

Direct Conversion of Methane to Valuable Chemicals Using Single-Atom Catalysis

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Major Goals and Objectives

This ACS PRF sponsored project builds around rational design of highly effective single-atom catalysts for the conversion of light alkanes, particularly methane, to valuable chemical products that will solve such problems as efficient utilization of natural and oil-associated gas, and environmental protection. The major goal of this PRF project is to create nanostructured site-isolated catalysts, in the form of “nanobowl” as well as intermetallics. Specifically, our research aims at understanding:

- Catalyst synthesis for optimizing the thermal stability using atomic layer deposition (ALD)
- The catalyst active site(s) under typical reaction conditions
- The selectivity to ethylene and aromatics controlled by the coordination and the accessibility of the active sites.

Achievements

With the support of PRF grant, great efforts have been taken to develop new synthesis strategy using ALD to design and synthesize advanced catalysts and kinetic test of the catalysts. In this period, the focus is to create site-isolated active sites in the form of intermetallic alloys which are expected to be thermodynamically favorable under reaction conditions.

One example of MO/M catalysts is shown in Figure 1 where inverse ZnO/Pt nanoparticles prepared by atomic layer deposition (ALD) are supported on spherical alumina support. In this catalyst, the thermal stability of the 1 nm sized Pt particles dramatically increases with the presence of the

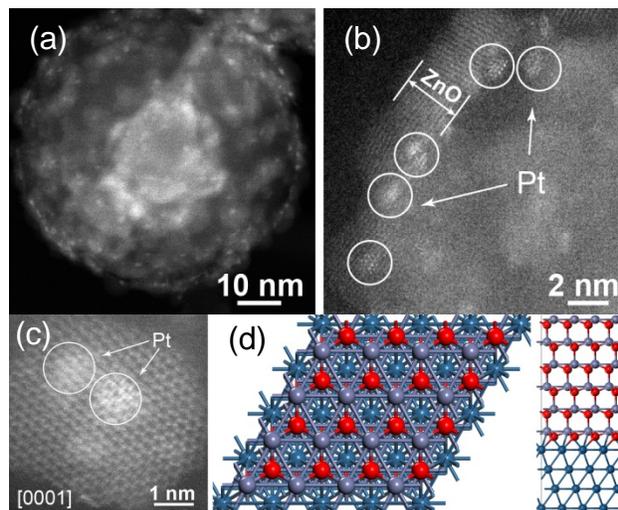


Figure 1. (a-b) Side-view and (c) top-view of HAADF-STEM images of ZnO/Pt/spherical Al_2O_3 , and (d) top-view and side-view of the monolayer ZnO supported on Pt. Pt-blue. Oxygen-red. Zinc-purple. Lattice mismatch is less than 10%.

overlayer ZnO. The catalysts exhibit interesting properties due to the presence of new interfaces as well as the metal-to-ligand charge transfer. In addition, the property of the catalysts can be further tuned by carrying out proper treatment, e.g., partially reduction in hydrogen. The catalyst could form an intermetallic PtZn-shell and Pt-core catalysts where the surface consists of uniformly isolated Pt sites which favor light alkane dehydrogenation and suppressed cracking and hydrogenolysis. The metallic Zn could lower the occupied Pt 5d valence bands and thus weaken the strength of surface adsorption, avoiding totally oxidation.

The composition and structure of intermetallics were carefully controlled by the number of ALD cycles and deposition sequence of each component. The existence of intermetallics were confirmed by Pt L₃ edge X-ray absorption spectroscopy (XAS) shown in Figure 2. The L edges (*p* → *d*) were employed to study the metal-to-ligand charge transfer because the valence *d* electrons are particularly relevant for catalysis. The X-ray absorption fine structure (EXAFS) revealed that the geometric structure of Pt evolved and the data fitting is illustrated in Table 1. A Pt-Zn contribution was fit in ZnO/Pt/Al₂O₃ with a coordination number of 4.5 ± 0.3 at an average bond distance of 2.61 Å. It indicates that the PtZn intermetallic phase was ready formed.

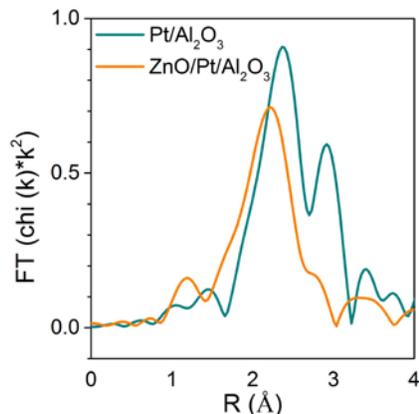


Figure 2. Pt L₃ edge EXAFS spectra of Pt/Al₂O₃ and ZnO/Pt/Al₂O₃.

Table 1. Pt L₃ EXAFS data fitting

Catalyst	Shell	CN	R(Å)
Pt/Al ₂ O ₃	Pt-Pt	5.9	2.69
ZnO/Pt/Al ₂ O ₃	Pt-Pt	2.5	2.78
	Pt-Zn	4.5	2.61

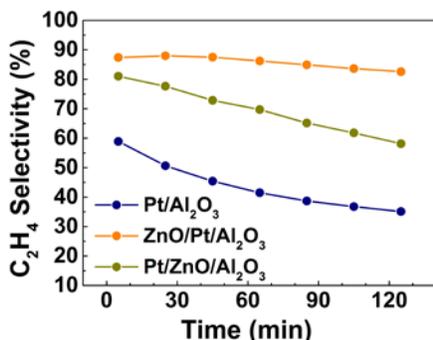


Figure 3. ODH of ethane tested at 833 K in 18% C₂H₆, 6% O₂, and balance with helium with flow rate 50 sccm.

As shown in Figure 3, it is possible to tune the reactivity and selectivity by combining the geometric and electronic effects of monolayer ZnO supported on Pt. In this kinetic test, ethane oxidative dehydrogenation (ODH) was used as the probing reaction. As ethane is one of the major components of the nature gas and the desired product ethylene is one of the most produced building blocks in petrochemical industry, the ODH of ethane reaction is strongly relevant to petroleum research. In the presence of ZnO as a promoter, the selectivity to ethylene dramatically improved as compared the unprompted Pt/Al₂O₃ catalysts. In addition, the inverse, monolayer ZnO/Pt/Al₂O₃ exhibited the best stability and reactivity possibly owing to having both ZnO/Pt and Pt/Al₂O₃ interfaces. The presence of overcoated ZnO may offer additional thermal stability to the 1 nm Pt catalysts.