

## Catalytic performance of surface-modified intermetallic In<sub>2</sub>Au for alcohol oxidation

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Nano porous gold (NPG) is a bulk gold with nano porous structure and is generally prepared by selective leaching of other elements than Au from precursor alloys. It shows high catalytic activity for various reactions including the oxidation of CO, primary and secondary alcohol [1]. Its catalytic activity is affected by some factors including residual species and surface morphology. While it is well known that active residues such as Ag play a key role in oxidation reactions due to the ability of O<sub>2</sub> dissociation, morphological effect on catalysis especially without them is not yet fully understood [2,3]. In this study, we focused on the effect of the surface structures of NPG by varying the leaching conditions. To this end, we conducted controlled leaching of In<sub>2</sub>Au intermetallic, which has well-ordered CaF<sub>2</sub> type structure, by hydrochloric acid and investigated the catalytic activity for benzyl alcohol oxidation.

In<sub>2</sub>Au intermetallic compound was crashed and sieved to a powder smaller than 20 μm and was immersed into hydrochloric acid for  $t$  (= 0, 0.25, 4, 20 h) to leach In. The structural change of the powder was studied as a function of  $t$  using XPS, ICP-MS, SEM, XRD. The XPS for the Au 4f shows the gradual peak shift from 84.8 eV to 83.8 eV, whereas the relative intensities of the In 3d peak (444.6 eV) with respect to Au 4f<sub>7/2</sub> peak decrease with  $t$  (Fig. 1). The ratio of Au in the powders were estimated by ICP-MS to be 32, 33, 35 and 75 at% at  $t$  = 0, 0.25, 4 and 20 h, respectively. These indicate that only the surface area of the In<sub>2</sub>Au powder was converted to Au<sup>0</sup> at  $t$  = 4 h, while the In<sub>2</sub>Au powder is completely converted to Au<sup>0</sup> at  $t$  = 20 h. SEM and XRD also support the assumption that only the surface was modified at  $t$  ≤ 4 h.

Figure 2 plots the turnover frequencies for catalytic oxidation of benzyl alcohol obtained by normalizing the reaction rate by the surface area. Notably, the powder obtained at  $t$  = 4 h shows much higher activity than that at  $t$  = 20 h, indicating that the catalytic properties of the Au<sup>0</sup> surface of the powders at  $t$  = 4 and 20 h are significantly different. One of the plausible explanations is that the surface of the powder prepared at  $t$  = 4 h has a larger population of coordinatively unsaturated Au sites active for oxidation reactions [3].

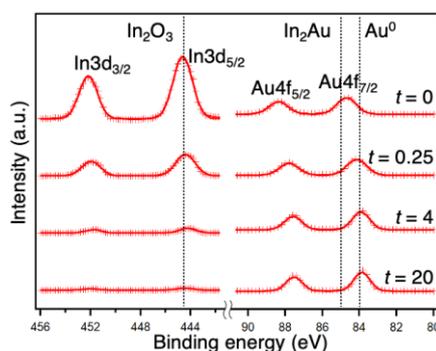


Figure 1. X-ray photoelectron spectra as a function of leaching time  $t$ .

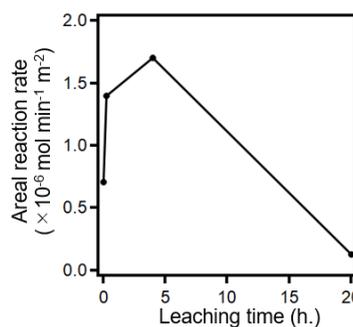
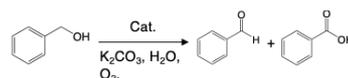


Figure 2. Reaction rates normalized by each surface area.

[1] Wittstock, A. and Bäumer, M. *Acc. Chem. Res.* **2014**, *47*, 731. [2] Wittstock, A. *et al J. Phys. Chem. C* **2009**, *113*, 5593. [3] Kameoka, S. *et al. J. Chem. Phys.* **2016**, *144*, 034703.