

Nanostructured Catalysts for Hydrogen Generation from Renewable Feedstocks

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Objectives

The research program is directed towards the development of highly active and selective catalysts for the production of hydrogen from renewable alcohols. The objective is to gain fundamental understanding of complex,

multi-component catalysts through an investigation of catalytic processes occurring on system sub-components (the metal phase and the support) and synergistic interactions among the catalyst system components. To facilitate the mechanistic and reaction studies, we synthesize catalysts that are well-defined: single phase, uniform composition metallic alloy powders. We also synthesize oxides of controlled morphology that expose well-defined single facets so that the role of the oxide phase can be studied. These catalysts are studied using novel analytical approaches including the use of in-situ microscopy and spectroscopy techniques.

Technical Barriers

Selective catalysts are increasingly multifunctional, and involve synergistic contributions from several components, including the catalyst support. The goal of achieving the ultimate performance in activity and selectivity demands control of particle size, composition, and achieving desired atomic connectivity, and structure in the catalytically active sites. Unraveling the contributions of each of these components in industrial catalysts is challenging because of the inherent heterogeneity of these catalysts. It is therefore necessary to find an approach that bridges the gap between the well-defined model catalysts used in surface science experiments and those that can be tested in a conventional flow reactor under industrially relevant conditions.

Abstract

Work carried out during this second year of the 3-year project renewal period continues to build on insight gained in the first year of this project, focusing on understanding the role played by ZnO as a promoter. Base metals (e.g., Co) and precious metals are active in C-C bond cleavage of ethanol, with metal oxide (e.g., ZrO₂, ZnO, CeO₂, etc) supported Co catalysts being less selective to CH₄ than precious metal catalysts. However, supported Co catalysts are prone to rapid deactivation, thus limiting their potential applications. On supported cobalt catalysts we have learnt that addition of the ZnO improves the selectivity towards CO₂ and suppresses methane formation. Although the mechanisms of CH₄ formation and catalyst deactivation are not fully understood yet, it is speculated that high oxygen mobility throughout the oxide support can facilitate the oxidation of CH_x species formed from C-C bond cleavage of ethanol, leading to reduced CH₄ formation and improved catalyst life. Our work on aerosol synthesis has helped in generating single phase metal alloys in the PdZn system, allowing us to determine the role of phase and composition on reactivity for methanol

steam reforming. In steam reforming of ethanol, we find that addition of Zn leads to improved H_2 yield in PdZn catalysts. Finally, we have learnt that isolated single atoms of Pd on alumina show exceptionally high activity for CO oxidation. We highlight two of the projects we have carried out this past year.

Progress Report

Steam Reforming of Acetone

The formation of acetone in ethanol steam reforming (ESR) and its oligomerization on the acidic/basic sites of the oxide support and the subsequent carbon deposition (mainly as filaments) on the active sites responsible for H_2O dissociation can result in insufficient oxygen-mobility, which causes catalyst deactivation under practical operating conditions. Therefore, acetone steam reforming (ASR) was studied to elucidate the detailed mechanisms on Co nanoparticles and to enable the rational design of highly active, selective, and stable catalysts for steam reforming of biomass-derived oxygenates. Co nanoparticles (~5 nm) were synthesized on an inert support (graphitized activated carbon) without addition of promoter to minimize the complications by either support and/or promoter. On the basis of experimental mechanistic investigations and theoretical understanding of the full reaction mechanism with density functional theory (DFT) calculations, we elucidated that Co nanoparticles (~5 nm) play dual roles of cleaving C-C bond of acetone while efficiently dissociating H_2O to oxidize CH_x^* and C^* . As a result, inert activated carbon-supported Co nanoparticle catalysts are very selective and stable for hydrogen production via ASR (Figure 1). The high selectivity is attributed to: 1) the facile C-H bond scission relative to the C-C bond cleavage of acetone suppresses the formation of CH_3^* species that lead to methane (Figure 2); 2) the hydrogenation of CH_x^* species has a higher barrier than dehydrogenation; and 3) the facile H_2O dissociation resulting in a higher water-gas-shift activity. On the other hand, the factors responsible for the exceptional catalyst stability are: 1) enhanced oxygen mobility by facile water dissociation on the cobalt nanoparticles (~5 nm); and 2) the lack of acid/base sites on the inert support. This work suggests that acetone, either formed as a by-product or present as a reactant, can be selectively steam-reformed to produce hydrogen without the catalyst deactivation issue as previously reported in the literature. Our fundamental understanding of the nature of Co nanoparticles further provides the insight into the rational design of catalysts for steam reforming of biomass-derived oxygenates with minimized formation of coke and methane.

CO oxidation on Pd/La-alumina

In recent work on Pd/La-alumina automotive exhaust catalysts, there was evidence suggesting that lanthana, which is used to stabilize gamma alumina, may play a role in

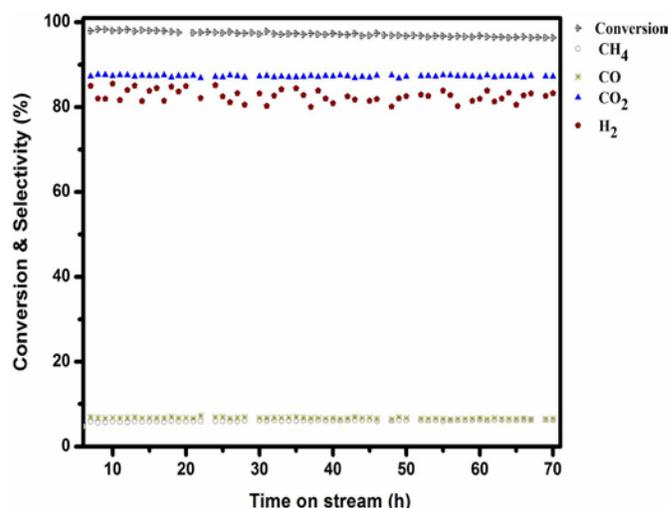


FIGURE 1. Co/C catalyst durability test during ASR (20 mg, 7.8 mol% C, steam/carbon=5, W/F= 0.094 g.s. STP mL⁻¹, T= 450°C). With the high space velocity and acetone partial pressure, at a conversion below 100%, no observable deactivation was found after 70 hrs time on stream operation.

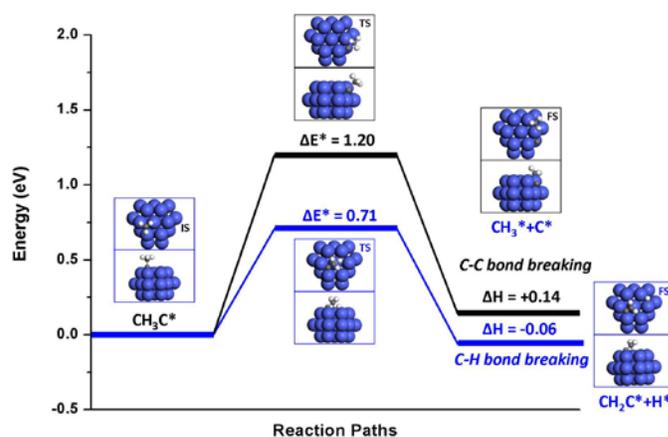


FIGURE 2. The C-H bond-breaking of CH_3C^* is more favorable than the C-C bond-breaking, indicating the CH_3 formation is least likely.

improved CO oxidation reactivity. Fig 3 shows the light off curve for CO oxidation on Pd/alumina and on Pd/La-alumina. We investigated the origins of this enhanced CO oxidation activity via EXAFS, XANES, FTIR and via HAADF STEM. It was found that the La-alumina support had smaller Pd particles than on Pd/alumina. More important, the Pd particles on La-alumina showed facile oxidation behavior, hence they allowed O_2 to compete with CO allowing for the onset of low temperature oxidation. Figure 4 shows a schematic of our observations.

To further investigate the reactivity of these Pd catalysts, we studied these catalysts via Aberration Corrected (AC) STEM. Fig. 5 shows how PdO was seen after heating the catalyst at 140 °C, a temperature where we would only expect metallic Pd. These STEM images confirm the facile

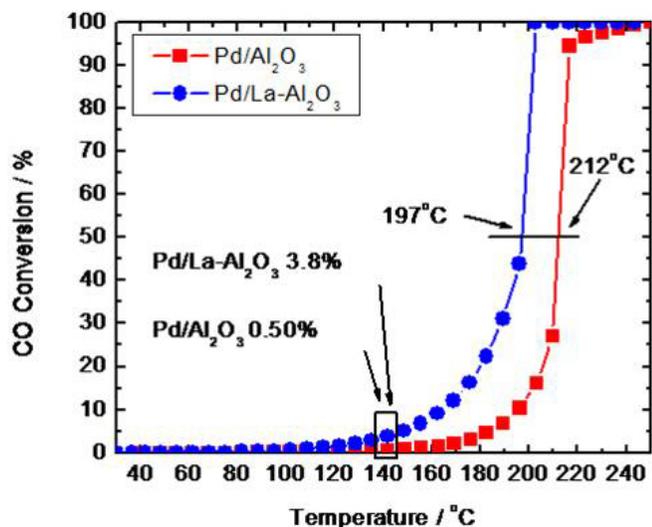


FIGURE 3. CO oxidation reactivity on Pd/alumina and Pd/La-alumina. The box shows % conversion at 140°C.

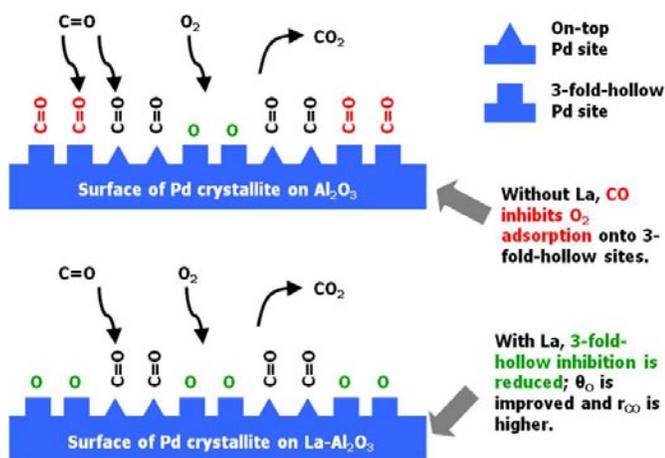


FIGURE 4. Schematic showing the observed behavior of Pd/La-alumina that leads to enhanced CO oxidation at 140°C.

redox behavior of Pd that was also seen by FTIR of adsorbed CO. These images also provide evidence for existence of atomically dispersed species, which we have confirmed to be La atoms as well as Pd atoms. To study the CO oxidation reactivity of the atomically dispersed species, we prepared a catalyst containing 0.5 wt% Pd. We saw a low onset temperature for reaction with significant CO oxidation reactivity at 60 °C. While the low onset temperature can also be seen on Pd/alumina, the Pd/La-alumina is much more stable. These results show that atomically dispersed Pd species can be stable and show high reactivity even on a non-reducible support like alumina. Understanding the conditions that lead to the stability of these isolated atoms of Pd should pave the way for future work on tapping the potential of atomically dispersed species in heterogeneous

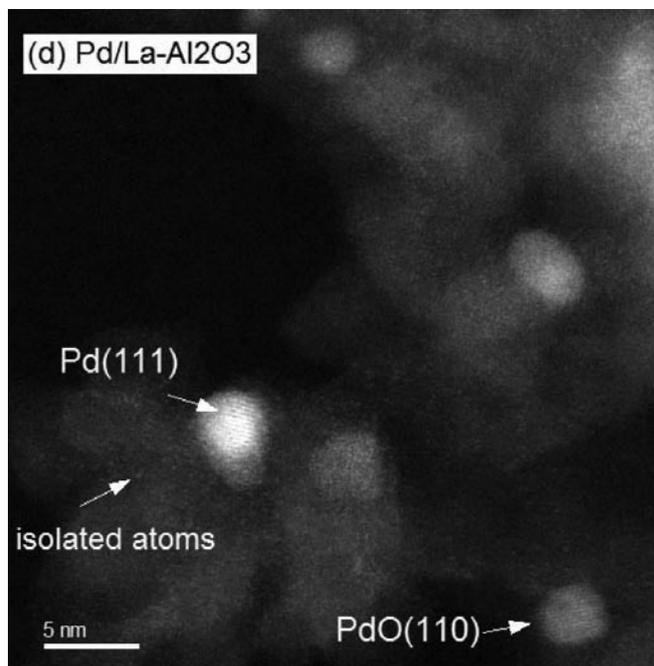


FIGURE 5. AC-STEM image of 2.5 wt% Pd/La-alumina. We see the presence of PdO in these catalysts at low temperatures. The facile oxidation of Pd helps explain the enhanced low temperature reactivity for CO oxidation.

catalysis. It will also help us bridge the gap between homogeneous and heterogeneous catalysts.

Future Directions

We will continue our work on alcohol reforming for hydrogen production using aerosol derived model catalysts as well as supported catalysts. In-situ studies of phase evolution of bimetallic catalysts will be carried out using model supported catalysts. We plan to complete our studies of CO oxidation on atomically dispersed Pd and move on to other reactions where the dispersed Pd may provide enhanced reactivity.

Publication list acknowledging the DOE grant since the last annual report

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