Promotional Effect of Carbon Monoxide on the Decomposition of Ethylene over an Iron Catalyst

N. M. RODRIGUEZ, M. S. KIM, AND R. T. K. BAKER[1]

Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

We have used the growth of filamentous carbon in conjunction with the gas-phase product distribution as a probe of the reactivity of a powdered iron catalyst when exposed to a carbon-containing gas environment. During the course of a series of reactions designed to examine the differences in carbon deposition characteristics exhibited by CO and C_2H_4 over iron, an unexpected pattern of behavior was found. Exposure of the metal to a C_2H_4–H_2 mixture at 600°C resulted in only minor decomposition of the olefin; however, upon addition of a small amount of CO to the system, there was a dramatic increase in the amount of filamentous carbon formed, of which the major fraction could be attributed to decomposition of C_2H_4. Maximum reactivity was achieved with a C_2H_4–CO–H_2 (3 : 1 : 1) mixture, and it was apparent that CO was responsible for not only promoting the formation of solid carbon, but also inducing the conversion of C_2H_4 to C_2H_6. Removal of CO from the system resulted in a rapid decline in catalytic activity, however, upon reintroduction of CO activity was restored to its initial high level, indicating that the reversible nature of the activation–deactivation processes. This behavior is rationalized in terms of a reconstruction of the iron surface in the presence of coadsorbed CO which results in the possible formation of various faces with differing reactivity characteristics, and a relaxation when CO is removed from the reactant. © 1993 Academic Press, Inc.

INTRODUCTION

The formation of carbonaceous solids over iron surfaces from the decomposition of carbon-containing gases has been studied extensively (*1–12*). The variation in carbon formation activities with different carbon sources over iron, cobalt, and nickel surfaces have been investigated previously, and it was reported that with CO as the carbon source, iron was the most active catalyst (*12*), whereas when the carbon deposition reaction was conducted in the presence of hydrocarbons iron showed little tendency to produce solid carbon (*6*). The high activity of iron with CO has only been observed when some additive gas such as hydrogen, water vapor, or other oxygenates were mixed with the reactant (*1, 3, 7*). Dry *et al.* (*3*) reported that in all the cases where

enhancement of carbon deposition was observed, hydrogen was shown to be present within the catalyst bed. They suggested that the increase in solid carbon formation was related to the ability of hydrogen to strengthen the adsorption characteristics of CO to the iron and as a consequence increase its rate of decomposition.

It is known that disproportionation of CO takes place via the Boudouard equilibrium,

$$2CO \rightarrow C + CO_2, \qquad (1)$$

which favors the right side at temperatures below 700°C. The promotional effects of hydrogen on the decomposition of CO have been interpreted in two ways. The first is the occurrence of a secondary reaction (CO hydrogenation) to produce solid carbon (*1, 7*):

$$CO + H_2 \rightarrow C + H_2O \qquad (2)$$
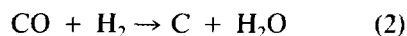
[1] To whom correspondence should be addressed.

In addition to this process, hydrogen adsorbed on the metal surface was also found to catalyze the Boudouard reaction, and this effect has been explained by the ability of hydrogen to decompose inactive metal carbides into the catalytically active metallic phase (1). There have been numerous investigations which have dealt with the interaction of CO and hydrogen on transition metal surfaces, and these have been comprehensibly reviewed by Vannice (14). It is generally agreed that the uptakes of CO and hydrogen are mutually enhanced by a coadsorption procedure compared to that of either gas alone, and this aspect was rationalized in terms of the formation of a surface complex between the two adsorbate molecules.

Examinations of the carbonaceous deposit formed on iron surfaces during interaction with CO–H_2 mixtures have been carried out by transmission electron microscopy, and the major fraction has been found to consist of filamentous carbon (1, 2, 4–9). The filaments are generally formed in a whisker-like mode where the catalyst particle is attached to the growing end, however, there are reports of ribbon-like structures and bidirectional growths in a braided conformation (15). One of the major sources of controversy surrounding the formation of this type of carbon concerns the chemical state of the catalyst particle responsible for catalyzing the growth of filaments. Some workers believe that the active entities are carbides (9, 16, 17), others favor the metallic state (11), and there is also a claim that γ-Fe_2O_3 is the catalytic species (4). This latter state, however, seems unlikely in view of surface science studies (18), which demonstrated a complete lack of any oxygen-containing species on the surface of an iron foil exposed to mixtures in the range 1 : 1 to 11 : 1 of H_2 : CO. Furthermore, it was found that a preoxidized iron surface was unstable under the reaction conditions and was rapidly reduced.

The current investigation was undertaken in an attempt to gain a fundamental understanding of the differences in carbon deposit-ing characteristics of iron when treated in CO and ethylene, both in the absence and presence of molecular hydrogen and in mixtures containing all three gases.

EXPERIMENTAL

The apparatus used in this study has been described in detail previously (19). It consists basically of a quartz reactor tube, which is connected to a gas supply line and operated at 1 atm total pressure under controlled flow conditions. There is provision for taking samples at various intervals during reaction for gas product analysis by gas chromatography. The reactor tube is heated by a conventional split tube furnace. Powdered catalyst samples (50 mg) were held in a ceramic boat which was placed at the center of the reactor tube. After reduction of the sample in a 10% H_2–He mixture for 2 h at 600°C, the system was flushed with helium and then the reactant, either pure CO, CO–H_2, C_2H_4–H_2, or CO–C_2H_4–H_2 mixtures, was introduced into the reactor and allowed to react with the iron catalyst at 600°C for periods of up to 5 h. The total amount of carbon deposited during the experiment was determined by weight difference.

The composition of the gas phase was monitored as a function of time from analysis performed in a Varian 3400 GC equipped with a 30-m megabore column (GS-Q). The column was temperature programmed to release hydrogen, CO, methane, carbon dioxide ethylene and ethane at 35°C and water vapor as the temperature was progressively raised to 180°C. Carbon and hydrogen atom balances in conjunction with the relative concentrations of the respective components were applied to obtain the various product yields. The accuracy of estimating the amount of solid carbon produced by using this approach was checked in a number of experiments where the reaction was terminated after selected time intervals and the amount of solid carbon determined directly from weight measurement differences. Under these circumstances the amounts of

solid carbon were within ±5% of those esti-
mated during continuous experiments by us-
ing mass balances of the reactant and
products.

Iron powder (200 mesh) was obtained
from Johnson Matthey, Inc. (99.99% pu-
rity), and had a BET nitrogen surface area
of 0.3 m^2/g^{-1} at $-196°C$. The adsorption
properties of the metal powder were mea-
sured in a Coulter Omnisorb 100CX unit.
The gases used in this work, CO (99.9%),
hydrogen (99.999%), ethylene (99.99%), and
helium (99.99%), were obtained from Alpha-
gaz company and used without further puri-
fication.

The morphological characteristics of the
solid carbon were established from exami-
nation of random sections of the deposit.
TEM specimens were prepared by applica-
tion of a drop of a dispersion of the solid
carbon in isobutanol onto either a carbon
film or a transmission specimen of single-
crystal graphite. When this combination
was inserted into a JEOL 200CX electron
microscope (resolution 0.18 nm) it was evi-
dent that the deposits from all the various
reactant mixtures consisted of a large frac-
tion of filamentous carbon structures.

RESULTS

(a) Iron-Catalyzed Decomposition of CO–H₂ Mixtures

The effect of hydrogen addition to the CO
feed on the amount of solid carbon depos-
ited on iron after 1.5 h reaction at 600°C is
presented in Fig. 1. Inspection of these data
shows a number of important features:

(i) The addition of only a small amount
of H_2 into the feed produces a remarkable
increase in the formation of solid carbon,
from 0.5% (in the absence of H_2) up to 20%
with a mixture containing 7% hydrogen.

(ii) A subsequent increase in the percent
of hydrogen in the reactant does not appear
to have a great deal of impact on the percent
of CO which is ultimately converted to solid
carbon.

In an attempt to determine the relative im-
portance between the Boudouard reaction
$(2CO \rightarrow C + CO_2)$, CO hydrogenation
$(CO + H_2 \rightarrow C + H_2O)$, and CO methana-
tion $(CO + 3H_2 \rightarrow CH_4 + H_2O)$ both the
solid and gas-phase products compositions
were determined. The results of the analysis
for CO–H₂ (4 : 1) and CO–H₂ (1 : 4) mixtures
are presented as a function of time in Figs.
2a and 2b, respectively. Here, each product
yield is defined as the moles of that product
divided by the moles of input CO. After a
short initial period, the product yields in-
cluding those of the solid carbon reached a
steady state with a CO–H₂ (4 : 1) mixture
(Fig. 2a). In this case, a larger fraction of
solid carbon is formed as a result of the
Boudouard reaction rather than CO hydro-
genation, and methane formation is almost
negligible.

On the other hand, with a CO–H₂ (1 : 4)
mixture (Fig. 2b), all product yields, with
the exception of CO_2, exhibit a gradual
change at reaction times in excess of 30 min.
Specifically, the methane yield exhibited a
steady increase for periods of up to 3 h. In
this case, the water yield is very high and
a larger fraction of solid carbon is formed
via CO hydrogenation rather than the Bou-
douard reaction. It is of interest to note that
the methane yield is relatively important un-
der these circumstances and is even higher
than that of carbon dioxide at the later stages
of the reaction. This suggests that in addi-
tion to the Boudouard reaction and CO hy-
drogenation, a third reaction to produce
methane is operative, namely, CO metha-
nation.

The regions where the three reactions pre-
dominate can be identified from the data
presented in Table 1, which shows the prod-
uct distributions obtained from the iron cat-
alyzed decomposition of a series of CO–H₂
mixtures after one hour reaction at 600°C.
At high CO–H₂ ratios the Boudouard reac-
tion is responsible for producing most of
the solid carbon, whereas with equimolar
mixtures about half of the deposit is found to
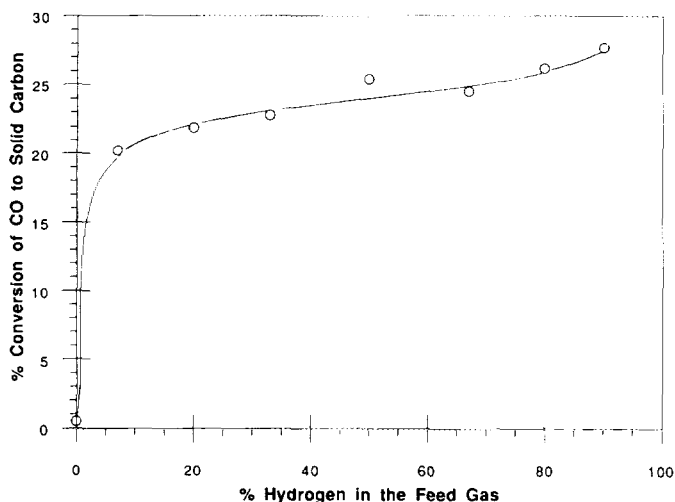arise from CO hydrogenation. In contrast, at

FIG. 1. Effect of hydrogen on the conversion of CO to solid carbon over iron at 600°C (reaction time 1.5 h).

high H_2 : CO ratios, CO hydrogenation and methanation become the dominant reaction pathways with the former been the major source of solid carbon.

Finally, we have also considered the possible contribution of the water-gas shift reaction (CO + $H_2O \rightarrow H_2$ + CO_2) on the product distribution. The equilibrium constant, $K = [CO_2][H_2]/[CO][H_2O]$, for this reaction at 600°C based on thermodynamic data is 2.59 (20). From the measured concentration ratios obtained in the current study for the reaction of CO : H_2 (1 : 4) and (4 : 1) mixtures the values were calculated to be 2.13 and 2.44, respectively. Since these values are very close to that of the equilibrium constant, the rate of this reaction will be very slow under the present experimental conditions. As a consequence, we assume that the shift reaction does not play a significant role in determining the composition of the product gas. This conclusion was also reached by Walker et al. (1) from their studies which were performed at similar conditions to those used in the present study.

(b) Iron-Catalyzed Decomposition of C_2H_4–H_2 and CO–C_2H_4–H_2 Mixtures

A comparison of the carbon deposition rates from the decomposition of CO–H_2

(4 : 1) and C_2H_4–H_2 (4 : 1) mixtures over reduced iron, nickel, and cobalt catalysts is presented in Table 2. It is apparent that the solid carbon formation rates from the iron-catalyzed decomposition of CO–H_2 are much higher than those produced from the other two metals. Conversely, when C_2H_4–H_2 is the reactant mixture, iron showed the lower activity for the formation of solid carbon.

When iron powder was reacted in a C_2H_4–H_2 (3 : 1) mixture the carbon formation activity was initially 0.43% and remained at this level for about 1 h, at which point CO was introduced into the feed gas in sufficient concentration to create a CO–C_2H_4–H_2 (1 : 3 : 1) mixture. The addition of CO to the feed resulted in a dramatic increase in the amount of solid carbon which was deposited on the catalyst, rising from 0.43 to 68%, over a 30-min period of time; see Fig. 3. It appears that the presence of CO may induce changes in the surface of the iron catalyst which are responsible for enhancing its ability to adsorb and decompose ethylene.

An equally fascinating result was obtained using a slightly different experimental procedure, as can be seen from the data given in Fig. 4. Initially a CO–C_2H_4–H_2
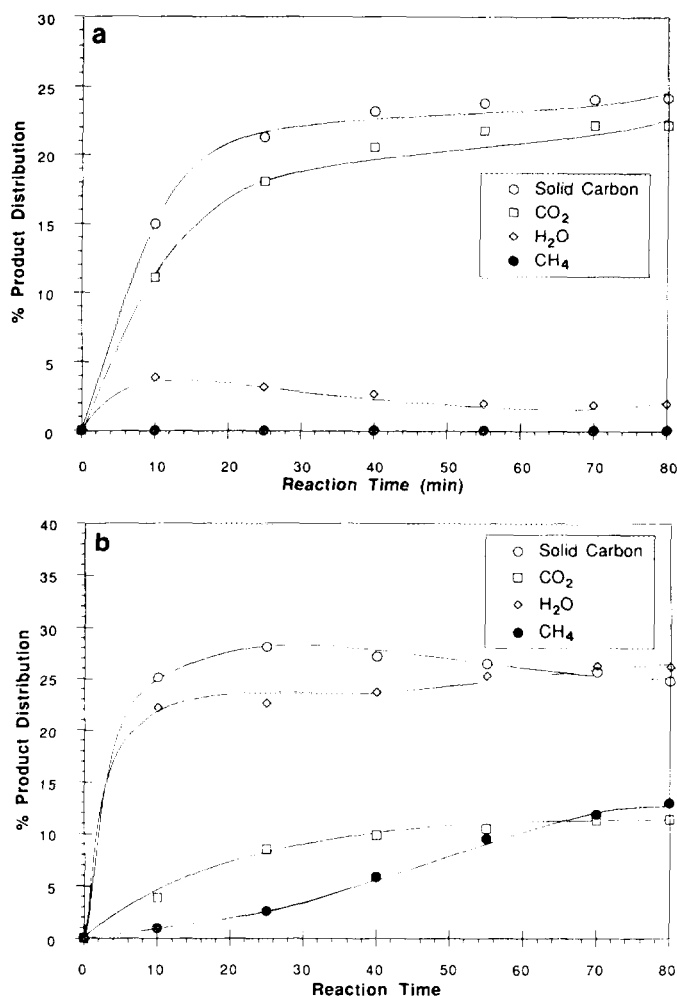
FIG. 2. Change in product distribution as a function of reaction time for various $CO-H_2$ mixtures over iron at 600°C. These data are calculated by mass balances and the units are moles of products/ moles of CO input. (a) $CO:H_2$ (4:1) and (b) $CO:H_2$ (1:4).

(1:3:1) mixture was passed over an iron catalyst, and the same level of high carbon yields as those produced in the previous experiment were obtained. After 80 min reaction time, the CO flow was stopped, and as a result of this action, the amount of solid carbon decreased to around 3%, a level comparable to that obtained with a $C_2H_4-H_2$ (3:1) mixture in the previous experiment. When the CO flow was reintroduced into the feed 45 min later, the amount of solid carbon recovered to the original high level.

This sequence of events indicates that the catalyst activation–deactivation process is reversible and the high carbon formation activity occurs only when CO is present in the reactant mixture.

In order to investigate the details of the influence of CO on the decomposition of ethylene, the ratio of CO in $CO-C_2H_4-H_2$ mixtures was varied from 0 to 1 (CO fraction = $CO/\{CO + C_2H_4\}$). The total product distribution obtained with the various mixtures is presented in Table 3. Ethane is prob-

TABLE 1

Effect of Gas Composition on Product Distribution from the Interaction of CO–H$_2$ Mixtures over Iron after 60 Min Reaction at 600°C

CO:H$_2$	% Product distribution			
	Solid carbon	Carbon dioxide	Water	Methane
100:0	0.49	0.49	—	—
93:7	20.2	19.6	0.62	0.02
80:20	21.9	19.9	2.05	0.05
67:33	22.8	17.7	5.51	0.41
50:50	25.4	16.3	10.4	1.27
33:67	24.5	14.1	16.5	6.10
20:80	25.7	10.4	24.8	9.5
10:90	27.7	6.80	35.6	14.7

ably produced by hydrogenation of ethylene molecules which are adsorbed in a parallel fashion on the metal surface. The solid carbon from ethylene and that from CO were calculated by assuming that all of the methane resulted from the decomposition of ethylene. Since the amount of methane produced was relatively small and that produced from CO was negligible with the feed containing a small portion of hydrogen, the error resulting from the approach should not be appreciable. Inspection of the data in Fig. 5 shows the relative amounts of solid carbon from ethylene and CO as a function of reactant composition, where it can be seen that the solid carbon from CO is almost independent of the composition of the feed

TABLE 2

Comparison of Carbon Deposition Rates from CO–H$_2$ and C$_2$H$_4$–H$_2$ Mixtures over Iron, Cobalt, and Nickel at 600°C

Catalyst	Reactant	Deposition rate (g carbon/g cat · h)
Iron		10.30
Cobalt	CO/H$_2$ (4:1)	0.47
Nickel		0.02
Iron		0.32
Cobalt	C$_2$H$_4$/H$_2$ (4:1)	4.50
Nickel		54.60

gas, whereas that from ethylene is extremely sensitive to the CO concentration. The carbon produced from ethylene increased significantly with addition of a small amount of CO, and did not exhibit a substantial change at CO concentrations higher than 25%. The procedure used to determine the relative amounts of solid carbon produced from CO and C$_2$H$_4$ is described in the Appendix.

(c) Electron Microscopy Examination of Carbonaceous Deposits

A number of samples of the carbonaceous deposits taken from selected flow reactor experiments were studied by transmission electron microscopy and found to consist of a network of carbon filaments, where the individual components varied from between 10 and 300 nm in width and up to 100 μm in length. Inspection of the filaments showed that their structure and the morphology of the associated catalyst particles was extremely sensitive to the composition of the gaseous reactant. Carbon filaments produced from the interaction of C$_2$H$_4$–H$_2$ mixtures with iron exhibited many similar physical characteristics to those found with filaments formed from the cobalt–C$_2$H$_4$–H$_2$ reaction (20). It was apparent that they had grown via a bidirectional mode where the diamond shaped catalyst particle was contained within the body of the filament. Once formed, both the size of the catalyst particle and the width of the filament remained relatively constant throughout the growth period, indicating a complete reluctance of the metal to undergo dispersion within the carbonaceous solid. A close examination of the filament structure failed to reveal the existence of any degree of crystalline order.

In contrast, when CO was present in the reactant mixture the characteristics of the carbon filaments were entirely different. In this case, the catalyst particle was located at the growing end demonstrating that the filaments had been formed via whisker-like process. Figure 6 is an electron micrograph showing the appearance of carbon filaments which were produced during the interaction
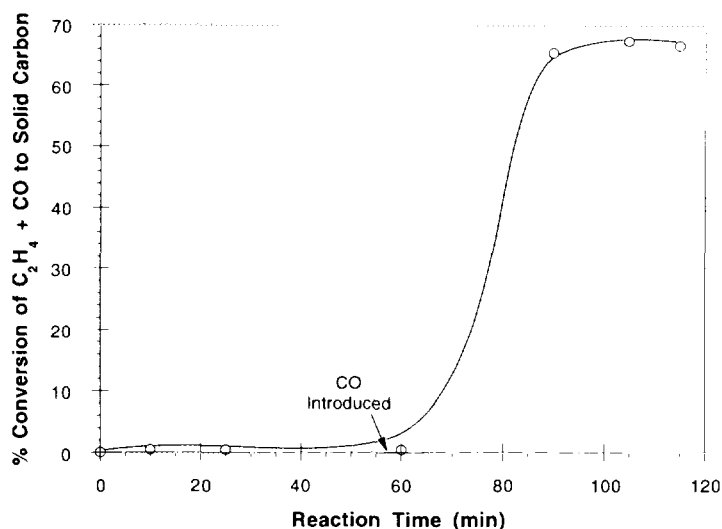
FIG. 3. Effect of CO addition on the decomposition of a C_2H_4–H_2 (3 : 1) mixture leading to the formation of solid carbon over iron at 600°C.

of iron with a CO–H_2 (4 : 1) mixture at 600°C. Also included as an inset in this figure is the selected area electron diffraction pattern showing the existence of sharp rings on which the 002 arcs are superimposed and are coincident with the graphitic platelets found perpendicular to the filament axis. It is significant that the platelets are aligned in a parallel direction to the base of the catalyst particles and this confers a "rib-cage" ar-

rangement to the filament structure. The unusual morphological shapes exhibited by the catalyst particles in these particular filaments is one which is normally associated with the establishment of a strong metal–support interaction.

In a complementary series of experiments, samples of these filaments were dispersed on transmission sections of single crystal graphite and then heated in the pres-
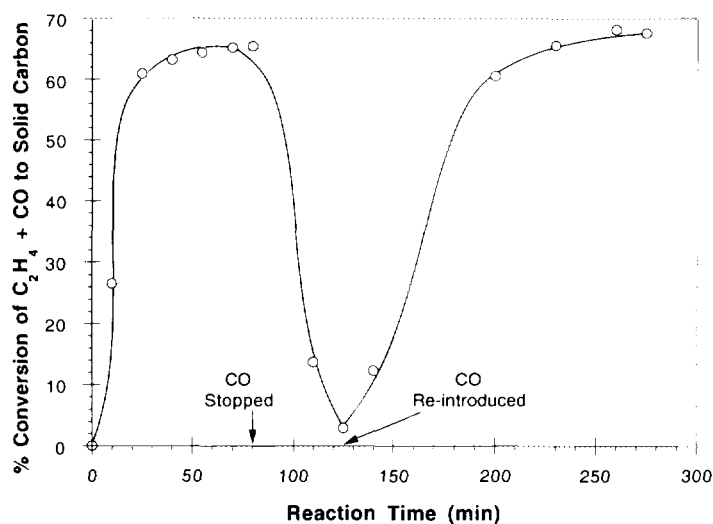

FIG. 4. Reversible behavior of an iron catalyst towards ethylene decomposition to form solid carbon in the presence and absence of CO at 600°C.

TABLE 3

Effect of Gas Composition on Product Distribution from the Interaction of C_2H_4–CO–H_2 Mixtures with Iron after 60 min at 600°C

C_2H_4:CO:H_2 molar ratio	$\dfrac{CO}{CO + C_2H_4}$ (mol/mol)	% Solid carbon yield[a]	% CH_4 yield[b]	% C_2H_6 yield[c]	% CO_2 yield[d]	% H_2O yield[e]	% CO conversion	% C_2H_4 conversion	$\dfrac{H_{2,\,out}}{H_{2,\,in}}$[f]
80:0:20	0	0.51	<0.01	8.1	0	0	0	9.8	0.53
73:7:20	0.09	20.3	0.73	8.5	1.1	30.1	32.3	29.0	1.84
68:12:20	0.15	50.3	0.58	9.4	2.7	29.9	35.4	61.9	3.68
60:20:20	0.25	68.1	1.07	10.3	5.9	23.5	32.5	86.4	4.95
38:42:20	0.525	67.9	2.7	5.5	9.1	17.5	38.5	96.8	5.41
17:63:20	0.788	45.9	2.6	5.8	18.1	5.8	42.0	93.8	4.88
0:80:20	1	21.9	0.05	—	19.9	2.1	40.9	—	0.91

[a] Number of carbon atoms in the solid carbon/number of carbon atoms in C_2H_4 + CO feed.
[b] Number of carbon atoms in the methane produced/number of carbon atoms in the C_2H_4 feed.
[c] Number of moles of C_2H_6 produced/number of moles of C_2H_4 fed.
[d] Number of moles of CO_2 produced/number of moles of CO fed.
[e] Number of moles of H_2O produced/number of moles of CO fed.
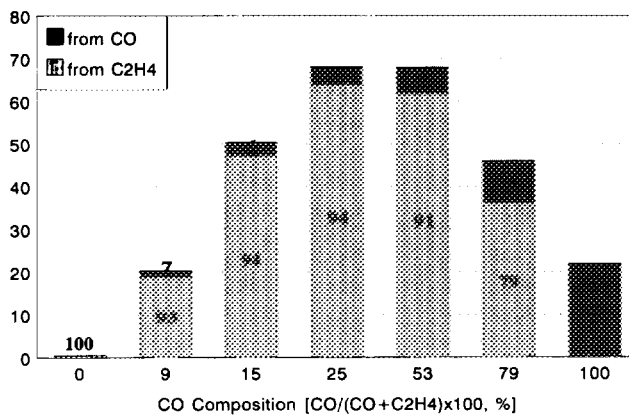[f] Number of moles of H_2 produced/number of moles of H_2 in the feed.

FIG. 5. Relative amounts of solid carbon produced from C_2H_4 and CO as a function of reactant gas composition over iron at 600°C.
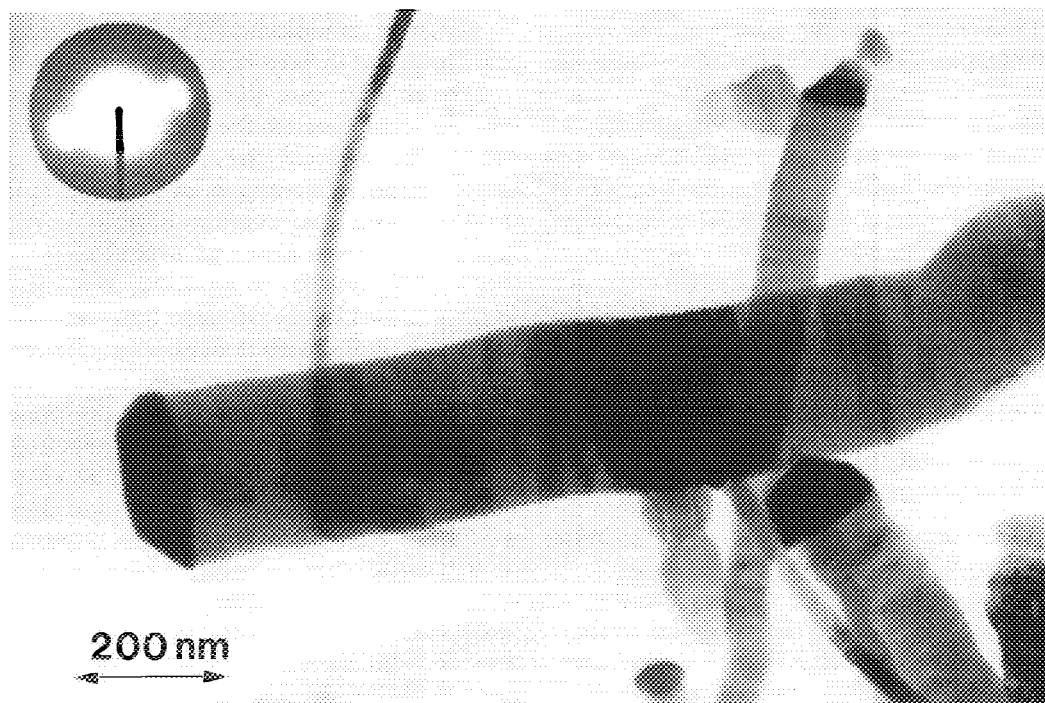

FIG. 6. Transmission electron micrograph showing the typical appearance of carbon filaments produced from the interaction of iron with a CO–H_2 (4:1) mixture at 600°C. The faceted iron catalyst particles can be seen at the head of the filaments, where the particle base is aligned parallel to the stacking direction of graphitic platelets in the filament. Inset shows the selected area electron diffraction pattern of the large filament.

ence of 0.2 Torr oxygen in the controlled atmosphere electron microscope. Continuous observation of this process showed that it was necessary to raise the temperature to 775°C in order to induce the oxidation reaction of the filaments, which appeared to take place at about the same rate as that of the surrounding graphite substrate. The onset of gasification is always dictated by the degree of crystalline perfection of the solid, amorphous carbon undergoing reaction at much lower temperatures than graphite. It was interesting to find that the iron particles associated with the filaments did not participate in the gasification reaction.

DISCUSSION

Over the years it has been tacitly assumed that the decomposition of hydrocarbons and CO over certain metal catalysts will lead to the formation of similar amounts of solid carbon deposits. More recently studies performed both in our laboratory and by other groups (13, 19) have demonstrated that the events occurring at the catalyst–gas interface are critical factors in determining the adsorption characteristics and mode of decomposition of the carbon-containing gas, a necessary step in the subsequent formation of filamentous carbon. As a consequence, the presence of additives, either in the gas phase or as inclusions in the catalyst can have a profound effect on carbon deposition by modifying the chemical nature of the metal surface.

(a) Iron-Catalyzed Decomposition of CO–H₂ Mixtures

There are numerous studies highlighting the complexity of the chemical nature and the role of the carbon species formed on metal surfaces during the decomposition of $CO-H_2$ mixtures (18, 21–28). It is now generally agreed that the carbonaceous deposit can be divided into three categories: (i) carbon which remains at the metal–gas interface and is probably combined with hydrogen as CHx species; (ii) carbon which is directly bonded to metal atoms and may be

partially dissolved in the bulk, which is referred to as carbidic carbon, and like type (i) may be an intermediate in the formation of various gaseous products; and (iii) a graphitic deposit, which initially accumulates at the rear faces of the metal in the form of a filament. The presence of this type of carbon does not result in immediate deactivation of the catalyst, since carbon grows at the rear of the metal particle leaving the upper surface of the catalyst free to undergo continued reaction with the gas phase. In the current work we have focused our attention on the events that precede the formation of filamentous carbon and mention of the other types of carbon will be restricted to circumstances where their existence impacts on the type (iii) deposit.

When iron was reacted in either pure CO or C_2H_4 the amount of solid carbon produced on the metal was below the detection limits of the techniques used in this work. Under these conditions it is highly probable that the metal surface was incapable of dissociatively adsorbing the carbon-containing gas. Examination of the data in Table 1 shows that whereas the introduction of a small amount of hydrogen into the reactant brought about a substantial increase in the amount of carbon filaments produced from the Fe–CO system. In contrast, when hydrogen was added to ethylene then very little change in the carbon depositing characteristics of iron were observed.

Dry et al. (3) suggested that the presence of chemisorbed hydrogen induces electron donation to the iron surface. Such an electron enrichment in the iron adsorption sites would result in an increase in the strength of the metal–carbon bond, which in turn weakens the C–O bond of the adsorbed CO molecule and facilitates the eventual formation of solid carbon. Attempts have also been made to identify the H_2–CO surface complexes from coadsorption experiments and although success in this endeavor has been limited (29, 30), many studies have provided indirect evidence for their existence on metal surfaces. The presence of such
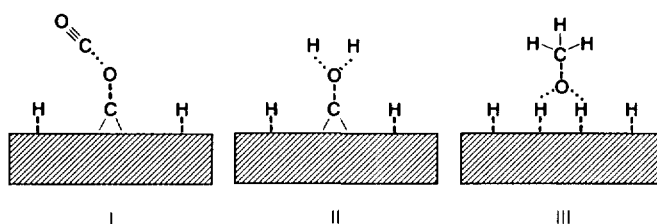
FIG. 7. Postulated mechanism of CO decomposition over iron in the presence of various amounts of hydrogen (see text for explanation of I–III).

complexes could be established by an increase in the heat of hydrogen adsorption, a change in the adsorption state of hydrogen and an enhancement in the gas adsorption capacity. Some workers (31, 32) have also found evidence for the creation of a strong CO–H interaction via electron transfer through the bonding electrons in the metal surface.

Perhaps the clearest understanding of the interaction of CO–H$_2$ with iron comes from recent surface science studies performed by Madix and co-workers (33, 34) of the coadsorption of CO and H$_2$ on Fe$_{(100)}$ surfaces. It was suggested that adsorbed CO induced a weakening in the strength of the Fe–H bond, which triggered the formation of a potentially more reactive hydrogen species. In a subsequent investigation Burke and Madix (35) demonstrated the validity of this argument in experiments where the introduction of CO onto an iron surface presaturated with hydrogen brought about the formation of ethane from coadsorbed ethylene, a reaction which did not occur in the absence of CO (36).

Based on the experimental data obtained in the current investigation, Table 1, we propose the following mechanistic pathways outlined in Fig. 7 to account for the interaction of CO–H$_2$ mixtures with the powdered iron catalyst. At low percentages of added hydrogen (7–20%) following reconstruction of the surface, CO is adsorbed in a manner where an oxygen atom in the weakened C–O bond will interact with the electron rich carbon in a second CO molecule (Fig. 7-I). This

will result in rupture of the C–O bond to produce a molecule of CO$_2$ and leave a carbon atom on the surface which can subsequently dissolve and diffuse through the metal particle and precipitate at the rear faces thus contributing to the formation of a carbon filament. It is possible that the presence of chemisorbed hydrogen on the surface enhances the population of the 2π* (37, 38) (antibonding) orbitals and consequently a weakening of the C–O bond is promoted. At higher hydrogen contents (~50%), then in addition to mechanism I there is a possibility that the extra H atoms will be available to interact with O in the adsorbed CO molecule, and under these circumstances both H$_2$O and carbidic carbon will be formed, which will eventually be transformed into solid carbon (Fig. 7-II). Finally, in the presence of excess hydrogen (>50%) a third pathway would become available where direct adsorption of CO over the hydrogen-saturated metal surface is blocked, and as a consequence the O atom in the CO molecule can then interact with the modified surface. Simultaneously, the carbon atom in the CO will also bond to other H atoms as illustrated in Fig. 7-III. The products of such an arrangement would be methane and water and since mechanism II is also operative under these conditions, solid carbon would be produced from this route. The above arguments are consistent with previous studies by White and co-workers (39–41), which indicated that CO will only adsorb on hydrogen precovered open faces of a metal crystallite, and will not bind to a

hydrogen precovered closed packed face. It would appear that in the presence of a $CO-H_2$ rich mixture, the metal surface can undergo reconstruction to generate several different faces, which simultaneously can catalyze several independent reactions.

(b) Iron-Catalyzed Decomposition of $C_2H_4-H_2$ and $CO-C_2H_4-H_2$ Mixtures

McCarty and co-workers (20, 42) have categorized the various forms of carbon deposited on nickel resulting from the reaction with ethylene according to their reactivity patterns with various gas environments such as hydrogen, oxygen and steam. Carbidic surface carbon species, designated as the $C\alpha$ state were formed from the interaction of the metal with either CO or C_2H_4 at ~300°C and found to be very reactive towards hydrogen, whereas $C\delta'$ (filamentous carbon) and $C\delta$ (encapsulating carbon) which only formed at temperatures in excess of 500°C, were more resistant to attack by hydrogen. Although there are not published reports relating to the extension of this treatment to Fe–CO and Fe–C_2H_4 systems, it is reasonable to assume that the carbon deposits formed in these reactions would exhibit similar reactivity patterns to those produced in the analogous reactions with nickel. Cooper and Trimm (43) performed a very comprehensive investigation of the deposition of carbon from the interaction of propylene over both single-crystal and polycrystalline iron surfaces. It was significant that in order to maintain the formation of solid carbon on the metal surface they found it was necessary to add hydrogen to the hydrocarbon feed. The rate of carbon deposition appeared to be higher on $Fe_{(100)}$ and polycrystalline iron surfaces than on $Fe_{(110)}$, however, the reasons for this trend were somewhat obscure. Although the nature of the carbon deposit was not characterized in this work, it is probable that filamentous carbon was the major component from reactions carried out at 600°C.

Although there have been a number of investigations dealing with the effect of ethylene addition on CO hydrogenation over various metal catalyst systems (44, 45), only a few of these have focused on the behavior of iron in this context (46–49). Hall et al. (46) found that when 1.0 to 1.25 mol% ethylene was added to a CO/H_2 (1 : 1) mixture, then in the presence of an iron catalyst at 225°C, approximately 12% of the hydrocarbon products originated from the olefin. Barrault et al. (47) also examined the influence of ethylene addition to CO/H_2 (1 : 1) over various iron-alumina catalysts at 470°C and reported that the olefin significantly enhanced both the formation of methane and C_3-C_4 hydrocarbons, and the hydrogenation to ethane. A similar trend towards the formation of higher molecular weight products was also demonstrated by Dwyer and Somorjai (48) from the interaction of CO/H_2 mixtures containing small concentrations of either ethylene or propylene over $Fe_{(111)}$ single-crystal surfaces.

In the current study we have extended the findings of Burke and Madix (35) relating to the CO-induced hydrogenation of ethylene to produce ethane over hydrogen-presaturated iron surfaces, to investigate how the alternative olefin decomposition pathways such as carbon deposition, are influenced by this promotional effect. Inspection of the data presented in Figs. 3–5 and Table 3 shows that coadsorption of CO on the iron catalyst not only promotes the formation of ethane via the hydrogenation step, but also has a tremendous impact on the fate of the carbon species produced on the metal surface from the C–C bond cleavage of the adsorbed ethylene molecules. It is known from previous studies (36) that in the absence of CO, ethylene adsorbs reversibly without dissociation on hydrogen presaturated iron surfaces and it is therefore not surprising to find that very little solid carbon is produced on the metal. In the presence of CO, the metal is activated towards ethylene decomposition and the carbon species formed at the surface proceed to dissolve

into the bulk of the particle and eventually precipitate at the rear faces in the form of a filament. This is obviously a facile process since filamentous carbon is formed in abundance and its growth is sustained for relatively long periods of time.

When CO is removed from the reactant then the fraction of ethylene which decomposed to form filamentous carbon rapidly declines to the level exhibited by the CO-free iron surface. On reintroduction of CO the formation of this form of carbon is quickly restored to a high level, demonstrating the reversible nature of the promotional effect. It is possible that adsorption of CO induces reconstruction of the surface to a configuration which facilitates rupture of the C=C bond in ethylene. Elimination of CO from the system causes a relaxation of the reconstructed surface to a structure which no longer favors ethylene decomposition. It is also worth taking into consideration the possibility that the presence of CO produces electron perturbations which alter the bonding characteristics between the ethylene and metal surface atoms.

Coadsorption of CO on a surface is not limited to stimulating the hydrogenation capacity of a metal catalyst, it can also promote other reactions. Somorjai and co-workers (38, 50) have reported that CO was capable of inducing the ordering of a number of organic molecules on selected metal surfaces. They found that when benzene was coadsorbed with CO on a $Rh_{(111)}$ surface, the organic molecules became tightly bound to the surface and it was suggested that under these circumstances the hydrocarbon would undergo distortion and eventual fragmentation rather than remaining intact. It was concluded that CO, being an electron acceptor, would induce rupture of the C–C bonds in the benzene molecule. Similar conclusions might be drawn from the present investigation where it is evident that the presence of CO promotes not only the adsorption of ethylene on iron, but also fosters the rupture of the C=C in ethylene to produce solid carbon. It would appear that the

CO stimulation phenomenon is not restricted to hydrocarbons. Sasaki et al. (51, 52) studied the CO induced decomposition of both ammonia and methylamine, respectively, on $Ru_{(001)}$ and found that well ordered (2 × 2) structures were formed in the presence of CO and that dissociation of ammonia and methylamine was considerably enhanced under these conditions. Based on these results they suggested that CO coadsorption caused the selective activation of a particular reaction pathway.

It is interesting to compare the relative amounts of methane formed in the present system with that produced from the decomposition of C_2H_4–H_2 mixtures over copper-nickel alloy particles (19) where over 20% of the ethylene decomposed to form methane. The excessive amount of methane generated in this latter system was purported to result from the formation of an "ethylidyne" intermediate. It would appear, therefore, that in the present system, where the methane yield under comparable conditions is less than 0.01%, the formation of an "ethylidyne" intermediate is not a favored step. Changes in the ratio of the reactive intermediates formed from the decomposition of ethylene on ruthenium surfaces have also been reported when CO was introduced into the system (53, 54). In the absence of CO, ethylene was found to decompose via the formation of comparable amounts of "acetylide" and "ethylidyne" intermediate states. Although both these states were generated in the presence of coadsorbed CO, "acetylide" was the major species.

From a consideration of the product distribution it is possible to make certain speculations regarding the mode by which which ethylene is adsorbed on the iron surface containing coadsorbed CO and H_2. The formation of a relatively large amount of ethane from the CO-induced hydrogenation of the olefin suggests that there is a strong tendency for the ethylene molecules to bind in an arrangement in which the C=C bond is "parallel" to the metal surface. Conversely,

the low amount of methane produced during this reaction indicates that a very small number of ethylene molecules adsorb in the "end-on" configuration, where one of the carbon atoms in the molecule is attached to three metal atoms in the form of an "ethylidyne" conformation. In such an arrangement the carbon atom attached to the surface would then proceed to diffuse into the metal and eventually precipitate in the form of carbon filament.

(c) Structural Characteristics of the Carbon Filaments

The most striking feature to emerge from the electron microscopic examination of the solid carbon deposits was the observation that filaments produced from the interaction of iron with $C_2H_4-H_2$ mixtures were relatively amorphous, whereas those grown from a reactant mixture containing CO were highly graphitic in nature. In a previous investigation (55) it was suggested that one of the necessary requirements to form highly ordered carbon filament structures was that, under reducing conditions, the metal utilized as the catalyst should readily wet graphite, a consequence of the existence of a strong interaction between the two phases.

Direct observation of the behavior of iron particles on graphite when heated in hydrogen was performed in the controlled atmosphere electron microscope (56) and from these experiments it was evident that the metal showed no propensity to wet the graphite at 600°C. Moreover, as the temperature was raised to 755°C those particles located on the basal plane regions became mobile—a characteristic associated with a weak metal–support interaction. Based on this information one would predict that filaments produced from the iron catalyzed decomposition of a hydrocarbon would adopt a somewhat amorphous structure. On the other hand, by analogy the formation of highly graphitic filaments from a $C_2H_4-H_2$ mixture containing a small amount of CO

would seem to imply that this environment induces a strong wetting action between iron and graphite.

SUMMARY

The rate of decomposition of pure CO over iron was found to be very slow, however, the addition of a small amount of hydrogen resulted in a dramatic increase in its reactivity. It is believed that the initial increase in catalytic activity is due to reconstruction of the iron surface induced by adsorbed hydrogen. At higher hydrogen concentrations, it is suggested that due to the weakening of the Fe–H bond in the presence of CO, there is the potential for desorbed H species to directly take part in the reaction via the abstraction of O from the CO molecule. It is also possible that under these conditions the reconstruction of the metal crystallites will result in the generation of various faces which exhibit distinct reactivity characteristics.

When iron was treated in $C_2H_4-H_2$ mixtures, adsorption and decomposition of the olefin was insignificant. The addition of CO to the reactant brought about a dramatic change in the catalytic activity of the iron particles. Under these circumstances not only was the metal transformed into a hydrogenation catalyst, but it also promoted the adsorption and decomposition of ethylene towards the growth of carbon filaments. Removal of CO from the system resulted in the complete deactivation of the catalyst, however, upon reintroduction of CO activity was restored to its initial high level, indicating that the activation–deactivation process was reversible.

APPENDIX

The relative amounts of solid carbon produced from ethylene and carbon monoxide as a function of the reactant gas composition, presented in Fig. 5, were calculated according to the following procedure:

If we consider the carbon atom atom balances in the two systems:

(a) Solid carbon yield from CO decomposition can be expressed as

$$\frac{CO_{input} - (CO + CO_2)_{output}}{CO_{input}} \quad \text{or}$$

$$\frac{CO_{input} - CO_{output}}{CO_{input}} - \frac{CO_{2\ output}}{CO_{input}},$$

which is

$$\{CO_{conversion} - CO_{2\ yield}\}\ \chi_{C\ atoms} \cdot$$

(b) Solid carbon yield from C_2H_4 decomposition can be written as

$$\frac{C_2H_{4\ input} - (CH_4/2 + C_2H_6 + C_2H_4)_{output}}{C_2H_{4\ input}},$$

which is

$$\{C_2H_{4\ conversion} - (CH_4 + C_2H_6)_{yield}\}\ \chi_{C\ atoms},$$

where, $\chi_{C\ atoms}$ = fraction of carbon atoms per mole.

Applying these expressions to the product distributions from a given mixture, e.g.,

$$C_2H_4 : CO : H_2 = 73 : 7 : 20 \quad \text{(Table 3)}$$

Yield of solid carbon from CO

$$= (31.2)\frac{7}{7 + 73 \times 2} = 1.4$$

Yield of solid carbon from C_2H_4

$$= (19.8)\frac{73 \times 2}{7 + 73 \times 2} = 18.9$$

Finally, % solid carbon from CO

$$= \frac{1.4}{20.3} \times 100 = 7\%$$

and, % solid carbon from C_2H_4

$$= \frac{18.9}{20.3} \times 100 = 93\%.$$

ACKNOWLEDGMENT

REFERENCES

1. Walker, P. L., Jr., Rakszaski, J. F., and Imperial, G. R., J. Phys. Chem. 63, 140 (1959).
2. Ruston, W. R., Warzee, M., Hennaut, J., and Waty, J., Carbon 7, 47 (1969).
3. Dry, M. E., Shingles, T., Boschoff, L. J., and Van Botha, H., C. S., J. Catal. 17, 347 (1970).
4. Renshaw, G. D., Roscoe, C., and Walker, P. L., Jr., J. Catal. 18, 164 (1970).
5. Baker, R. T. K., Harris, P. S., Thomas, R. B., and Waite, R. J., J. Catal. 30, 86 (1973).
6. Lobo, L. S., Trimm, D. L., and Figueiredo, J. L., in "Proceedings, 5th International Congress on Catalysis, Palm Beach, 1972" (J. W. Hightower, Ed.), p. 1125. North-Holland, Amsterdam, 1973.
7. Turkdogan, E. T., and Vinters, J. V., Met. Trans. 5, 11 and 21 (1974).
8. Baird, T., Fryer, J. R., and Grant, B., Carbon 12, 591 (1974).
9. Sacco, A., Jr., Thacker, P., Chang, T. N., and Chiang, A. T. S., J. Catal. 85, 224 (1984).
10. de Bokx, P. K., Kock, A. J. H. M., Boellaard, E., Klop, W., and Geus, J. W., J. Catal. 96, 454 (1985).
11. Baker, R. T. K., Chludzinski, J. J., and Lund, C. R. F., Carbon 25, 295 (1987).
12. Bianchini, E. C., and Lund, C. R. F., J. Catal. 117, 455 (1989).
13. Sacco, A. Jr., Geurts, F. W. A. H., Jablonski, G. A., Lee, S., and Gately, R. A., J. Catal. 119, 322 (1989).
14. Vannice, M. A., in "Catalysis Science and Technology" (J. R. Anderson and M. Boudart, Ed.), Vol. 3, p. 139. Springer-Verlag, New York, 1982.
15. Boehm, H. P., Carbon 11, 583 (1973).
16. Bradley, J. R., Chen, Y. L., and Sturner, H. W., Carbon 23, 715 (1985).
17. Kock, A. J. H. M., de Bokx, P. K., Boellard, E., Klop, W., and Geus, J. W., J. Catal. 96, 468 (1985).
18. Dwyer, D. J., and Somorjai, G. A., J. Catal. 52, 291 (1978).
19. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., J. Catal. 131, 60 (1991).
20. Rostrup-Nielsen, J. R., "Steam Reforming Catalysts," p. 24. Teknisk Forlag A/S, Danish Technical Press, Copenhagen, 1975.
21. McCarty, J. G. and Wise, H., J. Catal. 57, 406 (1979).
22. Biloen, P., Helle, J. N., and Sachtler, W. M. H., J. Catal. 58, 95 (1979).
23. Goodman, D. W., Kelley, R. D., Madey, T. E., and Yates, J. T., J. Catal. 63, 226 (1980).
24. Bonzel, H. P., and Krebs, H. J., Surf. Sci. 91, 499 (1980).
25. Biloen, P., Helle, J. N., van den Berg, F. G. A., and Sachtler, W. M. H., J. Catal. 81, 450 (1983).
26. Bianchi, D., Tau, L. M., Borcar, S., and Bennett, C. O., J. Catal. 84, 358 (1983).
27. Dwyer, D. J., and Hardenbergh, J. H., J. Catal. 87, 66 (1984).
28. Stockwell, D. M., Bianchi, D., and Bennett, C. O., J. Catal. 113, 13 (1988).

29. Blyholder, G., and Neft, L., *J. Phys. Chem.* **66**, 1664 (1962).

30. Demuth, G. E., and Ibach, H., *Chem. Phys. Lett.* **60**, 395 (1979).

31. Welder, G., Colb, K. G., Heinrich, W., and McElihiney, G., *Appl. Surf. Sci.* **2**, 85 (1978).

32. Rangelov, G., Bischler, N., Memmel, N., Bertel, E., and Dose, V., *Surf. Sci.* **273**, 61 (1992).

33. Benziger, J. B., and Madix, R. J., *Surf. Sci.* **115**, 279 (1982).

34. Burke, M. L., and Madix, R. J., *Surf. Sci.* **237**, 20 (1990).

35. Burke, M. L., and Madix, R. J., *J. Am. Chem. Soc.* **113**, 1475 (1991).

36. Burke, M. L., and Madix, R. J., *J. Am. Chem. Soc.* **113**, 3675 (1991).

37. Sung, S., and Hoffman, R., *J. Am. Chem. Soc.* **107**, 578 (1985).

38. Mate, C. M., and Somorjai, J. A., *Surf. Sci.* **160**, 542 (1985).

39. White, J. M., *J. Phys. Chem.* **87**, 915 (1987).

40. Akhter, S., and White, J. M., *J. Vac. Sci. Technol. A* **6**, 864 (1988).

41. Akhter, S., and White, J. M., *CRC Crit. Rev. Solid State Mater. Sci.* **14**, 131 (1988).

42. McCarty, J. G., Hou, P. Y., Sheridan, D., and Wise, H., *in* "Coke Formation on Metal Surfaces" (L. D. Albright and R. T. K. Baker, Eds.), ACS Symp. Ser., Vol. 202, p. 253. Am. Chem. Soc., Washington, DC, 1982.

43. Cooper, B. J., and Trimm, D. L., *J. Catal.* **62**, 35 (1980).

44. Bell, A. T., *Catal. Rev.-Sci. Eng.* **23**, 203 (1981).

45. Bell, A. T., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 5, p. 134. Chem. Institute of Canada, Ottawa, 1988.

46. Hall, W. K., Kokes, R. J., and Emmett, P. H., *J. Am. Chem. Soc.* **82**, 1027 (1960).

47. Barrault, J., Forguy, C., and Perrichon, V., *J. Mol. Catal.* **17**, 195 (1982).

48. Dwyer, D. J., and Somorjai, G. A., *J. Catal.* **56**, 249 (1979).

49. Satterfield, C. N., Huff, G. A., and Summerhayes, R. J., *J. Catal.* **80**, 486 (1983).

50. Van Hove, M. A., Lin, R. F., and Somorjai, G. A., *J. Am. Chem. Soc.* **108**, 2532 (1986).

51. Sasaki, T., Aruga, T., Kuroda, H., and Iwasawa, Y., *Surf. Sci.* **240**, 223 (1990).

52. Sasaki, T., Aruga, T., Kuroda, H., and Iwasawa, Y., *Surf. Sci.* **276**, 69 (1992).

53. Hills, M. M., Parmeter, J. E., and Weinberg, W. H. J., *J. Am. Chem. Soc.* **108**, 7215 (1986).

54. Henderson, M. A., Mitchell, G. E., and White, J. M., *Surf. Sci.* **203**, 378 (1988).

55. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **134**, 253 (1992).

56. Baker, R. T. K., Chludzinski, J. J., and Sherwood, R. D., *Carbon* **23**, 245 (1983).