

THE FISCHER-TROPSCH SYNTHESIS IN SLURRY PHASE REACTORS

Kinetics and Mass Transfer

proefschrift

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*Iemand is blij als hij de passende woorden vindt,
het juiste woord op het juiste moment is een weldaad.*

Spreuken 15 : 23

SUMMARY

Low olefins such as ethene and propene are important basic chemicals which are generally still obtained from crude oil nowadays, but it may well be that coal could become a major carbon source for the production of these and other hydrocarbons in the future.

With coal as the raw material, there are two main routes, i.e. extraction under simultaneous hydrogenation and gasification, followed by the production of synthesis gas, which, in turn, is converted to hydrocarbons and oxygenated chemicals by Fischer-Tropsch synthesis. This study is concerned with the latter of these routes, i.e. a variation of converting from coal-derived synthesis gas to low olefins.

An important characteristic of synthesis gas, is the H_2/CO ratio. This ratio may vary between 0.4 and 4.0, depending on which gasification process is chosen. In this study the major objective is the ability to convert synthesis gas, having a low H_2/CO ratio (0.46 - 0.68), directly to low olefins in a slurry reactor. Such synthesis gas is produced by modern coal gasifiers, because low H_2/CO ratio's have economic and process advantages.

For the goals set in the objective of this thesis to be fulfilled, it is necessary to apply a suitable catalyst system which not only gives the desired activity and selectivity characteristics for the desired performance in a slurry reactor, but the catalyst system should also be a good water-gas shift catalyst.

In this thesis the selective production of low olefins is investigated at relatively high pressures (e.g. 10 bar) and high measures of conversion from CO rich synthesis gas. Two catalysts are used in this investigation: $RuFe/SiO_2$ and potassium promoted fused iron.

$RuFe/SiO_2$ has been selected because of its high activity and olefin selectivity observed at low conversions. On the other hand, potassium promoted fused iron is a veteran in the field and therefore served as the best available basis for comparison.

The slurry bubble column seems promising for the industrial production of low olefins via the Fischer-Tropsch route. Therefore special attention is given to the effect of gas-liquid mass transfer in this type of reactor. The mass transfer of hydrogen is of particular importance because the conversion rate of synthesis gas depends mainly on the hydrogen pressure.

The influence the type of reactor has on olefin selectivity is investigated whereby a bubble column reactor is used which has external recycle of the gaseous reaction products and unconverted CO and H₂.

The experimental work consist of three parts:

1. A kinetic study of Fischer-Tropsch synthesis over RuFe/SiO₂ and fused iron in a stirred autoclave at 1.5 - 17 bar and 200 - 300°C for a maximum measure of conversion of 98%.
2. A study of the gas-liquid mass transfer coefficient of H₂ in a 5 cm diameter glass bubble column at atmospheric pressure and 250°C whereby the application of ethene hydrogenation over palladium was applied.
3. An investigation of CO and H₂ conversion to low olefins in a 5 cm diameter stainless steel bubble column at 9 bar and 250 - 270°C over fused iron. Part of the reactor outlet gas is recycled by means of a compressor. The liquid phase in this and the other reactors is squalane (C₃₀H₆₂) which can be considered as representative of a Fischer-Tropsch wax.

In the case of fused iron the extent of secondary hydrogenation of ethene and propene mainly determines the olefin selectivity of C₂ and C₃ respectively. The olefin selectivity depends entirely on the olefin/carbon monoxide pressure ratio in the reactor and is independent of the hydrogen pressure. This may be explained by considering carbon monoxide and olefin molecules produced competing for the same catalyst surface sites, whereas the order of hydrogen for secondary hydrogenation and synthesis gas conversion is equal. Thus, an increase of the CO conversion results in a higher olefin/CO pressure ratio and this causes an increase in the hydrogenation of olefins. In the case of ethene it would appear that incorporation also increases with increasing ethene/CO pressure ratio. The latter incorporation of ethene makes it clear why the C₂-point falls below the Schulz-Flory line at higher conversions.

The olefin selectivity observed with RuFe/SiO_2 is very low in comparison with fused iron, particularly after some time on stream. The olefin selectivity decreases extremely rapidly with increasing CO conversion. Since olefin selectivity appears to be equally low, whether using RuFe/SiO_2 or Ru/SiO_2 and the bimetallic phase appears to decompose, it is clear that it is the Ru particle which determines the performance of the RuFe/SiO_2 system and therefore the pronounced hydrogenation activity.

There are other properties of the fused iron catalyst which are superior to the RuFe/SiO_2 catalyst, such as higher activity and a considerably lower methane selectivity. The latter is even lower than what is predicted by the Schulz-Flory distribution under conditions almost complete CO conversion.

The activities of both fused iron and RuFe/SiO_2 are low to the extent that the mass transfer rate in a bubble column in which a Fischer-Tropsch reaction is operating, is sufficiently large.

The mass transfer coefficient k_{La} reaches exceptionally high values in the squalane liquid medium ($> 2 \text{ m}^3_{\text{L}}/\text{m}^3_{\text{L+G s}}$) by using a porous plate as a gas distributor, provided the concentration of the solid particles is low ($< 1 \text{ wt\%}$).

However, the addition of solids in the diameter range of 3 - 64 μm , which gives a suspension containing 1 - 20 wt% of solids, always results in a fall of the k_{La} . This decline of the k_{La} with increasing solid concentration is more pronounced for solids with larger particle diameters. The particles added to the system probably cause accelerated coalescence of gas bubbles. The advantage of a porous plate, which is meant to produce small bubbles, gets lost therefore, for a higher concentration of solid particles.

The olefin selectivity was much higher in a bubble column than in a stirred autoclave for equal conversions. This high olefin selectivity is caused by the mean lower olefin/CO pressure ratio and this, in return, is caused by the plug flow characteristic of the gas flow. The effect of "back-mixing" of product gas, investigated by recycling products of reaction and unconverted synthesis gas is less significant than the effect of the conversion taking place.

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