

## ISOBUTANOL SYNTHESIS FROM SYNGAS

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### INTRODUCTION

The hydrogenation of CO to oxygenates is a field of growing interest due to their properties as gasoline blends and the necessity to search for alternatives for future automotive fuels (1). While methanol synthesis from syngas is a well established process, the work on higher alcohol synthesis has been less successful. The demand for MTBE (Methyl-*tert*-butylether) is shifting the interest from higher linear alcohols towards the branched members, mainly isobutanol.

The application of slurry reactors for exothermic reactions has gained considerable interest in the industrial and academic world. For synthesis gas conversions the LPMeOH process by Air Products is a well known example (2). This prompted us to apply this technology to isobutanol synthesis which runs under more extreme reaction conditions.

Because of much easier and faster handling and the necessity to compare results from slurry reactions with the fixed bed reactions cited in literature fixed bed reactor systems are preferred for catalyst development and optimization. The main differences e.g. temperature gradients, backmixing and particle sizes will obviously have major influence on a reaction which mechanistically consists of a network from parallel and consecutive steps (3).

Due to this objective, a fixed bed reactor study has been performed running a typical isobutanol catalyst with different particle sizes and linear velocities. The catalyst developed by us consists of a potassium promoted  $ZrO_2/ZnO/MnO$  possessing high activity for isobutanol and methanol (4). These tests provide data to study the behaviour of residence time and temperature on reaction products. Furthermore mass transfer limitations which affect activity and selectivity (5) can be determined.

### EXPERIMENTAL AND EQUIPMENT

The catalyst was prepared by coprecipitation of the metal nitrates with potassium hydroxide at 80 °C, keeping the pH constant at  $11 \pm 0.2$ . The precipitate was washed, pelletized and dried at 130 °C. After calcination at 450 °C for 3 hours (heating rate: 4°/min) the resulting catalyst was powdered, pressed and sieved to sizes of 0.25-0.50 mm and 1.60-2.00 mm.

For catalytic testing a continuous lab scale unit was set up which can be operated at temperatures up to 500°C and pressures up to 40 MPa. The unit was constructed to switch directly from fixed bed to slurry reactor. A Process management system and on line GC analysis with gas partitioner as well as an automatic product sampler for off line analysis allows continuous operation.

Catalyst activations and reactions have been carried out in a fixed bed reactor from stainless steel with an inner diameter of 9 mm. Catalyst particles have been mixed with an equal amount of copper particles of the same size. Glass particles were added on top as a preheating zone.

The catalyst was activated in situ by pressurizing with hydrogen ( $30 \text{ Ni}\cdot\text{h}^{-1}$ , 3 MPa) and heated to 225 °C with a rate of 4°/min keeping this temperature constant for 120 min. Subsequently the reactor was pressurized with  $H_2/CO$  (1/1) to 25 MPa while temperature was increased up to reaction conditions with 4°/min.

All reactions were conducted at 25 MPa varying temperature from 430 °C to 370 °C in steps of 30°. Afterwards the measurements at 430 °C were repeated to test reproducibility. At each temperature linear gas velocity was changed in six steps from 24 to  $227 \text{ Ni}\cdot\text{h}^{-1}$ . All setpoints were allowed to come to steady state for 75 min. Then the first on line measurement was started followed by collecting one off line sample. A second on line measurement 75 minutes later ended each analysis.

Using this procedure, four test runs have been performed changing bed volume from 2 ml to 4 ml of catalyst and particle sizes from 0.25-0.50 mm to 1.60-2.00 mm.

### RESULTS AND DISCUSSION

Typical reaction conditions of the potassium promoted  $ZrO_2/ZnO/MnO$  catalysts are above 400 °C. Data to show yields of typical products from fixed bed reactions are given in Table 1. Runs up to 415 °C using a 300 ml CSTR with decalin as inert liquid proved the possibility to perform the isobutanol synthesis under slurry conditions. The advantage of removal of exothermic heat by an inert liquid is diminished by approaching the critical temperature. The differences in heat removal between decalin and the syngas itself become very small in high temperature reactions (6).

The fixed bed reactor study resulted that the CO conversion towards alcohols shows a clear dependence upon variation of particle size. All measurements show that activity increases with decreasing particle size which can be interpreted as mass transfer limitation by porous diffusion.

As presented in Figure 1, CO conversion to isobutanol is showing this behaviour in a typical way. Activity increases with increasing temperature following Arrhenius' law. The smaller particle sizes show higher conversions than the larger ones which is an effect of mass transfer limitation. The difference in activity between the two particle sizes grows with temperature due to the temperature dependence which is smaller for mass transfer than for chemical reaction kinetics.

The opposite behaviour can be observed in for the CO conversion to methanol (Figure 2). The activity decreases with temperature which can be explained through an approach to chemical equilibrium. At higher temperatures the values are close to equilibrium and no dependence on residence time can be seen. The measurement at 370 °C shows the characteristics discussed above reaching a steady state value at long residence times in the catalyst bed.

Film diffusion might be an additional limiting step in heterogeneously catalyzed reactions. The influence of film diffusion increases with temperature in the same way as porous diffusion and decreases with linear velocity by reducing laminary films covering the catalyst pellets. Figure 3 exhibits that film diffusion has no influence on CO conversion to isobutanol at 370 °C and only little effect at 430 °C.

The most accepted reaction network for higher alcohol synthesis given by Klier et al. for cesium promoted Cu/Zn-oxide catalysts describes the mechanistic differences between the reaction paths to methanol and isobutanol (3). The first step in higher alcohol synthesis is hydrogenation of CO to a surface intermediate which is very similar to methanol. Linear primary alcohols are built by linear chain growth including CO insertion steps. Isobutanol and 2-methylbutanol-1 origin from  $\beta$ -addition including aldolic condensation. Formation of 1-propanol can be reached via both pathways (Scheme 1).

Isobutanol and 2-methylbutanol-1 do not undergo consecutive reactions following this network. They cannot react further in aldolic condensations and the probability of linear chain growth is low. On the other hand the linear alcohols are able to undergo linear chain growth as well as  $\beta$ -addition.

The CO conversions to the afore mentioned alcohols ethanol, 1-propanol and 2-methylbutanol-1 are plotted in Figures 4, 5 and 6. The branched alcohol 2-methylbutanol-1 shows similarities to the conversion to isobutanol with an increasing activity with temperature (Figure 4). The conversions to ethanol (Figure 5) and 1-propanol (Figure 6) show a similar behaviour as described for methanol. They exhibit a lower activity at higher temperature and seem to be independent from linear gas velocity at 430 °C.

## CONCLUSIONS

The fixed bed reactor study with the potassium promoted  $ZrO_2/ZnO/MnO$  catalyst proved that mass transfer limitations occur at high temperatures even with lab scale particle sizes of 1.60-2.0 mm. Further it could be shown that CO conversion to methanol follows an equilibrium behaviour at higher temperatures, whereas isobutanol does not. For the conversion towards linear alcohols a similar behaviour as observed for methanol was found, where 2-methylbutanol-1 follows the characteristics as pointed out for the other branched member isobutanol.

Future studies adress a further optimization of the  $ZrO_2/ZnO/MnO$  system in order to achieve milder reaction conditions which will benefit slurry reactor operations.

## ACKNOWLEDGMENT

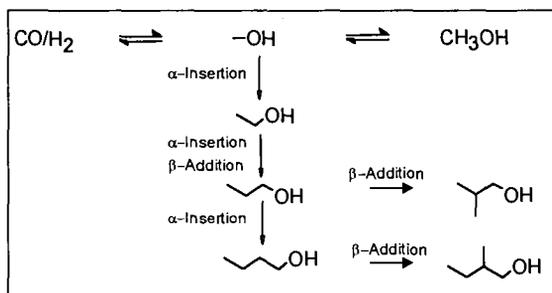
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## LITERATURE

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T [°C]	370		430	
GHSV [h <sup>-1</sup> ]	12000	23250	12000	23250
STY [g/(t·h)]				
Methanol	478	748	242	516
Ethanol	37	43	17	30
1-Propanol	34	38	15	29
Isobutanol	34	35	176	265
2-Methylbutanol-1	11	12	19	29
U <sub>CO</sub> [%]	25	16	48	42
S <sub>CO2</sub> [%]	50	39	56	49

Table 1. Space time yields to alcohols with ZrO<sub>2</sub>/ZnO/MnO/K catalyst in fixed bed reactor (V<sub>cat</sub> = 4 ml, Particle size: 0.25-0.50 mm)



Scheme 1. Reaction Network for alcohol synthesis from CO/H<sub>2</sub>

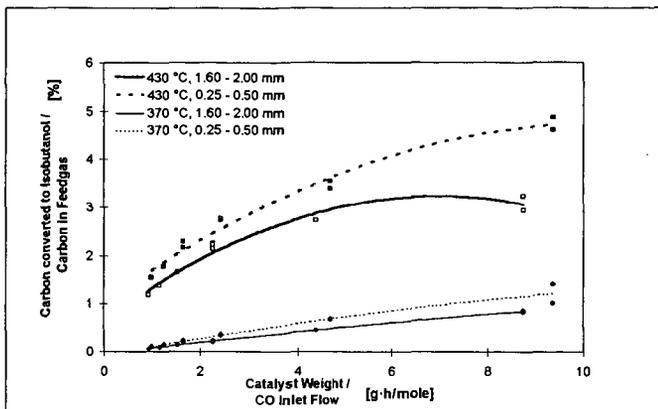


Figure 1. Effect of particle size on CO conversion to isobutanol ( $V_{Cat} = 4$  ml)

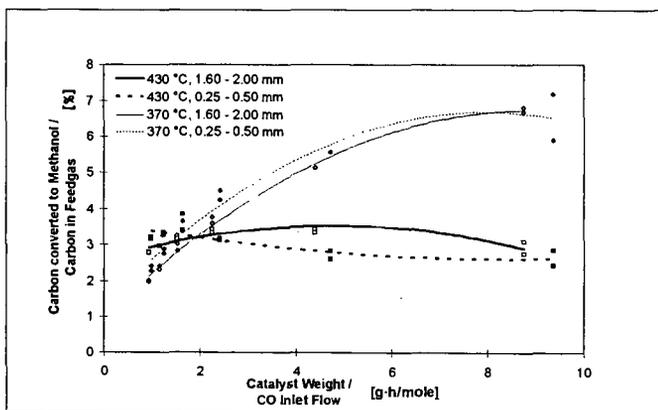


Figure 2. Effect of particle size on CO conversion to methanol ( $V_{Cat} = 4$  ml)

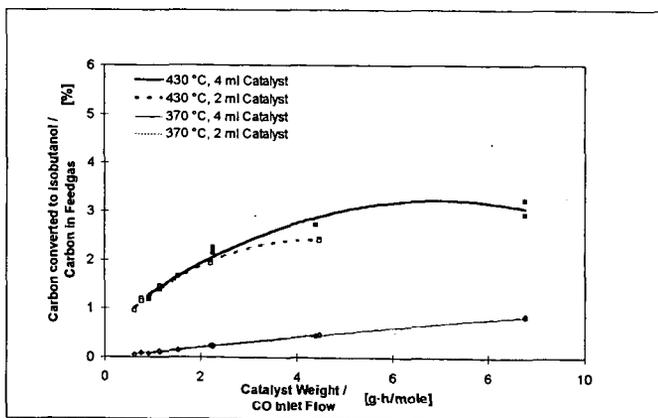


Figure 3. Influence of catalyst bed length on CO conversion to isobutanol (Particle Size: 1.60-2.00 mm)

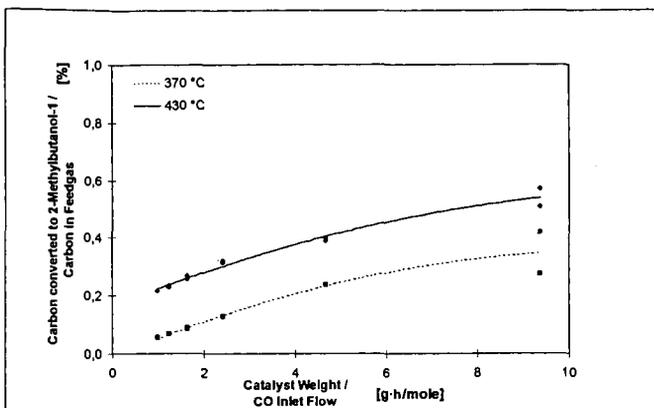


Figure 4. CO conversion to 2-methylbutanol-1 ( $V_{Cat} = 4$  ml, Particle Size: 0.25-0.50 mm)

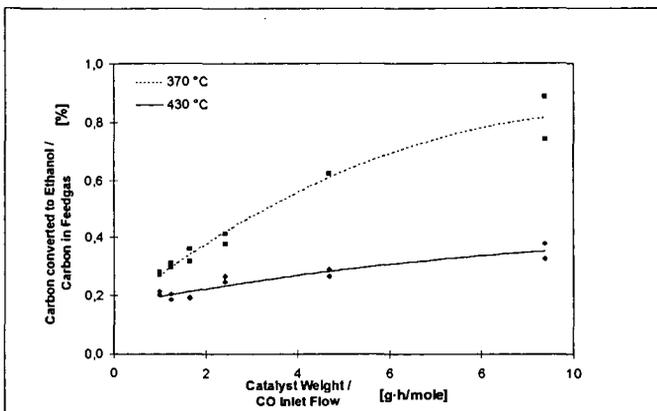


Figure 5. CO conversion to ethanol ( $V_{Cat} = 4$  ml, Particle Size: 0.25-0.50 mm)

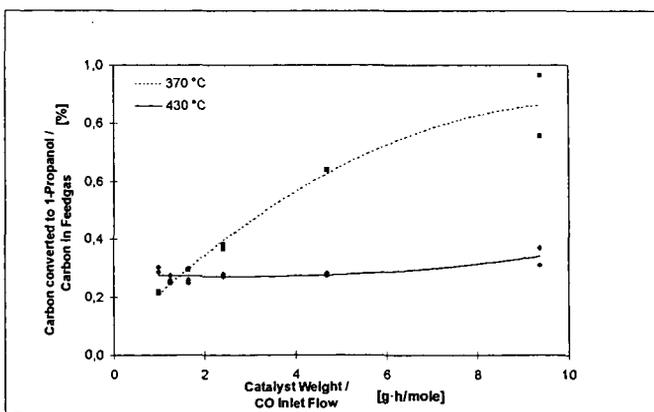


Figure 6. CO conversion to 1-propanol ( $V_{Cat} = 4$  ml, Particle Size: 0.25-0.50 mm)