

**Dissecting the steps of CO<sub>2</sub> reduction: 2. The interaction of CO and CO<sub>2</sub> with  
Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: *an in situ FTIR study***

János Szanyi\*, Ja Hun Kwak<sup>#</sup>

Institute for Integrated Catalysis, Pacific Northwest National Laboratory

Richland, WA 99352

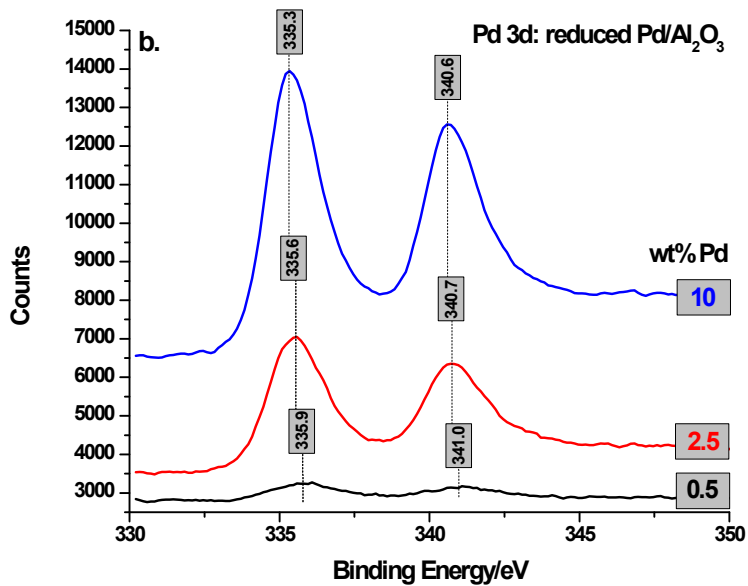
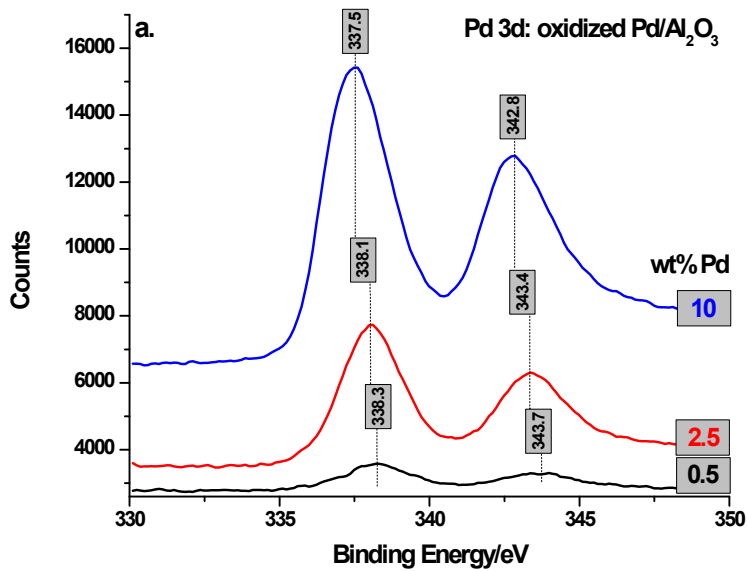
E-mail: [janos.szanyi@pnnl.gov](mailto:janos.szanyi@pnnl.gov)

<sup>#</sup>Current address: Department of Chemical Engineering, UNIST

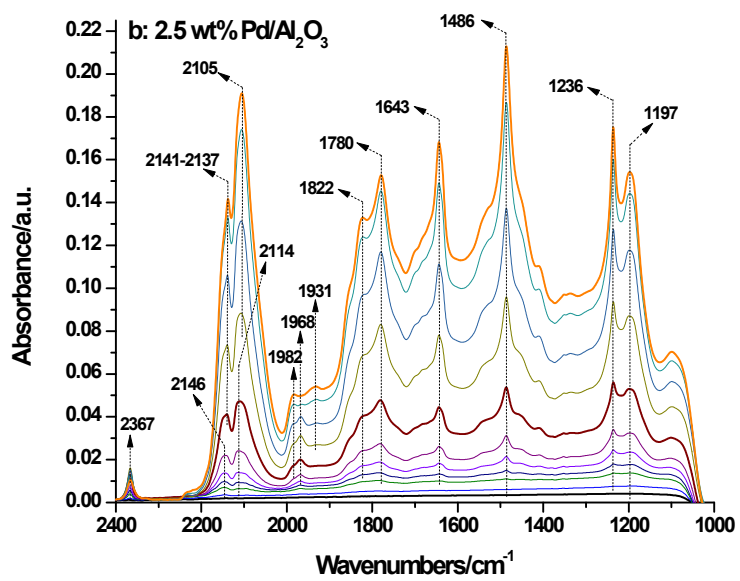
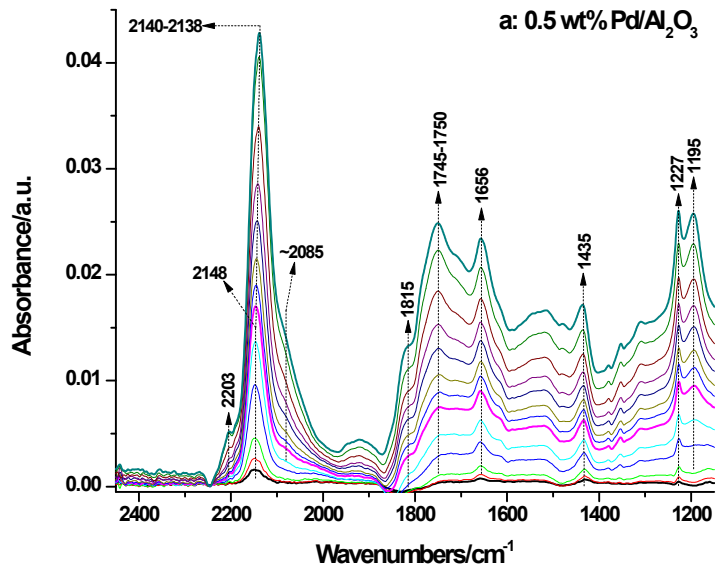
100 Banyeon-Ri, Ulsan 689-798, Korea

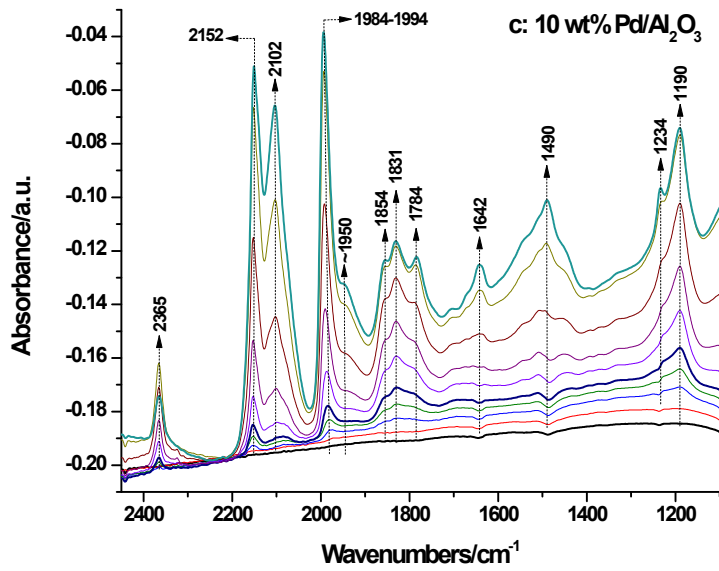
**Supplementary Information:**

**Figure S1.** XPS spectra of the oxidized (panel a) and reduced (panel b) Pd/Al<sub>2</sub>O<sub>3</sub> samples in the Pd 3d binding energy range. (Oxidation: at 773 K in 10 %/O<sub>2</sub>/He flow for 2 hrs. Reduction: 773 K, in 10 % H<sub>2</sub>/He flow for 30 min.)



**Figure S2.** Series of IR spectra obtained during the stepwise adsorption on oxidized 0.5 (a), 2.5 (b) and 10 wt% (c) Pd/Al<sub>2</sub>O<sub>3</sub> samples at 295 K.

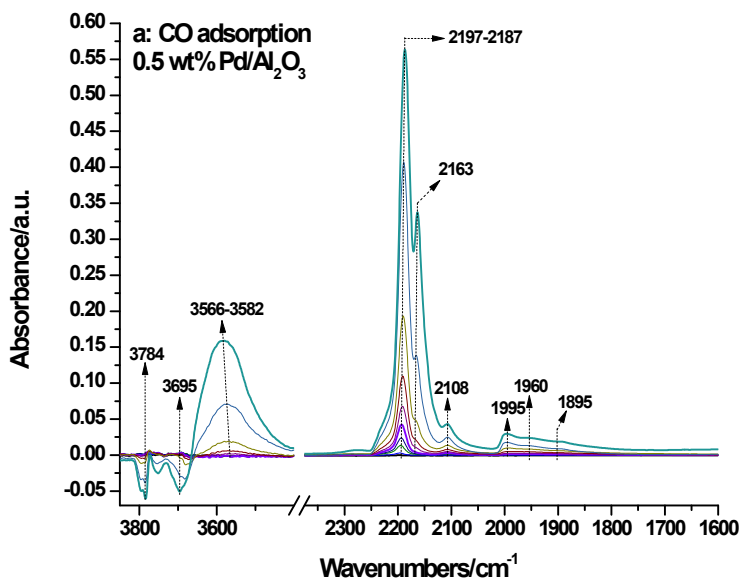




### Step-wise CO adsorption on oxidized and reduced Pd/Al<sub>2</sub>O<sub>3</sub> samples at 100 K:

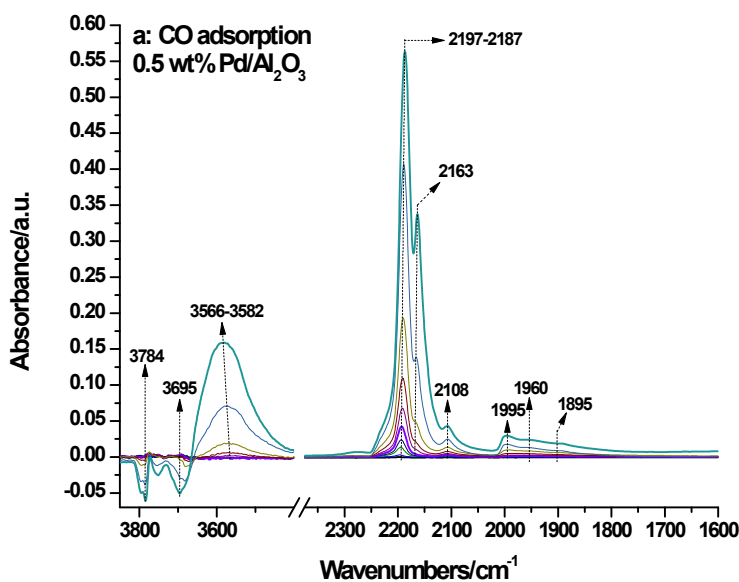
The series of IR spectra recorded during the stepwise CO adsorption on the oxidized 0.5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample at 100 K is displayed Fig. S3. In the stretching vibrational region of adsorbed CO (1850-2250 cm<sup>-1</sup>) the two main features represent CO adsorbed either onto Lewis acidic Al<sup>3+</sup> sites (2198-2187 cm<sup>-1</sup>) or surface hydroxyl groups (2168-2163 cm<sup>-1</sup>), just as we have seen for the Pd-free alumina support [Part 1 of this study]. The negative features in the OH stretching vibrational region between 3650 and 3800 cm<sup>-1</sup>, and the broad band centered around 3570 cm<sup>-1</sup> are clear evidence for the hydrogen bonding interaction between surface hydroxyls and CO molecules. The two weak shoulders at 2230 and 2140 cm<sup>-1</sup> belong to CO adsorbed onto defect sites on alumina and oxidized Pd (Pd<sup>2+</sup>), respectively. There is no indication for the formation of surface carbonates/bicarbonates at this low temperature.

**Figure S3.** FTIR spectra collected during the stepwise CO adsorption on the oxidized 0.5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> sample at 100 K.



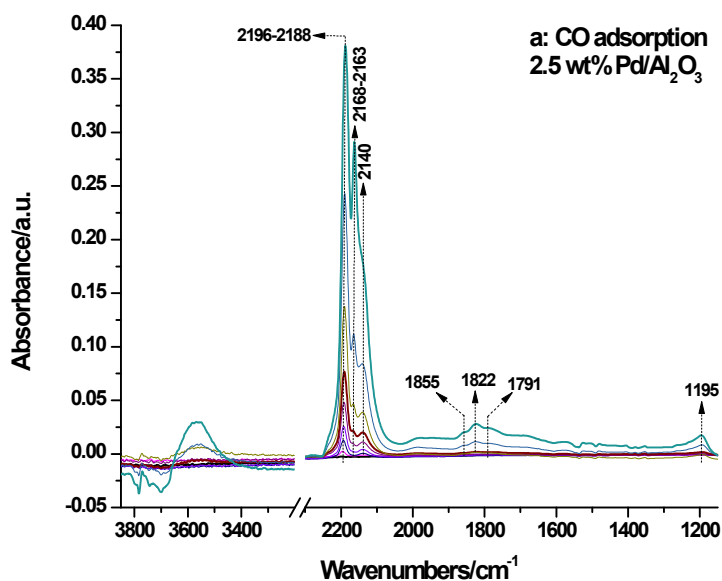
The series of IR spectra collected from the reduced 0.5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample (Fig. S4) during stepwise CO adsorption at 100 K shows significant differences from that obtained from the oxidized sample (Fig. S3). Although this series of spectra is also dominated by the features of the alumina support-bound CO (2163 and 2187-2197 cm<sup>-1</sup>), the presence of adsorbed CO on metallic Pd is clearly visible. The presence of characteristic vibrational bands of linear (2108 cm<sup>-1</sup>) and bridge-bound (1880-2000 cm<sup>-1</sup>) CO (in different bonding configurations) is in contrast to the oxidized sample where we detected adsorbed CO mostly on Pd<sup>2+</sup> sites. These results substantiate that the mild reduction process applied converted most of the oxidized Pd species to metallic ones (Due to the large intensity of the 2163 cm<sup>-1</sup> band we cannot observe CO that might be adsorbed on Pd<sup>+</sup> and Pd<sup>2+</sup> sites. The absence of a clearly discernible shoulder in this spectral region suggests that the number of oxidized Pd species is much smaller on this sample than on the oxidized one.) The appearance of bridge-bound CO features (1995, 1960 and 1895 cm<sup>-1</sup>) suggests the formation of metallic Pd particles with well defined crystal facets during the reduction process.

**Figure S4.** FTIR spectra collected during the stepwise CO adsorption on the reduced 0.5 wt% Pd/Al<sub>2</sub>O<sub>3</sub> sample at 100 K.

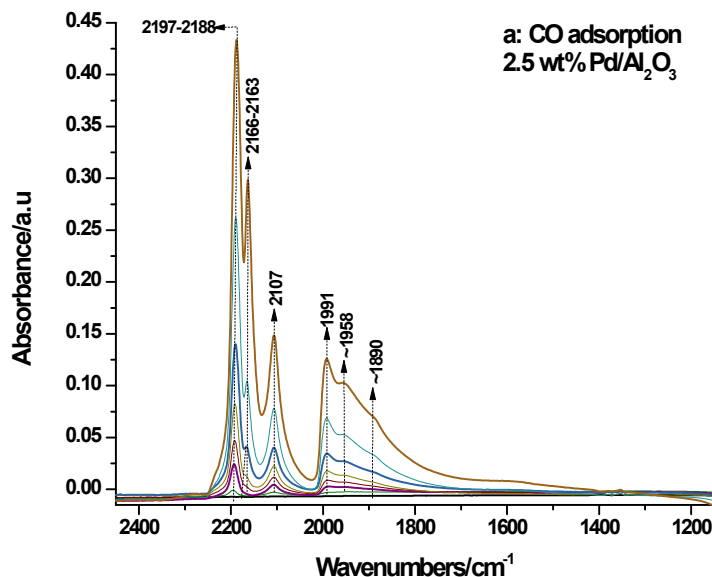


The series of IR spectra obtained during stepwise CO adsorption on the oxidized 2.5 wt% Pd/ $\gamma$ - $\text{Al}_2\text{O}_3$  sample at 100 K is shown in Fig. S4. The spectra are dominated by IR bands of the alumina support-bound CO (2196-2188 and 2168-2163  $\text{cm}^{-1}$ ), and a high intensity shoulder at  $\sim 2140 \text{ cm}^{-1}$  of  $\text{Pd}^{2+}$ -bound CO. At the two highest CO exposures (top two spectra) the formation of bridging carbonates on the alumina support can clearly be seen as well (IR bands centered at 1195 and 1791, 1822, 1855  $\text{cm}^{-1}$ ). In these two IR spectra we can also observe some intensity around 2000  $\text{cm}^{-1}$  that may arise from the adsorption of CO on  $\text{Pd}^+$  species in bridging configuration. This is in concert with the onset of PdO reduction by CO that is manifested itself by the appearance of surface carbonates as a result of  $\text{CO}_2$  formation.

**Figure S5.** FTIR spectra collected during the stepwise CO adsorption on the oxidized 2.5 wt% Pd/ $\text{Al}_2\text{O}_3$  sample at 100 K.



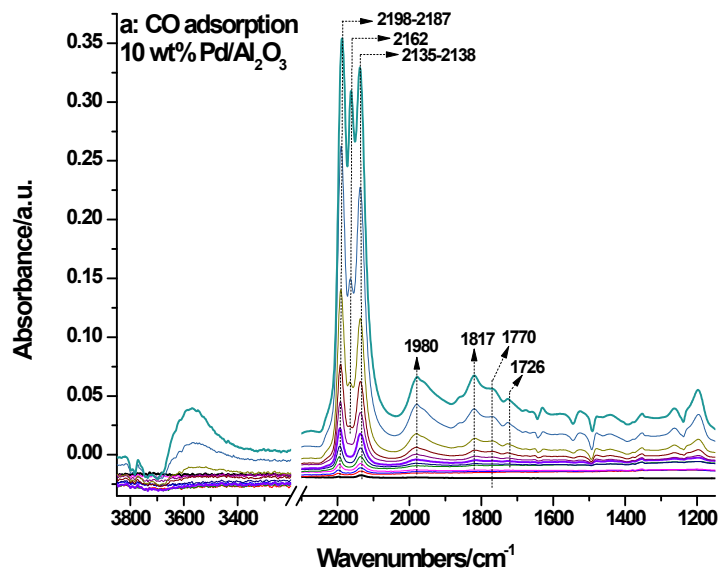
**Figure S6.** FTIR spectra collected during the stepwise CO adsorption on the reduced 2.5 wt% Pd/ $\text{Al}_2\text{O}_3$  sample at 100 K.



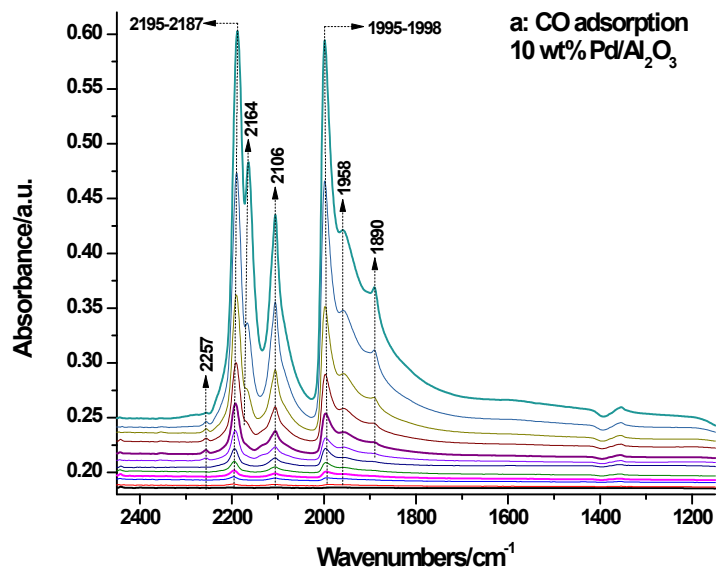
The IR spectra collected from the oxidized 10 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample (Fig. S7) during stepwise CO adsorption at 100 K show the development of two main features characteristic of CO adsorbed on either the Lewis acidic Al<sup>3+</sup> surface sites on the alumina support (2198-2187 cm<sup>-1</sup>), or on Pd<sup>2+</sup> sites (2135-2138 cm<sup>-1</sup>). The intensities of these two features increase simultaneously with increasing CO exposure, while the H-bonded CO feature (2162 cm<sup>-1</sup>) appears only at higher CO amounts. The very high intensity of the IR feature at ~2140 cm<sup>-1</sup> is consistent with the high Pd loading in this sample in comparison to that of the 0.5 and 2.5 wt% samples discussed above. Lower intensity features also develop as the CO exposure increases at 1980 cm<sup>-1</sup> (CO bridge bonded to Pd<sup>+</sup> ions), and those of bridging carbonates on the alumina support (1190, 1700-1850 cm<sup>-1</sup>).

**Figure S7.** FTIR spectra collected during the stepwise CO adsorption on the oxidized 10 wt% Pd/Al<sub>2</sub>O<sub>3</sub> sample at 100 K.





**Figure S8.** FTIR spectra collected during the stepwise CO adsorption on the reduced 10 wt% Pd/Al<sub>2</sub>O<sub>3</sub> sample at 100 K.



**Table. S1.** Assignment of IR features observed after CO adsorption on Pd- $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

<b>Wavenumbers/cm<sup>-1</sup></b>	<b>Assignment</b>	<b>Reference</b>
1890-1920	<b>three-fold hollow bound CO on Pd(111) facets</b>	20
1923-1959	<b>bridge-bound CO on Pd(100) facets</b>	20;22;24
1966-1970	<b>bridge-bound CO on Pd<sup>+</sup> ions</b>	20
1970-1998	<b>bridge-bound CO (compressed structures) on Pd<sup>0</sup></b>	21
2072-2082	<b>a-top bound CO on Pd<sup>0</sup></b>	18;21
2095-2110	<b>a-top bound CO on Pd<sup>0</sup></b>	26
2110-2120	<b>a-top bound CO on Pd<sup>+</sup></b>	20;21
2138-2154	<b>a-top bound CO on Pd<sup>2+</sup></b>	18-23