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Viewpoint

Oxide-supported $Au_n(SR)_m$ nanoclusters for CO oxidation

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1. Introduction

Supported Au nanoparticles have been extensively investigated in heterogeneous catalysis since the seminal work of Haruta's research group, in part because of their high activity in some reactions, especially CO oxidation [1–5]. Although many studies have been performed, two problems still remain: aggregation of Au nanoparticles and their catalytic reaction mechanism. Many strategies have been developed to increase Au nanoparticle stability, such as modification of metal nanoparticle composition, metal-support interfaces, and support nanostructures [6–9]. However, Au particles prepared by the deposition-precipitation method are usually larger than 2 nm. Au nanoparticles smaller than 2 nm easily aggregate, and how to stabilize them is an interesting topic. In addition, many studies on the reaction mechanism catalyzed by supported Au nanoparticles have been performed, but the conclusions are not in agreement. This is mainly because of the heterogeneous distribution of the active metal in the catalysts, which are usually prepared by the traditional deposition-precipitation method [10,11].

Benefiting from the development of the solution-phase synthesis of thiol ligand-protected Au clusters [12–15], a series of atomically precise Au clusters ($Au_n(SR)_m$, where n and m are the numbers of Au atoms and thiolate ligands SR, R = alkyl group) have been successfully prepared, and the exact composition and structure of some have been determined [16–20]. Differing from traditional Au nanoparticles, the size of $Au_n(SR)_m$ clusters are ultrasmall (< 2 nm, or less than 200 atoms), and the number of Au atoms and ligands are tunable. It is important to note that they are nearly monodispersed. Such properties of $Au_n(SR)_m$ nanoclusters make them an ideal model catalyst for mechanism study.

2. CO catalytic oxidation over supported $Au_n(SR)_m$ nanoclusters

Supported $Au_n(SR)_m$ nanoclusters for CO oxidation have been extensively studied. It is believed that the capping ligands block the adsorption of CO on the Au surface and S could poison the catalyst, so the thiolate ligands are conventionally removed

by oxidative or reductive pretreatment (Fig. 1) [21–24]. Gaur et al. [25,26] impregnated $Au_{38}(SC_{12}H_{25})_{24}$ clusters on TiO_2 , and then used a 5% H_2/He gas mixture at 400 °C for 1 h to remove the thiolate ligands. X-ray photoelectron spectroscopy and extended X-ray absorption fine structure (EXAFS) analysis of the supported catalyst showed trace levels of residual sulfides. High-resolution transmission electron microscopy (HRTEM) images (Fig. 2) showed that the particle size was 3.90 ± 0.96 nm, while the sizes of the untreated Au_{38}/TiO_2 catalyst and unsupported $Au_{38}(SC_{12}H_{25})_{24}$ were 2.8 ± 0.59 nm and 1.7 ± 0.2 nm, respectively. As shown elsewhere [25], pretreatment resulted in the growth of Au clusters, although the final size was still small. However, Ma et al. [27] constructed heterostructured transition-metal-oxide-mesoporous silica ($CuO-mSiO_2$) to support $Au_{144}(SR)_{60}$. The size of the clusters was maintained after removing the thiolate ligands by calcination at 300 °C in air. Scanning transmission electron microscopy showed that the particle size of the $Au_{144}(SR)_{60}$ clusters after calcination was 1.67 ± 0.2 nm, which is consistent with the size of bare $Au_{144}(SR)_{60}$ in the liquid phase (1.7 nm) [20]. The interaction

Fig. 1. General methodology for preparing heterogeneous catalysts from nanoparticle precursors. Reproduced from Ref. [23]. Note: MPCs means monolayer protected clusters.

Fig. 2. HRTEM image of Au_{38} nanoclusters with particle size distribution of unsupported (Up), supported (Down-a), and dethiolated supported nanoclusters (Down-b). Reproduced from Ref. [25].

between Au clusters and the support seems to play an important role in maintaining the size of Au clusters during pretreatment. In addition, the pretreatment method is also important, Menard et al. [21] found that the use of ozone at room temperature for ligand removal resulted in smaller cluster sizes than thermal treatment.

The $\text{Au}_n(\text{SR})_m$ nanoclusters as a whole, have unique structure and electrochemical properties. Their performances in aqueous phase organic reactions on either supported or unsupported Au nanoclusters take advantage of their intact structure [28,29]. In gas phase reaction, ligands seemingly cover the active sites and prevent CO from approaching Au surface. Tai et al. [30] proved by in situ diffuse reflectance infrared Fourier transform (DRIFT) that CO could not be adsorbed on uncalcined titania supported thiol-capped Au nanoparticles. Gaur et al. [25] also showed that intact $\text{Au}_{38}(\text{SC}_{12}\text{H}_{25})_{24}/\text{TiO}_2$ had no CO oxidation activity. But just regarding nanoclusters as a precursor of traditional Au/oxides catalysts, it neglects their most precious properties as a whole. Questions are then naturally raised, what the ligands behave during the CO oxidation reaction, and must all the ligands be removed to make them active?

Häkkinen and coworkers [31] carried out density functional theory (DFT) calculations, and found that ligands can alter the electronic structure of Au clusters. They showed that in lig-

Fig. 3. Reaction performance over $\text{Au}_{25}(\text{SR})_{18}/\text{MO}_x$ catalysts. Reproduced from Ref. [32].

and-capped Au nanoparticles ($d = 1.2\text{--}2.4$ nm), electronic quantum size effects, particularly the energy gap between the highest and lowest occupied molecular orbitals, significantly affects the binding energy between molecular O_2 and Au clusters. We deposited $\text{Au}_{25}(\text{SR})_{18}$ ($R = \text{C}_2\text{H}_4\text{Ph}$) onto various oxide supports (including TiO_2 , CeO_2 , and Fe_2O_3), and tested their CO oxidation activity [32]. The results showed that the $\text{Au}_{25}(\text{SR})_{18}/\text{CeO}_2$ catalyst was much more active than the other two catalysts (Fig. 3). In addition, O_2 pretreatment greatly increased the activity of the $\text{Au}_{25}(\text{SR})_{18}/\text{CeO}_2$ catalyst. After pretreating in O_2 for 1.5 h at 150°C , $\text{Au}_{25}(\text{SR})_{18}/\text{CeO}_2$ exhibited the highest activity. Thermal gravity analysis (TGA), TGA-mass spectroscopy (MS), O_2 -temperature-programmed oxidation-MS, and nuclear magnetic resonance confirmed that the CeO_2 -supported $\text{Au}_{25}(\text{SR})_{18}$ catalyst remained intact after O_2 treatment at 150°C . Removing the ligands did not lead to any further increase in activity. The enhancement effect of O_2 pretreatment was also observed for $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ [33], and thermal pretreatment at temperatures between 100 and 175°C greatly increased the catalytic activity, while pretreating at higher temperatures ($> 200^\circ\text{C}$) to remove the thiolate ligands led to a somewhat lower activity than 175°C pretreatment (Fig. 4). Ligands did not detach and remained on the $\text{Au}_n(\text{SR})_m$ cata-

Fig. 4. Effect of pretreatment temperature (T_{pre}) on CO conversion over the $\text{Au}_{38}(\text{SR})_{24}/\text{CeO}_2$ catalyst. Reproduced from Ref. [33].

Fig. 5. CO oxidation mechanism on intact, and partially and fully dethiolated $\text{Au}_{25}(\text{SR})_{18}/\text{CeO}_2$ -rod catalysts. Reproduced from Ref. [34].

lyst at the reaction temperature, but the change of the ligand structure during the pretreatment was still unclear.

A very recent study by Wu et al. [34] investigated the effect of thiolate ligands on the catalysis of CeO_2 -rod supported $\text{Au}_{25}(\text{SR})_{18}$ for CO oxidation. By in situ CO diffuse reflectance infrared Fourier transform spectroscopy, X-ray absorption near edge structure, and DFT calculations, they found that the intact $\text{Au}_{25}(\text{SR})_{18}$ nanoparticle on the CeO_2 rod was not able to adsorb CO, and only when the thiolate ligands were partially removed from the interface between the Au nanoclusters and CeO_2 support could CO be adsorbed. In situ infrared radiation and EXAFS correlated the removal of thiolate ligands with catalytic activity, the catalyst began to show weak activity at 150 °C, which is the starting temperature for ligand removal, and the catalytic activity reached its maximum at 250 °C when the ligands were completely removed. They proved the simultaneous existence of three types of Au sites: $\text{Au}^{\delta+}$ ($0 < \delta < 1$), Au^+ , and $\text{Au}^{\delta-}$ ($0 < \delta < 1$). For the first time, low-temperature CO oxidation on Au/CeO_2 via the Mars van Krevelen mechanism was confirmed with isotopic labeling experiments and Raman spectroscopy, where CeO_2 activates O_2 while CO is activated on the dethiolated Au sites and further oxidized by the CeO_2 lattice O_2 (Fig. 5).

3. Conclusions and outlook

Oxide-supported $\text{Au}_n(\text{SR})_m$ nanoclusters with ultrasmall size (< 2 nm) and atomic precision have the potential to shed light on the long puzzling area of Au catalysis. The existing studies on oxide-supported $\text{Au}_n(\text{SR})_m$ clusters open a new route to stabilize Au nanoparticles, and provide fundamental information for future studies on how ligand-protected Au nanoparticles can be efficiently used as gas-phase reaction catalysts. The interesting problems related to oxide-supported $\text{Au}_n(\text{SR})_m$ nanoclusters, e.g., why supported $\text{Au}_n(\text{SR})_m$ clusters exhibit different catalytic reaction behavior in liquid and gas phase media, how different types of ligands influence the interactions between $\text{Au}_n(\text{SR})_m$ and supports, and how to choose suitable $\text{Au}_n(\text{SR})_m$ clusters and oxide supports to efficiently catalyze gas phase reactions, will attract increasing attention in an attempt to solve these problems in the future.

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Graphical Abstract

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Metal oxide supported $Au_n(SR)_m$ with ultrasmall size (< 2 nm) and atomic precision have recently attracted increasing interest in CO oxidation, and the recent progress is highlighted in this perspective.

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