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HREELS CHARACTERIZATION OF THE ROOM TEMPERATURE PHASE OF PROPENE ADSORBED ON RUTHENIUM (001)

Dezheng WANG, Yongxue LI, Haiyang LIU, Runsheng ZHAI and Xiexian GUO

Laboratory for Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian, China

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Room temperature adsorption of propene on ruthenium (001) was studied by HREELS and UPS. Adsorption was mainly dissociative, with cleavage of both C-H and C-C bonds, and resulted in a mixture of surface species: naked carbon atoms, CH fragments, metal carbynes, ethylidyne, di-σ adsorbed alkene, and π-adsorbed alkene in order of their relative abundance.

Much work in recent years has described the electron energy loss spectroscopy (EELS) of ethene adsorbed on various single crystal faces of transition metals, and their interpretation in terms of the adsorbed species [1,2]. With particular reference to ruthenium (001), di-σ adsorbed species has been observed at low temperatures [3–5]. π-adsorbed ethene was seen on an oxidised surface [3]. Ethylidyne [3], and a mixture of ethylidyne and acetylide [4], was seen after flashing to room temperature and quenching. One type of CH species, deduced to be sp^2 hybridized with the C-H bond inclined to the surface normal, was seen after flashing to 450 K and quenching [3] though Hills et al. [4] assigned similar looking spectra taken under similar conditions to acetylide and methylidyne. A different type of CH species, deduced to be methylidyne, was seen after hydrogenation of surface carbon or hydrogenolysis of ethene [3]. The adsorption of propene has been less extensively studied. The works that have been done on it [2,6] suggest that the chemistry is essentially similar, i.e., adsorption as a di-σ adsorbed complex at low temperatures that transforms into propylidyne and then CH fragments with increasing temperature. The propene derived surface species are thermally a bit less stable than the ethane derived species, by ca. 50 K.

Somorjai and co-workers have noted an emerging correlation between position in the periodic table and the adsorptive chemistry with respect to alkenes. The room temperature phase on platinum and rhodium is known to be alkylidyne whereas on iron and tungsten, extensive bond breaking occurs [2].

The position of ruthenium is intermediate between these two groupings while its adsorptive chemistry, taking the stable room temperature phase as the char-

acterization of the adsorptive chemistry, is somewhat ambiguous. Barteau et al. [3], using HREELS, reported that adsorption of ethene at 170 K with subsequent heating gives an ethylidene phase that is stable to 310 K. This decomposes slowly from 320 K to 550 K. In this case ruthenium behaves like rhodium and should be grouped with that grouping, rhodium and platinum, with a stable room temperature phase. Hills et al. [4], using a similar experimental technique, reported a room temperature phase that is a mixture of ethylidyne and acetylide which decompose at ca. 360 K to give carbon atoms and methylidyne respectively. In this case, ruthenium can still be considered rhodium-like albeit with more activity for dissociation. Lauderback and Delgass [7], using SIMS, reported that adsorption of ethene at 323 K results in dissociation to a carbon layer. It can be conjectured that adsorption of ethene at room temperature, even if it gives a stable alkylidine phase, it is likely to give a phase that is on the verge of decomposition, and thus does not give an accurate characterization of the adsorptive chemistry. We report here a characterization of the room temperature phase from the adsorption of propene, which is expected to give slightly less stable surface species, and suggest that ruthenium should be grouped with iron in the grouping with the room temperature phase composed of extensively cleaved fragments.

By now EEL spectra have been sufficiently well analyzed to allow us to go beyond the need to stay within the bounds of the conditions for unique surface species. We were interested in an adsorption study at room temperature because the adspecies formed are more closely related to the surface state under reaction conditions. The spectra from this adsurface are rather complex and in our interpretation we assume that they result from a mixture of known surface species already identified through previous spectroscopic experiments [1–6] on the adsorption of ethene and propene. This assumption allows us to make use of previous EEL spectra of identified adsorbed species by the breakdown of our spectra as a superimposition of the spectra of those identified species. This incorporates the assumption that no new surface species or dissociated fragments are formed.

The EEL spectra were recorded using a Leybold-Heraeus ELS 22 spectrometer housed in a Leybold-Heraeus u.h.v. stainless steel chamber with a base pressure of 1×10^{-10} mbar. Spectra were recorded in specular reflection at an angle of 60° to the surface normal. The spectrometer was operated at 5 eV primary energy with a resolution of 80 cm^{-1} and count rates of 10^5 cps. UPS spectra were recorded with a Leybold-Heraeus He I resonance discharge lamp and a hemispherical electrostatic analyzer operated for 5×10^4 counts per second in the constant resolution mode. The photon flux was incident at an angle of 45° to the sample normal and the photoelectrons were analyzed normal to the sample. The peak positions are referenced to the Fermi level. Difference spectra were obtained by direct subtraction; after alignment of the Fermi levels, of curves taken under identical conditions of light intensity and crystal position. The chamber is also

equipped with LEED (Varian), Auger spectroscopy, and a Q 200 quadrupole mass spectrometer. Gas purity was verified with the mass spectrometer prior to use. Gases were exposed with the sample at room temperature (300 K). All exposures of gases were achieved by backfilling the chamber via a leak valve and using the readings of the supplied ion gauges.

The ruthenium (001) sample used was presented by Professor K. Wandelt of the Fritz Haber Institute in Berlin. This was cleaned in u.h.v. by cycles of heating to 900 K in 2×10^{-7} mbar oxygen and annealing in vacuum at 1200 K for 2 minutes. The final period of cleaning in oxygen and annealing was followed by reduction in 2×10^{-7} mbar of deuterium at 900 K and heating in vacuum at 900 K to desorb the deuterium. The final cycle of heating in oxygen, deuterium and annealing was repeated prior to each set of experiments. The Auger spectrum was identical to that reported in the AES Handbook [8] and the clean surface exhibited a sharp (1×1) LEED pattern. The clean surface was also evidenced by a clean EEL spectrum and a similarity in physicochemical behaviour for adsorption of CO and oxygen between this sample and many reports in the literature [9]. Temperatures were measured with a Pt-Pt/Rh thermocouple spotwelded to the side of the crystal.

Figure 1 shows the EEL spectra for various exposures of propene to the clean ruthenium surface. The spectra have been normalized to constant elastic peak intensity. The prominent feature is an intense peak that shifts from 570 cm^{-1} to 490 cm^{-1} with increased exposure. There are two possibilities for the assignment of this peak, namely, a metal-oxygen or a metal-carbon stretch. We reject a metal-oxygen assignment because we did not detect any oxygen contamination in the vacuum system on the mass spectrometer. Furthermore, this peak exhibits a frequency shift to lower frequency with increasing coverage and disappears above 650 K (cf. fig. 2(a)), effects which are not consistent with those of adsorbed oxygen [9,10]. By elimination of a metal-oxygen assignment, this peak in the 500 cm^{-1} region is then assigned to a metal-carbon stretch; to be more specific, a metal-naked carbon atom stretch because the spectra show only very weak features in the range where C-C features (1300 cm^{-1}–1500 cm^{-1}) are expected. Furthermore, the C-H stretch, being relatively very weak, is unlikely to be associated with the ca. 500 cm^{-1} peak. These are attributed to a small amount of coadsorbed hydrocarbon species. The intensity of the ca. 500 cm^{-1} peak, comparable to that of a metal-CO stretch, suggests that it is due to the dipolar mechanism, perhaps the more likely loss mechanism with a naked carbon atom.

An intense metal atom-carbon atom peak had been reported in two other instances, from CO on tungsten [11] and ethene on iron [12]. Ibach and co-workers have also assigned a peak at 550 cm^{-1} [13a] and a peak at 520 cm^{-1} [13b] on a stepped nickel surface to a naked carbon atom-metal atom stretch, though we should note that the peak on the stepped surface is not as intense. However, this is not a commonly seen peak and we conjecture that this is because carbon atoms tend to polymerize at high temperatures to give a form of carbon which gives only

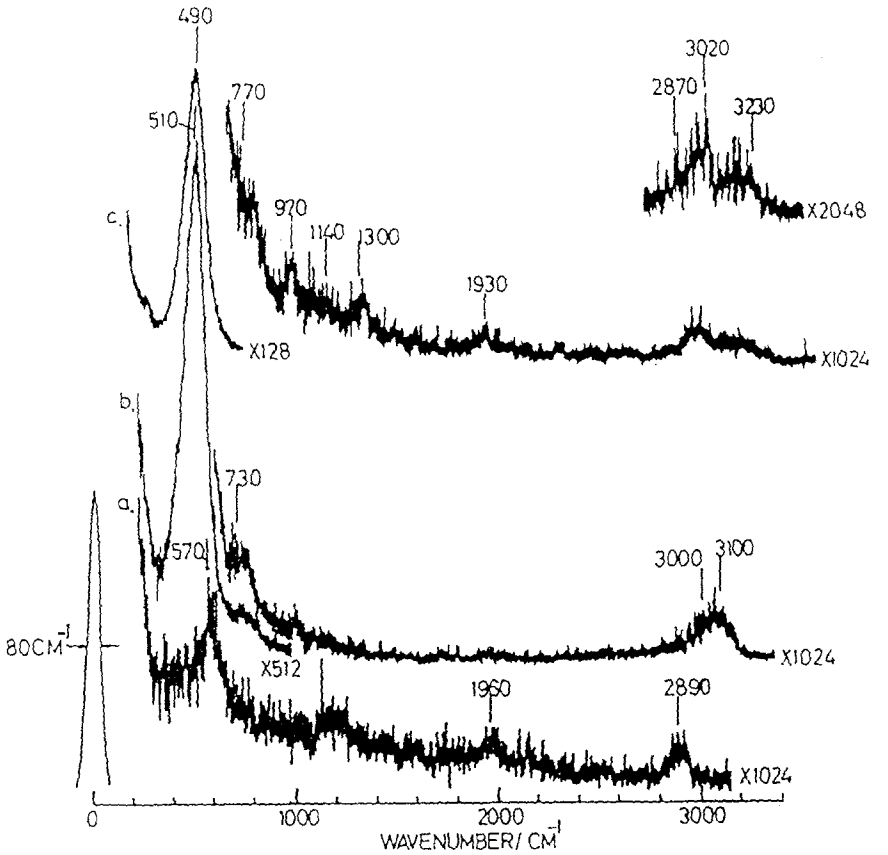

Fig. 1. EEL spectra of a room temperature adsorption of propene on ruthenium (001). The different spectra correspond to different exposures of propene as indicated: (a) 0.5 L, (b) 3 L, (c) 12 L.

very weak vibrational features (cf. fig. 2(a)), and situations with complete dissociation to carbon atoms at low temperatures are not common.

If the metal-carbon atom assignment is accepted, one thus also accepts that ruthenium is rather stronger in its adsorption behaviour than we had believed, though this is consistent with the report by Lauderback and Delgass [7] from SIMS observations of the dissociation of ethene at 323 K. The dissociative adsorption of propene to give naked carbon atoms is not likely to have been due to the "accidental" presence of steps since this surface does not exhibit a similar dissociative adsorption of carbon monoxide.

The other salient point about fig. 1 is the development of a peak at 3230 cm^{-1} with increased exposure of the surface to propene. Peaks in this frequency range are associated with C-H stretch. However, this frequency is rather higher than the C-H frequencies of those hydrocarbon spectra where adsorption results in sp^3 or sp^2 hybridization. This indicates a different kind of CH species, though we note that Ibach and co-workers [14] have assigned a rather high frequency, 3100 cm^{-1},

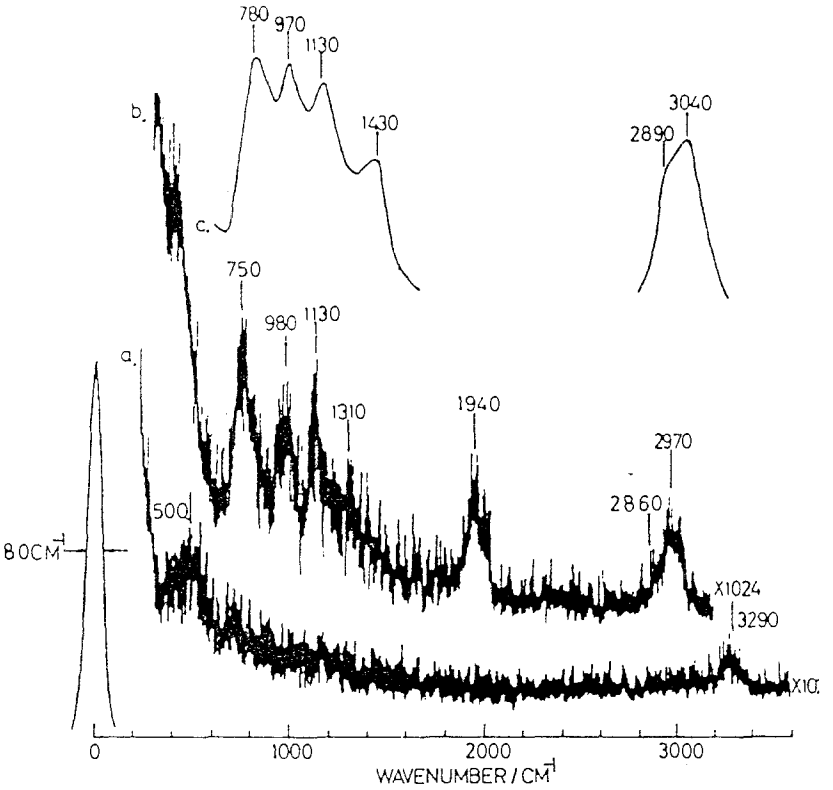

Fig. 2. EEL spectra of hydrocarbon species and fragments on ruthenium (001). (a) The surface from fig. 1(c) after heating at 650 K for 2 min. (b) 7 L exposure of propene to a surface that had been saturated with propene and then heated to 1100 K. (c) A simulated spectrum from the superimposition of spectra, simulated from the data of Barteau et al. [3], of (i) sp^2 CH fragments, (ii) ethylidyne, (iii) di-σ adsorbed alkene and (iv) π-adsorbed alkene with the weighting 10 : 2 : 2 : 1.

to a sp^2 CH species, attributing the high frequency to the simultaneous presence of carbon atoms. In this work, we shall associate sp^2 species with frequencies around 3000 cm^{-1}. We thus assign the 3230 cm^{-1} frequency to a different species; to a sp hybridized species based on the fact that the characteristic frequencies of sp hybridized species are reported as around 3300 cm^{-1} [15]. More specifically, we assign the peak to a metal carbyne because there was no corresponding development in the C-C region with the appearance of this peak. It is interesting that this species is stable to 650 K (cf. fig. 2(a)).

Figure 1(c) also shows some weak features that are due to adsorbed hydrocarbon that had not been completely dissociated. The resolution of the spectrum is not very good and for its interpretation, we assume that these weak features of this spectrum is the same as the features in the same frequency range in the spectrum from propene adsorbed on a graphitized surface (cf. fig. 2(b)). We assume that differences in peak frequencies between fig. 1(c) and fig. 2(b) are due to inadequate resolution, and differences in relative intensities of the peaks reflect

differing amounts of the different species present rather than a qualitative difference in the molecular structure of the hydrocarbon species.

Figure 2 shows EEL spectra, normalized to constant elastic peak, resulting from heating the surface with adsorbed propene of fig. 1 to 1100 K, and subsequent adsorption of propene, at room temperature, on this surface. We assume that the surface after heating to 1100 K is a graphitized surface and that adsorption occurs on those, presumably, weak metal sites that are produced, i.e., heating rearranges the carbon atoms to a more dense phase to produce some clean ruthenium atoms [7].

The main elements of fig. 2(b) are peaks at 750 cm^{-1}, 980 cm^{-1}, 1130 cm^{-1}, 1310 cm^{-1}, and a C-H stretch at 2970 cm^{-1} with a wing on the low energy side at 2860 cm^{-1}. The width of some of the peaks suggests that each of them is composed of many peaks. This implies that these peaks are made up from contributions from a number of surface species (rather than being the different modes of a single species). This belief is supported by the observations that these peaks do not always appear with the same relative intensities, and that they exhibit different stabilities: the peak at 750 cm^{-1} is stable to 570 K, the peak at 980 cm^{-1} is stable to 420 K, and the peaks at 1130 cm^{-1} and 1310 cm^{-1} are stable to 520 K. It is interesting to note that the corresponding species which we will assign to alkylidyne, di-σ adsorbed alkene, and π-adsorbed alkene are more stable on the "weak sites" here than their corresponding counterparts on clean platinum and rhodium.

In our reasoning for the identification of surface species present, we assume that the C-H peak having a wing at the low energy side is evidence of a sp^2 hybridized species with the wing representing a sp^3 hybridized species in conformity with their frequencies at 2970 cm^{-1} and 2860 cm^{-1}, We identify the species giving rise to the 750 cm^{-1} peak as the CH species, proposed by Demuth and Ibach [16], that is sp^2 hybridized with the C-H bond bent with respect to the surface normal since the spectrum of this shows a strong peak in the 750 cm^{-1} range [3,6,16]. A strong peak in the 750 cm^{-1} range can also come about from acetylide [4,17] though we disfavor this assignment because it requires a 1310 cm^{-1} peak with the same thermal stability. A comparison of the relative intensity of this peak with the C-H peak at 2970 cm^{-1} suggests that this species does not totally account for the fairly strong sp^2 C-H intensity observed. There must then be another type of sp^2 species, which implies a π-adsorbed species, and a comparison with typical π-adsorbed spectra suggests that the 980 cm^{-1} peak is due to this species. This leaves the peaks at 1130 cm^{-1}, 1310 cm^{-1} and a small C-H stretch at 2860 cm^{-1}. These may be due to the same species or two different species. The relative intensity of the fairly strong peak at 1130 cm^{-1} as compared to the 1310 cm^{-1} peak argues in favor of a mixture of d-σ adsorbed species and ethylidyne species. Surprisingly, there is possibly no propylidyne since this should give a C-C stretch of the ethyl group which would be expected to be fairly strong at 950 cm^{-1} [6] with the same thermal stability as the 1130 cm^{-1} and 1310 cm^{-1}

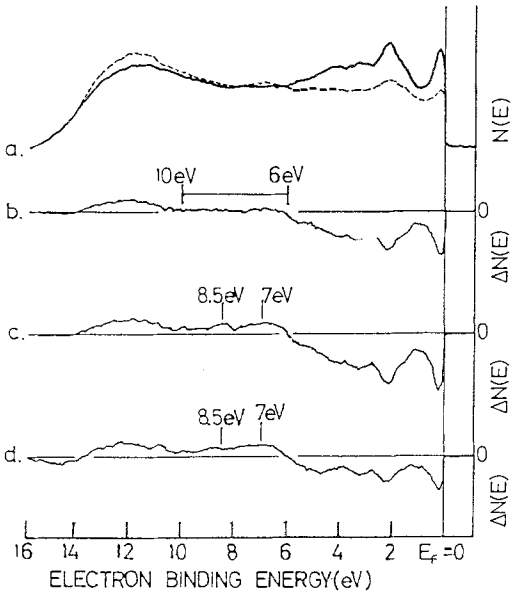

Fig. 3. He I UPS spectra of a room temperature adsorption of propene on ruthenium (001). (a) Clean surface (solid line) and after an exposure of 1 L propene (dashed line). The difference spectrum is shown in (b). (c) The difference spectrum due to a 3.5 L exposure of propene. (d) The difference spectrum due to a 2 L exposure of propene to a graphitized surface.

peaks. It is somewhat surprising that the alkylidyne species likely to be seen on the basis of EEL spectroscopic experiments via heating to room temperature and quenching [3,4] is indeed present as a minor species. It is possible that raising the temperature from a low temperature may steer the reaction pathway to the formation of more stable intermediates like the acetylide [4], and thus inhibit extensive fragmentation.

Thus, the hydrocarbon species present on the surface of fig. 2(b) (and fig. 1(c)) are deduced as a CH species (sp^2 hybridized), an ethylidyne, a di-σ adsorbed species, and a π-adsorbed species in order of their relative amounts. A simulated spectrum from the superimposition of spectra, simulated from the data of Barteau et al. [3], of (i)sp^2 CH fragments, (ii)ethylidyne, (iii)di-σ adsorbed alkene and (iv)π-adsorbed alkene with the weighting 10 : 2 : 2 : 1 respectively is shown in fig. 2(c). The weighting is only qualitative since we cannot correlate EELS intensity with surface concentration.

The spectra in fig. 3 show complementary UPS data in support of the HREELS characterization of the species present on the surface. Figure 3(a) shows the He I 21.2 eV UPS spectra for clean ruthenium (001) (solid line) and after a 1 L exposure to propene (dash line), both at room temperature. The difference in emission between the adsorbate covered surface and the clean surface is shown in fig. 3(b). Figure 3(c) shows a similar difference spectrum after a 3.5 L exposure to

propene. Higher exposures did not result in any discernible changes in the UPS difference spectra. There is a 0.2 eV decrease in the work function of the adsorbate covered surface relative to the clean surface. Figure 3(d) shows the difference spectrum due to a 2 L exposure of propene to a graphitized surface produced by heating a saturation propene exposure to 1100 K.

The dominant feature of the difference spectrum after a 1 L exposure to propene, fig. 3(b), is a strong adsorbate-induced attenuation in the d band region from the Fermi edge to 6 eV which is clear evidence of the presence of adsorbates. This spectrum is most notable for the absence of peaks due to molecular orbitals of species with C-C bonds which, based on UPS data and analysis from the adsorption of ethene and acetylene on various metals [18–23], would be expected in the region 6 to 10 eV, while even more peaks are expected in the case of species with a C-C-C skeleton by inference from the spectrum of gaseous propene [24]. This difference spectrum thus supports the HREELS assignments that the main species on the surface in the first stage of the adsorption of propene are species with single carbon atoms. The UPS data, because of the strong ruthenium (001) d band features from the Fermi edge to 5 eV which cannot be easily disentangled, do not allow any statement to be made on which of the many possible species this/these single carbon atom species may be. That the UPS spectrum of adsorbed carbon atoms is a broad and featureless band with strong attenuation and changes in the d band region is consistent with the work of Brucker and Rhodin [20] and Demuth [23]. AES analysis of the surface after this series of experiments shows the absence of any adatoms other than carbon, and probably hydrogen. We point out here that our count rates of 5×10^4 cps are sufficient for the observation of the molecular orbitals of C-C species should they be present, since we have no trouble observing CO and O orbitals in other experiments, and the d band features of ruthenium (001) are clearly seen and are in good agreement with those reported by Fuggle et al. [25].

The distinctive feature of figs. 3(c) and 3(d) is the appearance of small peaks at 8.5 and 7 eV in addition to the features of fig. 3(b), while there is a difference between fig. 3(c) and fig. 3(d) in a smaller change in the d band region in fig. 3(d). The peaks at 8.5 and 7 eV can be interpreted as collateral evidence for the HREELS assignments for fig. 1(c) and fig. 2(b). They can be viewed as the ionization features of CH species as suggested by Brucker and Rhodin [20] and Demuth [22]. Alternatively, one can suppose that these peaks correspond to the σ orbitals of species with a C-C skeleton with the other peaks being not visible since they are less intense and there are features from other surface species in the region where they are expected, or both cases are true, as suggested by our HREELS assignments. The smaller change in the d band region on the graphitized surface can be interpreted as the presence of a smaller amount of adsorbates and/or the absence of species causing a large change in the d band region. Thus, the UPS data of fig. 3, while not interpretable in terms of distinct surface species, is consistent with the HREELS assignments.

In summary, the room temperature adsorption of propene shows that a variety of sites that are qualitatively different exist, even on a flat HCP (001) surface. These sites give the following species: (1) complete dissociation to naked carbon atoms, (2) dissociation to CH fragments, (3) dissociation to metal carbynes, (4) ethylidyne, (5) di-σ adsorbed species, and (6) π-adsorbed species. This adsorptive chemistry is like that of iron [12].

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