

担持金クラスターのサイズ選択的合成と酸化触媒活性

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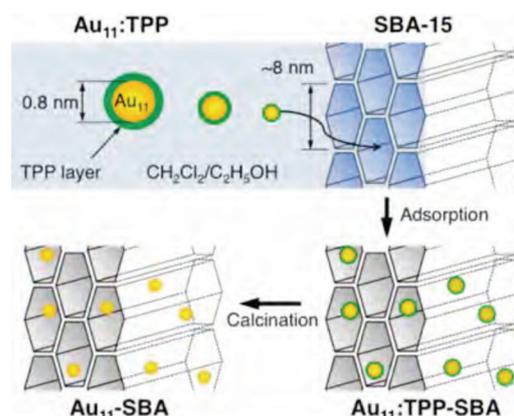
Oxidation over supported gold catalysts using molecular oxygen has gained much attention recently and is known to be affected by the chemical nature of the support as well as the particle size. Highly active Au catalysts may be developed even on chemically inert supports, such as SiO₂ and Al₂O₃, if the size of AuNPs can be reduced to below 1 nm, since small Au_n clusters ($n \leq 20$) are known to activate the O₂ molecule. However, immobilization of small, monodisperse Au clusters on silica is a technical challenge since the conventional methods such as deposition-precipitation (DP) and impregnation (IP) cannot be applied. The present work aims to develop a method to prepare subnanometer-sized Au clusters on mesoporous silicas with large surface areas (SBA-15, HMS, MCF) using phosphine-protected Au₁₁ clusters as precursors.

Scheme 1 shows the synthesis process of 0.8-nm Au₁₁ clusters within mesoporous channels of SBA-15 (pore diameter 8 nm, BET surface area 860 m²/g).

(1) First, the Au₁₁:TPP clusters and SBA-15 were dispersed for 2 hours in mixed solvents of CH₂Cl₂/C₂H₅OH and the composite of Au₁₁:TPP and SBA-15 was collected by filtration. The composites thus obtained are hereafter denoted using the Au content and solvent composition; for example, the composite prepared in the solvent with C₂H₅OH/CH₂Cl₂=20% is referred to as 0.16Au₁₁:TPP-SBA(20).

(2) The Au₁₁:TPP-SBA composite was then calcined at 200 °C for 2 hours to remove the organic ligands. A sample obtained by calcination of 0.16Au₁₁:TPP-SBA(20), for example, will be referred to as 0.16Au₁₁-SBA(20). The size of the gold clusters after calcination was probed by diffuse reflectance UV-vis spectroscopy. Figure 1A shows the optical spectra obtained after calcination of a series of Au₁₁:TPP-SBA composites (curves b-f). The surface plasmon (SP) band is absent in curve b, but is apparent when the concentration of C₂H₅OH is lower than 10 % (curves c-f). This indicates that the Au clusters in 0.16Au₁₁-SBA(20) are smaller than those in the other samples. The suppression of aggregation in 0.16Au₁₁-SBA(20) cannot be ascribed to a smaller amount of loading of the Au₁₁:TPP precursor (curve g), but is related to the composition of the dispersing media used for the adsorption of Au₁₁:TPP. It is believed that aggregation is suppressed because Au₁₁:TPP is adsorbed more homogeneously on SBA-15 as a result of weaker attractive force in the mixed solvent with C₂H₅OH/CH₂Cl₂=20% than in the other compositions.

The structure of 0.16Au₁₁-SBA(20), which contains the smallest Au clusters, is now considered. Given that optical spectroscopy probes the electronic structure of the ensemble of Au clusters and is highly sensitive to the presence of AuNPs (>2 nm), curve b in Figure 1A



SCHEME 1. Synthesis Procedure of Subnanometer-sized Au Clusters within SBA-15.

indicates that the population of Au clusters larger than 2 nm is negligibly small. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) confirmed that most of the clusters in 0.16Au₁₁-SBA(20) are ~1 nm in size (Figure 1B). Figure 1B represents a histogram of the Au cluster size determined by measuring ~120 particles. The average diameter is determined to be 0.8±0.3 nm. This size is comparable to the diameter of the Au₁₁ core and is the smallest so far reported for silica-supported Au clusters.

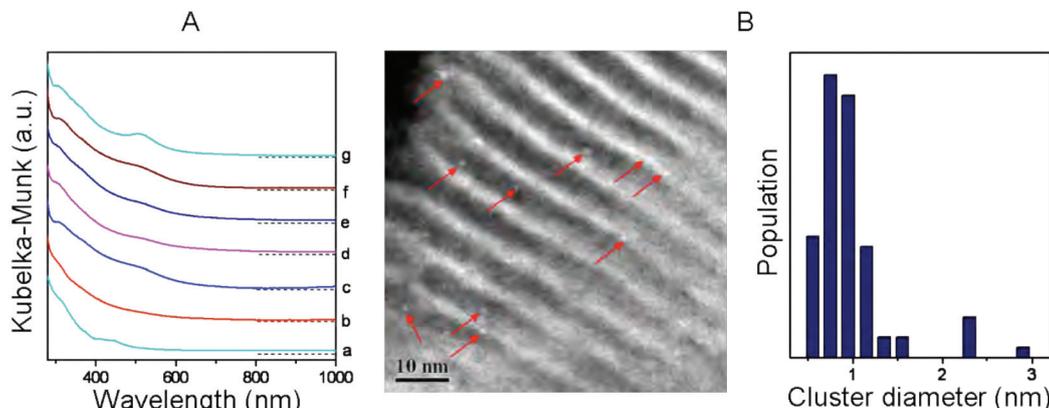


Figure 1. (A) Diffuse reflectance UV-vis spectra of a) 0.16Au₁₁:TPP-SBA(20), b) 0.16Au₁₁-SBA(20), c) 0.17Au₁₁-SBA(10), d) 0.18Au₁₁-SBA(5), e) 0.19Au₁₁-SBA(2.5), f) 0.20Au₁₁-SBA(1), g) 0.10Au₁₁-SBA(0). (B) Representative HAADF-STEM image and size distribution of Au clusters of 0.16Au₁₁-SBA(20).

The catalytic properties of the smallest Au clusters in 0.16Au₁₁-SBA(20) were studied using the oxidation of benzyl alcohol (**1**) in water as a model reaction. In this study, microwave heating was employed and H₂O₂ was used as an oxidant. The 0.16Au₁₁-SBA(20) catalyst showed higher activity than larger AuNPs (~10 nm) prepared by conventional IP and DP methods. The higher selectivity of 0.16Au₁₁-SBA(20) for the formation of **3** than 0.16Au-SBA(IP) and 0.16Au-SBA(DP) can be explained by higher oxidation ability of smaller clusters. The 0.16Au₁₁-SBA(20) catalyst can be recycled at least four times at 60 °C without any loss of activity.

TABLE 1: Oxidation of Benzyl Alcohol

Entry	Catalyst	Recovery (%)		Yield (%)	
		1	2	3	4
1	0.16Au ₁₁ -SBA(20)	0	6	91	2
2	0.16Au-SBA(IP)	24	42	15	2
3	0.16Au-SBA(DP)	29	20	36	0

In summary, a simple, effective method was introduced to immobilize ~1 nm Au clusters within mesoporous silicas (SBA-15, MCF, HMS) using Au₁₁:TPP as a precursor. It was found to be crucial to disperse the Au₁₁:TPP homogeneously on the silica before calcination. Homogeneous adsorption was achieved by adjusting the average permittivity of the dispersing media. The size of SBA-supported Au clusters after calcination was estimated to be 0.8±0.3 nm by HAADF-STEM observation. The 0.8-nm Au clusters confined within SBA-15 were shown to exhibit catalytic activity for oxidation of various alcohols by H₂O₂ under microwave irradiation and were found to be reusable. These results hint at the possibility that highly active and practical gold catalysts are developed even on chemically-inert silica support if the cluster size is reduced below 1 nm.