1185 – *In Situ* Study of the Motion of Supported Gold Nanoparticles

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Supported metal nanoparticles constitute an important class of materials in heterogeneous catalysts. The active sites are mainly found on the surface of the nanoparticles so an often used typical design parameter is to maximize the surface for a given volume of material, i.e. Optimize s/v ~d^{-1}. Thus, size distribution of nanoparticles becomes a key factor to evaluate a catalyst performance and deactivation, although other factors can influence both of these parameters.

Particle growth by sintering is one of the main catalyst deactivation mechanism. This is the process where the population of larger particles grow at the expense of smaller particles resulting in a loss of active surface area. Studies of nanoparticles sintering [1] are often carried out ex situ and do not provide information of how the process occurs. Especially the motion of the nanoparticles on the oxide support and the dynamics at interface between nanoparticle and support. In this work, we will present three different motions of nanoparticles on the oxide support: rigid-body sliding, rigid-body rotation and layered movement via mass transport studied with atomic resolution.

Au/CeO_2 is a widely studied system used for the catalytic conversion of carbon monoxide to carbon dioxide. The typical interfacial relationship between nanoparticle and CeO_2 support is {111}Au // {111}CeO_2 which can occur in two distinct configurations [2]. The lattice spacing is 0.235 and 0.312 nm for {111} Au and {111} CeO_2 respectively, giving a 25% mismatch in lattice spacing. To accommodate this mismatch, a dislocation network with edge dislocations (T symbols in Figure 1) is formed, where every four Au (111) layers match three CeO_2 (111) layers (Figure 1). Our results indicate that gold nanoparticles slide along the oxide support/nanoparticle interface in a rigid-body manner. Interestingly, it seems as if the sliding process does not occur between the first interface gold layer (Au1) and first oxide layer(s1), instead it happens at the Au1 and Au2 interface. The blue dotted line shown on the figure indicates a point of reference. The Au nanoparticle moves upward by one Au (111) lattice spacing (around 0.235 nm) between 38.4 s and 39.2 s. While the interface layers (Au1 and s1) both remain at the same positions, suggesting a strong interactions between ceria and Au.

Another mechanism through which the nanoparticle can migrate on the support is through a mass transport process. Figure 2 shows a sequence of HRTEM images indicating the motion a Au nanoparticle moving on the oxide support through by this mechanism. Within 2 s, one (111) layer (indicated by red arrow) at the bottom of the particle disappears and a new (100) layer (indicated by blue arrow) populate the right corner (100) facet. The diffusion of atoms continues to move from the new (100) facet to the other (111) facet (indicated by yellow arrow) of the nanoparticle. As a result the whole particle moves laterally on the oxide substrate by 0.235 nm with respect to the substrate, i.e. one (111) lattice space.

Apart from the above two migration processes, we also observed a rigid-body rotation of the nanoparticle with the rotation axis parallel to the interface, which is different from the phenomenon reported in [3].
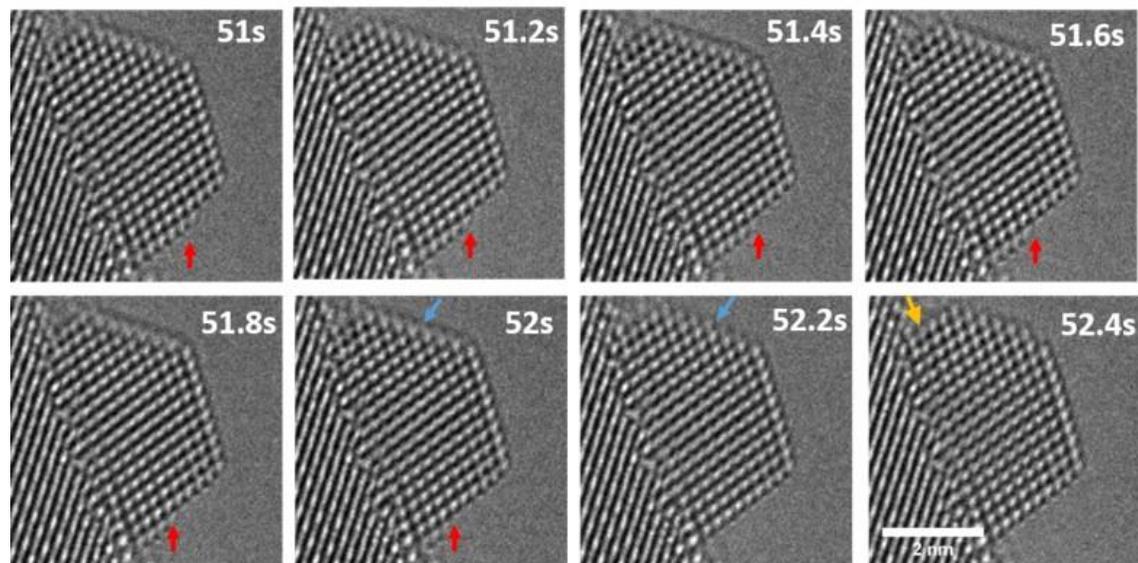
Our atomic scale observation of nanoparticle movement on oxide substrates sheds light on the underlying processes of sintering, especially through particle migration and coalescence.

Figure 1. Rigid-body motion of a supported gold nanoparticle. The three red lines indicate the positions of dislocations. The interface layers are labeled s1 and Au1. The layer labeled Au2 is the second layer inside the Au particle counting from the interface, s2 is the second CeO_2 layer counting from the interface. The "T" symbol indicates the position of dislocations at the interface, where additional Au columns are present.

Figure 2. Red arrows indicate an atomic layer disappearing column-by-column on the (111) facet from 51s to 52s. Blue arrows indicate a newly formed layer on the (100) facet. At 52.2s, four columns appear at the blue arrow indicated on the (100) facet, two more columns are present in the next frame. Experimental conditions: room temperature, 4.5 Pa CO.

References

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