JOURNAL OF CATALYSIS **89**, 159–163 (1984)

NOTES

XPS Study of β-Carbon Hydrogenation on Nickel(111) Surface

In recent years the methanation reaction has been studied extensively using conventional catalysis and modern surface science techniques (*1*). It is now well established that the mechanism of this reaction involves the dissociative adsorption of carbon monoxide to produce highly reactive "carbidic" carbon (α-carbon) which is subsequently hydrogenated to produce methane (*2*). Under conditions of low hydrogen concentration, and high temperature, however, the reactive α-C can be transformed into relatively less-reactive "graphitic" carbon (β-carbon) (*3, 4*). The nature of β-carbon has been suggested to be graphitic as characterised by Auger electron spectroscopy (AES) (*5*), X-ray photoelectron spectroscopy (XPS) (*6*), and temperature-programmed surface reaction (TPSR) in hydrogen (*7*).

Recently we used field emission microscopy to characterise α- and β-carbon deposits on nickel single crystal field emitter tips (*8*). An important observation was the direct confirmation of nucleation sites for β-carbon islands, found to be associated with steps vicinal to the (110) and (111) poles. After extensive carbon deposition, the stepped regions (111) and (110) planes were completely covered by β-carbon while the (100) regions remained essentially free of such deposits.

Since β-C deposits lead to loss of catalytic activity, processes for the removal of such deposits are of interest. The mechanism of β-C hydrogenation, however, has not been studied in great detail. The rate-limiting step in the catalytic hydrogenation of graphitic carbon has been suggested to be dissociative adsorption of hydrogen (*9*) and carbon–carbon bond breaking (*10*). The rate of hydrogenation has also been shown to be dependent on the type of carbon present (*11*). For the filamentary carbon deposits, the rate of gasification has been suggested to be limited by carbon diffusion through the metal particle (*12*).

Two mechanisms can be postulated for β-carbon hydrogenation, both requiring dissociative adsorption of hydrogen on the metal surface but differing in the nature of carbon species hydrogenated. In one case, hydrogen adatoms diffuse to the edge of β-carbon islands and react there, while in the other mechanism detachment of edge carbon atoms from β-carbon islands occur to produce α-carbon which is subsequently hydrogenated.

The latter mechanism would involve conversion of β-carbon into α-carbon at the β-carbon hydrogenation temperature. Also, if hydrogenation of β-carbon proceeds via α-carbon species, neither dissociative adsorption of hydrogen nor hydrogenation of β-carbon can be rate-determining since hydrogenation of α-carbon occurs readily at much lower temperatures. In the present work, using XPS, we demonstrate directly that conversion of β-carbon to α-carbon does occur at β-carbon hydrogenation temperature and that the rate-determining step in the hydrogenation of β-carbon may be the detachment of carbon atoms from β-carbon islands.

The experiments were carried out using a standard VG Scientific ESCALAB MkII spectrometer comprising a twin-anode X-ray source, LEG200 electron gun for AES

0021-9517/84 $3.00

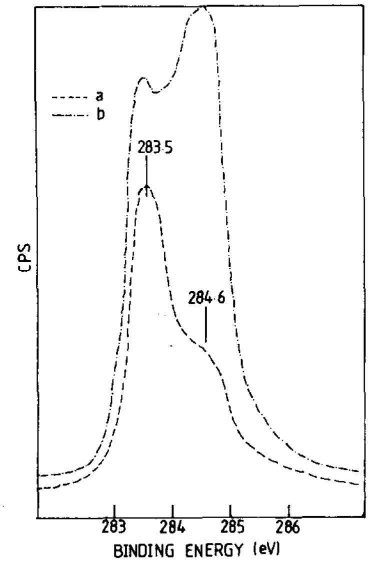

FIG. 1. Growth of α- and β-carbon on Ni(111), with C(1*s*) levels at 283.5 and 294.6 eV, respectively, after (a) 15 min and (b) 20 min in CO at 400°C.

and SQ300 quadrupole mass spectrometer. The Ni(111) single crystal surface was cleaned by a repeated sequence of argon ion bombardment and heating in hydrogen. The Ni surface was considered clean when no contaminants were detected in AES after prolonged annealing in UHV at the maximum temperature (500°C) used in the experiments. Hydrogen or carbon monoxide could be admitted to the preparation chamber and gas composition monitored with the mass spectrometer. Surface carbon was deposited by dissociative adsorption of CO in the temperature range 300–500°C and pressure 10^{-5}–10^{-2} mbar. The XPS spectra of the C(1*s*) level were taken with the Mg*K*α source at 15 kV, 300 W power, and for a spectrometer pass energy of 10 eV. The XPS binding energies reported here are referenced with respect to the binding energy of the Ni ($2P_{3/2}$) level, measured at 853.0 eV.

The α- and β-carbons were observed in XPS with C(1*s*) peak positions at 283.5 and 284.6 eV, respectively. Carbon deposited at temperatures below 300°C was seen to be essentially carbidic in nature whereas carbon deposition above 350°C resulted in rapid buildup of both α- and β-carbons (Fig. 1). The transformation, α- to β-carbon, occurred readily at 450°C though it was noted that even after prolonged heating at 450°C, small amounts of α-carbon still remained (Fig. 2). It is interesting to compare the β-carbon peak with the carbon peak taken from a single crystal graphite sample, (inset to Fig. 2). The carbon peak from the graphite sample is quite structureless while the β-carbon peak shows considerable structure. The reasons for these differences are not clear but one possibility is that the β-carbon signal comes from carbon atoms occupying multiply coordinated sites in the graphitic type islands on the nickel surface. Studies are being carried out to investigate this further.

In order to observe the reverse transformation (β- to α-carbon), the α-carbon present on the Ni surface was first selectively hydrogenated off. When the crystal with both α- and β-carbons present on it was exposed to hydrogen at 10^{-3} mbar

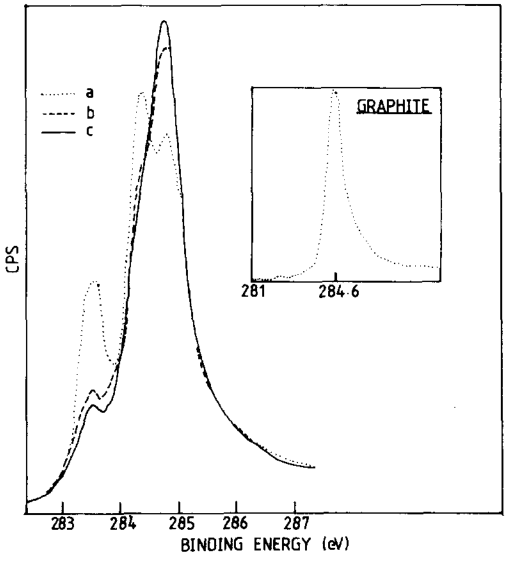

FIG. 2. Carbon 1*s* levels from α- and β-carbon on Ni(111), showing the transformation α → β by heating the crystal at 450°C in UHV. (a) Before heating; (b),(c) after successive heating cycles of 5 min duration. Inset shows the C 1*s* level from a graphite single crystal.

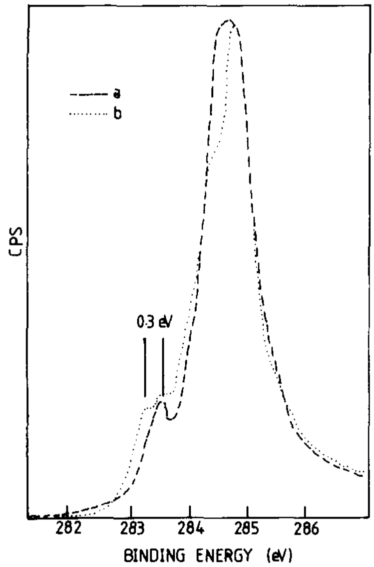

FIG. 3. The α- and β-carbon (1*s*) levels, (a) before and (b) after exposure to hydrogen at room temperature. The splitting of the α peak in (b) is probably due to the formation of CH_x-type species on the Ni surface.

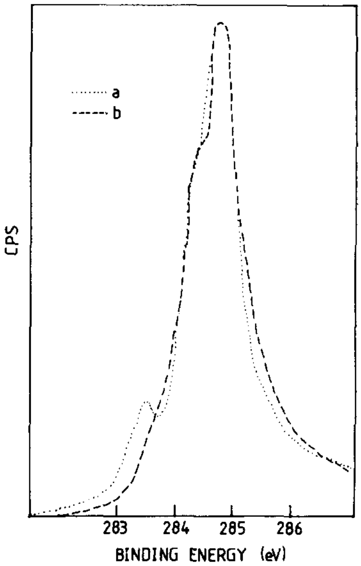

FIG. 4. Selective hydrogenation of α-carbon by heating the Ni crystal to 300°C in hydrogen. Carbon (1*s*) levels (a) before and (b) after heating in hydrogen.

pressure, a shoulder developed at about 0.3 eV below the α-carbon peak (Fig. 3). The appearance of this shoulder is probably associated with partial hydrogenation of some α-carbon to yield CH_x type species on the nickel surface, just as has been observed on iron surfaces (*13*). Heating the Ni crystal in H_2 at 300°C resulted in complete removal of α-carbon while the β-carbon peak remained unchanged (Fig. 4). The crystal was then heated at 450°C in UHV ($\leq 2 \times 10^{-10}$ mbar) for varying periods and XPS spectra recorded. Figure 5 shows that during the annealing period α-carbon reappeared on the surface with subsequent decline in the concentration of β-carbon, as evidenced by a decrease in the β-carbon peak height. The α-carbon peak that reappeared after prolonged heating at 450°C was similar in height to that seen remaining after conversion of α- to β-carbon (cf. Figs. 5 and 2). The appearance of this α-carbon level cannot be associated with carbon deposition from ambient CO since annealing the clean crystal under similar UHV conditions did not result in any α-carbon formation. These observations suggest that an equilibrium state is reached between α- and β-carbons and that α- to β-carbon conversion is not an

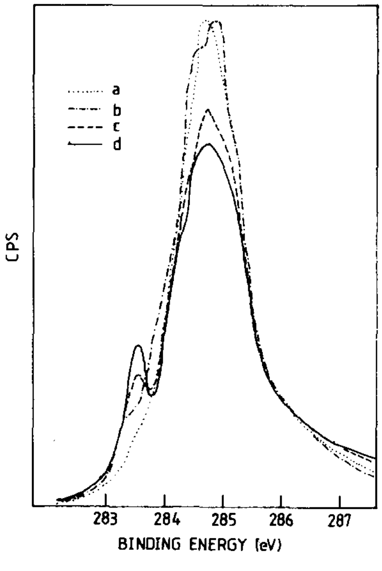

FIG. 5. Growth of α-carbon on the Ni(111) surface by β–α transformation at 450°C. Carbon (1*s*) levels (a) before and (b)–(d) after successive 5-min anneals in UHV.

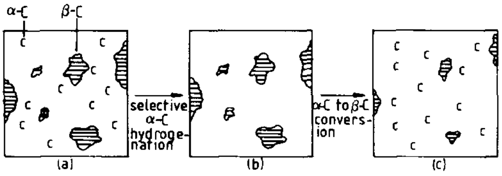

FIG. 6. Schematic drawing of the redistribution of β-carbon into α-carbon. (a) α- and β-carbon in equilibrium; (b) after selectively removing α-carbon by hydrogenation; (c) detachment of carbon atoms from β-carbon islands to reestablish $\alpha \leftrightharpoons \beta$ equilibrium.

irreversible process as previously suggested (*14*). The concentration of α-carbon that is in equilibrium probably depends strongly upon the temperature and the nickel crystal surface geometry. For example, the binding energy for carbidic type carbon is highest on Ni(100) as shown by Eizenberg and Blakely (*15*) and our studies (*8*), while for a Ni(111) surface β-carbon appears to be more stable.

It has recently been shown that during hydrogenation of CO a steady state carbidic carbon level is established on the catalyst surface (*16*). We propose that a similar situation can exist during hydrogenation of β-carbon by conversion of β-carbon to α-carbon followed by hydrogenation of the α-carbon species, as shown schematically in Fig. 6. Figueiredo and Trimm (*12*) have proposed a mechanism of filamentary carbon hydrogenation where diffusion of carbon through nickel particles occurs followed by hydrogenation of the surface carbon species. Studies of catalysed hydrogenation of graphite by platinum particles have led Santiesteban *et al.* (*17*) to conclude that the rate-determining step in this reaction is the breaking of C–C bonds as a result of interaction with the metals, supporting the original observation of Holstein and Boudart (*10*). Auger lineshape studies of carbon species on rhodium and nickel surfaces have led Houston *et al.* (*14*) to invoke the idea of the transformation of graphite to carbide in the case of rhodium. Recent studies by Bliznakov *et al.* of the hydrogenation of graphite by nickel indicates that an "active carbide" is present as an intermediate (*18*). The evidence and the mechanism proposed by us is in agreement with that proposed by these authors and shows clearly that the transformation α-carbon to β-carbon is not an irreversible process.

We have studied the kinetics of β- to α-carbon conversion and β-carbon hydrogenation on Ni/Al_2O_3 catalysts using TPSR methods and observed that the kinetics of the two processes were very similar (*19*). These results and the results of our present study lead us to conclude that the rate-determining step in the hydrogenation of β-carbon on nickel surfaces is detachment of carbon atoms from β-carbon islands.

REFERENCES

1. Biloen, P., and Sachtler, W. M. H., "Advances in Catalysis," Vol. 30, p. 165. Academic Press, New York, 1982.
2. Kelley, R. D., and Goodman, D. W., *in* "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis" (D. A. King and D. P. Woodruff, Eds.), Vol. 4, p. 427. Elsevier, New York, 1983.
3. Kelley, R. D., Madey, T. E., Revesz, K., and Yates, J. T., *Appl. Surf. Sci.* **1,** 266 (1978).
4. McCarty, J. G., and Wise, H., *J. Catal.* **57,** 406 (1979).
5. Goodman, D. W., Kelley, R. D., Madey, T. E., and Yates, J. T., *J. Catal.* **63,** 226 (1980).
6. De Deken, J., Menon, P. G., Froment, G. F., and Haemers, G., *J. Catal.* **70,** 225 (1981).
7. McCarty, J. G., Hou, P. Y., Sheridan, D., and Wise, H., *Amer. Chem. Soc. Symp. Ser.* **202,** 253 (1982).
8. Dost, A. A., Dhanak, V. R., and Bassett, D. W., *Vacuum* **33,** 687 (1983).
9. Rewick, R., Wentrcek, P., and Wise, H., *Fuel* **53,** 274 (1974).
10. Holstein, W. L., and Boudart, M., *J. Catal.* **72,** 328 (1981).
11. Tomita, A., and Tamai, Y., *J. Catal.* **27,** 293 (1972).
12. Figueiredo, J. L., and Trimm, D. L., *J. Catal.* **40,** 154 (1975).
13. Bonzel, H. P., and Krebs, H. J., *Surf. Sci.* **91,** 499 (1980).

14. Houston, J. E., Peebles, D. E., and Goodman, D. W., *J. Vac. Sci. Technol.* **A1**(2), 995 (1983).

15. Eizenberg, M., and Blakely, J. M., *J. Chem. Phys.* **71,** 3467 (1979).

16. Goodman, D. W., Kelley, R. D., Madey, T. E., and White, J. M., *J. Catal.* **64,** 479 (1980).

17. Santiesteban, J., Fuentes, S., and Yacaman, M. J., *J. Vac. Sci. Technol.* **A1**(2), 1198 (1983).

18. Bliznakov, G. M., Kiskinova, M. P., and Surnev, L. N., *J. Catal.* **81,** 1 (1983).

19. Dost, A. A., and Bassett, D. W., in press.

A. A. DOST
V. R. DHANAK[1]
S. BUCKINGHAM

VG Scientific Ltd.
Imberhorne Lane
East Grinstead
Sussex RH19 1UB
United Kingdom

Received June 29, 1983

---

[1] To whom correspondence should be addressed.