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Membrane application in Fischer–Tropsch synthesis reactors—Overview of concepts

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Abstract

Different applications of membranes have been proposed for Fischer–Tropsch synthesis in recent literature. Across membranes, reactants can be fed along the reactor axis or the inhibiting by-product H_2O can be selectively removed. Here, the concept of enhanced conversion of CO_2 containing synthesis gases to long-chain hydrocarbons by in situ H_2O removal is introduced. Experimental results of in situ H_2O removal under reactive conditions with an Fe-based catalyst show positive effects on conversion and yield. Additionally, catalytic membranes can be used as a defined reaction zone. In so-called plug-flow contactor membranes, high specific production rates can be achieved. Finally, a catalyst encapsulated by a zeolite membrane layer is presented as a possibility to modify product distribution.

Keywords: Membrane reactors; Catalytic membranes; Fischer–Tropsch synthesis; H_2O removal; CO hydrogenation; CO_2 hydrogenation

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1. Introduction

Different applications of membrane reactors have been proposed for Fischer–Tropsch (FT) synthesis in recent literature. This overview does not consider the application of oxygen transfer membranes in synthesis gas production or filter applications for slurry systems, as it focuses solely on the FT reactor unit. We apply the classification of catalytic membrane reactors according to Sanchez Marcano and Tsotsis [1] who categorize according to the type of membrane (permselective/non-permselective) and the location of the catalyst (within/outside the membrane).

Fig. 1 and Table 1 summarize the published concepts for membrane application in FT reactors without claiming that the list is complete. By the application of membranes, advanced feeding concepts (distributed feeding) may be realized to control the heat of the FT reaction and to enhance the selectivity to long-chain products (Eq. (1)). The selective removal of the by-product H_2O which deactivates FT catalysts and may inhibit the reaction rate can increase per-pass conversion, product yield and catalyst lifetime. Furthermore, in situ removal of H_2O enhances the conversion of CO_2 containing syngases to long-chain hydrocarbons by displacing the equilibrium composition of the water gas shift (WGS) reaction (Eq. (2)).

$$\text{FT}: \quad CO + 2H_2 \rightarrow (CH_2) + H_2O, \quad \Delta_r H = -158\,\text{kJ/mol}\,(T = 250\,^\circ\text{C}) \tag{1}$$

$$\text{WGS}: \quad CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta_r H = -39.5\,\text{kJ/mol}\,(T = 250\,^\circ\text{C}) \tag{2}$$

A catalytic membrane can offer a defined reaction zone while the reactants are forced through the membrane by a pressure gradient. Depending on the properties of the membrane, very high gas–liquid mass-transfer rate can be obtained, resulting in high volume specific production rates. In a new concept, the products of the FT synthesis are forced through a catalytic membrane resulting in a modified product distribution. Hence, the motivations for membrane application are: higher specific production rates, increased catalyst lifetime, and increased product selectivities. Especially for future small/medium-scale FT units, e.g. for off-shore applications and biomass-to-liquids (BTL) processes, membrane reactors may have potential.

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Table 1
Concepts of membrane application in FT synthesis reactors

	References	Concept	Reactors	Membrane/support	Catalyst	X_{CO}	$S_{C_{2+}}$	$Y_{C_{2+}}$
a	Léonard et al. [2–4]	Distributed feeding	PBNMR PBCMR	γ-Al_2O_3/α-Al_2O_3 ZSM-5/α-Al_2O_3	Co/Al_2O_3	$+^{a}$ /$-^{b}$	−/+	−/+
b	Espinoza et al. [5]	Selective H_2O removal	PBMR	Mordenite/ZSM-5/silicalite/stainless steel	n.a.			
b	Rohde et al. [6]	Selective H_2O removal reactant distribution	PBMR	$Si(OH)_xO_y$/γ-Al_2O_3/α-Al_2O_3	Fe/Al_2O_3/5K/Cu	$+^{c}$		$+^{c}$
b	Zhu et al. [7]	Selective H_2O removal	PBMR	4A-zeolite/TiO_2/stainless steel	n.a.			
c1	Khassin et al. [8]	Forced-through flow catalytic membrane	CNMR	Porous catalyst/copper structure	Co/Al_2O_3	+	+	+
c2	Bradford et al. [9]	Forced-through flow catalytic membrane	CNMR	Catalyst/γ-/α–Al_2O_3	P/Pt-Co/Al_2O_3	+	−	+
d	He et al. [10]	Control of product traffic	PBCMR	ZSM-5/catalyst pellet	Co/SiO_2	−	$+^{d}$	$+^{d}$

PBNMR: packed-bed non-permselective membrane reactor, PBMR: packed-bed MR, CMR: catalytic MR, CNMR: catalytic non-permselective MR.

[a] CO fed across membrane.

[b] H_2 fed across membrane.

[c] Based on CO_2.

[d] For C_1–C_{10}.

2. Concept of distributed feeding

Significant axial and radial temperature profiles can occur in multitubular packed bed reactors (PBR). Membranes as reactant distributor along the reactor axis have been proposed to control the heat production of the FT reaction. As the activity and product selectivity depend significantly on the H_2/CO-ratio in the case of Co-based catalysts, distributed feeding can positively affect the gas phase composition. Léonard et al. [2], Vanhove and Léonard [3] and Guillou et al. [4] presented a conceptual study on distributed feeding of H_2 and CO along the reactor axis. One of the reactants was fed through a tubular membrane, while the other was led through the catalyst bed located inside the membrane. The membrane was either inert (γ-Al_2O_3 on α-Al_2O_3) or coated with a ZSM-5 zeolite layer. The results obtained in the PBNMR and PBCMR setups were compared to PBR experiments operated under similar conditions (180 °C, 0.1 MPa, Co/Al_2O_3).

The observed results are in accordance with general kinetics of Co-based catalysts and the influence of H_2/CO-ratio on product selectivity [11–13]. With H_2 as feed gas and CO as distributed reactant, the H_2/CO-ratio maintains extremely high along the reactor axis. Hence, the inhibition of the FT reaction rate due to CO remains low and increased conversions were measured compared to the PBR. However, the formation of long-chain hydrocarbons is not favored and C_1–C_4 hydrocarbons were mainly recovered as product. Consequently, the distribution of H_2 into a CO feed stream resulted in lower conversions as the inhibition by CO is high. Due to the low H_2/CO-ratio, an increase in C_{10+} hydrocarbon yield and lower methane selectivity was observed. The application of the ZSM-5 membrane showed similar results, but it altered the product distribution additionally by secondary reactions at the acidic sites of the zeolite, resulting in higher yields of short-chain hydrocarbons. Another way of incorporating zeolites into FT reactors by means of membranes is the use of encapsulated catalysts (see further below).

3. Concept of H_2O removal

H_2O which is formed as a by-product during FT synthesis accumulates in the gas phase and decreases the partial pressures of the reactants. At high per-pass conversions, H_2O molar fractions of 40–50% for Co-based and as low as 8% for WGS active Fe-based catalysts can be met at the

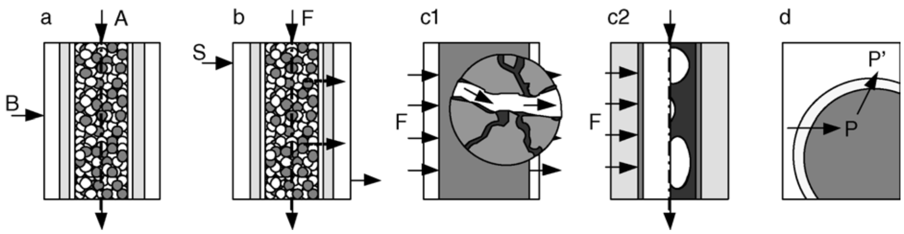

Fig. 1. Membrane reactors for FT synthesis proposed in literature. (a) Distributed feeding of the reactants A+B; (b) in situ H_2O removal by selective membrane, F: feed, S: sweep; (c1) plug-through contactor membrane (PCM) with wide transport pores; (c2) forced-through flow membrane contactor, product and heat removal by circulated liquid product; (d) zeolite encapsulated FT catalyst, P′: modified product. *Sources*: See Table 1.

reactor exit. The application of membranes for in situ H_2O removal has drawn a lot of attention particularly due to the fact that high H_2O partial pressures lead to reoxidation and reduced catalyst lifetime [5,7]. For Fe-based catalysts, H_2O inhibits the FT reaction rate and forces the formation of CO_2 via the WGS reaction (Eq. (2)). Here, in situ H_2O removal could accelerate the FT reaction rate and displace the equilibrium composition in favor of CO. The enhanced equilibrium displacement could facilitate the conversion of CO_2 containing synthesis gases [6].

The concept of in situ H_2O removal can be realized by the integration of a highly permselective membrane into the reaction compartment, i.e. slurry, packed or fluidized bed. High driving forces across the membrane are built up by a sweep gas at high flow rate (sweep ratio) and decreased pressure (pressure ratio). Reactor performance strongly depends on the permselectivity, hydrothermal and mechanical stability of the membrane. Hydrophilic inorganic materials have been proposed for selective removal of the polar molecule H_2O from mixtures with H_2 and CO.

Espinoza et al. [5] carried out a series of permeation experiments with silicalite-1/ZSM-5 and mordenite (on α-Al_2O_3/stainless steel support) under non-reactive conditions typical for FT (200–300 °C, 2 MPa). In particular mordenite membranes exhibited high H_2O fluxes ($\Pi_{H_2O} = 2 \times 10^{-7}$ mol/(s Pa m^2), 250 °C) and promising permselectivities. Recently, Zhu et al. [7] published results of single gas and binary permeation experiments for a 4A-zeolite membrane. This type of membrane – so far mainly applied in pervaporation for dehydration – may be a candidate for vapor separation from permanent gases. It offers high permeances for H_2O ($\Pi_{H_2O} = 2 \times 10^{-6}$ mol/(s Pa m^2), 30–102 °C) and high permselectivities of H_2O towards H_2, CO, CH_4. But the permselectivities drop with increasing temperatures, e.g. $S_{H_2O,CO} = 244$ at 30 °C, 30 at 102 °C (Fig. 2). Since the experiments were only carried out up to 102 °C, selectivity values can only be estimated in the range of 200–250 °C. Under FT conditions, it can be expected that the selective adsorption and surface diffusion of H_2O is less significant.

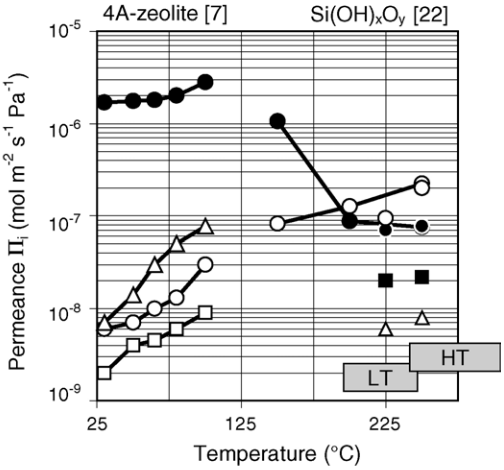

Fig. 2. Component permeances determined (–○–) from binary mixtures of H_2O vapor and a permanent gas; (○) from PBMR experiments [6]. (●) H_2O, (○) H_2, (▲) CO, (□) CH_4, (■) CO_2, bars: typical FT temperatures. *Source*: Refs. [7,22].

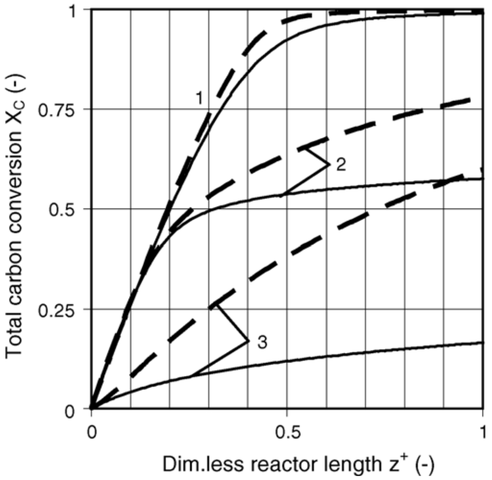

Fig. 3. Effect of in situ H_2O removal on total carbon conversion $X_{CO} + X_{CO_2}$: (—) PBR; (- - -) ideally permselective PBMR. (1) Co-based catalyst $H_2/CO = 2/1$; (2) Fe-based catalyst $H_2/CO = 2/1$; (3) Fe-based catalyst $H_2/CO_2 = 3/1$. *Conditions*: See Table 2.

In order to assess the effects of in situ H_2O removal, calculations for an isothermal, pseudo-homogeneous packed bed permselective membrane reactor (PBMR) were carried out, applying typical kinetics for Co-based [12] and Fe-based catalysts [16]. The results for an ideally permselective membrane ($\Pi_{H_2O} = 1 \times 10^{-7}$ mol/(s Pa m^2)) are shown in Fig. 3 (Table 2) and the findings can be summarized as follows:

(a) Removal of H_2O during FT reaction on a Co-based catalyst does not have a significant effect (curves 1), though the partial pressures of the reactants, the rate of reaction and the residence times are increased. Under varying conditions, the effects may be larger, but the increments in conversion do not exceed 10% in these calculations [17]. However, the mean H_2O partial pressure can be reduced significantly.

(b) The increments in total carbon conversion $X_{CO} + X_{CO_2}$, i.e. hydrocarbon yield are considerable for Fe-based catalysts and H_2/CO (2/1) syngas (curves 2). Here, H_2O removal helps to decrease CO_2 formation via WGS reaction and – if the CO partial pressure is low enough – to inverse the WGS reaction converting CO_2 to long-chain hydrocarbons. But the use of balanced H_2/CO (2/1) syngas on Fe-based catalysts appears unattractive unless the characteristic product distribution is desired. Application of membranes with H_2 deficient, e.g. coal- or biomass-derived syngases will lead to lower yields since the WGS shift reaction to H_2 is prohibited.

(c) The in situ H_2O removal effects significantly the conversion of H_2 balanced CO_2 containing synthesis

Table 2
Membrane permselectivities and conditions for membrane FT calculations, $p_{feed} = 1$ MPa, $T = 225$ °C, reference permeance $\Pi_{ref} = 1 \times 10^{-7}$ mol/(s Pa m^2), $\tau_{mod} = m_{cat}/\dot{V}_{feed,STP}$

	Sweep ratio ($\dot{V}_{sweep}/\dot{V}_{feed}$)	Pressure ratio (p_{sweep}/p_{feed})	Permselectivities, Π_i/Π_{ref}				τ_{mod} (kg s/m^3)	Feed gas	Sweep gas
			H_2	H_2O	CO	CO_2			
Fig. 3	1	0.1	–	1	–	–	8000	See Fig. 3	N_2
Fig. 4	3.3	1	0.94	0.70	0.06	0.22	4000	H_2/CO_2 (3/1)	See Fig. 4

gases [14,17]. The conversion of H_2/CO_2 (3/1) syngases is considerably accelerated (curves 3) because the WGS equilibrium is continuously displaced by the H_2O removal (Eq. (2)). Increased hydrocarbon yields can be expected with a product distribution similar to the one obtained with H_2/CO synthesis gases [18] as Fe-based catalysts are not as susceptible to high H_2/CO-ratios as Co-based catalysts. This approach appears interesting because CO_2 containing synthesis gases are encountered in many cases, e.g. low-temperature partial oxidation of natural gas [15], reforming of CO_2 containing natural gas, biomass (or coal) gasification balanced with H_2 from external sources [14]. The hydrogenation of CO_2 to long-chain hydrocarbons enhanced by in situ H_2O removal may be able to increase the overall carbon efficiency of FT processes. Therefore, practical interest in CO_2 conversion during FT synthesis results from CO_2 being a potential constituent of synthesis gases from coal, biomass or natural gas [19].

Membrane integration for in situ H_2O removal in a FT packed bed reactor was experimentally demonstrated by Rohde et al. [6]. A tubular packed bed permselective membrane reactor (PBMR, Fig. 1, b) was applied. The tube side was filled with 2 g of K-doped Fe-based catalyst and H_2/CO_2 (3/1) was chosen as feed gas as the largest measurable effects can be expected for this combination (Fig. 3, curves 3).

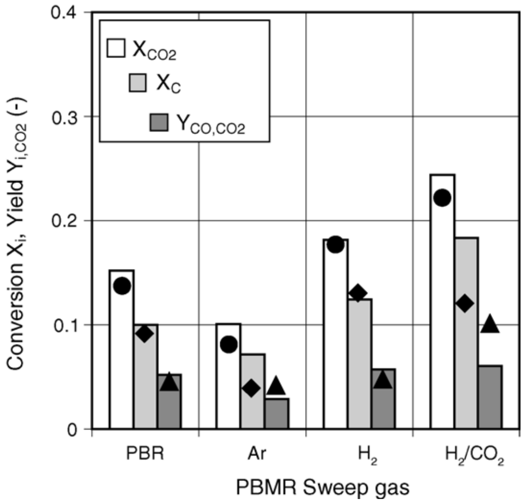

Fig. 4. Effect of sweep gas composition on conversion and yields in IMPBR [6], bars: experimental data, symbols: calculated. (●) X_{CO_2}, (◆) X_C, (▲) Y_{CO,CO_2}, Fe-based catalyst, Si(OH)$_x$O$_y$-Al$_2$O$_3$ membrane. Conditions and permselectivities: Table 2.

The tubular membranes (provided by ACA, Berlin) have a free permeation area of 59 cm^2 and consist of commercial ultrafiltration supports (γ-Al$_2$O$_3$ on α-Al$_2$O$_3$, $d_{Pore} < 5$ nm) with pore sizes reduced below 1 nm by in situ hydrolysis of tetraethyl-orthosilicate (TEOS) [20,21]. The polymeric Si(OH)$_x$O$_y$-structures in the pores offer hydrophilic properties. Permeation and pervaporation measurements under mild conditions show high selectivities towards H_2O. The shell side was swept with different sweep gases at varied flow rates and the pressures on the feed and shell side were both kept at 1 MPa (pressure ratio = 1). The experimental results show that the applied membrane was not permselective enough to remove H_2O selectively out of the reaction mixture. Fig. 2 summarizes permeance data collected from binary permeation experiments under non-reactive conditions and from the experiments under reactive conditions. The use of argon as sweep gas results in lower conversions and yields due to reactant loss. Nevertheless, the deficiency in permselectivities and the reactant can be reduced by H_2 and H_2/CO_2 (3/1) as sweep gas. Increased CO_2 conversions and product yields were observed (Fig. 4; Table 2). The evaluation of the experiments by model calculations showed clearly that the increase in conversion can be attributed to the removal of H_2O and not to dilution effects or co-feeding of reactants. The use of syngas as sweep gas seems to be a simple solution as it combines H_2O removal and co-feeding of reactants, but it contradicts the conceptual idea, since H_2O has to be removed in an additional process step from the sweep gas stream. The experimental results and model calculations demonstrate that (a) the permeances $\Pi_{H_2O} > 10^{-7}$ mol/(s Pa m^2) are high enough for in situ H_2O removal and (b) permselectivities of H_2O regarding H_2, CO, CO_2 should go beyond 50.

The alternative approach to separate FT synthesis and WGS, i.e. into a membrane reactor with low temperature WGS catalyst followed by a low temperature FT reactor with Co-based catalyst was investigated by the authors. This concept appears advantageous as the RWGS membrane reactor is free of liquid phases. However, model calculations revealed that the reverse shift reaction of CO_2 containing synthesis gas is only possible with highly selective membranes and extremely high sweep flow rates/low pressures at the shell side due to low partial pressures of H_2O in the vapor phase.

4. Concept of forced-through flow membrane

The exploitation of small natural gas fields, e.g. off-shore applications (flared gas on oil rigs) and the utilization of biomass-derived synthesis gas demand for small or medium-scale FT reactors that offer high specific production rates and safe and easy operability. Promising concepts could incorporate catalytic membranes which offer a defined reaction zone.

Khassin et al. [8] developed a proprietary method (sintering in the presence of a pore-producing agent) to prepare catalytic membranes with a high load (up to 800–1000 kg/m^3) of Co/Al_2O_3 catalyst and a high thermal conductivity addressing the problem of efficient heat removal. The catalytic membranes have tubular geometry and they exhibit a distinct three-modal pore distribution. Large pores (3–7 μm) run through the membrane and enable high permeation rates. The transport pores are interconnected by narrower pores which are filled with liquid due to capillary forces (Fig. 1, c1). The feed gas stream is forced through the membrane either inwards or outwards. The so-called plug-through contactor membranes (PCM) offer low pressure drop, flat temperature profiles, high reactor capacities, high gas–liquid mass-transfer rates and low diffusive constraints [8]. By varying the preparation methods, the porous structure can be adjusted so that the diffusion lengths are lowered significantly and CO depletion in the pores is reduced resulting in a high yield of long-chain hydrocarbons and a high olefin-to-paraffin ratio. The specific C_{2+} production rate achieves up to 18 kg/(m^3 h) at 210 °C and 0.1 MPa and up to 200 kg/(m^3 h) at 2 MPa [8].

Bradford et al. [9] propose a monolithic loop catalytic membrane reactor. A mesoporous honeycomb structure is coated with a microporous ceramic membrane and FT catalyst. The shell side of the monolith is pressurised with syngas. The syngas permeates through the support and is forced through the catalyst layer; the heat of the reaction and products are removed by a gas–liquid stream which is circulated through the channels of the monolith (Fig. 1, c2). In a conceptual study, Bradford carried out experiments in a tubular CMR without liquid circulation. The mesoporous support with a 45 μm layer of Al_2O_3 with a 2 nm nominal pore size was coated with a 200 μm layer of P/Pt-Co/γ-Al_2O_3 catalysts. A comparison of the experimental results with the results from a packed bed reactor reveals diffusive resistances in the catalytic membrane which lead to an undesired depletion of CO in the catalyst layer. Therefore, a higher CO conversion can be observed ($X_{\mathrm{CMR}} = 53.7\%$, $X_{\mathrm{PBR}} = 42\%$, $H_2/CO = 1.51$, 2.4 MPa, 205–207 °C, $\tau_{\mathrm{mod,\,STP}} = 1440$ kg s/m^3). However, a lower C_{2+} selectivity ($S_{C_{2+},\mathrm{CMR}} = 83.5\%$, $S_{C_{2+},\mathrm{PBR}} = 89.2\%$) and a lower olefin-to-paraffin ratio are obtained. The potential production capacity of a ML-CMR was estimated with a simplified reactor model, based on the experimental results. The maximum C_{2+} production rate for a honeycomb membrane module (0.25 m × 1.524 m) with 11,470 channels coated with a 300 μm catalyst layer is given with ca. 270 kg/(m^3 h) at 200 °C and 2 MPa [9].

5. Concept of encapsulated catalyst

Several authors proposed the combination of FT catalysts with acidic zeolites, e.g. in physical mixtures [23,24] or by dispersion of Co on zeolite. The aim is to modify the distribution of FT products by hydrocracking and isomerization as soon as the products are formed. He et al. [10] proposed the application of membranes on particle scale. They coated Co/SiO_2 catalyst pellets (0.38–0.5 mm, 0.85–1.7 mm) with ZSM-5 layer of about 10 μm thickness. The zeolite layer works as a catalytic membrane: the reactants permeate through the layer into the FT catalyst; the formed products are forced to diffuse through the zeolite layer in counter-current direction (Fig. 1, d). Main variables are size of zeolite channels, number of acidic sites (activity) and the layer thickness. The residence times in the pore system of the zeolite increase with chain length of hydrocarbons. Therefore, long-chain molecules undergo hydrocracking and isomerization reactions more frequently as short-chain hydrocarbons. The capsule has the advantages that extremely large specific membrane areas are achieved and cracks and pinholes do not have a significant effect on reactor performance. He et al. [10] carried out experiments with a Co/SiO_2-zeolite catalyst and compared the results with an uncoated Co/SiO_2 catalysts and a physical mixture with ZSM-5 at comparable conditions ($H_2/CO = 2$, 1 MPa, 260 °C, $\tau_{\mathrm{mod,STP,Co/SiO_2}} = 1600$ kg s/m^3). The results of their encapsulated catalysts can be summarized as follows: (a) conversion is slightly lower due to diffusional limitations. (b) Methane selectivity increases due to secondary reactions and unfavourable H_2/CO-ratio within the pellets. (c) Sharp hydrocarbon distributions are generated with a cut-off at C_9–C_{10} (Fig. 5). The adsorption cut-off diameter for ZSM-5 is about 0.65 nm (e.g. kinetic diameter of *i*-octane: 0.61 nm). Due to the forced secondary reactions in the zeolite layer, the selectivities to short-chain hydrocarbons, *iso*-paraffins and

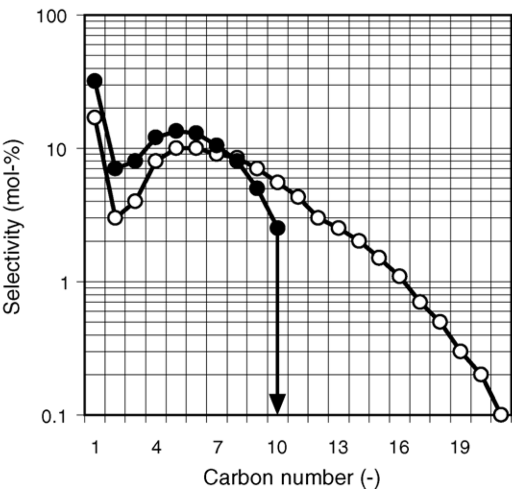

Fig. 5. Product hydrocarbon distribution in FT synthesis with Co/SiO_2 (○) and Co/SiO_2 coated with zeolite membrane (encapsulated catalyst, ●) [10]. *Conditions*: See text.

olefins are significantly higher compared to the physical mixture.

6. Conclusion and outlook

In light of various concepts of membrane application in FT synthesis, the following points should be addressed:

The required separate availability of H_2 and CO and high sensitivities of FT product distribution of Co-based catalyst with respect to local variations in H_2/CO-ratio appear as most critical aspects of distributed feeding. However, distributed feeding may be applied in the case of the conversion of biomass (or coal) derived H_2 deficient syngases. Additional H_2 from independent sources could be introduced along the reactor axis maintaining a medium H_2/CO-ratio advantageous for long-chain products.

Membranes for in situ H_2O removal offer possibilities to enhance catalyst lifetime and to convert CO_2 containing syngases. At this point, however, available membranes are not (yet) sufficiently selective and hydrothermally and mechanically stable. Most significant areas to be addressed for scale-up and application are geometric configurations, sweeping concepts (e.g. with N_2 from air separation unit or vacuum applied), staged concepts with monolith reactors and membrane stages in series. Presently, the authors are carrying out experiments under reactive conditions with a new type of membrane (ceramic supported polymer membranes) to cover the field of in situ H_2O removal as well for Fe- and Co-based catalysts.

The application of forced-through flow membranes is promising for small-/medium scale FT reactors. High specific reactor capacities, new concepts for heat removal and a well defined and fixed reaction zone are advantageous for safe and economic operability.

The FT synthesis in presence of acidic zeolites has drawn a lot of attention, e.g. for direct production of gasoline. The new concept of zeolite coated catalyst particles has the outstanding advantage that all product molecules have to pass through the zeolite layer. In physical mixtures or impregnated zeolites, product molecules undergo secondary reactions more or less randomly. In future, it has to be shown whether the encapsulated catalyst will also work stably over long time on stream, since coking of trapped hydrocarbons can be expected.

The field of membrane application in FT synthesis can be envisaged to be very active in research in the coming years. The development of new (membrane) materials and of reactor configurations may lead to improvements in reactor productivity and process economics.

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References

[1] J.G. Sanchez Marcano, T.T. Tsotsis, Catalytic Membranes and Membrane Reactors, Wiley–VCH, Weinheim, 2002.

[2] S. Léonard, S. Miachon, D. Vanhove, Récents Progres en Génie des Procédés 89 (2003) 226.

[3] D. Vanhove, S. Léonard, Récents Progres en Génie des Procédés 89 (2003) 194.

[4] L. Guillou, S. Léonard, V. Le Courtois, E. Payen, D. Vanhove, in: Proceedings of ICCMR-6, Lahnstein, 6–9 July 2004.

[5] R.L. Espinoza, et al. Stud. Surf. Sci. Catal. 130 (2000) 389.

[6] M.P. Rohde, D. Unruh, G. Schaub, Membrane application in Fischer–Tropsch synthesis to enhance CO_2 hydrogenation, Ind. Chem. Eng. Res., in press, available online: 15 June 2005, doi:10.1021/ie050289z.

[7] W. Zhu, L. Gora, A.W.C. van den Berg, F. Kapteijn, J.C. Jansen, J.A. Moulijn, J. Membr. Sci. 253 (2005) 57.

[8] A.A. Khassin, A.G. Sipatrov, G.K. Chermashetseva, T.M. Yurieva, V.N. Parmon, Top. Catal. 32 (1–2) (2005) 39.

[9] M.C.J. Bradford, M. Te, A. Pollack, Appl. Catal. A: Gen. 283 (2005) 39.

[10] J. He, Y. Yoneyama, B. Xu, N. Nishiyama, N. Tsubaki, Langmuir 21 (2005) 1699.

[11] G.P. van der Laan, Kinetics, selectivity and scale up of the FT-synthesis, Ph.D., University Groningen, 1999.

[12] I.C. Yates, C.N. Satterfield, Energy Fuels 5 (1) (1991) 168.

[13] H. Schulz, E. van Steen, M. Claeys, Top. Catal. 2 (1995) 223.

[14] D. Unruh, M. Rohde, G. Schaub, Stud. Surf. Sci. Catal. 153 (2004) 91.

[15] S. Rabe, T. B. Treong, F. Vogel, Low temperature catalytic partial oxidation of methane for gas-to-liquids applications, Appl. Catal. A, in press, available online: 27 July 2005, doi:10.1016/j.apcata.2005.06.001.

[16] W.H. Zimmerman, D.B. Bukur, Can. J. Chem. Eng. 68 (1990) 292.

[17] D. Unruh, M. Rohde, G. Schaub, Chances for innovative processes at the interface between refining and petrochemistry, in: Proceedings of the DGMK-Conference, Berlin, 9–11 October 2002, p. 287.

[18] T. Riedel, G. Schaub, K.-W. Jun, K.-W. Lee, Ind. Eng. Chem. Res. 40 (2001) 1355.

[19] G. Schaub, D. Unruh, M. Rohde, Stud. Surf. Sci. Catal. 153 (2004) 17.

[20] P. Kölsch, M. Noack, P. Druska, D. Müller, P. Toussaint, J. Caro, Chemie Ingenieur Technik 70 (1998) 860.

[21] M. Noack, P. Kölsch, J. Caro, M. Schneider, P. Toussaint, I. Sieber, Microporous Mesoporous Mater. 35–36 (2000) 253.

[22] D. Unruh, Fischer–Tropsch Synthese mit Synthesegasen aus Biomasse—Verbesserung der Kohlenstoffnutzung durch Anwendung eines Membranreaktors, Ph.D., Universität Karlsruhe, in preparation.

[23] F.G. Botes, W. Böhringer, Appl. Catal. A: Gen. 267 (2004) 217.

[24] X. Li, K. Asami, M. Luo, K. Michiki, N. Tsubaki, K. Fujimoto, Catal. Today 84 (2003) 59.