Proc. 7th Int. Conf. X-Ray Absorption Fine Structure, Kobe, 1992
Jpn. J. Appl. Phys. Vol. 32 (1993) Suppl. 32-2, pp. 454-456

The Influence of Metal-Support Interactions on the Whiteline Intensity

Marius VAARKAMP[1], Jeff T. MILLER[2], Frank S. MODICA[2], and Dick C. KONINGSBERGER[3]

[1] *Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*
[2] *Amoco Oil Company Research Centre, P.O. Box 400, Naperville, IL 60540, USA*
[3] *Debye Institute, Utrecht University, P.O. Box 80083, 3508 TB Utrecht, The Netherlands*

(Received August 25, 1992)

The whiteline intensity of Pt/K–LTL catalysts reduced at 300, 450, and 600°C decreases with increasing reduction temperature. This change in whiteline intensity was ascribed to the removal of hydrogen from the metal–support interface by reduction at higher temperature.
Keywords: electron deficiency; whiteline intensity; platinum catalysts; metal–support interaction

Introduction

The change in catalytic properties of metal–catalysts with a change in particle size is generally attributed to the geometric requirements of the reaction(s) under investigation[1]. However these changes might also occur due to a changing fraction of edge and corner atoms in the total amount of surface atoms, hence a change in average electronic density on the surface atoms of the catalyst. The electron density of atoms can be measured with X–ray Absorption Spectroscopy.

Although many factors are known to affect the electron density on atoms and small metal particles, their relative importance is not clear. Lytle and coworkers[2] have shown by studying a number of platinum compounds that the intensity of the L_{III} resonance of third row transition metals has an almost linear relationship with the so–called coordination charge. The whiteline intensity of supported small metal particles is known to be affected by absorption of oxygen at room temperature[2], removal of adsorbed hydrogen from the platinum surface[3, 4], and the type of support[5]. Lytle et al.[3] demonstrated that the intensity of the L_{II} edge decreases with hydrogen removal whereas the intensity of the L_{III} edge increases slightly with hydrogen removal. The important consequence of this work is that both the L_{III} and the L_{II} edge have to be examined before any statement about a change in electron density can be made. The same study showed a large influence of measuring temperature on the intensities of the whitelines with a decrease of both edges with increasing temperature.

Recently Local Density calculations[6] of the d–band density of states of charged Ir_4 and Ir_{10} clusters have shown that the d–band density of states decreases when the particle size decreases, hence the whiteline intensity increases when the particle size decreases. A consequence of these calculations is that comparison of whiteline intensities should be done for particles of the same size.

To access the relative importance of the effects described above we prepared platinum catalysts with different supports and particle size and we measured the changes in whiteline intensity after various treatments.

Experimental

Catalyst Preparation

A 1.0 wt% $Pt/\gamma\text{–}Al_2O_3$ was prepared by impregnation of Ketjen CK-300 (200 m^2/g, 0.6 cm^3/g) with an aqueous solution of hydrochloric platinic acid. The catalyst was dried in air overnight at 120°C before it was reduced at 300°C for 4 hours. After reduction the catalyst was passivated at room temperature.

K–LTL (zeolite L) was obtained from Linde. Excess alkali was reduced by water wash until the pH of the washed solution reached 9.5 to give a K/Al molar ratio of 1.05. H–LTL (K/Al molar ratio of 0.34) was prepared by repeated ammonium nitrate exchange of K–LTL, followed by calcination at 500°C. The zeolites were impregnated with an

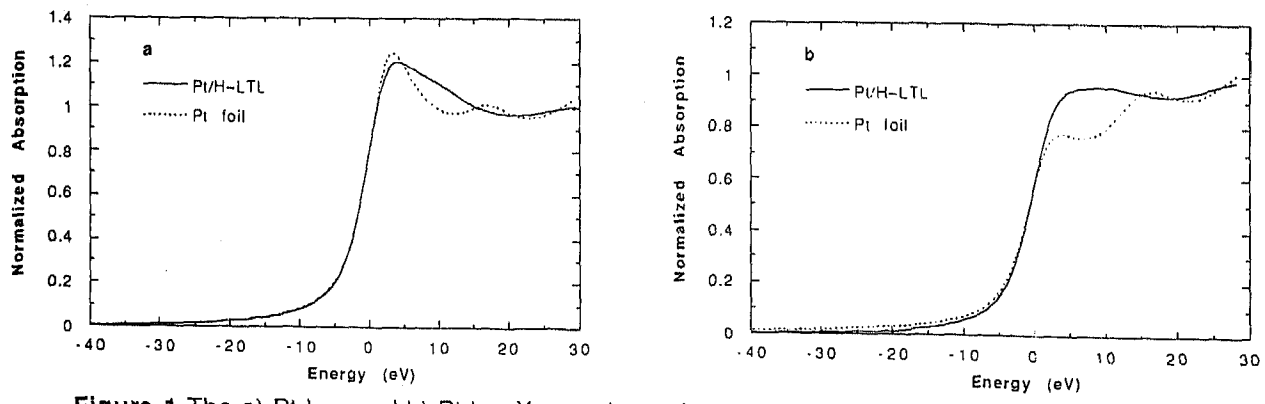

Figure 1 The a) Pt L_{III} and b) Pt L_{II} X–ray absorption edges of platinum foil (solid line) and Pt/H–LTL (dashed line) aligned with their inflection points.

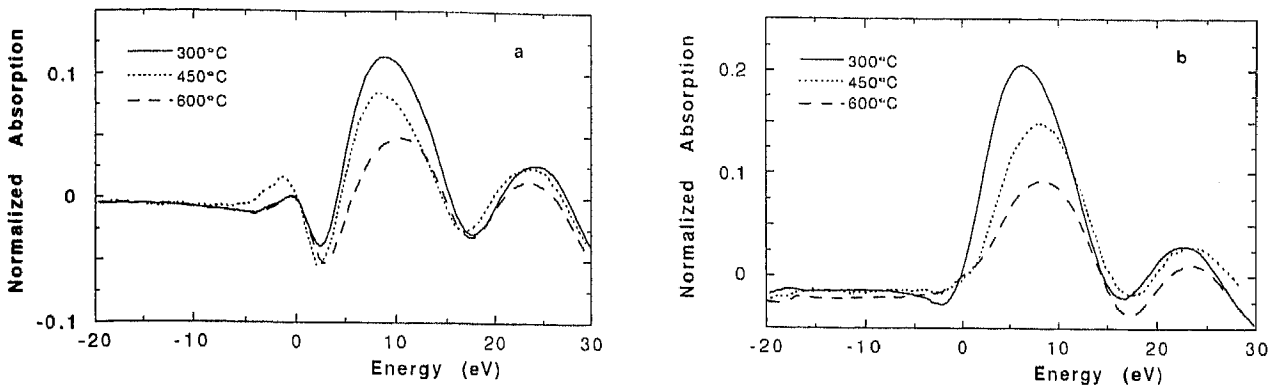

Figure 2 Platinum foil subtracted a) Pt L_{III} and b) Pt L_{II} X-ray absorption edge of Pt/K-LTL reduced at 300°C (solid line), 450°C (short dashed line), and 600°C (long dashed line).

aqueous solution of platinum(II)tetraamine nitrate to give a 1.2 wt% Pt/K-LTL and a 1.0 wt% Pt/H-LTL catalyst. The impregnated zeolites were dried at 120°C and stored till further use.

X-ray Absorption Measurements

Self-supporting wafers were reduced in H_2 in a controlled atmosphere *in-situ* cell[7]. The X-ray Absorption data were obtained at the Synchrotron Radiation Source in Daresbury, U. K., Wiggler Station 9.2 in the transmission mode at liquid nitrogen temperature in the presence of H_2. The estimated resolution at the Pt L_{III} (11564 eV) and L_{II} (13273 eV) edge is 4 eV. The Si(220) monochromator was detuned to 50% intensity to avoid the effects of higher harmonics. In order to obtain an absolute energy calibration of the data a third ionchamber was used with a platinum metal foil (thickness 4 μm) placed between the second and third ionchamber. Standard procedures were used to extract the EXAFS functions[8]. The spectra were normalized by the edge jump at 50 eV above the edge.

Whiteline Intensity Determination

To quantify the differences in whiteline intensity between the catalysts and the foil we used the approach described by Mansour et al.[9]. The normalized XAFS spectra of the Pt $L_{III, II}$ edge of the platinum foil and the catalyst were aligned at there inflection points (figure 1). After subtraction of the platinum foil data from the data of the catalyst, the resulting curves were numerically integrated between -2 and +17 eV for both the L_{III} (ΔA_3) and the L_{II} (ΔA_2) edge. The resulting areas were combined as proposed by Mansour et al.[9]:

$$\Delta h_T = 2.25\ (\Delta A_3 + 1.11\ \Delta A_2) \qquad (1)$$

Results and Discussion

The aligned Pt L_{III} X-ray absorption edges of platinum foil and Pt/H-LTL have been plotted in figure 1a, figure 1b shows the alignment of the L_{II} edge. Although alignment of the EXAFS wiggles ensures a better alignment of the Fermi energies, we choose to align the inflection points because the lack of common features in the EXAFS of the catalysts and the platinum foil makes such an alignment unreliable.

The curves resulting from subtraction of the platinum foil absorption edge from the spectra of Pt/K-LTL reduced at 300, 450, or 600°C are shown in Fig. 2(a) and 2(b) for the L_{III} and L_{II} edge respectively. Results of numerical integration of the areas below the curves are listed in table I, together with the first shell Pt-Pt coordination number[10]. The whiteline intensity decreases with increasing reduction temperature whereas the particle size increases with reduction temperature from 5-6 atoms after reduction at 300°C to approximately. 11 atoms after reduction at 600°C. It is thus tempting to conclude that there is a clear relation between particle size and whiteline intensity. However, in a recent paper[10] we have shown that the interaction between zeolite and platinum cluster changes with reduction temperature and moreover that hydrogen desorbs irreversibly from the platinum-zeolite interface during reduction at high temperature. Furthermore it is known[3] that the whiteline intensity is affected by the adsorbed gas and the interaction with the support[5]. Hence, the decrease in whiteline intensity of the Pt/K-LTL catalyst with increasing reduction temperature is no valid proof of the increase or decrease of the whiteline intensity with particle size.

The platinum foil subtracted Pt $L_{III, II}$ edges of

Table I Coordination numbers and whiteline intensities

Sample	reduced at (°C)	N_{Pt-Pt}	ΔA_3	ΔA_2	Δh_T
Pt/γ-Al_2O_3	300	4.1	0.64	1.62	5.49
Pt/H-LTL	300	4.9	0.61	1.68	5.55
Pt/K-LTL	300	4.0	0.71	1.74	5.95
Pt/K-LTL	450	4.4	0.38	1.24	3.73
Pt/K-LTL	600	4.9	0.09	0.71	1.98

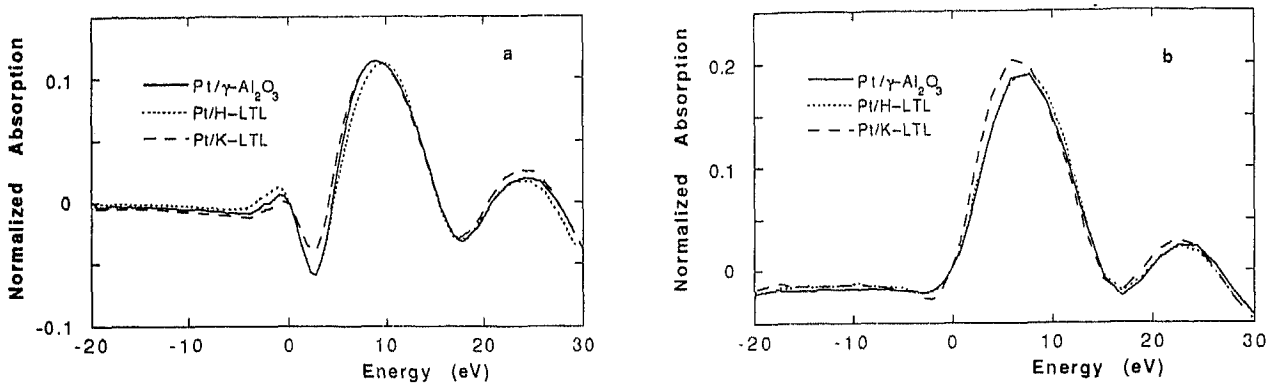

Figure 3 Platinum foil subtracted a) Pt L_{III} and b) Pt L_{II} X-ray absorption edge of Pt/γ–Al_2O_3 (solid line), Pt/H–LTL (short dashed line), and Pt/K–LTL (long dashed line).

Pt/γ–Al_2O_3, Pt/H–LTL, and Pt/K–LTL, all reduced at 300°C are shown in figure 3. The results of numerical integration of the areas below these whitelines are listed in table I together with the first shell Pt–Pt coordination number of these catalysts. The area of the X-ray absorption edge is the largest for the Pt/K–LTL catalyst while the areas of the Pt/γ–Al_2O_3 and the Pt/H–LTL catalyst are almost the same. The particle size is equal within the limits of accuracy for Pt/γ–Al_2O_3 and Pt/K–LTL, whereas Pt/H–LTL has significantly larger particles. The changes in whiteline intensity observed for these catalysts that are all reduced at 300°C, are much smaller than the changes in whiteline intensity for the Pt/K–LTL catalyst reduced at 300, 450, and 600°C. This suggests that the interfacial hydrogen which is present in the catalysts reduced at low temperature is the most important factor determining the whiteline intensity.

As the interfacial hydrogen contribution to the electron density has been kept constant for the samples reduced at 300°C we can use them to look for particle size or support effects on the whiteline intensity. Although the range of particle size for these catalysts is the same as for the Pt/K–LTL catalysts reduced at different temperatures, there is no clear decrease in whiteline intensity with particle size. Platinum particles on acidic supports like alumina and acidic zeolites are considered to be electron deficient compared to platinum particles on inert or basic supports like silica or K–LTL. In this study we observe a smaller electron density on platinum atoms supported by the inert K–LTL than on platinum atoms supported by the acidic supports. We propose that the platinum particles are shielded by the interfacial hydrogen from the electron donating or electron withdrawing capacity of the support.

Conclusion

We have shown that the whiteline intensity of small platinum particles is mainly determined by the structure of the metal-support interface. After reduction at 300°C when interfacial hydrogen is present in the metal-support interface the whiteline intensity is the highest. Increasing the reduction temperature which is accompanied by irreversible removal of interfacial hydrogen results in a decrease in whiteline intensity. The acidity of the support and the particle size are less important factors in determining whiteline intensity.

Acknowledgement

We thank the staff at the SRS for help during the measurements. M. V. and D. C. K. are indebted to NWO for providing travel funds and measuring time at the SRS.

References

1. M. Che and C. O. Bennett; Adv. Catal. **36** (1988) 55.
2. F. W. Lytle, P. S. P. Wei, R. B. Greegor, G. H. Via and J. H. Sinfelt; J. Chem. Phys. **70** (1979) 4849.
3. F. W. Lytle, R. B. Greegor, E. C. Marques, V. A. Biebesheimer, D. R. Sandstrom, J. A. Horsley, G. H. Via and J. H. Sinfelt; ACS Symp. Ser. **288** (1985) 280.
4. M. G. Samant and M. Boudart; J. Phys. Chem. **95** (1991) 4070.
5. A. N. Mansour, J. W. Cook Jr, D. E. Sayers, R. J. Emrich and J. R. Katzer; J. Catal. **89** (1984) 462.
6. W. Ravenek, A. P. J. Jansen and R. A. van Santen; J. Phys. Chem. **93** (1989) 6445 .
7. F. W. H. Kampers, T. M. J. Maas, J. van Grondelle, P. Brinkgreve and D. C. Koningsberger; Rev. Sci. Instr. **60** (1989) 2635.
8. J. W. Cook Jr., and D. E. Sayers; J. Appl. Phys. **52** (1981) 5024.
9. A. N. Mansour, J. W. Cook Jr., and D. E. Sayers; J. Phys. Chem. **88** (1984) 2330.
10. M. Vaarkamp, J. van Grondelle, R. A. van Santen, J. T. Miller, F. S. Modica, G. S. Lane and D. C. Koningsberger; *Proceedings of the 9th International Zeolite Conference, Montreal, July 5-10, 1992*, (Butterworth-Heinemann, London, in print).