

## OXYGENATES FROM SYNTHESIS GAS

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The direct synthesis of oxygenates starting from synthesis gas is feasible by homogeneous and heterogeneous catalysis. Homogeneous Rh and Ru based catalysts yielding methyl formate and alcohols will be presented.

Interestingly, modified heterogeneous catalysts based on "Isobutyl Oel" catalysis, practiced in Germany (BRD) up to 1952 and in the former DDR until recently, yield isobutanol in addition to methanol. These "Isobutyl Oel" catalysts are obtained by adding a base such as Li < Na < K < Cs to a Zn-Cr<sub>2</sub>O<sub>3</sub> methanol catalyst. Isobutanol is obtained in up to 15% yield.

J. Seibring [1] synthesized, with a ZrO<sub>2</sub>-In<sub>2</sub>O<sub>3</sub>-CuO-ZnO-K<sub>2</sub>O catalyst, isobutanol in yields up to 22%. G. Kollé-Gorgen [2] produced with a ZrO<sub>2</sub>-MnO<sub>2</sub>-Pd-K<sub>2</sub>O catalyst isobutanol in yields up to 30%.

Our best catalyst a Zr-Zn-Mn-Li-Pd catalyst produced isobutanol up to 60% at a rate of 740g isobutanol per liter catalyst and hour. The reaction conditions with T = 715K, p = 25 MPA, GHSV = 20,000 h<sup>-1</sup> are rather severe. With changing pressure the selectivity to isobutanol changes. There is a significant temperature impact, which is evident from Fig. 1

Whereas at 625K about 72% methanol is formed, this portion decreases to 6% at 725K. In parallel, the isobutanol portion in the liquid product increases from 4% to 625K to 45% at 715K. The catalyst is quite stable over a run of about 720 hours. In catalyst preparation, the pH of the precipitation is critical. Fig. 2 outlines best values for isobutanol rest and around pH-values. Finally Fig. 3 exhibits a typical selectivity pattern obtained in various runs.

1. J. Seibring. *Thesis RWTH Aachen* 1985.
2. G. Kollé-Gorgen, *Thesis RWTH Aachen* 1985.

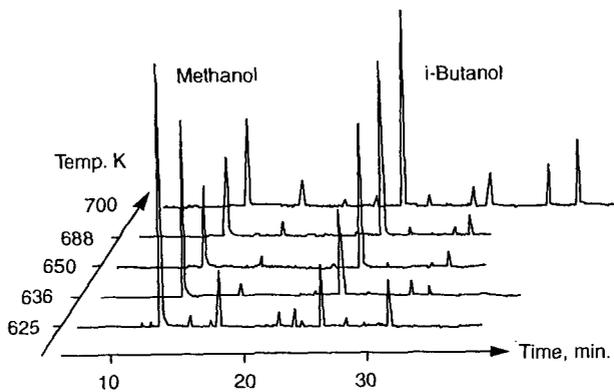


Figure 1. Temperature dependence i-BuOH selectivity (Zr-Zn-Mn-Li-Pd catalyst, 10 MPa, GHSV 10,000 h<sup>-1</sup>)

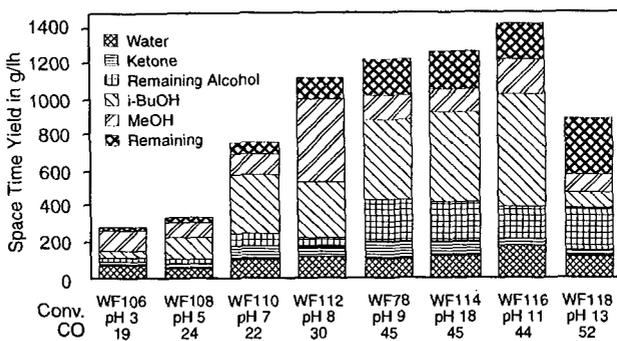


Figure 2. Impact of pH-value on catalyst preparation Zr-Zn-Mn-K-Pd, T = 700 K, p = 25 MPa, GHSV = 20,000 h<sup>-1</sup>

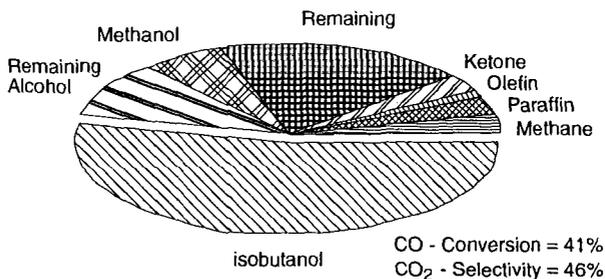


Figure 3. Product selectivity Zr-Zn-Mn-Li-Pd catalyst T = 715 K, p = 25 MPa, GHSV = 20,000 h<sup>-1</sup>