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DISSOCIATION OF CH SPECIES ON Ni(111): A HREELS STUDY

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The isothermal dissociation rate of CCH and CH on Ni(111) was measured by following, with HREEL spectroscopy, the intensity of the CH stretching peak as a function of time. By repeating the experiment at several different temperatures we obtained an activation energy of 8 ± 3 kcal/mol for the CCH dissociation reaction and of 12 ± 3 kcal/mol for the CH dissociation reaction. Pre-exponential factors were found to be $10^{3 \pm 1}$ s^{-1} in both cases. Independent thermal desorption spectra show a feature at 470 K and a tail extending up to 600 K which can be assigned to the CCH dissociation and the CH dissociation respectively. The two experiments are quantitatively consistent.

1. Introduction

One of the goals of this work is to show one way to use the high resolution electron energy loss spectroscopy (HREELS) technique not only as a qualitative but also as a quantitative tool in the study of dynamic surface processes.

A very important class of such processes are the so-called Fischer–Tropsch reactions. These are catalytic reactions in which CO and H_2 are the starting molecules and a hydrocarbon species $C_n H_m$ is the final product.

An intermediate step of such a reaction can be written as

$$C_x H_y + H \underset{k_{-1}}{\overset{k}{\rightleftarrows}} C_x H_{y+1} + *. \tag{1}$$

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For some of these reactions, for example for the methanation reaction, apparent activation energies for the overall process on different transition metal catalysts have been measured [1].

Our knowledge of the kinetic parameters (pre-exponentials, activation energies) of the individual intermediate steps of the reaction, on the other hand, is extremely limited. In recent years a small number of quantitative studies of the kinetic parameters of the CO dissociation step on single crystal transition metal surfaces has been carried out [2-5]. The situation concerning the existence, stability and role of $C_x H_y$ moieties is more complex and only a few scattered papers have appeared in the literature [6-10].

As a part of an ongoing program of study in our laboratory, we have started investigating the simplest intermediate steps described by eq. (1) with $y = 0$ and $x = 1$ or 2 on a Ni(111) model catalyst substrate.

In the following we report on the kinetic parameters of the inverse reactions (CCH and CH dissociation), which are important steps in a large number of dehydrogenation reactions, measured through the high resolution electron energy loss spectroscopy (HREELS) technique.

2. Experimental details

The experiments were performed in a two stage stainless steel UHV system. The first stage is dedicated to sample preparation and houses a LEED system, an Auger spectrometer, a sputter ion gun, gas dosers and a quadrupole mass spectrometer, and is pumped by a turbomolecular pump. The second stage of the system is pumped by an ion pump and a cryopump and reaches a base pressure of 6×10^{-11} mbar. It houses a commercial HREEL spectrometer (Leybold-Heraeus ELS 22) consisting of a double pass 127° cylindrical electrostatic monochromator and analyser. The best spectrometer resolution was 4.5 meV on the beam reflected from the sample, but because of the low coverage of the CH species and the low cross-section of their modes we chose to record our spectra at a resolution of typically 10 meV in order to increase the count rate. The incidence angle of the electrons was 60° and the spectra were taken 20° off specular.

The nickel single crystal was oriented within 1° of the (111) direction and mounted on two tungsten wires which allowed it to be heated resistively up to 1200 K. The temperatures were measured using a Chromel–Alumel thermocouple spot-welded to the back face of the sample. Surface impurities were removed through repeated annealing and Ar ion sputtering cycles. Residual carbon was removed by heating the sample to 900 K in an oxygen atmosphere (10^{-8} mbar). Contaminants were kept below 0.02 of a monolayer. High purity gases were used for the exposures and dosing was performed by flooding the first stage of the chamber.

The thermal desorption spectra were obtained recording the H_2 partial pressure during heating from 300 to 650 K at a rate of 5 K/s with the mass spectrometer placed in front of the sample.

3. Experimental results and discussion

In principle, C_xH_y species can be prepared either by direct hydrogenation of carbidic carbon or by thermal dissociation of molecules like ethylene or acetylene. Menzel and co-workers [11] have shown that carbidic carbon hydrogenates readily on a Ru(001) surface at moderate temperatures under UHV conditions.

So far, however, all our efforts to produce a CH species on our Ni(111) sample by direct hydrogenation of carbidic carbon by using hydrogen pressures up to 10^{-3} mbar (the highest allowed by our present system) have failed. Goodman and co-workers observed carbidic carbon hydrogenation but at substantially higher hydrogen pressure (100 Torr) [12]. Also direct hydrogenation of carbon on cobalt requires pressures of at least 1 Torr [13].

The dissociation paths of both acetylene and ethylene have been widely studied by many authors with the HREELS technique on different crystal faces of most of the transition metals [14–16] and it is well known that CH_2, CCH and CH species form as intermediate products of the dissociation path in many cases. Demuth and Ibach [14], by using HREELS, reported that a CH species is formed when an acetylene covered Ni(111) surface is flashed to 450 K. The spectrum showed distinct peaks at 98 and 370 meV (plus a small peak at 160 meV). The peak at 370 meV was identified as the CH stretching mode while the 98 meV peak was attributed to the CH bending mode. On adsorbing ethylene on Ni at room temperature, on the other hand, it dissociates immediately into adsorbed hydrogen and acetylene [17,18], which, upon heating, should dehydrogenate and follow the same dissociation path as pure acetylene or a very similar one.

We have therefore tried to produce C_xH_y species by adsorbing ethylene at room temperature and then flashing the sample at higher temperature (for instance 60 s at 383 K). After this treatment one expects to find C, CH_2, CH and CCH on the Ni(111) surface [14,15]. The energy loss spectrum obtained after this procedure is shown in fig. 1 (curve a). Apart from peaks originating from the C–H stretching and bending modes which could be due to CCH or CH [14,15], a loss around 160 meV can be seen. This structure could be due to a C–C stretching mode or to a CH_2 scissor mode [14]. In order to distinguish between these two possibilities we took a spectrum (not shown here) after the same heating procedure using deuterated ethylene as a starting product. The loss structures originating from the C–D stretching and bending modes are shifted with respect to those due to the hydrogen containing moieties as expected, but there is still a peak around 160 meV indicating the presence of a
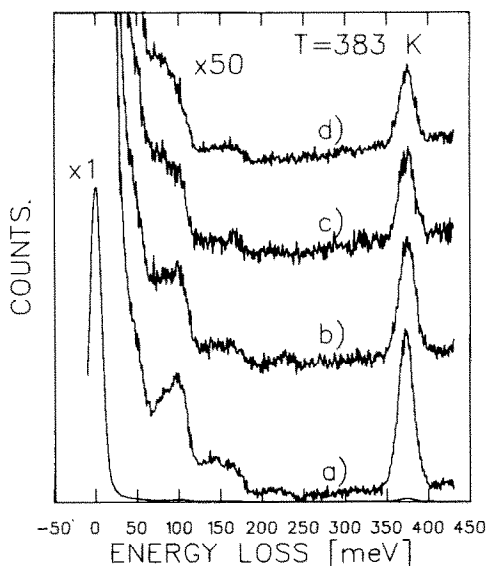
Fig. 1. HREELS spectra for 60 L exposure of ethylene to Ni(111) after heating at 383 K for 60 s (a), 150 s (b), 900 s (c), 1800 s (d). The primary energy was 5.1 eV and the spectra were taken 20° off specular. The peak at 225 meV is due to CO contamination.

moiety containing a C–C bond. We therefore think that both CH and CCH are present on the surface.

In order to measure quantitatively the kinetic parameters of the dissociation steps of these CH species, we proceeded as follows: after adsorbing ethylene at room temperature (typically 60 L), we heated the sample at a given prede- termined temperature, T, for a fixed amount of time and then cooled it back to room temperature (RT) in order to freeze the reaction during the data acquisition time of a complete HREEL spectrum. The sample was then cycled between RT and T varying the heating period and taking a spectrum after each cooling. Some of the spectra obtained during one of these "isothermal" dissociation reactions (at $T = 383$ K) are shown in fig. 1 for different total heating time. It is clearly seen that initially the three loss peaks decrease together with heating time.

To characterize the dissociation reaction, we have chosen to follow the intensity of the peak at 372 meV as a function of heating time since the bending mode at 95 meV sits on the tail of the carbon loss (C–M stretch) at 40 meV which would make the background subtraction procedure more difficult and uncertain. Since the CH stretch intensity does not change going away from the specular direction, while that of the electron–hole pair background decreases sharply, the spectra were taken at an angle of 20° from the specular direction in order to improve the signal to background ratio.
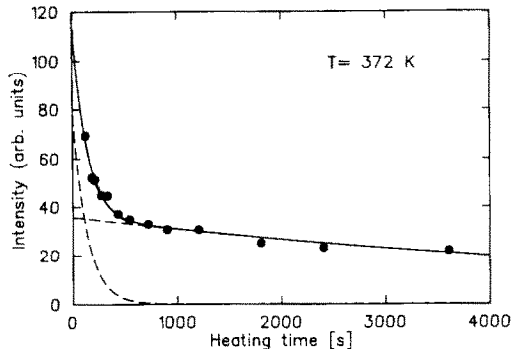
Fig. 2. Intensity of the CH stretching peak at 372 meV as a function of heating time at $T = 372$ K (dots). The continuous line shows the fit obtained by summing two exponential decays (dashed lines) [see eq. (2)].

Fig. 2 shows the intensity of the CH stretching peak versus total heating time (normalized to the incident beam intensity) at $T = 372$ K. As is well known, quantitative measurements are difficult with the HREELS technique since the relationship which links the peak intensity to the coverage is not always a linear one. In dipole scattering non-linearity may in fact be introduced by the coverage dependence of the electron beam reflectivity of the surface and by changes in the surface order [19]. Artefacts due to variations in reflectivity can be identified and corrected by repeating the measurements at different primary energies of the electron beam and normalizing the data to the elastic peak intensity. Non-linearity due to changes in surface order can be eliminated normalizing to the background [19].

Since in the case of the CH stretching mode the main scattering mechanism is impact scattering which does not involve an elastic reflection at the surface, these effects should be less severe if not negligible, also because the residual dipole scattering contribution was minimized by our scattering geometry. Furthermore the peak intensity is expected to depend linearly on the coverage θ if θ is small [19]. This should be true in our case where the CCH and CH coverages are estimated to be ≤ 0.1 monolayer (see TDS spectra below).

Nevertheless, we have made many checks by repeating the measurements at many different primary electron energies and by trying different normalization procedures, obtaining consistent results. We also checked for changes in the surface order looking at the LEED pattern after the first heating and at the end of a dissociation reaction, but found no appreciable changes.

The decay of the intensity, I, of the CH stretching peak shown in fig. 2 for $T = 372$ K, can be fitted by the sum of two exponentials:

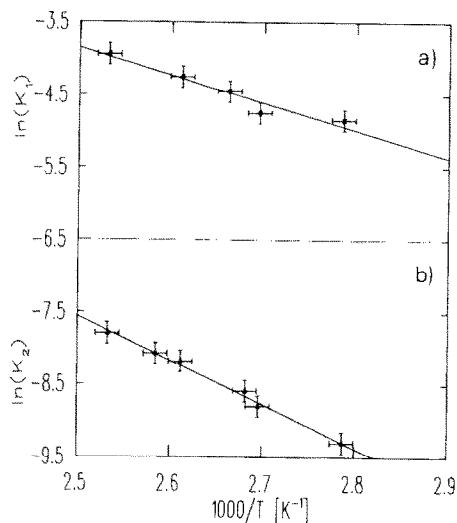$$I(t) = I_1 \exp(-K_1 t) + I_2 \exp(-K_2 t). \tag{2}$$

Fig. 3. Arrhenius plots of the CH species dissociation rates: (a) K_1 corresponding to the CCH dissociation, (b) K_2 corresponding to the CH dissociation.

This behaviour can be understood if we assume that two different first-order dissociation processes $(d\theta_i/dt = -K_i\theta_i, \; i = 1, 2)$ are taking place.

The dissociation reaction was repeated many times at several temperatures always using "isothermal" conditions. From each "isothermal" dissociation we evaluated the kinetic constants K_1 and K_2 through the fitting procedure explained before.

Figs. 3a and 3b show the temperature dependence of K_1 and K_2 which both follow an Arrhenius behaviour. A fit through the experimental points gives an activation energy of 8 ± 3 kcal/mol for the fast dissociation (K_1) and of 12 ± 3 kcal/mol for the slow dissociation (K_2). In both cases the resulting pre-exponential factor is of the order of $10^{3 \pm 1}$ s^{-1}.

The identification of K_1 with the CCH dissociation rate constant is suggested by the fact that we see the intensities of both CH peaks and the C–C peak decrease together upon heating as shown before. The CH moiety would then result as the more stable one on the Ni(111) surface, its dissociation being characterized by the rate constant K_2. This interpretation is supported by the literature since a similar dissociation path is seen on Ni(110) [15] and Ru(001) [20].

Regarding a theoretical evaluation of the activation energy for the CCH dissociation, we are not aware of anything published for Ni substrates but Kang and Anderson [21] found a value of 9 kcal/mol for CCH on Pt(111) in good agreement with our result.
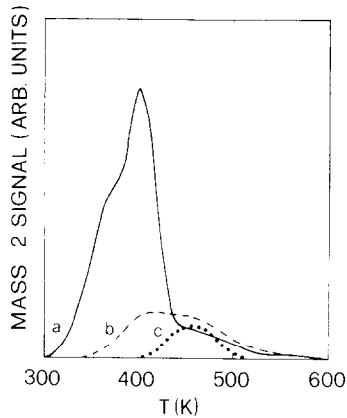
Fig. 4. Temperature programmed desorption after (a) 60 L exposure at 300 K, (b) 60 L exposure at 300 K and additional preheating up to 383 K, (c) thermal desorption spectrum calculated from our HREELS CCH dissociation parameters.

In order to obtain further insight into the dissociation steps (and more in general into the overall dissociation reaction of ethylene on Ni(111)), we have performed a number of thermal desorption spectroscopy (TDS) experiments by adsorbing C_2H_4 at room temperature and monitoring the H_2 evolution. The results are shown in fig. 4 (full line). The spectrum is dominated by two unresolved peaks at 370 and 400 K which are interpreted as originating from the hydrogen due to the initial ethylene to acetylene conversion and to acetylene dissociation respectively. At 470 K it is possible to distinguish a small bump which originates from the CCH dissociation. Finally a tail due to the CH dissociation extends to even higher temperatures. The dashed curve in fig. 4 shows the TDS spectrum after preheating at 383 K for 30 s. The feature at 470 K is more evident in this case.

In order to check the internal consistency of our experimental determinations, we have simulated with the computer the TDS spectrum which would be originated by the CCH and CH dissociation respectively (followed by hydrogen recombination and desorption), using the kinetic parameters we have obtained from the HREELS "isothermal" sets of data and the H desorption data of ref. [22]. The computed TDS for the CCH dissociation reported in fig. 4 (dotted curve) shows a peak at 470 K while the one for the CH dissociation (not drawn here) results in a peak around 550–600 K, in good agreement with the experimental TDS, giving convincing proof of the internal consistency of our data.

In conclusion, by using HREELS and thermal desorption spectroscopy, we have investigated in detail the dissociation path of ethylene on Ni(111) at high temperatures. On heating C_2H_4 absorbed on this Ni surface, ethylene dissoci-

ates into hydrogen and acetylene and then into CCH and CH species. We have measured in detail the dissociation kinetics of the CCH and CH species obtaining for the first time quantitative data for the pre-exponential factors and for the activation energies of the processes.

Acknowledgement

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