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Application of Conversion Electron Mössbauer Spectroscopy to the Study of Carbon Deposition on Iron[1]

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Carbon deposits were formed on iron foils by the catalytic decomposition of an acetone–carbon dioxide mixture. These deposits were studied by Conversion Electron Mössbauer Spectroscopy and weight change measurements. The results indicate that wüstite (FeO) catalyses the carbon deposition process and cementite (Fe_3C) plays a role in forming carbon filaments by disseminating the wüstite. A mechanism is proposed for carbon deposition in this system.

INTRODUCTION

Carbon deposition may occur when carbon-containing gases catalytically decompose over hot metals. A number of metals are known to catalyse the reaction (*1*) but the most active catalysts, and therefore the most studied metals, are iron, nickel, and cobalt. The deposit can occur in a number of forms, including filamentary, amorphous, and graphitic carbon (*2*).

The reaction is known to occur in many industrial situations including: catalyst beds, where it may poison the catalyst or block pores necessary for the free flow of reactants and products (*3*); chemical plant, where pipes can become blocked by the deposit (*4*); and in furnaces, where firebrick can deteriorate due to deposition on iron particles within the bricks (*5*). The metal catalyst often can suffer severe attack, causing it to powder, a process known industrially as "metal dusting" (*6*).

Previous studies of carbon deposition have included a wide range of gases (e.g., acetylene (*7*), methane (*8*), and carbon monoxide (*9*)) and analytical techniques (e.g., electron microscopy (*10*), Auger electron spectroscopy (*11*), and weight change measurements (*12*)). This paper deals with carbon deposition onto iron from acetone/carbon dioxide, studied mainly by Conversion Electron Mössbauer Spectroscopy (CEMS). CEMS is a nuclei specific (57-iron) surface sensitive technique allowing iron phases to be studied to a depth of approximately 300 nm.

EXPERIMENTAL

Materials. Iron foils, obtained from Johnson-Matthey, were of 99.98% purity and 1 "mil" thick (2.54×10^{-3} cm). Enriched (98%) iron-57 foils (1 μm thick) were obtained from Amersham International for use in the CEMS experiments. The carbon dioxide was British Oxygen Company CP grade (>99.9% purity) and the acetone was redistilled reagent grade (British Drug Houses). Reaction gas was produced by bubbling carbon dioxide through acetone at room temperature according to a method described by Bennett *et al.* (*13*). This method produced approx. 0.3 atm of acetone in carbon dioxide.

Method. Samples were prepared in two experimental arrangements. For CEMS

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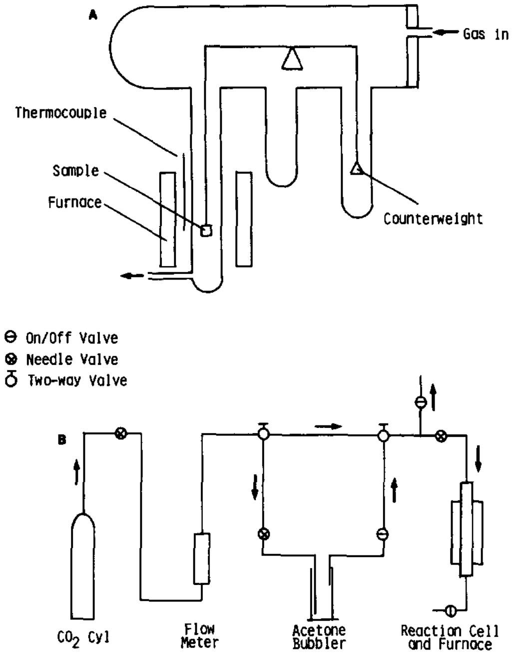

FIG. 1A. Experimental arrangement used for kinetic studies in the microbalance. B. Experimental arrangement used for producing samples for study by Conversion Electron Mössbauer Spectroscopy (CEMS).

studies the enriched iron foils (5 × 5 mm) were degreased in acetone followed by washing in methanol, then suspended by a gold hook in the reaction tube (Fig. 1b), and flushed with reaction gas (CO_2 containing 0.3 atm acetone). The sample was kept at room temperature in a cool part of the tube until the furnace had reached reaction temperature (±20°C) whereupon the sample was quickly lowered into the furnace. After a set time the sample was withdrawn into the cool zone and allowed to cool quickly to room temperature. Samples so prepared were studied by CEMS and scanning electron microscopy.

For kinetic data, unenriched iron foils (1 × 1.5 cm) were treated in a similar manner to the above and suspended in the furnace by a gold wire from one arm of a torsion microbalance (Cahn 2000), as shown in Fig. 1a. The system was flushed for 1 h with reactant gas and the furnace switched on. Weight change was followed continuously with time at a number of temperatures (±5°C). After reaction the samples were cooled slowly in the furnace to room temperature and a few were studied subsequently by electron microscopy and Mössbauer spectroscopy.

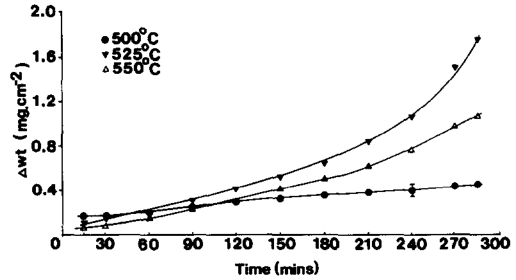

FIG. 2. Weight change versus time for an iron foil exposed to carbon dioxide/acetone at 500, 525, and 550°C. Typical error bars are shown.

RESULTS

Microbalance. The weight change versus time curves obtained in the microbalance studies are shown in Figs. 2 and 3. Typically the results indicate two different types of behaviour depending on the reaction temperature. At all temperatures, however, there was an initial period when little, if any, weight change was noted. Below 575°C (Fig. 2) the rate of carbon deposition was relatively slow and the total weight increase small, whereas at temperatures of 575 and 600°C (Fig. 3) deposition was very rapid, producing copious quantities of carbon with the iron foil eventually disintegrat-

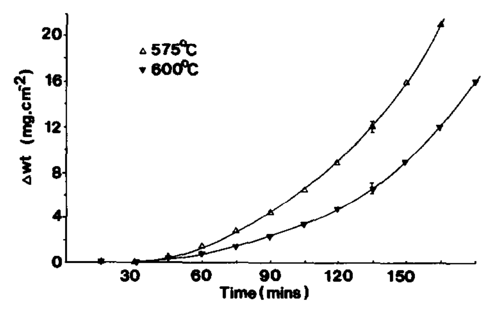

FIG. 3. Weight change versus time for an iron foil exposed to carbon dioxide/acetone at 575 and 600°C. Typical error bars are shown.

PLATE 1. (a) SEM of iron foil exposed to carbon dioxide/acetone at 500°C showing the uniform deposit formed at this temperature. (b) SEM of iron foil exposed to carbon dioxide/acetone at 550°C. Note the columnar carbonaceous deposit formed at this temperature.

ing. Experiments conducted on the oxidation of iron in carbon dioxide showed a weight increase of approximately 0.8 mg cm^{-2} after 180 min at 550°C and 1.4 mg cm^{-2} after 180 min at 600°C. This indicates that oxidation may be the main contributing factor to the weight increase at 500–550°C in acetone/carbon dioxide and that in the presence of acetone oxidation may be inhibited.

It should be noted at this time that above approximately 560–580°C wüstite is the stable iron oxide whereas below this temperature magnetite is stable.

At 500°C the total weight increase after 3 h was less than 300 μg cm^{-2}. Scanning electron microscopy (SEM) showed that the deposit was fairly uniform with some surface irregularities (Plate 1a). Conversion Electron Mössbauer spectroscopy revealed that Fe_3O_4 was the only iron species in the deposit, indicating that carbon deposition was associated with simultaneous oxidation of the iron.

At 525°C a total weight increase of 1700 μg cm^{-2} after ~300 min was observed (Fig. 2).

At 550°C (Plate 1b) the total weight increase after ~300 min was less (~1100 μg cm^{-2}, Fig. 2). SEM revealed that the deposit was much rougher in texture than the smoother deposits formed at 500°C.

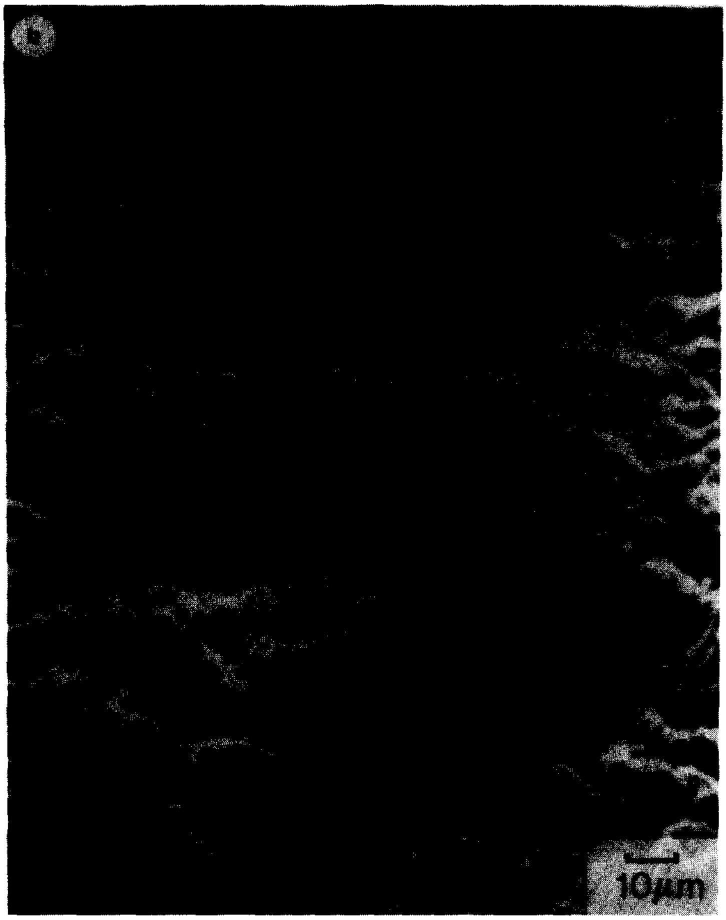

PLATE 1—*Continued.*

At 575°C (Fig. 3) there was little weight increase for the first 30 min, after which the reaction rate increased rapidly, giving rise to a total weight increase of approximately 16,000 μg cm^{-2} after only ~150 min.

At 600°C it was noted that, after an initial period of little weight change, the rate of weight increase was slower than at 575°C, as shown in Fig. 3. SEM on the sample heated at 600°C revealed that it was covered with a mass of carbon filaments (Plates 2a and b). These filaments appeared to grow on columns of carbon. Transmission electron microscopy of the copious carbon produced at this temperature revealed it to be almost solely filamentary in nature with electron dense tips (Plate 2c). Transmission Mössbauer spectroscopy of the filamentary carbon showed Fe_3O_4 was the only iron species in the deposit.

The observation of a larger weight increase for the sample treated at 525°C versus that at 550°C and for the sample treated at 575°C versus that at 600°C, could not be explained. These observations, however, were based on a single experiment at each temperature and therefore may not be general. What is most important is the observation that the rate of reaction increases rapidly above 550°C.

Mössbauer spectroscopy. Iron-57-enriched foils were exposed to CO_2/acetone at 550, 600, and 650°C for study by Conversion Electron Mössbauer Spectroscopy

PLATE 2. (a) SEM of columnar growths formed on an iron foil at 600°C. (b) SEM of columnar growths formed on an iron foil at 600°C showing the appearance of filamentary carbon on the columns. (c) TEM of carbon filaments formed on an iron foil exposed to carbon dioxide/acetone at 600°C for 3 h.

(CEMS). These samples were then quenched in reactant gas before being removed for analysis.

At 550°C the spectrum showed a gradual transition from Fe to Fe_3O_4 over a period of almost 7 h exposure (Fig. 4). At 600°C there was clear evidence for wüstite (FeO) and cementite (Fe_3C) as well as the iron substrate (Fig. 5). Dark areas were visible on this foil after approximately 10 min exposure.

At 650°C, cementite formed almost immediately, so that after only 2 min at this temperature dark areas were visible on the foil and CEMS showed the presence of Fe_3C and some FeO (Fig. 6a). The carbide phase continued to grow and was the only iron phase indicated by CEMS after 8 min (Fig. 6d). No other iron carbides or oxides were detected by CEMS.

The effect of slow cooling on samples from the gas handling rig was determined by heating an Fe-57-enriched foil to 650°C in acetone/carbon dioxide and holding it

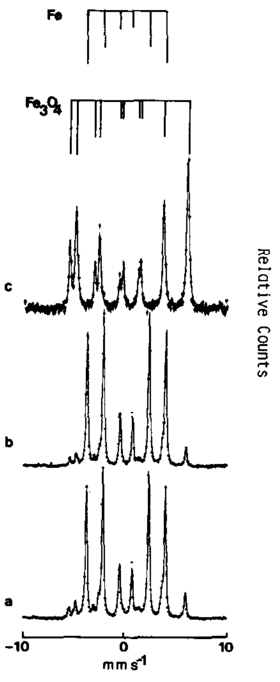

FIG. 4. CEMS of an iron foil exposed to carbon dioxide/acetone at 550°C for (a) 16 min, (b) 1.5. h, and (c) 5 h.

PLATE 2—*Continued.*

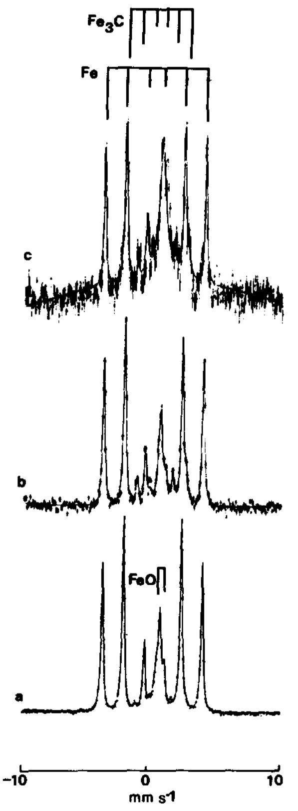

FIG. 5. CEMS of an iron foil exposed to carbon dioxide/acetone at 600°C after (a) 12, (b) 30, and (c) 50 min exposure, showing the formation of wüstite and then the gradual formation of cementite.

there for 2 min (conditions known to promote the formation of Fe_3C and FeO, cf. Fig. 6a). In this case, however, the sample was not quenched in a cooler part of the reaction tube, instead the furnace was switched off and the sample left to cool over a period of approximately 1 h in flowing reactant gas (conditions similar to those used in the microbalance). The CEM spectrum of this sample indicated that virtually none of the expected Fe_3C was present and that the major phase was Fe_3O_4 with some iron still present.

On the basis of the above experiment it is assumed that the phases present in the microbalance at reaction temperature change on cooling and that those indicated by CEMS studies of quenched samples from the gas rig are more representative of the phases present at reaction temperature.

DISCUSSION

A number of mechanisms have been proposed for carbon deposition, more specifically for the identity of the catalyst responsible for filamentary carbon formation on iron. In the present system a number of clear trends were observed. These are summarized below and in Fig. 7.

(i) Carbon deposition at 575 and 600°C occurred slowly at first, perhaps indicating an induction period. Microscopic evidence suggests that during this period, at temperatures greater than 550°C, small columns grow, and CEMS indicates the presence of cementite and wüstite. Below 550°C the deposit is smooth.

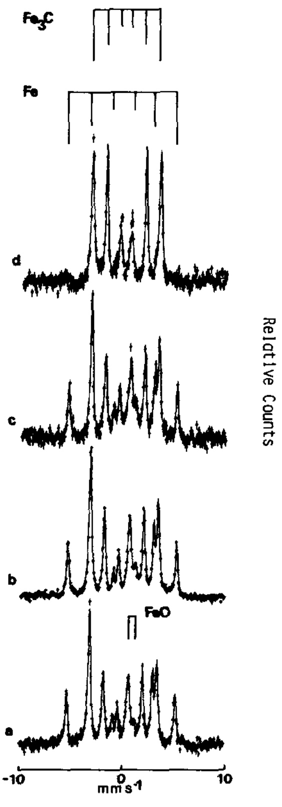

FIG. 6. CEMS of an iron foil exposed to carbon dioxide/acetone at 650°C for (a) 2 min, (b) 4 min, (c) 6 min, and (d) 8 min.

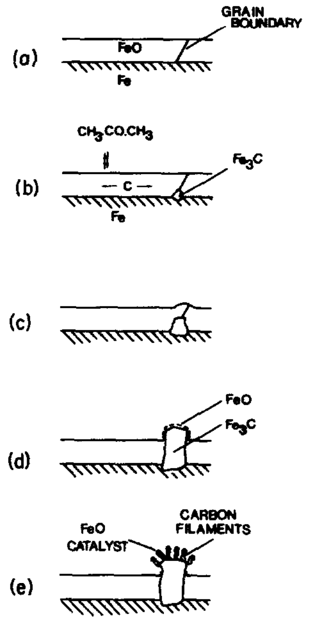

FIG. 7. Proposed mechanism for the formation of filamentary carbon on iron foils from carbon dioxide/acetone above 550°C. (a) Growth of wüstite on the iron foil; (b) decomposition of acetone on the wüstite film and the diffusion of carbon to nucleation sites, where it is precipitated as cementite; (c) continued growth of cementite; (d) the cementite fractures the wüstite film, disseminating the catalyst. The source of iron for cementite formation (iron substrate) has now been cut off; (e) the dissolved carbon now precipitates out as carbon at the wüstite/cementite interface (area of mismatch). Carbon filaments form and propagate according to the mechanism proposed by Baker *et al.* (*2*).

(ii) Immediately following this induction period there is an increase in the reaction rate, and above 550°C copious quantities of carbon filaments are produced. This change in reaction kinetics could be associated with the appearance of wüstite, which is the stable oxide above ~560–580°C (*14*).

(iii) Electron dense tips were observed on the filamentous deposits (Plate 1b).

From the above the following is suggested.

Nucleation and Formation of Catalytic Particles above 550°C

There remains some controversy over the identity of the catalytic system responsible for filamentary growth, although there seems little doubt that this occurs during the induction period. Most authors agree that iron carbides (of one variety or another) play a role in the formation of the catalyst (*15*) and some consider iron carbides to be the catalyst (*16*).

In the present work information relevant to the induction period was revealed and the following scheme is suggested.

(a) During the early stages of exposure to CO_2/acetone, FeO (wüstite) forms on the iron surface. Wüstite is stable above 560°C and is cation deficient. Its structure is of the rock salt type but with cation deficiencies and an appropriate proportion of ferric ions to achieve electroneutrality: $Fe^{3+}_{1-3x}Fe^{2+}_{2x}\square_xO$. A major observation of this work is that copious quantities of filamentary carbon were produced at temperatures where wüstite became the stable iron oxide phase, suggesting that FeO formation plays an important role in the overall catalytic system. A clue to its possible role can be found from the work of Renshaw *et al.* (*9*). These authors suggested that cation vacancies in γ-Fe_2O_3 play an important role in the dissociation of CO, by providing a pathway for the diffusion of cations through the oxide layer to the gas–solid interface. These cations, it was suggested, facilitate the chemisorption and subsequent rupture of the CO bond on the oxide surface. Wüstite is also cation deficient and, in a similar manner, could therefore influence the decomposition of acetone.

However, in the present studies, the results of a single experiment on an iron foil, on which FeO had previously been grown (verified by CEMS), conflict with this view. The oxidised foil was subsequently exposed to CO_2/acetone at 550°C; no carbide phases were present in the CEM spectra, as might be expected from the microbalance results. This would suggest that it is not sufficient to have wüstite present, but rather that the wüstite formed in the presence of acetone is altered in some way. Support for this hypothesis comes from the

PLATE 3. "Breakaway-type" oxide formed on the surface of an iron foil exposed to carbon dioxide/acetone at 600°C in the microbalance.

work of Taylor (*17*) and Keep *et al.* (*18*). In the latter work it was found that preoxidation of steel in air reduces the propensity for carbon deposition whereas preoxidation in carbon dioxide increases the propensity for carbon deposition compared with untreated steel. This enhancement was attributed to the presence of highly mobile carbon in the oxide film during carbon dioxide pretreatment. It is therefore thought that the wüstite layer formed from acetone/carbon dioxide has been altered by the incorporation of carbon, and resembles the oxide normally associated with breakaway oxidation (Plate 3 and Ref. (*19*)). For the sake of clarity this oxide will be called "breakaway-type wüstite" in the following discussion.

(b) The oxide film continues to grow and reaches some limiting thickness, approximately 50 nm, before further growth is inhibited. If the carbon-depositing reaction continues, then eventually the oxide will become saturated with carbon and if no mechanism is available for the removal of carbon, decomposition will stop. In the present system the carbon precipitates out as cementite, preferentially at grain boundaries, and therefore the reaction continues.

The precipitation of carbon as cementite has an important bearing on the formation of filamentary carbon. The precipitation of cementite appears to fracture the original oxide (wüstite) skin on the iron substrate leaving wüstite attached to cementite, isolated from the iron substrate. If wüstite is responsible for the catalytic decomposition of the acetone then the increase in surface area brought about by breakthrough would lead to an increase in reaction rate, as observed. A similar effect was observed by Baker *et al.* (*20*), who observed that fragmentation of a wüstite layer into smaller particles exposed further active regions for deposition, during the reaction of iron oxides with carbon depositing gases. The production of small particles of wüstite, each catalysing carbon deposition, would prevent the diffusion of carbon within the disseminated oxide to remote nucleation points (e.g., grain boundaries). The oxide would also be cut off from the sink of iron atoms, needed for carbide formation, by the cementite column. The overall effect therefore would be for carbon to be deposited at the oxide/carbide interface where sites would be available due to mismatch.

Further reaction will stress this interface, leading to the detachment of loosely held oxide catalyst particles and the formation of filaments, with the catalyst particles making up the electron dense tips observed in Plate 2c.

Once formed, the filaments could propagate according to the mechanism proposed by Baker *et al.* (*2*).

Most of the above dealt with carbon deposition above 550°C. It is probable, however, that a similar mechanism to that described above operates below this temperature, with "breakaway magnetite" acting as the catalyst.

Therefore, the major conclusion from this work is that the production of filamentary carbon from carbon dioxide–acetone occurs in two main stages and involves the participation of at least two iron-containing phases. In the first step (Fig. 7) a conditioned oxide, breakaway-type wüstite, is formed which is an efficient catalyst for the disproportionation of acetone. In the second step the precipitation of carbon, as cementite, fractures and disseminates the oxide phase causing an increase in catalytic surface area and the production of filaments. This mechanism is, however, generally applicable, since any combination of a catalyst for the disproportionation of a carbon-depositing gas, and a mechanism for carbon precipitation, should lead to the formation of carbon filaments.

On the basis of this mechanism, additives which suppress deposition could have many functions, including (a) decreasing the effectiveness of the disproportionation reaction by, in this case, occupying cation vacancies or reducing the mobility/solubility of carbon in the oxide; (b) preventing the precipitation of carbon; (c) stabilising the oxide; (d) producing a stable oxide film between the substrate and outer oxide layer such as by the deposition of SiO_2 films on stainless steels (*21*).

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