

STRUCTURAL MODELS OF BIMETALLIC NANOPARTICLES THE IMPORTANCE OF ALLOYING EXTENT AS STUDIED BY X-RAY ABSORPTION SPECTROSCOPY

Studies of bimetallic nanoparticles (NPs) received great attention from both a scientific and technological communities because most of the nanoparticles catalytic activity depends on their structural aspects [1]. Among the various structural aspects it is of most important to control the homogeneity, dispersion, and alloying extent as they have profound influence on the surface properties which affect the catalytic activity and stability of the bimetallic NPs. Hence methods to get more insights into structural aspects are highly needed. Even though alloying is a well-known phenomenon, detailed studies on quantitative assessment of alloying extent in bimetallic NPs have been lacking so far. By deriving the structural parameters from X-ray absorption spectroscopy (XAS) analysis we proposed a general methodology to estimate the alloying extent or atomic distribution in bimetallic NPs and demonstrated the results on two commercially available carbon-supported Pt-Ru NPs [2].

The XAS spectra were recorded in the transmission mode on two commercial Pt-Ru/C catalysts (ca. 2-3 nm, 20% Pt/10% Ru with a Pt/Ru atomic ratio of 1:1) at beamline **BL12B2**. By estimating the ratio of the coordination number (CN) of A around B and also the CN of B around A to the

total CNs, we have deduced the alloying extent of A (J_A) and B (J_B) in A-B bimetallic NPs. The parameters that are needed to derive the extent of alloying are represented as P_{observed} , R_{observed} , P_{random} , and R_{random} . The parameter P_{observed} can be defined as a ratio of the scattering atoms 'B' CN around absorbing 'A' atoms (N_{A-B}) to the total CN of absorbing atoms ($\sum N_{A-i}$), ($P_{\text{observed}} = N_{A-B}/\sum N_{A-i}$). Similarly, R_{observed} can be defined as a ratio of the scattering atoms 'A' CN around absorbing 'B' atoms (N_{B-A}) to the total CNs of absorbing atoms ($\sum N_{B-i}$), ($R_{\text{observed}} = N_{B-A}/\sum N_{B-i}$). Whereas, P_{random} and R_{random} can be taken as 0.5 for perfect alloyed bimetallic NPs if the atomic ratio of 'A' and 'B' is 1:1. The J_A and J_B for 1:1 A-B bimetallic NPs can then be estimated by using the equations (1) and (2) respectively.

$$J_A = (P_{\text{observed}}/P_{\text{random}}) \cdot 100\% \quad (1)$$

$$J_B = (R_{\text{observed}}/R_{\text{random}}) \cdot 100\% \quad (2)$$

Based on the $\sum N_{A-i}$, $\sum N_{B-i}$, J_A and J_B it is possible to predict the structural models of NPs. Seven possible cases were discussed and schematics of the corresponding models are shown in Fig. 1. In case if $\sum N_{A-i} > \sum N_{B-i}$ there appears core is rich in 'A' atoms

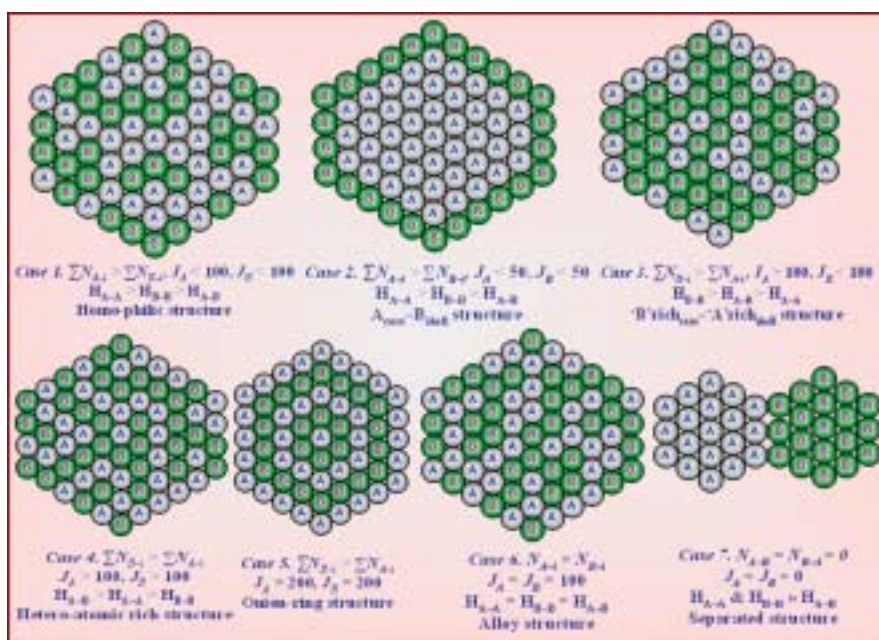


Fig. 1. Schematics of bimetallic nanoparticles at various degrees of alloying.

and shell is rich in 'B' atoms. In this case if both J_A & $J_B < 100\%$ then the extent of homo-atomic interactions will become more ($H_{A-A} > H_{B-B} > H_{A-B}$) and results in a homo-philic structure (case 1, Fig. 1). However if J_A & $J_B < 50\%$ with a coordination number relationship of $\Sigma N_{A-i} > \Sigma N_{B-i}$ then bimetallic NPs structure is close to $A_{\text{core}}-B_{\text{shell}}$ (case 2, Fig. 1). In another case, if $\Sigma N_{B-i} > \Sigma N_{A-i}$ then the resultant structure is similar to 'B' rich in core-'A' rich in shell (case 3, Fig. 1). Here if $J_A > 100\%$ & $J_B < 100\%$ it indicates that 'B' atoms prefers 'B' atoms rather than 'A' and 'A' atoms prefer 'B' atoms rather than 'A' atoms, as a result atomic distribution of 'A' atoms is better than 'B' atoms. In other words we can say that the segregation of 'A' atoms are less pronounced than 'B' atoms with the order of interactions $H_{B-B} > H_{A-B} > H_{A-A}$. However if both J_A and $J_B > 100$ then the atomic distribution of both 'A' and 'B' atoms are improved with more hetero-atomic interactions than the homo-atomic interactions and bimetallic NPs adopt hetero-atomic rich structure ($H_{A-B} > H_{A-A}$ and H_{B-B} , see case. 4 of Fig. 1). In case 5, if $J_A = 200\%$ & $J_B = 200\%$ indicates that 'A' atoms always prefer 'B' atoms and vice-versa and the resulting structure look like an onion ring (case 5, Fig. 1). In case 6, if $\Sigma N_{A-i} = \Sigma N_{B-i}$ and $J_A = J_B = 100\%$ then bimetallic NPs adopt an alloy structure (case 6, Fig. 1). However if $J_A = J_B = 0$ results in a separated structure (case 7, Fig. 1).

The alloying extent of Pt (J_{Pt}) and Ru (J_{Ru}) for commercial catalysts viz JM 30 and E-TEK 30 Pt-Ru/C catalysts can be obtained from the expression (1) and (2), respectively. The J_{Pt} and J_{Ru} values are calculated as 40 and 78% respectively for JM 30 Pt-Ru/C with P_{observed} and R_{observed} as 0.20 and 0.39 respectively. For E-TEK 30 catalyst the structural parameters P_{observed} and R_{observed} are calculated as 0.13 and 0.24 respectively and the J_{Pt} and J_{Ru} values are 26 and 48% respectively. For both the catalysts it was found that $\Sigma N_{Pt-i} > \Sigma N_{Ru-i}$ and $J_{Ru} > J_{Pt}$ and it indicates that the catalysts adopt a Pt rich in core and Ru rich in shell structure (Fig. 2).

From the quantitative extent of alloying values we infer that in both the catalysts considerable amount of Ru is segregated on the shell layer but its extent is higher in E-TEK 30 when compared to the JM 30. The increased value of J_{Ru} in JM 30 catalyst indicated that most of the Ru is involved in alloying and hence less segregation of Ru in the shell whereas in the case of ETEK 30 catalyst lesser extent of Ru is involved in the alloying and considerable extent of segregation of Ru can be expected in the shell region.

The higher segregation of Ru in the case of ETEK 30 in part may be responsible for its lower methanol oxidation activity compared to JM 30. Increase in J_{Pt} and J_{Ru} values in JM 30 compared to E-TEK 30 indicates that the atomic distribution of Pt and Ru atoms are much facilitated. Increase in atomic distribution can be taken as a measure for enhanced homogeneity.

The alloying extent in bimetallic NPs can easily be estimated by the proposed XAS methodology. From this approach it is possible to provide a quantitative index measuring the changes in atomic distribution in bimetallic NPs which have strong influence on physico-chemical properties of NPs. This methodology can also convenient to extend to other multi-metallic NPs.



JM 30 Pt-Ru/C catalyst E-TEK 30 Pt-Ru/C catalyst

Fig. 2. Structural models deduced for JM 30 (a) and E-TEK 30 Pt-Ru/C catalysts (b) based on XAS parameters.

Bing-Joe Hwang^{a,b,*}, Jyh-Fu Lee^b and Mau-Tsu Tang^b

^a Nanoelectrochemistry Laboratory, National Taiwan University of Science and Technology, Taiwan ROC

^b National Synchrotron Radiation Research Center, Taiwan ROC

*E-mail: bjh@mail.ntust.edu.tw

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