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Addition Compounds of Boron Nitride with Alkali Metals and Their Catalytic Activity

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Boron nitride consists of parallel-layer planes, in each of which boron and nitrogen atoms occupy alternate sites on regular hexagonal lattice. Therefore, the structure of boron nitride (BN) bears a relation to graphite; the distance between the planes (3.30 Å) is almost the same as in graphite (3.345 Å), and their interatomic distances in the hexagonal plane are close, 1.45 Å (for boron nitride) and 1.42 Å (for graphite). However, because of the greater electronegativity of nitrogen as compared with that of boron, there is an uneven distribution of the electrons, giving a partly ionic character to the lattice. The nuclear magnetic resonance study of the bonding has led to the conclusion that boron nitride has a 45% double-bond resonating configuration.[1)]

It is well known that graphite reacts with striking readiness with the molten alkali metals, potassium, rubidium and cesium, or their vapours, to form alkali metal-graphite lamellar compounds.

Recently, a strong chemisorption was found on these lamellar compounds of graphite by the methods of hydrogen-deuterium exchange reaction and ortho-parahydrogen conversion.[2)]

The similarity of the structures of graphite and boron nitride led Croft and Rudorff to attempt the preparation of boron nitride intercalation compounds.[3,4)] However, because of the difficulty of preparing and identifying them, there remains some ambiguity.

In this paper, we will discuss the preparation of boron nitride alkali metal compounds and their catalytic activity.

Experimental Procedures

Boron nitride, a white powder provided by Borax Consolidated, Ltd., and the Showa Denko Co., was used to prepare its alkali metal complexes.

Among the alkali metals, commercial-grade sodium and potassium metals were employed, while the rubidium and cesium were obtained by the reduction of their chlorides by calcium metal. The purified alkali metal was admitted into a vacuum reaction vessel, in which a degassed boron nitride powder was kept, by distillation. By further heating at 200°C for two or three days in an electric furnace, the reaction between alkali metal and boron nitride was completed. The Cs-BN complex was deep blue.

The principle of the kinetic studies of parahydrogen-orthohydrogen conversion and of hydrogen-deuterium equilibration over these complexes has already been reported.[2)] These studies were carried out at room temperature and at 77°K in a constant-volume reaction system which was protected from grease and other condensable gases by traps cooled in liquid nitrogen.

For electrical conductivity measurements, a small piece of boron nitride (3.7 mm in diameter, 1.5 mm thick) was fused at around 3000°C in an arc-imaging furnace to make a fused specimen. The thin aluminum films evaporated onto both sides of the fused specimen were used as electrodes.

Results and Discussion

Boron nitride is a typical electric insulator, its observed electrical conductivity at 15°C and apparent activation energy being 10^{-17}—10^{-22} Ω^{-1} cm^{-1} and ~ 1 eV respectively. The ionization potential, estimated from its photoemission in a vacuum ultra-violet region, was about 5.6 eV.[*1] The details of the experimental procedure have already been reported.[6)]

No catalytic activity was found on the powder specimen of boron nitride at all. However, the complexes between BN and alkali metals revealed a marked catalytic activity for such reactions as para-orthohydrogen conversion and hydrogen-deuterium equilibration. Table 1 summarizes their kinetic data. It can be seen form Table 1 that

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1) A. H. Silver and P. J. Bray, *J. Chem. Phys.*, **32**, 288 (1960).

2) H. Inokuchi, N. Wakayama, T. Kondow and Y. Mori, *ibid.*, **46**, 837 (1967).

3) R. C. Croft, *Austral. J. Chem.*, **9**, 206 (1956).

4) W. Rudorff and E. Stumpp, *Z. Naturforsch.*, **13b**, 459 (1958).

[*1] Taylor and Coulson have calculated an electronic structure of boron nitride with a tight-binding approximation. They reported that the electrons of the BN crystal cocupy one band, approximately 2.4 eV in width, separated from the next-higher band by a gap of about 4.6 eV.[5)]

5) R. Taylor and C. A. Coulson, *Proc. Phys. Soc.*, **A65**, 834 (1952).

6) Y. Harada and H. Inokuchi, This Bulletin, **39**, 1443 (1966); M. Kochi, Y. Harada and H. Inokuchi, This Bulletin, **40**, 531 (1967).

the rate constants have about the same magnitude for both the reactions at room temperature, and that only para-$H_2 \rightleftharpoons$ortho-H_2 conversion can be catalyzed at 77°K, implying that at higher temperatures the reactions occur by the chemical mechanism, and at lower temperatures, by the physical one.

We have already reported that graphite makes lamellar complexes with alkali metals, which are very active in the above catalytic reactions.[2] Though a quantitative comparison of catalytic activity can not be made between BN- and graphite-alkali metals complexes since the surface area has not yet been measured, it seems that boron nitride complexes have an activity comparable with graphite.

What is the cause of this activity over the BN-complexes? The promotion may take place by means of an electron transfer from the alkali metal to a partner molecule: ($nM^+ \cdot BN^{n-}$). The excess charge on the B–N hexagonal skeleton may give a predominant mechanism of catalytic activity. However, we could not find any detectable change in the crystal structure of boron nitride upon the addition of alkali metals.

A more detailed and systematic study will be required to establish the structures of these complexes and the nature of the catalytic active sites.

TABLE 1. THE CONVERSION AND THE EXCHANGE OF HYDROGEN WITH BORON NITRIDE-ALKALI METALS SYSTEM

Complex	Reaction	Temperature (°K)	$min^{-1}g^{-1}$*
BN-K	$H_2+D_2 \rightleftharpoons 2HD$	295	0.8×10^{-2}
		77	non-detectable
	$pH_2 \rightleftharpoons oH_2$	295	1.3×10^{-2}
		77	1.2×10^{-3}
BN-Rb	$H_2+D_2 \rightleftharpoons 2HD$	295	1.0×10^{-2}
		77	non-detectable
	$pH_2 \rightleftharpoons oH_2$	295	1.0×10^{-2}
		77	1.3×10^{-3}
BN-Cs	$H_2+D_2 \rightleftharpoons 2HD$	295	1.4×10^{-2}
		77	non-detectable
	$pH_2 \rightleftharpoons oH_2$	295	4.2×10^{-2}
		77	1.4×10^{-3}

* $k=\frac{2.303}{t}\log\left(\frac{C_0-C_e}{C_t-C_0}\right)$; where C_0, C_e and C_t are concentrations of para-H_2 at the initial point, in equilibrium at the given temperature, and after t min, respectively. For D_2, the similar calculation is applied.