Investigation of Tetraalkylammonium Bromide Stabilized Palladium/Platinum Bimetallic Clusters Using Extended X-ray Absorption Fine Structure Spectroscopy

Uwe Kolb,* Stefan A. Quaiser, Martin Winter, and Manfred T. Reetz

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim/Ruhr, Germany

Received January 30, 1996. Revised Manuscript Received May 21, 1996[⊗]

Structural investigations using EXAFS spectroscopy and standard analytical methods were performed on electrochemically synthesized tetrabutylammonium bromide stabilized Pd/Pt bimetallic clusters with different Pd/Pt ratios. The results of these investigations allow the determination of a detailed model concerning the structure of these 3.5 nm sized bimetallic clusters. The cores of the clusters are enriched in platinum metal, while the outer shell is enriched in palladium metal. The nanostructured particles are partially oxidized. The amounts of oxide in the outer shells are larger than in the cores of the clusters. Also, a small amount of the metal is present as metal bromide. The ammonium salt stabilizer forms a protective layer around the cluster.

Introduction

Transition-metal clusters in the nanometer size range are of interest as catalysts in organic and inorganic reactions, as electrocatalysts in fuel cells and as components for materials with special electronic properties.[1−4] In most cases stabilizers such as special ligands,[5] polymers,[6] or tetraalkylammonium salts[7] are needed in order to prevent undesired particle agglomeration.[1−4] The same applies to nanostructured bimetallic clusters.[1−4] In all cases the stabilizer is believed to form a mantle which surrounds the metal core, although convincing structural proof of this generally accepted model is rare.[8,9] To date the precise physical basis of the stabilizing interaction has not been elucidated satisfactorily, i.e., the details of possible steric and electronic factors remain unclear in most systems studied. The fact that the nature of the stabilizer varies considerably increases the complexity of the discussion. For example, Pd and Pt clusters and Pd/Pt bimetallic clusters are known to be stabilized by such different compounds as poly(*N*-vinyl-2-pyrrolidone) and tetraalkylammonium salts.[1−8] Another factor that complicates the situation is the fact that the metal core may consist not solely of metal atoms but also of an oxidized outer metal layer in the form of the metal oxide. Although this possibility is occasionally mentioned in the literature,[1−4] it is usually not explicitly considered.

In the case of bimetallic clusters, the structure of the metal core is of great theoretical and practical interest.[1−4,10−13] This applies to homogeneous solutions of stabilized clusters and to materials immobilized on solid supports. The spatial distribution of the two metal components in the metal core is not necessarily random. For example, in pioneering studies on bimetallic clusters, Sinfelt showed that, for example, Ru/Cu bimetallic clusters have a structure in which the surface consists of copper in the form of an outer monolayer and the inside of the core consists of ruthenium.[10] Related effects have been observed in the case of other bimetallic combinations.[1−4,10−12] Generally, extended X-ray absorption fine structure analysis (EXAFS) is used as the analytical tool. For example, Toshima recently elucidated the structure of Pd/Pt bimetallic clusters stabi-

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) (a) *Clusters and Colloids*; Schmid, G., Ed.; VCH: Weinheim, 1994. (b) Henglein, A. *J. Phys. Chem.* **1993**, *97*, 5457. (c) Davis, S. C.; Klabunde, K. J. *Chem. Rev.* **1982**, *82*, 153.

(2) (a) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693. (b) Schmid, G. *Chem. Rev.* **1992**, *92*, 1709. (c) Gates, B. C.; Guczi, L.; Knözinger, H. *Metal Cluster in Catalysis*; Elsevier: Amsterdam, 1986. (d) Conway, B.; Tilak. B. In *Advances in Catalysis;* Eley, D.; Pines, H., Weisz, P., Eds.; Academic Press: New York, 1992; Vol. 38. (e) Wendt, H. *Electrochemical Hydrogen Technology*; Elsevier: Amsterdam, 1990.

(3) Schön, G.; Simon, U. *Colloid Polym. Sci.* **1995**, *273*, 101.

(4) Reetz, M. T.; Helbig, W.; Quaiser, S. A. In *Active Metals: Preparation, Characterization, Applications*; Fürstner, A., Ed.; VCH: Weinheim, 1996.

(5) (a) Schmid, G.; Morun, B.; Malm, J.-O. *Angew. Chem.* **1989**, *101*, 772; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 778. (b) Vargaftik, M. N.; Zagorodnikov, V. P.; Stolarov, I. P.; Moiseev, I. I. *Mol. Catal.* **1989**, *53*, 315.

(6) (a) Bradley, J. S.; Millar, J. M.; Hill, E. W. *J. Am. Chem. Soc.* **1991**, *113*, 4016. (b) Porta, F.; Ragaini, F.; Cenini, S.; Scari, G. *Gazz. Chim. Ital.* **1992**, *122*, 361.

(7) (a) Kiwi, J.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 7214. (b) Blum, J.; Sasson, Y.; Zoran, A. *J. Mol. Catal.* **1981**, *11*, 293. (c) Boutonnet, M.; Kizling, J.; Stenius, P.; Maire, G. *Colloids Surf.* **1982**, *5*, 209. (d) Toshima, N.; Takahashi, T.; Hirai, H. *Chem. Lett.* **1985**, 1245. (e) Boutonnet, M.; Kizling, J.; Touroude, R.; Maire, G.; Stenius, P. *Appl. Catal.* **1986**, *20*, 163. (f) Meguro, K.; Toriyuka, M.; Esumi, K. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 341. (g) Wiesner, J.; Wokaun, A.; Hoffmann. H. *Prog. Colloid Polym. Sci.* **1988**, *76*, 271. (h) Satoh, N.; Kimura, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1758. (i) Bönnemann, H.; Brijoux, W.; Brinkmann, R.; Dinjus, E.; Joussen, T.; Korall, B. *Angew. Chem.* **1991**, *103*, 1344; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1312. (j) Toshima, N.; Takahashi, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 400.

(8) Reetz, M. T.; Helbig, W.; Quaiser, S. A.; Stimming, U.; Breuer, N.; Vogel, R. *Science* **1995**, *267*, 367.

(9) Yonezawa, T.; Tominaga, T.; Toshima, N. *Langmuir* **1995**, *11*, 4601.

(10) (a) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. *J. Chem. Phys.* **1980**, *72*, 4832. (b) Sinfelt, J. H. *Acc. Chem. Res.* **1987**, *20*, 134.

(11) (a) Toshima, N.; Harada, M.; Yonezawa, T.; Kushihashi, K.; Asakura, K. *J. Phys. Chem.* **1991**, *95*, 7448. (b) Harada, M.; Asakura, K.; Ueki, Y.; Toshima, N. *J. Phys. Chem.* **1992**, *96*, 9730.

(12) (a) Bradley, J. S.; Hill, E. W.; Klein, C.; Chaudret, B.; Duteil, A. *Chem. Mater.* **1993**, *5*, 254. (b) Esumi, K.; Shiratori, M.; Ishizuka, H.; Tano, T.; Torigoe, K.; Meguro, K. *Langmuir* **1991**, *7*, 457. (c) Lee, A. F.; Baddeley, C. J.; Hardacre, C.; Ormerod, R. M.; Lambert, R. M.; Schmid, G.; West, H. *J. Phys. Chem.* **1995**, *99*, 6096. (d) Li, Y.-X.; Klabunde, K. *J. Catal.* **1990**, *126*, 173.

(13) (a) Reetz, M. T.; Quaiser, S. A. *Angew. Chem.* **1995**, *107*, 2461; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2240. (b) Reetz, M. T.; Helbig, W.; Quaiser, S. A. *Chem. Mater.* **1995**, *7*, 2227.

S0897-4756(96)00062-2 CCC: $12.00

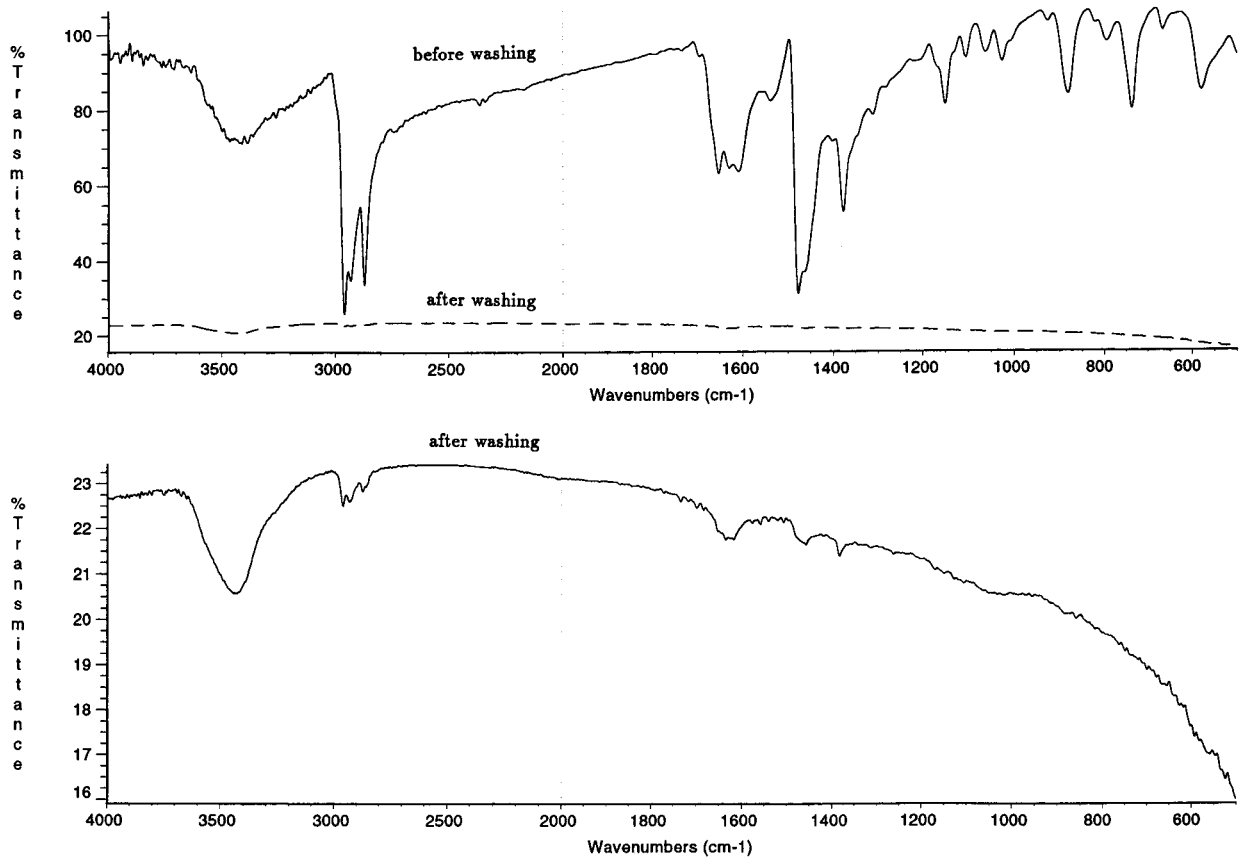

Figure 1. IR spectra of the particle (Pd/Pt ratio 5.18) before (solid line) and after (dashed line) washing with an ethanole/ether mixture (top) and the spectrum of the washed particles with another extinction scale (bottom).

Table 1. Elemental Analyses and Calculated Total Formulas of the Samples

		elemental analysis					
sample with Pd/Pt ratio	total formula	Pd	Pt	Br	C	H	N
1.72	$Pd_{4.91}Pt_{2.85}Br_{1.33}O_x \cdot NBu_4Br$	32.12	34.21	11.44	12.21	2.39	0.86
2.64	$Pd_{4.76}Pt_{1.80}Br_{1.68}O_x \cdot NBu_4Br$	31.45	21.85	13.30	11.64	2.29	0.87
5.18	$Pd_{3.97}Pt_{0.77}Br_{1.55}O_x \cdot NBu_4Br$	31.08	11.01	14.99	13.60	2.53	1.03
5.18 (washed)	$Pd_{3.97}Pt_{1.02}Br_{1.80}O_x \cdot 0.35\ NBu_4Br$	33.99	15.97	13.79	5.36	0.74	0.43

lized by poly(*N*-vinyl-2-pyrrolidone) on the basis of a detailed EXAFS study.[11] Toshima used reference compounds and theoretical phase shifts and amplitudes tabulated by Teo[14] to determine the structural parameter of the samples. Today theoretical phase shifts and amplitudes are available with less deviations from experimental data which lead to more reliable results (for example, data calculated with FEFF).[15] Accordingly, the outer surface of the metal core is enriched in palladium, whereas the inner part consists mainly of platinum. Furthermore, interaction with oxygen leads to an oxidized surface containing Pd−O bonds.[11]

Since different research groups use different metal salt precursors, reducing agents, stabilizers, and reaction conditions, it is not clear whether conclusions regarding a particular metal pair in a specific case are general. In particular the question arises as to whether the structural features of the metal core of a bimetallic cluster depend upon the nature of the stabilizer. In this paper we present the results of an EXAFS study of Pd/Pt bimetallic clusters stabilized by tetrabutylammonium bromide. All clusters were prepared by our previously published electrochemical method.[4,13]

(14) (a) Teo, B. K.; Lee, P. *J. Am. Chem. Soc.* **1979**, *101*, 2815. (b) Teo, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 3990.

(15) Rehr, J. J.; Mustre de Leon, J.; Zabinsky, S. I.; Albers, R. C. *J. Am. Chem. Soc.* **1991**, *113*, 5135.

Experimental Section

Sample Preparation. Palladium/platinum bimetallic clusters with different Pd/Pt ratios (see Table 1) were synthesized via an electochemical reaction with tetrabutylammonium bromide as stabilizer and as electrolyte as previously published,[4,13] except that the workup was different (see below). The metal sources were a sacrificial anode consisting of Pd bulk metal and $PtCl_2$ in the solution. The concentration of the electrolyte NBu_4Br in THF was ~0.06 mol L^{-1}. The samples were prepared using a current density of 5 mA cm^{-2}. As the electrolysis proceeded, the Bu_4NBr-stabilized bimetallic cluster precipitated out. Every 3−4 h the electrolysis was stopped, the solution decanted and the precipate washed with ether. Then the electrolysis was continued until the next sample was isolated. In this way samples of bimetallic clusters with different Pd/Pt ratios were obtained (the $PtCl_2$ concentration diminishes with time). The particles turned out to have an average size of about 3.5 nm. They were studied by TEM and EDX analyses as previously described.[13] A reference compound was obtained by repeatedly washing a part of the sample (with the Pd/Pt ratio of 5.18) thoroughly with an ethanol/ether mixture to remove the stabilizer. This was monitored by IR spectroscopy (Figure 1). The powder cannot be redispersed in THF.

All three substances were mixed with an organic matrix material (urea) and pressed using a pressure of 9 tons/cm^2 to produce pellets (less than 0.5 mm thickness). The concentration of the substances in the matrix material was precalculated to have an average absorption of ~85% of the X-ray beam intensity in the sample.

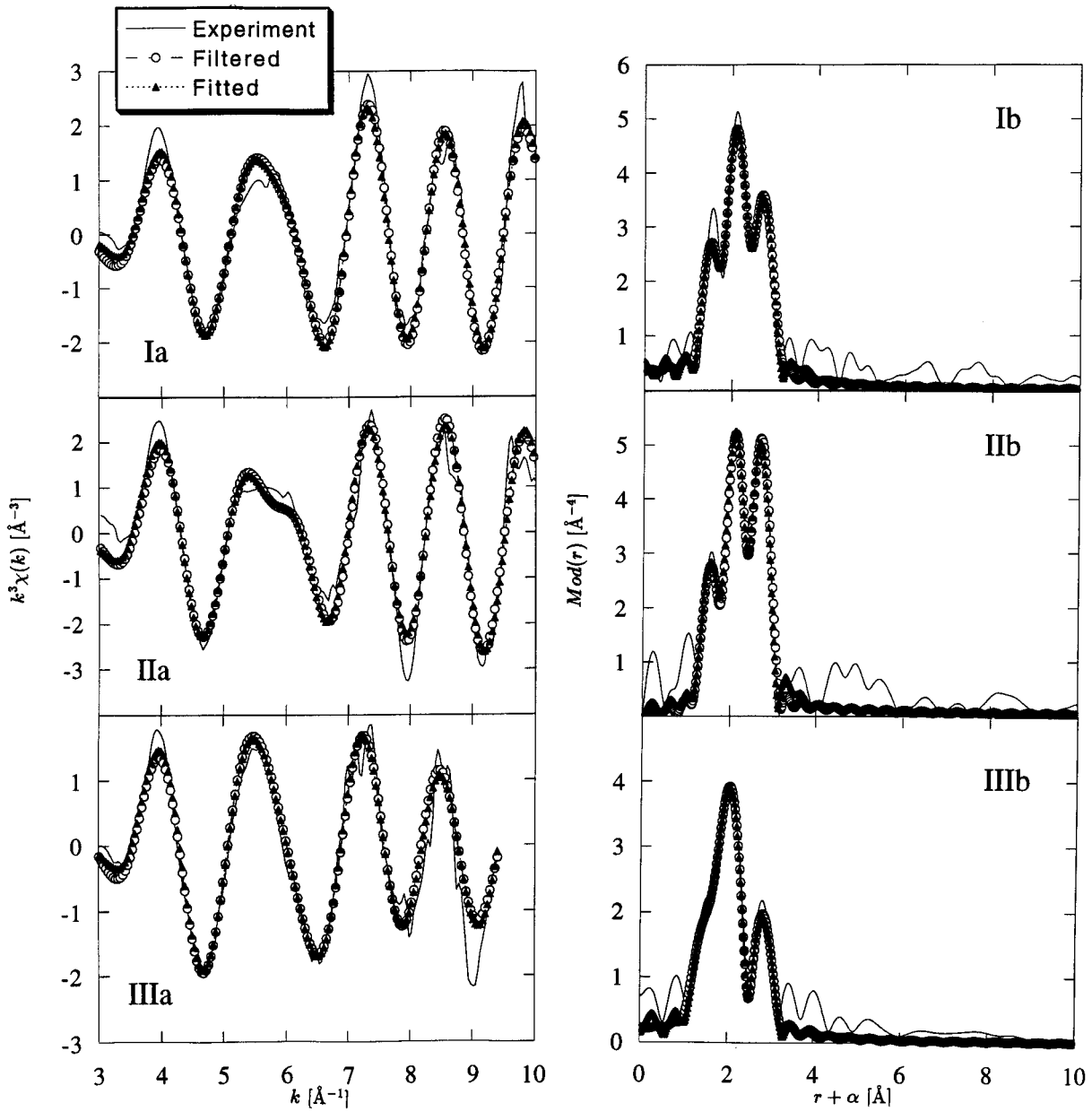

Figure 2. Experimental, filtered, and fitted EXAFS functions $\chi(k)\cdot k^{3-}$ (a) and their Fourier transformed functions (b) (not phase corrected) on the Pt L_{III} edge of the nanostructured particles with Pd/Pt = 1.72 (I), 2.64 (II), and 5.18 (III).

EXAFS Data Acquisition and Analysis. The EXAFS experiments were performed at the Pt L_{III} edge (11 564 eV) and the Pd K edge (24 350 eV) at the beamline ROEMO II at HASYLAB, Hamburg, with a Si⟨311⟩ double-crystal monochromator (~4.4 GeV, 75−135 mA beam current). In all cases data were collected in transmission mode with ion chambers. The second crystal was detuned by about 50% (Pt edge) or 35% (Pd edge) from its maximum flux position to discard higher harmonics. Energy calibration was performed with a Pt foil or Pd foil, respectively.

The data were evaluated with a program package which was specially developed for the requirements of liquid and amorphous samples and which is described in detail in ref 16. The curve-fitting procedure was performed with amplitude and phase functions calculated with the program FEFF V 3.1[15] implemented in the program package.[16] Only the absorber backscatterer distance r, coordination number N, and the damping factor σ^2 (often called EXAFS Debye−Waller factor) were fitted. The energy shift was fixed to 0.0 and the amplitude reducing factor was fixed to 1.0 to reduce the number of free parameters. The data are shown in Figures 2 and 3 and the results of the curve fitting procedure in Tables 2 and 3.

The minimization of the number of parameters causes a large error in the absorber backscatterer distance r. This leads to implausible short distances for the metal−metal interaction and to an inconsistency between the Pd−Pt and the Pt−Pd distance in the determination of the structural parameters in the curve-fitting procedure.

Reliable distances and consistent results were obtained with the energy shifts as additional parameters. For the determination of the absolute coordination numbers, we calculated the theoretical $\chi(k)\cdot k^3$ function with fixed distances r_i and fixed energy shifts ΔE. These values were taken from the curve-fitting procedure using a Levenberg−Marquardt algorithm. The coordination numbers N_i, the EXAFS Debye−Waller factors σ_i and the amplitude reducing factor $S0$ were varied systematically over a wide range. The values of N_i, σ_i, and $S0$ were determined by the minimum of the deviation between the calculated and the experimental $\chi(k)\cdot k^3$ function. The results are shown in Tables 4 and 5. [The energy shifts should have the same value. In the used theoretical phase data the polarization of bonds between absorber and backscatterer is not taken into consideration. The different values for the energy shifts may compensate this. However, the results were

(16) Ertel, T. S.; Bertagnolli, H.; Hückmann, S.; Kolb, U.; Peter, D. *Appl. Spectrosc.* **1992**, *46*, 690.

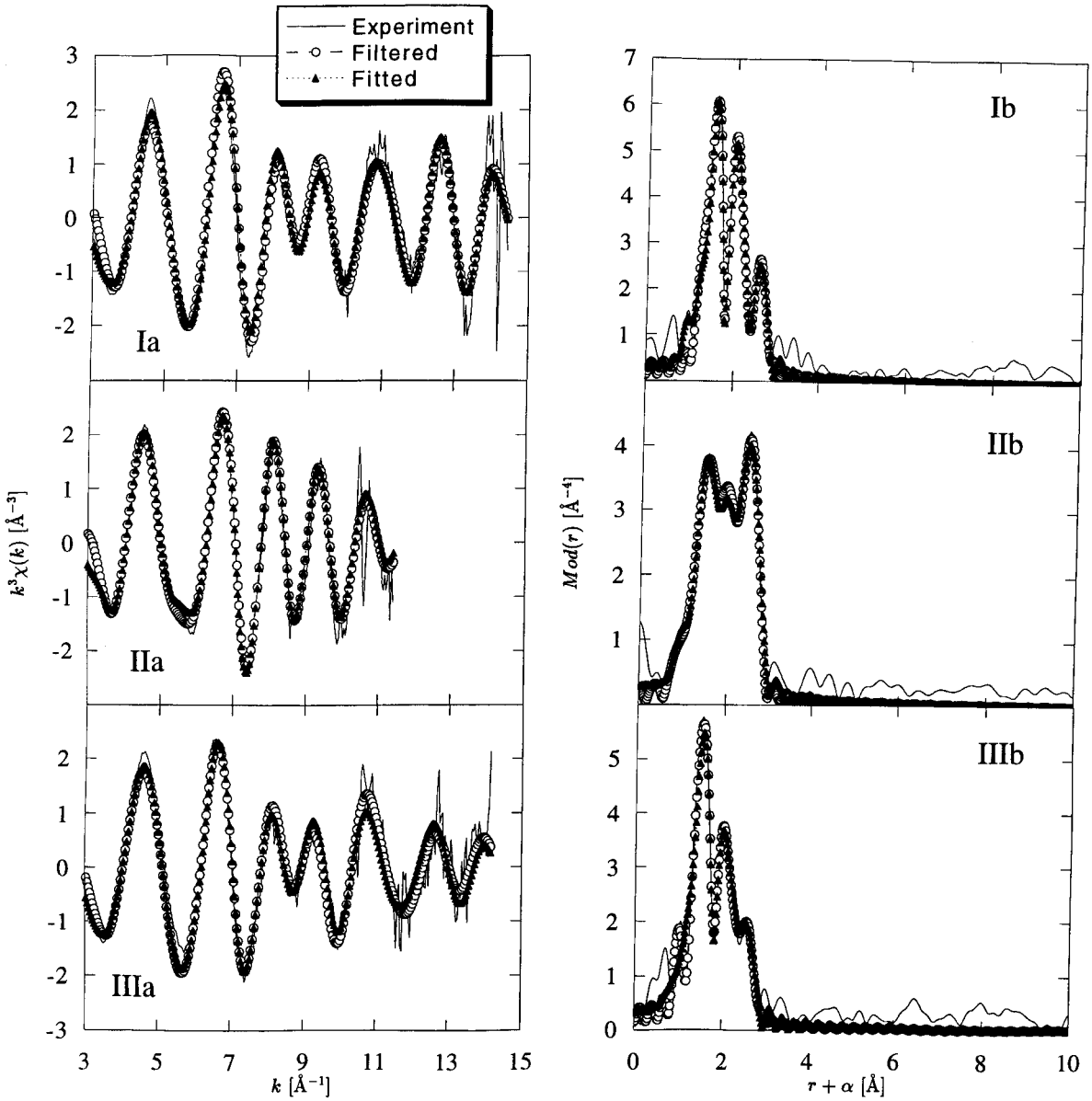

Figure 3. Experimental, filtered, and fitted EXAFS functions $\chi(k)\cdot k^{3-}$ (a) and their Fourier transformed functions (b) (not phase corrected) on the Pd K edge of the nanostructured particles with Pd/Pt = 1.72 (I), 2.64 (II), and 5.18 (III).

checked with the program FEFF6 using one value for the energy shift.]

To verify these results, simplified models on the basis of these values were calculated with the common known program FEFF6 and the parameters were slightly improved manually. The parameter sets for the FEFF6 ab initio calculations are shown in the Tables 6 and 7.

Results and Discussion

The results of the curve-fitting procedure for the EXAFS spectra with the minimum of fit parameters are listed in Tables 2 and 3 (see Figures 2 and 3). Depending on the high degree of correlation between the absolute coordination number N and the damping factor σ^2 and the fact that the amplitude reducing factor $S(k)$ is unknown, no absolute coordination numbers can be given. The ratio of the coordination numbers from a multiple shell fit can be given with a tolerable error of a maximal factor of 2. This can be determined by data analysis and curve fitting of model substances with well-known structures in a comparable way. Despite such possible sources of errors, it is possible to deduce a fairly detailed model of the structure of these tetrabutylam-

Table 2. Results of the Curve-Fitting Procedure (Reduced Set of Parameters) with Amplitude and Phase Data Calculated with the Program FEFF V3.1 for the Nanostructured Particles[a]

	backscatterer dist r (Å)		relative coordination no. N		damping factor σ	
Pd/Pt ratio	exp	fil	exp	fil	exp	fil
1.72						
O	1.94	1.93	0.16	0.12	0.0839	0.0472
Br	2.56	2.57	0.17	0.18	0.0836	0.0994
Pt	2.61	2.62	1.0	1.0	0.0853	0.0848
Pd	2.62	2.62	0.22	0.17	0.0849	0.0625
2.64						
O	1.89	1.89	0.26	0.25	0.1006	0.0924
Br	2.53	2.53	0.11	0.10	0.0473	0.0494
Pt	2.63	2.63	1.0	1.0	0.0837	0.0770
Pd	2.63	2.63	0.71	0.71	0.0990	0.0934
5.18						
O	1.97	1.95	0.19	0.13	0.0762	0.0583
Br	2.56	2.53	0.25	0.27	0.0842	0.1099
Pt	2.61	2.63	1.0	1.0	0.0945	0.1074
Pd	2.60	2.60	0.20	0.20	0.0939	0.0905

[a] exp: signs the result of the curve-fitting procedure for the nonfiltered; fil: for the filtered EXAFS spectra on the Pt L_{III} Edge.

Table 3. Results of the Curve-Fitting Procedure (Reduced Set of Parameters) with Amplitude and Phase Data Calculated with the Program FEFF V3.1 for the Nanostructured Particles[a]

	backscatterer dist r (Å)		relative coordination no. N		damping factor σ	
Pd/Pt ratio	exp	fil	exp	fil	exp	fil
1.72						
N	1.99	2.00	2.6	2.2	0.0401	0.0401
O	2.10	2.12	0.98	0.72	0.0400	0.0423
Br	2.46	2.46	1.7	1.5	0.0923	0.0906
Pt	2.70	2.70	0.69	0.83	0.0529	0.0642
Pd	2.69	2.70	1.0	1.0	0.0966	0.1144
2.64						
N	1.96	1.96	0.84	0.80	0.0439	0.0401
O	2.08	2.07	0.90	0.84	0.0562	0.0423
Br	2.42	2.43	0.52	0.21	0.0835	0.0442
Pt	2.71	2.67	0.89	0.83	0.0901	0.0854
Pd	2.73	2.73	1.0	1.0	0.0718	0.0850
5.18						
N	2.07	2.09	1.7	1.2	0.0497	0.0407
O	1.95	1.96	1.5	1.9	0.0423	0.0423
Br	2.46	2.46	1.6	1.9	0.0921	0.0984
Pt	2.69	2.70	0.40	0.62	0.0461	0.0569
Pd	2.71	2.71	1.0	1.0	0.0908	0.0823

[a] exp: signs the result of the curve-fitting procedure for the nonfiltered; fil: for the filtered EXAFS spectra on the Pd K Edge.

Table 4. Results of the Curve-Fitting Procedure (Full Set of Parameters) for the Filtered EXAFS Spectra on the Pt L_{III} Edge with Amplitude and Phase Data Calculated with the Program FEFF V3.1 for the Nanostructured Particles

Pd/Pt ratio	backscatterer dist r (Å)	coordination no. N	damping factor σ	energy shift ΔE (eV)
1.72 ($S0 = 0.89$)				
O	2.00	1.08	0.0493	10.3
Br	2.46	0.68	0.1128	10.9
Pt	2.75	8.45	0.1584	8.4
Pd	2.74	1.81	0.0818	7.2
2.64 ($S0 = 0.80$)				
O	1.99	1.32	0.0965	11.02
Br	2.45	0.46	0.0926	8.03
Pt	2.75	6.90	0.1588	8.05
Pd	2.75	3.30	0.0908	7.95
5.18 ($S0 = 0.80$)				
O	2.00	1.06	0.0441	6.58
Br	2.53	1.30	0.1007	6.13
Pt	2.75	7.64	0.1576	6.73
Pd	2.72	1.72	0.0913	5.92

Table 5. Results of the Curve-Fitting Procedure (Full Set of Parameters) for the Filtered EXAFS Spectra on the Pd K Edge with Amplitude and Phase Data Calculated with the Program FEFF V3.1 for the Nanostructured Particles

Pd/Pt ratio	backscatterer dist r([Å)	coordination no. N	damping factor σ	energy shift ΔE (eV)
1.72 ($S0 = 0.63$)				
N	2.23	1.27	0.0441	6.0
O	2.01	3.25	0.0570	6.0
Br	2.44	1.93	0.0918	0.0
Pt	2.73	1.18	0.0780	7.0
Pd	2.75	1.15	0.0925	2.0
2.64 ($S0 = 0.63$)				
N	1.99	2.53	0.0431	3.0
O	2.12	1.88	0.0508	3.0
Br	2.43	0.85	0.0489	2.95
Pt	2.73	1.63	0.0908	0.0
Pd	2.75	1.68	0.0519	0.0
5.18 ($S0 = 0.63$)				
N	2.00	3.25	0.0431	2.97
O	2.12	1.78	0.0443	2.89
Br	2.47	0.95	0.0700	2.99
Pt	2.72	1.48	0.0913	3.05
Pd	2.75	0.83	0.0773	2.91

Table 6. Input Parameters of Simplified Models of the Samples To Calculate the EXAFS Spectra on the Pt L_{III} Edge with the Program FEFF6 for the Nanostructured Particles

Pd/Pt ratio	backscatterer dist r (Å)	coordination no. N	damping factor σ
1.72 ($S0^a = 0.89$, $\Delta E^b = 9.0$ eV)			
O	1.99	1	0.0802
Br	2.46	1	0.1127
Pt	2.75	8	0.1584
Pd	2.74	2	0.0837
2.64 ($S0^a = 0.84$, $\Delta E^b = 10.0$ eV)			
O	1.99	1	0.0912
Br	2.45	1	0.1248
Pt	2.75	7	0.1421
Pd	2.75	4	0.0951
5.18 ($S0^a = 0.92$, $\Delta E^b = 8.0$ eV)			
O	2.00	1	0.0703
Br	2.53	1	0.1007
Pt	2.75	8	0.1549
Pd	2.72	2	0.0987

[a] Please notice that the FEFF input is $S0^2$ in the HOLE card. [b] The imaginary energy shift in the CORRECTION card was 1.0 eV.

monium bromide stabilized clusters by interpreting the fit parameters carefully. Curve fitting, which includes the variation of the energy shift ΔE and the amplitude reducing factor $S0$ (calculated without k dependency), was also done and the results were verified by calculating the theoretical $\chi(k)\cdot k^3$ function using the program FEFF6.[15] The results of the curve-fitting procedure are tabulated in Tables 4 and 5, and the parameters of the FEFF inputs are shown in Tables 6 and 7. The portion of the palladium compound in the cluster is, in all cases, much higher than the portion of the platinum metal. In contrast to this, it was found in the curve-fitting procedure that there is an always greater contribution of platinum backscatterers to the $\chi(k)\cdot k^3$ function on the Pt L_{III} edge. Hence, an enrichment of platinum in the core and of palladium in the outer shell can be deduced. This interpretation is in agreement with the results determined for similar Pd/Pt clusters stabilized by poly(N-vinyl-2-pyrrolidone).[11] Thus, an important conclusion of the present study is evident. The gross structural features regarding the two metals in the metal core do not depend upon the nature of the stabilizer.

A small contribution of a light backscatterer (oxygen) to the Pt L_{III} edge implies that the clusters are partially oxidized. This behavior has been reported as well by Toshima in the case of poly(N-vinyl-2-pyrrolidone)-stabilized Pd/Pt bimetallic clusters.[11] The significantly greater contribution of light backscatterers to the Pd K edge is a result of a partial oxidation of the cluster on the one hand and of stabilizer molecules being very close to the surface of the cluster on the other hand. This contribution to the Pd K edge was fitted with an oxygen and a nitrogen backscatterer. We are certain that there must actually be an overlap of oxygen (metal oxide), nitrogen, and carbon (stabilizer) backscatterers. However, these contributions could not be resolved in the curve-fitting procedure. We conclude on the basis of the EXAFS data that the Bu_4NBr stabilizer surrounds the outer part of the bimetallic cluster. This is in agreement with a combined STM/TEM study of R_4NX-stabilized Pd clusters, in which a structural model with a monomolecular protective coat was deduced.[8] The partial oxidation of the palladium-enriched outer part of the cluster can also be deduced on the basis of the total number of

Table 7. Input Parameters of Simplified Models of the Samples To Calculate the EXAFS Spectra on the Pd K Edge with the Program FEFF6 for the Nanostructured Particles

Pd/Pt ratio	backscatterer dist r (Å)	coordination no. N	damping factor σ
1.72 ($S0^a = 0.71$, $\Delta E^b = 5.0$ eV)			
N	2.23	2	0.0440
O	2.01	3	0.0570
Br	2.44	2	0.0918
Pt	2.73	1	0.0780
Pd	2.75	1	0.0925
2.64 ($S0^a = 0.62$, $\Delta E^b = 2.0$)			
N	1.99	3	0.0431
O	2.12	2	0.0508
Br	2.43	1	0.0489
Pt	2.73	2	0.0908
Pd	2.75	2	0.0592
5.18 ($S0^a = 0.63$, $\Delta E^b = 5.0$)			
N	2.00	3	0.0316
O	2.12	2	0.0443
Br	2.47	1	0.0728
Pt	2.72	1	0.0693
Pd	2.75	1	0.0775

[a] Please notice that the FEFF input is $S0^2$ in the HOLE card. [b] The imaginary energy shift in the CORRECTION card was 1.0 eV.

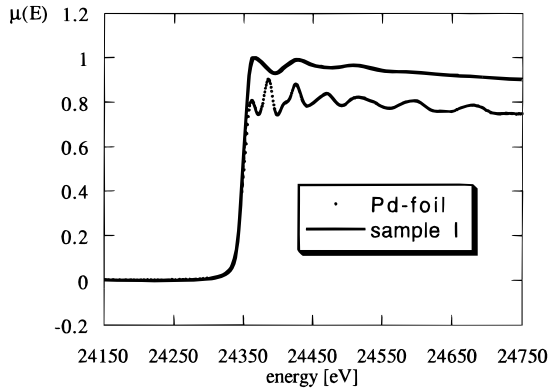

Figure 4. Normalized EXAFS spectra (near edge region) on the Pd K edge of palladium foil (dotted line) and sample I (Pd/Pt = 1.72 (I)) (solid line).

atoms surrounding the palladium. In pure metal the number of neighbors should be 12. A total number of neighbors less than this indicates a greater portion of oxide in the outer part of the cluster. This conclusion is also supported by the number of metal neighbors on the Pd K and the Pt L_{III} absorption edge, respectively. These aspects lead to the conclusion that a small part of oxide is included in the cores and a larger amount of oxide is part of the outer shells of the clusters. Figure 4 shows the near edge region of the EXAFS spectra of a palladium foil and sample I on the Pd K edge. The differences between the spectra and the smaller amplitude of the oscillations of the spectrum of sample I show that the local environment of the palladium absorber in the cluster is completely different from the environment in the pure metal.

The existence of a bromine backscatterer on the Pt L_{III} edge shows that a small part of the platinum appears to be present in the sample as metal bromide. The counterion is bromide and not chloride because of the greater amount of bromide ions in the solution during the preparation procedure. However, the EXAFS data do not allow for a clear conclusion as to where the platinum bromide is located in the sample (in the metal core, as part of the stabilizer or simply as an impurity). Washing the samples with THF to remove possible Pt salts in order to obtain clusters with higher purity was not performed in the present study.

The elemental analysis (Table 1) also speaks for the conclusion that part of the bromide is associated with a metal, i.e., not solely with the ammonium cations. On the Pd K edge a significant contribution of bromine backscatterers to the $\chi(k)\cdot k^3$ functions was also found. On the basis of a careful interpretation of the coordination numbers, it can be said that the amount of palladium bromide is equal or a little bit larger than the amount of platinum bromide. Further EXAFS studies on the Br K edge will help to clarify the question where the bromide is precisely located.

It is difficult to give a precise and reliable value for the amount of nonreduced metal in the sample. However, an approximation is possible. A careful interpretation of the ratio of the coordination numbers and the result of the elemental analyses lead to the conclusion that about 20−40% of the total metal is unreduced, i.e., it occurs to this extent as oxide and bromide, the latter making up 9−18%.

Conclusions

A structural model of Bu_4NBr-stabilized Pd/Pt bimetallic clusters has been deduced from EXAFS data. Accordingly, the outer part of the bimetallic core is enriched in palladium, the inner part being enriched in platinum. Similar structures were previously found for poly(N-vinyl-2-pyrrolidone)-stabilized Pd/Pt bimetallic clusters.[11] Thus, such structural features appear to be independent of the type of stabilizer. The metal particles are partially oxidized and part of the metal is present in the cluster in an unreduced form as metal bromides. The nanostructured particles have a protective coat consisting of ammonium ions with bromide as the counterions. The stabilizer appears to be close to the surface of the cluster.

As far as application in catalysis is concerned, the presence of some metal oxide is often beneficial.[11] This does not necessarily apply to the presence of metal halides. However, cluster preparations in the absence of halides are known.[1−4] For example, we have reported an alternative electrochemical fabrication of metal clusters using tetrabutylammonium acetates as electrolyte and stabilizer.[13] Structural studies of crude and purified forms of such materials are in progress in our laboratories.

Acknowledgment. U.K. wishes to thank J. Tölle for his general assistance and Dr. Seevogel and Mrs. Dittrich for performing the IR spectroscopic measurements.

CM960062H