114f Combinatorial Synthesis and High Throughput Screening of Carbide and Nitride Supported Methanol Steam Reforming Catalysts

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Transition metal carbides and nitrides possess a number of interesting properties and are known to catalyze a variety of reactions. Recently, we demonstrated that carbide and nitride supported metal catalysts are active for the water gas shift (WGS) and methanol steam reforming (MSR) reactions. The goal of the research described in this paper is to identify catalysts that exhibit both high activity and high CO_2 selectivity for MSR. A library of catalysts was synthesized using a specially designed combinatorial synthesis reactor and tested using a high-throughput screening reactor. The database also allowed us to explore interactions between the early transition metal carbides and nitrides and a variety of late transition metals.

Base metals including Cu, Co, Fe, Ni and Sn and noble metals including Pt, Pd, and Ru were impregnated onto high surface area Mo_2C and Mo_2N supports. Following an experimental design, we prepared approximately 400 different catalyst formulations. The monometallic base metal catalysts had high CO_2 selectivities but low H_2 production rates. In contrast, the noble metal catalysts exhibited high activities and low CO_2 selectivities. Among the monometallic materials, the Mo_2N supported Pt catalyst was very promising exhibiting an activity that was significantly higher than that for the commercial Cu-Zn-Al catalyst.

From results for the monometallic catalysts, we hypothesized that a combination of noble and base metals might produce catalysts that possess high activities and high CO_2 selectivities. Simultaneous or sequential impregnation methods were used to prepare catalysts with noble-base and base-base metal combinations. Noble-noble metal combinations were not attempted because of the potential for very high cost. The base-base metal combinations were synthesized with the expectation that the bimetallic materials might have higher activity than the monometallic base metal catalysts. Results for the bimetallic catalysts showed a trend similar to that for the monometallic catalysts, but with a slight improvement in selectivity. Base-base metal combinations synthesized using the sequential method exhibited higher activities than those synthesized using the simultaneous method.

Assuming that MSR is a combination of methanol decomposition and WGS, the low CO_2 selectivities suggested that the surfaces were dominated by methanol and that CO or H_2O adsorption was limited. Surface characterization using techniques including pulsed chemisorption, temperature programmed desorption and temperature program reaction revealed that the poor CO_2 selectivities were a consequence of competition between CO and methanol for the active sites, particularly the sites required for WGS. Methanol may block these sites for CO thus giving low CO_2 selectivity in MSR.

In conclusion, we have identified a number of promising candidates with good selectivities and moderate MSR rates. Continued screening and characterization of the existing formulations holds promise for identifying additional promising candidates.