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Catalyst Optimization from Structural and Chemical Analysis of Individual Au-Pd Nanoparticles Using Aberration Corrected STEM

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Structural and chemical information acquired from individual bimetallic nanoparticles are indispensable for understanding and optimizing their catalytic properties. In this work, Au-Pd/TiO_2 catalysts prepared by different methods are compared by HAADF imaging and XEDS analysis in an aberration corrected JEOL 2200FS STEM. Developing preparation-structure-performance correlations in this way has allowed us to devise a novel catalyst preparation method for Au-Pd/TiO_2 catalysts, which display a 3-fold improvement in catalytic performance, without changing the metal content or precursor, for the direct synthesis of hydrogen peroxide from molecular hydrogen and oxygen.

We first studied two commonly used synthesis methods for preparing Au-Pd/TiO_2 catalysts, namely conventional wet-impregnation (C_{Im}) and sol-immobilization (S_{Im}). The C_{Im} method involves adsorption of aqueous solutions of $HAuCl_4$ and $PdCl_2$ salts onto the TiO_2 support, followed by drying and a calcination treatment in air. This results in the formation ~10 nm Pd-rich shell/Au-rich core particles, along with um scale Au-rich particles and sub-nm Pd–rich clusters. Despite the limited control over particle size and composition, the C_{Im} method has the important merit of simplicity. In the case of the S_{Im} method, Au-Pd nanoparticles were pre-formed in the aqueous phase by simultaneously reducing $HAuCl_4$ and $PdCl_2$ in the presence of a stabilizer ligand PVA, and subsequently immobilized onto the TiO_2 support. This results on the formation of 1-6 nm homogeneous Au-Pd alloy particles, which display a superior catalytic performance to the C_{Im} materials. However a systematic size-dependent composition variation was also identified in S_{Im} materials, indicating that the composition control by S_{Im} is limited. Furthermore, the S_{Im} method is not easy to scale-up for mass production.

Our goal was to develop a new synthesis method that is as simple as C_{Im}, yet provides even better size and composition control than S_{Im}. We achieved this by first adding an excess amount of Cl^-, in the form of HCl, into the precursor solution used in the original C_{Im} route, and then replacing the air calcination treatment with a heat treatment in a reducing 5% H_2/Ar atmosphere. There are several benefits of using this so-called modified impregnation method (M_{Im}). Firstly, the heat treatment in a reducing atmosphere shrinks the mean particle size and also eliminates core-shell morphology structures. As shown in Figure 1, the M_{Im} catalyst subjected to a reducing atmosphere has a 1-6 nm particle size and a homogeneous alloy structure (Figs. 1 (a) & (b)), In comparison, the M_{Im} material calcined in air generates particles which are ~10 nm in size and have distinctive Pd-rich shell/Au-rich core structures (Figs. 1 (c) & (d)). Secondly, the effect of the excess Cl^- was to direct Au into the bimetallic nanoparticles, instead of the um-scale

particles. As shown in Figure 2, the average Pd concentration in the nanoparticles progressively drops from 75wt% to 51wt% to 30wt% if using 0M (black triangles), 0.58M (red squares) or 2M (blue circles) excess HCl respectively. It is remarkable that using this simple M_{Im} technique, the size, structure and composition of the Au-Pd alloy particles could all be successfully controlled to a much higher degree of precision than the C_{Im} or S_{Im} methods. The optimum productivity of hydrogen peroxide for the M_{Im} material reached 99 mol $H_2O_2 kg_{cat}^{-1} h^{-1}$, which is at least a factor of three better than materials prepared by the more conventional methods (32 mol $H_2O_2 kg_{cat}^{-1} h^{-1}$ for S_{Im} material and 23 mol $H_2O_2 kg_{cat}^{-1} h^{-1}$ for C_{Im} material).

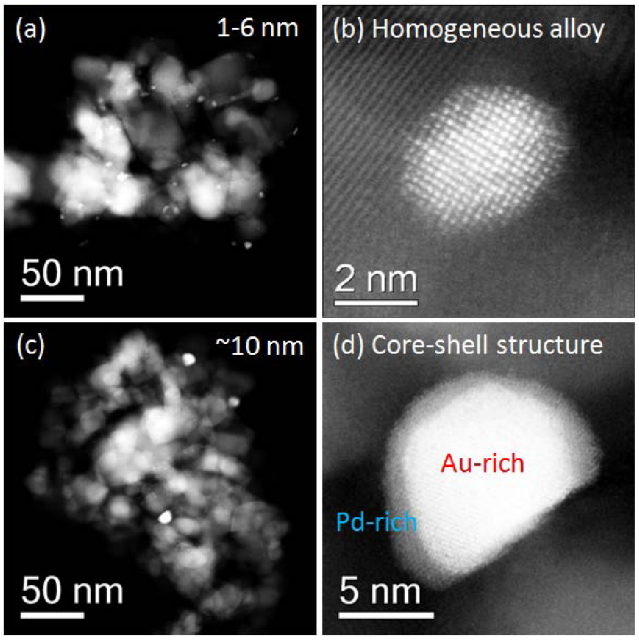

Figure 1 HAADF images of Au-Pd/TiO_2 catalysts prepared by M_{Im} with 0.58M excess HCl, but subjected to different heat treatments. The sample in (a, b) was heat treated at 400°C in a reducing (5% H_2/Ar) atmosphere, whereas that shown in (c, d) was calcined at 400°C in air. It is clear that treatment in a reducing atmosphere gives rise to smaller homogeneous alloy particles, whereas calcination in air creates larger Au-rich core-Pd rich shell particles.

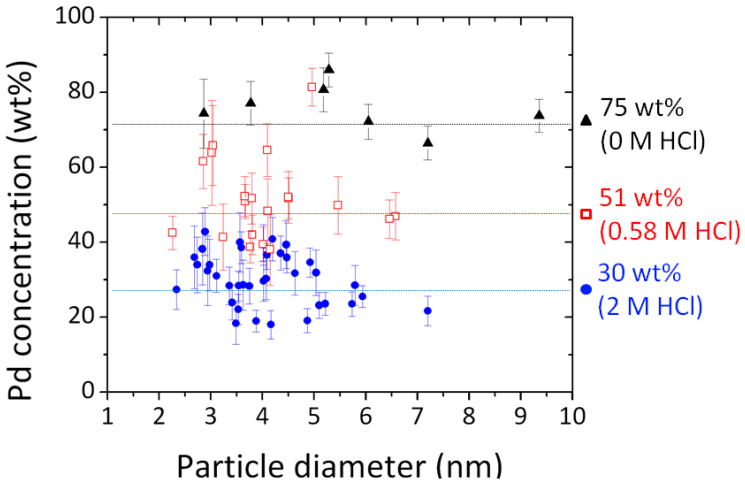

Figure 2 Individual particle compositions plotted against particle diameter for Au-Pd/TiO_2 catalysts prepared by M_{Im} with 0 M (black triangles), 0.58M (red squares) and 2M excess HCl (blue circles) added. The average Pd concentration drops from 75wt% to 30wt% with the increase in amount of excess HCl used, indicating that Au is being more efficiently incorporated into the nanoparticles.

Reference: 1. Sankar, M., He, Q., Kiely CJ., Hutchings GJ. *et al. ACS Nano*, 2012, **6**, 6600-6613.

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