

## SUPPORTING INFORMATION

### Interaction of Alkali Acetates with silica supported PdAu

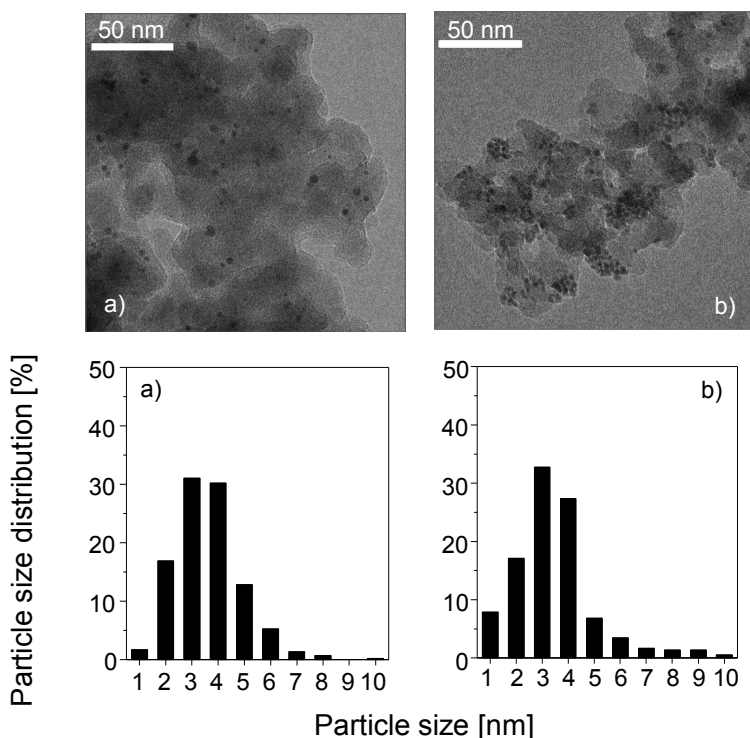
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#### Transmission Electron Microscopy

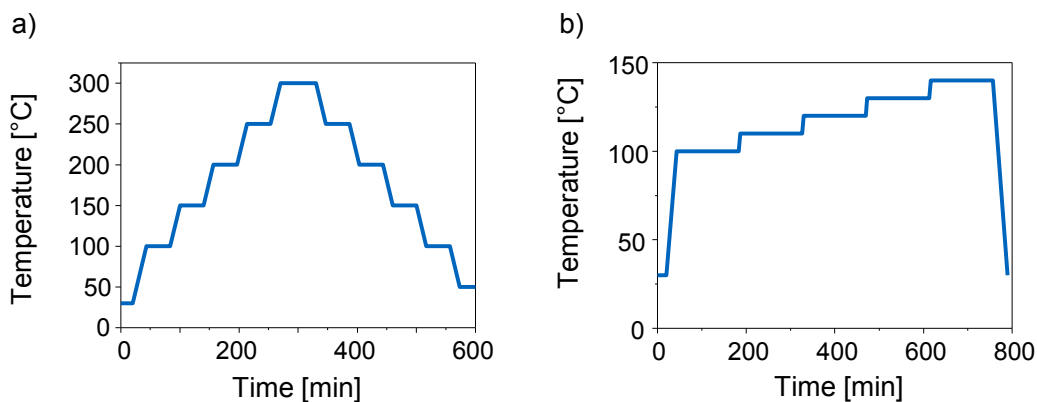
TEM images were collected on a *JEM-2010-JEOL* microscope applying an acceleration voltage of 120 kV to electrons generated by a LaB<sub>6</sub> source. The resolution of the microscope is 0.2 nm. Before measurement the samples were dispersed in ethanol and dropped on a copper-grid supported film.



**Figure S1:** TEM images and particle size distribution of (a) unpromoted and (b) KOAc promoted PdAu/SiO<sub>2</sub>.

The particle size distribution of PdAu/SiO<sub>2</sub> and PdAu/KOAc/SiO<sub>2</sub> revealed an average particle size of ~3.6 nm and 3.7 nm, respectively. The promotion with KOAc does not affect the PdAu particle size but their mobility to form particle groups which may undergo sintering during subsequent reaction to form agglomerates.

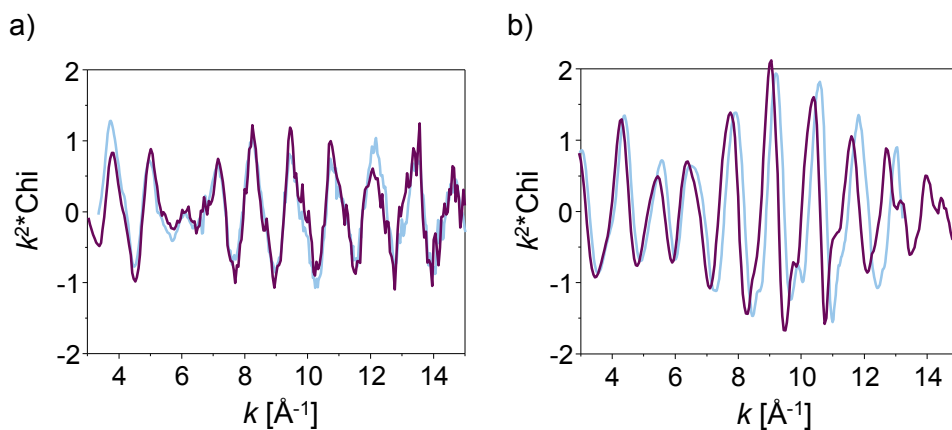
### In Situ X-Ray Diffraction Programs



**Figure S2.** In situ XRD temperature programs. (a) The temperature was increased from 30 to 300 °C and cooled to 50 °C with a heating/cooling rate of 3 °C/min. At each temperature level, a 20min XRD pattern was recorded after equilibrating the temperature for 20 min. (b) The temperature was raised from 30 °C to 100 °C and then in steps of 10 °C to 140 °C (heating rate 3 °C/min). In contrast to program (a), the temperature was equilibrated for 2h prior to a 20 min XRD measurement.

### EXAFS at the Pd-K and Au-L<sub>3</sub> Edge of Unpromoted and Li- and K-acetate Promoted PdAu/SiO<sub>2</sub>

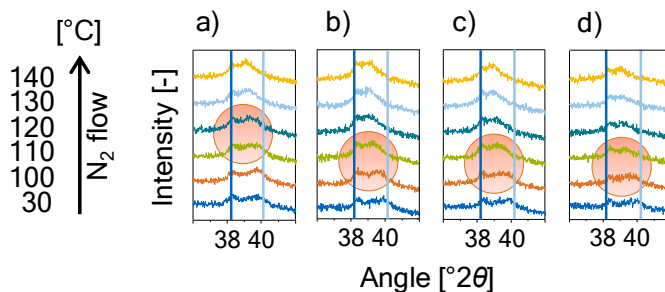
The  $k^2$  weighted EXAFS functions of (a) Au and (b) Pd edges differ slightly between unpromoted (blue) and LiOAc promoted (violet) PdAu/SiO<sub>2</sub> catalysts. The addition of LiOAc to PdAu/SiO<sub>2</sub> qualitatively induced changes in metal-metal distances. Additional oscillations reveal changing surroundings of Pd and Au.



**Figure S3.** EXAFS function at the a) Pd-K and b) Au-L<sub>3</sub> edge of PdAu/SiO<sub>2</sub> (blue) and PdAu/LiOAc/SiO<sub>2</sub> (violet),  $k^2$  weighted.

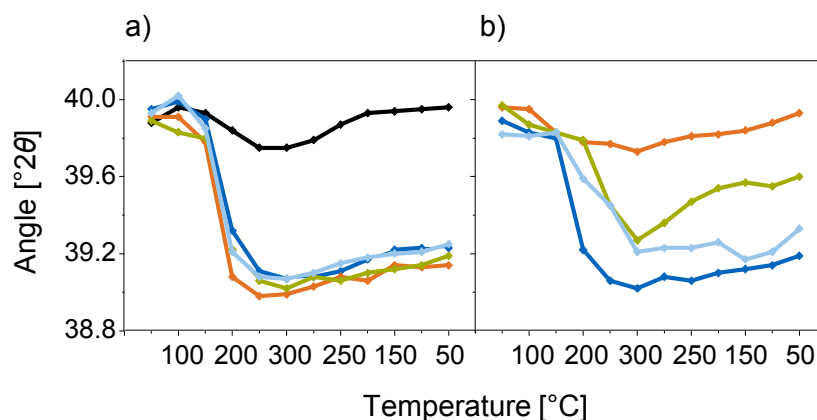
### In situ X-Ray Diffraction Studies

Radius dependent Pd(111) peak shifts were investigated by applying (a) LiOAc, (b) NaOAc, (c) KOAc and (d) CsOAc impregnated PdAu/SiO<sub>2</sub> to the in situ XRD program in Figure S2b.



**Figure S4.** In situ XRD profiles for Pd<sub>x</sub>Au<sub>y</sub>(111) of (a) PdAu/LiOAc/SiO<sub>2</sub> (b) PdAu/NaOAc/SiO<sub>2</sub>, (c) PdAu/KOAc/SiO<sub>2</sub> and (d) PdAu/CsOAc/SiO<sub>2</sub> in flowing N<sub>2</sub>. The bimetallic phase is located between those of the pure metals: Au(111) ( $2\theta = 38.3^\circ$ , blue bar) and Pd(111) ( $2\theta = 40.1^\circ$ , bright blue bar).

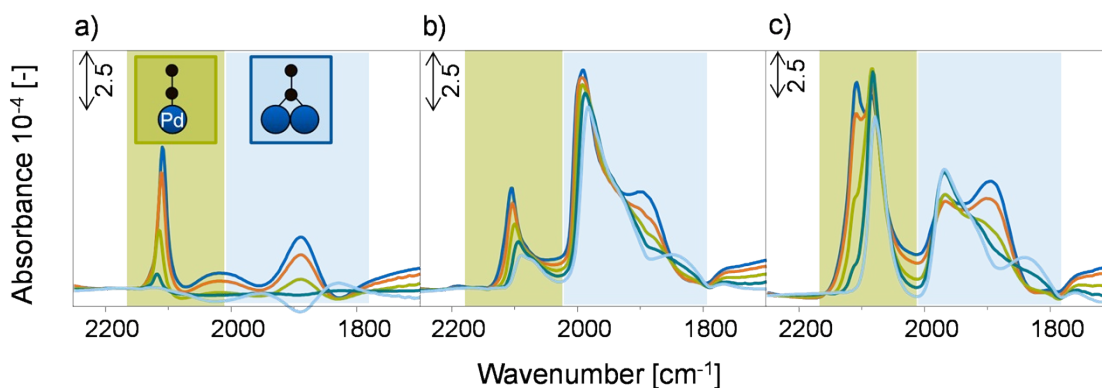
Figure S5 depicts the peak position of Pd(111) of (a) unpromoted as well as alkali acetate promoted PdAu/SiO<sub>2</sub> and (b) of KOH, K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and KOAc impregnated PdAu/SiO<sub>2</sub> as function of the temperature for the in situ XRD program in Figure S2a.



**Figure S5.** Temperature dependent position of Pd(111) of PdAu/SiO<sub>2</sub> promoted with (a) promoter-free (black), LiOAc (blue), NaOAc (orange), KOAc (green), CsOAc (bright blue) and (b) KOAc (blue), KOH (orange), K<sub>2</sub>CO<sub>3</sub> (green), K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (bright blue).

### Temperature Dependent CO Adsorption on Au/SiO<sub>2</sub>, Pd/SiO<sub>2</sub> and PdAu/SiO<sub>2</sub> Followed by IR spectroscopy

In order to determine the effect of temperature<sup>1</sup> on CO band positions, CO was adsorbed on Au/SiO<sub>2</sub>, Pd/SiO<sub>2</sub> and PdAu/SiO<sub>2</sub> at -89, -50, 0, 50 and 100 °C (Figure S6). On Au/SiO<sub>2</sub>, CO linearly adsorbed at 2104 cm<sup>-1</sup> while the broad bands at 2020 and 1890 cm<sup>-1</sup> derived from subtraction errors with the spectrum of the activated sample measured at 50 °C (Figure S6a). CO linearly adsorbed on Pd at 2109 and 1991 cm<sup>-1</sup> at -89 °C (Figure S6b). With increasing temperature, the CO band areas and frequencies decreased due to lower CO coverages and thus less CO dipole coupling.<sup>1-3</sup> In the bimetallic case (Figure S6c), CO adsorbed on Au in contact to Pd at 2109 cm<sup>-1</sup> and on Pd close to Au at 2083 cm<sup>-1</sup> at -89 °C. Thus, the contact of Au with Pd leads to an increase and the contact of Pd to Au to a decrease of CO band frequencies according to the electronic Pd-Au interactions described in the two band model.<sup>4,5</sup> However, an increase in temperature leads to a slight upshift of CO on Au (~ 3 cm<sup>-1</sup>) like observed from Rainer<sup>6</sup> and France et al.<sup>7</sup> and a downshift of linear CO on Pd (~7 cm<sup>-1</sup>). CO/Au shows a large negative shift which offsets the positive dipolar shift as CO coverage increases. The upshift can be explained by the weakening of the Au-C bond upon temperature increase. The downshift of CO on Pd might be due to the reduction in CO dipole couplings (transition from a compressed to an uncompressed CO overlayer).



**Figure S6.** IR spectra of 1.0 mbar CO adsorbed on (a) Au/SiO<sub>2</sub>, on (b) Pd/SiO<sub>2</sub> and on (c) PdAu/SiO<sub>2</sub> at -89 °C (blue), -50 °C (orange), 0 °C (green), 50 °C (dark green) and 100 °C (bright blue).

At 100 °C, linear and bridged adsorption modes were observed at 2090 cm<sup>-1</sup> and 1984 cm<sup>-1</sup> on Pd/SiO<sub>2</sub>, whereas on Au/SiO<sub>2</sub>, CO adsorbed only in a linear mode at 2118 cm<sup>-1</sup> (50 °C).<sup>8</sup> The temperature dependent spectra revealed that CO adsorbed exclusively on Pd above 50 °C.

## References

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