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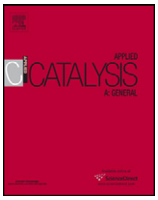

Addition of olefins to acetylacetone catalyzed by cooperation of Brønsted acid site of zeolite and gold cluster

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ABSTRACT

HY zeolite-supported Au clusters (Au^0HY) prepared by deposition–precipitation method, well characterized by XANES, EXAFS, and NH_3- and acetyl acetone-adsorption IR, were tested for addition of acetyl acetone to alkenes. Au^0HY showed higher selectivity to the addition product than HY zeolite-supported $Au(OH)_3$ and Au clusters supported on NH_4^+-exchanged Y zeolite, Al_2O_3, MgO, SiO_2, and TiO_2. Studies on the effect of Au oxidation state, Au cluster size and Brønsted acidity of zeolite on the catalytic showed that co-presence of metallic Au with smaller cluster size and the acidic OH groups of the zeolite was necessary to the selective formation of the addition product. Cooperation mechanism of the Brønsted acid sites of the zeolite and Au clusters is proposed.

1. Introduction

Since the first reports of the spectacular performance of gold clusters in the aerobic oxidation of CO, many publications have been devoted to clarify the factors controlling the activity of gold catalysts mostly for oxidation reactions [1–7]. In many cases, not only nanometer-sized Au clusters but also cooperative supports or additives play an important role in the Au cluster catalysis. Generally, reducible oxide supports, such as TiO_2 and Fe_2O_3, or basic additives are used as a co-catalyst, which significantly increase the catalytic efficiency of Au clusters. On the other hand, there are less investigation on effect of acidic supports on the catalytic property of Au cluster. This is mainly due to difficulty in the deposition of the frequently used precursor, $Au(OH)_3$ in an aqueous alkaline solution, on the acidic surface. However, Okumura et al. [7] showed that $Au(OH)_3$ was successfully prepared in the micropore of HY zeolite, which was then converted, by heating it in He at ca. 225 °C, to the Au cluster in the micropore of the zeolite. From Au–Au coordination numbers of EXAFS analysis, the structure of Au clusters in HY zeolite has been proposed as two-shell structure of a cuboctahedron (Au_{55}) with 1.3 nm in diameter.

"Gold rush" is occurring also in the field of organic synthesis as exemplified by the number of articles on the Au-catalyzed carbon–carbon and carbon–heteroatom bonds formation reactions that recently appeared [2,8–22]. In most of the reports on homogeneous [8–19] and heterogeneous [20–22] gold catalysis, soft Lewis acidity of cationic Au^+/Au^{3+} species has been used to activate unsaturated functionalities such as alkynes, alkenes, and allenes [8–22]. An elegant example is the $AuCl_3$/AgOTf-catalyzed intermolecular addition of activated methylene compounds (such as acetyl acetone) to alkenes developed by Li and Yao [8,9]. High efficiency of this catalytic system is believed to be due to the Lewis acidity of $Au(OTf)_3$, but the exact nature of the catalytically active species is still not known. As pointed our by Hashmi [12], there are a number of examples for Brønsted acids serving as co-catalysts and promoters of Au^+/Au^{3+} catalyst, but there are quite a few example of cooperating effect of Brønsted acids and Au clusters in gold-catalyzed organic reactions.

The alkylation of 1,3-dicarbonyl compounds is one of the most common method for carbon–carbon bonds formation. Traditionally, this reaction requires the use of a stoichiometric amount of base and an organic halide. An alternative reaction via metal-catalyzed addition of 1,3-dicarbonyl compounds to alkenes would provide a more atom-economical approach and has attracted much interest [8,9,23–32]. However, most of the reported method with homogeneous [23–30] and heterogeneous catalysts [32] suffer from low catalytic activity for unactivated olefins, requirement of additives such as HCl or Lewis acids, difficult catalyst synthesis, or difficult catalyst separation. To our knowledge, there is only one successful example of heterogeneous catalysis for

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Table 1
List of supported gold catalysts.

Catalysts	Support	*D* (nm)[a]	*M* (wt%)	Preparation method	T_{cal} (°C)[b]
Au^{3+}NHY	NH_4^+-Y zeolite	–	5.0	Deposition–precipitation	–
Au^{3+}HY	H^+-Y zeolite	–	5.0	Deposition–precipitation	–
Au^0HY	H^+-Y zeolite	1.1	5.0	Deposition–precipitation	300
Au^0NHY	NH_4^+-Y zeolite	1.4	5.0	Deposition–precipitation	300
Au^0HY600	H^+-Y zeolite	2.1	5.0	Deposition–precipitation	600
Au^0Al[c]	γ-Al_2O_3	2.5	1.0	Colloid deposition	300
Au^0Mg[c]	MgO	3.0	1.0	Colloid deposition	300
Au^0Si[c]	SiO_2	1.9	2.5	Colloid deposition	300
Au^0/Ti[d]	TiO_2	3.5	1.5	Deposition–precipitation	–

[a] Average particle size (nm) of metallic Au species estimated from EXAFS except for Au^0/Ti.
[b] Calcination temperature.
[c] From Ref. [34].
[d] Standard catalyst supplied from World Gold Council.

the addition of 1,3-dicarbonyl compounds to unactivated alkenes [31].

As a part of our ongoing studies on d^{10} (Ag, Au) metal-cluster catalyzed green organic reactions [33,34], we report the catalytic addition of acetyl acetone to an unactivated alkene, norbornene, promoted by a collaboration of Au clusters and strong Brønsted acid sites of zeolite. Effect of Au oxidation state, Au cluster size and Brønsted acidity of zeolite on the catalytic properties is investigated to establish the factors affecting catalytic properties.

2. Experimental

A World Gold Council (WGC) test catalyst, TiO_2-supported Au (Au1.5/TiO_2, Au = 1.5 wt%, average Au particle size = 3.6 ± 0.28 nm) was purchased from the WGC. γ-Al_2O_3 with surface area (S_{BET}) of 224 $m^2\,g^{-1}$ was prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) at 600 °C for 3 h. FAU-type zeolites, i.e., HY (Si/Al_2O_3 = 5.5, JRC-ZHY5.5) and MgO (JRC-MGO-1, S_{BET} = 55 $m^2\,g^{-1}$) were supplied from the Catalysis Society of Japan. Preparation method of SiO_2 is reported in our previous paper [34]

According to the method by Okumura et al. [7], HY-supported gold catalyst was prepared with a deposition–precipitation method. To 100 mL of $HAuCl_4$ (Wako Chemical Co.) solution heated in a water bath at 70 °C was added 0.5 g of zeolite. The pH of the solution was adjusted at 6.5 by the addition of ammonia solution (2.8%) under vigorous stirring. The slurry continued to stir for an additional 1 h. After the filtration, the sample was thoroughly washed with deionized water. Finally, it was dried in air at 60 °C for 12 h. The loading of Au (5 wt%) was measured with ICP analysis. After the preparation, most of the H^+ ions in HY should be exchanged to NH_4^+ cation, and $Au(OH)_3$ is deposited in the NH_4^+-exchanged Y zeolite as will be confirmed in the following section. Hence, this sample is named Au^{3+}NHY. The most representative catalyst, named Au^0HY, was prepared by calcination of Au^{3+}NHY at 300 °C in air for 3 h.

According to the method by Tai and Tajiri [4], Au clusters supported on various supports (Al_2O_3, SiO_2, MgO) were prepared by the colloid deposition method [34]. The support was added to the colloidal gold (2.3 ± 0.41 nm) solution under stirring and kept in contact until total adsorption occurred, indicated by decoloration of the solution. The solids were collected by filtration followed by washing the solids with toluene to remove all the soluble species. The resulting composites were dried at room temperature and calcined at 300 °C for 4 h under air for the combustion of thiols [4].

Au L_3-edge X-ray absorption fine structure (XAFS) measurements were performed in transmission mode at the BL01B1 in the SPring-8. The storage ring was operated at 8 GeV. A Si(1 1 1) single crystal was used to obtain a monochromatic X-ray beam. Samples were sealed in cells made of polyethylene under ambient atmosphere and XAFS spectra were taken at room temperature. The analyses of the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structures (XANES) were performed using the REX version 2.5 program (RIGAKU). The Fourier transformation of the k^3-weighted EXAFS oscillation from *k* space to *r* space was performed over the range of 30–140 nm^{-1} to obtain a radial distribution function. The inversely Fourier filtered (in a range 0.10–0.35 nm) data were analyzed with a usual curve fitting method in *k*-space in a range of 39–140 nm^{-1}. For the curve-fitting analysis, the empirical phase shift and amplitude functions for Au–Au and Au–O shells were extracted from the data for Au foil and Au_2O_3, respectively.

In situ FTIR spectra were recorded on a JASCO FT/IR-620 equipped with a quartz IR cell connected to a conventional flow reaction system. The sample was pressed into a 10 mg of self-supporting wafer and mounted into the quartz IR cell with CaF_2 windows. Spectra were measured accumulating 5–20 scans at a resolution of 4 cm^{-1}. A reference spectrum of the catalyst wafer (typically 20 mg) in He taken at measurement temperature was subtracted from each spectrum. Prior to each experiment the catalyst disk was heated in He flow (100 $cm^3\,min^{-1}$) at 150 °C for 0.5 h, followed by cooling to 100 °C under He flow. For the introduction of acetyl acetone to the IR disc, the liquid compound was injected under the He flow preheated at 100 °C which was fed to the in situ IR cell, followed by purging with He for 600 s at 100 °C.

Commercially available organic compounds were used without further purification. Typical procedures for the addition of acetyl acetone to norbornene is as follows. Au^0HY powder (0.1 g, 2.5 mol% Au with respect to norbornene) was added to the mixture of acetyl acetone (1.1 mmol) and norbornene (1.0 mmol) in CH_3NO_2 (3.0 g) in a reaction vessel equipped with a condenser under N_2. The resulting mixture was vigorously stirred at 100 °C. Conversion and yield of the addition products were determined based on norbornene using GC (Shimadzu GC-14B) equipped with DB-1 capillary column (Shimadzu) using *n*-dodecane as an internal standard. The products were identified by gas chromatography/mass spectrometry (Shimazu GCMS-QP5000) equipped with the same column and in the same conditions as GC and also by comparison with commercially pure products.

3. Results and discussion

3.1. Characterization of catalysts

As summarized in Table 1, a series of Y zeolite-supported Au catalysts were prepared. Au L_3-edge XANES and EXAFS experiments were performed to identify the structure of Au species at each preparation step (Fig. 1). The Au–O and Au–Au coordination numbers (N_{Au-O}, N_{Au-Au}) and interatomic distances (*R*) derived from the curve-fitting analysis of EXAFS are listed in Table 2. Since the precursor of the catalyst was prepared by deposition–precipitation at pH 6.5 using ammonia solution, $HAuCl_4$, and HY zeolite, fol-