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Infrared spectra of adsorbed ethene on the EUROPT-1 catalyst

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Abstract

The infrared spectra from the adsorption of ethene on the EUROPT-1 catalyst, at room temperature, indicate a complex surface hydrocarbon-phase consisting of four species. Three are identified as ethylidyne, π-ethene and di-σ adsorbed ethene. The most likely identity of the fourth is a C_4 species derived from the dimerisation of the other adsorbed C_2 hydrocarbons.

Key words: Adsorbed species; EUROPT-1 catalyst; ethene; infrared spectroscopy.

Espectros infrarrojos de eteno adsorbido sobre el catalizador EUROPT-1

Resumen

Los espectros infrarrojos de la adsorción de eteno sobre el catalizador EUROPT-1, a temperatura ambiental, produce una compleja fase superficial de hidrocarburos, que contiene de cuatro especies. Tres fueron identificadas como etilidino, π-eteno and di-σ eteno adsorbido. Es probable que la cuarta sea una especie C_4 producto de la dimerización de los hidrocarburos C_2 adsorbidos.

Palabras clave Catalizador EUROPT-1; espectroscopía infrarroja; especies adsorbidas; eteno.

Introduction

One of the prime difficulties in basic in catalysis research is to obtain reproducible results from different laboratories because of the sensitivity of catalyst behaviour to details on the preparation procedure. EUROPT-1 is a standard silica-supported platinum (Pt/SiO_2) catalyst produced in quantity and distributed by the Research Group on Catalysis, (Council of Europe), to many laboratories for characterization (1-6). It is prepared from $Pt(NH_3)_4Cl_2$ and $Pt(NH_3)_4(OH)_2$ on Sorbsil silica and has a Pt loading of 6.3 wt % after reduction in hydrogen at 673 K. The Pt particles are rather uniform in size with a mean diameter of circa 2 nm and are reported to have a raft-like structure with added top-surface Pt-atoms (7).

In this paper we analyse the infrared spectra obtained from ethane (ethylene) adsorbed on the EUROPT-1 catalyst in terms of the presence of four species. We also com-

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pare the ethane spectra on EUROPT-1 with those obtained on another silica-supported Pt catalyst, prepared from the reduction of hexachloroplatinic acid in hydrogen, in hydrogen at 650 K and which has a notably higher metal loading (circa 16 Pt wt %). This contains many larger metal crystallites with diameters in the range 5 to 20 nm (8, 9).

Experimental

Transmission infrared spectra from ethane adsorbed on the EUROPT-1 catalyst were collected from a 25 mm diameter pressed disc of approximately 50 mg on the final ground catalyst using a Biorad FTS-20 Fourier transform infrared spectrometer. The samples were contained within a Pyrex glass cell fitted with NaCl windows which allowed exposure to the catalyst to either static or a flow of gas under reduced pressure.

The sample could be also heated to allow in situ reduction prior to the infrared adsorption studies. The reduction procedure typically involved heating the catalyst to between 600 and 670 K under flow of H_2 at 200 torr for approximately 3 hours followed by outgassing into vacuum at 480 K for a further 3 hours before cooling to room temperature for adsorption measurements.

The gaseosus reagents used in this study were of research grade and supplied by B.O.C. Ltd.

Results and Discussion

Figure 1 shows a spectrum of ethene adsorbed to saturation on the EUROPT-1 catalyst. The spectrum is the ratio of two 4 cm^{-1} resolution single beam spectra recorded before and after exposure of the catalyst to 12 torr of ethane for 5 minutes.

The carbon-hydrogen bond stretching region displays a total of seven distinct peaks while the deformation region shows only three. Although there are only ten clear maxima, the total number of vibrations contributing to the spectrum may be higher. The half-width of the 3040, 3012, 2885, 2800, 1500 and 1342 cm^{-1} peaks all of the order of 15 cm^{-1}. The half-width of the band centred near 1420 cm^{-1} is almost this value perhaps suggesting two or more closely adjacent overlapping peaks. Similarly, the appearance of the spectrum between 2990 and 2900 cm^{-1} suggests the superposition of a number of peaks giving the three maxima shown at 2970, 2950 and 2920 cm^{-1}.

The above spectrum is broadly similar to earlier spectra of ethane adsorbed on either silica or alumina supported Pt catalysts (10) and so some general conclusions may be drawn as to the origin of the major features in the spectrum; i.e. these can be associated with following surface complexes: π-C_2H_4 (3012 and 1500 cm^{-1}), di-σ C_2H_4 (1920 and 1428 cm^{-1}) and ethylidyne (2885 and 1342 cm^{-1}) (11, 12). However, much of the

Intensity in the spectrum between 2990 and 2920 cm^{-1} and a component of the broad feature centred on 1420 cm^{-1} remains to be accounted and suggests the presence of one or more further species in addition to the π, di-σ and ethylidyne species already noted.

For a multicomponent mixture such as this surface phase, it is normally reasonable to assume that bands which consistently vary in parallel fashion with experimental parameters belong to the same component. Figure 2 shows the variation in appearance of the spectrum of ethene adsorbed on EUROPT-1 as the surface coverage varies with increasing exposure time. Single beam spectra were recorded at regular time intervals with a constant flow of 10^{-2} torr of ethane across the sample. These spectra them ratioed against a single beam spectrum of the clean sample to generated the spectra 2a to2f. The sharp and very weak absorption at 2990 cm^{-1} denotes non-cancellation of the gaseous ethene spectrum. Notice that partial increase in the intensities of the 2885 and 1342 cm^{-1}peaks in going from spectrum 2a to 2f, and drop in intensity of the 3012 and 1500 cm^{-1} peaks is obvious. The detailed

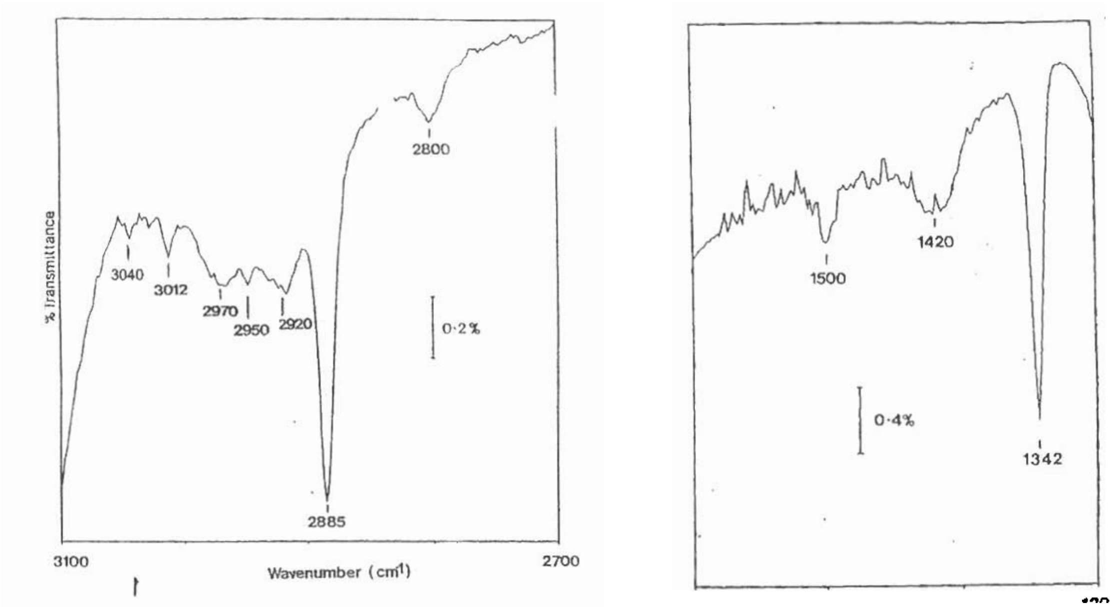

Figure 1. The CH streching and CH_2 deformation regions of the infrared spectrom from ethene on a EUROPT-1 catalyst.

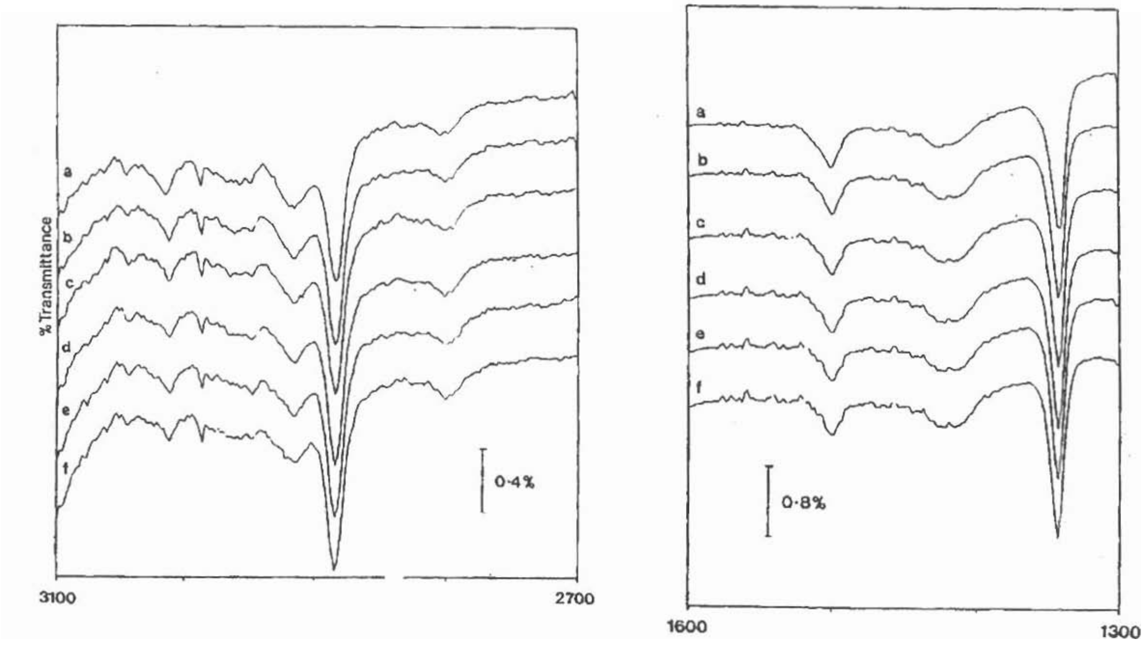

Figure 2. A series of infrared spectra showing the variation in peak intensities as a function of exposure time to ethylene at 10^{-2} torr (For the exposure times see Figure 3).

variation in intensities of all peaks is shown in the plot of Figure 3. This shows the intensity of each peak, measured as transmittance, as a function of time (i. e. minutes of exposure at 10^{-2} torr). The two most intense peaks in the spectrum at 2885 and 1342 cm^{-1} grow together towards saturation at a almost identical rate (the ratio of their intensities is more or less constant at 1:1.6 and the intensities of these peaks saturate at exactly the same point, i.e. spectrum 2d). The intensity of the weakest peak in the spectrum at 2800 cm^{-1} also parallels the 2885 and 1342 cm^{-1} peaks, confirming that the 2885, 2800 and 1342 cm^{-1} peaks belong to the same surface species, namely ethylidyne (11).

The intensity of the 3012 and 1500 cm^{-1} peaks vary in an identical fashion to another but differently from the 2885, 2800 and 1342 cm^{-1}. This again confirms that both bands are attributed to vibrational modes of a second surface species which is undoubtedly p adsorbed ethene. Unlike the 2885, 2800 and 13442 cm^{-1}, which grow steadily towards a saturation value, the 3012 and 1500 cm^{-1} peaks drop in intensity from an initial maximum value. As the bands from the p species fall in intensity while all the others continue to grow towards maximum values, it is possible that the p species decomposes with time to form other surface hydrocarbon fragment. Alternatively, the p species may be removed from the surface by hydrogenation to form ethane by the hydrogen released in the dissociative formation of the ethylidyne species.

The only other peaks in the spectra, which could be measured with any degree of accuracy were that at 2920 cm^{-1} and the broader composite absorption centred near 1420 cm^{-1}. The behaviour of the 2920 cm^{-1} peak differs from both the 2885, 2800 and 1342 cm^{-1} 3012 and 1500 cm^{-1} sets of peaks inasmuch as the intensity of this feature grows towards a saturation value but reaches a maximum intensity at a very early stage of the experiment (spectrum 2b). This behaviuor clearly marks the 2920 cm^{-1} peak as due to a third surface; the di-s adsorbed ethene. The early saturation of this species is important as it allows generation of simpler spectra showing the continuing of the other surface species towards saturation (or continuing decrease in intensity due to surface reaction in the case of the p species). By using the single beam spectrum recorded at the point where the intensity of the 2920 cm^{-1} peak saturates as a background for the subsequent single bema spectra, recorded at lower exposure times, a second set of ratioed spectra may be generated. In these spectra the 2920 cm^{-1} peak, and any other peak associated with the di-σ species, should ratio out. This secondary set of ratioed spectra is shown in Figure 4.

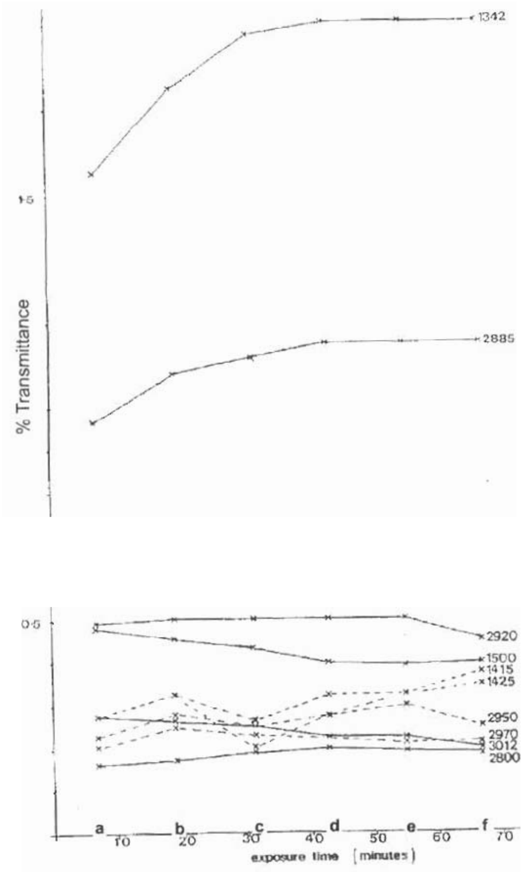

Figure 3. A plot of intensity against exposure time for the spectra shown in Figure 2.

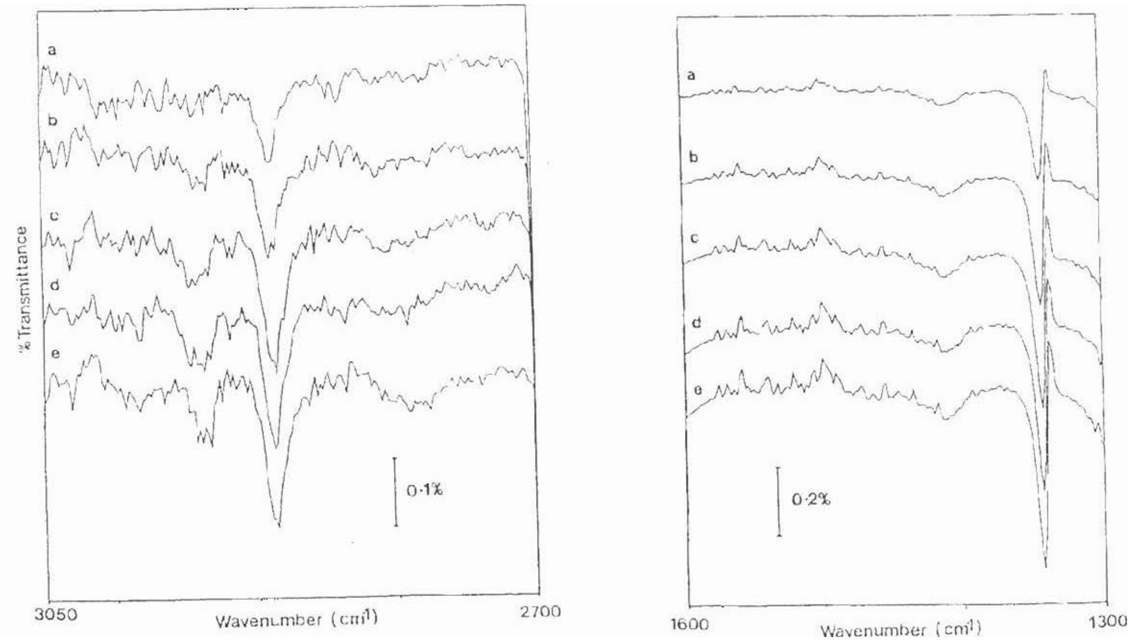

Figure 4. A set "second ratioed" spectra showing the continuing variation of peak intensity as a function of exposure time to athylele at 10^{-2} torr.

As expected the spectra of Figure 4 are much simpler. Once again the 2885 and 1342 cm^{-1} peaks can be seen to grow towards saturation at similar rate. It is also apparent that the 1342 cm^{-1} peaks shifts slightly higher wavenumber with increasing coverage. As in the previous set of spectra, the 1500 cm^{-1} peak decreases in intensity with increasing exposure times. The important difference between the initial ser and this secondary set is that "ratioing out" the bands from the di-σ species, giving the at **2930 cm^{-1}, reveals that a peak at 2940 cm^{-1}** and a component of the original broad band at 1420 cm^{-1} also grow in parallel fashion to the 2885 and 1342 cm^{-1}. This suggests that vibrations at 2940, 2885, 2800, 1415 and 1342 cm^{-1} all belong to the same surface ethylidyne species. Comparing these frequencies with those of the model compound $[Co_3(CCh_3)(CO)_9]$ (13) shows that the peak at 2800 cm^{-1} is consistent with the totally symmetric component of the overtone of the *d(CH$_3$)-as* mode of ethylidyne. The additional peaks at 2940 and 1451 cm-1 almost exactly match those expected from the asymetric stretching and deformation modes of the methyl group in an ethylidyne hydrocarbon group. Together with the totally symmetric vibrations at 2885, 2800 and 1342 cm^{-1} (Figure 5), these comprise the complete set of infrared active expected for the ethylene surface ligand. These non-totally symmetric modes are normally considered forbidden in the by the Metal Surface Selection Rule (MSSR) (14, 15).

The physical basis of the MSSR often adopted for the small metal particle system considers the components of an electric field E, in this case arising from an incident infrared electromagnetic wave, in direction radial, E_r, and tangential, E_t, to the surface of the metal particle. For an extended planar surface (an "infinitely" large spherical particle) of a perfect metal, E_t is zero while E_r is by a factor of two (15). The resulting field may therefore only excite a vibration of an adsorbed molecule if the

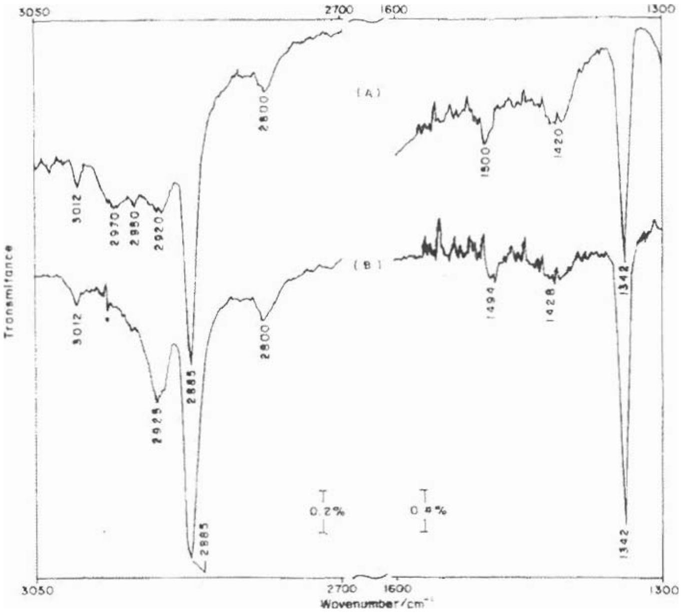

Figure 5. A comparision of the infrared spectra from (A) the adsorption of ethene on EUROPT-1, and (B) on another widely used Pt/SiO_2 catalysts but with larger metal particles

normal mode of the vibration produces an oscillating dipole in the radial direction, i. e. perpendicular to the metal surface. This constitutes the MSSR. The tangential component of the field experienced by an adsorbed species on a curved surface is however a function of both the distance of the adsorbate from the metal/vacuum interface and the curvature of the surface. As the radius of curvature of the surface decreases E_t increase until, for a small particles, normal modes of adsorbates both parallel and perpendicular to the local surface normal normal may be excited. Greenler et al. (15) concluded that relaxation of the selection rule for monolayer distances would become significant for particles smaller than 2 nm. As 75% of the Pt crystallites in the EUROPT-1 sample are believed to be smaller than 2 nm (1-7), the observation of weak non-totally symmetric modes is to be expected. Some contributions to the intensities of the latter modes may also arise from local distortions on the small metal particles.

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