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SURFACE SCIENCE LETTERS

KINETICS OF THE C_2H_2 DISSOCIATION ON Ni(111): A HREELS STUDY

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The C_2H_2 isothermal dissociation rate 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 have obtained an activation energy of 1.2 ± 0.1 eV/molecule and a pre-exponential factor of $10^{14 \pm 1}$ s^{-1} for the first step of the C_2H_2 dissociation reaction.

The dissociation path of acetylene has been widely studied by many authors with the HREELS technique on different crystal faces of most of the transition metals (see for example refs. [1–5]). Generally these studies have identified the intermediate species formed during the process but have provided no quantitative information on the activation energies of the single steps. Such kinetic data are usually obtained from TDS measurements, which, however, cannot be used when the products of the dissociation do not evolve immediately into the gas phase. Furthermore, the pre-exponential factor is not extracted from the TDS data but is usually an input parameter to the fitting procedure [6].

HREELS studies have shown that acetylene adsorbs molecularly on Ni(111) at room temperature and dissociates into CH_2, CH and C upon heating to higher temperature [7]. The hydrogen evolution during the dissociation has been monitored through TDS but no kinetic data have been extracted on any of the single steps [8]. On the other hand, recently the interest in a quantitative determination of these data, also from a theoretical point of view has grown considerably, as shown for example by the work of Shustorovich and Bell [9].

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In the following we report on the determination of the activation energy and the pre-exponential factor of the first step of the C_2H_2 dissociation reaction on Ni(111), performed by monitoring the intensity of the CH stretching peak as a function of heating time at various temperatures. The power of the relatively novel application of the HREEL technique to the determination of the kinetics of surface reactions has been recently shown (see for example refs. [10–12]).

The experiments were performed in a previously described two stage UHV system [13] housing a commercial HREEL spectrometer (Leybold-Heraeus ELS 22) consisting of 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 cross section of CH stretching mode we choose to record our spectra at a resolution of typically 15 meV in order to increase the count rate. The primary energy was 5 eV, the incidence angle of the electrons 60° from the surface normal and the electrons were collected 10°, 20° and 25° off the specular direction towards the surface normal. No evidence for resonance effects on the cross sections of the loss processes was found, in agreement with Ibach and Lehwald [14].

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. Impurities in the sample were removed following standard procedures [13]. Contaminants were kept below 0.02 of a monolayer. The initial C_2H_2 coverage was chosen to be 0.25 monolayers (corresponding to a 2 L exposure at room temperature [15]) in order to maximize the HREEL signal of the CH stretching peak without having partially dissociated molecules already at 300 K [7]. Further measurements at different coverages are in progress.

Fig. 1 shows the HREEL spectra measured on Ni(111) exposed to 2 L of C_2H_2 at room temperature and heated to 352 K for different periods of time. During the data aquisition time the sample was cooled to room temperature which proved to be sufficient to freeze the dissociation reaction (typical heating and cooling times were about 20 s). The spectrum obtained immediately after exposure (fig. 1a) is in agreement with the one reported in the literature for molecularly adsorbed C_2H_2 in the impact scattering regime [14]. With increasing heating time the CH stretching peak decreases in intensity and shifts from 361 meV, characteristic energy for the molecularly adsorbed C_2H_2 to the equivalent energy for the dissociated CH containing radicals which amounts to 371 meV as reported in the literature [16]. Hence we have taken as a measure for the coverage of C_2H_2 molecules at each total heating time the area of the unresolved CH stretching peaks minus the area of the 371 meV peak, left after the completion of the first reaction step. These data, normalized to the incident electron flux, are represented in fig. 2 for three different
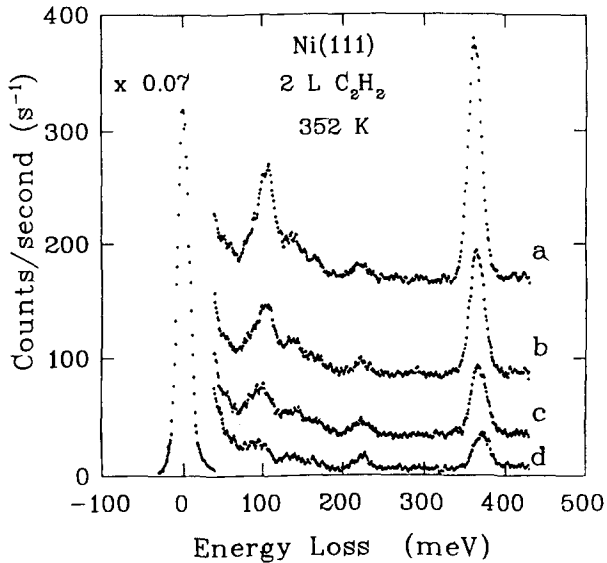
Fig. 1. HREELS spectra for 2 L exposure of acetylene to Ni(111) (a); after heating a 352 K for 40 s (b); 2 min (c); 13 min (d). The primary energy was 5 eV and the spectra were taken 25° off specular. The peak at 226 meV is due to very small CO contamination.

temperatures out of the many at which the dissociation was followed. The decay curves are well fitted by exponentials as one expects for a first-order kinetic process.
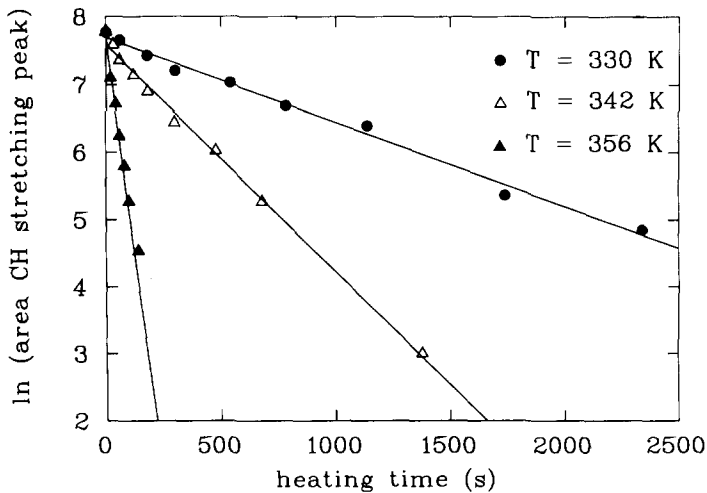

Fig. 2. Intensity of the CH stretching peak at 361 meV as a function of heating time at $T_1 = 330$ K, $T_2 = 342$ K and $T_3 = 356$ K. The data were taken 20° off specular.
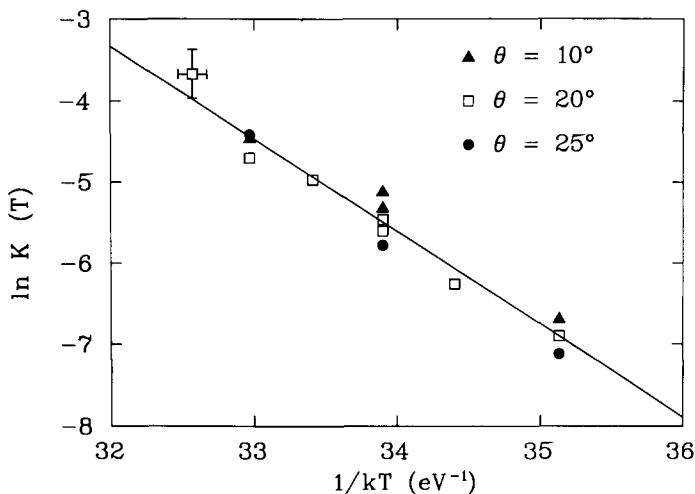
Fig. 3. Arrhenius plot of the C_2H_2 dissociation rate. $K(T)$ determined from spectra taken 25°, 20° and 10° off specular.

The slope of each curve gives the kinetic constant $K(T)$. We have recorded the spectra at 3 different scattering angles finding no dependence of $K(T)$ on the electron collection geometry. This result, together with the fact that the main scattering mechanism in our case is impact scattering, rules out the possibility that the measured scattering cross section is influenced by changes in surface order or in electron reflectivity and allows us to assume a linear relationship between the calculated area and the coverage of C_2H_2 molecules [13,17]. Changes of the work function with coverages should not affect our data, since no resonance effect was observed for the CH stretch intensity.

The $K(T)$ have also been evaluated by calculating the area of the 361 meV peak from a fit of the unresolved CH stretching peaks with two gaussians, obtained the same results.

Fig. 3 shows the temperature dependence of K, from which an activation energy for dissociation of 1.2 ± 0.1 eV/molecule and a pre-exponential factor K^0 of $10^{14 \pm 1}$ s^{-1} are obtained.

The species which form upon C_2H_2 dissociation involve moieties which contain CH and CC and/or CH_2 groups as evidenced by the vibrations at 100 and 371 meV (CH) and at 140–160 meV (CC and/or CH_2) [7]. The present study refers to coverage and temperature ranges different from those investigated by Demuth and Ibach [7]. At the high coverages of their study C_2H_2 is already partially dissociated at RT and, upon heating at 450 and 500 K, it decomposes in CH first and then in CH_2. When we decompose C_2D_2 the structure at 140–160 meV splits in two components, one at about 100 meV (corresponding to a CD_2 scissor mode), the other at about 150 meV (corre-

sponding to a C–C stretching mode). This finding suggests the presence of both CC and CH_2 (CD_2) radicals in the final products. These results are in good agreement with the theoretical calculations by Shustorovich and Bell [9]. According to these authors the dissociation path which has the lowest activation energy (about 1 eV/molecule) is the one corresponding to the formation of CH_2C species.

In conclusion by using HREELS we have measured the first step of the dissociation of acetylene on Ni(111) obtaining for the first time quantitative data for the pre-exponential and the activation energy of the process.

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