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X-Ray Photoelectron Spectroscopy of Nickel Boride Catalysts: Correlation of Surface States with Reaction Products in the Hydrogenation of Acrylonitrile

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X-Ray photoelectron spectroscopy has been employed to characterize the surface of nickel boride hydrogenation catalysts. The data indicate that the surface stoichiometry is identical to the bulk, Ni_2B. A typical catalyst has a surface composed of a boron oxide and a boride species. The oxide is produced during the preparation of the catalyst as a contaminant overlayer. The oxide : boride ratio is a function of the method of preparation of the catalyst. The oxide is water soluble and is therefore dominant when the catalyst is prepared by precipitation from a 95% ethanol solution. The boride species catalyzes the simple hydrogenation of acrylonitrile to propionitrile while the oxide catalyzes the conversion of acrylonitrile to 3-ethoxypropionitrile via a Michael addition.

INTRODUCTION

The reduction of an inorganic nickel salt with sodium borohydride in solution gives a finely divided black precipitate that contains boron (*1*). If the borohydride reduction is performed in aqueous solution, the product is referred to as a P-1 nickel boride. If the reduction is performed in 95% ethanol, the product is called a P-2 nickel boride (*2, 3*). Nickel borides produced in this fashion have been shown to be very active hydrogenation catalysts for aldehydes (*4*), olefins (*5*), and unsaturated compounds containing oxygen and nitrogen (*6, 7*).

The activity of a nickel boride catalyst has been shown to vary according to its method of preparation (*1, 8*). Generally, the P-2 catalyst is more active than the P-1 catalyst. The bulk stoichiometry of the nickel borides is also slightly variable (*1, 8, 9*). When boron and nickel were quantitatively determined in the borides, the total weight percentage did not equal 100%. Schlesinger *et al.* (*1*) attributed this to a partial oxidation. A more detailed investigation by Maybury and co-workers (*8*) indicated that part of the discrepancy could be accounted for by the presence of tightly bound hydrogen. All of the available data, however, are consistent in that the Ni : B ratio is 2 : 1. The studies of Schlesinger *et al.* (*1*) and Maybury *et al.* (*8*) were performed on nickel borides precipitated from different salts and solvents. Thus it appears that the bulk stoichiometry is independent of the metal salt and solvent used to prepare the catalyst.

In heterogeneous catalysis the catalytic activity is a function of surface properties. Therefore, the determination of surface stoichiometry and chemical state(s) of the surface play a most important role in understanding the activity of the nickel boride catalysts. One instrumental technique capable of elucidating the chemial nature of surface states in a quantitative fashion is X-ray photoelectron spectroscopy (XPS). Numerous XPS investigations of catalytic surfaces have been reported (*10*). These studies have mainly been concerned with the use of XPS to achieve an understanding of the effect various preparative methods and treatments have on the surface chemis-

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try of the catalyst. For example, Wu *et al.* (*11*) have studied the nature of the nickel species on the surface as a function of the support for a series of nickel catalysts. Brinen and Armstrong (*12*) have studied the nature of the surface chemical composition for a series of hydrodesulfurization catalysts (Co–Mo–Al_2O_3). The effects are discussed in terms of sulfiding with a mixture of H_2S and H_2 at elevated temperatures. A similar study on Ni–W–Al_2O_3 catalysts was performed by Ng and Hercules (*13*). Schreifels *et al.* (*14*) have studied the effect of heat treatments on the oxidation states of copper and chromium present on the surface of copper chromite catalysts.

Very few reports have attempted to correlate surface composition as determined via XPS with catalytic activity for specific reactions. One such investigation has been reported by Okamoto and co-workers (*15*). The authors studied the surface composition of SnO_2–MoO_3 catalysts with XPS and correlated the data with the catalytic activity in the dehydration and dehydrogenation of *sec*-butanol. Their data demonstrate that the determination of the surface composition of binary oxides is necessary in order to discuss their catalytic activity in detail. Carberry and Kuczinski (*16*) found that a silver catalyst was more active for the conversion of ethylene to ethylene oxide when surface calcium was present.

In the present study, XPS has been employed to elucidate the qualitative and quantitative chemical nature of the surface of a series of nickel boride catalysts as a function of preparative method. The surface characteristics will be correlated with the reaction products formed in the hydrogenation of acrylonitrile.

EXPERIMENTAL

Apparatus. The vessel used for catalyst preparation consisted of a 500-ml flask with a side arm. Attached to the side arm was a high-vacuum stopcock through which the sodium borohydride, wash solution, or solvent could be added without atmospheric exposure. The neck of the flask was fitted with a filtering adapter which consisted of a coarse-fitted funnel with a high-vacuum stopcock attached to the stem. A 24/40 ground-glass joint was attached to the mouth of the funnel. This apparatus allowed one to prepare the catalyst without exposure to the atmosphere.

The hydrogenations were carried out in a constant-pressure Parr-like hydrogenator at 6 atm and 70°C.

The X-ray photoelectron spectra were recorded using a GCA-McPherson Instrument Corporation ESCA 36 photoelectron spectrometer. The base pressure in the sample chamber was routinely 10^{-7} Torr. Mg$K\alpha$ X rays ($h\nu$ = 1253.6 eV) were used for excitation of the photoelectron spectra. The spectra were calibrated by adjusting the energy scale such that the C(1*s*) binding energy from the adventitious hydrocarbon contaminant layer was 285.0 eV.

To ensure that the integrity of the catalytic surface had been maintained, a device was fabricated which allowed one to transfer the pyrophoric nickel boride from the preparation flask to the sample chamber of the spectrometer without exposure to the atmosphere (*17*). The boride was transferred from the flask to the device in a glove box containing dry nitrogen. The valve of the device was then closed and the transfer chamber was bolted to the sample chamber.

Preparation of the nickel boride. A 0.8 *M* nickel solution was prepared by dissolving nickel acetate in the appropriate solvent (e.g., a P-1.75 catalyst would be made from a 75% ethanol–water solution). A 1.1 *M* solution of sodium borohydride was prepared in the same solvent that contained 0.5 ml of 0.2 *M* sodium hydroxide. Once the sodium borohydride was completely dissolved, the resulting cloudy solution was filtered.

To prepare 1 mmole of catalyst, 12 ml of the nickel acetate solution was poured into the catalyst preparation flask. One milliliter of the filtered sodium borohydride solution was then poured into the reservoir attached to the side arm of the flask. The reaction flask was attached to a vacuum line via standard-taper ground-glass joints. Both the reservoir containing the sodium borohydride and the reaction flask were then evacuated. The reservoir was then refilled with hydrogen.

Reduction of the nickel was accomplished by simultaneously shaking the reduction flask and opening the stopcock on the side arm. After the vigorous evolution of hydrogen had ceased, the reaction flask was isolated by closing the stopcocks on the fritted adapter and on the side arm. The reaction flask was then disconnected from the vacuum system. Filtration was accomplished by connecting a vacuum line to the end of the fritted adapter, inverting the reaction flask, and opening the stopcock. After filtration was complete, the catalyst was washed twice with 5-ml aliquots of 95% ethanol. It should be noted that the P-1.75 and P-2.00 catalysts had such a small average particle size that a significant amount of the catalyst would pass through the frit during filtration. Therefore, all of the catalysts were dispersed in Kieselguhr to facilitate filtration. This was accomplished by mixing 1.00 g of Kieselguhr with the nickel acetate solution for 10 min immediately prior to reduction.

Materials. The acrylonitrile was obtained from the Aldrich Chemical Company in 99+% purity and was freshly distilled prior to use. The nickel boride (99% NiB), nickel acetate, sodium borohydride, nickel foil, and Kieselguhr were obtained from Ventron Corporation. The nickel borides (99% Ni_2B and 99% Ni_3B) were obtained from CERAC, Incorporated. Elemental boron, 99.8% purity, was obtained from Apache Chemicals, Incorporated. The various boron oxides and nickel oxide were obtained from Scientific Products in reagent-grade purity.

RESULTS AND DISCUSSION

Determination of surface chemistry. Comparisons with standards must be made if one is to determine the chemical nature of surface species with XPS. Thus, correlations between core electron binding energy and chemical state are possible. Table 1 contains the binding energies for a number of boron and nickel compounds. From these data, it is evident that the borohydride anion (BH_4^-), the boron oxides, and elemental boron can easily be differentiated from one another. The $NaBH_4$ undergoes a photooxidation with X-ray exposure as indicated by the growth of an oxide peak as a function of exposure time. Also included in Table 1 are data from a number of commercially available nickel borides of varying stoichiometry that were prepared by thermal fusion techniques. To obtain these data, the powders were ground in a mortar and pestle immediately prior to analysis. All of the XPS spectra for the fused borides contained two B(1*s*) photoelectron lines. The

TABLE 1

Binding Energies (eV) of Nickel and Boron Standards and Nickel Boride Catalysts

	B(1*s*)			Ni($2p_{3/2}$)
	Line 1	Line 2	Line 3	
Standards				
B			186.7	
$NaBH_4$	193.3[a]	188.7		
H_3BO_3	193.2			
B_2O_3	193.3			
$Na_2B_4O_7$	192.0			
Ni				852.6
NiO				856.2
NiB	193.7	189.1		853.4
Ni_2B	194.3	190.1		852.6
Ni_3B	192.1	187.6		853.2
Catalysts				
Ni_2B P-1.00	192.3	187.9		852.0
P-1.50[b]	192.2	188.0		852.1
P-1.50[c]	193.5	—		852.9
P-1.75	192.2	187.9		851.9
P-2.00	193.0	187.8		852.0

[a] Initially weak, intensifies with X-ray exposure.

[b] Atmospheric exposure followed by H_2 reduction at 400°C.

[c] No atmospheric exposure.

relative intensities of the two lines were a function of the thoroughness of grinding. The lower-energy line, which increased in relative intensity with grinding, was assigned to the boride species. The higher-binding-energy component was attributed to a surface oxide. It is also worthy of note that the B(1*s*) binding energy for the boride species is higher than that for elemental boron. The Ni($2p_{3/2}$) photoelectron binding energies are listed for Ni, NiO, and the commercial nickel borides. The Ni($2p_{3/2}$) binding energies for the borides are slightly higher than that of elemental nickel.

Also included in Table 1 are B(1*s*) and Ni($2p_{3/2}$) binding energies for nickel borides produced by reduction with sodium borohydride. The B(1*s*) energies correspond closely to those for the thermally fused borides. Thus the boron species produced by the two techniques are, within the resolution of the XPS technique, chemically similar. However, the nickel species appear to be slightly different. Notice that nickel in the fused borides has a higher binding energy than elemental nickel. On the other hand, the nickel in the borohydride reduced borides has a lower binding energy than elemental nickel. The relative charge on nickel in the reduced borides may play an important role in the determination of their catalytic properties (i.e., activity, selectivity, and resistance to poisoning). The fused nickel borides show no catalytic activity in hydrogenation reactions.

Slight exposure of the nickel borides to the atmosphere produces significant oxidation of the active surface. Therefore, it is necessary to determine whether the catalytic surface could be regenerated by reduction with H_2. A P-1.50 catalyst was prepared and dried *in vacuo*. When air was bled into the preparation flask, the catalyst immediately ignited. The resulting gray powder was placed into a tube furnace and heated to 400°C in a dynamic hydrogen atmosphere. After 1 hr of reduction, the reaction tube was carefully sealed to avoid reexposure to the atmosphere. The reduced powder was placed into the transfer device in an inert atmosphere such that it could be transferred to the photoelectron spectrometer. Figure 1 contains the Ni($2p_{3/2}$) and B(1*s*) spectra for the fresh catalyst (A) and the "regenerated" catalyst (B). In each case, the Ni($2p_{3/2}$) spectra are characteristic of elemental nickel. However, the B(1*s*) spectrum in Fig. 1B contains only a contribution from an oxidized boron whereas the B(1*s*) spectrum in Fig. 1A contains both a boride and a boron oxide. These data indicate that "regeneration" of the catalytic surface in a dynamic hydrogen atmosphere at 400°C reduces only the nickel. The boron remains in an oxidized state. After the boron has been oxidized, reduction back to the boride is difficult if not impossible. The data imply that if the nickel boride as a unit is the active species, extreme care must be taken to ensure that oxidation does not occur. Total reactivation of a spent catalyst will, therefore, be difficult, if not impossible.

Determination of surface stoichiometry. As discussed above, the *bulk* stoichiometry of the nickel borides is such that the Ni : B ratio is 2 : 1. One must be certain that the *surface* stoichiometry is known if a thorough understanding of the catalytic system is to be obtained. It is possible to obtain stoichiometric data from XPS spectra by the analysis of relative peak areas. Since XPS samples only the first 15–20 Å, these stoichiometries are the average over the first several layers of the sample. In such an analysis, errors resulting from consideration of electron escape depths must be minimized. This can be accomplished by analyzing photoelectron data obtained for photoelectrons of approximately the same binding energy. The main source of error is the thickness of any contaminant layers found on the surface. If the thickness varies from sample to sample and electrons of drastically different energies are employed for analysis, large variations in peak area ratios result.

The binding energies of the Ni($2p_{3/2}$),

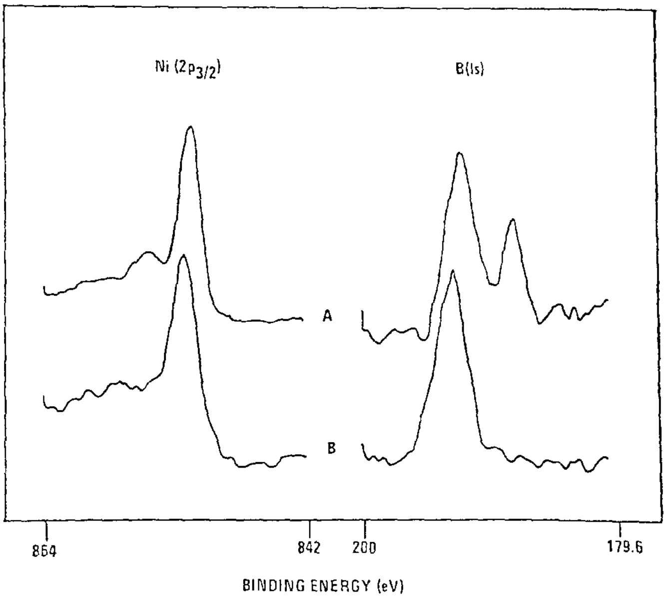


FIG. 1. Ni($2p_{3/2}$) and B($1s$) spectra of a P-1.50 nickel boride catalyst: (A) with no atmospheric exposure and (B) after atmospheric exposure followed by H_2 reduction at 400°C.

Ni($3s$), and Ni($3p$) electrons differ from the B($1s$) binding energy by 650, 80, and 120 eV, respectively. Since the ΔE between the Ni($2p_{3/2}$) and B($1s$) electrons is so large, a considerable error would be introduced if these photoelectron lines were employed in quantitative measurements for nickel and boron. To minimize errors from surface contamination, the Ni($3s$) and Ni($3p$) electrons were chosen for intensity correlations with the B($1s$) electrons.

Matrix effects can also severely affect the accuracy of quantitative determinations employing XPS data. Wyatt *et al.* (*18*) found that using a $PbSO_4$ calibration curve for lead analyses in a PbI_2 system would result in errors as large as 50%. To determine the severity of matrix effects in the determination of stoichiometry in the nickel boride system, two calibration curves were established for nickel and boron. The first curve was generated by intimately mixing NiO and B_2O_3 powders such that the Ni : B ratios were 1, 2, and 3. The appropriate nickel and boron XPS data were then collected on the mixtures. Figure 2 contains the calibration curves obtained by plotting the Ni($3p$) : B($1s$) and Ni($3s$) : B($1s$) peak area ratios versus the Ni : B atom ratios. Notice that the relationship is essentially linear.

A second set of calibration curves was generated by measuring the identical spectra for a series of commercial nickel borides (NiB, Ni_2B, and Ni_3B) synthesized by thermal fusion techniques. These data are also plotted in Fig. 2. Note that the two calibration curves differ significantly in slope. The largest deviation occurs at lower boron concentrations where the estimate of Ni : B can vary by as much as 40–50%. Since the fused borides are closer in chemical nature to the nickel boride catalysts, any matrix effects would be minimized by use of the calibration curve obtained on the fused materials. As discussed above, the effect of surface contamination would be minimized by use of photoelectrons with similar energies. For this reason, the Ni($3s$) : B($1s$) calibration curve should provide the best stoichiometric data.

When the Ni($2p_{3/2}$), Ni($3s$), and B($1s$) were recorded for P-1.00, P-1.50, P-1.75, and P-2.00 catalysts, the boron was invari-

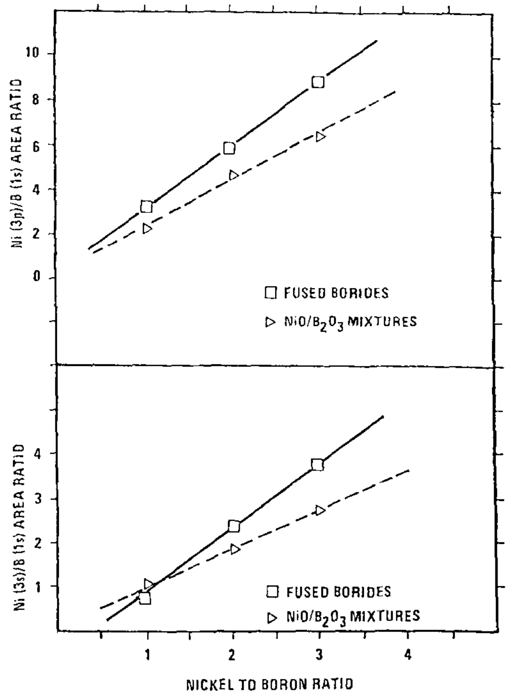


FIG. 2. Calibration curves for the determination of nickel : boron ratios in nickel boride catalysts.

ably present in two states: an "oxide" at higher binding energy than the "boride." The spectra in Fig. 1A represent typical data. However, from catalyst to catalyst, the intensity of the oxide line varied relative to that attributable to the boride. The P-1.00 catalyst had the least oxide and the P-2.00 catalyst contained the most. Figure 3 is a plot of oxide : boride ratio versus catalyst preparation. As the solvent becomes more ethanolic (P-2.00 is formed via reduction in 95% ethanol) the ratio sharply increases to a maximum. Thus, there is a significant solvent effect on the relative amounts of oxide and boride present on the surface. This effect could be due to an alteration of the surface (e.g., surface oxidation of the boride) or may be attributed to the deposition of an oxidized boron compound during or after precipitation of the nickel boride. Table 2 contains the Ni(3*s*) : B(1*s*) peak area ratios. The third column contains the ratios obtained using the total B(1*s*) signal (oxide + boride) while the fourth column contains that obtained using only the B(1*s*) boride signal. None of the data yield a single, unambiguous stoichiometry. The data using the total B(1*s*) area suggest two stoichiometries. The P-1.00 and P-1.50 catalysts have one stoichiometry while the P-1.75 and P-2.00 have another. If the boron oxide peak is a deposited oxide, the Ni(3*s*) signal relative to the boride B(1*s*) signal should vary in intensity as more of the boron oxide is deposited. As shown in Fig. 3, the boron oxide contribution increases as one moves from a P-1.00 to a P-2.00 catalyst. Thus, the Ni(3*s*) : B(1*s*) ratio would be expected to change for these

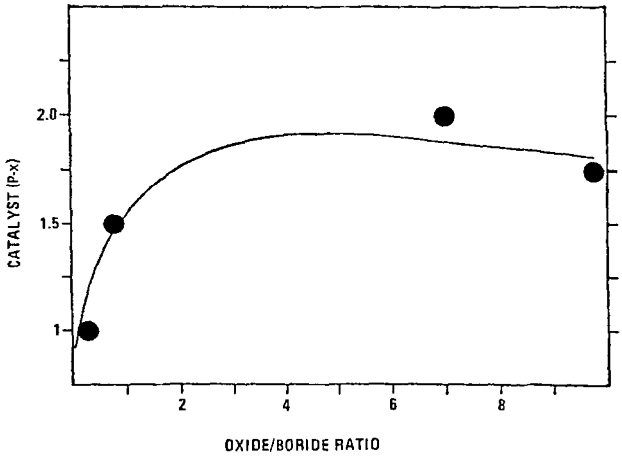


FIG. 3. Variation of oxide/boride ratio as a function of catalyst preparation.

TABLE 2

Nickel : Boron Photoelectron Area Ratios as a Function of Catalyst Preparation

	Surface area (m^2/g)	$Ni(3s)/B(1s)_{oxide+boride}$	$Ni(3s)/B(1s)_{boride}$
P-1.00	24.1	2.02	2.86
P-1.50	40.8	2.10	3.75
P-1.75	39.5	0.61	5.25
P-2.00	58.0	0.97	6.53

catalysts. The ratio in Table 2 changes as a function of the solvent used in preparation of the catalyst. The greater the ethanol content of the solvent, the greater is the Ni(3*s*) : B(1*s*) ratio. Thus, either the stoichiometry is varying or there is a significant attenuation of the signal due to a surface impurity.

It is possible that the solvent does not affect the stoichiometry beneath the oxide layer. If this were true, the solvent may be affecting only the thickness of the oxide overlayer. By use of solvents that cause the oxide layer to vary, it should be possible to determine the dependence of the Ni(3*s*) : B(1*s*) and Ni(3*p*) : B(1*s*) ratios on surface oxide contamination. In Figs. 4 and 5 the dependence of both the Ni(3*p*) : $B(1s)_{boride}$ and the Ni(3*s*) : $B(1s)_{boride}$ area ratios on the $B(1s)_{oxide}$: $B(1s)_{boride}$ ratio is shown. Figures 4 and 5 indicate a dependence that is nearly linear. Thus, the assumptions that the oxide is a surface contaminant and that the stoichiometry of the nickel boride under the contaminant is constant for different preparations appear to be true. Extrapolation of the data to zero contamination leads to unattenuated ratios for Ni(3*p*) : B(1*s*) and Ni(3*s*) : B(1*s*) of 7.2 and 2.8, respectively. These extrapolated ratios correspond to a Ni : B ratio of 2.2 as determined using the calibration curve obtained for the fused borides. This is well within experimental error of 2.0. Thus, the nickel boride surface stoichiometry appears to be identical to the bulk, Ni_2B.

The oxide layer is a contaminant whose concentration (thickness) is associated with the solvent used in preparation of the catalyst. Therefore, one can surmise that the boron oxide layer is soluble in water. Furthermore, the removal of this contam-

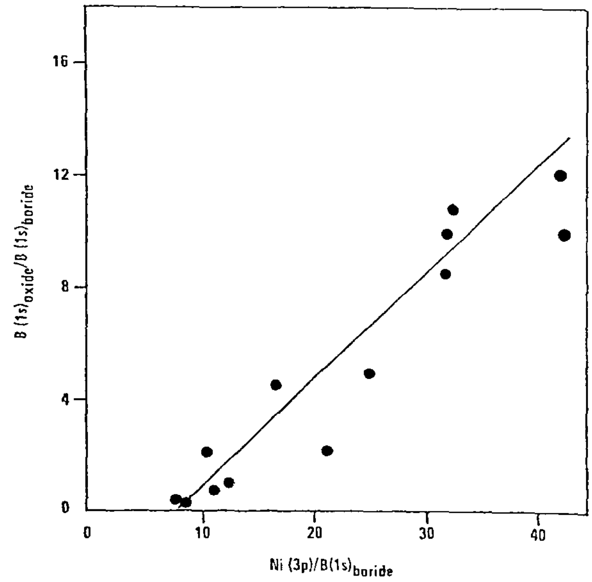


FIG. 4. Effect of oxide contamination on the relative intensities of the Ni(3*p*) and $B(1s)_{boride}$ photoelectron lines.

inant should significantly alter the Ni(3s) : B(1s)$_{\text{boride}}$ ratio. After washing a P-2.00 catalyst with water, the amount of oxide relative to the boride decreased from a B(1s)$_{\text{oixde}}$: B(1s)$_{\text{boride}}$ ratio of 9.3 to 0.27. The Ni(3s) : B(1s)$_{\text{boride}}$ ratio likewise changed from 7.3 to 2.9 which agrees well with the extrapolated value of 2.8. During the reduction of nickel acetate with $NaBH_4$, boric acid is produced (*19*). Once some nickel boride has been produced, the boride itself will catalyze the hydrolysis of $NaBH_4$ to $NaBO_2$ (*1*). These boron oxides produced via side reactions are less soluble in ethanol than in water. Thus, it is not surprising that more boron oxides will precipitate from an ethanolic solvent than an aqueous solvent during and after the precipitation of the nickel boride.

One can calculate the thickness of overlayers by using photoelectron peak intensities. The peak intensity, I, has been shown to vary exponentially with overlayer thickness, t (*20*):

$$I = I_0 \exp(-kt), \tag{1}$$

where

$$k = 1/\lambda(\sin\theta)^{-1}, \tag{2}$$

I_0 is the intensity of a photoelectron line from an uncontaminated surface, λ is the escape depth of the photoelectron, and θ is the photoelectron takeoff angle. For the McPherson ESCA 36, $\theta = 45°$. For $t = 2\lambda$, I is $\sim$ 6% of I_0. In other words, the signal is attenuated by 94%. For the P-2.00 catalyst, the B(1s)$_{\text{boride}}$ was approximately 6% of that for the water-washed catalyst.

It has been shown (*21, 22*) theoretically that

$$\lambda_T(\epsilon_i) = \epsilon_i / \{a_T(\ln \epsilon_i + b_T)\}, \tag{3}$$

where a_T and b_T are constants for a particular material and ϵ_i is the kinetic energy of the electron. Penn (*22*) has calculated $\lambda_T(\epsilon_i)$ for many of the elements. He has also given values for a_T and b_T for many materials. Using Penn's values, the escape depth for photoelectrons with a kinetic energy of 1056 eV [B(1s)$_{\text{oxide}}$] was calculated to be 18.2 Å. This implies that the oxide overlayer on a P-2.00 catalyst is approximately 36 Å thick.

Correlation of reaction products with surface chemistry. It was of interest in this laboratory to study the hydrogenation kinetics of different organic functional groups using the P-2.00 nickel boride catalyst. The catalyst was dispersed in Kieselguhr for ease of handling. During the course of studies of the reduction of acrylonitrile to propionitrile in ethanol, a side reaction [1] was observed:

$$H_2 + CH_2{=}CH{-}CN \xrightarrow[\text{P-2.00 catalyst}]{\text{EtOH}} CH_3CH_2{-}CN \tag{1}$$

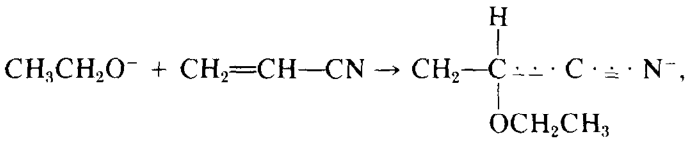
The side reaction was evidenced by the fact that less than one equivalent of hydrogen was taken up during the course of the reaction. Gas chromatographic analysis indicated the presence of a compound with a much longer retention time than either acrylonitrile or propionitrile. The side product was isolated via vacuum distillation and was found to have a boiling point of 173.5–174.5°C. The infrared spectrum contained a nitrile stretch (2240 cm^{-1}) and a very intense C–O–C stretch (1120 cm^{-1}). The NMR spectrum of the compound contained the following absorbances and relative integrations: 3.5δ(multiplet,4); 2.5δ(triplet,2); 1.2δ(triplet,3). The mass spectrum indicated a molecular ion peak at 99 amu. These data are consistent with the structure of 3-ethoxypropionitrile:

$$CH_3{-}CH_2{-}O{-}CH_2{-}CH_2{-}CN$$

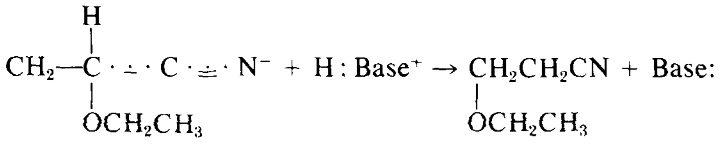
The NMR spectrum of 3-ethoxypropionitrile listed in Sadtler's Index of NMR spectra (4933M) was identical with that of the pure compound produced in the side reaction.

Addition of an ethoxy group to an olefinic bond, normally referred to as the Michael reaction, is common (*23*). In particular, acrylonitrile is known to generally undergo reactions with alkoxide ions (*24*). The condensation takes place under the influence of alkaline reagents, typically metal alkoxides. The Michael addition is believed to proceed by the following mechanism:

$$CH_3CH_2OH + Base: \rightarrow H:Base^+ + CH_3CH_2O^-, \qquad [2]$$



$$CH_3CH_2O^- + CH_2{=}CH{-}CN \rightarrow CH_2{-}\overset{H}{\underset{OCH_2CH_3}{C}}\cdot\overset{-}{\cdot}\cdot C\cdot\overset{=}{\cdot}\cdot N^-, \qquad [3]$$



$$CH_2{-}\overset{H}{\underset{OCH_2CH_3}{C}}\cdot\overset{-}{\cdot}\cdot C\cdot\overset{=}{\cdot}\cdot N^- + H:Base^+ \rightarrow \underset{OCH_2CH_3}{C}H_2CH_2CN + Base: \qquad [4]$$

Some of the bases commonly employed are alkoxides, ammonia, amines, metallic sodium or potassium, and potassium carbonate.

The production of 3-ethoxypropionitrile in the reduction of acrylonitrile was surprising in that no base has been added to the reaction mixture. However, as indicated above, the P-2.00 catalyst contained a significant layer of an absorbed boron oxide. Furthermore, it is well known that borates are quite basic. For example, boric acid has a pK_a of 9.24. Thus, it is likely that the presence of a basic boron oxide on the surface of the P-2.00 nickel boride catalyst would catalyze the formation of 3-ethoxypropionitrile via a Michael-type addition. If this were true, one would expect to observe a dependence of 3-ethoxypropionitrile production on the specific catalyst preparation used. Since, as shown in Fig. 3, the amount of oxide varies with preparative technique, a P-1.00 catalyst should produce the smallest amount of 3-ethoxypropionitrile and a P-2.00 catalyst should produce the most.

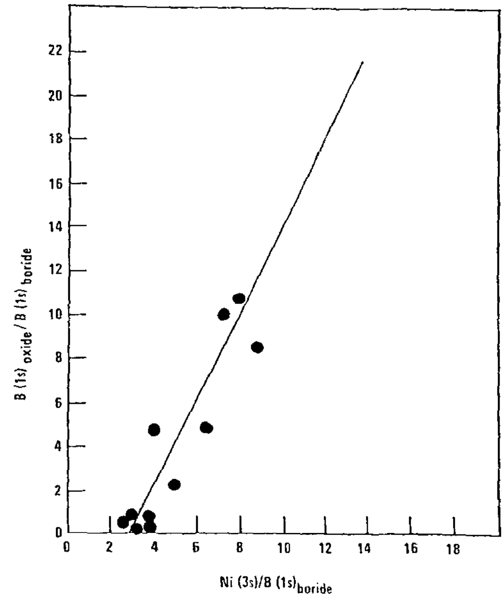


FIG. 5. Effect of oxide contamination on the relative intensities of the Ni(3*s*) and B(1*s*)$_{boride}$ photoelectron lines.

P-1.00, P-1.50, and P-1.75 nickel boride catalysts were prepared and the hydrogenation of acrylonitrile was performed under identical conditions to those of the P-2.00 hydrogenation. The reaction was considered complete when the uptake of hydrogen ceased. The resulting reaction mixtures were analyzed via gas chromatography. Figure 6 shows the dependence of the production of 3-ethoxypropionitrile on catalyst preparation. As predicted, as the solvent used to prepare the catalyst becomes more ethanolic, there is an increase in the production of 3-ethoxypro-

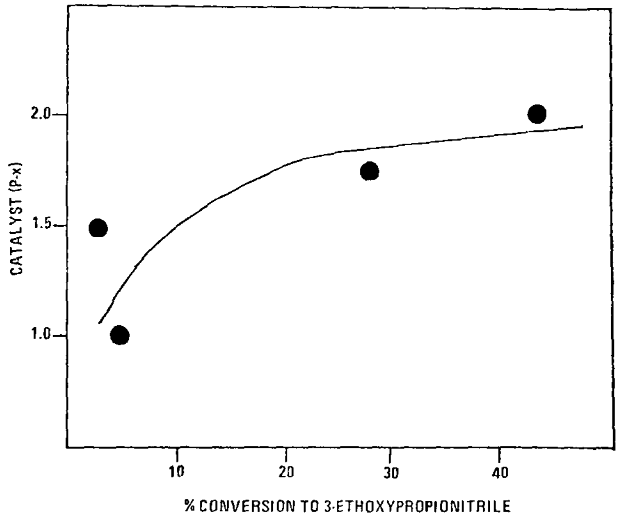


FIG. 6. Effect of catalyst preparation on the conversion of acrylonitrile to 3-ethoxypropionitrile.

pionitrile. If a comparison is made between the amount of oxide present on the catalyst surface (oxide/boride ratio) and the amount of 3-ethoxypropionitrile produced (Fig. 7). A linear relationship is observed.

As was previously mentioned, a P-2.00 catalyst that had been washed with water after preparation contains less oxidized boron than it did before washing. Therefore, this washed catalyst should convert much less of the acrylonitrile to 3-ethoxypropionitrile than the unwashed P-2.00 catalyst. In Fig. 7 the half-filled circle represents the result obtained in the hydrogenation using a water-washed P-2.00 catalyst. Note that within experimental error, the water-washed catalyst produces the expected amount of 3-ethoxypropionitrile. Obviously, there is a strong dependence of conversion of acrylonitrile to 3-ethoxypropionitrile on the amount of oxide present on the surface of nickel boride catalysts.

The surface oxide necessarily represents a very small percentage of the total weight of the catalyst. If this were not true, the analyses discussed above would have noted

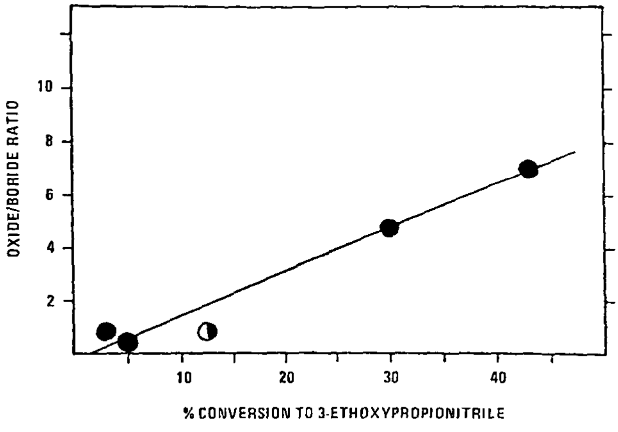


FIG. 7. The percentage conversion of acrylonitrile to 3-ethoxypropionitrile as a function of oxide/boride ratio.

large variations in the Ni : B ratio as different solvents were used. As discussed, all preparations resulted in analyses whose Ni : B ratios are 2 : 1. In the acrylonitrile hydrogenations, the substrate (acrylonitrile) to catalyst ratio was 1000 : 1. Since the 36Å-thick oxide layer necessarily represented a very small percentage of the P-2.00 catalyst, the substrate to surface oxide ratio must be extremely high. If the conversion of acrylonitrile to 3-ethoxypropionitrile can compete so successfully with the simple hydrogenation reaction, the surface oxide must have an extremely high catalytic activity.

Typically, the Michael reaction requires the use of a large amount of base as the catalyst (*23*). In the present case, much smaller relative amounts of catalyst are required. Normally, the Michael reaction is reversible in that higher temperatures favor rearrangement and retrogression (*25*). Thus, the 70°C reaction temperature employed in the present case would normally be expected to inhibit the formation of the addition product. It is obvious that the oxide overlayer on the nickel borides produces 3-ethoxypropionitrile via a Michael-type reaction much more efficiently than the bases typically employed.

CONCLUSIONS

1. The surface of a nickel boride catalyst is covered with an oxidized boron species that varies in thickness with the method of preparation. As the preparation solvent becomes more ethanolic, the layer of oxidized boron increases. A P-2.00 catalyst has a layer of the oxidized species that is approximately 36 Å thick.

2. The surface stoichiometry of nickel boride, Ni_2B, is essentially identical to that of the bulk.

3. In the hydrogenation of acrylonitrile in an ethanolic solvent, 3-ethoxypropionitrile is produced as a side product. The extent of production of 3-ethoxypropionitrile is a function of the oxide/boride ratio on the catalytic surface. This ratio is a function of the method of preparation of the catalyst.

4. The characterization of a catalytic surface with X-ray photoelectron spectroscopy can provide both qualitative and quantitative information as to the course taken by a chemical reaction employing the catalyst.

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