

Catalyst design and fabrication for ethanol oxidation

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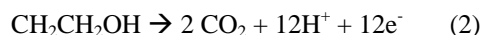
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Ethanol is easy to store and transport, and can be simply produced in great quantity through fermentation of sugar containing raw materials. The high energy density of 8.01 kWh kg⁻¹ of ethanol is comparable to that of methanol. The direct alcohol fuel cells (DAFCs) working with ethanol have received therefore growing attention for applications as power sources of electric vehicles.

The electrooxidation of ethanol may proceed via two pathways, i.e.



and



It is obvious that the path (2) is more desirable for energy conversion of DAFC, because it can release 12 electrons per ethanol molecule. The key issue to catalyze ethanol oxidation through the path (2) consists in that the catalyst should have a high reactivity to break the C-C bond in ethanol molecule. As platinum group metals (PGMs) are actually the irreplaceable catalyst materials employed in the DAFCs, to design and fabricate PGMs and Pt-based catalysts with high activity, selectivity and durability is one of key issues in electrocatalysis, especially those catalysts that could bear a high reactivity to break the C-C bond are most important for developing the direct ethanol fuel cells (DEFCs).

This communication will report our recent progresses made on the catalyst design and synthesis for ethanol oxidation to promote the efficiency of energy conversion in DEFCs. As the ethanol oxidation takes place at the surface of catalysts, the surface structure of catalysts is the crucial parameter to determine their performances. Based on our long-term studies on the surface structure-catalytic functionality by employing single crystal planes as model catalysts, we have focused on, in recent years, the design of PGMs and Pt-based catalysts of high performances from a microstructure point of view, and have made achievements in the following three aspects:

- (1) **Tailoring the surface atomic arrangement of well-defined nanocrystal catalysts.** Through developing the electrochemically shape-controlled synthesis¹, well-defined Pt and Pd nanocrystal catalysts have been successfully obtained, such as tetrahedral nanocrystals (THH NCs) enclosed with {hk0} high-index facets, and Trapezohedral nanocrystals (TPH NCs) bind with {hkk} high-index facets. As the high-index facets of these face centered cubic (fcc) metals contain a high density of step atoms that constitute the catalytic active centers, these well-defined Pt and Pd nanocrystals of high-index facets exhibited high activity for ethanol oxidation¹⁻⁶;
- (2) **Tuning the electronic structure of Pt-based nanocatalysts.** The electronic structure of catalysts determines also the catalytic performances, and can

be turned either by surface decoration using foreign adatoms, or through alloying Pt with other metals. Different adatoms such as Bi, Ru and Au were used to decorate the THH Pt NCs^{7,8}, and both THH and TPS Pt-based alloy nanocatalysts were prepared by electrochemically shape-controlled synthesis⁹;

- (3) **Tuning the chemical structure of Pt-based nanocatalysts.** The chemical structure was tuned by preparation of platinum-lead oxide nanocomposite (Pt-PbO_x NC)¹⁰. The PbO₂ has good resistance to corrosion, high electronic conductivity, excellent stability, and low cost. It has a high reactivity for degradation of organic pollutant molecules through electro-generation of •OH radicals. Thus the design and preparation of the Pt-PbO_x NC has confirmed the high activity to break the C-C bond in ethanol, and 27 folds long-term catalytic performance was achieved on the Pt-PbO_x NC catalyst referring to that of commercial Pt black catalyst.

The above strategy of design and fabrication of high efficient catalyst for ethanol oxidation has been also proved by in situ FTIR studies at a molecule level. The spectral results revealed that the catalysts obtained through the mentioned strategy exhibit a high reactivity to break the C-C bond of ethanol that is at least 2 folds larger than that of commercial Pt catalysts.

Acknowledgement: The study was supported by natural science foundation of China (21021002).

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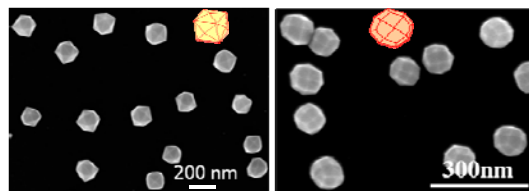


Figure 1. SEM imagies of THH and TPH Pt NCs and corresponding models.