Low Temperature Infrared Spectra of Ethylene Adsorbed on Alumina-supported Platinum and Palladium

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Summary Infrared spectra of π-bonded ethylene on Pt and Pd surfaces observed at low temperature revealed an interesting difference in the metal–ethylene bonding.

π-BONDED olefinic species adsorbed on transition-metal surfaces are considered to be intermediates for hydrogenation or deuterium exchange reactions. Sheppard and his colleagues recently showed the presence of π-bonded ethylenic species on Pd or Pt on the basis of the i.r. difference spectra of adsorbed species before and after hydrogenation at room temperature.[1]

Measurements on a highly dispersed metal surface at low temperature have now shown that: (i) the i.r. spectra of π-bonded ethylene could be observed easily not only in the CH stretching region but also in the C=C stretching region, which is important in clarifying the detailed interaction of the ethylene π-orbital with metal surface and in distinguishing between π-bonded and the σ-bonded species; (ii) the spectrum of π-bonded ethylene on Pt was reproducible whereas difficulty in observing reproducible spectra has been reported.[1]

Ethylene or [$^2H_4$]ethylene was adsorbed on Al_2O_3 (Degussa)—supported Pt and Pd at low temperature (−86 °C), using a cryogenic cell similar to the one used by Avery.[2] Ethylene was chemisorbed on the sample for 30 min at −86 °C, evacuated to 10^{-3} Torr, and then argon was

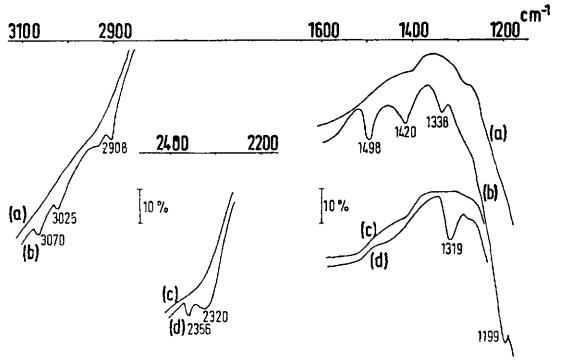

FIGURE. I.r. spectra of ethylene adsorbed on alumina-supported platinum at −86 °C. (a) Background spectrum of spectrum (b). (b) Spectrum of C_2H_4 chemisorbed on Pt. (c) Background spectrum of spectrum (d). The catalyst was reduced by deuterium. (d) Spectrum of C_2D_4 chemisorbed on Pt.

introduced to maintain the cell temperature in the i.r. beam. In this procedure physically adsorbed ethylene with absorption bands at 1610, 1440, and 1340 cm^{-1} was removed.

The Figure shows the spectra of ethylene chemisorbed on $Pt–Al_2O_3$ at −86 °C. In the lower frequency region, co-ordinated C=C stretching bands were observed at 1498 cm^{-1} for C_2H_4 (and 1319 cm^{-1} for C_2D_4), as well as a CH_2 scissors mode at 1420 cm^{-1} and another CH_2 scissors mode at 1199 cm^{-1}. The frequencies of the bands were slightly lower than those of Zeise's salt, where the corresponding bands were observed at 1515, 1353, 1426, and 1243 cm^{-1}.[3] According to vibrational analysis of Zeise's salt and analogous compounds,[4] the lower frequency CH_2 scissors vibration is strongly coupled with the C=C double-bond stretching vibration. In the case of Zeise's salt the band at 1243 cm^{-1} involves much C=C stretching character. On the other hand with C_2D_4-Zeise's salt, the band at 1353 cm^{-1} consists mainly of C=C stretching vibration, so the frequency directly reflects the strength of bonding interaction between ethylene and Pt.

Also, a band was observed at 1338 cm^{-1} in C_2H_4 adsorption the intensity of which changed with the experimental conditions. When the spectra were measured without argon in the cell allowing the catalyst to warm up gradually in the i.r. beam, the intensity of the band at 1338 cm^{-1} increased with time. Also, in the CH stretching region the bands at *ca.* 2940 and 2880 cm^{-1} increased in intensity. Hence, the band at 1338 cm^{-1} could be attributed to the CH deformation vibration of the σ-bonded species.

On $Pd–Al_2O_3$, co-ordinated C=C stretching bands were observed at 1515 cm^{-1} for C_2H_4 and 1430 cm^{-1} for C_2D_4. A CH_2 scissors band was observed at 1430 cm^{-1}, and a sharp band was observed at 1325 cm^{-1}, which may be attributed to the σ-bonded species. In comparison with the results for C_2H_4 adsorption on $Pd–SiO_2$ by Sheppard,[1] no effect on the C=C stretching band frequency was observed with a change in suppport.

It is interesting to note that the % changes in the frequencies of the C=C stretching bands from that of free C_2D_4 were 6·3% for Pd and 12·9% for Pt, which suggest a considerable difference in the strength of the π-adsorption of ethylene on those metals.

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