PHYSICAL REVIEW B VOLUME 29, NUMBER 3 1 FEBRUARY 1984

Determination of graphitic carbon structure adsorbed on Ni(110) by surface extended energy-loss fine-structure analysis

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(Received 12 July 1983)

A model is proposed for the geometrical structure of graphitic carbon chemisorbed on a Ni(110) single crystal which reproduces with good accuracy the experimental radial distribution function $F(R)$ obtained for the first time by surface extended energy-loss fine-structure spectroscopy. The graphitic layer strongly interacts with the Ni substrate. We find that some carbon atoms are placed in the fivefold symmetry site of Ni.

When carbon monoxide adsorbed on Ni dissociates, a carbonaceous overlayer forms which, depending on the substrate temperature, shows at least two different states: a "carbidic" carbon which is very active in the catalytic methanation reaction, and a "graphitic" carbon which drastically reduces any catalytic activity. The existence of these two species has been experimentally demonstrated by observing strong modifications in the carbon Auger line shape; that means that different electronic properties and geometries for the two adsorbed species occur.[1-5]

Some recent band-structure calculations to identify the geometry of a carbon overlayer on Ru and Rh have been made,[6,7] but up to now few experiments are available to verify the model.

In this Rapid Communication we report on carbon near-edge electron-energy loss and surface extended energy-loss fine-structure (SEELFS) experiments on a graphitic carbon layer on Ni(110) surface. The SEELFS technique, made in the reflection mode, was recently successfully tested on clean metal surfaces and overlayers.[8-10] It is very simple experimentally and uses the same formalism and computational technique as extended x-ray absorption fine structure (EXAFS).

Spectra have been taken in an UHV system at a base pressure $\lesssim 5\times10^{-10}$ torr. A Ni(110) crystal oriented within 1° was polished and cleaned by Ar^+ ions and thermal annealing cycles to obtain an Auger clean surface with a contamination level lower than 1%. To obtain energy-loss spectra an electron beam (1000—1600 eV) coaxial to the cylindrical mirror analyzer (CMA) was used. The CMA (in the second derivative mode) monitored the losses suffered by primary electrons.

A graphitic overlayer was obtained by reacting CO at a pressure of 5×10^{-5} torr with Ni(110) at a temperature $T \simeq 600$ K for about 30 min (at this temperature a carbidic carbon overlayer transforms in graphitic carbon[11]).

Figures 1(a) and 1(b) show the carbon *K*-edge loss structure for carbidic and graphitic carbon, respectively. The technique strongly discriminates between the two different phases: Carbidic and graphitic carbon spectra show a dramatic change in line shapes. In the carbidic carbon, only one prominent peak centered at 286-eV loss energy is visible; in the graphitic layer, a second peak is clearly evident. Figure 2(a) shows the same *K*-edge loss for graphitic carbon in comparison with that of a single-crystal graphite taken in the identical experimental conditions [Fig. 2(b)]. As indicated in the figure, the two strong features are related to $1s$-π and $1s$-σ transitions.[12,13] In Fig. 2(c) a spectrum from Ref. 14 for a graphitic layer on Ni(111) is reported for comparison. As in the x-ray-absorption near-edge structure (XANES) regime, *K*-edge loss spectrum should be very sensitive to the local arrangement of atoms:[15,16] The differences in the relative intensities and energy location of *K*-edge loss peaks means different site symmetry and/or chemical bonding distances. Graphitic carbon on Ni(111) is very similar to graphite single crystal while the graphitic overlayer on Ni(110) shows (i) a strong difference in relative peak intensities ($1s\rightarrow\pi, 1s\rightarrow\sigma$); (ii) a 0.5-eV higher-energy separation in the π and σ transitions with respect to graphite.

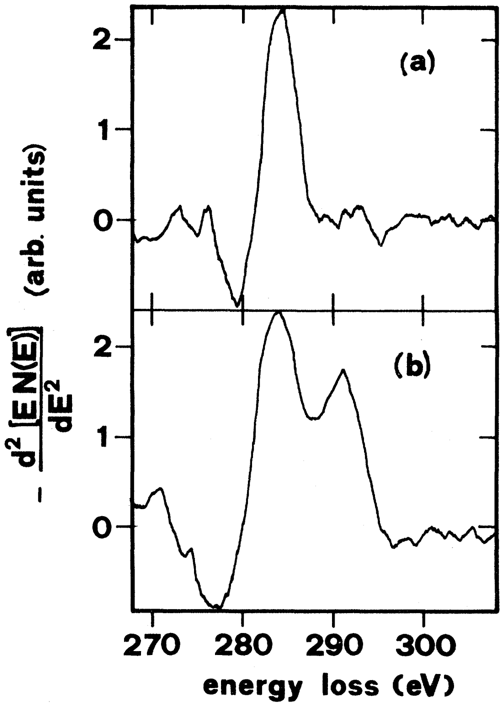

FIG. 1. Carbidic (a) and graphitic (b) carbon *K*-edge loss spectra obtained with a primary electron beam energy E_p of 1600 eV.

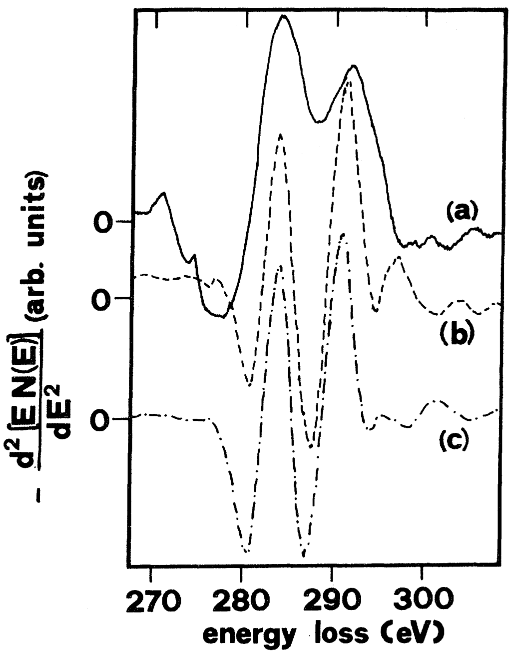

FIG. 2. Carbon K-edge loss spectra (a) for graphitic overlayer on Ni(110), (b) for single-crystal graphite, and (c) for graphitic overlayer on Ni(111).

The Ni(110) is a rough surface with respect to Ni(111) so that carbon atoms cannot coordinate well with other carbon atoms placed along the [100] direction of Ni substrate. In the Ni(111) a complete graphitic layer in register with Ni substrate can be obtained just stretching the carbon-carbon bonding distances from 1.42 to 1.44 Å to fit the threefold hollow site distances of the substrate.[14] These observations suggest that a graphitic layer in registry with the Ni(110) surface can be obtained along a [110] direction. We checked within the experimental resolution that Ni substrate did not relax during carbon adsorption by analyzing the SEELFS oscillation above the Ni M_{23} edge before and after graphitic overlayer formation.

Figure 3(a) shows a SEELFS spectrum of the graphitic carbon layer on Ni(110) obtained at a primary energy $E_p = 1600$ eV with a modulation voltage of 8 V peak to peak, at a primary electron beam current of $\sim 2\ \mu$A. The strong peak at ~ 286-eV energy loss is due to the carbon K edge while visible oscillations extend up to about 200 eV higher. The radial distribution function $F(R)$ obtained by Fourier transform of the energy-loss spectrum in $\vec{k}$ space, $\chi(k)$, is reported in Fig. 3(b). A broad peak centered at 2.40 ± 0.08 Å is seen with a bump at 4.15 Å.

Two model calculations for graphitic carbon adsorption on

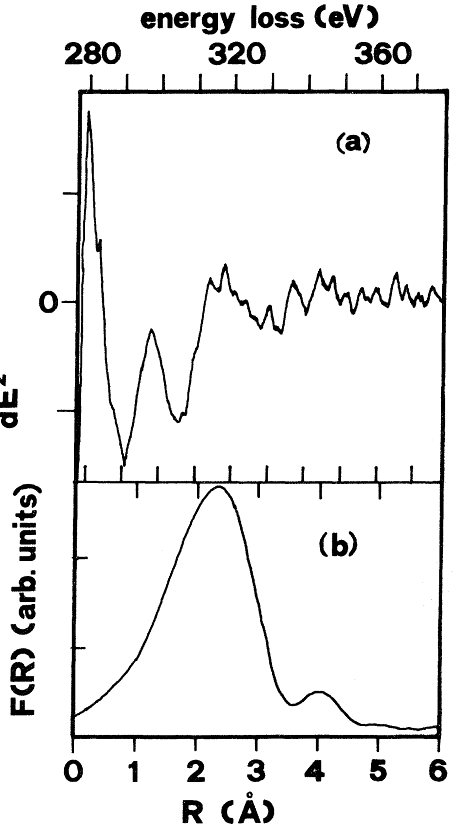

FIG. 3. (a) SEELFS spectrum in the second derivative mode of the graphitic layer on Ni(110) obtained with $E_p = 1600$ eV and a modulation voltage of 8 V peak to peak, and (b) radial distribution function $F(R)$ obtained with integration limits $k_{\min} = 2.33$ Å^{-1} and $k_{\max} = 7.13$ Å^{-1}.

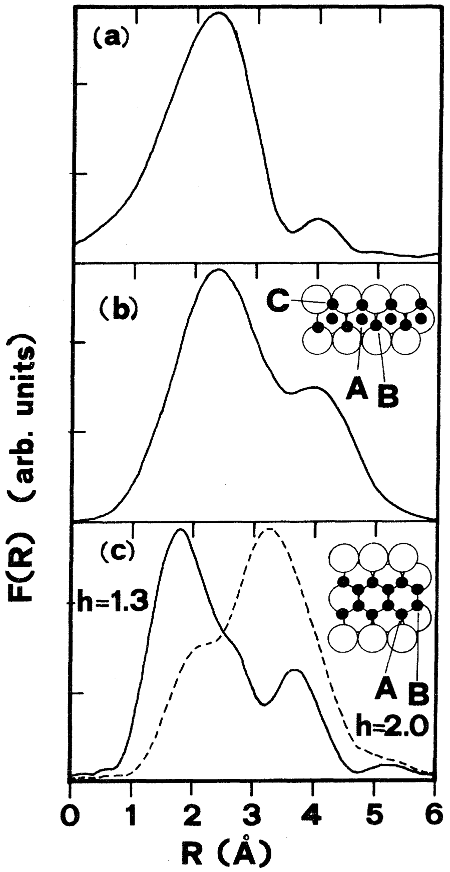

FIG. 4. (a) Experimental $F(R)$ as in Fig. 3(b), and theoretical $F(R)$'s [(b) and (c)] obtained using the EXAFS formalism for carbon adsorption configurations depicted in the insets. The dotted and solid lines in (c) refer to different distances h between graphitic layer and first Ni layer.

TABLE I. Coordination numbers and bonding length distances relative to the two models presented in this work for a graphitic overlayer on Ni(110). In model II figures in parentheses refer to the $h = 2.0$ Å case.

	Model I			Model II		
	Shell	Coordination number	Distance (Å)	Shell	Coordination number	Distance (Å)
A	1	5	2.49	1	1	1.95 (2.49)
	2	2	3.52	2	1	2.49 (2.91)
	3	2	4.31	3	2	2.88 (3.52)
	4			4	2	3.17
B	1	1	1.95	1	2	1.95 (2.49)
	2	1	2.93	2	1	2.78 (3.44)
	3	2	3.07	3	2	3.35 (3.68)
	4	2	3.16	4	2	3.73 (4.25)
C	1	2	1.95			
	2	1	3.10			
	3	1	3.40			
	4	2	3.77			

Ni(110) have been tested to reproduce the experimental $F(R)$. Due to the low backscattering amplitude of carbon with respect to Ni atoms,[17] in both models only carbon-nickel distances are considered. A theoretical $\chi(E)$ has been constructed using the EXAFS formalism with the calculated backscattering amplitudes and phase shifts.[17] Because of the second derivative technique used in our experiments, the $d^2X(E)/dE^2 = \chi(E)$ has been performed.

The Fourier transform of $\chi(k)$ has been compared with the experimental one using the same limits of integration.

Model I is depicted in the inset of Fig. 4(b); carbon atoms of type *A* have five Ni atoms in the first coordination shell at a distance of 2.49 Å. Atoms *B* have one Ni atom as first neighbor at a distance of 1.95 Å, which is supposed to be the minimum allowed carbon-nickel distance. Atom *C* has two Ni atoms as first neighbors at 1.95 Å. Carbon-*A*-carbon-*B* distance is longer (1.49 Å) than C-C distance in graphite (1.42 Å) to obtain a graphitic layer in the [110] direction in registry with the substrate.

In model II [inset of Fig. 4(c)], only two types of carbon atoms exist. Both of them have the same distance for the first coordination shell which consists of one Ni atom and two Ni atoms for carbons *A* and *B*, respectively. The distance *h* between the graphitic layer and first Ni layer has been varied from 1.32 Å (corresponding to a C-Ni minimum distance of 1.95 Å) to 2.03 Å (corresponding to a C-Ni distance of 2.49 Å). The C-C distance is 1.44 Å in this model to obtain registry with Ni periodicity in the [110] direction.

In Table I all coordination numbers and shell distances used in the calculation are reported. Theoretical $F(R)$'s obtained for the two models are compared with the experimental one in Fig. 4. Model II does not reproduce the experiment adequately either by varying the distance between graphitic layer and first nickel layer.

Model I shows very good agreement not only in reproducing the position of the main peak 2.40 ±0.08 Å but also in the general behavior of the curve: A peak at 4.15 Å is also found in the experimental $F(R)$.

Summarizing, carbidic and graphitic carbon can be formed on Ni(110) by thermal cracking at low CO pressure and *K*-edge loss spectroscopy can very well discriminate between different carbonaceous layers; graphitic carbon shows a strong interaction with Ni(110) substrate as shown by the two broad $1s$-π and $1s$-σ transitions of Fig. 2(a); furthermore, a possible model is proposed for chemisorption of graphitic carbon which reproduces with good accuracy the experimental $F(R)$ curve.

ACKNOWLEDGMENTS

This work was partially supported by Ente Nazionale Energie Alternative, Casaccia, Roma, Italy.

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