Catalytic Behavior of Graphite Nanofiber Supported Nickel Particles. 2. The Influence of the Nanofiber Structure

Colin Park and R. Terry K. Baker*

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115 Received: February 19, 1998; In Final Form: April 22, 1998

The hydrogenation of ethylene, 1-butene, and 1,3-butadiene has been used as a probe reaction in an attempt to monitor any possible changes in catalytic behavior induced by supporting nickel on different types of graphite nanofiber support materials. This study is designed to compare the catalytic behavior of the metal particles when dispersed on three types of nanofibers, where the orientation of the graphite platelets within the structures is significantly different in each case. The metal crystallites are located in such a manner that the majority of particles are in direct contact with graphite edge regions. It should be emphasized, however, that there are subtle differences in the spacing between adjacent exposed carbon atoms in the various nanofiber structures. As a consequence, it is highly probable that the atomic arrangement of the surfaces of nickel particles that nucleate on these different graphite edges will be dictated to a large degree by the interaction with the atoms in nanofiber supports. Under such circumstances one might reasonably expect that different crystallographic faces of nickel will be exposed to the reactant gas depending on which type of nanofiber structure is used as the supporting medium. For comparison purposes, the same set of hydrogenation reactions were carried out under similar conditions over γ -alumina supported nickel particles.

Introduction

The discovery of buckminsterfullerene, the so-called "bucky ball" molecule,¹ along with carbon nanotubes² and the development of catalytically grown carbon nanofibers³ have led to a subsequent avalanche of papers dealing with the characterization and potential uses of these carbonaceous structures. These unique materials all possess chemical and physical properties that could be of significant importance in a number of areas, including gas storage and separation, reinforcement agents in polymeric matrixes, electronic devices, and novel support materials for metal catalyst particles.

The more conventional form of graphite, while offering several desirable features as a catalyst support, does have major limitations. The most serious of these is the fact that graphite has a relatively low surface area, approximately 1.0 m² g⁻¹. Amorphous carbon offers substantial advantages as a catalyst support when compared with the traditional oxide support materials. This form of carbon is relatively inexpensive to produce and exhibits a range of surface areas, up to 1000 m² g⁻¹ in its activated form. Catalyst precursors supported upon carbon media are readily reduced to the metallic state, a condition that generally requires prolonged treatment in hydrogen when the same metal salts are dispersed on an oxide support.⁴

It is now being recognized that the recently developed types of carbon materials, which possess a variety of extraordinary structures, afford some exciting opportunities for exploiting the potential of nanofibers as novel catalyst supports for metal particles. The interaction of transition metals with buckminsterfullerene has been investigated by Vijayakrishnan and coworkers⁵ using photoemission spectroscopy. These workers established that, in contrast to the situation encountered with graphite, nickel strongly interacted with C₆₀, causing significant changes in the C(1s) and C(2s) binding energies. In addition to this finding, they observed that at low nickel loadings a significantly greater increase in the nickel(2p) binding energy occurred on C_{60} than on graphite surfaces, indicating the existence of a much stronger metal—support interaction in the former system. In a further aspect relating to carbonaceous support materials, Schlogl and co-workers⁶ have recently demonstrated that ruthenium particles appear to be extremely stable with respect to sintering when dispersed on fullerene-based support media. It was suggested that this behavior was due to the interaction of the metal clusters with the non-sixmembered carbon rings in the support structure. It was also claimed that the ability of the support to anchor the ruthenium moieties was responsible for the observed high catalytic hydrogenation activity exhibited by this system.⁷

Planeix and co-workers ⁸ investigated the hydrogenation of cinnamaldehyde and reported that 0.2 wt % ruthenium supported on carbon nanotubes was a highly selective catalyst for this reaction, up to 92% cinnamyl alcohol being produced at an overall high conversion of cinnamaldehyde. While these results are extremely encouraging there are several drawbacks associated with the use of carbon nanotubes, not least being the fact that they are expensive to generate in large quantities and possess a relatively low surface area, typically of the order of $25 \text{ m}^2 \text{ g}^{-1}$. The majority of any impregnated metal species is located on the outer carbon shell, a condition that would be expected if the proposed tubular model for the structure of the material is correct. This factor will tend to limit both the number and the different types of interaction that can be created between the metal particles and the carbon nanotube surfaces.

The development of methods to tailor both the degree of crystalline perfection and the orientation of graphite platelets that constitute the nanofibers has overcome many of the limitations encountered with other more traditional forms of carbon.^{9,10} One of the most outstanding features of these structures is the presence of a large number of edges, which in

^{*} To whom correspondence should be addressed.

turn constitute sites that are readily available for chemical and physical interactions. Perhaps one of the most unexpected findings is that such ordered crystalline solids can exhibit high surface areas ($50-500 \text{ m}^2 \text{ g}^{-1}$), where the totality of the surface area is chemically active. It this these characteristics that we have attempted to take advantage of in the present study.

The growth and characterization of carbon nanofibers produced from the interaction of a variety of pure metals and bimetallic catalysts with hydrocarbons have been extensively investigated by Baker and co-workers.^{11–14} By judicious choice of the catalyst and careful control of the reaction conditions, it is possible to tailor the growth of graphite nanofibers to generate structures of a desired conformation where the platelets are oriented in a particular direction with respect to the fiber axis.

While the electron microscopy studies demonstrate that graphite nanofiber supported metal particles exhibit structural features that are generally associated with the existence of a strong interfacial reaction,¹⁵ the data acquired up to this point in time do not allow one to reach any definitive conclusions with regard to the possibility of preferred growth locations. If the metal establishes a very strong interaction with carbon atoms located at the "armchair" face, then one could speculate that the particles would adopt a different morphology with these sites compared to that found at either the "zigzag" or basal plane sites, and as a consequence, one might expect to find concomitant variations in catalytic activity and selectivity. It has been well documented in the literature that specific faces of a metal particle are required to catalyze certain reactions.^{16–18} Yang and Chen¹⁹ demonstrated by selected area electron diffraction that Ni₍₁₀₀₎ and Ni₍₁₁₀₎ faces were present at the metal/gas interface, whereas Ni(111) and Ni(311) faces were in contact with a graphite substrate during the formation of carbon nanofibers from the metal-catalyzed decomposition of hydrocarbons.

Initial studies by Rodriguez and co-workers²⁰ showed that Fe-Cu particles supported on graphite nanofibers exhibited a significantly higher catalytic activity for the conversion of hydrocarbons than when the same loadings of the bimetallic were supported on either activated carbon or γ -alumina. A subsequent study by Chambers and co-workers¹⁵ established that the performance of nickel particles supported on carbonaceous materials was extremely sensitive to the degree of crystalline perfection of the substrate; the highest activity for the hydrogenation of 1-butene and 1,3-butadiene was displayed by a system in which the metal was dispersed on nanofibers possessing a high graphitic content. These results were in accord with those from earlier work by Brownlie and coworkers,²¹ who reported that, for the hydrogenation of selected hydrocarbons, catalysts based on palladium decorated graphite samples exhibited a significantly higher activity and selectivity compared to that where the metal was impregnated on other less ordered carbonaceous solids.

In the current investigation we have used the hydrogenation of simple alkenes and dienes including, ethylene, 1-butene, and 1,3-butadiene as probe reactions in an attempt to monitor any possible changes in catalytic behavior induced by supporting nickel on three different types of nanofibers, where the orientation of the graphite platelets within the structures is significantly different in each case. These experiments have enabled us to evaluate not only the potential of the graphite nanofibers as a support medium but also the impact of the orientation of the graphite platelets on the catalytic activity and selectivity of the metal. For comparison purposes, the same set of hydrogenation reactions were carried out under similar conditions over γ -alumina supported nickel particles.



Figure 1. Schematic representation of the three unique conformations of graphite nanofibers used as a catalyst support material.

The use of 1,3-butadiene has long been recognized as being a convenient and proficient method to probe the surface characteristics of supported metal catalysts.^{22–24} For a series of supported metal catalysts the hydrogenation of 1,3-butadiene offers an ideal means of simultaneously comparing the activity and selectivity of these systems. The selective hydrogenation of 1,3-butadiene has been studied extensively by Wells and coworkers^{25–27} for a range of catalyst systems.

Experimental Section

Materials. The three types of graphite nanofibers used in this work, which are shown in the schematic diagram, Figure 1, were produced by passing a desired mixture of a carboncontaining gas-ethylene and/or carbon monoxide-and hydrogen over a specific mono- or bimetallic catalyst powder for periods of up to 3 h. The nanofibers are classified as possessing a "platelet" structure where the graphite platelets in the carbon material are oriented perpendicular to the fiber axis, (Figure 1a), a "spiral" form where the platelets in the helical nanofibers are oriented parallel to the fiber axis, (Figure 1c), and a "ribbon" structure where the graphite platelets are aligned parallel to the fiber axis (Figure 1b). The exact conditions used to grow these nanofibers have been described in detail in previous papers.^{9,13,14,28} The resultant structures were demineralized in dilute nitric acid over a period of 7 days to remove the original metal catalyst. The nanofibers were then thoroughly washed in deionized water before being dried overnight at 110 °C and then stored in sealed vessels.

The 5 wt % supported nickel catalysts used in this study were prepared by a standard incipient wetness technique. Each support medium was impregnated with a solution of nickel nitrate containing the appropriate amount of the precursor salt necessary to achieve the desired 5 wt % metal loading. The nickel nitrate was dissolved in 25 mL of ethanol, since in the "as-prepared condition" the graphite nanofibers are hydrophobic in nature and poor metal dispersion was achieved when an aqueous solvent was used. After drying overnight at 110 °C, the impregnated materials were calcined in air at 250 °C for 4 h to convert the metal nitrate to the oxide and then reduced at 350 °C in a 10% H₂/He mixture for 20 h. The reduced catalysts were cooled in He before being passivated at ambient temperature in a 2% O₂/He mixture for 1 h prior to removal from the reactor. The catalyst precursor was deliberately calcined at a lower temperature to avoid gasification of the graphite nanofiber support material. With this safeguard no loss of support material was recorded during the catalyst preparation. In the case of the γ -alumina supported metal catalyst samples the time of the hydrogen treatment at 350 °C was varied from 20 to 60 h in order to check that complete reduction of the nickel oxide was being achieved. It was significant to find that the subsequent performance of these catalysts appeared to be the same, within experimental error, indicating that in all cases the supported particles were in the metallic state.

The gases used in this work, helium (99.999%), hydrogen (99.999%), carbon monoxide (99.99%), ethylene (99.95%), 1-butene (99.95%), and 1,3-butadiene (99.95%), were obtained from MG Industries and used without any further purification. Reagent grade nickel nitrate [Ni(NO₃)₂·6H₂O] was obtained from Fisher Scientific for the catalyst preparation. The γ -alumina was supplied by the Degussa Corporation and was used as received.

Apparatus and Procedures. The apparatus used for the catalyst studies consisted of a quartz flow reactor, fitted with a quartz frit at the midpoint of the tube, and this assembly was located within 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 to the system. Catalyst samples (100 mg) were placed on the quartz frit, and the tube was aligned in such a manner that this region of the reactor was always in approximately the same position in the furnace. After reduction in a 10% H₂/He mixture for 2 h at 400 °C, the system was cooled to the desired reaction temperature, and the reactant hydrocarbon gas, or a predetermined hydrocarbon/H2/He mixture, was introduced to the catalyst sample for periods of up to 3 h. The reaction was monitored as a function of time by sampling the inlet and outlet gas streams at regular intervals. The reactants and products were analyzed by gas chromatography (Varian 3400 unit) using a 30 m megabore (GS-Q) capillary column for reactions involving ethylene and a 30 m megabore (GS-AL) capillary column for those where 1-butene and 1,3-butadiene were the reactants. Turnover frequencies (TOF) for all reactions were estimated using the average metal particle sizes as determined from TEM measurements and calculated according to the accepted procedure.²⁹

The characteristics of all the support materials and catalyst samples were established using a combination of techniques, including high-resolution transmission electron microscopy (HRTEM), temperature-programmed oxidation (TPO), X-ray diffraction (XRD), and nitrogen BET surface area measurements. In addition, the nickel catalysts were examined after use by HRTEM to ascertain any changes in either the support structure or the morphology of the metal particles induced by exposure to a hydrocarbon/hydrogen environment. These studies were carried out in a JEOL 2000EXII electron microscope fitted with a high-resolution pole piece capable of a lattice resolution of 0.14 nm. Suitable transmission specimens were prepared by ultrasonic dispersion of catalyst samples in isobutanol and application of a drop of the resultant suspension to a holey carbon support grid.

Temperature-programmed oxidation studies were carried out on the demineralized graphite nanofibers in the presence of CO_2 at a constant heating rate using a Cahn 2000 microbalance as outlined previously.¹⁴ This procedure has been shown to provide an ideal means of establishing the graphitic content of a carbonaceous solid. BET surface areas, calculated from nitrogen adsorption isotherms at -196 °C, were carried out on the various support media using a Coulter Omnisorp 100CX surface analysis unit. Powder XRD patterns of the graphite nanofibers and all catalyst samples were obtained with a Scintag diffractometer using nickel filtered Cu K α radiation. Diffraction patterns were recorded over a range of 2θ angles from 10° to



Figure 2. Comparison of the CO₂ temperature-programmed oxidation profiles of the graphite nanofibers.

 90° and compared with the known X-ray powder files to determine the phase identities.

Efforts were made to determine metal particle sizes by standard hydrogen chemisorption procedures; however, serious difficulties were encountered with the graphite nanofiber supported nickel systems, since copious amounts of hydrogen were absorbed by these types of carbon solids, and as a consequence, meaningful data were only obtained for the metal particles dispersed on γ -alumina.

Results

1. Characterization Studies. *1.1. XRD Analysis.* X-ray diffraction studies of the nanofibers failed to detect the presence of any of the original catalyst in the demineralized sample, indicating that removal of metal by treatment in acid was a satisfactory method. The predominant peak was identified as being the (002) peak of graphite, giving a clear indication of the highly crystalline nature of these nanofiber structures. The average interlayer spacing of each graphitic nanofiber structure was also determined using XRD. The "spiral-like" nanofibers had a *d* spacing of 0.337 nm, 0.002 nm larger than that of either the "platelet" or "ribbon" types of nanofiber structures.

1.2. Temperature-Programmed Oxidation. CO_2 temperatureprogrammed oxidation profiles indicate the degree of crystalline perfection, that is the graphitic nature, of each type of nanofiber support material. A carbonaceous material that has a high degree of crystalline perfection will start to gasify under these conditions at approximately 850 °C. In the other extreme, if the material is amorphous in nature, the material will start to undergo gasification at approximately 600 °C. It is evident from Figure 2 that the nanofibers used in this study are highly graphitic materials with an extremely low amorphous carbon content. The graphite nanofibers that were comprised of a "ribbon" structure were identified as being the most graphitic in nature followed by the "platelet" and the "spiral" conformations.

1.3. Surface Area Measurements. The N₂ BET surface area of demineralized samples of each catalyst support, measured at -196 °C, are summarized in Table 1. The surface area of the demineralized graphite nanofibers varied according to the type of conformation, but in all cases these values were substantially higher than that of a conventional graphite sample, typically $<1 \text{ m}^2/\text{g}$, due to the extremely large number of edge regions that are exposed in the former materials. The surface area of the nanofibers can be significantly enhanced by careful activation in CO₂ at 850 °C to achieve values of up to 700 m² g⁻¹.

 TABLE 1: Calculated Nitrogen BET Surface Areas of the

 Catalyst Support Materials

support material	surface area (m ² g ^{-1})
"ribbon-like" graphite nanofibers	85
"spiral-like" graphite nanofibers	45
"platelet-like" graphite nanofibers	120
γ -alumina	115

 TABLE 2: Average Size of Nickel Crystallites Dispersed on the Various Types of Support Material Measured from Transmission Electron Micrographs

support material	av particle size (nm)
"ribbon-like" graphite nanofibers	8.1
"spiral-like" graphite nanofibers	7.2
"platelet-like" graphite nanofibers	6.4
γ-alumina	1.4

The surface area of the more traditional catalyst support, γ -alumina, was found to be similar to that of the graphite nanofibers.

1.4. Transmission Electron Microscopy Examination. Highresolution transmission electron microscopy studies indicated that the graphite nanofibers were between 100 and 150 nm in width and varied from 5 to 50 μ m in length. Examination of the nanofiber supported nickel catalyst samples revealed that, in all cases, the metal particles were located along the edges of each particular graphite nanofiber structure. When nickel was supported on the graphite nanofibers, the average crystallite size, as determined from measurements of over 400 particles in each sample, was found to be significantly greater than that where the metal was dispersed on γ -alumina, as outlined in Table 2. It was an arduous task to discern the appearance of metal particles on γ -alumina specimens due to the interference of the support texture; however, it was possible to establish that in this case the metal particles did not adopt any preferred geometrical shape. In sharp contrast, metal particles supported on the three types of graphitic nanofibers acquired definite hexagonal shapes, an example of which is presented in Figure 3. The morphological characteristics exhibited by these particles are generally those associated with a system that exhibits a strong metal-support interaction.

2. Flow Reactor Studies. 2.1. Catalytic Hydrogenation of Ethylene by Supported Nickel Particles. From the data presented in Table 3 it is evident that the ability of nickel to catalytically hydrogenate ethylene at a relatively low temperature, 100 °C, does not appear to exhibit any substantial variations when the metal is dispersed on the different support media. An overall high conversion of ethylene, primarily to ethane and to a lesser extent solid carbon, was achieved when a C_2H_4/H_2 (1:1) mixture was passed over each supported nickel catalyst system. The introduction of nickel onto graphite nanofibers possessing a "ribbon-like" structure did, however result in a marginally higher activity for this reaction than that of the other systems. It is evident that the turnover frequencies (TOF) for the hydrogenation of ethylene are similar for all these supported nickel systems.

An interesting feature was observed with a catalyst consisting of nickel supported on the "platelet" type of graphite nanofibers. At 100 °C an induction period of 35 min was required for this system to achieve an overall conversion of ethylene similar to that displayed by the other supported nickel catalysts. This reactivity sequence was found to persist when the temperature was increased up to a maximum level of 200 °C.

2.2. Catalytic Hydrogenation of 1-Butene by Nickel. In an attempt to gain further insights into the catalytic behavior of these supported nickel catalysts, in a second series of experi-

ments a larger probe molecule, 1-butene, was used. This particular reactant molecule was chosen since it offers the possibility of isomerization in addition to hydrogenation pathways, thus highlighting changes in the selectivity pattern due to the influence of the support medium. From Figure 4 and Table 4 it is apparent that when a 1-butene/hydrogen (1:1) reactant mixture was passed over nickel at 90 °C, the observed catalytic activity and the selectivity patterns were strongly dependent upon the nature of the supporting medium. Under these conditions a much higher activity was attained with nickel deposited on the three types of graphite nanofibers compared to that where the metal particles were supported on γ -alumina. In all cases, however, the primary product of this reaction was *n*-butane, resulting from the complete hydrogenation, and this was followed by isomerization of the reactant molecules to cis- and trans-2-butene in varying ratios, which were highly dependent upon the particular catalyst system employed. Inspection of the reaction profiles shows that when nickel was supported on either the "platelet" or "spiral" forms of graphitic nanofibers, an induction period of between 35 and 60 min was required in order to achieve a high conversion rate, a criterion that was not observed when the metal was dispersed on either the "ribbonlike" nanofibers.

On close scrutiny of the data in Table 4 showing the percent product distribution from the hydrogenation of 1-butene at 90 °C over these supported nickel catalysts, several salient features can be identified. It is evident that the particular orientation of the graphite platelets within the nanofiber structures exerts a strong influence on the selectivity of the supported nickel particles for this reaction. The selectivity toward the formation of 2-butenes, S₁, is similar for all three types of graphite nanofiber supported nickel systems and appreciably higher than that realized from the nickel/ γ -alumina catalyst. It is also noticeable that the *trans/cis-2*-butene ratio is extremely sensitive to orientation of the graphite platelets in the nanofiber structures, decreasing according to the sequence "ribbon-like" >"spiral" > "platelet" forms. Clearly therefore, a change in orientation of the graphite platelets from being aligned parallel to being perpendicular to the fiber axis modifies the structure of the supported nickel crystallites in such a manner that favors the formation of cis-2-butene over that of trans-2-butene.

The turnover frequencies for the hydrogenation of 1-butene over the various nickel catalysts exhibit a dramatic change as a function of the support media. Nickel deposited on the "ribbon" type of nanofibers is seen to exhibit the highest TOF, more than twice that observed when the same metal loading is dispersed on the "platelet" nanofibers. An intermediate value is found for nickel supported on the "spiral" form of nanofibers, which is similar to that calculated for the hydrogenation of ethylene over this catalyst system.

2.3. Catalytic Hydrogenation Studies of 1,3-Butadiene by Nickel. In this series of experiments an attempt was made to ascertain the impact that the arrangement of the graphite platelets in the nanofiber support materials exerted on the hydrogenation activity and selectivity of nickel for 1,3-butadiene, a more demanding and sensitive probe molecule than 1-butene. The hydrogenation of the diene can occur by several different reaction pathways giving rise to numerous products, thereby allowing for the simultaneous comparison of the activity and selectivity.

Figure 5 shows the overall conversion of a 1,3-butadiene/ hydrogen (1:1) mixture at 90 °C over the various supported Ni catalyst systems. From these plots it is apparent that the overall conversion of the diene is very limited over all these catalyst



Figure 3. High-resolution transmission electron micrograph highlighting the morphology and size of Ni particles deposited on the "platelet" form of graphite nanofibers. The direction of the lattice fringes of the nanofibers are indicated.

TABLE 3:	Selectivity of S	Supported	Nickel	Catalysts	for a
C_2H_4/H_2 (1:	1) Reactant M	ixture at 1	00 °C		

	% conversion of ethylene to selected products					
catalyst support	methane	ethane	solid C	% conversn	TOF (s ⁻¹)	
"ribbon-like" GNF "spiral-like" GNF "platelet-like" GNF γ-alumina	0.02 0.04 0.01 0.03	63.69 71.64 52.16 68.78	8.60 11.61 7.37 10.58	72.31 83.29 59.54 79.39	0.376 0.384 0.242 0.301	

systems, being approximately 7% for all graphite nanofiber supported metal systems and less than 4% when nickel was deposited on γ -alumina. When nickel was supported on the "spiral" type of nanofibers, the system exhibited a significant decrease in activity for this reaction over the first 35 min on stream settling down to level comparable to that obtained with the other nickel/graphite nanofiber catalysts. Despite the low activity achieved with these supported nickel catalysts, a comparison of the product selectivities raises several very key points. One general feature to emerge was that butenes, partially hydrogenated molecules, were the major products. In this series of experiments conditions were deliberately selected so as to minimize the complete hydrogenation of 1,3-butadiene to butane, and this situation was achieved by limiting the concentration of hydrogen in the reactant mixture.

When the reaction was conducted with a 1,3-butadiene/ hydrogen (1:2) mixture at 90 °C over the same series of supported nickel, a dramatic enhancement in catalytic activity of some of the systems was observed as evidenced from the



Figure 4. Effect of the support on the catalytic activity of 5 wt % Ni in the hydrogenation of a C_4H_8/H_2 (1:1) reactant mixture at 75 °C.

data presented in Figure 6. Under these conditions, the catalytic activity of nickel supported on graphite nanofibers possessing either "platelet" or "spiral" conformations exhibited a dramatic increase over that where the reaction was performed in a equimolar reactant mixture; however, in both cases an induction period of about 35 min is required to reach the optimum conversion level. On the other hand, the activity of systems where the metal particles were supported on γ -alumina and or on nanofibers with a "ribbon" conformation did not change to any significant degree upon exposure to the reactant feed containing a larger fraction of hydrogen.

TABLE 4: Selectivity of Supported Nickel Catalysts for a C₄H₈/H₂ (1:1) Reactant Mixture at 90 °C^a

	% conversion of 1-butene to selected products						
catalyst support	<i>i</i> -butane	<i>n</i> -butane	trans-2-butene	cis-2-butene	S_1	T/C	TOF (s^{-1})
"ribbon-like" GNF "spiral-like" GNF "platelet-like"GNF γ-alumina	0.11 0.10 0.09 0.08	67.81 61.52 42.48 0.38	13.88 11.90 4.98 0	10.34 10.26 9.01 0	0.26 0.26 0.25 0	1.34 1.09 0.55 0	$\begin{array}{c} 0.479 \\ 0.386 \\ 0.230 \\ 2.0 \times 10^{-3} \end{array}$

 $a_{S_1} = (trans-2$ -butene + cis-2-butene)/(trans-2-butene + cis-2-butene + butane). T/C = trans-2-butene/cis-2-butene.



Figure 5. Effect of the support on the catalytic activity of 5 wt % Ni in the hydrogenation of a C_4H_6/H_2 (1:1) reactant mixture at 90 °C.



Figure 6. Effect of the support on the catalytic activity of 5 wt % Ni in the hydrogenation of a C_4H_6/H_2 (1:2) reactant mixture at 90 °C.

Examination of the product distributions, given in Table 5, shows that the major product from all catalysts is *n*-butane, which produced as a result of the complete hydrogenation of 1,3-butadiene. Although nickel particles supported on both the "spiral" and "platelet" types of graphite nanofiber conformations exhibited a similar overall activity, substantial differences are apparent in the product distributions derived from these two systems. It can be seen that when the metal was supported on graphite nanofibers possessing a "spiral" conformation, the major route was the complete hydrogenation of the diene to *n*-butane, whereas when nickel was dispersed on "platelet-like" nanofibers, the pathways leading to partial hydrogenation to 1-butene and complete hydrogenation to *n*-butane were equally favored. This aspect is highlighted in Table 5 where S_2 , the selectivity to the partially hydrogenated products, is observed to be substantially higher when nickel was supported upon "platelet" nanofibers rather than on "spiral" nanofibers. Significant differences between these two catalysts can also be seen from a comparison of the ratios of trans/cis-2-butene and 1-butene/2-butene, respectively. The formation of trans-2butene is favored when nickel was supported on "spiral" nanofibers, whereas *cis*-2-butene was the preferred isomer when the metal was dispersed on the "platelet" form. In contrast, the 1-butene to 2-butene ratio is substantially higher when the "platelet" nanofibers are used as the catalyst support. Although nickel supported on the "ribbon-like" graphite nanofibers exhibited an extremely low overall activity for the hydrogenation of 1,3-butadiene, it was found to display the highest selectivity toward the formation of butenes, and in particular to *trans*-2-butene.

Finally, the turnover frequency for the hydrogenation of 1,3butadiene over nickel supported on the "ribbon-like" nanofibers decreased dramatically when compared to the corresponding values calculated for the hydrogenation of ethylene and 1-butene. In sharp contrast, this trend was reversed, to a somewhat lesser degree, when the metal was supported on either the "platelet" or "spiral" graphite nanofiber forms.

Discussion

The most important feature to emerge from this investigation is the finding that when nickel is supported on graphite nanofibers, the system can exhibit some unusual patterns of behavior with respect to the catalytic hydrogenation of olefins and dienes. Moreover, the performance of the supported metal catalyst for a given reaction is extremely sensitive to the particular geometric arrangement adopted by the graphite platelets constituting the structure of the nanofibers. We have demonstrated that it is possible to create a highly selective and active catalyst for the hydrogenation of both ethylene and 1-butene to the corresponding alkanes by supporting 5 wt % nickel on certain types of graphite nanofibers. The optimum performance for these reactions was achieved with a catalyst in which the nickel was dispersed on graphite nanofibers possessing a "ribbon-like" conformation. A comparison of graphite nanofiber supported nickel catalysts with a more conventional oxide supported metal system, nickel/ γ -alumina, showed that in all cases the former combinations exhibited the superior performance.

Conventional wisdom might suggest that the observed behavior of the latter system could be rationalized according to the notion that when nickel was dispersed on the oxide support, complete reduction to the active metallic state was not achieved during the preparation step. There are a number of factors that argue against this possibility; hydrogen chemisorption measurements were consistent with a dispersion corresponding to an average metal particle size of about 1.5 nm. The catalytic behavior of alumina supported nickel particles did not appear to exhibit any significant changes as a result of increasing the time of reduction in the preparative step from 20 to 60 h. The 5 wt % nickel/alumina catalyst exhibited a relatively high activity for the hydrogenation of ethylene, and portions of this same sample were subsequently used for the hydrogenation reactions of 1-butene and 1,3-butadiene.

Perhaps the most intriguing aspect of these reactions is the manner by which the selectivity patterns exhibited by nickel

TABLE 5: Conversion of a C_4H_6/H_2 (1:2) Reactant Mixture at 90 °C to Selected Products for a Series of Supported Nickel Catalysts^{*a*}

	% conversion of 1,3-butadiene to selected products							
catalyst support	<i>n</i> -butane	1-butene	cis-2-butene	trans-2-butene	S_2	B_{1}/B_{2}	T/C	$TOF(s^{-1})$
"ribbon-like" GNF	1.10	3.68	0.92	1.51	0.85	1.51	1.64	0.038
"spiral-like" GNF	62.77	10.40	11.58	15.28	0.37	0.39	1.32	0.461
"platelet-like" GNF	39.26	34.89	14.83	14.09	0.60	1.43	0.95	0.401
γ-alumina	0	0.04	0.20	0.03	1	0.17	0.15	5.1×10^{-3}

 ${}^{a}S_{2} = (1-butene + trans-2-butene + cis-2-butene)/(1-butene + trans-2-butene + cis-2-butene + butane). B_{1}/B_{2} = 1-butene/(trans-2-butene + cis-2-butene). T/C = trans-2-butene/cis-2-butene.$

are modified by the structural characteristics of the supporting medium. For the most part, all the catalyst systems behaved in a similar fashion during reaction in an ethylene/hydrogen (1:1) mixture. As the complexity of the hydrocarbon reactant molecule was increased, so differences in the overall catalytic activity and selectivity of the various systems became apparent. The predominant product from the 1-butene/hydrogen reaction was *n*-butane; however, when graphite nanofibers were used as the support, an appreciable fraction of the reactant underwent isomerization to either *trans-* or *cis-*2-butene. The observed increase in the formation of isomerization products when nanofibers were used as the support is believed to be directly related to the modification in morphological characteristics of the nickel crystallites induced by the interaction with these types of novel graphite materials.

The nickel-catalyzed hydrogenation of 1,3-butadiene is a more demanding reaction that presents the opportunity to probe the existence of any further nuances contained within the various product distributions that might be associated with the structural characteristics of the supporting medium. In this series of experiments nickel supported on both the "platelet" and "ribbon-like" forms of graphitic nanofibers was found to be highly selective toward the partial hydrogenation of 1,3-butadiene to 1-butene rather than proceeding to undergo complete hydrogenation to *n*-butane. The relatively low activity of the metal when supported on the "ribbon" type of nanofibers was unexpected, especially since this particular catalyst system had displayed the highest activity for the hydrogenation of both ethylene and 1-butene.

1. Influence of the Support on the Morphological Characteristics of Nickel Particles. High-resolution transmission electron microscopy studies provided some key insights regarding the morphological characteristics adopted by the nickel crystallites on the graphite nanofibers. It was apparent that many of the metal particle characteristics were similar on all three types of graphite nanofibers and quite different to those observed when alumina was used as the catalyst support. On the graphite supports the crystallites were found to adopt very thin, hexagonal morphologies, and since the electron density was uniform across a given particle, one may tentatively conclude that they were relatively flat. These growth features are generally believed to originate from the creation of a strong metal-support interaction that induces a spreading action of the metal on a carrier surface. In contrast, a more globular particle geometry was prevalent when nickel was supported on γ -alumina, consistent with the existence of a somewhat weaker metal-support interaction. For comparison purposes it would have been desirable to generate similar sized particles on all the support media; however, even when the metal loading was increased by an order of magnitude with the nickel/ γ -alumina system, the crystallites were still significantly smaller than those formed from the lighter loading on the carbon materials.

In this regard it is instructive to examine the data obtained from controlled atmosphere electron microscopy studies of the



Figure 7. Schematic representation of the "armchair" and "zigzag" faces of a graphite platelet.

nickel/graphite-hydrogen system performed by Baker and coworkers.^{30–33} They observed that catalytic hydrogenation of the graphite proceeded by a channeling mode and that the tracks propagated by active nickel particles tended to be straight with occasional 60° and 120° bends and aligned along the $\langle 1120 \rangle$ crystallographic orientations of the graphite. These findings indicated that in the presence of hydrogen the metal exhibited a preferential wetting action with respect to the "armchair" faces of graphite and that the particles moved in such a manner so as to maintain contact with carbon atoms in this arrangement. It is therefore not unreasonable to assume that the interaction of nickel with the "zigzag" faces of graphite will be somewhat weaker. These experimental observations were found to be in complete agreement with the theoretical studies reported by Abrahamson,³⁴ who calculated the surface energies of a number of metals on the different faces of graphite. On the basis of these conclusions, one can confidently predict that subtle differences are likely to exist in both the morphological and chemical characteristics of metal particles that are formed on the "armchair" and "zigzag" faces of graphite, respectively. In the present circumstances the graphite nanofiber surfaces are in essence acting as templates for the generation of metal particles in a desired orientation. Upon consideration of the arrangement of carbon atoms in the prismatic faces of graphite, the so-called "armchair" {1120} and "zigzag" {1010} faces, it is very easy to visualize from Figure 7 that the former face presents a much more open structure for the deposition of metal when compared to that of the "zigzag" face. Since the ratio of "armchair" to "zigzag" sites will vary from one type of graphite nanofiber structure to another, dramatic changes in both the catalytic activity and selectivity of nickel may be explained in terms of the variations in crystallographic orientations of the particles associated with the differing structures of the supporting media.

2. Ramifications of Graphite Nanofiber Structure on the Catalytic Behavior of Nickel. It is an interesting exercise to examine the catalytic data obtained for nickel dispersed on the three types of graphite nanofibers in light of the possible differences in morphological characteristics of the metal particles that can exist on these particular support structures. For this purpose it is necessary to refer to the schematic structures presented in Figure 1. It can be seen that the surfaces exposed by the "ribbon-like" nanofibers consist of two relatively large basal plane regions, each of which are bounded by two long and two short edge regions. At this time it is not possible to establish the precise orientation of these two edges; however, since they are aligned in directions that are perpendicular to one another, one can state with certainty that the grouping of the carbon atoms along these two regions will be different, i.e., one edge will adopt the "armchair" configuration and the other will be in the "zigzag" arrangement. Preliminary theoretical calculations and modeling studies have indicated that the long edge region of this type of nanofiber is most likely to be in the "zigzag" orientation. On this type of material the majority of the metal species will tend to accumulate on the long edge region, and those particles that collect on other locations are not likely to make a significant contribution to the overall catalytic performance of the system. By comparison, graphite nanofibers that possess a "platelet" structure have two edges of approximately the same length that are oriented to an equal degree in either the "armchair" or "zigzag" configurations. Finally, the "spiral-like" nanofibers are comprised of graphitic platelets that are oriented in a manner similar to the "ribbonlike" material; however, in this case the geometrical requirements associated with these structures place a great deal of strain on the platelets, resulting in an average d spacing of 0.337 nm, a value that is 0.002 nm larger than that of single-crystal graphite. This expansion of the layers will result in a modification of the interaction between the nanofiber surface and the impregnated metal atoms. We believe that this feature accounts for the observed difference in behavior of this system and where the nickel is dispersed on the "ribbon-like" nanofibers. Indeed, a significant difference in the hydrogenation behavior of nickel was observed when the metal was supported on the these two types of carbon structures. Nickel was found to be highly active for the hydrogenation of 1,3-butadiene when supported on the "spiral" type of nanofibers, but in contrast, the metal was virtually inactive when dispersed on the "ribbonlike" material.

A comparison of the *trans/cis*-2-butene (T/C) ratios for both the hydrogenation of 1-butene and 1,3-butadiene obtained in this investigation allows one to make a number of important deductions. The formation of 2-butenes from the hydrogenation of 1,3-butadiene has been purported to occur via two separate pathways: isomerization of the partially hydrogenated product 1-butene prior to its desorption from the catalyst surface and by a 1,4 addition of hydrogen to 1,3-butadiene.¹⁰⁻¹² Both pathways are equally valid, but if the trans/cis ratio is similar for both hydrogenation reactions, then the formation of 2-butenes has been postulated to proceed mainly via the isomerization of 1-butene. On the other hand, if significant differences in the trans/cis ratios are found for the two systems, the reaction will proceed via a 1,4 addition of hydrogen. Inspection of the data presented in Tables 4 and 5 shows that the *trans/cis-2*-butene ratios for these two hydrogenation reactions were similar when nickel was supported on either the "spiral" or "ribbon-like" forms of graphite nanofibers, indicating that in these cases the formation of 2-butenes occurs primarily via the isomerization of 1-butene. It is evident, however, that when the metal was supported on the "platelet" type of nanofibers, a significant difference in the trans/cis ratio for the same set of reactions

was observed. As a consequence, it is probable that under these circumstances the formation of 2-butenes would appear to proceed via both pathways to similar extents.

It was significant to find that when nickel was supported on γ -alumina, the trans/cis ratios, calculated from the hydrogenation of 1-butene and 1,3-butadiene, became increasingly different, indicating that on this particular catalyst system 2-butenes appear to be produced directly by the 1,4 addition of hydrogen to diene. Based on these data, it is evident that there is a divergence in the isomerization ability of these catalysts. Nickel itself has been reported to be a highly effective catalyst for the isomerization of alkenes, but when supported on various materials, the ability of the metal to perform this function can be radically changed.³⁵ Once again it becomes apparent that the orientation of the graphite platelets in the graphite nanofiber supports and the associated surface atomic arrangement of the dispersed nickel crystallites play a critical role in determining the activity and selectivity of the catalyst system. Moreover, it is clear that major differences exist in the catalytic performance of the supported nickel particles depending on whether the graphite platelets constituting the nanofiber supports are oriented parallel or perpendicular to the fiber axis.

Catalytic hydrogenation was originally considered to be a structure-insensitive reaction, but it has become increasingly evident from experimental data that this is not the case.³⁶ Brownlie and co-workers¹⁷ claimed that the observed enhancement in the catalytic activity of palladium particles that were located at graphite edges compared to that exhibited by those particles in contact with the basal plane region was directly related to the strong metal-support interaction that existed at the former regions, which was responsible for maintaining a fine dispersion of metal crystallites. These conclusions were later confirmed by Masson and co-workers,37-39 who demonstrated that the rate of hydrogenation of ethylene occurred much faster over small rather than large platinum particles when the metal was dispersed on silica. This particle size effect has been also observed with nickel³⁸ and palladium^{40,41} supported on alumina, silica, and carbon media.18,39

It is clear that the data obtained in present investigation are at variance with the previous conclusions, since the hydrogenation activity of the relatively large nickel particles dispersed on the graphite nanofibers is significantly higher than that obtained from an equal loading of very small crystallites of the same metal supported on a traditional carrier, such as γ -alumina. In this context it is important to emphasize the work of Boitiaux and co-workers,^{42,43} who challenged the previously held notions regarding the relationship between particle size and catalytic activity. These workers investigated the performance of supported palladium catalysts for the hydrogenation of 1-butyne, 1,3-butadiene, and isoprene and demonstrated that there was indeed a strong particle size dependency; however, they observed a dramatic decrease in the catalytic activity when extremely small metal particles (<3 nm) were used for these reactions. This trend was explained in terms of a stronger adsorption of a these unsaturated, electron-rich molecules on the smaller metal particles.^{42–44} It was somewhat surprising that the hydrogenation of 1-butene was unaffected by the size of the supported palladium particles. These results have since been reproduced for a variety of metals and support combinations.⁴⁴⁻⁴⁶

The inactivity displayed by nickel in the current investigation when supported on γ -alumina cannot be readily explained in similar terms as those proposed by Boitiaux and co-workers,^{42,43} since the system displayed a low activity for both the hydrogenation of 1-butene and 1,3-butadiene but, on the other hand, exhibited a high activity for the hydrogenation of ethylene. The extremely small nickel particles, 1.4 nm in diameter, may strongly adsorb both 1-butene and 1,3-butadiene but do not appear to exert the same effect on ethylene.

Based on these criteria, it is apparent that one cannot account for the observed higher activity displayed by nickel when supported on graphite nanofibers for specific hydrogenation reactions by merely presenting arguments based on average metal particle sizes. While a reasonably high metal dispersion on a given support material is desirable, it may not be the most critical factor in determining the catalytic behavior of the system in certain hydrogenation reactions. Clearly, the reasons for the unexpected performance of the graphite nanofiber supported metal systems require a more profound understanding. We therefore offer an alternative explanation that focuses attention on the morphological characteristics of the metal particles, a property in which the support location site plays a pivotal role. When one considers the structural features of the various types of graphite nanofibers, these materials are unique in that for the most part they present an abundance of edge sites to the gas phase. With the choice of two distinct adsorption sites on the graphitic platelets, the "armchair" and "zigzag" faces, metal particles may be expected to adopt unusual geometries when they nucleate and grow on these template regions. It is this factor that we believe is largely responsible for dictating the arrangement of metal atoms in the exposed faces of the particles and, as a consequence, is responsible for controlling the catalytic behavior of the system toward specific hydrogenation reactions. An analogous set of arguments were proposed by Massardier and co-workers47 to account for the observations that in the hydrogenation of 1,3-butadiene over palladium, where the $Pd_{(110)}$ face was found to be significantly more active than the $Pd_{(111)}$ face.

Taking into consideration the data obtained here for the hydrogenation of 1-butene and 1,3-butadiene along with that derived from previous CAEM studies of the nickel/graphitehydrogen system,³⁰⁻³³ and if one assumes that the metal crystallites adopt different orientations on the "armchair" and "zigzag" faces, respectively, then it is possible to develop a rationale to account for the catalytic behavior of the nickel/ graphite nanofiber systems. We suggest that the hydrogenation of alkenes may be favored via adsorption at certain crystallographic faces of the nickel particles, which are generated from the interaction of the metal atoms with one particular face of the graphitic nanofibers. This argument is predicated on the notion that the graphite platelets act as templates for the creation of nickel particles that possess a more accessible structure with a smaller coordination number and, as such, generates conditions for the formation of a more stable adsorbate. Further detailed high-resolution transmission electron microscopy studies designed to examine the relationship between the crystallographic features of the metal particles and the orientation of the graphite platelets in the various nanofiber structures are currently in progress.

Corroboration for some of the arguments outlined above can be obtained from the work of other groups. Dalmai-Imelik and co-workers⁴⁸ prepared nickel/silica catalysts where the crystallites were oriented with either the Ni₍₁₁₁₎ or the Ni₍₁₁₀₎ planes parallel to the support surface, a procedure that resulted in a higher catalytic activity for the hydrogenation of ethylene than that achieved from a system in which the metal particles were distributed in a random fashion. In a further investigation Dalmai-Imelik and Massardier⁴⁹ examined the hydrogenation of ethylene at 25 °C over three low index planes of nickel single crystals and found that the (100) face was virtually inactive while the activity of the (111) face was about twice that of the (100) face. Gallezot and co-workers⁵⁰ reported significant differences in the activity and selectivity of platinum for the hydrogenation of cinnamaldehyde when the metal particles were supported on graphite and charcoal. These variations were attributed to the existence of a strong interaction between platinum crystallites and the graphite support, a condition that was not observed with charcoal. Goetz and co-workers⁵¹ stressed the importance of metal particle morphology in their studies of the palladium-catalyzed hydrogenation of 1-butene and 1,3-butadiene. They claimed that when palladium underwent a strong interaction with γ -alumina to form thin, flat particles, isomerization reactions tended to be highly favored. In contrast, when the metal particles did not interact strongly with the oxide support, hydrogenation was found to be the predominant reaction.

The induction period required to achieve a steady-state conversion observed when nickel was supported on the various graphitic nanofibers might be an indication that a surface reconstruction phenomenon is operative during the initial stages of many of these reactions. The reconstruction of a solid surface has been attributed to the enhanced mobility of surface atoms, resulting from a weakening of the metal-metal bond brought about by the chemisorption of gaseous molecules.⁵²⁻⁵⁵ This phenomenon has, however, been shown to be reversible in nature, the surface eventually relaxing back to its original arrangement upon desorption of the chemisorbed species. A further factor that cannot be ignored is the possibility that the delocalized π -electrons present within these graphitic nanofiber structures might perturb the electronic structure of the metal particles and, as a consequence, exert an impact on their catalytic behavior. Finally, one should not overlook the possibility that differences in the architectural features of the various types of graphite nanofibers may have a profound effect on the manner by which the hydrocarbon reactant molecules can be adsorbed on the carbon structure in the vicinity of the metal particles. If such behavior was operative, then one would expect it to be most pronounced with the larger molecules, 1-butene and 1,3butadiene, rather than the less demanding matching requirements encountered with ethylene.

Conclusions

We have shown that the catalytic performance of nickel for the hydrogenation of alkenes and dienes at moderate temperatures is extremely sensitive to the nature of the support medium. When nickel was dispersed on three unique forms of graphite nanofibers, significant improvements in the catalytic activity and selectivity to specific products were attained over that using the same metal loading on a more traditional support material, γ -alumina. The observed variations in catalytic activity and selectivity are attributed to the different orientations adopted by the nickel particles on the support materials. It is suggested that the graphite platelets in the nanofiber support media act as templates for the dispersed nickel crystallites, which adopt a specific geometry that is determined by their specific site location.

In all cases studied in this work the metal crystallites are located in such a manner that the majority of particles are in direct contact with graphite edge regions. It should be emphasized, however, that there are subtle differences in the spacing between adjacent exposed carbon atoms in the various nanofiber structures. As a consequence, it is highly probable that the atomic arrangement of the surfaces of nickel particles

that nucleate on these different graphite edges will be dictated to a large degree by the interaction with the atoms in nanofiber supports. Under such circumstances one might reasonably expect that different crystallographic faces of nickel will be exposed to the reactant gas depending on which type of nanofiber structure is used as the supporting medium. The ramifications of this remarkable example of a metal-support interaction is that it opens up the possibility of a tailoring the morphological characteristics of metal particles in such a fashion so to achieve a desired catalytic performance.

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