344e Alcohol Steam Reforming for Hydrogen Production

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Steam reforming has been a process of major importance for production of hydrogen, synthesis gas and town gas for several decades. Classical steam reforming is the process by which methane, and other hydrocarbons in natural gas, is converted into hydrogen and carbon monoxide by reaction with steam over a nickel catalyst on a ceramic support. The hydrogen and carbon monoxide are used as feedstock for many other industrial processes. For a developed hydrogen infrastructure that will allow for new and renewable hydrogen carriers in the future, there is a desperate need for efficient and cost-effective reforming technologies for converting lower alcohol fuels to hydrogen. The availability of highly effective and stable catalytic systems for fuel reforming of methanol and ethanol will play a critical role in the advancement of fuel utilization for hydrogen production. Methanol is potentially a good source of hydrogen for mobile fuel cells since it is a liquid at ambient conditions, has a high hydrogen to carbon ratio, and can be converted to hydrogen using either steam or oxygen at relatively low temperatures compared to other fuels. Hydrogen can also be produced in a renewable manner from lignocelluloses biomass with the use of several methods, including pyrolysis, gasification, and steam reforming. Of commercial promise are methods in which biomass is converted to ethanol by saccharification/fermentation. Steam reforming of bio-ethanol offers a highly attractive route for converting bio-mass to hydrogen. In this talk we present an overview of our past and present work in alcohol reforming of methanol and ethanol. We address how catalyst synthesis methods affect oxidation state, structure, metal dispersion, and particle size and in-turn, catalytic performance in steam reforming for hydrogen production. Of particular interest is operation under minimized S/C ratios, understanding carbonaceous deposit formation from high molecular weight molecules, particularly at lower S/C, and preventing loss of active surface area and metal-agglomeration during reforming. Catalysts prepared using an incipient wetness impregnation used nitrate salts and pure oxide supports obtained commercially. Coprecipitated catalysts were prepared from nitrate precursors and a carbonate precipitant, however, ammonium hydroxide was sometimes used as a precipitant. Activity was examined using packed bed reactor flow systems with on-line gas chromatography. Activity was measured using varying space velocities, steam to carbon ratios, and compositions. The feed was delivered via liquid saturators or, where applicable, liquid micro pumps in conjunction with a vaporizer. When necessary, a ruthenium methanizer was implemented to detect small levels of carbon monoxide. Reducibility was evaluated either using a temperature-programmed system equipped with a TCD detector or a GC/MS flow system. Volumetric chemisorptions were used to determine metallic surface area and dispersion of reduced catalysts. The surface reactions occurring over these catalysts during reduction pre-treatment and reaction were analyzed with diffuse reflectance FT-IR spectroscopy (DRIFTS). Post-reaction analysis was accomplished using inert atmosphere transfer to an X-ray photo-electron spectroscopy instrument. Zirconia-containing CuO/ZnO catalysts were examined for their use in the steam reforming of methanol. Catalyst samples with varying compositions were prepared by means of a coprecipitation method, and the effect of different pretreatment conditions was examined. Activity testing shows that the catalysts do not require pre-reduction to obtain good activity for the steam reforming of methanol, although pre-reduction with diluted H_2 increases activity in some cases. X-Ray Diffraction (XRD) and Thermo-Gravimetric Analysis (TGA) show that the bulk CuO phase of all the catalysts is reduced to Cuo when reduced with hydrogen, methanol, or methanol and water. Additionally, the catalysts were characterized using BET surface area analysis, Cu surface area analysis, temperature-programmed reduction (TPR), temperature-programmed desorption (TPD), and XPS. A cobalt-based catalyst system has been developed that is effective for ethanol reforming to produce hydrogen. A series of supported cobalt catalysts have been synthesized via incipient wetness impregnation. Catalyst testing showed the best performance for the zirconia supported catalyst. We address many fundamental questions involved in catalytic steam reforming of ethanol, such as the identity and nature of active sites, the correlation between catalytic properties and catalytic performance,

the kinetic mechanisms involved in the reaction network, and the catalyst deactivation and stability characteristics. The optimal catalyst parameters (cobalt loading, reduction temperature) were determined using BET surface area analysis, TPR, CO and H2 chemisorption, and TGA. DRIFT Spectroscopy also gives valuable insight into the surface transformation occurring during ethanol steam reforming.