DOI: 10.1002/ange.200802844

Surface Chemistry

On the Role of Surface Modifications of Palladium Catalysts in the Selective Hydrogenation of Acetylene**

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Dedicated to the Catalysis Society of Japan on the occasion of the 50th Anniversary

The ethylene used in the production of polymers is produced in steam crackers and typically contains on the order of 1% acetylene.[1,2] The acetylene content needs to be reduced to a few ppm so as not to affect the polymerization process,[3,4] and one method to achieve this is by its selective hydrogenation to ethylene. This process demands highly optimized catalysts that are very selective, since any ethylene that is hydrogenated together with the acetylene results in losses. Palladium-based catalysts modified with silver are often used industrially.[5]

Apart from Pd-Ag catalysts, other palladium-based catalysts have also been found to be highly selective, for example, Pd-Ga,[6] Pd-Au,[7,8] and Pd-Pb.[9] Recently, DFT calculations indicated that nonprecious-metal hydrogenation catalysts based on Ni-Zn would be practical, and their significantly improved selectivity compared to pure Ni catalysts was verified experimentally.[10] It has also been found that palladium itself can be made selective if the reaction is performed under conditions where subsurface carbon is formed.[11]

Herein, we report on the use of density functional theory calculations to identify the underlying principles that determine the selectivity of hydrogenation catalysts. We show that the effects of alloying and subsurface carbon can be understood in the same conceptual framework. We also discuss the role of hydride formation for the reactivity and selectivity of palladium catalysts.

Several theoretical studies have addressed the issue of selectivity in the hydrogenation of acetylene and ethylene over Pd and Pd-Ag surfaces.[10,12–14] The heats of adsorption of acetylene and ethylene were identified as the main factors that determine the selectivity.[10,15] Since the activation barrier for hydrogenation is less affected by a change in the surface activity, the rate of ethylene desorption increases relative to the rate of further hydrogenation on more noble surfaces. This results in the selectivity increasing the more noble the surface is.[10,12–14] A weakening of the adsorption of acetylene, however, will eventually lead to a decrease in the rate of acetylene hydrogenation. A catalyst must, therefore, bind acetylene strongly and ethylene weakly to be simultaneously active and selective.

The acetylene and ethylene adsorption energies have been found to scale with the carbon–surface bond energy as measured by, for example, the adsorption energy of CH_3 groups. This relationship links the difference between desorption and hydrogenation rates to the binding energy of a methyl group.[10,16] Figure 1 shows the acetylene and ethylene adsorption energies on various transition-metal surfaces as a function of the adsorption energy of a methyl group. The scaling laws are seen to be quite simple: ethylene, which forms two σ bonds with the surface, has an adsorption energy that scales with twice the adsorption energy of a methyl group, while acetylene, which forms four σ bonds, has a scaling coefficient of four versus a methyl group.

As the acetylene and ethylene adsorption energies are correlated, the best catalyst will be a compromise between selectivity and activity. Based on this scaling behavior, it was possible to identify an energy window (in terms of the adsorption energy of a methyl group, ΔE_{CH_3}) where metals and alloys are found that have an optimal combination of high selectivity and high activity. Surfaces in this energy window are predicted to bind ethylene rather weakly but bind acetylene sufficiently strongly to allow its hydrogenation.

The effect of adding Ag to the Pd catalyst is shown in Figure 2. Palladium becomes more selective on addition of silver because the adsorption of a methyl group is weakened, and in accordance with the scaling relation, the same is true for the adsorption of ethylene. The same behavior is observed with other alloy systems (see Figure 1). This rather simple concept allowed the fast screening for selective hydrogenation catalysts, and allowed Ni-Zn alloys to be identified as a

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[**] Funding from the Lundbeck Foundation, the Danish National Research Foundation, the Danish Research Councils (STVF), and the Danish Center for Scientific Computing is gratefully acknowledged.

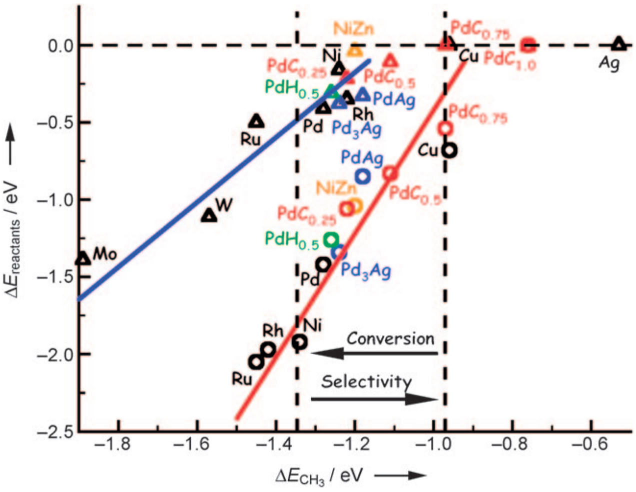

Figure 1. Adsorption energies for acetylene (circles) and ethylene (triangles) plotted against the adsorption energy of a methyl group. The adsorption energies of acetylene and ethylene represent the most stable adsorption site and are defined as the total energy of the surface with the adsorbed species minus the sum of the total energy of the clean surface and the adsorbate in a vacuum. The solid lines show the predicted acetylene (red line) and ethylene (blue line) adsorption energies from scaling. The adsorption geometry of ethylene on Ni and Rh surfaces has been accounted for by specifically choosing the methyl binding site corresponding to the site of adsorption of the carbon atoms in ethylene. The dotted lines indicate the energy window.

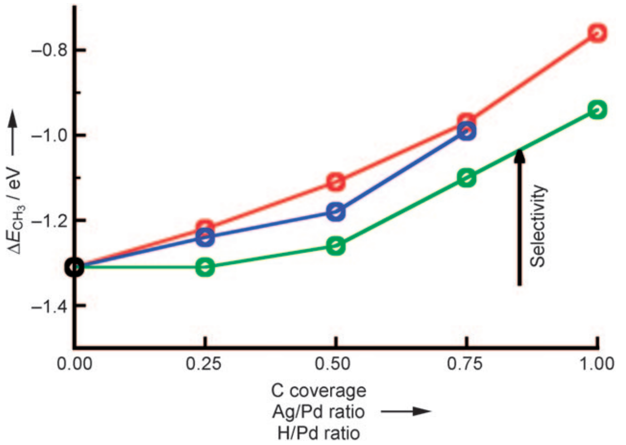

Figure 2. Differential adsorption energy of a methyl group as a function of the carbon coverage as well as the Ag/Pd and H/Pd ratios. Red: palladium with subsurface carbon, blue: Pd-Ag alloys, green: palladium hydrides. Weakening of the adsorption energy of methyl groups should increase the selectivity towards ethylene.

new promising potential nonprecious-metal catalyst.[10] The discovery was verified experimentally with the observation that Ni-Zn catalysts were indeed much more selective towards ethylene than were pure Ni catalysts.

We now use this concept to discuss the effect of subsurface carbon on a Pd catalyst in the selective hydrogenation of alkynes. We calculated the adsorption of carbon on a Pd(111) and a Pd(211) surface and in the subsurface octahedral sites (Figure 3).

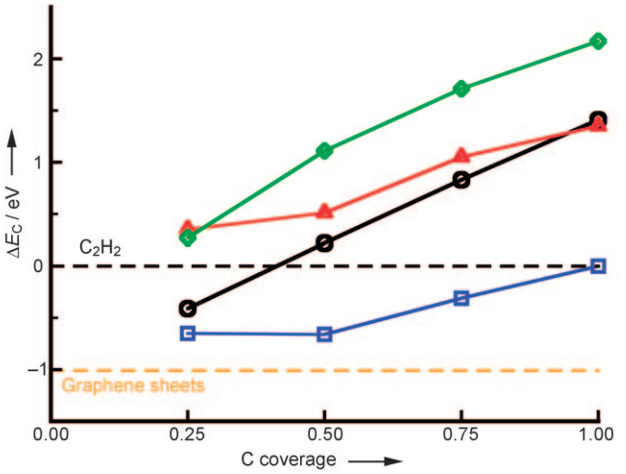

Figure 3. Differential adsorption energies of carbon in different sites on the palladium surface and subsurface (blue squares: adsorption on the Pd(211) steps; green diamonds: adsorption in the hcp sites of the surface; red triangles: adsorption in the tetrahedral subsurface sites (tss); black circles: adsorption in the octahedral subsurface sites (oss)). The energies are given with respect to the decomposition of gas-phase acetylene (dotted line at 0 eV) to adsorbed carbon and gas-phase H_2. The orange line represents the formation of graphene sheets from the different adsorbed carbon species.

Carbon adsorbs most strongly on the Pd(211) step sites. At coverages above 0.5 along the step, the bond strength decreases as a result of carbon–carbon repulsion. The step sites will thus be decorated (poisoned) immediately once some carbon deposits are formed. The next stable adsorption sites for carbon are the subsurface octahedral sites, where the adsorption strength of carbon is also coverage-dependent. Adsorption of carbon in the threefold site of the Pd(111) surface and in the subsurface tetrahedral site is weaker compared to the octahedral subsurface site by as much as approximately 0.7 eV. These findings are in qualitative agreement with DFT calculations of carbon adsorption on Pd clusters.[17] Diffusion of carbon from the threefold hexagonal close-packed (hcp) site on the surface to form subsurface carbon was calculated to have a barrier of 1.33 eV. Importantly, carbon will stay in the subsurface layer since it becomes significantly less stable when moving further into the bulk of the palladium (+0.89 eV at a carbon coverage of 0.25). It is, therefore, reasonable to assume that the step sites will be occupied first and that the addition of more carbon will form subsurface carbon that is located in the octahedral sites.

The effect of carbon deposits on the chemisorption energy of a methyl group is included in Figure 2. The binding of a methyl group weakens when the Pd(111) has subsurface carbon, thus shifting Δ_{CH_3} into the window where selective catalysts are expected to be found.[10] This weaker binding of methyl groups leads to a weaker binding of acetylene and ethylene, as expected (see Figure 1). The carbon-modified surface shows exactly the same scaling behavior as monometallic transition metals and bimetallic alloys. The weaker adsorption of ethylene may explain the high selectivity that is observed experimentally for palladium with subsurface carbon.[11] Interestingly, the effect of the subsurface carbon is comparable to the effect of the addition of silver to palladium if the carbon coverage is compared with the silver/palladium ratio of the binary alloy (see Figure 1 and Figure 2).

The binding of a methyl group on palladium hydrides is also shown in Figure 2. It is known that a bulk palladium hydride, the so-called β-hydride phase, is formed under high hydrogen pressures. The H/Pd ratio is pressure-dependent, and it has been reported that it can reach as much as 0.69:1 at a hydrogen pressure of 990 atm.[18] A H/Pd ratio of up to 0.5:1 can be expected under the conditions that are normally used for the selective hydrogenation of acetylene.[19] The hydrogen occupies the octahedral sites[20] and the formation of the β-hydride is accompanied by an expansion of the Pd lattice by approximately 3.47 %.[21] We calculated four different palladium hydride structures in the bulk phase with a hydride content ranging from 0.25:1 to 1.0:1. Figure 4 shows the stability (compared to gas-phase H_2) and lattice expansion of the palladium hydride as a function of hydrogen content. We find that the PdH structure with a H/Pd ratio of 0.75:1 is the most stable; the calculated expansion of the Pd lattice by 3.2 % fits well with the experimental values. It should be noted that the adsorption energies of hydrogen in the threefold sites on the Pd(111) surface are approximately −0.44 eV. Thus, hydrogen adsorption is preferred on the surface, and bulk hydride is only formed when high hydrogen pressures are applied.

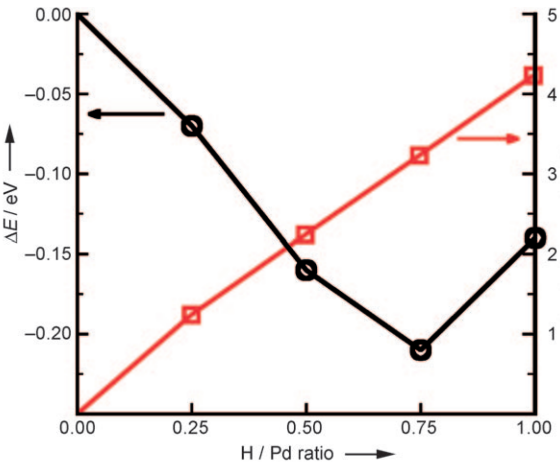

Figure 4. Formation energies and lattice expansions of different palladium hydrides as a function of the H/Pd ratio. The formation energies are calculated relative to pure Pd and gas-phase hydrogen.

The effect of hydride formation is less pronounced than the effect of alloying with Ag or subsurface carbon (see Figure 2). As discussed above, only a H/Pd ratio of 0.5:1 is expected under normal reaction conditions. Here, we find the chemisorption of a methyl group to be only slightly weaker than on the clean Pd(111) surface. The same applies to the adsorption of acetylene and ethylene. Strong modifications of the surface that will alter the adsorption energies significantly are only observed for H/Pd ratios of 0.75:1 and higher. Notably, these modifications for ratios of 0.75:1 and 1.0:1 of the bulk palladium hydride are calculated to have a significantly less pronounced effect on the selectivity/reactivity of the Pd surface than the effect observed for subsurface carbon and the addition of Ag (see Figure 2). This finding is in agreement with earlier calculations for subsurface hydrogen (not the hydride).[12]

We conclude that the underlying physical principles of subsurface carbon are identical to the effect of alloying Pd with, for example, Ag. Modification of the surface with carbon leads to weaker adsorption of CH_3 groups and hence other carbon species, including acetylene and ethylene. This effect increases the ethylene selectivity of the catalyst in the hydrogenation of acetylene. This effect is also present, but is considerably less pronounced for the palladium hydride structures.

Methods

Density functional theory calculations were carried out using the DACAPO code,[22] which uses a plane wave implementation to describe the valence electrons and Vanderbilt ultrasoft pseudopotentials[23] to represent the core electrons. The kinetic energy cut-off was 340 eV. All calculations were performed using the generalized gradient approximation (GGA) and the RPBE functional.[24] The self-consistent electron density was determined by iterative diagonalization of the Kohn–Sham Hamiltonian, with the occupation of the Kohn–Sham states being smeared according to a Fermi–Dirac distribution with a smearing factor of $k_B T = 0.1$ eV and Pulay mixing of the resulting electron density.[25] All energies have been extrapolated to $k_B T = 0$ eV. Slabs consistent with four layers separated by 11 Å of vacuum were periodically repeated in a 2 × 2 unit cell for the Pd(111) surfaces and 1 × 2 unit cell for the Pd(211) surfaces. A Monkhorst–Pack 4 × 4 × 1 k-point sampling was applied.[26] Nudged-elastic-band calculations were performed to obtain the transition state.[27,28]

Received: June 15, 2008

Keywords: acetylene · density functional calculations · hydrogenation · selectivity · surface chemistry

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