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PHOTOEMISSION SPECTROSCOPY INVESTIGATION OF THE ELECTRONIC STRUCTURE OF CARBIDIC AND GRAPHITIC CARBON ON Ni (1 1 1)

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Photoemission measurements have been carried out on different forms of carbon deposits of catalytic importance on the (1 1 1) face of nickel, and give a picture of the electronic structure of "carbidic" and "graphitic" carbon.

The photoemission spectra of graphitic overlayers strongly resemble spectra taken on graphite bulk samples but show an (almost) rigid shift of the levels with respect to the Fermi level.

The results we obtain for carbidic carbon can be understood on the basis of recent surface electronic structure calculations. In particular a p-like state has been observed very near the Fermi level, which is probably responsible for the high chemical reactivity of carbidic carbon.

1. INTRODUCTION

CARBON MONOXIDE IS KNOWN to dissociate on selected transition metal surfaces in appropriate temperature and partial pressure ranges, leaving carbonaceus deposits [1, 2]. These deposits play an important role in the catalytic methanation reaction and Fisher–Tropsch synthesis in general [3–7].

Carbon monoxide adsorbes molecularly and reversibly at room temperature on Ni and its irreversible dissociation occurs for $T > 150^\circ$C and $p_{CO} > 10^{-8}$ torr [1, 8]. Possible mechanisms for carbon deposition are [1]:

$$2CO_* \rightleftarrows C_* + (CO_2)_{gas} \tag{1a}$$

$$\left\{\begin{array}{l} CO_* + * \rightleftarrows C_* + O_* \\ (CO)_{gas} + O_* \rightarrow (CO_2)_{gas} + * \end{array}\right. \tag{1b}$$

Two different forms of the adsorbed carbon may be distinguished:

(1) in a low temeprature regime ($T \leqslant 280^\circ$C) and for low coverages ($\theta_c \lesssim 0.3$ ML), carbon is dispersed on the surface. A few ordered phases are also known to exist [9]. In this form, carbon reacts readily with hydrogen above room temperature to form methane [3–7]. Because of its peculiar Auger lineshape (reminiscent of the carbon KVV Auger lineshape of transition metal carbides) this form has been termed "carbidic" carbon (C_{carb}) [10],

(2) in a higher temperature regime ($T \gtrsim 280^\circ$C) the overlayer morphology changes dramatically. A hexagonal structure develops very similar to that of a graphite layer (as shown by the LEED pattern) [11]. This species is much less reactive towards hydrogen than the carbidic form and effectively poisons the catalyst surface [6]. The KVV Auger lineshape takes the form usually recorded for graphite crystals [6]. For this reason this adsorbed carbon species has been termed "graphitic" carbon (C_{graph}). The understanding of the electronic structure of these overlayers is of great relevance for furthering our knowledge of the catalytic hydrogenation of carbon monoxide. This kind of investigation has been scarce [12], however, despite its relevance to fuel production problems. Important questions which remain to be answered include:

(a) the exact mechanism of formation of C_{carb} and its dependence on geometric and electronic properties of different transition metal catalyst surfaces;

(b) why C_{carb} is so highly reactive toward hydrogen;

(c) whether it is possible to avoid the formation of C_{graph}, and if so, how.

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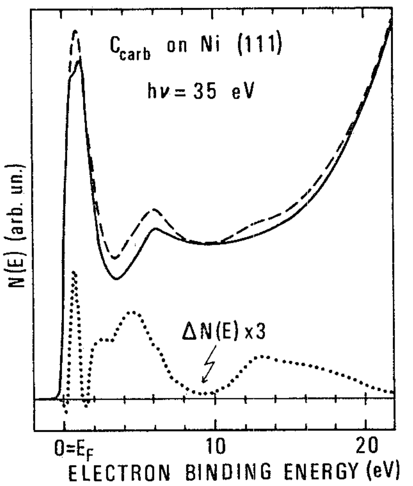

Fig. 1. Photoemission energy distribution curves for the Ni–C_{carb} system. Solid line, clean Ni; dashed line, Ni + 0.2 ML of C_{carb}; dotted line, difference spectrum (Ni + C_{carb} – clean Ni).

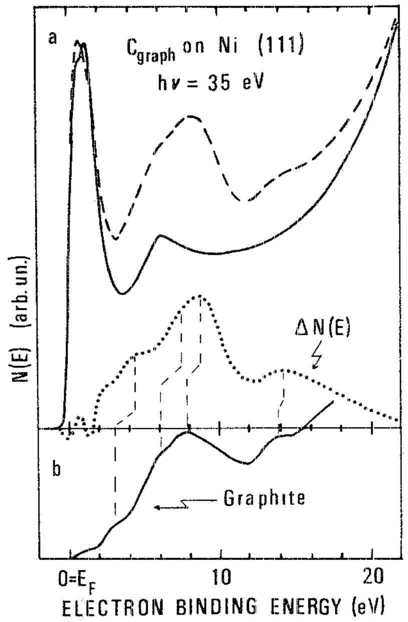

Fig. 2. (a) Photoemission energy distribution curves for the Ni–C_{graph} system. Solid line, clean Ni; dashed line, Ni + 0.4 ML of C_{graph}; dotted line, difference spectrum (Ni + C_{graph} – clean Ni). (b) Photoemission spectrum for graphite single crystal taken from [17]. Photon energy $h\nu = 34$ eV.

In the following we report UPS results on C_{carb} and C_{graph} absorbed on Ni(1 1 1) which provide the first detailed experimental picture of the electronic properties of carbidic and graphitic carbon on Ni(1 1 1).

2. EXPERIMENTAL SETUP AND RESULTS

The vacuum chamber was pumped with ion pumps and liquid nitrogen cooled titanium sublimator. Typical operating pressures were in the low 10^{-10} torr range. The experimental chamber contains facilities for LEED, AES and UPS analysis. Photoemission studies were performed with a double pass cylindrical mirror analyzer (CMA) and Synchrotron Radiation from the Storage Ring in Frascati. The light was impinging on the sample at 45° in *p* polarization.

The Ni(1 1 1) sample, oriented within 1° and cut to a size of 6 x 6 x 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 sample at 900°C in 10^{-7} torr oxygen pressure and by argon ion sputtering cycles. Residual contaminants (mainly sulphur) were kept below 1% of a monolayer.

Carbidic carbon overlayers were reproducibly obtained by heating the sample for 5–10 minutes at 200–250°C in a 10^{-5}–10^{-6} torr pressure range of CO. Details of the growth kinetics of carbon adlayers in this low CO pressure range will be published elsewhere [13].

Graphitic carbon overlayers were readily produced by heating the sample above 300°C. In the intermediate temperature range (250–300°C), carbidic and graphitic carbon mixed phases were produced. LEED observations showed that graphitic carbon formed an ordered 1 x 1 pattern (as expected, since the Ni nearest neighbours distance in the Ni(1 1 1) surface, i.e. 2.48 Å, is close to the graphitic lattice parameter, i.e. 2.46 Å [14]). The carbidic carbon also shows an ordered LEED pattern, but with more complicated geometry [15].

Electronic levels of atomic adlayers usually have much smaller photoemission cross-sections than molecular adsorbates, and so are best revealed by difference spectra obtained by carefully subtracting spectra of the overlayer system and of the clean substrate.

Figure 1 shows UPS spectra of Ni(1 1 1) and of the Ni + C_{carb} system taken at $h\nu = 35$ eV. As expected, carbidic carbon does not show pronounced peaks. On subtracting the clean Ni spectrum, however, three distinct feature show up at 1, 4.2 and 13 eV binding energies (b.e.) while a weak shoulder is present at 6.6 eV. The estimated C_{carb} coverage from the Auger carbon intensity, is $\theta \simeq 0.2$ ML.

Figure 2 shows the UPS spectra of the Ni(1 1 1) and Ni + C_{graph} system for a graphitic carbon coverage $\theta \simeq 0.4$ ML. In this case structures appear at 4.2, 8.4 and 14 eV. A UPS spectrum of graphite single crystal (taken from [16]) is also shown for comparison [Fig. 2(b)].

3. DISCUSSION

The contribution of the graphitic layer to the UPS spectra shows strong similarities with the spectra taken on graphite bulk sample [16] (see Fig. 2). In fact there is a one to one correspondence in the peaks with an overall shift of 1 eV towards higher binding energies. This observation strongly suggests that the electronic structure of the graphitic overlayer can be interpreted in terms of graphite band structure calculations [17]. It also provides striking experimental evidence that a single layer of graphite already has the complete electronic structure of a bulk sample. Moreover Fig. 2 shows that the UPS spectrum of the Ni–C_{graph} system can be considered, as a good approximation, a simple superposition of the EDC's of pure Ni and of graphite. We deduce that the interaction of the graphite overlayer with the metal substrate is very small and shows up mainly as a charge transfer leading to a shift of major features by about 1 eV. In analogy with UPS results on alkali metal intercalated graphite [18, 19], we interpret the average increase in binding energy as a rise of the Fermi level. An approximate estimate of the charge transfer necessary to induce such a shift gives ~ 0.02 electrons per carbon atom [2]. The 14 eV peak makes an exception, as its position in bulk graphite and in the graphitic overlayer differs negligibly, pointing out that band shifts are not perfectly rigid. Similar non-rigid-band shifts have been detected in Li intercalated graphite [21, 22].

Our UPS spectra of the Ni–C_{carb} system can be interpeted with the aid of Feibelman's calculations for a carbidic layer on a (0001) Ru surface [23]. The calculated electronic levels consist of carbon 2*s* states 11 eV below the Fermi level (E_F), bonding *p* states centered at 4 eV b.e., non-binding states (mainly p_z) near E_F ("dangling bond" states) and antibonding *p* states above E_F. The broad peak which appears at 13 eV b.e. in our difference spectrum (Fig. 1) originates from carbon 2*s* states. The small feature appearing at 6.6 eV below the Fermi level can be associated with the lower p_x, p_y states (which become an s–p_z mixture at Γ) in the theoretical calculations. The main bump centered at 4.2 eV b.e. is certainly correlated with the p_x, p_y states which Feibelman puts at 3.5 eV below E_F. The structure appearing at about 1 eV b.e. is associated with a "dangling bond" structure and hence is of particular interest. Unfortunately it overlaps with the Ni *d* band requiring a very delicate subtraction procedure owing to the depletion and masking of the Ni *d* states. The carbidic carbon induced structure is however clearly detectable also in spectra taken at different photon energies [24] and quite independent of the normalization procedure.

This peak is associated with the p_z states which Feibelman finds in the proximity of the Fermi level and which are presumably responsible for the high chemical reactivity of the carbidic species. Indeed the *p* state probably extends above the Fermi level [24] forming a sort of dangling bond, as predicted [23].

4. CONCLUSIONS

In conclusion we have presented in this communication the first detailed experimental results on the electronic structure of carbidic carbon on Ni. The agreement with theoretical calculations is surprisingly good, especially if it is taken into account that these were performed for carbidic carbon on a Ru(0001) surface. In particular, we have proved the existence of carbon *p* states in close proximity of the Fermi level. This finding can be of paramount importance owing to its catalytic implications.

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