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利用課題名 (日本語) : その場雰囲気での分散型 X 線吸収分光実験によるロジウムナノ粒子の水素吸蔵機構解明
Program Title (English) : Investigation on size-dependent hydrogen-storage properties in Rh nanoparticles
by *in-situ* XAFS
利用者名 (日本語) : 宋哲昊¹⁾, 廣井 慧¹⁾, 坂田 修身¹⁾, Seo Okkyun¹⁾, 崔 藝濤²⁾
Username (English) : Chulho Song¹⁾, Satoshi Hiroi¹⁾, Osami Sakata¹⁾, Seo Okkyun¹⁾, Yi-Tao Cui²⁾
所属名 (日本語) : 1) (国) 物質・材料研究機構, 2) 東京大学
Affiliation (English) : 1) National Institute for Materials Science, 2) The University of Tokyo
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1. 概要 (Summary)

Metal nanoparticles (NPs) have recently attracted much attention as advanced materials related to hydrogen-storage. Rh is an effective catalyst for various chemical reactions in the 4d transition metal series. The synthesis of metal NPs for improving catalytic activities and obtain unexpected properties is a very hot topic owing to the quantum size effects and high surface area-to-volume ratios exhibited by NPs. For instance, while bulk Rh metal does not absorb hydrogen, Rh NPs do. Kusada *et al.* observed that the hydrogen-storage capacity of Rh NPs increases with decreasing particle size [1]. These phenomena might be caused by a change in an electronic state of Rh with decreasing particle size. However, an origin of the hydrogen-storage property and performance of Rh NPs can hardly be described as one parameter and has not yet been. Therefore, investigating the local crystal structure of such NPs is very important for understanding their catalyst properties.

2. 実験(目的,方法) (Experimental)

We investigated the relation between the local crystal structure and the hydrogen-storage property of Rh NPs having various particle sizes (4.0, 7.1, and 10.5 nm). Rh K-edge *in-situ* XAFS spectra were measured by an energy dispersive and time-resolved mode with Laue configuration at the bending magnet beamline BL14B1, SPring-8, Japan. Sample temperatures used were room temperature and 373 K and a sampling rate was 0.67 Hz (1.5 s).

A sample, which weighted 30 mg, composed of Rh NPs and BN mixture powders was packed in a cylindrical sample holder ($\phi 10 \times \phi 7 \times 10 \text{ mm}^3$) and pressed by hand to make a disk pellet ($\phi = 7 \text{ mm}$). The sample pellet in the holder was placed in an *in-situ* flow type XAFS cell. H₂ and N₂ gases were flowed at 100 cc/min as an adsorption and desorption gases, respectively.

3. 結果と考察 (Results and Discussion)

An *in-situ* XAFS measurement with dispersive optics is a powerful tool observing small local structural change. From the XAFS spectra between before and after H₂ absorption and desorption on various sized Rh NPs, we were able to observe the small difference in a near edge structure, EXAFS functions, and Fourier transform intensity. However, in normal sense for spectra comparison, it is difficult to judge that H₂ absorption and desorption brings about local structural change of Rh NPs because the difference in the spectra is so small that normal error value clouds the justification of the effect of H₂ absorption and desorption. Such time-resolved observation by *in-situ* XAFS measurement enables us to detect small changes of local structure. From the results of *in-situ* XAFS for Rh NPs, it is confirmed as follows, during H₂ absorption and desorption, (1) the difference of interatomic distance increases with decreasing particle size at a same temperature. (2) the difference of interatomic distance decreases with increasing temperature at a same particle. (3) Debye-Waller (DW) factor for All Rh NPs was not affected by H₂ absorption and desorption. To analyze the obtained data in

detailed about the dynamic local structural change, during H₂ absorption and desorption, will enable understanding of the hydrogen absorption property of metal NPs with more deeply interesting hydrogenate on mechanism.

4. その他・特記事項 (Others)

[1] K. Kusada *et al.*, *Chem. Lett.* **42** (2013) 55-56