Surface-Bonded Precursor Determines Particle Size Effects for Alkene Hydrogenation on Palladium**

Aidan M. Doyle, Shamil K. Shaikhutdinov, and Hans-Joachim Freund*

Reactions of linear alkenes with metal surfaces have been previously studied on model catalyst systems with varying degrees of complexity, from single crystals to metal particles deposited on well-ordered oxide films.[1–15] Based on these studies, the majority of which were conducted with ethene, it has been suggested that alkene hydrogenation is structure insensitive. This means that the reaction only depends on the number of metal atoms on the surface and is independent of the crystallographic orientation of the particle facets and particle size. These size effects are difficult to study in real catalytic systems because the mean particle size and distribution cannot be controlled accurately. Herein, we report the particle size effects on alkene reactivity (ethene and *trans*-2-pentene) using well-defined Pd/Al_2O_3 model catalysts, where the particle size can be varied in a controllable manner. Temperature-programmed desorption (TPD) indicated that alkene adsorption exhibits site-specific behavior, which is assigned to the reactions occurring separately on facets and on low-coordination-number atoms such as edge and corner atoms. A strong particle size effect (within the 1–5-nm range) is observed for the hydrogenation of pentene over a hydrogen-precovered surface, whereas the reaction for ethene is independent of size. These effects are explained by the reactions proceeding via di-σ-bonded pentene, which is favored on the terrace sites of large particles, and π-bonded ethene.

The morphology of the Pd model system has been studied intensively in our laboratory by scanning tunneling microscopy.[9,16] Thin alumina films were grown on a clean NiAl(110) single crystal, and subsequently Pd was vapor-deposited onto the films (see the Experimental Section for details). An average particle size was determined from the amount of Pd deposited and could be varied within the range 1–5 nm with a narrow particle-size distribution (20%);[16] the corresponding relationship is presented in reference [9]. To exclude any effects of morphology changes on Pd particles during TPD measurements, the samples were preannealed at 500 K before the adsorption experiments.

The TPD spectra showed that ethene desorption occurs from at least two distinct states.[9,10] Weakly bonded ethene in a π configuration desorbs at temperatures below 200 K, while the high-temperature (HT) state at about 300 K is associated with di-σ-bonded molecules, which is in agreement with calculations showing that di-σ-bonded alkenes (e.g., ethene, various butene isomers) are more strongly bound on the Pd(111) surface.[8,15,17] A similar desorption behavior is observed for various pentene isomers.[18,19] Weakly bound pentene in a π-bonded geometry desorbs at about 170 K. Accordingly, the HT state at about 230 K is associated with di-σ-bonded molecules. At elevated temperature, alkene molecules undergo stepwise dehydrogenation as evidenced by multiple hydrogen peaks in the TPD spectra.

Deuterium presaturation on the Pd surface suppresses alkene adsorption in the di-σ state and favors π bonding.[9,12,15] A H–D exchange reaction is clearly observed by detecting the desorption of $C_2H_{4-x}D_x$ and $C_5H_{10-x}D_x$ molecules for ethene and *trans*-2-pentene, respectively, on Pd particles as well as Pd(111). The D-substituted molecules desorb in the same temperature range as the HT state observed on D-free Pd surfaces.[19] This observation implies that the di-σ-bonded alkenes rapidly exchange H atoms with D atoms present on the surface via half-hydrogenated ethyl and pentyl species from which alkenes desorb, thus resulting in the HT peak in the TPD spectra. This finding is in line with results previously reported by Vasquez Jr. and Madix[20] for 1-hexene on Pd(111) and by Sekitani et al.[21] for ethene on Pd(110), and can explain the H–D exchange reaction observed. Stacchiola et al.[13] have recently proposed the formation of an η^1-allyl species for propene on Pd(111), based on infrared spectroscopic measurements. In principle, the adsorbed allyl groups (in particular π-allyl species), which are in a dynamic equilibrium with di-σ-bonded species, could also result in a H–D exchange reaction. However, Zaera and Chrysostomou[22] provided evidence against this mechanism, at least for Pt(111), and further supported the proposal that the half-hydrogenated (2-propyl) species is an intermediate in both the exchange and hydrogenation reactions.

Figure 1 shows a series of TPD spectra recorded for *trans*-2-pentene adsorbed on D_2-presaturated particles as a function of the nominal thickness of a Pd overlayer. The H–D exchange and hydrogenation reactions clearly occur under these conditions, as seen by the formation of [D_1]pentene ($C_5H_9D_1$) and [D_2]pentane ($C_5H_{10}D_2$) which desorb at 200–250 K (Figure 1 a,b). As pentane desorbs from Pd at a much lower temperature, the desorption of [D_x]pentane during the TPD experiment is reaction limited. Again, this is the temperature range where the pentene desorbs from the di-σ-bonded state. Therefore, the results indicate that the hydrogenation reaction proceeds by the addition of H/D to di-σ-bonded pentene to form a pentyl species, which may transform back to D-substituted di-σ-bonded pentene, or react by further H/D addition to form pentane.

Figure 1 a,b shows that the desorption temperatures for both [D_1]pentene and [D_2]pentane continuously shift as the Pd coverage increases from 0.4 to 14 Å, which indicates a particle size effect for the reaction. The size effect is more clearly seen by monitoring the H_2 and D_2 signals (see

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[*] Dr. A. M. Doyle, Dr. S. K. Shaikhutdinov, Prof. H.-J. Freund
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4–6
14195 Berlin (Germany)
Fax: (+49) 30-8413-4105
E-mail: shaikhutdinov@fhi-berlin.mpg.de

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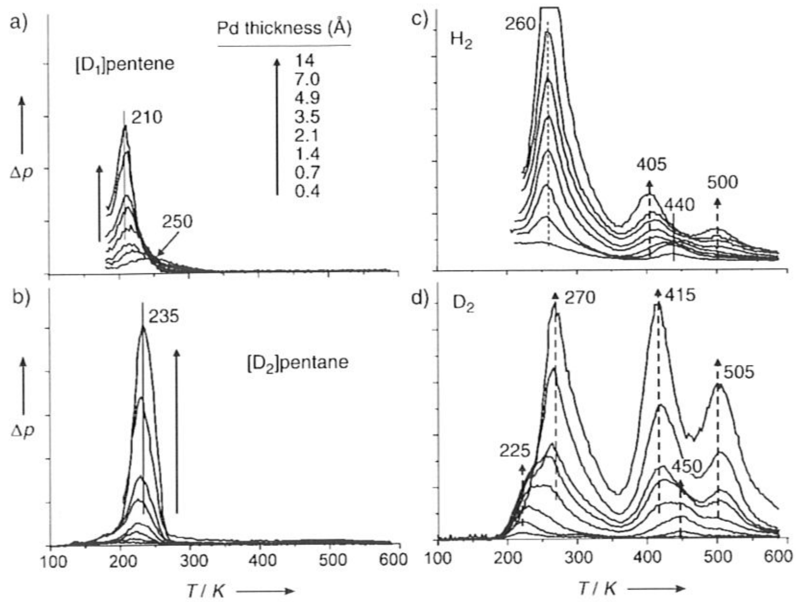

Figure 1. TPD spectra of 1 L of *trans*-2-pentene adsorbed at 100 K on Pd/Al_2O_3/NiAl(110) presaturated with D_2 at 200 K as a function of nominal thickness of the Pd overlayer. [D_1]pentene (a), [D_2]pentane (b), H_2 (c), and D_2 (d) desorption signals are shown.

Figure 1 c,d). For the lowest Pd coverage, a small quantity of desorption-limited D_2 is detected at 225 K, and a single, reaction-limited D_2 peak at 450 K is observed. As the particle size is increased, additional D_2 peaks emerge at 415 and 505 K, which prevail for the largest Pd coverage such that the signal at 450 K is only seen as a shoulder at intermediate Pd coverage. Similar trends are found for the H_2 signal. For the smallest particles, peaks at 260 and 440 K are detected. Peaks at 260, 405, and 500 K are prominent at the highest Pd coverage. At intermediate Pd coverage, both groups of peaks are present with corresponding weighting factors. In other words, *de*hydrogenation of D-exchanged pentenes proceeds separately on two types of sites.

It is known that particles expose both low-coordination sites, such as edges and corners, and regular terrace sites on facets. Clearly, the small particles are composed mainly of low-coordination atoms while terrace sites dominate the larger particles. Therefore, the H_2 peaks at 260 and 440 K, as well as the D_2 peaks at 225 and 450 K, recorded for the smaller particles may correspond to dehydrogenation reactions of H(D)-containing molecules that occur on low-coordination atoms. Consequently, the signals at 260 K (270 K for D_2), 405 (415) K, and 500 (505) K, which prevail for higher Pd coverage, may result from dehydrogenation on the (111) facets dominating the large Pd particles.

Such a site specificity of the pentene reactions on Pd particles is further supported by the correlation between hydrogenation activity and Pd particle size (Figure 2a). The activity was measured by the TPD areas of the [D_2]pentane desorption signal per Pd surface area as determined from STM studies.[9] The diagram clearly shows that the activity increases by a factor of 4 over the range 1.5 to 4.5 nm. The increase in hydrogenation activity correlates well with the ratio of terrace sites to total surface Pd atoms shown on the same diagram in Figure 2a. This correlation strongly indicates that the terrace sites favor *trans*-2-pentene hydrogenation. This result also supports the conclusion that pentene hydrogenation proceeds via the di-σ-bonded species as the precursor. Indeed, adsorption in a di-σ-bonded geometry occurs preferentially on flat surfaces, which are characteristic for the larger particles.[9] As a result, the activity increases with particle size, which indicates that *trans*-2-pentene hydrogenation is structure sensitive.

In comparison, Figure 2b shows the [D_6]ethane production for ethene (C_2D_4) hydrogenation determined in a similar manner. We only observed a slight decrease in activity over the 1–3.5-nm range. This means that this reaction is essentially structure insensitive. This difference in the size dependence observed for ethene and pentene is considerable, even though the di-σ state is more favorable on terraces for both molecules and, therefore, one would expect similar behavior for both alkenes. However, Neurock and van Santen,[8] using cluster and DFT calculations, showed that it is π-bonded ethene, rather than di-σ-bonded ethene, that converts to an ethyl group (and subsequently to ethane) when adsorbed at high coverage on the H-precovered Pd(111) surface. This finding is consistent with experimental data showing that π-bonded ethene is the active species in ethene hydrogenation,[1,6,14,22] and may explain its structure insensitivity.

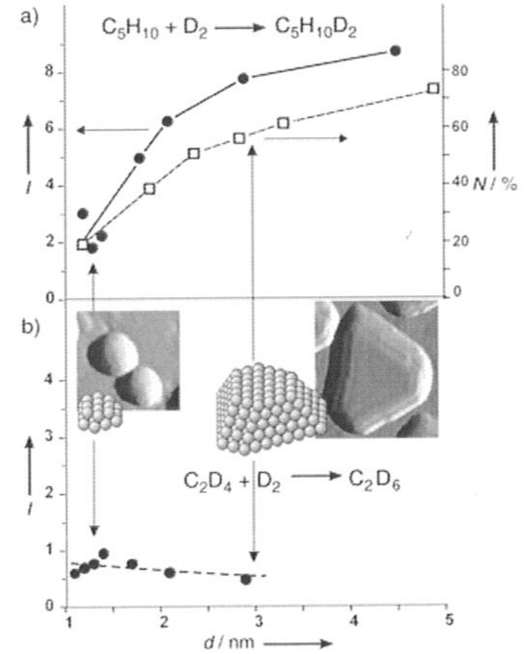

Figure 2. a, b) Integral [D_2]alkane desorption signals per Pd surface area as a function of particle size (●). The ratio of terrace sites (□) to the total number of surface atoms on the particles (*N*) of the same aspect (height/diameter) ratio is shown for comparison. The insets in (b) show typical STM images of the Pd nanoparticles[9] (presented in differentiated contrast as if they are illuminated from the right-hand side) and schematic representations of their structures.

To our knowledge, there are no similar calculations for pentene. However, it is expected that hydrocarbons, beginning with propene, adsorb in a less distorted geometry (π bonded) in a *second* layer[13,22] on top of the most strongly bound di-σ species. In other words, π-bonded species may not be in direct contact with the Pd surface. Therefore, it seems plausible that π-bonded pentene on the H(D)-precovered Pd surface desorbs intact, and the hydrogenation proceeds only via di-σ-bonded pentene, in contrast to π- and di-σ-bonded ethene, which transform into ethyl intermediates.

In summary, we have shown that reactions of *trans*-2-pentene exhibit site-specific behavior, assigned to the reactions occurring separately on facets, and on low-coordination sites such as edge and corner atoms. Under the conditions studied, a strong particle size effect is observed for pentene hydrogenation, while ethene hydrogenation is structure insensitive. The results are explained by hydrogenation proceeding via di-σ-bonded pentene, which is favored on the terrace sites of large particles, and π-bonded ethene. Certainly, the question remains as to what extent these results can be extrapolated to high-pressure conditions. However, our previous experiments with ethene at nearly atmospheric pressure showed a good match with the results obtained by TPD.[23]

Experimental Section

The experiments were performed in an ultrahigh-vacuum chamber (base pressure $<10^{-10}$ mbar) equipped for low-energy electron diffraction and Auger electron spectroscopy, and with a differentially pumped quadrupole mass spectrometer for TPD experiments. Thin alumina films were grown on a clean NiAl(110) single crystal as described elsewhere.[16] Palladium (99.99%) was deposited onto the alumina films using a commercial evaporator (Focus EM3). The sample was biased with a retarding voltage to prevent metal ions from being accelerated toward the sample and creating nucleation centers on the surface. A deposition rate of 1 Å min^{-1} was used, calibrated with a quartz microbalance. The amount of Pd deposited is presented in the text as a nominal thickness.

All gas exposures (measured in Langmuirs, 1 L = 10^{-6} Torr s) were performed with a calibrated directional gas doser. Deuterium (99.9%, isotopic content 99.5%) and C_2H_4 (99.5%) were supplied by AGA Gas, and *trans*-2-pentene (99%) by Fluka. C_2D_4 (isotopic content 99%) was supplied by Isotec Inc. *trans*-2-pentene was purified by a number of freeze–thaw cycles before adsorption. To increase sensitivity, the signals for fragmented masses[24] were used to analyze the hydrocarbon molecules: 56 amu for $C_5H_9D_1$ and 45 amu for $C_5H_{10}D_2$. We checked that these signals fully described the desorption of the corresponding molecules. The full mass signals were used for the reactions of deuterated ethene.

The TPD spectra presented here were not corrected for ionization gauge sensitivities. In all TPD experiments, deuterium was adsorbed at 200 K and pentene at 100 K. A linear temperature ramp with a heating rate of 5 K s^{-1} was generated using a feedback control system. A new alumina film was grown for each Pd sample. Clean alumina films did not show any reactivity toward ethene or pentene.

Pd was deposited at 90 K and subsequently oxidized in O_2 at 500 K for 30 min and reduced with CO at 300 K until no CO_2 was produced. The individual alkene and hydrogen adsorptions on these Pd/Al_2O_3 samples were essentially similar to those obtained for the nontreated system. In addition, both systems were previously shown to exhibit identical behavior in CO adsorption and oxidation reactions.[25]

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