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The benefit of design of support architectures for zeolite coated structured catalysts for methanol-to-olefin conversion

**Reference:**

Lefevere Jasper, Gysen Marijn, Mullens Steven, Meynen Vera, van Noyen J.- The benefit of design of support architectures for zeolite coated structured catalysts for methanol-to-olefin conversion

Catalysis today - ISSN 0920-5861 - 216(2013), p. 18-23

Full text (Publishers DOI): <http://dx.doi.org/doi:10.1016/j.cattod.2013.05.020>

To cite this reference: <http://hdl.handle.net/10067/1105620151162165141>



32 technologies for ethylene and propylene. Nowadays, thermal cracking of naphtha is the  
33 main production process for these light olefins. Due to the increase in crude oil prices  
34 and a fast growth of the world propylene demand, new processes for olefin production  
35 using alternative feedstocks receive increasing attention. A high selectivity towards  
36 propylene is favourable in these new processes, as the market for propylene grows even  
37 faster than that for ethylene [1,2]. One alternative for the steam cracking process is the  
38 production of light olefins out of methanol (methanol-to-olefins, MTO). Methanol can  
39 be produced with proven and mature technologies such as steam reforming of natural  
40 gas or gasification of coal using syngas technology [3]. The MTO technology is a very  
41 promising way of converting alternative feedstock such as natural gas and coal to  
42 chemicals and fuels with methanol as an intermediate. The MTO technology has been  
43 proven successful with a first commercial plant start-up in China in 2010, and more  
44 being constructed [4,5].

45 Zeolites are, to the best of our knowledge, the only type of catalysts that are currently  
46 being used in industrial MTO processes. Two types of zeolite are effectively used: SAPO-  
47 34 by UOP/Ineos and Dalian Institute of Chemical Physics, and ZSM-5 used in the Lurgi  
48 process [5,6]. SAPO-34 is a silicoaluminophosphate with small 8 membered pores, and  
49 has been proven to have a good selectivity to light olefins. However, it shows fast  
50 deactivation due to coke formation [7]. On the other hand, the ZSM-5 catalyst, a  
51 medium-pore zeolite composed of intersecting straight ( $5.3 \times 5.6 \text{ \AA}$ ) and sinusoidal ( $5.1$   
52  $\times 5.5 \text{ \AA}$ ) 10-ring pores, generally has a much better stability [8]. ZSM-5 however shows  
53 inferior selectivity for ethylene and propylene as compared to SAPO-34 [4]. Due to its  
54 larger pores the selectivity towards heavier products such as butylene is higher for the  
55 ZSM-5 catalyst. This catalyst is generally shaped as microgranules or extruded pellets  
56 and used in a random packed bed. These packed beds have a number of disadvantages,  
57 including limited heat- and mass transfer, high pressure drop and unevenly distributed  
58 flows, leading to differences in contact time and loss of selectivity. In recent years, the  
59 interest for zeolite coated structured catalysts has been growing as they allow a low  
60 pressure drop in combination with high mass- and heat transfer and controlled

61 residence times. The zeolite coating can be prepared using different techniques such as  
62 wash coating [9], and hydrothermal coating [10–17] or a combination of both [18]. A  
63 broad spectrum of porous or non-porous support materials can be used, such as Al<sub>2</sub>O<sub>3</sub>  
64 [11], glass [12], stainless steel [10,13], alumina ceramic foam [14], cordierite honeycomb  
65 [15,16,19], or SiC [17,20,21].

66 The architecture of the support is of crucial importance for the mass- and heat transfer,  
67 pressure drop and contact time. By “robocasting” or 3 dimensional fiber deposition  
68 (3DFD) an optimal architecture can be manufactured, combining good mass transfer  
69 with low pressure drop [22–25]. This technique comprises a layer by layer build-up of a  
70 ceramic or metallic support structure. With the 3DFD technique an unprecedented  
71 freedom of design and degree of control over the architecture is possible, allowing  
72 optimization for different applications [26]. Rapid prototyping of ceramic and metallic  
73 supports allows an almost unlimited amount of unique architectures with an excellent  
74 reproducibility. By combination of modelling and testing, a fast and good choice of  
75 supports with adequate mechanical properties and low pressure drop can be achieved  
76 [25].

77 In this study, the influence of different architectures of the 3DFD support structures on  
78 the conversion of methanol to light olefins has been studied. A comparison has been  
79 made with cordierite honeycombs and a packed bed of pelletized ZSM-5 powder. The  
80 influence of the support architecture on the catalytic properties of the zeolite has been  
81 studied. First, the wash coating process of ZSM-5 on the structured stainless steel  
82 supports was optimized and characterised with regard to coating adhesion. Then, the  
83 coated structured catalysts have been evaluated for their catalytic performance in the  
84 methanol dehydration and MTO reaction. The effect of architecture of the support  
85 structure on the selectivity and activity of the reaction is demonstrated.

86

## 87 **2. Experimental**

88

### 89 *2.1 Preparation of the catalysts*

90 The stainless steel (316L) support structures were prepared using 3DFD technology, as  
91 described in literature [27,28]. 3DFD structures with 1-1 and 1-3 stacking were  
92 manufactured using a 0.9 mm nozzle and a programmed inter fibre distance of 1.1 mm.  
93 The 1-1 stacked 3DFD structure has straight channels in the direction of the flow (1.1 x  
94 1.1 mm) in combination with smaller radial channels (1.1 x 0.45 mm) in the two  
95 directions (Table 1). The 1-3 stacked 3DFD structure consists out of zigzag channels in  
96 the direction of the flow (1.1 x 1.1 mm) and smaller straight channels (1.1 x 0.45 mm) in  
97 the two radial directions. The fibers of the 1-1 structure show a tetragonal symmetry  
98 while the 1-3 stacked structure shows a face centered symmetry (See supplementary  
99 information) [29]. After synthesis, the stainless steel 3DFD samples were sintered at  
100 1300°C for 4 hours. The monoliths used in the comparison were commercially available  
101 cordierite honeycomb structures with 400 cells per square inch (cpsi) and a wall  
102 thickness of 6.5 mil (0.165 mm) (NGK Insulators). The honeycomb structures have  
103 straight channels with a size of 1 x 1 mm and no radial channels. The support structures  
104 were cut into cylinders with a diameter of 21 mm and a length of 25 mm. All supports  
105 were cleaned in acetone, ethanol and distilled water for 10 minutes under ultrasonic  
106 conditions and dried overnight at 100°C.

107 The coating slurry was prepared as follows: ZSM-5 (TZP302, Süd-chemie, Si/Al ratio 25,  
108  $d_{50}$  8.77  $\mu\text{m}$ ) powder was dispersed in distilled water and colloidal silica (LUDOX HS-40,  
109 Sigma-Aldrich) was added. The final composition of the wash coating slurry consisted of  
110 30wt% ZSM-5, 1wt% methylcellulose and 1wt% LUDOX HS-40.

111 The support structures were coated by a wash coating procedure. The structures were  
112 placed vertically and the coating slurry was perfused through the substrate using a  
113 peristaltic pump. After a contact time of 10 seconds at which the slurry remained  
114 immobile, the excess of slurry was discharged using an air flow. The coated structures  
115 were dried overnight at 100°C. Finally, the samples were calcined for 3 hours at 550°C  
116 with a heating rate of 60 °C/h in ambient atmosphere to remove all organic compounds  
117 from the coating.

118

119 *2.2 Characterization*

120 Rheology was used to determine the viscosity of the slurry as a function of the shear  
121 rate (kinexus rheometer, Malvern Instruments, Worcestershire, United Kingdom). Shear  
122 rates were varied between 0.01 and 1000 s<sup>-1</sup> at a temperature of 25°C.

123 Particle size distribution was measured using laser diffraction (Mastersizer X, Malvern  
124 Instruments, Worcestershire, United Kingdom) using a beam length of 10 mm.

125 The amount of zeolite deposited was calculated from the weight increase after  
126 calcination. The adhesion strength of the coating onto the stainless steel supports was  
127 evaluated by resistance to ultrasonic treatment. The dried samples were weighed  
128 before and after treatment in an ultrasonic bath during 1 minute. The weight loss of the  
129 coating gives an indication of the adhesion strength of the coating to the structured  
130 support [30,31].

131 The apparent specific surface area of the different catalysts was measured by N<sub>2</sub>  
132 sorption at -196°C using the BET method (Autosorb-1, Quantachrome, Germany). Prior  
133 to N<sub>2</sub> sorption measurements, the samples were outgassed for 16h at 200°C in order to  
134 remove all adsorbed water from the zeolite.

135 X-ray diffraction (XRD; X'pert PRO, Philips, Eindhoven, The Netherlands) was used to  
136 examine the phase and crystallinity of the coating using a Cu-K<sub>α</sub> X-ray source (λ=  
137 1.54056 Å).

138 The surface and cross-sections of the catalyst were observed using a cold field emission  
139 scanning electron microscope (FEG-SEM) type JSM6340F (JEOL, Tokyo, Japan) at an  
140 acceleration voltage of 5 keV. To avoid charging under the electron beam during SEM,  
141 all samples were coated with a thin Pt(80)/Pd(20) (surfaces) or Au (cross-sections) layer  
142 (~1.5 nm), using a Cressington 208 HR (UK) and a Balzers Union SCD 040 (Balzers,  
143 Liechtenstein) high resolution sputter-coater, respectively. The thickness of the coating  
144 deposited onto the fiber was observed.

145 NH<sub>3</sub>-Temperature Programmed Desorption (NH<sub>3</sub>-TPD) was performed on the pure  
146 zeolite powder and the coating to measure their acidity (Autosorb-iQ-Chemi,  
147 Quantachrome, Germany). Prior to TPD measurements, the samples were outgassed for

148 16h at 200°C under vacuum in order to remove all adsorbed water from the zeolite.  
149 After the pre-treatment the samples were saturated with ammonia at 100°C. The excess  
150 of ammonia was removed with a helium flow for 30 minutes. The temperature was  
151 raised from 100°C to 750°C at a rate of 10°C/min for the desorption of ammonia. The  
152 desorbed ammonia was detected using a thermal conductivity detector (TCD).

153

### 154 *2.3 Catalytic testing and reaction data analysis*

155 Catalytic testing was performed in a fixed bed reactor with an inner diameter of 25 mm  
156 and a length of 300 mm at atmospheric pressure and temperatures of 350°C. The  
157 catalyst structures with a length of 25 mm were packed in thin layer of quartz wool and  
158 placed in the middle of the reactor. The zeolite powder used for the comparison was  
159 pelletized and sieved (0.125-0.250 mm fraction). The pelletized particles were diluted  
160 with inert, sintered Al<sub>2</sub>O<sub>3</sub> pellets and placed in the same reactor volume as the  
161 structured catalysts. Table 1 gives an overview of the different catalysts tested.

162

163

164

165 Nitrogen gas was co-fed (300 ml/min) and used as diluent for methanol (Merck, ≥99.9  
166 %). The reaction was carried out at a weight hourly space velocity (WHSV) in the range  
167 of 4.56-36.46 h<sup>-1</sup>. The product distribution has been analyzed with a gas chromatograph  
168 using a dual thermal conductivity detector and flame ionization detector (450-GC,  
169 Bruker, Bremen, Germany). After achieving equilibrium at each flow rate an isothermal  
170 period of 1 hour was kept and 4 gas measurements were performed. After each run the  
171 catalyst samples were regenerated by burning of the coke at 550°C for 2 hours in a  
172 stream of air. In the data analysis all C<sub>5</sub>+ species are combined in one group as this is not  
173 the main focus of this research.

174 The conversion of methanol was calculated as:

$$X_{MeOH} = 1 - \frac{C_{MeOH,outlet}}{C_{MeOH,inlet}}$$

175

176 The selectivity and yield of the different components was defined as:

$$S_i = \frac{C_i}{\sum_n C_n} \quad y_i = S_i * X_{MeOH+DME}$$

177

178 with n representing all components in the product stream except methanol and DME.

179

### 180 **3. Results and discussion**

#### 181 *3.1 Preparation and characterization of the catalysts*

182 Initially, a coating slurry was used containing 30 wt% ZSM-5, 1 wt% methylcellulose and  
183 69% distilled water. After wash coating and calcination, the adhesion of this coating was  
184 evaluated. After 1 minute of ultrasonic treatment, 47 % of the coating was removed  
185 from the structure. A weight loss of maximum 5 wt% of the coating was targeted as this  
186 is required for catalytic applications [32]. Therefore, colloidal silica was added as a  
187 binder to the coating suspension which improved the adhesion to the support (Figure 1).  
188 A decrease of the weight loss was observed from 47 % loss without silica addition down  
189 to 5 % loss at 2 wt% silica. In addition to the better adhesion, the amount of zeolite  
190 deposited increases with higher colloidal silica concentrations, from 0.1 g/cm<sup>3</sup> with no  
191 silica to 0.18 g/cm<sup>3</sup> with 2 wt% silica. Rheology measurements show a shear-thinning  
192 effect for all coating suspensions with an increase of the viscosity for higher silica  
193 concentrations especially at low shear rates (Figure 2). This effect can explain the higher  
194 loadings deposited with increasing silica concentration [33]. It seems that the adhesion  
195 of the zeolite particles to each other and to the support is improved by the colloidal  
196 binder due to an increased contact surface between the large particles themselves and  
197 the particles and support. With increasing colloidal silica concentration the amount of  
198 particles in the suspension rises so more silica particles hold the zeolite particles  
199 together, leading to a coating with better adhesion. At 2 wt% silica the viscosity is so  
200 high that removal of the excess wash coat from the porous substrate and thus the  
201 uniformity of the coating becomes an issue, so in further testing 1 wt% silica is used.

202 Further improvement of the coating adhesion was made by milling the zeolite before  
203 the coating process [34]. The initial zeolite powder had a d<sub>50</sub> (50% of the particles

204 smaller than this size) of 8.77  $\mu\text{m}$  and  $d_{90}$  (90% of the particles smaller than this size) of  
205 14.1  $\mu\text{m}$ . By planetary ball milling (250 rpm using 3 mm zirconia beads), the  $d_{50}$  reduced  
206 to 3.40  $\mu\text{m}$  after 15 minutes of milling and 2.73  $\mu\text{m}$  after 30 minutes of milling. After 30  
207 minutes the  $d_{90}$  was reduced to 10.01  $\mu\text{m}$ . The particle size distribution showed a  
208 bimodal distribution with a first peak of particles smaller than 2  $\mu\text{m}$  and a second peak  
209 with particles between 2 and 10  $\mu\text{m}$ . XRD measurements show a slight decrease in  
210 crystal size by milling from 63.0 nm before milling to 53.2 nm after milling. Rheology  
211 measurements confirm that the larger amount of smaller particles in the coating slurry  
212 after milling results in higher viscosity at low shear rate (data not shown). Figure 3  
213 shows the beneficial effect of milling on the adhesion of the coating. The combination of  
214 the effect of milling and an addition of 1 wt% of silica leads to a further improvement of  
215 the coating adhesion (Figure 3). The amount of zeolite deposited before ultrasonic  
216 treatment increases by milling if no silica is present. At a concentration of 1 % of silica  
217 the loading does not increase by milling. It is supposed that smaller zeolite particles  
218 have a better anchoring at the rough surface of the support leading to a better  
219 adhesion. After these modifications, the weight loss during ultrasonic treatment (1  
220 minute) has been reduced to 4 %. At longer ultrasonic treatment (10 minutes) the  
221 weight loss of the coating only slightly increased up to 6 %. These structures with stable  
222 coating were used for catalytic testing (Figure 4). Furthermore, by repeated coating the  
223 loading of the structures could be increased from 0.1 to 0.4  $\text{g}/\text{cm}^3$ . XRD measurements  
224 confirm that the crystallinity of the ZSM-5 is preserved in the coating (See  
225 Supplementary Information). Moreover  $\text{N}_2$  sorption shows similar apparent surface  
226 areas for the pure zeolite as for the coated zeolite (pure zeolite 434  $\text{m}^2/\text{g}$  compared to  
227 428  $\text{m}^2/\text{g}$  of the coated layer).  $\text{NH}_3$ -TPD measurements of the pure zeolite and the  
228 coating confirm that all acid sites on the zeolite surface are preserved during the coating  
229 process and that no pore blocking occurs (See Supplementary Information). The  
230 distribution of strong and weak acid sites on the zeolite surface remains similar after the  
231 wash coating process (See Supplementary information) and is in line with literature  
232 values [31,35].

## 233 3.2 Catalytic testing

### 234 3.2.1 Methanol dehydration

235 At low temperatures (250°C) the dehydration of methanol to dimethylether (DME) is the  
236 main reaction. As this reaction is exothermic, structured catalysts can be very use-full  
237 for efficient removal of the heat of the reaction. This could be beneficial in applications  
238 where high yield of dimethylether is desired such as DME as transportation fuel. In table  
239 2 the results of the catalytic conversion of methanol at 250°C with a WHSV of 4.56 h<sup>-1</sup>  
240 are given. The reaction data show a high selectivity (over 99 %) towards DME at 250°C.  
241 All structured catalysts show similar behavior, reaching a conversion of 84.5 %, about  
242 20 % higher than for the packed bed. These results indicate a higher effectiveness of the  
243 catalyst in the coating. These structured types of catalyst show promising results for the  
244 methanol dehydration reaction. The stability of this high DME yield was not tested as  
245 this was not within the scope of this paper but could be of interest for future work.

246

247

### 248 3.2.2 Methanol-to-olefins

249 At higher temperatures the selectivity of the reaction shifts to heavier products such as  
250 olefins, alkanes and aromatics. The conversion of methanol was monitored at 350°C and  
251 different WHSVs between 4.56 and 36.48 h<sup>-1</sup> (Figure 5). In the results of this catalytic  
252 testing dimethylether is included in the reactant pool and not considered as a product.  
253 The results show that the conversion of the structured catalysts is higher than that of  
254 the packed bed at all tested WHSVs. At the lowest WHSV of 4.56 h<sup>-1</sup> the packed bed  
255 gives 84.60% conversion while the structured packing show full conversion of methanol.  
256 It was already suggested by Patcas [36] that the reason for the higher effectiveness of  
257 the coated structures over a packed bed is due to diffusional transport limitations. As  
258 the bulk phase of the packed bed pellets is larger and has a higher density than the  
259 coating, the effectiveness of the coating is higher because of internal diffusion limitation  
260 in the pellets of the packed bed. At higher WHSV the conversion of the packed bed  
261 progressively declines. The catalyst deposited onto the surface of a support is more

262 effective at converting methanol and DME. All structured catalysts reach 100%  
263 conversion at WHSVs from 4.56-9.12 h<sup>-1</sup>. The conversion of the ZSM-5 coated 3DFD 1-1  
264 catalyst starts to drop at a WHSV of 18.24 h<sup>-1</sup> while the conversion of the honeycomb  
265 and 3DFD 1-3 sample only start to decline at a WHSV of 27.35 h<sup>-1</sup>. Interestingly, at very  
266 high WHSV the conversion of the 3DFD 1-3 sample is higher than all other samples,  
267 which can probably be ascribed to better mass- and heat transfer properties of this  
268 structure [22,23,25].

269

270 The combined ethylene and propylene yield was studied at different WHSVs at 350°C  
271 (Figure 6). The results show that the 3DFD 1-3 sample achieves the highest light olefin  
272 yield of all tested samples at a WHSV of 27.35 h<sup>-1</sup> and 350°C. At the same conditions and  
273 comparable conversion the 1-3 3DFD achieves higher ethylene and propylene yield than  
274 the straight channel honeycomb. In the honeycomb catalyst the formation of heavier  
275 products is higher. It is proposed that the better mass transfer of the 1-3 3DFD structure  
276 leads faster evacuation of the light products and so better selectivity. The catalytic  
277 testing also suggests that at different reaction conditions there is a different optimal  
278 catalyst for this reaction. It is suggested that the different mass- and heat transfer  
279 properties of the catalytic structures lead to different optimal operating conditions.  
280 These results also suggest that the highest olefin yield is achieved at below 100%  
281 conversion. Indeed figure 7 shows that the ethylene/propylene selectivity increases with  
282 decreasing conversion. At an equal conversion (80%) of all catalysts, the 3DFD type  
283 samples achieve the highest ethylene and propylene selectivity. The honeycomb catalyst  
284 shows a higher selectivity towards butylene, C<sub>2</sub>-C<sub>4</sub> alkanes and larger C<sub>5</sub><sup>+</sup> products at  
285 WHSVs ranging from 4.56 h<sup>-1</sup> to 27.35 h<sup>-1</sup> than the 3DFD structured catalysts. The packed  
286 bed shows a higher tendency for the undesired formation of C<sub>2</sub>-C<sub>4</sub> alkanes at all WHSVs  
287 tested compared the structured catalysts (See supplementary information).

288

289

290

291 **4. Conclusions**

292 The use of rapid prototyping techniques such as three dimensional fiber deposition  
293 allows fast manufacturing of highly reproducible supports with different architectures.  
294 The optimized coating method enables the deposition of a homogenous catalytic layer  
295 of zeolite on the surface of the support. By addition of colloidal silica and milling of the  
296 zeolite, the deposited coatings show a good adhesion to the surface of the support, due  
297 to a better interaction with the support surface and interaction between the zeolite  
298 particles. A hierarchical porous catalyst is obtained after coating by the combination of  
299 the macroporous support with the microporous zeolite layer.

300 The ZSM-5 coated structures were benchmarked for the conversion of methanol to  
301 dimethylether and to olefins. The influence of the architecture on the catalytic  
302 performance of the zeolite was studied rather than the intrinsic properties of the zeolite  
303 catalyst. At low temperature the catalytic testing indicates that high selectivity towards  
304 DME can be achieved using a structured catalyst with straight channels. The contact  
305 time distribution is of key importance to achieve high DME selectivity. At 350°C the  
306 structured catalyst are effective in converting methanol to olefins even at high methanol  
307 feed rates. It was shown that a 3DFD support structure with 1-3 architecture, having  
308 tortuous channels, exhibits the highest yield of light olefins at high WHSV. The main  
309 reason for this is the better mass and heat transfer properties of this type of structured  
310 catalyst.

311 Further improvement of the catalyst structures can be made by optimization of the fiber  
312 thickness and spacing between the fibers of the 3DFD structure. This could lead to an  
313 even more effective catalytic layer. In future work the stability of these catalyst in a  
314 relation to the heat and mass transfer properties of different architecture structured  
315 catalyst will be considered.

316 By using innovative rapid prototyping techniques, combined with an optimized wash  
317 coating method, new structured catalysts have been manufactured. These novel  
318 catalysts have been compared with packed bed and a honeycomb type support for the  
319 conversion of methanol at different temperatures, and show excellent catalytic

320 properties. This work demonstrates that the optimal catalyst structure depends on the  
321 application and the reaction conditions used. Rapid prototyping allows fast synthesis of  
322 different types of structured catalysts in function of the application. These types of  
323 catalysts are very promising for the conversion alcohols to olefins.

324

### 325 **Acknowledgements**

326 The authors want to express their thanks to the VITO personnel for their continuous  
327 support, especially R. Kemps, M. Mertens, I. Thijs, W. Bouwen (Sustainable Materials  
328 Management Department, VITO). J. Lefevere thankfully acknowledges a PhD scholarship  
329 provided by VITO and the University of Antwerp. This work was done in the frame of a  
330 project of the fund for scientific research (FWO) in Belgium (G. 007113N).

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391 **Figure captions**

392 **Figure 1** Effect of SiO<sub>2</sub> concentration on the adhesion of the coating.

393 **Figure 2** Effect of silica addition on the rheology of the coating suspension.

394 **Figure 3** Effect of milling and combination of milling and silica addition on the adhesion.

395 **Figure 4** (a) 3DFD structure, (b) 1-1 (top) and 1-3 stacking (bottom) of 3DFD structure,  
396 (c) Cross section of fiber coated with the optimized coating method.

397 **Figure 5** Hydrocarbon reagents pool (methanol + DME) conversion as function of WHSV  
398 for different coated structures and packed bed at 350°C.

399 **Figure 6** Yield of ethylene and propylene as function of WHSV for different coated  
400 structures and packed bed at 350°C.

401 **Figure 7** Ethylene + propylene selectivity as function of conversion for different coated  
402 structures and packed bed at 350°C.

403

404 **Table caption**

405 **Table 1** Samples used in the catalytic testing.

406 **Table 2** Results of catalytic conversion of methanol at 250°C and a WHSV of 4.56 h<sup>-1</sup> for  
407 different catalytic structures and packed bed of catalyst.