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NOTES

An Infrared Spectroscopic Study of C–C Bond-Breaking during the Thermal Decomposition of the Chemisorbed Species from Ethane on a Pt/SiO_2 Catalyst

INTRODUCTION

Although many studies have been made on the infrared spectra of unsaturated hydrocarbons (alkenes, alkynes, and benzenes) and of cycloparaffins chemisorbed on metal surfaces (*1*), very few such studies have been made on adsorbed alkanes. In the pioneering era of such research, Eischens and Pliskin (*2*) reported qualitatively that ethane adsorbed on Ni/SiO_2 catalysts gave spectra similar to those from adsorbed ethylene on the hydrogen-free Ni surface, but very weak ones on the hydrogen-covered surfaces. Lee *et al.* (*3*) have shown that methane molecules incident with high kinetic energy chemisorb on Ni(111) to give surface methyl groups below 150 K.

McDougall (*4*) showed that ethane was chemisorbed at room temperature on a finely divided silica-supported platinum catalyst (EUROPT-1) and gave rise to a spectrum characteristic of surface ethylidyne groups CH_3CPt_3. Such surface species have previously been identified from the adsorption of ethene (ethylene) on various oxide-supported Pt catalysts (*5–9*), and on Pt(111) (*10–13*) and Pt(100) (5 × 20) (*14*) single-crystal surfaces. In the present paper we report the effects of heating to 573 K from room temperature (294 K) on the surface species, including ethylidyne, derived from ethane chemisorbed on an impregnated finely divided Pt/SiO_2 catalyst. Direct evidence is found for C–C bond-breaking processes.

EXPERIMENTAL

The procedure used in the preparation of the impregnated Pt/SiO_2 catalyst has been described in detail elsewhere (*15, 16*). Briefly, a hexachloroplatinic acid impregnated silica powder (Cabosil H5) was pressed into a disk for transmission infrared work. The H_2PtCl_6 was reduced in hydrogen for 6 h at 673 K to give a 16% w/w Pt-on-silica catalyst, from which electron micrographs showed the majority of metal particles to have diameters between 5 and 15 nm. After reduction at 673 K the Pt/SiO_2 sample was evacuated overnight at 10^{-6} Torr to give a "hydrogen-free" or "hydrogen-depleted" catalyst. Infrared spectra were measured at 4 cm^{-1} resolution using a Digilab FTS20 Fourier-transform spectrometer.

RESULTS AND DISCUSSION

Figure 1A shows the infrared spectrum of the adsorbed species after room temperature (294 K) adsorption of ethane (5 Torr) followed by a single evacuation of the gas phase to 5×10^{-5} Torr. The original spectrum was ratioed against that of the Pt/SiO_2 catalyst before introduction of the hydrocarbon, so as to show only absorptions from the adsorbed species.

Figures 1B, 1C, and 1D show analogous spectra obtained after heating the catalyst plus adsorbed species to 413, 513, and 573 K, respectively, in a closed cell, so that the spectra of any gas-phase species generated could also be recorded. In each case heating to the specified temperature was followed by cooling to room temperature before recording the spectrum.

The room temperature spectrum (Fig. 1A) clearly shows absorptions at 2881(s), 2795(w), and 1348 cm^{-1} (vs) which are now well known to characterise the presence of

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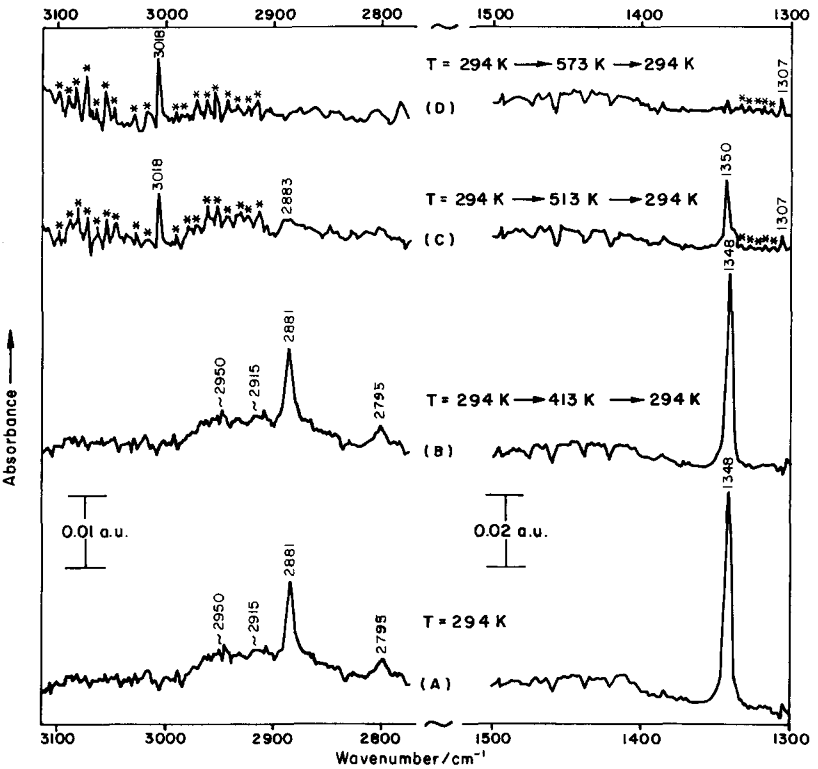

Fig 1. Infrared spectra, measured at room temperature after (A) adsorption of 5 Torr ethane at 294 K, on a Pt/SiO$_2$ catalyst, followed by evacuation to 5×10^{-5} Torr; and then after subsequent heating *in a closed cell* to (B) 413 K, (C) 513 K, and (D) 573 K. In the region 1500 to 1350 cm^{-1} the unlabelled sharp features are caused by water vapour miscancellation. The features indicated by asterisks are lines in the vibration–rotation spectrum of methane.

the ethylidyne surface species (*5–14, 17*) on Pt/SiO$_2$ disks (*5, 6, 18*) which are opaque below 1300 cm^{-1}. It should be noted however that the relative strength of the 2881 cm^{-1} band relative to that at 1348 cm^{-1} is notably less than that when the spectrum is derived from ethene absorption. Additional absorptions occur at ca. 2950 cm^{-1} (bd) and ca. 2915 cm^{-1}, both with medium intensity. The ca. 2915 cm^{-1} feature may denote the presence of the di-σ chemisorbed species, PtCH$_2$CH$_2$Pt, previously identified following ethene adsorption on the same type of catalyst (*18, 19*). The origin of the ca. 2950 cm^{-1} band, characteristic of CH$_3$ groups, is not clear. It may possibly represent the presence of a small amount of gas-phase ethane, reformed under equilibrium conditions by gradual rehydrogenation of unsaturated adsorbed species by surface-adsorbed H, following the initial removal of the gas-phase ethane.

Heating to 413 K (Fig. 1B) produced no detectable changes in the spectrum observed, but by 513 K (Fig. 1C) the prominent absorptions from the ethylidyne species had much weakened and simultaneously new absorptions from gas-phase methane (Q-branches at 3018 and 1307 cm^{-1} accompanied by vibration–rotation PR lines) had appeared (*20*). At this temperature little change was observed from the absorptions near 2950 and 2915 cm^{-1}. By 573 K (Fig. 1D) all the absorptions from adsorbed species had virtually been eliminated, and the methane spectrum was correspondingly strengthened. The gradual growth of the methane spectrum shows unambiguously that C–C bond-breaking of the original adsorbed species occurred at some temperature between 413 and 513 K, with this process well advanced at the latter temperature and complete by 573 K. Furthermore the ethylidyne species was the first and principal one to give rise to C–C bond scission.

Although no related experiments seem to have been carried out following ethane adsorption, several previous studies on the adsorption of ethene have identified the ethylidyne species on Pt and considered its temperature range of stability. In an NMR study on Pt/Al_2O_3, Wang *et al.* (*21*) found that C–C bond-breaking of predominantly ethylidyne species commenced at 380 K and was complete by 480 K. On Pt(111) and Pt(100) (5 × 20), the latter representing a close-packed (111)-type metal monolayer, electron energy loss (EEL) spectroscopic studies of ethylidyne species showed decomposition at the temperatures 450–550 K (*11*) and near 450 K (*14*), respectively. However, in these cases it has been concluded that the resulting species are predominantly of type C_2H, although the presence of some CH surface species, implying C–C bond-breaking, was also envisaged (*22*). It remains not unlikely that the continuous pumping away of gas-phase H_2 in the EELS work could give rise to a different decomposition pathway for ethylidyne from that occurring under the closed-cell procedure used in the present work. In the EELS studies (*11, 14*) the overall surface composition after ethylidyne decomposition was estimated from the integrated loss of hydrogen from the surface as monitored by thermal-programmed desorption (TPD). However, in the latter experiments only mass numbers characteristic of ethene and H_2 (*11, 14*) and ethane (*11*) were monitored. Our experiments suggest that the mass-number characteristic of methane might also be profitably studied during TPD experiments involving hydrocarbon adsorbates.

CONCLUSIONS

The species chemisorbed on Pt/SiO_2 from ethane at room temperatures include ethylidyne CH_3CPt_3 and possibly the di-σ bonded species $PtCH_2CH_2Pt$. Between 413 and 573 K these species are decomposed to give predominantly gas-phase methane, implying C–C bond-breaking which, for the ethylidyne species, is largely complete by 513 K.

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REFERENCES

1. Sheppard, N., *Ann. Rev. Phys. Chem.* **39,** 589 (1988).
2. Eischens, R. P., and Pliskin, W. A., *Adv. Catal.* **10,** 1 (1958).
3. Lee, M. B., Yang, Q. Y., and Ceyer, S. T., *J. Chem. Phys.* **87,** 2724 (1987).
4. McDougall, G. S., Ph.D. thesis, University of East Anglia, 1984.
5. Sheppard, N., James, D. I., Lesiunas, A., and Prentice, J. D., *Commun. Dept. Chem. Bulgarian Acad. Sci.* **17,** 95 (1984).
6. Bandy, B. J., Chesters, M. A., James, D. I., McDougall, G. S., Pemble, M. E., and Sheppard, N., *Philos. Trans. R. Soc. London A* **318,** 141 (1986).
7. Beebe, Jr., T. P., Albert, M. R., and Yates, Jr., J. T., *J. Catal.* **91,** 254 (1987).
8. Beebe, Jr., T. P., and Yates, Jr., J. T., *J. Phys. Chem.* **91,** 254 (1987).
9. Sheppard, N., and De La Cruz, C., *React. Kinet. Catal. Lett.* **35,** 21 (1987).
10. Ibach, H., and Lehwald, S., *J. Vac. Sci. Technol.* **15,** 407 (1978).
11. Steininger, H., Ibach, H., and Lehwald, S., *Surf. Sci.* **117,** 685 (1982).
12. Chesters, M. A., and McCash, E. M., *Surf. Sci.* **187,** L639 (1987).
13. Malik, I. J., Brubaker, M. E., Mohsin, S. B., and Trenary, M., *J. Chem. Phys.* **87,** 5554 (1987).
14. Hatzikos, G. H., and Masel, R. I., *Surf. Sci.* **185,** 479 (1987).
15. De La Cruz, C., Ph.D. thesis, University of East Anglia, 1987.

16. De La Cruz, C., and Sheppard, N., *J. Mol. Struct.*, in press.
17. Skinner, P., Howard, M. W., Oxton, I. A., Kettle, S. F. A., Powell, D. B., and Sheppard, N., *J. Chem. Soc. Faraday Trans. 2* **77,** 1203 (1981).
18. De la Cruz, C., and Sheppard, N., *J. Chem. Soc. Chem. Commun.*, 1854 (1987).
19. Mohsin, S. B., Trenary, M., and Robota, J. J., *J. Phys. Chem.* **92,** 5229 (1988).
20. Cole, A. R. H., "Tables of Wavenumbers for the Calibration of Infra-red Spectrometers; IUPAC," Butterworths, London, 1961.
21. Wang, P. K., Slichter, C. P., and Sinfelt, J. H., *J. Phys. Chem.* **89,** 3606 (1985).
22. Somorjai, G. A., Van Hove, M. A., and Bent, B. E., *J. Phys. Chem.* **92,** 973 (1988).

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