

***In situ* Environmental TEM and DFT Studies on the Highly Stable AuIr Bimetallic Catalyst**

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Since the report by Haruta *et al.* in 1987 of high catalytic activity of supported nanocrystalline Au catalysts in CO oxidation at low temperature [1], Au catalysts have attracted significant amount of interest from researchers. Despite the remarkable activity of Au catalysts in various oxidation processes, a wide range of uses of Au catalysts in industry is limited due to the lack of stability against sintering [2,3]. In this regard, stabilization of supported Au nanoparticles (NPs) is of utmost importance in the field of Au catalysis. With the purpose of increasing the stability of Au catalysts, various methods for increasing the stability have been developed [4,5]. One of the successful methods for increasing the stability is through adding a second metal into Au NPs [6–9]. Specifically, R. Zanella *et al.* reported that AuIr bimetallic NPs on TiO₂ support show enhanced stability and activity compared to Au on TiO₂ [7]. Considering several reports of the improved catalytic activity as well as on the improved stability of supported Au-based bimetallic catalysts, it can be expected that Au catalysts for industrial applications will be comprise bimetallic NPs rather than pure Au. Therefore, the mechanism behind the increased stability of Au-based bimetallic catalysts needs to be clearly understood. Despite the importance of Au-based bimetallic catalysts, however, the *in situ* investigations of their dynamic behaviors during the “real” catalytic process have been limited.

In this study, we performed *in situ* environmental TEM and DFT calculations to investigate the highly stable anatase TiO₂ supported AuIr bimetallic NPs, prepared by the deposition-precipitation by urea (DPU) method [6,7]. Particularly, as an effort to understand the activity as well as the increased stability of AuIr catalyst, the dynamic behaviors (i.e., morphological variation and/or surface reconstruction) of AuIr NPs during room temperature CO oxidation process were investigated using *in situ* E-TEM technique. In all the experiments performed, significant care was taken to avoid electron beam damage by using of low-dose irradiation to avoid structural transformation of the Au NPs [10]. A mixture of CO and He (ratio= 1:1) was fed into the differentially pumped environmental cell of the FEI Titan E-TEM and the pressure was maintained at ~ 0.55 Torr. Figure 1 shows the morphological variation of AuIr NPs in the CO and He ambient at room temperature. Fig. 1(a) displays a faceted AuIr NP at the onset of the experiment. Structural reconstruction occurs during the reaction and after 9 minutes of reaction time the morphology as shown in Fig. 1(b) is that of a rounded NP. Considering the fact that low-coordinated Au atoms [11], locating on the corners and edges of the NPs are attributed to the catalytic activity, the morphological variation can be correlated with the measured temporal variation of catalytic activity of AuIr NPs in CO oxidation. We also performed a series of density functional theory (DFT) calculations for single crystal AuIr alloy slabs on the TiO₂ surface [Fig. 2], as a first approximation, to understand the higher stability of TiO₂ supported AuIr NPs, as compared to Au NP. At the vacuum/metal interface, Au atoms prefer to segregate to the surface, but at the TiO₂ interface, oxygen reverses this trend and draws

the more oxophilic Ir atoms to the interface. The segregated Ir atoms near the TiO₂ surface leads to the increase in stability of AuIr on TiO₂. The results of *in situ* E-TEM analysis and DFT calculations will be provided and the correlation between the morphological changes of AuIr NPs with the activity in CO oxidation. Moreover, the mechanism of the increased stability will be discussed in the aspect of the theoretically calculated adsorption energies of AuIr slabs on TiO₂.

References

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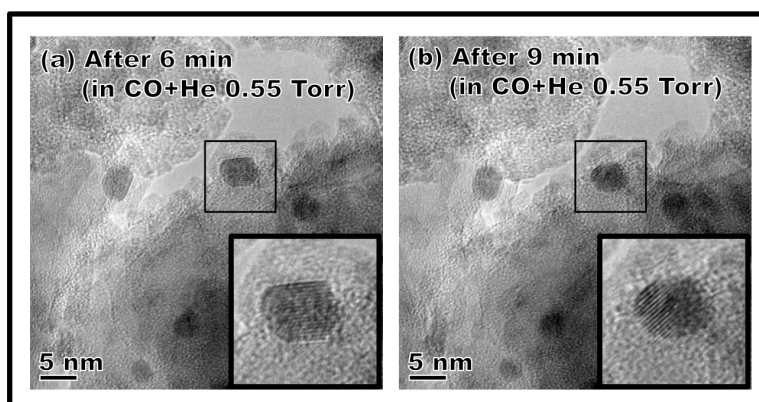


Figure 1. *In situ* E-TEM images of AuIr NPs on TiO₂ after feeding the CO and He gas mixture. Morphological variation of a AuIr NP from the strongly faceted (Fig. 1a) to the rounded (Fig. 1b) is observed.

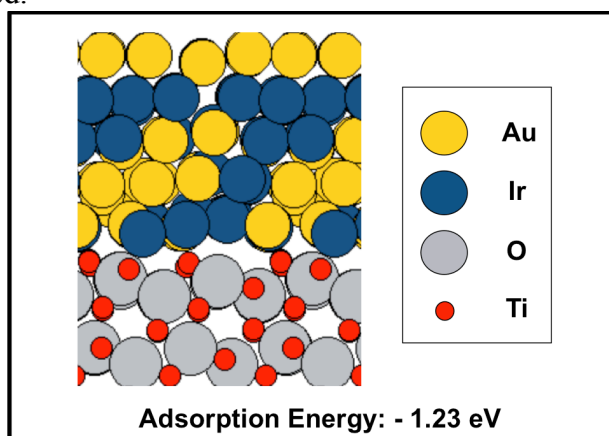


Figure 2. AuIr slab on anatase TiO₂ surface showing segregation of Au to the vacuum interface and Ir to the support interface. Adsorption energy reported below figure.