Effects of Adsorbate Coverage and Bond-Length Disorder on the d-Band Center of Carbon-Supported Pt Catalysts

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Determination of the factors that affect the d-band center of catalysts is required to explain their catalytic properties. Resonant inelastic X-ray scattering (RIXS) enables direct imaging of electronic transitions in the d-band of Pt catalysts in real time and in realistic environmental conditions. Through a combination of in situ, temperature-resolved RIXS measurements and theoretical simulations we isolated and quantified the effects of bond-length disorder and adsorbate coverage (CO and H_2) on the d-band center of 1.25 nm size Pt catalysts supported on carbon. We found that the decrease in adsorbate coverage at elevated temperatures is responsible for the d band shifts towards higher energies relative to the Fermi level, whereas the effect of the increase in bond-length disorder on the d-band center is negligible. Although these results were obtained for a specific case of non-interacting support and weak temperature dependence of the metal–metal bond length in a model catalyst, this work can be extended to a broad range of real catalysts.

Catalytic descriptors are global variables, which provide a quantitative characterization of the multitudinous factors that influence catalytic properties. One of the most commonly used descriptors in catalysis and electrocatalysis[1] is the d-band center,[2] which can be directly measured using resonant inelastic X-ray scattering (RIXS) techniques.[3] RIXS experiments require synchrotron radiation and are performed by measuring intensities of X-ray radiation emitted by the sample as a function of both incident and emitted photon energies in the vicinity of the X-ray absorption edge.[4] Many effects related to changes in the electronic properties of metal catalysts during a reaction may affect the d-band center, such as the charge transfer between catalyst particles and the support and/or adsorbates[2b, 5] or changes in particle size.[6] In addition, bond-length changes on the nanoparticle surface (due to thermal expansion as well as temperature-dependent bond-length disorder) may have an influence.[7] How such factors mediate shifts of the d-band center in complex chemical environments, for which multiple perturbations are to be expected, remains poorly understood and is subject of intense research.[8]

In this paper we use experimental valence-band RIXS (VB-RIXS) to investigate the sensitivity of the d-band center of monodispersed supported Pt nanoclusters to adsorbate type, coverage, and thermally induced disorder. Through a combination of experimental design and simulations, we are able to isolate and disentangle these effects, and give a measure to the relative importance of each factor in determining the d-band center. To this end, a systematic, in situ study over a broad temperature range is required. The equilibrium adsorbate coverage,[9] desorption activation energy,[10] particle–support interaction,[8d] metal–metal bond length, and bond disorder all depend on temperature and adsorbate pressure. Distinguishing the roles of these effects on RIXS behavior is possible only if their characterizations are done self-consistently, under the same conditions, and on the same nanoparticle system. In this work we examined a prototypical system: 1.25 ± 0.37 nm Pt clusters supported on carbon under both H_2 and CO atmospheres and at temperatures of 34 and 400 °C. One key point of our experimental design was to use (from an electronic perspective) a weakly-interacting support (in this case C) to exclude the support effect that, otherwise, would have been difficult to isolate from adsorbate interactions[11] and, in general, made the RIXS much more difficult to interpret. The same sample and in situ conditions used were as in our previous work,[11] in which we investigated the effects of adsorbate pressure and temperature on both the structural and the electronic properties of supported Pt catalysts using high energy resolution fluorescence detection (HERFD) measurements of X-ray absorption spectra.

Figure 1 shows the experimental RIXS results grouped by temperature and gas type. The RIXS data are shown as contour maps in a plane of incident and transferred photon energies, where the vertical axis represents the energy transfer as a function of incident energy, and as specific line profiles extracted from these data (Figure 1 a–c for CO and Figure 1 d–f for H_2).

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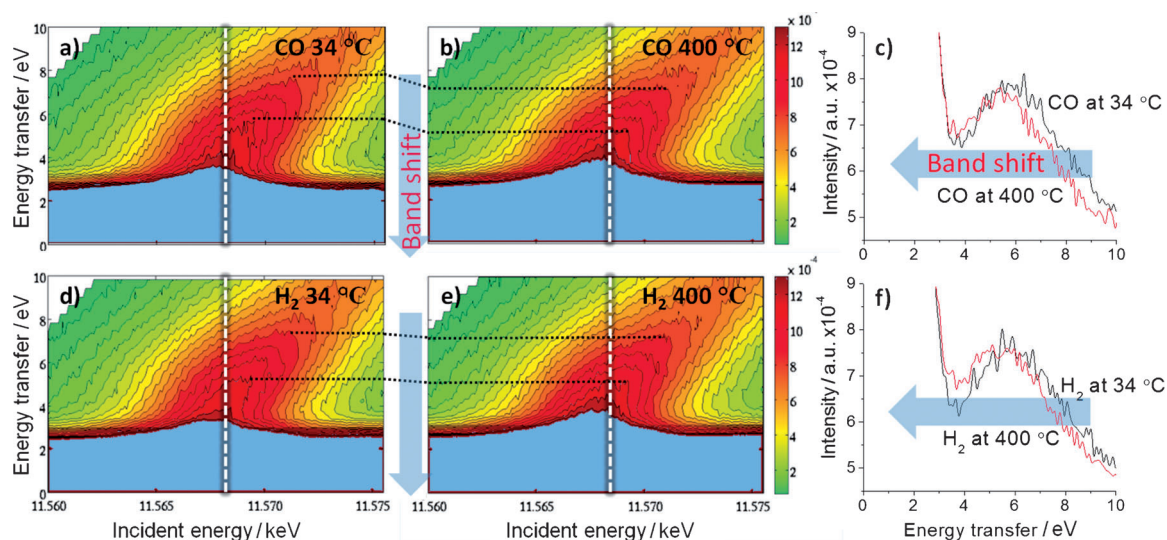E-mail: moniek.tromp@tum.de

Figure 1. Pt RIXS maps and their intensity profiles visualizing the density of photo-excited electronic transitions between Pt 5d states in Pt/C nanoparticles for different atmospheres [CO (a–c) and H_2 (d–f)] and temperatures (34 °C and 400 °C). The transition densities shown in (a, d) are shifted toward lower energy transfers in (b, e) at elevated temperatures for both gases. The fully saturated detection near the elastic peak is shown by blue color. Visualizations of the downward shifts of the d band at elevated temperature for each atmosphere are aided by the dotted horizontal lines corresponding to the same intensity at each temperature, and by vertical arrows. Vertical dashed lines illustrate the direction of the intensity profiles obtained for each map at the same incident energy of 11568.4 eV and are shown in (c, f). The same band shifts towards lower energy-transfer values at elevated temperatures (a, b and d, e) are shown by horizontal arrows in (c, f).

Except for the detector saturation near the elastic peak (colored blue) the color variations correspond to different scattering intensities, with dark red being the highest intensity. The broad bands from ~ -2.5 to $+2.5$ eV (Figure 1 a,b,d,e) are the elastic scattering bands, which are relatively large in the setup used and overlap partly with the inelastic peaks of interest. The shape and position of the inelastic scattering peak in each, however, is visible and can be extracted more accurately using a line profile plot, as shown in Figure 1 c,f. Fitting these line profiles shows that the peak centers shift to lower energy transfers by approximately 0.5 eV for each adsorbate (H_2 or CO) at higher temperature. The details of the fits are in the Supporting Information. Detection of the relative displacements of the VB RIXS features, best seen in the line profiles, enables us to directly image and, in principle, quantitatively measure the displacements of the corresponding d-band centers.

As discussed above, these changes may be caused by multiple physical factors affecting the electronic structure of the metal particles. We first theoretically examine structural contributions to RIXS. Structural information was previously obtained from EXAFS analysis of the same samples and under the same re-

gimes reported here.[11] These results demonstrated that the Pt–Pt bond lengths in this system are relatively insensitive to applied changes in temperature and/or the adsorbate.[11] Hence, the bond-length dependence on the operating conditions can be ignored in this experiment, and we focus on the effects of disorder and adsorbate coverage on the RIXS behavior. Specifically, we examine two separate effects on the d-band center shift: 1) Variable Pt–Pt bond-length disorder, and 2) variable coverage of H and CO adsorbates.
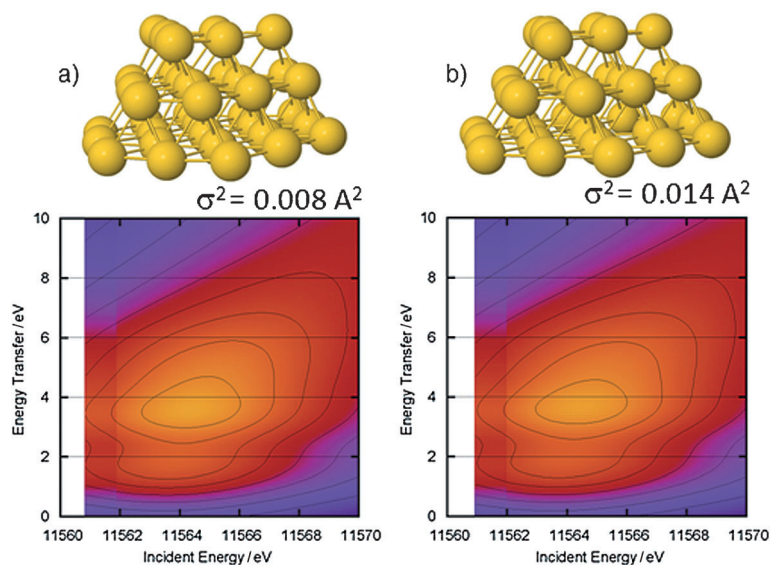

Figure 2. Models of Pt clusters (top) constructed to simulate experimental RIXS data (bottom) by varying the mean square bond-length disorder: a) $\sigma^2 = 0.008$ A², b) $\sigma^2 = 0.014$ A².
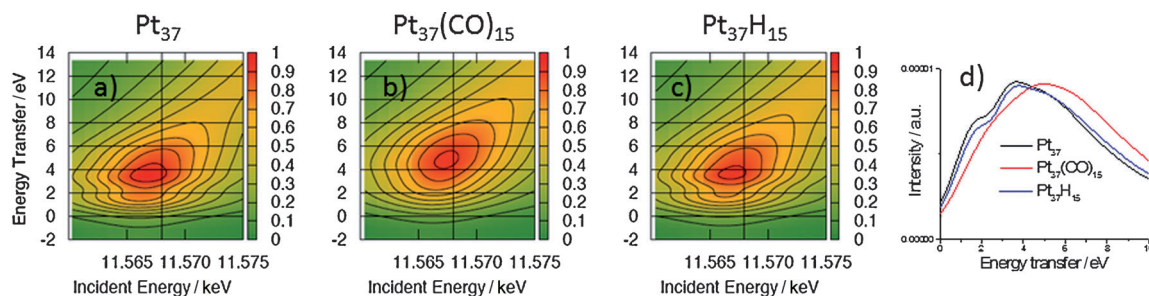
Figure 3. Simulated RIXS data for a 37-atom Pt cluster: bare (a), with CO (b) and H (c) adsorbed. The profile along the 11586 eV energy [shown as a vertical line in (a–c]) is shown in (d). The bare cluster's features are shifted towards lower energy transfers by 0.304 ± 0.009 eV and 1.04 ± 0.01 eV for H_2 and CO, respectively (see the Supporting Information).

These effects were modeled theoretically using representative, 37-atom clusters (Figure 2). The cluster's diameter was 1.1 nm, in agreement with the experimental data (vide supra). First principles RIXS simulations were conducted using a modification of the real-space multiple scattering Green's function code FEFF9.[11,12] In this formalism, the RIXS is given as a convolution of the X-ray emission spectrum with an effective X-ray absorption spectrum.

Calculations were performed separately for each of the Pt atoms in the cluster, and averaged to produce the final spectrum. Potentials were calculated self-consistently, and unique potentials were used for each of the atoms in the cluster to ensure stability of the Fermi level. The full multiple scattering method was used in the calculations of the Green's function, with the maximum radius set to include all atoms in the cluster, and with a maximum angular momentum cut-off of three for the Pt atoms, and two for the C, O, and H atoms.

To model the effect of the disorder on RIXS, the clusters were randomly distorted from the ideal periodic fcc structure according to the experimentally measured Pt–Pt bond-length disorder.[11] Atomic positions in the clusters were disordered using a random-number generator. In this procedure, every atom was shifted in a random direction by the same distance, so that the mean square disorder of the first nearest-neighbor distance matched the experimentally obtained value. The average Pt–Pt bond length in each type of cluster was constrained to the experimentally observed value of 2.74 Å.[11] The cluster models with mean square bond-length disorder values of 0.008 and 0.014 Å² corresponding to temperatures of 34 and 400 °C, respectively, are shown in Figure 2 a,b.

Simulations of the disorder effects resulted in no visible vertical shift of the RIXS maps (Figure 2). If the average bond length does not change between the two models (as in the present case), local variations in the bond lengths on either side of the average length exert opposite effects on the shape of the d band: The longer bonds tend to narrow the d band (and thus raise the Fermi level relative to the d-band center), and the shorter bonds broaden it, thus lowering the Fermi level.[2b,7,13] Therefore, it is reasonable to conclude that when the average bond length does not change with temperature, these two effects cancel each other, as can be seen by RIXS, which provides a snapshot of the valence electron properties averaged over all atoms in the cluster.

At 400 °C and these partial pressures, the H and CO adsorbate coverages on Pt clusters are negligible and their upper limit can be estimated as less than 9% for each gas (for more details see the Supporting Information). At 34 °C, the clusters are almost completely covered by adsorbates.[14] Therefore, we simulated the effect of adsorbate coverage by comparing the bare and fully covered (with H and CO) clusters. Full coverage (H or CO) was simulated by placing an adsorbate on each of the 15 Pt atoms that reside on the surface of the simulated clusters, thus excluding the Pt atoms in the direct contact with the support. Simulations of bare and covered clusters were performed for a cluster with the same (0.008 Å²) Pt–Pt bond length disorder (Figure 2 a). The results of these simulations are summarized in Figure 3. Calculated 5d density-of-states are shown in Figure S5 in the Supporting Information.

As shown in Figure 3, and as observed in an earlier work, CO adsorption causes an upward shift of the d-band center.[3] Since the coverage of both CO and H adsorbates decreases with temperature (at constant pressure), the results of these simulations are in qualitative agreement with the experimental data (Figure 1). Hence, we conclude that ligand adsorption is dominating the RIXS behavior. This conclusion is not affected by the fact that Pt particles have finite size distribution, because the differences in adsorbate coverage (between 1 and 0) across the temperature changes (between 34 and 400 °C, respectively) are both large and not sensitive to the difference in the particle sizes in the 1 nm range studied in this work.

In summary, we have directly imaged the changes of the d-band center position of an important prototype catalyst in response to variable temperature and type of adsorbates. Our simulations we used an idealized model (bare vs. fully covered cluster), nevertheless we obtained semi-quantitative agreement with experimental energy-transfer values. We have isolated the dominating effect of the adsorbate coverage compared to the effect of bond-length disorder on the d-band center behavior. In this Communication we reported a study which benefitted from several competing factors being either negligible (e.g. support effect) or constant (e.g. bond length). We believe that the analytical power of d-band imaging by VB RIXS will offer the possibility to account for support interaction, cluster size, and changes in compressive or tensile strain within a catalyst in the process of chemical reaction, and their separate effects on the electronic state of the catalyst.

Experimental Section

Pt clusters supported on C were prepared by impregnating Vulcan X-72 with $NH_4Pt(OH)_2$ to attain a Pt loading of 0.5 wt%. After drying the samples, they were each reduced at room temperature using pure H_2 for 30 min prior to being heated to 500 °C at a heating rate of 3.4 °C min^{-1}. This temperature was maintained for 1 h before the samples were allowed to cool to room temperature and were flushed with Ar. Sample sizes and distributions were obtained using a JEOL 2010-F scanning transmission electron microscope.[11]

RIXS measurements were performed at the European Synchrotron Radiation Facility (ESRF) high brilliance XAS/XES beamline ID26. The incident energy was selected using the $< 111 >$ reflection from a double Si crystal monochromator. Rejection of higher harmonics was achieved by using three Pd/Cr mirrors at an angle of 2.5 mrad relative to the incident beam. The size of the X-ray beam was 0.3 mm (horizontal) × 1 mm (vertical). RIXS spectra were measured using an X-ray emission spectrometer with the sample, crystal analyzer and photon detector (avalanche photodiode) arranged in a vertical Rowland geometry. The full RIXS plane was measured by scanning the incident energy at different emission energies. The emission energy was selected using the $< 933 >$ reflection of three spherically bent Si crystal analyzers (with a 1 m bending radius). The intensity was normalized to the incident flux. A combined (incident convoluted with emitted) energy resolution of 2.1 eV was obtained as determined by measuring the full width at half maximum (FWHM) of the elastic peak. Samples of Pt/C catalysts were loaded in a microreactor cell consisting of 0.5 mm ID quartz capillary, the heater block with cartridge heaters and gas-flow connections for gas input and gas analysis. Each sample was investigated at 34 and 400 °C using both $\delta = 50$ ppm CO (balance He) and 100 % H_2 at a pressure of 1 atm. Prior to the X-ray measurements the sample was loaded into the cell and flushed under pure H_2 at room temperature for 30 min. The sample was then heated to 400 °C in pure H_2 and kept at this temperature for 20 min. The temperature was lowered to 34 °C and held there until the absorption edge spectra stopped changing (within statistical noise) and the RIXS at this temperature was acquired. The temperature was then returned to 400 °C and, once the absorption edge stabilized, RIXS data were acquired. After acquiring the H_2 data at 400 °C, the feed gas was switched to $\delta = 50$ ppm CO and RIXS was conducted after the absorption edge had stabilized. Finally, the temperature was lowered to 34 °C in $\delta = 50$ ppm CO and the last RIXS spectrum was acquired.

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