ATOMIC DISTRIBUTION OF PtCo/C NANOPARTICLES AS INVESTIGATED BY X-RAY ABSORPTION SPECTROSCOPY

Abdul Hamid Budiman[1], Eniya Listiani Dewi[2], Widodo Wahyu Purwanto[1], Rinaldy Dalimi[3] and Bing Joe Hwang[4]

[1]*Chemical Engineering Department-University of Indonesia*
New Campus UI, Depok 16424, Indonesia
[2]*Centre of Material Technology-Agency for the Assessment and Application of Technology*
Jl. MH. Thamrin No. 8, BPPT II Bld, 22 Fl, Jakarta 10340
[3]*Electrical Engineering Department-University of Indonesia*
New Campus UI, Depok 16424 Indonesia
[4]*Department of Chemical Engineering-National Taiwan University of Science and Technology*
43 Keelung Road section 4 Taipei, Taiwan
e-mail : widodo@che.ui.ac.id

ABSTRACT

ATOMIC DISTRIBUTION OF PtCo/C NANOPARTICLES AS INVESTIGATED BY X-RAY ABSORPTION SPECTROSCOPY. X-Ray Absorption Spectroscopy (XAS) was utilized to deduce the structural parameters that can provide information on atomic distribution and extent of alloying as well as the surface population of bimetallic nanoparticles (NPs). In this study, we focused on PtCo/C NPs treated by CO with various of time. XAS measurement showed that this experiment is related to the Case 3, which is $J_{Pt} < 100 \%$ and $J_{Co} < 100 \%$, then both Pt and Co atoms are not preferred to be alloyed, and it indicates that a higher extent of Pt/Co atoms prefer only to a lesser extent alloying between Pt and Co atoms. If $J_{Co} > J_{Pt}$, it appears that the core is rich in Pt atoms and shell is rich in Co atoms. On the contrary if $J_{Pt} > J_{Co}$ resulting in Co atoms are rich in the core and Pt atoms are rich in the shell. The XAS results reveal that the time of treatment influences the surface population hence the structure of the catalyst. Catalyst treated CO for 0, 3 and 5 hours leads to higher population of Pt on the core and Co was moved to the surface resulting to Pt rich in core Co rich in shell, while treated for 7 and 15 hours leads to higher population of Pt on the shell and Co on the core resulting to Pt rich in shell Co rich in core.

Key words : Atomic distribution, X-Ray Absorption Spectroscopy, Coordination number, Alloy extent

ABSTRAK

DISTRIBUSI ATOM NANOPRATIKEL PtCo/C HASIL INVESTIGASI DENGAN *X-RAY ABSORPTION SPECTROSCOPY*. *X-Ray Absorption Spectroscopy* (*XAS*) telah digunakan untuk memperkirakan parameter struktur yang dapat memberikan informasi tentang distribusi atom dan batas pemaduan sebagaimana halnya populasi permukaan nanopartikel (NP) bimetal. Pada penelitian ini, pembahasan difokuskan pada NP PtCo/C dengan perlakuan CO divariasi waktu. Hasil pengukuran *XAS* menunjukkan bahwa percobaan ini berhubungan dengan *Case* 3, dimana $J_{Pt} < 100 \%$ dan $J_{Co} < 100 \%$ maka kedua atom Pt dan Co tidak disarankan untuk dipadukan dan hal ini menunjukkan bahwa semakin banyak atom Pt/Co hanya sedikit antara atom Pt dan Co yang membentuk *alloy*. Bila $J_{Co} > J_{Pt}$, maka bagian *core* kaya dengan atom Pt dan bagian *shell* kaya dengan atom Co. Sebaliknya jika $J_{Pt} > J_{Co}$ menghasilkan atom Co kaya di bagian *core* dan atom Pt kaya dibagian *shell*. Hasil *XAS* menunjukkan bahwa lama waktu perlakuan mempengaruhi populasi permukaan sehingga mempengaruhi struktur katalis. Katalis yang dikenai perlakuan selama 1 jam hingga 5 jam mendorong terjadinya populasi Pt yang tinggi pada *core* dan Co bergeser ke permukaan sehingga kaya Pt di bagian *core* kaya Co di bagian *shell*, sedangkan perlakuan selama 7 jam hingga 15 jam mengakibatkan populasi Pt yang tinggi pada *shell* dan Co pada *core* sehingga kaya Pt di bagian *shell* kaya C di bagian *core*.

Kata kunci : Distribusi atomis, *X-Ray Absorption Spectroscopy*, Bilangan koordinasi, Penyebaran *alloy*

INTRODUCTION

Bimetallic nanoparticles (NPs) are of great interest from both a scientific and technological perspective because of the modification of physical and chemical properties not only due to quantum size effects but also as a result of the combination of different metals [1-2]. Bimetallic NPs display fascinating electronic and optical properties different from those of the bulk metal [2]. In order to understand the nanostructure-property relationships, it is really necessary to investigate both the chemical states and the atomic distribution in bimetallic NPs.

In the field of heterogeneous catalysis, study of the surface composition of bimetallic NPs is being fundamental. The interaction of surface atoms of the catalyst with reactants will play a significant role in catalysis. In many cases, the surface composition of bimetallic NPs differ from that of the bulk and has a significant influence on NP activity, selectivity and stability [3].

In the last two decades X-ray absorption spectroscopy (XAS) has increasingly been applied to study the structure of metal cluster. This is may be attributed to its unique potential to provide information regarding to the oxidation state and local coordination, number and identity of neighbors of absorbing atom [1,4,6]. XAS techniques also can provide information on the morphology of the considered species, as well as the distribution of the two metals inside the species.

XAS studies can be distinguished into two parts : XANES and EXAFS. X-ray absorption near edge structure (XANES) provides critical information about the oxidation state and fractional d-electron density and electronic environment of the absorbing atoms. While extended X-ray absorption fine structure (EXAFS) provides details about the number, type and distance of backscattering atom surrounding the central absorbing atom, investigation on the short range ordering and provide geometric information. The XAS techniques has been proved as a powerful technique for the characterization of bimetallic catalysts, since it is difficult to obtain structural information on such system by means of conventional material analysis method at the early stages [7-8].

PtCo bimetallic catalyst have been studied exhaustively during the past decade. It was reported that Pt alloyed with Co on the carbon support yield better catalytic activity than pure Pt, where the most study were PtCo with ratio of 1:1 to 1:3 [9-11]. Few reasons for the high catalytic activity for these alloy are ascribed to the modification of the electronic structure of Pt on alloying with Co and structural effect on Pt. A novel preparation procedure of such core shell nanoparticle using an adsorbate- induced surface segregation effect has been demonstrated by Mayrhofer et al [12]. The composition of the surface of a bimetallic system can be

vary different from the bulk, it depends on the heat of segregation and the surface mixing energy. He found that utilizing this strategy resulting in a highly active catalyst with a low amount of noble metal.

In this study, we focused on PtCo/C NPs treated by CO with various of time. The XAS techniques is used to extract the structural parameters required for understanding the atomic distribution and alloying extent and the corresponding structure is revealed.

EXPERIMENTAL METHOD

Catalyst Preparation

A commercial Carbon supported PtCo supported at Carbon Vulcan XC 72 (nominal atomic ratio 50 : 50) with 20 wt% metal loading electrocatalyst from PREMETEK was prepared by treated with CO as adsorbate at the temperature of 200 °C for different time 0, 3, 5, 7, and 15 hours by using U tube reactor. Prior to CO treatment, the catalyst was treated with flowing H_2 at 300 °C for 2 hours to clean the impurities and to eliminate the oxide contribution.

XAS Measurement

The X-ray absorption spectra were recorded at the beamline 17C1, National Synchrotron Radiation Research Centre, Hsinchu, Taiwan. The electron storage ring was operated at 1.5 GeV with a current of 300 mA. A Si (111) double crystal monochromator was employed for the energy selection with a resolution $\Delta E/E$ better than 2×10^{-4} at both the Pt L_{III}-edge (11564 eV) and the Co K-edge (7709 eV). All of the experiments on bimetallic nanoparticles were conducted on a homemade cells fabricated with stainless steel for an XAS powder study. Prior to the XAS measurements, sample were reduced with 10 % H_2 for 1 hours at 300 °C to remove the oxidized species if any remained on the surface during catalyst preparation. The total amount of the sample was adjusted to reach the optimum absorption thickness ($\Delta \mu x = 1.0$, $\Delta \mu$ is the absorption edge, x is the thickness of the sample) so that the proper edge jump step could be achieved during measurements. All of the spectra were recorded at room temperature in a transmission mode. Higher harmonics were eliminated by detuning the double crystal Si(111) monochromator. Three gas filled ionization chambers were used in series to measure the intensities of the incident beam (I_0), the beam transmitted by the sample (I_t) and the beam subsequently transmitted by the reference foil (I_r). The third ion chamber was used in conjunction with the reference sample, which was a Pt foil for Pt L_{III}-edge measurements and a Co foil for the Co K-edge measurements. The control of parameters for EXAFS measurements, data collection modes, and calculation of errors were all carried out according to the guidelines

set by the International XAFS Society Standards and Criteria Committee.

EXAFS Data Analysis

The XAS experimental data were treated by utilizing the standard procedures. The EXAFS function, χ, was obtained by subtracting the post edge background from the overall absorption and then normalized with respect to the edge jump step. The normalized χ(E) was transformed from energy space to k-space, were "k" is the photoelectron wave vector. The χ(k) data were multiplied by k^2 to compensate for the damping of EXAFS oscillations in the high k-region. Subsequently, k^2 weighted χ(k) data in k-space ranging from 3.53 to 13.95 Å^{-1} for the Pt L $_{III}$-edge and from 3.53 to 10.36 Å^{-1} for the Co K-edge were Fourier transformed (FT) into r-space to separate the EXAFS contribution from the different coordination shells. A non linear least squares algorithm was applied to the curve fitting of an EXAFS in the r-space between 1.8 and 3.2 Å for both Pt and Co depending on the bond to be fitted.

The PtCo reference file was determined by a theoretical calculation. Reference phase and amplitude for the Pt-Pt absorber scatter pairs were obtained from a Pt foil. For the Co-Co and Co-O absorber scatter pairs, the phase and amplitude were obtained from the reference Co foil and CoO, respectively. All of the computer programs were implemented in the UWXAFS 3.0 package, with the backscattering amplitude and the phase shift for the specific atom pairs being theoretically calculated by using the Feff7 code. From these analysis, structural parameters such as coordination numbers (N), bond distance (R), Debye-Waller factor ($\Delta\sigma_j^2$) and inner potential shift (ΔE_0) have been calculated. For the amplitude reduction factor, S_0^2, values for the Pt and Co were obtained by analyzing the Pt and Co foil reference sample respectively, and by fixing the coordination number in the FEFFIT input file.

RESULTS AND DISCUSSION

The structure of bimetallic NPs which contains two kinds of metal elements, may posses the crystal structure similar either to the bulk alloy or another type that is the distribution of each metal elements is different from the bulk.

Many reports have appeared describe the applicability of XAS to figure the structural models for bimetallic NPs, but researchers have proposed only qualitatively the structural models of bimetallic NPs such as random alloy, cluster and core shell structure.

It is of interest to estimate the alloy extent or atomic distribution of element in bimetallic NPs to get more detail about the structure and

the composition. In this direction, we have analyzed the bimetallic NPs of type A-B by XAS. Firstly we estimate the ratio of the coordination number of Pt around Co and also coordination number of Co around Pt to the total coordination number, then we deduced the qualitative parameter, J_{Pt} and J_{Co} for the alloying extent in PtCo bimetallic NPs. These structural parameter are not only helpful to distinguish random and non random alloying Pt and Co in a PtCo cluster but also give information about the extent Pt and Co atomic distribution in nanoparticle [3-5].

The calculation of J_{Pt} and J_{Co} of PtCo bimetallic NPs involves, obtaining the ratio of scattering atom Co coordination number around absorbing Pt atom (N_{Pt-Co}) to the total coordination number of absorbing platinum atom ("$N_{Pt-i} = N_{Pt-Co} + N_{Pt-Pt}$) denoted as $P_{observed}$ ($P_{observed} = N_{Pt-Co}/"N_{Pt-i}$). The $P_{observed}$ provides information on the probability of Pt bonds with a Co atom and serves as an index to Pt atomic distribution in a PtCo cluster. Similarly, the ratio of the scattering atom Pt coordination number around absorbing Co atom to the total coordination number of absorbing cobalt atom ("$N_{Co-i} = N_{Co-Pt} + N_{Co-Co}$) denoted as $R_{observed}$. ($R_{observed} = N_{Co-Pt}/"N_{Co-i}$). $R_{observed}$ provides information on the Co atomic distribution in a PtCo cluster.

Once $P_{observed}$ and $R_{observed}$ values are determined from XAS coordination number parameter, the value of J_{Pt} dan J_{Co} can be estimated by using the Equation (1) and Equation (2) respectively

$$J_{Pt} = \frac{P_{observed}}{P_{random}} x100 \quad \text{.................................} \quad (1)$$

$$J_{Co} = \frac{R_{observed}}{R_{random}} x100 \quad \text{.................................} \quad (2)$$

Where :

P_{random} = Calculated from the atomic ratio of Pt and Co
R_{random} = Calculated from the atomic ratio in PtCo NPs

From Table 1, we can see that for PtCo treated CO for 0, 3 and 5 hours, the total coordination number parameter relationship of $\Sigma N_{Pt-i} > \Sigma N_{Co-i}$ and the alloying extent $J_{Pt} < J_{Co}$ indicate that Co atom are segregating at the surface of the nanoparticle and Pt atom at the core resulting Pt-rich$_{core}$-Co-rich$_{shell}$ structure. Meanwhile for PtCo treated CO for 7 and 15 hours, the total coordination number parameter relationship of $\Sigma N_{Pt-i} < \Sigma N_{Co-i}$ and alloying extent $J_{Pt} > J_{Co}$ indicate that Pt atom are

Table 1. Coordination number and alloying extent PtCo/C

No.	Time of CO treatmet	ΣN_{Pt-i}	ΣN_{Co-i}	J_{Pt}	J_{Co}
1.	0 h	8.65	7.28	70.51	78.40
2.	3 h	8.93	6.78	64.88	80.12
3.	5 h	8.78	7.37	65.99	73.70
4.	7 h	8.56	8.63	69.59	64.77
5.	15 h	8.56	8.69	61.04	56.39

Case 1. $J_A=0, J_B=0$
H_{A-A} & $H_{B-B} >> H_{A-B}$
Separated structure

Case 2. $J_A=J_B=100$
$H_{A-A}=H_{B-B}=H_{A-B}$
Alloy structure

Case 3. $J_A< 100, J_B< 100$
$H_{A-A}>H_{B-B}>H_{A-B}$
Homo-philic structure

Case 4. $J_A> 100, J_B< 100;$
$H_{B-B}>H_{A-B}>H_{A-A}$
'B'rich$_{core}$-'A'rich$_{shell}$ structure

Case 5. $J_A> 100, J_B> 100$
$H_{A-B}>H_{A-A}$ (or) H_{A-B}
Heteratomic-rich structure

Case 6. $J_A< 50, J_B< 50$
$H_{A-A}>H_{B-B}>H_{A-B}$
A_{core}-B_{shell} structure

Case 7. $J_A= 200, J_B= 200$
Onion-ring structure
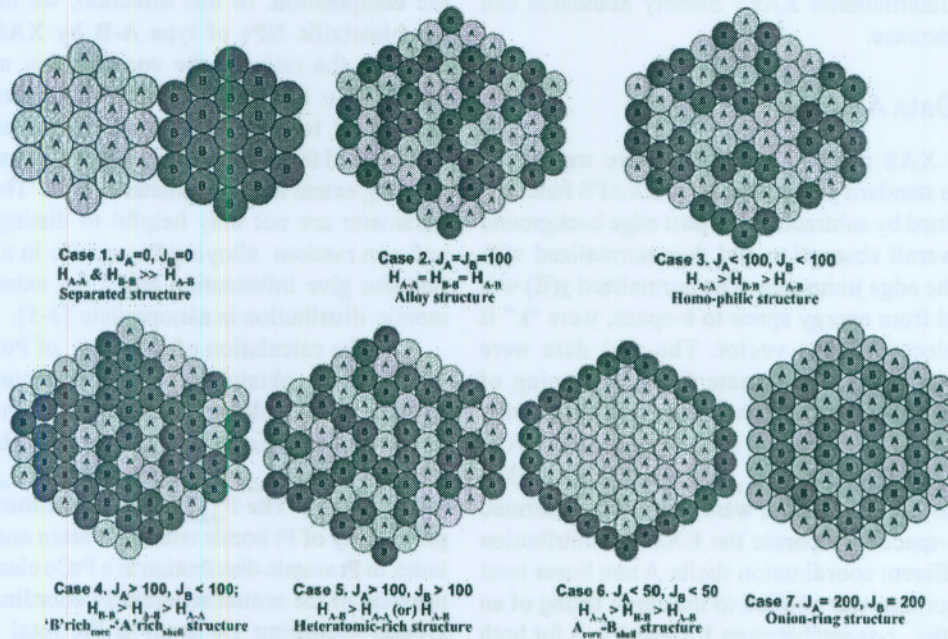
Figure 1. Schematic of bimetallic nanoparticles at various degree of alloying [1]

CO induced surface segregation

● Pt   ○ Co
Alloy structure

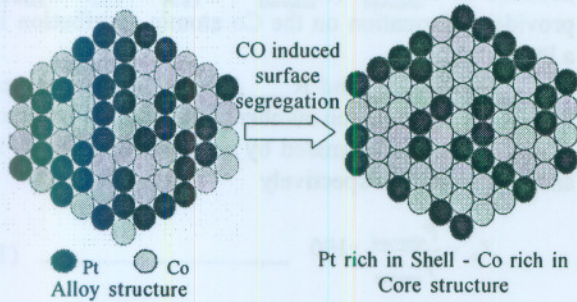Pt rich in Shell - Co rich in Core structure

Figure 2. Structure Catalyst was changed by induced surface segregation

segregating at the surface of the nanoparticle and Co atom at the core resulting in Pt-rich$_{shell}$-Co-rich$_{core}$ structure.

The atomic structure of PtCo/C nanoparticle are derived from experimentally obtained XAS structural parameter and the alloying extent of Platinum (J_{Pt}) as well as Cobalt (J_{Co}). These structural parameter are not only helpful to distinguish random and non random alloying Pt and Co in a PtCo cluster but also give information about the extent Pt and Co atomic distribution in nanoparticle as shown in Figure 1.

The surface of a bimetallic system can be vary different from the bulk, it depends on the heat of segregation and the surface mixing energy. The chemical potential of the gas phase is also influence the system since the strong bonding of adsorbates will result in a gain in energy of the system [12]. An adsorbate induce to the system will control the surface segregation as shown in the Figure 2.

From the XAS measurement it can be concluded that this experiment is related to the Case 3, which is J_{Pt} < 100% and J_{Co} < 100%, then both Pt and Co atoms are not preferred to be alloyed, and it indicates that a higher

extent of Pt/Co atoms prefer only to a lesser extent alloying between Pt and Co atoms. If $J_{Co} > J_{Pt}$, it appears that the core is rich in Pt atoms and shell is rich in Co atoms. On the contrary if $J_{Pt} > J_{Co}$ resulting in Co atoms are rich in the core and Pt atoms are rich in the shell.

CONCLUSION

The relationship between alloying extent and Pt d-band vacancies in PtCo/C electrocatalyst has been established, which is tunable with Pt and Co composition and strongly impact on the catalytic activity for ORR. It is found that the catalytic activity of PtCo/C treated CO for 3 hours, the ORR is the highest due to its higher alloying extent. The XAS results reveal that the time of treatment influences the surface population hence the structure of the catalyst. Catalyst treated for 0, 3 and 5 hours leads to higher population of Pt on the core and Co was moved to the surface resulting to Pt rich in core Co rich in shell, while treated for 7 and 15 hours leads to higher population of Pt on the shell and Co on the core resulting to Pt rich in shell Co rich in core.

ACKNOWLEDGEMENTS

REFERENCES

[1]. B.J. HWANG, L.S. SARMA, J.M. CHEN, C.H. CHEN, S.C. SHIH, G.R. WANG, D.G. LIU, J.F. LEE and M.T. TANG, *J.Am.Chem.Soc.*, **127** (2005) 11140-11145

[2]. C.H. CHEN, B.J. HWANG, G.R. WANG, L.S. SARMA, M.T. TANG, D.G. LIU and J.F. LEE, *J. Phys. Chem. B*, **109** (2005) 21566-21575

[3]. B.J. HWANG, L.S. SARMA, G.R. WANG, C.H. CHEN, D.G. LIU, H.S. SHEU and J.F. LEE, *J. Chem. Eur. J*, **13** (2007) 6255-6264

[4]. B.J. HWANG, L.S. SARMA, C.H. CHEN, M.T. TANG, D.G. LIU and J.F. LEE, *Applied Physics Letter*, **91** (2007) 023108

[5]. F.J. LAI, L.S. SARMA, H.L. CHOU, D.G. LIU, C.A. HSICH, J.F. LEE and B.J. HWANG, *J. Phys. Chem. C*, **113** (2009) 12674-12681

[6]. B.J. HWANG, L.S. SARMA, C.H. CHEN, C. BOCK, F.J. LAI, S.H. CHANG, S.C. YEN, D.G. LIU, H.S. SHEU and J.F. LEE, *J. Phys. Chem C*, **112** (2008) 19922-19929

[7]. B.J. HWANG, C.H. CHEN, L.S. SARMA, J.M. CHEN, G.R. WANG, M.T. TANG, D.G. LIU and J.F. LEE, *J. Phys. Chem. B*,**110** (2006) 6475-6482

[8]. L.S. SARMA, C.H. CHEN, S.M.S. KUMAR, G.R. WANG, S.C. YEN, D.G. LIU, H.S. SHEU, K.L. YU, M.T. TANG, J.F. LEE, C. BOCK, K.H. CHEN and B.J. HWANG, *Langmuir*, **23** (2007) 5802-5809

[9]. U.A. PAULUS, A. WOKAUN, G.G. SCHERER, T.J. SCHMIDT, V. STAMENKOVIC, V. RADMILOVIC, N.M. MARKOVIC and P.N. ROSS, *J. Phys. Chem. B*, **106** (2002) 4181

[10]. N. TRAVITSKY, T. RIPENBEIN, D. GOLODNITSKY, Y. ROSENBERG, L. BURSHTEIN and E. PELED, *J. Power Sources*, **161** (2006) 782-789

[11]. H.A. GASTEIGER, S.S. KOCHA, B. SOMPALLI and F.T. WAGNER, *Appl. Catal. B*, **56** (2005) 9-35

[12]. K.J.J. MAYRHOFER, V. JUHART, K. HARTL, M. HANZLIK and M. ARENZ, *Angew. Chem. Int. Ed.*, **48** (2009) 3529-3531