

The use of a localized heating protocol in heterogeneous catalysis

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Abstract

The catalyzed decomposition of ethylene has been used as a probe reaction to ascertain the advantages of exclusive heating of a supported metal catalyst by a current stimulated technique. This approach has been found to result in the elimination of certain side reactions generally encountered in conventional catalytic reactor systems associated with thermal decomposition of gas phase molecules. We have found that by restricting the heated zone to the catalyst surface the ubiquitous formation of pyrolytic carbon arising from thermal decomposition of hydrocarbons can be effectively mitigated. In addition, major differences in the selectivity patterns were observed from the localized heating system compared to that found when the same catalyst was reacted in a conventional flow system. The difference in behavior of the catalyst under these diverse conditions is rationalized according to the notion that the flow of an electric current through the support not only served to resistively heat the sample, but also induced electronic perturbations in the metal surface atoms.

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1. Introduction

Carbon deposition on catalysts, reactor tubes, and heat exchanger surfaces adversely affects the performance of a large number of industrial processes, particularly those involving the conversion of hydrocarbons. Several review articles have highlighted the complex structure of carbon deposits [1–8], which can be divided into three main classes: pyrolytic, filamentous, and graphite shell-like structures. These different types would not be distinguished during a routine analysis of a carbonaceous deposit, but merely referred to collectively as “coke.” The potential for carbon formation exists in any system in which

hydrocarbons undergo thermal decomposition and it is well known that certain metals can increase the overall rate of this process by catalyzing the growth of filamentous and the graphitic types of deposit. The highest catalytic activity for carbon deposition is exhibited by iron, cobalt and nickel, and alloys containing these metals.

Available evidence indicates that the pyrolytic carbon component is amorphous in nature and is formed via condensation and polymerization reactions. This type of material originates from uncatalyzed thermal processes. It is conceivable that a significant amount of hydrogen is incorporated in the deposit, however, as the temperature is raised dehydrogenation reactions will tend to reduce the hydrogen content [9]. Evidence indicates that the acidic nature of a surface can exert a profound effect on the amount of this type of carbon that accumulates [10]. There is now a general consensus that the formation of the filamentous and

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graphitic forms of carbon requires the participation of a catalytic entity that usually operates in a particulate form during the growth process.

Over the past few years, a level of understanding regarding the dissociative interaction of carbon-containing gases with metals and alloys has been attained so that it is now possible to control the manner by which such particles catalyze the formation of carbon deposits [11–15]. While it is not possible to completely suppress this action, by modifying the surface chemistry of metal catalyst particles we have identified conditions where the active surfaces remain clean and available for continuous reaction with a gaseous reactant. This state is achieved despite the fact that other faces of the crystallites are generating significant amounts of solid carbon [16]. It should be recognized, however, that in several processes a large fraction of the carbonaceous deposit that accumulates on a metal surface arises from uncatalyzed sources. The most common route being the thermal decomposition of unsaturated hydrocarbons, which gives rise to the deposition of so-called “pyrolytic carbon” [2,17]. This condition is encountered in a variety of commercial operations, including steam-reforming [18], catalytic reforming [19–22], and steam cracking of paraffinic feed stocks [23–26].

In this regard, it is worthwhile to examine the fundamentals by which the majority of heterogeneous catalytic processes are performed. In general, heterogeneous catalysts consist of very small metal particles (1–2 nm diameter) dispersed on either a powdered or pelleted oxide support medium. In a typical catalytic process this combination is then positioned in a suitable reactor vessel and exposed to a reactant gas while the whole assembly is radiantly heated in a furnace to temperatures over the range 150–800 °C. While this conventional approach generally results in the transformation of a major fraction of the reactants into the desired products, the process is energy intensive since one is heating not only the catalyst, but also the gas stream. As a consequence, thermal decomposition of certain reactants can lead to the formation of unwanted products and an increase in the rate of various catalyst deactivation steps [27].

It is reasonable to expect that the problem of pyrolytic carbon deposition could be attenuated or even completely avoided if one used an approach where localized heating of the catalyst component

was adopted. With such an arrangement only those gas molecules that are very close or in direct contact with the catalyst surface will be thermally excited. The ramifications of this procedure is that one could circumvent problems of gas phase polymerization reactions, the precursor step to pyrolytic carbon formation, which ultimately leads to premature catalyst deactivation. We have endeavored to combat this problem by utilizing an approach whereby the catalyst sample is exclusively heated by passage of an electric current through a conductive carbon support. In this resistive heating method only the catalyst is subjected to the elevated temperatures while the reactor walls and feed gases remain relatively cool.

The benefits of localized heating has already been proved to some extent from the direct observations of early controlled atmosphere electron microscopy experiments where specimens were heated resistively by passing a DC current through a platinum strip [28]. Comparison of the behavior of supported metal particles undergoing reaction with acetylene at temperature up to 800 °C demonstrated that with this arrangement very little carbon decomposition attributable to uncatalyzed routes was observed [29]. In contrast, when similar samples were treated in a conventional flow reactor system in the same partial pressure of acetylene, copious amounts of pyrolytic carbon were found to accumulate on the surface.

The growth of carbon nanofibers from metal catalyzed decomposition of ethylene was used as a probe to ascertain any differences in the gas and solid phase product distributions compared to those measured when the same reactions were performed in a conventional reactor system. It should be stressed that we did not intend results of this study to simulate the events occurring in a commercial reactor system. In addition, variations in the morphological characteristics of the nanofibers arising from the two diverse growth methods were determined from high-resolution transmission electron microscopy studies. Previous work from this laboratory has demonstrated that the initial shape of the metal catalyst particle is the key factor that ultimately determines the structure of the nanofiber [30].

In this context, one must be aware that the potential and current flow through the support medium creates electric and magnetic fields, which can induce perturbations leading to differences in the catalytic behavior

of the metal particles and concomitant modifications in nanofiber morphology. Pacchioni et al. [31] investigated the effects of electric fields on heterogeneous catalyst systems and concluded that the rates of oxidation of organic molecules increased by several orders of magnitude when a potential was applied to metal particles supported on solid electrolyte ion conductors. Theoretical calculations by Ajiki and Ando [32] predicted that magnetic fields perpendicular to the axis of carbon nanotubes could result in distortion of the lattice with a corresponding lowering of the electronic energy gap. It is also interesting to find that resistive or Joule-heating effects have produced unexpected crystalline products from amorphous metallic ribbons [33].

2. Experimental

2.1. Materials

The conductive support medium used in these experiments was ThermaGraph graphite fabric that was supplied by Amoco Performance Products. Prior to use the material was washed in acetone and then calcined in air at 500 °C. The 5 wt.% supported nickel catalyst was prepared by a standard incipient wetness technique. The graphite fabric support was impregnated with an ethanol solution containing the appropriate amount of the metal nitrate required to achieve the desired nickel loading. After drying overnight in air at 110 °C, the impregnated material was calcined in air at 250 °C for 4 h and then reduced at 350 °C for 24 h in a 10% H₂/He mixture. The reduced catalyst sample was cooled in He and finally, passivated in 2% O₂/He for 1 h prior to being removed from the reactor. In another set of experiments the introduction of a nickel-rich copper phase onto the graphite fabric was accomplished by addition of an ethanol solution containing both metal nitrates mixed in amounts designed to produce bimetallic particles having a Cu–Ni ratio of 3:7 and a 5 wt.% total metal loading. A similar sequence of steps was employed for the preparation of this catalyst to that followed for the nickel system. In all cases examination of sections of the supported catalyst systems by transmission electron microscopy confirmed that the metal particles were uniformly dispersed over the carrier surface.

The gases used in this work, helium (99.999%), hydrogen (99.999%), and ethylene (99.95%) were obtained from Med Tech Gases and used without further purification. Reagent grade nickel nitrate [Ni(NO₃)₂·6H₂O] and cupric nitrate [Cu(NO₃)₂·3H₂O] were purchased from Fischer Scientific for the catalyst preparation.

2.2. Apparatus and procedures

A novel reactor unit was constructed that allows for localized heating of the catalyst whilst maintaining the rest of the system at ambient conditions. A schematic rendition of the unit showing the rudiments of this approach is presented in Fig. 1. The power is supplied from a low voltage/high current ac source. The catalyst sample is clamped between two copper electrodes to provide good electrical contact. During any given experiment the temperature of the sample was measured by a thermocouple placed that was in direct contact with the central region of the support material. The extent of heat transfer from the hot catalyst surface to the surrounding gas environment and reactor walls was determined in a series of calibration experiments by placing a bank of thermocouples at incremental distances from the reacting sample. It was found that under conditions when the sample was at 600 °C and the gas flow 50 ml/min, the temperature of the gas phase close to the catalyst was 300 °C and the walls of the Pyrex reaction vessel reached 150 °C. Under these conditions the rate of uncatalyzed decomposition of ethylene and other hydrocarbons is negligible. It is also significant to note that the localized heating approach uses between 75 and 85% less electrical power than the conventional flow reactor system.

Sets of comparison experiments were carried out in a horizontal quartz flow reactor system. In all cases, prior to reaction, the catalyst samples were reduced in 10% H₂/He at 400 °C for 2 h and then brought to the desired reaction temperature. Following this step, a C₂H₄/H₂ (4:1) mixture was passed over the catalyst at a flow rate of 50 ml/min at temperatures ranging from 400 to 800 °C for a period of 3 h. The gas flow to the reactor was precisely regulated by the use of MKS mass controllers allowing a constant composition of a reactant feed to be delivered, reactions were followed as a function of time by sampling the inlet and outlet gas streams at regular intervals and analyzing

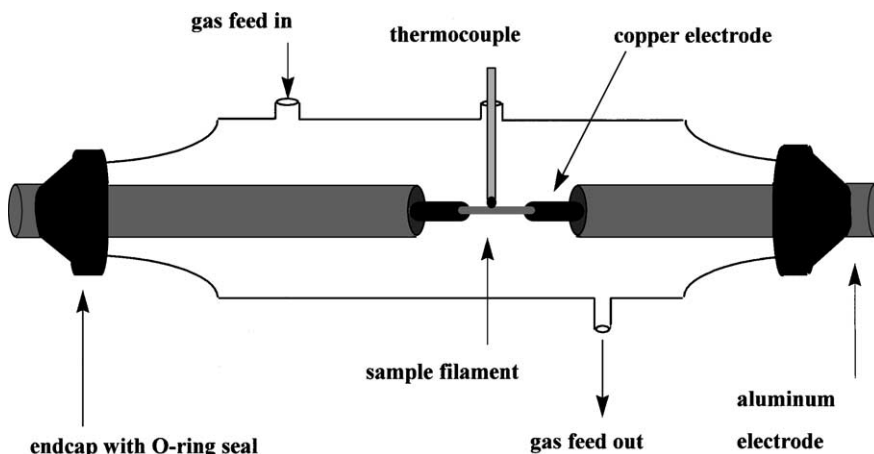


Fig. 1. Schematic diagram showing the main features of the localized heating reactor.

the reactants and products by gas chromatography using a 30 m megabore (GS-Q) capillary column in a Varian 3400 GC unit. At the conclusion of each experiment the solid carbon product was removed from the reactor, weighed and then stored for subsequent structural analysis. In order to verify that uncatalyzed reactions were not exerting an influence on the reactivity behavior of the hydrocarbon, experiments were performed on the graphite support material in the absence of metal particles.

The details of the structural characteristics of individual constituents of the solid carbon products were obtained from examination of a number of specimens from each experiment in a JEOL 2000 EXII transmission electron microscope (0.18 nm lattice resolution). Suitable transmission specimens were prepared by application of a drop of an ultrasonic dispersion of the solid carbon in iso-butanol to a carbon support film. The topographical features of the samples were ascertained from examinations performed in a JEOL JSM 6320 FV high-resolution scanning electron microscope.

The overall degree of crystalline of the solid carbon product was assessed by temperature programmed oxidation studies carried out in the presence of a CO₂/He (5:1) mixture with a Cahn 2000 microbalance at a heating rate of 5 °C/min. Under these conditions the onset of gasification of amorphous carbon is observed at 550 °C whereas the corresponding value for high purity single crystal graphite is 860 °C [35]. From a

comparison of the oxidation profiles of the two standard forms of carbon with that of the uncharacterized sample it is possible to gain an estimate of the crystalline perfection of the material. In order to overcome potential problems associated with the participation of impurities on the gasification reaction, the solid carbons were initially demineralized in 1 M hydrochloric acid for 3 days. This operation was necessary since nickel and copper–nickel particles responsible for the growth of certain types of carbon are present as inclusions and can amount to about 5% of the weight of the deposit.

3. Results

3.1. Flow reaction studies

Figs. 2 and 3 show the gas phase and solid carbon product data as a function of temperature for the respective nickel catalyzed C₂H₄/H₂ (4:1) systems. In order to obtain a meaningful comparison between the two systems the product yields have been normalized at each temperature to the same ethylene conversion levels. It is evident that when the reaction is conducted by Joule heating of the catalyst hydrogenation of the olefin to form ethane is favored over the solid carbon formation step. On the other hand, the formation of methane is significantly higher when the reaction is carried out in the conventional reactor system.

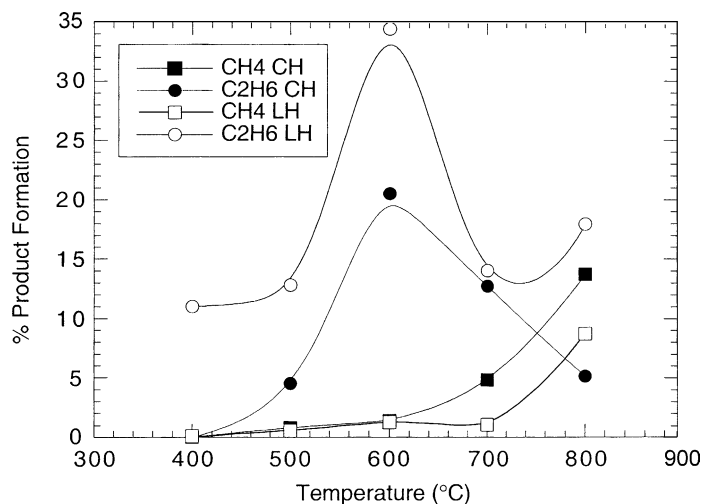


Fig. 2. Percent gas product distribution as a function of temperature for the conventional and localized heated nickel catalyzed C_2H_4/H_2 (4:1) systems.

Inspection of the data presented in Fig. 3 shows similar trends in solid carbon formation are obtained in both systems, with the maximum yield occurring at about 600 °C. As the temperature is raised to 700 °C production of solid carbon exhibits a sharp decline, however, on continued heating catalytic activity is restored.

The corresponding set of data obtained from the copper–nickel (3:7) catalyzed decomposition of

C_2H_4/H_2 (4:1) are presented in Figs. 4 and 5. It is apparent that once again hydrogenation of ethylene to form ethane is the predominant gas phase reaction in the case of the resistively heated catalyst system. The yields of methane generated from the bimetallic catalyst treated in the conventional flow reactor are appreciably higher compared with those from the former system. In contrast, the amounts of solid car-

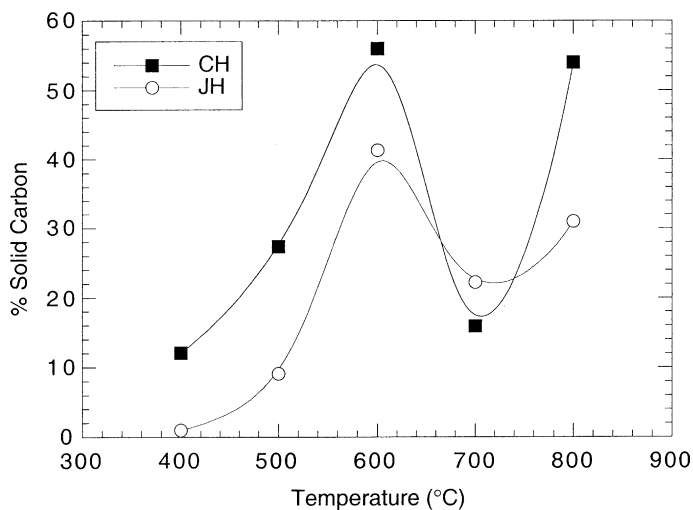


Fig. 3. Percent solid carbon generated from the conventional and localized heated nickel catalyzed C_2H_4/H_2 (4:1) systems as a function of reaction temperature.

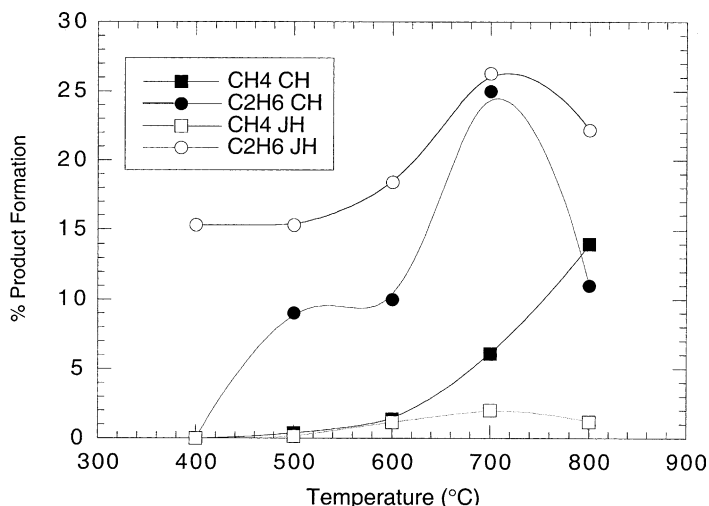


Fig. 4. Percent gas product distribution as a function of temperature for the conventional and localized heated copper–nickel (3:7) catalyzed C_2H_4/H_2 (4:1) systems.

bon formed from the two systems are also identical at all temperatures with the maximum level being observed at about 700 °C. Visual examination of the reacted samples indicated that the deposited carbon was fairly uniformly distributed across the catalyst bed. Moreover, the material was not easily removed from the catalyst surface implying the existence of

strong adhesive forces between the two components. It should be stressed that at temperatures of about 800 °C and higher, the walls of the entire length of the reactor tube in the conventional furnace became coated with a dark brown polymeric residue. In sharp contrast, this phenomenon was completely absent when the specimen was subjected to Joule heating.

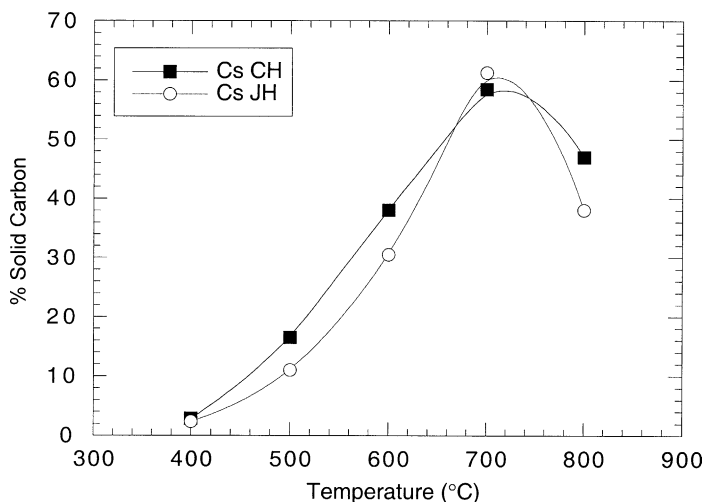


Fig. 5. Percent solid carbon generated from the conventional and localized heated copper–nickel (3:7) catalyzed C_2H_4/H_2 (4:1) systems as a function of reaction temperature.

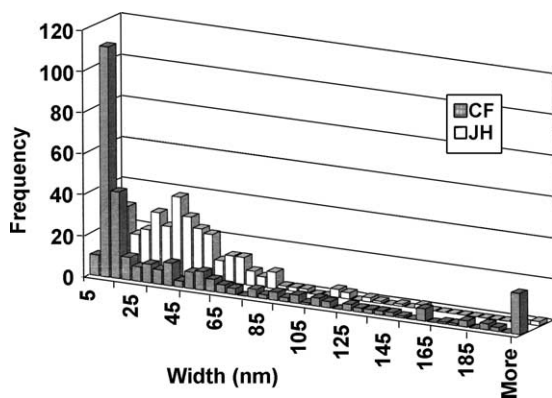


Fig. 6. Comparison of the width distributions of graphite nanofibers generated in the two reactor systems from the nickel catalyzed decomposition of C_2H_4/H_2 (4:1) at $600^\circ C$.

3.2. Characterization of solid carbon deposits

The catalyzed formation of graphite nanofibers is an ideal probe reaction since the structural characteristics of the material are extremely sensitive to the crystallographic arrangement of the metal catalyst particles used in the synthesis. A further advantage of this process is that the deposited carbon effectively constrains the shape of the catalyst in its active state thereby

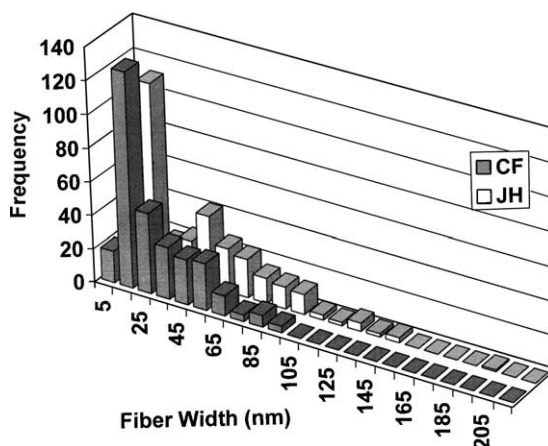


Fig. 7. Comparison of the width distributions of graphite nanofibers generated in the two reactor systems from the copper–nickel (3:7) catalyzed decomposition of C_2H_4/H_2 (4:1) at $600^\circ C$.

enabling one to pinpoint modifications in particle morphology arising from changes in reaction conditions.

Inspection of the solid carbon product that had accumulated on the catalyst by transmission electron microscopy showed that in all cases the deposit consisted entirely of graphite nanofibers. Variations in the width of the nanofibers as a function of both catalyst

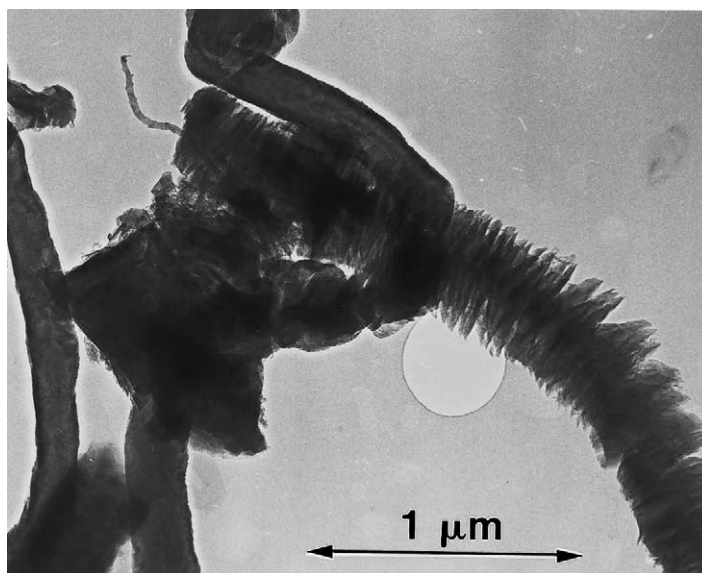


Fig. 8. Transmission electron micrograph showing the appearance of nanofibers produced from the nickel catalyzed decomposition of C_2H_4/H_2 (4:1) at $600^\circ C$.

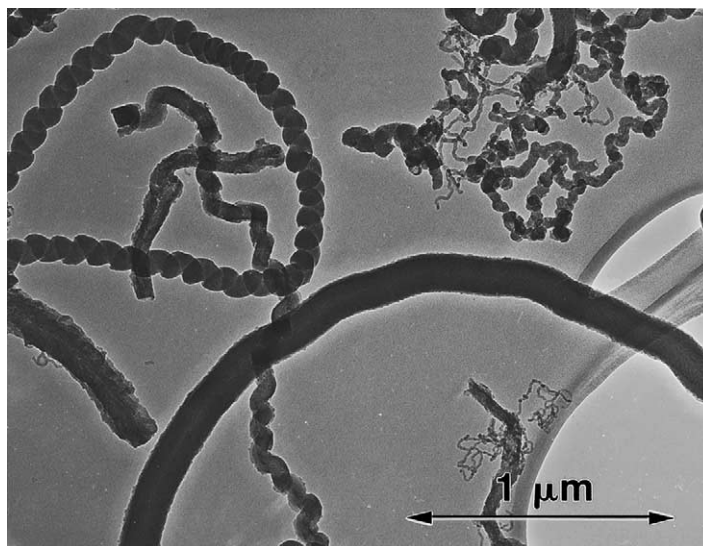


Fig. 9. Transmission electron micrograph showing the appearance of nanofibers produced from the copper–nickel (3:7) catalyzed decomposition of C_2H_4/H_2 (4:1) at 600 °C.

composition and growth conditions were determined from the measurements of over 300 such structures in each sample. Figs. 6 and 7 show the nanofiber width distributions obtained for both reactor systems using nickel and nickel–copper (3:7), respectively. It is apparent that while there are some slight differences for nanofibers derived from the localized and conventional heating methods, the average widths fall within the range, 25–50 nm. Fig. 8 shows the typical appearance of the structures generated from the nickel/graphite catalyzed decomposition of ethylene at 600 °C. It can be seen that the nanofibers tend to acquire a bi-directional helical form and these characteristics were independent of the type of reactor system used generate the material. The results of a corresponding examination is shown in Fig. 9 for the copper–nickel (3:7)/graphite system. In this case, nanofibers grown in both of the reactors once again adopt a spiral conformation.

4. Discussion

Carbon deposition on reactor tubes and heat exchanger surfaces adversely affects the performance of a large number of industrial processes, particularly

those involving the conversion of hydrocarbons. Available evidence indicates that pyrolytic carbon is formed via condensation and polymerization reactions and this material originates from thermal processes. It is generally agreed that this form of carbon is initially formed by a radical precursor mechanism [2]. In a conventional reactor system catalyzed decomposition reactions involving olefins are generally restricted to temperature regions below 700 °C because thermal instability of the compounds leads deposition of carbonaceous residues on the reactor walls. Previous efforts to control the formation of this form of carbon have tended to focus on the use of radical scavenging agents such as *N,N*-diethylhydroxylamine [34].

The current investigation has highlighted the existence of a number of advantages that can be realized by utilizing a localized heating concept in heterogeneous catalysis. One of the major benefits of such a procedure is that the rate of uncatalyzed reactions, which can alter the chemical nature of the reactants and also the selectivity towards certain products, is significantly decreased. In experiments involving the decomposition of ethylene, it was significant that during localized heating the walls of the reactor remained perfectly clean indicating that uncatalyzed decomposition of the olefin was not occurring. Based on high-resolution

transmission electron examinations, we have been able to characterize the form of the deposit and establish that its origin is exclusively catalytic in nature, demonstrating that contributions via uncatalyzed reactions are effectively eliminated by this novel procedure. In sharp contrast, when the reaction was performed in a conventional reactor system copious amounts of pyrolytic carbon collected on the walls of the tube.

It is evident that the overall activity of nickel and copper–nickel (3:7) towards the decomposition of ethylene do not appear to be influenced by the mode of heating of these catalysts. In contrast, resistive heating of the respective catalysts exerted a major change in the gas phase selectivity patterns of the two systems. In both cases, there was an enhancement in the hydrogenation product, ethane, and a corresponding reduction in methane formation.

In a previous investigation it was shown that the distribution of gas phase products was directly related to the manner by which ethylene was adsorbed on the metal catalyst surface [35]. When ethylene was bonded to the surface in an “end-on” arrangement, the adsorbed molecule would rapidly undergo a rearrangement to form an “ethylidyne” intermediate. This entity would subsequently undergo C–C bond rupture to produce a methane molecule, leaving a residual carbon atom on the metal surface that would eventually contribute towards the growth of a carbon nanofiber. On the other hand, when the olefin is bonded in a conformation where the C=C bond is “parallel” to the metal surface, hydrogenation proceeds and ethane is formed. The difference in behavior of the metal catalysts under these diverse conditions suggests that the flow of an electric current through the support exerts at least two effects. This procedure not only serves to resistively heat the specimen, but also induces electronic perturbations in the metal particles that is manifested in a dramatic change in the selectivity patterns.

It was apparent, however, that the structural characteristics of the graphite nanofibers generated from the respective catalysts were independent the mode of heating. In this regard, it is important to consider the critical steps involved in the growth of graphite nanofibers. Initially the hydrocarbon must adsorb on a metal crystallographic face that favors C=C bond rupture. Following this interaction a fraction of the surface carbon species are required to dissolve in the metal particle and diffuse through the bulk to regions

where precipitation in the form of graphite is facilitated. If these various events proceed in a symmetrical fashion then the nanofiber will tend to acquire a relatively straight conformation. On the other hand, when an element of asymmetry exists in the catalyst particle that causes an imbalance in the carbon diffusion characteristics, then the nanofiber will tend to adopt a spiral or helical geometry. This latter condition is frequently encountered when sulfur, chlorine or phosphorus is present in the gas phase [13,36,37]. The finding that the nanofiber conformation was not influenced by the mode of heating would imply that electron transfer effects do not exert an influence on the diffusion characteristics of dissolved carbon species.

The likelihood that electronic effects are operative in catalytic reactions has been a source of controversy for many years. Such an effect was invoked to account for the unusual behavior exhibited by various metals supported on certain oxides when heated in the presence of hydrogen at about 500 °C [38–42]. The counter argument was based on a geometric effect resulting from the blocking of metal sites due to the migration of reduced oxide species [43–47]. In more recent years, we have re-visited this area and examined the effect of dispersing nickel on a number of dielectric oxide media using the hydrogenation of various olefins as probe reactions [48,49]. It was found that at certain critical reaction temperatures the performance of these catalyst systems could be enhanced to a substantial degree. The optimum activity was attributed to electronic perturbations in the nickel particles that were induced as a result of structural and electronic changes occurring in the support at the Curie temperature.

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