

Dynamic Self-Organization of Supported Pd/Au Catalysts during Vinyl Acetate Synthesis

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Supporting information

Results of the EXAFS analysis

The results of the EXAFS analysis for the Pd/Au samples before and after reaction are listed in Table 1

Table 1: EXAFS fit results for Pd/Au samples before reaction (b.r.) and after reaction (a.r)

	Au-Pd		Au-Au		Pd-Au		Pd-Pd		$E_0(\text{Au})$	$\sigma^2(\text{AuAu})$	$E_0(\text{Pd})$	$\sigma^2(\text{PdPd})$	$\sigma^2(\text{PdAu}) = \sigma^2(\text{AuPd})$	R-factor
	N	d/nm	N	d/nm	N	d/nm	N	d/nm						
1.1 b.r.	4.0	0.277	7.8	0.279	4.5	0.277	4.7	0.275	3.0	0.009	-6.2	0.006	0.007	0.002
1.1 a.r.	6.5	0.278	4.6	0.279	5.9	0.278	4.5	0.281	3.0	0.002	-6.8	0.004	0.001	0.015
2.0 b.r.	4.5	0.277	7.3	0.280	2.2	0.277	7.9	0.275	3.8	0.009	-3.7	0.004	0.005	0.008
2.0 a.r.	7.4	0.277	3.9	0.278	4.1	0.277	5.9	0.280	2.5	0.001	-8.2	0.003	0.005	0.012
6.0 b.r.	5.4	0.276	6.5	0.280	1.1	0.276	9.3	0.275	5.1	0.009	-4.7	0.003	0.005	0.006
6.0 a.r.	7.2	0.277	3.8	0.279	1.2	0.277	8.8	0.281	3.1	0.009	-4.9	0.004	0.008	0.012

CO adsorption on reference samples

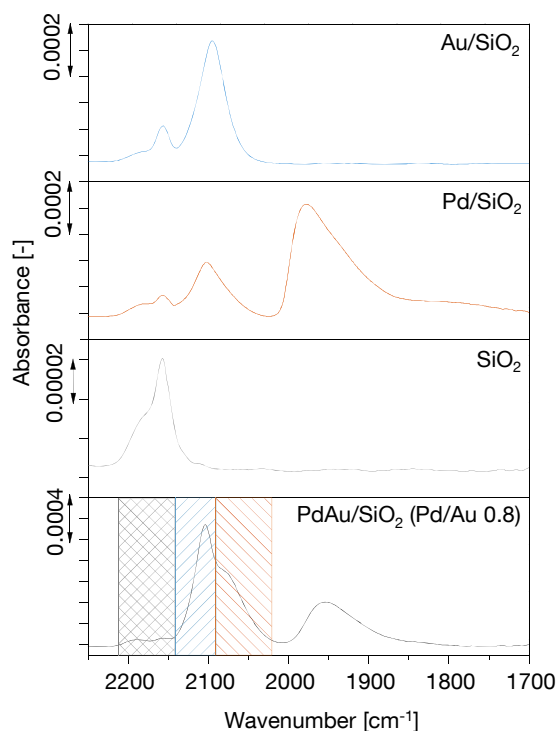


Figure 1: FTIR spectra of CO adsorbed at -150 °C at maximum coverage (1 mbar) on Au/SiO₂, Pd/SiO₂, pure SiO₂ and a bimetallic sample with a Pd/Au molar ratio of 0.8. Dashed regions in grey, blue and orange account for CO adsorption on the support, Au and Pd.

Figure 1 shows the transmission infrared spectra of CO adsorbed at -150 °C on a series of reference samples and a bimetallic Pd/Au sample with a Pd/Au molar ratio of 0.8. The low Pd/Au ratio was chosen as example in order to provide equally pronounced linear adsorption on both metals. Spectra were taken at 1 mbar CO partial pressure. On the monometallic Pd sample, CO adsorbs predominantly in multifold mode (2000 – 1700 cm⁻¹). Linearly adsorbed CO is found at a wavenumber of approximately 2095 cm⁻¹.

CO adsorbed on monometallic Au is exclusively present in linear adsorption mode and was detected at wavenumbers around 2098 cm⁻¹. No multifold adsorbed CO species were found.

For bimetallic samples, the linear adsorption mode is more dominant as it was found for monometallic palladium sample. As well known in literature^{1,2}, the introduction of Au to monometallic palladium leads to a shift towards lower wavenumbers for adsorption features representing CO on Pd. The adsorption features of Au are less affected in terms of wavenumber shifts, however small shifts towards higher wavenumbers are distinguishable.

At -150 °C CO also adsorbs on the silica support. Two adsorption features are evident. CO adsorbed on OH-groups is found at a wavenumber of approximately 2153 cm⁻¹, which is in good agreement to literature.^{3,4} CO adsorption at surface impurities leads to a weaker adsorption feature at higher wavenumbers (~2180cm⁻¹).

Dashed regions in figure 1 represent the wavenumber regions for CO on Pd, which is electronically altered by Au and CO on Au, which frequencies are shifted due to close neighborhood to Pd. The deconvolution of the FTIR spectra of CO adsorbed on the bimetallic samples is shown and discussed in the main part of this work.

Pressure dependence of CO adsorption

Figure 2 shows the pressure dependence of the adsorption of CO for Pd/Au 2.0 in a CO partial pressure range of 0.005 mbar – 1.000 mbar.

With increasing coverage the intensity of the multifold adsorption feature at 1968 cm^{-1} is intensified, whereas relative to this feature the shoulder around 1900 cm^{-1} shows only small variations. Similar behavior with increasing partial pressure of CO was found by McKenna and Anderson⁵ on monometallic palladium. The adsorption features representing linearly adsorbed CO on Pd and Au ($\sim 2120\text{--}2015\text{cm}^{-1}$) show pronounced variations until the maximum coverage is reached. For low coverages CO adsorbs predominately on Pd and only low intensities for the adsorption of CO on Au are found ($> 2100\text{ cm}^{-1}$). With increasing partial pressure (and increasing coverage), CO adsorption on Au is favored and the adsorption features representing CO on Au increase in intensity.

The adsorption of CO on the support also shows pressure dependency. At low partial pressures, the adsorption of CO on OH-groups ($\sim 2153\text{ cm}^{-1}$ at maximum coverage) is weak. With increasing partial pressures the adsorption of CO on OH-groups is enhanced. The adsorption on cationic surface impurities ($\sim 2180\text{ cm}^{-1}$) is weak and less effected by an increasing CO partial pressure. The pressure dependence of the CO adsorption on the support is in perfect agreement to studies of Busca et al.^{3,4}

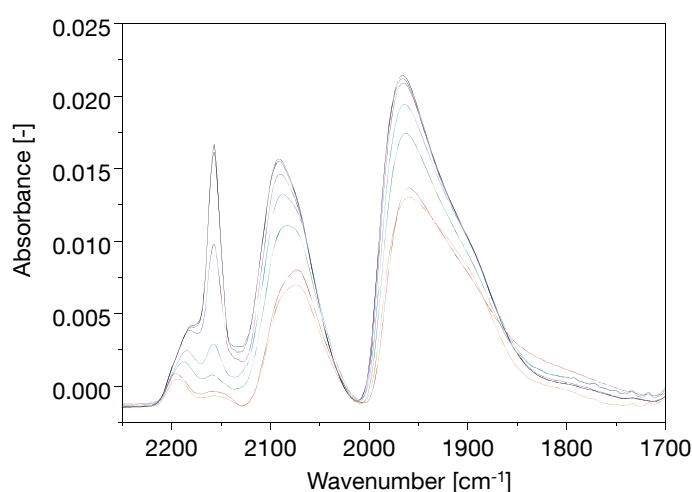


Figure 2: FTIR spectra of CO adsorbed at $-150\text{ }^{\circ}\text{C}$ at increasing pressures. 0.005 mbar – 0.010 mbar – 0.050 mbar – 0.100 mbar – 0.500 mbar – 0.750 mbar – 1.000 mbar.

Complete author list of reference 2 in main contribution:

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