# Benzyl alcohol oxidation over gold catalyst supported on SBA-16 mesostructured silica

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## Introduction

The development of effective heterogeneous catalysts for the oxidation of alcohols to the corresponding aldehydes or ketones using molecular $O_2$ as an oxidant is highly desired from a green chemistry point of view. Recently, supported gold nanoparticles have attracted considerable attention because of their extraordinarily high activity and selectivity [1]. The outstanding catalytic ability of gold is related to the size and shape of the nanoparticles, the degree of coordinative unsaturation of the gold atoms, and the interactions between gold and the oxide supported [2]. The mesoporous silica, such as MCM-41, SBA-15, and SBA-16, possess the advantages of high area (~1000 $m^2/g$) and uniform pore size (2.0-10.0 nm). The strong confinement of the pore system would provide a uniform distribution of the Au nanoparticles. Herein, the superior catalytic performances of Au/SBA-16 were reported in the solvent-free aerobic oxidation of benzyl alcohol.

## Materials and Methods

SBA-16 synthesized using F127-butanol-$H_2O$ mixture at low HCl concentration reported elsewhere [3]. Au/SBA-16 was prepared by a method using surface-functionalized mesoporous silica to adsorb the gold precursor. In a typical preparation, 1.0 g of SBA-16 sample was suspended in 30 ml of toluene solution containing 1.0 % (3-aminopropyl) triethoxysilane (APS) and refluxed for 5 h. The resulting materials were filtered off, washed with toluene, and then dried at 80 $^oC$ to remove the remaining solvent. Immobilization of gold nanoparticles was conducted by adding the resulting sample to 100 ml $10^{-3}$ M $HAuCl_4$ aqueous solution, followed by stirring at 80 $^oC$ for 5 h. The mixture was filtered, washed with deionized water, and dried at 80 $^oC$.The final gold loading was measured by ICP. The solvent-free oxidation of benzyl alcohol with molecular $O_2$ was carried out using a bath-type reactor operated under atmospheric condition. In a typical reaction run, 200 mg of catalyst was loaded to a glass flask pre-charged with 10 ml (98.5 mmol) benzyl alcohol, the mixture was then heated to the reaction temperature (160 $^oC$) under vigorous stirring. Oxygen flow was bubbled at a flow rate of 20 mL $min^{-1}$ into the mixture to start the reaction once the reaction temperature is reached. After reaction, the solid catalyst was filtered off filtered off and the liquid samples were analyzed by GC after adding an internal standard.

## Results and discussion

From TEM observations, a homogeneous distribution of Au nanoparticles can be discerned in the Au/SBA-16 catalyst. The particles are mostly observed in the size range of 2-9 nm, with a maximum of size distribution at 5-6 nm. Considering the channel structure of SBA-16, it is reasonable to conclude that most of Au nanoparticles are confined inside the cage of SBA-16 structure. On the other hand, relatively large Au nanoparticles with sizes more than ca. 7 nm can be observed in Au/SBA-15 and Au/MCM-41 catalysts. Gold nanoparticles are not well confined in the pore structure of SBA-15 and MCM-41, and many large particles may appear outside of the pores. Moreover, the size distributions of Au particles over SBA-15 and MCM-41 are much broader than that of SBA-16. Thus, it is clear that the unique pore structure of SBA-16 is superior to MCM-41 and SBA-15 for confining Au nanoparticles. Combined the catalytic performances of Au-containing samples, it can be suggested that the Au nanoparticles with a mean size of 5-6 nm confined within the SBA-16 cage are more active for benzyl alcohol oxidation with molecular $O_2$.

**Table 1. Results of benzyl alcohol oxidation over Au-containing mesoporous silica catalysts[a]**

| Catalyst | Pre-treatment | TOF ($h^{-1}$) | Conv. (%) | Benzyldehyde select. (%) |
|---|---|---|---|---|
| SBA-16 | - | - | < 1.0 | - |
| Au/SBA-16-80 | Air, 80 $^oC$ | 803 | 6.3 | > 99 |
| Au/SBA-16-540 | Air, 540 $^oC$ | 484 | 3.8 | > 99 |
| Au/SBA-16-200H | $H_2$, 200 $^oC$ | 1655 | 13.0 | > 99 |
| Au/SBA-16-400H | $H_2$, 400 $^oC$ | 2419 | 19.0 | > 99 |
| Au/SBA-15-400H | $H_2$, 400 $^oC$ | 2048 | 16.1 | > 99 |
| Au/MCM-41-400H | $H_2$, 400 $^oC$ | 827 | 6.5 | > 99 |

[a] Reaction conditions in this work: the amount of Au in each catalyst $2.5\times10^{-3}$ mmol; benzyl alcohol 10 mL (98.5 mmol), 160 $^oC$, $O_2$ flow rate 20 mL $min^{-1}$, reaction time 3 h.

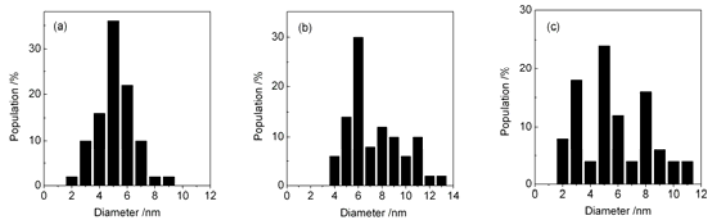


**Figure 1.** Size distribution of Au nanoparticles in mesoporous silica samples: (a) Au/SBA-16, (b) Au/SBA-15, (c) Au/MCM-41.

## Significance

The unique pore structure of SBA-16 can be used to encapsulate Au nanoparticles; the well confined Au nanoparticles with a mean size of 5-6 nm are highly active in solvent-free benzyl alcohol selective oxidation with molecular $O_2$.

## References

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