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# Chloride-free and water-soluble Au complex for preparation of supported small nanoparticles by impregnation method



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#### ABSTRACT

A novel simple and easy impregnation method for preparation of small gold (Au) nanoparticle (NP) catalysts (<3 nm) deposited on various supports including silica, which is difficult to be applied for conventional methods, has been developed. Chloride-free and water-soluble precursor, Au complexes coordinated with  $\beta$ -alanine, were successful for the preparing Au NPs, which exhibited an average diameter less than 3 nm. Thermal behavior of the Au complex was investigated by TG-DTA and in situ XAFS. XAFS analyses and DFT calculations revealed a molecular structure of the Au complex to be square-planar coordination structure and mononuclear complex of Au<sup>3+</sup>. Lower decomposition and reduction temperature of the chloride-free Au complex prevented Au atoms from aggregating and from following growth of Au particles. The prepared Au/SiO<sub>2</sub> showed high selectivity for hydrogenation of 1-nitro-4vinylbenzene into 1-ethyl-4-nitorobenzene and good performance for removal of unpalatable aroma by means of adsorption of polysulfide molecules.

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## 1. Introduction

Gold (Au) nanoparticles (NPs) on supports such as metal oxides, active carbons, and polymers, have received considerable attentions in recent years as catalysts [1,2], adsorbents [3], and optical and electronic devices [4]. Generally, the size effect is critical to the functions of Au NPs, i.e., smaller (<5 nm) particles are indispensable for high catalytic activity [5–11]. Therefore, special techniques have been established for preparing supported Au NPs, including deposition-precipitation (DP) and co-precipitation (CP) methods. These techniques are applicable to various metal oxides except for acidic materials such as SiO<sub>2</sub>, because of electrostatic repulsion between the  $Au(OH)_{4}^{-}$  precursor and the support surface, which is negatively charged. In contrast, the most conventional impregnation (IP) method using the standard precursor chloroauric acid (HAuCl<sub>4</sub>·4H<sub>2</sub>O) is unsuccessful for the preparing small Au NPs, because it results in the growth of particles via the aggregation of Au atoms [12]. Density functional theory (DFT) calculation studies have revealed that the adsorption of  $Cl^-$  ion onto an oxygen defect site of  $TiO_2$  enhances the aggregation of Au atoms [13,14].

For practical use in the industry, the IP methods have advantages that are suitable for large scale preparing of catalysts. Postimpregnation treatments to obtain supported small Au NPs have been reported. High-temperature hydrogen reduction is effective for Au/TiO<sub>2</sub> and Au/C prepared by an IP method with AuCl<sub>3</sub> [15]. To remove Cl<sup>-</sup> ions, washing with ammonia has been used as the post-treatment of IP methods [16-20]. Delannoy et al. have reported that small Au NPs (3-4 nm) on any type of oxides including SiO<sub>2</sub> were obtained by a modified incipient wetness IP method with HAuCl<sub>4</sub>·4H<sub>2</sub>O [20]. In the procedure, the IP using HAuCl<sub>4</sub> aqueous solution was followed by a post-treatment with an aqueous ammonia solution. The ammonia washing removes chloride ligands from Au<sup>3+</sup> precursor and forms an amino-hydroxo-aquo cationic gold complex, which interacts with supports. When ammonia contacts Au in solution, the formation of explosive Auammonia complexes are provoked [21,22]. For the sake of safety, the remains of no Au in the solution is a prerequisite.

Another means to obtain supported small Au NPs has been reported that using of chloride-free precursors such as  $Au(OAc)_3$  for the preparation [23,24]. Recently, Sakurai et al. have reported



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a detailed study of the IP method of preparing Au NPs with Au  $(OAc)_3$  as a precursor [24]. Au NPs supported on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, and SiO<sub>2</sub> have successfully been prepared with diameters between 3 and 6 nm. However, because of the poor solubility of Au(OAc)<sub>3</sub>, a tedious alkaline solution treatment is required to prepare the Au solution and is followed by evaporation of the dilute aqueous solution for IP. In addition, the synthesis of Au(OAc)<sub>3</sub> requires two steps via unstable Au(OH)<sub>3</sub>.

One of the simplest approaches to realize direct IP method for the preparing small Au NPs on various supports including SiO<sub>2</sub> is the use of chloride–free and water–soluble Au precursors. Rai et al. have reported that the reaction between chloroauric acid and  $\iota$ -asparagine results in the formation of 1:1 complex [25]. On the basis of the reaction, Kazachenko et al. have synthesized the water–soluble Au complexes coordinated with glycine, histidine, and tryptophan [26]. However the structures of the Au complexes have scarcely been characterized. Exploiting the high solubility of these complexes in water, we developed an incipient wetness method involving only a very small amount of water. In the field of preparing colloidal Au NPs, amino acids and amines have been used as reducing and capping agents [27,28]. In our experiments, amino acids act as ligands of Au complexes, which are completely different from the roles of them in the synthesis of colloidal NPs.

In this paper, we describe a novel IP method followed by calcination in air, which is fit for practical use, using readily accessible Au complexes coordinated with  $\beta$ -alanine (Au–( $\beta$ -ala)) as precursors. Our method enables anchoring of the Au NPs onto acidic supports such as SiO<sub>2</sub>, which are difficult to coat via DP and CP methods. We determine the coordination structure and thermal behavior of the Au–( $\beta$ -ala) and oxidation state of Au in the complex by analyses of Au  $L_{III}$ -edge X-ray absorption fine structure (XAFS) spectra, thermogravimetry-differential thermal analysis (TG-DTA), and DFT calculations. Catalytic performance of the prepared Au/SiO<sub>2</sub> was investigated by hydrogenation of 1-nitro-4-vinylbenzene, which has been a reaction studied using Au NPs on various supports. In addition, adsorption of unpalatable aroma in drinks, which is one of the possible applications of the Au/SiO<sub>2</sub> other than catalysts, was demonstrated.

#### 2. Experimental

#### 2.1. Synthesis of Au complexes

Au complexes coordinated with  $\beta$ -alanine (Au–( $\beta$ -ala)) were prepared using examples from synthetic procedures reported by Kazachenko et al. [26]. Ethanol (3 mL) was added to 2 mL of a NaOH aqueous solution (1.25 M) in which  $\beta$ -alanine (H<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>-COOH) (Tokyo Chemical Industry Co., Ltd.) (1.82 mmol) was dissolved. A second solution was prepared by adding 1 mL of a HAuCl<sub>4</sub>·4H<sub>2</sub>O (Tanaka Kikinzoku Kogyo K.K.) (0.227 M) aqueous solution to 4 mL of ethanol. The first solution containing  $\beta$ -alanine and NaOH was then added to the second solution. The mixed solution was left at –18 °C for 12 h. The precipitates were collected by centrifugation and washed with water/ethanol (3/7 v/v%) solution, in which  $\beta$ -alanine was soluble, but Au–( $\beta$ -ala) was insoluble. The solid was dried under vacuum to obtain Au–( $\beta$ -ala) powder.

#### 2.2. Preparation of supported Au NPs

Supported Au NPs were prepared by the incipient wetness IP method. In addition to the Au–( $\beta$ -ala), HAuCl<sub>4</sub>·4H<sub>2</sub>O was used as a precursor. The precursor was dissolved in 1.20 mL of water, and the solution was added to 0.99 g of SiO<sub>2</sub> (CARiACT Q-15, Fuji Silysia Chemical Ltd.). The volume of Au solutions were decided

by total pore volume of the supports measured by nitrogen adsorption. For impregnation on 0.99 g of TiO<sub>2</sub>, MCM-41, and Ketchen black, the volume of Au solutions were 0.43 mL, 0.93 mL, and 1.51 mL, respectively. The Au loading amounts were 1 wt% (10 mg of Au). After impregnation, the solid was calcined in air. The heating rate was kept at 5 °C/min until 300 °C and then the temperature was kept for 0.5 h.

## 2.3. Sample characterization

High-angle annular dark field scanning transmission electron microscope (HAADF-STEM) images were acquired with a IEM-ARM200F microscope (JEOL) operated at 200 kV. Powder X-ray diffraction (XRD) data were collected on a MiniFlex600 (Rigaku Co.) diffractometer using Cu K $\alpha$  radiation. Au  $L_{m}$ -edge XAFS spectra were collected at the BL14B2 beamline of SPring-8 (Hyogo, Japan). Synchrotron radiation from the storage ring was monochromated by a Si<sub>311</sub> double-crystal. The experiments were conducted in the transmission mode at room temperature. The XAFS spectra were analyzed by using the program REX2000 (Rigaku Co.). During the calcination process of preparing the supported Au NPs, in situ XAFS spectra were also collected using the same optical system with the XAFS measurements. The silica supported Au precursors were placed in a quartz tube reactor and were heated by using the same temperature program as that used in the preparation method. The collection of a XAFS spectrum required approximately 3.5 min. TG-DTA data were collected on a STA7300 (Hitachi High-Tech) thermal analyzer. The samples were heated by using the same temperature program as that used in the preparation method.

#### 2.4. DFT calculations

Using DFT calculations, we optimized the geometry of the Au complex with  $\beta$ -alanine. The PBEO functional was used for these calculations. The SDD basis set was used for the Au atom, and the 6-31+G(d,p) basis set was for N, C, O, and H atoms. In these calculations, we assumed that the net charge of this complex was neutral.

# 2.5. Hydrogenation of 1-nitro-4-vinylbenzene and adsorption of dimethyl trisulfide (DMTS) experiments

The Au NPs prepared by our method, 1-nitro-4-vinylbenzene (74.6 mg, 0.5 mmol), triethylene glycol dimethyl ether (30  $\mu$ L) as an internal standard, and ethyl acetate (2.0 mL) as solvent were introduced into a glass inner tube of a stainless steel autoclave. The autoclave was sealed, following the filling of hydrogen at 2.0 MPa. Catalytic reactions were then performed at 100 °C for 24 h. After the reactions, the mixture was filtered and analyzed by a gas chromatography (GC) using an Agilent GC 6850 series II equipped with an Agilent J&W HP-1 capillary column (0.32 mm i. d., 30 m). For the adsorption experiments, the silica supported Au NPs (Au/SiO<sub>2</sub>) was added to 4 mL of ethanol solution of DMTS (Tokyo Chemical Industry Co., Ltd.) (4.7 mg/L) and the mixture was then kept at room temperature. The concentration of DMTS was analyzed by GC. The adsorption amounts of DMTS were estimated as differences from the initial concentration of DMTS.

#### 3. Results and discussion

#### 3.1. Sizes of Au NPs on various supports

The Au loading per obtained catalyst (Au/SiO<sub>2</sub>) was analyzed by microwave plasma–atomic emission spectrometry to be 0.94 wt%. Fig. 1a shows a portion of a HAADF–STEM image of the Au/SiO<sub>2</sub>



**Fig. 1.** HAADF–STEM image of the Au/SiO<sub>2</sub> prepared by using the Au–( $\beta$ -ala) (a). The inset shows size distribution of Au particles. XRD patterns for the Au/SiO<sub>2</sub> prepared by using the Au–( $\beta$ -ala) and HAuCl<sub>4</sub>·4H<sub>2</sub>O (b). Schematic view of the preparation of Au/SiO<sub>2</sub> using the Au–( $\beta$ -ala) and HAuCl<sub>4</sub>·4H<sub>2</sub>O (c).

prepared by using the Au–( $\beta$ -ala). The size distribution of the observed spherical particles is displayed in a histogram in the inset of Fig. 1a; their average diameter was  $2.8 \pm 0.8$  nm. Moreover, HAADF–STEM images of the Au NPs dispersed on various supports, including TiO<sub>2</sub>, MCM-41, and Ketchen black, using the Au–( $\beta$ -ala) as a precursor are displayed in the supporting information, Fig. S1, which shows spherical NPs with the average diameters of 2.8 ± 0.7 nm, 2.5 ± 0.6 nm, and 2.9 ± 1.0 nm, respectively.

The Au–( $\beta$ -ala) is thus applicable to the preparation of small Au NPs on various supports. The Au/SiO<sub>2</sub> were also characterized by powder XRD. The XRD patterns (Fig. 1b) showed some sharp small peaks and broad peaks. The sharp small peaks observed at 38.2°, 44.4°, 64.4°, and 77.6° in the pattern of the Au/SiO<sub>2</sub> prepared by using  $HAuCl_4 \cdot 4H_2O$  were assigned to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes of Au metal, respectively. The small broad 111 peak of Au metal was also observed at the same angle in the diffraction pattern for Au/SiO<sub>2</sub> prepared by using Au–( $\beta$ -ala). The crystallite size was estimated to be 2.6 nm for the Au–( $\beta$ -ala) sample according to the Scherrer equation and the FWHM value of the 111 peak. The average diameter of the spherical particles observed in the HAADF-STEM images was approximately the same as the crystallite size estimated from the XRD pattern, thus indicating that the Au NPs were supported on the SiO<sub>2</sub> as small single Au metal crystals. The crystallite size of Au NPs on the chloroauric acid sample was also estimated to be 30.8 nm. Compared with the preparation using the conventional precursor, HAuCl<sub>4</sub>·4H<sub>2</sub>O, the Au–( $\beta$ -ala) yielded smaller Au NPs that were highly dispersed on the SiO<sub>2</sub> supports. The relationships between the obtained particle sizes and the procedures for preparation are summarized in Fig. 1c. The broad peaks observed at approximately 20-30° were due to amorphous SiO<sub>2</sub>.

#### 3.2. Thermal analyses of the Au–( $\beta$ -ala)

In general, heating enhances aggregation of metal atoms during the reduction and calcination process. Therefore thermal behavior, e.g., the decomposition temperature and reduction temperature, of the precursors is important for preparing small metal NPs. The thermal decomposition profile of the Au–( $\beta$ -ala) was investigated using TG-DTA. Three mass losses were observed at approximately 65 °C, 135 °C, and 300 °C, as shown in Fig. 2. The slow mass loss from room temperature to 135 °C was identified as dehydration of contained moisture, i.e., a drying process, on the basis of the very small endothermic DTA peaks. Other mass losses observed at approximately 135 °C and 300 °C with exothermic DTA peaks were indicative of ligand dissociation of the Au–( $\beta$ -ala).

To determine the reduction temperature of the Au–( $\beta$ -ala) and chloroauric acid samples, in situ Au  $L_{III}$ -edge XAFS spectra collected during the calcination process were analyzed. Before calcination, a characteristic peak, the 'white line', which was attributed to the excitation from the  $2p_{3/2}$  to the 5 d or 6 s states, was observed at 11,922 eV in the spectra of Au–( $\beta$ -ala) and chloroauric acid, as shown in Fig.3a and b, respectively [29,30].

Analyses of the white line intensity can be used to identify the oxidation state [30]. The intensity of the white line for Au–( $\beta$ -ala) was approximately the same as that for Au<sub>2</sub>O<sub>3</sub>, thus indicating that



Fig. 2. TG-DTA curves of the Au-(β-ala).



**Fig. 3.** Normalized X-ray absorption near-edge structure (XANES) spectra for silica supported  $Au-(\beta-ala)(a)$ ,  $HAuCl_4(b)$ , and the fraction of  $Au^0$ , x, determined by the pattern fitting analyses for silica supported  $Au-(\beta-ala)$  and  $HAuCl_4$  during the calcination process as a function of temperature in flowing air (c). The inset shows the XANES spectrum observed at 190 °C (open circle) and corresponding curve fitted (solid line) from initial state (long dashed short dashed line) and final state (dashed line).

the Au oxidation state of the Au-( $\beta$ -ala) was +3. As a result of the calcination, the white line intensity became weak and finally disappeared. The samples obtained after the calcination were identified as Au<sup>0</sup> by fingerprint analyses of their spectra. In addition, two isosbestic points were observed at 11,928 eV and 11,954 eV for Au–( $\beta$ -ala) and at 11,925 eV and 11,953 eV for chloroauric acid. These results indicate that the Au–( $\beta$ -ala) and chloroauric acid were reduced via a one-step reaction and that the oxidation state of Au was changed from +3 to 0 without forming intermediates. Hence, the XANES spectra were deconvoluted into the initialstate and the final-state spectra. The inset in Fig. 3a shows the XANES spectrum obtained at 190 °C and the corresponding curves fitted from the Au–( $\beta$ -ala) complex (initial-sate) and the Au<sup>0</sup> spectra (final-state) as a representative fitting result. The pattern fitting converged, yielding an *R*-factor of 0.072%. This fitting result indicates that the sample contained 22% Au<sup>3+</sup> and 78% Au<sup>0</sup>. The fractions of  $Au^0$ , x, at each temperature were determined from the pattern fitting analyses and the following relationship: [100% = x]% Au<sup>0</sup> + (100 – x)% Au<sup>3+</sup>]. Fig. 3c shows a plot of the x values obtained at each temperature, which indicates that the reduction temperature (x = 50%) of the Au–( $\beta$ -ala) and chloroauric acid were 170 °C and 200 °C, respectively. Compared with chloroauric acid, the Au–( $\beta$ -ala) was reduced at a lower temperature.

The reduction temperature for the Au–( $\beta$ -ala) determined by the XANES analyses is in accordance with the temperature of main mass loss observed via the TG-DTA analysis, as shown in Fig. 2. At this temperature, the Au–( $\beta$ -ala) decomposed via reduction from the Au<sup>3+</sup> complex to Au<sup>0</sup> metal. The third mass loss at 300 °C shown in the TG-DTA curves was attributed to a later decomposition of ligands that weakly interacted with the Au<sup>0</sup> metal.

Given that the Au concentration of the prepared complex powder was determined to be 39 wt% by microwave plasma atomic emission spectrometry (MP-AES), the molar ratio of  $\beta$ -ala ligand/ Au was estimated to be 1.2. The details of this estimation are described in Fig. S2 in the supporting information.

#### 3.3. Structure of the Au–( $\beta$ -ala)

We expected the Au–( $\beta$ -ala) to not contain Cl<sup>-</sup> ions because the aggregation of Au atoms was inhibited. In Raman spectra of the Au/SiO<sub>2</sub> prepared by using the Au–( $\beta$ -ala) (Fig. S3a), no peak is observed before and after calcination. On the other hand, Raman spectrum of before calcined Au/SiO<sub>2</sub> from HAuCl<sub>4</sub> exhibits two peaks at 322.3 cm<sup>-1</sup> and 345.0 cm<sup>-1</sup>, which are characteristic of Au–Cl vibrations [20]. The peaks disappeared after calcination. These results indicate that there is no Au–Cl coordination in the Au–( $\beta$ -ala). The structure of the Au–( $\beta$ -ala) was determined by analyses of Au *L*<sub>III</sub>-edge XAFS spectra as shown in Fig. 4.

The frequency and the relative amplitude of the  $k^3$ -weighted oscillation for the Au–( $\beta$ -ala) were similar to those for Au<sub>2</sub>O<sub>3</sub>, as is the dominant peak intensity of the Fourier transform function, which appeared in the range from 0.13 to 0.20 nm. In contrast, they differed from those for the AuCl<sub>3</sub>, as shown in Fig. 4a and b. A dominant peak in the Fourier transform function for the AuCl<sub>3</sub>, which was attributed to the scattering of photoelectrons ejected from the Cl atoms located at the nearest distances from the absorber



**Fig. 4.**  $k^3$ -weighted EXAFS oscillation (a) and Fourier transform (b) (without phase correction) of the Au-( $\beta$ -ala) pellet (black solid line), Au<sub>2</sub>O<sub>3</sub> (red dashed line), and AuCl<sub>3</sub> (blue long dashed short dashed line) (30.5  $\leq \Delta k \leq$  133.5 nm was used).

Table 1	
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Summary of curve-fitting analysis for the Au–( $\beta$ -ala).

N <sup>a</sup>	r <sup>b</sup> /nm	d <i>E</i> <sup>c</sup> /eV	$d\sigma^d/nm$
$3.7 \pm 0.7$	$0.204 \pm 0.001$	$-0.13 \pm 3.0$	$-0.001 \pm 0.003$

<sup>a</sup> Coordination number.

<sup>b</sup> Coordination distance.

<sup>c</sup> Energy difference in the absorption threshold between the reference compound,  $Au_2O_3$ , and  $Au-(\beta-ala)$ .

<sup>d</sup> Difference of Debye-Waller factor between  $Au_2O_3$  and  $Au-(\beta-ala)$ .

Au atom, was observed in the range from 0.15 to 0.23 nm. These results indicate that the coordination of the Au-( $\beta$ -ala) can be assigned to Au-O but not to Au-Cl. Here, we successfully prepared a chloride-free precursor. Table 1 shows structure parameters for the Au–( $\beta$ -ala) obtained by curve-fitting analyses of its Fourier filtered function. The peak discernible at 0.13–0.20 nm in the Fourier transform function shown in the Fig. 4b was attributed to the scattering of photoelectrons ejected from the O atoms located at the nearest distances from the absorber Au atom. This scattering occurred because the frequency and the relative amplitude of the  $k^3$ -weighted oscillation for the Au–( $\beta$ -ala) were similar to those for the Au<sub>2</sub>O<sub>3</sub> previously described. The peak was subsequently back-transformed into k space and fitted by considering the contribution from the Au-O shells to determine the structural parameters for the Au–( $\beta$ -ala). The backscattering amplitude and phase shift for the Au–O bond were obtained experimentally from the

# Table 2

The optimized geometries of the Au–( $\beta$ -ala).

Distance/nm		Angle and dihedral angle	e/°
R(10Au-9O) R(10Au-11O) R(10Au-13O) R(10Au-13N)	0.201999 0.196876 0.195472 0.208235	A(110-10Au-130) A(130-10Au-90) A(110-10Au-1N) A(90-10Au-1N)	90.472 89.059 84.341 96.131
		D(110-150-90-IN)	1.080



**Fig. 5.** Top-view (a) and side-view (b) of the optimized geometry of the Au-( $\beta$ -ala).



**Fig. 6.** Molecular structure of the Au–( $\beta$ -ala).

XAFS spectrum of the Au<sub>2</sub>O<sub>3</sub> (coordination number, N = 4 and coordination distance, r = 0.201 nm) [31]. Their Debye-Waller factor was assumed to be 0.006 nm. The curve-fittings converged to give R-factor of 0.26%. The coordination number of 3.7 and the coordination distance of 0.204 nm for the Au-( $\beta$ -ala) were consistent with those for Au<sub>2</sub>O<sub>3</sub> within the estimated range of errors, respectively. In addition, the differences of the threshold energy and the Debye-Waller factor were sufficiently small. The local structure around the Au atoms in Au-( $\beta$ -ala) was very similar to that around the Au atoms in Au<sub>2</sub>O<sub>3</sub>. Because the molar ratio of  $\beta$ -ala ligand/Au was 1.2, and  $\beta$ -ala can be a bidentate ligand, the amino group and

#### Table 3

Hydrogenation of 1-nitro-4-vinylbenzene by the Au/SiO2 and Au/TiO2.



Catalyst		Conv./%	Yield/%		
	Precursor		A	В	С
Au/SiO <sub>2</sub>	Au-(β-ala) HAuCl₄	66 0	59 0	2 0	2 0
Au/TiO <sub>2</sub>	Au-(β-ala)	100	0	70	2

carboxyl group of a  $\beta$ -ala can be assumed to be bound to Au<sup>3+</sup>. Because the scattering cross-section of an N atom is similar to that of an O atom, the structure of the Au–( $\beta$ -ala) given by the fitting results shows good agreement with the structure of Au<sub>2</sub>O<sub>3</sub>.

Using DFT calculations, the geometry of the Au–( $\beta$ -ala) were optimized. The obtained structure is shown in Table 2 and Fig. 5.

These results indicate that the geometry around the Au ions in this complex is square planar and the deformation from the proper square planar one is small. Therefore, this result indicates that the valence of Au ions in this complex is trivalent because the square-planar structure is typical of the Au<sup>3+</sup> complex.

We propose a molecular structure of the Au-( $\beta$ -ala), as shown in Fig. 6. The mononuclear complex of Au<sup>3+</sup> has a square-planar coordination structure. The amino group and carboxyl group of a  $\beta$ -ala molecule, which is bidentate, are bound to Au<sup>3+</sup>. The other two coordination of Au<sup>3+</sup> are bound to hydroxyl groups, respectively.

#### 3.4. Application for hydrogenation reaction and for adsorbents

The catalytic performances, selectivity, of the Au/SiO<sub>2</sub> and Au/ TiO<sub>2</sub> for reduction of 1-nitro-4-vinvlbenzene were investigated. As shown in table 3, the Au/SiO<sub>2</sub> prepared by the Au-( $\beta$ -ala) exhibits high selectivity for hydrogenation of vinyl group of 1-nitro-4-vinylbenzene into 1-ethyl-4-nitrobenzene (A). On the other hand, nitro group of 1-nitro-4-vinylbenzene was hydrogenated into 4-vinylaniline (**B**) by the Au/TiO<sub>2</sub>. Probably, polymerization of 4-vinylaniline can be occurred as a side reaction. The over-reduced product, 4-ethylaniline (C) was formed at negligible levels. Boronat et al. have reported that favorable adsorption of nitro group on TiO<sub>2</sub> afforded nitro-selective hydrogenation of 1nitro-3-vinylbenzene into 3-vinylaniline when Au/TiO<sub>2</sub> was used [32]. Meanwhile, poor interactions between the substrate and SiO<sub>2</sub> resulted in a low regioselectivity and yielded over-reduced 3-ethylaniline as major product using Au/SiO<sub>2</sub>. The result that Au/SiO<sub>2</sub> selectively hydrogenates vinyl group is consistent with the selectivity of Au NPs on silica previously reported. Turnover frequency of Au/SiO<sub>2</sub> for the hydrogenation of styrene has been larger than that of nitrobenzene [32]. Au NPs on silica have been highly selective for the hydrogenation of C=C bond in cinnamaldehyde to form hydrocinnamaldehyde [33]. We expect the nitro group on the para-position withdraws electrons more efficiently than meta-position which brought the higher reactivity of vinyl group of 1-nitro-4-vinylbenzene compared to 1-nitro-3vinylbenzene. In addition, size-effect of Au NPs might be obtained because the Au/SiO<sub>2</sub> prepared by HAuCl<sub>4</sub>, having an average diameter about 30 nm, showed no catalytic activity.

One of the possible practical application of the  $Au/SiO_2$  obtained by our method is described. We subsequently applied the  $Au/SiO_2$ to an adsorption test using DMTS in ethanol, which is responsible



Fig. 7. Time dependence of the adsorption amounts of DMTS on Au/SiO<sub>2</sub>.

for the unpalatable aroma of drinks such as Japanese sake [34,35], beer [36], whiskey [37], and wine [38]. Silica is allowed to use for Japanese Sake brewing by the National Tax Administration Agency of Japan. Fig. 7 shows time dependence of the adsorption amount of DMTS on the Au/SiO<sub>2</sub> prepared by using the Au–( $\beta$ -ala), on the Au/SiO<sub>2</sub> prepared by using HAuCl<sub>4</sub>·4H<sub>2</sub>O, and on commercial Au/ SiO<sub>2</sub> (Haruta Gold, Inc.) prepared by the deposition-reduction method using Au(en)<sub>2</sub>Cl<sub>3</sub> as a precursor. The rate and quantity of adsorbed DMTS on the Au/SiO<sub>2</sub> prepared by using the Au–( $\beta$ -ala) were markedly higher than those on the Au/SiO<sub>2</sub> prepared by using HAuCl<sub>4</sub>·4H<sub>2</sub>O.

Compared with the adsorbed amount on the commercial Au/ SiO<sub>2</sub>, whose Au NP size was 7 nm, smaller Au NPs on SiO<sub>2</sub> adsorbed a larger amount of DMTS, thus indicating that the DMTS molecules adsorbed onto the surfaces of the Au NPs. The Au/SiO<sub>2</sub> prepared by using the Au–( $\beta$ -ala) showed high performance for removal of unpalatable aroma, although bulk Au particles, such as Au/SiO<sub>2</sub> prepared by using HAuCl<sub>4</sub>·4H<sub>2</sub>O, scarcely adsorbed any DMTS molecules. For further detailed discussion of these phenomena, other kinds of studies, such as investigation for adsorption mechanisms and spectroscopic measurements for adsorbates, are necessary, which is a future research topic.

#### 4. Conclusion

The Au NPs were highly dispersed on various supports, especially on silica, through use of a novel incipient wetness IP method. The average diameter of the Au NPs was determined to be less than 3 nm on the basis of TEM observations. The preparation of smaller Au NPs on silica supports was achieved by using Au–( $\beta$ -ala) complexes, whose structure is similar to that of Au<sub>2</sub>O<sub>3</sub> (Fig. 6), as chloride-free precursors. The decomposition and

reduction temperatures of the Au–( $\beta$ -ala), which were investigated by in situ XAFS and TG-DTA, were lower than those of HAuCl<sub>4</sub>·4H<sub>2</sub>-O. These behaviors prevented Au atoms from aggregating. We expect that Au complexes coordinated with another kind of amino acid are also precursors for preparing supported small Au NPs. The Au/SiO<sub>2</sub> prepared by our method showed high activity and selectivity for hydrogenation of 1-nitro-4-vinylbenzene into 1-ethyl-4nitrobenzene and good performance for removal of unpalatable aroma.

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#### **Appendix A. Supplementary material**

HAADF–STEM images of the Au NPs supported on TiO<sub>2</sub>, MCM-41, and Kethen black, details of estimation of the molar ratio of  $\beta$ -ala ligands/Au in Au–( $\beta$ -ala) complex on the basis of the TG-DTA data, and Raman spectra for the Au/SiO<sub>2</sub> prepared by using the Au–( $\beta$ -ala) and HAuCl<sub>4</sub> can be found in the online version. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2017.07.002.

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