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Atmospheric pressure studies of selective 1,3-butadiene hydrogenation on well-defined Pd/Al_2O_3/NiAl(110) model catalysts: Effect of Pd particle size

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Abstract

The selective hydrogenation of 1,3-butadiene was studied on a series of Pd/Al_2O_3/NiAl(110) model catalysts with mean Pd particle sizes of 2–8 nm. While Pd nanoparticles $\geqslant$4 nm exhibit a near zero-order reaction kinetics with respect to butadiene, the rate behavior on smaller Pd particles is more complex, and the rate increases with decreasing butadiene pressure. This indicates a change in the rate-limiting step from a regime governed by adsorption to a regime governed by the surface reactions. When the total number of Pd surface atoms is used for rate normalization, the turnover frequency (TOF) of 1,3-butadiene hydrogenation increases linearly with increasing particle size. But this is only an *apparent particle size dependence*. Considering a realistic structural model of the Pd nanoparticles [i.e., with incomplete (111) terraces] for rate normalization, 1,3-butadiene hydrogenation becomes *particle size independent*, even though the reaction is *structure sensitive*, as corroborated by reactivity studies on Pd(111) and Pd(110) single crystals. For 1,3-butadiene hydrogenation, well-faceted Pd nanoparticles $\geqslant$4 nm behave like Pd(111).

Keywords: Selective hydrogenation; Palladium; Nanoparticles; Butadiene; Model catalysts; Size effects

1. Introduction

Control of selectivity is the most important aspect in the hydrogenation of dienes such as 1,3-butadiene. Typically, a high 1-butene/2-butene ratio should be obtained while full hydrogenation to *n*-butane should not occur. For example, in the petrochemical industry, olefins are often produced by catalytic cracking of petroleum and contain significant amounts of dienes [1,2]. Before subsequent processing, these dienes must be selectively converted to 1-butene while hydrogenation of the olefinic stream must be avoided. Pd-based catalysts are widely used for the selective hydrogenation of 1,3-butadiene to 1-butene, due to the high activity and selectivity even in the presence of an excess of olefins [3–6].

Atmospheric pressure studies of selective 1,3-butadiene hydrogenation on Pd(111) and Pd(110) single-crystal surfaces have shown that the reaction is structure sensitive, with the catalytic activity [i.e., the turnover frequency (TOF)] being fivefold higher for the more open (110) surface [7,8]. A higher hydrogen concentration on the Pd(110) surface, due to the higher sticking probability on more open surfaces, was considered responsible for the observed behavior [7,9].

Studies on technical Pd catalysts have shown that the Pd particle size, the support, and the presence of additional transition metals (promoters) have a significant effect on both the catalytic activity and the selectivity of the hydrogenation reaction. For example, for Pd/Al_2O_3 and Pd/SiO_2 powder catalysts, Boitiaux et al. observed an activity decrease with decreasing particle size [10]. A similar conclusion was obtained by Tardy et al. for Pd aggregates supported on activated carbon [11]. This decrease was explained by changes in the electronic structure of small (<3 nm) Pd nanoparticles, leading to stronger interaction with 1,3-butadiene and to stronger deactivation. Unfortunately, the high surface area and porous structure of the powder catalysts often prevented a detailed characterization of the particle surface structure and composition.

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The use of clean and well-defined Pd/Al_2O_3 model catalysts [12–14] may be helpful in improving understanding of 1,3-butadiene hydrogenation. In a previous paper we reported results on Pd(111) and Pd(110) [8], and a short account of studies on Pd nanoparticles was reported in [15]. In this paper we present a detailed investigation of particle size effects on 1,3-butadiene hydrogenation, including a description of catalyst structure data. The Pd particle size affects both the kinetic behavior and the reaction selectivity. When the common procedure is used to calculate TOFs, a linear increase is observed for a particle size range of 2–8 nm. However, a detailed characterization of particle size and surface structure by scanning tunneling microscopy (STM) allows us to propose a model that indicates that the TOF is in fact independent of Pd particle size. Pd atoms of incomplete (111) terraces are suggested as active sites. Ultrahigh-vacuum (UHV) studies of olefin hydrogenation on Pd particles and Pd(111) were reported previously [16,17].

2. Experimental

A series of different Pd/Al_2O_3/NiAl(110) model catalysts with Pd particle size ranging from 2 to 8 nm were prepared by evaporation methods under UHV [12,14,18]. First, an ordered Al_2O_3 thin film (around 0.5 nm thick) was grown on a NiAl(110) single crystal by two sequences of oxidation (1×10^{-6} mbar O_2 at 543 K) and subsequent annealing to 1100 K in vacuum [19]. The atomic structure of the Al_2O_3 film was recently characterized by low-temperature (4 K) STM [20]. Pd (99.99%) was then deposited by electron beam evaporation at two different support temperatures, 90 and 303 K. Varying the amount of Pd finally produced different catalysts with mean Pd particle sizes ranging from 2 to 8 nm. Two STM images are shown in Fig. 1 as an inset [13]. (Atomically resolved STM images of individual particles are available elsewhere [21].) As revealed by STM, the as-grown Pd nanoparticles had the shape of truncated cubo-octahedra when the evaporation was carried out at 303 K ($\sim 1 \times 10^{12}$ particles/cm^2), and more disordered particles were seen after evaporation at 90 K ($\sim 5 \times 10^{12}$ particles/cm^2) [19,21]. However, in this study both the 90 and 303 K Pd particles were annealed to 373 K before the reaction, and thus both preparations yielded particles with ordered surfaces. All catalysts prepared exhibited a rather narrow particle size distribution (mean particle size $\pm \sim 1$ nm).

Once a Pd/Al_2O_3/NiAl(110) catalyst was prepared, the sample was transferred under UHV to a high-pressure reaction chamber attached to the UHV system [8,14,18]. Kinetic measurements of 1,3-butadiene hydrogenation were performed at atmospheric pressure (reaction mixture: $P_{1,3\text{-butadiene}}$, 5 mbar; P_{H_2}, 10 mbar; Ar added up to 1 bar) at 373 K. At this (high) reaction temperature and low hydrogen pressure, the formation of β-Pd-hydride (requiring at least 200 mbar H_2) can be excluded. Kinetic measurements were done in batch mode with the gas recirculated over the catalyst by a metal bellows pump (reactor volume 755 cm^3 exchanged 4 times/min) and were reproducible within 5%. Reaction products were analyzed by on-line gas chromatography (GC), using a HP-PLOT/Al_2O_3 (50 m × 0.53 mm) capillary column and a flame ionization detector. Retention times and sensitivity factors for the reactant and the products were calibrated using a number of different gas mixtures. The absence of background (wall) reactions under typical operating conditions was confirmed using Al_2O_3 films on NiAl(110) as "inert" catalysts.

Under the relatively "mild" reaction conditions, structural changes of the Pd nanoparticles can be mostly excluded. Postreaction surface characterization by chemisorption or vibrational spectroscopy (using CO as probe molecule) did not indicate any surface restructuring, such as particle sintering or strong surface structure changes. Furthermore, repeated kinetic measurements after several hours of reaction time showed only very small variations. Surface restructuring *during* the reaction cannot be fully excluded but is unlikely, because it must have been fully reversible.

Pd(111) and Pd(110) single crystals ($\varnothing \sim 10 \times 2$ mm) were used as reference samples [8]. The crystals were cleaned by annealing to 1100 K, Ar ion etching (beam voltage 900 V at 6×10^{-6} mbar Ar at 298 K), heating to 1100 K, oxidation during cooling down in 5×10^{-7} mbar O_2 between 1100 and 600 K, and a final flash to 1100 K in UHV. After cooling to 90 K, well-ordered and clean surface structures were confirmed by LEED and CO-TPD. For the single-crystal Pd, atoms on both surfaces [front and back; both of (111) orientation] and on the perimeter were considered for the TOF calculations, because carbon impurities easily dissolve in Pd on flashing above 700 K.

3. Results and discussion

3.1. Catalytic behavior

3.1.1. Rate measurements

Figs. 1a–1e show the reaction kinetics of 1,3-butadiene hydrogenation at 373 K for different Pd catalysts with 2–8 nm mean particle size. For all samples, independent of Pd particle size, 1-butene, *trans*-2-butene, and *cis*-2-butene were the primary products, with the thermodynamically least stable 1-butene being the main product (100% selectivity toward butene formation). Interestingly, in the first minutes of the reaction (before complete butadiene consumption), the relative proportion of these three products was quite independent of particle size; that is, a 1-butene/2-butene ratio of around 1.3 and a *trans*-/*cis*-2-butene ratio of around 3.4 were observed. The similarity in the relative amount of the three reaction products points to an identical reaction mechanism for the (first) butadiene hydrogenation step on the different Pd clusters, that is, independent of particle size, most probably through 1,2- and 1,4-H addition to 1,3-butadiene to produce 1-butene and *trans*-/*cis*-2-butene, respectively [8,22]. Although the product distribution followed a similar trend for all particle sizes examined, the kinetic behavior was clearly size dependent (Fig. 1). For the smallest particle size (2 nm; Fig. 1a), the catalytic activity increased with reaction time. In fact, at high butadiene pressure (i.e., low reaction time), the catalyst exhibited a constant activity. However, after the butadiene pressure was reduced to a certain value (∼30% butadiene conversion), the activity suddenly increased until 1,3-butadiene was completely