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Structure of graphitic carbon on Ni(111): A surface extended-energy-loss fine-structure study

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The structural parameters of the graphitic carbon overlayer on a Ni(111) substrate has been determined by using surface extended-energy-loss fine-structure spectroscopy. We find that graphitic carbon is very similar to a graphite single-crystal plane, but slightly expanded (~ 2%), with C-C_1 and C-C_2 distances of 1.45 ± 0.03 and 2.50 ± 0.03 Å, respectively. The graphite overlayer floats at 2.80 ± 0.08 Å above the Ni(111) face. The C-Ni interaction is strong enough to force the overlayer in registry with the substrate. However, we find that the Ni-Ni distance remains identical, showing that the substrate is not affected by the growth of the graphitic overlayer.

Nickel is an efficient methanation catalyst and it is well known that during CO hydrogenation its surface is covered by carbon deposits.[1-7] When the reaction is run too hot, "coking" occurs and the catalytic activity is greatly reduced.[6] Single-crystal studies have shown that the Auger spectra of the carbon overlayer formed in these conditions are very similar to those recorded on graphite.[6] These carbon species were therefore termed "graphitic" carbon.

Quite recently, using photoemission spectroscopy, we have shown[8] that the electronic structure of the graphitic carbon overlayer is very similar to the electronic structure of a graphite single crystal. Ultraviolet photoemission spectroscopy spectra, in fact, resembled those recorded on graphite except for a small, almost rigid, shift of the structures.

Despite the obvious importance from both a fundamental and an applicative point of view, detailed structural studies of carbon overlayers of catalytic relevance are still scarce.

We present here a complete geometrical structure determination of the graphitic carbon overlayer on Ni(111) by using surface extended-energy-loss fine-structure (SEELFS) spectroscopy.[9-13] This technique, which has been developed recently in our laboratory,[14] promises to be extremely valuable for structural studies of clean surfaces and overlayers. It is a comparatively simple technique (it only needs the basic apparatus used for Auger spectroscopy). The experimental data manipulation is also simple [using the same formalism and computational techniques of extended x-ray absorption fine structure (EXAFS) (Refs. 15 and 16) and surface EXAFS (SEXAFS) (Refs. 17 and 18)].

The overall sensitivity of SEELFS compares very favorably with SEXAFS (Refs. 19 and 20) and very good signal-to-noise ratios are usually obtained even with limited data collection periods (~ 15 min.).

The technique seems especially suitable for studying overlayers of the light elements of technological importance (C,O,N) which are very difficult to handle with SEXAFS.

It also appears to be much more appealing than extended appearance-potential fine structure (EAPFS) (Refs. 21 and 22) (which also uses an electron beam excitation probe) because of the comparatively straightforward simplicity of analysis.

In the following we show that SEELFS allows a complete determination of the geometrical parameters of the graphitic overlayer including the carbon-nickel distance.

Indeed the SEELFS technique is so sensitive that it can give information also on the variations of geometry of the metal substrate upon absorption of an adsorbate.[13] In the present case we will show that the formation of the graphitic overlayer does not disturb at all the Ni substrate.

The Ni(111) sample, oriented within 1° and cut to a size of $6 \times 6 \times 1.5$ mm^3, was polished in order to obtain a stress-free mirror-finished surface. The cleaning procedure was performed *in situ* by heating the Ni substrate at 900°C in 10^{-7}-Torr oxygen pressure and by argon ion sputtering cycles. Residual contaminants (mainly sulfur) were kept below 1% of a monolayer. The experimental vacuum chamber, operating at 10^{-10}-Torr range, contained facilities for low-energy electron diffraction (LEED) and Auger spectroscopy. Energy-loss spectra in reflection mode were recorded with a double-pass cylindrical mirror analyzer (CMA) and its coaxial electron gun. Primary electron energies between 1000 and 1600 eV were used with currents of ~ 5 μA. Peak-to-peak modulation voltages in the CMA of 5–10 V were used and the signal detected in the second derivative mode. Graphitic carbon overlayers were readily produced by heating the sample above 300°C, for 5–10 min, in a 10^{-5}–10^{-6}-Torr range of CO. LEED observations showed that graphitic carbon formed an ordered (1×1) pattern.

Figure 1 shows SEELFS spectra for a clean Ni(111) surface and for the same surface, covered with the graphitic overlayer, at a primary beam energy $E_p = 1600$ eV, in the 0–500 energy-loss range. The structures observed for the clean (111) surface are identical to those observed on a Ni(100) (Ref. 13) surface and a Ni polycrystalline[10] sample, as expected.

The carbon-covered surface shows a strong signal originating from the carbon K edge (very similar to the one observed on a graphite single crystal[12]) and fine structures above it which extend for about 250 eV. The procedure of analysis of the experimental data,[9] and the theoretical justification of the use of the dipole approximation in the reflection low-energy scattering matrix element[13] have been already outlined and will not be repeated here. The k-space transformed experimental spectrum $X(k)$ of the carbon-covered surface is shown in Fig. 2(a). Figure 2(b) shows the function $\tilde{F}(R)$ obtained by Fourier transforming the function $X(k)$ with integration limits $k_{\min} = 2.3$ Å^{-1} and $k_{\max} = 8.3$ Å^{-1}. Since the data are obtained in the second derivative mode the function $\tilde{F}(R)$ gives a radial distribution function multiplied for a factor $\sim R^2$.[23] The function $\tilde{F}(R)$ shows strong well-defined peaks at 1.10 ± 0.03, 2.19 ± 0.03, and 2.95 ± 0.03 Å. The dotted line in Fig. 2(b) shows the Fourier transform of the Ni surface integrated in the identical k range. It provides, therefore, the limits of reliability of the observed peaks. Three more peaks appear at higher R values which seem to be above the noise level. In a conventional SEXAFS (Refs. 17, 19, and 20) transform the high R peaks would be very small. The second derivative technique seems, therefore, very promising for enhancing the contribution of the outer shells.[24]

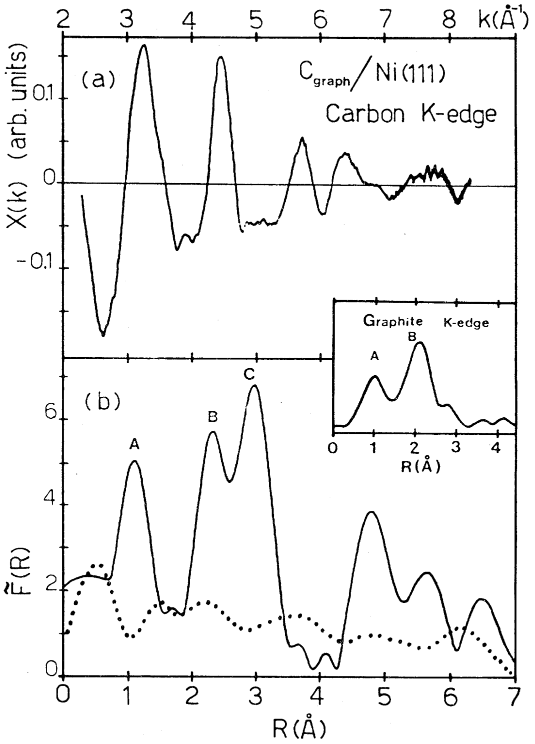

FIG. 2. (a) SEELFS signal $X(k)$ extracted above the K edge of the graphitic carbon formed on Ni(111). (b) Fourier transform of the above spectrum between $k_{\min} = 2.3$ Å^{-1} and $k_{\max} = 8.3$ Å^{-1}. The dotted line is the Fourier transform of the Ni(111) spectrum performed in the same energy range used for the curve (b). The inset shows the Fourier transform of a graphite single crystal (Ref. 12) obtained with the same primary beam energy and with the same integration limits.

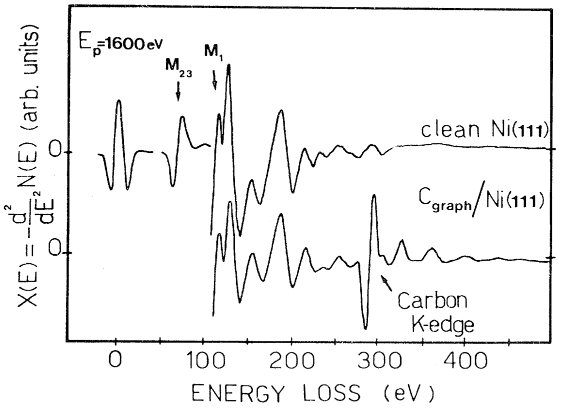

FIG. 1. Electron energy-loss spectra of a Ni(111) surface recorded before (upper curve) and after the formation of an overlayer of graphitic carbon. The primary beam energy was $E_p = 1600$ eV and the curves are displayed in function of the second derivative of the electron yield $N(E)$. The SEELFS extend up to about ~ 300 eV above the M_{23} (68-eV) Ni core level and for ~ 200 eV above the carbon K edge (285 eV).

Our present results for the function $\tilde{F}(R)$ show strong analogies with the radial distribution function obtained for a graphite single crystal[12] (obtained with the same primary beam energy and Fourier transform limits, see inset in Fig. 2). The first two peaks (A and B) are almost identical while the third peak (at 2.95 Å in the present data), appears only as a shoulder in pure graphite.

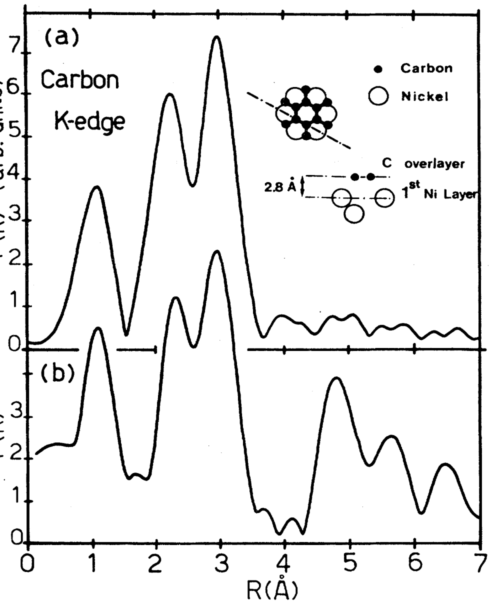

FIG. 3. (a) Fourier transform of an EXAFS model calculation for the system C_{graph}/Ni(111) around the carbon K edge. Phase shifts and amplitudes are taken from Ref. 25. The parameters used were the following: C-C_1 = 1.45 Å, $\sigma_1^2 = 0.003$ Å^2, and $N_1 = 3$; C-C_2 = 2.50 Å, $\sigma_2^2 = 0.009$ Å^2, and $N_2 = 6$; C-Ni = 3.10 Å, and $\sigma_3^2 = 0.009$ Å^2, $N_{Ni} = 3$. The Fourier integration is performed with the same limits used for the experimental $\tilde{F}(R)$ [curve (b)].

In Ref. 12 the first two peaks were interpreted as the first- and second-nearest neighbors in the graphite basal plane. Similarly we interpret the first two peaks as the analogous shells in the graphitic overlayer. We interpret the third strong peak as arising from the backscattering of the Ni atoms of the substrate. Indeed Ni has a much higher backscattering amplitude than carbon so that this difference is expected.

Figure 3(a) shows the results of a theoretical EXAFS model[25] for $\tilde{F}(R)$, including three-neighbors coordination shells, while Fig. 3(b) shows again the experimental $\tilde{F}(R)$ for comparison. The model has been obtained by constructing the theoretical $X(E)$. The second derivative of $X(E)$ was Fourier transformed using the same integration limits and weight functions used for the experimental results. We find the C-C nearest neighbors at 1.45 ± 0.03 Å and the second-nearest neighbors at 2.50 ± 0.03 Å. These values are slightly larger than the corresponding distances in pure graphite (1.42 and 2.46 Å, respectively) although the difference is within the experimental error. The C-Ni distance is 3.10 ± 0.05 Å (Ref. 26) which corresponds to a 2.80 ± 0.08-Å distance between the carbon and the first (111) Ni layer.

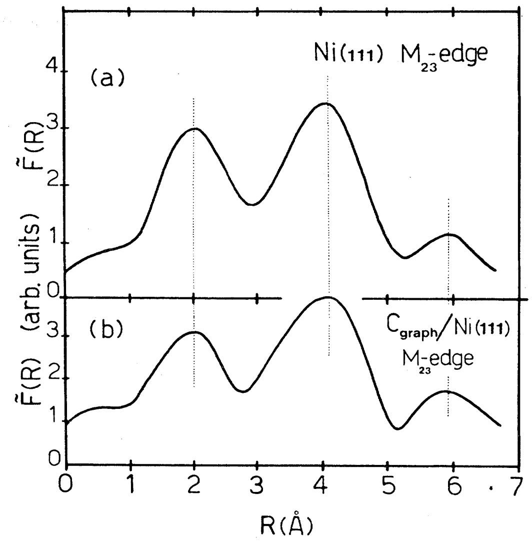

FIG. 4. $\tilde{F}(R)$ obtained above the Ni(111) M_{23} core level for (a) clean surface and (b) surface covered with graphitic carbon. The experimental $X(k)$ (Fig. 1) are integrated in the same integration limits (3.0–7.5 Å^{-1}).

For the calculation we have used, for the C-C phase shifts, experimental values obtained from Ref. 12, since calculated phase shifts of light elements are usually not reliable.[19] The use of theoretical phase shifts did not give, however, different results in this case. For the C-Ni distance we have used instead theoretical phase shifts.

The agreement between the theoretical model and the experimental results is gratifying. Although the carbon overlayer is floating well above the Ni surface our data seem to indicate that the interaction is still strong enough to force a slight expansion (~ 2%) of the carbon-carbon distance to bring it into register with the substrate periodicity. This conclusion is supported by LEED inspection which shows [for the graphitic overlayer on Ni(111)] a (1 × 1) without extra rings. Figure 4 shows the Fourier transform $\tilde{F}(R)$ of the fine structures above the M_{23} Ni core levels for (a) the clean sample (Ref. 27) and (b) the carbon-covered surface. The $\tilde{F}(R)$ were integrated in the same integration limits ($k_{min} = 3.0$ Å^{-1} and $k_{max} = 7.5$ Å^{-1}). The peak positions are identical within the experimental accuracy, showing that the nickel substrate is not affected by the growth of the graphitic overlayer.

In conclusion this paper reports a complete structural determination of the graphitic carbon on a Ni(111) substrate by using surface extended-energy-loss fine-structure spectroscopy. We have been able to determine the structure up to the third-nearest-neighbor shell (C-C_1, C-C_2, and C-Ni). We have also been able to show that the Ni substrate is not disturbed by the growth of the graphitic overlayer since the Ni-Ni distance remains identical.

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[23] For this reason we prefer to identify the radial distribution function we obtain with the notation $\tilde{F}(R)$.

[24] The structural information in SEXAFS spectra of light overlayers is usually restricted to the first coordination shell. See, for instance, Ref. 20.

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[26] The larger error in this case takes into account the uncertainty in the carbon-nickel phase shift and the possibility of weighting contiguous carbon-nickel shells. A similar orientational effect has been detected in single-crystal graphite (Ref. 12).

[27] $\tilde{F}(R)$ for clean nickel has been reported already in Refs. 9 and 13. The structures observed in Refs. 9 and 13 were sharper because of the different integration limits.