

PREPARATION OF METAL BORIDES IN AN APROTIC SYSTEM

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ABSTRACT

A novel technique to prepare Nickel Borides using Diborane-THF complex generated "in-situ" as reducing agent, is presented. The Nickel Borides series were prepared using two ways, the HETEROGENEOUS and HOMOGENEOUS route. Solid NiCl₂ of different mesh size was added to the reducing complex to prepare nickel boride by HETEROGENEOUS route. While Ni(AcO)₂.4H₂O dissolved in methanol was used to obtain nickel boride by the HOMOGENEOUS one. The advantage of this technique is that by using an aprotic medium, borides of metals which form stable oxoanions are obtained.

INTRODUCTION

For the most part, borides are very hard, high-melting, refractory substances whose structure and stoichiometries do not conform to the ordinary concepts of valence. Borides with low boron-to-metal ratios (M₄B, M₃B, M₂B) contain isolated boron atoms. However, as the proportion of boron increases (M₃B₂, M₄B₃, M₃B₄), borides with single and double chains of boron appear. Borides with formulae like MB₄, MB₆, and MB₁₂ exist in three dimensional arrays with open networks of boron atoms interpenetrating a regular metal atom lattice. See Fig.1 and Fig.2.

The use of metal borides as catalysts in many reduction processes has been widely reported in the literature (1). In most of these contributions metal borides were prepared by following the pioneer Schlesinger method (2). In the preparation of nickel borides catalysts, sodium borohydride is generally used to reduce a nickel salt. The catalyst obtained is dependent on the reaction medium. P-1 nickel boride was obtained in an aqueous solution, whereas P-2 nickel boride was obtained when 95% ethanolic solution was used. Both P-1 and P-2 are active catalysts. Other versions of this synthesis have been conducted in alcohol or ether solvents, under an inert atmosphere like nitrogen, or under hydrogen pressure. Borides have been deposited in the presence of a second (promoter) metal, on inert solid

support, or as colloidal suspensions on solvent-swollen polymers. As will be seen, small variations in the method of preparation can affect dramatically the activity, selectivity, physical and chemical properties of the boride. The major drawback of these methods is that they can not be used when the involved metal forms stable oxoanions. In this contribution we present an alternative way that overcomes this limitation.

EXPERIMENTAL

PREPARATION OF CATALYST

The reducing solution was obtained by reacting 1 g. of NaBH_4 (Aldrich) with 1 ml of distilled water in 100 ml of THF (Mallinckrodt) at 25°C . This solution was used to reduce the metal salts, which were added to the system either as solid (HETEROGENEOUS ROUTE) or dissolved in methanol (HOMOGENEOUS ROUTE).

Within the heterogeneous route, solid nickel chloride (Merck) was used. Different preparation conditions were checked changing reaction temperature, stirring speed, particle sizes of the solid and aging time.

When the homogeneous route was used, 23.5 ml of a 0.125M solution of $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ in methanol was added.

Aging time, the time between catalyst preparation and catalytic activity determination, was specified at three different values (0.5, 48 and 72 hours). During this stage the catalyst slurry was maintained at a constant temperature of 25°C .

In both preparations the reaction goes on quickly producing hydrogen and a powdered black solid (boride).

CHARACTERIZATION

Elemental chemical analysis for determination of nickel and boron contents were carried out. The nickel boride was dissolved in $\text{HNO}_3:\text{HCl}$ (1:3) after been washed with water, alcohol and ether followed by drying under vacuum. The nickel was determined complexometrically and boron, as H_3BO_3 , potentiometrically using NaOH in presence of mannitol.

The studies of boride structure were carried out with the help of an X-Ray analyzer Type Phillips, using filtered Cu K α radiation.

The specific surface area was measured by a gravimetric technique using n-hexane as adsorbate in a Cahn RG electrobalance (3).

For the catalyst prepared via heterogeneous route the particle size distribution was determined by SEM, using a Jeol 35 cf Electronic Microscope.

HYDROGENATION OVER NICKEL BORIDE

Catalytic activity was evaluated in the liquid phase hydrogenation of nitrobenzene.

Fresh catalyst samples, not dried, were used. Several of them were prepared at the same time to test the reproducibility of each experience. The catalyst was added to nitrobenzene solution (1M) in methanol.

The air in the reactor system (Parr Model 3911) was removed using hydrogen at room temperature. The system was heated up until the reaction temperature and then pressurized.

The hydrogen uptake, under essentially constant volume conditions, was followed manometrically.

RESULTS

Reduction of nickel chloride (solid) with complex Borane-THF (HETEROGENEOUS ROUTE) yielded a black precipitate. Products with the same chemical composition, but different surface area, were obtained using different preparation conditions (e.g. different temperature reaction, stirring speed, particle size distribution and aging time).

The powdered boride was non pyrophoric. It hydrolyzed readily in HCl with vigorous H₂ evolution. Since elementary boron is insoluble in HCl, so nickel and boron exist in a combined state.

Elemental analysis indicated a Ni/B ratio of 4/3 (Table 1). Because of the BH₃ ability as Lewis acid, a possible reaction mechanism for the nickel boride formation was proposed. According to this, the global stoichiometry was deduced (1); which was verified by chemical analysis.

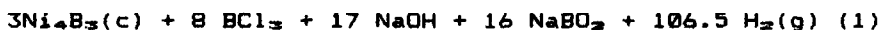
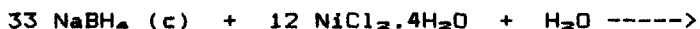


TABLE 1 : Elemental analysis and BET surface area, nickel boride catalysts.

Catalyst	Ni% wt	B% wt	Ni:B (mol ratio)	BET surface area m ² /g
NiB _{HETER.}	87.9%	12.1%	4:3	40
NiB _{HOMOG.}	88.6%	5.5%	3:1	140

BET surface area ranges between 10-120 m²/g. An average value of 40 m²/g was found when nickel chloride 100/200 mesh, medium stirring speed and 25°C were used. See Table 2.

TABLE 2 : BET surface area of nickel boride (HETEROGENEOUS) under different preparation conditions.

Series T*	Preparation Vol. H ₂ O (K)	Conditions Cl ₂ Ni granulomet.	Aging Time(°)	BET surface area m ² /g	
A	278	1.0	As such	72 hs.	33
	278	1.0	As such	0.5 hs.	148
	278	1.0	As such	48 hs.	33
B	278	1.0	100/200 mesh	48 hs.	47
	278	1.0	100/200 mesh	48 hs.	36
	278	1.0	100/200 mesh	48 hs.	37

a) Time between catalyst preparation and catalytic activity determination.

Fig.3 shows a transmission micrograph of nickel boride. The catalyst consists of small grains with a spongy solid structure like bronzes. The SEM analysis give an average particle size of 187 nm. See Fig.4

X-Ray catalyst diffractions show that they are all amorphous when the aging time is less than 24 hs. For longer aging time the catalyst shows a structure like B₃Ni₂.

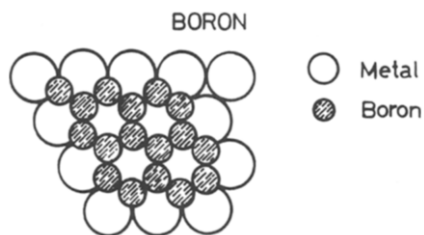
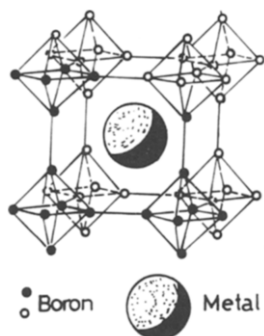
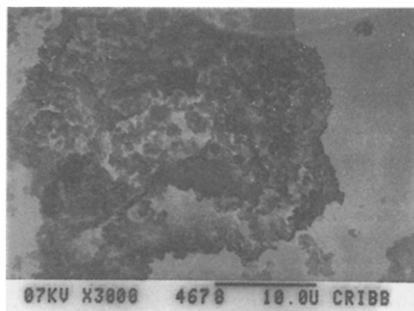
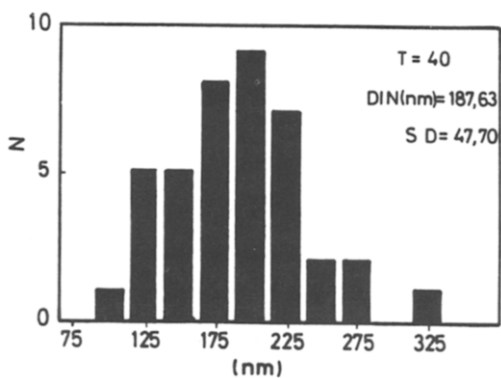
The liquid phase hydrogenation of nitrobenzene on these borides was first order in H₂ partial pressure and independent of nitrobenzene concentration. See Fig.5 and 6. The Fig.7 shows dependence of k with temperature.

The specific rate constant values showed a good reproducibility regardless of catalyst surface area changes. They suggest that the active surface sites are the same in all cases (Table 3).

TABLE 3 : Specific rate constant value at different aging time. (HETEROGENEOUS ROUTE)

Series	Aging Time(°)	BET surface area m ² /gr	Catalytic Activity kp 10 ¹² (mol/s.m ² kPa)
A	72 hs.	33	3.6
	0.5 hs.	148	2.9
	48 hs.	33	3.6
B	48 hs.	47	6.8
	48 hs.	36	9.9
	48 hs.	37	9.5

Conditions: Hydrogen pressure 375 kPa, T° 323K,
Nitrobenzene 1M and Ni 0.1M

Fig. 1. Boride structures type MB_2 .Fig. 2. Boride structures type MB_6 .Fig. 3. Ni_4B_3 transmission micrograph.Fig. 4. Ni_4B_3 distribution particle size by SEM. Preparation conditions: $NiCl_2$ solid 100/200 mesh; aging time 4h h.

When the HOMOGENEOUS ROUTE was used, again the product obtained was a non pyrophoric and soluble in HCl black solid. Its surface area varied between 130-150 m²/g. The chemical analysis gave a 3/1, Ni/B ratio. See Table 1.

On Ni₃B "Homogeneous" the specific rate constants for the nitrobenzene hydrogenation are much higher than on Ni₄B₃.

Table 4 summarizes the specific rate constant values for the liquid phase hydrogenation of nitrobenzene using both type of borides at three different temperatures. Borides Ni₄B₃ type were prepared using the conditions of "B Series" (see Table 2), to obtain the specific rate constant values.

TABLE 4 : Specific rate constant for the nitrobenzene hydrogenation over nickel borides.

T (K)	k 10 ¹² (Ni ₃ B ₄) (mol of H ₂ /s.kPa. m ²)	k 10 ¹² (Ni ₃ B) (mol of H ₂ /s.kPa. m ²)
328	9.9	238
338	14.1	263
348	20.4	332

Conditions: Hydrogen pressure 375 kPa, nitrobenzene concentration 1M and Ni 0.1M

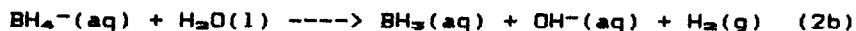
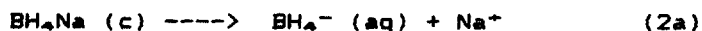
DISCUSSION

Most of the methods previously described, involve the use of sodium borohydride as reducing agent. The alkali borohydrides are crystalline solids which are soluble in protic solvents but only slightly soluble in aprotic ones. Behaviour that greatly limits its use.

The aqueous solutions of sodium borohydride are relatively stable. However, the following reaction take place:



This reaction could be formulated following the sequence:



The BH₃ produced in reaction (2b) forms a complex compound with water H₂O:BH₃. It gives a series of complex species with BH₄⁻ ions. The reaction (2c) is slow but it

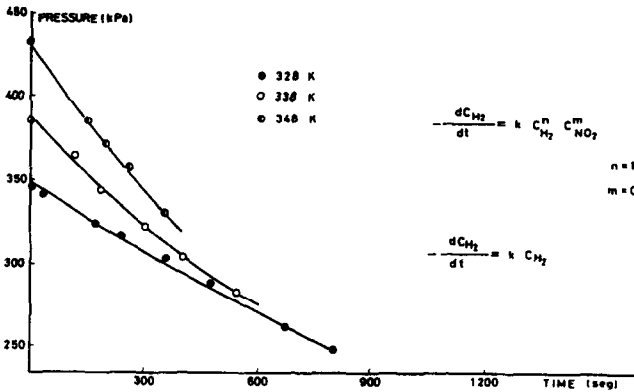
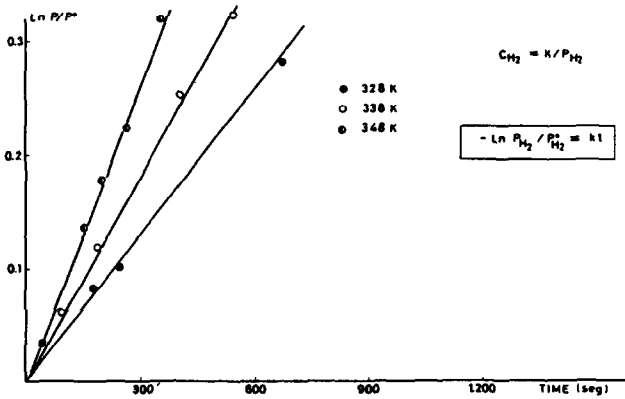
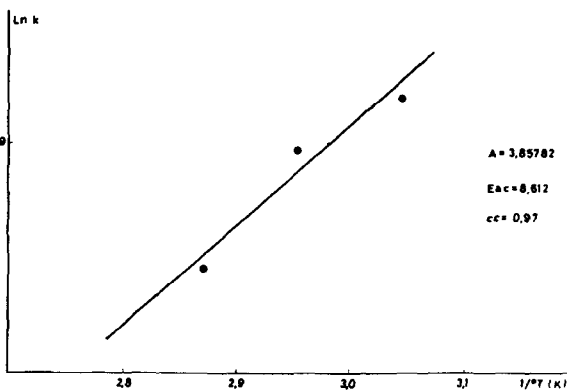


Fig. 5. Nitrobenzene hydrogenation kinetics.

Fig. 6. Dependence of $\ln P/P^*$ with time.Fig. 7. Dependence of k with temperature.

is catalyzed by the metal boride. Therefore, by introducing the metal salt into the borohydride solution, this latter reagent is rapidly decomposed. Only a small portion is used in the boride formation.

For metals which form stable oxoanions, the reaction goes on totally through step (2c) interrupting the boride formation.

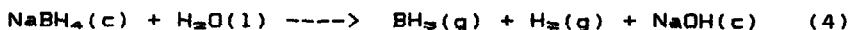
Nevertheless, reaction (2b) can be avoided by using an aprotic solvent such as THF. It forms a stable complex with BH_3 , which could act as the reducing agent.

The solution of the $THF:BH_3$ complex in THF is stabilized by adding $NaBH_4$, according to the following equilibrium reaction:



The $THF:BH_3$ complex stabilization generated by bubbling BH_3 in THF with $NaBH_4$ was demonstrated by Hopps (4). This reducing complex was used by Brown et al. (5) to direct reduction of carboxylic acid to alcohol.

In the present method the $THF:BH_3$ complex was produced in situ, by combining stoichiometric quantities of sodium borohydride and water eq. (4), in THF medium. The borane formed was retained as a complex, according to the following reaction scheme:



Using amounts of water just below stoichiometry relation, the equilibrium shown by eq.(3) is achieved and the stabilization of the borane solution is improved. This is the principal difference with the method proposed by Rei (6).

We were able to prepare Mo, Cr and Ni borides by using this new method. Molybdenum borides were prepared using solid Molybdenum(V) Chloride within an inert atmosphere and added to the complex Borane-THF. Chromium borides were obtained using solid Chromium(III) Chloride "anhydrous" in the same conditions as before. In both preparations the reaction goes on quickly producing hydrogen and a powdered black solid. We have been studying more extensively the Ni borides due to the data availability of their catalytic and structural properties.

The nitrobenzene to aniline reduction mechanism was deduced by Haber in 1898 and verified by Burge and Collins (7). This mechanism consists of two stages, the catalytic reduction from nitrobenzene to nitrosobenzene and the non catalytic reduction from nitrosobenzene to aniline. Therefore, the solvent influence has a main role in nitrosobenzene reduction, due to solvent polarity. So a low polar solvent decreases the reduction potential H_2/H^+ . We have experimentally verified that using this

sort of solvent the reduction was inhibited, while adding methanol in a further step the hydrogenation capacity was restored.

The nitrobenzene hydrogenation in liquid phase under the same conditions as ours, on nickel boride catalyst, but prepared by the Schlesinger-Brown method (Ni_2B), was studied by Collins (8).

The Collins' rate constant values are not specific ones. To compare these values with ours, a surface area of $150 \text{ m}^2/\text{g}$ was assumed for Collins' catalyst, although he didn't report them. This assumption came from the results obtained by us using his procedure (Brown-Technique). According to these considerations the new Collins' specific rate constant values are in the same order of magnitude than ours. (See Table 5).

TABLE 5 : Specific rate constants comparison

T (K)	$k^a \cdot 10^{12}$ (Collins) (Ni_2B)	$k^b \cdot 10^{12}$ (Ni_3B_4)	$k^b \cdot 10^{12}$ (Ni_3B)
328	353	9.9	238
353	747	23.9	349
473	1974	46.4	1362

a) Collins et al (1982) (8) (mol of H_2 / s. kPa m^2)

b) This work (mol of H_2 / s. kPa m^2)

It is interesting to note that with the new method, nickel borides with different B/Ni ratio and (B-B)/(Ni-Ni) bonds can be obtained. These present different activities and selectivities (9). Borides of metals which form stable oxoanions, e.g. chromium and molybdenum were also possible to be obtained.

CONCLUSIONS

- * It is possible to reduce metals in aprotic system using BH_3 -THF complex "in-situ"
- * Using this method it is possible to prepare borides with metals which forms stable oxoanions. e.g.: Mo, Cr.
- * It is possible to prepare borides with different B/Ni ratios.
- * The specific rate constant values for Ni_4B_3 show a good reproducibility regardless catalyst surface area changes. This suggest that the active surface sites are the same in all cases.
- * These borides (Ni_4B_3 and Ni_3B) are active in the nitrobenzene hydrogenations.
- * The reaction of nitrobenzene hydrogenation is the first order in H_2 partial pressure and independent on nitrobenzene concentration.

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