Higher alcohol synthesis from syngas over Molybdenum based catalysts.

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Introduction

The need for reduction of greenhouse gas emissions, the depletion of fossil energy reserves and an increased fuel demand in the world makes renewable energy sources very attractive. Ethanol is an excellent motor fuel and it is used both as neat fuel and as gasoline additive. Today ethanol is primarily produced by the fermentation technique which limits the use of the biomass feedstock to a few raw materials. The supply of this type of raw materials, like corn and wheat, competes with food production and very large production areas are needed if ethanol is going to be used instead of oil. An alternative route is to gasify the biomass to synthesis gas (H_2/CO) and convert the synthesis gas to ethanol (and higher alcohols) using a heterogeneous catalysis process. By this method, virtually all types of biomass feedstock can be used and it makes it possible to produce much more fuel for each ton of raw material. This also makes it possible to use undesirable products like various kinds of organic waste. Alkali promoted Co-MoS_2 and Ni-MoS_2 catalysts experience great alcohol selectivity and high water-gas-shift activity, which makes the catalyst an interesting choice for alcohols synthesis for synthesis gas derived from biomass (H_2/CO ratio near 1) [1,2]. The objective of this work, is first to design a catalyst with high catalytic activity and high selectivity to ethanol and higher alcohols, and second to test the effect of methanol recirculation on the higher alcohol selectivity. To reach this goal, different catalyst preparation methods were investigated to obtain different particle size, promotor dispersion etc.

Materials and Methods

Supported and unsupported K-MoS_2 catalysts with Ni or Co promotors were prepared by co-precipitation, impregnation and microemulsion techniques, from thiomolybdate and molybdate precursors. Catalysts prepared from thiomolybdate were decomposed under N_2 atmosphere. MoO_3 samples were converted to their sulfide form with H_2S. The catalysts were characterized by TEM, XRD, TPD, chemisorption and N_2 adsorption analysis. CO hydrogenation reactions were performed using a high-pressure 20 ml fixed-bed reactor. Product analysis was carried out on-line with a gas chromatograph (Varian 3800) equipped with TCD and FID detectors. In all measurements a premixed syngas with fixed H_2/CO ratio (2:1 or 1:1) and 4% N_2 (internal standard) was used. The catalytic tests were carried out at high pressure (10-90 bar), temperatures ranging from 280-360°C and space velocities between 2400-24000 ml/g/h.

Results and Discussion

MoS_2 based catalysts show high alcohol selectivity and increased pressure leads to higher CO conversion. All catalysts show high-water-gas shift activity. At high space velocity and low temperature, the alcohol products almost follow polymerization kinetics (ASF distribution), while at low space velocities and high temperature, a great drop in methanol selectivity can be seen and higher alcohol selectivity is increased as well as methane selectivity. This might indicate that methanol is involved in secondary reactions. The results obtained from different preparation methods, H_2/CO ratios and nature of the promoters, on conversion and product distribution as well as effect of methanol recirculation will be reported and discussed.

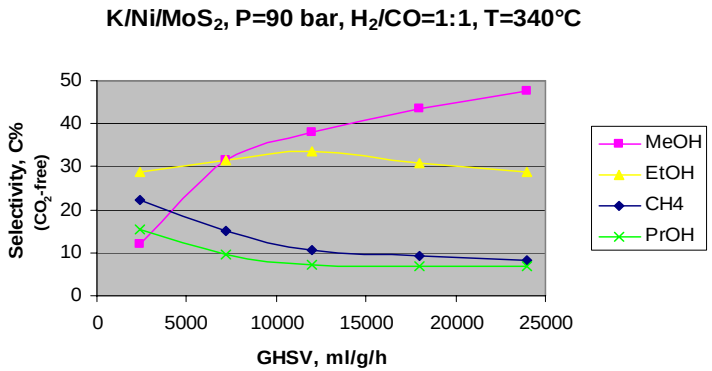

Figure 1. Product distribution (CO_2-free) over an unsupported K-Ni-MoS_2 at various space velocities (GHSV).

Significance

To produce ethanol and higher alcohols from syngas, a process which is of great interest from an industrial point of view, more active and selective catalysts are needed. Suitable preparation methods for catalysts have to be developed in order to achieve high syngas conversion to ethanol and higher alcohols.

References

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2. Li, Y., Wang, R., and Chang, L. *Catal. Today* 51, 25 (1999).