Structure-Reactivity Correlations in the Catalytic Coupling of Ethyne over Novel Bimetallic Pd/Sn Catalysts

Adam F. Lee, Christopher J. Baddeley, Christopher Hardacre,[†] Geoffrey D. Moggridge,[‡] R. Mark Ormerod,[§] and Richard M. Lambert*

Department of Chemistry, University of Cambridge, Cambridge CB2 1EW, England

Jean P. Candy and Jean-M. Basset

Laboratoire de Chimie Organométallique de Surface, UMR CNRS-CPE 9986, CPE Villeurbanne, France Received: November 18, 1996; In Final Form: January 28, 1997[®]

The structure, thermal stability, and catalytic behavior of a novel highly dispersed silica-supported Pd/Sn catalyst prepared by an organometallic route have been examined by X-ray photoelectron, X-ray diffraction, and X-ray absorption, fine structure spectroscopies, the latter two measurements being carried out with an *in situ* reaction cell. Additional reactor measurements were performed on a more Sn-rich catalyst and on a pure Pd catalyst. Varying the temperature of reduction induced large variations in catalytic performance toward ethyne-coupling reactions. These changes are understandable in terms of the destruction of SnO₂-like structures surrounding the Pd core, yielding a skin of metallic Sn which subsequently undergoes intermixing with Pd. The overall thermal and catalytic behavior of these highly dispersed materials accords well with the analogous single-crystal model system.

Introduction

The catalytic coupling of ethyne over Pd and Pd-derived surfaces provides a relatively complex network of reactions which exhibit very pronounced sensitivity to the structure¹ and composition² of the metal surface. It is therefore a useful system for examining mechanistic aspects of hydrocarbon conversion. The application of alloy catalysts provides an additional dimension and can yield results that are of wider significance in fields such as catalytic hydrocarbon reforming.^{3,4}

Our earlier work on Au{111}/Pd⁵ and Pd{111}/Au² model catalysts gave results that were of value in illuminating the behavior of practical, dispersed Au/Pd core/shell catalysts.⁶ Recently, we reported on the structural and thermal properties of the Pd{111}/Sn model planar system.⁷ Here we describe corresponding structural and catalytic results obtained with a novel type of a highly dispersed Pd/Sn catalyst in which a coating of Sn is applied to a Pd core by an organometallic route. For comparison purposes, additional catalytic measurements were carried out on a more Sn-rich catalyst and on a pure Pd catalyst; the Pd content was identical in the three cases. It is found that large variations in catalytic perfomance are understandable in terms of the deliberately induced changes in surface structure and composition. Furthermore, in this case too, Pd{111}/Sn single-crystal data provide relevant insight. Comparisons are made with the related Pt{111}/Sn system.⁷

Experimental Section

Two silica-supported Pd/Sn bimetallic catalysts were prepared by the controlled surface organometallic reaction (CSOR) method developed by Basset and co-workers.⁸ The Pd/SiO₂

monometallic catalysts were prepared by ion exchange of [PdCl- $(NH_3)_5]^{2+}$ onto a 250 m² g⁻¹ silica support. The resulting surface complex was calcined in air at 673 K and reduced at 673 K in H₂ to yield 10–20 Å Pd particles with a dispersion of ~ 0.75 ,⁹ and metal loading of 2 wt % Pd. The subsequent surface reaction was performed in the liquid phase (n-hexane solvent) in a stainless steel autoclave between the desired amounts of tetra-n-butyl tin $Sn(n-C_4H_9)_4$ and the monometallic Pd catalyst by reduction at 473 K under 30 mbar hydrogen. The resulting slurry was refluxed in boiling *n*-hexane under Ar at 370 K for 24 h to remove unreacted Sn(n-C₄H₉)₄ and was dried in Ar, and the catalyst samples were sealed under an Ar atmosphere for transportation. All measurements were performed on deliberately air-exposed samples. The amounts of monometallic Pd/SiO₂ and Sn(n-C₄H₉)₄ were chosen to give a ratio of Sn to *surface* Pd atoms of $Sn:Pd_s = 0.5$ and $Sn:Pd_s =$ 0.66. Hereafter, these samples are designated Pd₂Sn and Pd₃- Sn_2 by reference to the idealized surface stoichiometries.

In situ X-ray diffraction (XRD) experiments were performed at 300 K, in 1 bar He with a Siemens D500 diffractometer using Cu K α radiation (154 pm), and with a specially constructed silica reaction cell.¹⁰ This cell permits both XRD and X-ray fine absorption structure (XAFS) studies to be carried out in controlled, reactive atmospheres. Powdered catalyst samples, typically ~ 100 mg, were placed on a ceramic/silica sinter fitted into a recess of the hollow silica sample holder. The XRD/ XAS (XAS = X-ray absorption spectroscopy) cell was attached to a Perkin-Elmer 700HWD GC (Poropak-N and 5X molecular sieve), allowing precise monitoring of the catalyst environment. The sample cell could also be operated as a single-pass flow reactor, and the catalytic data presented here were obtained in this way. Reductions were performed in H_2 (10 mL min⁻¹, distillers 4.6, 20 K/min) at temperatures between 300-873 K for 20 min, followed by purging and cooling in He. Data were collected between $2\theta = 35-85^{\circ}$ at 0.02° increments with spectral acquisition times of 500-1000 min/scan.

XAFS measurements were performed as a function of catalyst reduction temperature on Stations 9.2 and 9.3 of the Daresbury

 $^{^{\}dagger}$ School of Chemistry, Queen's University, Belfast BT9 5AG, Northern Ireland.

[‡] Department of Chemical Engineering, University of Cambridge, Cambridge CB2 3RA, England.

[§] Department of Chemistry, University of Keele, Keele, Staffs ST5 5BG, England.

^{*} Corresponding author.

[®] Abstract published in Advance ACS Abstracts, March 1, 1997.



Figure 1. XRD pattern from Pd₂Sn/SiO₂ reduced in H₂ at 873 K.

SRS facility using the *in situ* reaction cell. Both the Pd and Sn K-edges (at 24.35 and 29.19 keV, respectively) were monitored in fluorescence mode at 300 K in He, using a Canberra solidstate multichannel detector, mounted in the horizontal plane. Transmission spectra of 8 μ m Pd and Sn foils, together with SnO and SnO₂ powder standards, were also measured. Signal to noise ratio was optimized by acquiring multiple scans for every spectrum. Data analysis employed the Daresbury EXBROOK and EXCURVE92 packages for background sub-traction and subsequent theoretical fitting, respectively. Fourier-filtering procedures were not employed in this study, due to the quality of background subtraction and absence of significant artifacts adjacent to the principal fitted coordination shells.

Catalyst testing was performed under steady-state conditions as a function of the H₂:C₂H₂ reactant ratio and as a function of the reaction or reduction temperature at 1 bar total reaction pressure. Product yields stabilized after ~45 min and remained constant for >5 h. The errors in quoted yields and selectivities are ~±5% for the major (C₆) products and ±10% for the minor (C₄) products. The activity was calculated *via* carbon massbalance, thus

> activity = no. of moles of C₂H₂ consumed = $\sum_{n=4,6} {n/2}$ (no. of moles of C_n product)

and product selectivity is defined as

$$S_{\text{product}} = \frac{\text{moles of } C_n \text{ product}}{\sum_{n=4,6} \text{moles of } C_n \text{ product}}$$

X-ray photoelectron spectra were recorded at 300 K in a VSW ARIES system¹¹ equipped with a HA100 spectrometer (Mg K α) at 40 eV pass energy. The sample was prepared as a homogeneous powder supported on adhesive tape, with energy referencing made to the adventitious carbon line at 284.3 eV to compensate for charging effects.

Results

X-ray Diffraction Studies. Very weak, common diffraction features were observed for all Pd_xSn/SiO_2 samples irrespective of the reductive pretreatment or scan time used. Figure 1 illustrates the XRD pattern for a Pd_2Sn/SiO_2 sample prereduced at 873 K in H₂. Three weak, broad peaks associated with a metal phase are visible at ~40°, 46° and 68°, the corresponding positions for bulk fcc Pd and α -Sn are shown for comparison. The sloping background and poor signal to noise reflects the low counts detected from the dilute samples and the absence of large metal particles. From the 40° ([111]) diffraction peak



Figure 2. (a) Pd 3d and (b) Sn 3d photoemission core-level spectra from air-exposed Pd₂Sn/SiO₂.

of the 300–873 K reduced samples, the Scherrer equation yields a constant fcc lattice parameter of ~3.9 Å and corresponding volume-averaged particle size of \leq 35 Å for cubeoctahedral/ spherical particle morphologies. Note the errors in the XRDderived lattice parameter (~±0.1%), and particle diameters (±20 Å) are significant, due to the low signal intensities and limiting particle sizes. This lattice parameter and the additional refelections match well to those of pure Pd. No reflections characteristic of tin oxide or crystalline Pd/Sn alloys were observed for any sample. Minority, intermediate Pd_xSn were also undetected; note that no random substitutional Pd/Sn alloys are reported in the literature.¹²

X-ray Photoelectron Spectroscopy. Photoelectron spectra of the as-prepared Pd₂Sn/SiO₂ sample were measured in order to determine the electronic state of both metallic components. The principal Pd and Sn $3d_{3/2,5/2}$ X-ray photoemission transitions at ~336 and ~485 eV binding energy (BE), respectively, are presented in Figure 2a,b. A single Pd $3d_{5/2}$ line is present at ~336.3 eV BE (Figure 2a), with a shape characteristic of the bulk material but shifted by ~1 eV to higher BE.¹³ The Sn $3d_{5/2}$ line has a composite shape (Figure 2b), which standard Shirley background subtraction and deconvolution procedures reveal to comprise a majority component at ~486.8 eV BE, together with a weaker lower BE state at ~484.5 eV. For reference, the $3d_{5/2}$ line of bulk α -Sn occurs at 484 eV.¹⁴

X-ray Absorption Fine Structure Studies. The local structural and electronic environment of each metal component in the Pd₂Sn sample were investigated by X-ray absorption spectroscopy as a function of H_2 prereduction temperature. Additional measurements on the Pd₃Sn₂ sample gave quantitatively similar results to those for Pd₂Sn and are thus not reported here. Results from the deliberately air-exposed and control samples were in good quantitative agreement. Figure 3a,b show the respective raw Pd and Sn K-edge EXAFS (extended X-ray absorption fine structure spectroscopy) data



Figure 3. Raw (a) Pd and (b) Sn K-edge EXAFS spectra from Pd₂-Sn/SiO₂ as a function of H_2 reduction temperature. Spectra from Pd and Sn foils and SnO/SnO₂ powder standards are shown for comparison.

for Pd₂Sn together with standard transmission spectra from 8 μ m Pd and Sn foils and SnO/SnO₂ powders for comparison. The raw Pd-edge data for Pd₂Sn display no clear variation with increasing reduction temperature and closely resemble the standard foil spectrum, hence only the as-received and 873 K reduced spectra are discussed. In contrast, the raw Sn-edge spectra display a dramatic decrease in the white line (edge–step height) intensity and in the amplitude and periodicity of the EXAFS oscillations, with increasing reduction temperature. Comparison of the raw Pd₂Sn data with the Sn standards suggests a progressive transformation from a SnO₂/SnO-like phase at 300 K to a metallic phase after 873 K reduction.

The background-subtracted, k^3 -weighted Pd and Sn raw EXAFS functions appear in Figure 4a,b, respectively, together with their associated theoretical fits for various reduction treatments. No variation is apparent between the Pd-edge spectra, which are directly superimposable. In contrast, upon reduction, the Sn-edge spectra exhibit gross changes. Again, the as-received and 300 K reduced Sn-edge spectra resemble that of SnO₂, while the 873 K spectrum closely matches the Sn foil EXAFS function. The structural transformations accompanying reduction are more apparent from the Pd- and Sn-edge unfiltered RDFs, shown together with their theoretical fit functions in Figure 5a,b, respectively. The fitted parameters derived for these figures are quantified in Table 1.

The as-prepared (air-exposed) Sn-edge (RDF) of Pd₂Sn exhibits a single major peak at ~ 2 Å, Figure 5b. The presence of *tert*-butyl groups on unreduced Ni_xSn/SiO₂ catalysts yields a similar peak attributed to a Sn–C shell distance.¹⁵ By analogy, the present peak distance is too short to correspond to a Sn–metal scattering coordination shell, while organometallic



Figure 4. Background-subtracted raw k^3 -weighted (a) Pd and (b) Sn χ data from Pd₂Sn/SiO₂ as a function of H₂ reduction temperature.

Sn-C and oxidic Sn-O bond lengths are both ~ 2 Å. In the absence of surface hydrocarbon fragments⁹ this shell is assigned to Sn-O scattering. An excellent fit to the unreduced Pd₂Sn data was achieved using bulk SnO₂ fit parameters as well as a constrained iteration of the Sn-O Debye–Waller and phase-shift correction factors ($\sigma 1_{Sn-O}$ and E_f). No fit could be achieved using the parameters of SnO.

Increasing reduction temperatures induce a gradual decrease in the number of nearest-neighbor O atoms from \sim 6 at 300 K to effectively zero following an 873 K reduction (Figure 5b). A new sharp, high R scattering shell simultaneously emerges at $\sim 2.6-2.7$ Å. This shell could not be fitted using oxygen scatterers, and in any case it does not correspond to any known bulk oxide of Sn. This interatomic distance is thus assigned to heavier, metallic scatterers, although distinguishing beween Sn and Pd nearest-neighbor atoms is not trivial, due to their similar scattering power. The Sn-Sn nearest-neighbor distance varies from 3.02 to 2.8 Å between bulk α - and β -Sn structures, and therefore complicates the accurate estimation of Sn-Pd bond distances in fcc-like bimetallic particles. The bulk Pd-Pd separation of 2.75 Å is closest to the observed 2.65 Å shell distance (which may be contracted due to Sn charge-polarization). This shell is thus reasonably attributed to nearest-neighbor Pd atoms, an assumption supported by the final "high" coordination of ~5 attained after an 873 K reduction. Sn-Sn coordination of \sim 5 is unlikely considering the low initial Sn: Pd atom ratio and the resultant relatively low maximum possible Sn surface concentration of $\sim 0.66^{16}$ via seeding with bulky tertbutyl ligands. The absence of Sn X-ray diffraction features is



Figure 5. Unfiltered (a) Pd and (b) Sn K-edge pseudo-radialdistribution functions obtained from Pd_2Sn/SiO_2 as a function of H_2 reduction temperature. Data from a pure SnO_2 bulk standard are shown for comparison.

TABLE 1

	300/K	473/K	673/K	873/K
Sn K-edge				
$N1_{Sn-O}$	6	3	1	
$N2_{Sn-Pd}$		3.3	3.1	4.7
$R1_{Sn-O}/Å$	2.05	2.02	2.01	
$R2_{Sn-Pd}/Å$		2.64	2.67	2.65
$\sigma 1_{\text{Sn-O}}/\text{Å}^2$	0.008	0.013	0.007	
$\sigma 2_{\mathrm{Sn-Pd}}/\mathrm{\AA}^2$		0.017	0.015	0.0174
Pd K-edge				
$N1_{\rm Pd-Pd}$	8			8.2
$N2_{\rm Pd-Pd}$	4.7			4.7
$R1_{\rm Pd-Pd}/{\rm \AA}$	2.77			2.77
$R2_{\mathrm{Pd-Pd}}/\mathrm{\AA}$	3.87			3.94
$\sigma 1_{\mathrm{Pd-Pd}}/\mathrm{\AA}^2$	0.023			0.022
$\sigma 2_{ ext{Pd-Pd}}/ ext{\AA}^2$	0.039			0.034

in accord with this view. Discriminating between possible Sn–Sn and Sn–Pd scattering pairs from the theoretical fits alone proved inconclusive, although disorder factors were in better agreement with those from Pd foil as opposed to Sn foil. Reduction treatments thus result in the progressive elimination of Sn–O nearest neighbors and their replacement by Sn–Pd nearest neighbors. This process was essentially complete above 673 K.

The Pd-edge RDFs exhibit a single, major peak at $\sim 2.7-2.8$ Å for all reduction temperatures. This feature can be accurately fitted using bulk Pd foil parameters and a reduced Pd-Pd nearest-neighbor atom coordination of ~ 8 . The inclusion of Pd-Sn scattering pairs served only to worsen the fit



Figure 6. Normalized, derivative (a) Pd and (b) Sn K-edge XANES spectra from Pd_2Sn/SiO_2 as a function of reduction temperature. Spectra from Pd and Sn foils and SnO/SnO₂ powder standards are shown for comparison.

and confirmed that Pd atoms reside in a truncated bulk Pd-like environment. A weak shoulder to low R on the principal Pd peak is a termination error resulting from Fourier transformation of the EXAFS data over a finite *k*-range.¹⁷

Absorption features in the energy range $\sim 0-50$ eV above the edge jump can also provide information on the valence electronic structure of the excited atom.¹⁸ Core-ionized photoelectrons possessing a sufficiently low kinetic energy may become trapped in bound or quasibound unoccupied states close to the Fermi energy of a sample,¹⁹ thus modulating the smooth atomic absorption function. The occurrence of such transitions is controlled by the dipole-selection rule ($\Delta l = \pm 1$), and where this is satisfied, their intensity reflects the local excited atom density of states.²⁰ The Sn K-edge X-ray absorption near edge structure (XANES) is thus dominated at low energies by allowed $1s \rightarrow 5p$ transitions (analogous to L₁-edge spectra²⁰) and can yield information on the Sn 5p occupancy. In contrast, the Pd valence band possesses primarily d-orbital character. Consequently, $1s \rightarrow 4d$ transitions are only weakly allowed (*via* p-d rehybridisation), and low-energy Pd K-edge XANES features are thus weak and are less sensitive probes of the Pd d-band occupancy.

Analysis of fine structure within the XANES region is usually performed on the normalized, derivative spectra. Differences in the relative intensities of absorption features are thus greatly enhanced. Figure 6a,b show the resultant Sn and Pd derivative XANES spectra as a function of reduction temperature. The energy scale of each spectrum is referenced to the first maximum (E_0) to compensate for experimental variations in the raw data.

The Sn XANES exhibits a sharp maximum at E_0 and a sharp minimum at \sim +10 eV. The magnitude of both features for the as-received sample closely matches both oxide standards and decreases systematically with increasing reduction temperature. (The difference between the oxidized and reduced cases is indicated by the double-headed arrows in Figure 6b). The



Figure 7. Activity of Pd_xSn/SiO_2 catalysts as a function of reactant mix and Sn loading. $T_{reaction} = 540$ K.

first peak maximum is assigned to $1s \rightarrow 5s$,p transitions,²⁰ and thus reflects the Sn valence band occupancy. It is apparent that, following reduction at either 673 or 873 K, the features above $\sim 10 \text{ eV}$ are significantly shifted. In contrast, the phase and magnitude of the principal Pd XANES maxima and minima are unperturbed by reduction, mirroring those of the Pd foil standard.

Catalytic Measurements

The *in-situ* reaction data, which provide a complementary surface sensitive probe to the preceding spectroscopic measurements, reveal the exclusive formation of C_4 and C_6 cyclization products at elevated temperature over all 3 Pd_xSn/SiO_2 samples. The principal reaction products observed under all reaction conditions, for all sample pretreatments, in order of yield, were benzene, *n*-hexane, isobutene, and *trans*- and *cis*-2-butene. Trace cyclohexene and cyclohexane were also observed.

Influence of Reactant Gas Composition. Figure 7 shows the catalytic activity at 540 K as a function of the loading ratios of H₂:C₂H₂ and Sn:Pd for samples prereduced at 540 K. The steady-state activities of all three catalysts exhibit very similar hydrogen partial pressure dependence. A rapid increase occurs from essentially zero conversion in pure ethyne to a maximum for H₂:C₂H₂ \sim 1–1.5, decaying slowly to low (nonzero) activities for ratios >5. The maximum activity increases with Pd: Sn ratio, corresponding to 58, 86, and 95% conversion for the Pd, Pd₂Sn, and Pd₃Sn₂ samples, respectively. The peak Pd₃-Sn₂ activity also occurs at a slightly lower H₂:C₂H₂ ratio than for the other samples. For H₂:C₂H₂ ratios <1, all rates exhibit positive order in H₂, while for H₂:C₂H₂ ratios >2, all rates show negative order in H₂.

The principal reaction products for all H₂:C₂H₂, and Sn:Pd ratios were benzene and n-hexane. The yields of these two products exhibit strong anticorrelation as a function of the H₂: C₂H₂ ratio (Figure 8a). All samples exhibit similar dependencies for increasing $H_2:C_2H_2$ ratios between 0–1.2. Sbenzene falls from ~90 to 50%, while $S_{n-\text{hexane}}$ increases in the same manner from \sim 0 to 50% over this regime. This transition, from essentially pure benzene to predominantly *n*-hexane production, continues for the Pd and Pd₂Sn catalysts at higher H₂ partial pressures, and is complete for $H_2:C_2H_2 \ge 1.75$. In contrast, the trends in the Pd₃Sn₂ catalyst selectivity are much less pronounced for H₂:C₂H₂ ratios \geq 1.2, yielding limiting S_{benzene} and S_{n-hexane} values of $\sim 20\%$ and 75%, respectively. Note that all the minority C₄ product selectivities track the variation in S_{benzene} with H₂:C₂H₂ for the Pd and Pd₂Sn samples. Figure 8b illustrates the case for $S_{trans-butene}$. The Pd₃Sn₂ C₄ selectivities display a similar dependence (tending to zero production), and thus appear to deviate from S_{benzene} for ratios ≥ 2 . This



Figure 8. Selectivity toward (a) C₆ and (b) C₄ products of Pd_xSn/SiO₂ catalysts as a function of reactant mix and Sn loading. $T_{\text{reaction}} = 540 \text{ K.}$



Figure 9. Activity of Pd_xSn/SiO_2 catalysts as a function of H_2 prereduction temperature and Sn loading. $T_{reaction} = 540$ K.

observation may reflect the very low C₄ yields, and thus large measurement error in these latter data points. The peak C₄ selectivities decrease in the order $S_{trans-butene}$ (~6%) > S_{isobutene} (~5%) > S_{cis-butene} (~3%).

Influence of Reduction Temperature. The activities of the Pd_xSn catalysts as a function of prereduction temperature and Sn:Pd loading are shown in Figure 9. The dependence of activity on reduction temperature increases with Sn loading. Thus the activity of the pure Pd sample was completely insensitive to all reduction treatments employed, while the Pd₂-Sn and Pd₃Sn₂ activities decrease by ~8 and 13%, respectively, following reduction between 300–1073 K. The maximum activities again equate to 58, 86, and 95% for the Pd, Pd₂Sn, and Pd₃Sn₂ samples, respectively. Figure 10 shows the corresponding C₆ selectivities of the Pd and Pd₂Sn samples. Data for the monometallic catalyst do not exhibit any significant



Figure 10. Selectivity toward C₆ products of Pd_xSn/SiO₂ catalysts as a function of H₂ prereduction temperature and Sn loading. $T_{\text{reaction}} = 540 \text{ K}.$



Figure 11. Selectivity toward C_6 products of a 540 K prereduced Pd_2 -Sn/SiO₂ catalyst as a function of reaction temperature.

trends. However, for Pd₂Sn, a rise in S_{benzene} and a corresponding fall in $S_{n-\text{bexane}}$ (both by ~12%) with reduction temperature are apparent. A similar, less pronounced transition between benzene and *n*-hexane production also occurs for the Pd₃Sn₂ sample (not shown for clarity)—these smaller changes may reflect the initial high S_{benzene} (~85%) and low $S_{n-\text{hexane}}$ (~4%) of the as-prepared samples. The C₄ selectivities display no systematic variations, and individual product selectivities remain at levels <5%. In all cases the maximum total C₄ selectivity is <7%, and the measurement error for these small yields is significant.

Influence of Reaction Temperature. The dependence of C₆ selectivities on reaction temperature is shown in Figure 11. The selectivities toward all C₄ products (not shown) exhibited a slight decrease with increasing reaction temperature: S_{iso-butene} from 5% to 4%, S_{cis-butene} from ~5% to ~2%, S_{trans-butene} from ~2% to ~1%.

Discussion

Structural Characterization of the Pd₂Sn Catalyst. Previous studies of the Rh,Ni/Sn systems prepared by CSOR routes indicate that submonolayer quantities of $Sn(n-C_4H_9)_4$ are selectively anchored to, and undergo hydrogenolysis exclusively at, the surface of small (~10–15 Å) metallic Rh and Ni particles. Low reduction temperatures stabilize the M_s[Sn($n-C_4H_9$)_x]_y surface organometallic fragments.⁹ In the present case, the hydrogenolysis reaction was performed at 473 K, sufficient to remove the ($n-C_4H_9$)₄ ligands, yielding pure metallic Pd particles partially encapsulated by a Sn overlayer.

The XRD-derived lattice parameter for the Pd_2Sn sample indicates the presence of small Pd clusters with an average

particle size of ≤ 30 Å. Pd K-edge EXAFS data (Figure 5a), which indicate bulk Pd-Pd separations and the absence of Pd-Sn nearest neighbors, confirm the majority of Pd atoms are initially located in a "pure" Pd phase. An independent estimate of the Pd cluster size may be obtained from the nearest-neighbor coordination number. For average particle sizes below ~ 100 Å, high-temperature (\geq 300 K) EXAFS analysis yields artifically reduced coordination numbers due to anharmonic atom vibrations.²¹ Employing the correction factors determined by Clausen et al., the average, "true" EXAFS-derived Pd particle size is $\sim 10-30$ Å, in agreement with the XRD measurements. This is in line with the observed high Pd 3d BE (\sim 336.3 eV), which is shifted by $\sim +1$ eV relative to the bulk. For small metal clusters supported on insulating substrates with which they weakly interact (e.g. SiO₂), such core-level shifts predominantly reflect changes in final-state, core-hole screening processes relative to the bulk environment.²² The magnitude of the shift is thus a strong function of the cluster size, with which it is inversely correlated; previous studies of Pd clusters deposited on silica indicate that a 1 eV shift is associated with $\sim 10-20$ Å particles.²³

Basset et al. have shown the CSOR method is highly selective, localizing the SnR4 ligands exclusively on the metallic clusters-interaction with silanol groups on the support is negligible.⁹ The absence of significant Sn-Pd scattering in the as-prepared sample presumably reflects the effect which might be expected to result in tin oxide formation at the cluster surface. Indeed, studies of ultrathin Sn films grown on a Pd{111} singlecrystal demonstrate that the low-pressure oxidation of submonolayer Sn deposits is extremely facile and proceeds rapidly at 300 K.²⁴ These findings are in accord with our Sn K-edge EXAFS data which indicate that the majority of Sn atoms are initially present within a SnO₂ film, Figure 5b. However, the Sn 3d XPS spectra do provide clear evidence for the retention of some Sn (~10% of the grafted overlayer) within a metallic environment. These Sn⁰ atoms may be either localized on the surface of the Pd particles, as a partial encapsulating overlayer, or present within a Pd/Sn surface alloy phase. In contrast with unannealed Sn overlayers, single-crystal studies show that Sn atoms incorporated within Pd/Sn surface alloys are highly resistant to oxidation even at pressures of >50 Torr O₂.²⁴

Oxidation ($\geq 10^{-4}$ Torr O₂) induces cracking of thin Sn films supported on Pd{111}.²⁴ It is thus unlikely that the SnO₂ phase formed during room temperature air-exposure constitutes a continuous encapsulating layer around the Pd clusters. Exposure of bare Pd sites following disruption of the Sn oxide overlayer may also contribute to the room temperature reactivity of the as-prepared Pd₂Sn sample, discussed later. This cracked oxide phase is XRD invisible, and given the absence of higher Sn-O coordination shells in the Sn EXAFS, it could be little more than a monolayer thick. EXAFS measurements on silicasupported Ge/Ru bimetallic clusters prepared by CSOR²⁵ also indicate that air exposure yields a partially encapsulating GeO_x structure, similar to that proposed here. Note also that our results eliminate the possibility that substantial Sn oxide agglomerates were present at the cluster/silica interface.

Reduction temperatures above 300 K progressively destroy the Sn oxide phase: Sn K-edge EXAFS shows that nearestneighbor oxygen scatterers around each Sn atom are progressively replaced by Pd, Figure 5b. Although this process becomes detectable after reduction at room temperature, significant oxygen loss only occurs above 473 K, with an accompanying reduction in the Sn–O coordination from 6 to \sim 3. A scheme which is consistent with our results is illustrated in Figure 12 which represents the conversion of the SnO₂ *via*

Figure 12. Schematic illustrating progressive destruction of surface SnO_2 particles and subsequent Pd/Sn surface alloying for Pd_xSn/SiO_2 catalysts as a function of reduction in H₂.

disordered/nonstoichiometric SnO to a bimetallic system. In this connection, it is worth noting that ultrathin Sn oxide films on Pd{111} also begin to decompose at \sim 473 K.²⁴ In contrast, bulk SnO₂ and SnO are stable up to 1000 K,^{26,27} illustrating the much lower stability of the supported Sn oxide layer on both clusters and extended Pd surfaces. This scheme is supported by a recent EELS, XPS, and ISS study of Hoflund²⁸ showing that step 1, representing the direct reduction of SnO₂ to SnO without passage via a transitional oxide phase, occurs for bulk SnO₂ samples following 473 K reduction in 40 Torr H₂. The subsequent high-temperature reduction of SnO to Sn⁰ incorporated within ordered Pd/Sn surface alloys, step 2 of the scheme, is also observed during in vacuo annealing of ultrathin, stoichiometric SnO films supported on Pd{111}. This behavior contrasts with that of bulk SnO, for which annealing treaments between 473-873 K actually reoxidise the selvedge to SnO₂ via a transitional Sn₂O₃ phase.²⁶

The short Sn–Pd distance found for the "473 K reduced" sample (2.65 Å *versus* > 2.75 Å for a bulk substitutional Pd/Sn alloy¹²) is consistent with stage 2 of the scheme shown in Figure 12 with interfacial Sn atoms residing between the Pd substrate and an oxygen top layer. (Goursot *et al.*²⁹ recently calculated a similar metal-metal separation for Sn on a Ru₉{111} cluster.) Reduction in Sn radius due to Sn–O charge polarization (*e.g.*, in SnO and SnO₂: 0.93 and 0.73 Å, respectively²⁷) would also contribute to the contracted Pd–Sn separation.

It might be expected that Sn surface \rightarrow bulk diffusion would be thermodynamically disfavored for small Pd particles where the low Sn:Pd atom ratio prohibits intermetallic compound formation,¹² the proposed driving force for Sn bulk diffusion into Pt particles.³⁰ This is what we find. Thus our EXAFS data suggest that reduction of the surface Sn oxide phase is complete at temperatures >673 K and that the total Sn nearestneighbor coordination remains low, even after reduction at the highest temperature. This points to Sn atoms predominantly occupying surface sites, as anticipated from the very large difference in Pd and Sn surface free energies (0.71 and 2.1 J m⁻², respectively²⁷). Correspondingly, the XRD results confirm the absence of bulk Pd/Sn alloy phases.

Again, the behavior of the dispersed Pd/Sn system accords well with that found for macroscopic model planar catalysts. Heating of Sn monolayers deposited on Pd{111} under vacuum conditions leads to surface alloy formation.⁷ A $\sqrt{3}$ (Pd₂Sn) surface structure is formed at ~773-873 K, its thermal stability increasing with initial Sn overlayer thickness. High temperature reduction of supported Pd-Sn catalyst particles should therefore induce Sn-Pd surface alloy formation and our catalytic measurements (see below) do in fact indicate the continued presence Sn atoms at the surface, even after reduction at 873 K.

The Pd XANES results (Figure 6a) confirm that reduction does not significantly perturb the average local electronic and structural environment of Pd atoms within the Pd₂Sn catalyst. In contrast, the Sn XANES (Figure 6b) shows a progressive transformation from an oxidic (electron deficient) to metallic

environment, in accord with the EXAFS data. However, the 873 K reduced Sn XANES still exhibit a significant shift relative to the bulk Sn standard, suggesting incorporation of Sn within an electronically distinct Pd–Sn surface alloy.

Our observations regarding the structural evolution of these cluster-derived Pd/Sn catalysts are in general accord with studies of supported Pt/Sn catalysts prepared by wet-impregnation/ coprecipitation.^{3,30,31} These report that low-temperature reduction yields Sn²⁺ and/or Sn⁴⁺, although there is disagreement as to whether the Sn oxide is coordinated to the support material. Reduction at >673 K results in loss of oxygen and induces strong Sn–Pt interaction, although in contrast with the present system, complete reduction of Sn to the metallic state is not generally observed.^{30,31} Our CSOR method appears to produce better defined precursor material in which the Sn is apparently associated exclusively with the Pd clusters, resulting in efficient and complete reduction to a true bimetallic system.

Ethyne Coupling over Pd_xSn Catalysts. Both the pure Pd and bimetallic Pd_xSn catalysts were active for ethyne coupling, yielding only C₄ and C₆ products. Furthermore, the yields of the C₄ products and benzene from each sample were closely correlated under all pretreatment or reaction conditions (Figure 8a-b) and C₃ and C₅ products were never observed. We have already demonstrated that formation of a C₄H₄ intermediate is the key reaction initiating step in the coupling chemistry of ethyne on single-crystal Pd and Pd alloy surfaces under UHV conditions.^{2,32} The present observations emphatically confirm the view that the same C₄H₄ intermediate plays a crucial role in catalysis by practical materials operated at atmospheric pressure.

The absence of ethene, even at high H₂:C₂H₂ ratios, at first sight suprising, is not without precedent. Szanyi and Paffett³³ report an almost identical range of products resulting from ethyne coupling over extensively carbided Pt{111} and { $\sqrt{3} \times \sqrt{3}$ R30°-Sn/Pt{111} single-crystal surface alloys under similar reaction conditions (400–550 K, 20–100 Torr, H₂:C₂H₂ = 2.5–50). Furthermore, alkyne hydrogenation over supported Pd is a strong function of particle size,³⁴ *e.g.*, rates of vinylacetylene hydrogenation over 2 wt % Pd/SiO₂ decrease by an order of magnitude for Pd/SiO₂ catalysts with decreasing particle size from 40 to 10 Å.³⁵ Note that under our conditions (T_{reax} \geq 3 73 K and/or H₂ partial pressures \leq 1 bar), with small small (\leq 20 Å) Pd particles, complications due to phase transformation to β Pd-H may be discounted.

Influence of Reactant Mix. The activity dependence of all three catalysts on the H₂:C₂H₂ ratio (Figure 7) is readily understood in terms of site-blocking effects. At low H₂ partial pressures, extensive decomposition of both ethyne and its coupling products occurs over both Pd³⁶ single-crystal surfaces and Pd/SiO₂ catalysts prepared by conventional wet-impregnation.³⁷ Carbiding of the active surface results in rapid catalyst deactivation on a time scale of minutes. Increasing hydrogen concentration inhibits dissociative chemisorption,^{1,38} and it facilitates clean-off reactions. Beyond an optimum reactant ratio, competitive chemisorption of ethyne results in a rate decrease as would be expected under Langmuir-Hinshelwood kinetics. The dependence of reaction orders of individual products on hydrogen partial pressure (determined at <10% ethyne conversion) is in line with this. Closely similar kinetic behavior is found for ethyne coupling over the $\sqrt{3}$ Sn/Pd{111},-Pt{111} alloy surfaces,^{33,38} confirming the close connection between the model systems and supported Pd_xSn catalysts.

The samples used for testing contained, within the experimental error, identical amounts of Pd. Activity differences between the three catalysts cannot simply be ascribed to differences in dispersion because the XRD results indicate similar particle sizes in all three cases. Differences in maximum activities (Figure 7) are attributed to the differing amounts of Sn at the surface. The XAFS measurements show that Sn atoms are predominantly in metallic form after reduction at >473 K, the temperature regime in which stable Pd/Sn surface alloys are formed on Pd{111}.⁷ The most Sn rich catalyst exhibits the highest activity because Sn surface atoms act to inhibit the decomposition of reactants and products as a result of C–C and C–H cleavage,^{4,38–40} they also facilitate the desorption of products by reducing chemisorption bond strengths.^{7,40,41} The net result of these effects is to enhance the total activity of Pd₃Sn₂ by ~50% with respect to the pure Pd.

Under all conditions examined, the product distributions from the Pd_xSn catalysts were heavily weighted in favor of C_6 over C_4 species; i.e., addition of a third ethyne molecule to the C_4H_4 intermediate is strongly favored over its hydrogenation, even in hydrogen-rich atmospheres. This stands in interesting contrast to measurements on $Sn/Pt\{111\}$ single-crystal³³ which showed that C_4 production always exceeded C_6 production and that the $C_4:C_6$ relative yield increased slightly with H_2 pressure. It is possible that this reflects the reduced hydrogenation activity of Pd relative to Pt.

The benzene and *n*-hexane yields for all samples display a strong inverse correlation, respectively decreasing and increasing with rising hydrogen partial pressure (Figure 8). This suggests that these two products derive from a common reaction intermediate and are related sequentially, as follows:

$$C_{2}H_{2}(a) \xrightarrow{H_{2}, C_{2}H_{2}} C_{4}H_{4}(a) \xrightarrow{} C_{6}H_{6}(a) \xrightarrow{} C_{6}H_{6}(g)$$

$$H_{2} \xrightarrow{\downarrow} H_{2} \xrightarrow{\downarrow} H_{2} \xrightarrow{\downarrow} C_{6}H_{12,14}(g)$$

The observed formation of cyclohexane and cyclohexene (intermediates in benzene hydrogenolysis to n-hexane³³) under all reaction conditions is in accord with the above scheme.

In the absence of hydrogen, chemisorbed ethyne reacts to form benzene almost exclusively. Increasing hydrogen partial pressures progressively favors hydrogenation and the increasing production of cyclohexane and its hydrogenolysis product *n*-hexane at the expense of benzene formation. With the pure Pd and Pd₂Sn catalysts, almost 100% conversion to *n*-hexane occurs for H₂:C₂H₂ ratios > 1.75 (Figure 7). In the case of Pd₃-Sn₂, benzene production is *not* fully quenched, even at high hydrogen partial pressures, reflecting the effect of increased surface Sn concentration in limiting the number of Pd ensembles effective for hydrogenation/hydrogenolysis. This is consistent with a study by Xu and Koel⁴⁰ who showed that surface Sn atoms destabilise cyclohexene chemisorption on Pt{111}, inducing a transition from a di σ - to H-bonded adsorption geometry, resulting in increased benzene production.

Influence of Reduction Temperature. Ethyne coupling on Pd and Pd-based surfaces is a very structure-sensitive reaction: {111}-oriented facets are critically important.⁵ It is apparent that ethyne conversion over the Pd, Pd₂Sn, and Pd₃Sn₂ samples is relatively insensitive to reduction temperature, even up to \sim 1100 K (Figure 9). This indicates the particles are rather stable with respect to sintering, a conclusion that is supported by the corresponding XRD and Pd EXAFS. The activities of both bimetallic catalysts do however show some decrease with increasing reduction temperature—the magnitude of this decrease increasing with Sn content. This is understandable as follows.

EXAFS shows that after low temperature reduction, much of the Sn is present within 3D oxide structures; some metallic

Sn is present on the surface of the Pd particles where it promotes ethyne conversion, as discussed above. At higher reduction temperatures (>673 K) the remaining surface tin oxide undergoes progressive decomposition, liberating additional Sn which spreads over the Pd, increasing selectivity to benzene (Figure 10) and decreasing overall activity (Figure 9). The small Pd_xSn cluster size inhibits complete dissolution of Sn in the Pd core (which *does* occur above 523 K for Sn overlayers on bulk Pd⁷) even at reduction temperatures of 1100 K.

Influence of Reaction Temperature. The variation in C_6 selectivities with reaction temperatures between 300-500 K (Figure 11) cannot be attributed to changes in surface composition of the Pd₂Sn catalyst. An (admittedly oversimplified) rationalization in terms of the surface lifetime of reactively formed benzene may be offered as follows. It may be rationalized in terms of reduced surface lifetime of the reactively formed benzene with increasing temperature (desorption is the rate limiting step for appearance of benzene in the gas phase). This should reduce the probability of further conversion to hydrogenation and hydrogenolysis products, in keeping with observation. Interestingly, the benzene selectivity increases between 300 and \sim 450 K, which is just the temperature interval over which desorption of benzene form Pd{111} occurs.⁴² For T > 450 K, the surface lifetime of reactively formed benzene is very short and the yield of this product reaches a limiting value.

Conclusions

Conclusions are as follows: 1. Reduction of Pd/Sn catalyst precursors prepared by controlled surface organometallic reaction generates highly dispersed (<30 Å), thermally stable catalysts for ethyne coupling. These materials are resistant to particle growth but show important changes in surface composition as the reduction temperature is increased from 473 to 873 K.

2. Increasingly vigorous reduction leads to progressive destruction of the SnO₂-like 3D structures that surround the Pd core. Surface alloy formation ensues, followed eventually by more extensive Pd/Sn intermixing. This results in destruction of the critical ensembles necessary for structurally demanding hydrogenolysis reactions; significant modification of surface electronic properties also occurs.

3. The above changes are accompanied by pronounced changes in catalytic activity and very large changes in selectivity. Only C₆ and C₄ products were ever observed with benzene and *n*-hexane being the major species formed. Increased levels of surface Sn greatly increased benzene selectivity and inhibited hydrogenolysis. In the case of "Pd₂Sn", the product distribution could be varied from ~100% benzene to ~100% *n*-hexane. With "Pd₃Sn₂", benzene formation could never be totally quenched because of the limited bulk solubility of Sn in the very small particles.

4. The thermal properties and catalytic chemistry of these highly dispersed materials are in good accord with those reported for Pd{111}/Sn model planar catalysts, suggesting that the latter do provide a useful means of isolating and mimicking important aspects of the behavior of practical systems.

Acknowledgment. Financial support from the UK Engineering and Physical Sciences Research Council under Grant GR/ K45562 is gratefully acknowledged. We thank Johnson Matthey PLC for a loan of precious metals.

References and Notes

(1) Ormerod, R. M.; Lambert, R. M. J. Chem. Soc., Chem. Comm. 1990, 1421. Yoshinabu, J.; Seikitani, T.; Onchi, M.; Nishijima, M. J. Phys. Chem. 1990, 94, 4269.

- (2) Baddeley, C. J.; Hardacre, C.; Tikhov, M. S.; Lomas, J. R.; Lambert, R. M. J. Phys. Chem. 1996, 100, 2189.
 - (3) Srinavasan, R.; Davis, B. H. Platinum Met. Rev. 1992, 36, 151.
 - (4) Xu, C.; Tsai, Y. L.; Koel, B. E. J. Phys. Chem. 1994, 98, 585.
 (5) Baddeley, C. J.; Ormerod, R. M.; Stephenson, A. W.; Lambert, R.
- M. J. Phys. Chem. 1995, 99, 5146. (6) Lee, A. F.; Baddeley, C. J.; Hardacre, C.; Ormerod, R. M.; Lambert,
- R. M.; Schmid, G.; West, H. J. Phys. Chem. 1995, 99, 6096.
 (7) Lee, A. F.; Baddeley, C. J.; Tikhov, M. S.; Lambert, R. M. Surf. Sci. In press.
- (8) Didillon, B.; El Mansour, A.; Candy, J. P.; Bournonville, J. P.; Passat I. M. In Hydrogeneous Catching and Fine Chamicals III Crigaret
- Basset, J. M. In *Heterogeneous Catalysis and Fine Chemicals II*; Guisnet M., et al., Eds.; Elsevier: New York, 1991; 137.
- (9) Didillon, B.; Houtman, C.; Shay, T.; Candy, J. P.; Basset, J. M. J. Am. Chem. Soc. 1993, 115, 9380.
- (10) Moggridge, G. D; Rayment, T.; Lambert, R. M. J. Catal. 1992, 134, 242.
- (11) Horton J. H.; G. D. Moggridge; Ormerod R. M.; Kolobov, A. V.; Lambert, R. M. *Thin Solid Films* 1994, 237, 134.
- (12) Hansen, M. In *Constitution of Binary Alloys*; McGraw-Hill: New York, 1958; 1126.
- (13) Anderson, J. N.; Hennig, D.; Lundgren, E.; Methfessel, M.; Nyholm, R.; Scheffler, M. Phys. Rev. B 1994, 50, 17525.
 - (14) Cheung, T. T. P. Chem. Phys. Lett. 1984, 110, 219.
- (15) Lesage, P.; Clause, O.; Moral, P.; Didillon, B.; Candy, J. P.; Basset,
 J. M. J. Catal. 1995, 155, 238.
- (16) Candy, J. P.; Ferretti, O. A.; El Mansour, A.; Mabilon, G.; Bournonville, J. P.; Basset, J. M.; Martino, G. J. Catal. 1988, 112, 201.
- (17) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. J. Chem. Phys. 1980, 72, 4832.
- (18) Bianconi, A. In X-Ray Absorption; Koningsberger, D. C., Prins, R., Eds.; Wiley: New York, 1988; 573.
 - (19) Sham, T. K. Phys. Rev. B 1985, 31, 1888.
- (20) Kostroun, V. O.; Fairchild, R. W.; Kukkonen, C. A.; Wilkins, J. W. *Phys. Rev. B* 1976, *13*, 3268.

- (21) Clausen, B. S.; Grabaek, L.; Topsoe, H.; Hansen, L. B.; Stoltze, P.; Norskov, J. K.; Nielsen, O.-H. J. Catal. 1993, 141, 368.
- (22) Cheung, T. T. P. Surf. Sci. 1984, 140, 151.
- (23) Nosova, L. V.; Stenin, M. V.; Nogin, Y. N.; Ryndin, Y. A. Appl. Surf. Sci. 1992, 55, 43.
 - (24) Lee, A. F.; Lambert, R. M. Manuscript in preparation.
- (25) Coq, B.; Dutartre, R.; Bond, G. C.; Slaa, J. C.; Galvango, S.; Mercandante, L.; Garcia Ruiz, J.; Sanchez Sierra, M. C. In *Europacat II Conference Abstracts*; Maastricht 1995, 431.
- (26) Moreno, M. S.; Mercader, R. C.; Bilboni, A. G. J. Phys. C 1992, 4, 351.
- (27) Weast, R. C., Ed. CRC Handbook of Chemistry and Physics, 69th ed.; The Chemical Rubber Company: Cleveland, 1988.
 - (28) Hoflund, G. B. Chem. Mater. 1994, 6, 562.
 - (29) Goursot, A.; Pedocchi, L.; Coq, B. J. Phys. Chem. 1995, 99, 12718.
 - (30) Balakrishnan, K.; Schwank, J. J. Catal. 1991, 127, 287.
 - (31) Burch, R. J. Catal. 1981, 71, 348.
 - (32) Patterson, C. H.; Lambert, R. M. J. Am. Chem. Soc. 1988, 110,
- 6871. Patterson, C. H.; Lambert, R. M. J. Phys. Chem. 1988, 92, 1266. (33) Szanyi, J.; Paffett, M. T. J. Am. Chem. Soc. 1995, 117, 1034.
 - (34) Karpkinski, Z. *Adv. Catal.* 1990, *37*, 45.
- (35) Ryndin, Y. A.; Nosova, L. V.; Boronin, A. L.; Chuvilin, A. L. Appl. Catal. 1988, 42, 131.
- (36) Rucker, T. G.; Logan, M. A.; Gentle, T. M.; Mutterties, E. L.; Somorjai, G. A. J. Phys. Chem. 1986, 90, 2703.
- (37) Ormerod, R. M.; Lambert, R. M. J. Chem. Soc., Chem. Comm. 1990, 1492.
 - (38) Lee, A. F.; Lambert, R. M. Manuscript in preparation.
- (39) Xu, C.; Peck, J. W.; Koel, B. E. J. Am. Chem. Soc. 1993, 115, 751.
- (40) Xu, C.; Koel, B. E. Surf. Sci. 1994, 304, 249.
- (41) Xu, C.; Koel, B. E. Surf. Sci. 1994, 310, 198.
- (42) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. Surf. Sci. 1983, 135, 128.