Spectroscopic evidence for the formation of CH_x species in the hydrogenation of carbidic carbon on Ni(100)

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The CH_x species formed on Ni(100) by hydrogenation of carbidic carbon have been detected using high resolution electron energy-loss spectroscopy (HREELS). Exposures of carbidic carbon to 1×10^{-7} Torr H_2 and D_2 at 313 K for 20 min produce CH_x and CD_x species, respectively. These species are identified by two energy-loss peaks for CH_x at 2970 and 1380 cm^{-1} and only one peak for CD_x at 1980 cm^{-1}. Because of the existence of the intense peak at 1380 cm^{-1}, in the range of a scissors mode for CH_2 and a symmetric deformation mode for CH_3, the CH_x species are tentatively ascribed to CH_2 and/or CH_3. The CD_x species undergo decomposition at 330–370 K in UHV as well as in hydrogen below 10^{-7} Torr. No stable CH_x species are observed above 400 K, which is lower than the normal reaction temperature of the methanation reaction (500 K).

Keywords: CH_x species; carbide; methanation; hydrogenation; nickel

Surface science investigations have provided extensive information on the mechanism and kinetics of the methanation reaction, $CO + 3H_2 \rightarrow CH_4 + H_2O$, on Ni single crystals. Goodman et al. [1–3] have found that both Ni(100) and Ni(111) show almost equal catalytic activity, or turnover number, as Ni/Al_2O_3 for this reaction at near-atmospheric pressures. The agreement between the single crystal and supported catalyst indicates the reaction to be "structure insensitive" [1]. They have also reported that surface carbide formed by dissociation of CO is a reaction intermediate which is subsequently hydrogenated to CH_4 [1–3]. However, it is still unknown why the catalytic activity for methanation is independent of the crystallographic surface structure of Ni. With this problem, Hirano and Tanaka [4] have shown that the arrangement of carbon atoms in the carbide overlayer on Ni(111) is identical to that of the p4g carbide overlayer on Ni(100). The kinetics of hydrogenation of carbide to CH_4 have

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been reported on Ni(100) [3] and Ni(111) [5], while microscopic information on the surface hydrogenation process is, at present, scarce.

Partially hydrogenated carbon species, CH_x ($x = 1$–3), are believed to be important intermediates in the methanation as well as the Fischer–Tropsch synthesis [6]. CH_x species on single crystal surfaces of Fe [7], Ru [8,9], and Ni [10–13] have been studied by high resolution electron energy loss spectroscopy (HREELS). The energy-loss spectra of CH/Ni(111) were detected by decomposing ethylene [10], acetylene [11], and adsorbed CH_3 [12]. And the spectrum of CH_3 species on Ni(111) was detected at a low temperature (140 K) by HREELS [13]. The decomposition of CH_4 occurs on Ni(111) to yield CH_3 when CH_4 has sufficiently high translational energy, but no surface CH_2 was observed. So far, the CH_x on Ni single crystal by reaction of carbide with hydrogen has not been directly detected. In this paper, we wish to report the HREELS results on the formation of CH_x species formed by the hydrogenation of carbide and its decomposition on Ni(100).

Experiments were conducted in an ultrahigh vacuum (UHV) apparatus. It consists of a stainless steel UHV chamber and an attached small reactor. The UHV chamber is equipped with a cylindrical mirror analyser for Auger electron spectroscopy (AES), low energy electron diffraction (LEED) optics, a mass spectrometer (MS), and a spectrometer for HREELS. Base pressures in the 10^{-10} Torr range are routinely obtained in the UHV chamber, and the details have been described elsewhere [14]. A single crystal wafer of Ni(100) with an accuracy of $\pm 1°$ of the (100) plane was mechanically polished with 0.25 μm diamond paste. The sample (8 mm in diameter and 1 mm thick) was supported by two spot-welded tantalum wires and was heated resistively. The temperature was measured by a chromel–alumel thermocouple spot-welded to the edge of the Ni(100) sample. Cleaning the Ni(100) surface was achieved by repeating the cycle of the oxidation in 10^{-8} Torr O_2 at 800 K, Ar^+ ion bombardment at room temperature, and annealing at 1000 K in UHV.

Carbidic carbon was prepared by surface segregation at 550 K in UHV [15]. This temperature is necessary to form a monolayer of carbidic carbon. After a certain time of segregation, the formation of carbide overlayer was monitored by the Auger fine structure of the C(KVV) transition peak. The amount of carbidic carbon deposited on Ni(100) was adjusted so that the peak height ratio of C(KVV)/Ni(LMM) ≈ 0.1, which corresponds to 0.15–0.20 carbon atom per nickel surface atom ($\theta = 0.15$–0.20). We chose the low coverage of carbide since it is known that the steady state coverage of carbide during methanation reaction on Ni(100) at 450–700 K is below $\theta = 0.1$. The carbidic overlayer on Ni(100) has a p4g c(2×2) structure, of which the saturated coverage is $\theta = 0.5$. In this experiment, therefore, the Ni(100) surface is partly covered by the carbidic domain with a bare nickel surface. After preparation of surface carbon, no loss peak in HREELS was observed for the carbon deposited Ni(100) surface.

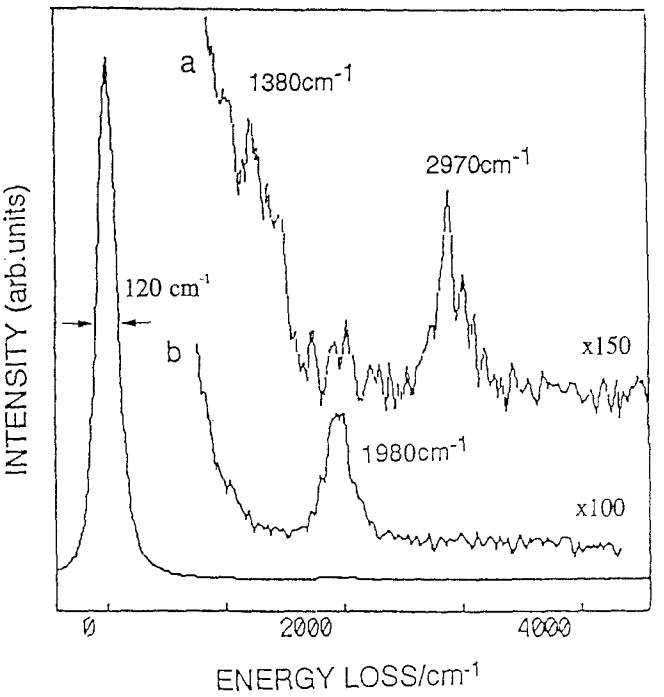

Fig. 1. Electron energy-loss spectra of (a) after exposure of carbide covered Ni(100) to 1×10^{-7} Torr of H_2 at 313 K for 20 min and (b) after exposure of carbide covered Ni(100) to 1×10^{-7} Torr of D_2 at 313 K for 20 min.

Fig. 1 shows typical spectra of HREELS obtained by exposing carbide covered Ni(100) to 1×10^{-7} Torr H_2 and D_2 at 313 K for 20 min. In the case of H_2 (spectrum (a)), two loss peaks are observed at 2970 and 1380 cm^{-1}. In addition, there seem to be loss peaks between 900 and 1100 cm^{-1} hidden in the shoulder of the elastic peak, which are frequently observed by exposing H_2 to the surface carbide at 313 K. The ratios of the intensity of the loss peaks at 2970 and 1380 cm^{-1} are always constant at any reaction condition, even when the amounts of CH_x are changed. This suggests that the CH_x species are not mixtures of CH_x with different numbers for x, but are, in fact, a specified species. The loss peak at 2970 cm^{-1} in (a) may correspond to the CH stretching vibration of the CH_x species. In spectrum (b), however, only one loss peak at 1980 cm^{-1} is recognized. The peak at 1980 cm^{-1} in (b) can be attributed to the CD stretching vibration. Careful adsorption and desorption studies have shown that the loss peak at 1980 cm^{-1} is not due to adsorbed CO. The intensity of the loss peak increased as the dosing time of D_2 (4×10^{-7} Torr) was increased up to 100 min. At a saturation coverage of carbidic carbon, no CH_x formation was observed in our study.

The loss peak at 1380 cm^{-1} seen in fig. 1a is in the range of a scissors mode of a CH_2 group or a symmetric deformation mode of a CH_3 group. Weinberg

and co-workers [8] assigned the loss peak at 1422 cm^{-1}, observed after dosing of CH_2N_2 on Ru(100), to the scissors mode of adsorbed CH_2. They tabulated the scissors mode of the CH_2 group for gaseous ethylene (1444 cm^{-1}), gaseous CH_2N_2 (1414 cm^{-1}), and methylene (1360 cm^{-1}) coordinated to metals in a cobalt complex, which have been measured by IR. Ibach and co-workers [7] have observed surface CH_x species over Fe(110) during the Fischer–Tropsch synthesis at a pressure of 1 atm. According to their assignments, the vibrational losses at 870 and 3100 cm^{-1} are characteristic of surface CH and those at 1420 and 3010 cm^{-1} are characteristic of a CH_2 group. On the other hand, Ceyer and co-workers [13] have reported an energy-loss spectrum for adsorbed CH_3 on Ni(111) at a low temperature as 140 K. The CH stretching mode in the CH_3 species is observed at 2660 cm^{-1}, while an intense loss peak at 1220 cm^{-1} is assigned to the symmetric deformation mode of CH_3 group. As CH species has no loss peak around 1300–1400 cm^{-1} on Ni(111) [10–12] and Ru(001) [9], they give loss peaks at 1200–1300 cm^{-1} being assigned to the bending mode of C–H. Because of the existence of intense peaks at 1380 cm^{-1}, we tentatively ascribe the CH_x species to CH_2 and/or CH_3. The loss peak for the scissors mode of CD_2 and the symmetric deformation mode of CD_3 should be located at around 1000 cm^{-1} [16] and 940 cm^{-1} [13], respectively. In our study, these peaks may be hidden in the shoulder of the elastic peak. The region of loss peaks for C–C bonds (around 1000 cm^{-1}) is also hidden in the shoulder. However, it is likely to form CH_x species as an intermediate of methanation on Ni(100).

The thermal stability of CD_x on Ni(100) in UHV and in 1×10^{-7} Torr D_2 was studied by raising the temperature as shown in figs. 2a and 2b, with the interval time between measurements being 20 min. The elastic peak intensity was almost constant during the heating. However, the intensity varied in different runs, (a) and (b), so that the difference of intensities between (a) and (b) for C–D stretching in arbitrary units has no quantitative meaning. The intensity of the loss peaks for CD_x starts to decrease at 330 K in UHV as well as in D_2 atmosphere, and the intensity of the loss peak falls to zero at temperatures higher than 370 K, indicating the decomposition of CD_x. D_2 was detected by MS at about 370 K during the heating.

It is noteworthy that the decomposition temperature (330–370 K) is far lower than the 500 K for the methanation reaction. Therefore, one must consider that the decomposition of CH_x species is thermodynamically favourable in hydrogen pressures below 10^{-7} Torr and temperatures above 370 K. However, the formation of CH_x and its hydrogenation will be rapid at higher temperatures. As a result, it is likely that the hydrogenation of CH_x to CH_4 is balanced by the formation of carbidic carbon during the methanation reaction. The very small reaction probability of the hydrogenation of surface carbide to CH_4 on Ni(100) [1] may be responsible for the instability of the CH_x species.

The stability of CH_x species on Ni(100) may be different from that on Ni(111). CH species were assigned on Ni(111) using HREELS by Demuth and

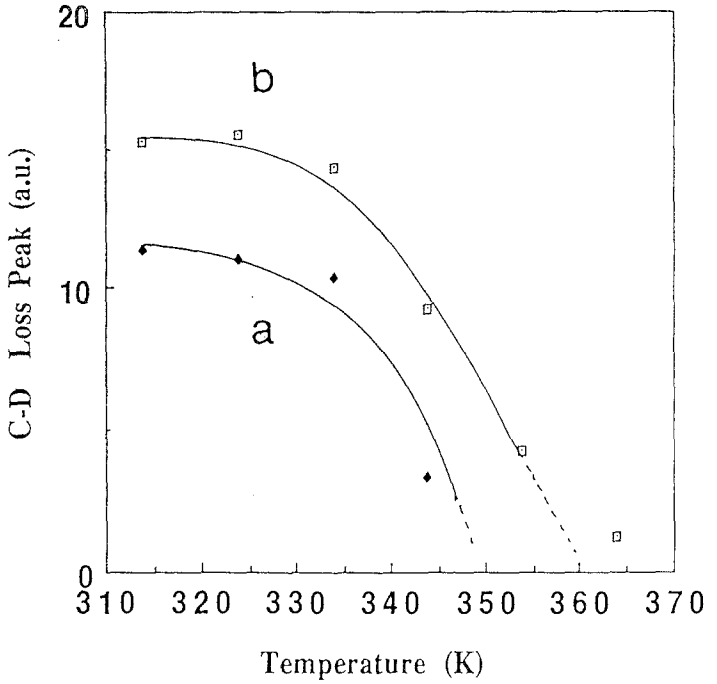

Fig. 2. Intensity of C–D stretching for CD_x as sample is heated in (a) 1×10^{-7} Torr D_2 and (b) UHV. Heating rate was 1 K s^{-1}. The spectra were measured at the corresponding temperature.

Ibach [11], Rosei and co-workers [10], and Ceyer [12], where the CH species were prepared by different ways. They found that the CH species on Ni(111) were stable up to 400 K. However, in the present study, no stable species was observed at 400 K on Ni(100) surface. In addition, no CH species were observed in our reaction conditions on Ni(100). It is quite possible that the difference in the local structure between CH_x on (100) and on (111) affects the thermal stability of CH_x. This contrasts with the identical kinetic parameters such as reaction rate and activation energy in the methanation on Ni(100) and Ni(111) [1], and the identical arrangement of carbon atoms in the carbide overlayer on Ni(100) and Ni(111) [4].

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