Towards Low-Temperature Dehydrogenation Catalysis: Isophorone Adsorbed on Pd(111)

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Supporting Information

Experimental Details

All experiments were performed at the Fritz-Haber-Institut, Berlin, in an ultrahigh vacuum (UHV) apparatus that has been described in detail before.[1] In brief, isophorone was dosed onto the sample cooled to 100 K through two doubly differentially pumped multi-channel array sources controlled by valves and shutters. The sources were operated at room temperature, and the beam diameter was chosen to exceed the sample size. Isophorone (Acros Organics, 98%) was further cleaned prior to the experiments by repeated freeze-pump-thaw cycles. The Pd(111) single crystal was cleaned prior to use by repeated cycles of Ar^+ ion bombardment at room temperature (ion current on sample $\sim 4\ \mu$A), annealing at 1000 K and oxidation in $1\cdot10^{-6}$ mbar O_2 at 750 K to remove residual carbon. The flatness and cleanliness of the Pd(111) single crystal surface was checked by

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*To whom correspondence should be addressed low energy electron diffraction (LEED) and infrared reflection-absorption spectroscopy (IRAS) of adsorbed CO. IRAS data were acquired using a vacuum Fourier-Transform Infrared (FT-IR) spectrometer (Bruker IFS 66v/S) with a spectral resolution of 2 cm^{-1} and using a mid-infrared (MIR) polarizer and p-polarized IR light. Temperature programmed desorption (TPD) experiments were carried out in the same vacuum system and by using an automated quadrupole mass spectrometer (QMS) system (Hiden Analytics). In TPD experiments the following masses were detected: 2, 3, 4, 16, 18, 28, 82, 83, 85, 86, 107, 108, 111, 112, 114, 115, 126, 127, 139, 139, 142 and 146.

The isophorone coverage was determined by TPD and IRAS: At greater than one monolayer coverage, a second desorption peak of intact isophorone molecules appears in TPD experiments at 254 K. This peak is assigned to molecules desorbing from the multilayer, whereas the peak observed at 272 K is considered to show desorption of molecules from the monolayer (see Fig. 4 in the main text). Moreover, the IR vibrational modes change significantly with increasing submonolayer coverage. As shown in Fig. 1, at low coverage of 0.3 ML, the IR spectra show only C–H deformation and the vibration modes are in the ranges of 2800-3000 cm^{-1} and 1100-1500 cm^{-1}. We also observed features in our calculated IR spectra at 420 and 470 wavenumbers. However, we are not able to experimentally measure the signal below 700 cm^{-1}, since we are using a KBr window and a Mecury-Cadmium-Telluride liquid N_2 cooled detector with a cutoff at relatively high wavenumbers. At higher coverage of 1.3 ML, however, the C=C and C=O vibrations also appear so that these spectra are similar to those of the gas phase.

References

(1) Libuda, J.; Meusel, I.; Hartmann, J.; Freund, H.-J. A Molecular Beam/Surface Spectroscopy Apparatus for the Study of Reactions on Complex Model Catalysts. *Rev. Sci. Instrum.* **2000**, *71*, 4395–4408.

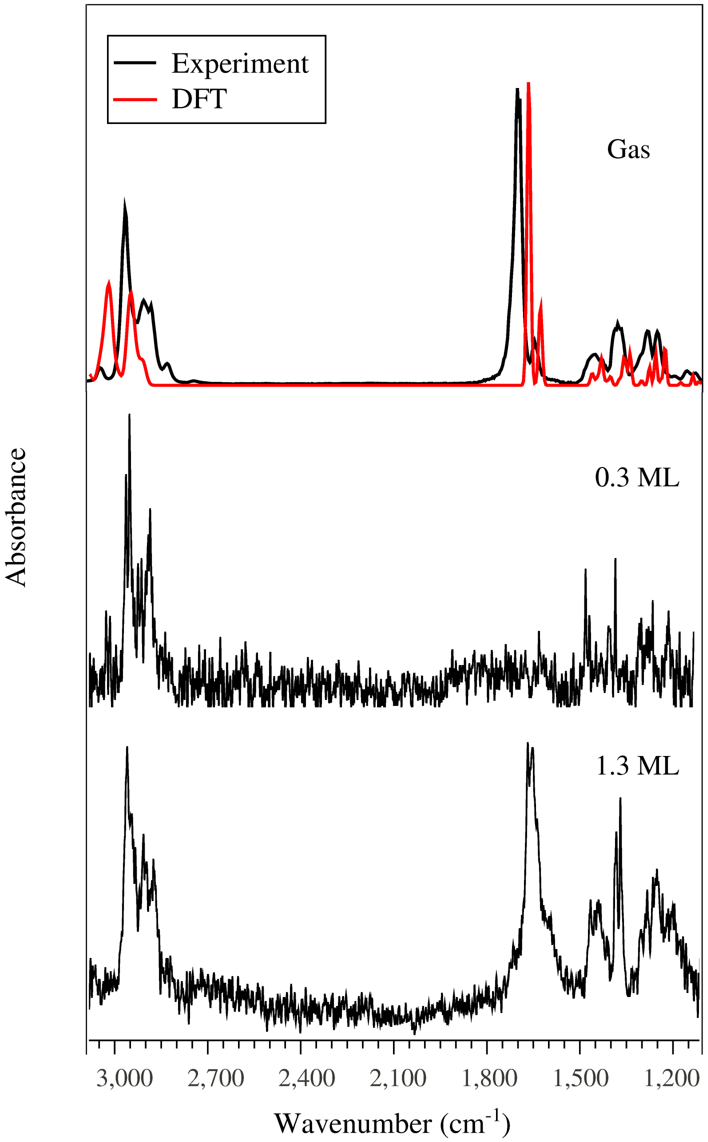

Figure 1: The experimental IR spectra of isophorone/Pd(111). (Gas), (0.3 ML), and (1.3 ML) show the results of the isophorone in the gas phase and on the Pd(111) surface at 130 K, respectively. The calculated gas phase IR spectrum is also depicted for a comparison purpose.