High Throughput Discovery of Noble Metal-free Ni-based Water-Gas-Shift Catalysts

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Introduction

We have developed high-throughput synthesis and screening methods for the discovery of families of high activity WGS catalysts. More than 250 wafers were screened and more than 250,000 experiments were conducted to comprehensively examine catalyst performance for various binary, ternary and higher-ordered compositions.

Materials and Methods

Discovery (primary screening) libraries consisted of 11x11 of 121 or 16x16 arrays of 256 catalysts on 3 inch or 4 inch quartz wafers, respectively. Catalysts were prepared by robotic liquid dispensing techniques and screened for catalytic activity in Symyx' Scanning Mass Spectrometer in the temperature range of 200°C to 450°C. The feed consisted of CO, CO_2, H_2, H_2O with Kr as internal standard in Ar carrier gas.

Results and Discussion

The discovered lead compounds include supported noble metal systems as well as base metal compositions [1-3]. Relative ranking of metals, classification of dopants and identification of synergistic building blocks has resulted in a WGS toolbox for the design of customized catalysts for specific applications.

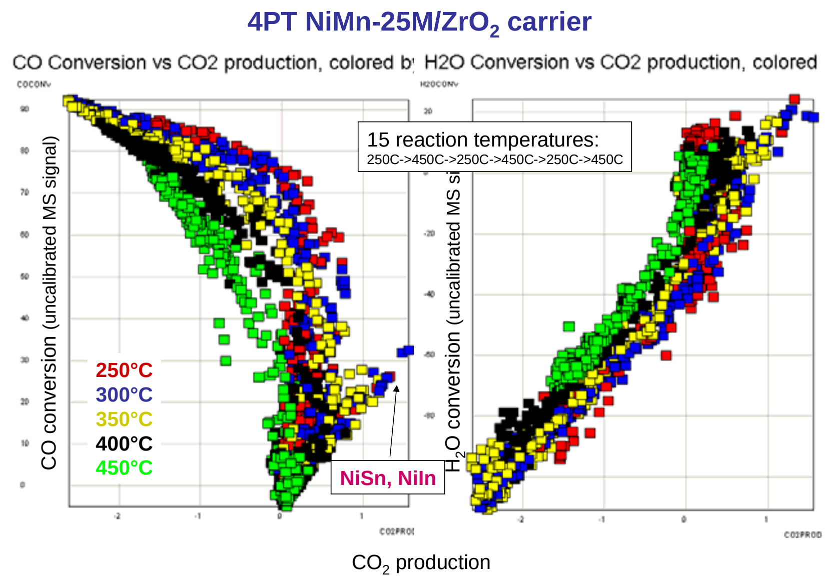
As a representative example of a Ni-based discovery wafer, figure 1a-b shows the library design as well as screening data at multiple temperatures (250C-450C) for Ni-Mn-M ternaries supported on a ZrO2 carrier (where Mn functions as a stabilizer preventing Ni deactivation by sintering). Each ternary is mapped out by 4 different compositions. The 11x11 element wafer accommodates 25 WGS systems. An in-situ temperature programmed reduction in scanning mass spec was carried out with 3 temperature scans in total (250C to 450C in 50C steps and 2 repeated cycles to study the effect of oxidized versus reduced metal dopants). Whereas most systems are unselective and catalyze the unwanted methanation (CO hydrogenation) side reaction two systems (NiSn and NiIn) are identified as selective shift catalysts obeying the WGS mass balance (straight line through the origin and the selective PtCe benchmarks; unselective methanizers deviate from the WGS mass balance line). In was found to be better than Sn when in-situ reduced while Sn was better than In when prereduced at high temperature. Moreover, the direct comparison on the same wafer allows a classification into methanizers and shifters as well as a relative ranking. The activity ranking of best (synergistic, i.e. displaying a branch on the WGS diagonal) Ni moderators is given by:

Fe > Cu > Sb > Sn > In > Te > Ge > Pb > Cd

with decreasing activity and increasing selectivity from left to right.

Although Ni is known to be methanizing it was possible to effectively moderate Ni by alloying with deactivating dopants and convert it into a selective shifter. The performance was poor under LTS conditions, however, the selectivity was steadily improving with temperature (moderators in reduced state). Therefore, novel cheap alloyed Ni systems are proposed as alternative to state-of-art Pt/CeO2 WGS catalysts, for instance, in fuel processors for mobile and stationary applications.

Figure 1. CO conversion (left) and water conversion (right) versus CO2 production colored by reaction temperature.



Significance

Highly active catalysts for methane oxychlorination were identified. The high throughput workflows used also demonstrated the ability to quickly generate detailed activity data on a difficult-to-implement chemistry.

References

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2. C. Brooks et al., Topics in Catalysis (2006), 38, 195-209.
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