Oxidation catalysis of Au nano-particles immobilized on thiol-functionalized mesoporous silicate supports

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Abstract: Novel Au nano-particle catalysts immobilized on thiol-functionalized mesoporous titanosilicates were developed. Aerobic alcohol oxidation activities of the catalysts depended on the amounts of thiol-group on the supports. Active sites were estimated as electron-rich Au nano-clusters formed on the support with highly dispersed thiol groups.

Keywords: Au nanoparticles, Aerobic oxidation, Thiol-functionalized silicate.

1. Introduction (11-point boldface)

Catalysis of nano-scale Au particles have been attracted much attention. Especially, oxidation catalyses of Au nano particles are interesting because of their applicability toward various oxidation reactions including dehydrogenative oxidation of alcohol and oxygenation of hydrocarbons. Catalytic performances of Au particles are affected by size of particles.[1] In order to controlling the particle sizes and preventing to aggregate the particles, interactions between Au and soft donors such as thiol and phosphine have been utilized. Especially, organic thiol-modified silicates have been employed as precursors of solid supports of Au nano particle catalysts. During immobilization process, Au(III) precursors are reduced to Au(I) species by thiols and stable Au-thiolate complexes are formed. Following reduction of the Au-thiolate compounds yields Au(0) nano particles. In the Au catalysts prepared by these procedures, loadings of the thiols are relatively high (~ 1 mmol g^{-1}), and these thiol functionalities removed by calcination.[2] The remaining thiols are believed to have negative effects toward the catalysis due to changing the electronic properties of the Au particle and preventing the access of substrates to active sites. However, correlation between the thiol loadings and properties of the supported Au nanoparticles catalysts has not been investigated systematically.

In order to improve the activity toward hydrocarbon oxidation, Au nano-particles catalysts are combined with other active species such as titanium(IV) sites of titanosilicates.[1, 3] The Ti(IV) site can activate H_2O_2 to oxidize hydrocarbons. It is known that aerobic alcohol oxidation is catalyzed by Au nano-particles catalysts. During the course of the alcohol oxidation, H_2O_2 would be formed and the resulting generated H_2O_2 could be utilized as an oxidant *in situ*. Therefore, combination of Au nano-particles catalysts and other species which activate H_2O_2 would become an aerobic oxidation catalysts applicable to various substrates including alkenes and alkanes. In this work, we have designed novel Au nano-particles catalysts immobilized on thiol-functionalized mesoporous silicates.

2. Experimental

The thiol-functionalized mesoporous titanosilicates were synthesized by one-pot condensation of alkoxide precursors in the presence of polymer micelle template. Molar ratio of precursors $Si(OEt)_4$: $Ti(OiPr)_4$: $Si(C_3H_6SH)(OEt)_3$ were controlled as $100 - (x + y) : x : y$ where $x = 0$ to 2.0 and $y = 0$ to 8.0, respectively. Reaction of the supports with EtOH solution of $NaAuCl_4$ yielded ionic Au-immobilized precursors. Following reduction by $NaBH_4$ yielded the catalyst Au/Ti(x)-SBA15-SH(y).

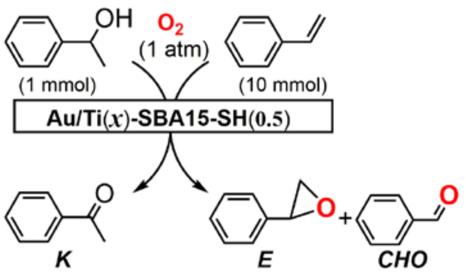
3. Results and discussion

TEM observation of the obtained catalysts Au/Ti(0.5)-SBA15-SH(y) revealed the correlation between the thiol loadings and the size of formed Au particles. On the lower thiol loading support (y = 0.5), the particle sizes of Au were 2 – 5 nm. The particle sizes of Au were decreased with increasing the loading amount of thiol on the supports. On the highest thiol loading support (when *y* = 8.0), Au particles which larger than 1 nm diameters did not exist. On the non-thiol-functionalized support, the formed Au particles were larger than 5 nm. The structures of the Au sites of the catalysts and their precursors (non-reduced ionic Au-anchored supports) were analyzed by EXAFS. On the precursors, Au-S bonds were observed. On the lower thiol functionalized support (*y* = 0.5), the reduction with $NaBH_4$ led to reduce the Au-S bonds whereas increase the Au-Au bonds due to the formation of Au cluster. In contrast, many Au-S bonds remained on the highest thiol-functionalized support (*y* = 8) even after the treatment with $NaBH_4$. Only a few amounts of Au-Au bonds appeared, and therefore, strong Au-S interaction would prevent the forming Au clusters. Electronic states of the resulting Au species were also varied according to the amounts of thiol loadings *y*. On the support with *y* = 0.5, the binding energy of XPS of the formed Au particles was slightly shifted to lower compared to that of the metallic Au formed on the non-thiol-functionalized support (*y* = 0). In contrast, increasing the thiol functionalities yielded cationic Au with higher binding energy.

Catalysis of the Au/Ti(0.5)-SBA15-SH(*y*) were assessed by oxidation of 1-phenylethanol with O_2 at 333 K. In our system, any base additives were not required. The non-thiol-functionalized (*y* = 0) and the highest thiol-loaded catalysts were almost inactive. The catalytic efficiency based on the immobilized amounts of Au atoms (= TON of Au) depended on the amounts of the thiol functionalities as $y = 0.25 \sim 0.5 > 0.75 > 1.0 >> 8.0 = 0$. Removal of the thiol functionalities by calcination influenced the catalytic activities. In the case of the catalyst with *y* = 8.0, the calcination and following washing with H_2O led to appear the alcohol oxidation activity, although that was still lower than the non-calcinated catalyst with *y* = 0.5. Also, the activity of the calcinated catalyst with *y* = 0.5 became lower than that of the non- calcinated one. XPS analysis of the calcinated catalysts on *y* = 8.0 and 0.5 revealed that oxidation states of Au on the both supports were zero. Therefore, the most active species are negatively charged Au sites which were stabilized by the electron donating thiol donors formed on the support with *y* = 0.5.

Then we have investigated the role of titanium sites on Au/Ti(*x*)-SBA15-SH(0.5) by assay of oxidation of styrene in the presence of 1-phenylethanol with O_2 (see Figure 1). In this reaction system, 1-phenylethanol was worked as a sacrificial reducing reagent and a hydrogen source for H_2O_2 generation. The yields of the styrene-oxidized products were correlated with the loading amounts of Ti(IV) (i.e. value of *x*), although major product derived from styrene was benzaldehyde. When the non-Ti(IV)-loaded catalyst was used, oxidation of styrene occurred. But the activity of styrene oxidation was improved on the Ti(IV)-containing catalysts and the most reactive one was *x* = 1.0 in the series of Au/Ti(*x*)-SBA15-SH(0.5).

Table 1. Aerobic oxidation of alkene with alcohol.



x / mol%	Yields / µmol		
	K	***E***	***CHO***
0	51.2	1.2	17.3
0.5	106.1	0.1	30.0
1	58.3	2.5	55.4
2	96.9	1.3	83.2
1*	—	4.8	9.1

*Without 1-phenylethanol

4. Conclusions

Novel Au nano-particle catalysts immobilized on thiol-functionalized mesoporous titanosilicates were developed. Size of formed Au particles and aerobic alcohol oxidation activities of the catalysts depended on the amounts of thiol-group on the supports. The incorporated titanium species contributed to the improvement of the catalytic activity of the aerobic oxidation of styrene with 1-phenylethanol.

References

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