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A Fourier-transform infrared spectroscopic study of the adsorbed species from perdeuteroethene on a deuterium-exchanged Pt-on-silica catalyst

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Fourier-transform infrared spectroscopy has been applied to study the adsorption and deuteration of perdeuteroethene (C_2D_4) at 298 K on a deuterium-exchanged Pt/SiO_2 catalyst. The spectra show absorptions associated with π- and di-σ-bonded (C_2D_4) and with (CCD_3), and a trace of (CCD_2H), ethylidyne surface species. These were identified by comparison with the closely-corresponding pattern of absorptions from the adsorption of C_2H_4. They are also correlated with previous spectroscopic results from C_2D_4 adsorption on Pt single-crystals and from analogous ligands in organometallic compounds. Deuteration of the initially-adsorbed species gives only gas-phase C_2D_6 and a trace of C_2D_5H.

Keywords: FT-IRS; perdeuteroethene; Pt/SiO_2 catalyst

1. Introduction

Two general approaches have been used to investigate adsorbed species or reaction intermediates associated with the interaction of hydrocarbons with catalyst surfaces. The first of these involves the postulation of intermediates through the kinetic analysis of isotopic variants of products of surface reactions, principally by means of mass spectrometry (for reviews of the kinetic literature see ref. [1]). The second approach involves the use of in situ infrared or other vibrational spectroscopy for the direct identification of surface species and the evaluation of their activities as reaction intermediates [2,4]. In order to provide interconnections between these two approaches as applied to hydrocarbons, the adsorption of deuterium- as well as hydrogen-containing molecules need to be studied by the infrared method. However, difficulties in the past have been caused by the reduced intensities of νCD compared with νCH absorptions, and by νCO absorption bands of comparable intensities in the same wavenumber range brought about by the absorption of residual CO in the vacuum line.

In this paper we analyse spectra from the adsorption of perdeuteroethene (C_2D_4) on a Pt/SiO_2 catalyst at ambient temperature. This has been deuterium-exchanged so as to replace surface OH groups on the silica surface by OD, and thereby to minimise H/D exchange of the adsorbed C_2D_4.

2. Experimental

The procedure used in the preparation of the initial Pt/SiO_2 catalyst has been described elsewhere [5]. Briefly an impregnated Pt/SiO_2 powder, with ca. 16% Pt by weight, was pressed at 550 kg cm^{-2} for 10 min into a self-supporting circular disc of 25 mm diameter and 0.1 mm thickness. The disc was reduced in H_2 at 673 K for 6 h in an evacuable infrared cell. In order to exchange OH for OD groups, the disc was exposed to five doses of D_2 (Messer-Grisheim, Germany) at 673 K, followed by a short evacuation of the gas phase. The high degree of SiOH replacement by SiOD was monitored by infrared analysis of the νOH and νOD absorptions at 3747 and 2756 cm^{-1} respectively. Electron micrographs showed that the majority of the metal particles of the disc were between 5 and 30 nm in diameter. The C_2D_4 was obtained from Merck, Sharp and Dohme, Canada in 1 ℓ × 1 bar Pyrex break-seal flasks and had a stated purity of 99 atom% deuterium. Infrared spectra were obtained at 4 cm^{-1} resolution using a Digilab FT-20V Fourier-transform, i.e. interferometric, spectrometer. In order to bring out the detailed features of the absorptions from the adsorbed species, each spectrum was absorbance-subtracted relative to that of the deuterium-exchanged Pt/SiO_2 catalyst prior to C_2D_4 adsorption.

3. Results and discussion

Fig. 1A shows the infrared spectra in the νCH and νCD regions in the presence of both gas-phase and surface species resulting from the adsorption of C_2D_4 on the deuterium-exchanged (OD-containing) Pt/SiO_2 catalyst at 298 K; (∗) and (●) denote gas-phase absorptions of C_2D_4 and C_2D_6 respectively. The presence of the latter shows the occurrence of a degree of self-deuteration over the catalyst. The 2345 and 2199 cm^{-1} absorptions are from the b_{2u} and b_{3u} infrared-active νCD_2 modes of C_2D_4 respectively; those at 2235 and 2087 cm^{-1} are from the e_u and a_{2u} νCD_3 modes of C_2D_6 [6].

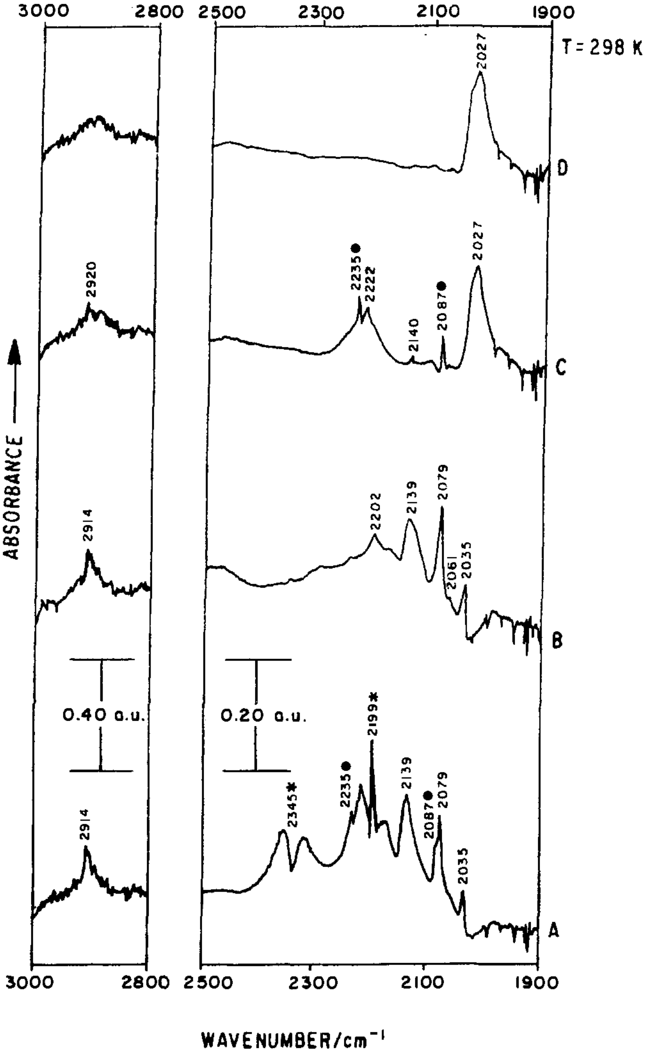

Fig. 1. The infrared spectra at 298 K resulting from the adsorption of 5 Torr of C_2D_4 on a deuterium-exchanged Pt/SiO_2 catalyst: (A) in the presence of the gas phase, (B) after the evacuation of the gas phase to 10^{-3} Torr, (C) after addition of 10 Torr D_2, and (D) after a second evacuation to 10^{-5} Torr.

The remaining bands in fig. 1A are from adsorbed species and are better observed after evacuation of the gas phase (fig. 1B). They appear at 2914 (w), 2202 (mw), 2139 (s), 2079 (s), ca. 2061 (w) and 2035 cm^{-1} (mw). With the exception of the first of these, from residual νCH in $M_3(CCD_2H)$, the overall spectral pattern, taking into account all of relative band-positions, intensities and band-widths, is closely analogous to that obtained from C_2H_4 adsorbed on the same catalyst [3,7]. This leads [3] to the following rather confident band-assignments: 2202 cm^{-1}, νCD_2 s, π-(C_2D_4) complex; 2139 cm^{-1}, νCD_2 s, di-$\sigma(C_2D_4)$ complex; 2079 cm^{-1}, νCD_3 s, and 2035 cm^{-1}, $2\delta CD_3$ as of ethylidyne, $M_3(CCD_3)$, M = metal. A weak feature at 2061 cm^{-1} may be from $2\delta CD_2$ of the di-σ complex. The assignments here, and from the earlier adsorption of C_2H_4, are guided by the considerations of the metal-surface selection rule [8,9] wich applies to spectra from flat metal-surfaces and from facets of large metal particles as used here. The selection rule allows only vibrations with associated dipole changes that are perpendicular to the metal surface to be prominent in the spectrum, i.e. a_1 modes for the effectively C_{2v} π-complex; a_1 or a for the di-σ complex depending on whether the C_2M_2 skeleton is planar (C_{2v}) or non-planar (C_2); and a_1 for the C_{3v} ethylidyne species.

Our results and interpretations are summarised in table 1 where they are compared with earlier vibrational electron energy loss (VEEL) spectroscopic data from C_2D_4 adsorbed on several single-crystal faces of Pt [10–14], and from analogous species as ligands in metal coordination/cluster compounds [15–18]. The overall agreement is most satisfactory. The infrared spectra give better resolution and precision of band-positions than in VEELS. The agreements in table 1 confirm a number of more tentative assignments in the single-crystal spectra where mixtures of surface-species are involved. We also include in table 1 some less-complete data from C_2D_4 adsorbed on a Pt/Al_2O_3 catalyst [19]. It is assumed that the absorptions attributed to the $2\delta CD_2$ and $2\delta CD_3$ modes of the di-σ species and ethylidyne respectively are increased in intensity by Fermi resonance with the adjacent fundamentals.

The spectrum of the $M_3(CCD_2H)$ species has been obtained before from the adsorption of H_2CCD_2 [20]. The νCH absorption of this adsorbed species at 2914 cm^{-1} probably originates in a small amount of C_2D_3H within the perdeuteroethene sample. The νCD_2 absorption of the same species is virtually coincident with the strong 2139 cm^{-1} absorption from the di-σ complex [20]. The value of 2914 cm^{-1} for νCH in the CHD_2 group can be used to calculate a CH internuclear distance from McKean's formula [21]:

$$r_{CH}\ (\text{Å}) = 1.402 - 1.035 \times 10^{-4}\ \nu CH\ (cm^{-1})$$

to give the value of 1.1000 ± 0.0005 Å, a value in good agreement with the results of neutron diffraction meas-

Table 1
The vibrational frequencies/wavenumbers and assignments of the absorption bands from C_2D_4 adsorbed at 298 K on a deuterium-exchanged Pt/SiO_2 catalyst in comparison with literature results from Pt single-crystals and related organometallic model compounds

Wavenumbers (cm^{-1})							Assignments
Pt[111] [10,11]	Pt[110] 1 × 1 [12]	Pt[110] 2 × 1 [13]	Pt[210] [14]	Pt/SiO_2 [this work]	Pt/Al_2O_3 [19]	model compounds [a,b] [15–18]	
π-complex							
c	2225	2220	2210	2202	2213	2193(a_1)	νCD_2 s
	1330	1290	1320	1320	1320	1353(a_1)	$\nu CC/\delta CD_2$
di-σ complex							
2160	2130			2139	2140	2139(a_1/a)	νCD_2 s
				2061?		2102(a_1/a)	$2\delta CD_2$
ethylidyne							
				2914		(2919)[e]	νCH, (CCD_2H)
2080				2079		d	νCD_3s, (CCD_3)
				2035			$2\delta CD_3$, (CCD_3)

[a] Zeise's salt, $K^+[(C_2D_4)PtCl_3]^-$ as the model for the π-complex [15,16]; $[Os_2(C_2D_4)(CO)_8]$ [17] as the model for the di-σ complex; $[Co_3(\mu_3CCD_3)(CO)_9]$, as the model for the ethylidyne complex [18].
[b] See the comments in the text about the symmetries of the allowed fundamentals under the metal-surface selection rule [8,9].
[c] The π-complex with bands at 2230 and 1370 cm^{-1} has also been observed on a Pt [111] surface with an 0.23 monolayer precoverage of oxygen [10], but not on a clean Pt [111] surface.
[d] This region is obscured by strong νCO absorptions of the model compound.
[e] Calculated value.

urements on similar organic [21] and organometallic compounds [22].

The addition of D_2 in the gas phase leads (fig. 1C) to C_2D_6 with its absorption bands at 2235 and 2087 cm^{-1} mentioned earlier, and a trace of C_2D_5H (2920 cm^{-1}). These are removed by evacuation leaving an absorption band at 2027 cm^{-1} from a small-fraction coverage by CO. On standing all the adsorbed hydrocarbon species were converted to ethane but earlier work involving adsorbed C_2H_4 on Pt/SiO_2 [3] or Pt/Al_2O_3 [19] showed that the π- and di-σ species are removed much more rapidly than the ethylidyne.

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