

THE RELATION BETWEEN CATALYTIC AND ELECTRONIC PROPERTIES OF SUPPORTED PLATINUM CATALYSTS: THE LOCAL DENSITY OF STATES AS DETERMINED BY X-RAY ABSORPTION SPECTROSCOPY

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Abstract

The intensity of the white line of the L_{II} and L_{III} X-ray absorption edge spectra of small platinum particles increases with decreasing particle size. The combined white line intensity of the L_{II} and L_{III} X-ray absorption spectra for platinum catalysts with comparable average particle size is higher when dispersed on acidic than on neutral supports. This indicates that platinum particles are more electron deficient on acidic than on neutral supports. The propane hydrogenolysis TOF for platinum supported on γ -Al₂O₃ or H-LTL is found to be more than an order of magnitude higher than for platinum supported on a non-acidic K-LTL zeolite. The differences in catalytic behavior are related to differences in the d-band density of states.

1. INTRODUCTION

Electronic properties of highly dispersed metal particles are thought to be affected by support and/or promoter ions [1]. Charge transfer or polarization at the metal-support or metal-promoter interface may change the d-band density of states leading to different catalytic properties.

Information about the d-band density of states in transition metal clusters can be obtained from the white line intensities of the L_{II} (transition from 2p_{1/2} to 5d_{3/2}) and L_{III} (transition from 2p_{3/2} to 5d_{5/2} and 5d_{3/2}) X-ray absorption edges. A basic theory of white lines has been given by Mott [2], Brown et al. [3] and Mattheiss and Dietz [4]. The theoretical calculations of the unoccupied Pt d-states show that the J=5/2 final state is predominant. Brown et al. [3] showed that the J=5/2 states contribute about 14 times more to the final d-states than the J=3/2 states. Mattheiss and Dietz [4] calculated that the ratio of the unoccupied states ($h_{5/2}/h_{3/2}$)

ranges from 3.5 within 0.5 eV of the Fermi level to 2.9 over the entire unoccupied conduction band. These calculations explain why the intensity of the white line of the L_{III} X-ray absorption edge is much higher than the intensity of the L_{II} edge in bulk platinum.

Several authors have used the L_{III} X-ray absorption edge spectra to characterize the chemical state of the absorbing atom in transition metal compounds. Lytle et al. [5,6] have shown for iridium, platinum, and gold that the intensity of the white line of the L_{III} X-ray absorption edge is proportional to the d-electron vacancies. Also, changes in the L_{III} white line intensity of the X-ray absorption spectrum for Pt/SiO₂ have been related to alterations in the d-band density of states resulting from a metal-support interaction at high reduction temperatures [7]. Gallezot et al. [8,9] reported that platinum clusters in Ce-promoted NaY zeolite have a larger number of d-holes than platinum in NaY zeolite.

While the support and promoter ions do affect the white line intensity, the metal particle size is also important. Gallezot et al. [8,9] reported that the white line intensity of the L_{III} edge of 1-nm Pt clusters in Pt/NaY is larger than 3-nm clusters. Mansour et al. [10] carried out a more quantitative study including the white line of the L_{II} absorption edge for Pt/SiO₂ with an average particle size of 15 Å (72 atoms) and determined that there were 14% more d-holes than in bulk platinum metal. For a series of Pt/SiO₂ catalysts with increasing particle size (with first shell EXAFS coordination numbers of $N=6.6$ and larger), the combined white line intensity of the L_{II} and L_{III} edge increased as the platinum particle size decreased [11].

Here we present the results of a study of the white lines of the L_{II} and L_{III} X-ray absorption edges for a series of platinum catalysts supported on γ -Al₂O₃, H-LTL and K-LTL zeolites. It will be shown that also for very small platinum clusters ($N=3.9$ to 4.9) in the Pt/K-LTL catalyst, the white lines of both the L_{II} and L_{III} edges are strongly influenced by particle size. After accounting for the particle size, platinum on acidic supports (γ -Al₂O₃ and H-LTL) is more electron deficient than on non-acidic supports (K-LTL). In addition, propane hydrogenolysis has been used as a catalytic reaction to investigate the influence of the changes in the d-band density of states due to support and/or promoter ions on the catalytic properties of the platinum particles.

2. EXPERIMENTAL

2.1. Catalyst Preparation

A 1.0 wt% Pt/ γ -Al₂O₃ catalyst (200 m²/g, 0.6 cm³/g) was prepared by impregnation with an aqueous solution of H₂PtCl₆. The catalyst was dried in air at 120°C, and reduced (heating rate 5°C/min) at 450°C for 4 hr, followed by passivation in air at RT.

K-LTL was obtained from Linde. Excess alkali was reduced by water wash until the pH of the wash solution was 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 NH₄NO₃ exchange of K-LTL followed by calcination at 500°C. The Pt was loaded (1.2 wt% Pt/K-LTL and 1.0 wt% Pt/H-LTL) by impregnation using tetraammine platinum (II) nitrate followed by drying at 120°C.

2.2. Propane Hydrogenolysis Reactions

The conversion of propane was conducted at 400°C and atmospheric pressure in a fixed-bed, bench-scale reactor using 3.78 vol% propane in H₂. The catalysts were prereduced at 450°C or 600°C, and the conversion was adjusted to between 2 to 10% by changing the propane space velocity. Turnover frequency (TOF) was determined using hydrogen chemisorption as a measure of the active platinum surface.

2.3. X-ray Absorption Experiments

X-ray Absorption experiments were carried out at the Synchrotron Radiation Source in Daresbury, U.K., Wiggler Station 9.2, using a Si (220) double crystal monochromator. At the Pt L_{III} edge (11564 eV), the estimated resolution was 3 eV. The monochromator was detuned to 50% intensity to avoid the effects of higher harmonics present in the X-ray beam. The measurements were done in the transmission mode. 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 2nd and the 3rd ionchamber. The data of the foil were used to calibrate the energy axis of the x-ray absorption data of the catalysts. Self-supporting wafers were reduced in a controlled-atmosphere cell [12]. The X-ray absorption data were obtained at liquid nitrogen temperature in the presence of H₂.

The Pt/γ-Al₂O₃ samples were rereduced at 300 and 450°C and are designated as Al(300) and Al(450), respectively. Similarly, Pt/K-LTL samples were reduced at 300 or 450°C and are designated as K-LTL(300) and K-LTL(450). K-LTL(600), which had been prereduced at 600°C, was rereduced in the cell at 450°C (the temperature limit of the EXAFS cell). Pt/H-LTL was reduced at 450°C, and is designated H-LTL(450).

3. RESULTS

3.1. Structural Characterization

Detailed structural characterizations of the catalysts by TPR, H₂ TPD, hydrogen chemisorption, and EXAFS are reported elsewhere for Pt/γ-Al₂O₃ [13], Pt/H-LTL [14] and Pt/K-LTL [15]. The EXAFS first-shell coordination numbers, which are important for an evaluation of the white line results are given in the Table 1.

3.2. Propane Hydrogenolysis

For each of the catalysts, hydrogenolysis of propane yielded methane and ethane in equal molar amounts. The catalytic turnover frequencies are given in the Table. For the Pt/K-LTL and Pt/γ-Al₂O₃ catalysts, there was little deactivation. The Pt/H-LTL catalyst, however, deactivated more rapidly, and conversion is reported at 10 minutes on stream and extrapolated to zero time on stream.

The catalytic activities fall into two groups, predominantly determined by the

Table 1
EXAFS coordination numbers and propane hydrogenolysis activity

Samples	Coordination number	Hydrogenolysis TOF ^(a)
K-LTL(300)	3.9	-
K-LTL(450)	4.4	0.063
K-LTL(600)	4.9	0.022
H-LTL(450)	5.4	0.53 ^(b) 0.40 ^(c)
AL(300)	4.7	-
AL(450)	5.6	0.62

^(a) 400°C and 1 atm, TOF (molecules/s/surface Pt).

^(b) Initial TOF extrapolated to zero time on stream.

^(c) TOF at 10 min on stream.

acidity of the support. The TOFs for platinum on acidic supports, e.g. H-LTL(450) and Al(450), were more than an order of magnitude higher than on the non-acidic support, e.g. K-LTL(450) and K-LTL(600). Of the acidic supports, platinum on chlorided alumina was more active.

3.3. White Line Spectra of Pt L_{II} and L_{III} X-ray Absorption Edges

A preedge background was subtracted over the entire range of data for both the L_{II} and L_{III} edges to remove the contribution of all other absorbers to the X-ray absorption spectrum [10]. This isolates the partial cross section being studied. To ensure that the X-ray absorption edge being studied was well separated from the background, the region used for fitting the preedge was extended from 200 to 80 eV below the X-ray absorption edge. The position of the absorption edge (Fermi energy) was defined as the inflection point of the spectrum. The energy scale for the absorption data was defined as the energy above this inflection point ($E - E_{\text{edge}}$).

In order to obtain an atomic cross section, the data were normalized by dividing the absorption intensity by the step height of the absorption edge. To do this, the fit of the preedge was extrapolated into the post-edge region. The postedge (EXAFS) region was smoothed by a cubic spline fit of the background and the step height was defined as the intensity difference between this background in the postedge region and the extrapolated preedge, determined at the normalization energy. The L_{II} edge was normalized at 58 eV and the L_{III} edge at 50 eV. This procedure guarantees a systematic approach with a normalization which is independent of the shape of the white line [8].

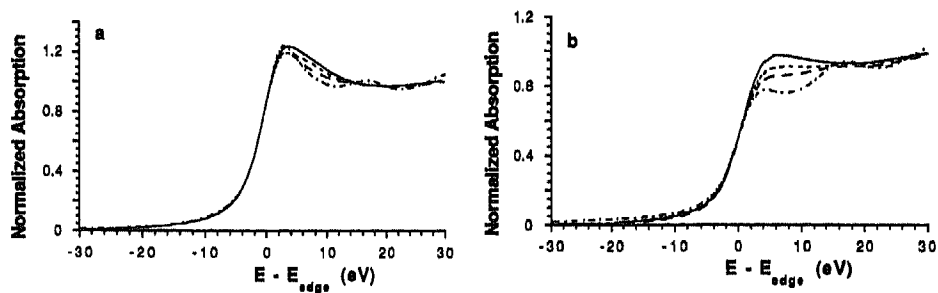


Figure 1. (a) L_{III} en (b) L_{II} x-ray absorption edge of Pt-foil (----), K-LTL(300) (—)K-LTL(450) (---) and K-LTL(600) (- - -).

Figure 1 shows the X-ray absorption data of the L_{III} (Figure 1a) and the L_{II} (Figure 1b) edge of platinum foil, K-LTL(300), K-LTL(450), and K-LTL(600). The white line intensities of both the L_{II} and the L_{III} edge decrease with increasing platinum particle size (or increasing reduction temperature).

Since the white line intensity is particle size dependent, the influence of the interaction of the platinum with the support and/or promoter ions on the white line intensity can be properly evaluated only when the particle size is taken into account. For example, despite the larger particle size for Al(300) ($N=4.7$), the white line intensity of both the L_{II} and the L_{III} edge is higher than for K-LTL(450) ($N=4.4$) (Figure 2). This indicates that the platinum in Al(300) is more electron deficient than in K-LTL(450).

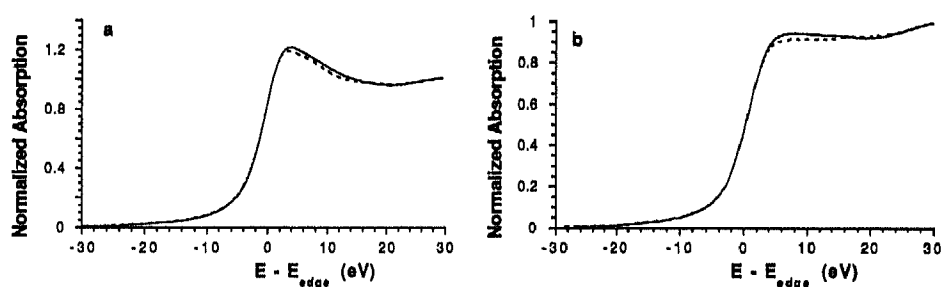


Figure 2. (a) L_{III} en (b) L_{II} x-ray absorption edge of Al(300) (—) en K-LTL(450) (---).

The X-ray absorption spectra for Al(450), H-LTL(450) and K-LTL(600) are shown in Figure 3. Since the Al(450) and H-LTL(450) have about the same particle size, the higher white line intensity of the Al(450) indicates greater electron deficiency than the H-LTL(450). On the other hand, in spite of the smaller platinum particle size in K-LTL(600), the white line intensity is still slightly larger than for H-LTL(450). Thus, after accounting for the effect of particle size, H-LTL(450) is shown to be more electron deficient than K-LTL(600).

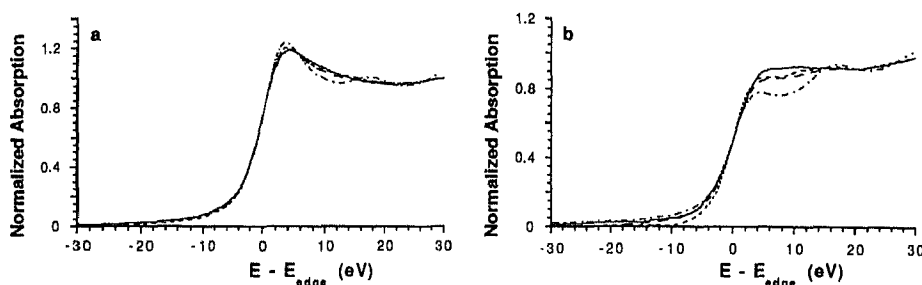


Figure 3. (a) L_{III} en (b) L_{II} x-ray absorption edge of Pt-foil (---), K-LTL(600) (— · —), H-LTL(450) (----) and Al(450) (—).

4. DISCUSSION

As pointed out by Pease [16] and Mansour [10], the white line can be described as a superposition of an arctangent function (representing the atomic cross section for X-ray absorption) and a Lorentzian distribution function (representing the $2p \rightarrow 5d$ electronic transitions). The absorption edge can be lowered below the Fermi energy, particularly if a white line is broadened by the resolution function of the spectrometer or due to lifetime effects of the excited states. The amount of lowering of the absorption edge increases with these broadening effects and the strength of the white line. As shown in Figure 1, the white lines of both the L_{II} and L_{III} edges are strongly dependent on the particle size. The width and the intensity (determined by the area) of both white lines increases with decreasing particle size. Since the degeneracy for the $2p_{3/2}$ state is twice that for the $2p_{1/2}$ state, the intensity of the L_{II} edge should be counted twice in determining the total d-hole density. Comparison of Figure 1a with 1b clearly shows that the intensity and shape of the L_{II} edge is more strongly influenced by the particle size than the intensity of the L_{III} edge, indicating that the final states with $J=3/2$ are more sensitive to the particle size than the $J=5/2$ states. Also apparent in Figure 1a and 1b, is that the onset of the L_{II} and L_{III} absorption edge of both catalysts originates at higher energy than for bulk platinum metal indicating that the small platinum particles are electron deficient compared to bulk platinum metal.

These results on Pt/K-LTL confirm the earlier results for Pt/SiO₂ that the white line intensity increases with decreasing particle size [11]. This may lead to the suggestion that small transition metal particles are more electron deficient than bulk metal. However, Hartree-Fock-Slater LCAO calculations on small copper particles [17] have clearly demonstrated that the Cu-Cu distance becomes shorter than in bulk metal. This is due to a decreased degree of delocalization (more electron density between the metal atoms) since metal atoms in small metal particles have, on average, fewer neighboring atoms than in bulk metal. An increase in the d-band density of states of surface atoms due to the same effect has been discussed by Cyrot-Lackman et al. [18] and Saillard et al. [19]. The decreased d-valence electron bandwidth for surface atoms leads to an increase of the d-valence electron band filling. These studies predict that small transition metal particles have a higher electron density than bulk metal, which is in contradiction with the interpretation above for the results of the white line. The apparent contradiction has been solved by a recent theoretical study of Ravenek et al. on Ir₄ and Ir₁₀ clusters [20]. Hartree-Fock-Slater LCAO calculations, indeed, indicate a higher number of d-electrons for the Ir₄ cluster in comparison to Ir₁₀. However, introduction of a core hole, to mimic the X-ray absorption process, into the calculations results in a lower number of d-electrons for the Ir₄⁺ compared to the Ir₁₀⁺ cluster. The higher electron deficiency for the smaller cluster, as suggested by the larger white line intensity, for example, is actually due to a less efficient screening of the core hole induced by the absorption of the X-ray photon in smaller clusters. The electron density of the neutral metal particle, however, is higher for the smaller particle in contrast to the white line results.

In order to determine the influence of the support and/or promoter ions on the d-band density of states, one must first account for the contribution to the white line resulting from differences in particle size. In Figure 2 the white lines are compared for Al(300) and K-LTL(450), i.e., platinum dispersed on an acidic and non-acidic support. In addition to the differences in the support composition, the platinum particles are larger on the alumina catalyst. Inspection of Figure 2 clearly indicates that the d-band density of states does depend on the type of support. If the platinum particles had been of identical size, the differences in the white line intensity would have been even larger. Nevertheless, it can be concluded that the platinum particles supported on γ -Al₂O₃ are more electron deficient than those dispersed in K-LTL zeolite. For this comparison, however, it is not possible to separate the influence of the potassium ion, i.e., a base promoter, from the effect of the support composition on the d-band density of states.

In Figure 3, the L_{II} and L_{III} white line intensities are shown for Al(450), H-LTL(450) and K-LTL(600). The total white line intensity (L_{II} plus L_{III}) of the acidic Al(450), coordination number 5.6, is higher than for H-LTL(450), coordination number 5.4. Although both supports are acidic, the platinum in the Al(450) is clearly more electron deficient than in H-LTL(450). Without accounting for the particle size, the white line intensity for H-LTL(450) and K-LTL(600) would suggest a slightly larger or similar electron deficiency. However, the platinum particles are smaller in K-LTL(600) than in H-LTL(450), N = 4.9 and 5.4, respectively. Since the white line intensity decreases with increasing particle size,

a H-LTL(450) catalyst with $N=5.4$ would have a lower white line intensity than K-LTL(600). Therefore, after accounting for particle size effects, the platinum in H-LTL(450) is seen to be more electron deficient than K-LTL(600).

The propane hydrogenolysis TOF was determined for K-LTL(450), K-LTL(600), H-LTL(450) and Al(450) and increased in the order K-LTL < H-LTL < Al. As previously observed for hydrogenolysis of neopentane [21,22] and ethane [23], the propane TOF is higher for platinum on acidic supports, i.e., γ -Al₂O₃ and H-LTL. In each of the previous studies, the increase in activity has been attributed to electron-deficient platinum. The electron deficient nature of the platinum was thought to be an intrinsic property of the small metal particles [23] or the result of donation of platinum electron density to the support [21,22]. In a recent study, Samant and Boudart investigated the electron deficiency of platinum in a series of Pt/Y catalysts of similar platinum particle size by several techniques, including XANES [24]. They concluded that all of the observations ascribed to electron deficiency were the result of the intrinsic properties of the very small platinum particles which form on acidic supports. If the electron deficiency is only the result of the small particle size, then the smallest platinum particles would have the highest hydrogenolysis activity. In this study, the most active catalysts for hydrogenolysis of propane, e.g., the acidic supported catalysts, have the largest particle size. Furthermore, after accounting for the differences in particle size, we determine that the platinum on the acidic supports is more electron deficient as judged by the combined white line intensity. We conclude, therefore, that the support acidity and/or promoter ions do affect the d-band density of states, and that these perturbations in the electronic structure affect the catalytic activity, at least, for hydrogenolysis.

In [13] we show that the nature of the metal-support interface in Pt/K-LTL changes with increasing reduction temperature. Table 1 shows that the propane hydrogenolysis activity decreases by a factor 3 by changing the reduction temperature from 450°C at 600°C. A more systematic study of the white line intensity is needed before the influence of the nature of the metal-support interface can be distinguished from that of promoter ions. The presence of chemisorbed hydrogen also influences the intensity of the white line [7] and this influence should be evaluated as well.

5. CONCLUSIONS

The white line intensity of both the platinum L_{II} and L_{III} X-ray absorption edges increase with decreasing particle size. The changes in the intensity are much larger for the L_{II} edge. This means that the intensity of the L_{II} edge whiteline must be taken into account before any conclusion can be drawn about changes in d-band density of states. After correcting for the differences in particle size, platinum on acidic supports is more electron deficient than on non-acidic supports. The electron deficiency of the platinum increased in the same order as the activity for propane hydrogenolysis. Changes in support acidity and/or promoter ions alters the platinum d-band density of states, affecting the reactivity for hydrogenolysis reactions.

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DISCUSSION**Q:** T. Uematsu (Japan)

Surface activity or reactivity is strongly dependent on the particle size. You have demonstrated the charge transfer and metal-support interaction by EXAFS. The interaction was controlled by the platinum particle size. However, such interaction would be also influenced by the activities of supporting oxides. In this view, the effects of particle sizes of the support must be taken into account, especially for metal clusters (superfine particles) supported on fine particle of supporting metal oxides. What is your opinion ?

A: D. C. Koningsberger

The total white-line intensity of supported small metal particles is in my opinion determined by metal (i) particle size/shape, (ii) type of adsorbate, (iii) type of support and (iv) structure of metal-support interface. The influence of the support is most probably due to a charge transfer from or to the metal particle. However, there is still no conclusive experimental evidence for this. I do not see how the particle size of the oxide support can influence the d-band density of states of the supported metal particles, as you suggest. There is may be an indirect effect, the support particle size may influence the size/shape of the metal particles, which in turn influence the white-line intensity of the supported metal particles.

Q: G. L. Haller (USA)

Because the effects you observed for both Pt L_{II} and L_{III} edges as a function of support acidity and or Pt particle size are changes in line width rather than intensity at the edge, this suggests you may be measuring changes in the 5d bond shape rather than charge transfer. Charge transfer can be measured quantitatively by measuring shifts in the absorption edge (relations to the simultaneously measured edge of a Pt foil references). How did you look at your edge shifts and are they consistent with the charge transfer interpretation ?

A: D. C. Koningsberger

The shape of both the L_{II} and the L_{III} white-line is indeed changing as a function of particle size and type of support. However, we have determined also the total white-line area of both the L_{II} and the L_{III} edge and the total white-line intensity is showing the results which we discussed in the paper. We have not yet measured enough accurate edge position data to relate changes in white-line intensity to changes in edge position.

Q: V. Haensel (USA)

Particle size depends to a large extent on treatment following impregnation. For example, with a γ -alumina support the treatment with air following impregnation (at up to 500 °C) and subsequent reduction with H₂ produces highly dispersed catalyst particles while H₂ treatment only produces larger catalyst particles and lower catalyst activity.

A: D. C. Koningsberger

I fully agree that particle size depends on the treatment following impregnation. We have found that also direct reduction in hydrogen using a very small temperature ramp (5 K/min) leads to very stable highly active small metal particles.

Q: K. Klier (USA)

Do you have data that could be quantitatively evaluated as to the amount of charge transferred upon chemisorption of "electron accepting" adsorbates, e.g. oxygen, hydrogen and chlorine? Does the L_{II} intensity change correlate with electronegativity of these adsorbates ?

A: D. C. Koningsberger

We do not have yet enough data to correlate the electronegativity of different adsorbates with changes in white-line intensities. We do have found that desorption of chemisorbed hydrogen leads to a decrease in white-line intensity, showing that the chemisorption of hydrogen withdraw electrons from platinum.

Q: A. Renouprez (France)

The normalization, subtraction procedure is known to be a critical step in absorption edge data treatment. Did you try to interpret your results using the $L_{III} - k \times L_{II}$ method or $L_{III}(\text{foil}) - L_{III}(\text{sample})$? Do you not think that the larger L_{II} modifications compared to L_{III} (also observed in alloys) could be better interpreted in terms of spd-hybridization or d-rearrangements rather than pure charge transfer?

A: D. C. Koningsberger

We do have subtracted the white-line data of the samples from the corresponding white-line of the platinum foil to establish the change in white-line intensity. As demonstrated in the paper the spd rehybridization (as we believe to be the origin of the particle size effect on the white-line) is separated from the effect of the support by trying to compare catalysts with the same average metal particle size.

Q: R. W. Joyner (United Kingdom)

In interpreting small changes in X-ray white lines it is important to recall the lessons from XPS studies of small particles. XPS binding energy shifts are observed, but are now considered largely to be caused by final state relaxation effects.

You are careful to limit and define the ways your comparison are made. However, even if two catalysts have the same average (nearest neighbor coordination number, then size distribution and shape may vary. Thus, even when carefully controlled, white line charges may reflect final state effects rather than electron transfer to or from the support.

A: D. C. Koningsberger

The white-line intensity is most probably determined by final state effects, which means that the white-line is sensitive to the averaged particle size and shape of the metal particles. We have not yet fully established how large this effect is. We have tried in the paper to correct for the particle size effect by trying to compare catalyst with the same averaged particle size. We do not believe that the shape of the platinum particles in H-L and K-L for these small clusters is different. More research is needed before the influence of the shape of the metal particles on the white-line intensity is determined.

Q: R. Prins (Switzerland)

The largest change in white line intensity is observed in the L_{II} edge. However, this line is due to the $2p_{1/2} \rightarrow 5d_{3/2}$ transition, and since the $5d_{3/2}$ band should be completely filled, actually the intensity of the L_{II} line should be very small. Changes in the L_{II} intensity are then induced by mixing of the $d_{3/2}$ and $d_{5/2}$ bands and this will be very sensitive to the Fermi surface, and thus to metal particle size, shape and metal atom packing. Since most of the change in white line intensity is seen in the L_{II} edge, the total white line intensity change is very sensitive to several factors. If that is true, is there then any hope to use the white line intensity and say something about particle size and charge?

A: D. C. Koningsberger

As already mentioned in my answer to the question made by T. Uematsu I agree that the total white-line intensity is determined by several factors: (i) particle size/shape, (ii) type of adsorbate, (iii) type of support and (iv) structure of metal-support interface. It must be possible to separate support effects from other effects by careful elimination; for

instance by studying metal particles with the same average size reduced at the same temperature (i.e. same metal-support interface) covered with (and without) the same adsorbate.

Q: E. Iglesia (USA)

I concur fully with your experimental observation that the rates of propane reactions increase with increasing acidity of the support. We have observed similar increases in the bifunctional hydrocracking of higher alkanes with increasing support acidity. I disagree, however, with:

- 1) your description of the process as hydrogenolysis on Pt clusters and
- 2) your explanation of the phenomenon as one arising from differences in the electronic properties of Pt clusters.

The process is likely to occur by a bifunctional mechanism where the rate-limiting step is the reaction of equilibrium concentrations of propene on acid sites. Therefore, your choice of Pt sites for turnover calculations is the predominant reason for the apparent turnover rate changes. Would you comment on my disagreement? Have you measured the rates of propene cracking on your catalyst supports ?

A: D. C. Koningsberger

While bifunctional hydrocracking of higher alkanes is well known, we do not believe that the enhanced activity for propane conversion we observe for Pt on acidic supports is the result of a bifunctional reaction path. Monomolecular cracking of propene is not possible since neither α -hydrogen elimination from a secondary carbenium ion, nor β -hydrogen elimination can lead to the formation of stable products. Bimolecular reaction of propene (i.e. oligomerization followed by cracking) does not yield methane and, additionally, yields C_3^+ products, which were not observed. Since the reaction products are methane and ethane in a molar ratio of 1:1, the bifunctional reaction pathway can be ruled out.