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Study of the Rhodium Nanoparticles in ZrO_2-CeO_2 Based Catalytic Materials using Nano Beam Diffraction and High Resolution TEM

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Rhodium is an essential component in three-way catalyst for NO_X reduction and also one of the most expensive precious metals. Since mixed ZrO_2-CeO_2 (CZ) based oxides are widely regarded as Rh support due to the catalyst thermal stability and unique surface properties, extensive studies have been focused on the understanding of the chemical, textural and nano-structural properties of CZ based catalytic materials. As the dispersion and morphology of Rh in the Rh-CZ system has strong influence on the Rh-CZ catalyst activity, high resolution TEM (HRTEM) has been used to characterize dispersed Rh nanoparticles previously [1, 2]. However in the HRTEM, a particle structure and orientation can be determined only when it is oriented along low index zone axis parallel to the incident beam. Furthermore, high irradiation dose is needed in HRTEM. Nano-beam diffraction (NBD) gives a direct indication of the particle structure and orientation at doses significantly lower than HRTEM [3]. NBD is insensitive to sample drift and the TEM lab instabilities [4].

In this work, Ceria-Zirconia based support was prepared by a powder supplier using co-precipitation process. 2 wt% of Rh as $Rh(NH_3)_2(NO_2)_2$ aqueous solutions were loaded into the CZ powder solution using the conventional wet impregnation method. The fresh Rh in CZ support was calcined in air at 500ºC for 2 hours and subsequently aged in 5% CO/N_2 at 950ºC for 5 hours. HRTEM investigation was carried out in a JEOL JEM-2200FS at 200kV and Hitachi HF 3300 and NBD was preformed in a Hitachi HF 3300, an instrument equipped with cold field emission gun at 300kV.

Fig. 1a is a HRTEM image of a metal Rh nanoparticle on CZ support. An enlarged image of this particle is shown in the right inset in Fig 1a. The corresponding NBD pattern, shown in the up left inset in Fig. 1a, reveals that the nanoparticle is metallic Rh single crystal. The indexing of the NBD pattern shows that Rh particle is oriented with $[011]_{Rh}$ parallel to the incident beam. The reflections belonging to {111} of CZ are indicated by red arrows. It can be seen that the two arrowed spots are aligned with reflections of $\{111\}_{Rh,}$ suggesting $\{111\}_{Rh}$ parallel to $\{111\}_{CZ}$. Fig. 1b shows another nanoparticle marked by a green square and the corresponding NBD pattern is shown in the upper left inset. Again the NBD pattern suggests the nanoparticle is metallic Rh single crystal. The indexing shows the zone axis is [-112].

In the HRTEM observation, {111} plane is the most commonly observed. Because the surface energy of different planes of Rh crystal is in a sequence of $(111)_{Rh}<(200)_{Rh}<(220)_{Rh}$ [5], the existence of $\{111\}_{Rh}$ suggests the oriented attachment controls the growth of Rh nanoparticle: during the anisotropic growth of the nanoparticle, the facets of seeds with high surface energy are attached while the ones with lower surface energy are conserved. Fig. 2 shows a Rh nanoparticle with apparent truncated octahedron morphology. The misfit between $\{111\}_{Rh}$ and $\{111\}_{CZ}$ is accommodated by misfit dislocations on every third CZ plane indicated by arrows. The truncation observed on this particle reduces its total energy. The edge dislocations found at the interface between Rh and CZ decreases the metal-support interaction and reduces the total energy by decreasing its adhesion energy at the Rh-CZ interface. A truncated octahedral shape is an often observed equilibrium shape of a face centered cubic (FCC) metal cluster. The apparent existence of this morphology suggests that the heat treatment under CO provides sufficient time and thermal energy for the cluster to form an equilibrium shape.

References

1. J. M. Gatica, R. T. Baker, P. Fornasiero, et al. J. Phys. Chem. B, 104(2000) 4667.
2. N. Y. Jin-Phillipp, P. Nolte, A. Stierle, H. Dosch, Surf. Sci., 603 (2009) 2551.
3. J.-O. Malm, M. A. O'keefe, Ultramicroscopy, 68 (1997)13.
4. M. Malac, M. Beleggia, Y. Taniguch, R. F. Egerton and Y. M. Zhu, Ultramicroscopy, 109 (2008) 14.
5. Q. Jiang, H. M. Lu, M. Zhao, J. Phys. Cond. Mater., 16 (2004) 521.

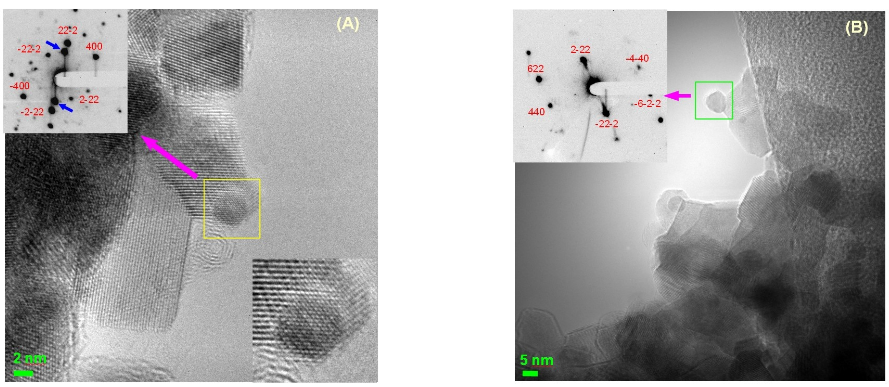

Fig. 1a HRTEM of Rh on Ceria-Zirconia oxide based support with HRTEM (low right inset) NBD diffraction pattern (up left inset). Fig. 1b shows an Rh nanoparticle on CZ support and the NBD pattern (up left inset). Both NBD patterns reveal that the metal Rh nan nanoparticles formed a single crystal.

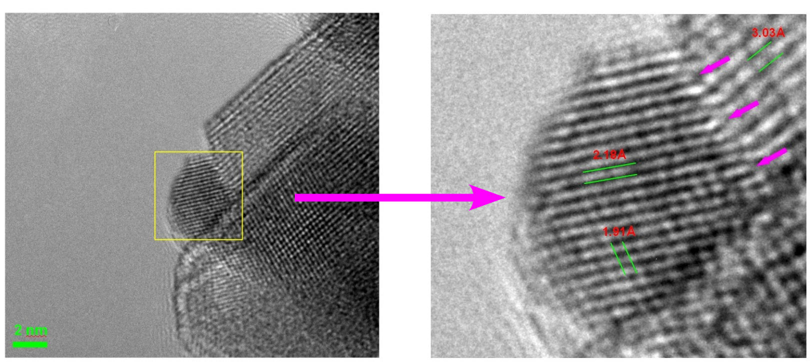

Fig. 2. Rh nanoparticle on CZ support. The misfit between {111} planes of Rh and CZ is accommodated by dislocations at the interface (indicated by arrows in the enlarged image left).

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