

Studies of Auger Electron Spectroscopy and Characteristic-Energy-Loss Spectra of Alloy Catalysts for the Gasification of Graphite in Water Vapor and Hydrogen¹

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Auger spectroscopy studies have been performed on Fe-Co, Fe-Ni, Ni-Cu, and Co-Ni alloy catalysts used in the gasification of graphite in wet hydrogen. Small (~200 Å diameter) metal particles were formed on the surface of graphite disks by annealing vapor-deposited films of a nominal thickness of 50 Å, corresponding to only 0.0015 wt% of the graphite sample prior to gasification. The variation of catalytic activity with composition has shown maxima in Fe-Co and Fe-Ni alloys at 30 atom% Co and 20 atom% Ni, respectively. Characteristic-energy-loss spectra of dilute alloys of Fe in Co have confirmed that small changes in bulk Fe concentration are related to marked variations in catalytic activity. Auger studies have revealed the presence of a carbide phase (Fe₃C) on the surface of iron foils used to catalyze the gasification of carbon, this phase presumably formed during cooling from the reaction temperature. Auger analysis has also demonstrated that surface segregation of Fe-Co alloy catalysts is dependent on the composition of the reacting gas.

I. INTRODUCTION

The catalytic gasification of carbon in water vapor and hydrogen is of much interest because of its importance in coal-conversion processes. The influence of transition metal catalysts on the rate of gasification has been studied by several workers (1-6), whose studies have included measurements of reaction kinetics in bulk samples and light and electron optical observations of the morphology of the surface of graphite single crystals after partial gasification. However, to date there has been no work on the catalytic gasification of

carbon by alloy catalysts. Such an investigation is needed to elucidate the role of *d*-electron concentration and band-structure effects in catalytic activity. Part of this paper is devoted to an investigation of the gasification of carbon by Fe-Co, Fe-Ni, Co-Ni, and Ni-Cu catalysts. Specifically, the bulk and surface natures of some of these alloy catalysts have been investigated by Auger and characteristic energy-loss spectroscopy in relation to their activity.

Another question of paramount importance to the development of a detailed model of the reaction mechanism is the composition and structure of pure-element and alloy-catalyst particles during the gasification process. In the case of the pure Fe catalyst there has been some evidence from magnetic studies (3) of the occurrence of the carbide phase Fe₃C under particular conditions of reaction temperature and gas composition. In this paper we show that the technique of Auger spectroscopy can, under favorable circumstances, demonstrate the formation of small amounts of a carbide phase in a very direct manner.

¹ It is understood that the material in this paper is intended for general information only and should not be used in relation to any specific application without independent examination and verification of its applicability and suitability by professionally qualified personnel. Those making use thereof or relying thereon assume all risk and liability arising from such use or reliance.

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II. EXPERIMENTAL

High-purity graphite planchets (disks) used in the experiments were obtained from Ultra Carbon Corporation. The planchets were 2.5 cm in diameter and 0.15 cm in thickness. Impurities such as Cu, Si, Ni, Mg, Fe, and Al were below the 1-ppm level.

Metal films of high-purity Fe, Co, Ni, or Cu were deposited on one side of the graphite planchet to nominal thicknesses of 50, 500, or 1000 Å by vacuum evaporation. These thicknesses amounted to about 0.0015, 0.015, and 0.03 wt% of the metal on graphite, respectively. Chemical analysis using atomic absorption of dissolved films

from several representative samples showed that the calculated and actual film thicknesses agreed to within $\pm 10\%$.

The binary alloys between Fe, Co, Cu, and Ni were first prepared as 2-g ingots by induction melting on a water-cooled copper boat in a gettered argon atmosphere. The samples were remelted several times to ensure homogeneity. The required amounts were cut from the alloy buttons for vacuum evaporation. The alloy films of the desired thickness were deposited in the same manner as the pure metals noted earlier.

The metal or alloy film on the graphite planchet was first heated for a period of 0.5 hr at 750°C in a stream of high-purity, dry

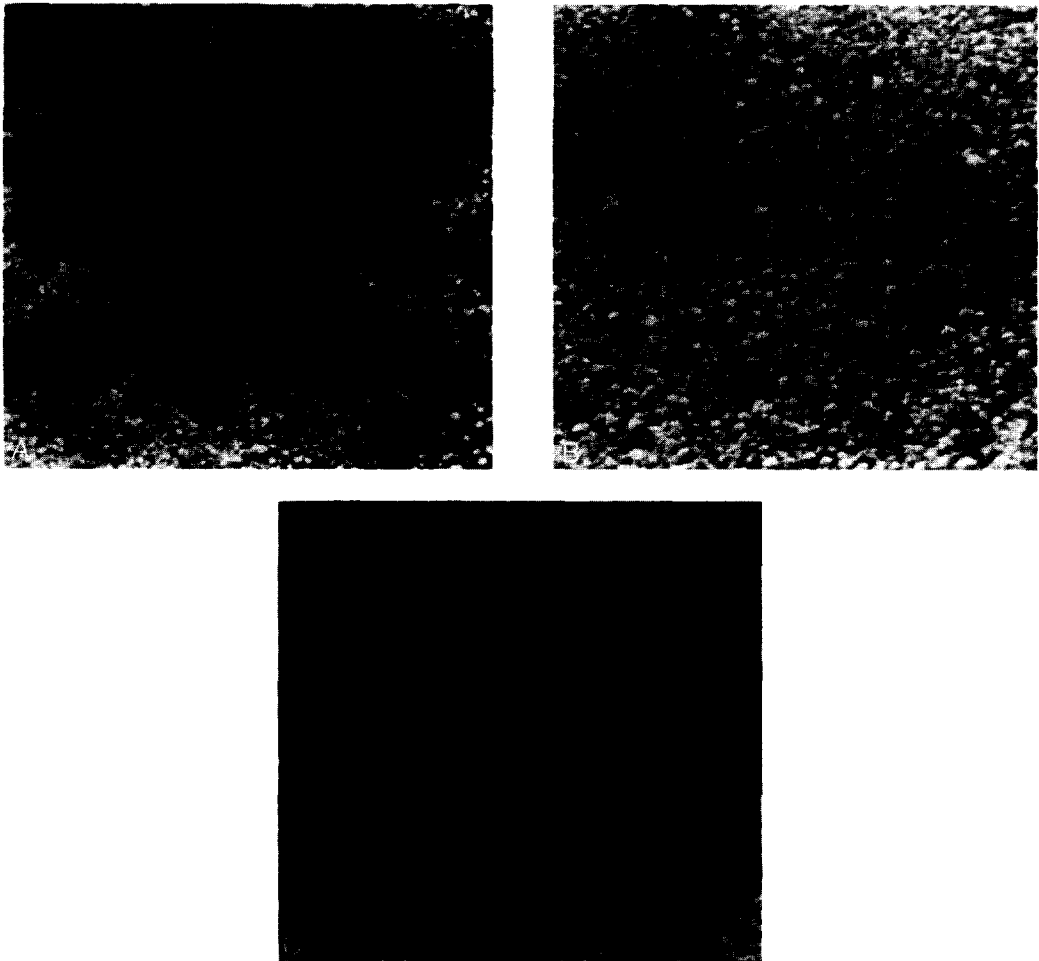


FIG. 1. Electron micrographs showing the breakup of 50-Å-thick Fe film on a graphite planchet upon heat treatment in dry H_2 at 750°C for (A) 5, (B) 15, and (C) 30 min. $\times 18,000$.

H₂ to remove any metallic oxide. This procedure also results in the breakup and dispersal of the film into fine particles, as shown in the electron micrographs of Fig. 1. It is evident that there is some gasification of carbon in a dry H₂ atmosphere, resulting in the gradual movement of the particles to the interior of the graphite.

After the reduction treatment, samples were reacted with water vapor and hydrogen by bubbling the high-purity hydrogen at a rate of 930 ml/min through a steam saturator maintained at 22°C. This provided a partial pressure of about 20 mm Hg for the water vapor at the inlet to the reaction chamber. During the experiment, the partial pressure of H₂O was monitored with an oxygen sensor and analyzer (Applied Electrochemistry Inc.).

The activity of the various catalysts was measured by the amount of CO and CH₄ liberated in the reaction with wet H₂ at 1000°C, which was continued for 30 min. The concentrations of CO and CH₄ in the product gas were measured by gas

chromatography at intervals of 3 min. The amount of CO₂ liberated, as measured by mass spectrometry and gas chromatography, was found to be 40 ppm or less.

Electron micrographs of the surface of the graphite planchet after the reaction with wet H₂ showed extensive attack (Fig. 2) accompanied by tunneling of the catalyst particles into the interior of the graphite. Consequently, it was not possible to analyze the catalysts by Auger spectroscopy after the reaction with wet H₂. Hence the Auger analysis on the fine-particle catalyst has to be performed before reacting samples with wet H₂. Some catalyzed gasification experiments were conducted by using metal foils (0.0025 cm in thickness) with small blocks (32 × 3 × 10 mm) of graphite resting on top covering about 20% of the surface.

High-resolution Auger spectra were recorded by using a Varian Model 981-2730 spectrometer. Samples were placed in the bell jar and evacuated to 10⁻¹⁰ Torr for 2 days prior to examination by AES. Spectra were obtained with a primary beam of 5

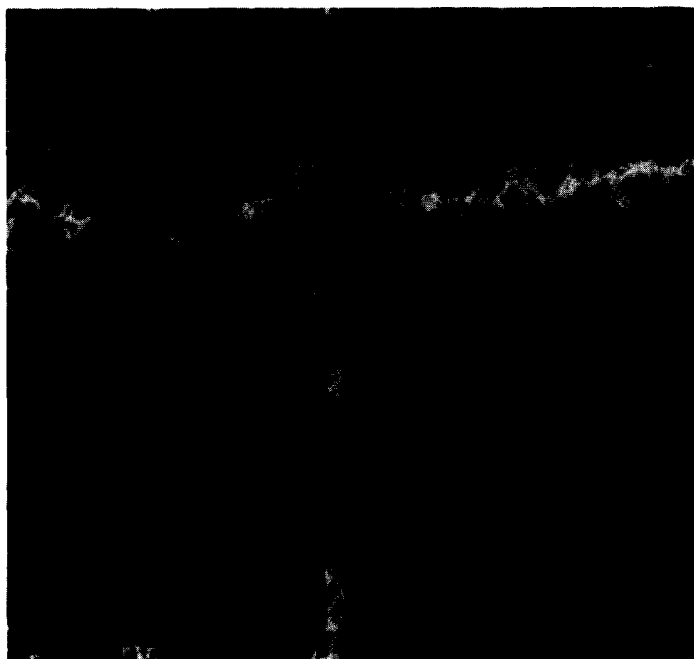


FIG. 2. Scanning electron micrograph of graphite with vapor-deposited Fe catalyst showing extensive attack in wet H₂ at 1000°C. The central diamond region and the crosslines were free of catalyst.

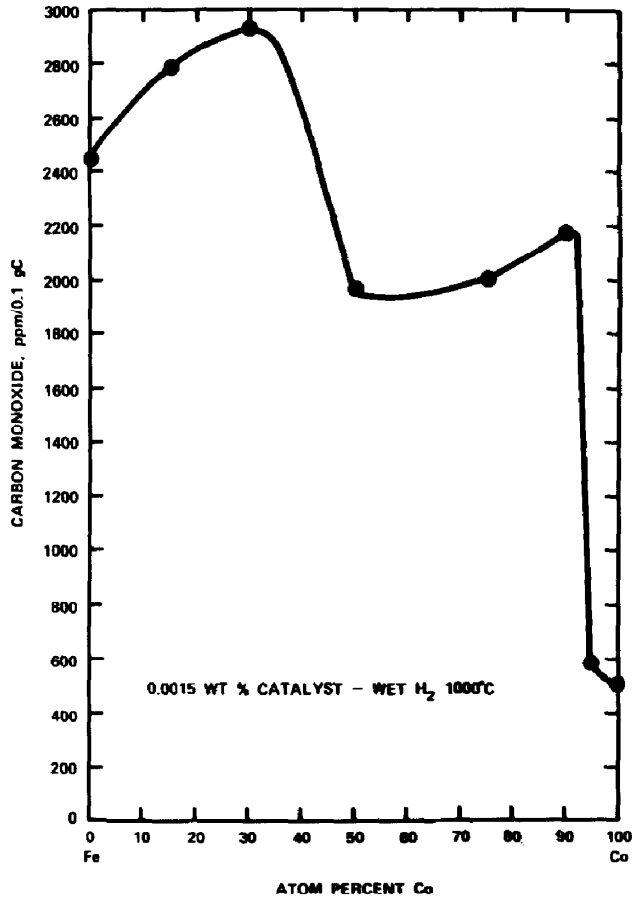


FIG. 3. Rate of carbon gasification by Fe-Co alloy catalysts as determined by carbon monoxide concentration in effluent gas.

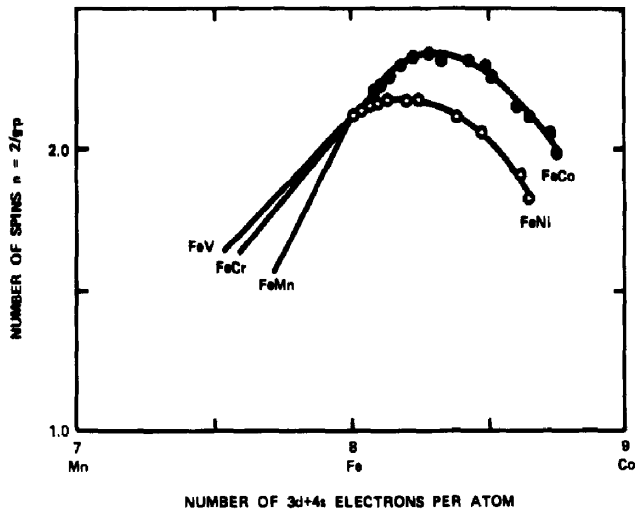


FIG. 4. Variation of the average atomic moment with alloy composition for bcc iron alloys (after Crangle (8)).

keV and $1 \mu\text{A}/\text{cm}^2$. A 100-kHz and 2-V peak-to-peak modulation was applied to the cylindrical mirror analyzer. Characteristic-energy-loss spectra were obtained at a primary beam energy of 2000 eV.

In an attempt to determine whether the carbide phase Fe_3C plays a role in the catalytic process, a high-purity Fe foil of thickness 0.0025 cm was laid on the graphite planchet. The reaction with wet H_2 was conducted in the same manner as described earlier. The carbon Auger signal from the surface of the foil was then recorded to investigate the nature of the carbon-containing phases, if any. For comparison, the carbon Auger spectrum was also recorded from bulk graphite and Fe_3C prepared by a method described earlier (7).

III. RESULTS AND DISCUSSION

A. DEPENDENCE OF GASIFICATION RATE ON ALLOY COMPOSITION

It was found that the main component in the product gas during the reaction with wet H_2 was CO. The amounts of CH_4 and CO_2 liberated were together less than 2% of the amount of CO liberated. Hence, the amount of CO liberated per 0.1 g of graphite expressed as parts per million of the outgoing gas from the reaction chamber was taken as a measure of the catalytic activity of the alloy.

1. Fe-Co Alloys

The rate of gasification as a function of alloy composition in Fe-Co is shown in Fig.

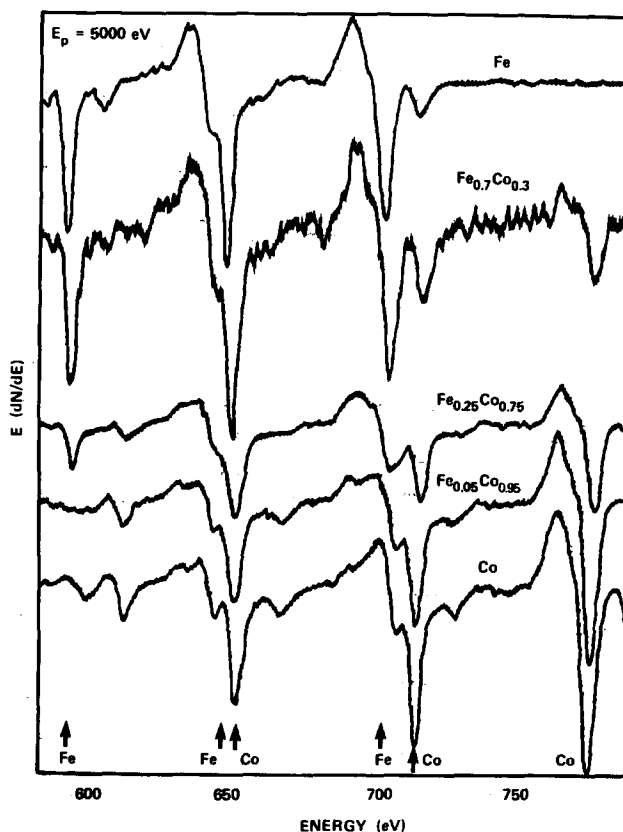


FIG. 5. Auger spectra of Fe-Co alloy catalysts before the reduction step. The main Fe and Co peak positions are shown.

3. The two interesting features of the curve in Fig. 3 are the following.

a. Peak in catalytic activity at 30 atom% cobalt in Fe-Co. The behavior is somewhat reminiscent of the Slater-Pauling curve (8) for the variation of the average atomic moment with alloy composition as shown in Fig. 4. As discussed in section B, this similarity supports the possibility of band-structure effects, especially the density of 3d states at the Fermi level being important factors in determining the catalytic activity, as has been proposed for pure elements. However, a detailed correlation between the catalytic and band-structure effects should include a consideration of the magnetic transitions on the latter. Auger spectra of the Fe-Co alloy catalysts, shown in Fig. 5, confirmed that the vapor-deposited film corresponded to the source composition. There was no variation in the alloy composition of as-deposited film as detected by Auger analysis over the entire specimen. Electron microscopy studies showed no detectable changes in dispersion between the various Fe-Co alloy catalysts.

b. Large variation of catalytic activity in the range 5 to 10 atom% Fe in Co. This is clearly seen in the extreme right of the curve in Fig. 3. The catalytic activity of 10 atom% Fe in Co was found to be 3.6 times higher than that of 5 atom% Fe in Co. This was a surprising result since the variation was relatively gradual with composition in the rest of the range. It was of course important to establish that this sudden variation of catalytic activity with composition on the Co-rich side was definitely due to a small change in Co content. As seen in Fig. 5, the Auger electron spectrum is unable to detect the presence of such a small amount of Fe in the background of the Co spectrum. The most intense peak in the Auger spectrum of Fe happens to nearly coincide in position with a Co peak (Fig. 5).

Therefore the characteristic-energy-loss (CEL) spectra of $\text{Fe}_{0.05}\text{Co}_{0.95}$ and $\text{Fe}_{0.1}\text{Co}_{0.9}$ were studied (Fig. 6). The CEL peaks of Fe and Co were sufficiently resolved to confirm

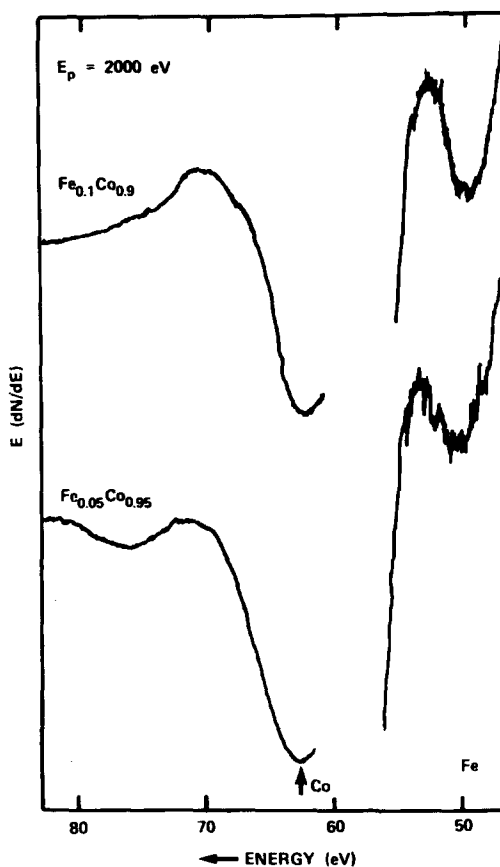


FIG. 6. Characteristic-energy-loss spectra of $\text{Fe}_{0.1}\text{Co}_{0.9}$ and $\text{Fe}_{0.05}\text{Co}_{0.95}$. The discontinuities in the traces are caused by adjustments in the instrument sensitivity to reveal the weak Fe signal.

the difference in composition of the two catalysts, and no evidence for point-to-point inhomogeneity was found in either catalyst sample. Additional experimentation aimed at understanding the abrupt drop from the high catalytic activity of $\text{Fe}_{0.1}\text{Co}_{0.9}$ to the much lower value of $\text{Fe}_{0.05}\text{Co}_{0.95}$ is described in a following section.

2. Fe-Ni Alloys

The dependence of the rate of gasification on the Fe-Ni alloy composition is shown in Fig. 7. As in the case of the Fe-Co catalysts, the initial increase of catalytic activity with Ni content resembles the Slater-Pauling behavior for the variation of the atomic moment with composition (Fig.

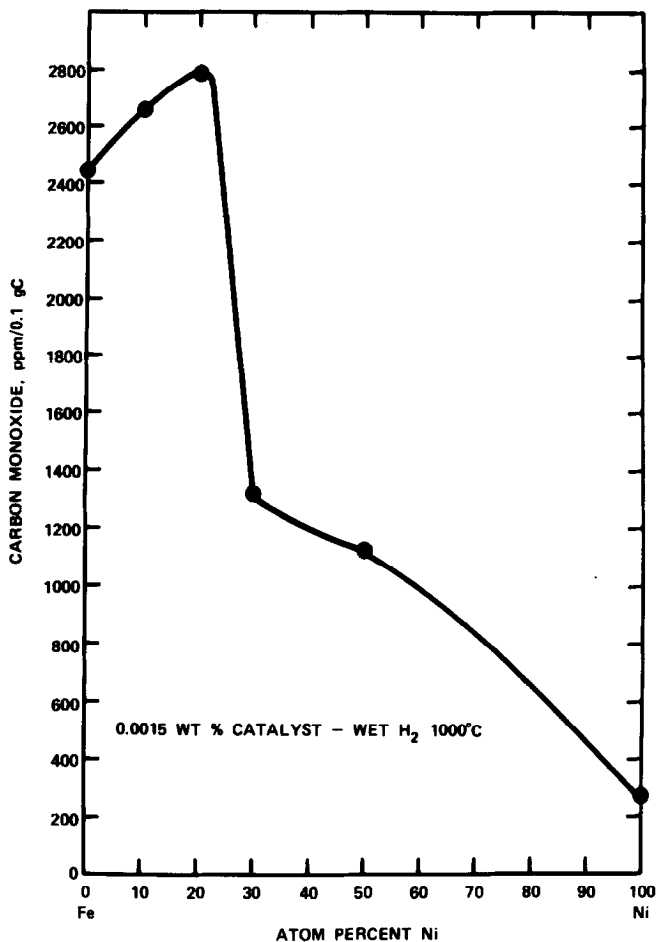


FIG. 7. Rate of carbon gasification by Fe-Ni alloy catalysts.

4). The Auger spectra of the as-deposited Fe-Ni catalyst (Fig. 8) were in accordance with the compositions of the starting materials and did not show any evidence of bulk segregation effects. No changes in dispersion among Fe-Ni alloy catalysts could be detected.

However, it seems probable that surface segregation of the more volatile component plays a dominant role. Burton and Hyman (9) have shown that the surface concentration of Cu in nickel alloys may approach 100% in some cases and is above 80% in even rather dilute (5% Cu) alloys at low temperature (below 450°C) and only drops to 40% surface concentration in these alloys at 1000°C.

Their analysis is based on regular solution theory and does not take the composition of the atmosphere into account. However, as shown in a following section, the extent of surface segregation in $\text{Fe}_{0.85}\text{Co}_{0.15}$ is very high when the surface is exposed to H_2 - H_2O , whereas there is only slight surface enrichment when the atmosphere is primarily H_2 -CO.

3. Co-Ni Alloys

The rate of gasification in wet H_2 versus composition of Co-Ni alloy catalysts is shown in Fig. 9. The noticeable features are the maximum in catalytic activity at $\text{Co}_{0.5}\text{Ni}_{0.5}$ and a surprisingly low reaction rate at $\text{Co}_{0.25}\text{Ni}_{0.75}$. The Auger spectra (Fig.

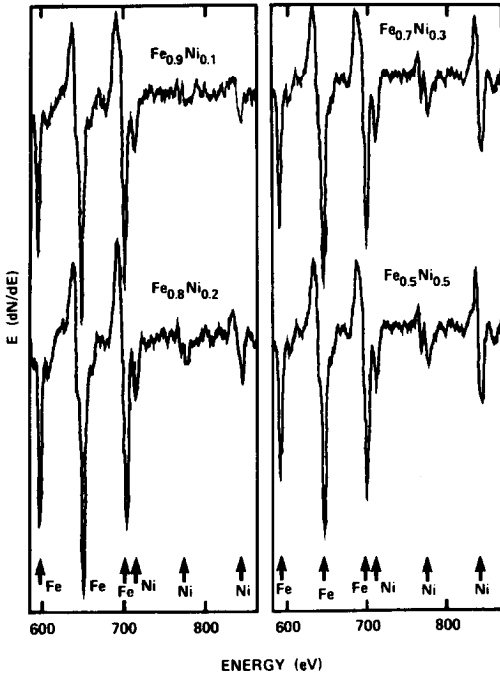


FIG. 8. Auger spectra of Fe-Ni alloy catalysts.

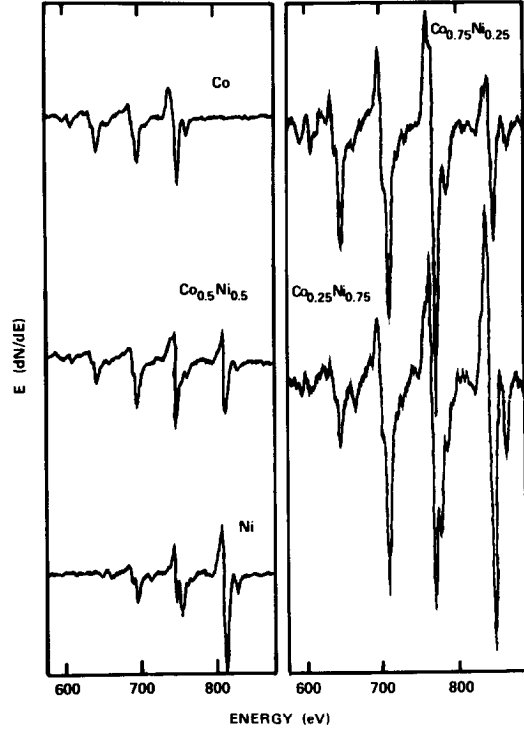


FIG. 10. Auger spectra of Co-Ni alloy catalysts.

10) clearly showed that the catalysts had the same composition as the as-melted alloy buttons. There was no evidence for compositional inhomogeneity of the specimens or for changes in dispersion. In general, the

reactivities of the Co-Ni catalysts for CO production are rather low, although they are relatively effective methanation catalysts (10).

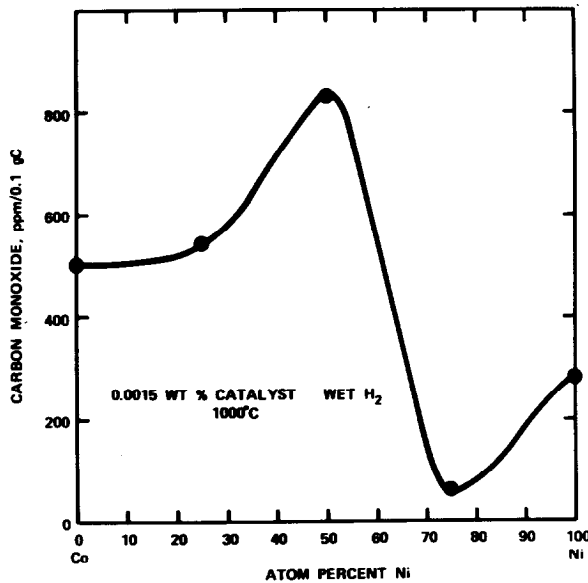


FIG. 9. Rate of carbon gasification by Co-Ni alloy catalysts.

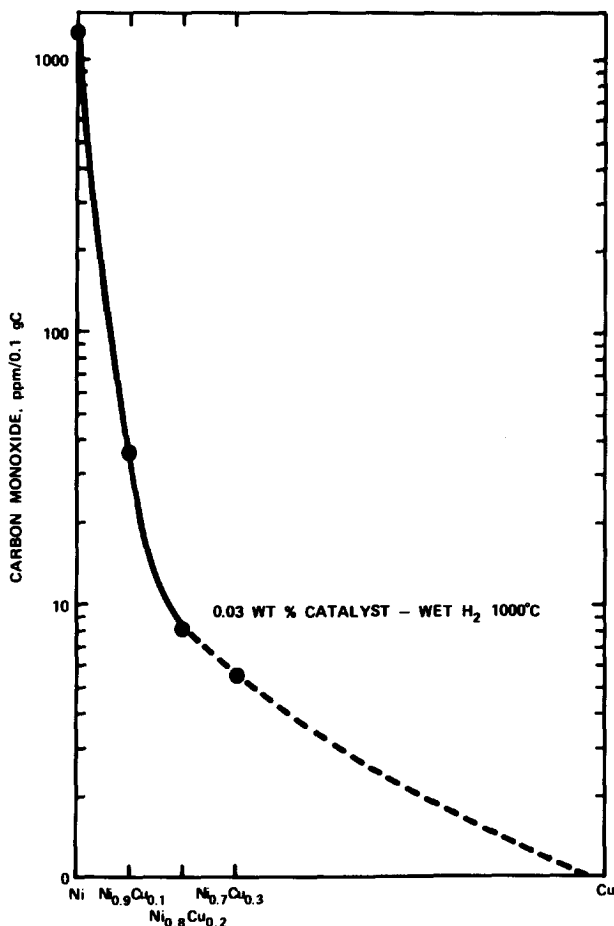


FIG. 11. Rate of carbon gasification by Ni-Cu alloy catalysts.

4. Ni-Cu Alloys

The rate of carbon gasification in wet H₂ for several Ni-Cu alloys is shown in Fig. 11. In this case the catalytic activity falls off rapidly with increasing Cu content and drops to a very low value for pure copper. The Auger spectrum, shown in Fig. 12 for one of the alloys, confirms again that the composition of the evaporated films corresponds to that of the bulk alloys. However, the surface composition will be altered due to segregation during heating in the gasification atmosphere as discussed below. The extent of such segregation will be extremely difficult to determine at the reaction temperature because of rather slow cooling rates with the apparatus. The pronounced

effect of small Cu additions on reducing the catalytic activity of Ni has been reviewed by Burton and Garten (11).

5. Surface Composition after Reaction

As mentioned previously, Auger analysis of the metal-alloy catalyst particles was not successful because they burrowed beneath the surface of the graphite planchet. An alternative approach, to "invert" the experiment and put carbon on solid metal, proved to be successful. It provided valuable information about the role of kinetics and was more amenable to postreaction studies by Auger spectroscopy, including a search for carbide formation (discussed in the following section B) and evidence for surface segregation.

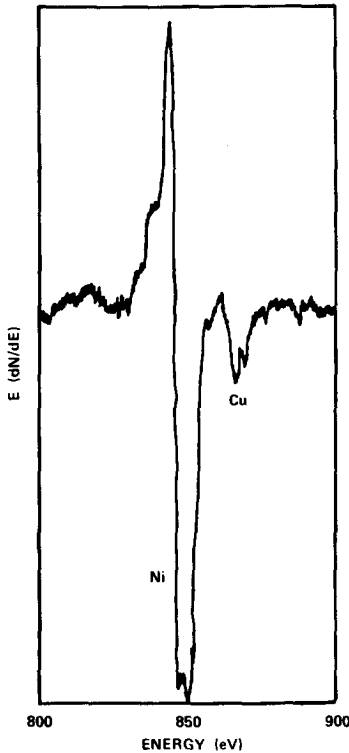


FIG. 12. Auger spectrum of $\text{Ni}_{0.9}\text{Cu}_{0.1}$ catalyst.

Auger spectra of a bulk sample of $\text{Fe}_{0.85}\text{Co}_{0.15}$ which was used to catalyze gasification of a block of graphite in wet H_2 at 1000°C are shown in Fig. 13. Areas well away from the reacted area and influence of the product gases CO and CH_4 exhibit Co segregation of about three times the base composition (where Co and Fe concentration are about equal, Fig. 13A) whereas under the reacted area the surface is only slightly enriched in Co (Fig. 13C). Much of the surface in this region is covered with very adherent carbon particles, and the spectra are from patches of base metal between them. After sputtering for a short time to remove approximately 100 \AA , the composition of both regions equals the alloy composition, as shown in Figs. 13B and D. Similar effects of CO in enhancing segregation of Ni in Ni–Cu alloys and Pt in Pt–Au alloys have been reported previously (12, 13).

6. Discussion

The close parallelism in the catalytic behavior on the Fe-rich side for Fe–Co and Fe–Ni catalysts seems to emphasize the role of electron concentration and consequent band-structure effects often mentioned in the catalysis literature. The maximum catalytic activity appears to occur for the $3d + 4s$ electron concentration per atom lying between 8.3 and 8.4, similar to the Slater–Pauling case (Fig. 4). Of course, the Slater–Pauling curve applies to bcc Fe–Co and Fe–Ni alloys whereas, at the temperature of our reaction, namely, 1000°C , the bulk Fe–Co and Fe–Ni alloys will occur as the fcc phase. Furthermore (as seen in the electron micrographs), the alloy catalysts are in the form of very fine particles, so that the curvature of the surfaces will be important. Obviously, much more experimental and theoretical work is needed to understand the nature of the catalytic particles under actual conditions of carbon gasification.

B. EVIDENCE FOR THE OCCURRENCE OF IRON CARBIDE

Inasmuch as graphite is stable with respect to iron and cementite (Fe_3C), the direct formation of carbide during gasification is not expected. However any fcc γ -phase of Fe in contact with graphite at 1000°C should contain about 1.5 wt% C in solution, so that some carbide should precipitate on cooling. To investigate this question, Auger spectra of bulk Fe_3C and graphite were first studied to permit direct interpretation of spectra obtained from the surfaces of Fe foils used as catalysts.

1. Auger Spectrum of Bulk Fe_3C

The Auger spectrum of carbon in bulk Fe_3C having the orthorhombic DO_{11} -type structure is shown in Fig. 14. For comparison, the spectrum of graphite is also shown in Fig. 14.

It is known (14–16) that the Auger spectrum of carbon displays “chemical effects”

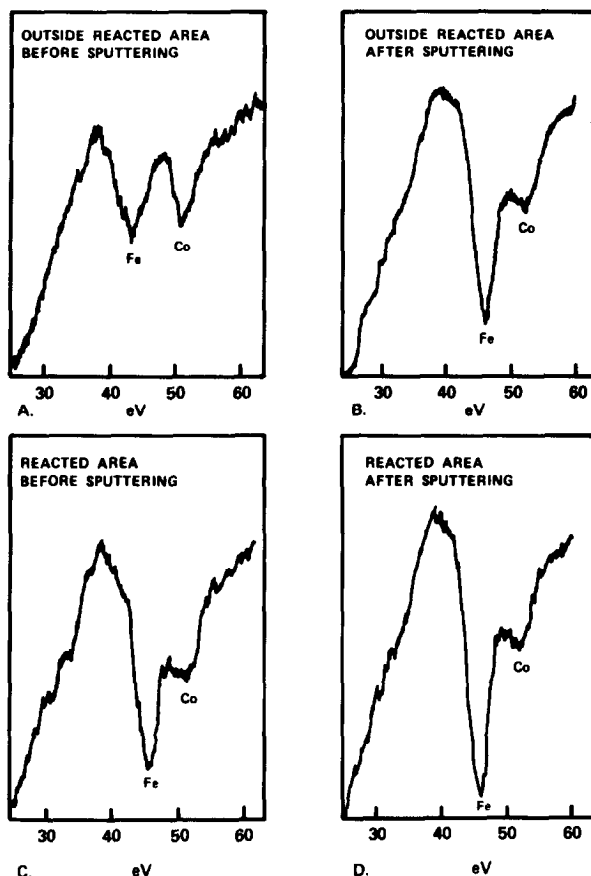


FIG. 13. Low-energy Auger peaks of Fe and Co in $\text{Fe}_{0.85}\text{Co}_{0.15}$ showing their relative intensities before and after sputtering in the reacted and unreacted areas.

stemming from the marked differences that can occur in the fine structure of the carbon KLL spectrum depending on whether carbon is bonded with silicon, a transition metal such as nickel (14), or with itself [as in graphite (17)]. The metal carbides are characterized by two relatively large peaks on the low-energy side of the main peak, whose positions have been specified by Siegbahn *et al.* (18) The fair agreement between the experimental and theoretical carbide spectra provides a sound footing for the identification of carbide phases in the catalysts.

2. Auger Spectrum of Fe Foils Used as Gasification Catalysts

The investigation of vapor-deposited fine-particle catalysts was supplemented

with corresponding Auger and CEL spectroscopy studies of the surface of metal foils. It was found that thin sheets of iron (and spheres and wires) placed on top of graphite crystals and planchets catalyzed the formation of CO and CH_4 in a manner comparable to vapor-deposited metal and were somewhat more amenable to Auger analysis, especially after considerable reaction has occurred.

Scanning electron micrographs of the bottom surface (in contact with graphite) of an Fe foil reacted in wet H_2 at 1000°C for 30 min are shown in Fig. 15. Much of the bottom surface is observed to be covered with small particles from the graphite planchet which were found to adhere very tightly to the iron foil.

The Auger spectrum of this surface of the

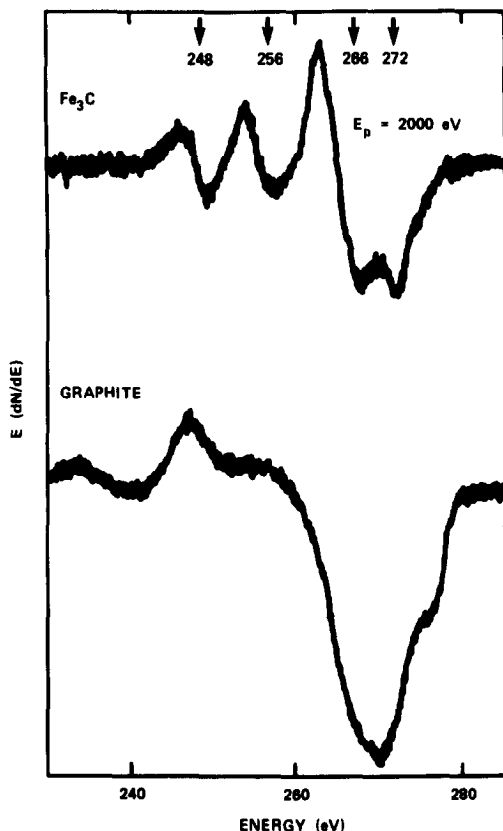


FIG. 14. Auger spectra of carbon in bulk cementite (Fe_3C) and graphite.

Fe foil, which was in contact with the planchet, initially yielded a spectrum similar to that of the graphite shown previously in Fig. 14. The surface was then etched by argon ion bombardment for 7 min. After this treatment the Auger spectrum showed unmistakable evidence for the presence of the Fe_3C phase on the surface (Fig. 16a).

However, the Fe_3C layer was extremely unstable under electron bombardment of even a few minutes duration. This is shown in the lower trace in Fig. 16, which was recorded immediately upon the completion of the first trace. Various areas with somewhat different surface appearance were examined. In all cases, after a 7-min argon ion etching period, an Fe_3C layer was detected throughout the surface of the foil that was in contact with the graphite planchet. Similarly, in every region of observation, the

Fe_3C layer was unstable under electron bombardment. This was a surprising result, indicating weak adherence of a very thin Fe_3C layer to the iron foil. No graphite or carbide was found on the surface (top) that was exposed to the wet H_2 gas.

3. Discussion

The observation of Fe_3C on the surfaces of the iron foil used to catalyze carbon gasification after cooling to room temperature can be understood by reference to the Fe-C phase diagram shown in Fig. 17.

In either wet or dry H_2 gas at the temperature of reaction (1000°C), the carbon activity will be essentially unity at the metal-graphite interface so that in this region the austenite ($\gamma\text{-Fe}$) phase will be saturated with carbon (~ 1.5 wt%). However at the surface exposed to $\text{H}_2\text{-H}_2\text{O}$, the activity will be zero and decarburization will be occurring (19, 20).

Although diffusion of C in Fe is very rapid at 1000°C , the decarburization reaction forming CO from dissociated H_2O is faster than carburization from solid graphite so that the carbon level will be low near the top surface of the Fe foil and will rise slowly to $\sim 1.5\%$ at the interface with the graphite (the back surface). As the solubility for carbon in austenite decreases during cooling, the excess carbon will be rejected from the austenites to form surface graphite on the back side, although it is masked by the presence of adherent graphite particles. Similar observations (and explanations) of the formation of graphite on the surface of catalyst foils have already been reported for nickel and iron.

Upon cooling below 910°C , the very-low-carbon austenite on the front surface will transform to bcc iron. As the transformation front progresses into the foil during cooling, the carbon will be concentrated in the austenite. At the ferrite-cementite eutectoid temperature (727°C), pearlite consisting of about 10% carbide and 90% ferrite should form from the remaining austenite. This characteristic structure was

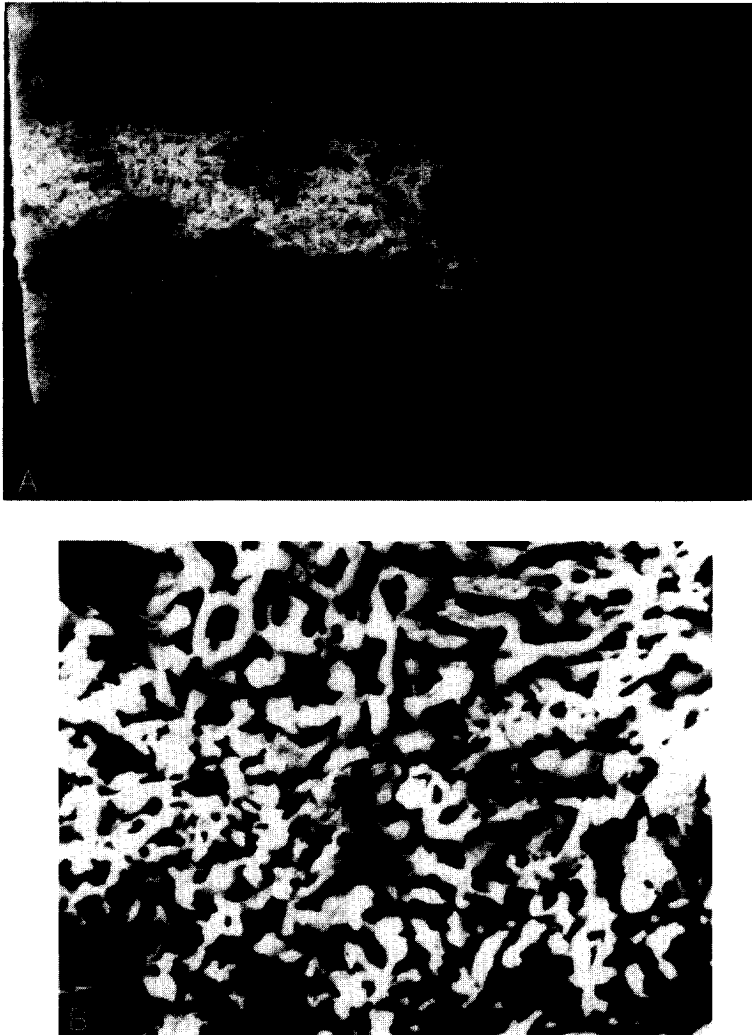


FIG. 15. Scanning electron micrographs of Fe foil used to catalyze a graphite block. (A) Light regions correspond to graphite adhesion to the metal surface. $\times 15$. (B) Higher magnification showing graphite particles. $\times 6000$.

not evident from metallographic examination of cross sections, confirming that the carbide forms on the surface as observed by Auger spectroscopy. Thus, although the presence of Fe_3C after catalytic gasification of graphite as reported earlier by Walker *et al.* (3) is confirmed, it appears to form during cooling and does not play a major role in the gasification reaction.

From the experiments with metal foils, it seems reasonable to conclude that little gasification of carbon at elevated temperatures occurs via the migration of dissolved

C through the catalyst to then combine with the O atoms (formed by dissociation of H_2O) or H atoms on the catalyst surface. Detailed measurements and electron microscope observations to be reported separately suggest that the dissolution process is not the dominant mechanism.

IV. CONCLUSIONS

Our studies have shown marked variations in the catalytic activities of the Group VIII alloys as a function of composition and the corresponding $3d$ -electron concentra-

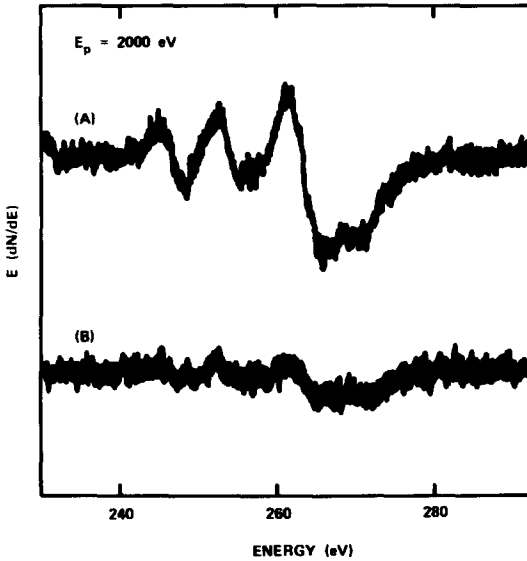


FIG. 16. Auger spectrum of carbon on the surface of a thin foil of Fe after catalyzation of the C-H₂O reaction at 1000°C. (A) Spectrum seen during the first scanning. (B) Spectrum seen during the second scanning on the same area showing the marked reduction in intensity.

by gas atmospheres.³ Auger and characteristic electron spectroscopy are indispensable tools for determining the bulk and surface compositions of catalysts that are active in carbon gasification. Auger studies also confirmed that the Fe₃C phase can be found on the surface of catalysts after cooling, although it appears that this phase does not play an important role in the gasification reaction mechanism.

ACKNOWLEDGMENTS

Dr. C. G. Shirley, now with Motorola, Inc. (Phoenix), participated in the initial stages of our catalysis program and was instrumental in establishing experimental procedures and program plans. We also wish to thank A. G. Moldovan (University of Pittsburgh) for his painstaking efforts in recording the Auger spectra and for several helpful discussions, and R. J. J. Martis and Nila Gupta for preparing the alloy buttons.

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tion. However, analogies to the magnetic behavior with band-structure effects for catalytic activity are complicated by surface segregation, especially as influenced

³ Vapor evaporation techniques can be used to deposit very small quantities (~0.0001–0.01 wt%) of pure metal or alloy catalysts which are at least as active as impregnation of ~2 to 5% of metal powders by conventional means (detailed studies of the effect of particle size and number of gasification rate will be reported separately).

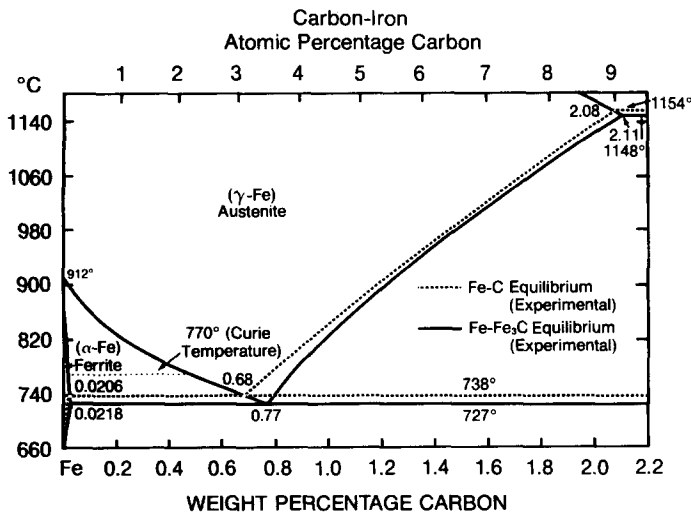


FIG. 17. Fe-C phase diagram (Reprinted with permission from Hawkins, D. T. and Hultgren, R., Constitution of Binary Alloys, "Metals Handbook, Metallurgy, Structures and Phase Diagrams," (Lyman, T., ed.), Vol. 8, 8th ed., p. 276, American Society for Metals, 1973.

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