Spectral Evidence for Hydrogen-induced Reversible Segregation of CO Adsorbed on Titania-supported Rhodium

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Supporting information

1. ADSORPTION OF CO

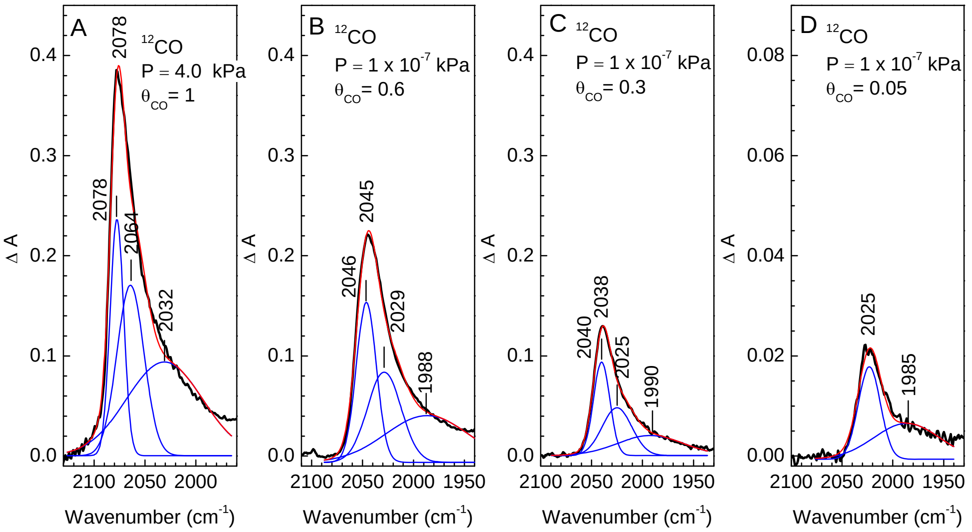

Figure S1. Deconvolution of the Rh^0-CO band observed in the FTIR spectra of CO adsorbed at 298 K on CO-reduced Rh/TiO$_2$, shown in Figure 1. (A) spectrum (a) obtained with CO saturated sample at 298 K; (B) spectrum (f) after 40 min evacuation at 448 K; (C) spectrum (h) after 60 min evacuation at 448 K; (D) spectrum (j) after 20 min evacuation at 523 K. The red curves are the sum of the deconvoluted bands.

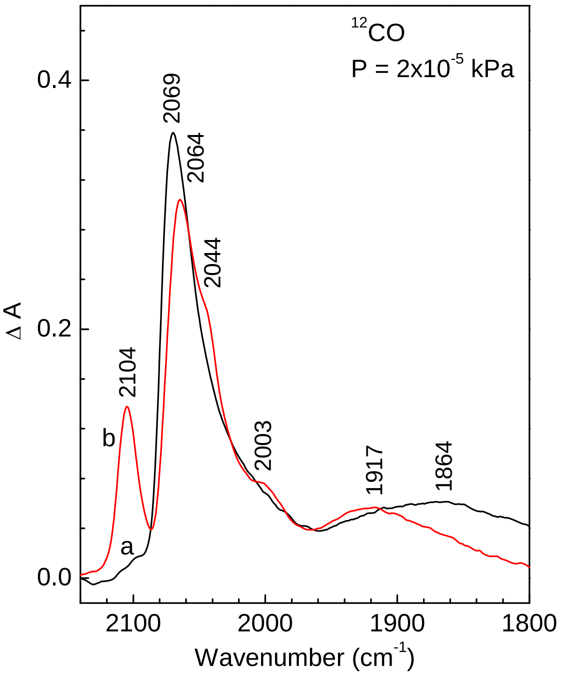

Figure S2. FTIR spectra of CO (4 kPa equilibrium pressure) adsorbed at 298 K on CO-reduced (*a*) and H_2-reduced sample (*b*). The CO-reduced sample is obtained after exposure to 4 kPa CO at 523 K for 1 min and evacuation at 298 K. The H_2-reduced sample is obtained after reduction in 4 kPa H_2 at 523 K for 10 min and evacuation at 298 K.

2. ADSORPTION OF H_2

In separate experiments, we examined the adsorption of H_2 on CO-reduced Rh/TiO_2. To obtain clean surface, the reduced sample was evacuated at 548 K for 20 min. Subsequent exposure of the sample to H_2 gas at 298 K led to immediate raise in the IR background absorbance as shown in Figure S3. The observed IR absorbance is featureless and increases exponentially from ~ 4000 to 1000 cm^{-1}. It was attributed to delocalized conduction band electrons that accumulate in TiO_2 with the H_2 exposure. Similar observations were recently reported for H_2 adsorption on Au/TiO_2.[1] The process behind is described by the following: H_2 dissociates on the metallic Rh particles and produces atomic hydrogen that spillover on the TiO_2 support; there, H atoms protonate surface oxygen atoms to OH groups while injecting electrons into the conduction band of TiO_2.[1,2] These spectral observations indicate the dissociative character of H_2 adsorption on Rh/TiO_2 surface at 298 K. In the experiments with co-adsorbed hydrogen, the spectra in the ν(CO) region were corrected for the background absorbance caused by the n-type donation of TiO_2. More details about the observed H-spillover process on Rh/TiO_2 are to be published.

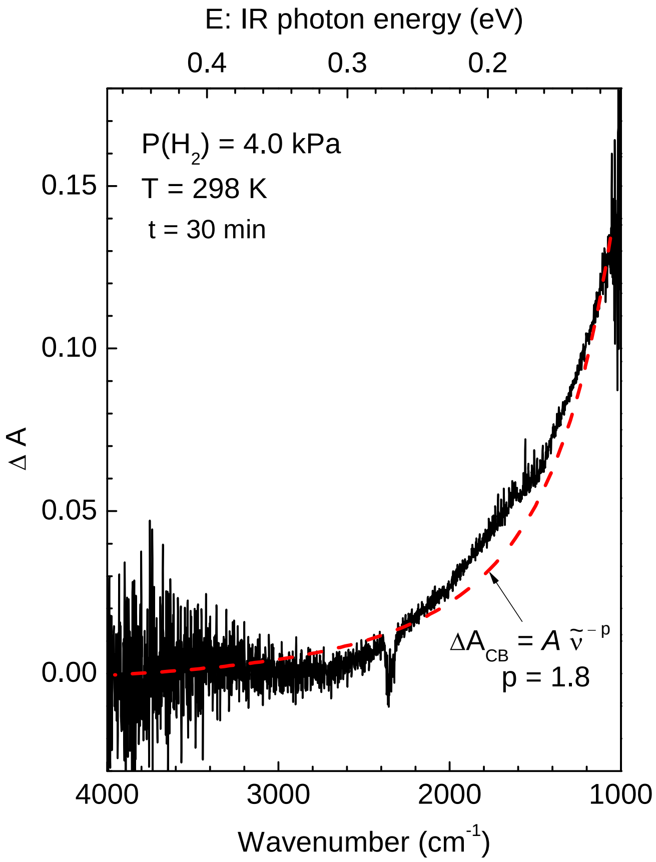

Figure S3. FTIR spectrum of Rh/TiO_2 sample recorded after 30 min exposure to 4 kPa H_2 at 298 K. Before the H_2 exposure, the CO-reduced Rh/TiO_2 sample was first evacuated at 548 K for 20 min and then cooled down to 295 K under dynamic vacuum. The red trace is a model for the spectral response of free electrons in the conduction band of the TiO_2 semiconductor.

According to the model, the absorption of light due to free conduction band electrons of a semiconductor varies in the mid-IR region as:[3-5]

$$\Delta(\text{Absorbance}) = A\,\nu^{-p}, \tag{1}$$

where A is a scaling parameter, ν is the wavenumber of IR light, and the exponent, p, is a characteristic of the scattering mechanism. That is, values for p = 1.5, 2.5, and 3 – 3.5 are predicted for acoustic-mode scattering, optic-mode scattering, and ionized-impurity scattering, respectively. IR absorption due to delocalized electrons that exhibit scattering constants in the range of 1.5 – 2, as observed here, is due to scattering processes involving acoustic phonons in TiO_2.

3. CO-ADSORPTION OF CO AND H_2

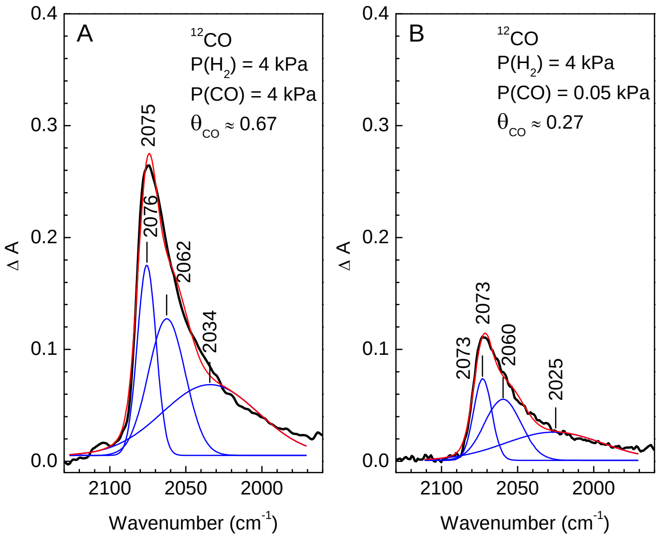

Figure S4. Deconvolution of the Rh^0-CO band observed in FTIR spectra of CO during the CO + H_2 co-adsorption experiment, shown in Figure 3. Admission of small doses of CO in the presence of 4.0 kPa H_2: (A) $\theta_{CO} = 0.67$; (B) $\theta_{CO} = 0.27$. The red curves are the sum of the deconvoluted bands.

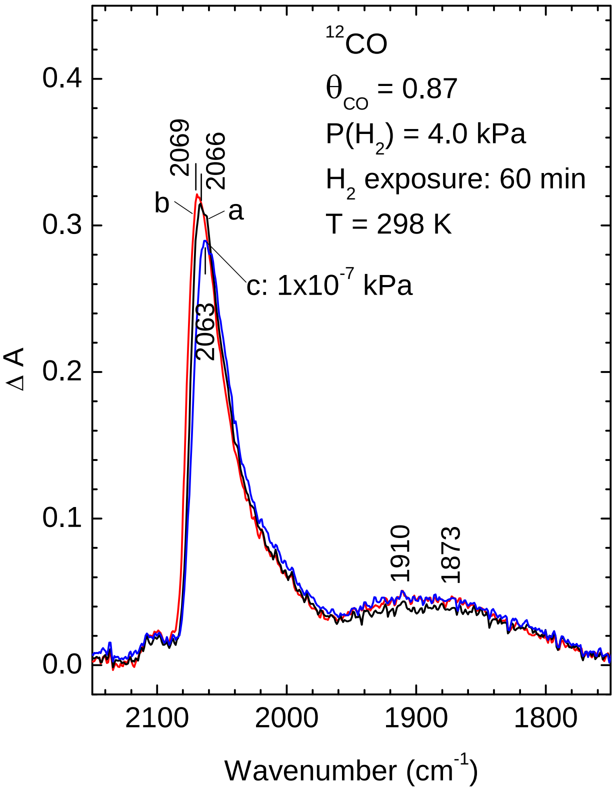

Figure S5. FTIR spectra in the carbonyl stretching region during the CO + H_2 co-adsorption experiment carried out at 298 K with Rh/TiO_2 that contained CO coverage close to that of CO-saturated sample, i.e. θ_{CO} = 0.87: (a) CO adsorbed on CO-reduced Rh/TiO_2 after evacuation at 298 K; (b) after interaction with 4 kPa H_2 at 298 K; (c) after evacuation at 298 K.

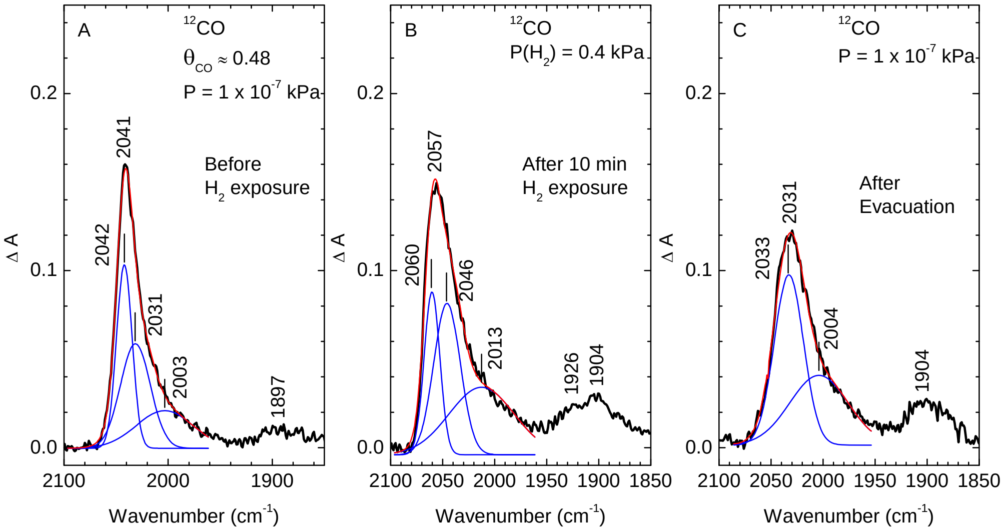

Figure S6. Deconvolution of the Rh^0-CO band observed in FTIR spectra of CO during the CO + H_2 co-adsorption experiments carried out at 298 K with Rh/TiO_2 that contained partial CO coverage, i.e. θ_{CO} = 0.48: (A) CO adsorbed on CO-reduced Rh/TiO_2 after evacuation at 298 K; (B) after interaction with 4 kPa H_2 at 298 K; (C) after evacuation at 298 K. The red curves are the sum of the deconvoluted bands.

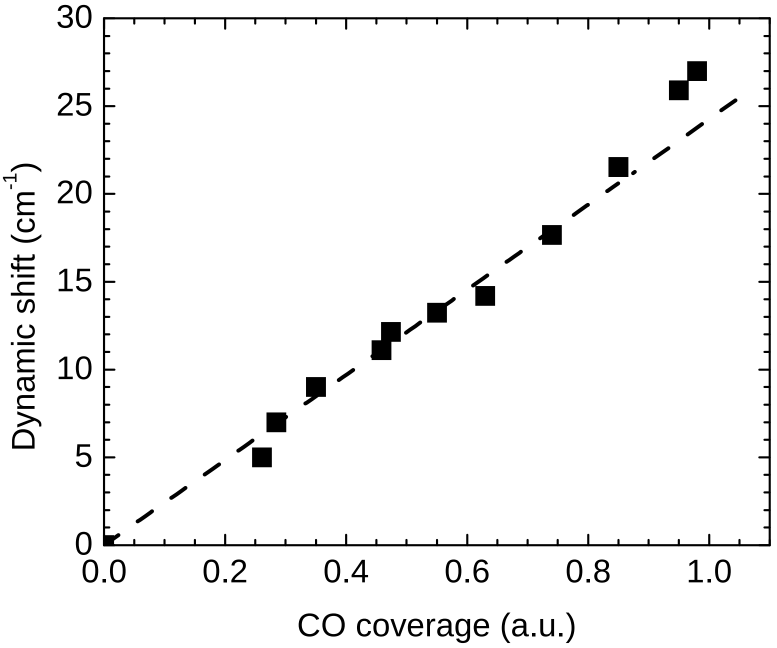

Figure S7. Dynamic shift of ν(CO) for linear Rh^0–CO species as measured (see the text) at increasing CO coverage in the presence of ^{12}CO + ^{13}CO isotopic mixture (1 : 9 molar ratio) at 298 K. The dash-dotted line is a guide for the eye.

REFERENCES

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