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Size Effect of Silica-supported Gold Clusters in the Microwave-assisted Oxidation of Benzyl Alcohol with H_2O_2

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Gold clusters with average diameters of 0.8, 1.5, and 1.9 nm were prepared on mesoporous silica (SBA-15) by controlling the calcination time of an $Au_{11}(PPh_3)_7Cl_3$/SBA-15 composite. It was found that the catalytic activity for benzyl alcohol oxidation decreased monotonically with the increase in size.

In the last two decades, gold-based catalysts have attracted growing attention due to their promise of potential application in various oxidation reactions.[1–4] However, a clear guiding principle for the fabrication of active and selective Au catalysts has not yet been established because a number of factors, such as cluster size, nature of support, and cluster/support interaction, are intricately interrelated in practical catalytic processes. One rational approach to Au oxidation catalyst is to utilize the potential ability of small Au clusters to activate O_2.[5] From this viewpoint, it is important to study the size effect on oxidation catalysis of Au clusters stabilized or supported by catalytically inert materials, such as organic polymers and silica. We have shown that small (ca. 1 nm) Au clusters stabilized by poly(vinylpyrrolidone) (PVP) can oxidize various alcohols using O_2 in air as an oxidant at ambient temperature.[6–9] Lambert and coworkers recently showed that Au clusters smaller than 2 nm on catalytically inert silica can oxidize styrene into styrene epoxide with a yield of ca. 5% using O_2.[10] These studies suggest that there is an optimal cluster size for efficient oxidation in the cluster size range below 2 nm. However, it is difficult to control the size of silica-supported Au clusters in this size range using conventional methods such as deposition precipitation and impregnation methods.

In this paper, we propose a simple bottom-up approach to prepare a series of small Au clusters having average diameters smaller than 2 nm by controlling the degree of aggregation of triphenylphosphine-protected Au_{11} clusters (Au_{11}:TPP) within mesoporous silica (SBA-15) during calcination. It was found that Au clusters on SBA-15 can oxidize benzyl alcohol under microwave irradiation using H_2O_2 as an oxidant and that the catalytic activity decreases drastically, even with only a slight increase in diameter from 0.8 to 1.9 nm.

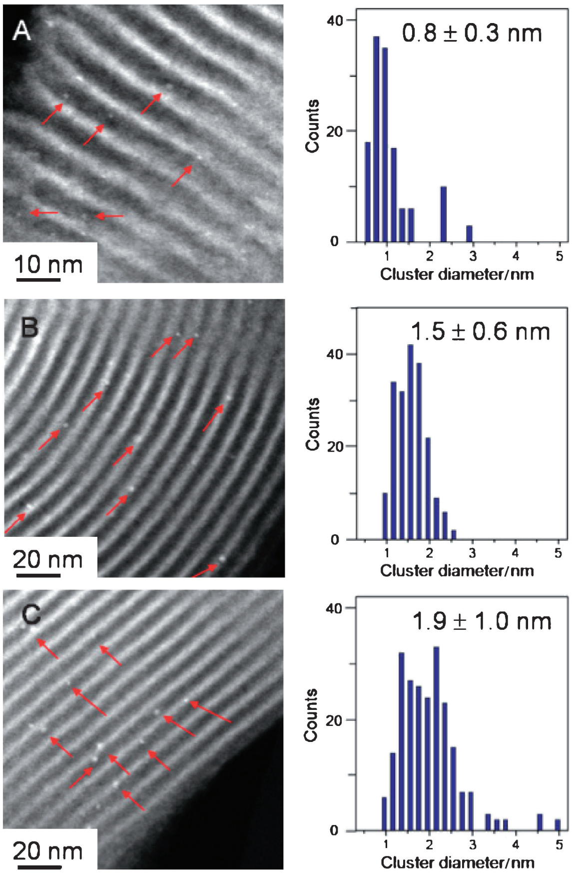


Figure 1. HAADF-STEM images and size distributions of Au clusters in A) $0.16Au_{11}$–SBA(2), B) $0.16Au_{11}$–SBA(8), and C) $0.16Au_{11}$–SBA(16).

As details of the preparation and characterization of SBA-15-supported Au clusters have been reported previously,[11] only a brief description is given here. First, 0.16 wt% of Au_{11}:TPP clusters (diameter; 0.8 nm) were deposited homogeneously over a large surface area of SBA-15 in a mixed solvent of CH_2Cl_2/C_2H_5OH (80/20). Then, the resulting composite Au_{11}:TPP–SBA was calcined at 200 °C under vacuum to remove the organic ligands. Calcination for 2, 8, and 16 h yielded the $0.16Au_{11}$–SBA(2), $0.16Au_{11}$–SBA(8), and $0.16Au_{11}$–SBA(16), respectively. We confirmed by thermogravimetric analysis that ligands are removed after calcination for 2 h.[11] The cluster size was evaluated by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and diffuse reflectance UV–vis spectroscopy. Figure 1 shows the HAADF-STEM image and the size distribution of the Au clusters. The average diameters were determined to be 0.8 ± 0.3, 1.5 ± 0.6, and 1.9 ± 1.0 nm for $0.16Au_{11}$–SBA(2), $0.16Au_{11}$–SBA(8), and $0.16Au_{11}$–SBA(16), respectively, by measuring the diameters of more than 200 particles. Figure 2 shows the diffuse reflectance UV–vis spectra of the three samples. The surface plasmon band of the Au clusters is absent for $0.16Au_{11}$–SBA(2), but it becomes more pronounced along with the increase in

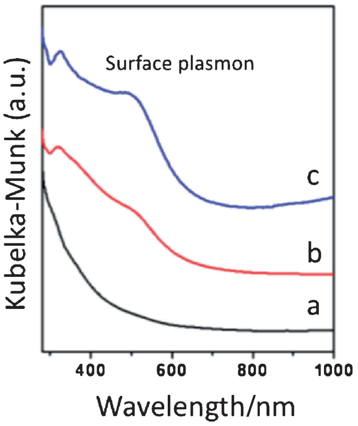


Figure 2. Diffuse reflectance UV–vis spectra of a) $0.16Au_{11}$–SBA(2), b) $0.16Au_{11}$–SBA(8), and c) $0.16Au_{11}$–SBA(16).

calcination time. This trend is consistent with the HAADF-STEM results and indicates that Au_{11} clusters aggregate into larger particles due to the thermally induced migration of Au_{11} clusters in $0.16Au_{11}$–SBA(8) and $0.16Au_{11}$–SBA(16). On the other hand, the Au_{11} clusters remain intact in $0.16Au_{11}$–SBA(2) as a result of the smaller possibility of aggregation during migration in a shorter calcination time.

The above results indicate that only cluster size can be fine adjusted simply by calcinating the common Au_{11}:TPP–SBA composite material for different times, without affecting other factors such as Au loading and preparation method. This approach facilitates the preliminary screening of the cluster size effect. To investigate the size effect on the activity of Au clusters on silica, catalytic performance was tested for oxidation of benzyl alcohol (**1**) as a test reaction.[12–14] In this study, H_2O_2 was used as an oxidant and the reaction was conducted at 60 °C, as the catalytic performance was not high enough under aerobic conditions and at ambient temperature. Microwave heating was essential to promote the reaction probably due to superheating,[15–17] in which the Au clusters are heated directly by microwave irradiation. Gas chromatographic (GC) analysis showed that benzaldehyde (**2**) and benzoic acid (**3**) were obtained as reaction products. We determined the conversion, X, from the recovery of **1** as a function of the reaction time. As shown in Figure 3, there is a linear relationship between $\log[1/(1 - X)]$ and the reaction time, indicating that the reaction is first order with respect to **1**. The rate constant, k, was obtained from the slope and is listed in Table 1. For the sake of comparison, the k values are normalized by the surface areas of the corresponding clusters by assuming spherical shapes with the diameters shown in Figure 1. The k' values listed in Table 1 represent the relative rate constants thus normalized with respect to that of $0.16Au_{11}$–SBA(2) and plotted in Figure 3B. The k' values show that the smallest (0.8 nm) Au clusters exhibit higher catalytic activity than the larger (1.5 and 1.9 nm) clusters. This result demonstrates that Au clusters supported even on inert silica support can catalyze the oxidation reactions when the cluster size is sufficiently small.

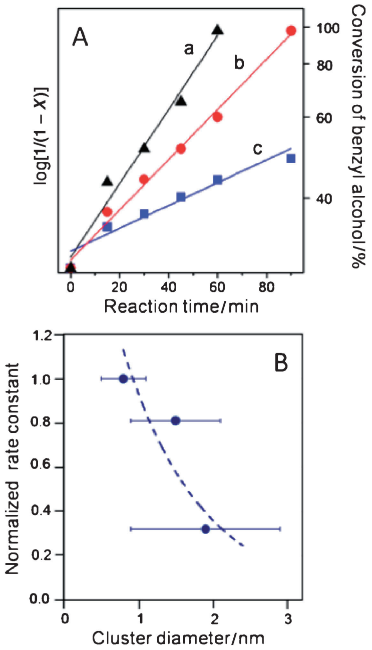
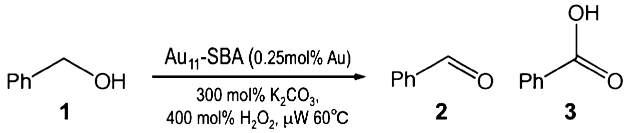


Figure 3. (A) Time course of the conversion and (B) normalized rate constants as a function of size for a) $0.16Au_{11}$–SBA(2), b) $0.16Au_{11}$–SBA(8), and c) $0.16Au_{11}$–SBA(16).

Table 1. Characterization of cluster size and catalytic activity for benzyl alcohol oxidation



Catalyst	d_{av}/nm	k/min^{-1}	k'	Yield/%[a]		
				1	**2**	**3**
$0.16Au_{11}$–SBA(2)	0.8 ± 0.3	1.7×10^{-2}	1	0	10	87
$0.16Au_{11}$–SBA(8)	1.5 ± 0.6	1.1×10^{-2}	0.81	20	11	67
$0.16Au_{11}$–SBA(16)	1.9 ± 1.0	3.8×10^{-3}	0.32	39	14	42

[a]Determined by GC after 60 min.

The size dependence of the activity of Au clusters on SBA-15 (Au:SBA-15) shown in Figure 3B appears to be similar to that of Au:PVP clusters; activity increases rapidly with decrease in the core size.[6–8] However, the origin of the size dependence is probably different between Au:SBA-15 and Au:PVP as discussed below. The small Au:PVP clusters with the size range of 1.0–1.3 nm show the highest catalytic activity in oxidation of various alcohols using O_2 in air as an oxidant at ambient temperature.[6–8] Spectroscopic measurement revealed that these small, catalytically active Au clusters are negatively charged by electron donation from PVP.[9] This result demonstrates that PVP not only stabilizes the cluster but also regulates the electronic structure of the Au clusters. It is known that small Au cluster anions in the gas phase show high activity to O_2 and generates superoxo-like species by electron transfer.[5] Based on the chemical nature of the free Au clusters, we propose that electron transfer from the small, anionic Au cores of Au:PVP to O_2 also generates superoxo- or peroxo-like species that plays a key role in oxidation of the alcohol.[18] This mechanism of O_2 activation is supported by the theoretical study on a model system in which icosahedral Au_{13} is stabilized by four ethylpyrrolidone (EP) molecules.[19] Namely, the size dependence of the catalytic activity of Au:PVP reflects that of O_2 activation. In contrast, Au:SBA-15 could not efficiently oxidize benzyl alcohol in the presence of O_2 although the Au cluster size is comparable to or even smaller than those of Au:PVP. This result suggests that the activity of Au:SBA-15 to O_2 is much lower than Au:PVP probably due to difference in the electronic structures of the Au clusters.[20] As shown in Table 1, however, Au:SBA-15 can oxidize benzyl alcohol using H_2O_2 as an oxidant under microwave heating. We believe that activation of H_2O_2 by the Au clusters[21] is the key for the alcohol oxidation by Au:SBA-15. In the framework of this model, Figure 3B suggests that smaller clusters show a higher activity to H_2O_2 because of the higher population of low-coordinated sites and/or larger structural fluctuation by microwave heating.

In summary, we have successfully prepared Au clusters with average sizes of 0.8, 1.6, and 1.9 nm on mesoporous silica (SBA-15) by controlling the calcination time of phosphine-protected Au_{11} clusters. It was shown that the catalytic activity of these Au clusters for the oxidation of benzyl alcohol increases along with a decrease in size.

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