EPR study of platinum supported on NaY

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Pt/NaY was prepared by the aqueous ion-exchange method and investigated by EPR spectroscopy. After reduction with H_2 using a static system, an orthorhombic EPR signal was observed with g_1 = 2.531, g_2 = 2.322, g_3 = 2.062, coaxial with the hyperfine components a_1 = 64.9 G, a_2 = 74.6 G, a_3 = 72.6 G; this signal is assigned to Pt^+ ions. Typical cation sites for location in the supercages are excluded for symmetry reasons.

Hetereogenous catalysts consisting of transition metal ions or small clusters supported on zeolites play a key role in important petrochemical reactions.[1] Since the activity and the selectivity of catalytic reactions depend on the size of clusters, characterization of the size, location, electronic and atomic structure by techniques such as TEM, EXAFS, XRD, XPS, TPR, TPD, H_2 chemisorption, ^{129}Xe NMR, IR or electron paramagnetic resonance (EPR) is indispensable. EPR has been shown to be an important tool for the characterization of many transition metals in zeolites.[2] In many cases it is possible to distinguish between different oxidation states, coordination numbers, complex symmetries and crystal field strengths. It is of importance for a further understanding of heterogenous catalysis to observe changes of the catalytically active transition metal centers during reactions. The site determines the accessibility by reacting molecules. In view of the importance of Pt on zeolites it is surprising that there have been no publications of EPR studies until today.

Samples were prepared *via* ion-exchange at 343 K over 48 h by dropwise addition of 0.003 M $[Pt(NH_3)_4]Cl_2$ solution to NaY slurry, resulting in a Pt loading of 4%. The exchanged zeolite was filtered, washed with deionized water in order to remove Cl^- ions, and dried at 296 K in air. Calcination was conducted by heating Pt/NaY from room temperature to 563 K at 0.5 K min^{-1} in flowing O_2 (270 ml min^{-1} g^{-1}), and holding at 563 K for 3 h. After this treatment platinum is located as PtO in the supercages of Y zeolite as has been shown using X-ray methods, electron microscopy and gas adsorption.[3,4] The zeolite was pumped at 523 K to remove water, and reduction was performed by heating from 296 K to 563 K at 0.5 K min^{-1} in a closed EPR tube with different molar ratios of Pt : H_2 (1 : 3 or 1 : 6), and holding at the final temperature for 6 h. X-Band EPR spectra were recorded on a Bruker EMX spectrometer in the temperature range 4 K to 150 K in H_2 atmosphere.

For reduction at a molar ratio of Pt : H_2 = 1 : 6, no EPR spectrum is observed. For a molar ratio Pt : H_2 = 1 : 3, the EPR spectrum at 4 K shows overlapping signals (Fig. 1). The spin concentration corresponds to about 0.5% of the total Pt loading. The main signal is orthorhombic with resolved ^{195}Pt hyperfine splitting (natural abundance 33.8%, $I = \frac{1}{2}$). Simulation[5] yields the spin Hamiltonian parameters g_1 = 2.531, g_2 = 2.322, g_3 = 2.062, a_1 = 64.9 G, a_2 = 74.6 G, a_3 = 72.6 G with coaxial g- and a-tensors. The orthorhombic symmetry allows us to exclude the possibility that the species is located at a typical cation site,[6] since axial symmetry should be expected for these sites. Going to higher temperatures, the lines broaden and the intensity decreases. Above 100 K only a very weak and broad spectrum is observed. This behavior may be caused by dynamic effects, for example by jump exchange of the observed species between different sites. At this point we have no explanation for the remaining minor features, which are superimposed mainly on the central line.

Several EPR spectra of formal Pt(I) complex compounds with organic ligands have been described.[7] The general sequence of g-values in all these spectra is $g_1 > g_2 \approx g_e >> g_3$, and the authors assign them to Pt^+, in contrast to expectation since for a d^9 system all g-values should be larger than g_e due to spin–orbit coupling.[8] Other authors[9] assume that during electrochemical preparation of these complexes a reduction of the organic ligands occurs, leading to species which are better described as $Pt^{II}(L^-)$ than as $Pt^I(L)$. The present case is different since a reduction of the zeolite lattice is more difficult than a reduction of unsaturated organic ligands. Indeed, g-values in the sequence $g_1 > g_2 > g_3 > g_e$ indicate the presence of platinum in the formal oxidation state of +1. For Pt^{3+} ions (d^7) $g_i > g_e$ is expected as well as for all ions with a more than half filled d-shell. Since we used an excess of hydrogen for the reduction of PtO it is unlikely that Pt^{3+} is formed.

Axial EPR spectra of Pt^+ ions with spin Hamiltonians characterized by $g_\parallel$ = 3.29, $g_\perp$ = 2.261, $a_\parallel \leqslant 10$ G and $a_\perp$ = 229 G for an Ar matrix and $g_\parallel$ = 3.13, $g_\perp$ = 2.214, $a_\parallel \leqslant 10$ G and $a_\perp$ = 311 G for a Kr matrix were reported.[10] Compared with the observed platinum species in Y zeolite, the g-anisotropy of Pt^+ was larger in the rare gas matrices because of the weaker crystal field.

The ^{195}Pt hyperfine splitting of about 70 G in NaY is equivalent to an s-orbital contribution of 0.6%, which is similar to the 1.4% for Pt^+ in Ar and 1.9% in Kr matrices.[10] The formation of Pt clusters during reduction is a well known process,[12] but based on the isotropic hyperfine coupling constant[11] of about 12000 G for Pt^0 a much higher s-character is expected for neutral clusters. We therefore exclude the possibility that the spectrum observed here represents clusters. The contribution of d-orbitals of Pt^+ in rare gas matrices is 54% for Ar and 76% for Kr.[10] The observed d-orbital contribution for Pt^+/NaY is only about 2%, possibly because of the contribution of excited p-orbitals.[10,13,14] Another possibility is the delocalization of spin density to ligands since the d-orbital contribution is smaller by about a factor 30 for Pt^+ in NaY than for Pt^+ in rare gas matrices. On the other hand, the high g-value allows us to exclude the possibility that the radical is localized on oxygen since $O^{\cdot -}$ or $O_2^{\cdot -}$ have g-values near g_e.[15,16] A more attractive interpretation is based on the assumption that one (or two) of the

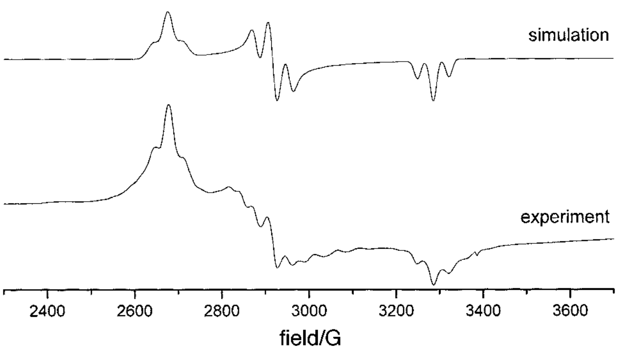

Fig. 1 Simulation and X-band EPR spectrum of Pt/NaY observed at 4 K.

hyperfine components is of negative sign, which is experimentally not distinguishable. This leads to near-zero s-character and somewhere of the order of 36% d-character, which is much closer to the results reported for Pt^+/Ar, and also compatible with the high g-values.

The present results introduce a new, non-invasive tool for the characterization of one of the most important catalysts. Further EPR experiments aiming at a better understanding of reaction mechanisms of heterogenous catalysis on Pt exchanged zeolites are in progress. This includes other preparation conditions and examinations of further zeolites which lead to Pt cations located at different sites, for example in sodalite cages,[3,4] and consequently to other environments which can be studied by EPR. Adsorption of organic compounds or oxidation may lead to the disappearance of the observed EPR signals, and perhaps to the appearance of other EPR active species. ESEEM experiments may give more detailed information about the nature of ligands around the observed species.

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