ISOBUTANOL FROM SYNGAS IN A THREE PHASE SYSTEM

Final Topical Report

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1 Introduction

With growing interest in oxygenates as octane booster for automotive fuels, various synthesis routes for these chemicals are being investigated. Among others, alternative routes to isobutene, the C4-components in MTBE-synthesis are under investigation.

A promising path to isobutene is the heterogeneously catalyzed CO-hydrogenation to isobutanol with following dehydration (Fig. 1).

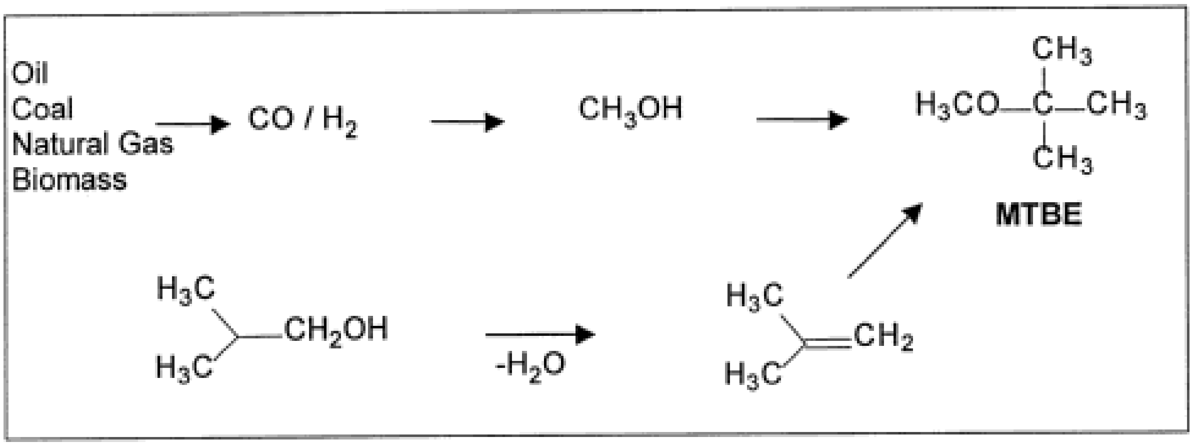


Fig. 1, Syngas-based synthesis of MTBE

Thermodynamics and reactor system

As shown by thermodynamical studies, the heterogenously catalyzed CO-hydrogenation to isobutanol is not expected to experience any thermodynamic constraints[1]. However, heterogeneous hydrogenation of CO is a very exothermic process, a problem which can only be partly solved when being conducted in a plug flow reactor. When carried out in reaction vessels with moving catalyst bed (e.g. three phase stirred tank), heat transfer problems can be resolved, along with additional benefits connected with this reactor type[2].

Catalyst system

Several heterogeneous catalytic systems have been under investigation for their capability of isobutanol synthesis from syngas. Most promising catalysts for an active and selective isobutanol synthesis from CO are modified high temperature methanol catalysts[3].

Research at Aachen

Early as 1982 we at the Institut für Technische Chemie und Petrolchemie at Aachen became interested in the synthesis gas based reaction of isobutanol. Based on the work of BASF, which introduced in 1935 a plant for "Isobutylölsynthese," which was commercial up to 1952, we wanted to apply modern catalyst and reactor design. In their theses of January and June 1985 Mr. Seibring (a chemist) and Mr. Kolle-Görgen (an engineer) designed a pilot plant, which could be used up to 325 bar and 450°C. They developed a catalyst on the basis of ZrO_2/In_2O_3,

	weight %
ZrO_2	81.4
In_2O_3	4.5
CuO	3.6
ZnO	8.5
K_2O	2.0

which produced isobutanol in up to 22 % yield thus being better compared to the BASF $ZnO\text{-}Cr_2O_3\text{-}K_2O$ catalyst.

In 1986 Mr. Falter continued the work by Seibring/Kolle-Görgen aiming at better catalysts, and catalysts operating at milder reaction conditions. Mr. Falter came up with a Zr-Zn-Mn-Li-Pd catalyst, which at 41 % CO conversion yielded up to 750 g isobutanol $l^{1}.h^{-1}$.

Falter's work was the basis for a collaboration with Air Products aimed at a better catalyst working at milder reaction conditions. Four theses were conducted by Finkeldei, Jaeger, Verkerk and Golob. Main emphasis rested on understanding the catalyst and developing a new catalyst (Jaeger, Verkerk, Golob). Due to the severe reaction conditions needed also chemical engineering approaches were undertaken (Finkeldei).

Besides the theses quoted above the work is described in the following papers:

1. W. Keim, W. Falter, Catalysis Letters 1989, 3, 59.
2. Prepr. Pap.-Am. Chem. Soc. Div. Fuel Chem. 1996, 41 (3), 875-879.
3. Isobutanol Synthesis from Syngas, C.H. Finkeldei, B. Jaeger, W. Keim, K.A.N. Verkerk in "Designing Transportation Fuels for a Cleaner environment", ed. J.B. Reynolds, M.R. Khan, Applied Energy Technology Series 1957.
4. Isobutanol from Syngas, W. Falter, C.H. Finkeldei, B. Jaeger, W. Keim, K.A.N. Verkerk in "Natural Gas Conversion", ed. A. Parmaliana, D. Sanfilippo, F. Frusteri, A. Vaccari and F. Arena, Elesvier 1998.
5. Prep. Pap. - Am. Chem. Soc. Div. Fuel Pet. Chem. 1999, 44(1), 28-30 (CA 130;354461c).
6. K.A.N. Verkerk, B. Jaeger, C.H. Finkeldei, W. Keim, Applied Catalysis A: General 186 (1999) 407-431.

2 Chemical engineering

Two high-pressure units were designed and built for the investigation of the heterogenously catalyzed CO-hydrogenation to isobutanol.

Unit I

Unit 1[6,7,8] is a fully automated high-pressure unit (pressures up to 400 bar at a temperature of 450°C) with a process management system (Tactician TCS2000) and an on-line system for analysis of liquid as well as gaseous products (Fig. 2). An automated off-line product sampling system for checking on-line results was installed additionally. Unit I was designed to allow a flexible usage of a continuous stirred tank reactor as well as a plug flow reactor.

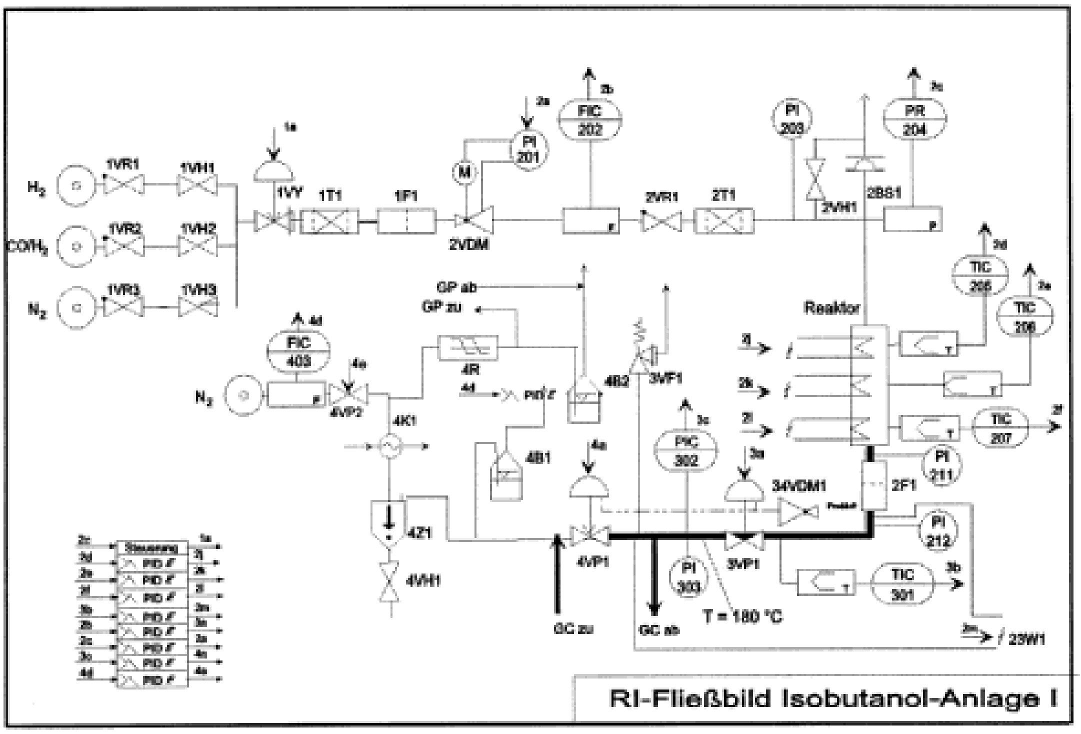


Fig. 2, P&ID Unit I

Continuous Stirred Tank Reactor (CSTR)

A continuous stirred tank reactor, withstanding high reaction conditions (pressure up to 350 bar at a temperature of 450°C), was designed and build at the institute[7]. Decalin showed to be a suitable inert liquid for isobutanol synthesis with sufficient stability at high reaction conditions[6]. Investigations were conducted investigating the influence of the stirring speed[14,18]. The yield to methanol increased with increasing stirring speed up to a speed of 2000 rpm. At higher stirring speeds, methanol yields remained constant.

Furthermore, calculations concerning mass and heat transfer in the CSTR were conducted[9,10,11,18]. Mass transfer limitation, caused by the use of decalin was excluded. The mathematical correlations were confirmed by experiments in the CSTR[9,10]. Mass transfer experiments were also conducted in the plug flow reactor by varying the particle size[10].

It could be shown that heat transfer in a two phase continuous stirred tank reactor is comparable to the heat transfer in a three phase continuous stirred tank reactor system[12].

The influence of pressure on alcohol synthesis in PFR and in 2-phase as well as 3-phase CSTR was studied[10]. Methanol follows thermodynamics at all reaction conditions, isobutanol shows a higher increase of yield with increasing pressure at lower temperatures. This effect can be explained by an increased formation of byproducts at high temperatures.

Unit II

Initially, catalyst screening was conducted in autoclave batch-equipment. The Zr/Zn/Mn-oxide[6] as well as various Zn/Cr-oxide catalysts were studied[13]. A second continuous high-pressure unit (Unit II)[14] was then designed and built for the purpose of catalyst screening. This unit was equipped with only off-line analytics (Fig. 3).

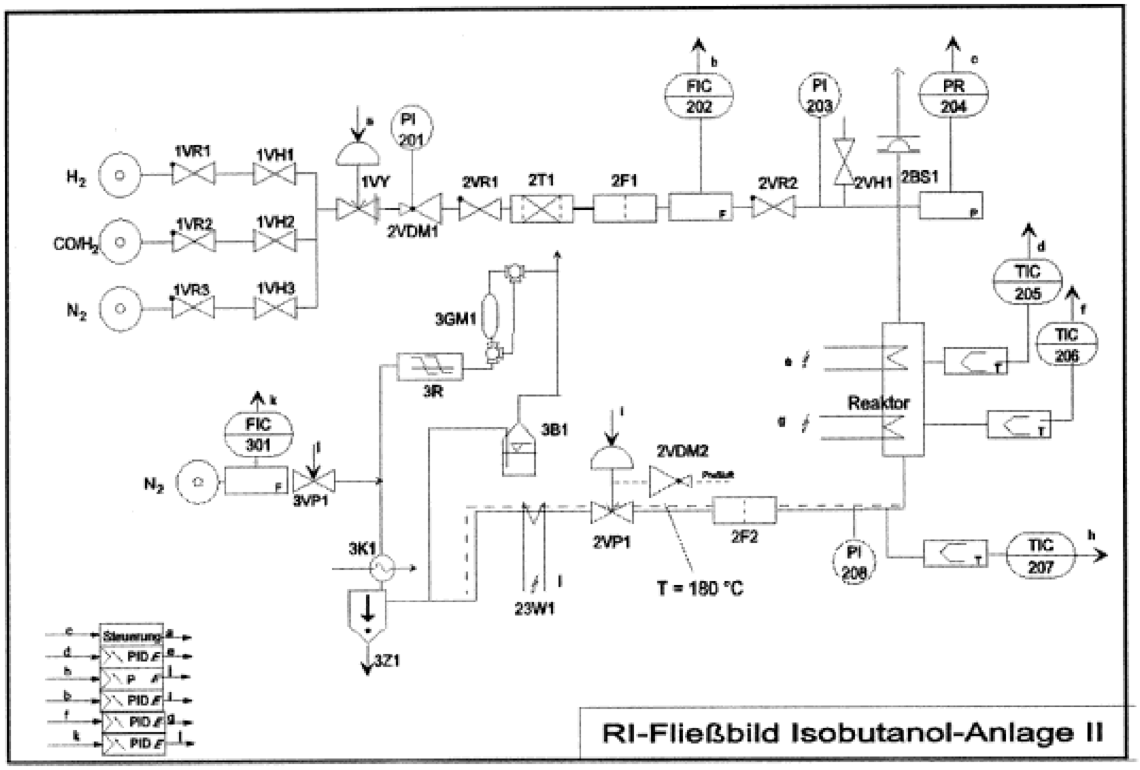


Fig. 3, P&ID Unit II

3 Comparison of PFR and CSTR

Influence of CO_2 *concentration in PFR and CSTR*

The different influences of backmixing in a plug flow reactor and CSTR on isobutanol synthesis were compared using a Zn/Cr-oxide catalyst as well as the Zr/Zn/Mn-oxide catalyst system. The CSTR was used as a 2-phase reactor with a so called spinning basket. This comparison shows a strong effect of the backmixing in the CSTR, which leads to high CO_2-concentrations[19]. When using the Zr/Zn/Mn-oxide catalyst, activity towards methanol and especially isobutanol show a sharp decrease, whereas activity towards ethanol and n-propanol are hardly affected by backmixing (Fig. 4).

This result shows clearly, that the $C_1 \rightarrow C_2$-step is not the only rate-limiting reaction step in isobutanol synthesis under the here used reaction conditions. Furthermore, methanol and isobutanol formation seem to proceed at the same reaction centre, which is being blocked at high CO_2-concentrations.

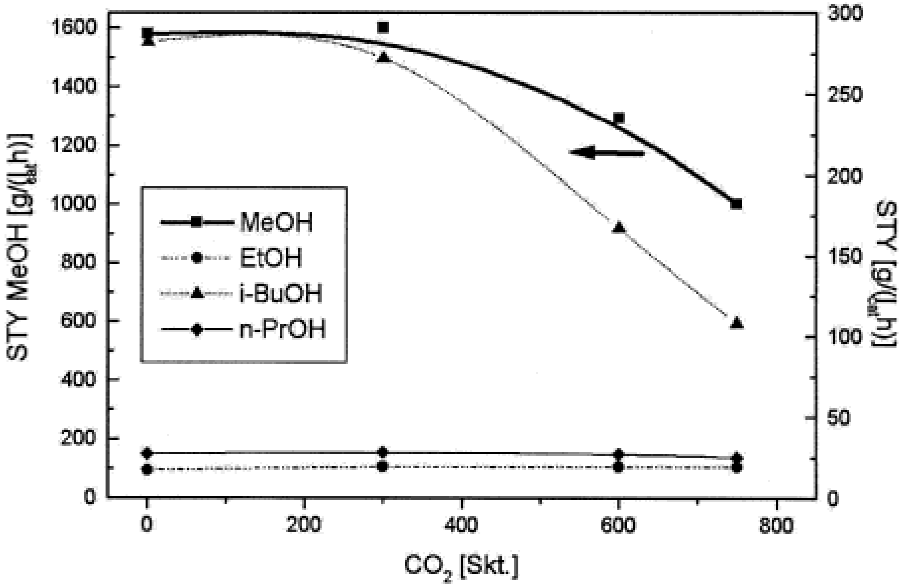


Fig. 4, Influence of CO2-addition in PFR on main products (Pd-Zr/Zn/Mn-oxide, PFR, Unit I, T = 400°C, p = 250bar, GHSV = 27,000 h $^{-1}$, V_{cat} = 2 ml, D_{cat} = 0,630,71 mm)

This result was reproduced in a backmixing-free system (plug flow reactor) by adding CO_2 to the syngas, thus showing the great impact influence of CO_2 on alcohol synthesis [15] (Fig. 5). However, for the Zn/Cr-oxide catalyst system, the effect of high CO_2 concentrations is less pronounced[17], showing the influence of the used catalyst system.

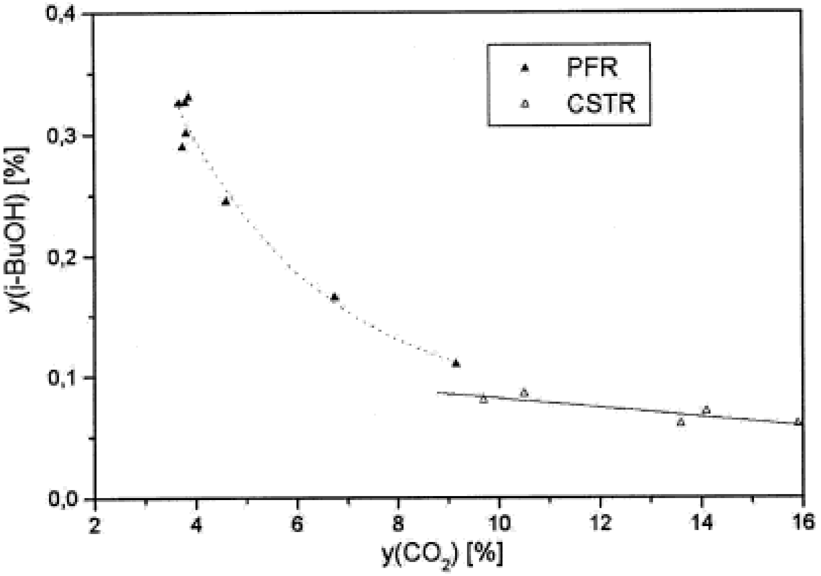


Fig. 5, Influence of CO2 content of gase phase at reactor outlet on isobutanol content in gas phase (Pd-Zr/Zn/Mn-oxide, PFR, Unit I, T = 400°C, p = 250 bar, GHSV = 27,000h^{-1} ,V_{cat} = 2 ml, D_{cat} = 0,63-0,71 mm)

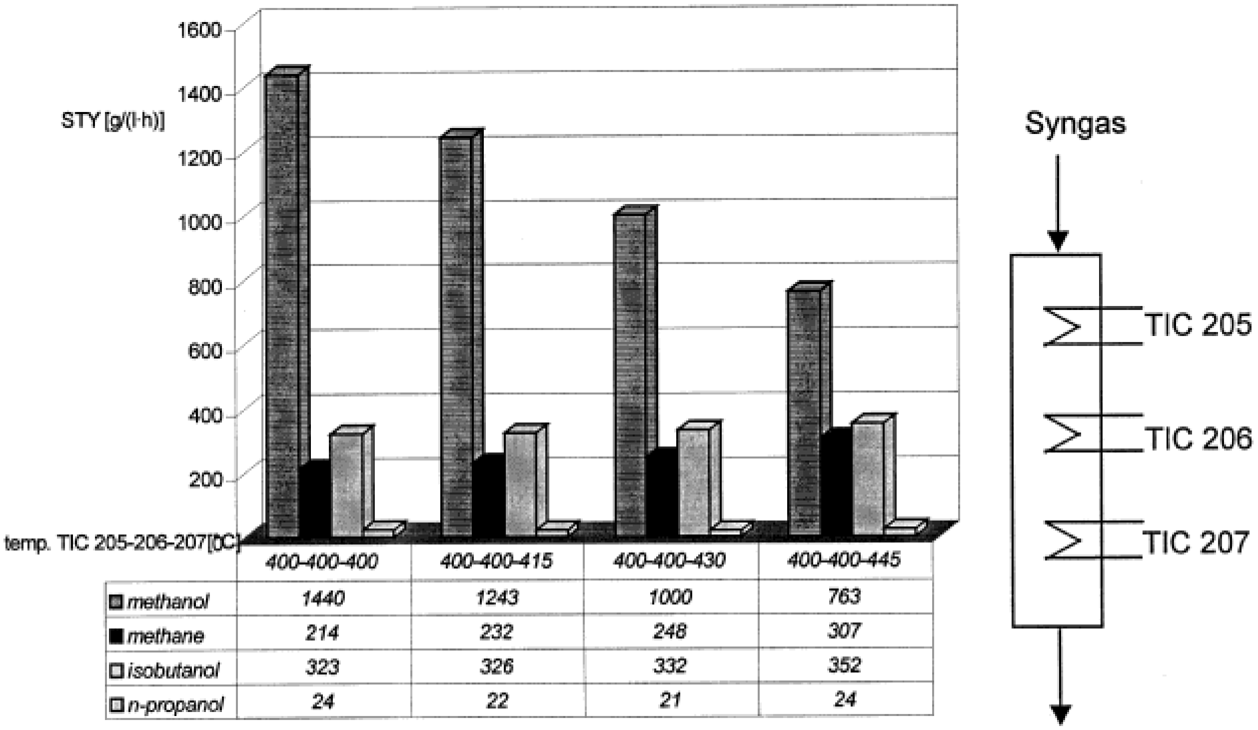
4 Reproduction of previous results

For the development of better catalysts than those made by Falter we first had to match Falter's results. We encountered great difficulties which finally were solved.

In catalyst synthesis, the washing procedure of the coprecipitated catalyst as well as the reduction procedure of the catalyst were studied[8]. Furthermore, calcination temperature was chosen below reaction temperature in previous' investigations, causing catalyst volume to decrease during reaction.

Initial high methanization activity observed in Unit I, could be strongly reduced by improved carbonyl-purification with activated carbon and by using a plug flow reactor with smoother inner surface[16]. A study of the previously used plug flow reactor showed that the construction of this reactor led to an axial temperature gradient, raising temperature at reactor outlet[8]. This led to a decrease in methanol selectivity, which is determined by thermodynamics.

For this reason, previously obtained isobutanol activities could be reproduced, whereas isobutanol selectivity could not be reached completely[14,16]. The influence of an axial temperature gradient on methanol activity, which shows thermodynamical limitation at the here used reaction conditions, and therefore on isobutanol selectivity, could be reproduced by an axial temperature gradient forced by external heating[17] (Fig. 6).



temp. TIC 205-206-207[°C]	400-400-400	400-400-415	400-400-430	400-400-445
▨ *methanol*	1440	1243	1000	763
■ *methane*	214	232	248	307
☐ *isobutanol*	323	326	332	352
☐ *n-propanol*	24	22	21	24

PFR Unit I, p=250 bar, V_{Cat} = 4 ml, temp. TIC 205-206 = 400 °C, GHSV = 26000 h^{-1}.

Fig. 6, Influence of an axial temperature gradient on yield to main products in the PFR

5 **Catalyst synthesis** (Thesis Jaeger, Verkerk, Golob)

Following catalyst synthesis methods were studied and compared[18]:

- Coprecipitation
- Precipitation
- Complexation[11]
- Sol-Gel chemistry
- Supported catalysts[19]

5.1 Zr/Zn/Mn-oxide catalysts

General remarks

- The optimal composition of the Zr/Zn/Mn-oxide catalyst showed to be 1:1:1.
- pH-value mainly influences the alkali content of the coprecipitated catalysts. This was shown with several solid material analytical methods (AAS/XRF, BET, XRD, DSC/TG)[16] Alkaline-free catalysts were synthesized. With these catalysts, the influence of alkaline content on isobutanol synthesis was investigated[14,16,18]
- Impregnation of the Zr/Zn/Mn-oxide catalyst with potassium improved isobutanol selectivity as well as activity[11,18]
- Zr/Zn/Mn-oxide catalysts, synthesized by impregnating a ZrO_2-support lead mainly to methanol and DME. This probably is related to the higher acidity of these catalysts[19].

Sol-Gel catalysts

Several aspects of this synthesis method were investigated:

- Addition of complexing agents (acetic acid, acetylacetone)[9]
- Influence of Cs/K-content[10,18]*:* A maximum both in activity and selectivity towards isobutanol are reached at a potassium promotion of 0.5 wt%.
- Effect of aging time[19]: catalysts with an medium long aging time of 7 days showed best results in isobutanol synthesis.
- Additional components (Ce, Cu, Co, Ni)[19]: especially addition of cerium or nickel to the Zr/Zn/Mn-oxide catalyst improved isobutanol yield.
- Influence of preparation method on surface area and pore size[10,11]. Highest isobutanol activity and selectivity are found for catalysts with high surface area and medium pore size.

5.2 Catalyst development at lower reaction conditions

For successful implementation of a heterogenous catalyst in a three phase isobutanol synthesis, the high reaction conditions used with Zr/Zn/Mn-oxide catalysts (temperature over 400°C, pressure = 250 bar) have to be lowered in order to lower process costs. For this reason known catalyst systems in isobutanol synthesis were compared. Then, it was tried to improve the catalytical properties of the most promising catalyst.

Comparison of known systems[20]*.*

Only modified high-temperature methanol catalysts showed high activity as well as selectivity towards isobutanol. Best results were obtained with a potassium promoted Cu/Co/Zr/Zn/Mn-oxide catalyst.

Impregnation of the Zr/Zn/Mn-oxide catalyst with hydrogenation metals[21]

A Zr/Zn/Mn-oxide catalyst was impregnated with different loads of various metals. These metals were chosen for their hydrogenation activity or for their ability to catalyze the $C_1 \rightarrow C_2$-reaction. Among the investigated metals (Cu, Co, Ru, Rh, Pd and Pt) only copper showed improved results in isobutanol activity as well as selectivity. For this reason, the influence of the copper content on a Cu/Zr/Zn/Mn-oxide catalyst system was investigated.

Investigation of the Cu/Zr/Zn/Mn-oxide catalyst system[22]

The addition of copper to a Zr/Zn/Mn-oxide catalyst lead to a significant improvement of catalyst activity. With increasing copper content, methanol activity, being only controlled by thermodynamics, remained constant. The yield of higher alcohols, on the contrary, increased with higher copper content. At very high levels of copper content, linear chain growth towards ethanol and n-propanol dominates over branching chain growth, especially at higher temperatures.

The investigated copper-containing catalysts show a remarkable thermal stability, especially at lower copper content. Reproduction measurements at 350 °C[1] show an even improvement of isobutanol activity as well as selectivity, as methanol activity decreases[18].

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[1] Order of experiment: measurement at 350, 385 and 350 °C.

Also, Cu/Zr/Zn-aerogel based catalysts were investigated[10,11,19]. These catalyst show a high selectivity and activity to isobutanol. Furthermore they exhibit an extraordinary thermal stability, which is most pronounced in the CSTR. Thermal deactivation of these catalyst leads to an increased lattice constant of copper, which cannot be observed in the CSTR and can be undone by reducing the catalyst a second time[19]. Calcination with CO or H_2 also leads to an increased lattice constant of copper, inducing that deactivation of the Cu/Zr/Zn-aerogel based catalyst is not only a thermal effect, but also an effect, induced by the presence of these gases at high temperatures.

Promotion of *the Cu/Zr/Zn/Mn-oxide catalyst with cobalt and palladium*

- Promotion with cobalt: Addition of cobalt to the Cu/Zr/Zn/Mn-oxide catalyst takes only minor influence on higher alcohol yield. However, by lowering methanol yield, selectivity towards higher alcohols can be changed considerably[23].
- Promotion with palladium: Addition of palladium to the Cu/Zr/Zn/Mn-oxide catalyst increases activity as well as selectivity towards higher alcohols[23].

Combinations of a *Zn/Cr-oxide catalyst with* a *Cu/Co-oxide catalyst*

It was also tried to combine a catalyst, active in linear chain growth at low reaction conditions (IFP Cu/Co-based catalyst system) with one, active in branched chain growth (BASF Zn/Cr catalyst system), in order to increase isobutanol activity and selectivity at milder reaction conditions[24,25]. Both catalysts were physically mixed in a ball mill.

Activity of the Zn/Cr-oxide catalyst can be greatly enhanced on adding Cu/Co-based catalyst. Activity and selectivity towards isobutanol are enhanced with increased Cu/Co content. At high Cu/Co-content of the mixed catalysts, however, preferred product in the C_{2+}-phase are linear alcohols. At higher temperatures, methanisation becomes a problem.

6 Summary of work carried out for Air Products

- Two high pressure units for isobutanol synthesis from syngas were designed and built for usage with CSTR as well as PFR.
- Previously obtained results in isobutanol synthesis from syngas could be reproduced.
- Isobutanol synthesis from syngas could be performed in a two- and three-phase CSTR, even at high reaction conditions. Isobutanol yields up to 80 g/(l_{cat} h) were reached.
- The influence of carbondioxide in PFR and CSTR on isobutanol synthesis from syngas could be shown for different catalytic systems. From these experiments, it could be demonstrated, that the $C_1 \rightarrow C_2$-step is not the only rate-limiting reaction step in isobutanol synthesis.
- Heat and mass transfer caculation and experiments in isobutanol synthesis from syngas were performed in PFR and CSTR.
- The sol-gel catalyst synthesis method was extensively studied leading to comparable catalysts.
- The activity of the Zr/Zn/Mn-oxide catalyst system could be enhanced at lower reaction conditions. Copper-containing catalysts showed high activity towards isobutanol with a remarkable thermal stability.
- The Falter catalyst proved to be the best.
- Comparing the work of the various other research groups in this field showed that Falter's catalyst is the best developed so far. However, the severe reaction conditions needed will make it difficult to operate this catalyst commercially.

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