NADH model compounds and  $[Co(acac)_3]$ , the charge of the micellar surface might play an important role in the heterolytic dissociation of the encounter complex. The anionic charge of SDS micelles accelerates the heterolytic dissociation of the encounter complex of  $[BNAH^+ Co(acac)_3^-]$  not only through stabilization of the positive charge of  $BNAH^{++}$  generated but also through the charge separation of acac<sup>-</sup> from the micellar surface. Thus, it is concluded that anionic SDS and SDeS promoted the photoreduction of [Co(acac)<sub>3</sub>] with BNAH and/or DNAH by concentrating them through the hydrophobic interaction and by lengthening the lifetime of the photoexcited NADH model compounds, while cationic DTAC and HTAB retarded the photoreaction by suppressing the heterolytic dissociation of the encounter complex between BNAH\* (or DNAH\*) and [Co(acac)<sub>3</sub>].

## **Bimetallic CuPt Particles Supported in Y Zeolite:** Structural Characterization by EXAFS

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The structures of bimetallic CuPt particles in freshly reduced and outgassed CuPt/NaY zeolites were characterized by extended X-ray absorption fine structure (EXAFS) at the Cu K-edge and Pt L<sub>3</sub>-edge. In order to understand the effect of copper on the coordinative environment of platinum, reduced Cu/NaY and Pt/NaY were also studied. It is found that the structure of CuPt bimetallic particles is dependent on the atomic ratio of Cu and Pt in the zeolites. At room temperature, some of the Cu atoms are oxidized, presumably by reacting with protons on the zeolite surface. By outgassing in helium at 500 °C, additional Cu atoms were leached from the surface of the CuPt particles to expose more Pt atoms on the surface. Thus, an enhancement in the activity of toluene hydrogenation was observed. Due to the leaching of Cu atoms upon outgassing in helium or under vacuum, hydrogen chemisorption is not an appropriate method to estimate the number of surface Pt atoms in bimetallic CuPt particles supported in NaY.

#### Introduction

Bimetallic catalysts have been widely used in heterogeneous catalysis.<sup>1,2</sup> One of the major applications is in the catalytic reforming of refinery naphtha. The main reason for their remarkable stability and selectivity compared to monometallic catalysts is due to the altered surface structure and composition. One of the major challenges in bimetallic catalyst research is obtaining particles with homogeneous composition. Most bimetallic catalysts are prepared by impregnation of metal salts into a support followed by activation in hydrogen. It is merely by chance that the two metallic components come together to form bimetallic particles on the support.<sup>3</sup> It was found by EXAFS analysis of a number of supported bimetallic catalysts (e.g., Cu-Ru,<sup>4</sup>-Os,<sup>5</sup>-Rh;<sup>6</sup> Ir-Pt,<sup>7</sup>-Rh;<sup>8</sup> Rh-Co;<sup>9,10</sup> Cu-Ni<sup>11</sup>) that the bulk composition often differed from that of the surface. An in situ EXAFS study by Esteban et al. also indicated that pure Pt and Ru particles as well as PtRu alloy aggregates were formed on alumina.<sup>12</sup> Anisotropy was also observed by transmission electron microscopy coupled with energy dispersive X-ray spectroscopy and electron diffraction to obtain morphological, analytical, and structural data on individual metal clusters in the catalysts. It was found that the composition of copper on ruthenium particles is not uniform in  $CuRu/SiO_2$  catalyts prepared from  $Cu(NO_3)_2$ 

- (4) Sinfelt, J. H.; Via, G. H.; Lytle, F. W. J. Chem. Phys. 1980, 72, 4832.
   (5) Sinfelt, J. H.; Via, G. H.; Lytle, F. W.; Greegor, R. B. J. Chem. Phys. 1981, 75, 5527.
- (6) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. J. Chem. Phys. 1983, 78, 882.
- (7) Sinfelt, J. H.; Via. G. H.; Lytle, F. W. J. Chem. Phys. 1982, 76, 2779.
  (8) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. J. Chem. Phys. 1983, 78, 2533.
- (9) Yokoyama, T.; Yamazaki, K.; Kosugi, N.; Kuroda, H.; Ichikawa, M.;
- Fukushima, T. J. Chem. Soc., Chem. Commun. 1984, 962. (10) Van'T Blik, H. F. J.; Koningberger, D. C.; Prins, R. J. Catal. 1986, 97, 210.
- (11) Sankar, G.; Vasudevan, S.; Rao, C. N. R. J. Phys. Chem. 1986, 90, 5325.
- (12) Esteban, P.; Diaz, G.; Guczi, L.; Garin, F.; Bernhardt, P.; Schmidt,
- J. L.; Marie, G. J. Chim. Phys. 1989, 86, 1727.
   (13) Shastri, A. G.; Schwank, J.; Galvagno, S. J. Catal. 1988, 100, 446. (14) Guczi, L. Stud. Surf. Sci. Catal. 1986, 29, 547.

and RuCl<sub>3</sub>.<sup>13</sup> One route to bimetallic catalysts is to use heterometallic molecular clusters as precursors.<sup>14</sup> This provides an opportunity to control the composition of the catalyst particles produced. However, this method is limited because of the availability of bimetallic clusters and possible segregation of the

<sup>(1)</sup> Sinfelt, J. H. Bimetallic Catalysts-Discoveries, Concepts and Appli-

<sup>(</sup>a) Onice y: New York, 1983.
(b) Ponec, V. In Advances in Catalysis; Eley, D. D., Pines, H., Weisz, P. B., Eds.; Acdemic Press: San Diego, 1987; Vol. 32, p 149.
(c) Margitfalvi, J.; Szabo, S.; Nagy, F. Stud. Surf. Sci. Catal. 1986, 27, Catal. 1986, 27, Catal. Sci. Catal. 1986, 27, Catal. 1986, 28, Catal. 1986, 28, Catal. 1986, 28, Catal. 1986, 28, Catal. 198

<sup>373.</sup> 

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different metals during deposition on the supports or during the activation process.<sup>15,17</sup>

Zeolites, particularly faujasite types, possess cation-exchange sites that can accommodate metal cations or complexes and micropores that can encapsulate metal particles produced during reduction. Previously, we proposed mechanisms to describe the formation of various sizes of Pt particles in different locations in NaY zeolite. (i) When Pt<sup>2+</sup> ions are in the supercages, small Pt particles with an average coordination number of 7.7, as determined by EXAFS measurements, are formed in the supercages.<sup>18</sup> (ii) If Pt<sup>2+</sup> ions are distributed in supercages and sodalite cages, Pt particles are formed by adding Pt atoms escaping from the sodalite cages onto the surface of Pt particles already formed in the supercages.<sup>19</sup> These two different cases of Pt particle formation could be extended to the design of bimetallic particles in NaY zeolites. If both metal ions are uniformly distributed in the supercages, bimetallic particles with a homogeneous composition could be generated in supercages after reduction. A typical example is PtRh on which results will be reported later.<sup>20</sup> On the other hand, if the two metal cations are located separately in supercages and sodalite cages, such as Pt<sup>2+</sup> and Cu<sup>2+</sup> ions, respectively, bimetallic CuPt particles formed by transfer of Cu atoms from the sodalite cages to Pt particles formed in the supercages can be expected.<sup>21</sup> The effect of copper in CuPt/Y on the selectivities toward isomerization of n-octane and ring opening of methylcyclopentane has been studied.<sup>21,22</sup> Other bimetallic particles in Y zeolites have also been studied, e.g. Cu-Rh, -Pt, -Ir;<sup>22</sup> Ru-Cu, -Ni;<sup>23</sup> Mo-Pt.<sup>24</sup> In this paper, we report on the formation and structure of bimetallic CuPt particles supported in NaY and the effect of outgassing on their structure.

#### **Experimental Section**

The bimetallic CuPt/NaY catalyst was prepared by ion exchange of NaY (Union Carbide, Lot 3606468) with an aqueous solution of 200 ppm platinum tetraammine chloride at 80 °C followed by ion exchange with an aqueous solution of 200 ppm copper nitrate at room temperature, as described previously.<sup>21</sup> Two CuPt/NaY samples with atomic ratios Cu/Pt = 1.0 and 3.0 were prepared and are referred to as CuPt/NaY(1.0) and CuPt/ NaY(3.0), respectively. The loading of Cu and Pt in CuPt/ NaY(1.0) were 0.8 and 2.4 wt % and in CuPt/NaY(3.0) were 2.4 and 2.4 wt %, respectively. Two reference samples, Cu/NaY with 1.0 wt % Cu and Pt/NaY with 2.0 wt % Pt, were also prepared by ion exchange. The three platinum-containing samples were first calcined in oxygen (1000 mL/(min g of zeolite), 0.5 °C/min to 300 °C, and at 300 °C for 2 h). Due to the low loading of copper and large X-ray absorption by zeolite support, CuPt/NaY was mixed with an appropriate amount of boron nitride so that the total X-ray absorption coefficient,  $\mu x$ , was less than 3. They were then reheated in  $O_2$  at 300 °C, evacuated and reduced by 5% H<sub>2</sub>/Ar from 25 to 500 °C at 10 °C/min, and held at 500 °C for another 2 h. After cooling to room temperature, the zeolite samples were transferred into glass sample cells with capton film windows and sealed under hydrogen without exposure to air. Another reduced sample, CuPt/NaY(1.0), which was

- (19) Tzou, M. S.; Sachtler, W. M. H. Stud. Surf. Sci. Catal. 1988, 38, 233
- (20) (a) Tzou, M. S.; Kusunoki, M.; Asakura, K.; Kuroda, H. To be published. (b) Tzou, M. S.; Kuroda, H.; Asakura, K. Presented at the First Tokyo Conference on Advances in Catalytic Science and Technology, July 1-5, 1990, Tokyo, Japan.
   (21) Moretti, G.; Sachtler, W. M. H. J. Catal. 1989, 115, 205.

(22) Tebassi, L.; Sayari, A.; Ghorbel, A.; Dufaux, M.; Ben Taarit, Y.; Naccache, C. In Proceedings of the 6th International Zeolite Conference; Olson, D., Bisio, A., Eds., Butterworth: Guildford, 1984; p 368. (23) Elliott, D. J., Lunsford, J. H. J. Catal. 1979, 57, 11.

- (24) Samant, M. G.; Bergert, G.; Gallezot, P.; Boudart, M. J. Phys. Chem. 1988, 92, 3547.



Figure 1. EXAFS  $k^3\chi(k)$  functions and Fourier transforms of freshly reduced Pt/NaY (a, b) and Cu/NaY (c, d).

further heated in helium at 500 °C for 1 h and sealed in helium was also prepared. The X-ray absorption measurements were carried out at room temperature at beam line 10B of the Photon Factory at the National Laboratory for High Energy Physics. The synchrotron energy, current, and resolution were 2.5 GeV, 200-300 mA, and 2 eV, respectively. A channel cut Si(311) was used as a monochromator, and ion chambers filled with nitrogen were used as detectors.

Hydrogenation of toluene on Pt/NaY and CuPt/NaY (60 mg) was carried out in a differential flow microreactor. In order to keep the conversion lower than 5%, the experimental conditions were T = 60 °C,  $P(H_2) = 732 \text{ Torr}$ , P(toluene) = 28 Torr, and flow rate = 230 mL/min. Analysis of the reactant and product gases was made using a Shimadzu CBP1-M50-025 capillary column with flame ionization detector in a Shimadzu GC 9A gas chromatograph.

The oxygen uptake during oxidation of CuPt/NaY (600 mg) at 500 °C, in which samples were prereduced in hydrogen and outgassed in helium at 500 °C, was carried out in a volumetric circulating reactor system. The size of the metal particles in all samples was characterized by HRTEM using an Akashi EM-002A electron microscope with an accelerating voltage of 120 K/V. Among the samples examined in this study, only in the case of Cu/NaY were large particles observed on the exterior of the zeolite.

#### **Results and Discussions**

**Pt/NaY and Cu/NaY.** Figure 1 shows the plot of the  $k^3\chi(k)$ function vs k, where k is the photoelectron wave vector and  $\chi(k)$ is the normalized EXAFS function for reduced Pt/NaY at the Pt L<sub>3</sub>-edge. Fourier transforms (phase shift uncorrected) of  $k^{3}\chi(k)$ , which is shown below the EXAFS plot, yield the radial distribution function  $\Psi(R)$ , where R is the distance from the absorber atom. There is a major peak at 2.5 Å (before phase correction) for Pt/NaY in Figure 1b. The small peak at 2.2 Å is caused by nonlinearity of the phase shift function for Pt-Pt bonding.<sup>25</sup> Such peaks at low R become intense, especially for small particles of third-row transition metals, such as supported Os, Ir, and Pt catalysts.<sup>26,27</sup> After curve-fitting analysis of the inverse Fourier transform (2.0-3.0 Å) with theoretical parameters, the bond distance and coordination number are 2.74 Å and 6.0  $\pm 1.0$ , respectively, as listed in Table I. The small coordination numbers for the first shell and the absence of peaks of higher coordination shells suggest that the Pt particles in Pt/NaY are small, which is consistent with reported data.<sup>18,24</sup>

Figure 1 also shows the  $k^3\chi(k)$  function and Fourier transform of Cu/NaY at the Cu K-edge absorption. The Fourier transform

(27) Via, G. H.; Sinfelt, J. H.; Lytle, F. W. J. Chem. Phys. 1979, 71, 690.

<sup>(15)</sup> Choplin, A.; Leconte, M.; Basset, J. M.; Shore, S. G.; Hsu, W.-L. J. Mol. Catal. 1983, 21, 389.

<sup>(16)</sup> Asakura, K.; Iwasawa, Y.; Yamada, M. J. Chem. Soc., Faraday Trans. 1 1988, 84, 2457

<sup>(17)</sup> Kelley, M. J.; Fung, A. S.; McDevitt, M. R.; Tooley, P. A.; Gates, B. C. Mater. Res. Soc. Symp. Proc. 1988, 111, 23. (18) Tzou, M. S.; Teo, B. K.; Sachtler, W. M. H. J. Catal. 1988, 113, 220.

<sup>(25)</sup> Teo, B. K.; Lee, P. A. J. Am. Chem. Soc. 1979, 101, 2815.
(26) Marques, E. C.; Sandstrom, D. R.; Lyte, F. W.; Greegor, R. B. J. Chem. Phys. 1982, 77, 1027.

TABLE I: Structure Parameters for Pt/NaY, Cu/NaY(1.0), and CuPt/NaY(3.0)<sup>a</sup>

samples	bonding pairs	<i>R</i> , Å	N	σ
Pt/NaY	Pt-Pt	2.74	6.0 ± 1	0.05
CuNaY	Cu-Cu	2.53	9.9 🌒 1.5	0.04
CuPt/NaY(1.0), freshly reduced	Pt-Pt	2.74	4.8 ± 0.6	0.06
	Pt-Cu	2.61	1.8 ± 0.4	0.08
	Cu-O	1.96	$1.0 \pm 0.2$	0.05
	Cu-Cu	2.48	$0.6 \pm 0.2$	0.05
	Cu-Pt	2.62	1.2 • 0.3	0.06
CuPt/NaY(1.0), outgassed	Pt-Pt	2.71	$4.9 \pm 0.6$	0.06
	Pt-Cu	2.59	$1.0 \pm 0.2$	0.08
	Cu-O	1.98	$1.2 \pm 0.3$	0.05
	Cu-Cu	2.48	$0.3 \pm 0.2$	0.05
	Cu-Pt	2.59	$0.7 \pm 0.3$	0.06
CuPt/NaY(3.0), freshly reduced	Pt-Pt	-	-	
	Pt-Cu	2.55	$7.4 \pm 1.5$	0.06
	Cu-Cu	2.51	$6.0 \pm 1.0$	0.05
	Cu_Dt	2 57	04 0 0 2	0.06

<sup>a</sup> R is the bonding distance, N the coordination number, and  $\sigma$  the Debye-Waller factor.



Figure 2. EXAFS  $k^3\chi(k)$  functions, Fourier transforms, and fitting analysis of freshly reduced CuPt/NaY(1.0) at the Pt L3-edge (a-c) and Cu K-edge (d-f).

clearly indicates the existence of 1st, 2nd, 3rd, and 4th coordination shells at 2.3, 3.4, 4.1, and 4.8 Å, respectively, before the phase correction. After curve-fitting analysis, the bond distance and coordination number of the first shell are 2.53 Å and 9.9, respectively, as listed in Table I. The presence of atoms in higher shells and the large coordination number for the first shell indicate that the Cu particles formed under the experimental conditions are large. Indeed, Cu particles with a face-centered cubic structure in the range 300-500 Å were clearly observed on the exterior of the zeolite crystals by HRTEM.

CuPt/NaY(1.0). The  $k^3\chi(k)$  weighted EXAFS function and Fourier transform of CuPt/NaY(1.0) at both the Pt  $L_3$ -edge and the Cu K-edge are shown in Figure 2. These are quite different from the corresponding functions of Pt/NaY and Cu/NaY in Figure 1. In the Fourier transform of the Pt  $L_3$ -edge absorption, there are two distinct peaks of equal intensity at 2.1 and 2.5 Å. Due to the lack of bimetallic cluster compounds and CuPt alloys with known compositions as reference materials for estimating the coordination numbers between Cu and Pt atoms in the CuPt



Figure 3. EXAFS  $k^3\chi(k)$  functions and Fourier transforms of freshly reduced CuPt/NaY(3.0) at the Pt  $L_3$ -edge (a, b) and Cu K-edge (c, d).

particles in NaY, an assumption of equal amplitude reduction factor, S, between Pt and Pt as well as Pt and Cu was made. The assumption is based on the near-equivalent amplitude reduction factors computed from the total electron shake-off probability among low- and high-Z (atomic number) elements.<sup>28-30</sup> Such an approximation may give rise to an error of about 10%. The best-fit analyses, as listed in Table I, are the bond distances R(Pt-Cu) = 2.61 Å and R(Pt-Pt) = 2.74 Å and coordination numbers N(Pt-Pt) = 4.8 and N(Pt-Cu) = 1.8. The coordinative distance of Pt-Pt is within experimental error of the results from X-ray crystallographic studies and is the same as in Pt/NaY. The bond distance of R(Pt-Cu) derived from the fitting analysis is about 0.04 Å shorter than the summation of the atomic radii of Pt and Cu atoms.

In the Cu K-edge, there is a major peak at 2.3 Å with two shoulders on both sides in the  $k^3$ -weighted Fourier transform, as shown in Figure 2e. Because these three peaks are not separable by the Hanning window technique, three terms fitting with oxygen, copper, and platinum as the possible backscattering atoms were used to analyze the inverse Fourier transform of CuPt/NaY(1.0)in the range R = 1.2-3.5 Å. After phase correction, the coordinative distances are R(Cu-O) = 1.96 Å, R(Cu-Cu) = 2.48 Å, and R(Cu-Pt) = 2.62 Å. The coordination numbers derived from fitting analysis are listed in Table I.

As listed in Table I, the coordination number, N(Pt-Pt), in CuPt/NaY(1.0) is smaller than that of Pt/NaY. However, the summation of N(Pt-Pt) and N(Pt-Cu) is slightly larger than N(Pt-Pt) of Pt/NaY. On the Cu K-edge absorption, the small N(Cu-Cu) and N(Cu-Pt) may indicate that copper does not exist as a separate phase or that is not well mixed with platinum. Based on the fitting results, the bimetallic CuPt particles in the CuPt/NaY(1.0) probably have a cherry type structure with platinum atoms in the center and copper atoms prevailing on the surface of Pt particles. Due to oxidation of part of the copper, which will be described in the section of oxidation of copper, the platinum surface may not be fully covered by copper atoms.

CuPt/NaY(3.0). Figure 3 shows the  $k^3$ -weighted EXAFS function and its Fourier transform of CuPt/NaY(3.0) at the Pt L3-edge and Cu K-edge absorption, which are quite different from the corresponding functions of CuPt/NaY(1.0) in Figure 2. The difference must be caused by the large amount of copper. There is only a main peak at 2.2 Å with a small shoulder at 2.6 Å in the Fourier transform (Pt  $L_3$ -edge) of CuPt/NaY(3.0). The curve-fitting analysis, also listed in Table I, gives only Pt-Cu bonding at 2.55 Å and N(Pt-Cu) = 7.4 and no significant con-

<sup>(28)</sup> Teo, B. K. EXAFS: Basic Principles and Data Analysis; Springer-Verlag: New York, 1986. (29) Teo, B. K.; Antonio, M. R.; Averill, B. A. J. Am. Chem. Soc. 1983,

<sup>105, 3571.</sup> 

<sup>(30)</sup> Stern, E. A.; Bunker, B. A.; Heald, S. M. Phys. Rev. B 1980, 21, 5521.

tribution for the bonding of Pt-Pt. In the Cu K-edge absorption, there is only a peak at 2.2 Å in the  $k^3$ -weighted Fourier transform. The fitting results in Table I indicate the neighboring atoms around copper are N(Cu-Cu) = 6.0 and N(Cu-Pt) = 0.4. In conclusion, the bimetallic CuPt particles in CuPt/NaY(3.0) have an alloy type structure in which platinum atoms are completely dissolved in copper particles.

It is known that both Cu and Pt have an fcc structure and form ordered solid solutions.<sup>31</sup> Ponec et al. also suggested that Cu and Pt can form a well-mixed solution over a wide range of composition.<sup>32</sup> The EXAFS studies of CuPt/SiO<sub>2</sub> by Sinfelt et al. revealed that about 40% of the first-shell coordinative atoms of platinum are copper, and vice versa.<sup>33</sup> However, the above results indicate that when Cu/Pt = 1.0, CuPt particles have a cherry type structure with Pt prevailing in the center and Cu atoms on the surface. As the amount of copper is increased to Cu/Pt = 3.0, platinum atoms are completely alloyed with copper atoms.

Formation of CuPt Bimetallic Particles. It is interesting to find that, with the same treatment conditions and similar metal loadings, the particle sizes in the four systems are quite different: large Cu particles on Cu/NaY, small Pt particles in Pt/NaY, and small CuPt bimetallic particles in CuPt/NaY(1.0) and CuPt/ NaY(3.0). Previously, we proposed mechanisms to explain the sizes and locations of Pt particles formed in Pt/NaY calcined at different temperatures.<sup>18,19</sup> Such mechanisms are suitable to explain the above observations.

(1) Cu/NaY. X-ray powder diffraction studies indicate that the distribution of copper ions in the exchange sites of Y type zeolite is dependent on the dehydration temperature, presence of guest molecules, and the loading.<sup>34</sup> The loading of copper in Cu/NaY is only 0.8 wt %, which is equivalent to about two copper atoms per unit cell. According to X-ray diffraction studies, Cu2+ ions in samples with such a low loading should be located in sodalite cages and hexagonal prisms after dehydration at 300 °C. Reduction of cupric ions is known to proceed in two steps: cupric to cuprous and cuprous to copper atom. Both reduction steps have been suggested to occur in the same cage.<sup>35</sup> Due to the high mobility of copper atoms at high reduction temperature, copper atoms that are finally produced could migrate rapidly through the six-oxygen ring of sodalite cages and through the supercages to the exterior of the zeolite crystals. Such processes are similar to the reduction of Pt/NaY (calcinated at 550 °C, with virtually all Pt<sup>2+</sup> ions in the sodalite cages) to produce large Pt particles on the outside of the zeolite crystals.<sup>19</sup>

(2) Pt/NaY. For Pt/NaY calcined at 300 °C, all of the platinum ions are in the supercages. This system can be reduced at low temperature to produce small platinum particles in the supercages.19

(3) CuPt/NaY(1.0) and CuPt/NaY(3.0). For CuPt/NaY(1.0) and CuPt/NaY(3.0), the absence of separate Cu particles on the external surface as revealed by HRTEM may indicate an interaction between copper and platinum. After dehydration at 300 °C, platinum ions should be located in the supercages and the copper ions should be in the sodalite cages. During reduction, first the easily reduced Pt is reduced and forms small particles in the supercages. This is followed by reduction of the copper in the sodalite cages and into the supercages where they attach to the Pt particles. Such processes are similar to the formation of Pt particles in Pt/NaY which was calcined at moderate temperature, e.g. 450 °C, such that platinum ions are distributed in the supercages and sodalite cages.<sup>19</sup> The present EXAFS results show that, in the CuPt/NaY(1.0), cherry type CuPt particles are apparently formed by such processes. However, in the CuPt/



Figure 4. X-ray absorption near-edge structure of (a) freshly reduced Cu/NaY, (b) CuPt/NaY(3.0), (c) CuPt/NaY(1.0), and (d) CuPt/ NaY(1.0) after 500 °C in He.

NaY(3.0), a reconstruction of platinum and copper atoms to form alloys may occur as the copper content is increased. In CuPt/ NaY(3.0), the large average coordination numbers, i.e. larger sizes of particles, may also suggest the attachment of more copper atoms onto the Pt particles as nucleation sites in supercages.

The effect of copper on the particle sizes of platinum was carefully studied by Tebassi et al., who compared the Pt/NaY and CuPt/NaY systems.<sup>22</sup> The average size of the particles increases from 10-15 Å in Pt/NaY to 15-20 Å in CuPt/NaY. Such an increase in particle size could be attributed to the addition of Cu atoms onto the Pt particles as described above. Elliott and Lunsford<sup>23</sup> also found that the particles of Cu in Cu/NaY and Ni in Ni/NaY were much larger than 50 Å. In contrast, the addition of Ru into Cu/NaY and Ni/NaY caused the sizes of the resulting particles to be dramatically decreased, becoming only slightly larger than the Ru particles in Ru/NaY.

Oxidation of Copper. Surprisingly, the above EXAFS results for the Cu K-edge absorption reveal that part of the copper in the CuPt/NaY(1.0) after reduction at 500 °C is in the oxidized state. This is contradictory to previous TPR studies of CuPt/ NaY(1.0) where both Cu and Pt ions were completely reduced below 400 °C.<sup>21</sup> Even for Cu/NaY reduced at 500 °C, only reduced Cu is detected as shown in Figure 1. It should be mentioned here that the same results have been obtained on the other three CuPt/NaY(1.0) samples which were individually prepared and whose X-ray absorptions were carried out at different beam times. An attempt was made to quench the CuPt/NaY(1.0)in liquid nitrogen immediately after reduction and measure its X-ray absorption at 100 K. In this case, similar results showing partial oxidation of copper were also observed. The X-ray absorptions in the near-edge region of CuPt/NaY(3.0), CuPt/ NaY(1.0), and Cu/NaY are shown in Figure 4, showing large white line transitions in the CuPt/NaY(1.0). The oxidation of copper may be due to reaction with surface protons in the zeolite generated during reduction of platinum and copper ions. Oxidation of copper also occurs on CuPt/NaY(3.0). Since the EXAFS data are normalized during analysis, the small fraction of oxidized copper that is formed cannot be easily identified in the Fourier transform of CuPt/NaY(3.0). However, the oxidation of part of copper is distinctive from the near-edge absorption, as shown in Figure 4b.

Additional results are given below. These include EXAFS, oxygen consumption, and hydrogenation of toluene to illustrate the effect of thermal treatment in helium or under vacuum. These are discussed in relationship to possible causes of the partial oxidation of Cu atoms in CuPt/NaY(1.0) reduced at 500 °C.

<sup>(31)</sup> Schneider, V. A.; Esch, U. Z. Electrochem. 1944, 50, 290.
(32) Dc Jongste, H. C.; Kuijers, F. J.; Ponec, V. In Proceedings of the 6th International Congress on Catalysis; Bond, G. C., et al., Eds.; Chemical Society: London, 1977; Vol. 2, p 915. (33) Meitzner, G.; Via, G. H.; Lytle, F. W.; Sinfelt, J. H. J. Chem. Phys.

<sup>1985, 83, 353.</sup> 

<sup>(34)</sup> Gallezot, P.; Ben Taarit, Y.; Imelik, B. J. Catal. 1972, 26, 295. (35) Herman, R. G.; Lunsford, J. H.; Beyer, H.; Jacobs, P. A.; Uytter-hoeven, J. B. J. Phys. Chem. 1975, 79, 2388.



Pt/NaY (outgassed at 500 °C)

Pt/NaY (freshly reduced)

catalysts

CuPt/NaY(3.0) (outgassed at 500 °C)

Reaction conditions: catalyst 60 mg, temperature 60 °C, flow rate 230 mL/min,  $P(H_2) = 732$  Torr, and P(toluene) = 28 Torr. <sup>b</sup>MCH = methylcyclohexane.

TABLE II: Outgassing Effect of Pt/NaY, CuPt/NaY(1.0), and CuPt/NaY(3.0) on the Hydrogenation Activities of Toluene

uptake data can provide the total numbers of moles of reduced metal after outgassing. The difference from the theoretical value to oxidize all reduced Cu and Pt allows for an estimate of the amount of oxidized copper after outgassing. It is assumed that platinum will not be oxidized during outgassing. As indicated by the EXAFS data, part of the Cu atoms are leached from the surface of CuPt particles upon outgassing. The numbers of platinum atoms exposed on the surface of CuPt particles should thus be increased which may consequently enhance the activity of hydrogenation reactions, such as the hydrogenation of toluene.

The amount of oxygen uptake during the oxidation of outgassed CuPt/NaY(1.0) at 500 °C was smaller than the calculated value. The difference of these two values is equivalent to 30% of the total number of copper in the CuPt/NaY(1.0)

The toluene hydrogenation activities of Pt/NaY, CuPt/NaY-(1.0), and CuPt/NaY(3.0) are expressed as the formation rates of methylcyclohexane in mmol/(h mmol of Pt). The results are listed in Table II. The activity decreases dramatically upon the addition of copper. This is consistent with the data reported for toluene and benzene hydrogenation on Pt/NaY and CuPt/ NaY 22,36,37 Outgassing of the CuPt/NaY increases the activity by 1 order of magnitude compared with freshly reduced CuPt/ NaY(1.0). However, it is still lower than that of Pt/NaY. The hydrogenation of unsaturated hydrocarbons is structure insensitive, and its activity should be higher on surfaces with more exposed platinum atoms. The results of toluene hydrogenation are consistent with the EXAFS results. As shown in Table II, the activity drops to the level of freshly reduced CuPt/NaY(1.0) if the degassed catalysts are rereduced. This may suggest that leached copper is rereduced and reattached to the CuPt particles.

Recently, it was also observed that Sn atoms in SnRh and SnNi alloy particles supported on silica were oxidized by silanol if the reduced alloy catalysts were heated in helium.<sup>38,39</sup> The oxidation of Cu atoms on the CuPt alloys might be related to the small size of particles and to the large number of OH groups around the bimetallic particles.

Chemisorption of hydrogen has been widely used to characterize the dispersion of supported metal and bimetallic particles. It has been found that, in silica-supported Cu-Ru and Cu-Os catalysts, the H/Ru and H/Os ratios decrease with the addition of copper where the Cu/Ru ratios are in the range from 0 to 1.0.40.41 The activities of reactions that require large ensembles of Ru and Os, e.g. hydrogenolysis of ethane, were greatly suppressed upon the addition of a small amount of copper. On the other hand, Wu et al.<sup>42</sup> and Rouco et al.<sup>43</sup> found no significant influence of Cu



(37) Bandiera, J.; Meriaudeau, P. React. Kinet. Catal. Lett. 1988, 37, 373. (38) Candy, J. P.; Ferretti, O. A.; Mabilon, G.; Bournonville, J. P.; El Mansour, A.; Basset, J. M.; Martino, G. J. Catal. 1988, 112, 210.

Figure 5. EXAFS  $k^{3}\chi(k)$  functions, Fourier transforms, and fitting analysis of CuPt/NaY(1.0) outgassed in helium at 500 °C at the Pt L<sub>3</sub>-edge (a-c) and Cu K-edge (d-f).

Degassed CuPt/NaY(1.0) at 500 °C in He. The X-ray absorption of CuPt/NaY(1.0) which was reduced at 500 °C and further degassed in helium at 500 °C for 1 h was also measured at the Cu K-edge and the Pt L<sub>3</sub>-edge. The  $k^3\chi(k)$  weighted EXAFS function and its Fourier transform are shown in Figure 5. The Fourier transforms of degassed CuPt/NaY(1.0) at both the Cu K-edge and Pt  $L_3$ -edge are dramatically different from those of freshly reduced sample. As shown in Figure 5b, there is only a shoulder on the short distance side of the main peak at 2.5 Å before phase correction in the Fourier transform of the Pt  $L_3$  absorption edge. This is in contrast to the two peaks with equal intensity that were observed for freshly reduced CuPt/NaY(1.0), as described in Figure 2b. For the Cu K-edge absorption, there are three peaks at 1.7, 2.2, and 2.6 Å (before phase correction) in the Fourier transform of CuPt/NaY(1.0) (see Figure 5e). The first peak intensity at 1.7 Å, which probably corresponds to bonding between copper and oxygen of zeolite framework, is much stronger than that of freshly reduced CuPt/NaY(1.0) in Figure 2e. However, the second peak at 2.2 Å for the Cu-Cu bond has a lower intensity and the third peak at 2.6 Å, probably due to Cu-Pt, has an intensity comparable to the corresponding Fourier transform of freshly reduced CuPt/NaY(1.0) in Figure 2e.

The fitting analysis was carried out in the same way as for the freshly reduced CuPt/NaY(1.0) and is shown in Figure 5c,f. The EXAFS results, also included in Table I, indicate that outgassing of the reduced CuPt/NaY(1.0) in helium at 500 °C causes (1) oxidation of more copper atoms, (2) unchanged coordination number between Pt and Pt, and (3) a decrease of coordination numbers between Pt and Cu as well as Cu and Cu. It is obvious that, after outgassing, the CuPt particles still have a cherry type structure with unchanged Pt aggregate in the center. However, more copper atoms have been leached from the CuPt surface. The oxidation of copper upon outgassing in helium at 500 °C may be again due to the reaction of copper atoms on the surface of CuPt particles with protons. The Cu K-edge absorption in the near edge of CuPt/NaY(1.0) outgassed in He at 500 °C is also included in Figure 4. It also shows large white line transition.

Oxygen Uptake and Hydrogenation of Toluene. In order to confirm the oxidation of Cu atoms on the CuPt particles, the oxygen uptake during the oxidation of outgassed CuPt/NaY(1.0)and the hydrogenation of toluene were investigated. The oxygen formation rates of MCH,<sup>b</sup>

mmol/(h mmol of Pt)

122

125

5

45

5

0.8

2.5

<sup>(39)</sup> Agnelli, M.; Candy, J. P.; Basset, J. M.; Bournonville, J.; Ferretti, O. A. J. Catal. 1990, 121, 236.

<sup>(40)</sup> Prestridge, E. B.; Via, G. H.; Sinfelt, J. H. J. Catal. 1977, 50, 115.
(41) Sinfelt, J. H. J. Catal. 1973, 29, 308.
(42) Wu, X.; Gerstein, B. C.; King, T. S. J. Catal. 1990, 121, 271.
(43) Rouco, A. J.; Haller, G. L.; Oliver, J. A.; Kemball, C. J. Catal. 1983, 127

<sup>84, 477.</sup> 

on the hydrogen chemisorption capacity of ruthenium, as characterized by <sup>1</sup>H NMR and hydrogen chemisorption. This finding was attributed to spillover of atomically adsorbed hydrogen from Ru to adjacent Cu after dissociative adsorption of molecular hydrogen on Ru. Tebassi et al.<sup>22</sup> and Moretti et al.<sup>21</sup> also used hydrogen chemisorption to characterize the reduced CuPt/NaY. They independently observed that the H/Pt ratios did not vary significantly for several CuPt/NaY samples with Cu/Pt ratios in the range 0.0-4.9. However, addition of copper has a dramatic effect on the activities and selectivities of hydrogenation and isomerization. In view of the EXAFS data discussed above, the unchanged H/Pt ratios for CuPt/NaY with a wide range of Cu/Pt ratios is due partly to the removal of Cu atoms from the surface of CuPt particles during outgassing or evacuation at high temperature which is always employed after reduction and prior to the chemisorption of hydrogen.

## Conclusions

In summary, two important findings have been made.

1. The structure of small bimetallic CuPt particles produced in Y zeolites is dependent on the composition. At Cu/Pt = 1.0, CuPt particles have a cherry type structure with platinum in the core and copper atoms prevailing on the surface. It is suggested that CuPt particles are formed by attachment of Cu atoms, escaping from sodalite ages, onto the surface of Pt particles in the supercages. When the Cu/Pt ratio equals 3.0, reconstruction may occur to give alloy type particles.

2. Part of the Cu atoms on the surface of CuPt particles are oxidized by reacting with protons on the zeolite surfaces, which occurs during cooling in  $H_2$  atmosphere at room temperature. At 500 °C in helium, 30% of the Cu atoms in CuPt/NaY(1.0) are leached out of the CuPt particles; the remaining metal particles expose large Pt ensembles on the surface.

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# The 100-Å-Order Depth Profile Control of Polypyrrole—Poly(3-methylthiophene) Composite Thin Film by Potential-Programmed Electropolymerization<sup>1</sup>

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The alternate layered and graded structures with 100-Å-order resolution are observed in polypyrrole-poly(3-methylthiophene) composite thin films by potential-programmed electropolymerization of a mixture of pyrrole and 3-methylthiophene. The compositional depth profiles of the resulting films are analyzed by transmission electron microscopy and electron-probe microanalysis.

## Introduction

Conducting polymers (CP) have provided a wide variety of research subjects during this past decade.<sup>3</sup> Molecular engineering of CP with their tailor-made properties involves (i) the design of the monomer by synthetic chemistry, (ii) the design of the first-order polymer structure by polymerization control, such as sequence-defined CP copolymers which has not been realized yet, and (iii) the arrangement of polymer chains and assembly of CP, i.e., the design of higher order polymer structures. The correlation between the structures and the optical, electric, and magnetic properties will be demonstrated by, at one's discretion, precise control of all the above in CP preparation. The studies on the first issue have been perused<sup>4</sup> ever since CP was discovered. Relating to the second, several works on electrochemical co-polymerization have been reported.<sup>5,6</sup> However, these reports indicated only the possibility of copolymerization without controlling their compositions and sequences of the copolymers, which will be a future target. The third has very recently been demonstrated<sup>7</sup> in the direction of the arrangement of the polymer and its assembly. Structural control of this assembly has the potential to accentuate properties that differ from those of the bulk. The Langmuir-Blodgett (LB) technique is one of the most powerful methods to manipulate a molecular-level thin film on water subphase and to cumulate monolayers one by one onto any substrate. We have constructed the CP multilayered films having polypyrrole (PPy), polythiophene, and polyaniline structures by several preparative routes with the LB technique.<sup>8</sup> The obtained multilayered film showed large anisotropic conductivity (up to

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<sup>(3)</sup> Skotheim, T. A. Handbook of Conducting Polymers; Marcel Dekker: New York, 1986.

<sup>(4)</sup> For example: Synth. Met. 1989, 28, 29, and 30 (Proceedings of the International Conference on Science and Technology of Synthetic Metals (ICSM '88)).

<sup>(5)</sup> Studies on electrocopolymerization of pyrrole and other monomers are as follows: (a) For poly(pyrrole-N-methylpyrrole): Kanazawa, K. K.; Diaz, A. F.; Krounbi, M. T.; Street, G. B. Synth. Met. 1981, 4, 119. (b) For poly(pyrrole-N-(p-nitrophenyl)pyrrole): Rosenthal, M. V.; Skotheim, T. A.; Melo, A.; Florit, M. I.; Salmon, M. J. Electroanal. Chem. 1985, 185, 297. (c) For poly(pyrrole-phenol): Kumar, N.; Malhotra, B. D.; Chandra, S. J. Polym. Sci., Polym. Lett. Ed. 1985, 23, 57. (d) For poly(pyrrole-ter-thiophene): Ingnäs, O.; Liedberg, B. O.; Chang-ru, W. U. Synth. Met. 1985, 11, 239. (e) For poly(Py-N-substituted pyrrole): Reynolds, J. R.; Poropatic, P. A.; Toyooka, R. L. Macromolecules 1987, 20, 958. (f) For poly(pyrrole-benzo[b]thiophene): Seki, M.; An, H.; Sato, K. Synth. Met. 1988, 26, 33. (6) Kuwabata, S.; Ito, S.; Yoneyama, H. J. Electrochem. Soc. 1988, 135, 1691. This paper is concerned with poly(opyrole-thonhene).

<sup>(6)</sup> Ruwabata, S.; 10, S.; Foneyama, H. J. Electrochem. Soc. 1968, 155, 1691. This paper is concerned with poly(pyrrole-thiophene).
(7) For example: (a) Akagi, K.; Shirakawa, H.; Araya, K.; Mukoh, A.; Narahara, T. Polym. J. 1967, 19, 185. (b) Araya, K.; Mukoh, A.; Narahara, T.; Akagi, K.; Shirakawa, H. Synth. Met. 1987, 17, 247. (c) Akagi, K.; Katayama, S.; Shirakawa, H.; Araya, K.; Mukoh, A.; Narahara, T. Synth. Met. 1987, 17, 241.
(8) (1) J. J. 2011.

<sup>(8) (</sup>a) Iyoda, T.; Ando, M.; Kaneko, T.; Ohtani, A.; Shimidzu, T.; Honda, K. Tetrahedron Lett. 1986, 27, 5633; Langmuir 1987, 3, 1169-1170.
(b) Shimidzu, T.; Iyoda, T.; Ando, M.; Kaneko, T.; Ohtani, A.; Honda, K. Thin Solid Films 1988, 160, 67-79.
(c) Ando, M.; Watanabe, Y.; Iyoda, T.; Honda, K.; Shimidzu, T. Thin Solid Films 1989, 179, 225.