Water Gas Shift Catalysts for H₂ Production in Membrane Reactors

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Polymers electrolyte fuel cells perform best on pure H₂. Low sulfur hydrocarbon fuels can be converted to PEM fuel grade H₂ using a compact membrane reactor architecture. Consequently United Technologies Research Center (UTRC) is developing integrated Pd Membrane reactors for H₂ production through reforming of fossil fuels and the subsequent conversion of the CO in the reformate to hydrogen through the Water Gas Shift (WGS) Reaction. This not only allows the shifting of the WGS equilibrium through H₂ removal but it greatly simplifies the system design by eliminating all the other reactors, as well as a major part of the multiple heat exchangers and the air mixers down steam of the reactor that are integrated with in the traditional fuel processing system for H₂ generation.

Metal supported tubular Pd membranes have high modularity and thus can be easily scaled up to any system capacity while they do not employ components with low reliability like frequently actuated rotating valves. This approach results in significant system cost savings and controls simplicity (thus higher system reliability) due to system and system controls simplification through component elimination. These are significant advantages over the currently applied and more mature technology for H₂ production, the Pressure Swing Adsorption. However this approach requires cost effective, air tolerant catalysts with high volumetric activity and high stability for prolonged operation at ~400 °C. On the basis of Gorte’s studies noble metal on nano-crystalline ceria-mixed metal oxide catalysts were explored to provide such a catalyst. Eventually a high temperature metal alloy on ceria based mixed metal oxide catalyst was found that gave excellent performance during an 880 hr test with synthetic reformate. This test included 560 hrs at ~240 °C. Although projecting life and stability has to be done cautiously the projected activity of this catalyst after 10,000 hrs at 420 °C was 73% of its 100 hr lined out activity or a turn over frequency TOF of ~2.4 CO/Pt-sec.

This catalyst was a member of a family of catalysts designed from the outset to have both high surface area and a network of pores sized to eliminate internal mass transfer. To this end a synthesis route to 2.5 to 3.5 nm doped ceria-zirconia or ceria hafnia oxide crystallites was devised. This route and its variants can accommodate a wide variety of both Ce/Zr or Ce/Hf ratios and dopants. The careful processing allows the recovery of a fractal structured material wherein the fundamental crystallites link through their high energy faces to form high porous ~100 nm particles. These particles link together forming even larger pores inside micro-sized aggregates. A typical Ce₁₋ₓZrₓO₂ with skeletal density of ~6 and a crystallite size of 3 nm by PXRD can be obtained with 270 m²/gm surface area. To put this in perspective this is about 70% of the theoretical surface area for the crystallite size. If the oxide had the same skeletal density as γ-Al₂O₃ then these catalysts would have a surface area of about 425 m²/gm. Surface area of ~200 m²/gm are typical of oxides designed for long term ~310 °C operation.

Significantly, the nano-crystallites are primarily cubic (Fm3m) in structure as determined by a combination of PXRD and Raman spectroscopy even at oxide compositions that in larger crystallites are tetragonal (P4/nmm) according to Kaspar. Raman is critical for determining the structure of these nano-crystalline materials as broader peaks caused by the small crystallite size tends to preclude definitive PXRD determination. Ce₁₋ₓZrₓO₂ crystallites with an average size of 3.45 nm by PXRD exhibits a major, broad Raman peak at ~465 cm⁻¹ with a low shoulder extending beyond 650 cm⁻¹ ascribed to oxygen vacancies. This shoulder appears even at 10% Zr and grows with Zr concentration. The Raman spectra of the nano-crystalline Ce₁₋ₓZrₓO₂ is dominated by a broad 465 cm⁻¹ peak though with a weaker ~640 cm⁻¹ peak. Ce₁₋ₓZrₓO₂ on the other hand is tetragonal by PXRD and had Raman spectra indicative of a tetragonal structure.

These oxides were converted to WGS catalysts by loading with noble metals either alone, in combination or with transition metal promoters. Gorte has demonstrated the major impact that Fe can have on Pd/CeO₂ activity. For the Ce₁₋ₓZrₓO₂ and Ce₁₋ₓZrₓDpₓO₂ prepared by our techniques Pt seems superior to the other metals. As prepared these supported Pt catalysts have 100% dispersion by CO chemisorption. High resolution TEM investigation is consistent with the majority of the Pt forming small, ~1-nm rafts. After loading with Pt these oxides are reducible at low temperatures by TPR. This is not a function of either Pt or oxide crystallite size. A Pt/Ce₁₋ₓZrₓO₂ catalyst was calcined at 1000 °C in air and had a major reduction peak at ~130°C despite very large Pt crystallites and nil surface area.

These high surface area catalysts were first explored for their low temperature water gas shift activity. Besides automated micro-reactor screening and kinetics studies, VASP atomistic modeling of the Ce₁₋ₓZrₓDpₓO₂ system along with in-situ CIR-FTIR studies were initiated. A range of compositions were examined as 80-120 mesh granules diluted with 40 mesh α-alumina run at high space velocity. Typically between 210 and 240 °C the kinetic expression r = Aexp(-Ea/RT)[CO][H₂O]α[H₂]β[H₂O]γ would fit the data with Ea values ranging from 66 to 73 kJ/mole. These results are consistent with a rate limiting step involving water. The modeling work predicted domination of the oxide surface by a formate like species, but that this domination could be lessened by doping the Ce-Zr oxide with any of several species, Mo among them. The in-situ FTIR spectra taken at low space velocity indeed indicated domination of the surface by a formate like species as well as carbonate for Pt/Ce₀.₅₋₀.₇₅ZrₐO₂. Doping with La apparently increased and changed the nature of the adsorbed CO while also enhancing peaks attributable to CO on Pt. Mo doping on the other hand decreased the apparent intensity of peaks attributed to CO and carbonate adsorbed on the oxide. These results were consistent with reactor studies where a Mo doped catalyst exhibited a lower apparent activation energy that the undoped material.

While Mo exhibited some low temperature promoting ability it did not increase high temperature activity. The catalysts suitable for long term ~320 °C deactivated when exposed to high temperatures for hundreds of hours. Catalysts deactivated even with UHP feed gases passed through activated carbon, mole sieve and Oxisorb™ traps as well as a heated ZnO bed. Analysis of these deactivated catalysts revealed only slight oxide crystallite growth or loss of surface area. Their PXRD patterns showed no evidence of severe Pt agglomeration and there were no drastic changes in their Raman spectra. Notably however the low temperature reduction peak so evident in the TPR of fresh catalysts was absent.

A promoter M was found for Pt / Ce₁₋ₓZrₓO₂. Kinetic studies were carried out and Athena software used to fit the data to Aeαt(1-β)R|T[CO][H₂O][CO₂][H₂O]² (1-β) where β is the approach to equilibrium. At low temperatures, below 250 °C, Ea

was 71 kJ/mole and $\alpha = -0.2$, $b = 0.8$, $\gamma = -0.12$, $\delta = -0.4$, while at high temperatures the activation dropped to 46 kJ/mole and $\alpha = 0.2$, $b = 0.4$, $\gamma = -0.2$, $\delta = -0.4$. This promoted catalyst still lacked the requisite high temperature stability. A Pt-M/Ce$_{1-x}$Hf$_x$Dp$_y$O$_2$ catalyst with a skeletal density >8.0 and a surface area of 146 m$^2$/gm and a crystallite size of 3.3 nm was synthesized. On a skeletal density adjusted basis its surface area was equivalent to about 190 m$^2$/gram for a 60% cerium, 40% zirconium oxide. This catalyst was tested for 880 hrs at 740,000 hr$^{-1}$ space velocity under a variety of conditions. Its activity retention was excellent. Under 7.5% CO, 5.5% CO$_2$, 27.6% H$_2$O, 28.9% H$_2$, bal. N$_2$ at 740,000 hr$^{-1}$ after -560 hours at 420 °C this catalyst’s TOF was 3.0 CO/Pt-sec.

On the basis of an activity versus log of time plot its projected activity at 10,000 hrs was > 2.4 CO/Pt-sec suggesting that it might retain 73% of its 100 hr activity at 10,000 hrs. United Technologies Research Center is working with HydrogenSource LLC and their suppliers to commercialise this catalyst technology for hydrogen production. Extended monolith tests are planned.

References