercury in Table I.

As can be seen from the data of Table I θ_{calc} appears to disagree with θ_{obs} , being about 40 times greater than the latter. The result is hence markedly contrasted with the case of $1ZnO + 1Cr_2O_3$ catalyst where the ratio of θ_{obs} to θ_{calc} was found to be almost unity.

TABLE I.
 θ_{calc} and θ_{obs} on $2\text{ZnO} + 1\text{Cr}_2\text{O}_3$ catalyst
 $T = 400^\circ\text{C}$.

P (mm. Hg)	θ_{calc}	θ_{obs}	$\theta_{\text{obs}}/\theta_{\text{calc}}$
0.01	2.9×10^{-2}	8.8×10^{-4}	0.03
0.001	9.1×10^{-3}	1.9×10^{-4}	0.02

Chemisorption of Carbon Dioxide on ZnO

Chemisorption isotherms of carbon dioxide on zinc oxide were determined similarly as the case of the binary catalyst at temperatures ranging from 350 to 500°C and at pressures below several mm. mercury. It was found that the outgassing of zinc oxide at 500°C gives rise to an increase of the chemisorption of carbon dioxide to an extent. The adsorbent was therefore repeatedly outgassed until reproducible results for the chemisorption of carbon dioxide could be reached. The log-log plots of chemisorption isotherms thus determined are shown in Fig. 2.

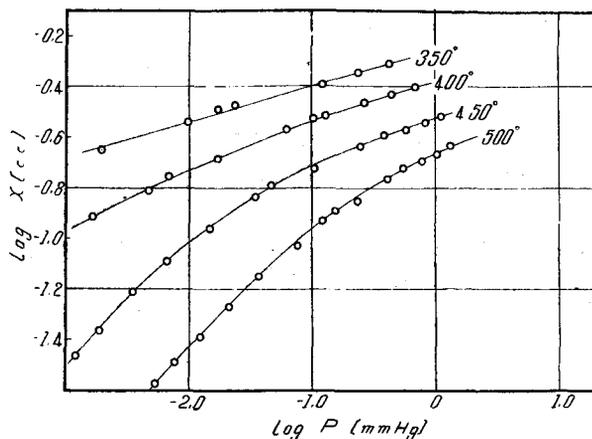


Fig. 2.
 Chemisorption isotherms of carbon dioxide on
 zinc oxide. ($3.7 \text{ g. } 23 \text{ M}^2$).

The chemisorption heat of carbon dioxide derived from the isotherms for a lower surface coverage was found to be $44 \pm 1 \text{ kcal./mole}$. This value is in good agreement with that on the binary oxide catalyst

within the limit of experimental error.

Substituting the value of chemisorption heat for $\Delta\varepsilon$ in eq. (1) θ_{calc} was similarly calculated and compared with θ_{obs} at equilibrium pressures of 0.01 and 0.001 mm. as shown in the accompanying Table II.

TABLE II.
 θ_{calc} and θ_{obs} on ZnO
 $T = 400^\circ\text{C}$

P (mm. Hg)	θ_{calc}	θ_{obs}	$\theta_{\text{obs}}/\theta_{\text{calc}}$
0.01	0.043	0.044	1.0
0.001	0.014	0.024	1.7

The last column of Table II indicates that θ_{calc} is reasonably coincident with θ_{obs} .

Electron Diffraction or X-ray Analysis of Zinc Chromium Oxide

The electron diffraction investigation of $2ZnO+1Cr_2O_3$ catalyst and also of $1ZnO+1Cr_2O_3$ for comparison was made respectively after the chemisorption experiments were finished. The diffraction patterns of these oxides are illustrated in Fig. 3b and 3c respectively. It can be shown from the figures that both patterns agree with the data required for zinc chromite with spinel structure and in the former that there is no indication of patterns characteristic of zinc oxide in spite of the presence of an excess zinc oxide. An application of X-ray diffraction to the oxide containing $2ZnO+1Cr_2O_3$, however, indicated that zinc oxide does exist, as verified by the diffraction photograph in Fig. 3d. The results hence suggest that zinc chromite particles are abundant in the surface of the binary oxide. Such structural features might be judged from the electron micrograph of this oxide as given by Fig. 3a.

Discussion

It should be especially remarked that the heat of chemisorption of carbon dioxide over $ZnO-ZnCr_2O_4$, allowing now to write the composition in this way on the basis of the X-ray investigation, agrees with



Fig. 3 a.

Electron micrograph of zinc chromium oxide in the composition of $2ZnO+1Cr_2O_3$ ($\times 30,000$).

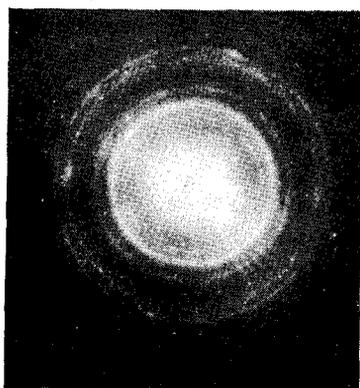


Fig. 3 b.

Electron diffraction patterns of zinc chromium oxide ($2ZnO+1Cr_2O_3$).

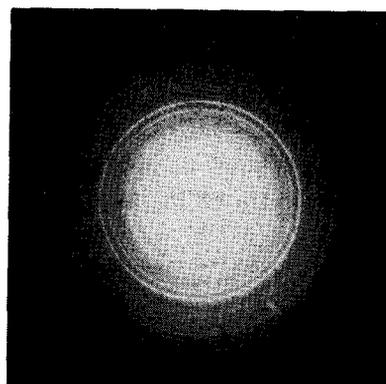


Fig. 3 c.

Electron diffraction patterns of zinc chromium oxide ($1ZnO+1Cr_2O_3$).

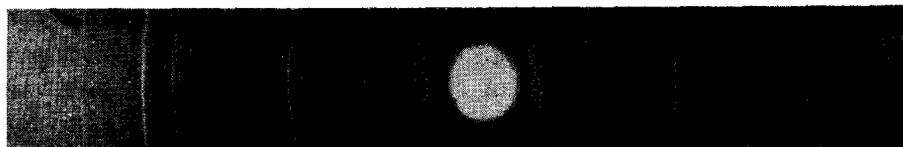


Fig. 3 d.

X-ray diffraction patterns of zinc chromium oxide ($2ZnO+1Cr_2O_3$).

that on ZnO alone. We, therefore, incline to a view that carbon dioxide chemisorption on the binary oxide catalyst $ZnO-ZnCr_2O_4$ is occurring exclusively on the surface of the component ZnO exposed to some extent toward gas phase. Another area of the surface of the binary oxide must expose zinc chromite, $ZnCr_2O_4$, which does not favour the chemisorption of carbon dioxide because of so small chemisorption heat as amounting to 16 kcal./mole.⁴⁾ Indeed, the chemisorption of carbon dioxide on zinc chromite was found immeasurably small under which conditions chemisorption of carbon dioxide was readily observed over zinc oxide-zinc chromite, $ZnO-ZnCr_2O_4$.

Assuming now that carbon dioxide chemisorption on $ZnO-ZnCr_2O_4$ catalyst is occurring preferentially on the side of ZnO surface, the values of θ_{calc} or θ_{obs} obtained above may be re-examined below.

The value of θ_{calc} given in Table I in regard to $ZnO-ZnCr_2O_4$ should signify a coverage of carbon dioxide on the surface of zinc oxide which is the component part of the binary oxide, and by reason of the fact of Table II this can be identified with θ_{obs} or x/n_1 where x is the chemisorbed quantity of carbon dioxide and n_1 the number of chemisorption sites on zinc oxide.

The value of θ_{obs} , however, is dependent of the B. E. T. surface area of $ZnO-ZnCr_2O_4$ catalyst and would probably be expressed by $x/(n_1+n_2)$ where n_2 is those on zinc chromite.

The ratio of θ_{obs} to θ_{calc} with $ZnO-ZnCr_2O_4$ catalyst is now given by

$$\frac{\theta_{obs}}{\theta_{calc}} = \frac{n_1}{n_1+n_2} = 0.02\sim 0.03$$

The conclusion is, therefore, that zinc oxide in the binary oxide catalyst $ZnO-ZnCr_2O_4$ exposes merely 2~3% of the B. E. T. surface area of the catalyst.

Since the B. E. T. surface area of zinc oxide by itself is appreciably less than that of zinc chromite (30 m² per g.) the very low area for zinc oxide on the surface of $ZnO-ZnCr_2O_4$ catalyst may be principally attributable to its ready sintering. Anyhow, the present investigation indicates that the zinc chromium oxide catalyst containing 50 atomic % zinc exposes the component zinc oxide only by a few % of the total surface area.

The binary oxide catalyst containing 75 atomic % zinc which is the most efficient of various compositions in many catalytic reactions and

gives, according to SATO⁸⁾, the electron diffraction patterns none other than those characteristic of zinc oxide and zinc chromite would expose more surfaces toward zinc oxide.

Although we are not yet in a position to understand the detailed mechanism of the high catalytic activities of the zinc and chromium oxide catalysts it seems probable that the activity is linked with the cooperative actions of two surfaces exposed without any predominance.

The binary oxide catalysts prepared by HÜTTIG *et al.*⁹⁾ by heating two oxides, for example $1ZnO$ and $1Cr_2O_3$, for different high temperatures exhibit various catalytic activities toward the decomposition of methanol, intermediate states from an oxide mixture to a spinel being, accordingly, linked with high activities. The superiority of the so-called intermediate states might be reduced to a similar basis as the "two surfaces" in the sense of the present investigation conduct catalytic activities.

The authors wish to express their sincere thanks to Professor J. HORIUTI for his valuable advice and suggestions and also to Mr. T. MATSUI for obtaining electron or X-ray diffraction data referred to in this work. They are also indebted to Mr. KAGAYA for his assistance throughout the work.

Summary

1. Chemisorption measurements for carbon dioxide have been made over zinc chromium oxide containing 50 atomic % zinc and zinc oxide alone respectively in the region of low surface coverage.
2. The chemisorption heat of carbon dioxide on the zinc chromium oxide was found to be almost coincident with that on zinc oxide.
3. The X-ray investigation of the zinc chromium oxide indicated that this binary oxide is composed of zinc chromite and zinc oxide.
4. Analysing the chemisorption data for the zinc chromium oxide with reference to that of zinc oxide, it has been shown that the surface of the zinc chromium oxide contains an excess of zinc chromite, zinc oxide being exposed merely by 2~3 % of the total surface.

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8) T. SATO, Rep. Gov. Chem. Ind. Res. Inst. Tokyo 46, 433 (1952).

9) G. F. HÜTTIG, *et al.*, Kolloid Z., 68, 258 (1934) and later papers.