ELSEVIER

Catalysis Today 79–80 (2003) 495–501

CATALYSIS TODAY

www.elsevier.com/locate/cattod

# Using monolithic catalysts for highly selective Fischer–Tropsch synthesis

Ronald M. de Deugd[1], Freek Kapteijn*, Jacob A. Moulijn

*Reactor and Catalysis Engineering, Faculty of Applied Sciences, Delft University of Technology,*
*Julianalaan 136, 2628 BL Delft, The Netherlands*

## Abstract

Reactor designs for Fischer–Tropsch synthesis (FTS) are illustrative for the struggle to combine the process needs concerning selectivity, heat removal, pressure drop and catalyst attrition and separation. A novel reactor type, the Monolithic Loop Reactor, may constitute a way out of these problems. Experimental data about activity and selectivity of monolithic catalysts are presented. The results show, besides competitive activity and chain growth probability, high olefin to paraffin ratios.

*Keywords:* Fischer–Tropsch synthesis; Monolithic catalysts; Catalyst testing; Selectivity

## 1. Introduction

Fischer–Tropsch synthesis (FTS) is a process to convert synthesis gas (mixtures of CO and $H_2$) to water and hydrocarbons that can be used as liquid fuels or base chemicals. Feedstocks for the generation of synthesis gas can be natural gas, coal and biomass. FTS is already an old process, but in the last decade, the interest is growing again under influence of the need to convert natural gas from remote sources to liquid fuels and to utilize associate gas from oil rigs.

Due to the polymerization-like mechanism (Fig. 1) of FTS a wide range of mainly non-branched products is formed ranging from methane to heavy waxes. Therefore, the selectivity to, for instance, diesel fuel is always limited. The selectivity of the process is usually described by the Anderson–Schulz–Flory (ASF) distribution and the characteristic chain growth probability, $\alpha$. High chain growth probabilities (>0.90) are regarded desirable as they lead to reasonable primary selectivities to fuel ranges and high selectivities to heavy components, which subsequently can be converted to liquid fuels rather easily. Especially, diesel range components are desirable as the linear FTS products have high cetane numbers.

The chain growth probability is determined by both catalyst properties and process conditions. Higher temperatures and super-stoichiometric concentrations of hydrogen lower the selectivity towards heavy products dramatically. Particle size and morphology are strongly connected to the composition of the reaction mixture near the catalytic sites. Different diffusion rates of CO and $H_2$ lead to super-stoichiometric concentrations of hydrogen in the catalyst particle with larger diffusion distances. Schanke et al. [1] report decreased selectivity to $C_{5+}$ products for particle sizes above 100 μm. Iglesia et al. [2] not only consider the transport of reactants, but also the readsorption and reinsertion of olefins. Chances of olefin readsorption

---

* Corresponding author.

*E-mail address:* f.kapteijn@tnw.tudelft.nl (F. Kapteijn).

[1] Present address: Shell Global Solutions International B.V., Badhuisweg 3, 1031 CM Amsterdam, The Netherlands.

0920-5861/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00073-7

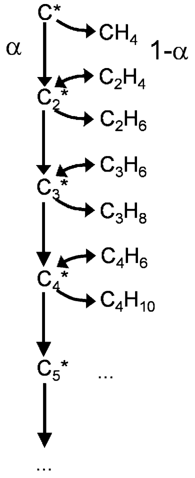

Fig. 1. Kinetic model scheme for the Fischer–Tropsch synthesis, including olefin production and reinsertion ($\alpha$ = chain growth probability).

rise with longer diffusion distances and higher carbon number, because of longer residence time in the catalyst and decreased mobility, respectively. The model combining reactant transport and olefin readsorption results in an optimum in $C_{5+}$ selectivity as a function of some catalyst parameter $\chi$ comprising properties as pore radius, porosity and characteristic length.

Considering the discussed impact on selectivity and the diffusion limitations on catalyst activity, short diffusion distances are to be preferred for Fischer–Tropsch synthesis. Short diffusion distances are also favorable for high α-olefin yields, which can be used as base chemicals. Existing reactor technologies meet all kinds of problems when complying with short diffusion distances, i.e. small catalyst particles [3]. Multi-tubular fixed-bed reactors are constrained to catalyst particles of a certain minimum size to stay below an acceptable pressure drop. Slurry bubble column reactors can operate with particles of 100 μm, but here one has to deal with problems as catalyst attrition and separation.

A structured catalyst such as a monolith [4,5] may provide an answer to the problems. Monoliths (Fig. 2) are ceramic structures with small parallel channels (0.5–2 mm internal diameter) separated by thin walls (60–300 μm) [6] consisting of cordierite or high surface area catalyst support material such as alumina or silica. Cordierite monoliths can be washcoated with thin layers of catalyst support. Application of the active phase on the monoliths can be done by several methods [7]. Hence, the characteristic diffusion length of the catalyst layer can be tuned by catalyst hold up and cell density.

A Monolith Loop Reactor (Fig. 3) [8] can be used to apply monolithic catalysts for large-scale FTS plants. Synthesis gas and liquid hydrocarbons flow co-currently down in Taylor flow mode. The liquid hydrocarbons are fed to the reactor to adsorb the heat generated along the reactor length. The gas flow is in single pass mode to benefit from the plug flow conditions in the monolith channels, while the liquid

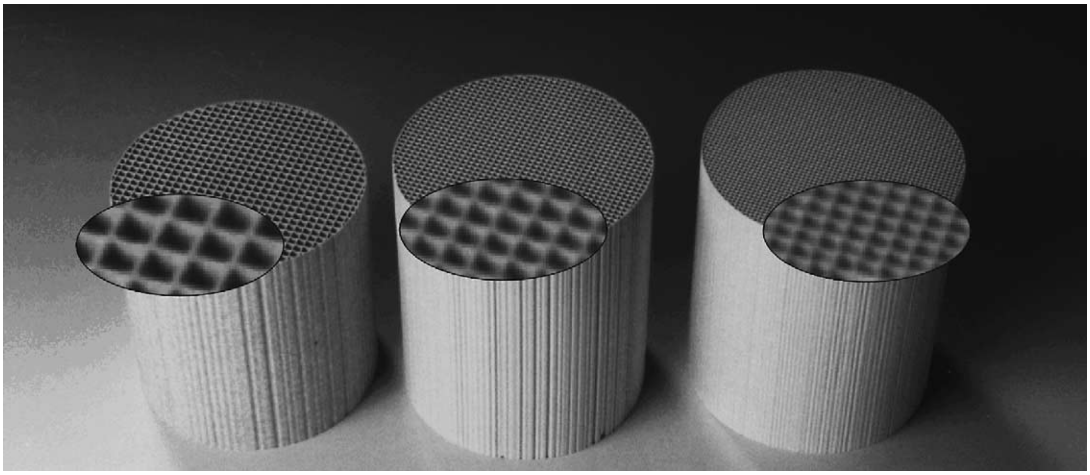

Fig. 2. Monolithic structures: from left to right 200, 400 and 600 cells per square inch (cpsi).

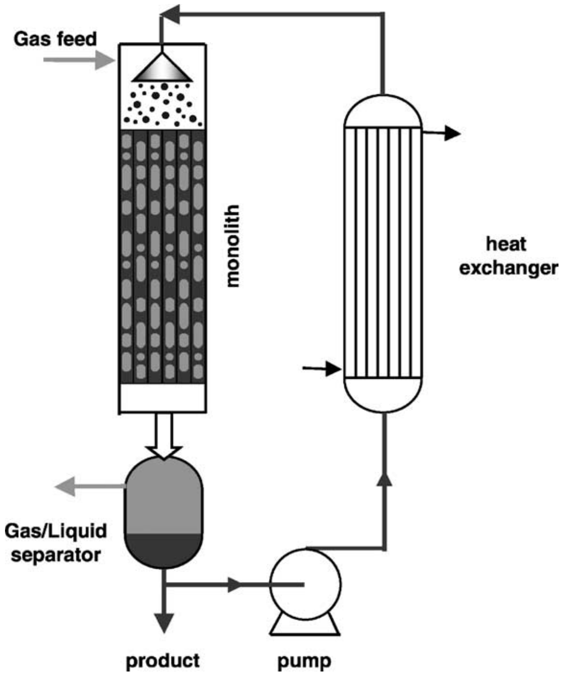

Fig. 3. Schematic drawing of a Monolith Loop Reactor with liquid recycle.

products are partially recycled through a heat exchanger to the top of the reactor. The Monolith Loop Reactor concept for Fischer–Tropsch Synthesis is considered in detail by de Deugd et al. [9].

In this contribution, the opportunities of monolithic catalysts for Fischer–Tropsch synthesis are explored from an experimental point of view.

## 2. Experimental

### 2.1. Monolith preparation

The monolithic catalyst used in this study is prepared on a cordierite support provided by Corning Inc. The alumina washcoat has been prepared using the slurry coating method described by Nijhuis et al. [7]. The alumina loading after a single dip in the alumina slurry was about 22 wt.%, which results in an alumina layer of about 50 μm on a 200 cells per square inch (cpsi) monolith. The active phase has been applied by homogeneous deposition precipitation from a solution of cobalt nitrate, rhenium oxide and urea [7]. The cobalt and rhenium loadings determined using XRF were 17 and 0.1 wt.%, respectively. $H_2$ chemisorption showed a codispersion of nearly 5%. The BET surface of the catalyst was 140 $m^2/g$, while the porosity was found to be 31%, both determined by $N_2$ adsorption.

### 2.2. Set-up

The monoliths have been tested in a dedicated six-flow set-up for Fischer–Tropsch synthesis. This approach allows testing of six catalysts in separate fixed-bed reactors simultaneously and is a powerful tool for catalyst testing and kinetic studies [10]. The configuration can be changed to five parallel fixed-bed reactors and one reactor suited for testing monoliths. The feed stream is mixed from high-pressure carbon monoxide, hydrogen and argon supply using separate mass flow controllers ensuring a fixed feed composition. Argon is added as internal standard. The mixed synthesis gas is supplied to the reactors using individual mass flow controllers. The pressure for each of the reactors can be adjusted individually. The temperature of the block containing the six fixed-bed reactors and the monolith reactor can be controlled separately. The configuration of the set-up ensures a maximum flexibility. The reactor effluent is led through a gas–liquid separator operating at 175 °C to remove waxy liquid products. The gaseous stream is sent to a Chrompack GC (CP9001) equipped with a CP-Sil5 column and a FID detector to detect $C_{5+}$ and a Molsieve 5 Å and a Porabond column coupled to a TCD detector for detection of CO, Ar, and methane. This GC configuration allows to analyze a Fischer–Tropsch synthesis reactor effluent quantitatively up to $C_{20}$ within 45 min. Several other options such as supply of liquids to the reactor are available in the set-up, but are not used for this study.

### 2.3. Operating conditions

The monoliths have been tested in a window of temperatures (180–230 °C) and feed compositions ($H_2$/CO ratio = 1–3) to gain more insight in the catalytic performance. The pressure has been fixed at 15 bar. The space velocity was also constant for all presented data, 0.13 mol synthesis gas $kg_{cat}^{-1}\,s^{-1}$, including 6.25 mol% argon as internal standard. All presented data are measured using a 200 cpsi monolith with a length of 25 cm and a diameter of 1 cm. The mass of catalyst washcoat on the cordierite structure was 2.754 g, corresponding to an average washcoat thickness of 50 μm.

## 3. Results and discussion

### 3.1. Activity

Fig. 4 presents the activity in moles CO converted per kilogram catalyst per second as function of temperature. The stoichiometric feed composition ($H_2/CO = 2$) shows the highest activity at high temperatures. However, at low temperatures super-stoichiometric amounts of hydrogen lead to a higher activity than a stoichiometric composition. Super-stoichiometric amounts of carbon monoxide show the lowest activity of the investigated feed compositions. The CO conversion level ranges from 6% at 180 °C and sub-stoichiometric amounts of hydrogen to 62% at 230 °C and stoichiometric feed composition. Schanke et al. [1] report an activity of about 0.01 mol CO $kg_{cat}^{-1}\,s^{-1}$ for a 400 cpsi monolith with a comparable cobalt (17 wt.%) and higher rhenium (1 wt.%) loading at 210 °C, 13 bar and stoichiometric feed composition. More recent experimental results [11] indicate that the difference in activity may be explained by diffusion limitations. In literature kinetic expressions for Fischer–Tropsch synthesis (e.g. [12]) carbon monoxide is present as an inhibiting component. The lower activity for excess carbon monoxide (higher $p_{CO}$) is therefore expected. A higher $H_2/CO$ ratio would lead to a higher activity. At lower temperature this is the case, but at higher temperature not. In the latter case, the diffusive intraparticle transport of carbon monoxide may become limiting for excess hydrogen conditions. Indeed, the apparent activation energy for the stoichiometric feed composition is 65 kJ/mol, while at $H_2/CO$ ratio of 3, this value drops to only 47 kJ/mol. The activation energy for the stoichiometric excess carbon monoxide feed composition was 53 kJ/mol. Schanke et al. [1] found indications for carbon monoxide depletion for particles larger than 100 μm, but for situations with sub-stoichiometric amounts of carbon monoxide it is to be expected that this effect is already present at shorter diffusional distances.

### 3.2. Selectivity

In Fig. 5 some product distributions are shown for operation at stoichiometric conditions. The chain growth probability, $\alpha$, ranges from 0.87 at 190 °C to

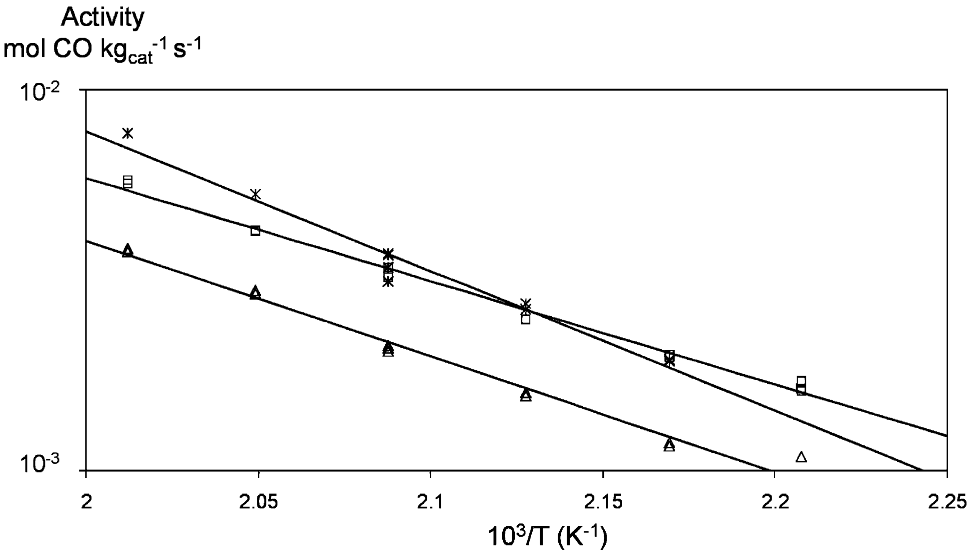

Fig. 4. CO conversion activity vs. reciprocal temperature. Conditions: pressure = 15 bar, space velocity = 0.13 mol synthesis gas $kg_{cat}^{-1}\,s^{-1}$; (△) $H_2/CO = 1$, (✱) $H_2/CO = 2$, (□) $H_2/CO = 3$.

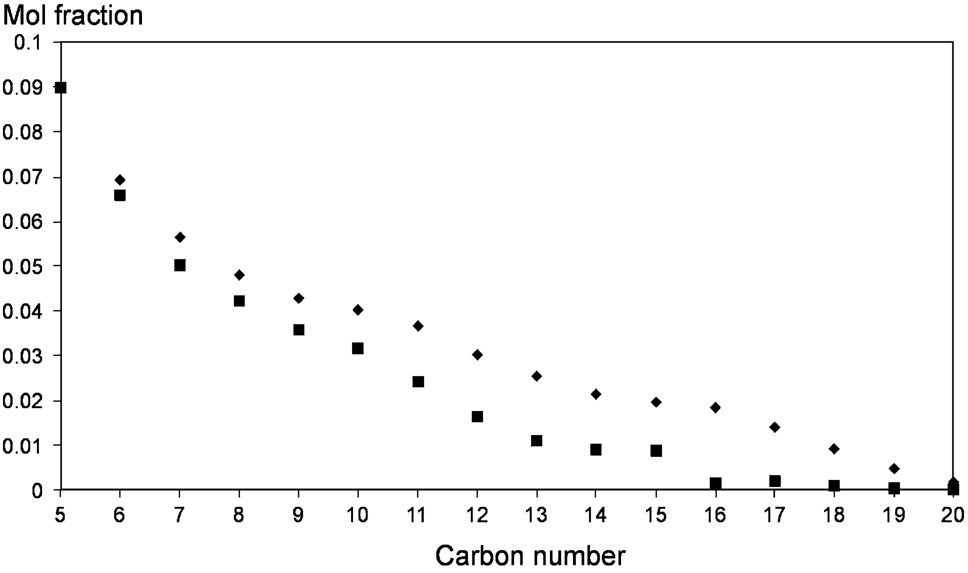

Fig. 5. FTS product (paraffins + olefins) distributions. Conditions: $p = 15$ bar, $H_2/CO = 2$, space velocity = 0.13 mol synthesis gas $kg_{cat}^{-1}\,s^{-1}$; (◆) $T = 200\,°C$, (■) $T = 230\,°C$.

0.78 at 230 °C. The heavy products at 200 °C show some deviation from the ASF distribution. The deviation is caused by the low concentrations as a result of the low conversion level at these conditions. The methane selectivity increases dramatically from 6% at 190 °C to 38% at 230 °C. The same trend is present for the other feed compositions. Especially the selectivity to methane is strongly dependent on the feed composition. Sub-stoichiometric concentrations of hydrogen have a maximum methane selectivity of 7% at 230 °C, while the other compositions show a selectivity of up to 38% at these conditions.

### 3.3. Olefin to paraffin ratio

The olefin content in the reactor effluent at stoichiometric conditions for different reaction temperatures is shown in Fig. 6. At low temperatures the olefin content is as high or higher than the paraffin content for shorter chain hydrocarbons. The olefin to paraffin (O/P) ratio decreases for increasing chain lengths and higher temperatures. Fig. 7 shows the olefin to paraffin ratios for the various feed compositions. As expected, the olefin content increases with higher concentrations of carbon monoxide in the feed, but the O/P ratio for the stoichiometric excess carbon monoxide feed composition is remarkably high. Results for $CoRe/Al_2O_3$ in particles of 75–100 μm shows a much lower olefin selectivity at comparable conditions [3].

The mechanism as shown in Fig. 1 can account for the differences in olefin to paraffin ratio. Under conditions with excess carbon monoxide termination by hydrogenation to paraffins and secondary hydrogenation of olefins is less likely by the lower hydrogen partial pressure. Schulz and Claeys [13,14] find comparable results and arrive at the same conclusions for particulate catalysts.

### 3.4. Stability

The activity of the catalyst decreased only 7% after 200 h of operation under conditions with stoichiometric and hydrogen super-stoichiometric feed composition and various temperatures up to 230 °C. After 300 h the activity had dropped to 76% of the original activity. In these last 100 h experiments with excess carbon monoxide have been conducted. The faster deactivation under conditions with excess carbon monoxide and, at least temporarily, high temperature are not surprising as these conditions favor coking.

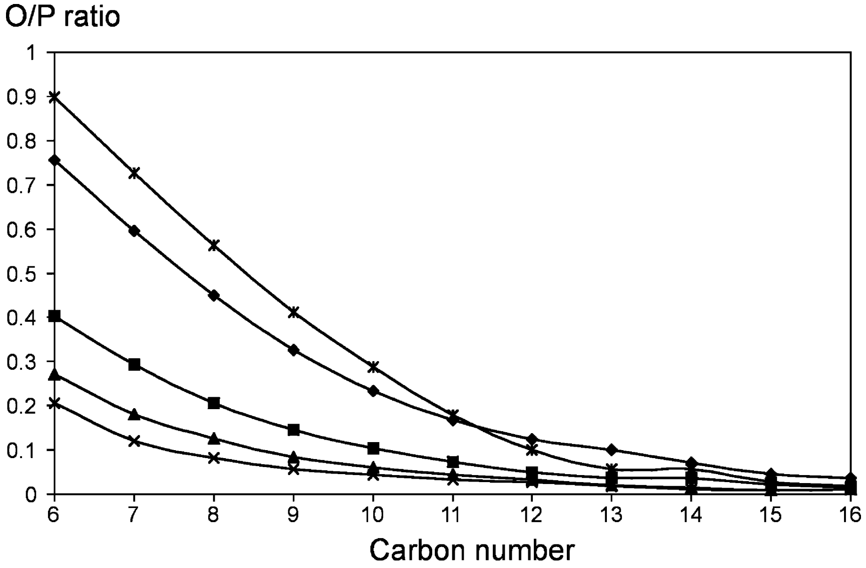

Fig. 6. Olefin to paraffin (O/P) product ratio as a function of carbon number and at different temperatures. Conditions: $H_2/CO = 2$, pressure = 15 bar, space velocity = 0.13 mol synthesis gas $kg_{cat}^{-1}\,s^{-1}$; (✱) $T = 190\,°C$, (◆) $T = 200\,°C$, (■) $T = 210\,°C$, (▲) $T = 220\,°C$, (×) $T = 230\,°C$.

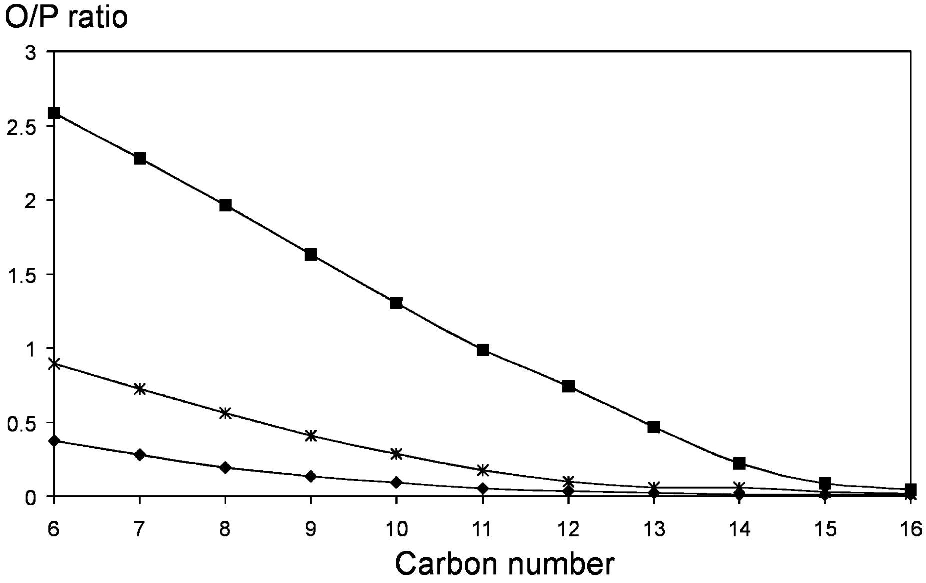

Fig. 7. Olefin to paraffin (O/P) product ratio as a function of carbon number at different feed compositions. Conditions: $T = 190\,°C$, pressure = 15 bar, space velocity = 0.13 mol synthesis gas $kg_{cat}^{-1}\,s^{-1}$; (■) $H_2/CO = 1$, (✱) $H_2/CO = 2$, (◆) $H_2/CO = 3$.

## 4. Concluding remarks

The experimental results for monolithic catalysts show an FTS activity level comparable to earlier reports in literature. Changing the $H_2/CO$ feed ratio either results in a much lower activity and a somewhat higher chain growth probability ($H_2/CO = 1$) or in a comparable activity and much higher yields to methane and other light products ($H_2/CO = 3$). The olefin content is relatively high for each of the investigated feed compositions, which is in agreement with the reaction–diffusion model for porous catalysts for short diffusional lengths. The stability of the catalyst is good, but strongly dependent on the feed composition.

Based on the presented results it can be concluded that monolithic catalysts may provide an alternative for existing FTS reactors. More research, especially concerning the effect of catalyst layer thickness on activity and selectivity is needed and ongoing at the moment.

## Acknowledgements

The authors would like to acknowledge Delft Interdisciplinary Research Center “Mastering the Molecules in Manufacturing” for financial support. Corning Inc. is acknowledged for supplying the cordierite monoliths.

## References

[1] D. Schanke, E. Bergene, A. Holmen, WO/38147 (1998) 199.

[2] E. Iglesia, S.C. Reyes, S. Soled, in: E.R. Becker, C.J. Pereira (Eds.), Computer-Aided Design of Catalysts, Marcel Dekker, New York, 1993.

[3] R.M. de Deugd, F. Kapteijn, J.A. Moulijn, Top. Catal., in press.

[4] F. Kapteijn, T.A. Nijhuis, J.J. Heiszwolf, J.A. Moulijn, Catal. Today 66 (2001) 133.

[5] F. Kapteijn, J.J. Heiszwolf, T.A. Nijhuis, J.A. Moulijn, Cattech 3 (1999) 24.

[6] Th. Vergunst, F. Kapteijn, J.A. Moulijn, Ind. Eng. Chem. Res. 40 (2001) 2801.

[7] T.A. Nijhuis, A.E.W. Beers, Th. Vergunst, I. Hoek, F. Kapteijn, J.A. Moulijn, Catal. Rev.-Sci. Eng. 43 (2001) 345.

[8] J.J. Heiszwolf, L.B. Engelvaart, M.G. van den Eijnden, M.T. Kreutzer, F. Kapteijn, J.A. Moulijn, Chem. Eng. Sci. 56 (2001) 805.

[9] R.M. de Deugd, R.B. Chougule, M.T. Kreutzer, F.M. Meeuse, J. Grievink, F. Kapteijn, J.A. Moulijn, Chem. Eng. Sci. 58 (2003) 583.

[10] J. Pérez-Ramirez, R.J. Berger, G. Mul, F. Kapteijn, J.A. Moulijn, Catal. Today 60 (2000) 93.

[11] R.M. de Deugd, Ph.D. Thesis, Delft University of Technology, 2003.

[12] I.C. Yates, C.N. Satterfield, Energy Fuels 5 (1991) 168.

[13] H. Schulz, M. Claeys, Appl. Catal. A: Gen. 186 (1999) 71.

[14] H. Schulz, M. Claeys, Appl. Catal. A: Gen. 186 (1999) 91.