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High activation of gold cluster-supported photocatalyst by elucidation of ligand elimination process

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Abstract

The creation of new heterogeneous catalysts using the unique electronic/geometric structures of small metal nanoclusters (NCs) has received considerable attention. However, to achieve this, it is extremely important to establish methods to remove the ligands from ligand-protected metal NCs while preventing the aggregation of metal NCs. In this study, the ligand-desorption process during calcination was followed for metal-oxide-supported 2-phenylethanethiolate-protected gold (Au) 25-atom metal NCs using four experimental techniques. The results clearly demonstrate that the ligand-desorption process consists of ligand dissociation on the surface of the metal NCs, adsorption of the generated compounds on the support and desorption of the compounds from the support, and the temperatures at which these processes occurred were elucidated. Based on the obtained knowledge, we established a method to form a metal-oxide layer on the surface of Au NCs while preventing their aggregation, thereby succeeding in creating a water-splitting photocatalyst with high activity and stability.

1. Introduction

In recent years, research on the creation of new heterogeneous catalysts utilizing the electronic/geometric structure of fine ligand-protected metal nanoclusters (NCs) has been actively conducted.1) In such catalyst creation, the ligand is generally removed by pretreatment such as calcination. However, when the ligand is removed without special treatment, the metal NCs easily aggregate on the support and lose size-specific nature. Therefore, it is extremely important to establish a method for removing ligands while preventing aggregation of metal NCs. In this study, for thiolate-protected gold (Au) 25-atom NC supported on a metal oxide, the ligand desorption process during calcination was tracked by a combination of four measurement methods.

2. Experiment

$Au_{25}(PET)_{18-n}(p\text{-MBA})_n$ (PET; 2-phenylethanethiolate, *p*-MBA: 4-mercaptobenzoic acid) was synthesized with atomic precision. The obtained $Au_{25}(PET)_{18-n}(p\text{-MBA})_n$ was stirred with $BaLa_4Ti_4O_{15}$ (which is one of the most advanced photocatalysts) in acetone solution for 1 h. The ligand desorption process during calcination in the obtained sample ($Au_{25}(PET)_{18-n}(p\text{-MBA})_n/BaLa_4Ti_4O_{15}$) was tracked by using direct insertion probe mass spectrometry (DIP-MS), X-ray absorption fine structure (XAFS) analysis, X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM).

3. Results and discussion

From DIP-MS of the unsupported Au NC ($Au_{25}(PET)_{18-n}(p\text{-}MBA)_n$), phenylethane (PE; m/z = 105; originated from PET) and *p*-MBA (m/z = 154) were appeared as the main peak (Fig.1ab). On the other hand, in the case of the Au NCs-adsorbed photocatalyst ($Au_{25}(PET)_{18-n}(p\text{-}MBA)_n/BaLa_4Ti_4O_{15}$), PE and *p*-MBA were not observed, while styrene (m/z = 104; originated from PET) and CO_2 (m/z = 44; originated from *p*-MBA) were observed at higher temperatures (Fig.1cd). It is interpreted that the ligands dissociated on the Au NC surface were once adsorbed on the photocatalyst and desorbed as styrene and CO_2 when the temperature was raised. XAFS analysis and XPS were also consistent with this interpretation. In addition, TEM observations revealed that calcining up to 300 °C causes almost no aggregation of Au NCs. The results obtained by the four measurements methods revealed the following facts regarding the calcination mechanism of $Au_{25}(SR)_{18}/BaLa_4Ti_4O_{15}$; 1) First, dissociation start from Au–S and then the desorbed compounds are again adsorbed on the support: 2) The compounds adsorbed on the support become styrene or CO_2 and desorbed from the support when the temperature is increased: 3) For this catalyst, heating at 300 °C can remove almost ligands from the Au NC surface while maintaining the size of Au NC: 4) Simultaneously, the catalyst contains a small amount of organic compounds and sulfur oxide on the support (Fig.2).[2)] Based on the obtained knowledge, we established a method to form a Cr_2O_3 film on the Au NC surface while preventing the aggregation of Au NCs, and succeeded in obtaining a highly active and stable water-splitting photocatalyst (Fig.3).

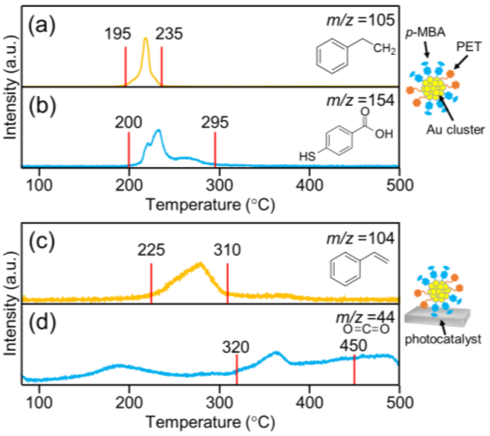

Fig.1 DIP-MS results of
(a, b) $Au_{25}(PET)_{18-n}(p\text{-}MBA)_n$ and
(c, d) $Au_{25}(PET)_{18-n}(p\text{-}MBA)_n/BaLa_4Ti_4O_{15}$.
(a) m/z = 105, (b) m/z = 154, (c) m/z = 104 and (d) m/z = 44. Each spectrum originated from (a, c) PET and (b, d) *p*-MBA.

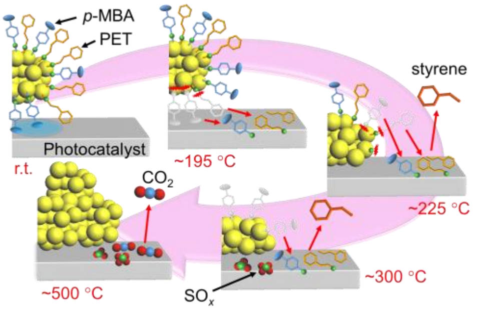

Fig.2 Proposed mechanism occurring at each temperature during calcination of $Au_{25}(PET)_{18-n}(p\text{-}MBA)_n/BaLa_4Ti_4O_{15}$.

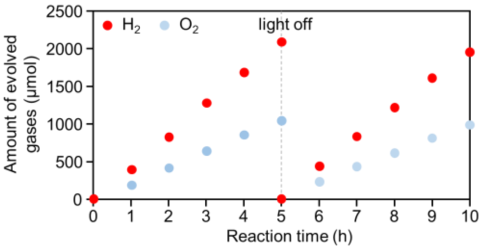

Fig.3 Time course of water-splitting activity of Cr_2O_3/Au NCs/$BaLa_4Ti_4O_{15}$.

4. Conclusions

We used multiple measurement methods to trace the ligand desorption process during calcination of Au NCs-supported catalysts. The ligands dissociated from the surface of the Au NCs were once adsorbed on the photocatalyst, and then decomposed by further heating and desorbed from the photocatalyst. Based on the obtained knowledges, we succeeded in creating a highly active and stable water-splitting photocatalyst.[2)]

References

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