Distinguishing surface adsorbed hydrogen from bulk-dissolved hydrogen in supported Pd nanoparticles using in situ Pd L$_3$-edge XANES

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Abstract. In situ X-ray absorption spectroscopy at the Pd L$_3$ edge was applied to determine the particle size effect on the formation of palladium hydride and on surface hydrogen adsorption at room temperature. Pd L$_3$ edge XANES spectra allow direct detection of hydride formation via a characteristic spectral feature caused by the formation of a Pd-H anti-bonding state. This feature showed strong particle size dependence. The L$_3$ edge spectra were reproduced using full multiple scattering analysis and density of states calculations and the contributions of bulk-dissolved and surface hydrogen to the XANES spectra could be distinguished. The ratio of hydrogen on the surface versus that in the bulk increased with decreasing particle size, and smaller particles dissolved less hydrogen.

1. Introduction

The particle size and support effects on catalytic performance are two well-known factors that affect the activity and selectivity of a reaction. For hydrogenation reaction catalyzed by palladium catalysts, the particle size effect can be critical because the formation of palladium hydride is particle size dependent. The amount of hydride that forms decreases with increasing dispersion of palladium in supported catalysts [1]. In contrast to the bulk metal, palladium particles smaller than 2.6 nm have been suggested to not form a hydride phase, even at high hydrogen pressures (P$_{H_2}$=1 atm and T=298 K) [2]. The hydride has higher mobility than the surface hydrogen and can hydrogenate surface adsorbates upon emerging to the surface [3]. Thus, the amount of bulk-dissolved hydrogen seriously affects the activity and selectivity of structure-sensitive hydrogenation reactions [4].

Geometrical and electronic information of palladium nano-particles and of palladium hydride can be obtained from X-ray absorption spectroscopy (XAS) at the K and L edges [5,6]. At the Pd K edge XAS, the formation of palladium hydrides was generally deduced from an increased interatomic distance in EXAFS analysis [5]. In contrast, Pd L$_3$ edge XANES allows the direct detection of palladium hydride via a signature peak at ~6 eV above the Fermi level, caused by the formation of a Pd-H anti-bonding state [6]. This ~6 eV peak can be theoretically simulated [7]. Distinction of bulk-dissolved hydrogen from surface hydrogen in a palladium-catalyzed process remains challenging. It was recently reported that nuclear reaction analysis can distinguish surface adsorbed and bulk-dissolved hydrogen on or in palladium nanocrystals on Al$_2$O$_3$NiAl (110) [8]. We performed XAS at the Pd L$_3$ edge to determine the electronic structural changes that occur in supported nano-sized...
palladium particles after exposure to hydrogen as function of their size. XANES analysis of the L₃ edge data enabled us to distinguish hydrogen that was adsorbed on the surface from that absorbed into the particle.

2. Experimental

2.1 Characteristics of samples
Two silica supported palladium catalysts, namely Pd/SiO₂(10.5) and Pd/SiO₂(2.8) were synthesized by an incipient-wetness impregnation method. A palladium weight loading of 1.9% was determined for both samples using inductive couple plasma. The dispersion of the palladium particles determined via carbon monoxide chemisorption was 0.9 for Pd/SiO₂(10.5) and 4.1 for Pd/SiO₂(2.8). A CO:Pd ratio of 1:1 was assumed. Scanning transmission electron microscopy (STEM) measurements showed that the size was 10.5 nm for Pd/SiO₂(10.5) and 2.8 nm for Pd/SiO₂(2.8). The details of the synthesis and characterisation were described elsewhere [9].

2.2 X-ray absorption spectroscopy
The XAS measurements were performed in fluorescence mode at the LUCIA beamline of the Swiss Light Source (Villigen, Switzerland). A water-cooled double crystal Si(111) monochromator was used in conjunction with a set of nickel-coated silicon mirrors to reduce high-order harmonics and thermal load. The Pd L₃ (3175 eV) edge XANES spectra were obtained using a silicon drift detector with an energy resolution of ~130 eV. A flow-through cell and covered by a kapton film, was placed on a heating block which can be heated to 800 K [10]. The palladium catalysts were first reduced at 2 K/min to 423 K in 4% H₂/He. The reduced catalysts were cooled down to room temperature in 4% H₂/He and subsequently exposed to hydrogen at room temperature to enable hydride formation and a spectrum was collected. The data were processed using XDAP software packages (Version 2.3) [11].

2.3 L₃ edge XANES calculations
The Pd L₃ XANES spectra were calculated using the JFEFF gui software code [12]. A β-palladium hydrides cluster of 27 atoms (PdH₆Pd₁₂H₈) was used. The β-palladium hydride has an FM-3M crystal structure. The cluster was generated by TKATOMS based on crystallographic data from literature [13]. To distinguish the effect of surface adsorbed hydrogen from that of bulk-dissolved hydrogen, the hydrogen atoms absorbed into the bulk in PdH₆Pd₁₂H₈ cluster were removed, so that a Pd_Pd₁₂H₈ cluster with only surface hydrogen was generated. A third Pd_Pd₁₂ cluster was used as a reference, which represents metallic palladium. A Hedin-Lundquist exchange correlation potential and the L₃ XANES, LDOS (angular projected density of states), complete core-hole screening, self-consistent field, and full multiple scattering cards were used in all calculations.

3. Results

3.1 Experimental L₃ edge XANES
Figure 1 shows the signatures of palladium hydrides of the samples obtained by subtracting experimental L₃ edge XANES spectra of palladium hydride with those of the corresponding metallic palladium. Under hydrogen, edge shift to higher energy, whiteline broadening and intensity loss was observed for both catalysts. The edge shift and whiteline intensity loss caused a negative peak at ~3174 eV. At the same time, a positive peak at ~6 eV above the whiteline (~3181 eV) appears. A second negative peak, which was broad, was also observed at the EXAFS region in between 3185 to 3195 eV. All these signatures were very sensitive to the particle size. Their intensities decrease following the decrease of particle size.

3.2 XANES calculations
Figure 1. Signatures of palladium hydrides obtained by subtracting experimental L₃ edge XANES spectra of palladium hydride with metallic palladium.

Figure 2. Signatures of palladium hydrides and surface hydrogen obtained by subtracting calculated L₃ edge XANES spectra of PdH₆Pd₁₂H₈ cluster and Pd₆Pd₁₂H₈ with that of Pd₆Pd₁₂.

Figure 2 shows the signatures obtained by subtracting the calculated Pd L₃ XANES of PdH₆Pd₁₂H₈ and Pd₆Pd₁₂H₈ clusters to that of Pd₆Pd₁₂ cluster. Two negative peaks at ~3173 and ~3187 eV and a positive peak at 3180 eV were observed, in agreement to those observed experimentally. Note that a clear broadening at ~3175 eV was observed with surface hydrogen alone. Because for noble metals the unoccupied d-DOS correlate to the L₃ edge XANES, the origin of the new ~6 eV peak could be revealed by over plotting the calculated L₃ edge XANES to the corresponding density of states. Figure 3 shows the DOS of palladium hydride of 27 atoms (PdH₆Pd₁₂H₈). After hydrogen dissolution into the palladium lattice, the Pd-d band center shifted downward by about 0.5 eV relative to the Fermi level. Meanwhile, a new bonding state of palladium hydride appeared at ~7 eV below the Fermi level whereas the corresponding anti-bonding states appeared at ~6 eV above the Fermi level. Figure 4 shows the calculated density of states of the Pd₆Pd₁₂H₈ cluster overplotted with the corresponding L₃ edge XANES. The calculated L₃ edge XANES of the Pd₆Pd₁₂H₈ cluster showed only whiteline broadening and an intensity increase at the region after the whiteline. No peak was observed at ~6 eV above the whiteline energy position. The Pd-d band center remained unchanged and the Pd-d-H's hybridization was much weaker. Intensity increase of the Pd-d band could be observed between 2.5 and 5 eV, which led to an overall intensity broadening of the corresponding XANES right after the whiteline (figure 2). This suggests surface adsorbed hydrogen does not contribute to the new ~6 eV peak, but to broadening of the whiteline.

4. Discussion
For noble metals, the L₃ edge XANES is very sensitive to changes in electronic structure and thus the resulting signatures (figure 1) were all very sensitive to the particle size. The formation of palladium hydride was observed for both Pd/SiO₂(10.5) and Pd/SiO₂(2.8), thus contradicting previous suggestions that a minimal particle size is required for hydrides to form. The signature peak at ~6 eV above the whiteline corresponds to the newly formed anti-bonding state and decreased with decreasing particle size. Signatures of surface hydrogen and bulk-dissolved hydrogen are different in Pd L₃ edge XANES. The calculated Pd L₃ edge XANES showed that bulk-dissolved hydrogen leads to a large edge shift and the formation of a new anti-bonding state. In contrast, surface hydrogen caused smaller edge shift and whiteline broadening. In the experimental spectra (figure 1) the signature of broadening at ~3175 eV overlapped with those of hydrides and was hence less pronounce as compared to the
calculated spectrum which showed exclusively the signal of the surface hydrogen. The appearance of the broad second negative peak in between 3185 and 3195 eV can be attributed to changes of the interatomic bond length and the peak intensity increased with more neighbouring atoms (and hence larger particle size).

Figure 3. Calculated palladium d and hydrogen s density of states overplotted with calculated L_3 edge XANES for palladium hydride.

Figure 4. Calculated palladium d and hydrogen s density of states overplotted with calculated L_3 edge XANES for a surface palladium atom set as absorbing atom.

Small particles have a higher surface to bulk ratio and relatively few interstitial sites. Thus more hydrogen adsorbs on the surface for small particles compared to the amount of hydrogen that dissolves into the palladium. The surface hydrogen does not contribute to the formation of hydride, which results in a lower intensity of the surface hydride compared to that of the surface hydrogen. The surface contribution of Pd/SiO_2(2.8) is observable and hence their signatures originate not only from the hydride but also from the surface hydrogen. In contrast, the experimental spectrum of Pd/SiO_2(10.5) under hydrogen showed only the anti-bonding state of the hydride. Because of its particle size of 10.5 nm and low surface contribution, the signatures originated purely from the hydride and no surface contributions were observed.

5. Conclusion
Pd L_3 edge XANES enables direct observation of the formation of palladium hydrides, based on the new anti-bonding state formed. The surface adsorbed hydrogen can be distinguished from the bulk-dissolved hydrogen in the Pd L_3 edge XANES. The formation of palladium hydrides is strongly particle size dependent, though all sizes showed the formation of interstitial hydrogen. Large particles have more interstitial places to accommodate bulk dissolved hydrogen and this leads to a more intense new anti-bonding state as compared to smaller particles. Due to higher surface to bulk ratio, more hydrogen adsorbed on the surface of smaller particles.

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