confirm the existence of the silvery CeC reported by Warf.[4] Several high carbon Ce–C and La–C alloys were examined in an attempt to confirm the existence of CeC_3 reported by Warf.[4] Microscopic examination and chemical and X-ray analyses show that alloys near the tricarbide composition (either quenched or slow cooled from the molten state) contain only free carbon and the rare earth dicarbide. It is possible that the presence of hydrogen in Warf's method of preparation may be the cause of this difference.

Hydrolytic Studies.—Investigation of gases liberated when various carbides react with water or dilute acids is in progress in this Laboratory. Examination of the R_3C indicates that the carbon atoms are approximately 3.5 Å. apart if carbon atoms occupy adjacent octahedral holes and, therefore, one would expect these compounds to form methane and hydrogen gas on hydrolysis. Mass spectrometric analysis of the gases liberated upon hydrolysis shows that only methane and hydrogen are formed, indicating that the R_3C compounds are methanides. Both the R_2C_3 and RC_2 compounds may be classified as acetylides, although they do not yield pure C_2H_2. The La_2C_3 yields approximately 50% C_2H_2, compared to 70% for LaC_2, and the amount of hydrogen liberated by the former is 2.5 times that of LaC_2. It is also significant that some C_3H_x (x = 4, 6 and 8) hydrocarbons are formed only from La_2C_3. The relative amounts of hydrogen liberated can be explained if one assumes that $C_2^=$ anions are formed and the extra La valence electrons contribute to the conduction band. For the sesquicarbide the number of conducting electrons per La atom is 1.5 and 1.0 for the dicarbide. Since the number of valence electrons per atom in the conduction band is related directly to the amount of hydrogen liberated, one would expect a higher yield of hydrogen for La_2C_3, and this is what is observed. The relative amount of C_2H_2 liberated can be explained by the number of $C_2^=$ groups per La atom. There is 1.0 group per La for LaC_2 and 0.75 for La_2C_3 and, therefore, the dicarbide would be expected to liberate more C_2H_2, which it does. Hydrolytic studies of YbC_2 show a slight increase in the amount of C_2H_2 and the absence of H_2 compared to LaC_2. The results of these hydrolytic studies and the fact that the lattice parameters of YbC_2 are abnormally small would indicate that YbC_2 is probably more closely related to the alkaline earth metal dicarbides than to the rare earth dicarbides. Similarities between the alkaline earth metals and ytterbium, and some of their compounds have been noted in other studies.

Acknowledgments.—The authors wish to thank Mr. N. Driscoll who gave much assistance in measuring films and performing calculations. Acknowledgment is also due Messrs. D. H. Dennison, C. Habermann and G. Wakefield who supplied most of the rare earth metals used in this research and also to Dr. H. Svec and Mr. J. Capellan who performed the gas analyses of the hydrolytic products.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF APPLIED CHEMISTRY, FACULTY OF ENGINEERING, UNIVERSITY OF TOKYO]

Exchange of Oxygen Atoms among Carbon Dioxide, Carbon Monoxide and Oxide Catalysts of Spinel Type

BY YUKIO YONEDA, SHOJI MAKISHIMA AND KATSUYOSHI HIRASA

RECEIVED NOVEMBER 12, 1957

The exchange of ^{18}O between CO_2, CO and oxide catalysts of the spinel type, *i.e.*, $ZnAl_2O_4$, $ZnCr_2O_4$ and $ZnFe_2O_4$, has been studied at 200–450°. (Attention was paid especially to the incorporation of ^{18}O to the surface layers of oxide.) Two mechanisms were proposed for the exchange reaction: at low temperatures ($T < 250°$), CO_2 exchanges its oxygen atom with oxide through the carbonate-formation mechanism I, $CO_2 + O_s^= \rightleftarrows CO_3^=$, without its dissociation into CO and an oxygen atom and without the participation of CO in the reaction; at high temperature ($T > 250°$), ^{18}O is transferred to CO from CO_2 through the oxide catalyst by the oxidation–reduction mechanism II, $CO + (K)O \rightleftarrows CO_2 + (K)$. The oxide catalysts are oxidized ($ZnAl_2O_4$) or reduced ($ZnCr_2O_4$ and $ZnFe_2O_4$) at high temperatures, although the rate of the exchange reaction is larger than that of the reduction or oxidation of the catalyst by at least several powers of ten; this is the difference between the rates of the forward and reverse reactions in mechanism II. The surface state of the catalysts is discussed.

Introduction

Today the catalyst is not considered as a *field* for a catalytic reaction, but rather as one of the *reactants*. The modern theory of solid state physics and isotope techniques can contribute to the elucidation of the mechanism by which the catalyst participates in a reaction.

The isotopic exchange reaction between carbon monoxide and dioxide has been studied by several authors[1-3] at high temperatures on rather inactive catalysts. They used ^{13}C or ^{14}C as the tracer, because the exchange of oxygen atoms between the gas phase and the catalyst, which was observed at about 900° on a silica surface, might complicate the measurement of the true rate of the exchange between the gaseous components.[1] Kul'kova, *et al.*,[4] also studied this exchange on a magnetic oxide catalyst with ^{18}O as the tracer. They did not take into consideration the exchange between the gaseous components and the solid catalyst, although they observed such an exchange at low temperatures.

In this paper we shall discuss the principal features of the exchange of oxygen atoms between the gaseous components and the oxide catalyst.

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[1] J. D. Brandner and H. C. Urey, *J. Chem. Phys.*, **13**, 351 (1945).

[2] T. H. Norris and S. Ruben, *ibid.*, **18**, 1595 (1950).

[3] T. Hayakawa, *Bull. Chem. Soc. Japan*, **26**, 165 (1953).

[4] N. V. Kul'kova, Z. D. Kuznets and M. I. Temkin, *Doklady Akad. Nauk*, **90**, 1067 (1953).

Experimental

Materials.—Three oxide spinels, $ZnAl_2O_4$, $ZnCr_2O_4$ and $ZnFe_2O_4$, were prepared by the solid phase reaction at high temperature between appropriate pairs of simple oxides. The starting materials were of A.R. purity. Chromia was prepared as follows: chromic hydroxide, precipitated from chromic sulfate solution with ammonium hydroxide, was dissolved in nitric acid and reprecipitated; this hydroxide was heated at 900° for 2 hr. to give chromia.

$ZnAl_2O_4$ was obtained by heating a stoichiometric, well-ground mixture of zinc oxide and alumina at 1100° for 5 hr. X-Ray diffraction analysis showed that several per cent. of the raw material was unchanged. The slightly bluish tint suggests the presence of defects, possibly of F′-centers. $ZnCr_2O_4$ and $ZnFe_2O_4$ were prepared similarly; the former was heated at 1100° for 9 hr. and the latter for 2 hr. at 930° and then 2 hr. of heating at 1000°. X-Ray diffraction analysis showed that the solid reaction was complete. $ZnCr_2O_4$ and $ZnFe_2O_4$ were grayish brown and reddish brown, respectively.

Two batches of carbon dioxide, containing 0.423 or 0.456% ^{18}O, were prepared by equilibrating ordinary carbon dioxide with water, enriched in ^{18}O, at room temperature. Carbon monoxide was produced by dehydration of formic acid which had been thoroughly evacuated. Carbon dioxide and water were removed through a train of phosphorus pentoxide, granular potassium hydroxide and a trap at −78°.

Exchange Reaction System.—The reaction system is outlined in Fig. 1. R is a reaction bulb, made of borosilicate glass, the volume of which is 55 cc.

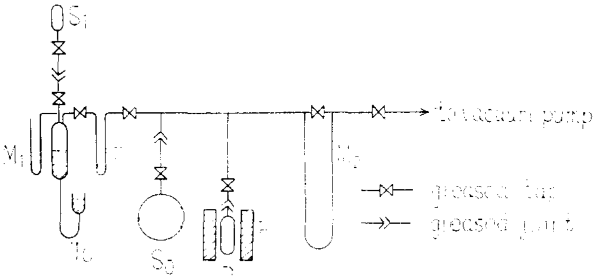

Fig. 1.—Exchange reaction system: M_1, M_2, mercury manometer; R, reactor bulb; S_0, reservoir; S_1, gas sampling pipet; To, Toepler pump; F, furnace; T, trap (liquid air).

Procedures.—The exchange reaction was studied by the static method.

(A) Exchange between Carbon Dioxide and Catalysts.—A weighed amount of catalyst, the apparent volume of which was *ca.* 0.5 cc., was placed in bulb R and outgassed for 2 hr. at 400° and 10^{-3} mm. The enriched carbon dioxide (^{18}O = 0.423%) was introduced so that p_{CO_2} was 40 mm. After 15 minutes, the bulb was cooled rapidly by removing the furnace. A gas sample collected in S_1 through the Toepler pump, To, was analyzed by the mass spectrometer.

(B) Exchange among Carbon Dioxide, Carbon Monoxide and Catalysts.—The amount of catalyst and the degassing procedure were the same as in (A). The furnace was then rapidly adjusted to give the appropriate temperature; the reaction was studied at temperatures ranging from 200–450°. A known amount, usually *ca.* 2.5 cc. (N.T.P.), of the gas mixture containing enriched carbon dioxide (^{18}O = 0.456%) and unlabeled carbon monoxide in a ratio of 1.04:1.00 was introduced into bulb R; the initial pressure of the gas mixture was *ca.* 35 mm. After 15 minutes, the bulb was cooled rapidly and the gas transferred to To through the cold trap T kept at −183°. After the carbon dioxide was frozen in T, the quantity of carbon monoxide collected in To was measured with manometer M_1. The sample of carbon monoxide, free from carbon dioxide, was transferred to S_1 and analyzed by the mass spectrometer. The quantity and isotope content of the carbon dioxide were measured in the same way. From the values thus obtained, the ratio of the two components of the gas mixture after the reaction was calculated.

Isotopic Analysis.—The mass spectrometer employed was Model 21-103A of Consolidated Electrodynamics, Inc. Abundances in CO_2* and CO* (free from carbon dioxide) were measured from the height of 44/46 and 28/30, respectively, since the contribution of ^{13}C or ^{17}O was negligible in this case. The accuracy of the values was ±2%.

Measurement of Surface Area.—The surface area was measured by the B.E.T. method, in which carbon dioxide at −78° was employed as the adsorbate. The areas of the catalysts are given in Table I; the method is not very accurate for areas smaller than 0.5 m.²/g.

TABLE I

EXCHANGE OF OXYGEN ATOMS BETWEEN CARBON DIOXIDE AND CATALYST AT 400°, EXPERIMENT A

Catalyst	$ZnAl_2O_4$	$ZnCr_2O_4$	$ZnFe_2O_4$
Weight of catalyst, (g).	0.645	0.615	1.015
Surface area, (m.²/g.)	8.5	0.8	0.1[a]
Atomic % of ^{18}O in CO_2 after reaction, α (%)	0.345	0.404	0.400
^{18}O transferred to catalyst, ($\times 10^{-8}$ g. atom/m.²)	3.7	10	59
Exchangeable surface oxygen, n_s ($\times 10^{-5}$ g. atom/m.²)	2.6	5.0	30
No. of exchangeable layers	1.3	2.5	15

[a] Not very accurate value.

Results and Discussions

(A) Exchange between Carbon Dioxide and Catalysts.—The experimental results are summarized in Table I. The quantity of oxygen which is exchangeable per unit surface area of the catalyst, n_s,[5] is estimated from the atoms of ^{18}O transferred to the catalyst divided by the excess atomic fraction of ^{18}O in the gaseous phase over its natural abundance, $(\alpha - 0.204) \times 10^{-2}$; it is assumed that there is isotopic equilibration between the ambient gas and a certain number of surface layers of the oxide. Assuming the lattice constant of these spinels to be 8.3 Å., a reasonable value, one obtains for the density of oxygen atoms in the surface the value 2×10^{-5} g. atom/m.². Then from this value and n_s we can calculate the number of exchangeable layers, *i.e.*, the average number of the net-planes of oxygen atoms which are able to exchange with the gaseous components (Table I).

Table I shows that the incorporation of oxygen atoms takes place to a considerable extent in $ZnFe_2O_4$ but to only a slight extent in $ZnAl_2O_4$. This might be explained by the difference of Tammann temperatures of the spinels. As the melting points of these spinels were not measured, we have used those of the appropriate simple oxides. The exchange of ^{18}O was found to vary inversely with the melting point of the oxide: alumina (2025°), chromia (1990°) and ferric oxide (1565°). The exchange is attributable to the carbonate-formation mechanism which is discussed below.

(B) Exchange among Carbon Dioxide, Carbon Monoxide and the Catalysts.—The experimental results are presented in Figs. 2–4. In this series of experiments, the oxygen atoms in carbon dioxide were exchanged with those in the oxide catalysts and carbon monoxide. The decrease of the atomic fraction of ^{18}O in carbon dioxide and its increase in carbon monoxide are presented in Figs. 2 and 3, respectively. The CO_2/CO ratio was altered by

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[5] This definition is slightly different from that of G. Houghton and E. R. S. Winter, *J. Chem. Soc.*, 1509 (1954).

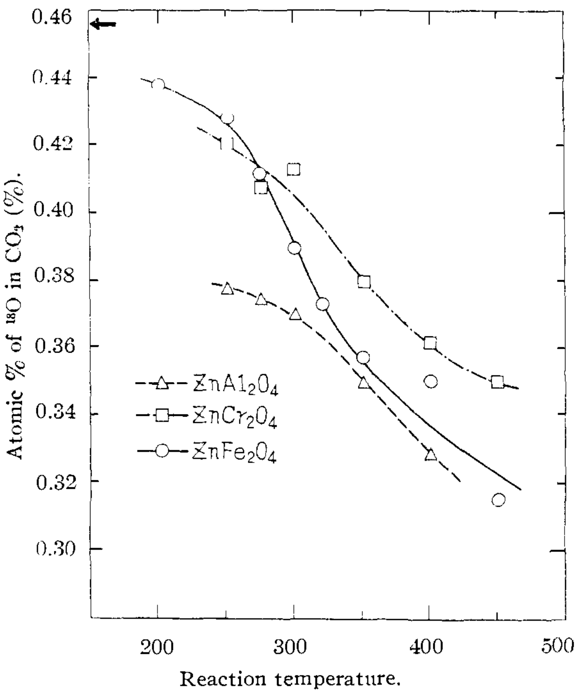

Fig. 2.—^{18}O in carbon dioxide: the arrow shows the atomic percentage of ^{18}O at the beginning of the reaction.

the reaction, as shown in Fig. 4, because the catalysts were either reduced or oxidized by the ambient gas mixture. The quantity of ^{18}O transferred to the catalyst was calculated from the material balance between the initially charged amount of gas mixture and the data in Figs. 2–4; see Fig. 5. The exchangeable surface oxygen, n_s, calculated as in (A) is also shown in Fig. 5.

Figures 2–4 show that at low temperatures ($T < 250°$), exchange of oxygen atoms occurred only between the catalysts and carbon dioxide, although while no exchange between carbon dioxide and monoxide, and no reduction or the oxidation of the catalysts by the ambient gas were detected. At high temperatures ($T > 250°$), the transfer of ^{18}O atoms from carbon dioxide to carbon monoxide increased as the reduction or the oxidation of catalysts gradually took place. Nevertheless, the amount of ^{18}O transferred to the catalyst was almost the same as that transferred at low temperatures.

These results have led us to propose two reaction mechanisms. At low temperatures, the oxygen atoms are transferred to the catalysts from carbon dioxide through the carbonate-formation mechanism I, while at high temperatures, the oxidation-reduction mechanism II will predominate.

$$\text{Mechanism I: } CO_2 + O_s^{=} \rightleftarrows CO_3^{=} \qquad (1)$$

$$\text{Mechanism II: } CO_2 + (K) \rightleftarrows CO + (K)O \qquad (2)$$

Low Temperature Range.—It is well known that the exchange between carbon dioxide and monoxide is observed only in the presence of a solid catalyst at this temperature range.[1–3] The experimental facts, that neither oxidation nor the reduction of the catalysts was observed, and that the ^{18}O content of the carbon monoxide was negligible, suggest that carbon monoxide does not participate in the reaction at this temperature range. This assumption is confirmed by the finding that the quantity of ^{18}O transferred to the catalyst when the ambient gas contains only carbon dioxide (A) is of the same order as the amount transferred when the gas contains both carbon dioxide and monoxide, even though experiment A was carried out at a high temperature (400°); see Fig. 5. This indicates that at low temperatures, carbon dioxide molecules exchange oxygen atoms with the catalyst without dissociation into carbon monoxide and oxygen atoms. The adsorbed molecules of carbon dioxide might prohibit the participation of carbon monoxide from the gas phase.

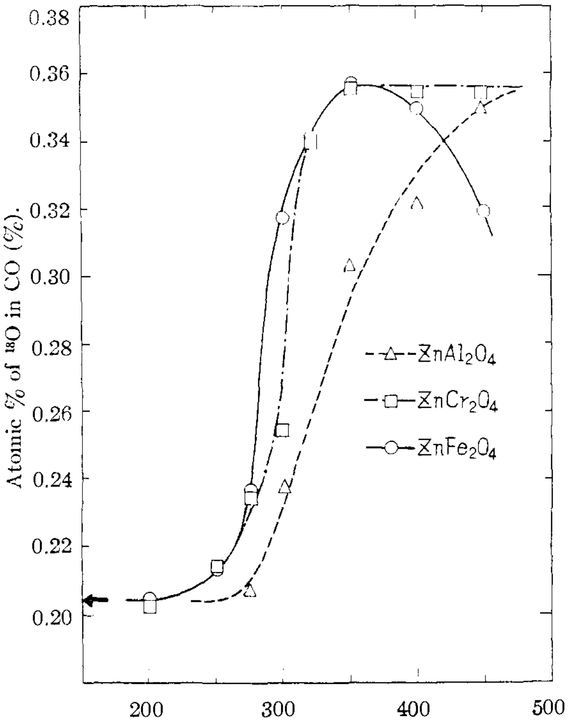

Fig. 3.—^{18}O in carbon monoxide: the arrow shows the atomic percentage of ^{18}O at the beginning of reaction.

Dell and Stone[6] also have suggested that a surface carbonate complex is formed between carbon dioxide from the gas phase and oxygen ion, $O_s^{=}$ on the surface of nickel oxide. Since the forward and reverse reactions of mechanism I are repeated quickly, ^{18}O atoms would be transferred to the catalyst surface from carbon dioxide even at low temperatures.

High Temperature Range.—As the temperature is raised, the oxidation or reduction of the catalysts and the transfer of ^{18}O to the catalyst and to carbon monoxide increase. The large amount of ^{18}O exchanged at high temperatures might be attributed to the incorporation of ^{18}O in the bulk of the oxide. In fact the number of exchangeable layers reaches 75 for $ZnFe_2O_4$ at 450°. However, the amount of ^{18}O transferred to the catalyst decreases at medium temperatures as is shown in Fig. 5, although it increases again at high temperatures.

[6] R. M. Dell and F. S. Stone, *Trans. Faraday Soc.*, **50**, 501 (1954).

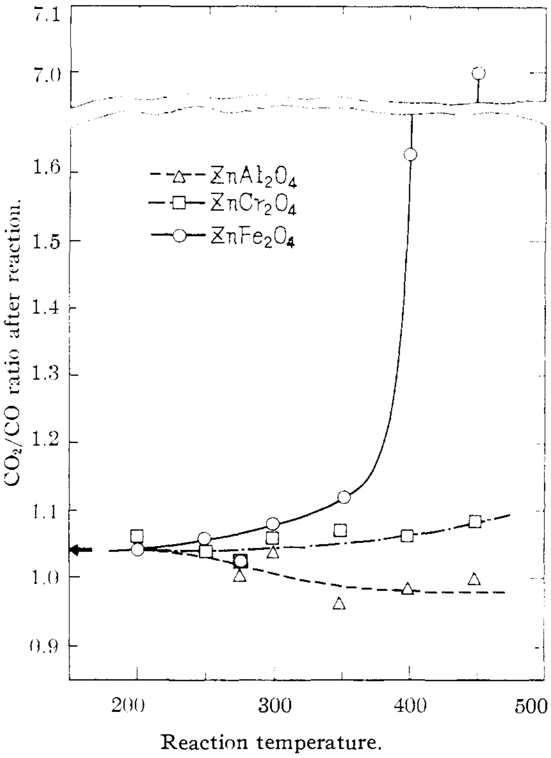

Fig. 4.—Ratio of CO_2 and CO after reaction: the arrow shows the ratio at the beginning of the reaction.

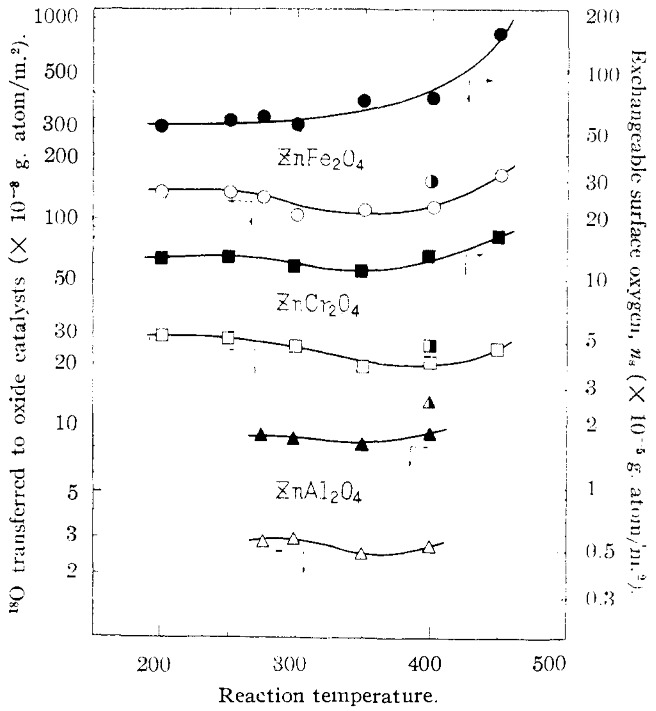

Fig. 5.—The amount of ^{18}O transferred to oxide catalysts and exchangeable surface oxygen, n_s. Open symbols indicate the amount of ^{18}O transferred, and solid ones the exchangeable surface oxygen. Semi-solid symbols indicate the former in series (A).

Except for $ZnAl_2O_4$, these values in experiment A (represented by the semi-solid symbols in Fig. 5), in which the ambient gas was carbon dioxide only, are lower than those obtained under the conditions of experiment B.

As the temperature is raised, the carbonate becomes less stable and its decomposition pressure becomes large; therefore, the exchange of oxygen atoms between carbon dioxide and the catalyst through mechanism I decreases gradually. On the other hand, the reduction or oxidation of the catalyst increases with the temperature; exchange due to mechanism II occurs and is superimposed on that due to I. This explains the slight minimum observed in Fig. 5 for the medium temperature range in which the exchanges due to both mechanisms I and II are low.

We shall now compare the rate of the exchange of oxygen atoms between the catalyst and carbon dioxide with the rate of the reduction or oxidation of the catalyst. The amount of reduction or oxidation of the catalyst is given in Table II in g. atom/m.^{2}.

The exchanged oxygen to CO, also included in Table II, was calculated as g. atom of ^{18}O transferred to carbon monoxide divided by $(\alpha - 0.204) \times 10^{-2}$, with the assumption of an isotopic equilibrium between carbon dioxide and the oxide catalyst. These values may be low, because the atom fraction of ^{18}O in the oxide catalyst, β, will be smaller than α at any time; β during the experiment may be smaller than that at the end of the reaction; and the reverse reaction is neglected. Nevertheless, as is seen in Table II, the rate of the exchange is larger than that of the reduction (or oxidation) by at least several powers of ten for the whole temperature range, except for $ZnFe_2O_4$ at high temperatures at which it is vigorously reduced. These comparisons serve to confirm mechanism II, *i.e.*, the rates of the forward and reverse reactions are rapid, one oxygen atom being exchanged as the reaction proceeds in either direction,

TABLE II

AMOUNT OF OXIDATION OR REDUCTION OF CATALYST AND ^{18}O TRANSFERRED TO CARBON MONOXIDE IN 15 MINUTES

Catalyst	Reaction temp. (°C.)	Amt. of oxidation or reduction of catalyst (g. atom O/m.^{2}) $\times 10^{-5}$	^{18}O transferred to CO (g. atom/m.^{2}) $\times 10^{-5}$	Exchanged oxygen atoms between CO and catalyst (g. atom/m.^{2}) $\times 10^{-5}$
	450	....	1.5	...
	400	0.032	1.2	0.96
$ZnAl_2O_4$	350	.039	0.96	.66
	300	.002	.31	.19
	275	.001	.04	.02
	450	.37	16.5	11.3
	400	.11	15	9.7
$ZnCr_2O_4$	350	.17	16	9.3
	300	.14	5.1	2.4
	275	.09	3.0	1.5
	250	.03	0.9	0.4
	200	.11	...	...
	450	42	17	15
	400	12	60	41
$ZnFe_2O_4$	350	2.1	79	51
	300	0.94	54	29
	275	....	15	7.2
	250	.60	3.9	1.7
	200	.09	0.0	0.0

and the reduction (or oxidation) is attributable to the difference between these two rates.

The exchangeable surface oxygen, n_s, of $ZnFe_2O_4$ is about five times larger than that of $ZnCr_2O_4$ and about thirty times larger than that of $ZnAl_2O_4$. This relationship is in qualitative agreement with the order of the amounts of ^{18}O transferred to carbon monoxide (Table II): $ZnFe_2O_4 > ZnCr_2O_4 > ZnAl_2O_4$. The tendency of the catalysts to be reduced or oxidized coincides with their oxidizing power; $ZnFe_2O_4$ will oxidize this gas more readily than $ZnCr_2O_4$, while $ZnAl_2O_4$ will reduce it slightly, as one might predict from its tint.

Now let us consider the nature of the surface state of these catalysts. No transfer of ^{18}O to carbon monoxide was observed even at 300° with grayish green $ZnCr_2O_4$ which had been slightly reduced with hydrogen at 100 mm. for 30 minutes at 480°. Another sample of $ZnCr_2O_4$, which had been evacuated at 10^{-3} mm. at 500° for 1 hr., also lost its catalytic activity. Neither treatment caused any change which could be observed by X-ray diffraction analysis. This suggests that the excess oxygen on the surface of $ZnCr_2O_4$, a p-type semi-conductor, is essential for its catalytic activity. Hence, for $ZnCr_2O_4$, (K)O in (2) represents the presence of excess oxygen and (K) its disappearance, which is caused by reduction by the ambient gas.

$ZnAl_2O_4$ and $ZnFe_2O_4$ are *n*-type semi-conductors; $ZnAl_2O_4$ prepared in this study was reduced somewhat from the stoichiometric composition. In $ZnFe_2O_4$, and inverse spinel, the iron ions distributed as Fe^{+++} both in the 8f and 16c positions are liable to exchange the valency as $Fe^{+++} \rightleftarrows Fe^{++}$. Accordingly, (K) and (K)O correspond in $ZnAl_2O_4$ to the defect of surface oxygen and to the state where the defect is filled with oxygen atoms; and in $ZnFe_2O_4$, to the site around a reduced iron ion, and to that around which all the iron ions are oxidized.

For the elucidation of the precise nature of (K)O and (K) and the identification of the rate-determining steps, further investigation is necessary.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Structure of Tetragonal Boron[1]

BY J. L. HOARD, R. E. HUGHES AND D. E. SANDS

RECEIVED MARCH 29, 1958

The fifty boron atoms of the tetragonal unit are divided among four approximately regular icosahedra centered in the positions $^1/_4\ ^1/_4\ ^1/_4$, $^3/_4\ ^3/_4\ ^1/_4$, $^3/_4\ ^1/_4\ ^3/_4$, $^1/_4\ ^3/_4\ ^3/_4$ of $P4_2/nnm$ with two individual atoms in 2b:00 $^1/_2$, $^1/_2\ ^1/_2$ 0. Each boron atom of an icosahedron forms six bonds directed toward the corners of a pentagonal pyramid, five within the same icosahedron, the sixth to an adjacent icosahedron or to an atom in 2b. The resulting framework is continuous in three dimensions. Typical intra- and intericosahedral bond distances are, respectively, 1.805 ± 0.015 and 1.68 ± 0.03 Å. Available single crystals of tetragonal boron are subject to a large and variable degree of internal disorder: the diffraction data afforded by different specimens are notably diverse as regards strength of diffuse scattering, distribution of Bragg intensities, and lattice constants. Typical values of lattice constants are $a = 8.75$, $c = 5.06$ Å.

Introduction

For many years only microcrystalline and often quite impure preparations of elemental boron were available, yielding X-ray powder diffraction patterns of notable complexity and diversity. Recent single crystal studies of three different modifications show boron exhibiting a remarkably wide range of structural complexity. The most recently discovered and structurally simplest modification[2] is *rhombohedral* with but one icosahedral B_{12} group within the unit cell. The structural arrangement[2] is intimately related to that of boron carbide,[3] $B_{12}C_3$. The most easily prepared but structurally by far the most complex modification of boron also is *rhombohedral*,[4] with 108 atoms in the unit cell. We have in progress intensive studies aimed at a determination of structure for this form. The *tetragonal*[5] modification of boron has been most studied.[6] The present paper reports the detailed structural investigation of the tetragonal single crystals (appearing in two widely dissimilar growth habits) prepared by Laubengayer, *et al.*,[6] through reduction of boron tribromide with hydrogen on a hot filament; the fundamental atomic arrangement within the fifty-atom cell of the earlier brief report[5] is confirmed.[7]

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[1] Supported by the Atomic Energy Commission under Contract No. AT(30-1)-878 and by the Research Corporation through a grant for purchase of major equipment used in this study.

[2] L. V. McCarty, J. S. Kasper, F. N. Horn, B. F. Decker and A. E. Newkirk, THIS JOURNAL, **80**, 2592 (1958).

[3] H. K. Clark and J. L. Hoard, *ibid.*, **65**, 2115 (1943); G. S. Zhdanov and N. G. Sevast'yanov, *Compt. rend. acad. sci. U.R.S.S.*, **32**, 432 (1941).

[4] D. E. Sands and J. L. Hoard, THIS JOURNAL, **79**, 5582 (1957).

[5] J. L. Hoard, S. Geller and R. E. Hughes, *ibid.*, **73**, 1892 (1951).

[6] A. W. Laubengayer, D. T. Hurd, A. E. Newkirk and J. L. Hoard, *ibid.*, **65**, 1924 (1943).

[7] Based on the free use of authoritative single crystal data, we expect to prepare (or persuade others[2] to prepare) for publication definitive tables for identifying the known modifications from X-ray powder data. We note here that the powder diff action pattern[6] for "needle crystals" includes lines not characteristic of tetragonal boron. In taking "clusters" of needles for powdering a good deal of the microcrystalline matrix (formed at a higher temperature since it directly ensheathed the filament) must have been included. The microcrystalline sheath formed in a run with a *filament* temperature of about 1350° gave a powder pattern now identifiable[4] as that of complex