

PROBING ACTIVE PHASE OF Pt-Fe MODEL CATALYSTS USING STM

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INTRODUCTION

Platinum Iron (PtFe) bi-component catalysts display prominent low-temperature activity towards preferential oxidation of the CO in the excess of H₂ (PROX) for the purpose of removal of trace CO in H₂ proton exchange membrane fuel cell (PEMFC), a promising and high efficient hydrogen energy converter from chemical energy to the electric energy^[1]. FeO nanostructures supported on the Pt(111), which contain density of coordinated unsaturated Fe (CUF) atoms at the metal/oxide interface, highly activate the O₂ molecules and therefore solve the CO-poisoning problem of Pt-based catalysts. In contrast, at the absence of the H₂ atmosphere, this FeO active phase would undergo deactivation with the reactivity of CO oxidation quickly dropping down.

The objective of this work is to get a better understanding of how the FeO active phase responds to the reaction condition and the corresponding deactivation mechanism. Furthermore, we investigated the active phase of PtFe alloy model catalyst, whose powders show high activity and enhanced stability of the CO oxidation in the excess /absence of H₂^[2].

EXPERIMENTS / FUNDAMENTAL OF THE PROBLEM / EXAMINATIONS

In this work, both low temperature and near ambient pressure Scanning Tunneling Microscopy (LT-STM & NAP-STM), were used for the in-situ investigation of the fine structure of well-defined FeO/Pt(111) and PtFe surface alloy model catalyst before and after exposure to reaction gas.

Preparation of supported FeO/Pt(111): The FeO nano-islands were deposited onto the Pt(111) surface by evaporating Fe atoms in 1.3×10^{-7} mbar O₂ at the clean Pt substrate temperature between 150 and 300 K. The as-deposited FeO nano-islands were then annealed to 600 K, leading to the formation of well-ordered Fe-edge terminated FeO nanostructures.

Preparation of FePt surface alloy: The PtFe surface alloy was prepared through the deposition of low coverage Fe ($\Theta_{\text{Fe}} < 1$ ML) onto Pt substrate at 460 K or high coverage Fe ($\Theta_{\text{Fe}} > 1$ ML) with post-annealing at 650 K. The as-prepared alloy surface exhibited network of stripes and consisted of Pt skin layer and Pt₃Fe layer underneath.

RESULTS AND DISCUSSION

The triangular Fe-edge terminated FeO nano-islands would reversibly transform to the O-edge terminated FeO at $\sim 10^{-8}$ mbar O₂. However, this bilayer FeO would gradually turned to the tri-layer FeO₂ when directly exposed to 0.26 mbar O₂. In contrast, FeO nano-island could remain stable under the PROX reaction gas with the pressure even increased to 1 bar.

Significant morphology changes occurred when the PtFe surface alloy exposed to 5×10^{-7} mbar O₂. A large density of nanoclusters, characteristic of one protrusion in the middle surrounded by dark contour, dominated the surface and could be attributed to the embedding Fe₃O_x nanostructures. Furthermore, massive segregation of subsurface Fe took place when exposed to the 0.05 mbar O₂, which dramatically increased the density of oxide-metal interface. Meanwhile, this PtFe surface alloy model catalyst also showed better activity of CO oxidation than Pt(111) at room temperature.

CONCLUSION

The bilayer FeO nanostructures exhibited advantages towards O₂ activation through the reversible transformation from Fe-edge to O-edge at lower O₂ pressure and remain stable even at realistic PROX condition. However, It would gradually transformed to tri-layer FeO₂ after exposure to O₂ at the near ambient pressure, which was the main deactivation mechanism of PtFe catalysts at H₂-lean reaction condition.

PtFe surface alloy, consisting of Pt-skin layer and Pt₃Fe subsurface layer, exhibited high reactivity and enhanced stability towards CO oxidation. Extremely small embedding Fe₃O_x nanoclusters formed at lower lower O₂ pressure. In contrast, significant segregation took place and supported FeO_x nanoclusters from subsurface layer dominated the surface after exposure to O₂ at the near ambient pressure. The newly-formed FeO_x nanoclusters with considerable metal/oxide interface and this segregation process should be responsible for high reactivity of CO oxidation and enhanced stability, respectively.

Since now, we have demonstrated the high performance of PtFe model catalysts in the solid-gas interface towards CO oxidation. However, the real PtFe catalysts of PEMFC operate at the solid-gas-liquid ternary phase interface, that is, the FeO/Pt nanoclusters are surrounded by the liquid atmosphere. So next step, we will keep on surveying whether the activity and stability of FeO/Pt(111) still remains at liquid atmosphere^[3].

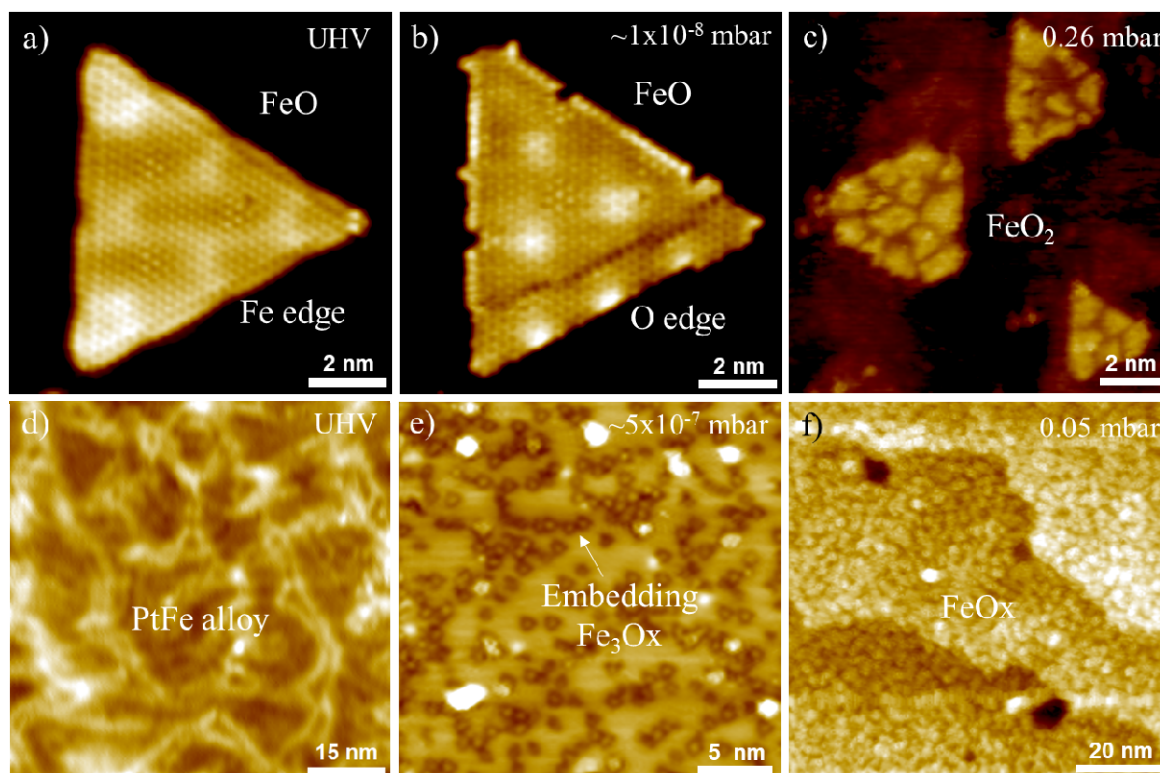


Fig.1 STM image of (a-c) FeO/Pt(111) and (d-f) PtFe alloy exposed to O₂ from UHV to NAP.

REFERENCES

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