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The formation of PdC_x over Pd-based catalysts in vapor-phase vinyl acetate synthesis: does a Pd–Au alloy catalyst resist carbide formation?

Y.-F. Han, D. Kumar, C. Sivadinarayana, A. Clearfield, and D.W. Goodman*

Department of Chemistry, Texas A&M University, College Station, Texas 77843, USA

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The formation of Pd carbide (PdC_x) during the synthesis of vinyl acetate (VA) was investigated over Pd/SiO_2 catalysts with two different Pd particle sizes, as well as over a $Pd–Au/SiO_2$ mixed-metal catalyst. XRD data show that PdC_x was produced in the pure Pd catalysts after reaction based on the downshift of the Pd(111) and (200) XRD features. The smaller Pd particles showed greater resistance to the formation of PdC_x. The XRD and XPS data are consistent with formation of a PdC_x species at the surface of the Pd–Au catalyst, however, the primary contributor to the downshift of the Pd(111) feature subsequent to reaction in the mixed-metal catalyst is believed to arise from reaction-induced alloying of Au with Pd. The alloying of Au with Pd is apparently very effective in preventing PdC_x formation in Pd-based catalysts for VA synthesis.

KEY WORDS: PdC_x; synthesis of vinyl acetate; Pd/SiO_2; $Pd–Au/SiO_2$; XRD.

1. Introduction

The formation of carbides over supported Pd catalysts was first reported in 1970 [1], and fully defined as Pd carbide (PdC_x) a decade later [2]. Interstitial carbon in Pd may significantly alter the bulk and surface structure of Pd and can lead to catalytic deactivation in reactions involving hydrocarbons [3–11]. It is well known that Pd–Au catalysts exhibit much higher reactivity than pure Pd catalysts for certain reactions, e.g., in vinyl acetate synthesis the reactivity is improved by a factor of 5–7 by mixing Au with Pd [12]. A key issue in Pd–Au catalysts is whether PdC_x is formed and, if so, to what extent. Except for a cursory study that addresses the formation of PdC_x [11] in a used Pd–Au catalyst, this issue has not been investigated thoroughly.

In this work, the goal was to investigate the effects of varying Pd particle size and mixing Pd and Au on the formation of PdC_x. X-ray diffraction (XRD) was used to monitor the nature of the phases formed in Pd and $Pd–Au/SiO_2$ catalysts subsequent to an extended VA synthesis reaction. X-ray photoelectron spectroscopy (XPS) was employed to explore carbon deposition on the used catalysts.

2. Experimental

2.1. Catalyst preparation and reaction

The catalysts, Pd(1.0 wt%)/SiO_2 and Pd(5.0 wt%)/SiO_2, and Pd(1.0 wt%)–Au(0.5 wt%)–K(2.5 wt%)/SiO_2, were prepared by incipient wet-impregnation. High surface area SiO_2 (Aldrich No. 7631-86-9) with a surface area of 600 m^2/g, mesh size of 230–400, and a pore volume of 1.1 mL/g, was used as the support. The catalyst preparation procedure is described in detail elsewhere [13, Y.-F. Han *et al.* Kinetics Study of Synthesis of Vinyl Acetate over Nano Sized Pd/SiO_2 Catalysts (unpublished)]. The VA synthesis reaction was carried out at 413 K in a reactant stream containing ethylene, acetic acid and oxygen. The rates were measured in a micro-reactor using online GC; before reaction the catalysts were pretreated (oxidized in a 20 mL/min of $O_2(10\%)/N_2$ at 673 K for 30 min followed by a reduction in pure H_2 (20 N mL/min) at 573 K for 30 min; the composition of the feed gas was 7 : 1 : 2 of ethylene : oxygen : acetic acid at atmospheric pressure and a flow rate of 30–60 N mL/min. The weight of the catalyst used was 1.0–1.6 g, and the reaction time, unless otherwise stated, was 1000 min.

2.2. X-ray diffraction

The X-ray powder diffraction data were collected with a Bruker D8 diffractometer using CuK_α radiation. The samples were scanned over the 2θ range from 36 to 52° using 0.2° steps for the Pd (5.0 wt%)/SiO_2 and 0.04° steps for the Pd (1.0 wt%)/SiO_2 and $Pd–Au/SiO_2$ catalysts. The Pd particle size was estimated using the Scherrer formula [14] where the particle diameter (D) in the direction perpendicular to the diffracting plane (111), $2\theta = 40.2°$, was obtained from the width of the diffraction profile. The Pd particle sizes before and after reaction for each catalyst studied are shown in table 1. The phase composition of the Pd–Au alloy was determined using Vegard's law [15,16].

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* To whom correspondence should be addressed.
E-mail: Goodman@mail.chem.tamu.edu

Table 1
Pd particle size over Pd/SiO_2 and $Pd–Au/SiO_2$ catalyst measured by XRD[a]

Sample	Freshly reduced/nm	After reaction/nm
Pd (5.0 wt%)/SiO_2	3.8	4.2
Pd (1.0 wt%)/SiO_2	ca. 2.5	< 2.5
Pd(1.0 wt%) Au(0.5 wt%)/SiO_2	2.0 (Au-rich), 1.4 (Pd-rich)	2.0 (Au-rich), 1.4 (Pd-rich)

[a] Crystallite size of Pd and Pd-rich Pd–Au alloy was estimated with reference to the diffraction feature of the Pd ⟨111⟩ plane, Au ⟨111⟩ for Au-rich Pd–Au alloy.

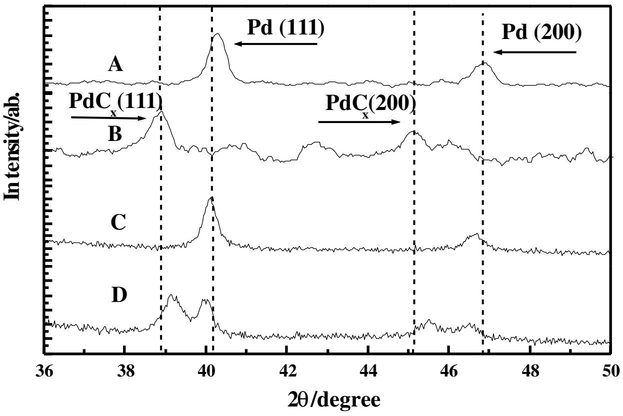

Figure 1. XRD data for Pd-only catalysts. (A,B) Pd(5.0 wt%)/SiO_2, (C,D) Pd(1.0 wt%)/SiO_2; A,C – freshly reduced; B,D – after reaction.

2.3. X-ray photoelectron spectroscopy

XPS measurements were carried out on a XPS 5500 spectrometer using MgK_α radiation (300 W, 58.7 eV pass energy). The base pressure of the spectrometer was 1×10^{-9} Torr. The background due to inelastic processes, B(E), was subtracted using the Shirley method [17]. The binding energies (BE) were referenced to the Si (2p) feature at 103.1 eV which was present in all the measurements.

3. Results and discussion

After 1000 min of reaction, the activity for VA formation relative to the maximum rate for the Pd(5.0 wt%)/SiO_2 and the Pd(1.0 wt%)/SiO_2 catalyst was ~50% and 35%, respectively. In contrast, a drop of only ~25% reactivity was observed for the Pd(1.0 wt%)–Au(0.5 wt%)/SiO_2 catalyst after 100 h time-on-stream. The ratio of reaction rates for VA formation is approximately 1 : 10 : 100 for Pd(5.0 wt%)/SiO_2 : Pd(1.0 wt%)/SiO_2 : Pd(1.0 wt%)–Au(0.5 wt%)/SiO_2, respectively. Obviously, the Pd–Au alloy catalyst exhibits a much higher stability and relative reactivity compared to the pure Pd catalysts.

XRD data for the pure Pd catalysts were recorded before and after reaction. For the Pd (5.0 wt%) catalyst, as shown figure 1A, the XRD peaks for the freshly reduced catalyst, indexed as ⟨111⟩ and ⟨200⟩ at a Bragg angle of 40.2° and 46.6°, respectively, correspond to a lattice constant of $a_0 = 0.389$ nm. These shift to 38.8° and 45.2° for the used catalyst, yielding a lattice constant of approximately $a_0 = 0.402$ nm (see figure 1B). This increase in the lattice constant suggests that carbon has penetrated into the bulk of the Pd. The subscript, x, in PdC_x is estimated to be 0.13–0.15 [5,7]. Over the Pd(1.0 wt%)/SiO_2 catalyst (see figure 1C), the diffraction profile of the freshly reduced sample is similar to that found for the Pd(5.0 wt%)/SiO_2 catalyst, but the corresponding peaks are lower in 2θ than the former by 0.1°, perhaps, due to the reduction in the size of the Pd particles [18]; however, two distinct peaks at 40.0° and 39.2° were observed for the used catalyst as shown in figure 1D. The peak at 40.0° suggests that some Pd particles remain carbide-free; however, the feature at 39.2°, greater than the 38.8° feature observed for Pd(5.0 wt%)/SiO_2, is indicative of intermediate PdC_x phases.

Obviously, the Pd(1.0 wt%)/SiO_2 appears to be more resistant to the formation of PdC_x under reaction conditions compared to Pd(5.0 wt%)/SiO_2. This difference in the tendency to form PdC_x between the two catalysts is attributed to the variation in the Pd particle sizes as seen in table 1. Pd particles of approximately 2.5 nm were detected for the freshly reduced Pd(1.0 wt%)/SiO_2 catalyst and 3.8 nm for the Pd(5.0 wt%)/SiO_2 catalyst. Two plausible reasons could lead to less PdC_x in the Pd(1.0 wt%)/SiO_2 catalyst: (i) an excess of oxygen may be present on the small Pd particles, thereby enhancing the combustion of carbon species and reducing the interaction between carbon and Pd. Previous studies in our laboratories [19,20] have shown that Pd particles undergo a metal to nonmetal transition at approximately 2.5 nm that could lead to significantly altered chemical properties. This, in turn, could influence the rate of dissociative adsorption of oxygen, known to be a limiting step in ethylene combustion in VA synthesis over Pd [Y.F. Han *et al.* Kinetics and Mechanism Study of Ethylene Combustion in the Synthesis of Vinyl Acetate over Large Surface Area SiO_2 Supported Pd Catalyst (unpublished)]; and/or (ii) Pd in small Pd clusters may be less reactive compared to bulk Pd with respect to the formation of carbides.

As illustrated in figure 2, a similar C1s XPS feature was recorded for all the used catalysts. A comparison of the C1s peak intensities shows that the amount of carbon on the Pd surface after reaction is essentially the same for each of the three catalysts. This observation is inconsistent with the above explanation (i) being the cause of PdC_x not forming in the Pd(1.0 wt%)/SiO_2 catalyst. In addition, the observed BE suggests that at

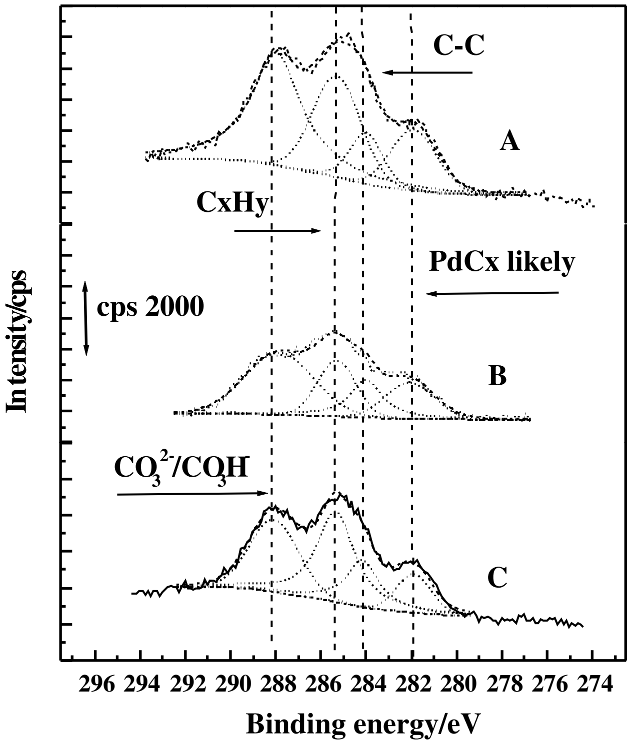

Figure 2. XPS C1s spectroscopy for the catalysts after reaction. A: Pd(1.0 wt%)/SiO$_2$; B: Pd(5.0-wt%)/SiO$_2$; C: Pd(1.0 wt%)–Au(0.5 wt%)/SiO$_2$.

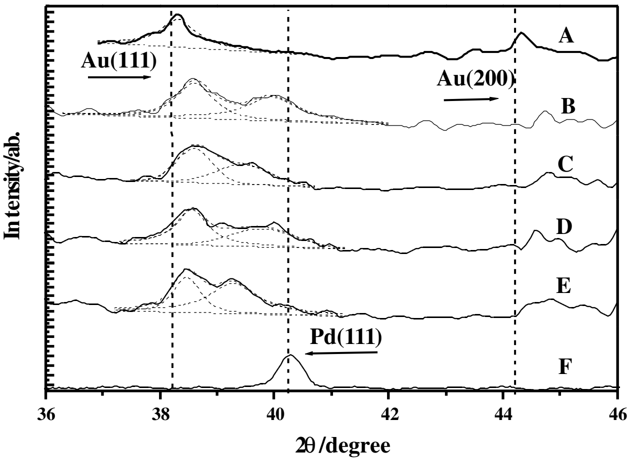

Figure 3. X-rays diffraction data for the Pd(1.0 wt%)–Au(0.5 wt%)/SiO$_2$ catalyst. A – freshly prepared; B – freshly reduced; C – after reaction (time-on-stream 100 h); D – reduced then 100 h time-on-stream in N$_2$ at 413 K; E – catalyst after reaction in C reduced in H$_2$ at 623 K for 4 h; F – freshly reduced Pd(5.0 wt%)/SiO$_2$.

least four carbon species, PdC$_x$ (ca. 282.0 eV), graphite C (284.0 eV), hydrocarbon C$_x$H$_y$ (285.2 eV) and carbonate/carbonoxyl (288.2 eV) are present on the used catalyst surface [21].

The XRD data for the phase-evolution of the Pd–Au catalyst are shown in figure 3. Results (figure 3A) for the untreated catalyst (the freshly prepared Pd–Au catalyst precursor dried at 393 K in air overnight after impregnation) show two features at 38.3°and 44.4°, slightly higher in 2θ (0.1°) than the corresponding values for Au(111) and (200). This change suggests that a small fraction of the Pd has alloyed with Au leading to an estimated composition of $Pd_{0.02}Au_{0.98}$; there is no evidence for a Pd phase. The XPS data showed that the freshly prepared SiO$_2$ was covered with a film of Pd oxide. After reduction, a new peak appears at 39.9° (figure 3B), a value lower than that for the Pd(111) phase by 0.3°, and is assigned to a Pd-rich phase with a composition of $Pd_{0.84}Au_{0.16}$. On the other hand, the peak corresponding to the Au-rich phase shifts to 38.6°, consistent with an alloy composition of $Pd_{0.21}Au_{0.79}$. Clearly, the Pd–Au catalyst consists of two well-defined phases, a Au-rich and a Pd-rich phase. After 100 h time-on-stream under VA synthesis reaction conditions (see figure 3C) the XRD feature corresponding to the Pd-rich phase moves to 39.5°, consistent with an alloy composition of $Pd_{0.63}Au_{0.37}$; the Au-rich phase remains unchanged. Bonarowska *et al.* [11], have reported an analogous shift in a Pd–Au alloy catalyst after hydrodechlorination of CCl_2F_2. It was suggested that the downshift of the Pd-rich feature was a result of carbon insertion into the Pd lattice. This conclusion was based on the fact that a carbon-free, Pd-rich phase was recovered subsequent to reduction of the used catalyst in H$_2$ at 623 K, a procedure known to remove interstitial carbon [11].

To demonstrate the dissolution of carbon into the bulk of the Pd–Au catalyst, a set of experiments shown in figure 3D was carried out. The freshly reduced Pd–Au catalyst was treated in a N$_2$ stream at 413 K for 100 h. The XRD data for the Pd(111) phase shifted to a lower value by 1° in 2θ ($Pd_{0.78}Au_{0.22}$) compared to the corresponding value for the freshly reduced catalyst in figure 3A. This result suggests that the diffusion of Au atoms into the Pd bulk is not likely responsible for the significant downshift in the used catalyst in figure 3C. On the other hand, after reducing the used Pd–Au alloy catalyst at 623 K in H$_2$ gas for 4 h, the peak related to the Pd(111) phase in the Pd–Au catalyst shifted down even more to 39.2° ($Pd_{0.52}Au_{0.48}$) (see figure 3E). The downshift of the Pd(111) peak in the Pd–Au alloy catalyst following reaction is believed to be due to a reaction-induced phase transformation rather than bulk Pd carbide formation. This argument is supported by the XPS sputter depth profile data for the used catalysts (not shown here for the sake for brevity), where the carbon species could not be removed completely from the Pd surface after sputtering. In contrast, essentially all the deposited carbon could be eliminated from the Pd–Au catalyst. On the other hand, XPS showed that following a simple reduction procedure, a carbon-free surface could be achieved for the Pd–Au catalyst; following an identical treatment, a significant carbon signal was evident on the pure Pd catalyst. Clearly, the interaction of carbon with the Pd–Au catalyst is significantly weaker compared to the corresponding interaction with Pd-only catalysts.

4. Summary

In summary, PdC_x is formed in a Pd-only catalyst during the synthesis of VA. Reducing the Pd particle size can enhance the resistance of Pd for carbide formation, this resistance likely being the reason for the improvement in stability seen for highly dispersed Pd for VA synthesis. On the other hand, there is no evidence for PdC_x in a Pd–Au alloy catalyst following VA synthesis. Alloying Au with Pd apparently inhibits the reaction between Pd and interstitial carbon and appears to be an effective way to prevent PdC_x formation in Pd-based catalysts.

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