

**Experiment title:**Active sites in metal-catalyzed reactions: in situ XAS study on the Pt and Au L<sub>3,2,1</sub> edges**Experiment number:**

CH-2129

**Beamline:**

BM26A

**Date of experiment:**

from: 02-12-2005 to: 06-12-2005

**Date of report:**

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**Shifts:**

12

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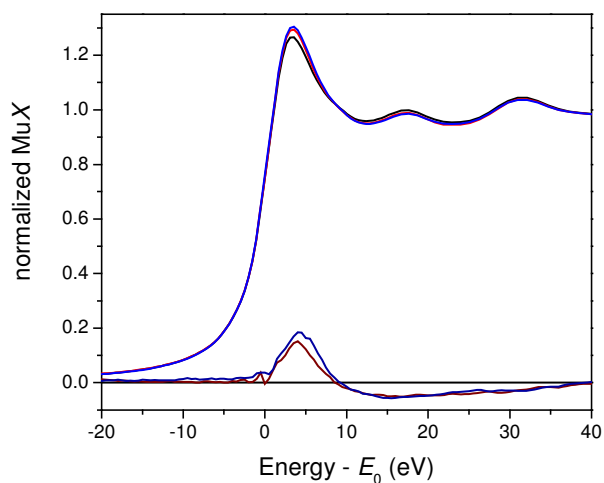
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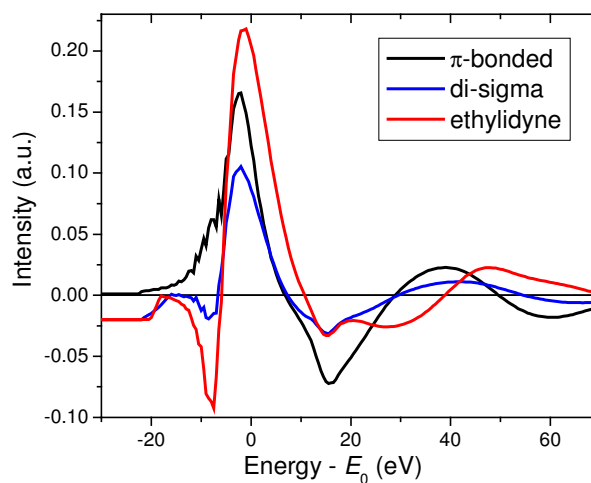
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**Report:**

We study the properties of supported metal catalysts as part of a larger project on structure-performance relationships in heterogeneous catalysis. The process of interest is the hydrogenation of aromatics and olefins over Pt, Au and PtAu-alloy clusters on metal oxides. The structure of the catalytic sites is elucidated through the interpretation of spectroscopic fingerprints in the Pt and Au L-edges, which are induced by the adsorption of reactants and intermediates on the metal. Extended X-ray Absorption Fine Structure (EXAFS) analyses provide the structure of the metal nanoclusters, before and after adsorption. Here, the adsorption of ethylene is discussed. During this beamtime, the adsorption of bigger hydrocarbons, namely cyclohexene, hexene, and 3-methylpentane, was also studied, as well as the co-adsorption of ethylene and hydrogen.



**Figure 1.** Pt L<sub>3</sub> edge of Pt/SiO<sub>2</sub> in vacuum at 303 K (black), with adsorbed ethylene at 303 K (blue) and 473 K (red) and the ethylene-induced fingerprint times five at 303 K (dark blue) and 473 K (dark red).

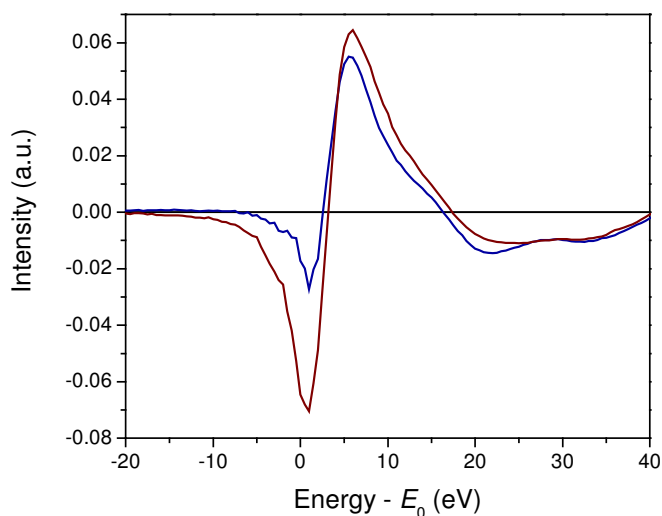


**Figure 2.** Ethylene spectroscopic fingerprints on Pt L<sub>3</sub> XANES calculated with FEFF8 for the three possible adsorption sites. The energy axis is not calibrated.

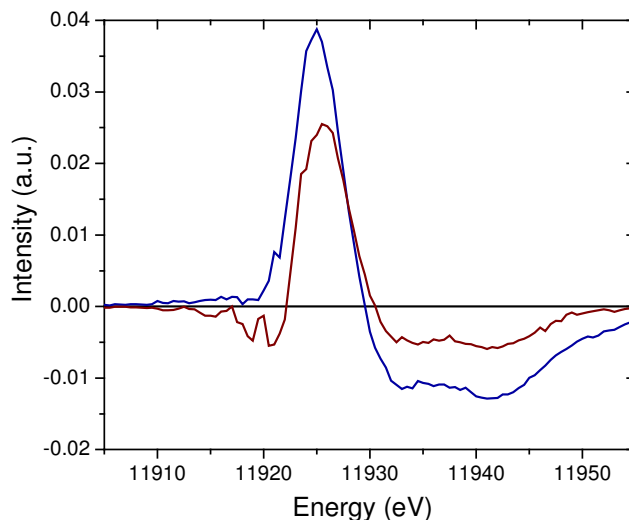
Pt clusters of  $\sim 2$  nm in size supported on  $\text{SiO}_2$  were reduced in pure hydrogen at 473 K, subsequently the hydrogen was desorbed at 673 K. XAS spectra of the Pt  $L_3$  and  $L_2$  edges were collected in vacuum at 303 K. Subsequently, ethylene was adsorbed at 303 K and the catalyst was heated to 473 K; at both temperatures XAS spectra of the  $L_{3,2}$  edges were collected. Figure 1 shows the  $L_3$  XANES, and the ethylene spectroscopic fingerprints, which are the changes in the  $L_3$  XANES compared to the spectrum in vacuum at the same temperature. The effect of ethylene on the Pt electronic structure changes with temperature. Changes were also observed in the Pt  $L_2$  edge. It has been shown before that the shape of the hydrogen fingerprint gives information on the adsorption site on Pt. With FEFF8 calculations a distinction can be made between a-top and n-fold sites [1]. We performed similar calculations for the adsorption of ethylene on Pt clusters. Ethylene can adsorb as a pi-, a di-sigma, or an ethylidyne complex on the Pt surface, as Somorjai *et al.* [2] have shown with sum frequency generation infrared spectroscopy. The  $\pi$ -mode needs only one metal atom and was mainly observed at high coverage and low temperature. The sigma-mode needs two metal atoms, and the ethylidyne mode three. The geometries of the adsorption modes as proposed by Somorjai *et al.* have been used in our calculations. The predicted signatures are shown in figure 2. Comparison of these with our experimental data suggests that at 303 to 473 K the ethylene is adsorbed in the  $\pi$ -mode. At the higher temperature less ethylene is adsorbed.

Pt clusters of  $\sim 1$  nm supported on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  were reduced in pure hydrogen at 573 K and the chemisorbed hydrogen was desorbed at 673 K. Ethylene was adsorbed at 303 K and the catalyst was heated to 473 K. Figure 3 shows the ethylene-induced fingerprint in the  $L_3$  edge at both temperatures. The ethylene adsorption mode is di-sigma at 303 K. Upon heating the ethylene dehydrogenates and the adsorption mode becomes ethylidyne.

Small Au clusters supported on  $\text{Al}_2\text{O}_3$  were formed by reducing the oxidic gold precursor at 473 K. Chemisorbed hydrogen was removed at 473 K. We have shown before that hydrogen chemisorption induces a change in the Au  $L_{3,2}$  edges [3]. Ethylene adsorption also induces a change in the Au L edges of Au nanoclusters, which differs from the hydrogen fingerprint. The ethylene fingerprint in the Au  $L_3$  edge at 303 and 373 K is shown in figure 4. It has a lower intensity than on Pt (figure 3), indicating either that less ethylene adsorbs on Au compared to Pt, or that the Au-ethylene interaction is weaker than the Pt-ethylene interaction, or both. The ethylene-adsorption mode on gold is pi at room temperature. Upon heating it changes towards di-sigma. The metal-ethylene interaction in the  $\pi$ -adsorption mode is weaker than for the other possible adsorption sites. Apparently, the Au-ethylene interaction is weaker than the Pt-ethylene interaction. This has also been observed for hydrogen.



**Figure 3.** Ethylene-induced fingerprint on the Pt  $L_3$  edge of Pt/ $\text{SiO}_2\text{-Al}_2\text{O}_3$  at 303 K (dark blue) and 473 K (dark red).



**Figure 4.** Ethylene-induced fingerprint on the Au  $L_3$  edge of Au/ $\text{Al}_2\text{O}_3$  at 303 K (dark blue) and 373 K (dark red).

Table 1 lists the results of the EXAFS analysis for all three catalysts. The larger Pt clusters supported on  $\text{SiO}_2$  hardly change upon ethylene adsorption. The coordination number is 9, thus the cluster size is about 2 nm. The Pt-Pt distance is 2.75 Å, which is slightly lower than the bulk value of 2.78 Å. It increases slightly upon ethylene adsorption at room temperature. In the smaller Pt clusters, supported on  $\text{SiO}_2\text{-Al}_2\text{O}_3$ , the Pt-Pt

distance is more contracted. It increases by 0.01 Å upon ethylene adsorption. The Pt-Pt coordination number is around 5, thus the clusters are about 1 nm in diameter. An oxygen contribution of the support of  $N = 0.2$  was included in the fits of the spectra collected in vacuum. This light-scatterer contribution increased to 0.6 upon ethylene adsorption, indicating that the carbon of the ethylene can be seen in the EXAFS. In the EXAFS fits of the gold clusters a support-oxygen contribution of 0.1 at 2.1 Å was included in the fits. The Au-Au coordination number is around 6, thus the clusters are about 1 nm in diameter. The Au-Au distance is contracted with respect to the bulk value of 2.88 Å and does not change upon ethylene adsorption.

**Table 1.** Coordination number ( $N$ ), interatomic distance ( $R$ ), and Debye-Waller factor ( $\Delta\sigma^2$ ) of the metal and the oxygen/carbon shell of Pt/SiO<sub>2</sub> and Au/Al<sub>2</sub>O<sub>3</sub> without adsorbates and with ethylene, at different temperatures. EXAFS analysis of Pt or Au L<sub>3</sub> edge.  $k^3$  weighing;  $k = 3 - 12 \text{ \AA}^{-1}$ ;  $R = 1.6 - 31 \text{ \AA}$ .

catalyst	T	atmosphere	$N$	$R$ (Å)	$\Delta\sigma^2$ ( $10^{-3} \text{ \AA}^2$ )
Pt/SiO <sub>2</sub>	303 K	vacuum	9.3	2.75	-1.3
		ethylene	9.3	2.76	-1.3
	473 K	vacuum	9.4	2.75	0.8
		ethylene	9.2	2.75	1.1
Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	303 K	vacuum	5.4	2.70	1.0
		ethylene	4.6	2.71	1.4
	473 K	vacuum	5.0	2.71	4.3
		ethylene	4.2	2.72	2.6
Au/Al <sub>2</sub> O <sub>3</sub>	303 K	vacuum	5.3	2.76	5.5
		ethylene	6.2	2.75	7.0
	373 K	vacuum	5.5	2.75	7.1
		ethylene	5.6	2.76	7.0

## Conclusion

The adsorption of olefins on metal clusters can be studied with *in situ* XAS of the metal L edges. The spectroscopic signatures and thus the adsorption mode of ethylene on Pt and Au were revealed.

## References

- (1) M.K. Oudenhuijzen, J.A. van Bokhoven, J.T. Miller, D.E. Ramaker, D.C. Koningsberger, *J. Am. Chem. Soc.* 127 (2005) 1530.
- (2) G.A. Somorjai, A.L. Marsh, *Phil. Trans. R. Soc. A* 363 (2005) 879.
- (3) E. Bus, J.T. Miller, J.A. van Bokhoven, *J. Phys. Chem. B* 109 (2005) 14581.