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A Study of Reaction Induced Sintering in Au Catalysts

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Reaction induced sintering has long been observed in catalysis studies, but very few studies have been carried out to characterize and provide a quantified description of reaction induced sintering. The major reason might be that the particle size change resulting from reaction is rather small. Another reason might lie in the difficulty of analyzing nanoparticles on a complicated surface, as in a real catalyst, where surface defects are prevalent.

In the study of Au/TiO_2 catalysis for CO oxidation at room temperature, it is well known that particle size plays a crucial role in the catalytic properties of Au catalysts. Since the as-prepared (uncalcined) Au/TiO_2 catalysts are the most active ones, and the initial gold particle size is extremely small (less than 2 nm), hence the change in gold particle size introduced by reaction heat is large. At the same time, Au/TiO_2 model catalysts were used as a simple and controllable environment. STEM Z-contrast imaging technique was used to accurately measure the size of gold particles due to its sensitivity to heavy elements and ease of interpretation.

Multiple (100)-oriented single crystal TiO_2 TEM samples were prepared by common TEM sample preparation methods and were annealed at high temperature in oxygen to obtain a (1x1) surface. TEM and XPS were carried out to verify the surface condition and cleanness. Gold nanoparticles were then deposited onto those TEM samples using a PVD method without exposure to air. The samples followed one of the treatments listed in Table 1, respectively. A JEOL 2100F microscope was then used to characterize these samples.

The STEM images of Au/TiO_2 model catalyst samples after various treatments are shown in Figure 1. Little difference can be seen between the as prepared sample (Figure 1a) and the sample annealed at 100^oC (Figure 1b). On the sample annealed at 200^oC, the number of ultra small (less than 2 nm) gold particles was drastically reduced, since sintering took place and small particles migrated and agglomerated with big particles. At 300^oC, the inter-particle space was increased and very large particles were formed. For samples which underwent reaction gas treatment, no apparent changes in particle size and morphology were observed (Figure 1e). Only carefully carried out statistical analysis can help tell the difference. In Figure 2a, the size of more than 300 particles was measured and counted. The trend of particle size increase can easily be seen for the as prepared sample, the sample annealed at 100^oC, and the sample treated in reaction gas. Similarly, a graph (Figure 2b) showing the increase in particle size for the samples annealed at 200^oC and 300^oC can be drawn, by measuring and counting more than 200 particles.

The above results indicate that the effect of reaction heat produced on the gold surface is similar

to annealing the whole sample at a temperature between 100°C and 200°C. This is a surprisingly high number compared to the temperature observed during reaction. Although it is extremely difficult to measure the local heating produced by reaction on the surface, this set of experiments essentially demonstrated a new way to roughly measure it by evaluating the effects of this local heating. That is, the temperature of the Au particle-support interface is probably between 100°C -200°C during reaction.

References

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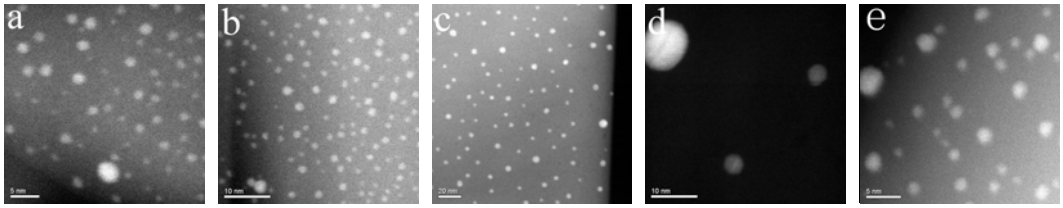

Fig. 1. STEM Z-contrast image of Au/TiO_2 model catalyst sample: (a) as prepared; (b) annealed in air for 1 hour at 100°C; (c) annealed in air for 1 hour at 200°C; (d) annealed in air for 1 hour at 300°C; (e) after 1 hour CO oxidation reaction gas treatment at room temperature.

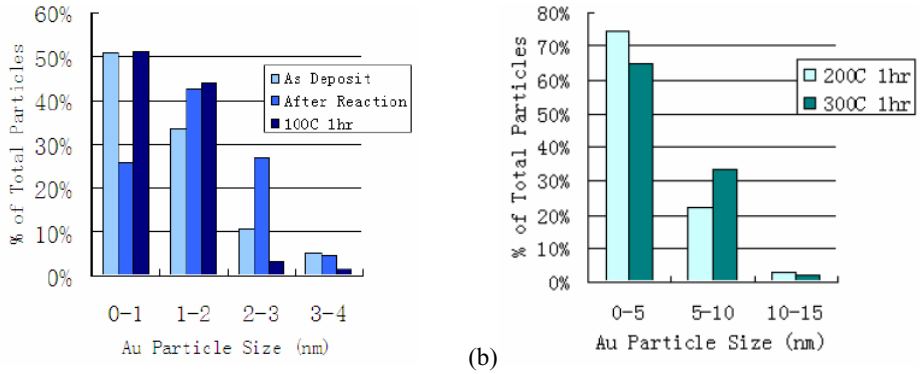

Fig. 2. (a) Size distribution of gold particles for as prepared sample, sample annealed in air for 1 hour at 100°C and sample treated by reaction gas for 1 hour at room temperature, respectively. (b) size distribution of gold particles for samples annealed in air for 1 hour at 200°C and 300°C respectively.

Table 1. Parameters used in reaction induced sintering experiments

Treatment	Temperature (°C)	Time (Hr)	Environment (1 atm)
Annealing	100	1	Air
Annealing	200	1	Air
Annealing	300	1	Air
Gas Treatment	RT	1	Reaction Gas (1%CO, 2.5%O_2, balance He)

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