

# Acetylene and ethylene hydrogenation on alumina supported Pd-Ag model catalysts

N.A. Khan,\* S. Shaikhutdinov, and H.-J. Freund

*Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, Berlin 14195, Germany*

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Adsorption and co-adsorption of ethylene, acetylene and hydrogen on Pd-Ag particles, supported on thin alumina films, have been studied by temperature programmed desorption (TPD). The TPD results show that adding of Ag to Pd suppresses overall hydrogenation activity but increases selectivity towards ethylene, i.e. similar to that observed on real catalysts. The results are rationalized on the basis of a complex interplay between surface and subsurface hydrogen species available in the system, whereby the latter species are the most critical for total hydrogenation of acetylene to ethane.

**KEY WORDS:** hydrogenation; bimetallic catalysts; acetylene; palladium; silver.

The selective hydrogenation of acetylene is an industrially important catalytic process in the large-scale production of polyethylene, where a small quantity of acetylene (<3%) is present in ethylene feedstock. Commercially, it is preferred to reduce the acetylene content to less than 10 ppm, which needs ~99% acetylene conversion in the excess of ethylene [1]. For the selective removal of acetylene, Pd catalysts are commonly used in industry [2], which are well known for their superior hydrogenation abilities. However, on monometallic Pd catalysts, the hydrogenation of ethylene to ethane is accelerated with high conversions of acetylene, which can lead to hydrocarbon deposits that decrease the catalyst lifetime [3]. For higher selectivity toward ethylene, Pd catalysts include promoters, such as silver [4–7], which generally lower the activity, increase selectivity and promote catalysts lifetime. However, a deeper understanding of reaction mechanisms on the Pd-Ag catalysts is necessary for a rational design of selective hydrogenation catalysts.

Within the “surface science” approach, the reaction of acetylene with Pd has been studied by numerous groups on Pd(111) single crystal using temperature programmed desorption (TPD) and vibrational (infrared, IRAS) spectroscopy [8–13]. Three main reaction pathways were observed such as dehydrogenation (decomposition), cyclotrimerization to benzene and hydrogenation (in the presence of hydrogen).

Data for supported Pd particles are relatively scarce [14,15]. Recently, our group has studied ethylene hydrogenation over Pd particles supported on a thin

alumina film both at low pressures (with TPD) and high pressures (up to 1 bar, using gas chromatography [16–18]). Under both conditions, the ethylene hydrogenation reaction was found to be structure insensitive. In contrast, hydrogenation of 2-pentenes exhibited a significant particle size effect [19]. These studies have demonstrated that metal particles deposited on well-ordered oxide films are suitable model systems for studying mechanisms of the hydrogenation reactions on supported metal particles.

We have also characterized Pd-Ag/alumina model systems by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS), which is discussed in detail in a separate paper [20]. Combined STM, XPS and CO adsorption studies showed formation of truly alloyed particles with Ag-rich surfaces. In this Letter, we have studied reactivity of bimetallic Pd-Ag nanoparticles towards acetylene and ethylene hydrogenation using TPD.

Figure 1 shows STM images of Pd (a), and Pd-Ag (b) particles formed by vapor deposition of metals onto the alumina film. It is clear that average particle size is nearly the same for both systems studied (at least, at low Ag: Pd ratio). Therefore, the differences, if any, in reactivity of mono- and bimetallic systems in the hydrogenation reaction cannot be attributed to the size effects.

First we have examined acetylene adsorption on pure Pd particles. Basically, acetylene is dehydrogenated on Pd giving rise to a hydrogen multi-peak desorption signal extending up to 500 K, i.e. similar to that observed for ethylene [21]. No ethane, but traces of ethylene were detected, desorbing at 250–300 K. These species can be assigned either to the self-hydrogenation reaction (as observed on Pd(111) [13]) or reaction with hydrogen from the vacuum background.

\*To whom correspondence should be addressed.

E-mail: khan@fhi-berlin.mpg.de, shaikhutdinov@fhi-berlin.mpg.de

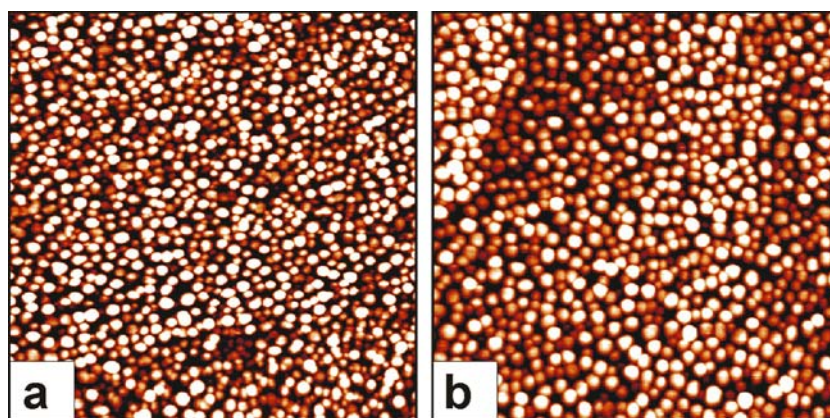


Figure 1. Room temperature STM images of 2 Å Pd (a) and 2 Å Pd + 0.4 Å Ag (b) deposited on alumina film at 100 K. (Image size 100×100 nm<sup>2</sup>).

We have previously shown that the production of ethane from ethylene critically depends on the amounts of hydrogen residing in the sub-surface region of Pd particles [17, 21]. In order to study this effect for hydrogenation of acetylene, we adsorbed hydrogen on pure Pd particles at different temperatures (200 – 300 K) followed by adsorption of acetylene at 100 K. Fig. 2a shows individual H<sub>2</sub> TPD spectra of the same samples right before the co-adsorption experiments, which allows one to determine the amount of different hydrogen species available in the system before acetylene adsorption. When the sample is exposed to H<sub>2</sub> at 300 K, a single “high temperature” (HT) state at ~330 K is observed in the TPD spectra, which exhibits

second-order kinetics on H<sub>2</sub> exposure [21] and has been assigned to the surface H species recombining and desorbing upon heating, similar to H<sub>2</sub> on Pd(111). However, when the Pd particles are exposed below 200 K to the same amounts of H<sub>2</sub>, desorption emerges at much lower temperatures than on Pd(111) [17]. The low temperature (LT) state(s) can be attributed to the recombination of surface H species, which are more weakly bonded to the surface in the presence of sub-surface hydrogen. The sub-surface hydrogen is available for the reaction on the particles due to their limited size in contrast to Pd crystals where hydrogen may migrate into the bulk far away from the surface [16, 17, 19, 22, 23]. Upon heating of the Pd particles, surface H species are

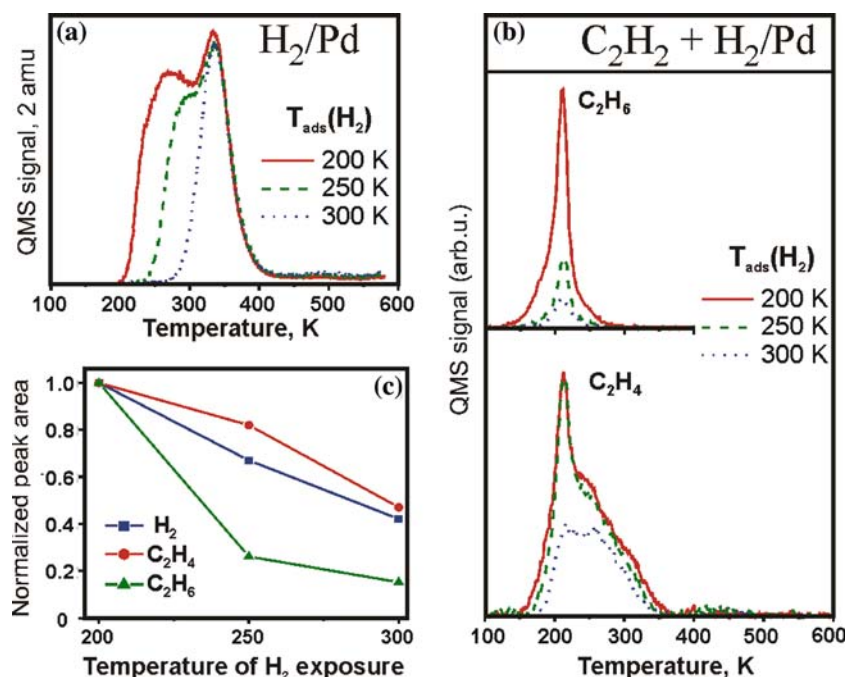


Figure 2. (a) H<sub>2</sub> TPD spectra as a function of hydrogen exposure temperature. (b) Ethane and ethylene desorption signals after 2 L of acetylene were dosed at 100 K to the H<sub>2</sub>-exposed surfaces at the temperatures as indicated. For each spectrum, the samples were exposed to 2 L of H<sub>2</sub>. (c) Normalized peak areas of ethylene and ethane signals evolved in co-adsorption (acetylene on H<sub>2</sub>/Pd) experiments and of hydrogen in the H<sub>2</sub> TPD experiments (see a).

re-populated by the H atoms from the sub-surface region, finally leading to the situation where sub-surface hydrogen is depleted and the desorption becomes similar to the case of adsorption at 300 K.

TPD signals of ethylene and ethane formed in the co-adsorption ( $C_2H_2$  on H/Pd) experiments are shown in Fig. 2b. It is clear that ethane production is strongly enhanced in the presence of sub-surface hydrogen. This behavior is essentially identical to that previously observed for ethylene in our work and in the literature [21, 24]. Stacchiola and Tysoe found that the presence of sub-surface hydrogen increased the amount of bonded ethylene on the surface of Pd(111) [24]. The desorption temperatures of ethane formed from acetylene (Fig. 2b) and ethylene [21] on the particles also show strong similarities (around 200 K). These results suggest that, under the conditions studied, full hydrogenation to alkane is always favored by sub-surface hydrogen independently of the nature of hydrocarbon precursor, alkyne or alkene. As expected, no ethane, but a small amount of ethylene, has been detected in similar experiments with Pd(111), consistent with previous studies by other groups [13], where weakly bonded hydrogen is not available for the reaction to occur.

Regarding ethylene, it should be mentioned that this signal contains a contribution from ethane cracking in the mass-spectrometer, which has been subtracted using the cracking pattern determined in the blank experiments. Therefore, the presence of a sharp peak of ethylene seen in Fig. 2b at  $\sim 210$  K (which is at the same temperature as of ethane) can partially be due to non-perfect subtraction procedure. Nonetheless, the ethylene signal is much broader than of ethane and extends up to 350 K, which suggests that formation of ethylene is less critical to the adsorption strength of H on Pd. In fact, the experiment with  $H_2$  pre-adsorption at 300 K shows that ethylene desorption emerges at  $\sim 200$  K, i.e. at the much lower temperature than  $H_2$  (see Fig. 2a). (Note that this low temperature ethylene cannot be assigned to impurities in acetylene feed. In addition, reaction with hydrogen from the vacuum background may only result in ethylene signal above 250 K). Therefore, these findings indicate that ethylene can be readily formed from the reaction of acetylene and hydrogen on Pd particles at low temperatures. Then ethylene can be hydrogenated further to ethane if weakly bonded hydrogen is available. Otherwise, ethylene desorbs or decomposes at elevated temperatures resulting in carbonaceous deposits.

The normalized area of the hydrogenation products is shown as a function of the temperature of  $H_2$  adsorption in Fig. 2c. The graph shows that the presence of sub-surface hydrogen strongly affects the ethane production, while the ethylene production basically follows the total amount of hydrogen in the Pd particles. (Note that in all these experiments we have observed only trace amounts of benzene, therefore we can neglect its formation.)

It is well known that Ag weakly interacts with  $H_2$  [25]. As a result, pure Ag particles are found to be inert towards  $H_2$ . Therefore, adding Ag to Pd was expected to suppress  $H_2$  adsorption as is observed in Fig. 3a, where  $H_2$  TPD spectra of Pd-Ag particles are shown as a function of amount of Ag added to Pd. However, adding Ag reduces the HT (surface) state to a more extent than LT (subsurface) state. These results are consistent with the assumption that the surface of bimetallic particles is enriched with Ag, which reduces the Pd surface area. Interestingly, a similar behavior (preferential suppression of the HT state) was observed for carbon deposited on Pd particles, which is believed to occupy hollow sites on Pd surface at low coverage [26]. However, the question whether the Pd-Ag surface is heterogeneous or forms a uniform alloy needs further investigations [20].

When ethylene has been adsorbed at 100 K on Pd-Ag particles saturated with  $H_2$  at 200 K, TPD spectra reveals formation of ethane desorbing at  $\sim 210$  K (Fig. 3b). The integral TPD areas of ethane normalized to the values of pure Pd particles shows that ethane production is gradually decreased upon adding Ag, see Fig. 3c. The graph in Fig. 4c also shows the normalized amounts of hydrogen present in the Pd-Ag system before ethylene was adsorbed. One can see that the ethane production at low Ag:Pd ratios decreases at a faster rate than the amount of hydrogen available in the system. It is important to note that at Ag:Pd ratios below 0.2, where the full hydrogenation activity drops by 80%, the desorption signals of molecular ethylene (not shown here) were almost identical, indicating that the interaction with hydrogen rather than with ethylene is responsible for the effects of Ag.

The results for hydrogenation of acetylene on Pd-Ag particles are summarized in Fig. 4. As compared to pure Pd, the amounts of reaction products decrease with an increase in Ag coverage such that the particles are essentially inactive at high Ag coverage. Again, the hydrogenation activity decreases at a faster rate than the amount of hydrogen available in the system. The desorption of ethylene and ethane occurs at the same temperatures as for pure Pd (see Fig. 2), which implies the same reaction mechanism is occurring on the bimetallic particles. Interestingly, ethane production is only 2–3 times less than that found in the previous experiments with ethylene instead of acetylene, for a given Ag:Pd ratio. This result suggests that acetylene can be hydrogenated efficiently to ethylene at low temperatures, which further reacts with weakly bound hydrogen to form ethane, which in turn desorbs intact upon formation. Fig. 4 also shows that the amount of ethylene product desorbed during the TPD decreases at a lower rate than ethane. It is important to note that some ethylene molecules may remain on the surface and be dehydrogenated on heating. If these ethylene molecules were included in the overall calculated ethylene

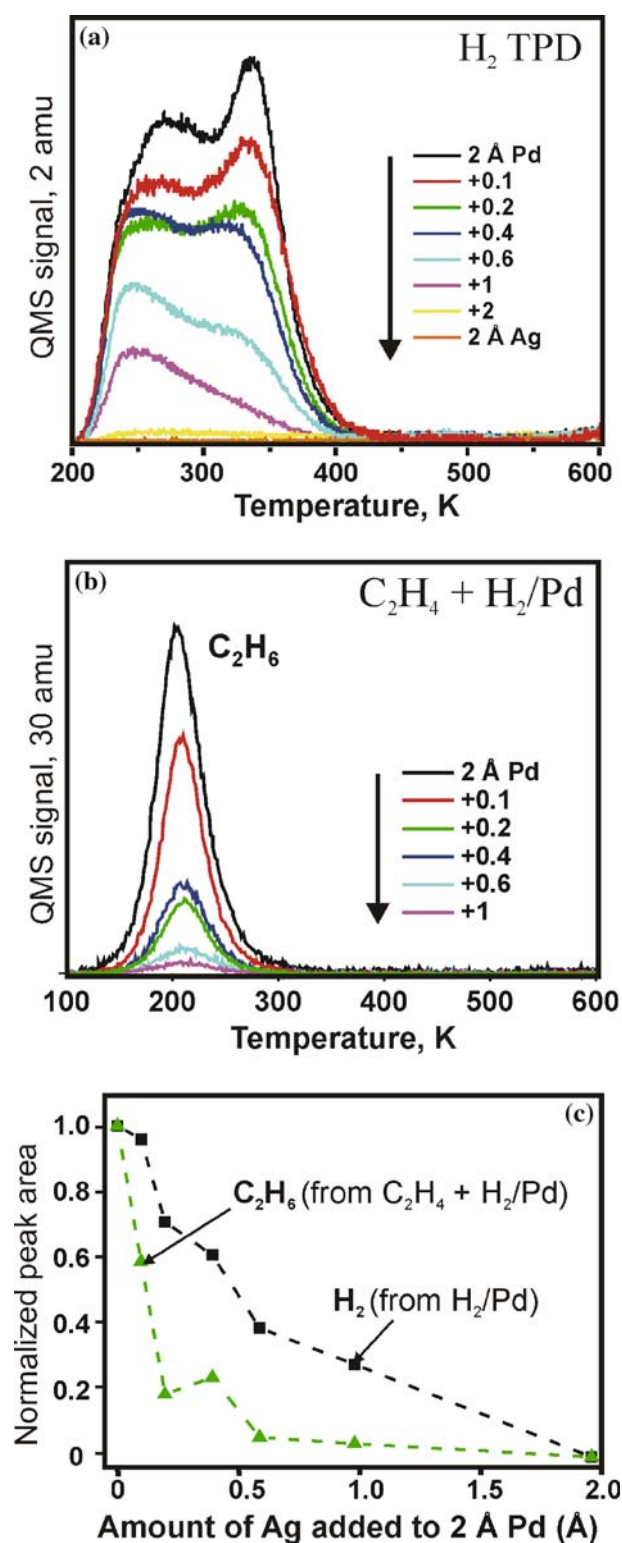


Figure 3. (a)  $\text{H}_2$  TPD spectra of Pd-Ag particles for different amounts of Ag added to 2 Å of Pd deposited on alumina film as indicated. The spectra for pure Pd and Ag are also included, for comparison. All samples were exposed to 2 L of  $\text{H}_2$  at 200 K. (b) TPD signals of ethane after 1.5 L of ethylene was dosed at 100 K to the surface pre-exposed to 2 L of  $\text{H}_2$  at 200 K. (c) Normalized peak areas of ethane produced in co-adsorption experiments and of hydrogen available in the system before ethylene adsorption.

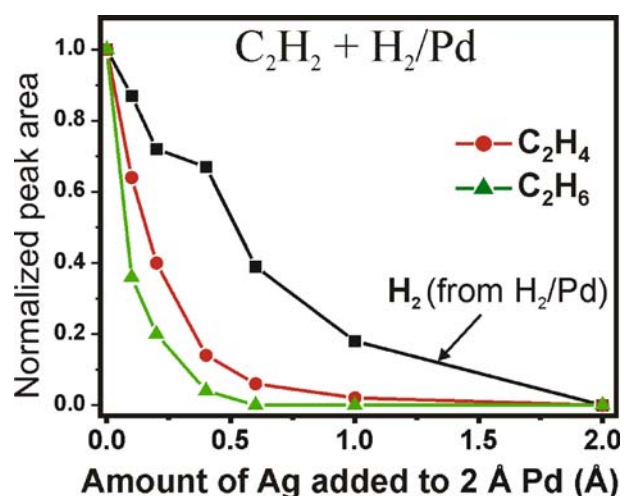


Figure 4. Normalized peak areas of ethane and ethylene produced in co-adsorption experiments (acetylene on H<sub>2</sub>-precovered surface) as a function of amounts of Ag added to Pd. The amounts of hydrogen available in the particles before acetylene adsorption is also shown.

production, the amount of ethylene produced is significantly increased, therefore further increasing the selectivity.

These results indicate that Pd-Ag system is more selective towards ethylene than pure Pd, although the overall activity decreases significantly. In general, this behavior is similar to what has been observed for real Pd-Ag catalysts [1, 27], thus suggesting that the model Pd-Ag catalysts studied here mimic the properties of the real catalysts.

It is generally believed that the hydrogenation of unsaturated hydrocarbons occurs via a Horiuti-Polanyi mechanism, where hydrogen atoms are sequentially added to the molecule. However, there has been some discussion on whether acetylene directly hydrogenates to ethane. The similarities in the formation of ethane from both ethylene and acetylene indicate that the consecutive reaction scheme (acetylene  $\rightarrow$  ethylene  $\rightarrow$  ethane) is the main reaction pathway.

In order to rationalize the effect of silver on selectivity, it is important to note that the ethylene  $\rightarrow$  ethane reaction is enhanced in the presence of the sub-surface hydrogen. Therefore, in order to suppress the full hydrogenation to ethane and hence increase selectivity to ethylene, one should suppress formation of sub-surface hydrogen. In other words, the Pd-Ag system should have, on the one hand, the Pd-rich surface to dissociate hydrogen and catalyze reaction with acetylene and, on the other hand, an Ag-rich core to prevent hydrogen migration into the particle. However, silver is known to have a lower surface energy than Pd [28] and therefore segregate on the Pd surface at above room temperature. This may explain relatively small differences between ethylene and ethane production observed in our experiments. However, the situation can be completely

reversed in a hydrogen ambient atmosphere due to much stronger interaction of hydrogen with Pd than Ag. Indeed, density functional theory calculations for the Pd-Ag system in oxygen ambient show that Pd segregates to the surface at increasing oxygen pressures [29]. It is plausible that this phenomenon occurs also in hydrogen atmosphere, with the effect being critically dependent on the hydrogen pressure. Therefore, under the realistic conditions, the Pd-Ag particles may exhibit in fact the Pd-rich surface and Ag-rich core, the latter suppresses formation of sub-surface hydrogen and hence inhibit ethylene to ethane hydrogenation.

Neurock and co-workers have recently shown that the presence of Ag in a Pd surface decreases the binding energy of ethylene, acetylene and reaction intermediates [30]. However, further theoretical studies are necessary to investigate the effect of hydrogen pressure on the surface composition of Pd-Ag surfaces, in particular cluster calculations as the particles may behave differently from the single crystal surfaces as has been shown for Pd particles forming interface oxide when supported on iron oxide [31].

## 1. Experimental

The TPD experiments were performed in a UHV chamber (base pressure below  $10^{-10}$  mbar) equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), a differentially pumped quadrupole mass spectrometer (QMS) for TPD measurements. All gases were introduced to the crystal using a calibrated directional gas doser.

The alumina film was grown on a clean NiAl(110) single crystal by two cycles of oxidation at  $10^{-6}$  mbar at 550 K for 20 min and annealing to 1140 K in UHV for 5 min. The quality of the alumina film was verified by the characteristic LEED pattern. Pd and Ag were deposited on the alumina film using an electron-beam assisted evaporator (Focus EFM3) with a deposition rate of  $\sim 0.2$ /min as calibrated *in situ* using a quartz microbalance. The pressure during metal deposition did not exceed  $5 \times 10^{-10}$  mbar. The coverages are reported as a nominal thickness (in Å).

The metals were deposited onto alumina at  $\sim 90$  K. The samples were then oxidized for  $\sim 10$  min in  $10^{-6}$  mbar of  $O_2$  at 500 K, reduced by CO at 300 K and flashed to 600 K. This procedure has been shown to prevent Pd from diffusing into the oxide film [32] and in addition resembles calcinations-reduction treatments of real catalysts.

The  $H_2$  (99.999%), CO (99.999%),  $O_2$  (99.999%) and ethylene (99.95%) used were of research grade, and were used without further purification. Acetylene (99.6%) was checked for impurities using gas chromatography, which showed that impurities were less than 1%. Up to 16 masses were simultaneously measured to discriminate cracking patterns of acetylene, ethylene, and ethane. For

each TPD experiment with hydrocarbons, new samples were prepared.

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