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Hydrogenation of crotonaldehyde over graphite nanofiber supported nickel

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Abstract

In the current investigation we have used the hydrogenation of crotonaldehyde as a probe reaction in an attempt to follow the changes in catalytic behavior induced by supporting nickel on different types of graphite nanofiber support materials. The hydrogenation of the α,β-unsaturated aldehyde to the desired product, crotyl alcohol, is a particularly difficult task since there is a strong tendency to hydrogenate both the C=C and C=O bonds in the reactant molecule. This study is designed to compare the catalytic behavior of the metal particles when dispersed on two 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. For comparison purposes, the same set of hydrogenation reactions were carried out under similar conditions over γ-Al_2O_3 supported nickel particles. The results demonstrate that when graphite nanofibers are used as a support media for nickel particles, these unusual carbonaceous materials exert a tremendous impact on the performance of the metal for the hydrogenation of crotonaldehyde to crotyl alcohol. Possible reasons for this unexpected pattern of behavior are presented. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Graphite nanofiber; Nickel

1. Introduction

The selective hydrogenation of α,β-unsaturated aldehydes and ketones over supported metal catalysts to form the corresponding unsaturated alcohols has gained increasing importance over recent years due to the use of the latter compounds as intermediates in the synthesis of a variety of fine chemicals. The selectivity of this reaction presents some difficult challenges, since one is attempting to simultaneously enhance the rate of hydrogenation of the C=O bond while suppressing that of the hydrogenation of the C=C bond in the aldehyde or ketone molecule [1–3]. It is well known that in their pristine state many metals, including nickel, palladium and platinum are intrinsically unselective and therefore unsuitable to perform this function [2,4].

A number of different approaches have been used in an attempt to improve the performance and in particular, the selectivity of the noble metals towards the formation of unsaturated alcohols. Such efforts have tended to focus on attempts to either modify the behavior of the metal by support effects [5–10], the use of organometallics to prepare clusters with, controlled structures [11] or the introduction of a second metal into the system [12–18]. While these methods have met with a certain degree of success, this is an area of heterogeneous catalysis that is ripe for exploitation by some unorthodox procedures.

Vannice and Sen [5] studied the gas phase hydrogenation of crotonaldehyde at low temperature and low conversions over a variety of platinum catalyst

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systems, including metal powder, and dispersions of the metal on SiO_2, Al_2O_3 and TiO_2 after reduction at either low or high temperatures. While some of these systems were found to produce 100% butanal from the hydrogenation of crotonaldehyde, significant perturbations from this general trend were observed when platinum was supported on TiO_2. Indeed, a Pt/TiO_2 that had been subjected to a reduction at 500°C, gave a selectivity of 37% crotyl alcohol, a finding that represented a major breakthrough in this technology. These results were rationalized according to the notion that the sites created at the $Pt–TiO_2$ interface were responsible for exhibiting preferential activation of the C=O bond in the reactant molecule [6].

Coloma and coworkers [9,10] investigated the effect of dispersing platinum on activated carbon as a catalyst for the gas phase hydrogenation of crotonaldehyde and reported that when the support medium was utilized in the ‘as received’ state the selectivity of the system towards crotyl alcohol was only 4%. However, when the concentration of surface oxygen groups was increased there was a concomitant enhancement in this value to ca.30%. Other workers have attempted to increase the yield of unsaturated alcohol resulting from the selective hydrogenation of the carbonyl bond by introducing various other metals into the platinum particles [12–18]. The addition of a small amount of tin to platinum was found to produce a major change in the product spectrum resulting from the hydrogenation of crotonaldehyde, where the reaction was found to proceed mainly through rupture of the C=O bond with the formation of crotyl alcohol [12]. This behavior was rationalized in terms of the acidic character of tin ions, which tended to enhance the reactivity of the C=O bond in preference to the C=C bond in the starting molecule. In sharp contrast, when nickel was added to platinum, the activity for hydrogenation of the C=O bond in crotonaldehyde was significantly decreased over that observed when the pristine noble metal was used for the same reaction [14].

Englisch and coworkers [19] demonstrated that the hydrogenation of crotonaldehyde over Pt/SiO_2 and Pt/TiO_2 was strongly dependent on the metal particle size and promotion by surface oxide species. They claimed that the selectivity was directly controlled by the mode of adsorption of the reactant molecule and that this pattern of behavior was identical for both oxide supported systems following reduction at 300°C provided that the platinum particle sizes were similar. The selectivity towards crotyl alcohol was found to increase as the metal particle size increased; a value of 11% being realized for a catalyst consisting of relatively small particles and this level could be improved to 41% with somewhat larger particles. It was also reported that if the Pt/TiO_2 catalyst was subjected to a higher initial reduction treatment of ca. 500°C then consistent with previous data [5], a significant increase in both the activity and selectivity towards the desired product could be achieved. This behavior was attributed to the participation of TiO_x species that are believed to decorate the surfaces of the metal particles after reduction at high temperatures [20] and offer the potential for interaction of Ti cations with electron pair donor sites of the reactant aldehyde molecules. In this regard, it is important to recognize that the oxygen of the C=O group of crotonaldehyde is strongest electron pair donor of this molecule and the reaction with Lewis acid sites of the catalyst is likely to be favored. It was significant to find that a similar behavioral pattern with regard to the effect of metal particle size and selectivity to the unsaturated alcohol prevailed when the hydrogenation reaction was performed in the liquid phase.

A theoretical treatment of the competitive C=C and C=O adsorption of α,β-unsaturated aldehydes on noble metal surfaces was performed by Delbecq and Sautet [21,22]. These workers used a semi-empirical extended Hückel molecular orbital calculation to investigate the adsorption characteristics of a series of α,β-unsaturated aldehydes on various platinum and palladium steps and faces. They concluded that both the nature of the metal and the type of exposed crystal face were critical factors in the determining the mode of adsorption of the aldehyde. One of the recommendations to emerge from this study was that in order to stimulate interaction of the C=O π-system with the metal, enrichment of the surface with electrons was a necessary step. This feature could be most easily achieved by the selection of the support medium, with graphite being one of the best materials for this purpose.

The electrical conductive properties of graphite offers some interesting possibilities when the material is used as a catalyst support medium for small metal particles [23,24]. Planeix and coworkers [25] examined the use 0.2% ruthenium on a novel form of carbon, namely nanotubes, as a support medium. They reported that when the hydrogenation of cinnamaldehyde was conducted over this system, up to 92% of the aldehyde was converted to cinnamyl alcohol. Unfortunately, like conventional graphite, this material possesses a relatively low surface area, $\approx 27\,\mathrm{m}^2/\mathrm{g}$, which creates a major drawback for such an application. This limitation can be readily overcome if one chooses to use graphite nanofibers for this purpose, since it is possible to tailor the orientation of the graphite platelet stacks that constitute the material and generate structures that exhibit high surface areas of between 100 and $700\,\mathrm{m}^2/\mathrm{g}$ [26,27]. Previous studies from this laboratory have demonstrated that when nickel particles were supported on various types of graphite nanofibers the catalyst system exhibited unusual properties with regard to the selectivity patterns obtained for hydrogenation of olefins and diolefins when compared to the behavior found when the metal was dispersed on oxide carriers [28,29]. This modification in catalytic performance of the metal particles was attributed to the different orientations adopted by the crystallites on the edges of graphite nanofibers. It was suggested that the graphite platelets in the nanofiber support media acted as templates for the dispersed nickel crystallites, which adopted a specific geometry that was dictated by their particular site location. In the current investigation, we have attempted to extend this approach to cover the behavior of a somewhat more demanding system, namely the selective hydrogenation of crotonaldehyde to crotyl alcohol.

2. Experimental

2.1. Materials

Two types of graphite nanofibers were used in this work and were grown according to the procedures outlined previously [30,31]. The nanofibers are classified as possessing a ‘platelet’ structure in which the graphite sheets are aligned perpendicular to the fiber axis, (Fig. 1(a)) and a ‘ribbon-like’ structure where the platelets are arranged parallel to the fiber axis (Fig. 1(b)). Prior to use as support media, the catalyst particles responsible for creating these nanofiber structures from the decomposition of various carbon-containing gases, were removed by dissolution in 1 M hydrochloric acid. This step was followed by a thorough washing in deionized water before drying overnight in air at 110°C. For comparison purposes, the same hydrogenation reactions were carried out under similar conditions over γ-alumina supported metal particles. The γ-alumina was supplied by Degussa and was used in the as-received condition.

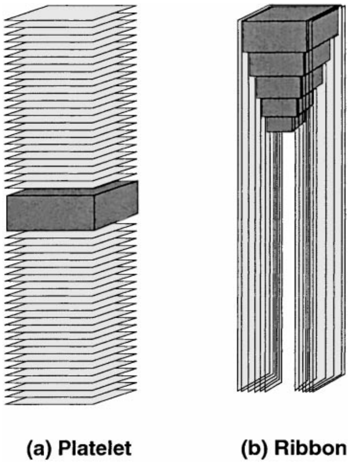

Fig. 1. Schematic representation of the two types of graphite nanofibers used in this investigation.

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 ethanol solution containing the appropriate amount of the precursor salt necessary to achieve the desired metal loading. After drying overnight in air at 110°C, the impregnated materials were calcined in air at 250°C for 4 h and then reduced at 350°C in a 10% H_2/He mixture for 20 h. The reduced catalyst samples were cooled in He and finally, passivated in 2% O_2/He for 1 h at room temperature before being removed from the reactor. This procedure creates a very thin oxide layer around the metal particles and protects the previously reduced surface from undergoing a highly exothermic reaction with air leading to extensive catalyst sintering. In the case of the γ-alumina supported nickel sample this protocol was modified, the reduction step in H_2 at 350°C was increased for periods up to 60 h in order to ensure that complete conversion of nickel to the metallic state was being realized.

The gases used in this work, helium (99.999%), hydrogen (99.999%), carbon monoxide (99.99%), ethylene (99.95%), were obtained from MG Industries and used without further purification. Reagent grade nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] and crotonaldehyde (99.9%) were obtained from Fisher Scientific and Aldrich, respectively.

2.2. Apparatus and procedures

Catalyst studies were performed in a coiled quartz flow reactor where the catalyst sample (100 mg) was positioned in the middle of the tube and this assembly was located within a heating mantle. The gas flow to the reactor was regulated by MKS mass flow controllers allowing for a constant composition of a desired reactant feed to be delivered to the system. Prior to reaction the catalyst sample was reduced in a 10% H_2/He mixture for 2 h at 350°C and the system was then cooled to the desired reaction temperature. At this point the gas, flowing at a rate of 20 sccm, was switched so that it now passed through a saturator containing the liquid crotonaldehyde maintained at a constant temperature of 20°C. The reaction was allowed to proceed for 24 h and its progress was monitored as a function of time by gas chromatographic analysis of the inlet and outlet streams at regular intervals. The reactions were conducted under differential conditions in order to avoid mass transfer limitations.

The supported nickel catalysts were characterized by a variety of techniques, including high resolution transmission electron microscopy (HRTEM), X-ray diffraction, temperature programmed oxidation (TPO) and BET surface area measurements. The former examinations were performed with a JEOL 2000 EXII instrument (lattice resolution of 0.14 nm) and efforts were made to identify any changes in either the support structure or morphology of the metal particles induced by treatment in the reactant mixture. Suitable transmission specimens were prepared by ultrasonic dispersion of the catalyst samples in isobutanol and the application of a drop of the supernatant to a carbon support film. The size distribution of metal particles on the three support media was determined from measurements of over 400 particles from various regions of each specimen. In addition, it was possible to discern the morphological characteristics of the particles and ascertain how these features were influenced by the nature of the support structure.

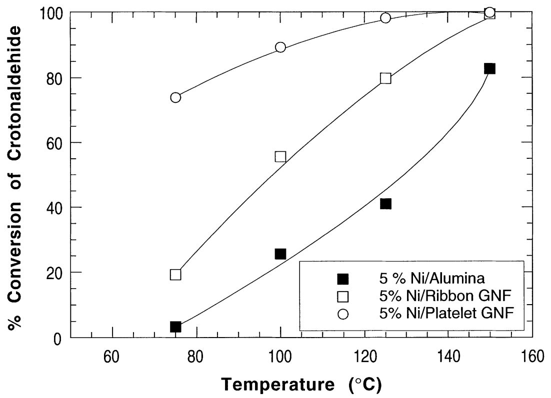

Fig. 2. Percentage conversion of crotonaldehyde over various supported nickel catalysts after 2.0 h reaction as a function of temperature.

3. Results

3.1. Flow reactor studies

Catalytic hydrogenation of crotonaldehyde over the various supported nickel systems was performed at temperatures over the range 75–150°C and analysis of the three major products, butanal, crotyl alcohol and butanol was carried out at regular intervals over a typical reaction time of 25 h. In most cases, the reactions appeared to reach steady conversion levels of crotonaldehyde after ca. 2 h on stream and these values are plotted for the three catalyst systems as a function of reaction temperature in Fig. 2. Inspection of these data indicates that at all temperatures, when the nickel is supported on either the ribbon or platelet types of graphite nanofibers a higher activity is obtained for the conversion of the α,β-unsaturated aldehyde than that displayed when the same loading of metal is dispersed on γ-alumina. Moreover, of the two GNF (graphite nanofibers) materials, the catalyst system based on the platelet form gives the best performance at all temperatures below 150°C.

It is interesting to find that the orientation of graphite platelets in the nanofiber supports exerts an impact not only on the overall activity, but also on the selectivity pattern. This latter feature can be readily observed from comparison of the data presented in Tables 1–3, which shows the percent product distributions obtained for the three catalyst systems at temperatures from 75 to 150°C. Inspection of these

Table 1
Product distributions obtained for the hydrogenation of crotonaldehyde over 5% Ni/platelet GNF after a period of 2.0 h reaction at various temperatures

Temperature (°C)	Butanal	Butanol	Crotyl alcohol[a]
75	58.94	0.60	13.47
100	16.63	32.68	39.70
125	16.32	16.47	65.38
150	21.72	0.07	78.18

[a] The sum of the product distributions is the total crotonaldehyde conversions shown in Fig. 2.

Table 2
Product distributions obtained for the hydrogenation of crotonaldehyde over 5% Ni/ribbon GNF after a period of 2.0 h reaction at various temperatures

Temperature (°C)	Butanal	Butanol	Crotyl acohol[a]
75	18.05	1.14	1.13
100	41.56	0.82	13.22
125	49.83	3.11	26.81
150	25.24	0.11	74.09

[a] The sum of the product distributions is the total crotonaldehyde conversions shown in Fig. 2.

Table 3
Product distributions obtained for the hydrogenation of crotonaldehyde over 5% Ni/γ-alumina after a period of 2.0 h reaction at various temperatures

Temperature (°C)	Butanal	Butanol	Crotyl alohol[a]
75	1.82	0.32	0.89
100	21.60	0.66	3.32
125	35.13	0.14	5.67
150	69.25	0.17	9.71

[a] The sum of the product distributions is the total crotonaldehyde conversions shown in Fig. 2.

data shows that at a reaction temperature of 100°C preferential hydrogenation of the C=C bond in the reactant molecule to form butanal ensued when nickel is supported on either the ribbon GNF or γ-alumina, whereas hydrogenation of the C=O bond takes place when the metal is dispersed on the platelet GNF. This pattern of behavior is maintained when the temperature is raised to 125°C. A dramatic change in the performance of the Ni/ribbon GNF system is observed at 150°C when it is evident that the selectivity pattern is almost identical to that displayed by the Ni/platelet GNF catalyst. On the other hand, when the reaction is conducted over the Ni/γ-alumina catalyst there is still a preference for the formation of butanal. In general, the complete hydrogenation step to butanol is relatively low, partial hydrogenation being heavily favored under the conditions utilized in these experiments.

In a final series of experiments, the catalytic activity of pristine samples of the respective GNF materials for the hydrogenation of crotonaldehyde was investigated at temperatures from 75 to 150°C. In all cases no evidence for decomposition of the reactant was found and so one may confidently conclude that these types of carbon materials do not exert any catalytic action on the conversion of the aldehyde in the absence of metal particles.

3.2. Characterization studies

A combination of CO_2 temperature programmed oxidation experiments and X-ray diffraction measurements established that all the nanofibers used in this work were highly graphitic in nature with an extremely low amorphous carbon content. TEM studies revealed that the nanofibers were between 100 and 150 nm in width and varied from 5 to 50 mm in length. Examination of the freshly prepared nanofiber supported nickel particles showed that in both systems, the metal particles tended to be located along the edge sites of each type of nanofiber structure. Particle size distributions on the two types of GNF support media are presented in Fig. 3. It is evident from inspection of these plots that the distribution profiles of nickel particles deposited on these materials are quite similar and relatively broad, ranging in size from 1.5 to 43.5 nm. From analysis of these data it was possible to establish that on these supports the weighted average size of the metal particles was ca. 7.0 nm.

The corresponding particle size distribution for the same loading of nickel on the γ-alumina support is presented in Fig. 4. In this case it is clear that the particle size range is quite narrow, 0.25–9.0 nm and analysis of this data gave a weighted average value of 1.4 nm. In sharp contrast to the nanofiber supported metal systems, with the γ-alumina support it was extremely difficult to determine the existence of any preferred shape of the particles and in general they appeared to be somewhat more rounded in outline. Despite this difference in particle morphology, the resistance to nickel particle growth on γ-alumina would certainly imply

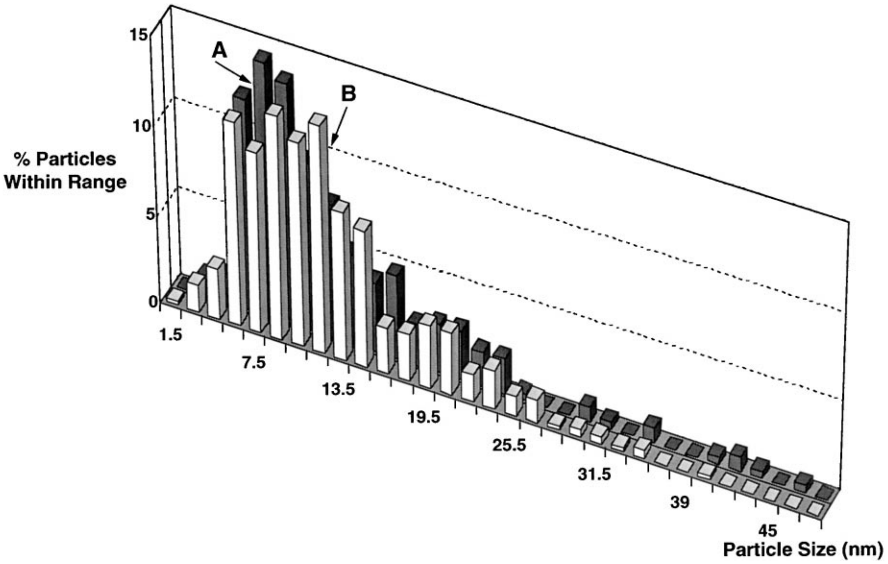

Fig. 3. Size distributions of 5 wt.% nickel particles supported on (A) platelet GNF and (B) ribbon GNF prior to reaction.

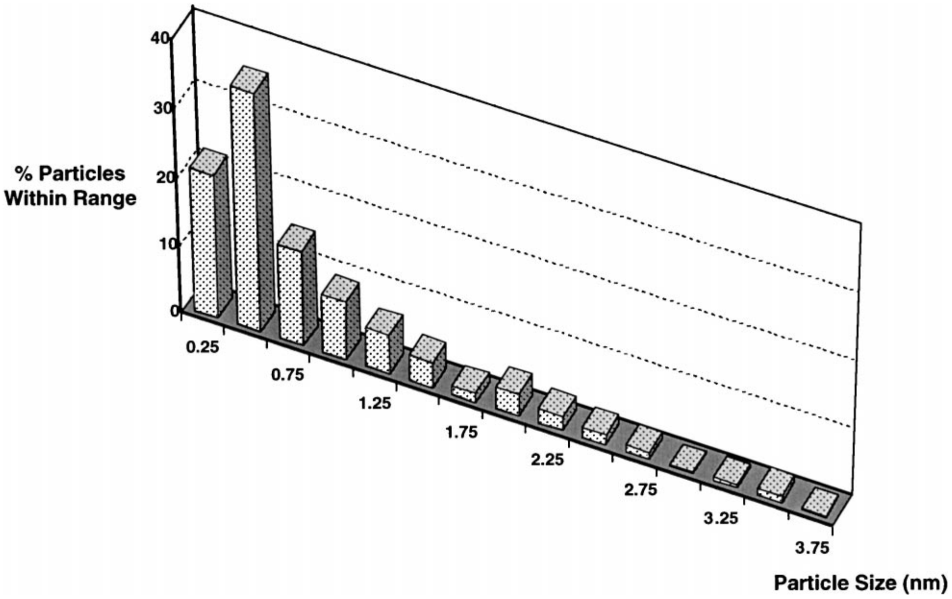

Fig. 4. Size distributions of 5 wt.% nickel particles supported on γ-alumina prior to reaction.

the existence of a relatively strong metal–support interaction.

High resolution examination of individual particles showed that the particles supported on GNF adopted a well-defined hexagonal outline and were thin enough to allow one to distinguish the structural features of the underlying support surface. It was apparent that as one scanned across a given particle the electron density remained fairly uniform, indicative of a flat geometry. This set of morphological characteristics is consistent with the existence of a strong metal–support interaction. Some of these features can be seen on the electron

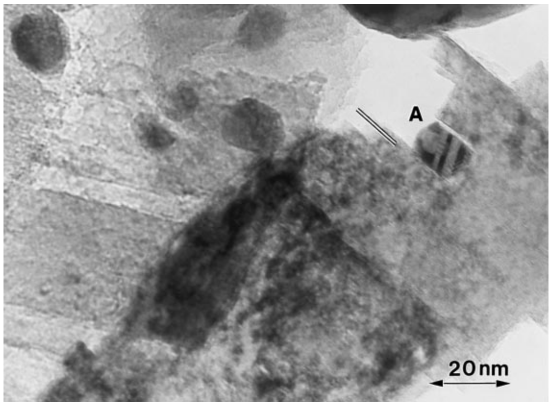

Fig. 5. High-resolution transmission electron micrograph of nickel particles supported on the platelet form of GNF prior to reaction. The direction of the graphite platelets constituting the nanofibers is shown by the parallel markers. Also, highlighted is a nickel particle (A) that has attacked the edge regions during the initial reduction step.

micrograph, Fig. 5, which is taken of a freshly prepared sample of nickel dispersed on the platelet form of GNF. The directions of the graphite platelets constituting the nanofiber structure are highlighted with the parallel lines. Close inspection of the particles shows that they are preferentially aligned with respect to the fiber axis. Furthermore, there is evidence in some cases that during the catalyst preparation procedure, the nickel particles have attacked the graphite nanofibers, an example of which is indicated (A). This phenomenon may well play a key role in dictating the orientation of the surfaces of metal crystallites with respect to subsequent gas phase reactions.

It was significant to find that following treatment in the crotonaldehyde/hydrogen environment at temperatures up to 150°C the nickel particles maintained their thin hexagonal form on both types of GNF supports and exhibited only a marginal increase in size under these conditions. A corresponding small increase in particle size was also observed for the nickel/γ–alumina system following the hydrogenation reaction.

4. Discussion

This study has demonstrated that when nickel particles are supported on certain types of graphite nanofibers this combination creates an exceptionally selective catalyst for the hydrogenation of crotonaldehyde to the desired unsaturated alcohol. In this regard, the platelet form of GNF provides the best structural support surface for the metal particles to achieve the desired reaction pathway. In order to understand the differences in the catalytic behavior exhibited by the same nickel loading on the two types of GNF materials it is necessary to examine some of the rudiments of the graphite structural characteristics.

Graphite consists of stacked layers of carbon atoms, arranged in a symmetrical hexagonal array, where the sheets are separated from each other by a distance of 0.335 nm. The material is comprised of three different faces; the basal plane (0 0 2), which possesses an associated cloud of delocalized π-electrons and two prismatic faces where the carbon atoms are arranged in either a ‘zig–zag’ $\{1\,1\,\bar{1}\,0\}$ or ‘arm-chair’ $\{1\,1\,\bar{2}\,0\}$ orientations. The nanofibers can be synthesized to produce a structural conformation consisting of a perfect assembly of graphite platelets where the exposed regions consist almost entirely of edges. The platelet form of GNF has therefore the two sets of prismatic faces exposed, whereas the ribbon type may only display a single surface carbon arrangement. The conformation of these novel materials is to be contrasted with that encountered with traditional graphitic materials, where the major fraction of the exposed structure consists of basal plane regions with a smaller fraction of available reactive edge sites.

It is probable that when nickel is supported on the nanofibers, the crystallites adopt morphological characteristics that are quite different to those that exist when the metal is dispersed on more traditional materials. While it is not possible to determine whether nickel particles will preferentially nucleate at one or other of the prismatic faces available on the GNF, it is clear that the atomic arrangements of the metal atoms will be quite different at these locations. As a consequence, it is expected that the interactions with the respective edge regions will dictate the catalytic behavior of the nickel crystallites.

Continuous observation of metal/graphite systems by controlled atmosphere electron microscopy (CAEM) has shown that particles which come into contact with edges tend to undergo a spreading action at certain temperatures. It was proposed that this phenomenon occurred at the stage where elimination of adsorbed oxygen groups from the graphite surface had been achieved by reaction with active hydrogen species, presumably generated via dissociation of molecular hydrogen on the metal particle. Such a 'clean-up' operation would create conditions that facilitated the formation of a strong bond between the metallic component and the oxygen-free graphite edge regions [32–34].

Baker and coworkers [35,36] used the CAEM technique to study the nickel/graphite–hydrogen system and were able to directly follow the interaction between the metal particles and the carbonaceous substrate. At a critical temperature, metal particles that had accumulated at the graphite edge sites were observed undergo a spreading action along these regions and following this behavior proceeded to propagate channels across the basal plane surfaces. The tracks generated by the active particles tended to be straight with occasional 60° and 120° bends, and were aligned parallel to the $\{1 1 \bar{2} 0\}$ crystallographic directions of the graphite. These findings indicated that in the presence of hydrogen the catalytic material exhibited a preferential wetting action with respect to the 'zig–zag' faces of the graphite and that particles move in such a manner to maintain contact with the carbon atoms in this arrangement. Since nickel interacts strongly with this face one may conclude that a somewhat weaker interaction will be realized when the metal comes into contact with the 'arm-chair' edge sites. These observations were found to be consistent with theoretical studies of Abrahamson [37] that were based on available surface tension data for the nickel/graphite system.

The existence of a strong metal–support interaction between nickel and the GNF surfaces was evident from the high resolution TEM studies as the particles adopted thin, flat, hexagonal morphological characteristics on these materials. It is therefore reasonable to assume that the metal particles form an epitaxial relationship with the graphite edges and adopt metal–metal atom spacings that are dictated to a large degree by the carbon atoms constituting the 'armchair' or 'zig–zag' faces of the graphite substrate. In this regard one can consider that the graphite platelets within the nanofiber structures are in essence acting as templates for the generation of metal crystallites in a particular orientation. Under these circumstances the dramatic changes in both the catalytic activity and selectivity of nickel may be accounted for in terms of the differing structures encountered with these two nanofiber conformations.

Comparison of the data presented in Tables 1 and 2 shows that the atomic arrangement of the metal particles supported on graphite GNF favors the adsorption of crotonaldehyde in such a manner that hydrogenation of the C=O bond is the preferred step, whereas activation of the C=C bond in the molecule takes place to a significantly lesser degree. This reactivity pattern becomes more pronounced as the temperature is progressively raised from 75 to 150°C, with the platelet form of GNF exhibiting the superior performance. At 150°C, however, the selectivity patterns of nickel dispersed on the platelet and ribbon forms of GNF are, within experimental error, virtually identical. This observation would seem to indicate that under these conditions the nature of the interactions between the metal particles and the two materials have reached a corresponding chemical and structural state.

The possibility that the behavior of the Ni/GNF system could be attributed to the existence of active sites at the metal/support interface was also taken into consideration. If, however, such a factor was important then one would expect to find that the rate of reaction would increase as the size of the metal crystallites is decreased. The results of the present investigation indicate that particle size is not a major factor in dictating the reactivity, therefore we can conclude that the reaction is not dependent upon the number of sites encountered at the metal–support interface.

While the unexpected enhancement in both activity and selectivity for the hydrogenation reaction of crotonaldehyde to crotyl alcohol that is achieved when nickel is dispersed on graphite nanofibers can be rationalized according to the geometric arguments presented above, one must also be aware that the presence of delocalized π-electrons in these electrically conductive supports, creates the possibility that electronic perturbations can be induced on the metal particles. Indeed, theoretical studies performed by Delbecq and Sautet [21,22] allow one to predict that a higher charge density on the nickel surface atoms could lead to a decrease in the binding energy of the C=C bond in the α,β-unsaturated aldehyde molecule due to the four-electron interaction. In contrast, this modification in the characteristics of the metal would tend to promote the back-bonding interaction with the $2\pi^*$ (antibonding) orbital and a consequent weakening of the C=O bond making it more reactive towards an interaction with hydrogen. A similar argument was invoked to account for the unexpected promotional effect of CO on the decomposition of ethylene over an iron catalyst [30].

5. Conclusions

The morphological characteristics of small metal particles and the role played by the supporting medium on such features is an area of extreme importance in heterogeneous catalysis. The results of the present investigation demonstrate that when graphite nanofibers are used as a support media for nickel particles, these unusual carbonaceous materials exert a tremendous impact on the performance of the metal for the hydrogenation of crotonaldehyde to crotyl alcohol. This enhancement in both activity and selectivity is attributed to the fact that for the most part nickel crystallites are located on the edge sites of the nanofibers and as a consequence, the arrangement of the metal atoms will be governed to a large degree by the interaction with the carbon atoms in these regions. Under such circumstances one might reasonably expect that different crystallographic faces of nickel will be exposed to the reactant gas compared to those that are present when the metal is dispersed on less ordered materials such as γ-alumina, silica or active carbon. A further aspect that must be taken into consideration is the possibility that electronic perturbations in the metal particles induced from the interactions with an electrically conductive support media, such as the GNF, could result in conditions that favor hydrogenation of the C=O bond rather than that of the C=C bond in the α,β-unsaturated aldehyde. We plan to extend these studies to cover the behavior of these catalyst systems for the liquid phase hydrogenation of the same reactant molecule.

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References

[1] J. Jenck, J.E. Germain, J. Catal. 65 (1980) 141.
[2] P.N. Rylander, Catalytic Hydrogenation in Organic Synthesis, Academic Press, New York, 1979, 72 pp.
[3] P. Gallezot, D. Richard, Catal. Rev.-Sci. Eng. 40 (1998) 81.
[4] T.B.L.W. Martinelli, S. Nabuurs, V. Ponec, J. Catal. 115 (1995) 431.
[5] M.A. Vannice, B. Sen, J. Catal. 115 (1989) 65.
[6] M.A. Vannice, J. Mol. Catal. 59 (1990) 165.
[7] A. Giroir-Fendler, D. Richard, P. Gallezot, in: M. Guisnet et al. (Eds.), Heterogeneous Catalysis and Fine Chemicals, Elsevier, Amsterdam, 1988, 171 pp.
[8] B. Coq, F. Figueras, P. Geneste, C. Moreau, P. Moreau, J. Warawdekar, J. Mol. Catal. 78 (1993) 211.
[9] F. Coloma, A. Sepulveda-Escibano, F. Rodriuez-Reinoso, Appl. Catal. A. 123 (1995) L1.
[10] F. Coloma, A. Sepulveda-Escibano, F. Rodriuez-Reinoso, Appl. Catal. 150 (1997) 165.
[11] M. Banares, A.N. Patil, T.P. Fehlner, E.E. Wolf, Catal. Lett. 34 (1995) 251.
[12] Z. Poltarzewski, S. Galvagno, P. Pietropaolo, P. Staiti, J. Catal. 102 (1986) 190.
[13] P. Beccat, J.C. Bertolini, Y. Glauthier, J. Massardier, P. Ruiz, J. Catal. 126 (1990) 451.
[14] C.G. Raab, J.A. Lercher, J. Mol. Catal. 75 (1992) 71.
[15] T.B.L.W. Marinelli, V. Ponec, J. Catal. 156 (1995) 51.
[16] A. Waghray, J. Wang, J. Oukaci, D.G. Blackmond, J. Phys. Chem. 96 (1992) 5954.
[17] B. Coq, F. Figueras, C. Moreau, P. Moreau, J. Warawdekar, Catal. Lett. 22 (1993) 189.
[18] U. Schroder, L. De Verdier, J. Catal. 142 (1993) 490.
[19] M. Englisch, A. Jentys, J.A. Lercher, J. Catal. 166 (1997) 25.
[20] Metal-Support Interactions in Catalysis, Sintering and Redispersion van Nostrand Reinhold Catalysis Series, in: S.A. Stevenson, J.A. Dumesic, R.T.K. Baker, E. Ruckenstein (Eds.), New York, 1987.
[21] F. Delbecq, P. Sautet, J. Catal. 152 (1995) 217.
[22] F. Delbecq, P. Sautet, J. Catal. 165 (1996) 152.
[23] I.C. Brownlie, J.R. Fryer, G. Webb, J. Catal. 64 (1969) 263.
[24] P. Gallezot, D. Richard, G. Bergeret, in: R.T.K. Baker, L.L. Murrell (Eds.), Novel Materials in Heterogeneous Catalysis, ACS Symposium Series 437, 1990, 150 pp.
[25] J.M. Planeix, N. Coustel, B. Coq, V. Brotons, P.M. Ajayan, J. Am. Chem. Soc. 116 (1994) 7935.
[26] N.M. Rodriguez, J. Mater. Res. 8 (1993) 3233.
[27] N.M. Rodriguez, A. Chambers, R.T.K. Baker, Langmuir 11 (1995) 3862.
[28] A. Chambers, T. Nemes, N.M. Rodriguez, R.T.K. Baker, J. Phys. Chem. 102 (1998) 2251.
[29] C. Park, R.T.K. Baker, J. Phys. Chem. 102 (1998) 5168.

[30] N.M. Rodriguez, M.S. Kim, R.T.K. Baker, J. Catal. 144 (1993) 93.
[31] C. Park, N.M. Rodriguez, R.T.K. Baker, J. Catal. 169 (1997) 212.
[32] R.T.K. Baker, J.J. Chludzinski, J. Phys. Chem. 90 (1986) 4734.
[33] R.T.K. Baker, R.D. Sherwood, J.A. Dumesic, J. Catal. 66 (1980) 56.
[34] R.T.K. Baker, K.S. Kim, A.E. Emerson, J.A. Dumesic, J. Phys. Chem. 90 (1986) 860.
[35] R.T.K. Baker, R.D. Sherwood, J. Catal. 70 (1981) 198.
[36] R.T.K. Baker, R.D. Sherwood, E.G. Derouane, J. Catal. 75 (1982) 382.
[37] J. Abrahamson, Carbon 11 (1973) 337.