JOURNAL OF CATALYSIS 77, 74–84 (1982)

Effect of the Surface State of Iron on Filamentous Carbon Formation

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Received December 9, 1981; revised March 16, 1982

The effect of oxygen and steam pretreatments of iron surfaces on their tendency to catalyze carbon formation during reaction with hydrocarbons has been investigated. Treatment of iron in steam at 700°C was found to have a dramatic influence on the carbon deposition reaction, the amount of carbon produced being at least an order of magnitude higher than that formed in the metal surface under comparable conditions. Spectroscopic analysis (Auger and Mössbauer) proved that this pretreatment converts the iron to FeO. Examination of the carbon deposit in the electron microscope shows that it is predominantly filamentous in nature. A detailed study using a variety of *in situ* surface chemical tools in conjunction with the more conventional bulk approaches has been used to compare the catalytic reactivity of Fe, FeO, and Fe_2O_3 precursors for the formation of filamentous carbon from ethane and acetylene. All these techniques lead to the same conclusion—that the order of activity is FeO > Fe ~ Fe_2O_3. It is also shown that Fe_3C is not an active catalyst for carbon filament formation.

INTRODUCTION

A number of investigations have highlighted the effect of the surface condition of metals on the subsequent deposition of carbon from the catalytic reaction of hydrocarbons with these surfaces (*1–5*). The most active catalysts for carbon deposition are those of the iron subgroup; however, the identity of the catalytic entities is still uncertain. This is hardly surprising in view of the diverse nature of systems that have been investigated, and it is possible that several species may be equally effective as catalysts. Renshaw *et al.* (*6*) emphasized this feature in a very comprehensive literature survey of carbon deposition from CO, stressing the uncertainties in the nature of the catalytic species responsible for the reactivity of iron surfaces. It is generally accepted that iron and not iron carbides catalyze carbon formation (*7*). There is, however, little direct information on the catalytic action of the various oxides of iron.

Bennett and co-workers (*8*) studied the deposition of carbon from acetone on a number of inorganic oxides including Fe_3O_4 and α-Fe_2O_3. They found that Fe_3O_4 was an extremely active catalyst for the formation of filamentous carbon when heated in acetone vapor at 600 to 700°C. In contrast the deposition rates on α-Fe_2O_3 were about an order of magnitude lower than those on Fe_3O_4, even though α-Fe_2O_3 was reduced to Fe_3O_4 at 600°C and to possibly a mixture of Fe_3O_4 and FeO at 700°C.

In the present study a variety of *in situ* surface chemical tools have been used in conjunction with the more conventional bulk approaches to compare the catalytic reactivity of Fe, FeO, and Fe_2O_3 precursors for the formation of filamentous carbon from ethane and acetylene. All these techniques lead to the same conclusion: that the order of activity is FeO > Fe ~ Fe_2O_3.

EXPERIMENTAL

Three types of experimental procedures were utilized in this work: controlled atmosphere microscopy techniques where the

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0021-9517/82/090074-11$02.00/0

changes in appearance of specimens was continuously followed during reaction, Mössbauer spectroscpy which enabled the state of the iron to be determined as a function of reaction conditions, and macroscale experiments conducted in a conventional flow reactor which gave data on the specific amount of carbon deposited on various surfaces under known conditions.

In the microscopy experiments acetylene was used as the hydrocarbon since it is a ready source of carbon even at low pressures. Earlier work showed that polymerization reactions of acetylene interfere with carbon filament formation at pressures in excess of 200 Torr (*9*). For this reason in the macroscale studies ethane was chosen as the reactant, as it is less reactive, and consequently a more convenient gas to use at atmospheric pressure.

Controlled atmosphere scanning electron microscopy. This technique, which has recently been developed, permits bulk specimens to be examined in the presence of gaseous environments at pressures of 1.0 Torr and temperatures up to 1300°C. The exhaust manifold from the microscope has been modified so that a portion of the gas effluent can be fed to the ionization source of a Hewlett–Packard 5992 GC–mass spectrometer. This arrangement provides a sensitive probe of the onset of any surface reaction occurring at the specimen, and in this respect partially compensates for the low resolving power using this cell, about 100 nm.

Specimens were prepared by cutting sections, 3 × 1 mm, from strips of iron and FeO, produced by a treatment described below. The higher oxide, Fe_2O_3, was obtained by heating iron foil, *in situ,* in 1 Torr O_2 at 750°C for 1 hr. In the first series of experiments, each iron catalyst was mounted and reacted independently with 0.3 Torr acetylene. Further experiments were performed where the FeO and Fe foils were reacted side by side on the same heater and both materials observed simultaneously. Finally, this approach was extended to cover the behavior of all three forms of iron.

Controlled atmosphere transmission electron microscopy (*CAEM*). The details of the CAEM technique have been given previously (*10*). Specimens were prepared according to two procedures. In the first, particles of bulk FeO derived from the macroscale experiments and powdered Fe_3C were separately deposited onto transmission sections of single crystal graphite substrates. The Fe_3C (*11*) was characterized by X-ray diffraction and the measured peaks found to have an excellent correspondence with those in the literature (*12*). In the second method iron was deposited as a thin film on graphite from a spectrographically pure wire, at a residual pressure of 5×10^{-6} Torr from a heated tungsten filament. The desired starting state of the iron was obtained by (a) heating the iron at 700°C in 1.0 Torr wet argon (bubbled through distilled water at 0°C) for 1 hr to produce FeO particles, or (b) treatment in 5 Torr oxygen at 600°C for 1 hr to form Fe_2O_3. All specimens were subsequently reacted in a 2 Torr acetylene.

In a separate set of experiments carbonaceous deposits produced in the macroscale and SEM studies were characterized by oxidizing the materials under controlled conditions in the CAEM.

Mössbauer spectroscopy. The Mössbauer spectroscopic techniques used in this work have been described by Phillips *et al.* (*13*). The sample was a 0.0127-mm-thick iron foil, of 99.99% purity, cut into the form of a disk 2.5 cm in diameter. Room temperature Mössbauer spectra were taken in the initial state, after treatment at 800°C for 30 min in 1 atm argon saturated with water at room temperature, and finally after reaction in 1 atm acetylene at 750°C for 0.5 min. Velocities were calibrated using the known Mössbauer parameters of metallic iron at 25°C, and zero velocity is with respect to this standard absorber.

Macroscale experiments. For studying filamentous carbon formation on a macroscale, the following apparatus was used. The reactor was a fused silica tube (2.54 cm in diameter) which was 90 cm long and externally heated via a three zone furnace, which was 61 cm long overall. The center zone was 46 cm long and it could be held at a set temperature to within ±1°C.

To enable samples to be loaded into the furnace at reproducible positions in the tube and facilitate their removal without disturbing the coke deposits, a holder shown in Fig. 1 was constructed. This consists of a series of six sections of silica tubing, each 3 cm long, 1.5 cm diameter, held together with a fused silica rod, the latter being long enough to reach to the exit of the reactor. This arrangement also had the advantage that the samples were held so that their maximum surface area was exposed to the gas phase.

The metallic iron used for these experiments was in the form of a foil, 0.013 cm thick, and had a stated purity of 99.99% (Materials Research Corp., Orangeburg, N.Y.). The foil was cut into pieces 3 × 0.6 cm. Before each experiment the metal foils were cleaned according to the following procedure: initial immersion in 190 proof ethyl alcohol, treatment in toluene, then ethyl alcohol again, washing in boiling distilled water, and then ethyl alcohol, and finally drying in air.

Well-defined samples of FeO were prepared by treating the iron foils with steam at temperatures above 700°C. In all cases, the extent of the reaction was followed by the weight difference of the iron before and after reaction with steam. Typical values obtained for fully reacted foils were $FeO_{1.04}$, $FeO_{0.85}$, and $FeO_{0.95}$, showing good reproducibility. The weight gains can, of course, only be attributed to FeO if an independent method of analysis is available. More definitive identification of the oxide was accomplished using Mössbauer and Auger electron spectroscopies, and X-ray diffraction techniques. The data obtained from the Mössbauer investigation are discussed later in this paper. The Auger elemental analysis were obtained by using the known relative sensitivities (*14*) of peaks of iron and oxygen. Small samples of the steam-treated foil were inserted into the vacuum chamber of the spectrometer. After recording the initial spectrum, argon ion bombardment was commenced and a series of spectra taken at various depths below the surface. As Auger electrons (*15*) have energies below 1000 eV, their escape depth is typically less than 5 nm. Accordingly, the information in the Auger spectrum is obtained mainly from the surface. Data collected in this manner showed that for depths down to 600 nm the composition was in the range $FeO_{0.90}$ to $FeO_{0.92}$.

Other portions of these samples were ground to a powder and examined by conventional X-ray diffraction techniques, which showed only peaks due to FeO. The Fe_2O_3 used in this work was initially in the

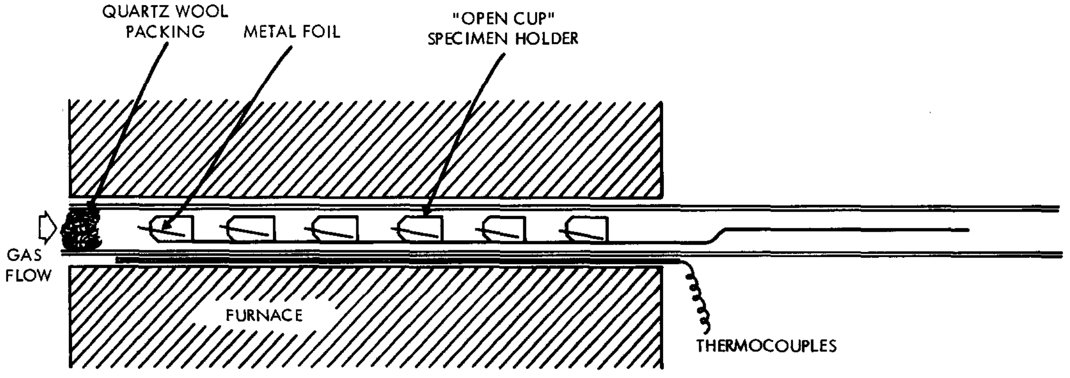

FIG. 1. Schematic representation of specimen holder for macroscale experiments.

form of a powder, stated purity 99.8% (Fischer Scientific Co.) and was pressed into self-supporting wafers, 2.5 cm in diameter.

After the specimens were loaded into the furnace tube they were given a mild oxidation at 700°C for 15 min in air saturated with water at room temperature. The tube was then flushed with N_2, prior to introduction of ethane. With the tube still maintained at 700°C, ethane was admitted at a flow rate of 94 cm^3/min and the reaction allowed to continue for periods of between 1.0 and 6.0 hr. The weight of deposited carbon was determined by difference of the starting and final specimen weights. In addition, the chemical state of iron in the FeO and Fe_2O_3 precursors was determined by room temperature Mössbauer spectroscopy after 2.0 hr of reaction in ethane at 700°C.

RESULTS

Controlled Atmosphere Scanning Electron Microscopy

When a pure metallic iron foil was heated in 0.3 Torr acetylene, carbon was observed to form on the edges of the specimen after about 1 min at 750°C. On continued reaction, growth started to accumulate on the foil surface causing it to acquire a matt appearance. The catalytic activity of the metal appeared to decay after about 10 min at this temperature. This observation was confirmed by the results from the mass spectrometer which showed a return to the original level in the acetylene concentration.

Under identical conditions, the FeO specimen not only appeared to catalyze carbon formation at a rate faster than that of the metal, but it also continued to decompose acetylene for the duration of an experiment, typically 2 hr. Figure 2 shows the crystalline surface of FeO prior to exposure to acetylene, exhibiting a high degree of specular reflectivity. The change in appearance of this area of the specimen after heating in 0.3 Torr acetylene for 2 hr at 750°C, is seen in Fig. 3. Carbon deposition was extremely heavy. The original crack region is almost obscured and during reaction it was apparent that considerable surface reorganization had occurred. At the resolution attainable with this instrument (100 nm) the deposit took the form of voluminous cauliflower-like clusters. Treatment of a portion of the deposit under oxidation conditions in the CAEM, revealed that each cluster was composed of carbon filaments, varying in width from 5 to 20 nm.

A side by side comparison of the catalytic activities of metallic iron and FeO precursors for carbon formation was made via experiments in which both materials were reacted with acetylene simultaneously. Figures 4 and 5 show the appearance of specimens before reaction and after 10 minutes in 0.3 Torr acetylene at 750°C, respectively. In this configuration it was clear that FeO was a superior catalyst compared to the pure metal. The deposit was uniformly thick over all the FeO surface, whereas it appeared to be restricted to edges in the case of the metal.

In a final series of experiments, the third material, Fe_2O_3 was added to this combination. Exposure of this system to acetylene at 750°C showed that under these conditions Fe_2O_3 was the least active catalyst for carbon formation. These experiments were terminated after a reaction time of 1 hr.

Controlled Atmosphere Transmission Electron Microscopy

In initial experiments micro-sized pieces of FeO, supported on graphite, were heated directly in 2 Torr acetylene. At 500°C the first signs of a change in the profile of the oxide were detected and this became more rapid at 575°C as filaments started to appear from the edges. These filaments, which ranged from 2.5 to 5 nm in width and up to 5000 nm in length, grew by rapid extrusion, with the catalyst particle remaining embedded in the FeO mass. As the temperature was gradually raised filamentous growth became more prolific and the vehemence of the reaction often resulted in rupture and

FIG. 2. Scanning electron micrograph of the surface of an FeO specimen.

fragmentation of the FeO sections into smaller particles, which resulted in the exposure of further active regions. Experiments were terminated at 800°C as the amount of deposit was so heavy that it was impossible to discern the growth of individual filaments.

In a second series of experiments FeO was made *in situ* by heating an evaporated film of iron on graphite in 1 Torr wet argon at 700°C for 1 hr, at a low flow rate. Inspection of specimens after this treatment revealed that the metal film had nucleated to form discrete particles, up to 50 nm in diameter.

When these specimens were subsequently reacted in 2 Torr acetylene, onset of filamentous carbon growth was observed at about 590°C. As with the previous system filament formation was via the extrusion mode; however, with this type of specimen arrangement it was possible to see some of the finer details of the growth process. In particular, the width of the filaments was generally much less than that of the catalyst particle from which they were derived, e.g., particles of about 50 nm diameter created filaments of between 2.5 and 5 nm in width. During such sequences it was also observed that the catalyst particles became progressively smaller as material was consumed in the growing filaments.

A further batch of these specimens was heated in 1.0 Torr H_2 at 675°C for 1 hr to reduce the oxide to the metallic state. After evacuation of the H_2, and cooling to room temperature, acetylene was introduced at a pressure of 2.0 Torr. Upon subsequent retreating, filaments were observed at 615°C. These filaments all grew by the commonly observed mode; i.e., the catalyst particle responsible for the growth remained at the head of a filament so that during the growth process it was carried away from the support. In this case there was a significantly wider size range of filaments compared to

FIG. 3. The appearance of the same area of FeO shown in Fig. 2. After treatment in 0.3 Torr acetylene for 2 hr at 750°C.

those formed on FeO, being 2.5 to 50 nm at 650°C. Although the number and size of filaments increased as the temperature was slowly raised to 825°C, it was quite apparent that the number of filaments formed in this system was far less than that produced from the interaction of FeO with acetylene.

The remainder of the specimens were pretreated in 5 Torr O_2 at 600°C for 1 hr, conditions where the metal is expected to form Fe_2O_3. When these specimens were exposed to 2 Torr acetylene, filamentous carbon formation was not detected until 700°C. Even at this temperature, reaction was restricted to only a few particles, the majority remaining quite inactive even at temperatures up to 900°C. The filaments that were formed grew by the extrusion mode, as with FeO.

Finally, particles of Fe_3C, supported on graphite were reacted in 2 Torr acetylene. In contrast to the behavior of previous systems, Fe_3C did not catalyze the formation of filamentous carbon. Indeed the particles showed very little change in appearance on heating up to 900°C.

The CAEM technique was also used to characterize the carbonaceous deposits produced in both the macroscale and scanning microscopy studies. In this case fragments of the various deposits were dispersed onto transmission specimens of graphite and subsequently heated in 5 Torr O_2. During this reaction the various carbonaceous components of the deposit oxidized at different rates and numerous details became evident. At 600°C the amorphous carbon was removed leaving behind a predominantly filamentous carbon residue. These structures, which formed an interconnected network, varied in width from 5 to 35 nm, and were up to 1×10^4 nm in length. Upon further oxidation up to 750°C, virtually all the carbonaceous mate-

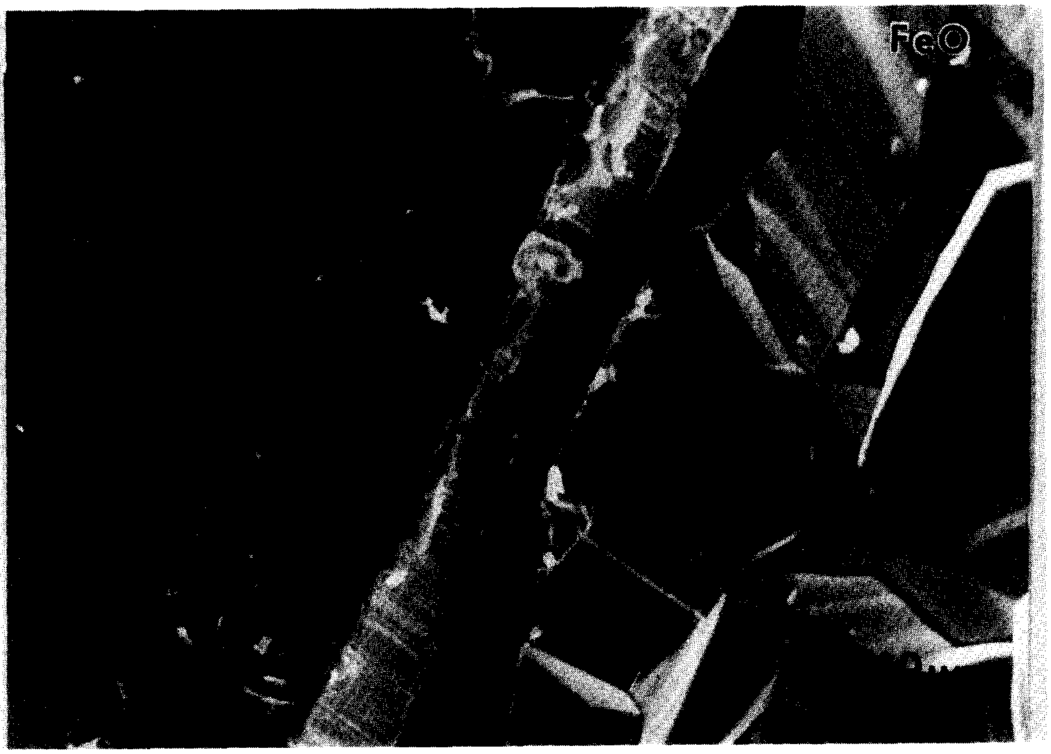

FIG. 4. Scanning micrograph of Fe and FeO before reaction.

rial had disappeared leaving a residue of metal or metal oxide particles.

Mössbauer Spectroscopy Experiments

The Mössbauer spectrum of the as received iron foil is presented in Fig. 6A and shows the six-peaked pattern characteristic of the pure metal. Figure 6B is the spectrum recorded after treatment with steam at 800°C and clearly demonstrates the dramatic change in the nature of the specimen. Although the six-peak spectral pattern of metallic iron still remains, it is clear that it is now no longer the major component; the majority of iron has been converted to another phase.

The corresponding spectral component is a quadrupole-split doublet having the following Mössbauer parameters: quadrupole splitting of 0.58 mm s^{-1} and isomer shift relative to metallic iron of 0.94 mm s^{-1}. These parameters are identical to those of FeO (*16*, *17*). Measurements of the total areas under the Fe and FeO peaks showed that only 12% of the iron remained in the metallic state after the steam treatment, assuming that Fe and FeO have equal recoil-free fractions. Finally, the specimen was heated in 1 atm acetylene at 750°C for 0.5 min and the spectrum shown in Fig. 6C was recorded. Compared to the spectrum collected after treatment in steam, the acetylene treatment leads to an increase in the amount of metallic iron at the expense of FeO. This can be made more quantitative from measurements of the areas under the Mössbauer spectra peaks which shows that Fe now accounts for 23% of the Fe species present. Also apparent in Fig. 6C is a small amount of the six-peak pattern characteristic of Fe_3C (*18*), as shown by the stick-diagram in this figure.

Macroscale Experiments

Table 1 summarizes the yields of carbon which were measured on the three types of

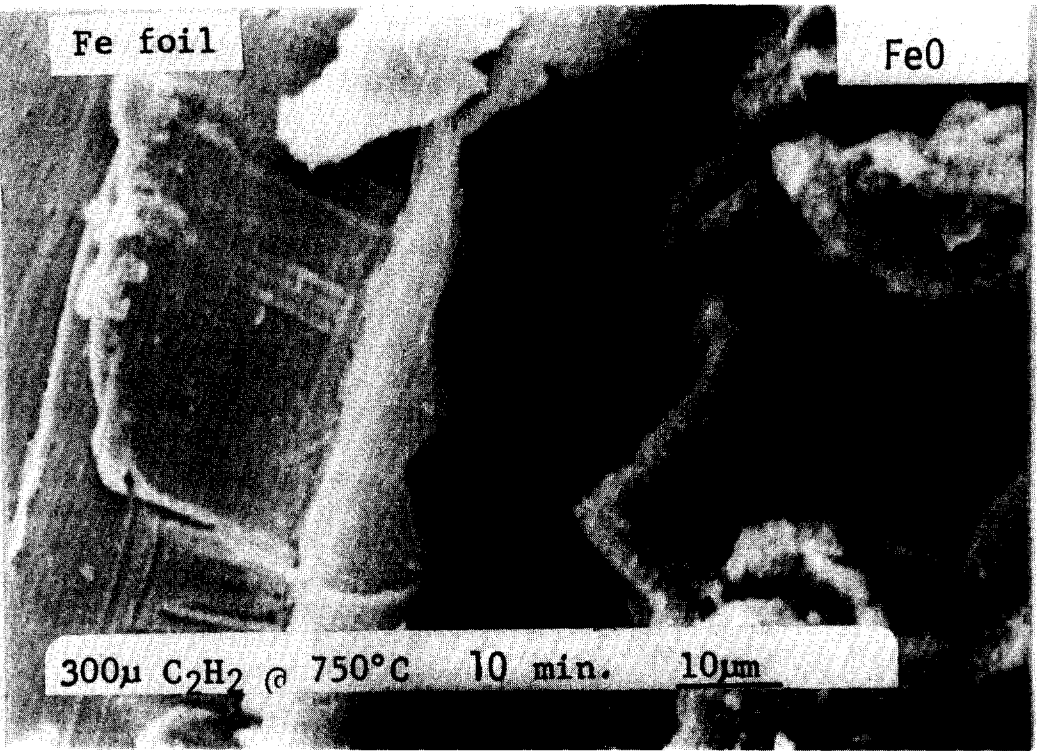

FIG. 5. The same region as shown in Fig. 4, after heating at 750°C in 0.3 Torr acetylene for 10 min.

specimens studied. It should be emphasized that data obtained for Fe_2O_3 are probably higher than they should be as the initial surface area of the starting powder was much higher than that of either of the foil specimens. Nevertheless, it is obvious that FeO is by far the most active surface for carbon growth. Indeed, the reaction was so extensive that upon examination of specimens that had been reacted in 1 atm ethane for 1 hr, no trace of the existence of the original foil could be found. Evidently during the reaction the foil had undergone complete disintegration into small particles intimately mixed with carbon. Portions of this deposit as well as those from Fe and Fe_2O_3 were subsequently oxidized in the CAEM where the carbon was found to be predominantly filamentous.

TABLE 1

Carbon Formation from Catalyzed Decomposition of Ethane at 700°C

State of iron	Carbon formed 10^{-4} g/cm^2/hr		
	Average	High	Low
Fe	114	148	60
FeO	1380	1870	1080
Fe_2O_3[a]	271	440	174

[a] The Fe_2O_3 was used as a pressed powder, with quite a high surface area, while the Fe and FeO were foils of essentially geometric surface area. Thus the rates given above for Fe_2O_3 are probably too high on a per cm^2 basis.

The Mössbauer spectroscopic analyses of the FeO and Fe_2O_3 precursors after reaction in ethane at 700°C for 2 hr showed the presence of only metallic iron and iron carbide (Fe_3C) in both samples, as can be seen in Fig. 7. Important is the observation that neither FeO nor Fe_2O_3 can be detected in either sample. For the FeO precursor, 14% of the iron is present as metallic iron after reaction in ethane, while less than 5% of the iron is metallic for the Fe_2O_3 precursor. (It

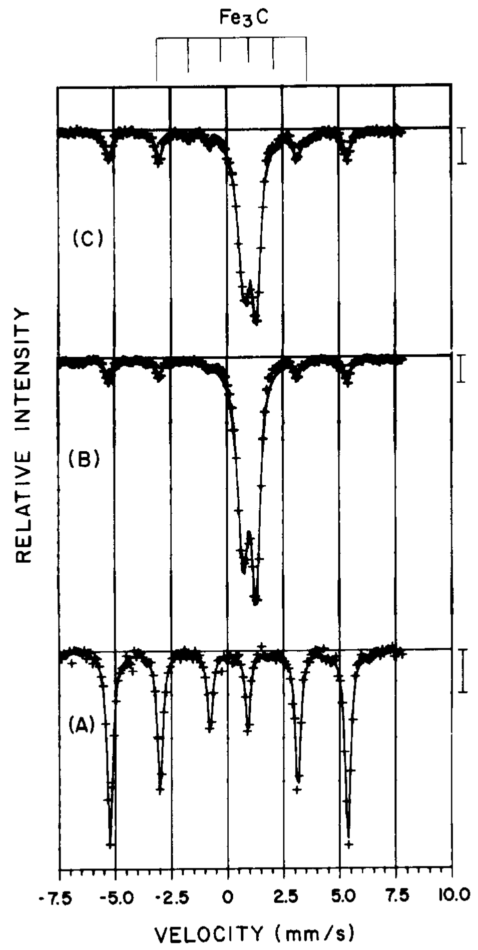

FIG. 6. Room temperature Mössbauer spectra of a metallic iron foil after treatments in steam and acetylene (A) Metallic iron foil as received. (B) From foil after treatment in steam at 800°C. (C) Sample of (B) after treatment in acetylene at 750°C.

is not known at present, however, whether this difference in the amount of metallic iron for the FeO and Fe_2O_3 precursors is significant since the amount of metallic iron for a given precursor varied from sample to sample.)

DISCUSSION

Both macroscale and SEM investigations showed that pretreatment of an iron surface with steam at 700°C induces a dramatic increase in the catalytic activity for carbon deposition from hydrocarbons. Spectroscopic analysis (Auger and Mössbauer) combined with weight increase measurements prove that treatment of iron with steam at 700°C results in the conversion of the surface of the iron to FeO. At 800°C, this process is not just limited to the uppermost surface layers but penetrates to an appreciable depth of the material after a 3 hr treatment. Indeed, the Mössbauer and weight gain data show that all of a 0.013 cm Fe foil is transformed to FeO in this time at 800°C. We realize that the equilibrium in the iron/oxide : H_2O/H_2 system predicts that Fe_3O_4 should be formed in pure steam at temperatures above 700°C (*19, 20*). However, we can only assume that under the present conditions thermodynamic equilibrium is not achieved, and so we make essentially pure FeO starting from Fe. Examination of these specimens while heating up in steam in the scanning electron microscope showed that the surface became rough and faceted beginning at 700°C. The nonstoichiometric nature of FeO has been the subject of a considerable number of papers. It is known, however, that the defects

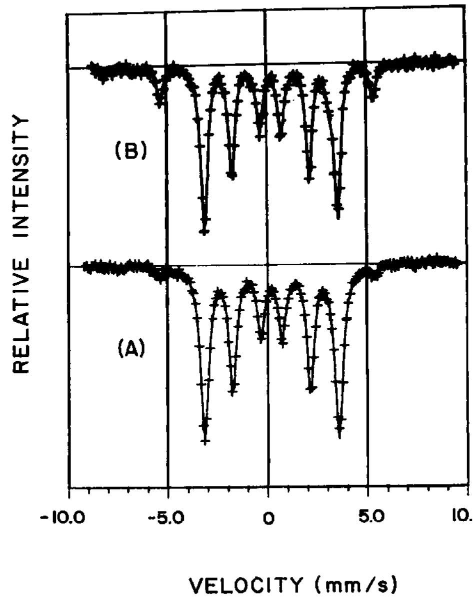

FIG. 7. Room temperature Mössbauer spectra of the Fe_2O_3 and FeO precursors after reaction in ethane at 700°C for 2 hr. (A) Fe_2O_3 precursor. (B) FeO precursor.

present in this material are vacant cation sites and trapped positive holes (*21*).

Comparison of the carbonaceous deposits produced on the macro- and microscale specimens shows that they are very similar in nature, the major constituent being filamentous carbon. Previous work on the formation of this type of carbon on supported metal particles thus becomes extremely relevant to the current investigation. A considerable body of information concerning this type of carbonaceous deposit has been built up over recent years (*22*). Baker and co-workers (*23*) proposed a mechanism for growth of filaments from the metal-catalyzed decomposition of acetylene by assuming that the diffusion process of carbon from the exposed metal faces to the rear of the particle was initiated by a temperature gradient created by the exothermic decomposition of acetylene.

In the present macroscale experiments the filaments have been formed following reaction of ethane with iron and iron oxides. The decomposition of ethane to elemental carbon and hydrogen is endothermic (*24*) and so, at first sight, it appears that the experimental results are in conflict with the above mechanism of filament growth. However, earlier work (*25*) has shown that the majority of carbon formed from ethane arises from the decomposition product ethylene. The latter decomposes exothermically (*24*) ($-\Delta H$ for C_2H_4 at 725°C is 9.2 kcal mole^{-1}) so that this mechanism is not contravened. A similar rationale was used by Keep, Baker and France (*26*) to account for the formation of carbon filaments during the nickel catalyzed decomposition of propane.

The key to the extremely high activity for filament production found with FeO may well reside in the defect structure of this compound. In such a structure the oxygen atoms in the surface will be readily accessible to extraction by protons generated by the hydrocarbon decomposition reaction and as a result the oxide could rapidly attain at the surface an iron-rich sponge-like arrangement, i.e., the role of FeO is that of a precursor for a high surface area Fe catalyst formed *in situ*. This hypothesis is supported by the Mössbauer spectroscopy data which clearly shows that Fe is being produced at the expense of FeO as carbon is being deposited. In addition, the iron in both the FeO and Fe_2O_3 precursors is present as metallic iron and iron carbide after reaction in ethane, indicating that the chemical state of iron is essentially the same in both samples after reaction; therefore the dramatic differences in reactivity of these two precursors for carbon deposition must be traced to differences in effective surface areas. This is despite the fact that the FeO was prepared from a low surface area foil of metallic iron while the Fe_2O_3 was present as a higher surface area powder. This suggests that small metallic particles are formed from the FeO precursor. This leads to the rapid production of many thin carbon filaments having small iron particles at their growing tips. The metallic iron particles formed from the Fe_2O_3 precursor, on the other hand, are evidently much larger than those formed from FeO. This leads to the slower growth of a smaller number of wider carbon filaments. A similar concept was proposed by Guinot *et al.* (*27*) who suggested that fragmentation of an iron–nickel low surface area catalyst by the carbon deposition from CO disproportionation was a necessary step in order to account for the high rate of reaction.

Finally, the CAEM studies do show that Fe_3C is not an active catalyst for carbon filament formation. This observation is also supported by the Mössbauer spectroscopy data which show that the iron carbide concentration increases as catalytic activity declines. This finding does not preclude the possibility that Fe_3C is a catalyst for other forms of carbon deposit.

ACKNOWLEDGMENTS

The authors would like to thank M. Estadt and J. J. Chludzinski for their assistance with the microscopy studies; J. McHenry who carried out the macroscale experiments; and J. Phillips and W. M. Shen (University of Wisconsin) who kindly performed the Mössbauer spectroscopy work presented here.

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