Catalytic Steam Reforming of Bio-Oil to Hydrogen Rich Gas

Bio-oil is a liquid produced by pyrolysis of biomass and its main advantage compared with biomass is an up to ten times higher energy density. This entails lower transportation costs associated with the utilization of biomass for production of energy and fuels. Nevertheless, the bio-oil has a low heating value and high content of oxygen, which makes it unsuited for direct utilization in engines. One prospective technology for upgrading of bio-oil is steam reforming (SR), which can be used to produce H2 for upgrading of bio-oil through hydrodeoxygenation or synthesis gas for processes like the Fischer-Tropsch synthesis. In the SR of bio-oil or biooil model compounds high degrees of conversion and high yields of H2 can be achieved, but stability with time-on-stream is rarely achieved. The deactivation is mainly due to carbon deposition and is one of the major hurdles in the SR of bio-oil. There are two main pathways to minimize carbon deposition in steam reforming; either through optimization of catalyst formulation or through changes to the process parameters, like changes in temperature, steam to carbon ratio (S/C), or adding O2 or H2 to the feed. In this thesis both pathways have been explored. Steam reforming of ethanol has been conducted over Ni-based catalysts in attempts to minimize carbon deposition through changes to the catalyst formulation. Furthermore the effect of temperature was investigated for Ni on MgAl2O4, CeZrO4/MgAl2O4, CeO2, and Ce0.6Zr0.4O2 at a S/C-ratio of 6. The support material affected the conversion and carbon deposition while the product distributions as function of temperature were similar. The yield of CO and H2 increased with increasing temperature while the yield of CO2, methane, and ethene decreased with temperature. The most abundant by-products were methene and ethene but acetic acid, acetone, and acetaldehyde were also produced in minor amounts. Ni/Co0.6Zr0.4O2 showed the highest activity, but also suffered from severe carbon deposition as carbon whiskers. Ni/CoZrO4/MgAl2O4 had the second highest activity and showed lower carbon deposition compared with both Ni/Co0.6Zr0.4O2 and Ni/MgAl2O4. The carbon deposition over Ni/Co0.6Zr0.4O2 and Ni/MgAl2O4 had a maximum at 500 °C, which coincided with the maximum in the ethene formation. This, along with estimations of the anity for carbon deposition from the gas composition, showed that ethene is the main precursor to carbon deposition. CeO2, ZrO2, K, or mixtures hereof were added to Ni/MgAl2O4, and all of them lowered the carbon deposition and increased the activity. The addition of CeO2 gave the lowest carbon deposition probably due to an increased oxidation of carbon by CeO2. Stability tests over 24 h at 600 °C over Ni-K/MgAl2O4 and Ni-K/CoO2/MgAl2O4 showed good deactivation with time-on-stream mainly due to carbon deposition as carbon whiskers. Sulfur was added as K2SO4 to Ni-CoO2/MgAl2O4 to selectively poison Ni-sites and inhibit carbon deposition. The sulfur poisoning induced a decrease in the carbon deposition and an increase in the yield of hydrocarbons indicating a lowering of the hydrocarbon SR activity. The optimal loading of sulfur was 0.03 wt% S added as K2SO4 and the lowest rate of carbon deposition of 1.2 mg C gCat h was achieved with this catalyst. The results from changes in the catalyst composition indicated that carbon free operation was not possible and so operational measures were investigated next. The effect of the S/C-ratio and addition of H2 or O2 to the feed on the products yields and carbon deposition in the SR of the ethanol over Ni/MgAl2O4, Ni/Co0.6Zr0.4O2, and Ni/CoO2 at 600 °C was investigated. Increasing the S/C-ratio from 1.6 to 8.2 over Ni/MgAl2O4 increased ethanol conversion from 53 % to 80 % as well as the yield of H2, while the carbon deposition and yield of hydrocarbons decreased. Oxygen addition increased conversion, decreased the yield of hydrocarbons and H2 as well as the carbon deposition. Carbon deposition was almost eliminated at an O/C-ratio of approximately 0.8. The penalty of adding O2 was a decrease in the yield of H2 corresponding to loss of 1 mole of H2 for 1 mole of ethanol converted compared with SR without O2. H2-addition had little influence on the catalyst performance, only a slight deactivation was observed at high H2/ethanol-ratios probably due to a high surface coverage of H-species inhibiting the reforming reactions. A 90 h test at O/C=1.1, S/C=6, and 600 °C over Ni/MgAl2O4 showed stable behavior and a total carbon deposition of less than 0.1 mg (rate of carbon deposition was 7 g C gCat h). The results indicate that stable operation in the SR of ethanol is only possible under oxidative conditions.

Bio-oil contains a wide range of oxygenated species ranging from acetic acid to guaiacol and it would be of interest to obtain knowledge about their behavior in reforming. Therefore SR of ethanol, acetic acid, acetone, acetol, 1-propanol, and propional was investigated over Ni/MgAl2O4 at temperatures between 400 and 700 °C and at S/C=6. The yield of H2 and conversion increased with increasing temperature while the yield of by-products decreased with temperature in the SR of the investigated compounds. The yield of H2 approached the thermodynamic limit at the highest temperatures investigated, where full conversion was achieved at the applied space velocity. No significant differences in conversion as function of temperature between the different model compounds were observed. However, the product distribution depended on the model compound and C3-oxygenates produced a larger fraction of byproducts compared to C2-oxygenates. Temperatures of 800 °C or above were generally needed to minimize the fraction of by-products and obtain a syngas containing mainly CO, CO2, H2, and H2O with only traces of CH4. Significant deactivation of the catalyst was observed for all of the compounds and was mainly due to carbon deposition. The carbon formation was highest for alcohols due to a higher formation of oleins, which are potent coke precursors. Steam reforming of 2-methylfuran, furfural, and guaiacol as function of temperature and time was investigated over one of the most promising catalysts, Ni/CoO2-K/MgAl2O4. The major products were, at all temperatures, CO, CO2, and H2, but formation of by-products, such as small hydrocarbons or fragments of the parent model compounds, was observed and the yield of these compounds decreased with increasing temperature. A large formation of aromatic compounds, benzenediols and phenol, was observed in the SR of guaiacol even at 600 °C and temperatures as high as 780 °C were needed to eliminate the formation of these compounds. Temperatures of 600 °C were needed to eliminate the formation of by-products in the SR of 2-methylfuran and furfural. Carbon deposition was apparent in the SR of the model compounds at 600 °C and S/C-ratio of 5 over Ni/CoO2-K/MgAl2O4 and was most pronounced for guaiacol followed by furfural and 2-methylfuran. The carbon deposition could almost be eliminated by adding oxygen to feed at the expense of a lower yield of H2.
operation over 24 h could not be achieved in the SR of guaiacol and furfural even under oxidative SR conditions.