TEM and STEM observation of the Au particle-NiO interface

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It is well-known that Au exhibits various catalytic properties when small Au particles in nano-scale are supported on the metal oxides [1,2]. The catalytic properties depending on the kind of the metal oxide supports are observed for various reactions. For example, high catalytic property is observed in the water-gas-shift reaction at the low temperature when the CeO_2 is used as support [3], and high activity is shown in the low temperature CO oxidation when TiO_2 is used for the support [2]. The origin of the catalytic properties of Au particles is not clear yet although it is suggested that the interface structure between the small Au particle and the metal oxide support is important [4,5]. In order to clarify the relation between the structure and the catalytic properties at the interface, we have carried out the structure analysis on the small Au particle supported on TiO_2 and CeO_2 with a transmission electron microscopy (TEM) and high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) [6,7]. Recently, it was reported that the Au/NiO catalyst exhibit high catalytic activity in direct aerobic oxidation of 1-octanol to octanoic acid. In this experiment, the basic structure of Au nano-particles supported on NiO was observed in atomic scale by HRTEM and HAADF-STEM.

The model structure of Au particles on NiO was prepared by vacuum deposition method by using poly-crystalline NiO substrate. A thin poly-crystalline NiO substrate was prepared by mechanical polishing and Ar ion beam milling. The NiO substrate was heated in air for 4 hours at 873K in order to remove contamination and damaged layer which introduced during sample preparation, and the flat low index faces were obtained at edge of the hole of the NiO substrate for profile-view observations. The Au particles were deposited on the NiO substrate by heating a piece of Au wire in a tungsten basket heater in vacuum chamber. Then, the Au/NiO sample was heated in air at 573K for 4 hours. The particle size of Au could be controlled to some extent by the amount of Au and changing the heating temperature.

Figure 1a shows typical profile-view TEM images of Au particle on NiO(111) surfaces. Small Au particles of approximately 2-5 nm in diameter are deposited on the edge of NiO substrate with sufficiently high population in this experiment. Gold particles also tend to be deposited on the NiO surface with the preferential orientation relationships of (111)[1-10]Au//(111)[1-10]NiO or (111)[-110]Au//(111)[1-10]NiO for the NiO(111) surface. The orientation relationship was estimated for 303 Au particles in HRTEM images, and Au particle with the orientation relationship of (111)[1-10]Au//(111)[1-10]NiO or (111)[-110]Au//(111)[1-10]NiO was 63%. Figure 1b shows profile-view HAADF-STEM images of Au particles on NiO(111). The incident electron beam direction was set along the NiO [1-10] zone axis, and atomic columns are observed clearly. The Au particle is also deposited with the orientation relationship of (111)[1-10]Au//(111)[1-10]NiO. It is possible to consider the bright contrast as atomic columns of Au and Ni in HAADF-STEM image. The oxygen columns in NiO are not

detected in these experiments because the oxygen is too light compared with the other atoms. The mean distance between Au and Ni atomic layers at the interface was estimated as 0.32±0.01nm from the HAADF-STEM images.

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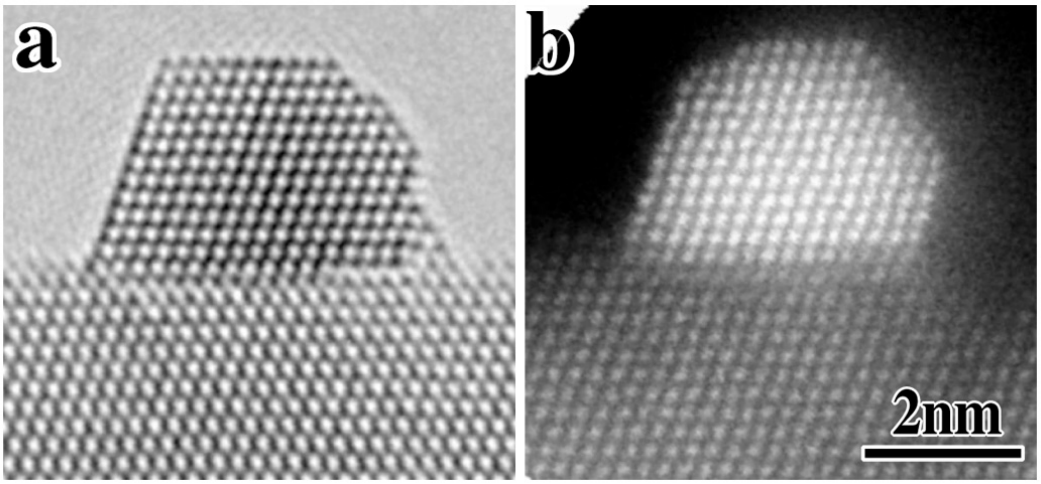

FIG. 1. HRTEM image of Au particle on NiO(111) surface (a) and HAADF-STEM image(b).