Type of presentation: Oral

MS-1-O-1786 Catalytically active structures in Au nanoparticulate catalysts studied by quantitative environmental TEM

Kuwauchi Y.[1], Yoshida H.[1], Takeda S.[1]

[1]The Institute of Scientific and Industrial Research, Osaka University

Email of the presenting author: takeda@sanken.osaka-u.ac.jp

To validate the usefulness of *in-situ* environmental TEM (ETEM) in catalyst chemistry, there remain several issues to be addressed such as electron irradiation effects, heterogeneity of real catalysts, temperature and pressure gaps [1]. It is recently shown that these issues in ETEM observation can be settled in supported gold nanoparticulate catalysts (AuNP catalysts) and others by quantitative data analyses [2-4]. These quantitative analyses can confirm that an area of interest under atomic resolution ETEM observation acts as catalyst. Based on the analyses, we show some recent results that can only be derived by quantitative atomic resolution ETEM.

We used a prototype ETEM [1] that is equipped with a corrector for the spherical aberration of the objective lens and was operated at 80, 200 and 300 kV. The basic part of the prototype ETEM is commercially available as FEI Titan ETEM G2. The sample was Au/CeO_2 powder that has exhibited high catalytic activity for the oxidation of CO even below room temperature. Details of the samples were already described before [2].

We have studied dynamic structures of AuNP catalysts. The observation proved that catalytically active AuNPs move reversibly and stepwise by approximately 0.09 nm on CeO_2 support surface at room temperature and in a reaction environment (Fig. 1). The lateral displacements and rotations indicate that AuNPs are loosely bound to oxygen-terminated CeO_2. The AuNPs are likely anchored to oxygen-deficient sites [5]. Observations indicate that the most probable activation sites in AuNP catalysts, which are the perimeter interfaces between an AuNP and a support, are not structurally rigid. It is also shown that the surfaces of AuNPs were structurally reconstructed under reaction conditions, via interactions with CO molecules [6]. CO molecules were observed on the surfaces of catalysts under reaction conditions (Fig. 2). We present more details on in-situ ETEM observation of the catalysts and others.

References

[1] S. Takeda and H. Yoshida, Microscopy. 62 (2013) 193-203.

[2] T. Uchiyama, H. Yoshida, Y. Kuwauchi, S. Ichikawa, S. Shimada, M. Haruta, and S. Takeda, Angew. Chem. Int. Ed. 50 (2011) 10157-10160.

[3] Y. Kuwauchi, H. Yoshida, T. Akita, M. Haruta, and S. Takeda, Angew. Chem. Int. Ed. 51 (2012) 7729-7733.

[4] H. Yoshida, K. Matsuura, Y. Kuwauchi, H. Kohno, S. Shimada, M. Haruta, and S. Takeda, Appl. Phys. Express 4 (2011) 065001/1-3.

[5] Y. Kuwauchi et al., Nano Lett. 13 (2013) 3073-3077.

[6] H. Yoshida, Y. Kuwauchi, J. R. Jinschek, K. Sun, S. Tanaka, M. Kohyama, S. Shimada, M. Haruta, S. Takeda, Science 335 (2012) 317-319.

Acknowledgement: This study was partially supported by a Grant-in-Aid for Scientific Research (A) , Grant No. 25246003 from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This research was partly supported by the Management Expenses Grants for National Universities Corporations from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

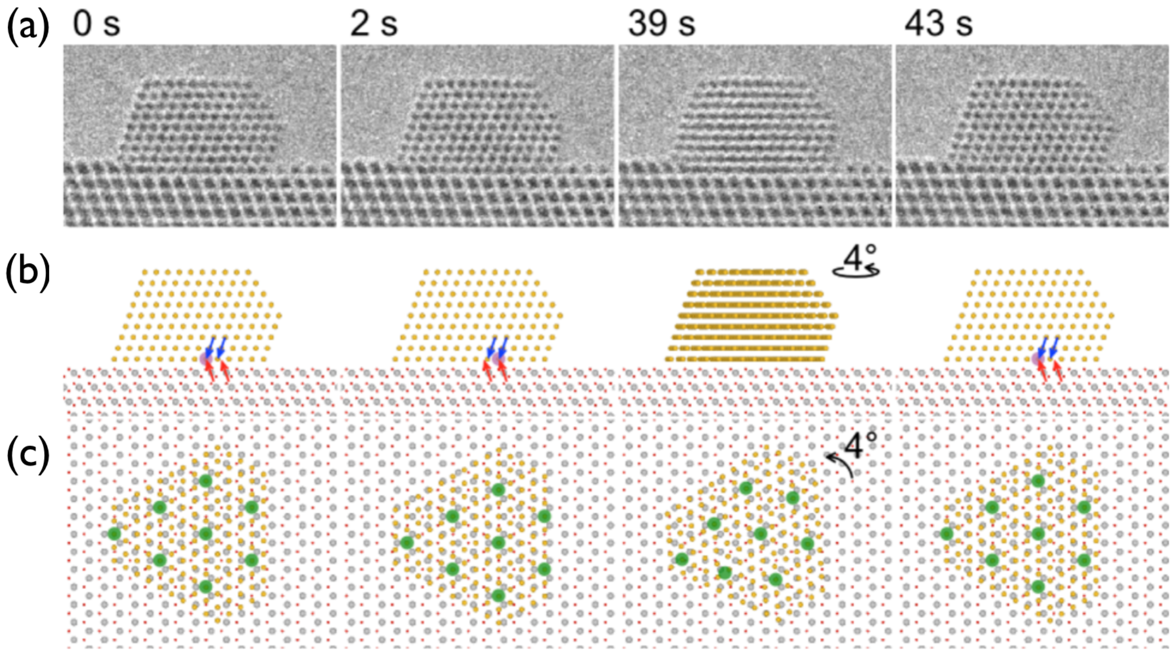

Fig. 1: Stepwise displacement and rotation of a AuNP supported on CeO_2 [5]. (a) In-situ observation. Observation time is indicated. (b) Instantaneous structural models that are depicted in lateral (b) and top (c) views.

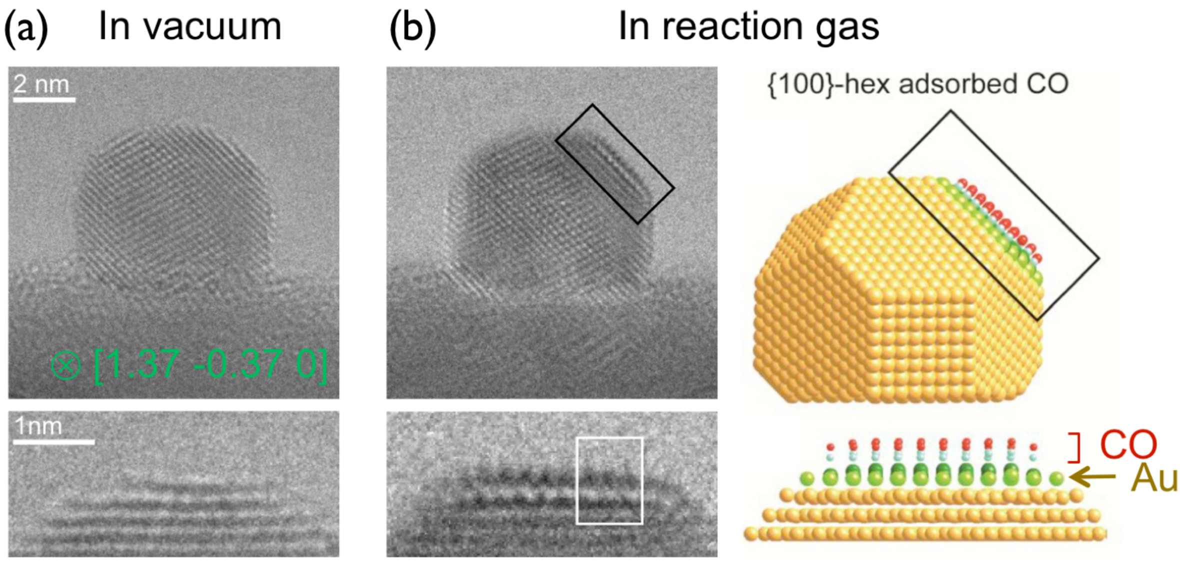

Fig. 2: Glimpse of gas molecules (CO) on the reconstructed surface of a AuNP [6]. In reaction gas in (b), the {100} facet, indicated by rectangle is structurally reconstructed, while in vacuum in (a) the facet is unreconstructed. Faint image contrast on the reconstructed facet in (b) can be accounted by adsorbates (CO molecules).