Abstract

Coal, biomass and natural gas are traditional energy carriers whose conversion via the Fischer-Tropsch process can be used to generate multiple hydrocarbon products such as fuels and fine chemicals. At the center of the Fischer-Tropsch process is the catalyst used for converting the syngas to hydrocarbons. Generally these catalysts using Co or Fe active sites are supported on high surface area inert materials such as silica and alumina. Our procedure in this thesis was to study some of the fundamental processes that affect Fischer-Tropsch catalysts (i.e. catalyst reduction, Ru as a reduction promoter and deactivation) using a so-called nanoreactor. This was done by loading metallic nanoparticles on either side of the nanoreactor surface. In this work hollow carbon sphere nanoreactors were mainly used as the catalyst support of choice to evaluate the processes mentioned above. First the effect of the hollow carbon sphere porosity on Fischer-Tropsch synthesis was evaluated using encapsulated Ru nanoparticles. Limited mass transfer limitations were observed on the mesoporous nanoreactor, thus suggesting the encapsulated nanoparticles were as accessible to reactants as the Ru nanoparticles loaded on the outside of the hollow spheres.

Using mesoporous hollow carbon spheres the effect of hydrogen spillover on Co Fischer-Tropsch nanoparticles using a Ru promoter was evaluated by controlling the nanoparticle intimacy [of Ru and Co] by exploiting the hollow carbon sphere morphology. Primary hydrogen spillover was found to be more favorable in enhancing the Co nanoparticles extent of reduction and Fischer-Tropsch activity. However, secondary hydrogen spillover from the Ru nanoparticles to Co nanoparticles on the carbon shell was responsible for a complete reduction of the cobalt oxide when compared to an unpromoted Co Fischer-Tropsch catalyst on the hollow carbon spheres. It was also shown that the secondary hydrogen spillover led to the formation of highly hydrogenated products during Fischer-Tropsch synthesis.

In terms of catalyst stability, the nanoparticles, by virtue of being embedded inside the carbon nanoreactor shell, showed good stability against sintering and re-oxidation by added water during process conditions. Furthermore a simple design of a highly sinter resistant catalyst is presented by making a compact nanoreactor on a titania supported Co Fischer-Tropsch catalyst.

This study illustrates the benefit of rationally designing and characterizing materials for a comprehensive understanding of important catalytic reaction processes; in this case our focus was on the reduction behavior and stability of Fischer-Tropsch catalysts.