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Local structure analysis of Rh catalysts prepared using arc-plasma

Keita IKEUE*, Satoshi HINOKUMA, Masato MACHIDA
Kumamoto University, Kurokami, Kumamoto 860-8555, Japan

Introduction

Recently, catalyst preparation using plasma has attached a lot of attentions. We reported a novel preparation method of supported Pt and Pd catalysts using pulsed arc-plasma, which enables the one-step deposition of highly dispersed metal nanoparticles from bulk metals in contrast to the multi-step preparation of conventional wet impregnation processes [1]. In the present work, we have applied this technique to a Rh catalyst supported on $AlPO_4$ to study the local structure and catalytic activity

Experimental

Rh loaded catalyst, Rh/$AlPO_4$(AP), was prepared using a pulsed cathodic arc-plasma source (Ulvac Inc., ARL-300) with a Rh cathode (ϕ10 mm, 99.99%, Furuya Metals, Co. Ltd.) under vacuum. The arc pulse with a period of 0.2 ms current amplitude of 2kA was generated with a frequency of 1 or 2 Hz. The plasma from the cathode entered into a container which contains powders of as-prepared $AlPO_4$ under mechanical stirring at ambient temperature. The catalysts were also prepared by a conventional wet impregnation method using an aqueous solution of $Rh(NO_3)_3$ (Rh/$AlPO_4$(imp)).

EXAFS of Rh K-edge was recorded at room temperature in a transmission mode on NW10A station at PF-AR. The XAFS data were processed by a REX 2000 program (Rigaku). The EXAFS oscillation was extracted by fitting a cubic spline function through the post-edge region. The k^3-weighted EXAFS oscillation in the 3.0-13.8 Å^{-1} regions was Fourier–transformed.

Results and discussion

CO oxidation measured in light-off mode using a conventional flow microreactor. As-prepared Rh/$AlPO_4$(AP) initiated the reaction at a low temperature of 100 °C, compared to more than 200 °C required for Rh/$AlPO_4$(imp). The reaction was also observed for C_3H_6 oxidation under oxygen-excess condition.

To explain such a catalytic behavior, we carried out local structure analysis by EXAFS and TEM observation. TEM images of Rh/$AlPO_4$ showed highly dispersed Rh nanoparticles with a uniform size. Rh/$AlPO_4$(AP) (2.4±0.1 nm) exhibited a narrower size distribution than Rh/$AlPO_4$(imp) (6.4±5.5 nm). Figure 1 shows Fourier transforms of Rh K-edge EXAFS for as-prepared Rh/$AlPO_4$ and two references (Rh and Rh_2O_3) without corrections for phase shifts. The peaks in the Fig.1 are therefore shifted to shorter r-value from atomic distances. When the first and second coordination shells were filtered, the best curve-fitting was obtained. Rh/$AlPO_4$(imp) catalysts showed the intense peak at around 2.0 Å, which is attributed to a Rh-O shell (r=2.03 Å, CN=4.3), but the second shell was quite different from that of Rh_2O_3. A curve-fitting analysis of the second shell was carefully performed on seven different types of possible shell combinations. The best fitting was finally achieved when the contribution of a Rh-O-P bonding suggested the presence of Rh species strongly interacting with $AlPO_4$ support. On the other hand, Rh/$AlPO_4$(AP) exhibited a much stronger peak due to a Rh-Rh shell (r=2.70, CN=2.0), suggesting the presence of metallic Rh, whereas the coordination number for a Rh-O-P shell was decreased significantly(CN=0.55). From these results, the supported Rh catalyst prepared using arc-plasma can be characterized by (i) the relative abundance of metallic state and (ii) weaker metal-support interaction. The higher fraction of metallic Rh in Rh/$AlPO_4$(AP) than in Rh/$AlPO_4$(imp) is considered as a common feature of arc-plasma catalyst preparation. Therefore, these results showed that high dispersion of metallic Rh nanoparticles should play a primary role in catalytic oxidation of CO at low temperatures.

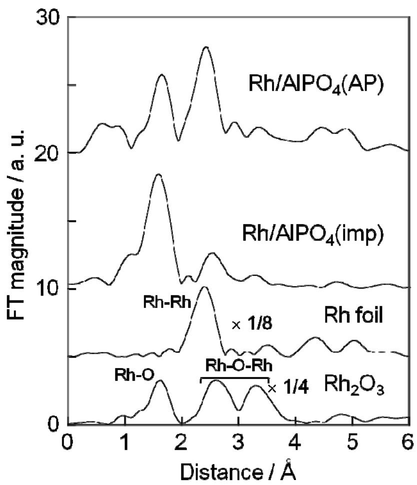

Figure 1 Fourier transformed Rh K-edge EXAFS for 0.4 wt% Rh/$AlPO_4$ as prepared by wet impregnation and arc-plasma process.

References
[1] S. Hinokuma, K. Murakami, K. Uemura, M. Matsuda, K. Ikeue, N. Tsukahara, M. Machida, Top. Catal, 52, 2108 (2009).; S. Hinokuma, M. Okamoto, E. Ando, K. Ikeue, M. Machida, Catal. Today, in press.

*ikeue@kumamoto-u.ac.jp