Novel Impregnated Support Combustion Synthesis of Stable Ni Catalysts for Hydrogen Production from Ethanol Reforming

Allison Cross¹, Khachatur Manukyan¹, Sergei Rouvimov¹, Alexander Mukasyan¹, and Eduardo Wolf*  
¹University of Notre Dame, Notre Dame, IN 46556 (USA)  
*ewolf@nd.edu

Introduction
During recent years our group has investigated transition metals (Ni, Cu, Fe) and their alloys in alcohol reforming [1] in an attempt to make on board hydrogen production for fuel cells economically viable. The catalysts studied previously show high activity and selectivity toward H₂ production at low temperature, but unfortunately undergo rapid deactivation, possibly due to several types of carbon deposition and sintering. The causes of deactivation will be discussed to design novel catalysts for highly active catalysts for long time on stream. To produce stable catalysts, several solutions were attempted here: adding Cu as a promoter, using an active support such as ceria, and preparing partially encapsulated active particles. The effectiveness of these solutions to provide high activity for long TOS will be characterized by stability reaction runs and TEM and UHV-XPS before and after the reaction.

Materials and Methods
The catalysts studied were prepared by a novel Solution Combustion Synthesis (SCS) called Impregnated Support Combustion Synthesis (ISCS). Aqueous solutions of Ni(NO₃)₂·6H₂O, Cu(NO₃)₂·3H₂O, and glycine with a fuel to oxidizer stoichiometric ratio, φ, of 1.75 was used to produce 10 wt.% of Ni, 10 wt.% Cu and 10-10 wt.% NiCu on each support of cerium (IV) oxide and silicon dioxide powders. The SCS method was also modified here to combust the precursors under pressures above atmospheric and under inert gases. We prepare 20% Ni on silica and combust it in a high pressure reactor under a 5 atm Ar atmosphere. Also for comparison, a 10% Ni on silica catalyst was prepared by standard wet impregnation techniques where Ni nitrate is dissolved and dispersed onto the silica and then calcined. All SCS catalysts and the impregnated catalyst were reduced at 500°C prior to reaction studies.

Catalytic activity was measured in a continuous flow fixed bed quartz reactor at atmospheric pressure as previously described.[2] The catalysts were imaged using a transmission electron microscope (FEI Titan 80-300 TEM). UHV powder X-ray photoelectron spectra (XPS) measurements were obtained under high power mode in a Kratos XSAM 800. A Multipak software package was used to determine the surface oxidation states and concentrations of the catalysts.

Results and Discussion
When comparing Ni/Coₓ and Ni/SiO₂ by the same synthesis method, the Ni/SiO₂ catalyst is stable for over 30 hours without any deactivation while Ni/Coₓ begins deactivating almost instantly due to massive carbon formation on the surface as detected by UHV-XPS. Ceria has been reported elsewhere to be able to remove residual surface carbon based on its redox and oxygen storage capacity properties. With the model reaction of ethanol decomposition (no added oxygen), we do not see the same effect, instead more carbon formation on the ceria supported catalysts is observed when compared to Ni/SiO₂. The reason for the drastic increase in stability is due to the Ni becoming partially encapsulated by the small silica particles during SCS, so that carbon formation is decreased. By alloying Ni with Cu, the stability increases due to a slower rate in carbon formation over the supported catalysts. The alloying of Ni prevents the metastable metal carbide formation, which is an intermediate stage of the growth of carbon.

Figure 1. Ethanol conversion over A) ISCS prepared single and bimetallic catalysts and B) Ni/SiO₂ prepared by SCS under 5 atm inert atm

Inert atmosphere SCS synthesis technique produces partially encapsulated Ni particles by the support particles. This produces highly stable catalysts that resist deactivation for 100 h TOS of the ethanol decomposition reaction. SCS under an inert atmosphere produces the most stable catalysts that show no change in activity, structure, or carbon formation during 100 h TOS. Under 5 atm of an inert atmosphere and with slightly higher porosity of the silica support, the active Ni particles can be more fully encapsulated than ISCS, protecting fully from any deactivation during reaction.

Significance
Partial encapsulation, the surrounding of the metal by the support preventing agglomeration and carbon deposition on surface Ni while still allowing the reactants to reach the active surface, is demonstrated to prevent catalyst deactivation. Ni/SiO₂ prepared by CS under 5 atm inert atmosphere demonstrates no change after 100 h TOS reaction.

References