**In situ XAS investigation of the formation of small Pt clusters in NaY zeolite and its degradation by CO**

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Small Pt$_{13}$ clusters in NaY zeolite are very reactive towards CO at room temperature. CO adsorption leads to a complete decomposition of the cluster and to the formation of new Pt$_2$(CO)$_m$ (m=4-5) species most probably stabilized by the zeolite walls. Small platinum metal clusters in NaY zeolite were prepared in situ and simultaneously the XAS spectra were recorded at the Pt L$_{III}$-edge. XAS investigation revealed the presence of Pt nano-clusters with average coordination number of 5.8. Subsequently, the hydrogen adsorbed platinum clusters were purged with argon gas and subjected to carbon monoxide treatment, also in situ. From the detailed EXAFS analysis, the degradation of nano-sized Pt clusters (under hydrogen atmosphere) into Pt$_2$(CO)$_m$ by CO was revealed.

The XAS measurements were carried out at beamline X1 of HASYLAB with a Si (111) double-crystal monochromator detuned to 65% of the incident intensity. Transmission mode spectra were measured using ionization chambers filled with argon gas. The oxygen calcined Pt/NaY sample was pressed into a pellet of 13 mm diameter and treated in a stainless-steel in situ cell with water-cooled Kapton windows, connected to a gas flow system. XAS scans at the Pt L$_{III}$-edge (11564 eV) were performed at room temperature after treating the sample in a 25 mL min$^{-1}$ flow of H$_2$ at 473 K for 1 hour, after argon gas flow at 50 mL min$^{-1}$ for 10 min, and after CO (1 bar) gas flow at 25 mL min$^{-1}$ for 20 min. The program AUTOBK implemented in the IFEFFIT program package was used for background correction, normalisation and background subtraction. The fit of the experimental data to the theory was obtained by adjustment of the common theoretical EXAFS expression according to the curved wave formalism of EXCURV98. The amplitude reduction factor was determined to be 0.8 in a previous work[1] and was fixed during the iteration procedure. When fitting experimental data with theoretical models an inner potential correction $E_f$ was included, that accounts for an overall phase shift between the experimental and the calculated spectra.

**XANES:** XANES spectra of the Pt metal foil, calcined Pt/NaY, reduced Pt/NaY, after subsequent Ar purging and CO adsorption on reduced Pt/NaY are given in Figure (see left). Both the shape and the intensity of the white line[2] in the XANES region are found to be completely different, although the absorption edge positions of the different Pt samples are similar to those of the reference metal foil. Compared to the metal foil, the calcined sample exhibits a relatively intense white line, which decreases in intensity upon reduction and further decreases upon Ar purging. Upon CO adsorption, there is a strong increase in the white line intensity. The white line in the L$_{III}$-edge of platinum reportedly corresponds to the electronic transition from the $2p_3/2$ to the $5d$ level[3] The reduction in the intensity and width of the white line upon Ar purging can be attributed to the partial desorption of adsorbed hydrogen. Increase in the white line upon CO adsorption, could be attributed to the decrease in electron density of the platinum centre due to bond formation with CO. Qualitatively, on moving from the metal foil to small Pt clusters in the zeolite with adsorbed H$_2$ or CO, the changes in the white line are attributed to an increase in d-band vacancies.

**EXAFS:** The Pt clusters in NaY were prepared under in situ conditions with a high flux of the reactant gases so air oxidation of the clusters could be safely ruled out. Insights into the size of the clusters, their location in the zeolite matrix and the effect of CO adsorption were obtained from the analysis of the local structure around Pt. In the Fourier transformed (FT) EXAFS spectrum of
Pt\textsubscript{13}H\textsubscript{m}/NaY, only a single intense peak at roughly 2.7 Å is present and further intense peaks, which are normally present in larger platinum clusters or bulk platinum metal are absent. This peak could be fitted with Pt at 2.77 Å as well as O at 2.72 Å with average coordination numbers of 5.8 and 3.8, respectively. The first shell Pt–Pt average coordination number of 5.8 provides evidence that very small, probably 13 atom clusters, are present in NaY. The clusters of this size (ca. 0.8 nm) could very well fit into the super cages of the NaY-zeolite with a free diameter of 1.3 nm. The observed Pt–Pt distance is comparable with its bulk value of 2.77 Å. In addition, a second near neighbour shell contribution from the zeolite oxygen atoms is present at 2.72 Å. Similar Pt–O distances have already been reported earlier for Pt in Y zeolites[4a]. The presence of the longer Pt-O distance in Pt\textsubscript{13}H\textsubscript{m}/NaY compared to that observed in PtO\textsubscript{2}, ~ 2.0 Å, and the absence of an oxygen shell at this distance exclude the possible oxidation of the platinum clusters and reiterate the necessity to use \textit{in situ} reduction to characterize such samples.

The \(k^2\) weighted experimental EXAFS function \(k^2\chi(k)\), and its Fourier transform for Pt\textsubscript{13}H\textsubscript{m}/NaY and Pt\textsubscript{2}(CO)\textsubscript{m}/NaY are shown in Figure 1 (Left). Significant changes upon CO exposure, at room temperature, like decrease in the intensity of the Fourier transform peak at roughly 2.7 Å and appearance of peaks near 2.0 Å are observed. In order to quantify the observed changes, experimental spectra were fitted with relevant structure models consisting of Pt–C, Pt–O and Pt–Pt contributions. The Pt–Pt distance in Pt\textsubscript{2}(CO)\textsubscript{m}/NaY decreases to 2.69 Å from 2.77 Å observed in Pt\textsubscript{13}H\textsubscript{m}/NaY, together with a decrease in the Pt–Pt average coordination number from 5.8 to 0.9. The changes in the structure parameters indicate a reconstruction of the Pt\textsubscript{13} cluster into smaller aggregates, most likely Pt\textsubscript{2}. Two Pt–C contributions, one at 1.95 Å and the next at 2.14 Å are obtained with average coordination numbers of 0.8 and 1.7, respectively. The short Pt–C distances are similar to Pt–C distances observed in compounds like Pt\textsubscript{3}(CO)\textsubscript{6} where CO molecules are linearly and bridge coordinated to Pt[4b]. In the present case, on an average, one linear and two bridged CO molecules coordinate to the Pt atom. Additionally, EXAFS contribution from zeolite oxygen is present at 2.72 Å with a coordination number 4.6, indicating that the Pt carbonyl clusters are in proximity to the zeolite framework. The use of other complementary techniques with XAS, like \textit{in situ} FTIR and EPR spectroscopy used in this study have already been published [5].

![Figure 1: Experimental EXAFS functions (top), its Fourier transform (bottom) and along with the fit to the data of Pt\textsubscript{13}H\textsubscript{m}/NaY (middle) CO-Pt\textsubscript{13}H\textsubscript{m}/NaY(right).](image)

\textbf{References}