Direct In Situ TEM Visualization and Insight into the Facet-Dependent Sintering Behaviors of Gold on TiO2

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Abstract: To prevent sintering of supported nanocatalysts is an important issue in nanocatalysis because the size of a nanoparticle (NP) is a critical parameter for its catalytic reactivity. A possible way to increase the durability of a nanocatalyst is to choose a suitable support. However, whether the metal-support interaction (MSI) promote or prevent the sintering process has not been fully identified due to the lack of confirmed experimental evidence. Herein, by combining spherical aberration corrected scanning transmission electron microscopy with environmental transmission electron microscopy, we report on completely different sintering behaviours of Au nanoparticles on distinct anatase TiO\(_2\) surfaces. The full in situ sintering processes of Au nanoparticles was visualized on TiO\(_2\) (101) surface, which couples the Ostwald ripening and particle migration coalescence. In contrast, no sintering of Au nanoparticles on TiO\(_2\) anatase (001) surface was observed under the same conditions. This facet-dependent sintering mechanism is fully explained by the density function theory calculations that the strong metal-support interactions highly increase the diffusion barriers of nanoparticles and adatoms, which prevent the sintering process. Our work not only offers the direct evidence of the important role of supports in the sintering process, but also provides insightful information for the design of sintering-resistant nanocatalysts.

Metal nanoparticles (NPs) supported on oxide are of great importance in many industrial chemical processes as heterogeneous catalysts\(^{[1]}\). One of the key parameters controlling the activity is the size of the NPs\(^{[2]}\). For example, Au NP will lose its reactivity rapidly when the diameter increases. However, many reactions take place at elevated temperatures, in which the highly dispersed nanocatalysts with high surface energies are prone to sintering and thereby lose activity.\(^{[3]}\) Therefore, understanding the sintering mechanism of supported catalysts is of considerable importance in nanoscience and nanocatalysis research. Two mechanisms are generally considered for the sintering of nanoparticles: Ostwald ripening (OR), which involves the migration of single atoms or small atomic clusters from smaller particles to larger particles; particle migration and coalescence (PMC), which involves the Brownian-like motion and coalescence of particles.\(^{[3a]}\) Tremendous efforts have been devoted to studying the two sintering mechanisms of supported catalysts.\(^{[3, 4]}\) Among these studies, the effect of the metal-support interaction (MSI) on the sintering behavior is a hot topic and has been extensively discussed.\(^{[5, 6]}\) Strong MSI is considered to prevent PMC by stabilizing the supported nanoparticle, however, it is also argued that it could promote the OR process. In this regard, the density function theory calculations that the strong metal-support interaction is fully explained by the density function theory calculations that the strong metal-support interactions highly increase the diffusion barriers of nanoparticles and adatoms, which prevent the sintering process. Our work not only offers the direct evidence of the important role of supports in the sintering process, but also provides insightful information for the design of sintering-resistant nanocatalysts.

To address this issue, direct experimental evidence linking the sintering behavior to MSI is necessary and demanding. As an emerging technology for sintering study, in situ transmission electron microscopy (TEM)\(^{[5a, 7]}\) could visualize sintering processes at the atomic level, which is extremely crucial for unveiling the underlying mechanism. Exciting advances have been reported in in situ TEM in several supported catalyst systems, for instance, Pt/Al\(_2\)O\(_3\)\(^{[7a]}\), Cu/SiO\(_2\)\(^{[7g]}\), Ni/MgAl\(_2\)O\(_4\)\(^{[7i]}\), etc. However, these studies focus on either determining the dominating sintering mechanism by statistical analysis of particle size evolution, or exploring the dynamic response of sintering behavior to environmental and support change, mostly from top view. The atomic-scale information of the interface between metal and support (from side view) during sintering is missing although such information is critical for the complete understanding of MSI-dependent sintering mechanisms.

In this article, combining spherical aberration corrected scanning transmission electron microscopy (STEM) with environmental transmission electron microscopy (ETEM), the sintering behaviours of Au nanoparticles on different TiO\(_2\) anatase crystal planes have been unveiled at the atomic level. Our TEM observation provides visualizations of complete sintering processes, involving both the OR mechanism and the PMC mechanism, of Au NPs on the TiO\(_2\) anatase (101) surface. Meanwhile, the resistance of sintering of Au NPs was observed on the TiO\(_2\) anatase (001) surface. Atomic TEM images of the interface structures show clear unwetting and wetting behaviours of Au NPs on these two surfaces, which links the different sintering behaviours directly to the different MSIs. Furthermore, density function theory (DFT) calculations confirmed that the facet-dependent sintering behavior is caused by the different adsorption and diffusion behaviours of Au on different TiO\(_2\) facets. The high angle annular dark field (HAADF) STEM analysis was performed in an FEI Titan G2 80-300 ST TEM (300 kV), equipped with a spherical aberration corrector. The TEM analysis and in situ observation of sintering behaviours were carried out in a Hitachi H9500 ETEM, operated at 300 kV. To examine the facet-dependent sintering behaviours, well-defined Au-TiO\(_2\) (101) and Au-TiO\(_2\) (001) model catalysts were prepared by loading Au nanoparticles (diameter: ~4-8 nm) on two typical anatase TiO\(_2\) supports [TiO\(_2\)-(101) and TiO\(_2\) (001)], through impregnation and in situ annealing methods. The TiO\(_2\)-(101) support is bipyramidal TiO\(_2\) nanocrystals (Figure 1a), which are dominated by (101) surfaces (Figures 1e, 1f, S1, S2 and S4; percentage of (101) area: >98%); The TiO\(_2\)-(001) support is TiO\(_2\) nanosheets (Figure 1c), which are mainly exposed by (001) surfaces (Figures 1h, 1i, S1, S3 and S4; percentage of (001) area: >80%). Therefore, by loading Au NPs on these two supports, most Au NPs located at the (101) (Au-TiO\(_2\) (101) catalysts) and (001) (Au-TiO\(_2\) (001) catalysts) surfaces, as evidenced by Figure S5. The typical Au-TiO\(_2\) catalysts are shown in Figure 1b [Au-TiO\(_2\) (101)] and Figure 1d [Au-TiO\(_2\) (001)].

The 3D visualizations and more details of these samples can be found in Figures S1-S4 and Movies S1-S4.
Firstly, the interface structures of Au-TiO$_2$ (101) and Au-TiO$_2$ (001) model nanocatalysts were investigated. Most observed Au-TiO$_2$ (101) interfaces (17 among 20, 85%) show incoherent structures with random orientation relationships. A typical HAADF-STEM image of the Au-TiO$_2$ (101) interface is shown in Figure 1g, viewing along TiO$_2$ [010] direction. A round-shape Au NP with a diameter of ~4.8 nm locates on TiO$_2$ (101) surface, and the interface does not show a preferential relationship. The (101) and (004) crystal planes of TiO$_2$ can be clearly identified, with interplanar spacings of 0.352 nm and 0.238 nm, respectively. The contacting interface is very small and the projection length of the interface is ~2.5 nm. The unwetting behavior shows a weak MSI between the Au NPs and the TiO$_2$ (101) surface. To illustrate intrinsic interfacial contact and get rid of the effect of size difference, we choose the ratio of interfacial length to diameter (IL/D) as a reference criterion. Several samples were further checked and the average IL/D is approximate 0.49 in a range from 0.44 to 0.58.

Different from Au-TiO$_2$ (101), most observed Au-TiO$_2$ (001) interfaces (15 among 20, 75%) have a preferential contacting relationship that TiO$_2$ (001) shares the plane with Au (111). A typical TEM image of the Au-TiO$_2$ (001) interface is shown in Figure 1j. The TiO$_2$ (002) lattice spacings are 0.475 nm, and the Au (111) lattice spacings are 0.236 nm. Compared with Au-TiO$_2$ (101) catalysts, the Au-TiO$_2$ (001) catalyst has a relatively larger interface, and the IL/D is 0.82 (Figure 1b), much larger than that of the Au-TiO$_2$ (101) interface (0.52, Figure 1a). The statistical analysis also shows the average IL/D ratio of the Au-TiO$_2$ (001) interface is 0.92 (in a range of 0.80-0.96), larger than that of Au-TiO$_2$ (101) interface (0.49). The different interface structures give direct evidence, that Au NPs attach more tightly on TiO$_2$ (001) surface than on TiO$_2$ (101) surface, which is consistent with previous theoretical prediction in literature.

Figure 1. The typical interface of the Au-TiO$_2$ catalysts. (a,b) Low-magnification HAADF-STEM images of TiO$_2$ (101) supports (a) and Au-TiO$_2$ (001) catalysts, respectively. (c,d) Low-magnification HAADF-STEM images of TiO$_2$ (101) catalysts (c) and Au-TiO$_2$ (001) catalysts (d), respectively. (e,f) High-magnification HAADF-STEM image (e) and the atomic structure (f) of TiO$_2$ (101) surface. (g) High-magnification HAADF-STEM image shows the typical interface between Au NP and TiO$_2$ (001) surface. (h,i) High-magnification HAADF-STEM image (h) and the atomic structure (i) of TiO$_2$ (001) surface. (j) The TEM image shows the typical interface between Au NP and TiO$_2$ (001) surface. The scale bars both in (e) and (h) represent 5 nm.

To explore how these two different MSIs affect the sintering behaviours of Au-TiO$_2$ catalysts, we performed in situ sintering experiments using Au-TiO$_2$ (001) and Au-TiO$_2$ (101) catalysts in ETEM. The samples were first heated to 500 °C at an oxygen environment (5×10$^{-2}$ Pa), and then we carried out the in situ observation. It should be noted that under such environments, the surface organic contaminants introduced during synthesis could be removed, as evidenced by EELS analysis (Figure S7). It has been discussed by Wang et al. that the reduction level of the TiO$_2$ supports are easily reduced by the electron beam irradiation, a fairly low electron beam dose was used in our experiments (~1 A/cm$^2$) to observe the intrinsic structure of Au-TiO$_2$ catalysts. Additionally, the reduction level of TiO$_2$ surfaces in the experiments is also controlled by inducing low pressure oxygen environment, which compensates the electron beam induced oxygen-loss (reduction) in the TiO$_2$ samples. The pressure is very low so that its effect on the sintering process can be neglected. During the sintering of Au-TiO$_2$ (101) catalysts, both PMC and OR processes were observed, and a typical sintering process is shown in Figure 2. At initial, seven particles with the similar size (~8 nm) are located on TiO$_2$ (101) surface, labeled from ① to ⑦, respectively (refer to Figure 2a). The projection area (PA) of each NP is estimated to quantify the contacting area, which indicates they started to coalesce. Meanwhile, the PA of particle ⑤, on the right side of the particle ⑥, changes from 66.5 nm$^2$ to 61.4 nm$^2$ (refer to Figure 2a and 2b), showing a typical ripening process. In the following process, the Au NPs ④ and ⑤ coalesced into one particle (Figure 2c), and the dynamic process is shown in Figure S8, and the PA evolves from 149.1 nm$^2$ to 160 nm$^2$. The PA of particle ⑤ decreased smoothly from 61.4 nm$^2$ to 23.4 nm$^2$ (Figure 2e). One large particle (PA: 172.1 nm$^2$) is left on the TiO$_2$ (101) surface (Figure 2d) in the end (708 s). Interestingly, the interface of the sintered large particle is also very small (Figure 2d), and the IL/D is ~0.45, similar with the unsintered Au NP (0.44 to 0.58). This also indicates the observed Au-TiO$_2$ (101) interface (Figure 1a) is an intrinsic structure and...
confirms a weak interfacial interaction between Au NP and TiO\textsubscript{2} (101) surface. In addition, the sintering between particles ② and ③ was also observed (Figure 2c-2d). The dynamic change of the projection area of each particle during the sintering process can be found in Figure 2e.

The situation was completely different on TiO\textsubscript{2} (001) surface. In the same experimental conditions (temperature: 500 °C; oxygen pressure: 5×10\textsuperscript{-2} Pa), neither notable PMC nor OR process of Au NPs was observed. A typical example is shown in Figures 3a and 3b, through a top view. At the beginning (Figure 3a), several Au NPs located on TiO\textsubscript{2} nanosheets, which dominated by (001) surface, separated with small distances (The minimum distance is less than 0.46 nm), which is the same order of magnitude as the sample in Figure 2. This time, these Au NPs were firmly attached to the substrate, in sharp contrast to the highly mobile Au NPs on TiO\textsubscript{2} (101) surface. Even after 2297 s, the sizes of the Au NPs did not show notable change (seeing Figure 3c), which shows a resistance of sintering of Au NPs on this surface. The side view images also confirms this conclusion and show strong interaction between Au NPs and TiO\textsubscript{2} (001) surface (Figures 3d and 3e). Since the TiO\textsubscript{2} nanosheets slightly rotated due to the damage of supporting carbon membrane, the locations of the Au NPs in Figure 3b are slightly different with those in Figure 3a. The Au NPs on (001) surface (between 10 and 40 nm\textsuperscript{2}) are smaller than those on (101) surface (between 40 and 160 nm\textsuperscript{2}). Normally, smaller NPs are considered to be easier to sinter due to their larger surface energies. The fact that the smaller Au NPs on (001) surface are more stable than the larger ones on (101) surface further verifies the sintering resistance of (001) surface. Note that the different size distribution of the Au NPs on the two surfaces could also be understood as a result from the facet-dependent sintering behaviour.

To understand this facet dependent sintering behavior, DFT calculations have been performed. The adsorptions of Au NP on the two surfaces (TiO\textsubscript{2} (001) and (101)) were studied firstly. A Au\textsubscript{20} cluster of pyramid structure with (111) surfaces was used as the model system\textsuperscript{[12]}. For Au\textsubscript{20} cluster, the adsorption energies on (001) surface ( -2.28 ~ -3.62 eV) is much larger than those on (101) surface ( -0.30 ~ -0.47 eV). It is consistent with the TEM observations that the preferential relationship exists between Au (111)-TiO\textsubscript{2} (001) interface, but not for Au-TiO\textsubscript{2} (101) interface. Further, the activation barriers in the two sintering mechanisms were investigated. The rate of PMC is mainly determined by the potential energy surface (PES) for the Au-TiO\textsubscript{2} interface. In this work, we estimate the roughness of the PES by calculating the adsorption energies ($E_{\text{ads}}$) of Au\textsubscript{20} on different adsorption sites of TiO\textsubscript{2} surfaces. The results show that the differences among $E_{\text{ads}}$ on different sites of TiO\textsubscript{2} (101) surface are quite small (within 0.18
eV), which indicates a rather flat PES. While, a rough PES is found for \( E_{ads} \) on TiO_2 (001) surface (\( E_{ads} \) differences reach 1.34 eV). This explains the prevented PMC of Au NPs on TiO_2 (001) surface and the mobility of Au NPs on TiO_2 (101) surface. The results are given in Figure 4. The same conclusion is also acquired from the DFT calculations of FCC Au_{79} cluster on the two surfaces (refer to Figure S9). In both sizes, the PES of TiO_2 (001) surface is much rougher than that of TiO_2 (101) surface, which indicates that the sizes of the NPs have little effects on the facet-dependent sintering behaviour.

Figure 4. The adsorption energies and configurations of a Au_{20} cluster on different adsorption sites of TiO_2 (101) surface and TiO_2 (001) surface, which shows the roughness of the potential energy surface of a Au NP on the two surfaces.

OR is caused by the net rate of the diffusion of the adatom on the substrate (AoS) from smaller NP to bigger NP.\(^{[13]}\) Apparently, the formation of the AoS is a prerequisite condition to OR. As shown in Figure 5, it is rate limited by a two-step interface-controlled detachment process. In step one, a metal atom moves off the NP through a transition intermediate state, referred as a “monomer on the particle” (MoP) by Wynnblatt and Gjostein, and becomes an adatom near the particle (AnP).\(^{[13]}\) The MoP is defined as a metal atom at the low-coordinated edge site of the NP that interacts weakly to the metal NP but strongly to the support.\(^{[14]}\) The activation barrier in this step comes mainly from the energetic difference between a MoP and an AnP, as shown below:

\[
E_1^s = E_{ads}^{MoP} - \left( E_{ads}^{MoP} + E_b \right) \tag{1}
\]

where \( E_b \) is the metal-metal bonding energy, and \( E_{ads}^{MoP} \) is the adsorption energy of MoP/AnP on the support surface.\(^{[14]}\) \( E_{ads}^{MoP} \) is coordination number dependent. As the coordination number of MoP is close to zero, the difference between \( E_{ads}^{MoP} \) and \( E_{ads}^{AnP} \) can be considered small. Therefore, \( E_1^s \) is mainly dependent on \( E_b \) which is independent on the MSI. In step two, the AnP diffuses away from the NP to become an AoS. The activation barrier in this step \( (E_2^s) \) is determined by the diffusion barrier of adatom \( (E_m) \) on the support surface. Thus, the MSI mainly affects the formation of AoS through \( E_m \). The pathways of the detachment processes of Au on anatase TiO_2 surfaces are shown in Figure 5. On TiO_2 (101) surface, the gold atom prefers to adsorb on the bridge site of the surface with the adsorption energy of -0.54 eV. The \( E_m^{101} \) is only 0.19 eV, which can be easily overcome at low temperature. On the other hand, the adsorption energy of a gold adatom on TiO_2 (001) surface is -2.74 eV and the \( E_m^{001} \) is much higher (1.31 eV). Thus, the AnP is difficult to move and to form AoS on the TiO_2 (001) surface. Without the formation of AoS, the OR could not occur. On the contrary, the easily formed AoS on TiO_2 (101) surface could help the OR to take place. Thus, the experimental observations are explained and it concludes that strong MSI can prevent OR process, while weak MSI can promote OR process.

Figure 5. (a) A schematic representation of the formation process of a Au adatom on the support TiO_2 anatase surface. (b, c) The energy pathway of the diffusion of a Au adatom on the TiO_2 (101) surface and TiO_2 (001) surface.

In conclusion, through Cs-corrected STEM and ETEM, we revealed a facet-dependent sintering behavior of Au-TiO_2 nanocatalysts. Through analyzing the interface structure, we found a preferential relationship could be formed at Au-TiO_2 (001) interface but not at Au-TiO_2 (101) interface, which indicates Au NPs attached on TiO_2 (001) surface more firmly than on TiO_2 (101) surface. During the in situ heating experiments, the sintering of Au NPs through both the OR and the PMC mechanisms was observed on TiO_2 (101) surface. Interestingly, the sintering-resistant Au NPs on TiO_2 (001) was unveiled. Through DFT calculations, the facet-dependent sintering behavior was fully explained by considering the adsorption energies of Au NP and diffusion barriers of Au adatom on different surfaces. This work not only gives the clear evidence of the atomic observation and theoretical understanding of the substrate effects on the sintering
of supported NPs, but paves the way for the rational design of efficient sintering-resistant catalysts.

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Keywords: sintering • Ostwald ripening (OR) • particle migration and coalescence (PMC) • metal–support interaction (MSI) • in situ TEM • Au-TiO2

Completely different sintering behaviours of Au nanoparticles on distinct anatase TiO$_2$ surfaces are unveiled by environmental TEM