

An Infrared Spectroscopic Investigation of the Species Chemisorbed from Ethylene over a Platinum/Silica Catalyst between 100 and 294 K; the Observation of di- σ Adsorbed PtCH₂CH₂Pt Surface Complexes

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Changes in the i.r. spectra of chemisorbed species from ethylene on a Pt/SiO₂ catalyst between 100 and 294 K allow the identification of the di- σ adsorbed species (3) at low temperatures with partial transformation to the ethylidyne species (2) at room temperature.

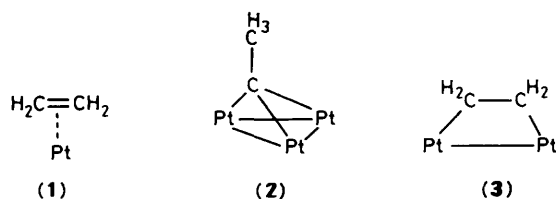
Much interest continues to be focussed on the identification of the chemisorbed species from ethylene on transition-metal surfaces,^{1,2} in pursuit of an understanding of the mechanism of catalysed reactions of alkenes.

The room temperature i.r. spectrum from ethylene chemisorbed on an impregnated Pt/SiO₂ catalyst is shown in Figure 1B. There is now fairly general agreement^{3,4} that the absorptions at 3016 and 1496 cm⁻¹ arise from the presence of the π -adsorbed species (1), and more recently it has been demonstrated^{1,2,5} that the strong absorptions at 2880 and 1342 cm⁻¹ are from surface ethylidyne species (CH₃-C)Pt₃ (2). These interpretations have been aided by the realisation that the metal-surface selection rule (that i.r. bands are only observable from vibrations perpendicular to the metal surface) might hold for particles down to as small as 2 nm in diameter.^{6,7} An earlier doubt as to whether the 2880 and 1342 cm⁻¹ bands both arise from the same species, caused by our observation of a differential weakening of the analogous 2887 cm⁻¹ band relative to that at 1342 cm⁻¹ from ethylene on Rh following CO co-adsorption,⁸ is resolved in the present low temperature study. The fact that both the 2880 and 1342 cm⁻¹ bands on Pt are from the same species has also recently been demonstrated by the observation of both absorptions in a room-temperature i.r. reflection/absorption study of ethylene on Pt(111).⁹ However an interpretation remains to be given to absorption bands at *ca.* 2922 and 1428 cm⁻¹, which we have previously tentatively attributed to the presence of the di- σ adsorbed species, (3), on the surface.^{1,5}

The earlier electron energy loss spectroscopic (EELS) study of ethylene on Pt(111) by Ibach and his colleagues^{10,11} showed

that at low temperatures (<250 K) the spectrum suggested the presence of the di- σ adsorbed species; this has since been confirmed by comparison with the i.r. spectrum of a model cluster compound.^{1,12} The EELS study showed that the low temperature species was converted at room temperature to another species, since identified as ethylidyne.^{11,13} In the earliest study from this laboratory on Pt/SiO₂, a low temperature spectrum at 128 K showed a single absorption at *ca.* 2907 cm⁻¹ which was at that time difficult to explain.¹⁴ We therefore decided to re-investigate the relationship between low- and room-temperature spectra from ethylene on the finely divided catalyst. A 16% Pt/SiO₂ catalyst was prepared by reduction of an H₂PtCl₆ impregnated silica disc at 673 K in hydrogen for 6 h. This procedure gives particle sizes between *ca.* 5 and 15 nm. Spectra were obtained from (a) the evacuated clean catalyst disc, (b) the disc + adsorbed species + gas phase, and (c) the gas phase alone, the latter by removal of the disc from the beam. The spectra of the adsorbed species at 189 and 294 K (Figures 1A and 1B) were obtained by absorbance subtraction of [(a) + (c)] from (b), during warming up from a straightforward multilayer at 100 K.¹⁵

It can be seen that at 189 K the bands previously attributed to species (1) (the π -complex) are present, but not those associated with (2) (ethylidyne). However two adjacent bands occur at 2922 and 2906 cm⁻¹. On warming to room temperature the second of these absorptions, plus some absorption near 1419 cm⁻¹, disappears to be replaced by the absorptions at 2881, 2795, and 1342 cm⁻¹, clearly attributable to ethylidyne.^{1,2,5} We interpret these changes as indicating that species (3) occurs at low temperatures on two different sites, only one of which is converted to (2) by room temperature. In other words we are observing on Pt/SiO₂ the same interconversions from the di- σ adsorbed to the ethylidyne species as is observed by EELS over a close similar temperature range on Pt(111).¹⁰ There is reasonably good agreement between the frequencies for these two species in comparison with the EELS measurements of 2930/1430 cm⁻¹, bearing in mind the poorer resolution of EELS. We assign the remaining pair of bands at 2922 and *ca.* 1428 cm⁻¹ to the ν (CH₂, sym.) and δ



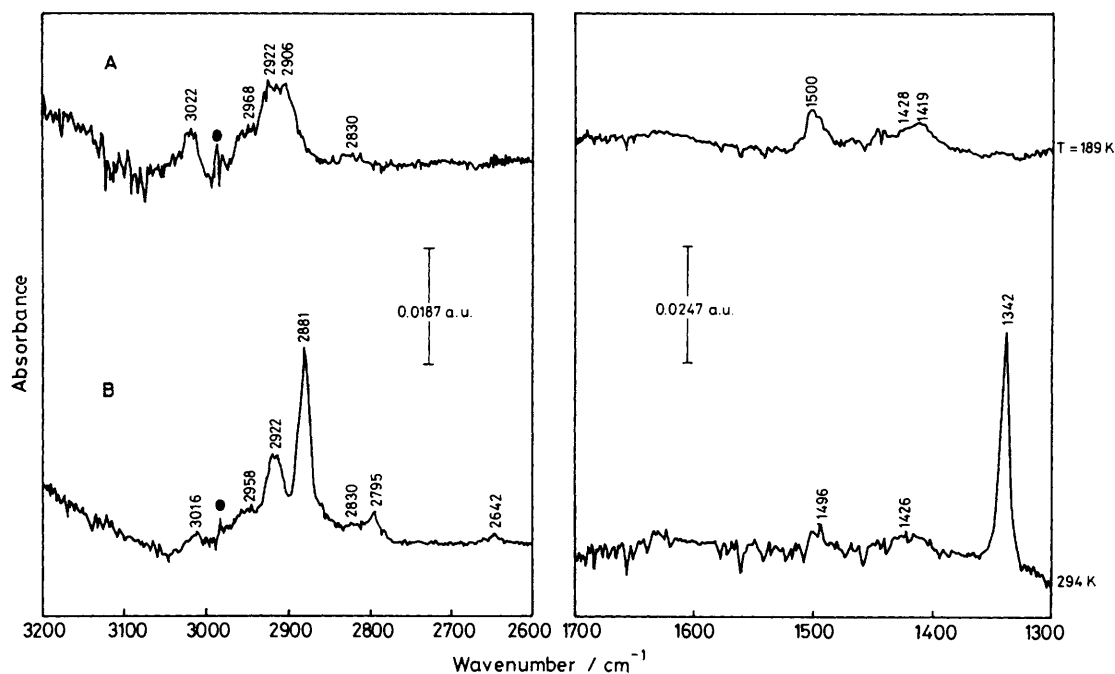


Figure 1. The i.r. spectra from ethylene adsorbed on a 16% Pt/SiO₂ catalyst (A) at 189 and (B) 294 K, in both cases after cancellation of gas-phase and SiO₂ background absorptions; • denotes slight miscancellation of the gas-phase bands.

(CH₂, sym.) modes of the di-σ species (3) possibly occurring on unreconstructed (100) planes. No other fundamentals are expected in the accessible region down to 1300 cm⁻¹ determined by silica absorptions. We consider that the new results now provide strong evidence for the successful identification of all three principal adsorbed species from ethylene on the Pt/SiO₂ catalyst.^{3,5} Finally the introduction of hydrogen in the gas phase leads to a more rapid removal of the absorptions from species (1) and (3) than from (2)^{15,16} together with the intermediate generation of absorptions attributable to surface ethyl groups.¹⁵

Our interpretation of the spectra of the species occurring on our Pt/SiO₂ samples is entirely consistent with the operation of the metal-surface selection rule. By contrast Beebe and Yates¹⁷ have observed somewhat similar spectra from ethylene on a Pt/Al₂O₃ catalyst but have assigned the at first sight related pair of absorptions at 2940 cm⁻¹ and 1411 cm⁻¹ to ν (CH₃, as.) and δ (CH₃, as.) vibrations of the ethylidyne species. Although the latter assignments imply a relaxation of the metal-surface selection rule (the above-assigned modes of vibrations would be expected to give dipole changes parallel to the metal surface) such behaviour would be consistent with the smaller mean size, ca. 2 nm, of their metal particles.^{7,17} Hence there is no necessary inconsistency between the two sets of results if the di-σ species are more abundant relative to ethylidyne, and the metal-surface selection rule has its expected stronger applicability, on the larger metal particles of the silica-supported catalyst.

Finally, it is of interest that the same set of well-defined bands for adsorbed ethylidyne have also been observed from the adsorption of ethane on Pt/SiO₂ at room temperature;^{15,18} spectra from some common species are to be expected as a catalyst operates on both the forward and backward reactions of an equilibrium such as C₂H₄ + H₂ ⇌ C₂H₆.

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