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Preparation and structure of a single Au atom on the TiO₂(110) surface: Control of the Au-metal oxide surface interaction

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Three-dimensional Au structures on bare and organic-compound-modified TiO₂(110) surfaces were interrogated by Au L₃-edge polarization dependent total reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) spectroscopy. On the bare TiO₂(110) surface, icosahedral Au₅₅ nanoclusters were the main product found. When the surfaces were modified with ortho or meso mercapto benzoic acid (*o*-MBA or *m*-MBA), Au was atomically dispersed. Sulfur atoms in the *o*- and *m*- MBA formed strong covalent bonds with Au to produce stable Au-MBA (*o*- and *m*- forms) surface complexes. On the other hand, only oxygen atoms on the surface did not make a strong enough interaction to stabilize the Au species. We discuss how the Au species formed on the modified TiO₂(110) surface and the possibility to control the Au structure by the surface modification method.

Introduction

Control of the structure of transition metal species on oxide surfaces is important for preparation of well-defined catalysts. For this purpose, we have to understand the origins of the metal-metal oxide interactions so that we can regulate the interaction. Recently, we have discussed this point using polarization dependent total reflection fluorescence X-ray absorption fine structure (PTRF-XAFS) studies of single crystal oxide surfaces.¹ XAFS is an oscillatory feature that appears near and above the X-ray absorption edge. XAFS provides information about the local environment around the X-ray absorbing atoms. Usually XAFS is applied to a powder sample to obtain the local structure of supported metal catalysts directly.² However, because the structural information derived from XAFS is averaged over all spatial directions, it is difficult to deduce the nature of the metal-support interactions directly. The XAFS signal ($\chi(k)$) is polarization dependent, as shown in Eqs.(1) and (2) where θ_j and $\chi_j(k)$ is the angle between the bond and polarization and XAFS oscillation for each bond, respectively. This polarization dependency can be leveraged in XAFS on single crystal oxide surfaces to obtain three-dimensional structural information and the metal support interaction can be determined.¹

$$\chi(k) = \sum_j 3 \cos^2 \theta_j \cdot \chi_j(k) \quad \text{for K-edge} \quad (1)$$

$$\chi(k) = \sum_j (0.7 + 0.9 \cos^2 \theta_j) \cdot \chi_j(k) \quad \text{for L}_{2,3}\text{-edge} \quad (2)$$

We have studied Ni, Mo, Cu, and Pt dispersed on Al₂O₃ (0001) and TiO₂ (110) single crystals. Overall, these PTRF-XAFS studies have demonstrated that the metal species binds to the crystal surface through the metal-anion bond or metal–O bond.⁹

The TiO₂(110) surface is a typical oxide surface that has several different adsorption sites, as shown in Fig. 1. These are referred to as three-fold hollow sites, bridge and atop sites of surface oxygen atoms, step edges and kinks, 5-fold Ti sites, and oxygen defect sites.³ In our previous XAFS studies we did not observe evidence for metal-cation bonds within the covalent bond

range. We concluded that even if there are interactions between the adsorbed metal species and surface cations (Ti), they are not strong enough to fix the metal species. Early transition metals form bonds with surface oxygen atoms to give monomers, dimers, or chains, depending on the surface structure and preparation conditions.^{4–6} The late transition metals also interact with oxygen dangling bonds. Atomically dispersed Ni was found at the kink site of a step where two oxygen dangling bonds were present.^{7,8} The Ni-O bond distances for the upper and lower terrace oxygen atoms were 0.199 and 0.204 nm, respectively. The Ni adsorbed at a Ti vacancy site, and the variation in Ni-O bond lengths for the upper and lower terrace oxygen atoms, reflected the different Ti-O bond lengths in the TiO₂ rutile crystal. Single-layer Ni clusters are stabilized by multiple bonds to surface oxygen atoms.⁹ Single-layer Ni was seen to deform to an fcc (110)-like structure to increase contact with the surface oxygen atoms. About 90% of the Ni atoms had averaged Ni-O bond distances of 2.3 ± 0.1 Å.

On the other hand, it was difficult to obtain a monoatomically dispersed Cu. When we deposited Cu on the bare TiO₂(110), we could not obtain Cu monomer species. Instead, three-dimensional Cu clusters formed, even at 0.02 ML where we obtained Ni monomer species as mentioned above.⁷ This was because the Cu-O binding energy was much smaller than that of Ni-O. The formation enthalpies of Cu₂O and CuO were -157.3 and -168.6 kJ/mol, respectively, while that of NiO was -239.7 kJ/mol.¹⁰ We were able to obtain Cu monomers in three different ways. The first approach was to deposit the Cu(dpm)₂ (dpm = dipivaloylmethane) complex. The Cu(dpm) species attached to the bridge site of the bridging oxygens, and was stabilized by the dpm ligand to form a tetrahedral structure.^{11,12} The monomer Cu species could be transformed into Cu trimers and hexamers with a low temperature reduction treatment.¹² The second way was achieved through surface modification by an anchored S-atom-containing organic molecule. Since Cu is a soft Lewis acid, it

should have a larger affinity toward sulfur (soft base) than oxygen (hard acid) and atomically dispersed Cu can be obtained. We used thiophene carboxylic acid (TCA) to modify the surface.¹³ Because the carboxylic acid stably adsorbed on the TiO₂ (110) surface, the TCA was fixed firmly on it through the carboxylic acid moiety and the S atom in the thiophene ring was directed upwards. Consequently, a S-modified TiO₂(110) surface was obtained. Cu deposited on this surface was atomically dispersed and had a sandwiched structure between S and O with a linear arrangement.¹³ Recently we successfully fixed Cu using mercapto benzoic acids (*o*-, *m*-, *p*-MBA)-modified TiO₂(110).¹⁴ Our third approach was to control diffusion of the Cu atom on the TiO₂(110) surface. As mentioned above, the Cu should have stronger interactions with bridging oxygen sites than with five-fold Ti sites. Cu may then diffuse along on the bridging oxygen rows. Through this facile diffusion, Cu atoms can easily migrate to find a Cu island and aggregate to give three-dimensional clusters. If the Cu diffusion was suppressed, Cu nucleation would occur locally before reaching a larger island, leading to smaller cluster formation. At the extreme case, atomically dispersed metal species would be created. We attempted to block Cu diffusion by depositing acetic anhydride on the TiO₂ surface; the acetic anhydride dissociatively absorbs on TiO₂ to produce two types of acetates.¹⁵ Acetate species A was located on the 5-fold Ti sites in a bridge-bidentate structure. On the other hand, acetate species B incorporated one of the TiO₂ bridging oxygen atoms, with its original carbonyl oxygen adsorbed on a five-fold Ti site. Acetate B species were therefore oriented perpendicular to the bridging oxygen row. Acetate B can be converted to acetate A by leaving the defect. On this surface, Cu diffusion was considerably restricted by the presence of acetate B and/or the oxygen defect. Finally, the Cu atoms were trapped by the nearby acetate and became fixed on the surface through bonds with two oxygen atoms: the acetate B carbonyl and the bridging oxygen atoms.¹⁶ In the latter two methods, the atomically dispersed Cu atoms were always stabilized by two bonding motifs: sandwiched by S and the bridging oxygen or by the acetate and the bridging oxygen.

Metallic Au is chemically stable and less reactive. Recently, Au nanoclusters have drawn much attention because of their low temperature activity toward CO oxidation.¹⁷ It was quite difficult to obtain atomically dispersed Au species because of the low affinity of surface oxygen. When Au was deposited on the TiO₂(110) (1 × 1) and (1 × 2) surfaces, the main product formed was an icosahedral Au₅₅.^{18,19} Even after surface modification with TCA, atomically dispersed Au could not be obtained, although the size of the Au clusters became smaller, as shown later. We further enhanced the Au-surface interaction by modification of the surface with *o*- and *m*-MBA compounds to obtain atomically dispersed Au species. In this paper, we report the local structure of Au as determined by PTRF-XAFS, and compared the local structures with other surface Au species to discuss the principles of Au atomic dispersion.

Experimental

Optically polished Nb-doped (0.05 wt%) TiO₂(110) samples (20 × 20 × 1 mm³, Furuuchi Co., Japan) were cleaned by immersion in 10% HF solution for 10 min, followed by annealing in air at 700°C for 1 h according to previous work.^{20,21} The

Figure 1 The TiO₂(110) model structure. Large and small spheres represent O and Ti, respectively. There are several adsorption sites on TiO₂(110) as labeled in the figure.

cleaned surface was immersed in 1 mM ethanol solutions of either *o*-MBA or *m*-MBA (Toronto Research Chemicals Inc, Canada) at room temperature for 24 h to modify the TiO₂(110) surface with the corresponding MBA monolayers.

The prepared sample was then transferred to the UHV PTRF-XAFS chamber. Au was evaporated onto the MBA-modified TiO₂(110) surfaces by resistive heating of a tungsten filament wrapped with Au wire (99.99+% purity, Nilaco Co., Japan). Au coverage was estimated from X-ray photoelectron spectroscopy (XPS) peak area ratios of Au 4f_{7/2} to Ti 2p_{3/2}. 1 ML was defined as 5.2 × 10¹⁴ cm⁻² corresponding to the TiO₂(1 × 1) unit cell. TCA was deposited on the Au surface as reported previously.¹³ PTRF-XAFS experiments were carried out at BL9A of the Photon Factory at the Institute of Material Structure Science (KEK-IMSS-PF). X-rays were monochromatized with a Si (111) double-crystal and focused using a pair of bent conical mirrors.²² The beam size on the sample was regulated with a pinhole (φ 0.4 mm) to reduce undesirable X-ray irradiation other than on the sample. The total reflection conditions were adjusted using a UHV-compatible high-precision six-axis goniometer as reported elsewhere.^{1,23} Considering the rectangular unit cell of the TiO₂(110) surface,³ XAFS measurements were carried out in three different orientations relative to the electric vector ($\vec{E}$) of the incident X-rays. PTRF-XAFS spectra for the orientation parallel to the surface were obtained from the $\vec{E} // [001]$ and $// [1\bar{1}0]$ directions. We acquired the structure in the perpendicular direction mainly from the $\vec{E} // [110]$ XAFS signal. The Au L_α fluorescence was detected by a 19-element Ge solid-state detector (GL0110S, Canberra, Meriden, USA). Self-absorption was negligible because the coverage was smaller than 1 ML.

XAFS analysis was carried out by a REX 2000 program (Rigaku Co. Tokyo, Japan).²⁴ The XAFS oscillations were extracted using a spline smoothing method and normalized by an edge height. The preliminary analysis was carried out by a least-squares curve fitting method using FEFF derived parameters:

$$\chi(k) = \frac{\sum_j (0.7 + 0.9 \cos^2 \theta_j) S_j F_j(k_j) e^{-2k_j^2 \sigma_j^2} \sin(2k_j r_j + \phi_j(k_j))}{k_j r_j^2}$$

$$k_j = \sqrt{k^2 - 2m\Delta E_j / \hbar^2}$$
(3)

Figure 2 XAFS oscillations $\chi(k)$ of Au on a TCA-modified $\text{TiO}_2(110)$ surface with different polarization dependencies, as indicated in the Figure.

Figure 3 XAFS oscillations $\chi(k)$ of Au on *o*-MBA-modified $\text{TiO}_2(110)$ surface with different polarization dependencies, as indicated in the Figure.

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directions, S_j , σ_j , r_j , ΔE_j are the amplitude reduction factor, Debye-Waller factor, bond distance, and the energy shift in the origin of the photoelectron kinetic energy of the j -th bond, respectively. $F_j(k)$ and $\phi_j(k)$ are the backscattering amplitude and the phase shift functions, respectively. We used the same fitting parameters within the same coordination shell. The final structure was determined by an iterative method using the FEFF8.04 code^{25,26} based on a real-space model structure.^{27,28} The FEFF calculation was carried out with a Hedin-Lundqvist potential. The Debye-Waller factor for Au-Au was fixed to one value for each polarization direction. The polarization dependence expressed in Eq. (2) was also considered in the simulation. To quantify the goodness of the fits we carried out a chi square test using the following equation:

$$\chi^2 = \frac{\nu}{(\nu-1)N_{data}} \sum \frac{[\chi_{obs}(k) - \chi_{cal}(k)]^2}{[\sigma_{obs}(k)]^2} \quad (4)$$

where $\chi_{obs}(k)$ and $\chi_{cal}(k)$ are the observed and calculated XAFS

oscillations, respectively. N_{data} is the number of data points, and $\sigma_{obs}(k)$ is the measurement error, estimated from the standard deviations of the observed data. To avoid confusion between the XAFS oscillation and the chi square test values, we here used symbol χ^2 instead of chi square (χ^2).

Results

First, we briefly reviewed the Au structure on the bare $\text{TiO}_2(110)$ surface reported elsewhere.^{18,19} There was little polarization dependence in the Au XAFS oscillations, indicating that three-dimensional Au nanoclusters were formed. The Au-Au distance of 2.70 Å was shorter than that of bulk Au (2.88 Å). The shorter bond distance resulted from the formation of small ~1-nm-diameter clusters.²⁹ A real space simulation showed that Au_{55} icosahedral structures were the main Au product formed on the bare $\text{TiO}_2(110)$ surface.

It was difficult to create an atomically dispersed Au. When Au was deposited on a $\text{TiO}_2(110)$ (1 × 2) surface, which contains more Ti^{3+} and has a rougher surface, we found that the same Au_{55} icosahedral species formed on this $\text{TiO}_2(110)$ surface.¹⁹ When the surface was modified with TCA, which helped to stabilize the Cu atoms on the $\text{TiO}_2(110)$ surface, we observed a reduction in the size of Au clusters formed on the surface.

Figure 4 Comparison between the observed XAFS oscillations $\chi(k)$ (solid line) of Au on the *o*-MBA-modified $\text{TiO}_2(110)$ surface and those calculated (broken line) based on the model structure illustrated in

Figure 5.

Figure 5 A model structure for Au on the *o*-MBA modified $\text{TiO}_2(110)$ surface. Yellow, purple and red spheres represent S, Au, and O, respectively.

Figure 6 Comparison between the observed XAFS oscillations $\chi(k)$ (solid line) of Au on the *m*-MBA-modified $\text{TiO}_2(110)$ surface and those calculated (broken line) based on the model structure illustrated in Figure 7.

Figure 7 A model structure of Au on the *m*-MBA modified $\text{TiO}_2(110)$ surface. Yellow, purple and red spheres represent S, Au, and O, respectively.

Figure 2 shows the XAFS oscillations after the deposition of Au on the TCA-modified TiO₂(110) surface. The amplitude of XAFS oscillations were smaller than those of Au deposited on the bare TiO₂(110) surface, even though Au-Au bonds were formed and agglomeration occurred, as mentioned in the introduction. The Au-Au distance was 2.68 Å, with smaller Au-Au coordination numbers relative to the unmodified(or bare) surface, as shown in Table 1, indicating that smaller nanoparticles were formed on the TCA-covered surface than on the bare surface. We also observed a polarization dependence. The polarization dependence of the coordination numbers in Table 1 indicated that two-layer fcc-like small Au₁₀ (~6 Å) nanoclusters were likely to be stabilized on the TCA surface. The TCA modified surface experienced stronger interactions with Au than the bare TiO₂(110) surface through the S-Au bond to stabilize the two-dimensional structure. However, the Au-TCA interaction was not strong enough to stabilize the Au monomer, as was seen with the Cu-TCA interaction.

Then we modified the TiO₂(110) surface with *o*-MBA. Figure 3 shows the polarization-dependent XAFS oscillations of the Au species deposited on the TiO₂(110) surface modified with *o*-MBA. For this surface, we observed totally different Au spectra when compared with those prepared on the TCA-modified TiO₂(110) surfaces. The preliminary curve fitting analysis indicated the presence of Au-S bond distances of 2.32 Å. We did not observe Au-Au interactions. We carried out the real space analysis based on the FEFF8 program. Figure 5 shows the model structure that could reproduce the XAFS oscillations in three directions, as shown in Fig. 4. In this structure, Au was sandwiched between sulfur and a bridging oxygen atom. The Au-S and Au-O bond lengths were 2.32 and 2.10 Å, respectively. The S-Au-O and C-S-Au bond angles were 155 and 143°, respectively. The angular deviation between the S-Au bond direction and the [001] direction was 59°. The atomically dispersed Au structure was thermally stable up to 473 K and no Au-Au bond was observed in the PTRF-XAFS. The Au was probably able to be efficiently captured by the S moiety in the *o*-MBA modified surface because of the S-atom positioning relative to the TiO₂ surface; S was seen to locate at about 4 Å above the surface in the proposed model structure which would be appropriate for the Au capture. On the other hand, the TCA modified surface had a S atom at 6.5 Å above the native surface. The monodentate form of the carboxylic structure was required to trap Cu atoms. An alternative reason for the superior Au trapping ability of the *o*-MBA surface could be that the S-Au bond formed on the MBA surface was stronger than that in TCA. To check this point, we modified the TiO₂ surface with *m*-MBA, which effectively moves the S atom to a position about 7 Å away from the TiO₂(110) surface when bridge-bidentate carboxylate adsorption was assumed. Fig. 6 shows the XAFS spectra of Au dispersed on the *m*-MBA-covered TiO₂(110). The observed spectra are similar to those of Au on the *o*-MBA-covered surfaces. The Au was atomically dispersed on the *m*-MBA-covered TiO₂(110) even though the S position was farther away from the surface. We carried out the real space analysis of the Au structure using the FEFF8 code and the fixed MBA molecular structure except the rotation around the S-C(benzene ring) bond. We found that the Au was again sandwiched by the sulfur and bridging oxygen, similar to the arrangement of Au on

the *o*-MBA-modified TiO₂(110) as shown in Fig. 7. Au-S and Au-O bond lengths of 2.32 and 2.10 Å, respectively, were deduced. The S-Au-O and C-S-Au bond angles were 166 and 147°, respectively. The angle between the S-Au direction and the [110] direction was 61°. In this case, we postulated a monodentate *m*-MBA structure on the TiO₂(110) surface. Otherwise the structure shown in Fig. 7 would be impossible and a strained structure would have to be considered. We concluded that the Au stabilization by *o*-MBA was not due to the suitable geometrical position to trap the Au, but was instead due to the formation of a strong S-Au bond.

Discussion

Structure of surface Au species

Au deposited on the bare TiO₂(110) surface easily aggregated to yield a three-dimensional structure. Although rather small Au nanoparticles were formed on the TCA-modified surface, atomically dispersed Au was difficult to obtain. The *o*- and *m*-MBA modified surfaces could provide atomically dispersed Au species. The Au-S bond distances in both *o*- and *m*-MBA were 2.32 Å. Table 2 shows the Au-S and Au-O bond distances in some selected compounds. The Au-S bond distances were found to be in the range of 2.29-2.34 Å, corresponding well to the ones found in the Au species on the *o*- and *m*-MBA modified surfaces. Thus the Au was fixed on the surface through Au-S and Au-O covalent bonds. In these compounds the X-Au-S angle was nearly linear and the O-Au-S angle on the TiO₂(110) surface was 160 ± 10°.

The reason why thiophene could not fix the atomic Au was based on the different affinity of Au to S atoms in TCA and in *o*- or *m*-MBA. To our knowledge, no Au-thiophene compounds are reported in the literature; however, there are many examples of Au-mercaptobenzene compounds and Au-hydrogenated TCA compounds called as THT=(Tetrahydrothiophene) which should have different bonding feature from that of TCA, as shown in Table 2. Further evidence for the stronger affinity of MBA to that of TCA can be found by examining the surface adsorption properties of mercaptobenzene and thiophene. Alkyl mercaptan and mercaptobenzene can be adsorbed on the Au surface up to full coverage to form a self-assembled thin film.^{30,31} On the other hand, only a small amount of thiophene was observed to adsorb on the defect sites of the Au (111) surface by vapor deposition at room temperature.^{32,33} Dishner et al. reported that the immersion method from ethanol solution could provide the thiophene film adsorbed on Au(111).³⁴ However, Sako et al. revealed that the thiophene was converted to butyl mercaptan in the immersion method.³⁵ Thus, molecular thiophene does not display stable adsorption characteristics on the Au surface. The Au atom can react with the S atom in mercaptobenzene, but not in thiophene. The mercapto moiety can make such a strong bond with Au that it can cleave an O(carboxylate of *m*-MBA)-Ti bond, transforming the MBA bridge-bidentate form to the monodentate form. Such monodentate species can be found in the Cu attached on the thiophene modified surface.¹⁸

The structure and morphology of Au species on the surface was determined by the balance of anion-Au and Au-Au interactions. As Hu et al. reported that Au-O formation enthalpy was more positive than the other metal oxide formation

enthalpies, Au on the bare TiO₂(110) grew three-dimensionally,³⁶ which corresponds well with our observations. The TCA-modified TiO₂ (110) failed to disperse the Au for the same reason. The Au-S interaction was stronger than that of Au-O because of the soft base-acid interactions. MBA could atomically disperse Au species. The Au-TCA interaction was moderate, resulting in smaller Au cluster formation, but not atomically dispersed.

Table 1 Curve fitting results of Au on the TCA-modified TiO₂(110) surface with three different polarization directions.

	Bond	N	R / Å	N(expected)*
E//[110]	Au-Au	5.4	2.67	5.2
E//[001]	Au-Au	5.0	2.67	5.2
E//[110]	Au-Au	3.9	2.68	3.9

* Coordination number calculated from a Au₁₀ nanocluster

Table 2 Au-S and Au-O distances in selected Au species

Compounds	Au-S / Å	Au-O/Å	Note	Ref
Au ₂₅ SR ₁₅	2.33		R=Phenylethly	37
R ₃ PAu{SC(OMe)=NC ₆ H ₄ NO ₂ -4}	2.31		R=Et,Cy,Ph ^{*1}	38
[(<i>t</i> -C ₄ H ₉ O) ₃ SiSAu] ₄	2.29		Au ₄ S ₄	39
Au ₂ Cl ₂ (μ-dppf)	2.30		Linear S-Au-P	40
(C ₆ H ₄ (COOH)S)-Au-(PPhMe ₂)-	2.31		Linear S-Au-P	41
[Au(C ₂ H ₃ O ₂)(C ₁₈ H ₁₅ P)]		2.063	Linear O-Au-P	42
[Au(NO ₃)(CNEt)]		2.033	Linear O-Au-C	43
Au(C ₇ H ₅ O ₂){PPh ₃ }.C ₆ H ₆		2.034	Linear O-Au-P	44
[Au(ppy)(tsc)] 1.5H ₂ O	2.276	2.057	Square	45
[Au(C ₆ F ₅) ₃ (THT)]	2.362		Square	46
(AuTHT ^{*2}) _∞	2.306, 2.335		S-Au-S	47

*1 Et=Ethyl, Cy=Cyclohexyl, Ph=Phenyl

*2 THT=tetrahydrothiophene

The formation mechanisms of atomically dispersed Au and small Au cluster on the modified TiO₂(110)

On the bare TiO₂(110) surface, deposited Au migrates to seek a stable absorption site. The Au-O bond is too weak to stabilize the Au monomer and the Au continues to diffuse until finding an Au island to aggregate and form three-dimensional clusters. In the case of *o*-MBA, the S dangling bond is directed toward the Au trapping site. The deposited Au is easily trapped by the S-Au-O bonding motif and stabilized. In *m*-MBA, the S atom has no bond directed toward the trapping site. The *m*-MBA exists in the following equilibrium between monodentate and bridge-bidentate adsorption structures.

The equilibrium between monodentate and bridge-bidentate carboxylate structures has been demonstrated by the STM observation of formic acid on TiO₂(110).⁴⁸ The monodentate *m*-MBA can change the orientation that can trap Au by bonding with the thiol species.

where O(bridging) means a bridging oxygen atom.

In equilibrium (6) the product side is more favorable, and the forward reaction in equilibrium (5) will proceed. Thus, the Au is trapped efficiently on the *m*-MBA-modified TiO₂(110) surface. In the case of TCA, similar equilibria might be present, but because of the weak interactions between thiophene and Au, the product

side would not be favorable in equilibrium (7) and trapped Au would not be stable.

However, the Au diffusion is limited by the TCA interaction, and Au aggregation occurs locally before reaching the larger Au islands. Consequently, smaller, two-layer Au clusters are formed on the TCA surface.

Conclusions

To stabilize atomic Au and small Au clusters on oxide surfaces, the Au-anion interaction is the most important. The Au-O bond is too weak to stabilize Au monomers, and Au atoms easily aggregate into a three-dimensional metal nanocluster. The Au is strongly stabilized by interaction with the mercapto moiety (-SH) of an MBA molecule, which is fixed to the surface through its carboxylic acid functionality. The Au-S bonds in Au-*o*-MBA and Au-*m*-MBA are both covalent with a bond length of 2.32 Å. The Au-S bond formed in TCA is not strong enough to fully stabilize atomic Au, but does serve to hinder Au diffusion on the oxide surface, which results in smaller Au clusters than on the bare oxide. The surface modification is useful to control the structures of Au species which have small interaction with the surface oxygen atoms.

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Notes and references

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- 1 K. Asakura, in *Catalysis Book Series*, ed. J. G. Catalano, 2012, vol. 24, pp. 281.
- 2 Y. Iwasawa, ed. *X-ray absorption spectroscopy for catalysts and surfaces*, World Science, Singapore, 1996.
- 3 U. Diebold, *Surface Science Reports*, 2003, **48**, 53.
- 4 W. J. Chun, K. Asakura and Y. Iwasawa, *Chem. Phys. Lett.*, 1998, **288**, 868.
- 5 W. J. Chun, K. Asakura and Y. Iwasawa, *J. Phys. Chem. B*, 1998, **102**, 9006.
- 6 W. J. Chun, K. Asakura and Y. Iwasawa, *Catal. Today*, 2001, **66**, 97.
- 7 Y. Koike, K. Ijima, W. J. Chun, H. Ashima, T. Yamamoto, K. Fujikawa, S. Suzuki, Y. Iwasawa, M. Nomura and K. Asakura, *Chem. Phys. Lett.*, 2006, **421**, 27.
- 8 Y. Koike, W. J. Chun, K. Ijima, S. Suzuki and K. Asakura, *Materials Trans.*, 2009, **50**, 509.
- 9 Y. Koike, K. Fujikawa, S. Suzuki, W. J. Chun, K. Ijima, M. Nomura, Y. Iwasawa and K. Asakura, *J. Phys. Chem. C*, 2008, **112**, 4667.
- 10 D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Churney and R. L. Nuttall, *J. Phys. Chem., Ref. Data*, 1982, **11**, **Supplement No.2**.
- 11 Y. Tanizawa, T. Shido, Y. Iwasawa, M. Nomura, W.-J. Chun and K. Asakura, *J. Phys. Chem. B*, 2003, **107**, 12917.
- 12 Y. Tanizawa, W. J. Chun, T. Shido, K. Asakura and Y. Iwasawa, *J. Synchro. Rad.*, 2001, **8**, 508.
- 13 W. J. Chun, Y. Koike, K. Ijima, K. Fujikawa, H. Ashima, M. Nomura, Y. Iwasawa and K. Asakura, *Chem. Phys. Lett.*, 2007, **433**, 345.
- 14 S. Takakusagi, H. Nojima, H. Ariga, K. Miyazaki, T. Wada, W.-J. Chun, M. Nomura, Y. Iwasawa, and K. Asakura *in preparation*
- 15 H. Ashima, W.-J. Chun and K. Asakura, *Surf. Sci.*, 2007, **601**, 1822.
- 16 W. J. Chun, Y. Koike, H. Ashima, K. Kinoshita, K. Ijima, K. Fujikawa, S. Suzuki, M. Nomura, Y. Iwasawa and K. Asakura, *Chem. Phys. Lett.*, 2009, **470**, 99.)
- 17 G. J. Hutchings and J. K. Edwards, in *Frontiers of Nanoscience*, eds. L. J. Roy and J. P. Wilcoxon, Elsevier, 2012, vol. Volume 3, pp. 249-293.
- 18 W. J. Chun, K. Miyazaki, N. Watanabe, Y. Koike, S. Takakusagi, K. Fujikawa, M. Nomura and K. Asakura, *J. Ceram. Soc. Jpn.*, 2011, **119**, 890.
- 19 W. J. Chun, K. Miyazaki, N. Watanabe, Y. Koike, S. Takakusagi, K. Fujikawa, M. Nomura, Y. Iwasawa and K. Asakura, *J. Phys. Chem.*, 2012, **in press**.
- 20 Y. Yamamoto, K. Nakajima, T. Ohsawa, Y. Matsumoto, H. Koinuma, *J. Appl. Phys.* 2005, **44**, L511.
- 21 R. Nakamura, N. Ohashi, A. Imanishi, T. Osawa, Y. Matsumoto, H. Koinuma, Y. Nakato, *J. Phys. Chem. B* 2005, **109**, 1648.
- 22 M. Nomura and A. Koyama, *KEK Report 98-194*, 1998.
- 23 W. J. Chun, Y. Tanizawa, T. Shido, Y. Iwasawa, M. Nomura and K. Asakura, *J. Synchro. Rad.*, 2001, **8**, 168-.
- 24 K. Asakura, in *X-ray Absorption Fine Structure for Catalysts and Surfaces*, ed. Y. Iwasawa, World Scientific, Singapore, 1 edn., 1996, vol. 2, pp. 33.
- 25 A. L. Ankudinov, Ravel.B., J. J. Rehr and S. D. Conradson, *Phys. Rev. B*, 1998, **58**, 7565.
- 26 A. L. Ankudinov, C. E. Bouldin, J. J. Rehr, J. Sims and H. Hung, *Phys. Rev. B*, 2002, **65**, 104107.
- 27 W. J. Chun, K. Asakura and Y. Iwasawa, *J. Phys. Chem. B*, 1998, **102**, 9006.
- 28 W. J. Chun, K. Asakura and Y. Iwasawa, *Catal. Today*, 1998, **44**, 309.
- 29 J. T. Miller, A. J. Kropf, Y. Zha, J. R. Regalbuto, L. Delannoy, C. Louis, E. Bus and J. A. van Bokhoven, *J. Catal.*, 2006, **240**, 222-234.
- 30 A. Ulman, *An introduction to Ultrathin organic films from BL to SAM*. Editor, Academic Press, San Diego, **1991**.
- 31 H. A. Biebuyck, C. D. Bain, G. M. Whitesides, *Langmuir* **1994**, **10**, 1825 -.
- 32 F. Elfeninat, C. Fredriksson, E. Sacher and A. Selmani, *J. Chem. Phys.*, 1995, **102**, 6153.
- 33 G. Liu, J. A. Rodriguez, J. Dvorak, J. Hrbek, T. Jirsak, *Surf. Sci.*, 2002, **505**, 295.
- 34 M. H. Dishner, J. C. Hemminger and F. J. Feher, *Langmuir*, 1996, **12**, 6176.
- 35 E. O. Sako, H. Kondoh, I. Nakai, A. Nambu, T. Nakamura, T. Ohta, *Chem. Phys. Lett.* **2005**, **413**, 267
- 36 M. Hu, S. Noda and H. Komiyama, *Surf. Sci.*, 2002, **513**, 530.
- 37 M. Zhu, C. M. Aikens, F. J. Hollander, G. C. Schatz and R. Jin, *J. Amer. Chem. Soc.*, 2008, **130**, 5883.
- 38 S. Y. Ho, E. C.-C. Cheng, E. R. T. Tiekink and V. W.-W. Yam, *Inorg. Chem.*, 2006, **45**, 8165.
- 39 W. Wojnowski, B. Becker, J. Saßmannshausen, E. M. Peters, K. Peters and H. G. Von Schnering, *Z. Anorg. Allgem. Chem.*, 1994, **620**, 1417
- 40 F. Canales, M. C. Gimeno, A. Laguna and P. G. Jones, *J. Amer. Chem. Soc.*, 1996, **118**, 4839.
- 41 U. Helmstedt, S. Lebedkin, T. Hofer, S. Blarrock and E. Hey-Hawkins, *Inorg. Chem.*, 2008, **47**, 5815.
- 42 P. G. Jones, *Acta Crystallogr. C*, 1984, **40**, 1320.
- 43 T. J. Mathieson, A. G. Langdon, N. B. Milestone and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1999, 201.
- 44 P. G. Jones, *Acta Crystallogr. C*, 1985, **41**, 905.
- 45 D. Fan, C.-T. Yang, J. D. Ranford, J. J. Vittal and P. Foo Lee, *Dalton Trans.*, 2003, 3376.
- 46 J. Coetzee, W. F. Gabrielli, K. Coetzee, O. Schuster, S. D. Nogai, S. Cronje and H. G. Raubenheimer, *Angew. Chem. Intern. ed.* 2007, **46**, 2497.
- 47 S. Ahlrand, B. Noren and A. Oskarsson, *Inorg. Chem.*, 1985, **24**, 1330.
- 48 M. Aizawa, Y. Morikawa, Y. Namai, H. Morikawa and Y. Iwasawa, *J. Phys. Chem. B*, 2005, **109**, 18831.