Abstract

Noble metals are widely used and researched in heterogeneous catalysis due to remarkable catalytic performances. First principle density functional theory (DFT) method provides a powerful way to perform large-scale and high-computing simulations to investigate the design rule in heterogeneous catalysis theoretically. In this thesis, we have investigated on the catalytic activity of palladium (Pd) and platinum (Pt) based bimetallic alloy with non-precious transition metals by density functional theory calculations. This thesis contains three parts: firstly, we have studied overlayer model of Pd-Cu and Pt-Cu bimetal alloy; secondly, we have studied the Pd monolayer model of Pd monolayer supported on Pd-M (M=Cu, Fe, Ni) intermetallic alloy; thirdly, we have studied the single atom alloy (SAA) model of dispersedly distributed Pt atoms doped in Cu(111) surfaces. The major results of the thesis are as follows. It is found out that the number of Pd (or Pt) cover layer can effectively influence the surface Pd (or Pt) activity. This is explained and supported by *d*-band center theory, where the *d*-band center of Pd (or Pt) atom is modulated by both the number of cover layer and substrate charge transfer. The proposed Pd-Cu bimetallic alloy is found to perform effectively as CO oxidation catalyst and the proposed Pt-Cu bimetallic alloy can be used as fuel cell anode materials with enhanced CO-tolerance ability. The famous Brønsted-Evans-Polanyi (BEP) relation is used to analyze the catalytic trend. For intermetallic alloy case, it is experimental proved that Pd-Cu alloy can be transformed from face-center cubic (*fcc*) alloy to body-center cubic (*bcc*) alloy, and Pd-Fe and Pd-Ni alloy can be transformed from *fcc* alloy to face-centered tetragonal (*fct*) alloy. We have investigated on the activity of these intermetallic alloy as electrocatalysts for oxygen reduction reaction (ORR). The enhanced performance is ascribed to moderate adsorption strength. For single atom alloy case, Pt atoms tend to dope on surface (slab model) or outmost shell (nanocluster model) sites. The H_2 dissociation ability is improved by subsequent subsurface or inner Pt dopant.

Publication list

1. Liu, J.; Fan, X.; Sun, C. Q.; Zhu, W., DFT Study on bimetallic Pt/Cu (111) as Efficient Catalyst for H_2 Dissociation. *Applied Surface Science* **2018**, 441, 23-28.

2. Liu, J.; Fan, X.; Sun, C. Q.; Zhu, W., DFT Study on Intermetallic Pd–Cu Alloy with Cover Layer Pd as Efficient Catalyst for Oxygen Reduction Reaction. *Materials* **2017**, 11 (1), 33.

3. Liu, J.; Fan, X.; Sun, C. Q.; Zhu, W., Layer effect on catalytic activity of Pd-Cu bimetal for CO oxidation. *Applied Catalysis A: General* **2017**, 538, 66-73.

4. Liu, J.; Fan, X.; Sun, C.; Zhu, W., Transparent conductivity modulation of ZnO by group-IVA doping. *Chemical Physics Letters* **2016**, 649, 78-83.

5. Liu, J.; Fan, X.; Sun, C.; Zhu, W., Oxidation of the titanium (0001) surface: diffusion processes of oxygen from DFT. *RSC Advances* **2016**, 6 (75), 71311-71318.

6. Liu, J.; Sun, C.; Zhu, W., Origin of efficient oxygen reduction reaction on Pd monolayer supported on Pd-M (M=Ni, Fe, Fe) intermetallic alloy. Submitted to *Electrochimica Acta*.

7. Liu, J.; Sun, C. Q.; Zhu, W., A comparative study on single atom alloy of Pt doped Cu flat surface and nanoclsuter. (In preparation)