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Electronic Supplementary Information

Experimental setup and catalysts preparation. The experiments were carried out in an ultrahigh vacuum (UHV) surface analysis system combined with a UHV-high pressure reaction cell[11]. For sample characterization, the UHV section (base pressure ~$1x10^{-10}$ mbar) was equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and temperature programmed desorption (TPD).

Pd-Al_2O_3/NiAl(110) model catalysts were prepared by growing a thin ordered Al_2O_3 film (thickness ~0.5 nm) on NiAl(110) by two cycles of oxidation in 10^{-6} mbar O_2 at 523 K, followed by Pd (purity $\geq$99.99%) electron beam evaporation at 300 K and 90 K[7,9]. Pd particles with a mean size from 2 to 8 nm were prepared by variation of the metal amount deposited and of the substrate temperature. All samples were annealed to 373 K prior to the reaction so that all preparations should yield crystalline particles. As revealed by scanning tunnelling microscopy (STM), Pd nanoparticles larger than 4 nm typically have the shape of truncated cubo-octahedra with distinct facets while smaller particles appear rather rounded (i.e. the facets are less pronounced and/or too small for atomic imaging)[9,16].

Pd(110) and (111) single crystals (~ø10 x 2 mm) were cleaned by annealing to 1100 K, Ar ion etching (beam voltage 900 V at $6x10^{-6}$ mbar Ar at 298 K), heating to 1100 K, oxidation during cooling down in $5x10^{-7}$ mbar O_2 between 1100 K and 600 K, and a final flash to 1100 K in UHV. After cooling to 90 K, well-ordered surface structures were confirmed by LEED (see inset in Fig. 1c) and TPD.

Catalytic measurements. The clean samples were then transferred under UHV to the reaction cell where catalytic measurements were performed at atmospheric pressure. The model catalysts were exposed to the reaction mixture ($P_{1,3\text{-butadiene}}$: 5 mbar; P_{H2} : 10 mbar; Ar added up to 1 bar) at temperatures between 298 and 373 K. Kinetic measurements were carried out in batch mode with the gas recirculated over the catalyst by a metal bellows pump (reactor volume exchanged 5 times per minute). The reaction products were analyzed by on-line gas chromatography (GC), using a HP-PLOT/Al_2O_3 (50 m x 0.53 mm) capillary column and an FID detector. Retention times and sensitivity factors for the reactant and products were calibrated using different gas mixtures. Employing Al_2O_3 films on NiAl(110) as "inert" catalysts the absence of background (wall) reactions was confirmed.