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XAS-Investigations of Colloidal Precursors for Pt/Rh Bimetallic Catalysts

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Abstract: Innovative transition metal catalysts prepared on the basis of preformed colloidal nano-particles and stabilized by surfactants are of special interest with regard to industrial applications. The physical characterization of the metal colloid precursors, i. e. the determination of their geometric and electronic structure prior to supporting, has been shown to be crucial for the optimization of new catalysts. Improved activity, selectivity and resistance against deactivation in case of bimetallic systems have been ascribed to 'synergetic effects' of the two metals present in the catalytically active components. The improved catalytic performance at a certain range of Pt:Rh atomic ratio in the precursor can be interpreted on the basis of a geometric lattice structure effect – rather than an electronic band structure effect. This has been shown by an investigation of both the near edge structure and the EXAFS-region of Pt L_{III} X-ray absorption measurements, performed on a series of ammonium salt stabilized bimetallic Pt/Rh resp. monometallic Pt colloids.

1 Introduction

Bimetallic nanoscale colloids are of current interest as precursors for heterogeneous catalysts [1][2]. These innovative catalysts reveal a synergetic effect in liquid phase hydrogenation reactions comparing their activity to the effect of combining the respective monometallic colloid catalysts. According to Bönemann et al. [3], surfactants are well suited as stabilizing agents for the preparation of metal colloids of group VI-XI elements by chemical reduction of metal salts in organic or aqueous solutions. Bimetallic Pt/Rh colloids protected by NR_4^+ (R =alkyl, C_6 - C_{12})-groups are accessible by coreduction of metal halogenides using hydrotriorganoborates in organic media. On coupling metal salts and tenside molecules before the reduction process, a wide range of reducing agents, e. g. H_2 , can be employed. The presence of both metals in the particle cores, which show a narrow size distribution with a mean diameter of about 2 nm, has been proved by EDX analysis with 1 nm point resolution. In order to get further information on alloy formation and electronic structure of Pt in the metal cores of the colloid particles, Pt L_{III} -XAFS measurements of $Pt_xRh_{100-x}[N(octyl)_4]^+$, $x=100, 70, 50, 30$, have been analyzed.

2 Experimental

All sample preparation and measuring steps were carried out strictly under inert gas conditions in order to avoid any air contact of the finely dispersed metal particles. Highly soluble metal-organic powders with metal contents of about 50 wt.% after purification of the raw colloids were produced by coreduction of different amounts of $[N(octyl)_4]^+PtCl_2Br_2$ and $[N(octyl)_4]^+_3RhCl_3Br_3$ – corresponding to the desired metal ratio – with $LiEt_3H$ in THF. X-ray absorption spectra were taken using synchrotron radiation from the Electron Stretcher and Accelerator ELSA at Bonn University, running in storage ring mode. The method of inert gas sample handling for measurements in standard transmission technique has been described elsewhere [4]. For measurements at the Pt L_{III} -edge (11.564 keV) the Lemmonier-type [5] X-ray monochromator was equipped with a pair of Ge(422) single-crystals ($2d=2.306$ Å). EXAFS-measurements have been analyzed according to the standard least-squares fitting technique [6] using the program package of Ertel et al. [7].

3 Results and Discussion

The influence of nano-scale alloy formation on dispersion and activity of colloid-based Pt/Rh/C catalysts has been checked by CO chemisorption. The synergetic effect of combining the two metals in the active sites can be deduced from the butyronitrile test reaction [2], which shows a maximum of catalytic activity between 10% and 30% Pt atoms in the particles – corresponding to the maximum of chemisorbed CO volume. The Fourier-filtered first coordination shell EXAFS-signals of $Pt_{70}Rh_{30}$, $Pt_{50}Rh_{50}$ and $Pt_{30}Rh_{70}$ in Fig. 1 indicate – by the characteristic beat structure – the presence of both Pt and Rh next neighbours of Pt absorbers in the colloid particles. Significant changes in the k^3 -weighted EXAFS-functions at different metal compositions of the colloid precursors can be observed. The structural parameters derived from least-squares fitting analysis are presented in Tab. 1. At first, a remarkable decrease of the first shell coordination number of 12 for Pt atoms in the *fcc*-type lattice to about half that value for Pt in Pt and Pt/Rh colloids has been found. This result cannot be explained solely by assuming a high degree of surface atoms with missing next neighbours in the colloid particles. An idealized 8 shell Pt or Rh cluster of about 2.2 nm diameter

would exhibit only 31% of atoms in surface positions, leading to an average coordination number much closer to 12. What seems to be more likely is the influence of static disorder, i. e. the presence of a large fraction of 'ill-coordinated' Pt atoms in the severely distorted nanoscale lattice, which has been proposed by Di Cicco et al. [8] to explain the decrease of coordination numbers in ball milled nm iron particles derived by EXAFS. To evaluate the influence of thermal disorder, a cumulant analysis might be necessary. Only a slight decrease of the interatomic distance has been found in the case of colloidal Pt (2.75 Å vs. 2.77 Å bulk-value), whereas the nanoscale alloying leads to Pt-Pt and Pt-Rh next neighbour distances which are close to the Rh bulk-value of 2.69 Å for Pt₇₀Rh₃₀ and Pt₅₀Rh₅₀.

Figure 1: Pt/Rh bimetallic colloids: first shell Pt_{LIII}-EXAFS signal (—) and best fit (•)

Table 1: Structural parameters and estimated errors derived from EXAFS analysis

colloid	backscat.	R ± 0.01 [Å]	N ± 0.5	σ² ± 0.002 [Å²]	ΔE ₀ ± 1 [eV]
Pt ₃₀ Rh ₇₀	Pt	2.65	3.4	0.0048	-2
	Rh	2.65	1.7	0.0049	6
Pt ₅₀ Rh ₅₀	Pt	2.71	4.5	0.0071	7
	Rh	2.69	1.3	0.0026	6
Pt ₇₀ Rh ₃₀	Pt	2.71	6.0	0.0088	6
	Rh	2.70	1.2	0.0096	8
Pt ₁₀₀	Pt	2.75	5.9	0.0066	9

Interestingly, in the case of Pt₃₀Rh₇₀ an even lower distance value of 2.65 Å has been found for both Pt and Rh backscatterers, indicating a somewhat stronger lattice contraction at excess Rh content in the colloid particles. Looking at the ratio of the first shell Pt and Rh coordination numbers, it becomes obvious that no statistical distribution of the metals results from coreduction of the respective halogenides. As it has been shown additionally by IR measurements on chemisorbed CO, Rh is enriched at the surface, giving rise to a higher Pt concentration in the centre of the bimetallic particles. Corresponding to this result, no significant deviations of white line intensities in the normalized Pt *L*_{III}-XANES spectra have been observed, indicating no change in density of unoccupied *d*-states localized at Pt sites with changing Rh concentration in the four colloid samples. Considering the low distance value of 2.65 Å for Pt₃₀Rh₇₀, in addition to the similarity of the near edge structures in the spectra of pure Pt and Pt/Rh alloy colloids, the improved catalytic performance might be explained by a geometric effect of the special particle structure due to the excess Rh concentration, rather than a change of the electronic structure of Pt atoms in the colloid precursors.

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