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Auger Electron Spectroscopy and Mass Spectroscopy Studies on Hydrogenation of Graphite in the Presence of Nickel and Tungsten

G. M. BLIZNAKOV, M. P. KISKINOVA, AND L. N. SURNEV

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1040 Sofia, Bulgaria

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Hydrogenation of polycrystalline graphite in the presence of nickel and tungsten was studied by means of Auger electron spectroscopy and mass spectroscopy at temperatures up to 850K and a hydrogen pressure ranging from 1.10^{-8} to 5.10^{-6} Torr. The changes in the carbon Auger lineshape with increasing metal surface concentration revealed a tendency to formation of a carbide phase, the latter being much stabler in the case of tungsten. The mass spectrometric studies of the interaction of hydrogen with the metal graphite systems showed the formation of CH_4 at temperatures higher than 750K. The electronic and adsorption properties of the metal–graphite systems and the formation of active surface "carbide" carbon were considered in explaining the different catalytic activities of nickel and tungsten.

INTRODUCTION

The energy-related catalytic gasification of carbon-containing solids has received much attention recently because of its importance in the production of synthetic gaseous fuel. To the commercially important reactions of carbon belongs the reaction with hydrogen according to the equation

$$C + 2H_2 = CH_4 \quad (\Delta H^\circ_{298} = -17.9 \text{ kcal mol}^{-1}).$$

This exothermic process occurs to a limited degree in many gasifiers and is highly desirable for reducing the heat requirements for the endothermic carbon–steam reaction. On the other hand, valuable hydrocarbons can be produced by direct hydrogenation. Since the rate of CH_4 formation is very low, this process requires a catalyst.

Various metal catalysts have been studied (*1–6*), but the mechanism of the catalytic action is not yet understood. Rewick and co-workers (*3*) interpreted the catalytic effect as enhancement of hydrogen dissociation on the metal surface, which is considered to be the rate-limiting step of the reaction. Tomita *et al.* (*1, 2*) have shown that along with the type of catalyst, the type of carbon also determines the rate of gasification.

During the last decade modern UHV techniques combined with surface-sensitive spectroscopies have been used in studies of the mechanism of catalytic reactions. Rao and co-workers (*7*) reported recently that Auger spectroscopy can be used in the studies of graphite gasification in the presence of alloy catalysts.

In this study a combination of Auger spectroscopy and mass spectroscopy measurements was used for studying the hydrogenation of graphite in the presence of Ni and W deposited on the graphite surface by vacuum evaporation. These two transition metals have different *d*-electron concentrations and exhibit different stabilities of the corresponding metal carbides (*8*). In the present paper we demonstrate that the Auger spectroscopy in combination with mass spectroscopy can give valuable information on the composition and adsorption properties of the surface after metal deposition, and on the formation of surface carbide and its relation to graphite gasification.

EXPERIMENTAL

All experiments were carried out in a stainless-steel UHV chamber pumped out

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by a 200 liters sec^{-1} ion pump and a liquid nitrogen-cooled titanium sublimation pump (base pressure 1.10^{-10} Torr). The system was equipped with a cylindrical mirror analyser and a quadrupole mass spectrometer (QMS).

A spectroscopically pure polycrystalline graphite planchet (12 × 6 × 0.06 mm) was used. It was mounted by means of two tungsten wires (d = 0.3 mm) to a precise manipulator. The sample was heated by direct electric current up to 900K. The temperature was monitored by a WRe 3%/WRe 26% thermocouple. No surface contaminants on the graphite were observed within the detection limit of the Auger spectrometer after heating the sample to 900K under UHV. Nickel evaporation was performed using a Knudsen oven. Tungsten was deposited by direct vacuum evaporation following electric current heating of a high-purity (99.999%) tungsten wire. The metal surface concentration was determined by calculations based on the C(KLL) and corresponding metal Auger peak-to-peak amplitude of the derivative spectra and the relative sensitivities of the Auger transitions for the pure element (*9*). The Auger spectra were obtained at a primary beam current of 1 $\mu A\ cm^{-2}$ and electron energies of 1500 and 3000 eV. The deposited metal layer can be removed by several hours of Ar ion bombardment (3 kV, 4 $\mu A\ cm^{-2}$) and heating to 900K.

The activitiy of the metal–graphite system in the hydrogenation reaction was evaluated by measuring the relative changes of the QMS signal for 15 and 16 amu when the sample was heated in a H_2 atmosphere. During the experiments the sample was situated in front of the mass spectrometer so that the latter "saw" only the flux of species leaving the sample. The measurements were performed within the pressure region 1.10^{-8}–5.10^{-6} Torr. The partial pressure of H_2 was monitored by measuring the changes in the QMS signal at 2 amu and calibrating the latter against the Bayard–Alpert gauge.

RESULTS

Figures 1 and 2 illustrate the changes in the Auger peak intensities of carbon and the W and Ni Auger peaks observed upon increasing the amount of metal deposited on the graphite surface. The W surface concentration, C_W, was estimated from the relative peak amplitudes of the C(KLL) and W(MNN) transitions using the relationship

$$C_X = \frac{I_X/S_X}{I_X/S_X + I_Y/S_Y},$$

where I_X and I_Y are the relative peak-to-peak amplitudes of the elements under consideration, and S_X and S_Y are the corresponding relative sensitivities between the element under consideration and silver, obtained from Ref. (*9*).

The relative Ni surface concentration, C_{Ni}, was estimated using the peak-to-peak amplitude of the C(KLL) and Ni(LMM) Auger transitions.

The values of the metal surface concentrations are the average over the results of at least 10 measurements in different surface spots. The deviations are within 5% of

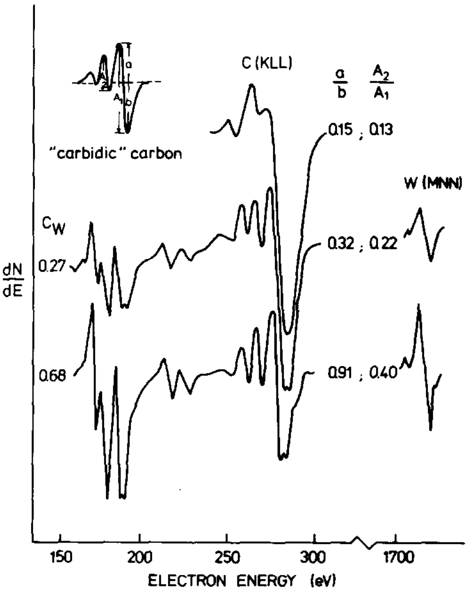

FIG. 1. Auger spectra of pure graphite and graphite with increasing concentration of deposited tungsten, C_W.

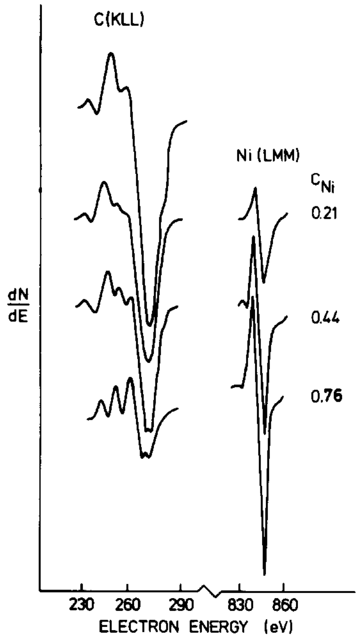

FIG. 2. Auger spectra of pure graphite and graphite with increasing concentration of deposited nickel, C_{Ni}.

the average value. This result is in good agreement with the mechanism reported by Egelhoff and Tibbets (*12*) for growth of metal films on polycrystalline graphite, where at low coverages the metal atoms were well dispersed over the surface.

As can be seen in Fig. 1, with increasing C_W the initial typical graphite shape of the carbon peak gradually changes, showing a tendency to formation of a carbide phase. The ratios a/b and A_2/A_1 were used in the present study to distinguish the detailed variation in the carbon peak shape (*10*). The values of a/b and A_2/A_1 gradually increase with increasing W concentration, approaching that found for pure W_2C. The values $a/b = 1$ and $A_2/A_1 = 0.45$ are reported for W_2C in Ref. (*11*).

In contrast to W, the deposition of Ni (see Fig. 2) on a graphite surface leads to no significant change of the C Auger lineshape at low Ni surface concentrations. More detailed inspection of the ratios a/b and A_2/A_1, however, has shown that a mixture of graphite and carbide carbon existed at C_{Ni} higher than 0.5. A typical carbide-like shape of the Auger C peaks was observed when C_{Ni} exceeds 0.7.

Heating of the sample at 900K after W and Ni deposition results in decreasing intensity of the corresponding metal Auger peaks. This effect becomes less pronounced with every following metal deposition and probably reflects the sinking of the metal into the subsurface carbon layers. For the sake of minimization of the effect of annealing on the surface metal concentration, the deposition and annealing runs were performed several times to ensure the saturation of the subsurface region. Thus the reaction with hydrogen was performed under steady-state conditions and negligible changes in the surface composition were found by comparing the Auger spectra recorded before and after the reaction.

A series of mass spectrometric measurements of the reaction of the graphite–metal system with hydrogen were carried out at a hydrogen partial pressure ranging from 1.10^{-8} to 5.10^{-6} Torr. It was found that the only gas-phase product of the reaction was CH_4, which was liberated at temperatures higher than 750K. For pure graphite, a very small amount of CH_4 was detected at temperatures higher than 850K. In the presence of Ni and W, the temperatures at which the formation of CH_4 was detected decreased down to 750K with increasing metal concentration. Figure 3 presents the changes in the amplitude of the QMS signal at 16 amu as a function of the metal surface concentration. The same trend shows the amplitude of the QMS signal at 15 amu. This figure shows the changes of the product CH_4 QMS signal at 16 amu, recorded 20 sec after opening the leak valve. We found that this time is sufficient for establishment of steady-state H_2 pressure conditions. It is evident that with increasing metal surface concentration the amount of CH_4 liberated as a reaction product increases. In the case of W (see curve 1 in Fig. 3b), the maximum CH_4 yield was detected at C_W of about 0.6. Further increase of C_W causes a decline of the CH_4 yield. By comparing this with the

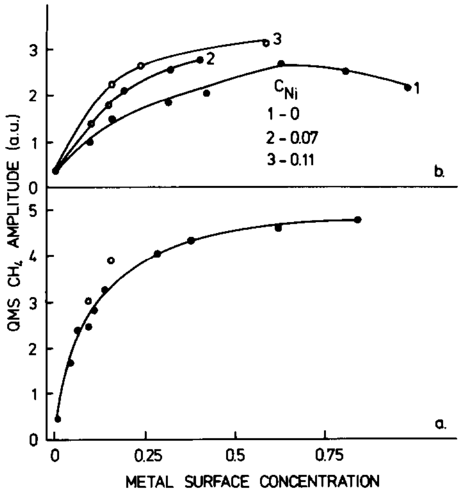

FIG. 3. Dependence of the amplitude of the CH_4 QMS signal (16 amu) on the deposited metal concentration. (a) Nickel, (b) tungsten.

results obtained for Ni (see Fig. 3a), the greater activity in methane production exhibited by Ni can be seen. In the latter case the amount of CH_4 liberated reaches its maximum value at C_{Ni} higher than 0.2. The studies of the activity of the mixed systems have shown that deposition of Ni on a graphite surface covered with W results in enhancement of the methane production as presented by curves 2 and 3 in Fig. 3. The effect becomes stronger with increasing Ni concentration. A certain promoting effect of W on the Ni–graphite system was detected only when C_{Ni} is lower than 0.2 (open circles in Fig. 3a).

Extended measurements of the QMS signal amplitude of CH_4 liberated in a hydrogen atmosphere at 850K as a function of the reaction time were also performed. The curves presented in Fig. 4 show that about 200 sec after the start of the reaction a strong increase of the CH_4 amount liberated was observed. A leveling off of the CH_4 production takes place about 1000 sec after the start, but this is not due to equilibrium limitation. The equilibrium pressure under our conditions is ca. 10^{-11} Torr, much higher than corresponds to these plateaux.

Studies of the dependence of methane production on the H_2 pressure within the pressure range 1.10^{-8}–5.10^{-6} Torr were carried out. As evaluated from the plot shown in Fig. 5, the amount of CH_4 liberated is proportional to the fourth root of the H_2 partial pressure, being independent on metal surface concentration for C_M higher than 0.2. At lower metal concentrations, because of the low CH_4 yield, the accuracy of the measurements was insufficient for drawing any qualitative conclusions.

Since the dissociative adsorption of H_2 was suggested by some authors to be the rate-limiting step of graphite hydrogenation, we studied hydrogen adsorption with the systems under consideration by means of thermal desorption. It was found that hydrogen adsorption on a graphite–metal system is strongly reduced in comparison with the corresponding clean metal surface. For the W–graphite system with C_W lower than 0.5 no H_2 desorption peak was detected after exposure to H_2 at 300K. Even at higher values of C_W, the desorbed H_2 amount was much less than that detected at comparable C_{Ni}. The H_2 desorption from the W–graphite surface occurs at lower temperatures than from a clean tungsten surface and the TD curves are similar to those observed by

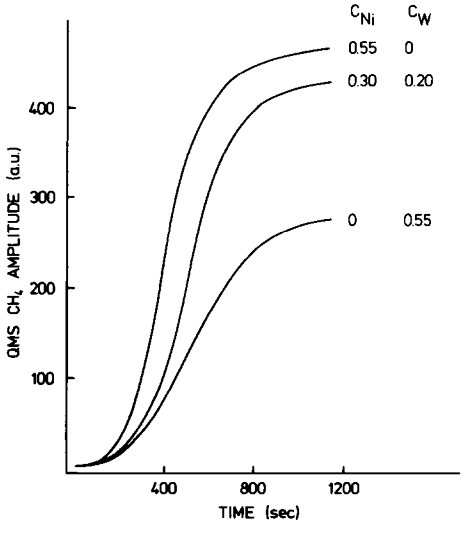

FIG. 4. Dependence of the amplitude of the CH_4 QMS signal (16 amu) on the reaction time at 850K.

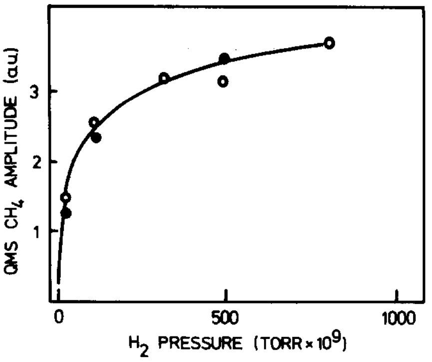

FIG. 5. Dependence of the amount of CH_4 liberated in the reaction on the H_2 partial pressure. ●, C_{Ni} = 0.52; ○, C_W = 0.43.

Benziger *et al.* with carburized W surface (*13*). The H_2 TD peak for a Ni–graphite surface (Fig. 6) appears in the same temperature range where H_2 desorption from a clean surface occurs. A similar desorption behavior of H_2 in the case of graphitized Ni(110) was reported in Ref. (*14*). It was explained by assuming the formation of separated surface nickel and graphite islands where the former are responsible for H_2 adsorption. This assumption might be applied to the present study since appreciable H_2 desorption was detected at relatively high C_{Ni}(0.25) when the formation of Ni islands is possible by filling the gaps between the uniformly adsorbed Ni atoms (*12*).

DISCUSSIONS

The results presented here demonstrate the role of several factors that are related to the elucidation of the catalytic activity of metals in graphite gasification to methane. The two metals under consideration (W and Ni) exhibit different catalytic activity, which, on the basis of the present experimental data, can be ascribed to three factors, which we now discuss in turn.

The first factor is the difference in the percentage of the *d*-electron character, which, according to Pauling's theory, is 40 for Ni and 43 for W (*15*). The role of the electronic properties of the metal catalysts is very often considered an important factor in explaining catalytic activity. The catalytic activity is usually assumed to increase with increasing percentage of *d*-character of the metal. The results in the present study, however, contradict the expected correlations based on the properties of the pure metals under investigation. This result is not surprising because, as demonstrated by the Auger spectra in Fig. 1, the catalytic properties of tungsten carbide rather than those of pure tungsten have to be considered. Indeed, the formation of a metal–carbon bond will cause removal of the metal valence electrons to the covalent metal–carbide orbitals, which undoubtedly will lead to changes of the adsorption and catalytic properties. Therefore, the nature and electronic structure of the active catalytic species under the actual reaction conditions have to be clarified, which introduces additional difficulties in elucidating the role of the electronic factor.

The second factor is the difference in the abilities of the W–graphite and Ni–graphite surfaces to effect the dissociative adsorption of hydrogen. As mentioned in the Introduction, many authors have related the catalytic activity of metals in graphite methanation to the enhancement of the probability for hydrogen chemisorption. The reaction sequence can formally be described as (1) hydrogen dissociative adsorption on the catalyst, (2) diffusion of the hy-

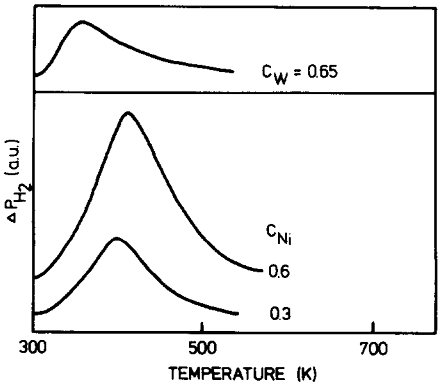

FIG. 6. H_2 spectra recorded after hydrogen exposure 60L (1L = 1×10^{-6} Torr sec^{-1}) at 300K.

drogen adatoms to the neighbouring carbon sites, and (3) formation of C–H bonds.

The H_2 thermal desorption experiments reported here demonstrate that it is hard to seek a correlation between the adsorption properties of the clean metal surfaces and the properties of the corresponding graphite–metal system. It was found that although reduced in comparison with a clean metal surface, some hydrogen adsorption takes place on the surface of the two systems. Since hydrogen does not chemisorb on a graphite surface, the observed hydrogen adsorption in the presence of the deposited metal atoms indicates the existence of a correlation between the ability for hydrogen chemisorption and the activity in hydrogenation. Indeed, the Ni–graphite system exhibits a higher adsorption and catalytic activity, which might be ascribed to the existence of free nickel atoms whose adsorption behavior is almost the same as that of a clean nickel surface. In the case of W, however, the Auger spectra give no evidence of the existence of free metal areas, since a stable carbide phase is formed. The chemisorption of hydrogen is found to be negligible when C_W is lower than 0.5. However, the dependence of the relative CH_4 yield on the H_2 partial pressure observed in the present study is weaker than expected assuming that the rate of methane formation is determined only by the rate of hydrogen dissociative adsorption as mentioned in Ref. (*3*). This fact implies that additional factors have to be involved in explaining the mechanism of the catalytic action.

The third factor to be considered is the formation of active carbon species in the presence of the metal catalysts. Recent studies of CO methanation (*16, 17*) give evidence that a mechanism involving hydrogenation of active surface "carbide" appears to be most consistent with the experimental data. The formation of a graphitic carbon surface layer significantly deactivated the catalysts. As reported under Results, it is possible to distinguish between "graphite" and "carbide" carbon on the basis of a comparison with the carbon Auger spectrum for a pure graphite and nickel or tungsten carbides. This enables one to trace the formation of a "carbide" surface phase as a result of the metal deposition. The results shown in Figs. 1 and 2 imply that the W atoms deposited on the graphite surface are involved in the formation of a stable carbide phase, whereas in the case of Ni the typical carbide-like shape of the C Auger spectra was detected only at sufficiently high nickel surface concentrations. Indeed, more detailed inspection of the carbon Auger spectra revealed that some carbide carbon was existing on the surface even at lower C_{Ni}. It is worth noting here that a continuous transition of nickel carbide to graphite occurs in the temperature interval 300–900K (*18*).

It seems reasonable to assume that the active surface "carbide" carbon is that which does not form a very stable bond with the metal atoms. This assumption is consistent with the observed different activities of W and Ni. In the latter case, the carbide phase, even if formed, is not stable and the carbon atoms are more active.

Assuming that the creation of active surface "carbide" species plays an important role, one can satisfactorily explain the observed increase of the CH_4 yield with the reaction time (Fig. 4). Probably the annealing of the sample facilitates the catalytic channeling of graphite by metal particles, as observed in Ref. (*1*), leading to the formation of more active carbon species. The leveling off in the CH_4 yield can be explained by the competition between two processes, namely, the formation of active "carbide" carbon and the reaction of these species with hydrogen.

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