Atomically Precise Synthesis of Au_{25} Cluster Catalyst on Double Metal Hydroxide by Long-term Oxidative Aging of $Au_{25}(SR)_{18}$

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One of the promising approaches for atomically precise synthesis of heterogeneous Au cluster catalysts is to activate ligand-protected Au clusters by pretreatment on a solid support. The most conventional pretreatment is removal of the ligands by calcination at >250 °C in vacuum,[1] but it also induced aggregation of the clusters. Another pretreatment method reported so far includes aging at a low temperature (~150 °C) in the presence of oxygen. However, much less is known about the structural change of the clusters during oxidative aging. In the present work, we focused on the structural change of $Au_{25}(BaET)_{18}$ (BaET: 2-(Boc-amino)ethanethiolate) during long-term oxidative aging at low temperature on double metal hydroxide (DMH) support composed of Co and Ce (Co_3Ce).

The structural change of $Au_{25}(BaET)_{18}$ on Co_3Ce during the aging was studied by Au L_3-edge X-ray absorption fine structure (XAFS) measurement. Time course of coordination numbers (*CN*s) determined by curve-fitting analyses of extended XAFS are plotted in Fig. 1. Firstly, the $CN_{Au–S}$ values monotonically reduced by aging for ≤8 h and became ~0 by aging for ≥12 h, suggesting the ligands were completely removed. Secondly, the $CN_{Au–Au}$ values became 4–5 after aging for 12 h. Such small *CN* values suggest that Au_{25} clusters take a flattened structure since the $CN_{Au–Au}$ for a hemisphere structure is estimated to be ~6 and that for monolayer of (111) plane in face-centered cubic structure is estimated to be 4.2. This structure was stabilized owing to the strong anchoring of gold by oxygen atoms on this support since $CN_{Au–O}$ was appeared after aging.

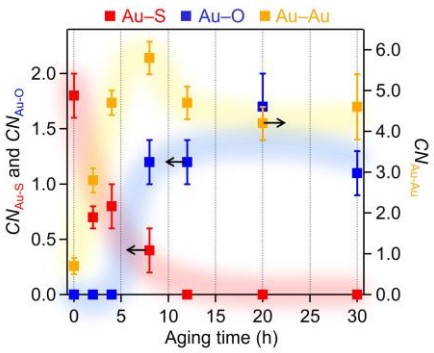

Fig. 1. Time course of coordination numbers (*CN*s) of Au–S, Au–O, and Au–Au bonds during the aging.

Finally, obtained Au_{25}/Co_3Ce catalyst exhibited quite high activity in the benzyl alcohol oxidation to benzoic acid under mild condition.[2]

1) S. Yamazoe, T. Yoskamtorn, S. Takano, S. Yadnum, J. Limtrakul, T. Tsukuda, *Chem. Rec.* **2016**, *16*, 2338. 2) S. Masuda, S. Takano, S. Yamazoe, T. Tsukuda, *Nanoscale,* in press.