Structured catalysts for methanol-to-olefins conversion : a review

Structured catalysts for methanol-to-olefins: a review

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The conversion of methanol to light olefins is a promising alternative for the conversion of new feedstocks such as gas, coal or biomass to ethylene and propylene, via methanol-to-olefins. During the last decade, structured catalysts have received increasing attention for this reaction. The effect of such structured catalysts on the stability and selectivity is discussed in this review. The reaction and coking mechanism show the importance of good mass transfer properties of the catalyst in the MTO reaction. Important aspects such as thickness of the coating, crystal size of the zeolite and architecture of the support on the mass transfer properties of the final catalyst are highlighted. An overview of the catalytic results of structured catalysts for the MTO reaction is presented.

Keywords: methanol-to-olefins, structured catalyst, zeolites, SAPO-34, ZSM-5

Introduction

For more than 50 years the thermal cracking of naphtha has been the major production process for ethylene and propylene. These two platform molecules are key intermediates in

the chemical industry. Using polymerization, oxidation, halogenation,… reactions they are the building blocks of a whole range of products. The rise of shale gas technology in the US in the past decades has led to the construction of ethane crackers as well as retrofitting of naphta crackers, as ethane crackers are economically more favourable over naphta crackers. This trend has resulted in an increasing shortage of propylene supply and an increasing attraction for tuning the methanol-to-olefins (MTO) reaction towards higher propylene yield (Rahimi & Karimzadeh, 2011; Yilmaz & Müller, 2009). The ever rising demand for light olefins, specifically for propylene, combined with an increase in oil prices, are the main drivers for the investigation for alternative methods for ethylene and propylene production. The conversion of methanol to light olefins could offer an alternative process for light olefin production, due to its higher selectivity towards propylene. Furthermore, the low CO_2 emissions increase the appeal of the MTO technology (J. Q. Chen, Bozzano, Glover, Fuglerud, & Kvisle, 2005). Methanol can be produced from alternative feedstocks with proven technologies such as steam reforming of natural gas, gasification of coal or gasification of biomass (T Ren, Patel, & Blok, 2008). The location of methanol production plays a crucial role in the economic viability of the methanol to olefin technology. Most of the natural gas reserves are found in remote locations and the transportation of this gas would not be economical. Converting this stranded gas to higher value chemicals could be beneficial for the chemical industry (T Ren et al., 2008; Tao Ren, Daniëls, Patel, & Blok, 2009). In addition, the MTO technology offers the possibility for production of light olefins in regions with gas and coal reserves but without oil. The Lurgi process for methanol-to-propylene (MTP) has been proven commercially viable in China. Recently 3 plants using the Lurgi technology have started up for the production of olefins from coal: Shenhua Ningxia Coal Industry Group (500 kton/year MTP, 2010); Shenhua Group (Baotou) (600 kton/year MTO, 2010) and Datang International Power Generation (460 kton/year MTP, 2011) (D. Chen, Moljord, & Holmen, 2012). Alternatively, the UOP/Hydro MTO process developed by UOP and Norsk Hydro (now Ineos) has been proven successful in the semi-commercial test-plant in Belgium in 2008 (TOTAL, 2008). The test reactor uses an additional olefin cracking step for the production of propylene and ethylene. After the MTO reaction all C4+ products are lead to an additional cracking reactor. By adjusting the operating conditions of this reactor the ethylene and propylene yield in this process can be modified. Several plants combining the UOP/Hydro MTO process and the Total Petrochemicals/UOP Olefin Cracking process for the production of light olefins from methanol, synthesized from coal, are planned for four sites with an overall production capacity of about 1.2 Mton/year (J. Q. Chen et al., 2005).

The conversion of methanol-to-olefins is catalyzed by zeolites, which are, to the best of our knowledge, the only type of catalysts commercially used for MTO. The two most commonly used zeolites in MTO processes are ZSM-5 (MFI-Type) and SAPO-34 (CHA-Type). ZSM-5 is a medium sized pore aluminosilicate with 10-membered ring pores. In general, it has a high selectivity towards propylene and butylene and a long catalyst life, but with a lower yield of light olefins compared to SAPO-34. SAPO-34 is a silicoaluminophosphate with small 8-membered ring pores. It has a high selectivity towards ethylene but it suffers from fast deactivation due to coke formation (Chae, Song, Jeong, Kim, & Jeong, 2010; J. Q. Chen et al., 2005; Li et al., 2011). The ZSM-5 zeolite is used in the Lurgi process in a packed bed configuration, while the UOP/Hydro process uses SAPO-34 as a catalyst in a fluidized bed configuration due to the fast deactivation. Operation in coupled fluidized beds allows for continuous regeneration of the catalyst, analogous to an FCC process. As several literature reviews deal with the general aspects of the different catalysts, the operating conditions, the reaction mechanism and the deactivation of methanol to hydrocarbons, they will not be discussed in great detail in this review and focus will be put on the specific influence of using structured catalysts (D. Chen et al., 2012; Keil, 1999; McCann et al., 2008; Olsbye et al., 2012; Sano, Kiyozumi, & Shin, 1992; Stöcker, 1999; Wender, 1996).

Structured catalytic reactors can offer great advantages over traditional packed catalytic beds, as they combine a lower pressure drop with a high surface-to-volume ratio. The catalyst is generally applied as a thin coated layer onto a support structure. This thin coated layer in combination with the large pores of the structured packing reduces the pressure drop over the reactor in comparison with a packed bed. The use of macroporous structured catalysts can increase both the mass and heat transfer properties of a catalytic bed, which is especially of interest in exothermic reactions such as MTO. Due to these important benefits, the use of structured catalysts in the MTO reaction has received increasing attention over the last years. This paper highlights some important properties of the reaction mechanism and the selectivity of the reaction, as well as the progress made in recent years for structured catalysts in MTO technology. The coating methods for depositing a thin zeolite film on a structured support are summarized. The effect of mass transfer properties of catalytic systems on the stability and selectivity of the reaction is highlighted. Both thickness of the coating and the architecture of the support material influence the mass transfer properties of the final catalyst. Their influence on the selectivity and stability are described in detail, including the benefits and drawbacks of the use of a structured catalyst. Alternatively

to a coated catalyst, a self-supporting zeolite monolith catalyst can be used in order to overcome certain problems related to a coated monolith system but still keep the benefits of a macroporous monolith. In order to give a clear understanding of the benefits of a structured catalyst for MTO the reaction is briefly discussed. The possible opportunities of structured catalysts in improving the selectivity, activity and stability of the reaction are highlighted. In a second part different structured supports and the coating of these supports is covered followed by examples of coated structured catalysts for MTO. In a final part of this paper the self-supporting structured catalysts are discussed.

Reaction mechanism and selectivity

Over time several mechanisms have been proposed. Studies of the reaction mechanism by Dahl and Kolboe (Bjorgen et al. 2007; Dahl and S Kolboe 1994; Dahl and Stein Kolboe 1993; Mores et al. 2008; Unni Olsbye et al. 2005; S Svelle et al. 2005; Stian Svelle, Rønning, and Stein Kolboe 2004) in SAPO-34 have suggested the hydrocarbon pool mechanism which is now generally accepted (Hemelsoet, Van der Mynsbrugge, De Wispelaere, Waroquier, & Van Speybroeck, 2013). In ZSM-5 however, the observations point to a dual cycle mechanism shown in Figure 1, with a hydrocarbon pool mechanism responsible for ethylene formation and a repeated methylation-cracking reaction for the formation of propylene (S Svelle et al., 2005; Stian Svelle et al., 2004). The questions whether both these cycles operate independently of each other is still of great interest to researchers as this has a great influence on the selectivity of the reaction (Olsbye et al., 2012).

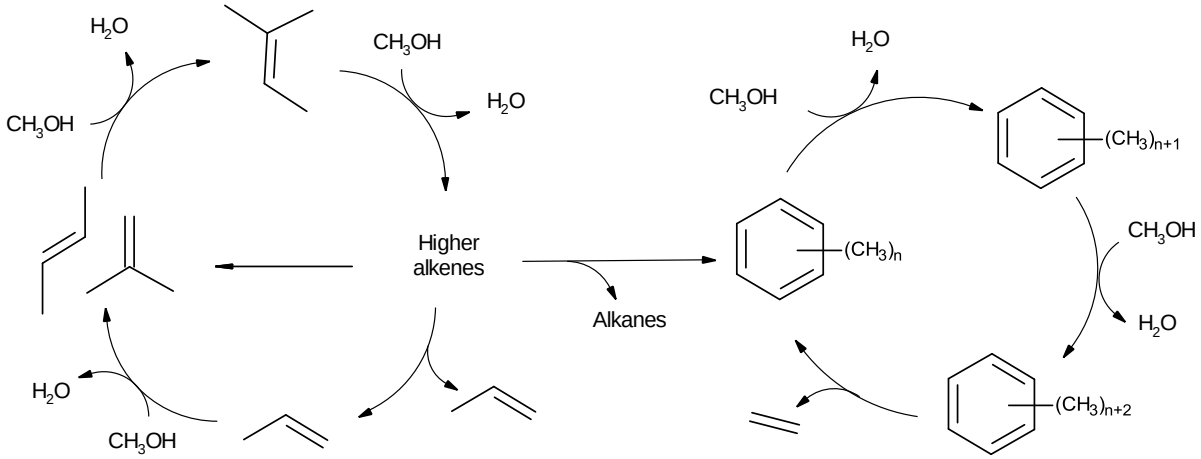

Figure 1: Representation of dual cycle mechanism in H-ZSM-5 (after Olsbye et al., 2005).

Intrinsic catalyst properties such as strength and density of the acid sites (Aramburo et al., 2011; Furumoto et al., 2011; Park, Kim, et al., 2008; Tago, Iwakai, Morita, Tanaka, & Masuda, 2005; Westgård Erichsen, Svelle, & Olsbye, 2013; W. Wu, Guo, Xiao, & Luo, 2011) and zeolite topology (Hereijgers et al., 2009; Li et al., 2011; Mccann et al., 2008; Ocampo et al., 2010; Park, Lee, Kim, Hong, & Seo, 2008) have an influence on the selectivity of the MTO reaction. In the past decade, research has focused on the modification of the acidity of the catalysts by changing the Si/Al ratio (Ferreira Madeira et al., 2012; Inoue, Okabe, Inaba, Takahara, & Murata, 2010), by incorporation of metal or phosphor in the zeolite (Kaarsholm et al., 2007; Rahimi & Karimzadeh, 2011; Takahashi, Xia, Nakamura, Shimada, & Fujitani, 2012; Valle, Alonso, Atutxa, Gayubo, & Bilbao, 2005; Y. Yang et al., 2012) or via modification by a binder (Yun-Jo Lee, Kim, Viswanadham, Jun, & Bae, 2010; Menges & Kraushaar-Czarnetzki, 2012). It was observed that lower acid site density, especially lower strong acid site density results in better selectivity and stability due to sparse distribution of alkylaromatics in the pores, suppressing the coke formation. The effect of reaction conditions (Taheri Najafabadi, Fatemi, Sohrabi, & Salmasi, 2012) and feed composition (X. Wu & Anthony, 2001) on the selectivity has also been explored. The most important reaction parameters influencing the selectivity and stability of the reaction are the temperature, the methanol space-time and the inlet water-methanol ratio. The co-addition of water to the reaction mixture has a double effect: it both influences the selectivity by shifting the methanol dehydration equilibrium and decreases the deactivation by coking by blocking the strongest acid sites.

The selectivity is also influenced by the diffusion properties of the catalyst, such as the crystal size of the zeolite (Bleken et al., 2012; De Chen, Moljord, Fuglerud, & Holmen, 1999; Dahl et al., 1999; Meng, Mao, Guo, & Lu, 2012; Möller & Böhringer, 1999; Rownaghi, Rezaei, & Hedlund, 2011). Modeling and catalytic experiments have shown that the diffusion is altered by the macroscopic properties of the catalyst structure, which has its consequences for the selectivity, activity and stability of the catalyst (Guo, Wu, Luo, & Xiao, 2012; Zhuang, Gao, Zhu, & Luo, 2012). The reaction mechanism suggest that fast evacuation of the reaction products from the catalyst is needed as further reaction of products such as propylene and butylene is possible. Kinetic studies performed by Svelle et al. have shown the importance of the contact time (S Svelle et al., 2005; Stian Svelle et al., 2004). It was shown that long contact times led to an increased yield of aromatics and alkanes whereas by fast evacuation of the alkene products, the formation of aromatics can be reduced and high $C_3^=/C_2^=$ ratios can be achieved. Moreover, the fast evacuation of products can reduce the coke formation on the zeolite surface thus increasing the stability. To control the residence time, contact time and kinetics of molecules in a chemical reaction three factors are crucial: the residence time in the zeolite micropores, in the catalyst bulk phase and in the gas phase of the reactor. By using a structured catalyst, all three time components can be modified independently. To do so, the zeolite crystal size, the thickness and porosity of the zeolite coating, and the architecture of the macroporous structure can be altered respectively. By modification of these three variables, the yield of valuable products of the MTO reaction can be improved and optimized.

Structured catalysts

Catalysts in industrial applications are generally shaped as pellets, micro granules or extrudates and used in a random packed bed. Fast evacuation of the products can be achieved by applying zeolites with small crystal sizes and introducing good mass transfer properties in the catalyst and/or catalytic bed. The mass transfer in a reactor with a packed bed of zeolite pellets can be improved by reducing the size of the zeolites pellets. However, this will lead to a higher pressure drop over the reactor and can lead to a serious operating cost in industrial installations. This high pressure drop can be avoided by using hierarchical porous catalysts, either by applying a macroporous support coated with the catalyst or by introduction of meso- and macropores in the zeolite particle. Mitchell et al. have shown that the stability of a hierarchical ZSM-5 is significantly higher than a conventional ZSM-5 catalyst for the MTO

reaction in a packed bed (Mitchell, Michels, Kunze, & Pérez-Ramirez, 2012; Mitchell, Michels, & Pérez-Ramírez, 2013). In this way, high mass transfer can be achieved without the high pressure drop penalty, additionally the stability of the zeolite can be increased (Guo, Wu, et al., 2012). The architecture of the structured catalysts has an impact on the residence time distribution of the molecules and thus the selectivity. A well designed structured catalyst can improve the selectivity and the stability of the catalyst system by achieving a narrower residence time distribution (Pangarkar et al., 2008). Structured catalysts are therefore a promising alternative as they allow a low pressure drop in combination with high mass- and heat transfer and controlled residence times (Dai, Lei, Li, & Chen, 2012; Lefevere, Gysen, Mullens, Meynen, & Van Noyen, 2013). In Figure 2 the pressure drop of different honeycomb monolith structures is compared to packed beds of spheres and rings. It is shown that the pressure drop increases with smaller particles or smaller channels. At the same specific surface area the samples show different pressure drop, respectively from high to low: spheres (packed bed), foams ≈3DFD 1-3, 3DFD 1-1 and honeycombs. The void fraction of a packed bed of spheres is low (40 %) as compared to the structured packings were the macroporous architecture results in a void fraction of 70-80 %. The results shown in figure 3 indicate a large influence of the porous architecture on the pressure drop of the structured packing.

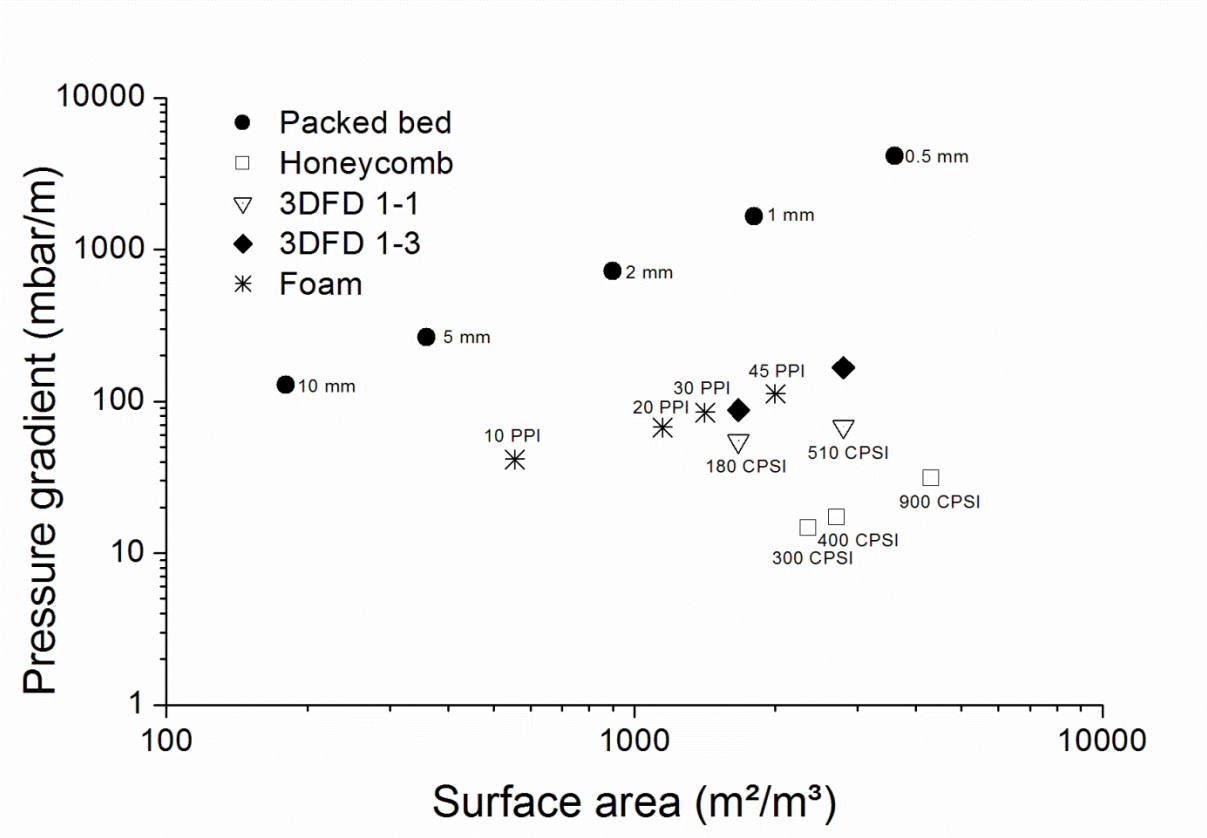

Figure 2: Pressure drop as function of specific geometric surface area of foams, honeycombs, 3DFD structures and spheres. Data are for air at 20 °C and 1 bar and a superficial gas velocity of 2.5 m/s (at STP) (CPSI: cells per square inch; PPI: Pores per inch) (Dietrich, 2012).

Many types of structured support materials have been proposed in literature. Conventional structured packings can be subdivided in four different classes: (1) ceramic or metallic monoliths with straight parallel channels, (2) sheet/gauze metallic packings, (3) knitted metallic wire packings and (4) open cell ceramic or metallic foams. The type of support material will have an impact on the mass and heat transfer properties, the pressure drop and the catalyst hold up. Alternatively, a new type of structured packing with high flexibility of the porous architecture was proposed. Recently the use of 3D-printing or 3 dimensional fiber deposition (3DFD) for manufacturing catalyst support structures has been proposed. This flexible technique allows optimization of the architecture of the support combining good mass and heat transfer properties with low pressure drop (Ferrizz, Stuecker, Cesarano III, & Miller, 2005; Lefevere et al., 2013; Lewis, Smay, Stuecker, & Cesarano, 2006; Stuecker, Miller, Ferrizz, Mudd, & Cesarano, 2004; Van Noyen, Wilde, Schroeven, Mullens, & Luyten, 2012). By constructing the catalyst support material layer by layer there is large freedom of design of the architecture of the support (Figure 3). The thickness of the

fibers, the distance between the fibers, the stacking of the fibers can be varied and manufactured in different materials such as stainless steel, cordierite or titania. The stacking of the fibers will have a major impact on the mass and heat transfer properties and pressure drop of the final catalyst (Ferrizz et al., 2005; Stuecker et al., 2004). The flexibility of the 3DFD technology allows to specifically enhance properties of the structured packing allowing research on the impact of these properties of the architecture of the support material for different types of reactions (Leong, Cheah, & Chua, 2003). Rapid prototyping of ceramic and metallic supports allows an almost unlimited amount of unique architectures with an excellent reproducibility. By combination of modeling and testing, a fast and good choice of supports with adequate mechanical properties and low pressure drop can be achieved (Van Noyen et al., 2012).

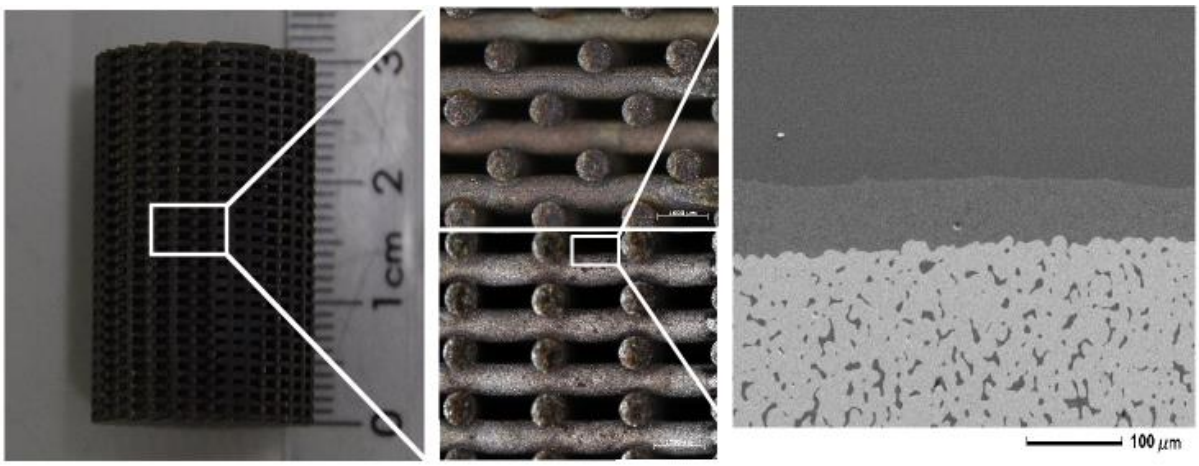

Figure 3: Different scales of 3DFD support structure respectively: full scale structure, different stacking of the layers of the 3DFD structure (1-3 on top and 1-1 on the bottom) and ZSM-5 coating on the 3DFD surface.

The straight channels of standard cordierite honeycombs have some disadvantages like problems with the bulk gas-solid mass transfer and problems with heat transfer in exothermal reactions such as MTO which can lead to hot spots. These problems can be overcome by different types of materials like foams or 3D ordered structures or metallic honeycombs with higher heat conductivity (Pangarkar et al., 2008). These structures promote turbulent flow and allow inter channel diffusion leading to better mass and heat transfer (Ferrizz et al., 2005; Stuecker et al., 2004). Structures with a predetermined 3D porous network are of great interest as these are highly reproducible and the ideal flow pattern in the structure can be chosen in

advance. In Table 1 an overview is given of the different properties of the classes of structured packings.

Parameter	*Packed bed*	*Ceramic/ metallic monolith*	*Sheet/gauze metallic packing*	*Knitted wire packing*	*Foam*	*3DFD*
Radial mass transfer	medium	no	good	no data	good	good
Radial heat transfer	medium	no	good	no data	good	good
Tortuosity of fluid	yes	no	yes	yes	yes	yes
Pressure drop	high	low	low	low	low	low
Geometric macroporosity	low	high	high	high	high	high
Price	low	low	medium	medium-low	medium-low	medium-high
Flexibility	low	low	medium	low	low	high

Table 1: Properties of conventional structured packings and 3DFD structured packings.(Pangarkar et al., 2008)

To obtain the active catalyst, coatings of zeolite particles are deposited on the inert structured surface (Ulla et al., 2003). There are two main techniques used to deposit a coating of the active zeolite on the surface of the support: wash coating (Zhu, Fan, & Xu, 2011) and hydrothermal coating (Ivanova et al., 2009; Louis, Ocampo, Yun, Tessonnier, & Pereira, 2010; Perdana, Creaser, Lindmark, & Hedlund, 2010; Seijger & Oudshoorn, 2000; Shan & Kooten, 2000; H. Yang, Liu, Gao, & Xie, 2010; Yao, Zeng, Zhang, & Xu, 2008; Zampieri et al., 2006). The most important differences between wash coatings and hydrothermal coatings are the presence or absence of intra crystalline porosity, the bonding strength of the zeolites to the support, the thickness of the coating and the uniformity of the coating (Table 2) (Seijger & Oudshoorn, 2000; J. M. Zamaro & Miró, 2010).

Method	*Intra crystalline porosity*	*Bonding strength*	*Thickness coating*	*Uniformity coating*
Wash coating	+	-	+	+
Hydrothermal coating	-	+	-	-

Table 2: Differences between properties of the coated zeolites layer when using wash or hydrothermal coating.

Although hydrothermal coatings result in high bounding strengths, they also suffer some drawbacks such as tendency for crystallization in the liquid rather than on the surface of the support. The most important variables in selectivity between zeolite deposited on the support and in the coating solution are (i) decreasing the ratio of the synthesis mixture volume to the packing surface area (ii) agitating the synthesis solution during synthesis (iii) lowering

the amount of reagent concentration of the synthesis mixture (iv) increasing the template concentration near the support surface and (v) creating a seeding surface on the support surface (Seijger & Oudshoorn, 2000; Shan & Kooten, 2000). Moreover, the loading of zeolite on the support using hydrothermal synthesis is limited in a single coating step. Prolonged synthesis time initially leads to an increase in loading but this effect decreases with increasing time. By repeated hydrothermal coating steps with a fresh synthesis solution on the same carrier, the loading increases proportionally with the number of coatings. Not only the thickness of the layer increases but also the density and the crystal size of the layer, as the first layer acts as a seeding for further coatings (Shan & Kooten, 2000; Van Noyen et al., 2012). It should be noted that the Si/Al ratio changes with repeated coatings, which has a direct impact on the acidity and the catalytic properties of the zeolite layer (Shan & Kooten, 2000). Another issue with hydrothermal coating is the high density of the coated layer, as a porous layer is beneficial for good mass transfer inside the zeolite coating (S. Lopez-Orozco, A. Inayat, A. Schwab, 2011).

On the other hand, the adhesion of zeolite wash coatings to the support structure is often an issue. Additional inorganic binders can be used in low concentration to improve the adhesion of the zeolite to the surface of the support (Buciuman & Kraushaar-Czarnetzki, 2001). However, the binder can inhibit the diffusion of reactants and products in the coating as it is usually smaller than the zeolite particles, possibly blocking the entrance of the pores of the zeolite. Buciuman & Kraushaar-Czarnetski showed it was possible to wash coat ZSM-5 and silicalite-1 directly onto a foam without the use of additives (Buciuman & Kraushaar-Czarnetzki, 2001). Uniform zeolite coatings were obtained for different carriers at a suspension zeolite concentration of 0.1-10 wt%. By increasing the zeolite concentration of the dipping suspension higher loadings on the foam could be achieved. The adhesion strength of the coating was tested using high air flow. A weight loss of about 10% of the zeolite loading was observed after 48h in a 1 m/s air flow, which is still too high for industrial applications. Another more demanding test for the adhesion of the coating is the use of ultrasonic conditions. By optimization of the particle size and the addition of binders a stable coating of ZSM-5 on cordierite honeycomb can be obtained as shown by Zamaro et al. and Lefevere et al. (Lefevere et al., 2013; J. Zamaro, Ulla, & Miro, 2005).

ZSM-5 is commonly used as catalyst in structured supports for methanol-to-olefins, because the deactivation by coking is too fast for SAPO-34 (Bleken et al., 2012). ZSM-5

coatings have been deposited on different types of support materials such as stainless steel (Shan & Kooten, 2000; H. Yang et al., 2010), Al_2O_3 (Seijger & Oudshoorn, 2000), glass (Louis et al., 2010), ceramic (Ivanova et al., 2009), cordierite (Perdana et al., 2010; Yao et al., 2008; J. Zamaro et al., 2005) or SiC (Ivanova, Louis, Madani, Tessonnier, & Ledoux, 2007; Jiao, Jiang, Yang, & Zhang, 2012; Zampieri et al., 2006). The architecture of the support as well as thickness of the coating and crystal size of the zeolite are of crucial importance for the mass- and heat transfer, pressure drop and contact time during the reaction. Combined with the intrinsic properties of the zeolite used they determine the selectivity and stability of the catalyst. Patcas (Patcas, 2005) has shown that a thick coating layer leads to low catalyst effectiveness and low olefin yield. On the other hand, when applying a very thin layer of catalyst it is difficult to keep the catalytic species confined in the micropores. This leads to a too fast evacuation of the reaction species and thus lowers the production of dimethylether, resulting in a low selectivity to light olefins. In conclusion a certain minimum amount/critical thickness of the catalyst coating is needed, although thick coatings should be avoided.

MTO with structured catalyst

In Table 3 some examples of catalytic results of ZSM-5 coated structured catalysts for the MTO reaction are given and are compared with a packed bed at the same conditions. Initial work performed by Patcas (2005) shows the better effectiveness of the coated structured catalyst. The use of the coated foam catalyst resulted in a 2.5 times higher production of light olefins per volume of reactor as compared to a packed bed. The results also suggest that the highest light olefin selectivity at 380 °C is achieved at 90 % conversion. Ivanova et al. (2007) have shown that the thickness of the coated layer is an important factor determining the selectivity. The use of thin coatings results in a fast evacuation of the products and a high selectivity to light olefins. On the other hand, conversion seems to be lower when thin coatings are applied. Although the catalyst hold up per reactor volume is lower using coated structured packings, these types of catalyst can be industrially relevant as the catalyst layer is more effective than in a packed bed. This was shown by Jiao et al. (2012), by comparing a coated foam with a diluted and undiluted packed bed at equal methanol feed per reactor volume. The packed bed of pellets diluted with quartz sand operating at the same WHSV as the coated catalyst showed initially the same selectivity as the composite however, the selectivity and conversion decreased rapidly with time on stream (TOS). On the other hand the undiluted packed bed of pellets working at lower WHSV showed comparable stability and

activity as the coated foam but showed significant lower selectivity to propylene. Due to enhanced mass- and heat transfer properties of the structured catalyst better catalytic results are achieved with less catalyst. These results were confirmed in the work of Bleken et al. (2012) were the propylene yield of zeolite coated glass monolith was higher than that for the packed bed. Moreover, at the same WHSV the reference zeolite particles showed faster deactivation than the coated sample. Lefevere et al. (2013) have shown that the importance of the architecture and material of the support structure on the performance of the final catalyst. The 3DFD 1-3 structure, with zigzag channels in the direction of the flow, shows the best yield of light olefins. Interestingly, the 3DFD 1-1 with straight channels shows higher selectivity than the honeycomb structure with straight channels and the same loading. This could be a result of the higher thermal conductivity of the steel support or the radial channels of the 3DFD support allowing radial mass- and heat transfer. The importance of porosity in the coated layer was highlighted by Jiao et al. (2013). A conventional hydrothermal coated structure was compared to a sample coated using a two-step coating. The second method resulted in a zeolite layer with high porosity at the surface of the layer and a denser zeolite layer at the surface of the support. This gradient coating combines the good adherence of the coating to the support with excellent accessibility of the zeolite. The catalytic results show that the improved mass transfer properties in the gradient sample result in higher propylene selectivity and longer stability than the conventional sample.

Catalyst structure	*Temp. (°C)*	*WHSV (h^{-1})*	*Conv. (%)*	*C_2H_4 (%)*	*C_3H_6 (%)*	*C_4H_8 (%)*	*Stability (h)*	*Ref.*
5 µm coating α-alumina foam	380	27	90		34	-	-	(Patcas, 2005)
18 µm coating α-alumina foam	380	40	90		32	-	-	(Patcas, 2005)
Packed bed	380	8	90		22	-	-	(Patcas, 2005)
Single coated SiC foam	500	-	76		$C_2^=$-$C_4^=$: 65		8	(Ivanova et al., 2007)
Double coated SiC foam	500	-	90		$C_2^=$-$C_4^=$: 60		10	(Ivanova et al., 2007)
Packed bed	500	-	70		$C_2^=$-$C_4^=$: 55		12	(Ivanova et al., 2007)
ZSM-5 coated SiC foam	500	4.46	100	-	37	-	50+	(Jiao et al., 2012)
Packed bed ZSM-5 diluted	500	4.46	95	-	30	-	35	(Jiao et al., 2012)

Packed bed ZSM-5 undiluted	500	0.75	100	-	25	-	50+	(Jiao et al., 2012)
ZSM-5 Packed bed	350	1.8	99	15	27	14	-	(Bleken et al., 2012)
ZSM-5 coating on glass monolith	350	1.8	99	12	30	18	-	(Bleken et al., 2012)
Coated cordierite honeycomb	350	18	99.7	$C_2^=$-$C_3^=$: 41.1		-	-	(Lefevere et al., 2013)
Coated stainless steel 3DFD straight channels	350	18	87.6	$C_2^=$-$C_3^=$: 65.8		-	-	(Lefevere et al., 2013)
Coated stainless steel 3DFD zigzag channels	350	18	98.9	$C_2^=$-$C_3^=$: 55.5		-	-	(Lefevere et al., 2013)
Packed bed	350	4.5	84.6	$C_2^=$-$C_3^=$: 48.7		-	-	(Lefevere et al., 2013)
SiC foam conventional ZSM-5 coating	500	0.6	97.5	8.2	37.8	19.9	-	(Jiao et al., 2013)
SiC foam gradient ZSM-5 coating	500	0.6	99.5	7.1	45.1	24.6	-	(Jiao et al., 2013)

Table 3: Overview of catalytic results for the MTO reaction using zeolite coated monolith catalysts.

Bulk monolithic catalyst

Monoliths with the catalyst incorporated in the structure, so called 'bulk monolithic catalysts' offer some advantages over the coated monolithic structures. First of all it is clear that synthesis of a coated catalyst needs more process steps than preparation of a bulk monolithic catalyst. For coated structures repeated coatings are often needed in order to obtain the necessary catalyst loading, this can lead to non-uniformity of the coating. Non-uniformity of the coating affects the mechanical properties as well as the mass- and heat transfer of the final catalyst. One of the most important drawbacks of a coated catalyst is the limited loading of catalyst per reactor volume. Using a bulk monolithic catalyst these shortcomings are overcome, a high amount of catalyst can be uniformly introduced in the reactor (Zamaniyan, Mortazavi, Khodadadi, & Manafi, 2010).

Modeling studies by Guo et al. (Guo, Wu, et al., 2012; Guo, Xiao, & Luo, 2012) have shown that a major improvement of the mass transfer properties is made by using a self-supporting

zeolite honeycomb over a randomly packed bed of particles. By using the zeolite ZSM-5 honeycomb it was calculated that the efficiency of the catalyst in the reactor went up five times, so lower space times were needed to obtain the higher conversion. Moreover, the selectivity to propylene was raised by using the honeycomb structure. It was found that the wall thickness of the monolith affects the product distribution, especially of C_3-C_6 alkanes. It was suggested that monoliths with high cell density and thin walls achieved the highest propylene yield, a zeolitic honeycomb structure with 400 cells per square inch and 200 µm was proposed.

Some work has already been done on the formation of ZSM-5 self-supporting monolith structures. Aranzabal et al. (Aranzabal et al., 2010) have optimized direct extrusion of ZSM-5 zeolite paste into a honeycomb shape. A series of process steps (kneading, extruding, drying, calcination) are crucial to obtain a highly stable defect-free structure. Good rheology of the paste is needed in order to ensure successful extrusion. Good mechanical properties are obtained using a colloidal silica binder in a concentration of 10-25 wt% of the final catalyst. An alternative method for the synthesis of a self-supporting ZSM-5 monolith is the use of a template. In this method a hydrothermal synthesis of zeolite on the template surface is performed, afterwards the template is removed in order to leave a macroporous self-supporting monolith. The use of polyurethane foam in order to synthesize a ZSM-5 self-supporting foam was proposed by Lee et al. (Y.-J. Lee, Lee, Park, & Yoon, 2001; Yun-Jo Lee et al., 2009). Foams with three different Si/Al ratios were synthesized, their catalytic properties were compared for conversion of methanol to light olefins. As reference material the foam with the best performance (Si/Al = 250) was pelletized and compared with the monolithic structure. The catalytic results at 450°C (Table 4) show that the monoliths have good selectivity to light olefins however the selectivity is only slightly higher than that of the packed bed. The main difference between the ZSM-5 foam and the pelletized zeolite is revealed in the testing of the conversion at higher WHSV. The monolith shows superior activity at high WHSV confirming the better efficiency of a structured self-supporting catalyst. Overall, the results of the modeling studies in combination with the catalytic study show promising opportunities for self-supporting ZSM-5 structures in the methanol-to-olefins reaction especially if high propylene selectivity is desired.

Catalyst structure	*Temp. (°C)*	*WHSV (h^{-1})*	*Conv. (%)*	*C_2H_4 (%)*	*C_3H_6 (%)*	*C_4H_8 (%)*	*Stability (h)*	*Ref.*

ZSM-5 foam (Si/Al= 140)	450	2.55	100	11.0	28.6	19.5	-	(Yun-Jo Lee et al., 2009)
ZSM-5 foam (Si/Al= 250)	450	2.55	100	11.4	43.9	20.1	-	(Yun-Jo Lee et al., 2009)
ZSM-5 foam (Si/Al= 500)	450	2.55	75.5	5.4	39.6	20.2	-	(Yun-Jo Lee et al., 2009)
Packed bed pelletized ZSM-5 (Si/Al= 250)	450	2.55	100	10.4	41.5	20.8	-	(Yun-Jo Lee et al., 2009)

Table 4: Overview of catalytic results for the MTO reaction using self-supporting zeolite monolith catalysts.

Conclusions

The reaction mechanism of the MTO process has shown that next to the intrinsic properties of the zeolite also the crystal size of the zeolite, the porous architecture of the catalyst are important. Fast removal of the products and heat of the MTO reaction and narrower contact time distribution can be achieved by using structured macroporous catalyst systems. The catalytic results of different research groups have shown that higher selectivity towards propylene and longer stability of the catalyst can be achieved. The higher mass- and heat transfer properties of these hierarchical materials lead to faster evacuation of the desired products. Moreover, the results of the coated systems point out the higher effectiveness of the catalyst layer and in this way overcoming the lower amount of catalyst per volume of these systems. On the other hand, the self-supporting zeolite monoliths offer an alternative to raise the loading of zeolite per reactor volume and reducing the number of manufacturing steps of the catalyst. Combining the high selectivity and stability of the structured catalysts and high loading of catalyst per reactor volume these self-supporting monoliths offer a promising route for process intensification.

In future work, the optimization of the architecture of the macroporous material can lead to further improvement of the stability and selectivity of the catalyst. 3D printing of the support using 3DFD technology can be an interesting tool to investigate the effect of architecture as it allows a high freedom of design of the catalyst structure. In combination with modeling studies faster optimization of the architecture of the support with the 3DFD technology can be achieved, which can lead to optimization of the propylene yield of the catalyst.

References

Aramburo, L. R., Karwacki, L., Cubillas, P., Asahina, S., de Winter, D. a M., Drury, M. R., … Weckhuysen, B. M. (2011). The porosity, acidity, and reactivity of dealuminated zeolite ZSM-5 at the single particle level: the influence of the zeolite architecture. *Chemistry a European Journal*, *17*(49), 13773–81. doi:10.1002/chem.201101361

Aranzabal, A., Iturbe, D., Romero-Sáez, M., González-Marcos, M. P., González-Velasco, J. R., & González-Marcos, J. a. (2010). Optimization of process parameters on the extrusion of honeycomb shaped monolith of H-ZSM-5 zeolite. *Chemical Engineering Journal*, *162*(1), 415–423. doi:10.1016/j.cej.2010.05.043

Bjorgen, M., Svelle, S., Joensen, F., Nerlov, J., Kolboe, S., Bonino, F., … Olsbye, U. (2007). Conversion of methanol to hydrocarbons over zeolite H-ZSM-5: On the origin of the olefinic species. *Journal of Catalysis*, *249*(2), 195–207. doi:10.1016/j.jcat.2007.04.006

Bleken, F. L., Chavan, S., Olsbye, U., Boltz, M., Ocampo, F., & Louis, B. (2012). Conversion of methanol into light olefins over ZSM-5 zeolite: Strategy to enhance propene selectivity. *Applied Catalysis A: General*, *447-448*, 178–185. doi:10.1016/j.apcata.2012.09.025

Buciuman, F., & Kraushaar-Czarnetzki, B. (2001). Preparation and characterization of ceramic foam supported nanocrystalline zeolite catalysts. *Catalysis today*, *69*, 337–342. doi:10.1016/S0920-5861(01)00387-X

Chae, H.-J., Song, Y.-H., Jeong, K.-E., Kim, C.-U., & Jeong, S.-Y. (2010). Physicochemical characteristics of ZSM-5/SAPO-34 composite catalyst for MTO reaction. *Journal of Physics and Chemistry of Solids*, *71*(4), 600–603. doi:10.1016/j.jpcs.2009.12.046

Chen, D., Moljord, K., & Holmen, a. (2012). A methanol to olefins review: Diffusion, coke formation and deactivation on SAPO type catalysts. *Microporous and Mesoporous Materials*, *164*, 239–250. doi:10.1016/j.micromeso.2012.06.046

Chen, De, Moljord, K., Fuglerud, T., & Holmen, A. (1999). The effect of crystal size of SAPO-34 on the selectivity and deactivation of the MTO reaction. *Microporous and Mesoporous Materials*, *29*(1-2), 191–203. doi:10.1016/S1387-1811(98)00331-X

Chen, J. Q., Bozzano, A., Glover, B., Fuglerud, T., & Kvisle, S. (2005). Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process. *Catalysis Today*, *106*(1-4), 103–107. doi:10.1016/j.cattod.2005.07.178

Dahl, I. M., & Kolboe, S. (1993). On the reaction mechanism for propene formation in the MTO reaction over SAPO-34. *Catalysis Letters*, *20*(3-4), 329–336. doi:10.1007/BF00769305

Dahl, I. M., & Kolboe, S. (1994). On the reaction mechanism for hydrocarbon formation from Methanol over SAPO-34 1 isotopic labeling studies. *Journal of Catalysis*, *149*, 458–464. doi:10.1006/jcat.1996.0188

Dahl, I. M., Wendelbo, R., Andersen, A., Akporiaye, D., Mostad, H., & Fuglerud, T. (1999). The effect of crystallite size on the activity and selectivity of the reaction of ethanol and 2-propanol over SAPO-34. *Microporous and Mesoporous Materials*, *29*(1-2), 159–171. doi:10.1016/S1387-1811(98)00328-X

Dai, C., Lei, Z., Li, Q., & Chen, B. (2012). Pressure drop and mass transfer study in structured catalytic packings. *Separation and Purification Technology*, *98*, 78–87. doi:10.1016/j.seppur.2012.06.035

Dietrich, B. (2012). Pressure drop correlation for ceramic and metal sponges. *Chemical Engineering Science*, *74*, 192–199. doi:10.1016/j.ces.2012.02.047

Ferreira Madeira, F., Ben Tayeb, K., Pinard, L., Vezin, H., Maury, S., & Cadran, N. (2012). Ethanol transformation into hydrocarbons on ZSM-5 zeolites: Influence of Si/Al ratio on catalytic performances and deactivation rate. Study of the radical species role. *Applied Catalysis A: General*, *443-444*, 171–180. doi:10.1016/j.apcata.2012.07.037

Ferrizz, R., Stuecker, J., Cesarano III, J., & Miller, J. (2005). Monolithic supports with unique geometries and enhanced mass transfer. *Ind.& Eng. Chem. Res.*, *44*(2), 302–308. doi:10.1021/ie049468r

Furumoto, Y., Harada, Y., Tsunoji, N., Takahashi, A., Fujitani, T., Ide, Y., … Sano, T. (2011). Effect of acidity of ZSM-5 zeolite on conversion of ethanol to propylene. *Applied Catalysis A: General*, *399*(1-2), 262–267. doi:10.1016/j.apcata.2011.04.009

Guo, W., Wu, W., Luo, M., & Xiao, W. (2012). Modeling of diffusion and reaction in monolithic catalysts for the methanol-to-propylene process. *Fuel Processing Technology*, 6–11. doi:10.1016/j.fuproc.2012.06.005

Guo, W., Xiao, W., & Luo, M. (2012). Comparison among monolithic and randomly packed reactors for the methanol-to-propylene process. *Chemical Engineering Journal*, *207-208*, 734–745. doi:10.1016/j.cej.2012.07.046

Hemelsoet, K., Van der Mynsbrugge, J., De Wispelaere, K., Waroquier, M., & Van Speybroeck, V. (2013). Unraveling the reaction mechanisms governing methanol-to-olefins catalysis by theory and experiment. *Chemphyschem : a European journal of chemical physics and physical chemistry*, *14*, 1526–45. doi:10.1002/cphc.201201023

Hereijgers, B. P. C., Bleken, F., Nilsen, M. H., Svelle, S., Lillerud, K.-P., Bjørgen, M., … Olsbye, U. (2009). Product shape selectivity dominates the Methanol-to-Olefins (MTO) reaction over H-SAPO-34 catalysts. *Journal of Catalysis*, *264*(1), 77–87. doi:10.1016/j.jcat.2009.03.009

Inoue, K., Okabe, K., Inaba, M., Takahara, I., & Murata, K. (2010). Metal modification effects on ethanol conversion to propylene by H-ZSM-5 with Si/Al2 ratio of 150. *Reaction Kinetics, Mechanisms and Catalysis*, *101*(2), 477–489. doi:10.1007/s11144-010-0245-4

Ivanova, S., Louis, B., Madani, B., Tessonnier, J. P., & Ledoux, M. J. (2007). ZSM-5 Coatings on -SiC Monoliths : Possible New Structured Catalyst for the Methanol-to-Olefins Process. *J. Phys. Chem. C*, *111*, 4368–4374. doi:10.1021/jp067535k

Ivanova, S., Vanhaecke, E., Dreibine, L., Louis, B., Pham, C., & Pham-huu, C. (2009). General Binderless HZSM-5 coating on b -SiC for different alcohols dehydration. *Applied Catalysis A: General*, *359*, 151–157. doi:10.1016/j.apcata.2009.02.024

Jiao, Y., Jiang, C., Yang, Z., Liu, J., & Zhang, J. (2013). Synthesis of highly accessible ZSM-5 coatings on SiC foam support for MTP reaction. *Microporous and Mesoporous Materials*, *181*, 201–207. doi:10.1016/j.micromeso.2013.07.013

Jiao, Y., Jiang, C., Yang, Z., & Zhang, J. (2012). Controllable synthesis of ZSM-5 coatings on SiC foam support for MTP application. *Microporous and Mesoporous Materials*, *162*, 152–158. doi:10.1016/j.micromeso.2012.05.034

Kaarsholm, M., Joensen, F., Nerlov, J., Cenni, R., Chaouki, J., & Patience, G. S. (2007). Phosphorous modified ZSM-5: Deactivation and product distribution for MTO. *Chemical Engineering Science*, *62*(18-20), 5527–5532. doi:10.1016/j.ces.2006.12.076

Keil, F. J. (1999). Methanol-to-hydrocarbons: process technology. *Microporous and Mesoporous Materials*, *29*(1-2), 49–66. doi:10.1016/S1387-1811(98)00320-5

Lee, Y.-J., Lee, J. S., Park, Y. S., & Yoon, K. B. (2001). Synthesis of Large Monolithic Zeolite Foams with Variable Macropore Architectures. *Advanced Materials*, *13*(16), 1259. doi:10.1002/1521-4095(200108)13:16<1259::AID-ADMA1259>3.0.CO;2-U

Lee, Yun-Jo, Kim, Y.-W., Jun, K.-W., Viswanadham, N., Bae, J. W., & Park, H.-S. (2009). Textural Properties and Catalytic Applications of ZSM-5 Monolith Foam for Methanol Conversion. *Catalysis Letters*, *129*(3-4), 408–415. doi:10.1007/s10562-008-9811-z

Lee, Yun-Jo, Kim, Y.-W., Viswanadham, N., Jun, K.-W., & Bae, J. W. (2010). Novel aluminophosphate (AlPO) bound ZSM-5 extrudates with improved catalytic properties for methanol to propylene (MTP) reaction. *Applied Catalysis A: General*, *374*(1-2), 18–25. doi:10.1016/j.apcata.2009.11.019

Lefevere, J., Gysen, M., Mullens, S., Meynen, V., & Van Noyen, J. (2013). The benefit of design of support architectures for zeolite coated structured catalysts for alcohol-to-olefin conversion. *Catalysis Today*, *216*, 18–23. doi:10.1016/j.cattod.2013.05.020

Leong, K. F., Cheah, C. M., & Chua, C. K. (2003). Solid freeform fabrication of three-dimensional scaffolds for engineering replacement tissues and organs. *Biomaterials*, *24*(13), 2363–2378. doi:10.1016/S0142-9612(03)00030-9

Lewis, J. a., Smay, J. E., Stuecker, J., & Cesarano, J. (2006). Direct Ink Writing of Three-Dimensional Ceramic Structures. *Journal of the American Ceramic Society*, *89*(12), 3599–3609. doi:10.1111/j.1551-2916.2006.01382.x

Li, J., Wei, Y., Liu, G., Qi, Y., Tian, P., Li, B., … Liu, Z. (2011). Comparative study of MTO conversion over SAPO-34, H-ZSM-5 and H-ZSM-22: Correlating catalytic performance

and reaction mechanism to zeolite topology. *Catalysis Today*, *171*(1), 221–228. doi:10.1016/j.cattod.2011.02.027

Louis, B., Ocampo, F., Yun, H. S., Tessonnier, J. P., & Pereira, M. M. (2010). Hierarchical pore ZSM-5 zeolite structures: From micro- to macro-engineering of structured catalysts. *Chemical Engineering Journal*, *161*(3), 397–402. doi:10.1016/j.cej.2009.09.041

Mccann, D. M., Lesthaeghe, D., Kletnieks, P. W., Guenther, D. R., Hayman, M. J., Speybroeck, V. Van, … Haw, J. F. (2008). A Complete Catalytic Cycle for Supramolecular Methanol-to-Olefins Conversion by Linking Theory with Experiment **, 5179–5182. doi:10.1002/anie.200705453

McCann, D. M., Lesthaeghe, D., Kletnieks, P. W., Guenther, D. R., Hayman, M. J., Van Speybroeck, V., … Haw, J. F. (2008). A Complete Catalytic Cycle for Supramolecular Methanol-to-Olefins Conversion by Linking Theory with Experiment. *Angewandte Chemie*, *120*(28), 5257–5260. doi:10.1002/ange.200705453

Meng, T., Mao, D., Guo, Q., & Lu, G. (2012). The effect of crystal sizes of HZSM-5 zeolites in ethanol conversion to propylene. *Catalysis Communications*, *21*(3), 52–57. doi:10.1016/j.catcom.2012.01.030

Menges, M., & Kraushaar-Czarnetzki, B. (2012). Kinetics of methanol to olefins over AlPO4-bound ZSM-5 extrudates in a two-stage unit with dimethyl ether pre-reactor. *Microporous and Mesoporous Materials*. doi:10.1016/j.micromeso.2012.07.012

Mitchell, S., Michels, N.-L., Kunze, K., & Pérez-Ramirez, J. (2012). Visualisation of hierarchically structured zeolite bodies from macro to nano length scales. *Nature chemistry*, *4*, 825–831. doi:10.1038/NCHEM.1403

Mitchell, S., Michels, N.-L., & Pérez-Ramírez, J. (2013). From powder to technical body: the undervalued science of catalyst scale up. *Chemical Society reviews*. doi:10.1039/c3cs60076a

Möller, K., & Böhringer, W. (1999). The use of a jet loop reactor to study the effect of crystal size and the co-feeding of olefins and water on the conversion of methanol over HZSM-5. *Microporous and …*, *29*, 127–144. doi:http://dx.doi.org/10.1016/S1387-1811(98)00326-6

Mores, D., Stavitski, E., Kox, M. H. F., Kornatowski, J., Olsbye, U., & Weckhuysen, B. M. (2008). Space- and time-resolved in-situ spectroscopy on the coke formation in molecular sieves: methanol-to-olefin conversion over H-ZSM-5 and H-SAPO-34. *Chemistry a European Journal*, *14*(36), 11320–7. doi:10.1002/chem.200801293

Ocampo, F., Cunha, J. a., de Lima Santos, M. R., Tessonnier, J. P., Pereira, M. M., & Louis, B. (2010). Synthesis of zeolite crystals with unusual morphology: Application in acid catalysis. *Applied Catalysis A: General*, *390*(1-2), 102–109. doi:10.1016/j.apcata.2010.09.037

583 Olsbye, U., Bjørgen, M., Svelle, S., Lillerud, K.-P., & Kolboe, S. (2005). Mechanistic insight
584 into the methanol-to-hydrocarbons reaction. *Catalysis Today*, *106*(1-4), 108–111.
585 doi:10.1016/j.cattod.2005.07.135

586 Olsbye, U., Svelle, S., Bjørgen, M., Beato, P., Janssens, T. V. W., Joensen, F., … Lillerud, K.
587 P. (2012). Conversion of methanol to hydrocarbons: how zeolite cavity and pore size
588 controls product selectivity. *Angewandte Chemie (International ed. in English)*, *51*(24),
589 5810–31. doi:10.1002/anie.201103657

590 Pangarkar, K., Schildhauer, T. J., van Ommen, J. R., Nijenhuis, J., Kapteijn, F., & Moulijn, J.
591 a. (2008). *Structured Packings for Multiphase Catalytic Reactors*. *Industrial &*
592 *Engineering Chemistry Research* (Vol. 47, pp. 3720–3751). doi:10.1021/ie800067r

593 Park, J. W., Kim, S. J., Seo, M., Kim, S. Y., Sugi, Y., & Seo, G. (2008). Product selectivity
594 and catalytic deactivation of MOR zeolites with different acid site densities in methanol-
595 to-olefin (MTO) reactions. *Applied Catalysis A: General*, *349*(1-2), 76–85.
596 doi:10.1016/j.apcata.2008.07.006

597 Park, J. W., Lee, J. Y., Kim, K. S., Hong, S. B., & Seo, G. (2008). Effects of cage shape and
598 size of 8-membered ring molecular sieves on their deactivation in methanol-to-olefin
599 (MTO) reactions. *Applied Catalysis A: General*, *339*(1), 36–44.
600 doi:10.1016/j.apcata.2008.01.005

601 Patcas, F. (2005). The methanol-to-olefins conversion over zeolite-coated ceramic foams.
602 *Journal of Catalysis*, *231*, 194–200. doi:10.1016/j.jcat.2005.01.016

603 Perdana, I., Creaser, D., Lindmark, J., & Hedlund, J. (2010). Influence of NOx adsorbed
604 species on component permeation through ZSM-5 membranes. *Journal of Membrane*
605 *Science*, *349*(1-2), 83–89. doi:10.1016/j.memsci.2009.11.030

606 Rahimi, N., & Karimzadeh, R. (2011). Catalytic cracking of hydrocarbons over modified
607 ZSM-5 zeolites to produce light olefins: A review. *Applied Catalysis A: General*, *398*(1-
608 2), 1–17. doi:10.1016/j.apcata.2011.03.009

609 Ren, T, Patel, M., & Blok, K. (2008). Steam cracking and methane to olefins: Energy use,
610 CO2 emissions and production costs. *Energy*, *33*, 817–833.
611 doi:10.1016/j.energy.2008.01.002

612 Ren, Tao, Daniëls, B., Patel, M. K., & Blok, K. (2009). Petrochemicals from oil, natural gas,
613 coal and biomass: Production costs in 2030–2050. *Resources, Conservation and*
614 *Recycling*, *53*(12), 653–663. doi:10.1016/j.resconrec.2009.04.016

615 Rownaghi, A. a., Rezaei, F., & Hedlund, J. (2011). Yield of gasoline-range hydrocarbons as a
616 function of uniform ZSM-5 crystal size. *Catalysis Communications*, *14*(1), 37–41.
617 doi:10.1016/j.catcom.2011.07.015

618 S. Lopez-Orozco, A. Inayat, A. Schwab, T. S. (2011). Zeolitic Materials with Hierarchical
619 Porous Structures. *Advanced Materials*, *23*, 2602–2615. doi:10.1002/adma.201100462

Sano, T., Kiyozumi, Y., & Shin, S. (1992). Synthesis of light olefins from methanol using ZSM-5 type zeolite catalysts. *Sekiyu Gakkai Shi*, *35*(6), 429–440. Retrieved from http://cat.inist.fr/?aModele=afficheN&cpsidt=4540858

Seijger, G., & Oudshoorn, O. (2000). In situ synthesis of binderless ZSM-5 zeolitic coatings on ceramic foam supports. *Microporous and Mesoporous Materials*, *39*, 195–204. doi:10.1016/S1387-1811(00)00196-7

Shan, Z., & Kooten, W. Van. (2000). Optimization of the preparation of binderless ZSM-5 coatings on stainless steel monoliths by in situ hydrothermal synthesis. *Microporous and …*, *34*, 81–91. doi:10.1016/S1387-1811(99)00161-4

Stöcker, M. (1999). Methanol-to-hydrocarbons: catalytic materials and their behavior. *Microporous and Mesoporous Materials*, *29*, 3–48. doi:10.1016/S1387-1811(98)00319-9

Stuecker, J. N., Miller, J. E., Ferrizz, R. E., Mudd, J. E., & Cesarano, J. (2004). Advanced Support Structures for Enhanced Catalytic Activity. *Industrial & Engineering Chemistry Research*, *43*(1), 51–55. doi:10.1021/ie030291v

Svelle, S, Ronning, P., Olsbye, U., & Kolboe, S. (2005). Kinetic studies of zeolite-catalyzed methylation reactions. Part 2. Co-reaction of [12C]propene or [12C]n-butene and [13C]methanol. *Journal of Catalysis*, *234*(2), 385–400. doi:10.1016/j.jcat.2005.06.028

Svelle, Stian, Rønning, P. O., & Kolboe, S. (2004). Kinetic studies of zeolite-catalyzed methylation reactions1. Coreaction of [12C]ethene and [13C]methanol. *Journal of Catalysis*, *224*(1), 115–123. doi:10.1016/j.jcat.2004.02.022

Tago, T., Iwakai, K., Morita, K., Tanaka, K., & Masuda, T. (2005). Control of acid-site location of ZSM-5 zeolite membrane and its application to the MTO reaction. *Catalysis Today*, *105*(3-4), 662–666. doi:10.1016/j.cattod.2005.06.009

Taheri Najafabadi, A., Fatemi, S., Sohrabi, M., & Salmasi, M. (2012). Kinetic modeling and optimization of the operating condition of MTO process on SAPO-34 catalyst. *Journal of Industrial and Engineering Chemistry*, *18*(1), 29–37. doi:10.1016/j.jiec.2011.11.088

Takahashi, A., Xia, W., Nakamura, I., Shimada, H., & Fujitani, T. (2012). Effects of added phosphorus on conversion of ethanol to propylene over ZSM-5 catalysts. *Applied Catalysis A: General*, *423-424*, 162–167. doi:10.1016/j.apcata.2012.02.029

TOTAL. (2008). *MTO / OCP : a strategic research project Testing innovative processes for making plastics* (p. 8).

Ulla, M., Mallada, R., Coronas, J., Gutierrez, L., Miro, E., & Santamaria, J. (2003). Synthesis and characterization of ZSM-5 coatings onto cordierite honeycomb supports. *Applied Catalysis A: …*, *253*, 257–269. doi:10.1016/S0926-860X(03)00498-8

Valle, B., Alonso, a., Atutxa, a., Gayubo, a. G., & Bilbao, J. (2005). Effect of nickel incorporation on the acidity and stability of HZSM-5 zeolite in the MTO process. *Catalysis Today*, *106*(1-4), 118–122. doi:10.1016/j.cattod.2005.07.132

Van Noyen, J., Wilde, A., Schroeven, M., Mullens, S., & Luyten, J. (2012). Ceramic Processing Techniques for Catalyst Design: Formation, Properties, and Catalytic Example of ZSM-5 on 3-Dimensional Fiber Deposition Support Structures. *International Journal of Applied Ceramic Technology*, *9*(5), 902–910. doi:10.1111/j.1744-7402.2012.02781.x

Wender, I. (1996). Reactions of synthesis gas. *Fuel Processing Technology*, *48*(I 996), 189–297. doi:10.1016/S0378-3820(96)01048-X

Westgård Erichsen, M., Svelle, S., & Olsbye, U. (2013). H-SAPO-5 as methanol-to-olefins (MTO) model catalyst: Towards elucidating the effects of acid strength. *Journal of Catalysis*, *298*, 94–101. doi:10.1016/j.jcat.2012.11.004

Wu, W., Guo, W., Xiao, W., & Luo, M. (2011). Dominant reaction pathway for methanol conversion to propene over high silicon H-ZSM-5. *Chemical Engineering Science*, *66*(20), 4722–4732. doi:10.1016/j.ces.2011.06.036

Wu, X., & Anthony, R. G. (2001). Effect of feed composition on methanol conversion to light olefins over SAPO-34. *Applied Catalysis A: General*, *218*(1-2), 241–250. doi:10.1016/S0926-860X(01)00651-2

Yang, H., Liu, Z., Gao, H., & Xie, Z. (2010). Synthesis and catalytic performances of hierarchical SAPO-34 monolith. *Journal of Materials Chemistry*, *20*(16), 3227. doi:10.1039/b924736j

Yang, Y., Sun, C., Du, J., Yue, Y., Hua, W., Zhang, C., … Xu, H. (2012). The synthesis of endurable B–Al–ZSM-5 catalysts with tunable acidity for methanol to propylene reaction. *Catalysis Communications*, *24*, 44–47. doi:10.1016/j.catcom.2012.03.013

Yao, J., Zeng, C., Zhang, L., & Xu, N. (2008). Vapor phase transport synthesis of SAPO-34 films on cordierite honeycombs. *Materials Chemistry and Physics*, *112*, 637–640. doi:10.1016/j.matchemphys.2008.06.019

Yilmaz, B., & Müller, U. (2009). Catalytic applications of zeolites in chemical industry. *Topics in Catalysis*, *52*, 888–895. doi:10.1007/s11244-009-9226-0

Zamaniyan, A., Mortazavi, Y., Khodadadi, A. A., & Manafi, H. (2010). Tube fitted bulk monolithic catalyst as novel structured reactor for gas–solid reactions. *Applied Catalysis A: General*, *385*(1-2), 214–223. doi:10.1016/j.apcata.2010.07.014

Zamaro, J. M., & Miró, E. E. (2010). Novel binderless zeolite-coated monolith reactor for environmental applications. *Chemical Engineering Journal*, *165*(2), 701–708. doi:10.1016/j.cej.2010.10.014

Zamaro, J., Ulla, M., & Miro, E. (2005). Zeolite washcoating onto cordierite honeycomb reactors for environmental applications. *Chemical Engineering Journal*, *106*(1), 25–33. doi:10.1016/j.cej.2004.11.003

Zampieri, A., Kullmann, S., Selvam, T., Bauer, J., Schwieger, W., Sieber, H., … Greil, P. (2006). Bioinspired Rattan-Derived SiSiC/Zeolite Monoliths: Preparation and

695 Characterisation. *Microporous and Mesoporous Materials*, *90*(1-3), 162–174.
696 doi:10.1016/j.micromeso.2005.10.049

697 Zhu, J., Fan, Y., & Xu, N. (2011). Modified dip-coating method for preparation of pinhole-
698 free ceramic membranes. *Journal of Membrane Science*, *367*(1-2), 14–20.
699 doi:10.1016/j.memsci.2010.10.024

700 Zhuang, Y., Gao, X., Zhu, Y., & Luo, Z. (2012). CFD modeling of methanol to olefins
701 process in a fixed-bed reactor. *Powder Technology*, *221*, 419–430.
702 doi:10.1016/j.powtec.2012.01.041

703