

**Experiment title:**Active sites in metal-catalyzed reactions: *in situ* XAS study on the metal $L_{3/2/1}$ edges**Experiment number:**

CH-1961

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Report:

Metals catalysts are widely used in large-scale processes such as petroleum refining, hydrogenation of chemicals, and automobile exhaust conversion. Our group studies the physical-chemical properties of supported metal catalysts, their interaction with reactive intermediates, and relates these properties to catalytic performance. Specifically, the activity and selectivity of supported metal clusters in the hydrogenation of benzene is investigated. The intermediate product cyclohexene is a starting material for synthesis of adipic acid, nylons, polyamides, and polyesters. The selective formation of cyclohexene from benzene is more favorable than the traditional route via cyclohexane oxidation.

The design of a selective catalyst is facilitated by knowledge of the hydrocarbon adsorption sites on the metal. Somorjai et al. [1] have applied the sum frequency generation (SFG) technique to determine the reactive intermediates for (de)hydrogenation reactions of hydrocarbon molecules, like hexane and cyclohexene, in the presence and absence of hydrogen on Pt(111), and obtained insight into the elementary steps in the reaction mechanism. However, SFG is insensitive for the metal and the adsorption sites of the hydrocarbons remain unknown [1]. Gates et al. [2] investigated the structural changes of small metal particles, however, their detailed EXAFS-analyses do not provide information on the participating surface sites. We aim at the experimental determination of the adsorption sites for reactants and of the reactive intermediates using X-ray absorption spectroscopy.

In this experiment, the adsorption of benzene, cyclohexene, and 1-hexene on Pt clusters supported on Al_2O_3 and SiO_2 was studied. 2 wt% Pt/ Al_2O_3 was prepared by incipient wetness impregnation of $\gamma-Al_2O_3$ with an aqueous solution of tetra ammine platinum nitrate (PTA). After impregnation, the powders were dried and calcined at 673 K. 1 wt% Pt/ SiO_2 was prepared by adding an aqueous solution of PTA to a slurry of SiO_2 in an NH_4OH solution with a pH of 10. After adsorption of the PTA, the powder was filtered, washed, and dried at 373 K. The Pt catalysts were pressed in a self-supported wafer and placed in our *in situ* XAS cell. Prior to the XAS experiments Pt/ Al_2O_3 was reduced in pure hydrogen at 723 K and Pt/ SiO_2 at 473 K. Chemisorbed hydrogen was removed by heating in vacuum ($<10^{-3}$ Pa). Spectra of the Pt $L_{3, 2, 1}$ edges were collected in vacuum at room temperature. Subsequently, one of the hydrocarbons was absorbed by filling the cell with He saturated with the hydrocarbon. Again, spectra of the Pt L edges were collected, at 303 and 343 K. The hydrocarbon-induced fingerprint was extracted by the following procedure: The L_2 edges were aligned on

their onset, i.e. at 0.4 of the step height. The L_3 EXAFS between 50 and 120 eV was aligned on the EXAFS of the corresponding L_2 edge. The difference between the L_3 edge with the adsorbed hydrocarbon and the L_3 edge collected in vacuum, is the absorbent-specific fingerprint. EXAFS fits of the L_3 EXAFS were performed in R -space with $3.2 < k < 12 \text{ \AA}^{-1}$ and $1.5 < R < 3.2 \text{ \AA}$.

In figure 1 the Pt L_3 edges of Pt/ Al_2O_3 and Pt/ SiO_2 are shown with and without adsorbed benzene, and the benzene fingerprint. The adsorption of benzene on the Pt clusters induces a change in the Pt L_3 XANES, as well as in the L_2 and L_1 XANES. From comparison of the fingerprint with calculated fingerprints for ethylene and hydrogen chemisorption, we can conclude that with increasing temperature the benzene-induced fingerprint changes towards more hydrogen. Thus, benzene dehydrogenates upon heating. On Pt/ Al_2O_3 there is more dehydrogenation than on Pt/ SiO_2 . In figure 2 the Pt L_3 edges of Pt/ SiO_2 with and without adsorbed cyclohexene are shown, together with the cyclohexene fingerprint at 303 K. Cyclohexene adsorption also induces a change in the Pt L edges, which differs from the benzene-induced fingerprint. Figure 3 shows the Pt L_3 edge of Pt/ SiO_2 with and without adsorbed 1-hexene and the hexene fingerprint at 303 and 343 K. Hexene dehydrogenates upon heating.

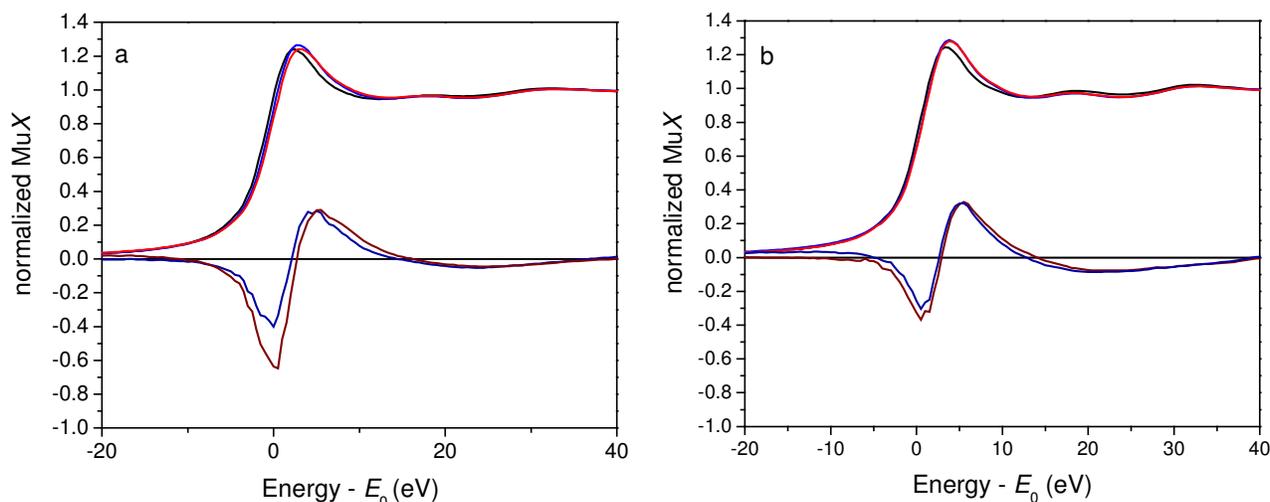


Figure 1. Pt L_3 edge of **a.** Pt/ Al_2O_3 and **b.** Pt/ SiO_2 . Without adsorbates (black), with adsorbed benzene at 303 K (blue) and at 343 K (red), and their differences with the spectrum in vacuum times five (303 K: dark blue; 343 K: dark red).

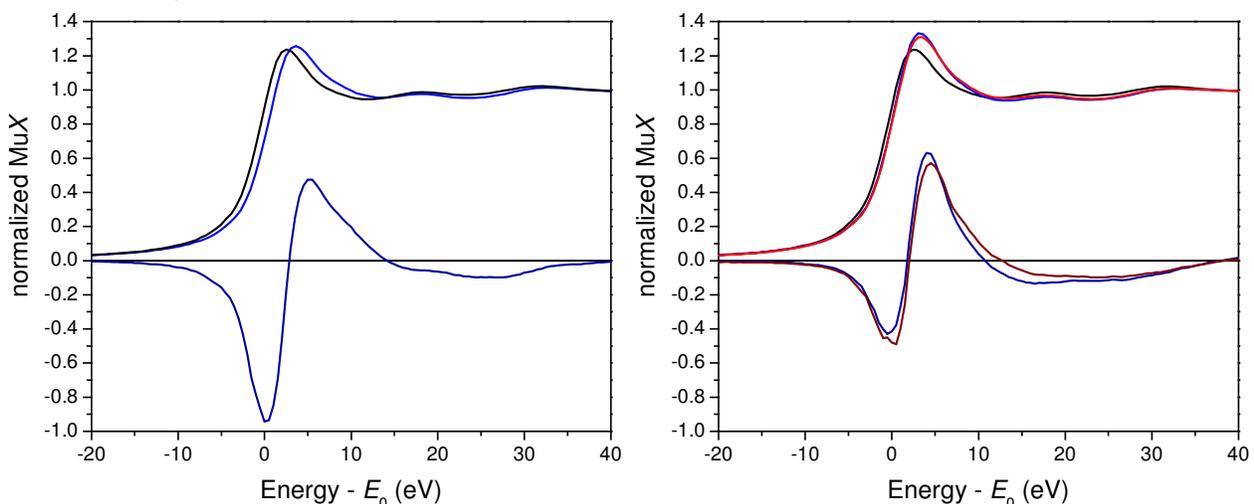


Figure 2. Pt L_3 edge of Pt/ SiO_2 . In vacuum (black), with cyclohexene at 303 K (blue) and their difference times five (dark blue).

Figure 3. Pt L_3 edge of Pt/ SiO_2 . Without adsorbates (black), with adsorbed 1-hexene at 303 K (blue) and at 343 K (red) and their difference with the spectrum in vacuum times five (303 K: dark blue; 343 K: dark red).

For the Pt clusters supported on Al₂O₃ the Pt-Pt coordination number is around 5 with and without adsorbed benzene. The interatomic distance is 2.70 Å in vacuum, compared to 2.78 Å in the bulk. The contracted distance does not increase significantly upon benzene adsorption, in contrast to hydrogen chemisorption, for which a bond relaxation is observed [3]. A support-oxygen contribution was included in the fits, with a coordination number of around 0.5. The Pt-Pt coordination number for Pt/SiO₂ is around 6, thus the clusters diameter is about 1 nm. The coordination number increases slightly upon adsorption of a hydrocarbon. The Pt-Pt interatomic distance in the clusters is 2.71 Å in vacuum and does not change upon adsorption.

Conclusion

The adsorption of benzene, cyclohexene, and 1-hexene on supported Pt clusters induces a change in the XANES of the Pt L edges. The shape and intensity of the hydrocarbon induced fingerprint depends on the type of adsorbed hydrocarbon, the support, and the temperature. Upon heating the hydrocarbons are dehydrogenated on Pt.

References

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