Combinatorial Approaches for Developing New Catalysts for Polyols

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Introduction

Formation of ethylene glycol (EG) and propylene glycol (PG) from sugars offers potential renewable resources for solvents, deicers, antifreeze and other products. The chemistry is attractive for starch derived glucose, hemicellulose derived five-carbon sugars xylose and arabinose, or biodiesel derived glycerol. The mechanism for hydrogenolysis is complex. At the minimum it involves dehydrogenation, accompanied with isomerization, retro-aldol (C-C cleavage), dehydration (C-O cleavage) and re-hydrogenation [1 – 3]. This is shown in a simplified manner in Figure 1.

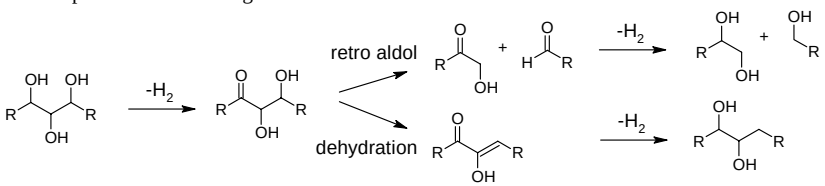

Figure 1. Simplified view at mechanisms operative during hydrogenolysis

Numerous precious metals and mixed metal systems on various supports along with various base or acid promoters have been used to catalyze the reaction [4 – 5]. The complexity of the mechanism and the variety of metals, supports and promoters possible in optimal catalytic systems makes combinatorial methodology ideal for advanced catalyst development.

Materials and Methods

The work was carried out at PNNL's high-throughput combinatorial laboratory which is based on the Symyx Renaissance platform. Catalyst development was done using 96-well plates with each well approximately 1 mL in volume. A variety of commercial and exploratory supports were used consisting of carbon, titania, zirconia, silica or niobia. Catalysts were prepared by adding supports to each well. The amount of support added was accurately controlled by a solids-handling robotic system and typically consisted of 25 - 40 mg of material. To the supports metal solutions were added using a modified insipient wetness technique. This was done with a second liquids-handling robotic system. The 96 catalysts were then calcined/reduced under the appropriate flowing gas atmosphere and temperature gradient. Commercial catalysts, from Engelhard or Degussa, were used as benchmarks. Various promoters ranging in pK_a, and feed solutions were added to the catalysts in each of the 96 wells under inert atmosphere. The plate was covered with gas-permeable tops to prevent cross-contamination of the wells while allowing free gas flow. The 96-well plates were then sealed in a nitrided stainless steel reactor, degassed and pressurized to desired pressures (up to 100 bar) using hydrogen and heated to a desired temperatures (up to 200 °C). Mixing was accomplished using orbitol shaking at 600 - 800 rpm. At the conclusion of the experiment the reactors were cooled, the 96-well plates removed and subjected to centrifugation followed by filtration and dilution using robotic systems. The 96-well plates were placed in an HPLC and each cell individually analyzed using a high-throughput column. Results were analyzed by informatic tools associated with Symyx Renaissance software.

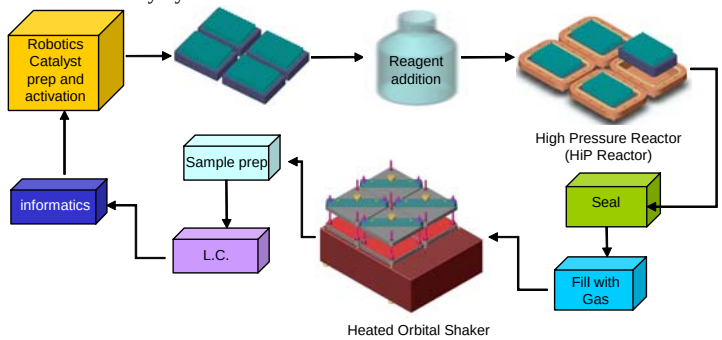

Figure 2. Process flow diagram for combinatorial catalysis discovery

Results and Discussion

The combinatorial approach has allowed us to rapidly prepare and screen in excess of 4,000 individual experiments in a matter of months. Surprising results were found on preferred supports, metal combinations and promoters. Catalysts systems screened included one or two central metals with up to two additional promoter metals (i.e. up to quaternary metal systems). The exact catalyst compositions will not be presented at this time. Rather, the presentation will focus on the process of catalyst discovery using mechanism-based along with statistical-based design enabled by high-throughput combinatorial discovery tools.

Significance

High-throughput combinatorial techniques, particularly when used with mechanism-based design and statistical tools can rapidly advance catalyst discovery. This is of particular important in new areas of catalysis, such as condensed aqueous phase systems often found with biomass.

References

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