Fraunhofer IKTS

TECHNISCHE UNIVERSITÄT DRESDEN

# OPTIMIZATION OF SUPPORTED IRON-BASED FISCHER-TROPSCH CATALYSTS FOR HIGHER ALCOHOL PRODUCTION

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## MOTIVATION

Fischer-Tropsch Synthesis (FTS) has recently experienced increasing interest again, since hydrocarbon chains can be built up from hydrogen and carbon monoxide (syngas) via the heterogeneously catalyzed polymerization reaction [1]. Syngas cannot only be produced from crude oil, natural gas and coal, but also from biogas and $CO_2$ [2]. Although sustainability could be increased by applying FTS for e.g. fuel production, it is still not economically competitive. But in addition to alkanes and alkenes, oxygenates, e.g. alcohols, can be produced by FTS as well. Especially higher alcohols (HA) that contain more than two carbon atoms per molecule, are value-added products and are accessible via FTS on iron based catalysts. This approach could be competitive with the established, complex multi-step reactions that are currently used for HA-production.

Selectivity of Fe catalysts towards higher alcohols can be further tuned by applying chemical or structural promotion [3]. While comprehensive literature on the former is available, it is scarce on structuring and shaping of iron FTS catalysts for HA production. Consequently, systematic approaches are needed to transfer this process from lab to pilot-scale.

Therefore, powder aluminum oxides of different modifications and crystallite sizes were impregnated and tested in FTS. Especially $\alpha$-$Al_2O_3$ was considered as promising support, because of its similar crystal structure to $\alpha$-$Fe_2O_3$. Accordingly epitaxial growth could be supposed to occur, which could give an extra impact on the long-time stability and reveal beneficial catalyst-support interactions [4].

## EXPERIMENTAL SECTION

### Catalyst Preparation

- Stepwise incipient wetness impregnation of the alumina powders with aqueous iron III nitrate or Ammonium iron (III) citrate solution
- calcination at 500 °C for 8 h

### Catalytic Tests

- Fixed-bed tube reactor
- Reduction: 10 % $H_2/N_2$ (GHSV = 200 $h^{-1}$) at 400 °C and atmospheric pressure for 10 h.
- Fischer-Tropsch synthesis: $H_2/CO/N_2$ (6:3:1) (GHSV = 60 $h^{-1}$), 20 bar, 200 °C
- Online gas phase monitoring by GC measurement

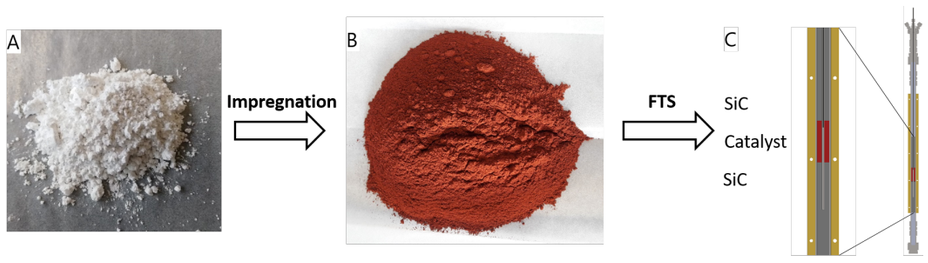


Figure 1: Schematic approach for catalyst production and testing: $Al_2O_3$ support (A), supported $Fe_2O_3/Al_2O_3$ catalyst (B) scheme of applied fixed-bed reactor.

## CATALYST CHARACTERIZATION

Table 1: Catalyst characteristics according to $N_2$ physisorption (BET) and XRD. Catalyst I was co-precipitated pure $Fe_2O_3$, while II-VI were $Al_2O_3$ supported catalysts synthesized by impregnation with either iron (III) nitrate or citrate.

| No. | $Al_2O_3$ phases | $D_{XRD}(\alpha\text{-}Al_2O_3)$ [nm] | Fe precursor | Spec. surface area [$m^2\ g^{-1}$] |
|---|---|---|---|---|
| I | - | - | - | 17 |
| II | α, δ | 11 | nitrate | 81 |
| III | α, δ | 47 | nitrate | 27 |
| IV | α | 66 | nitrate | 12 |
| V | α | 160 | nitrate | 5 |
| VI | α | 66 | citrate | 29 |

- Catalyst II experienced phase transition and surface area loss during calcination
- Citrate-derived catalyst exhibited higher surface area and iron distribution

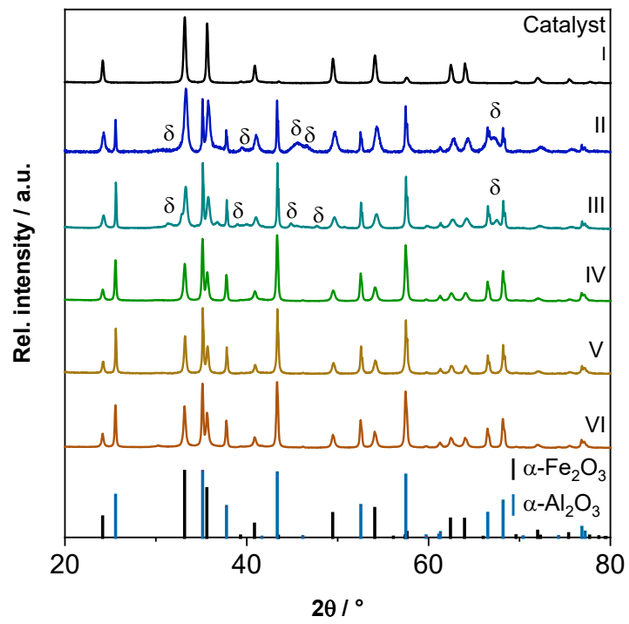


Figure 2: XRDs of the catalysts. References: α-, δ-$Al_2O_3$ and α-$Fe_2O_3$.

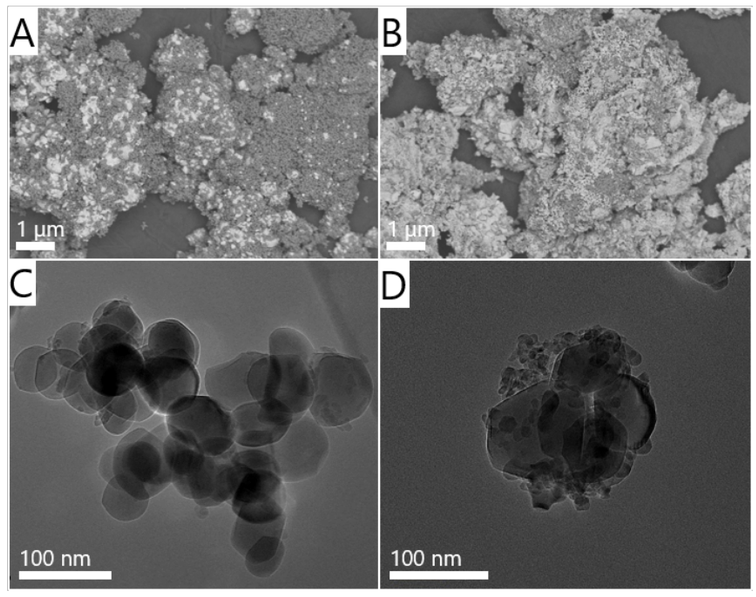


Figure 3: FESEM images ESB and TEM images of nitrate – (A, C) and citrate-derived (B, D) supported catalysts.

## CATALYTIC RESULTS

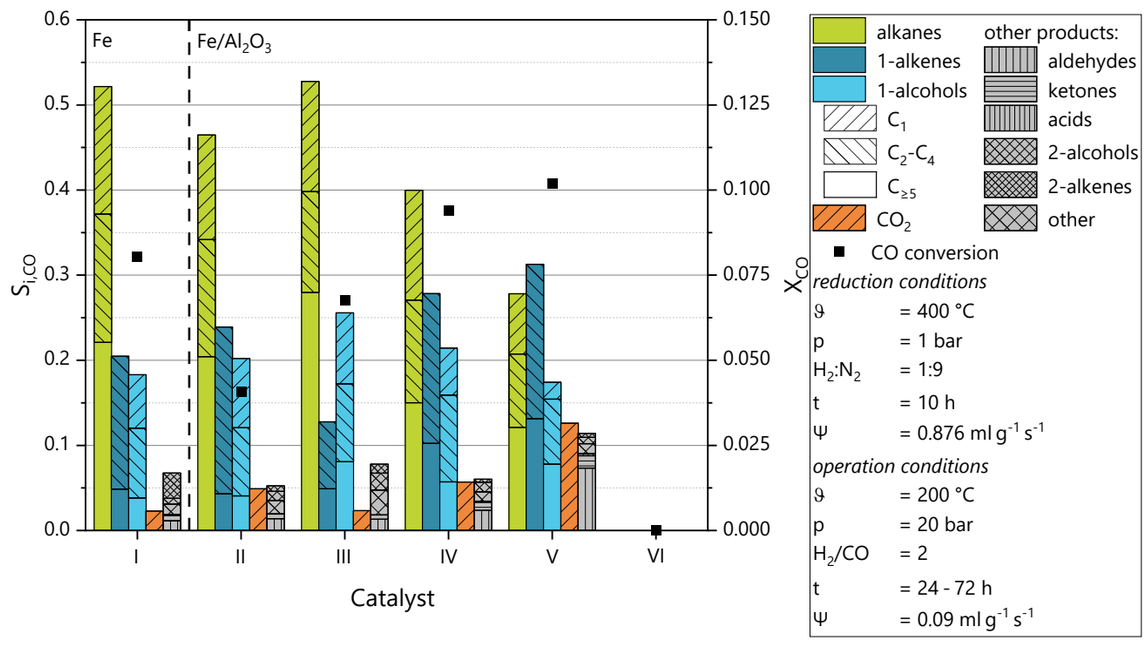


Figure 4: CO conversions and selectivity for the tested catalysts.

- Better selectivity for higher alcohols on supported catalysts
- Iron III citrate is not an appropriate catalyst precursor
- Conversion increases with crystallite size and mass fraction of $\alpha$-$Al_2O_3$ for supported catalysts
- Catalyst III:
  - Highest overall $C_{5+}$ selectivity
  - Beneficial catalyst-support interaction probably due to synergy between δ- and $\alpha$-$Al_2O_3$

## CONCLUSION AND OUTLOOK

### Conclusion

- Synthesis of supported $Fe/Al_2O_3$ catalysts successful
- Catalysts reveal beneficial catalyst-support-interactions for HA-synthesis
- Most promising results with catalyst III support
- Conversion and selectivity influenced by phase composition and crystallite size of support
- Citrate precursor not suitable for HA-synthesis

### Outlook

- Application of both chemical and structural promoters
- Shaping and structuring of supported catalysts

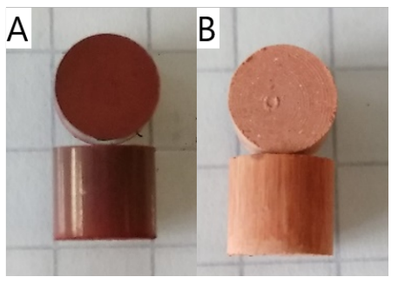


Figure 5: Shaped catalysts made by tableting A) pure co-precipitated $Fe_2O_3$ and B) a mixture of co-precipitated $Fe_2O_3$ and $Al_2O_3$.

## REFERENCES

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