## Magnetization of Pt<sub>13</sub> clusters supported in a NaY zeolite: a XAS and XMCD study.

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Zeolites are frequently used as support of Pt species in catalysis. Pt in I and III valence states, and forming dimers are known to yield to paramagnetic signals in EPR [1]. Recently, small Pt clusters supported in NaY zeolites, containing 13 atoms have been reported [2,3]. These Pt particles are prepared in two chemical states:  $Pt_{13}$  particles covered by H adsorbed atoms in one case, and  $Pt_{13}$  particles in the bare neutral cluster case [2]. They are dispersed in a zeolite matrix, with a maximum Pt charging of 6% in weight. The cluster may sit on a puckered 6-ring window (SII site of the faujasite structure) (Fig. 1), in which three oxygen atoms point towards the cluster and three away from it.

X-ray Absortion (XAS) and Magnetic Circular Dichroism (XMCD) spectra have been recorded at the L<sub>2,3</sub> edges of Pt of Pt<sub>13</sub> and hydrogenated Pt<sub>13</sub>H<sub>m</sub> clusters dispersed in NaY zeolite. From the XAS measurements the number of holes nh in the 5d band of these systems is found. From the difference of the L<sub>2,3</sub> edge spectra the Pt-H antibonding state, created by the hydrogenation embedded in the Pt d-band, is characterized by a shape resonance with energy  $E_{res} = 2.3$  eV. The average orbital and spin moments m<sub>L</sub> and m<sub>S</sub> for Pt atom have been determined from the XMCD measurements (Fig. 2). The total magnetic moment field dependence XMCD(H) was determined and scaled to the absolute value of the average moment per Pt atom. The fit of XMCD(H) to a Langevin function yields a magnetic moment per cluster of  $\mu = 3.7 \ \mu_B$  (Fig. 3). It is shown that non-magnetic clusters coexist with those giving a non-zero magnetic signal. The amount of Pt constituting the magnetic Pt<sub>13</sub> clusters is 15-20% of the total Pt. The XMCD data are compared with SQUID magnetization measurements. The moment found is consistent with density of state (DOS) calculations which predict a stable state for Pt<sub>13</sub> clusters with J = 3 - 4 angular momentum.

## **References:**

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Fig. 1. Left: NaY zeolite. Right: Pt<sub>13</sub>H<sub>1</sub><sup>+1</sup> cluster [1]



Fig. 2. Normalized XMCD spectra at the  $L_{2,3}$  Pt edges. (top) spectra of Pt<sub>13</sub>, (lower panel) Pt<sub>13</sub>H<sub>m</sub>. (dots) experimental points. (red line) fit to Lorenzian functions as guide to the eye. (green) Area integral. The arrows indicate the higher limit of the *p* and *q* integrals.



Fig. 3. XMCD M(H) data of  $Pt_{13}(\blacksquare)$ , and  $Pt_{13}H_m(\bullet)$ . Fits of the to a Langevin function (-).

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