The Preparation of Colloidal Pt/Rh Alloys Stabilized by NR4+- and PR4+-Groups and their Characterization by X-Ray-Absorption Spectroscopy

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Bimetallic Pt/Rh colloids protected by NR4+- or PR4+- groups are accessible by the co-reduction of PtCl2 and RhCl3 using hydrotriorganoborates in organic media. According to TEM the particle size ranges from 1.9 to 2.5 nm. EDX point analysis of several samples has shown that both metals are present in the particles. The metallic character of the Pt/Rh core confirmed by XANES, and EXAFS data clearly indicate the formation of nanometalic alloys. Colloidal Pt/Rh alloys prepared in this way are very soluble and highly stable in organic phases and serve as sources for heterogeneous hydrogenation catalysts.

Introduction

Bimetallic nanoscale clusters and colloids are of current interest as precursors for heterogeneous catalysts [1–5]. In 1990 we described the formation of a Fe0.7Co0.3 nanopowder by simple coreduction of FeCl3 and CoCl2 using hydrotriorganoborates in organic solvent [6]. Mössbauer spectroscopy provided unambiguous proof for the presence of an Fe/Co alloy [7 page 140]. By coreducing two different metal salts with NR4BR3H, a number of bimetallic nanometal colloids are obtained. In the case of colloidal Pt/Rh, EDX point analysis reveals that both Pt and Rh are present in every metal colloid particle analyzed (size ~ 2.3 nm) [7 page 155]. The finding that catalysts based on these bimetallic Pt/Rh colloids reveal a synergetic effect in liquid phase hydrogenation further indicates the presence of an alloy in the precursor [7 page 168]. Here we report results of a XANES and EXAFS study which confirm both the metallic character and the alloy formation in nanoscale Pt/Rh colloids stabilized by NR4+- and PR4+-groups.

Results and Discussion

Syntheses

The preparation of the N(Octyl)4+ – stabilized Pt0.5Rh0.5 colloids 1 and 2 was carried out according to the coreduction procedure previously described [7 page 172].

\[
m \text{PtCl}_2 + n \text{RhCl}_3 + (2m + 3n) \text{N(Octyl)}_4 \text{B}_{12} \text{Et}_3 \text{H} \xrightarrow{\text{THF, 18 h}} \text{Pt}_m \text{Rh}_n \text{colloid} + (2m + 3n) \text{N(Octyl)}_4 \text{Cl} + (2m + 3n) \text{BEt}_3 + (2m + 3n)/2 \text{H}_2
\]

alloy 1: T = 50 °C; alloy 2: T = 25 °C.

In order to check whether the reduction mode and the temperature influence the homogeneity of the resulting alloy, the reaction was preformed at 50 °C (alloy 1) and 25 °C (alloy 2) for comparison. According to TEM the mean particle size of the resulting Pt0.5Rh0.5 colloids 1 and 2 are 2.1 and 1.9 nm, resp. Under the microscope a number of particles of the colloids 1 and 2 were analyzed employing EDX with a point resolution of 1 nm showing that both Pt and Rh were present. The synthesis of a PR4+-stabilized Pt0.5Rh0.5 colloid was achieved for the first time by coupling the phosphonium protecting group to BR3H+ prior to the reduction step.

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Fig. 1. Section of the HRTEM image of the Pt/Rh alloy 3.

\[
\text{PtCl}_2 + \text{RhCl}_3 + 5 \text{PEt(octyl)BEt}_3 \text{H} \xrightarrow{\text{THF, 50 °C, 16 h}} \text{PtRh colloid} + 5 \text{PEt(octyl)Cl} + 3 \text{BEt}_3 + 2.5 \text{H}_2
\]  

Metal precipitation was not observed during the coreduction (eq. (2)), and the resulting bimetallic colloid 3 was found to yield one molar solutions, e.g. in THF, stable for months. Hence the solubility and stability of PR$_4^+$- and NR$_4^+$- protected Pt/Rh colloids are very similar. The colloid 3 may be purified after precipitation using an ether/ethanol mixture. The purified colloid 3 was characterized by elemental analysis, $^{31}$P and $^{13}$C NMR, HRTEM and EDX of the particles. Electron microscopy of 3 (Fig. 1) showed a mean particle size of 2.5 nm, which is very similar to the size of the NR$_4^+$- stabilized colloids 1 and 2. An EDX point analysis (resolution = 1 nm) of 3 has confirmed the presence of both Pt and Rh in a sufficient number of particles verifying that the material is truly bimetallic (Fig. 2).

In summary, the replacement of NR$_4^+$ by PR$_4^+$ as the protecting group has no significant influence on the chemical properties, the particle size, or the bimetallic character of the particles in colloid 3.

**XANES and EXAFS measurements**

In order to confirm the metallic character of Pt and Rh in the bimetallic Pt/Rh-colloids 1–3, i.e. to prove that both metal salts have been completely reduced during the colloid synthesis, XANES (X-ray Absorption Near Edge Structure) and EXAFS (Extended X-ray Absorption Fine Structure) measurements were carried out. Furthermore, information on the homogeneous or heterogeneous structure of the alloy particles was desirable. The preliminary results are described here.

**Platinum-LIII-edge**

XANES-measurements at the Pt-LIII-edge were performed on the colloid samples 1–3 and, for comparison, on Pt powder, a Pt/Rh reference-alloy (Rh$_{0.3}$Pt$_{0.7}$), and on PtO$_2$. The normalized absorption spectra in the energy range between 11,500 eV and 11,650 eV are shown in Fig. 3a. In Fig. 3b the magnification of the spectra in the region of the edge is shown.

First of all, the position of the inflection points of all absorption edges obtained by the numerical differentiation of the absorption spectra (except for PtO$_2$) indicates the metallic valency of platinum for the colloid samples 1–3 and the reference alloy. The positions differ only within the resolution of the Ge(220)-crystal at the Pt-2p$_{3/2}$-binding energy, whereas the shift of the absorption threshold (~3 eV) in the case of PtO$_2$ clearly corresponds to the valency four. The normalized spectra show different intensities of the threshold resonance (“white line”) and a broadening in the case of the Pt/Rh reference alloy and the colloid alloy 1. The decrease of the white line intensity in bi-
metallic particles has been attributed to a partial filling of empty electron states (the Pt–LIII white line is correlated to an electronic transition from the 2P3/2 to the 5d5/2 state [8]) by the interaction of two metals in an alloy [9]. This interpretation leads to the assumption of a rather pure Pt phase in the case of the colloid alloy 2. In contrast, in colloids 1 and 3 an increasing alloy character of the particles may be deduced. In other words, the synthesis of 2 at 25 °C leads to a more heterogeneous Pt/Rh colloid alloy than the syntheses of 1 and 3 performed at 50 °C. In order to determine the distribution of the nearest neighbours of Pt in the colloid particles, EXAFS measurements were carried out up to 700 eV behind the Pt–LIII-edge. Additionally, an EXAFS measurement was performed on the Pt/Rh reference alloy. Data reduction was achieved according to the standard procedure to separate the EXAFS oscillations using the EXAFS program package developed by T. S. Ertel and U. Kolb [10]. Fig. 4 shows the Fourier filtered (Hanning-Square-window from 1.3 to 3.2 Å in R-space), weighted EXAFS oscillations k·χ(k) for the colloid samples 1–3 and the reference alloy.

The similarity of the oscillations both in phase and amplitude is obvious for the reference alloy and the colloids 1 and 2, whereas the curve in the case of colloid 3 deviates significantly. Attempts to determine the structural parameters by least-
square fitting of the Fourier filtered EXAFS have been made indicating Pt and Rh backscatterers which are closer to the Pt central atom than the first coordination shell neighbours in fcc-Pt (2.76 Å) and fcc-Rh (2.69 Å). Probably non-standard EXAFS analysis methods [11] have to be applied with respect to the small size of the colloid particles. A more detailed analysis of the data is in progress.

Rhodium – $L_{III}$-edge

Fig. 5a shows XANES spectra at the Rh–$L_{III}$-edge in the energy range between 2,960 and 3,120 eV and Fig. 5b the magnification of the spectra in the region of the edge of the colloid samples 1–3, as well as RhCl$_3$ and a Rh foil which served as references. As compared to metallic Rh, the white lines of all 3 colloids are broadened and slightly shifted to higher energies. In principle, both observations could be explained by assuming the spectra of the colloids being a superposition of those of RhCl$_3$ and metallic Rh. However, by simulating such spectra it turned out that this assumption could not be confirmed as it was not possible to fit position and width of the lines simultaneously. As was already observed in the EXAFS spectra at the Pt–$L_{III}$-edge, the Rh–$L_{III}$-XANES spectra also show that colloid 3 differs significantly from the colloids 1 and 2. Here the white line of colloid 3 is not only more intense than those of the colloids 1 and 2, but even higher than for metallic Rh. The decrease of the white line intensity in the case of the very similar spectra of colloid 1 and 2 could be interpreted in the same way as in the Pt–$L_{III}$-measurements.

Catalytic Applications

The catalytic activities of the colloidal Pt$_{0.5}$Rh$_{0.5}$ alloys 1–3 (5% metal supported on charcoal) in heterogeneous liquid phase hydrogenation reactions were compared using the butyronitrile standard test [7 page 174].

As shown in Fig. 6, the Pt$_{0.5}$Rh$_{0.5}$ alloys 1 and 2 stabilized by NR$_4^+$ are more active than the corresponding Pt$_{0.5}$Rh$_{0.5}$ colloid 3 stabilized by PR$_4^-$groups. Obviously, traces of P(Octyl)$_3$ formed from PEt(Octyl)$_3^+$ under the reductive conditions of (eq. (2)) are sufficient to poison the catalyst. In this test the more homogeneously alloyed catalyst precursor 1 exhibits a substantially higher activity than precursor 2 where the XANES measurements indicate a heterogeneous structure of the Pt$_{0.5}$Rh$_{0.5}$ particles.
Experimental

All experiments were carried out strictly under argon. The XANES and EXAFS measurements on the Pt/Rh colloid samples were conducted using synchrotron radiation at beamline BN3 of the storage ring ELSA at Bonn University. The synchrotron radiation was monochromatized by means of a double crystal monochromator: Ge[220] at Pt–LIII-edge (11,564 eV) and InSb[111] at the Rh–LIII-edge (3004 eV). All measurements have been performed in transmission mode using ionization chambers as detector and primary intensity monitor. The HRTEM image has been recorded by a HITACHI HF-2000 field emission microscope at 200 kV, and the EDX measurement has been performed using a NORAN EDX-analyzer type Voyager with Si/Li detector and NOVAR window. NMR measurements have been performed by a Bruker AC 200 spectrometer at room temperature. $^{31}$P: $\delta_P$ rel. external aqueous 85% H$_3$PO$_4$. $^{13}$C: $\delta_C$ rel. TMS. The $\beta$-CD$_2$ signal of the D$_8$-THF solvent was used as standard and the chemical shifts were converted to the TMS scale [$\delta_C$(CD$_2$) = 2.53].

$N$(octyl)$_4$BEt$_3$H

$N$(octyl)$_4$BEt$_3$H was prepared from $N$(octyl)$_4$Br and K(BEt$_3$H) following the general procedure given previously, viz. in Refs. [12–14].

$P$(Et)(octyl)$_3$BEt$_3$H

The preparation of $P$(Et)(octyl)$_3$BEt$_3$H was the same as that for $N$(octyl)$_4$BEt$_3$H, only using $P$(Et)(octyl)$_3$Br instead of $N$(octyl)$_4$Br.

(alloy 1) Colloidal platinum$_{0.46}$rhodium$_{0.54}$ alloy

0.885 g (3.36 mmol) of RhCl$_3$ were dissolved in a solution of 5.795 g (10.6 mmol) of $N$(octyl)$_4$Br in 50 ml of THF and dried in a vacuum (10$^{-3}$ mbar) at 25–50 °C. This procedure was repeated twice, and the resulting residue was dissolved in 50 ml of THF. 0.885 g (3.33 mmol) of PtCl$_2$ were stirred in a solution of 3.71 g (6.78 mmol) of $N$(octyl)$_4$Br in 50 ml of THF for 72 h at 20 °C. The resulting solution was mixed with the solution of the prepared rhodate [RhCl$_3$$\times$3 $N$(octyl)$_4$Br] and 800 ml of THF were added. Then a solution of $N$(octyl)$_4$BEt$_3$H in THF (0.309 M; 55 ml) was added dropwise at 50 °C over a period of 16 h. After stirring for an additional 2 h a black-brown solution was formed and the volatile compounds were removed through evaporation. The black-brown, waxy residue was dried at 25–50 °C and 10$^{-3}$ mbar for 16 h. The product (21.13 g) proved soluble in THF, toluene, ether and acetone, but insoluble in pentane and ethanol, and contained 2.79 wt% of platinum and 1.45 wt% of rhodium. Thereafter, the residue was dissolved in 25 ml of technical quality diethyl ether without using an inert gas atmosphere. Addition of 250 ml of technical ethanol to the ether solution caused the formation of a grayish-brown precipitate. The precipitate was allowed to settle for several hours before the clear supernatant solution was removed by applying pressure of an inert gas on the liquid surface. Drying in a vacuum (10$^{-3}$ mbar, 20 °C, 16 h) yielded a gray colloidal alloy powder (3.96 g) which proved to be very soluble in THF. Metal content: 16.03 wt% platinum and 9.94 wt% rhodium (Pt$_{0.46}$Rh$_{0.54}$). TEM: mean particle size, 2.1 nm.

(alloy 2) Colloidal platinum$_{0.43}$rhodium$_{0.55}$ alloy

The experiment was carried out analogous by to alloy 1, with the exception of the addition step. The solutions of the preprepared platinum [PtCl$_2$$\times$2 N(octyl)$_4$Br] and rhodate [RhCl$_3$$\times$3 N(octyl)$_4$Br] were added dropwise at 25 °C to the solution of the $N$(octyl)$_4$BEt$_3$H in THF (0.11 M, 155 ml). Yield: 3.8 g. Metal content: 12.99 wt% platinum and 8.36 wt% rhodium (Pt$_{0.43}$Rh$_{0.55}$). TEM: mean particle size, 1.9 nm.

(alloy 3) Colloidal platinum$_{0.55}$rhodium$_{0.48}$ alloy

To a suspension of PtCl$_2$ (1.77 g; 6.68 mmol) and RhCl$_3$ (1.41 g; 6.74 mmol) in THF (450 ml) a solution of $P$(Et)(octyl)$_3$BEt$_3$H (150 ml; 0.277 M) was added at 50 °C in 16 h. After stirring for an ad-
ditional 2 h at 50 °C a black-brown solution was formed and the volatile compounds were removed through evaporation. The black-brown, waxy residue was dried at 25–50 °C and 10⁻³ mbar for 16 h. The product (20.67 g) proved soluble in THF, toluene, ether and acetone, but insoluble in pentane and ethanol. Thereafter, the residue was dissolved in 25 ml of technical quality diethyl ether without using an inert gas atmosphere. Addition of 300 ml of technical ethanol to the ether solution caused the formation of a grayish-brown precipitate. For the isolation and drying of the gray colloidal alloy powder see preparation of alloy 1. Yield: 3.34 g. Elemental analysis: Pt 34.04; Rh 16.68; C 31.42; H 6.29; Br 0.60 wt.%. Metal ratio: Pt0.52Rh0.48. ¹³C NMR spectra (d₈-THF): δ = 32.77, 31.81, 30.05, 29.92, 23.48, 22.66, 19.36, 14.42 Hz. ³¹P NMR spectra (d₈-THF): δ = 35.53 Hz. TEM: mean particle size, 2.5 nm.

Conclusions

The coreduction of PtCl₂ and RhCl₃ using NR₄⁺- or PR₄⁺-hydrotriorganoborates leads to ammonium- and, for the first time, phosphonium-stabilized Pt/Rh alloy colloids. XANES measurements at the Pt-LIII-edge of 3 bimetallic Pt/Rh colloids indicate a complete reduction of PtCl₂ during the synthesis. Differences in shape and intensity of the white lines may be an indication of differing homogeneity of the colloidal alloy particles. The spectra suggest that the Pt/Rh colloids 1 and 3 are more homogeneously alloyed than the Pt/Rh particles of sample 2. The EXAFS analysis has proved difficult because of the shape and small size of the bimetallic colloids. This leads to a very asymmetric (not gaussian) pair distribution function for the first shell neighbours. EXAFS measurements at the Rh-K-edge (23,220 eV) could provide additional structural information, but have not been conducted so far. The small shift in the peak position at the Rh-LIII-edge may be due to partial oxidation at the surface of the particles, where Rh is obviously enriched. Pt−LIII-EXAFS and Rh−LIII-XANES data indicate structural differences between colloids 1 and 2 and colloid 3 which also has the lowest catalytic activity. If it would be possible to correlate these observations, the structural characterization of the precursor particles by physical methods would open promising perspectives for catalyst design and optimization.

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