Infrared Spectroscopic Evidence for π-Complex Formation from Ethylene Chemisorbed on Palladium and Platinum

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Summary I.r. absorption bands near 1500 and 3000 cm^{-1} indicate the presence of π-bonded species from ethylene chemisorbed on silica-supported Pd and Pt catalysts; these co-exist with σ-bonded M-CH_2CH_2-M species but are more readily removed than the latter by hydrogen.

Previously published i.r. spectra from ethylene chemisorbed by 'hydrogen-covered' silica-supported metals have been interpreted in terms of the presence of the σ-bonded associatively adsorbed species M-CH_2CH_2-M (M = surface metal atom).[1] On Pt the strongest absorption band at 2885 cm^{-1} and a weaker companion at 2800 cm^{-1} have been assigned to this species. This type of spectrum has been observed at room temperature on Pt,[1] Pd,[2] Rh,[3] and at −78 °C on Ni.[1] Weaker bands have been assigned to dissociatively adsorbed species.

Some years ago Kemball and his colleagues[4] postulated that π-complexes are intermediates in heterogeneously catalysed exchange reactions involving hydrocarbons and deuterium on metals. Later Bond[5] revived these ideas in the context of the similarity between homogeneous and heterogeneous catalytic activities of transition-metal catalysts and discussed explicitly hydrogenation reactions of olefins. However at that time,[6] and also to date, no i.r. spectroscopic evidence has been forthcoming for π-bonded species from ethylenes on metal surfaces although σ-bonded species are well characterised by this means.[1,6]

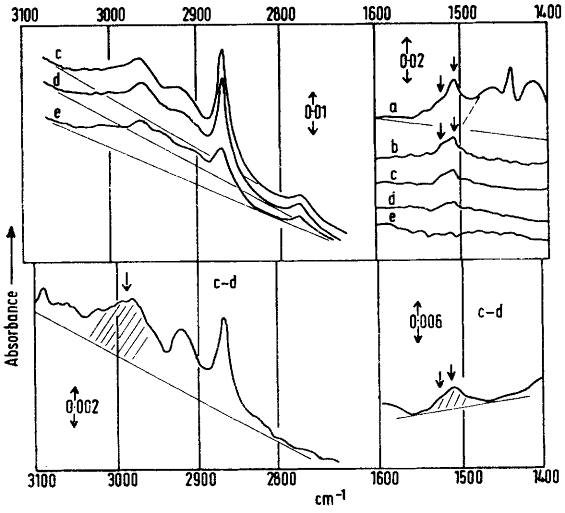

Figure. I.r. spectra of the species from the chemisorption of ethylene on silica-supported palladium: (a) in the presence of 10 Torr of ethylene; (b) after evacuation of ethylene for 5 min; (c) after further standing for 2 h; (d) after contact with 1·2 × 10^{-3} Torr of H_2 for 10 min; (e) after contact with 4·0 × 10^{-3} Torr of H_2 for 1 h; (c) — (d) the difference between the spectra (c) and (d). All spectra are expressed in absorbance units; note the different scales in different parts of the Figure.

The most definitive i.r. band for a π-bonded ethylenic species that would be accessible in the mid-i.r. region with silica-supported metals (4000—1300 cm^{-1}) is an absorption near 1500 cm^{-1}. Such absorptions are well known from the spectra of many π-bonded transition-metal compounds of known structure. They involve in part vibrations of the complexed C=C bond.[7]

In the course of repeating and extending earlier i.r. work on ethylene on Pt,[1] a somewhat 'different-from-normal' spectrum was obtained in the ν(CH) bond stretching region (3100—2800 cm^{-1}) from a Pt sample that had undergone multiple hydrocarbon and CO adsorptions, followed by regeneration by hydrogen reduction. Strong bands from the σ-bonded species were still present, but (a) an additional absorption occurred at 2955 cm^{-1}, (b) a band previously observed near 2930 cm^{-1} was shifted to 2920 cm^{-1} and (c) the single absorption above 3000 cm^{-1} (at 3020 cm^{-1}) was notably enhanced in intensity. By use of the exceptionally high sensitivity of a Digilab FTS-14 i.r. interferometer, and the facility for accurate ratioing of spectra provided by its minicomputer, it is now possible to obtain much better quality spectra than previously in the region (1800—1300 cm^{-1}) where silica absorptions are strong and change rapidly in intensity with frequency. It was thereby found that a band of moderate intensity at 1500 cm^{-1} occurred in conjunction with the changes in the 3000 cm^{-1} region. Controlled addition of hydrogen showed that the 1500 cm^{-1} band, together with the band at 3020 cm^{-1} attributable to olefinic CH bonds, disappeared most rapidly, followed by bands from the σ-bonded species, M-CH_2CH_2-M. This sensitivity to small amounts of added hydrogen is what would be expected for catalytically active species. Although we have so far been unsuccessful in obtaining another Pt sample giving the modified spectrum, the spectrum itself has been repeatedly obtained on this particular sample, even after treatment of the surface with oxygen, followed by re-reduction with hydrogen. This latter observation leads us to discount the possibility that this modified spectrum is associated with a metal surface contaminated with carbonaceous residues.

Subsequent i.r. studies of the adsorption of ethylene on Pd have now regularly shown the presence of an absorption at 1510 cm^{-1} together with a substantial shoulder at 1520 cm^{-1}. These are strongest in the presence of gas-phase ethylene but persist after evacuation of the latter (Figure). In this case there is no sharp absorption band apparent above 3000 cm^{-1}, but instead a broad region of absorption which stretches across this frequency. The spectrum in the ν(CH) region is otherwise similar to that found from the 'different-from-normal' Pt sample. Again the presence of the M-CH_2CH_2-M species is shown on this metal from the well defined pair of bands at 2868s and 2780w cm^{-1}. Controlled addition of hydrogen leads to the removal of the spectra from both associatively adsorbed species, but again it is the band in the 1500—1520 cm^{-1} region, and a companion broad absorption centred near 2980 cm^{-1}, which disappear more rapidly than the 2868/2780 cm^{-1} absorptions (Figure). Further addition of hydrogen, as in spectrum (e) of the Figure, leads to removal of only a small remaining amount of the species giving the 1510—1520 cm^{-1} absorptions, but extensive further removal of the species giving the 2868 and 2780 cm^{-1} absorptions assigned to the σ-bonded M-CH_2CH_2-M species. Bands in the 1500 cm^{-1} region have not so far been obtained from ethylene adsorbed on Rh[3] or Ni[8] catalysts.

Olefins containing $C{=}CH_2$ groups normally give strong absorptions near 3080 cm^{-1} as well as others near 3000 cm^{-1} and the former wavenumber region is usually considered to be particularly diagnostic of this group.[9] However, for molecules adsorbed on bulk metals, there is an optical selection rule which only allows the observation of absorptions resulting from dipole charges perpendicular to the surface.[10] There seem to be good grounds for considering that this selection rule is also operative to a considerable degree for the metal particles of diameter 20—100 Å normally found for oxide-supported metals.[3,11]. If so, this would lead to the expectation of only one strong i.r.-active ν(CH) band (symmetry A_1) of frequency near 3000 cm^{-1} for π-bonded ethylene, in agreement with the experimental results. Our assignment of the 1510—1520 cm^{-1} bands to the π-complexed ethylene species on palladium is reinforced by a recent observation of absorption bands in just this wavenumber region (1513 and 1522 cm^{-1}) when Pd atoms are allowed to react with ethylene[12] to give what was considered to be the complex $Pd(C_2H_4)_3$.

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