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PARTIAL OXIDATION OF UNSATURATED HYDROCARBONS OVER Pd(111): OXYGEN SCAVENGING OF REACTIVE INTERMEDIATES AND THE FORMATION OF FURAN FROM C_2H_2 AND C_4H_4

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Furan is formed by selective oxidation of both C_2H_2 and C_4H_4 over Pd(111). In the former case, oxygen scavenging of reactively formed C_4H_4 directly demonstrates that this species is the key intermediate in acetylene cyclotrimerisation. In the latter case, overall selectivity towards furan formation can be as high as ~ 80%.

1. Introduction

The low temperature cyclotrimerisation of acetylene to benzene on Pd(111) is an efficient and unusual heterogeneous reaction which can occur under conditions of ultra high vacuum [1–4]. Although the initial discovery of this surface reaction was made under low pressure conditions, subsequent work [5] has shown that the process can be operated as *a true catalytic reaction under conditions of steady state turnover* at 1 bar pressure over Pd catalysts on a variety of supports. The mechanism of this interesting process has been studied by a variety of methods [6–9] including molecular beam measurements which indicated that the reaction proceeds via a C_4 intermediate [6]; isotope labelling experiments [8] suggested that the stoichiometry of this surface intermediate was C_4H_4. It was also demonstrated that dissociative chemisorption of cis-3,4-dichlorocyclobutene ($C_4H_4Cl_2$; DCB) could be used to seed the metal surface with the relevant C_4H_4 species; i.e. this entity reacts with C_2H_2 to yield benzene with identical kinetics to those exhibited by the overall acetylene trimerisation reaction [7,8]. NEXAFS, ARUPS and HREELS observations [9,10] have indicated that this C_4H_4 species is likely to be a tilted metallocycle. The present paper describes the partial oxidation of acetylene to furan (C_4H_4O) on oxygen precovered Pd(111): such a reaction could not have been readily predicted in the absence of a detailed understanding of the structure and properties of the C_4 intermediate. These observations strongly support our early hypothesis that the cyclotrimerisation

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reaction proceeds via a C_4H_4 intermediate. It is also shown that furan is generated by selective oxidation of the species deposited by dissociative chemisorption of DCB confirming that the latter can indeed be used as a reagent for dosing the surface with the C_4 intermediate which evidently plays a crucial role in the chemistry of acetylene on Pd(111). Earlier work has demonstrated the partial oxidation of various higher alkenes on single crystal surfaces of Ag [11–13]. In the case of Pd(111) Davis and Barteau [14] have observed the conversion of primary alcohols to aldehydes while Gentle et al. [15] reported the formation of thiophene from acetylene on the sulphided surface–a process analogous to that reported here. The present work appears to be the first report of the heterogeneous partial oxidation of an alkyne at a transition metal surface.

2. Experimental

Temperature programmed reaction (TPR) measurements were carried out in an ion-pumped chamber (base pressure $< 5 \times 10^{-11}$ Torr) equipped with a 4-grid RFA and a computer multiplexed quadrupole mass spectrometer. The Pd(111) sample was prepared by standard methods and cleaned by repeated cycles of argon ion bombardment and annealing to 950 K. Final traces of subsurface carbon were removed by heating in 5×10^{-7} Torr of oxygen at 850 K followed by annealing to 1200 K. This procedure was repeated until room temperature oxygen adsorption resulted in no detectable CO desorption on subsequent heating of the sample to 1100 K. The specimen was mounted on a rotatable manipulator and could be resistively heated to > 1200 K and also cooled to < 100 K. The cooling arrangement employed a moveable heat sink which permitted very rapid specimen cooling, enabling the sample to be dosed with oxygen at ~ 300 K, followed by immediate cooling to ≤ 170 K prior to dosing with the organic adsorbate which was admitted to the system via a calibrated quartz capillary array doser. Photoemission measurements were carried out in a VG ADES chamber operating at a base pressure of 2×10^{-11} Torr.

3. Results and discussion

The clean Pd(111) surface could be saturated with oxygen with a 4 L exposure ($1L = 10^{-6}$ Torr s) at 300 K; this corresponds to the completion of a $p(2 \times 2)$ surface structure [16,17] and appropriate experiments were carried out in order to establish the exposures necessary to produce any desired oxygen precoverage.

TPR observations following acetylene chemisorption at 170 K on such oxygen precovered surfaces showed that CO_2, CO, H_2O, H_2, C_6H_6 and a small amount of C_4H_4O were produced. The product distribution varied markedly with oxygen/acetylene stoichiometry and total surface coverage. It can be shown [18]

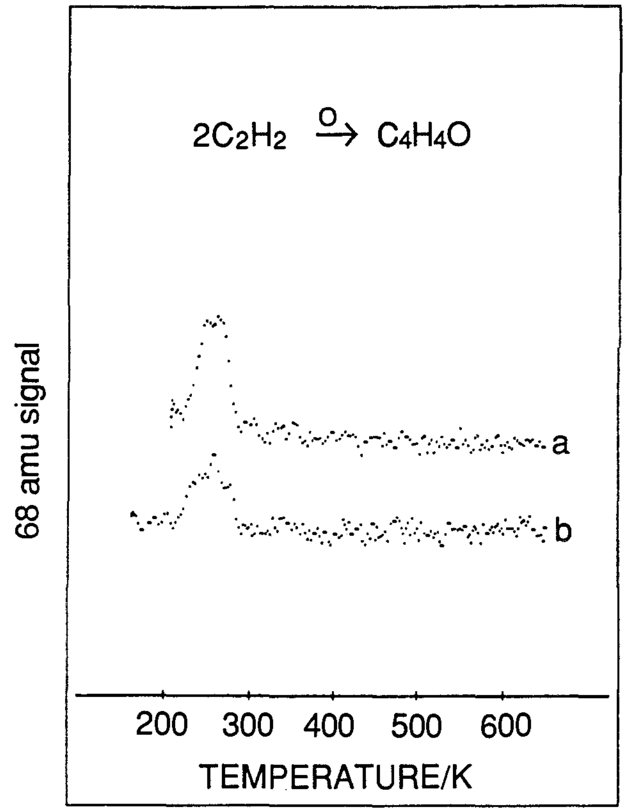

Fig. 1. Partial oxidation of acetylene to furan. TPR spectra obtained after adsorption of acetylene on oxygen precovered Pd(111). $\theta_{ox} = 0.12$; a: acetylene exposure 0.8 L; b: acetylene exposure 2.0 L.

that CO_2, CO and H_2O are produced by the combustion of acetylene and its decomposition products, while C_6H_6 and H_2 result from acetylene cyclotrimerisation and decomposition respectively. The formation of furan was verified by measurement of its mass spectrometer fragmentation pattern: the relative intensities of signals at 68 and 39 amu are particularly diagnostic. Although the yield of C_4H_4O was low, the fact that any is formed at all in such a highly oxidising environment is of considerable significance. Figure 1 shows the furan yield monitored at 68 amu at an oxygen precoverage of $\theta = 0.12$ and for two different acetylene coverages. The formation of furan by oxygen adatom scavenging provides the first *direct* evidence for the presence of a C_4H_4 species on the metal surface during acetylene cyclotrimerisation.

In order to confirm the above conclusion, further experiments were carried out in which the C_4 intermediate was produced directly by dosing the oxygenated surface with DCB at 270 K. Angle-resolved UP spectra (fig. 2) show that on the oxygenated surface DCB adsorbs non-dissociatively at 200 K with dissociation to C_4H_4 occurring at ~ 260 K; at higher temperatures (~ 350 K) decomposition to vinylidene and smaller fragments occurs. Figures 2A,B show the furan yield obtained under TPR conditions as a function of DCB coverage for two different oxygen precoverages. Note that the threshold DCB coverage for the onset of furan formation occurs at lower DCB coverage when the oxygen precoverage is lower (fig. 3B) as would be expected (see below). In the case of DCB oxidation, the yield of C_4H_4O is substantially greater than that produced by acetylene oxidation. Several factors appear to be at work here. First, the very efficient competing reaction ($C_4 + C_2 \rightarrow C_6$) to form benzene cannot occur since no acetylene molecules are present. Secondly, the use of DCB results in much higher coverages of C_4H_4. Third, C_4H_4 appears to be far less susceptible to hydrogen abstraction by oxygen than does acetylene itself [18,19]. Finally, it is possible that the presence of chlorine on the surface may moderate the tendency of adsorbed oxygen to initiate combustion reactions [12]. It can be seen that the furan desorption peak temperatures resulting from C_4H_4 oxidation and C_2H_2 oxidation

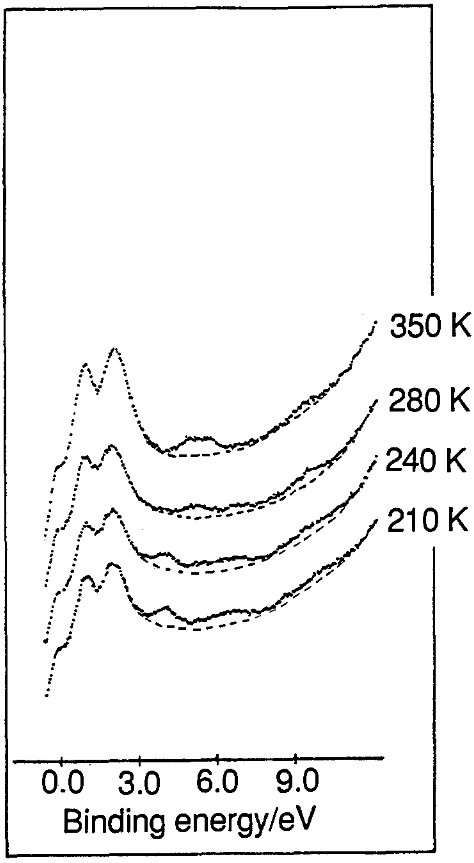

Fig. 2. He I UP spectra showing thermal evolution of species resulting from initial chemisorption of DCB on oxygen precovered Pd(111).

are significantly different (figs. 1, 2). This reflects the marked dependence of the furan peak temperature on total surface coverage [18,19].

Figure 4 shows the effect of varying oxygen precoverages on furan formation, following a fixed 1.75 L exposure to DCB. It can clearly be seen that more furan is formed at lower oxygen precoverages and this may be attributed to a combination of two factors. First, and most importantly, at higher oxygen coverages more complete oxidation to CO_2, CO and H_2O becomes favoured. Second, at lower oxygen precoverages a greater uptake of C_4H_4 is possible, due simply to the increased metal area available. This observation stands in marked contrast to the results of Gentle et al. [15] who found that with sulphided surfaces thiophene was only formed at the highest sulphur coverages employed ($\theta_S = 0.33$), suggesting that furan formation is favoured relative to thiophene formation. Figure 5 shows typical TPR spectra of furan, CO_2, CO and H_2O resulting from a single experiment using a low oxygen precoverage ($\theta = 0.025$). Taking account of the

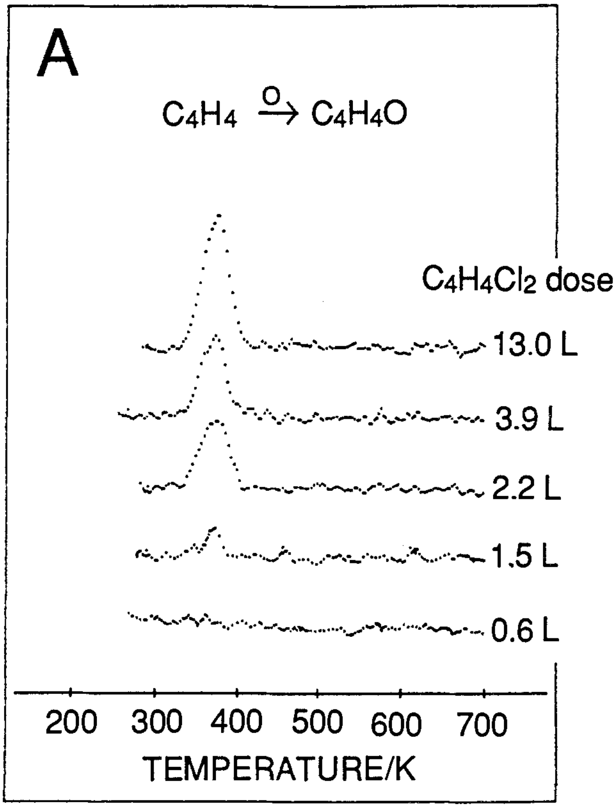

Fig. 3. Partial oxidation of C_4H_4 intermediate to furan. TPR spectra from oxygen precovered Pd(111) obtained after DCB adsorption at 270 K. A: $\theta_{ox} = 0.25$; B: $\theta_{ox} = 0.025$.

relative mass spectrometer sensitivities of the various species, we calculate an overall selectivity of ~ 80% towards furan formation under these conditions.

It is apparent from fig. 5 that the desorption maxima for CO_2, H_2O and furan are almost coincident (330 K). The evolution of both CO_2 and H_2O is known to be reaction-rate limited (as opposed to desorption-rate limited) [18], indicating that the interaction of oxygen with C_4H_4 to form CO_2 and H_2O occurs at this temperature. This could be taken to suggest that the almost coincident evolution of furan may also be limited by the incorporation of oxygen into the C_4 metallocycle rather than by its rate of desorption from the Pd surface. However, chemisorption of furan itself on oxygen precovered Pd(111) gives rise to a sharp C_4H_4O desorption maximum at 342 K, while desorption of the molecule from clean Pd(111) occurs at 360 K [19]. Thus it seems more likely that evolution of reactively formed furan is limited by the rate of product desorption, with oxygen incorporation into the metallocycle occurring at a lower temperature than does the combustion of C_4H_4. (The latter process is thought to proceed via a vinylidene species [9,19].)

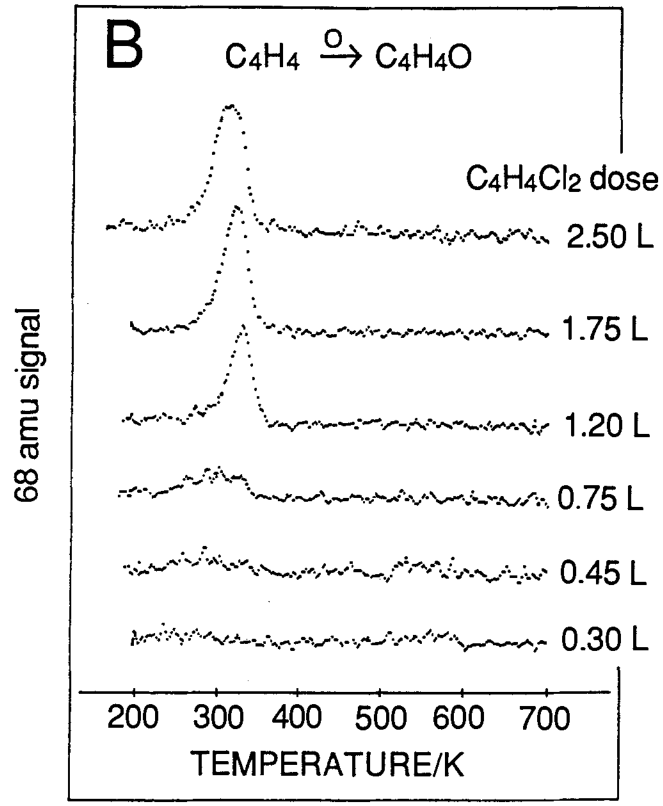

Fig. 3 (continued).

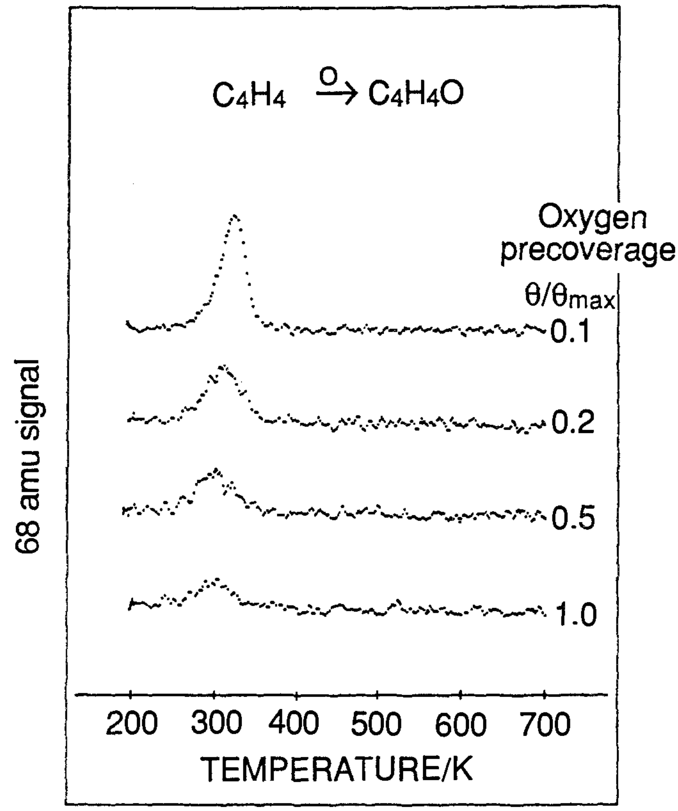

Fig. 4. Partial oxidation of C_4H_4 showing effect of oxygen precoverage. DCB exposure = 1.75 L.

4. Conclusions

Furan can be reactively formed and desorbed from Pd(111) during the selective oxidation of both acetylene and C_4H_4. In the latter case, the overall selectivity towards partial oxidation can be as high as ~ 80%. The results provide strong direct evidence that acetylene cyclotrimerisation does proceed via a C_4H_4 intermediate and that the latter may also be formed by dissociative chemisorption of cis-3,4-dichlorocyclobutene. Furan formation is favoured at low oxygen coverages, combustion to CO_2, CO and H_2O being favoured at higher oxygen coverages.

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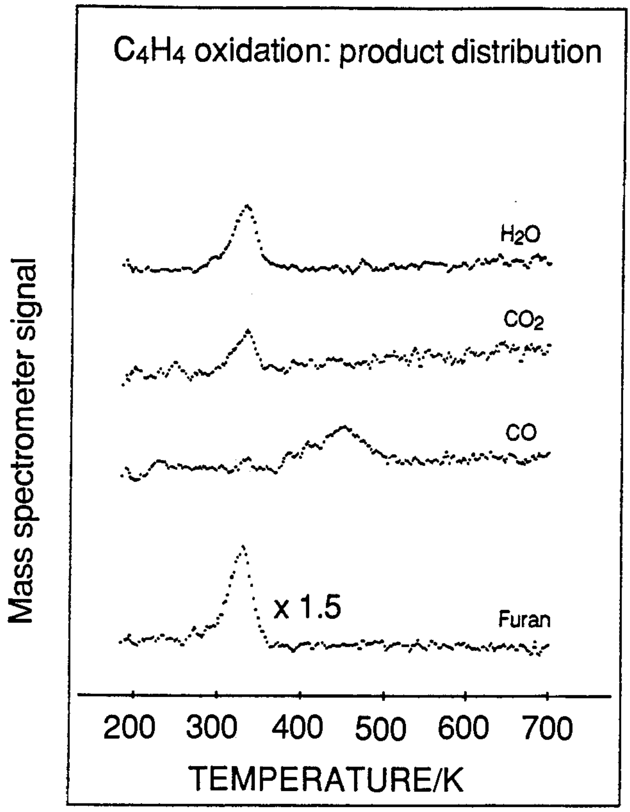

Fig. 5. Showing overall reaction selectivity during oxidation of C_4H_4 in TPR mode. $\theta_{ox} = 0.025$; DCB exposure 2.0 L at 200 K.

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