114e Selective High Throughput Combinatorial Studies of Oxidative Methanol Reforming to Hydrogen on Multi-Component Catalysts

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Hydrogen for fuel cells to power vehicles or small electronic devices can be extracted from sources including natural gas, water, biomass, or other more complex hydrocarbons [1]. Despite the numerous advantages that fuel cells provide, there are still significant difficulties including transportation, storage, and handling of hydrogen. An attractive alternative solution to problems associated with storing molecular hydrogen involves on- board catalytic production of hydrogen from high-energy liquid fuel such as methanol [2]. In this research, the partial oxidation of methanol was chosen for being exothermic and to minimize CO, (a fuel cell electrode poison) since CO_2 is a primary reaction product.

Copper-Zinc based catalysts are reported to be active for oxidative methanol decomposition [3-4]. However, such catalysts are not stable enough to give reliable on-board hydrogen production under a variety of operating conditions. This research focuses on using high throughput combinatorial methods for the discovery of novel multi-component catalysts, mechanistic studies, and catalyst characterization. In this work, a literature search revealed that (among others) catalysts containing elements Cu, Zn, Zr, Ce, and Pd are active and selective for methanol reforming reactions. A catalytic library based on Cu/Zn was formulated using Zr, Ce, and Pd as promoter materials to increase activity and selectivity. The catalytic library was prepared via Na_2CO_3 coprecipitation with variable Cu/Zn ratio. The promoted catalyst combinations were selected to study the effect of Zr, Ce, and Pd as promoters to the Cu/Zn basis composition.

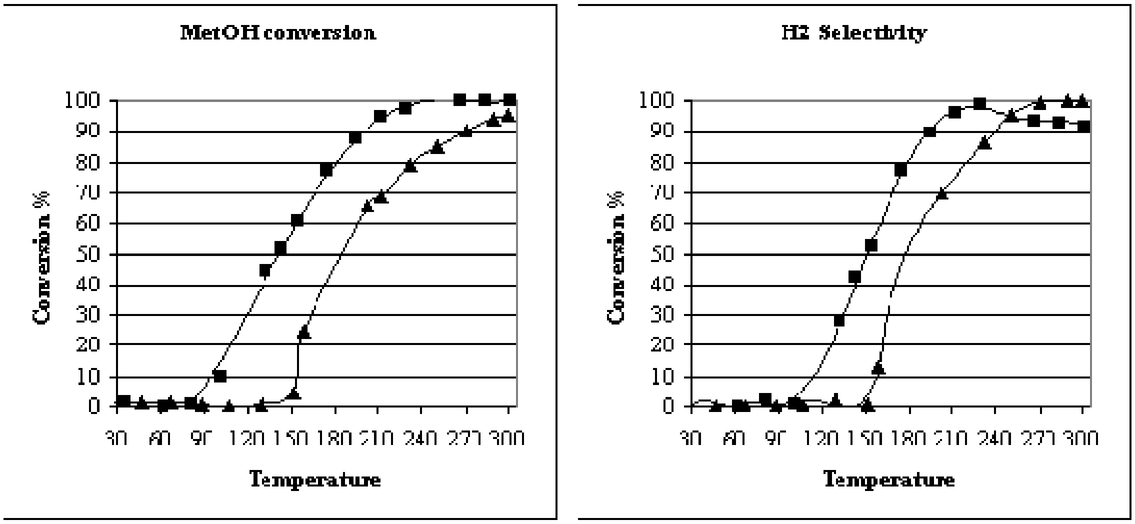
Catalytic activity is evaluated in a high throughput three-step process wherein each progressive step yields more detailed information regarding the activity of a catalyst formulation. Each step allows easy identification of under performing formulations, which eliminates them from further study. The most active and selective catalysts are studied in detail to obtain kinetic rate and reaction mechanism information in conjunction with XPS, XRD, BET, DRIFTS, EXAFS, etc. characterization techniques. Information gained from studying promising catalytic formulations is applied to building successive catalytic libraries to achieve better catalyst characteristics while gaining better fundamental understanding of catalytic behavior through the use of computer modeling.

The first and highest throughput level of catalytic activity experimentation involves using infrared thermography (IRT) to evaluate catalyst activity. Catalyst samples are packed into an array allowing study of up to 50 individual catalyst formulations. Then the array is placed in an infrared cell under a flowing reaction mixture. Total thermal activity of individual catalysts is evaluated with a broad-spectrum, 1.6 to 6.0 μm IR camera (Thermovision 782). The difference in temperature measured by the camera between reaction and non-reaction conditions is an indication of the catalytic activity. In this instance, the partial oxidation of methanol is an exothermic reaction yielding a larger temperature increase from active catalysts.

Thermally active catalysts discovered via IRT are placed into a 10-port parallel reaction system, the second level of activity evaluation. In this stage, catalytic activity can be evaluated from conversion and selectivity data obtained via gas chromatography. For all parallel reactor experiments, methanol is added via a saturator in the nitrogen line at an oxygen to methanol ratio of 0.5. This experimental setup provides more detailed catalyst performance information at a medium throughput level.

The most active and selective catalysts are further evaluated in a recycle reactor under variable reaction conditions. By eliminating under performing catalysts in the first two stages of experimentation, the number of catalysts studied in this detailed manner is greatly reduced. This reactor setup allows for detailed kinetic experiments in order to better understand the reaction mechanism. Catalysts evaluated in the recycle reactor may also be characterized by methods described above (XPS, XRD, BET, DRIFTS, EXAFS, etc.) to help give a complete picture of how catalytic components interact to increase activity.

Utilizing the method described above, we studied an initial library with variable Cu/Zn ratio to form a basis. Other combinations were selected to study the effect of Zr and Ce as promoters to a Cu/Zn/Pd catalyst. Zr promoted catalysts were quickly identified as active in IRT studies, and selective in parallel reaction studies. Activity-selectivity results obtained in the recycle reactor show ignition type behavior at approximately 120 to 150°C, then an increase in the reactor temperature to about 300°C yields conversion approaching 100% with hydrogen and CO_2 selectivity peaking at >95%. The most active and selective catalysts so far were Zr promoted (Cu/Zn/Zr), compared to unpromoted Cu/Zn catalysts, figures 1&2.



Figures 1&2: Conversion and selectivity results comparing Zr promoted Cu/Zn ● Cu/Zn/Zr catalysts to non-promoted Cu/Zn ▲ Cu/Zn.

Preliminary characterization via XPS indicates significant Zn enrichment of the surface relative to the bulk preparation. Addition of Ce and Zr may enhance the Pd on the surface. BET results also show an increase of surface area upon promotion of Cu/Zn with Zr and/or Ce. Other characterization methods and reaction mechanistic studies are currently in progress to better understand the role of Ce and Zr promoters. New strategies of catalyst preparation are also being developed to enhance the noble metal surface concentration.

References

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