Dynamic self-organization of supported Pd/Au catalysts during vinyl acetate synthesis

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ABSTRACT: Vinyl acetate monomer synthesis over bimetallic PdAu catalysts is known to be highly structure sensitive and that structures are dynamically formed and disintegrated in reactant gas atmosphere. Here we show via a combination of bulk and surface sensitive methods that independent of their nominal composition, Pd/Au bimetallic particles undergo marked reconstruction and phase partition during vinyl acetate synthesis. While temperature induced reorganization of SiO₂ supported Pd_xAu_y particles leads to all three thermodynamically meta-stable phases, i.e., Pd₃Au₁, Pd₁Au₁, Pd₁Au₃, with mainly Au enriched surface compositions, the reactive atmosphere induces selectively the formation of the Pd₁Au₁ phase and separated Pd particles. The Pd in the Pd₁Au₁ has higher specific activity and selectivity than the sole Pd nanoparticles exemplifying the importance of changing its electronic nature. As the Pd₁Au₁ phase dominates the catalytic activity, novel tailored catalysts could be produced limiting the presence of dispersed Pd.

KEYWORDS: Dynamic surface adaptation; Pd-Au; reactive self-organization, Pd-Au; vinyl acetate synthesis; reconstruction, acetate induced.

PdAu bimetallic catalysts supported on oxides such as SiO₂ and Al₂O₃ are used in a variety of important processes, including vinyl acetate monomer (VAM) synthesis from acetic acid (AcOH), ethylene (C₂H₄) and oxygen (O₂).^[1,2] Au acts as promoter without being alone catalytically active for this reaction, leading to higher selectivity, activity, and especially stability.^[3] This has been attributed to ligands and structural (ensemble) effects.^[4] Similar positive effects were induced by Au to Pd for the benzyl alcohol oxidation.^[5]

The impact of Au on the catalytically active Pd has been widely studied and led to contradictory models for the active ensembles.^[6] Specifically, the dynamic reconstruction during VAM synthesis is still unclear, but the insight would provide essential guidelines for the optimization of the catalyst, the catalyst pretreatment and the operation conditions.

The physicochemical properties (electronegativity, metal radii, number of valence electrons) of palladium and gold are similar.^[7] The mixing enthalpies for Pd and Au are positive and similar; thus phase separation is not expected.^[8,9] On the other hand, three ordered phases are reported. Okamoto and Massalski^[10], for example, describe solid phases with compositions of Au₃Pd₁, Au₁Pd₃ and, below 200°C, Au₁Pd₁.^[11] The authors reported relatively high ordering temperatures for Au₃Pd₁ and Au₁Pd₃ of 850 and 870°C, respectively, which were challenged by Sluiter et al.^[12] indicating order-disorder temperatures for Au₃Pd₁ and Au₁Pd₃ between 400 and 500°C and an order-disorder temperature of the Pd₁Au₁ phase of 150°C. Since other fcc-based systems with two ordered phases A₃B₁ and A₁B₃ type show order-disorder temperatures twice as high as the one of an intermediate A₁B₁ structure, the phase diagram proposed by Sluiter appears more probable.

Christensen et al.^[13] used the surface free energies to construct a Pd-Au phase diagram for surface alloys. The calculated segregation energies for Pd on Au were positive and negative for Au on Pd. Thus, Pd is expected to preferentially diffuse into the bulk, whereas Au should remain in the surface layer. For evaluation of the mixing degree in the surface layer, the curvature of the surface energy per surface atom was used. The curvature exhibits positive values for Pd atoms on Au and for Au atoms on Pd. Thus surface intermixing is preferred in both cases. However for Pd atoms on Au the curvature is higher than for Au atoms on Pd, resulting in higher tendencies towards surface intermixing for Pd atoms in a Au-rich surface. The surface intermixing of Pd and Au was confirmed by Soto-Verdugo and Metiu^[14], who calculated the relative energies for Pd atoms in the surface layer and in the bulk using density functional theory. These calculations are in good agreement with the experimental data of Goodman et al.^[15], describing neighboring Pd atoms in a low index surface plane as active sites for vinyl acetate synthesis. Studying the impact of the particle size, it was demonstrated that high activity was found for Pd-Au particles between 2 and 4 nm. For smaller particles the concentration of Pd atoms on low index surfaces was too low, while for larger particles the metal dispersion was not sufficient to reach a high activity.

However, the surface composition depends also on the particle size. Ferrer et al.^[16] observed a weakly enriched Pd outer shell on a bimetallic core for particles smaller than 5 nm, while larger particles had high Pd concentrations in the core and the outer shell, separated by a Au rich layer. Concerning the temperature dependence of ordered phases, Jiang et al.^[17] showed a shape and size effect on the disorder-order temperatures for the Pd₃Au₁, Pd₁Au₃ and the Pd₁Au₁ phases of supported metal particles. Brückner et al.^[18] addressed the changes in the particle morphology of supported PdAu catalysts for VAM formation at 155°C - 190°C in order to explore reasons for

catalyst deactivation. Besides sintering, surface enrichment in Pd was observed qualitatively by IR spectroscopy of adsorbed CO samples aged at 155, 170°C and 190°C.

In order to understand the consequences and causes of the potential rearrangement of the metal partners in the alloy, we explore the reactant induced formation and restructuring of PdAu bimetallic particles supported on SiO₂ during vinyl acetate synthesis at a reaction temperature of 150 °C. For evaluation of the alloy formation, catalysts with Pd/Au molar ratios of 1.1, 2.0 and 6.0 were prepared. Potassium was added to the catalyst as KOAc, crucial for reaching high conversion levels by enhancing the adsorption of acetic acid monomers on the catalytically active Pd sites^[19]. Fresh catalysts and used samples after 120 h time-on-stream were characterized by low temperature CO adsorption, X-ray absorption spectroscopy and X-ray diffraction. Samples were also characterized after thermal treatments in reducing and inert atmosphere.

The X-ray diffraction patterns of fresh samples showed the presence of multiple Pd_xAu_y phases (Fig. 1 - fresh), while after reaction at 150 °C for 120 h all catalysts showed only a single XRD reflection of a metal phase, specific for Pd₁Au₁ (Fig. 1 used). During the reaction a pronounced increase in conversion was observed for the first 25 hours on stream before reaching the steady state level. The phase compositions of the catalysts at steady state after 120 h on stream given in Table 2 were analyzed from XRD patterns by applying Vegard's law^[20]. The differences between the phase compositions observed by XRD and the Pd/Au ratios used in the synthesis indicate that an X-ray amorphous Pd phase must be present after reaction. Its presence has also been postulated by Macleod et al.^[21] The fraction of this highly dispersed Pd phase is given in Table 1. We identified it as Pd(OAc)₂ via analysis of the water collected after washing the catalysts post usage.

Because the formation of a Pd_1Au_1 phase and the concurrent formation of dispersed Pd were independent of the initial Pd/Au ratio, we conclude that a liquid surface layer consisting of acetic acid and water was present under reaction conditions. Pd atoms in Pd-rich particles are easier to oxidize compared to Pd atoms in close proximity to Au^[22]. Thus, especially in Pd rich particles, the acetic acid environment formed Pd acetate. Pd segregated so to the surface and was subsequently dissolved. As soon as the surface of the bimetallic particle was highly intermixed, (electronic) effects of Au on Pd inhibited the oxidation of Pd and led to the formation of bimetallic particles with a bulk composition of Pd_1Au_1 . Only for initially Au-rich samples the composition of the bimetallic particles was rich in Au. On the other hand Pd was deposited on Au-rich particles, e.g., via acetate bridges formed between dissolved Pd acetate and Pd in the surface layer of the bimetallic particle.

Figure 1. Left: X-ray diffraction profiles for fresh (green), thermally altered (orange) and used (blue) samples. Bimetallic phases of the corresponding planes are located in between those of the pure metals: Au (111) ($2\Theta=38.3^\circ$), Pd (111) ($2\Theta=40.0^\circ$), Au (002) ($2\Theta=44.5^\circ$), Pd (002) ($2\Theta=46.7^\circ$), Au (022) ($2\Theta=64.6^\circ$), Pd (022) ($2\Theta=67.9^\circ$). Right: fitted profiles for 111 surface of thermally altered (orange) and used (blue) samples.

Table 1. Concentrations of dispersed Pd after 120 hours on stream.

Pd/Au molar ratio	Fraction of dispersed Pd (Atom %)
1.1	3.8
2.0	39.4
6.0	70.9

Pronounced increase in the reaction rate was found for all bimetallic catalysts during the first hours on stream. Next to VAM only a relatively minor concentration of CO₂ was observed as reaction product. In order to investigate this induction period, Pd(OAc)₂ was impregnated onto the silica support. As an induction period was not observed for these catalysts (see supplementary information) we relate the increase in activity with time on stream to the reactive reconstruction of the bimetallic particles and the contribution of Pd(OAc)₂. Similar results were obtained by an additional impregnation with the KOAc promoter.

The increasing selectivity with time on stream (see supplementary information) indicates that the bimetallic particles tend towards the formation of a more active ensemble, i.e., bimetallic particles of Pd₁Au₁ nature as discussed below. Among the three ordered bimetallic PdAu phases, the Pd₁Au₁ phase is the most selective catalyzing vinyl acetate formation. The Pd₃Au₁ phase contains large surface ensembles of Pd atoms, which favor total oxidation of C₂H₄, while on the

Au-rich Pd₁Au₃ phase too few Pd atoms in close proximity are present, to form an appreciable concentration of the catalytically active ensembles.^[2]

To confirm that this specific reconstruction of the bimetallic particles towards a Pd₁Au₁ phase and a dispersed monometallic Pd phase occurred only under reaction conditions, the catalysts were subjected to a thermal treatment in He for 120 hours. Changes in the composition of the bimetallic phase were not detected by XRD, which is attributed to the lower mobility of the metal atoms in the presence of partially oxidized Pd surface atoms formed during exposure to the (ambient) gas atmosphere. Without reduction of surface Pd-O species, the atoms in the bimetallic particles did not reconstruct.

In contrast, thermal treatment of the catalyst after reduction in H₂ led to the formation of three distinct intermetallic compounds (i.e., Au₁Pd₁, Au₃Pd₁ and Au₁Pd₃) in agreement with the phase diagram discussed above.^[10] In order to avoid Pd hydride formation, the thermal treatment in reducing atmosphere consisted of the reduction period (up to 300 °C) followed by flushing with He from 300°C down to ambient temperature. This procedure decomposed the Pd hydride phase formed during reduction in H₂ and yielded diffractograms with lattice parameters of typical PdAu alloys. Note that the presence of Pd hydride would expand the lattice of the metal particles leading to a shift of the X-ray diffraction peaks to lower angles. The relative fractions of the bimetallic phases present in the catalyst depend on the overall Pd/Au ratio of the catalyst and on the gas composition applied (Table 2).

Table 2. Alloy compositions determined by XRD of samples aged in reactant atmosphere and via thermal treatment.

Pd/Au molar ratio	Pd _x Au _y after 120 h on stream	Pd _x Au _y after thermal treatment in reducing atmosphere (with He flushing to remove Pd-H species)
1.1	Pd _{0.42} Au _{0.58}	Pd _{0.17} Au _{0.83} , Pd _{0.51} Au _{0.49} , Pd _{0.81} Au _{0.19}
2.0	Pd _{0.47} Au _{0.53}	Pd _{0.12} Au _{0.88} , Pd _{0.52} Au _{0.48} , Pd _{0.80} Au _{0.20}
6.0	Pd _{0.51} Au _{0.49}	Pd _{0.20} Au _{0.80} , Pd _{0.48} Au _{0.59} , Pd _{0.81} Au _{0.19}

To characterize the surface composition of the bimetallic Pd-Au particles, the IR spectra of CO adsorbed at -150 °C was used. Spectra of CO adsorbed on monometallic Au and Pd, as well as on the pure silica support can be found in the supporting information. Moreover pressure dependent CO adsorption on bimetallic samples ranging from 0.005 mbar to the maximum coverage at 1 mbar are shown in the supporting information. Before reaction, the IR spectra showed two bands of CO adsorbed linearly on Pd and Au (see Figure 2-i). The band at 2090 cm⁻¹ is attributed to CO adsorbed on Pd in larger monometallic domains (linear CO on Pd next to Pd). The band at 2060-2040 cm⁻¹ corresponds to CO adsorbed on Pd in close proximity to Au (linear CO on Pd next to Au). CO adsorbed on Au led to a band between 2130 and 2100 cm⁻¹. On monometallic samples CO absorbs at 2098 cm⁻¹ on Au and at 2094 cm⁻¹ on Pd, which is in good agreement to literature. [23, 24]

Figure 2. IR spectra of adsorbed CO at -150 °C and 1 mbar partial pressure of CO on Pd/Au wt. molar ratios a) 1.1, b) 2.0 and c) 6.0. Blue lines represent CO on gold, red on palladium. i) Fresh samples, ii) thermally reconstructed samples and iii) reactively reconstructed samples. Pie charts represent intensities of the respective CO species.

Table 3. Ratios of neighbor pair types from IR of adsorbed CO species on fresh catalysts.

Pd/Au	molar ratio	Au-Pd/Au-Au	Pd-Au/Pd-Pd	linear/bridged
	1.1	0.4	0.5	0.8
	2.0	0.5	0.7	0.4
	6.0	0.2	0.4	0.2

Table 4. Ratios of CO species adsorbed on Pd and Au in catalysts thermally reconstructed under reducing conditions.

Pd/Au	molar ratio	Au-Pd/Au-Au	Pd-Au/Pd-Pd	Linear/bridged
	1.1	0.1	0.4	0.9
	2.0	0.4	0.6	0.7
	6.0	0.2	0.5	0.3

Table 5. Ratios of CO species adsorbed on Pd and Au in catalysts reconstructed in reactant atmosphere.

Pd/Au	molar ratio	Au-Pd/Au-Au	Pd-Au/Pd-Pd	Linear/bridged
	1.1	0.6	0.2	0.9
	2.0	1.3	0.2	0.9
	6.0	1.3	0.2	1.4

The assignments are supported by calculations by Liu and Nørskov^[25], estimating that the change in adsorption energy reflects changes in the d-band level of Pd resulting from an increasing number of Au atoms in contact with Pd. Due to an electron transfer from Au to Pd, an increased back donation from the d-level electrons of Pd to the anti-bonding π^* -orbitals of the adsorbed CO takes place.^[26] This leads to a red-shift of the CO stretching frequency adsorbed on Pd influenced by Au. Back donation to the anti-bonding CO orbitals is reduced for electronically altered Au, which leads to shifts to higher wavenumbers. The extent of the blue-, respectively red-shift in regard to the pure metal depends on the degree of intermixing. The adsorption of CO on the silica support led to bands at 2156 – 2185 cm^{-1} , which are attributed to the interaction of CO with terminal hydroxyl groups and cations.^[27, 28] For reasons of clarity, however, we will only show and discuss the deconvolution of metal related features of the CO adsorption.

To study the catalysts after VAM synthesis by IR spectroscopy, the KOAc promoter had to be removed by washing the catalyst with deionized water. The subsequent analysis of the washing water indicated the removal of Pd from the dispersed Pd phase in the form of $\text{Pd}(\text{OAc})_2$ as described above. To confirm this, the IR spectra of CO on a fresh catalyst, which was first loaded with KOAc and subsequently washed, and on a catalyst without KOAc impregnation were compared. As both spectra were identical, we conclude that Pd is not removed from the bimetallic Pd_1Au_1 alloy formed during reaction. As CO does not form bridged species between Pd and Au^[24] the linearly adsorbed CO species were predominantly found on alloyed surfaces, where the Pd atoms are separated by Au. The spectra of CO adsorbed on the catalysts before reaction are shown in Fig. 2i. The ratios of the intensities from CO linearly adsorbed on Pd or Au are compiled in Table 3. Before contact with reactants this ratio varies with the Pd/Au ratio used for catalyst synthesis, while a correlation with the initially applied metal ratios was not found. For example the ratio for Au-Pd/Au-Au slightly increased from 0.4 to 0.5 for Pd/Au with molar ratios of 1.1 and 2.0 but decreased to 0.2 for a Pd/Au molar ratio of 6.0 (see Table 3). In agreement with XRD data, this suggests that on fresh samples several bimetallic compositions and surface ensembles of Pd and Au were present. The blue-shifts with regard to CO adsorbed on pure Au (2098 cm^{-1}) and for CO adsorbed on Au-Au and Au-Pd species in bimetallic particles were similar for all samples before reaction. The shifts are in a range of 5 cm^{-1} for Au-Au species and of 25 cm^{-1} for highly intermixed Au-Pd species. As expected, the ratio in the intensities of linear to bridged adsorbed CO (two-fold and three-fold hollow sites) decreased with increasing Pd content, because a smaller fraction of the Pd was incorporated into bimetallic particles.^[29] Figs. 2i and 2iii show that the intensity of the bands of CO species adsorbed on the catalysts after reaction on Pd increased with respect to the fraction of CO adsorbed on Au compared to the

fresh sample. This indicates that the reaction induced surface enrichment in Pd results from a reconstruction or an oxidative leaching of Pd from the core of the bimetallic particles. By this process large surface ensembles of Au were removed and a highly intermixed metallic surface was created.

While not including the effects of a reactive atmosphere, thermodynamic calculations by Christensen et al.^[13] predict a pronounced Au surface enrichment, suggesting that for bimetallic PdAu particles Pd diffuses into the bulk phase, while Au forms a surface layer on the Pd rich bulk phase. This is in agreement with the IR data obtained for fresh and thermally altered samples, where intensive adsorption bands for CO on Au were observed (see Figure 2i and ii, 2130 – 2100 cm⁻¹). Thus, the low temperature CO adsorption indicates that the reconstruction induced by reactant gases is significantly different from the thermodynamic predictions.

In agreement with the present study, Brückner et al.^[18] observed surface depletion of Au for catalysts treated at 190, 170 and 155°C applying total pressures of 9 bar and a gas composition close to industrial applications.^[30] Their CO adsorption data showed that the ratio of linear to bridged adsorbed CO decreased significantly for samples after application to VAM synthesis.

We observed, in contrast, a significantly higher degree of alloying on samples after reaction. The blue shift in respect to pure Au was found to be about 8 cm⁻¹ for CO on Au-Au species and increased up to 30 cm⁻¹ for Au-Pd. For CO adsorbed on palladium we observed a red shift with respect to pure Pd of 20 cm⁻¹ and 45 cm⁻¹ for Pd-Pd and Pd-Au species, respectively. The increased shift for Pd compared to Au is attributed to the presence of residual potassium on the catalyst surface, which is known to cause a red-shift and a significant peak-broadening of vibrations of CO adsorbed on Pd.^{[31], [32]} Since Pd is the active metal and, thus, must be in close

contact to potassium, the influence of residual potassium is mainly observed for Pd after reaction and the peak broadening is more pronounced for samples with higher Pd concentrations. Within the Pd species (Pd-Pd and Pd-Au), peak broadening is enhanced for the Pd-Pd species. This can be attributed to potassium remaining as a Pd-K mixed phase^[33] formed during the reduction of KOAc and Pd(OAc)₂ in close proximity. Peak broadening and peak shifts were more pronounced for Pd-rich samples, since the concentration of dispersed Pd was higher (compare Table 1). Residual potassium is also responsible for the increase in intensity of the band around 2155 cm⁻¹. Montanari et al.^[27] found that the bands of CO adsorbed on potassium cations and on terminal hydroxyl groups overlap. Table 5 summarizes the ratios of the intensities for the bands of CO adsorbed on used catalysts. The degree of alloying is significantly enhanced after contact to the reactant atmosphere. The ratios between the intensities of linearly adsorbed CO species on Au (Au-Pd/Au-Au) are strongly increased. The slightly lower Au-Pd/Au-Au ratio for the more Au rich sample with a Pd/Au molar ratio of 1.1 can be explained by the presence of small, highly Au-rich clusters. The restructuring process is more pronounced on palladium rich particles, since the restructuring is based on the formation of Pd(OAc)₂ and the subsequent Pd leaching from the particle surface. For Au rich particles the restructuring and subsequent surface enrichment in palladium is not as pronounced and, thus, the surface of Au rich particles remains Au rich. The ratios between the intensities of linearly adsorbed CO species on Pd (Pd Au/Pd Pd) are equal for all three samples, but are lower compared to fresh samples. This is due to the more pronounced broadening of CO linearly adsorbed on Pd-Pd species compared to linearly bound CO on Pd-Au species as discussed above. Thus, we conclude that all bimetallic particles on the catalysts studied had similar surface concentrations of Au and Pd after application in vinyl acetate synthesis.

In contrast, low temperature CO adsorption on samples thermally aged under reducing atmosphere did not show significant shifts in wavenumbers. Noteworthy changes in absorption frequencies were found for CO adsorbed on the Au-Pd species in highly Pd rich samples and the Pd-Au species in the more Au-rich sample with an atomic ratio of Pd/Au 1.1. This is attributed to an increase in the degree of alloying. The restructuring of the surface, however, was less pronounced as found for samples after reaction. Comparing Figures 2 i and ii, shows that the intensity of the absorption features assigned to CO adsorbed on Au (light blue and dark blue Peaks) and on Pd (red and orange Peaks) are similar. However, small variations in the peak ratios of CO adsorbed on Au (Au-Pd/Au-Au) and on Pd (Pd-Au/Pd-Pd) are detected. Thermal reconstruction of as synthesized particles is highly dependent on the respective compositions of the metallic particles, as it can only occur within the particle and thus surface changes are less evident than for samples after reaction (compare Tables 3-5).

Table 6. Results of the EXAFS analysis for Au-L_{III} edge and Pd-K edge of fresh samples.

Pd/Au ratio	molar	Au-Pd		Au-Au		Pd-Au		Pd-Pd	
		d / nm	N	d / nm	N	d / nm	N	d / nm	N
1.1		0.277	4.0	0.279	7.8	0.277	4.5	0.275	4.7
2.0		0.277	4.5	0.279	7.3	0.277	2.2	0.275	7.9
6.0		0.276	5.4	0.280	6.5	0.276	1.1	0.275	9.3

Table 7. Results of the EXAFS analysis for and Pd-K edge of reactively reconstructed samples.

Pd/Au molar ratio	Au-Pd		Au-Au		Pd-Au		Pd-Pd	
	d / nm	N	d / nm	N	d / nm	N	d / nm	N
1.1	0.278	6.5	0.279	4.6	0.278	5.9	0.281	4.5
2.0	0.277	7.4	0.278	3.9	0.277	4.1	0.280	5.9

6.0	0.277	7.2	0.279	3.8	0.277	1.2	0.281	8.8
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Evidence for the above discussed formation of a Pd-K phase was also found in the EXAFS. Samples after reaction showed a significant expansion of the Pd-Pd distance of about 0.05 Å compared to the distance in fresh catalysts (compare Tables 6. and 7.). The analysis of the EXAFS of fresh and reactively reconstructed samples confirms the formation of a single PdAu phase under reaction conditions. The EXAFS at the Au-L_{III} edge of all reactively reconstructed samples indicated an ordered phase with an alloy composition of approximately Pd₁Au₁. An ordered 1:1 phase in a fcc lattice leads to a ratio of 2:1 for the coordination numbers of the mixed contributions relative to the monometallic ones, which was found at the Au-L_{III} edge.^[34] In contrast, randomly distributed PdAu alloys with a molar composition of 1/1 should show similar coordination numbers for both adsorbing and back scattering pairs.^[35] XRD and low temperature CO adsorption showed slightly Au-rich bimetallic particles after reaction for the PdAu 1.1 sample. This is confirmed via EXAFS analysis. $N_{\text{AuPd}}/N_{\text{AuAu}}$ is slightly lower as observed for the PdAu 2.0 and 6.0 samples (see Table 7). Since the alloy compositions derived from XRD data are consistent with the one obtained from EXAFS analysis, we conclude that all Au is incorporated into a Pd₁Au₁ phase forming bimetallic particles. The EXAFS at the Pd-K edge after reaction showed high coordination numbers for Pd-Pd neighbors, which resulted from the additional contribution of the monometallic Pd phase on the silica surface. Note that the coordination number of Pd includes both, the (bimetallic) neighbors from the PdAu phase and the atoms from the monometallic Pd phase. Since the samples were re-reduced before the XAS measurements, the disperse Pd phase, present in the form of Pd-acetate after reaction (not removed for the XAS experiments), was reduced to monometallic Pd particles. The increase in

the distances between the metal atoms in the samples after reaction (2.75 – 2.80 Å) was assigned to a Pd-K mixed phase formed from dispersed Pd(OAc)₂ and KOAc as discussed above. In summary, reactive reconstruction of Pd-Au bimetallic particles was detected by surface and bulk sensitive methods. While thermal treatment of the bimetallic particles led to the formation of bimetallic particles with Pd/Au of various compositions, in the presence of the reactant gases during vinyl acetate synthesis a single Pd-Au phase close to the equimolar composition was formed. Besides this single equimolar phase, Pd dispersed as Pd(OAc)₂ or as a highly dispersed monometallic Pd phase was present, independent of the initial Pd/Au ratio. The reconstruction process is attributed to the oxidation of Pd⁰ (present in larger Pd ensembles), the formation of Pd(OAc)₂ by a reaction with the reactant and subsequent extraction from the bimetallic particle into the liquid phase consisting of AcOH and H₂O. The temperature dependent phase composition of the bimetallic particles was identified to have a large impact on the activity for VAM formation. We expect that the observed formation of the bimetallic surface phase independently of the Pd/Au ratio and the presence of the isolated Pd are the key to understand the relation of the structural properties of bimetallic catalysts and the kinetic data observed for VAM synthesis. As the Pd₁Au₁ phase dominates the catalytic activity, novel tailored catalysts could be produced limiting the presence of dispersed Pd.

Experimental Methods

Synthesis: Pd-Au/SiO₂ catalysts with Pd to Au weight ratios of 0.3, 1, 2, 3 and 4 were prepared via incipient wetness impregnation of SiO₂ with an aqueous solution of HAuCl₃ and PdCl₂ according to DE102006058800 A1^[36], which includes a precipitation with carbonate and

subsequent washing with aqueous ammonia to remove chlorides. The Pd-Au/SiO₂ catalysts were reduced in flowing H₂ at 300 °C for 1 hour with a heating rate of 3 °C/min.

Characterization: X-ray absorption spectroscopy measurements were conducted at HASYLAB, DESY, Germany on the beamlines X1 and C. The storage ring energy was 4.5 GeV and the current decay during a typical fill was from 110 mA to 90 mA. The theta goniometer was equipped with a Heidenhain encoder within a tolerance of 10⁻⁵ degrees. The intensity of the higher order reflections was minimized by detuning the second crystal of the monochromator to 60 % of the maximum intensity. The Au-L_{III} (11919 eV) edge was measured with a pair of Si(111) crystals. For the Pd-K edge (24350 eV) the monochromator was equipped with a pair of Si(311) crystals. The samples were prepared as self-supporting wafers, having a total absorbance of 2.0. The samples were flushed with He inside the sample chamber and cooled to liquid N₂ temperature. Prior to measurements the samples were re-reduced in flowing H₂ at 300 °C for 1 hour with a heating rate of 5 °C/min. After reduction the samples were flushed with He for 15 minutes at 300 °C.

For EXAFS analysis, the scattering contributions in the pre- and post- edge background were removed from the X-ray absorption by a third-order polynomial function. The oscillations were weighted with k^2 and Fourier transformed within the limits $k=2.1-12 \text{ \AA}^{-1}$ for the Pd-K edge and $k=2.8-12 \text{ \AA}^{-1}$ for the Au-L_{III} edge. XAS data processing and EXAFS analysis were performed using IFEFFIT^[37] with the Horae package^[38] (Athena and Artemis). The amplitude, i.e. S_0^2 , was derived from EXAFS data analysis of known references with known coordination numbers and were fixed during analysis. S_0^2 was found to be 0.9 for Au and 1.0 for Pd. The multiple-edge fitting was carried out with the constraints (1)-(3).^[39]

$$(1) N_{\text{AuPd}} = N_{\text{PdAu}} * X_{\text{Pd}}/X_{\text{Au}} \quad (2) d_{\text{AuPd}} = d_{\text{PdAu}} \quad (3) \sigma_{\text{AuPd}} = \sigma_{\text{PdAu}}$$

The infrared spectra were recorded on a Vertex 70 spectrometer from Bruker Optics at a resolution of 4 cm⁻¹. The samples were prepared as self-supporting wafers with a density of 10 mg/cm². Samples were first activated in vacuum (1.0*10⁻⁷ mbar or less) at 300 °C for 1 hour with a heating rate of 5 °C/min, cooled to room temperature and subsequently re-reduced in 20 mbar H₂ at 300 °C with a heating rate of 5 °C/min. After re-reduction, the samples were outgassed at 300 °C in vacuum for 30 minutes. After pretreatment of the samples, the system was cooled to -150 °C with liquid nitrogen in 10 mbar He added to enhance the thermal conductivity. At -150 °C a spectrum was taken, the cell was evacuated and 1 mbar CO was introduced. To increase thermal conductivity, 10 mbar He were again added to the system. All spectra during CO adsorption were taken at -150 °C.

X-ray powder diffraction measurements were conducted on a Philips X'Pert Pro System using Cu-K α radiation (0.154056 nm) generated at 45 kV and 40 mA. The samples were mounted on a rotating powder holder. The XRD patterns were measured in a 2 Θ range of 5° to 70° with a step size of 0.019°/s. In-situ reduction measurements were performed in an Anton Paar HTK 1200 oven under flowing H₂ with a heating rate of 3 K/min and a cooling rate of 2 K/min. Data analysis was performed with High Score Plus software.

ASSOCIATED CONTENT

Supporting Information. Activity and selectivity behavior with time on stream for bimetallic samples and Pd(OAc)₂ impregnated onto SiO₂. Detailed results of EXFAS analysis including

R-factors and σ^2 are provided. Experimental details for vinyl acetate formation are listed. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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