4P079

Atomic-level control of size and composition of Au-based clusters and their oxidation catalysis

Songhai Xie[1], Hironori Tsunoyama[1], Wataru Kurashige[2], Yuichi Negishi[2], Tatsuya Tsukuda[1]
([1]Catalysis Research Center, Hokkaido University,[2] Tokyo University of Science)

【Introduction】 Gold clusters exhibit interesting chemical properties depending on the atomic numbers (size); for instance, gold cluster anions in the gas phase can react with oxygen molecules only when the size is small and even numbers [1]. Model gold catalysts on a metal oxide surface prepared by a soft-landing method can catalyze CO oxidation when the size is larger than 8 [2]. In addition, a theoretically study predicted that doping of even a single impurity atom greatly enhances the catalytic activity [2]. These studies on the model system illustrate that the catalysis of gold clusters can be manipulated by controlling the cluster size and composition at the atomic level. However, it is a challenge to realize this idea in real catalytic system. Recently, we developed a method to control the size of Au clusters at the atomic level using thiolate-protected Au clusters as precursors [5,6]. In this work, we extended this approach toward the synthesis of bimetallic Au-based clusters using dodecanethiolate-protected Pd_1Au_{24} clusters [4]. We successfully prepared a series of Au_{25}, Pd_1Au_{24}, Au_{38} and Au_{144} clusters on carbon nanotubes (CNTs). The catalytic properties of these catalysts were compared for aerobic oxidation of benzyl alcohol. Clear effect of cluster size and single-atom doping on catalysis were observed for the first time.

【Experimental】 Dodecanethiolate-protected Au-based clusters were synthesized according to the methods described in refs [3,4]. For Au_{25}, Au_{38} and Au_{144} clusters, the Brust-Schiffrin method [3] was employed to obtain a mixture of dodecanthiolate-protected Au clusters. After removing by-products and unreacted starting materials, clusters with specified sizes are purified by extracting with different solvents or mix-solvent. Dodecanethiolate-protected Pd_1Au_{24} binary clusters were prepared by following the protocol for the phenylethanethiolate-protected Pd_1Au_{24} clusters reported before [4].

CNTs (Nanocyl, NC-7000) were dispersed in toluene and sonicated for ~1 hr. The toluene solution containing calculated amount (0.2 wt%) of $Au_n(Pd)(SC_{12}H_{25})_m$ clusters were injected into the suspension of CNTs under vigorous magnetic stirring. After 1 hr, the $Au_n(Pd)(SC_{12}H_{25})_m$/CNTs composites are filtered and dried in vacuum 12 hr.

The calcination of the composites was performed in a quartz-tube oven under vacuum conditions: the temperature was raised to 300 or 450^{o}C with a heating rate of 2^{o}C/min. The aerobic oxidation of benzyl alcohol was studied under the same conditions as in ref. [5].

【Results and discussion】 Optical spectroscopy of the filtrates indicated a complete addition of $Au_n(Pd)(SC_{12}H_{25})_m$ clusters onto CNTs. The $Au_n(Pd)(SC_{12}H_{25})_m$/CNTs composites before and after calcinations were observed by TEM as well. The fresh prepared $Au_n(Pd)(SC_{12}H_{25})_m$/CNTs composites images clearly show that clusters are highly dispersed on CNTs and kept the original sizes. The size distribution of catalysts after the calcination increased a little and only small amount of aggregated clusters are found (Fig. 1). These results demonstrated the present method is effective for atomic-level control of size and composition of Au-based catalysts.

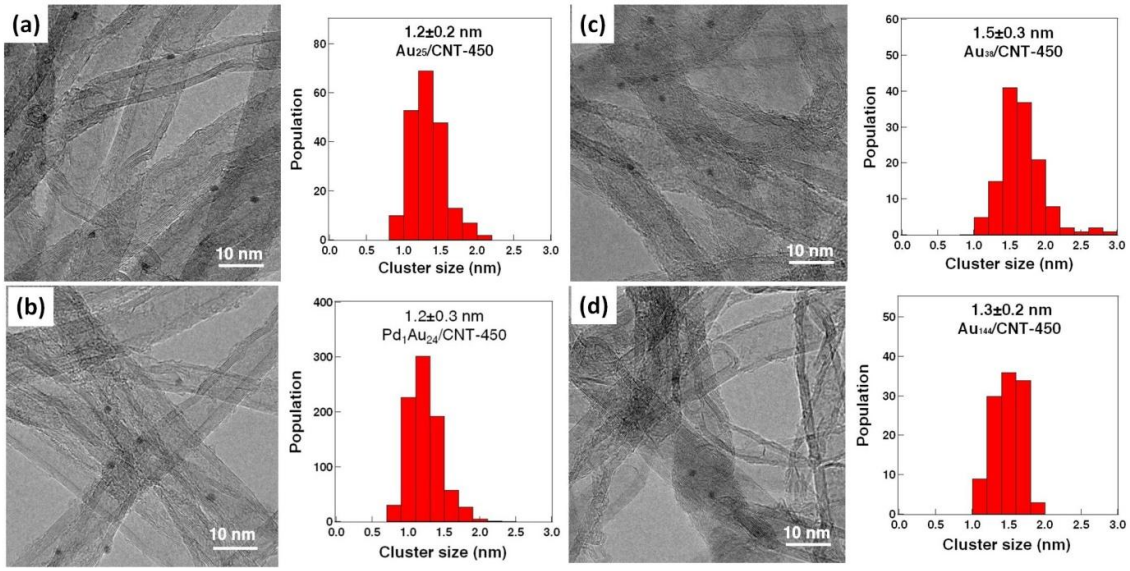

Fig 1. Typical TEM images and corresponding size distribution of Au_n(Pd)/CNTs (calcination under 450^{o}C)

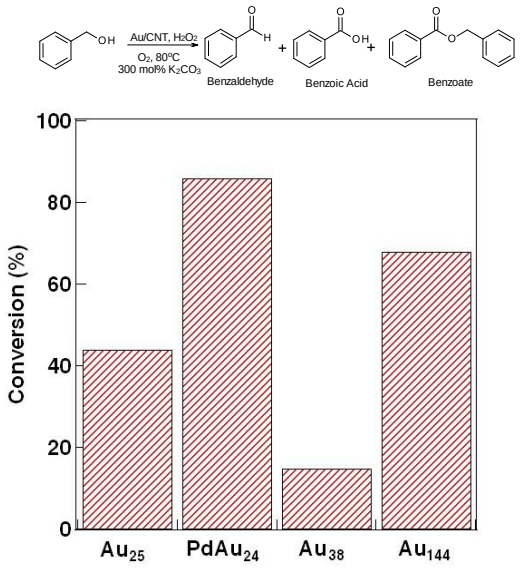

Fig 2. Phenyl alcohol oxidation activities of Au_n(Pd)/CNTs calcined under 450^{o}C

Oxidation of benzyl alcohol was used as a test reaction. Typically, benzaldehyde was the main product when the conversion was lower than 20% and benzoic acid dominated the product when the conversion became higher than 40%. Figure 2 shows the conversion by the catalysts calcinated at 450^{o}C. Interestingly, Pd_1Au_{24}/CNTs showed much higher activities than Au_{25}/CNTs (Fig. 2). This is, to the best of our knowledge, the first demonstration of single atom doping effect on gold catalysis. Size dependence and single atomic doping effects were clearly observed. Au_{144}/CNTs showed higher activity than Au_{25}/CNTs and Au_{38}/CNTs. The origin of this size effect is not clear at this moment, but the interaction of Au clusters with CNTs may play a role.

【Reference】

[1]. R. Meyer et al. *Gold Bull.* **2004**, 37, 72-124.

[2]. U. Heiz and U. Landman, *Nanocatalysis*

[3]. N. K. Chaki et al. *J. Am. Chem. Soc.* **2008**, 130, 8608–8610.

[4]. Y. Negishi et al. *Phys.Chem.Chem.Phys.*, **2010**, 12, 6219–6225.

[5]. Y. Liu et al. *J. Phys. Chem. C*, **2009**, 113, 31, 13457-13461.

[6]. Y. Liu et al. *ACS Catal.* **2011**, 1, 2–6.