Catalytic Behavior of Graphite Nanofiber Supported Nickel Particles. 3. The Effect of Chemical Blocking on the Performance of the System

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Graphite nanofibers are a newly developed type of material produced by the catalytic decomposition of carbon containing gases at high temperatures. The individual components of these conformations, small-sized graphite crystallites, are arranged in such a manner that only the edge regions are exposed. The carbon atoms at these sites that are arranged in two conformations, "armchair" or "zigzag", act as templates for the nucleation of metal crystallites. Treatment of graphite with certain phosphorus compounds is a process that is known to result in preferential blocking of the "armchair" faces, whereas boron oxide selectively substitutes into the "zigzag" faces. In the current investigation pretreatment in phosphorus oxide was found to exert little or no effect on the subsequent catalytic performance of graphite nanofiber supported nickel with respect to hydrogenation of ethylene and 1-butene. In contrast, incorporation of boron into the carbonaceous support, which resulted in blockage of the "zigzag" sites of the graphite nanofibers rendered the supported metal system virtually inactive toward hydrogenation of either of the olefins. These results suggest that the active state of nickel is one where the particles are preferentially located on the "zigzag" faces of the nanofiber structures. Under these conditions the metal particles adopt a crystallographic arrangement that is favorable toward reaction with both reactant molecules. It is evident that one can control the catalytic behavior of a given metal by careful tailoring the support structure at the atomic level.

Introduction

The use of additives in catalysis to selectively promote or inhibit specific reactions in hydrocarbon decomposition reactions is widely practiced.^{1–3} In this context, the most commonly studied nonmetal additives are sulfur and chlorine.^{4–13} The addition of sulfur in large amounts poisons a metal catalyst; however, trace amounts of the element can enhance the selectivity to aromatic products and decrease the hydrogenolysis activity of a reforming catalyst.^{4–8} Chlorine is a well-known promoter of isomerization reactions and is frequently added to catalysts to enhance the acidic nature of a support material such as γ -Al₂O₃. The acidity of the catalyst has been used to control the relative rates of hydrocracking and isomerization reactions and also inhibit the deposition of carbon.^{9,10} The use of additives must, however, be carried out under the correct conditions, with the appropriate loading in order to achieve the desired effect.

The use of phosphorus as an additive to various metals has been used in several catalytic studies involving hydrodesulfurization reactions.^{14–17} Eijsbouts and co-workers¹⁷ reported that the hydrodesulfurization activity of a carbon-supported nickel catalyst was enhanced, whereas the performance of other transition metal catalysts for this reaction were inhibited by the presence of phosphorus. The effect of introducing phosphorus into supported metal particles for various hydrogenation reactions has been examined by a number of research groups.^{18–23} Ko and Chou¹⁸ demonstrated that P-Ni/Al₂O₃ catalysts were highly selective for the hydrogenation of α -pinene to *cis*-pinene when compared to the performance of a Ni/Al₂O₃ catalyst. In another investigation, Yoshida and co-workers,^{19,20} using pretreated amorphous Ni-P and Ni-B alloys, claimed that these catalysts were highly active for the hydrogenation of olefins. These workers also concluded that di-olefins were less readily

hydrogenated than mono-olefins. In a reactant mixture containing both sets of compounds, however, it was found that the di-olefins were so strongly adsorbed on the catalyst surface that inhibition of the hydrogenation of the mono-olefins occurred. The use of Ni–P catalysts has also been found to exhibit a high activity for the reduction of nitrobenzene to aniline.²¹

Graphite nanofibers are produced by the thermal decomposition of carbon-containing gases over selected metal catalysts. These solids consist of extremely small graphite crystallites stacked in various directions with respect to the fiber axis, with only edges exposed. It is this feature that makes the material different from any other form of carbon because, since there is no basal plane exposed, interaction of the solid with other phases occurs solely at these edges. Research in the area of carbon nanofibers that possess unique tailored structures has gained momentum in the last 10 years as potential applications for these novel materials are identified.²⁴⁻³⁰ In previous studies, both nanofibers and nanotubes have been utilized as novel catalyst support media with exciting results.³⁰⁻³⁴ Park and co-workers³³ found that the structural characteristics adopted by particular types of graphite nanofibers exerted a significant impact on the catalytic behavior of supported nickel particles. This difference in performance was attributed to the ability of the nickel to adopt specific orientations following nucleation on either the "zigzag" $(10\overline{10})$ or the "armchair" $(11\overline{20})$ faces of the graphitic nanofibers. In this respect it is important to consider the work of Yang and Chen³⁵ who reported that a given crystallographic orientation of nickel would preferentially decompose carbon monoxide while a different set of faces favored the precipitation of dissolved carbon in the form of graphite.

A similar pattern of behavior was found by Cooper and Trimm³⁶ during a study of the decomposition of propylene over



Figure 1. Schematic representation showing the proposed structural arrangements involved in the bonding of (a) phosphorus and (b) boron oxide species to the respective "armchair" and "zigzag" faces of graphite nanofibers. Functionality has been omitted from many of the layers for the sake of clarity.

iron catalysts possessing different crystallographic orientations. These workers found that only certain crystal faces were capable of decomposing propylene, while others exhibited a limited activity toward the reaction. It is reasonable to assume therefore, that if one could impregnate a metal in a desired orientation onto a support material it would be possible to tailor both the activity and selectivity of the system to a desired level.

In this regard, it is well established that phosphorus species will preferentially bond to the graphite "armchair" (1120) faces while boron species tend to favor attachment to the "zigzag" (1010) faces.^{37–40} A schematic rendition of the manner by which these additives bond to the respective faces of the graphite structure is shown in Figure 1a,b. It should be emphasized that these observations have provided the rudiments for the development of surface treatments designed to protect graphite against oxidation at high temperatures.³⁷

In the current investigation, we have endeavored to exploit this concept by depositing nickel onto graphite nanofibers that have been pretreated with either phosphorus- or boron-containing compounds. From such studies it should be feasible to discriminate between the behavior of nickel on the pristine and modified nanofiber surfaces. One might argue that this procedure would merely result in a moderation in the catalytic behavior of the metal crystallites located on the capped regions of the surface. Previous studies, however, have indicated that when a metal is introduced onto such treated graphite surfaces then complete suppression of catalytic activity of the crystallites that form on the phosphorus- and boron-substituted regions of the substrate occurs, whereas those that accumulate on the unprotected faces exhibited normal behavior.^{38,39}

Experimental Section

Materials. The graphite nanofibers chosen for this present study were the "platelet" variety, in which the graphite platelets constituting the material were aligned in a direction perpendicular to the fiber axis. In this particular arrangement, the nanofibers expose an equivalent number of "armchair" and "zigzag" faces to the gas phase. These structures were grown according to the protocol described in a previous paper⁴¹ by passing a desired mixture of ethylene, carbon monoxide, and hydrogen over iron powder at 600 °C for periods of up to 3 h. The resultant carbon nanofibers were demineralized in dilute HNO₃ acid for a period of 7 days to remove any of the original metal catalyst particles. The effectiveness of this step was checked by X-ray diffraction analysis, which showed a complete absence of any metallic components at this stage. The nanofibers were then thoroughly washed in deionized water prior to being dried overnight in air at 110 °C and stored until required for use.

The graphitic nanofibers were subsequently impregnated with an aqueous solution of either methylphosphonic acid or ammonium pentaborate to realize a 5 wt % additive loading. The aqueous solution was added slowly to the carbonaceous solid with constant stirring at 90 °C until the consistency attained that of a thick paste. This doped nanofiber mixture was dried overnight in an oven at 110 °C. The treated nanofibers were then subjected to an oxidation treatment in a 50% air/helium mixture where the temperature of the sample was progressively raised to 850 °C at a rate of 5 °C/min and held at this level for 3 h before being cooled to ambient conditions. This oxidation treatment of the doped nanofiber precursors creates the conditions necessary to chemically bond phosphorus species onto the "armchair" faces of the graphite nanofibers and create the conditions necessary for boron to spread and interact with the "zigzag" regions. Phosphorus oxides not bound to the graphite face would undergo decomposition at much lower temperatures (ca. 350 °C). Prior to the introduction of nickel onto the nanofiber support, any unbound phosphorus and boron oxides were eliminated by thorough washing in dilute acid solution.

The 5 wt % Ni graphite nanofiber supported catalysts used in this study were prepared by a standard incipient wetness technique, as described in detail in a previous paper.³³ The catalyst precursor was initially calcined in air at 250 °C for 4 h to convert the metal nitrate to the thermally stable oxide state. The calcined catalyst was then flushed in He at ambient temperature before being reduced at 350 °C in a 10% H₂/He mixture for 20 h. The reduced catalyst was cooled in He, passivated at ambient temperature in a 2% O₂/He mixture for 1 h before the catalyst was removed from the reactor and finally stored in a sealed container for future use.

The gases used in this work, helium (99.999%), hydrogen (99.999%), carbon monoxide (99.99%), 1-butene (99.95%), and ethylene (99.95%) were obtained from Medical Technical Gases and used without any further purification. The dopants, methyl-phosphonic acid (98%) and ammonium pentaborate (99.99%), were obtained from Alpha Products and Aldrich Chemical Co., respectively; reagent grade nickel nitrate [Ni(NO₃)₂·6H₂O] was purchased from Fisher Scientific for the catalyst preparation.

Apparatus and Procedures. The catalysis unit used throughout this study consisted of a vertical quartz flow reactor, fitted with a quartz frit located in the central region of the reactor tube, which was heated with a split vertical tube furnace. The gas flow to the reactor was precisely regulated by the use of MKS mass flow controllers, allowing a constant composition of a desired reactant feed to be delivered. Catalyst samples (100 mg) were placed on the quartz frit and the tube was positioned in such a manner that the frit was always in approximately the same point in the reactor. After reduction in a 10% H_2/He mixture for 2 h at 350 °C the system was cooled to the desired reaction temperature while maintaining this gas flow. Once the desired reaction temperature was attained, the reactant hydrocarbon gas, or a predetermined hydrocarbon/H₂/He mixture, was introduced to the reduced catalyst sample at a flow rate of 100 sccm and the reaction was allowed to proceed for periods of up to 3 h. The product distribution was followed as a function of time by sampling the inlet and outlet gas streams at regular intervals. The concentrations of reactants and products were analyzed by gas chromatography using a 30 m megabore (GS-Q) capillary column for reactions involving ethylene and a 30 m megabore (GS-AL) capillary column for reactions involving 1-butene in a Varian 3400 GC unit.

The nature and characteristics of all the graphite nanofiber supported nickel catalysts were established using a combination



Figure 2. Comparison of the gasification characteristics of doped and untreated "platelet" graphite nanofibers in air.

of techniques, including high-resolution transmission electron microscopy (HRTEM), electron diffraction, and temperatureprogrammed oxidation (TPO) studies. The nickel catalysts were studied before and after use by HRTEM to establish any changes in the support structure and in the morphological characteristics of the impregnated metal particles. These examinations were carried out in a JEOL 2000EX II transmission electron microscope fitted with a high-resolution pole piece capable of giving a lattice resolution of 0.18 nm. Suitable transmission specimens were prepared by the ultrasonic dispersion of catalyst samples in isobutanol and application of a drop of the resultant suspension to a holey carbon support grid. Using this approach, it was possible to locate sections of the catalyst that protruded over the edge of the carbon, thereby permitting an examination of the sample without interference from the substrate. Images of very many different fields were displayed on the TV monitor, and the high-magnification images were transferred to a Mitsubishi printer unit for subsequent analysis. The size distribution plots were constructed from the measurements of over 500 particles in both the pristine and phosphorus-doped systems. In the case of the boron-doped material, far fewer metal particles were present and in this system the average size was estimated from about 150 particles. When operated in the diffraction mode, it was possible to determine the chemical state of the catalyst before and after reaction in the respective olefin/ hydrogen environments.

Temperature-programmed oxidation studies were carried out using a Cahn 2000 microbalance on demineralized and both doped graphite nanofiber samples in an air/Ar (1:1) mixture at a constant heating rate of 5 deg/min, as outlined in a previous paper from this laboratory.¹¹ This method was used to establish the effectiveness of the doping procedures by comparing the oxidation profiles of the phosphorus- and boron-treated nanofibers against that of an ostensibly clean demineralized sample.

Results

1. Catalyst Characterization Studies. *1.1. Temperature-Programmed Oxidation.* A comparison of the reactivity of phosphorus- and boron-doped platelet graphite nanofibers with that of the pristine material toward air is presented in Figure



Figure 3. Transmission electron micrograph showing the typical appearance of nickel particles supported on "platelet" GNF following reaction in 1-butene/hydrogen (1:1) mixture at 125 °C.

2. From these three profiles it can be seen that the introduction of phosphorus or boron onto the support surfaces exerts an appreciable retarding effect on the gasification of this type of nanofibers. Untreated graphitic nanofibers start to gasify under these conditions at 725 °C while the corresponding doped materials do not exhibit any significant weight loss until the temperature is raised to 940 °C. One may therefore assume that the objective of selectively blocking of the "armchair" faces of these nanofibers by phosphorus and the "zigzag" faces by boron has been successfully achieved in this study.

1.2. Transmission Electron Microscopy Examination. A representative example of the appearance of nickel particles on the untreated platelet type of graphite nanofiber (GNF) support following reaction in a 1-butene/hydrogen (1:1) mixture at 125 °C is presented in Figure 3. High-resolution electron microscopy examination of these specimens has enabled one to determine the location and morphology of the metal particles on these materials. Nickel particles were found to adopt a well-defined faceted shape, as shown in Figure 4. These morphological



Figure 4. High-resolution transmission electron micrograph showing the details of the nickel particle morphology when dispersed on "platelet" GNF.

characteristics are consistent with the existence of a relatively strong interaction between the metal particles and the support medium, whereas, in the case of a weak metal—support interaction, the metal particles would tend to acquire a more dense globular geometry⁴² and readily undergo sintering with a concomitant loss of catalytic activity.

Particle size distribution measurements of the fresh and reacted Ni/platelet GNF and the corresponding samples of Ni/ phosphorus-doped GNF are displayed in Figures 5 and 6, respectively. These plots are based on the measurements of over 500 particles in each sample. Inspection of the two sets of data reveal the existence of major differences in the distribution profiles of the untreated and phosphorus-doped GNF supported metal catalysts. While the profiles of the two fresh catalysts are very similar, after reaction in a 1-butene/hydrogen (1:1) mixture at 125 °C, a significantly narrower size range is attained when nickel was impregnated on the phosphorus-treated nanofiber surface, indicating that particle sintering is impeded to an appreciable extent under these circumstances. Table 1 highlights the differences in average particle size when one edge of the graphite nanofiber has been excluded from the impregnation process and the effect of a 3.0 h treatment in a 1-butene/ hydrogen reactant mixture at 125 °C.

Examination of Ni/boron-doped GNF revealed the existence of a very sparse collection of metal particles. It was evident that the few particles that were present adopted a globular morphology and exhibited a nonwetting behavior with respect to the interaction with the support. These are characteristics generally associated with the existence of a weak metal-support interaction. Since boron substitutes into the "zigzag" edges of graphite it is highly likely that these regions of the nanofibers will be masked and unavailable for the nucleation and growth of nickel crystallites following the metal nitrate impregnation step. Under such circumstances the only available unadulterated locations of the nanofibers will be the "armchair" faces. In this configuration the interfacial properties between the components may not favor the establishment of a strong metal-support interaction, and as a consequence, the growth characteristics of nickel crystallites on such surfaces will be quite different from those prevailing on the "zigzag" faces. On the other hand, in the case of the phosphorus-doped system, the location for the collection of metal species will be restricted to the "zigzag" faces of the graphite nanofiber support, where conditions exist for the creation of a strong metal-support interaction.

Electron diffraction analysis was carried out on phosphorusand boron-doped platelet GNF samples that had been impregnated with 5 wt % nickel. These experiments showed that nickel particles were in the metallic state in both systems, and no evidence was found for the existence of either Ni-P or Ni-B species in either the fresh or reacted catalyst samples.

2. Flow Reactor Studies. *2.1. Catalytic Hydrogenation of Ethylene by Graphite Nanofiber Supported Nickel Particles.* In this set of experiments both untreated 5 wt % nickel/platelet GNF and the analogous phosphorus- and boron-doped catalyst systems were tested over a period of 3.0 h at 120 °C to compare their ability to hydrogenate a simple probe molecule, ethylene. The results of these experiments are presented in Table 2, from which it can be seen that almost identical activities and selectivities were obtained with the former two catalyst systems, whereas the 5 wt % Ni/B-platelet GNF system was virtually inactive for this reaction. This overall pattern of behavior was maintained when the reaction was carried out at the slightly higher temperature of 140 °C over the same time period.

2.2. Catalytic Hydrogenation of 1-Butene by Graphite Nanofiber Supported Nickel Particles. When the degree of complexity of the reactant probe molecule was increased, significant differences were observed in the reactivity patterns of the three catalyst systems. Table 3 shows the product distributions obtained when the pristine and treated catalysts were treated in a 1-butene/hydrogen (1:1) mixture at 125 °C for 3.0 h. Once again, the Ni supported on boron-doped GNF samples exhibited an extremely low activity, which did not improve when the temperature was changed. Examination of the data from the other catalyst systems indicates that in both cases the major product is *n*-butane, which is formed from the complete hydrogenation of the reactant molecule. Under these conditions, however, the phosphorus-doped catalyst exhibited a significantly higher activity and a modification in the selectivity pattern that is reflected in lower yields of the isomerization products, cis- and trans-2-butenes.

In a final series of experiments the catalytic activity of the pristine, phosphorus- and boron-doped GNF materials for the hydrogenation of both olefins was investigated over the temperature range 100 to 140 °C. No evidence for decomposition of the respective reactants was found, indicating that in the absence of nickel, none of these supports was exerting any catalytic action on the hydrocarbon conversion reactions.

Discussion

In the current study, the impregnation of a platelet type of graphitic nanofiber with either phosphorus or boron species has been shown by TPO studies to offer a certain degree of protection of the material toward gasification by oxygen. These results are consistent with those obtained by Oh and Rodriguez,38 who used a variety of techniques, including controlled atmosphere electron microscopy, to directly observe the effect of phosphorus species on the graphite-oxygen reaction and concluded that the additive preferentially bonded to the "armchair" faces, leaving the "zigzag" regions vulnerable to oxidation. When these specimens were simultaneously examined by in-situ electron diffraction techniques, the d spacings were attributed to the establishment of a chemical bond between phosphorus oxide species and the coated carbon edge atoms. Others workers^{43–45} have reported on the ability of phosphorus to act as an inhibitor for graphite oxidation and suggested that physical blockage of edge sites was responsible for the action of the additive.

If one considers the action of the phosphorus dopant, which effectively blocks the access to the "armchair" faces of the



Figure 5. Particle size distribution profiles of metal particles supported on both fresh and used 5 wt % Ni/platelet GNF catalysts.



Figure 6. Particle size distribution profiles of Ni particles supported on both fresh and used 5 wt % Ni/phosphorus treated-platelet GNF catalysts.

TABLE 1: Comparison of the Average Nickel Particle Size Supported on Pristine and Phosphorus- and Boron-Treated GNF before and after Reaction in 1-Butene/Hydrogen (1:1) at 125 $^{\circ}$ C for 3.0 h

5 wt % Ni/GNF	av particle size (nm)
platelet GNF	7.92
platelet GNF(used)	13.61
phosphorus-platelet GNF	7.51
phosphorus-platelet GNF (used)	10.23
boron-platelet GNF	29.82
boron-platelet GNF (used)	36.70

nanofiber support, then it may be assumed that under these circumstances only nickel particles that collect on the "zigzag" edges will be active in the olefin hydrogenation reactions. It has been previously demonstrated that in a reducing environment, nickel preferentially wets and spreads along the "zigzag" faces of single-crystal graphite, leading to an epitaxial relationship metal and the substrate medium.^{46–48} These results were consistent with the theoretical studies of the surface energetics of the nickel/graphite system presented by Abrahamson,⁴⁹ who concluded that metal particles could adopt different morphologies on the two prismatic faces.

TABLE 2: Selectivity of Graphite Nanofiber Supported 5 wt% Nickel Catalysts for a C2H4/H2 (1:1) Reactant Mixture atVarious Temperatures

	% conversion of ethylene to selected products			
catalyst support	methane	ethane	solid carbon	% con- version
"platelet" GNF (120 °C)	0.03	51.4	8.50	59.6
P-doped "platelet" GNF (120 °C)	0.03	51.0	10.1	61.8
B-doped "platelet" GNF (120 °C)	0.00	1.2	0.01	1.41
"platelet" GNF (140 °C)	0.02	45.9	7.0	51.8
P-doped "platelet" GNF (140 °C)	0.01	46.1	9.0	54.2
B-doped "platelet" GNF (140 °C)	0.00	1.0	0.01	1.22

Since the "zigzag" edges are the preferred location for nickel particles on a graphite substrate, one would not expect that the presence of phosphorus on the adjacent edge sites would interfere with the catalytic activity of the system to any appreciable degree. On the other hand, since boron selectively interacts with the "zigzag" faces of graphite, access to these regions will be blocked and nickel will be forced to accumulate on the "armchair" faces. Under the conditions used in the current experiments, it is not entirely unexpected that any beneficial effects afforded by the interaction of certain edge sites with

TABLE 3: Selectivity of Graphite Nanofiber Supported 5 wt % Nickel Catalysts for a 1-C₄H₈/H₂ (1:1) Reactant Mixture at 125 $^{\circ}$ C

	1-1	% conversion of 1-butene to selected products			
catalyst support	<i>n</i> -butane	<i>trans</i> - 2-butene	<i>cis</i> - 2-butene	% conversion	
"platelet" GNF	39.2	12.6	14.5	67.8	
P-doped "platelet" GNF	79.6	6.2	5.5	92.0	
B-doped "platelet" GNF	2.4	0.6	0.8	3.8	

metal crystallites will be eliminated in the presence of this additive. These types of studies are being extended to other metals, such as copper, palladium, and platinum, to ascertain the preferential wetting behavior of these respective metals on the prismatic faces of graphite. This information will then enable us to develop more profound arguments with regard to the controlling factors on the metal particle morphology.

One might argue that impregnation of either a phosphorusor boron-treated nanofiber material with nickel would lead to the formation of the respective Ni–P or Ni–B compounds. Electron diffraction analysis failed to reveal the presence of such compounds either before or after reaction. It should be stressed, however, that this technique is limited to the determination of the bulk state and does not allow one to ascertain the chemical characteristics of the surfaces of the metal particles. Studies using a nickel phosphide as a catalyst have demonstrated that significant changes in the catalytic activity could be induced when compared to a similar untreated nickel catalyst.^{18–23}

In the current investigation, the catalytic hydrogenation of ethylene and 1-butene over both Ni/platelet GNF and the corresponding Ni/phosphorus-platelet GNF system were identical above 120 °C. This result would therefore tend to rule out the possibility of such a Ni-P species being the active catalyst in this study. In contrast, the use of a 5 wt % Ni/B-platelet GNF catalyst brought about significant changes in the catalytic behavior of the metal with respect to the hydrogenation of both ethylene and 1-butene. At all temperatures investigated in this study the boron-doped catalyst exhibited an extremely low activity toward the hydrogenation of both olefins. One possible explanation for this behavior is that the presence of boron in the catalyst acts as a poison to nickel, thereby inhibiting the hydrogenation of olefins. This explanation is somewhat tenuous since nickel-boron has been shown to exert a high activity for the hydrogenation of olefins. Indeed, the presence of a partially oxidized boron species on the catalyst surface was postulated to be responsible for the observed high selectivity and activity of the catalyst system.19,20,23

A more plausible rationale may lie in the notion that boron forms a strong interaction with the "zigzag" edges and effectively blocks the interaction of nickel with these sites. As a consequence, any beneficial metal—support interaction will not be realized and nickel will only exist in a weakly bound state to the "armchair" faces. Under these circumstances, the potential decrease in catalytic activity due to sintering of nickel crystallites will be greatly enhanced. Transmission electron microscopic examination of these specimens showed that the metal particles were relatively large and acquired a globular shape, features that are consistent with the above arguments. This behavior will result in a loss of nickel surface area and concomitant decrease in the catalytic performance of the system.

It is apparent that graphite nanofibers represent a new type of support media, where two crystal faces are available for subsequent impregnation and nucleation of metal particles. Each of the faces will exert a distinct effect on the eventual crystallographic arrangement adopted by the metal particles, which will ultimately be manifested in a different catalytic reactivity pattern. The results of the present investigation clearly demonstrate that the catalytic behavior of a given metal can be manipulated by careful tailoring of the support structure at the atomic level.

Conclusions

The use of phosphorus to selectively block the "armchair" faces of graphite nanofibers has been shown to exert little or no effect on the catalytic behavior of nickel with respect to hydrogenation of ethylene and 1-butene but did appear to result in a narrower particle size distribution following reaction. In contrast, addition of boron onto the carbonaceous support resulted in blocking of the "zigzag" faces, a step that appeared to subsequently render the supported metal system virtually inactive toward hydrogenation of either of the olefins. Based on these findings it is concluded that the active state of nickel is one where the particles are preferentially located on the "zigzag" faces of the graphite nanofibers. Under these conditions the metal particles adopt a crystallographic arrangement that is conducive toward reaction with both olefin molecules.

Transmission electron microscopy examination of the various nanofiber supported metal catalyst samples provides a picture that is consistent with these arguments. Nickel particles supported on pristine and phosphorus-treated platelet GNF exhibited a similar appearance, being relatively thin, flat, and hexagonal shaped, morphological characteristics that are associated with the existence of a strong metal—support interaction. On the other hand, those present on the corresponding boron-treated nanofibers were relatively large and globular in outline, features that are indicative of a weak metal—support interaction.

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