



# Atomic-scale insight into the structural effect of a supported Au catalyst based on a size-distribution analysis using Cs-STEM and morphological image-processing



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## ABSTRACT

Alumina-supported gold catalysts (Au/Al<sub>2</sub>O<sub>3</sub>) prepared under various conditions were observed on an atomic scale using aberration-corrected scanning transmission electron microscopy (Cs-STEM). The Au particles, including single Au atoms, on Cs-STEM images were extracted using morphological image-processing, and the size distributions for reaction site candidates, such as the corner, edge, and surface of Au clusters, in a unit weight of Au/Al<sub>2</sub>O<sub>3</sub> catalyst were calculated. Based on the size distributions for these reaction site candidates, we inspected the effective sites and sizes of Au catalysts for the hydrogenation of aldehydes (5-hydroxymethylfurfural and benzaldehyde) and a nitro compound (nitrobenzene). The results suggested that the corner atoms are a key site for the hydrogenation of aldehydes and the nitro compound because the dissociative adsorption of H<sub>2</sub> on corner atoms controls the reaction rate. Meanwhile, the effective size for the aldehydes was smaller than that for the nitro compound due to their different adsorption sites: while the aldehydes are adsorbed on the corners of Au clusters, the nitro group is adsorbed on their edges. The adsorption of the reactants was supported by reaction kinetics and X-ray absorption spectroscopy analyses. The specific active size for hydrogenation reactions was also investigated based on the size distributions.

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## 1. Introduction

Supported Au nanoparticles have been intensively studied not only because they provide unique catalytic activities for various reactions, but also because their catalytic effect is often size-dependent [1–3]. It is well known that Au nanoparticles show high catalytic activity for the CO oxidation reaction [1–3]. The catalytic activity drastically increases when the particle size decreases to below 3 nm. Such a unique size effect can also be observed in the hydrogenation reaction, where Au catalysts often show unique selectivity that is not observed with Pt group metal catalysts [3–9]. For example, unsaturated aldehydes and nitro compounds are selectively hydrogenated to the corresponding alcohols and amines on supported Au catalysts due to their preferential adsorption of aldehydes and nitro groups compared to a C=C group [4–11]. In hydrogenation reactions on Au catalysts, the activation

of H<sub>2</sub> is a key step [12–14]. It has been demonstrated that H<sub>2</sub> is dissociatively adsorbed on low-coordinated Au atoms on the corners or edges of Au nanoparticles, while H<sub>2</sub> is not adsorbed on a clean Au surface with the properties of bulk Au [15,16]. Furthermore, the dissociative adsorption of H<sub>2</sub> has been suggested to occur at the interface between Au nanoparticles and metal oxide supports such as Al<sub>2</sub>O<sub>3</sub> [13,17]. Au<sup>3+</sup> has also been proposed to be the active species for the hydrogenation reaction on Au/MgO [18]. The Au active site, size, and species for the hydrogenation reaction are still not clear. Meanwhile, techniques for particle structure (size and shape) analysis and nanomaterial synthesis have recently been developed, and, accordingly, the catalytic activities of Au cluster catalysts with diameters of less than 2 nm have been explored [19–24]. Such small Au clusters can show extraordinary catalytic activity based on their unique structures and electronic state, and the catalytic activity can vary according to differences at the atomic scale [3,25]. Therefore, the size effect of Au clusters has attracted intense attention.

Atomic-scale observation using aberration-corrected (scanning) transmission electron microscopy (Cs-(S)TEM) is a powerful technique for investigating the size-dependent catalytic activity of Au

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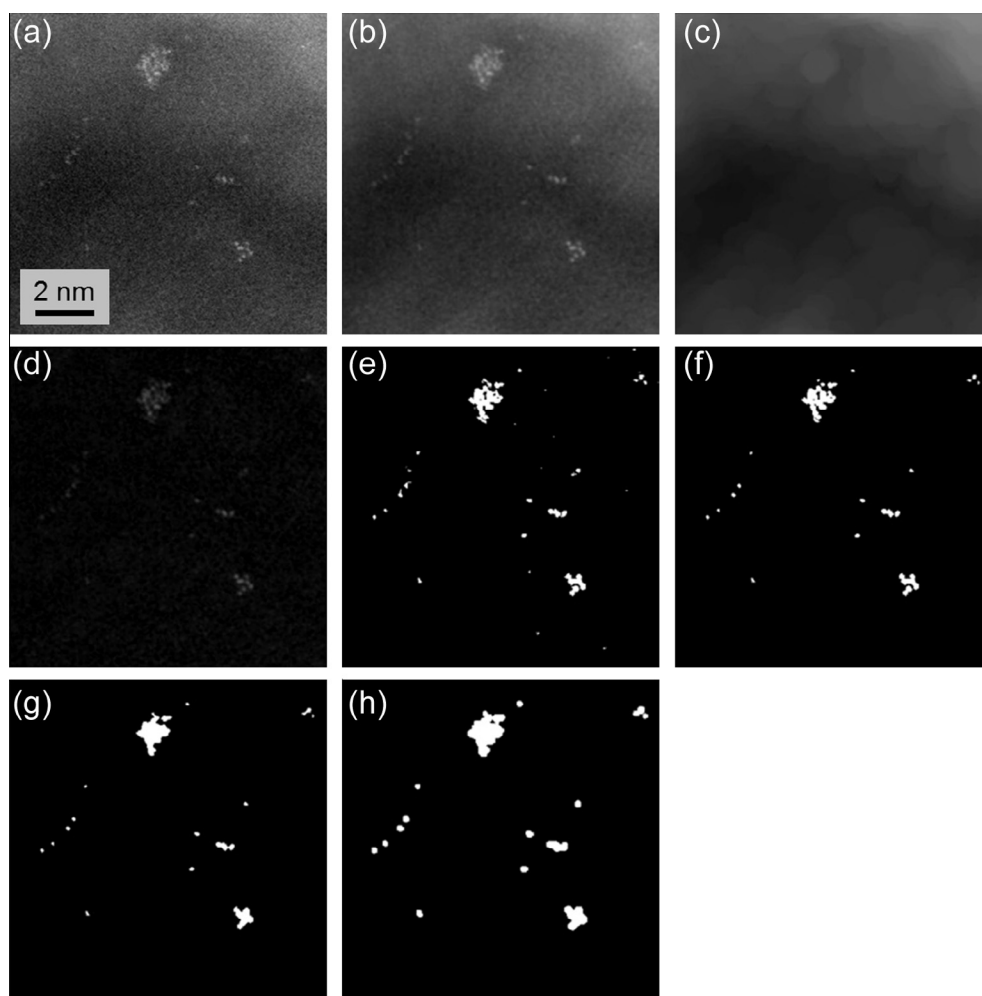
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clusters [19,20,26,27]. A pioneering study on the Au cluster size effect using Cs-STEM by Herzing et al. demonstrated that a Au cluster of  $\sim 10$  atoms with a bilayer structure has high catalytic activity for CO oxidation [19]. Very recently, Corma et al. showed that Au clusters of 5–10 atoms are extremely active for the oxidation of thiophenol [20]. Interestingly, both of these studies indicated that single Au atoms have little or no catalytic activity, while tiny clusters are specifically active. Cs-(S)TEM can also provide more structural information than just the particle size, since it can be used to visualize the atomic alignment in a metal cluster [28–30]. Akita et al. used Cs-TEM for a detailed investigation of the interface between Au clusters and their supports, which can play a critical role in their catalytic activities [28]. Long et al. and Sanchez et al. used Cs-(S)TEM to reveal the crystallinity of supported metal clusters [29,30]. They clarified that the crystallinity of metal clusters varies according to their size, metal–support interaction, and the nature of the metal. Our recent study on the use of a Ru catalyst for the hydrogen oxidation reaction showed that size-dependent crystallinity significantly affected the catalytic performance [31]. Therefore, Cs-STEM analysis can provide new and detailed structural information, which should promote our understanding of the structure-dependent catalytic activities of supported metal

clusters, and could lead to the development of highly active catalysts for industrial applications.

When Cs-STEM is used to observe supported metal catalysts, we can observe all of the supported metal species, from single metal atoms to nanoparticles (if the metal species shows high contrast against the support) [19,20,26,32–36]. Thus, if we can evaluate the particle size of all of the supported metal species on STEM images, we can obtain a quantitative size distribution for the number of metal particles, and then can estimate the number of Au atoms at potential reaction sites, such as the corners, edges, and surface of metal particles. Such a particle size distribution analysis may be used to elucidate the active site and effective size of metal catalysts.

To obtain more realistic size distributions based on atomic-scale observation, we have developed a new automatic STEM image-processing method that uses a mathematical morphological operation (Fig. 1) [32]. We demonstrated that this morphological image-processing method extracts supported Au particles (Au/Al<sub>2</sub>O<sub>3</sub>) more accurately (i.e., with fewer artifacts) than conventional image-processing methods. Furthermore, the morphological operation can connect atoms in an Au cluster showing the atomic structure on a STEM image, and allow us to evaluate the cluster



**Fig. 1.** A typical morphological image-processing of a HAADF STEM image: (a) Raw image of Au/Al<sub>2</sub>O<sub>3</sub>; (b) the image was smoothed using a convolution filter to reduce quantum and electrical noise; (c) a background image was prepared from the smoothed image by a morphological opening operation using a disk larger than a Au atom; (d) the background image was subtracted from the smoothed image; (e) the contrast of the background-subtracted image was changed by using a threshold, and transformed to a binary image; (f) any remaining noise was removed using another morphological opening operation. (g) Au atoms in a cluster on the binary image were connected. (h) The shapes of Au particles were corrected by a dilation operation that took into account the sizes of the electron probe and the Au atom.

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