Supporting information

Model Approach In Heterogeneous Catalysis: Kinetics and Thermodynamics of Surface Reactions

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Preparation and characterization of Pd nanoparticles.

The Pd/Fe₃O₄/Pt(111) model catalyst was prepared by growing a thin (~50 Å) Fe₃O₄(111) film on a Pt(111) single crystal by repeated cycles of Fe (>99.99%, Goodfellow) physical vapor deposition at a substrate temperature of ~120 K and subsequent oxidation at 875 K (see [1] for details). The cleanliness and the quality of the oxide film were checked by AES and LEED. Pd particles were grown *in-situ* by physical vapor deposition from a Pd rod (Goodfellow, >99.9 %) using a commercial evaporator (Focus, EFM 3) with a deposition rate of 0.3 Å/min ($2.04 \cdot 10^{14}$ atoms cm⁻²·min⁻¹). During metal evaporation, the single crystal sample was held at 115 K, and biased to +800 V to avoid formation of defects by metal ions. The mean diameter of the resulting Pd particles was controlled by the amount of deposited Pd, which was varied from $2.04 \cdot 10^{14}$ to $4.8 \cdot 10^{15}$ atoms cm⁻² using four nominal deposition thickness values (0.6, 1.5, 4.0, and 7.0 Å, where 1 Å corresponds to $7 \cdot 10^{14}$ atoms cm⁻² assuming the bulk density of Pd). Directly after Pd deposition, the sample was annealed to 600 K and cooled to 300 K, and a microcalorimetric measurement of oxygen adsorption heats was performed. The

evaporation rates of Fe and Pd were calibrated by a quartz-crystal microbalance (QCM, Sigma instruments).

Suppl. Figure 1 shows the scanning tunneling microscopy (STM) images of the investigated Pd supported systems obtained in a different UHV-STM setup. The $Fe_3O_4/Pt(111)$ support and the Pd nanoparticles were prepared in this chamber in the way identical to described above. Low energy electron diffraction (LEED) and CO temperature programmed desorption (TPD) were used as two common methods available in both setups to characterize and compare the prepared model surfaces. In all cases, both LEED patterns of the $Fe_3O_4(111)$ films and the CO-TPDs measured on Pd nanoparticles, were nearly identical when comparing the samples prepared in two different setups.



Suppl. Figure 1. STM images of the Pd/Fe₃O₄/Pt(111) model catalyst as a function of Pd coverage after preparation and annealing at 600 K for nominal Pd coverage of (a) 0.3 Å, (b) 4 Å, (c) 7 Å. (from [1])

For C-modification Pd model catalysts were precovered with deuterium (280 L D_2 at 100 K) then exposed to 0.85 L *cis*-2-butene at 100 K and subsequently heated in vacuum to 485 K. It was established spectroscopically (IRAS) by using CO as a probe molecule for different adsorption sites that carbon occupies predominately edge sites of the Pd nanoparticles while leaving the regular (111) terraces nearly unchanged.²

References:

(1) Schalow, T.; Brandt, B.; Starr, D. E.; Laurin, M.; Shaikhutdinov, S. K.; Schauermann, S.; Libuda, J.; Freund, H. J. Particle size dependent adsorption and reaction kinetics on reduced and partially oxidized Pd nanoparticles. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1347-1361.

(2) Brandt, B.; Fischer, J.-H.; Ludwig, W.; Libuda, J.; Zaera, F.; Schauermann, S.; Freund, H.-J. Isomerization and Hydrogenation of cis-2-Butene on Pd Model Catalyst. *The Journal of Physical Chemistry C* **2008**, *112*, 11408-11420.