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Cyclopropyl Species on Cu(110): Area Selective Activation of Adsorbed Cyclopropane Using a Dispersion Compensation HREELS Spectrometer

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The combined electron impact activation of cyclopropane localized on a 0.02-cm^2 area of a Cu(110) surface and the subsequent vibrational analysis of the adsorbed cyclopropyl product were achieved using a high-throughput HREELS (high-resolution electron energy loss spectroscopy) spectrometer. The use of low-energy electrons to induce surface processes has been widely studied, principally in the context of electron-stimulated desorption.[1] More recently, attention has been focused on the use of electron impact as a means of directing chemistry,[2] or migration,[3] on surfaces. For example, Zhou et al.[4] have reported the preparation of vinyl and phenyl fragments on Ag(111) using 50-eV electrons emitted from the biased filament of a quadrupole mass spectrometer. Similarly, Koel et al. prepared cyclohexyl groups on Pt(111) through electron-induced CH bond breaking in condensed cyclohexane multilayers.[5] It is clear that electron-induced dissociation (EID) is an efficient way to prepare catalytically important adsorbed hydrocarbon fragments.[4,5] However, the mechanisms for EID show a dependence on the impact energy.[6] For example, by using very low energy electrons one can work below the threshold for dipolar dissociation (DD).[6,7] As a result, it may be possible to achieve better control of the induced chemistry by working with variable energy electron sources. Furthermore, electrons may easily be focused onto a small area of the surface thereby achieving area selective bond activation. Finally, electrons are ubiquitous probes or carriers of information in ultrahigh vacuum surface studies; hence the electron beam can also be used to analyze the irradiated spot. The latter three points are taken into account in the present study, which uses a dispersion compensation (DC) HREELS spectrometer both as a local tool to induce chemistry and as a probe of that chemistry. As described below, the activation and the analysis are done in two different operating modes of the spectrometer; hence it is not a simple autoscopic experiment. The combination of molecularly specific technique (HREELS) and the ability to perform area and energy (or possibly bond) selective activation of adsorbates constitutes a highly significant entry to a whole range of surface chemistry experiments related to reactivity and diffusion.

The DC-HREELS spectrometer consists of a hemispherical (SDA 180) electron monochromator and a hemispherical electron analyzer in tandem. These selectors are placed in a symmetrical geometry allowing the analyzer to compensate for the aberrations inherent to the monochromator.[8] Kevan et al.[9] have shown that the application of the dispersion compensation principle to the design of HREELS spectrometers greatly increases the electron current onto the sample while maintaining the desired high resolution. Conventional HREELS spectrometers typically deliver less than 1 nA to the sample.[9,10] Given that the cross section for EID is typically in the range 10^{-19}–10^{-16} cm^2,[4–6] this means that a HREELS spectrometer would not be an efficient tool for producing spectroscopically detectable amounts of adsorbed products of EID processes. However, since DC-HREELS systems involve current levels of up to 100 times higher, they do provide enough current at the target to do such experiments.

Two different modes of operation of the DC-HREELS spectrometer are used in the electron activation and vibrational analysis experiment. In the *monoenergetic electron gun mode*, the impact energy is selected within the range 1–20 eV and the resolution of the monochromator is degraded so as to get as much current to the sample as possible. Subsequently, about 2 min of retuning is required to return to the *high-resolution mode*, or HREELS mode, so as to perform surface vibrational analysis on the irradiated spot. Typical spectrometer settings and performances are as follows. In the HREELS mode, the pass energies of both selectors are set at 1.2 eV and a resolution of 6–8 meV is obtained. In the monoenergetic electron gun mode, the current measured at the sample is increased from 0.01 to 0.07 μA by degrading the resolution of the monochromator to a base width of 135 meV.[11] In both modes of operation, due to the imaging properties of the spectrometer, the electron beam impacts onto the same 0.02-cm^2 area of the Cu(110) surface.

A typical DC-HREELS spectrum obtained following a 1.6-L exposure to C_3H_6 at 90 K is shown in Figure 1a. The spectrum may be assigned to approximately a monolayer of physisorbed cyclopropane. Desorption from the physisorbed layer occurs at 120 K. The DC-HREELS and related TPD results are consistent with HREELS, TPD,[12] and ESDIAD[13] results for cyclopropane on Ru(001). Figure 1b displays a DC-HREELS spectrum of the irradiated area, taken after dosing the surface with 1.1 × 10^{17} e cm^{-2} at 10 eV. Three new vibrational modes at 2830, 979, and 401 cm^{-1} appear and grow in intensity with increasing irradiation time. The growth of these features is accompanied by a decrease in the intensity of those associated with molecular c-C_3H_6. Furthermore, displacement of the sample using an XY manipulator, so that a new 0.02-cm^2 area is probed, reveals essentially the same spectrum as Figure 1a. This indicates that the modification is localized within the area irradiated by the electron beam. The differences between spectra 1a and 1b clearly show that a new surface species is present following electron bombardment. By a brief heating of the sample to 145 K, the nonactivated C_3H_6 is removed from the surface, isolating the DC-HREELS spectrum of the new species, as shown in Figure 1c. The active modes of this new species are listed in Table 1 for comparison with those for physisorbed C_3H_6. The mode at 401 cm^{-1} is primary evidence for the formation of a carbon–metal bond as adsorbed alkyl species on copper display metal–carbon stretching frequencies in the neighborhood of 400 cm^{-1}.[14] Futhermore, the observed CH stretching mode at 2820 cm^{-1} is consistent with the softening expected for an α-CH stretching mode of a chemisorbed alkyl

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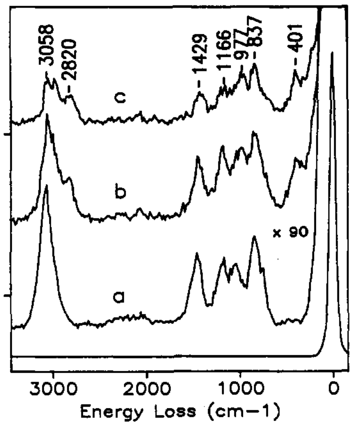

Figure 1. Specular high-resolution EELS spectra for condensed and electron-irradiated cyclopropane on a Cu(110) surface. (a) Spectrum of condensed cyclopropane, 1.6-L exposure at 90 K, taken at an impact energy of 6.1 eV. (b) Spectrum taken following electron bombardment at 10 eV for 2 h. The current on the irradiated area (0.02 cm^2) was 0.07 μA. (c) Spectrum of the same area following annealing to 145 K to desorb cyclpropane.

Table 1

	vibrational frequency (cm^{-1})		
mode	C$_3$H$_6$, 1.6 L[a]	C$_3$H$_6$ + electrons[b]	145 K[c]
CH stretch	3075	3055	3058 2978
α CH stretch		2830	2820
CH$_2$ scissor	1461	1446	1429
ring breathing	1186	1183	1166
CH$_2$ wag	1052	979	977
sym ring deformation	843	842	837
CH$_2$ rock	752		
C–Cu stretch		400	401

[a] Spectrum 1a. [b] Spectrum 1b taken after 1.1 × 10^{17} e cm^{-2} at 10 eV on a 0.02-cm^2 spot. [c] Spectrum 1c.

species.[15] By comparison with the spectrum of physisorbed C$_3$H$_6$ the spectrum of the new species reveals the presence of a ring breathing mode at 1166 cm^{-1} and ring deformation mode at 837 cm^{-1}. The persistence of these modes indicates that electron impact induced ring opening does not occur, at least for impact energies of 10 eV. This leads to the conclusion that the predominant species giving rise to spectrum 1c is adsorbed cyclopropyl. From the work of Bent et al.,[15] the softened α C–H stretching mode for a linear alkyl chemisorbed on Cu(111) appears at around 2740 cm^{-1}. This is almost 100 cm^{-1} lower than the soft mode found here. However, the difference can be explained by comparing the C–H bond strength of cyclopropane with that of linear alkanes. A larger p character in the cyclopropane C–C bonds induces a larger s character in the C–H bonds[16] and results in higher CH stretching frequencies. The observed frequency of 2820 cm^{-1} for the soft mode is thus further proof that the chemisorbed product of the EID process is a cyclopropyl species rather than a linear alkyl.

Measurements as a function of electron impact energy in the range below 20 eV[17] show that the cross section for EID of cyclopropane on Cu(110) peaks at around 10 eV and decreases rapidly below and above this maximum. However, the cross section rises again for impact energies of 18 eV or above.[17] These observations are interpreted as evidence for a dissociative electron attachment (DEA) mechanism at 10 eV. Evidence for such a mechanism has been observed previously by Sanche et al. in the case of multilayers of linear alkanes condensed on a Pt substrate.[18,19] Using a mass spectrometer they measured hydride ion production as a function of electron impact energy and observed a resonance with a FWHM of ≃3 eV centered at 10 eV. This resonance arises through electron capture to form a transient anion.[6,20,21] The resonant state dissociates by homolytic CH bond breaking yielding a hydride anion and a radical alkyl species. Our results are consistent with the formation of a cyclopropyl radical and its reaction with the copper surface to form a carbon–metal bond. The energy dependence of the excitation cross section, in particular the decrease at energies immediately above the 10-eV resonance, suggests that secondary electrons do not play a dominant role in the CH bond breaking process. A detailed discussion of the activation mechanisms and an estimation of the cross sections will be presented elsewhere.[17]

The present experiment adds several important new elements to the study of electron-induced phenomena at surfaces. First, the ability to vary the electron impact energy and to subsequently analyze the surface species provides a powerful means for the elucidation of the excitation mechanisms involved. Second, the ability to vary the impact energy holds the promise of bond selective activation. Finally, the experiment permits the low-temperature preparation of a well-defined species in a localized region of the surface. With respect to the latter point, we report the first observation of an adsorbed cyclopropyl species.

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