Highly catalytic performance of porous gold with twin boundary defects

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Since discovery of extraordinary catalytic properties such as CO oxidation [1] of porous gold (PG) this remarkable material has become a new class of catalysts with potential applications in a wide range of fields [2]. Samples of PG can be prepared, e.g., by leaching from alloys of Au with less noble elements such as Ag, Cu or Al. The origin of the catalytic activity of porous gold has been in literature widely discussed. To date, it is generally accepted that just the residual elements as, e.g., Ag which binds oxygen and its traces always remain in samples of porous gold play very important role in explanation of the extraordinary catalytic activity of porous gold. Recently, we reported that porous gold (PG(Al2Au)) prepared by de-alloying the Al2Au compound (i.e., despite missing Ag) with 10% NaOH aqueous solution which exhibited highly active for CO oxidation [3]. The mechanism of formation of the catalytically active sites described in our work represents thus a different contribution to the catalytic activity of porous gold than the effect of the residual elements. At this presentation, we will report high catalytic performance of PG(Al2Au) for CO oxidation and selective hydrogenation of acetylene and propose their possible reaction mechanism.

As shown in Fig. 1(a), PG(Al2Au) exhibited the higher catalytic performance than a conventional supported gold nanoparticles catalyst (Au/TiO2 (WGC)). The origin of these high activities of PG(Al2Au) is attributed to the high density of defects in the three-dimensional network of nanoscale ligaments (Fig. 1(b)). In high-resolution TEM images of the ligaments we observed high density of twin boundaries (TB) with nanoscale domain sizes (ca. 3 - 10 nm). As shown in Fig. 1(c), these TB defects in the fcc lattice of PG(Al2Au) are able to form active sites for the catalytic reaction on the surface because low-coordinated Au sites created by the TB defects (Colors indicates the coordination numbers (CN) of surface atoms). The twinning defects on the 211 surfaces of PG(Al2Au) can create highly reactive closed-packed rows of Au sites with coordinations CN = 6 and CN = 5 as the W-chains (Fig. 1(c): see Top view). Using DFT methods, it is shown that on these under-coordinated atomic sites oxygen or hydrogen adsorption, and subsequent reaction can proceed via Langmuir-Hinshelwood (LH) mechanism. The reactivity of the W-chains in the PG(Al2Au) can thus explain not only the catalytic activity toward the CO oxidation but also toward the semi-hydrogenation of C2H2. Twinning in the fcc lattice is a new systematic mechanism for formation of highly reactive under-coordinated surface atoms (i.e., CN = 6 and 5) in nanostructured catalysts.

Figure 1. (a) Catalytic properties of various gold catalysts, (b) HRTEM and SEM images of PG(Al2Au) and (c) Schematic views of the fcc Au(11-2) surface with the twin boundary (TB) defects.

References

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