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Maximum hydrogen chemisorption on KL zeolite supported Pt clusters

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5 Platinum clusters supported on KL zeolite were characterized by EPR, HRTEM, and EXAFS. Two kinds of hydrogen chemisorption experiments both result in a saturation value of 2.9 hydrogen atoms per platinum atom, significantly more than so far reported. A hydrogen coverage-dependent cluster restructuring is suggested.

Small noble metal clusters dispersed in zeolites are highly active catalysts for important petrochemical reactions like hydrogenation, naphtha reforming and isomerization. They were therefore extensively investigated by experimental and theoretical methods. Hydrogen chemisorption is often used to determine the dispersion, defined as the fraction of surface atoms of Pt catalyst particles. Thereby it is generally assumed that one surface atom chemisorbs only a single hydrogen atom, as in Figure 1a, although Cho *et al.* reported a value of 1.9±0.2 for H/Pt of small KL zeolite supported Pt clusters with a Pt–Pt coordination number (CN) around 4, independent of the Pt content.¹ Ji *et al.* showed that the hydrogen coverage of supported Pt particles with CN(Pt–Pt) around 6.5 depends strongly on the support ionicity and recommended to be cautious in interpreting H₂ chemisorption only in terms of Pt dispersion. Their experiments demonstrated a clearly decreasing trend of the H/Pt value with decreasing electron richness of the support oxygen atoms: 1.63 (Pt/NaY) > 1.55 (Pt/MgY) > 1.21 (Pt/LaY) > 0.88 (Pt/H-USY).²

10 In their theoretical work of unsupported Pt₁₃ clusters Chen *et al.* reported a phase transition from icosahedral to fcc morphology depending on hydrogen coverage.³ MD simulations and bond distance distribution analysis indicated that the hydrogen saturation point of free Pt₁₃ is reached at 44 chemisorbed hydrogen atoms, resulting in a value near 3.4 for H/Pt. 36 hydrogen atoms can chemisorb at the edge and corner sites of the fcc Pt₁₃ cluster surface. Additional H atoms were predicted to penetrate into the cluster and interact with the core Pt atom.³ Recent DFT calculations for γ -Al₂O₃ supported Pt₁₃ predict a reconstruction from a biplanar morphology on the support to a cuboctahedral structure at a coverage near 18 H per cluster and a maximum coverage of 3 H/Pt.⁴ Chemisorption sites on icosahedral Pt₁₃ clusters are shown in Figure 1. The preferential adsorption site on a Pt(111) single crystal surface is the three-fold hollow site,⁵ but for a cuboctahedral cluster it is predicted to be preferentially the bridge site followed by the on-top site.⁴

50 **Figure 1** Hydrogen chemisorption on icosahedral Pt₁₃ cluster on-top Pt (a, 12 sites), in three-fold holes (b, 20 sites) and edge-bridging (c, 30 sites).

Pt clusters were prepared from KL zeolite (Chemie Uetikon AG (CU) in Switzerland), and iron-free KL (Süd Chemie AG (SC)) by aqueous ion exchange with [Pt(NH₃)₄]Cl₂, leading to a Pt content of 5.3 wt% (CU) and 5.5 wt% (SC), and for both zeolites to a K/Al ratio of ~0.72, showing the extent of exchange with Pt. The samples were calcined in flowing O₂ and thereafter reduced in flowing H₂ following a procedure given in detail in the Electronic Supplementary Information (ESI).

X-Band EPR spectra were recorded at 4 K on a Bruker EMX spectrometer. The spin concentration of a Pt/KL sample was calibrated against a standard sample. EPR spectral simulation was done as described in previous work.⁶ An EPR spectrum obtained with partially hydrogen covered Pt clusters supported on KL(CU) zeolite is given in Figure S1 of the ESI. The multiplet represents a magic number Pt₁₃ cluster with 12 equivalent Pt atoms on the surface of an icosahedron or cuboctahedron, and one Pt nucleus in the center of the cluster possessing only a small spin density. The Pt₁₃ clusters are likely arranged within the zeolite pores, as confirmed elsewhere by means of ¹²⁹Xe NMR.¹ These hexagonally packed channels are the main structure element of the L zeolite containing K⁺ in the only exchangeable cation site at room temperature.⁷

HRTEM measurements using a JEOL JEM-4000FX electron microscope. An image of Pt particles dispersed in the zeolite is shown as Figure S2 of the ESI. The corresponding histogram of the size distribution reveals a cluster size near 1 nm.

EXAFS is the most reliable method to determine the average particle size of very small clusters. Experiments were conducted at the Pt L₃ edge at the beamline X1 of the HASYLAB synchrotron in Hamburg, Germany (for details see the ESI). EXAFS data for the two extreme states of the initial hydrogen reduced Pt/KL(CU) sample and for a fully hydrogen

desorbed Pt/KL(CU) sample are listed in Table 1 (for spectra see Figure S3 of the ESI). In both samples, a two shell model consisting of a Pt–O and a Pt–Pt contribution lead to the best approximation of the experimental data. The bond distances are in good agreement with the literature if size effects are taken into account.⁸ The value of 5.5 for CN(Pt–Pt) in case of the hydrogen reduced sample agrees very well with the expected value of 5.5 for an ideal cuboctahedron. Previously, (CN(Pt–Pt) = 5.4) was observed for a Pt/NaY sample.⁹

Table 1 EXAFS results for coordination number CN, backscatterer Bs, distance R, and Debye-Waller factor σ of Pt/KL(CU)

Sample	CN	R(Bs)/Å	$\sigma/10^{-3}\text{Å}^{-2}$
Hydrogen reduced	Pt-O 1.0 ± 0.1	2.60 ± 0.02	2 ± 0.2
	Pt-Pt 5.5 ± 0.6	2.70 ± 0.02	15 ± 1.5
Hydrogen desorbed	Pt-O 1.8 ± 0.1	2.52 ± 0.02	2 ± 0.2
	Pt-Pt 4.3 ± 0.6	2.59 ± 0.02	13 ± 1.3

The presence of a significant fraction of larger particles can be excluded as they would dominate the CN of the first Pt shell, leading to higher values.¹⁰ The presence of a Pt₁₃ cluster is also supported by the XANES spectra given in the ESI (Figure S4).¹¹ They exhibit a shift of the white line in comparison to bulk Pt by 2.2 and 2.6 eV for the hydrogen desorbed and reduced sample. According to Behafarid *et al.* this is in agreement with a cluster size <1 nm.¹² In comparison with this work, the larger shift of the white line is ascribed to adsorbed hydrogen.⁴ Ramaker *et al.* ascribed a similar edge shift as in the present work (ca. 2.6 eV) to support effects.¹³ However, on hydrogen desorption at 573 K, structural modifications are observed, as the Pt–Pt coordination number decreases by 20%, which is in agreement with the predicted coverage-dependent reconstruction of the cluster on an alumina support,⁴ and with a previous experimental observation.¹ Due to the higher interaction of the bare cluster with the support, it is likely that the clusters assume a structure that adapts to the elliptical shape of the cages in KL zeolite. The shortened Pt–O distance obtained by EXAFS analysis is compatible with this conclusion.

Figure 2 shows the EPR spectrum of a partially hydrogen covered Pt₁₃ cluster after hydrogen desorption at 423 K for 30 min (curve a). The small signals in the magnetic field range from 3250 to 3400 G arise from copper impurities and from the KL(SC) zeolite itself and are not in the focus of this work.

The EPR signal of Pt/KL(SC) where hydrogen was completely desorbed by heating the sample in a small oven at 573 K for 3 h under vacuum is given in Figure 2b. The splitting pattern of the Pt₁₃ cluster multiplet disappeared and a broad signal resulting from a different platinum species, perhaps the reconstructed bare cluster, appeared. On readsorption of hydrogen the multiplet reappeared with the same parameters, independent of coverage, but the intensity was not fully recovered, and for lower loadings it varied slightly over a period of days. In this context it is important to note that the EXAFS data represent all Pt in the sample and confirm the quantitative existence of small clusters. For EPR active Pt₁₃ clusters with spin $S = 1/2$, calibration against our standard reveals that less than 1% of the total number of Pt

Figure 2 EPR spectra of 5.5 wt% Pt/KL(SC) samples representing a partially hydrogen covered Pt₁₃ cluster multiplet (a), a fully hydrogen desorbed sample (b), Pt₁₃H₁₀ (c) and Pt₁₃H₃₈ (d) clusters after hydrogen readsorption at 540 mbar.

atoms in the sample contribute to the EPR multiplet, the remaining fraction is EPR silent. It was concluded previously for Pt/NaY that 15–20% of the Pt is in a high spin state and the major fraction is diamagnetic.¹⁴

The desorption of initially hydrogen reduced Pt clusters at gentle temperatures between approximately 393 K and 423 K for ~30 min first always results in a rising EPR intensity of the cluster multiplet, which must mean that formerly EPR-silent clusters become visible during gentle desorption and change of the coverage.¹⁵ This is one of several indications which let us conclude that the EPR visible Pt₁₃ clusters are in equilibrium with an EPR invisible reservoir of similar clusters. Even though the clusters have a narrow size distribution or consist of the same number of atoms their environment can be different, e.g. because of the inhomogeneous distribution of Al sites. Detailed information about hydrogen exchange, desorption and readsorption mechanism including chemisorption sites will be given in further work.

The EPR results suggest a reconstruction between the initial reduced cluster which is hydrogen saturated at 1 bar, and the gently desorbed but still hydrogen covered Pt₁₃ cluster states as predicted from theoretical calculations.^{3,4} Such an effect was not observed by Liu *et al.* for the Pt₁₃ clusters supported on NaY(CU) zeolite,¹⁶ which may indicate that less hydrogen can chemisorb on Pt clusters in NaY (Si/Al = 2.3) versus KL (Si/Al = 3.0) zeolite due to its lower support ionicity and different cation.² Alternatively, the shape of the zeolite cage may also play the structure-directing role.

The fully desorbed state (2b) is the starting point of the quantitative readsorption experiments which were carried out by sequentially adding known aliquotes of hydrogen and monitoring pressure equilibration, supported by EPR. Addition of the first aliquote leads to the reappearance of the Pt₁₃ multiplet pattern with small amplitude and to an increase of the signal of the other Pt species, as shown in Figure 4c. Adding further aliquotes results in increasing intensity of the multiplet and in a decrease in the signal intensity of the second Pt species (Figure 2d). The equilibrium pressure

reading after addition of the last aliquote was 540 mbar. At this point the accumulated amount of adsorbed hydrogen corresponded to 2.9 H/Pt, a key information that is independent of cluster structure. If a fraction of Pt atoms is inaccessible, as the center atom in cuboctahedral or icosahedral clusters, the number of H atoms per accessible surface Pt atoms would exceed the value of 2.9. This “manual” adsorption experiment is time-consuming, the endpoint not so well defined, and there is no distinction between chemisorption and physisorption.

A much better alternative are automated measurements of hydrogen adsorption isotherms using a Micromeritics ASAP 2000 apparatus. For a full hydrogen desorption after initial reduction the 5.3 wt% Pt/KL(CU) sample was evacuated at 623 K for 3 h (50 K higher than in the previous chemisorption experiment). The 308 K isotherms are shown in Figure 3. In agreement with common practise measuring two isotherms with evacuation in between allows distinguishing chemisorption from physisorption. The difference curve in Figure 3 is nearly pressure independent. It represents chemisorption and gives a H/Pt saturation value of 2.90, in good agreement with the value of 2.9 obtained from the manual chemisorption experiment described above. A value of 2.9 H/Pt corresponds to 38 chemisorbed H atoms per Pt₁₃ cluster. This number cannot bind at a single type of sites. Icosahedral clusters could accommodate 32 atoms if all on-top and hollow sites were filled, 42 for all edge and on-top sites, or 50 for all edge and hollow sites. Cuboctahedral (fcc) type clusters can fit 36 atoms if all 24 edge and 12 on-top sites are filled.³ No steps were detectable in the adsorption isotherms which would indicate a phase transition or a change of site filling, which means that the sites are of similar binding energy and the potential for surface diffusion is quite flat, in agreement with calculations.³

Figure 3 Hydrogen isotherm for the total amount of adsorbed hydrogen (squares). Subtraction of the isotherm for physisorbed hydrogen (triangles) results in the amount of chemisorbed hydrogen (circles).

In summary, we found perfect agreement in a H/Pt ratio of 2.9 (plateau value) for two different hydrogen chemisorption experiments on Pt clusters supported in KL zeolites. This value also agrees well with recent theoretical predictions for the same clusters in somewhat different environment^{3,4} but

was hitherto never reported from experiments. Furthermore, also in line with predictions, the EXAFS data confirm a hydrogen coverage-dependent restructuring of the clusters, or perhaps to some extent a disintegration.

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Notes and references

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Electronic Supplementary Information

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Details of sample preparation:

KL zeolite was obtained from Chemie Uetikon AG (CU) in Switzerland, and in view of magnetization measurements an iron-free KL zeolite was obtained from Süd Chemie AG (SC) in Germany. The zeolites were calcined in air to burn off any residual organic impurities. To exchange any ions other than K⁺ 5 g KL zeolite were stirred in 125 ml of 1 M aqueous KCl solution at room temperature (RT) for 24 h. The zeolite was filtered off, washed with doubly distilled water to remove Cl⁻ ions, and dried in an oven at 353 K overnight. This step was repeated three times. Chemical analysis using ICP-OES resulted in Si/Al = 3.0 and K/Al = 0.98 for KL(CU) zeolite, and Si/Al = 2.8 and K/Al = 0.98 KL(SC) zeolite. Pt/KL zeolites were prepared by aqueous ion exchange with 3 mM solution of [Pt(NH₃)₄]Cl₂ (Aldrich) that was added dropwise to a flask containing a suspension of 1 g KL zeolite in 500 ml of water which was stirred for at least 3 days at 343 K. The exchanged zeolite was filtered, washed again with doubly distilled water, and dried overnight in an oven at 353 K. This procedure led to a Pt content of 5.3 wt% (CU) and 5.5 wt% (SC), and for both zeolites to a K/Al ratio of ~0.72, showing the extent of exchange with Pt. Calcination was carried out in flowing O₂ (120 ml min⁻¹) using a heating rate of 0.5 K min⁻¹ from RT to 623 K and holding this temperature for 5 h. After the sample had cooled to RT, residual O₂ in the reactor was purged with N₂. Reduction was then performed in flowing H₂ (80 ml min⁻¹) at a heating rate of 4 K min⁻¹ from RT to 503 K and keeping the sample at 503 K for 1 h. After the sample had cooled to RT in hydrogen atmosphere, the reactor was purged with N₂, and the samples were transferred to EPR tubes in a glove box under nitrogen atmosphere, and then evacuated.

X-Band EPR spectra were recorded on a Bruker EMX spectrometer with a microwave frequency and power of about 9.47 GHz and 1.01 mW at 4 K. The spin concentration of a Pt/KL sample was calibrated against a standard sample (ultramarine blue diluted by KCl).

Characterization by EPR:

60 **Figure S1** a) EPR spectrum of a partially hydrogen covered Pt₁₃ cluster supported on KL(CU) zeolite. b) Simulation using the parameters $g_{\perp} = 2.3528$, $g_{\parallel} = 2.3729$, Pt hyperfine splitting due to 12 equivalent nuclei with $A_{\perp} = 67.1$ G, $A_{\parallel} = 68.1$ G and an intrinsic (single-crystal) line width of 9 G.

65 The multiplet represents a platinum species since its g value is much larger than g_e of the free electron, as expected for unpaired electrons in a more than half-filled d-shell of simple transition metal centers.¹ Isotopically enriched Pt samples proved unambiguously that the splitting is due to Pt.²

Characterization by HRTEM:

75 **Figure S2** (a) HRTEM image of a 5.3 wt% Pt/KL(CU) sample showing the dispersion of the Pt particles (black dots) in the zeolite after initial hydrogen reduction. (b) Histogram of size distribution.

The particle sizes were measured from intensity profiles of a set of five images across their contrasts using Digital MicrographTM software. Only the contrasts of well isolated particles in thin specimen areas were measured in order to avoid artefacts due to clustering or projection effects. The mean value indicated in Figure 3b overestimates the true mean particle size, since the contrast of particles of 1 nm and smaller is too weak to be measured reliably. This manifests itself also in an asymmetry of the histogram. The weak contrast and blurred images result partly from the embedding of the small particles within the zeolite.

Details of the EXAFS experiment and data treatment:

EXAFS samples were stored in a glove-box with an atmosphere of H₂O <0.1 ppm and O₂ <0.1 ppm, and filled in a container gas tight up to 200 bar. No further treatment with H₂ prior to the measurements was carried out in order to avoid any changes on the reduced and desorbed samples. EXAFS and XANES measurements were performed at beamline X1 (HASYLAB, Hamburg). A Si(111) double crystal monochromator was used for measurements at the Pt L_{III} edge (11.564 keV). The second monochromator crystal was tilt for optimal harmonic rejection. The spectra were recorded in transmission mode with ionisation chambers filled with nitrogen and argon. The individual pressures were adjusted to optimize the signal to noise ratio. Energy calibration was performed with a platinum metal foil. To avoid mistakes in the XANES region due to small changes in the energy calibration between two measurements, all spectra were corrected to the edge position with a platinum foil, which was measured parallel to the samples between the second and third ionisation chamber.

Data evaluation started with background absorption removal from the experimental absorption spectrum by subtracting a Victoreen-type polynomial. Due to several turning points in the absorption edge, the threshold energy E_0 was determined consequently by taking the energy at half of the edge jump.^{3,4} To determine the smooth part of the spectrum, corrected for pre-edge absorption, a polynomial was used piecewise. It was adjusted in such a way that the low-R components of the resulting Fourier transform were minimal. After division of the background-subtracted spectrum by its smooth part, the photon energy was converted to photoelectron wave numbers k . The resulting $\chi(k)$ -function was weighted with k^3 and Fourier transformed using a Henning window function. Data analysis was performed in k -space on unfiltered data.

Fitting was performed using the familiar theoretical EXAFS expression

$$\chi(k) = \sum_j \frac{N_j}{k r_j^2} S_0^2(k) F_j(k) e^{-2k^2 \sigma_j^2} e^{-2r_j/\lambda} \sin[2kr_j + \delta_j(k)]$$

according to the curved wave formalism of the EXCURV98 program with XALPHA phase and amplitude functions.⁵ The mean free path of the scattered electrons was calculated from the imaginary part of the potential (VPI set to -4.00 eV). The same amplitude reduction factor as achieved in a previous study was used.⁶ An inner potential correction E_f was introduced when fitting experimental data with theoretical models that account for

an overall phase shift between the experimental and calculated spectra.

In the fitting procedure, care was taken that the number of fitted parameters (N_{pars}) did not exceed the degrees of freedom (N_{ind}) which are calculated according to $N_{\text{ind}} = (2\Delta k \Delta R / \pi)$.⁷ The applied ranges were $\Delta k = 15 - 4 \text{ \AA}^{-1} = 11 \text{ \AA}^{-1}$ and $\Delta R = 2.5 \text{ \AA}$. The quality of fit is given in terms of the R-factor according to⁸

$$R = \sum_i \frac{k^3 |\chi^{\text{exp}}(k_i) - \chi^{\text{theo}}(k_i)|}{k^3 |\chi^{\text{exp}}(k_i)|} \cdot 100\%$$

Experimental EXAFS data:

Figure S3 (Top) Experimental EXAFS functions (black) for the hydrogen desorbed sample (bottom) and hydrogen reduced sample (top) together with the corresponding fits (red). **(Bottom)** Corresponding Fourier transformed functions showing nicely the shift of the main peak.

In Figure S4, the XANES spectra of the hydrogen reduced and desorbed samples in comparison to bulk platinum are shown. According to Behafarid *et al.*,⁹ the rather large shift of the white line compared to bulk platinum is characteristic of very small clusters. Moreover, while in the hydrogen reduced sample the signature of icosahedral Pt₁₃ at around 11.575 keV is clearly

visible,¹⁰ it disappears for the hydrogen desorbed sample. Instead, considering the still apparent large shift compared to bulk Pt, the XANES spectrum is now characteristic of a flat cluster geometry.⁹ Again, as already pointed out in the main text, a significant fraction of larger clusters can be ruled out based on these results, since this would lead to a much smaller shift in the XANES spectra.

Figure S4 XANES spectra of the hydrogen reduced and desorbed samples in comparison to bulk platinum. The spectral signature of the Pt₁₃ cluster after the white line is highlighted.

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Graphical Abstract:

2.9 hydrogen atoms can adsorb per Pt atom on 13 atom Pt₅ nanoclusters.