doi:10.1017/S1431927613010313
Microsc. Microanal. 19 (Suppl 2), 2013

In-Situ Observation of the Changes in Shape and Surface Structure of Pt Nanoparticulate Catalysts in Reactant Gases by Aberration-Corrected Environmental Transmission Electron Microscopy

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The catalytic activity of supported metal nanoparticles frequently depends on the size, shape, and surface structure of metal nanoparticles. It is well-known that the adsorption of gases induces changes in the shape and surface structure of metal nanoparticles. Thus, it is important to obtain structural information about metal nanoparticles under reaction conditions to elucidate the mechanism of catalysis at atomic scale. Environmental transmission electron microscopy (ETEM) is one of the powerful methods for the study of catalyst chemistry [1,2]. In this study, we have investigated the shape and surface structure of Pt nanoparticles that are supported on CeO_2 (Pt/CeO_2) in reactant gases by ETEM.

Pt/CeO_2 catalysts were prepared by solid grinding method which could produce halogen-free supported metal catalysts. $Pt(C_5H_7O_2)_2$ and CeO_2 powders were ground in an agate mortar in air for 20 minutes at room temperature (RT). The mixture was calcined in air at 300 ^oC for 4 hours and then reduced in a mixture of H_2:N_2 = 1:9 at 300 ^oC for 2 hours to form Pt nanoparticles on CeO_2 supports. The Pt content in the catalyst was estimated to be 9.1 wt%. The catalytic activity of Pt/CeO_2 catalysts for CO oxidation was measured by using a fix bed flow reactor by passing 1 vol% CO in air at a space velocity of 20,000 h^{-1} ml g_{cat}^{-1}. The conversion of CO to CO_2 was about 10% at RT and reached 100% at above 50 ^oC. The Pt/CeO_2 catalysts were supported on a Cu micro grid with a carbon supporting film. ETEM observation was performed using an FEI Tecnai F20 equipped with an environmental-cell and an FEI Titan ETEM G2. We observed the samples in vacuum and gases of N_2, O_2, CO, and CO/air (CO 1 vol %, O_2 21 vol %, N_2 78 vol %) of 100 Pa. The samples were observed at RT and 100 ^oC.

As shown in Figure 1, the shape of Pt nanoparticles changes depending on the gas species. Pt nanoparticles are stable polyhedra and faceted with low index crystal planes such as {111} and {100} in N_2 as well as in vacuum as shown in Figures 1a and 1b. In general, N_2 molecules are not adsorbed on the surface of Pt. This indicates that the impact of N_2 molecules does not cause the detectable shape change of the nanoparticles. In contrast, Pt nanoparticles become round and the shape is unstable in O_2 and CO (Figures 2c and 2d). It is very likely that such shape changes of Pt nanoparticles were caused by the adsorption of CO molecules and the dissociative adsorption of O_2 molecules [3].

We found that the Pt nanoparticles show temperature-dependent shape changes under reaction conditions. In CO/air at RT, Pt nanoparticle becomes round (Fig. 2b). The major {111} facet clearly shrinks, while the minor {110} and {311} facets appear (Fig. 2d). When the temperature increased to 100 °C in CO/air, the Pt nanoparticle becomes partially faceted (Fig. 2c). The {110} and {311} facets shrink and the {100} facet extends (Fig. 2d). Based on a comparison between the shapes of the Pt

nanoparticles in vacuum, N_2, O_2, CO, and CO/air at RT and 100 °C, we suggest that the Pt nanoparticles in CO/air are mainly covered by CO molecules at RT and by O atoms at elevated temperatures [3].

Moreover, we will present the dynamic change in the surface structure of Pt nanoparticles at atomic scale in gases by means of aberration-corrected ETEM.

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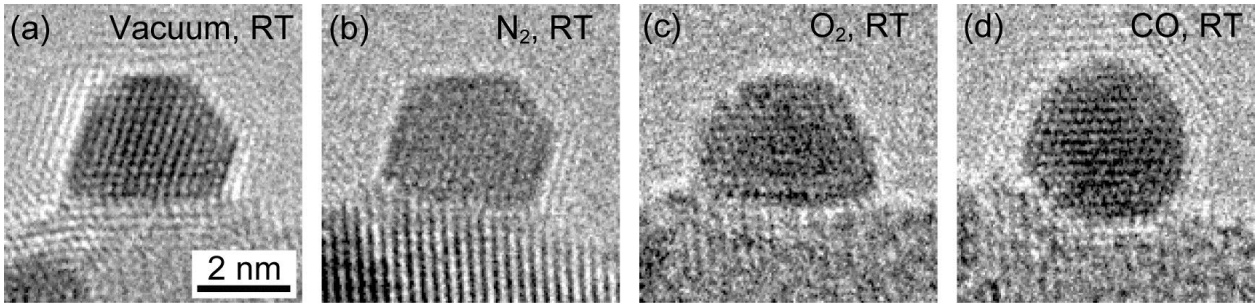

Figure 1. ETEM images showing the shape change of a Pt nanoparticle on CeO_2 depending on gas species. The same Pt nanoparticle is observed in (a) vacuum, (b) N_2 of 100 Pa, (c) O_2 of 100 Pa, and (d) CO of 100 Pa at RT [3].

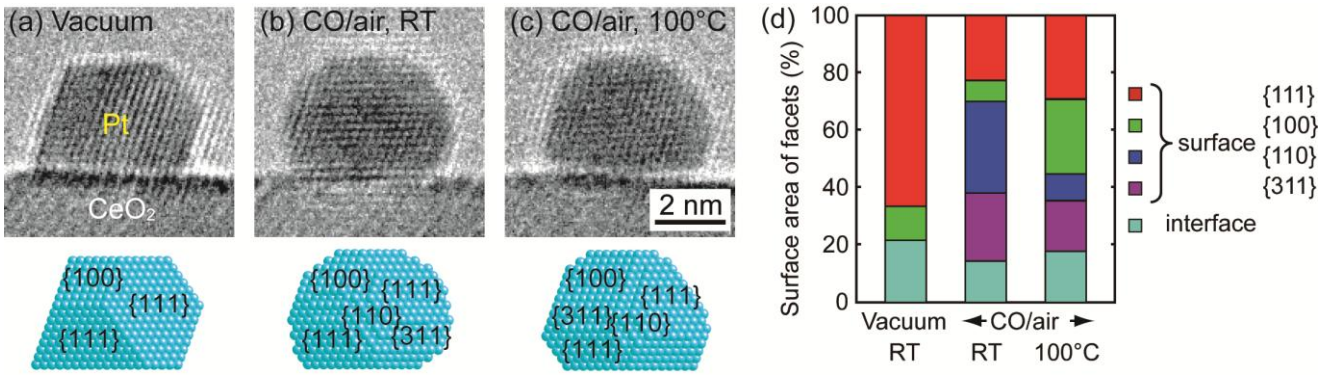

Figure 2. ETEM images and the corresponding atomic models of a Pt nanoparticle on CeO_2 in (a) vacuum at RT, (b) CO/air of 100 Pa at RT, and (c) CO/air of 100 Pa at 100 °C [3]. (d) The percentage of area of various facets on the Pt nanoparticle and the Pt-CeO_2 interface in vacuum at RT, CO/air of 100 Pa at RT, and CO/air of 100 Pa at 100 °C which are determined from Figure 2a, 2b, and 2c.

https://doi.org/10.1017/S1431927613010313 Published online by Cambridge University Press