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The Boron Content of Brown Palladium Catalyst

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It has been reported that nickel, cobalt, platinum, palladium, rhodium, ruthenium, osmium, and iridium catalysts prepared from their salts with sodium borohydride were effective, according to Paul[2] and Brown,[3] in catalytic hydrogenation reactions. It was well accepted[2-5] that the first two of these catalysts contain boron like Ni_2B–Ni_3B of nickel boride or that the nickel catalyst is a nickel boride precipitate. On the other hand, next three, according to Balandin, *et al.*,[6] also contained boron in such a stoichiometric ratio as Me_2B, and it was called as "palladium boride." But Brown[3] has shown that the platinum catalyst prepared by such procedure was essentially pure. In spite of such vague situation, noble metal catalysts, prepared from their salts with sodium borohydride, were often called as "metal boride" catalyst.[7]

We have found that the "palladium boride" catalyst leads to much more selective production of L-idonate from D-xylo-5-hexulosonate in its reduction than usual palladium black or 5% palladium charcoal catalyst.[8] This great improvement in the selectivity has led us to pay attention to the content of boron in the "palladium boride." In this note, the boron content in the so-called "palladium boride" will be investigated by both chemical and instrumental techniques, and compared with that of nickel boride, the chemical stoichiometry of which has been well established.

Results and Discussion

The content of boron in the "palladium boride" catalyst was reinvestigated first by the standard chemical analysis[9] after Paul[2] and others.[3-6] The result indicated that the amount of boron in the "palladium boride" is too small to detect and comparable with that of blank test or of ordinary palladium black. On the other hand, the boron content of nickel catalyst, prepared by sodium borohydride, was significant, and its composition was estimated as Ni_4B, the stoichiometry of which appeared to be not so far from those reported earlier,[2-4] that is, Ni_2B–Ni_3B. It may be considered therefore that the "palladium boride" is essentially pure or that the content of boron in the "palladium boride" is very small.

1) Location: *7-3 Hongo, Bunkyo-ku, Tokyo.*
2) R. Paul, P. Buisson and N. Joseph, *Compt. Rend.*, **232**, 627 (1951); R. Paul, P. Buisson and N. Joseph, *Ind. Eng. Chem.*, **44**, 1006 (1952).
3) H.C. Brown and C.A. Brown, *J. Am. Chem. Soc.*, **84**, 1493 (1962); H.C. Brown and C.A. Brown, *J. Am. Chem. Soc.*, **84**, 1495 (1962).
4) W. Romanowski, *Roczniki Chemii. Soc. Polonorum*, **41**, 423 (1967).
5) R.L. Augustine, "Catalytic Hydrogenation," Marcell Dekker, Inc., New York, 1965. p. 25.
6) A.M. Taber, B.D. Polkovnikov, N.N. Maltseva, V.I. Mikheeva and A.A. Balandin, *Dokl. Akad. Nauk. SSSR.*, **152**, 119 (1963).
7) M. Kawai, T. Imanaka and S. Teranishi, *Nippon Kagaku Zasshi*, **90**, 42 (1969).
8) C.Y. Chen, H. Yamamoto and T. Kwan, *Catalyst*, **10**, 77p (1968).
9) "Standard Methods of Chemical Analysis," Vol. 1, ed. by W.W. Scott. D. Van Nostrand Company Inc., New York, 1925, p. 86.

However, the preliminary qualitative analysis of the "palladium boride" with curcumine tincture[10] had shown that a trace of boron was present even in the sample scrapped by an inorganic acid.

Then, in view of the difficulty in accurate determination of a small amount of boron in the sample by chemical methods, an attempt was made to determine the amount of boron in the sample by an atomic absorption spectrophotometer. Samples of equal concentration (100 mg/ml) were prepared for ordinary palladium black and "palladium boride" respectively, and the concentration of boron in each sample was determined on the basis of calibration curve obtained for standard solutions of sodium borate. The results are shown in Table I together with that of nickel boride.

Table I. Determination of Boron by Atomic Absorption Spectrophotometry

Sample	Boron content		
	ppm	wt. %	Metal: Boron
Palladium black	<20	<0.02	—
"Palladium boride"	1050	1.05	10 : 1
Nickel boride	6800	6.80	2.5: 1

It is apparent from Table I that the boron content of the "palladium boride" is much less than that of nickel boride, and that the chemical stoichiometry of nickel boride is in good agreement with those reported earlier.[2-4] The disagreement of the present analysis result with that of the chemical analysis would perhaps be due to the obscure end point of the titration in the latter method.

Thus, atomic ratio of boron to palladium of the "palladium boride" catalyst is calculated as 1/10, hence being fairly less than the stoichiometric ratio of palladium boride, Pd_3B–Pd_5B_2, as prepared by a fusion method.[11]

Further attempt was made to detect boron of the "palladium boride" by an electron microprobe X-ray analyzer because of the importance of surface composition in catalysis. The result indicated that no detectable boron on the "palladium boride" surface layer is present within the experimental accuracy while nickel boride gives rise to a strong K_α signal of boron. It is concluded from the experimental accuracy of this method that the boron content of the "palladium boride" sample is below about 1 wt. % on the surface. The boron content near the surface layer would probably be not much different from that in the bulk.

Finally, analysis of the "palladium boride" was carried out by an atomic emission spectroscopy and led to the result that the sample contains traces of Cu and Mg together with boron. These impurities were detectable, however also in the sample of palladium black.

It is pointed out by utilizing the modern analytical instrumentations that the Brown palladium catalyst has the composition of $Pd_{10}B$ and contains traces of Cu and Mg, and that there is no evidence that shows accumulation of boron near the surface layer.

Experimental

Palladium chloride and palladium black were supplied from Japan Engelhard Co., and nickel chloride and sodium borohydride were from Koso Chemical Co. and Yoshitomi Pharmaceutical Co. respectively. They were used without further purification. The "palladium boride" was prepared in the following way according to Brown[3] and Balandin.[6] The sodium borohydride solution (2.0%) was added slowly into an aqueous solution of palladium chloride (0.1M) at 25° until finely-divided black precipitates were formed.

10) M. Ishidate, "Biryou Teisei Bunseki," Nanzando, Inc., Tokyo, 1958. p. 299.
11) N.N. Greenwood, R.V. Parish and P. Thornton, *Quart. Rev.*, **20**, 441 (1966).

The precipitates were repeatedly washed with distilled water, until the filtrate became colorless with phenolphthalein test. The nickel boride was prepared in a similar way.

Chemical analysis of the catalyst was carried out for about 1 g sample. The sample of "palladium boride" or nickel boride was dissolved in hydrochloric acid containing a small amount of nitric acid. Then, the metal ions were excluded as dichlorodiaminepalladium (II) or as nickel hydroxide in the case of nickel boride. Collected filtrates and washings were titrated as usual.[9] The dichlorodiaminepalladium (II) or nickel hydroxide was then dissolved in dilute hydrochloric acid and the amount of the metal was determined gravimetrically as its oxide.

The curcumine tincture test was undertaken for the extract as methyl borate from the evaporated residue of the dissolved "metal boride" solution.

The atomic absorption spectrophotometry was performed by use of the Jarrell-Ash Atomic Absorption Spectrophotometer Model AA-1. A high-temperature nitrous oxide-acetylene burner was used with the slot reduced to 5 cm. The instrument was set at 3000 Å and at 5X scale expansion. The dissolved solutions of palladium samples, adjusted to 50 mg/ml, were subjected to analysis. Sodium borate solutions ranging from 50 to 500 ppm boron content were prepared and employed as the standard for the calibration of the instrument. The calibration curve was a good straight line towards origin.

The Shimadzu-ARL Electron Microprobe X-ray Analyzer Model EMX-2A was used for the analysis of surface layer boron content. Samples of "palladium boride" and nickel boride were respectively mounted on the surface of aluminium electrode by means of an electroconductive paste. Accelerating potential of 15 KV was applied with sample current 0.4 A in each case.

A strong peak due to BK_α was obtained with a shoulder corresponding to NiL_α ($n=5$) in the case of nickel boride while no appreciable BK_α line was detected for "palladium boride" in spite of 40 seconds integration.

Shimadzu Atomic Emission Spectrometer Type-QL-170 was employed. Analysis was carried out under the conditions: primary potential; 50 V (2A), discharge potential; 210 V (55A), discharge time; 45 sec. wavelength range: 2500—3500 Å, slit width; 10 μ.

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