

## Carbon Supported $\text{Au}_{25}(\text{SR})_{18-x}$ Catalyst: Metastable State Observed during Calcination and Catalytic Activity

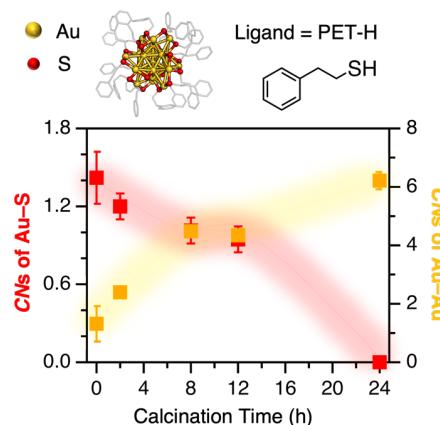
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Removal of protecting ligands (L) from atomically-precise  $\text{Au}_m\text{L}_n$  clusters on solid supports is a promising method for synthesizing active Au cluster catalysts.<sup>1</sup> However, aggregation of the Au clusters was often induced when the interaction between Au clusters and the solid supports is weak and the loading of Au cluster is high.<sup>2</sup> It was reported that the desorption of the thiolate ( $\text{RS}^-$ ) ligands from porous carbon-supported  $\text{Au}_{25}(\text{SR})_{18}$  required much higher temperature ( $\sim 500^\circ\text{C}$ ) than that of the non-supported cluster.<sup>3</sup> This suggests existence of strong interaction between the thiolates and the carbon support. In this study, we utilized such interaction as an anchor to develop novel methods to avoid aggregation during calcination.

1.0 wt% of the presynthesized  $\text{Au}_{25}(\text{PET})_{18}$  (PET = 2-phenylethanethiolate) clusters were adsorbed on commercially available carbon support and the resulting composite  $\text{Au}_{25}(\text{PET})_{18}/\text{C}$  was calcined at  $450^\circ\text{C}$  *in vacuo* to remove the thiolate ligands. The coordination numbers of Au–S bonds ( $CN_{\text{Au-S}}$ ) obtained from curve fitting analysis of Au L<sub>3</sub>-edge extended X-ray absorption fine structure (EXAFS) retained nearly constant value of  $\sim 0.9$  after the calcination for 8–12 h and gradually decreased to  $\sim 0$  after calcination for 24 h. This stepwise behavior indicates formation of an intermediate state,  $\text{Au}_{25}(\text{PET})_{18-x}/\text{C}$ , during the ligand removal process. The  $\text{Au}_{25}(\text{PET})_{18-x}/\text{C}$  intermediates prepared by calcination for 8, 12, and 24 h showed comparable catalytic activity and selectivity for oxidation of benzyl alcohol. This performance is in contrast to that by  $\text{Au}_{25}(\text{PET})_{18-x}$ /porous carbon where the activity and selectivity depend strongly on the calcination condition.<sup>3</sup> These differences suggest the  $\text{Au}_{25}(\text{PET})_{18-x}$  clusters of the intermediates provide comparable exposed Au surface by preferential desorption of the PET ligands exposed to vacuum.

- 1) S. Yamazoe *et al.* *Acc. Chem. Res.* **2014**, *47*, 816. 2) S. Xie *et al.* *ACS Catal.* **2012**, *2*, 1519. 3) T. Yoskamtorn *et al.* *ACS Catal.* **2014**, *4*, 3696.



**Fig. 1.** CNs of the Au–S (red) and Au–Au (yellow) bonds as a function of calcination time.