In Situ Observation of a Surface Chemical Reaction by Fast X-Ray Photoelectron Spectroscopy

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Despite their immense socioeconomic importance the discovery and optimization of new heterogeneous catalysts remains inefficient. This reflects the empirical methodologies often adopted and, in most cases, the absence of a microscopic understanding of catalyst behavior. By studying reactions on well-defined single-crystal surfaces, in conjunction with measurements on the corresponding practical dispersed catalysts, it is possible to obtain fundamental insight into reaction pathways and to develop predictive capabilities.[1,2] However, to further the rational design of catalytically active materials, new in situ analytical techniques are required. In particular, it would be valuable to obtain time-resolved information about the temperature-dependent evolution of the reacting adsorbed layer. Here, we demonstrate the first use of time-resolved fast X-ray photoelectron spectroscopy (XPS) as a chemically specific, quantitative probe in a study of the trimerization of ethyne to benzene over a catalytically active Pd(111) surface. We have measured the threshold temperature and activation barrier for trimerization, elucidated details of the reaction pathway, and identified configurational changes in the adsorbed layer.

The potential of fast XPS as a probe in studies of molecular desorption processes was recently demonstrated for the CO/Rh-(110) system.[3] The success of this technique hinges on the high photon flux and high resolution available at current third-generation synchrotrons. These attributes permit rapid acquisition of time-resolved XP spectra while ramping the sample temperature. Here, we extend the technique to follow a surface-catalyzed reaction: the trimerization of ethyne to benzene on a Pd(111) single-crystal surface. This reaction may be regarded as the prototypical metal-catalyzed alkyne coupling reaction. These processes are of interest because they constitute a versatile network of relatively complex reactions which, depending on the conditions, can yield a variety of products including linear and cyclic hydrocarbons and even heterocycles. In addition, they can be operated over a wide range of pressure ranging from ultra high vacuum to 1 bar using both single-crystal samples and dispersed catalysts. They therefore provide a valuable testing ground for many concepts that are central to catalytic science (see ref 4 and refs therein).[4]

Experiments were performed at the SuperESCA beamline of the ELETTRA (Trieste) synchrotron radiation source using on a Pd(111) single-crystal substrate prepared by standard procedures and maintained under ultra-high vacuum (system pressure ∼1 × 10^{-10} Torr). Quoted exposures are given in langmuirs (1 langmuir = 1 × 10^{-6} Torr s^{-1}). Carbon 1s XP spectra were acquired with

a photon energy of 400 eV and energy resolution of ∼100 meV. Temperature-programmed reaction data were acquired by application of a linear heating ramp (∼0.4 Ks^{-1}) to the ethyne-covered sample.

Ethyne trimerization occurs at low temperatures (<180 K). Therefore, adsorption was carried out with the sample held at 100 K so as to avoid immediate benzene formation. Figure 1 shows a sequence of C 1s XP spectra as a function of ethyne coverage. These data were obtained during continuous exposure of the initially clean Pd(111) sample over a time interval of ∼850 s, each spectrum being recorded in ∼10 s. All of the background-subtracted, low temperature C 1s spectra can be readily fitted using a single peak centered at 283.88 eV modeled by a Doniach−Sunjic function convoluted with a Gaussian. Derived peak parameters are given in Table 1 and the resulting C 1s integrated intensities are shown in the inset to Figure 1. This shows the presence just a single ethyne adsorption state at all coverages. We also obtained near-edge X-ray absorption spectra (NEXAFS, not shown) which show that the C−C axis of the reactant molecule remained parallel to the metal surface under all conditions. The surface coverage of ethyne increases linearly with exposure up to the saturation value of $\theta = 0.43$ monolayers (1 ML = 1 × 10^{-15} molecules cm^{-2}), indicative of precursor-mediated adsorption kinetics, consistent with previous studies.[5] Ethyne adsorption is accompanied by significant attenuation of the clean Pd(111) surface-state emission at 335.34 eV, relative to the emission from bulk Pd at 335.94 eV (Figure 2). The surface-state emission is associated with the topmost layer of Pd atoms,[6] and its quenching signifies Pd−ethyne bond formation.

Temperature-programmed C 1s XP spectra resulting from heating a saturated C_2H_2 overlayer are shown in Figure 3. Large temperature-dependent binding energy (BE) shifts and variations in peak width are apparent, due to changes in both the chemical state and number density of adsorbed hydrocarbon species. The initial peak shift to ∼1 eV higher BE is accompanied by little change in the overall C 1s intensity. However subsequent temperature rises induce a monotonic drop in C surface coverage and a gradual shift back towards lower BE. Using comparative C 1s spectra obtained during the low temperature chemisorption of benzene overlayers on Pd(111), all spectra in Figure 3 can be fitted by three components centered at 283.88, 284.54, and 285.01 eV, possessing a common lineshape. The fitted peak parameters are given in Table 1. The sequence in which these components are populated allows their assignment as unreacted ethyne, strongly chemisorbed flat-lying benzene, and weakly-bound tilted benzene, respectively. The temperature-dependent intensity variations of these components, and their sum (after correction for relative photon excitation cross-sections) are shown in Figure 4.

The interpretation we offer below is fully in accord with all of the available experimental data,[7] especially the isotope tracing and temperature-programmed reaction data.[8] The results show clearly that the primary chemical process is formation of flat-lying (η^6) benzene which commences at ∼150 K. The associated activation energy (obtained by analysis of the leading edge of the η^6 intensities shown in Figure 4) is ∼5 ± 1 kJ mol^{-1}. At ∼280 K, where ∼50% of the ethyne has reacted and a substantial amount of η^6 benzene is present, tilted (η^1) benzene appears on the surface. The formation of this species, either via direct reaction from ethyne and/or by tilting of η^6 benzene, reflects changing intermolecular interactions in the adsorbed layer. By ∼300 K most

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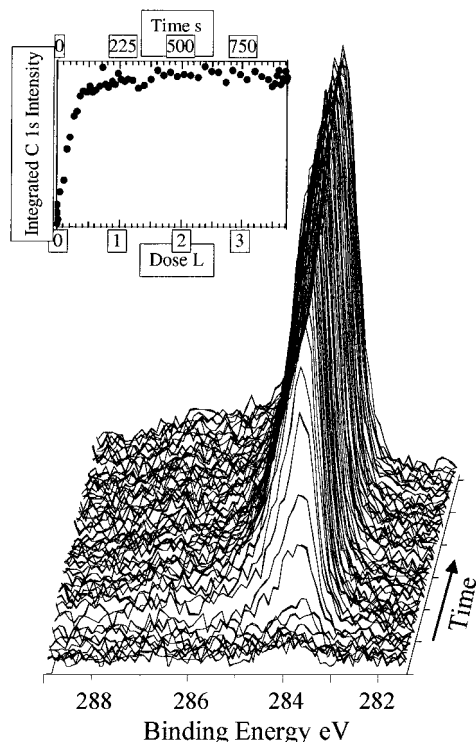
Figure 1. Main: C 1s XP spectra obtained during C_2H_2 uptake at 100 K over a clean Pd(111) surface. Inset: fitted, integrated C 1s peak intensities as a function of C_2H_2 exposure.

Table 1[a]

molecular assignment	binding energy, eV
C_2H_2	283.88
η^6 C_6H_6	284.54
η^1 C_6H_6	285.01

[a] Lorentzian FWHM $= 0.115$ eV, gaussian FWHM $= 0.522$ eV, asymmetry factor $= 0.188$.

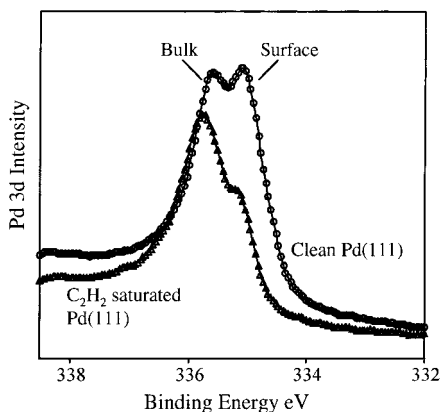**Figure 2.** Pd 3d XP spectra from clean (○) and C_2H_2-saturated (△) Pd-(111) surfaces showing quenching of clean Pd surface state.

Figure 3. C 1s XP spectra obtained from a C_2H_2-saturated Pd(111) surface as a function of temperature.

Figure 4. Fitted, integrated C 1s peak intensities derived from a C_2H_2-saturated Pd(111) surface as a function of temperature, showing C_2H_2) (—), η^6 C_6H_6 (○), and η^1 C_6H_6 (◆) components.

of the ethyne has been removed by desorption or reaction, but important changes continue within the predominately benzene containing adsorbed phase. At ~330 K ethyne is no longer present and it is clear that tilted η^1 tilted benzene starts to convert into η^6 flat benzene, presumably due to reduced adsorbate density. Closer insepection of the η^6 and η^1 intensities in this temperature regime shows that η^1 depletion exceeds η^6 accumulation, implying that in addition to the tilted → flat conversion, some of the tilted benzene actually desorbs. This desorption acts to deplete the surface of adsorbate, thus assisting the tilted → flat conversion. At ~500 K the coverage of η^6 (flat) benzene starts to decrease due to its desorption. At this point the Pd surface is rather bare and, quite unexpectedly, the η^1 population apparently starts to rise again. It
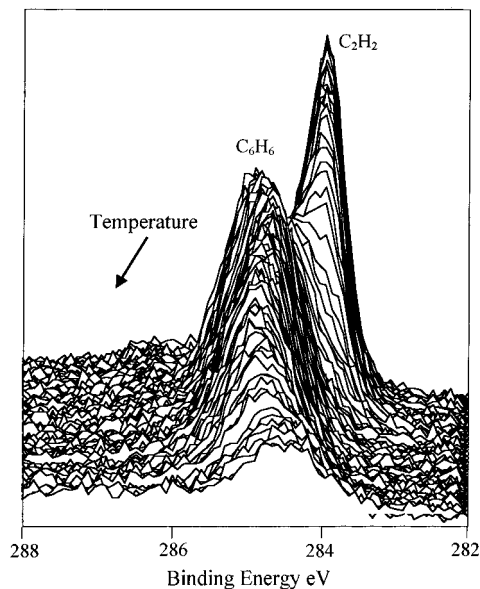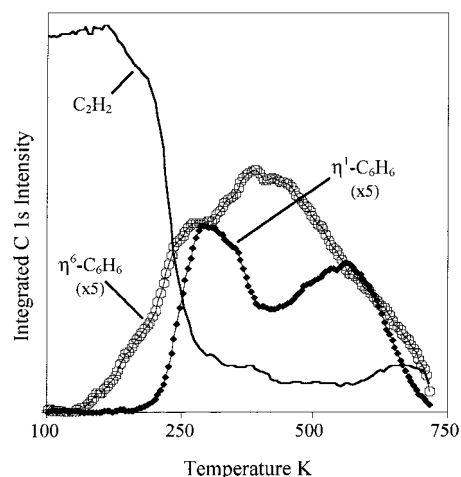
is hard to see how this high temperature species could be ascribed to conversion of strongly adsorbed η^6 benzene to weakly adsorbed η^1 benzene. A much more likely explanation is as follows. The nearly bare Pd(111) surface is efficient at inducing C–H cleavage in adsorbed benzene.[9] The resulting η^1 and η^2 phenyl species would be strongly adsorbed but also tilted with respect to the surface, resulting in a C 1s binding energy very similar to that of η^1 benzene. Finally, these phenyl species are lost by disproportionation, yielding gaseous benzene and residual adsorbed carbon.

Our observations provide the first direct evidence that surface reactions are not rate-limiting for the appearance of the gaseous benzene product: the desorption step is rate-limiting. They also demonstrate that important configurational changes occur in the adsorbed product as the the reaction proceeds. These changes are critically important in determining the kinetics of the overall reaction. Kinetic control can be achieved by designing the catalyst surface (e.g., by alloying Pd with Au)[10,11] so as to favour the formation of η^1 (tilted) benzene thus maximizing activity and optimizing selectivity.

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