Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information to

The importance of heat effects in the Methanol to Hydrocarbons reaction over ZSM-5: on the role of mesoporosity on catalyst performance

Irina Yarulina[a], Freek Kapteijn[a] and Jorge Gascon[a,*]

[a] Catalysis Engineering, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

Experimental Section

Catalytic Tests

The product mixture was analyzed online with an Interscience CompactGC equipped with a 15 m capillary RTX-1 (1% diphenyl-, 99% dimethylpolysiloxane) column and a flame ionization detector.
Conversion, selectivities and yields were calculated on a molar carbon basis. Thus, conversion was defined as the carbon-based fraction of light oxygenates (methanol and dimethyl ether) consumed during the reaction:

$$X = \frac{n_{C,MeOH_{in}} - n_{C,MeOH_{out}} - 2 \cdot n_{C,DME_{out}}}{n_{C,MeOH_{in}}} \cdot 100\% \qquad \textbf{(1)}$$

the selectivity towards produced hydrocarbons was calculated according to the carbon number of the product. I.e. for ethylene (2) and propylene (3):

$$S_{ethylene} = \frac{2 \cdot n_{C_2H_4}}{n_{C,MeOH_{in}} - n_{C,oxy_{out}}} \cdot 100\% \qquad \textbf{(2)}$$

$$S_{propylene} = \frac{3 \cdot n_{C_3H_6}}{n_{C,MeOH_{in}} - n_{C,oxy_{out}}} \cdot 100\% \qquad \textbf{(3)}$$

and the yield of a component *i* was defined from its selectivity and methanol conversion:

$$Y_i = \frac{S_i \cdot X}{100} \qquad \textbf{(4)}$$

Note that the selectivities and yields presented in the time-on-stream graphs (main text) are the instantaneous values. The bar graphs (Figures S2 and S3) represent the integral values over the whole experiment.

Tables

Table S1. Detailed characteristics of the catalyst bed in dilution experiments performed at $WHSV$ = 8 h^{-1}, $m_{catalyst}$ = 0.5 g, MeOH:N_2 = 1:1 and reactor ID 9 mm.

ZSM-5 :SiC (wt/wt)	ZSM-5 : SiC (vol / vol)	L_{bed} (cm)	$F(MeOH)$ (mmol min^{-1})
1:0	1:0	1.4	2.1
1:3	1:0.9	2.7	2.1
1:6	1:1.8	3.9	2.1

Table S2. Detailed characteristics of the catalyst bed and conditions in 3 TC experiments ($WHSV$ = 4 h^{-1}, MeOH:N_2 = 1:1, reactor ID 9 mm).

Catalyst	L_{bed} (cm)	m_{cat} (g)	m_{SiC} (g)	$F(MeOH)$ (mmol min^{-1})
ZSM-5	5	1.75	0	3.6
ZSM-5 + SiC	5	0.63	3.78	1.3
Meso-ZSM-5	5	1.44	0	3.0

Figures

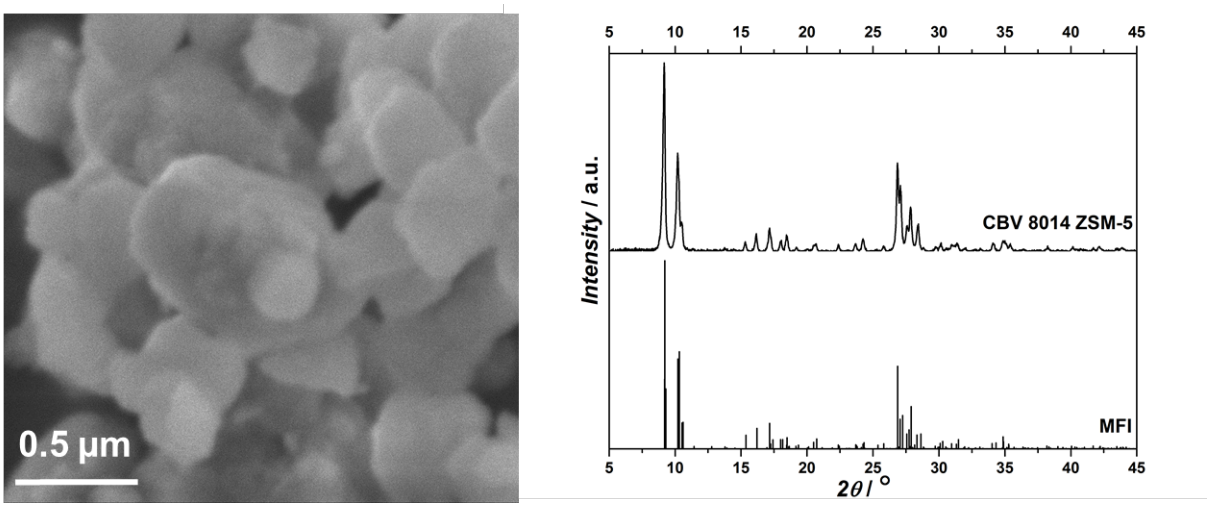

Figure S1. (*Left*) SEM picture of parent ZSM-5 material. (*Right*) XRD patterns of parent ZSM-5 and reference MFI structure.

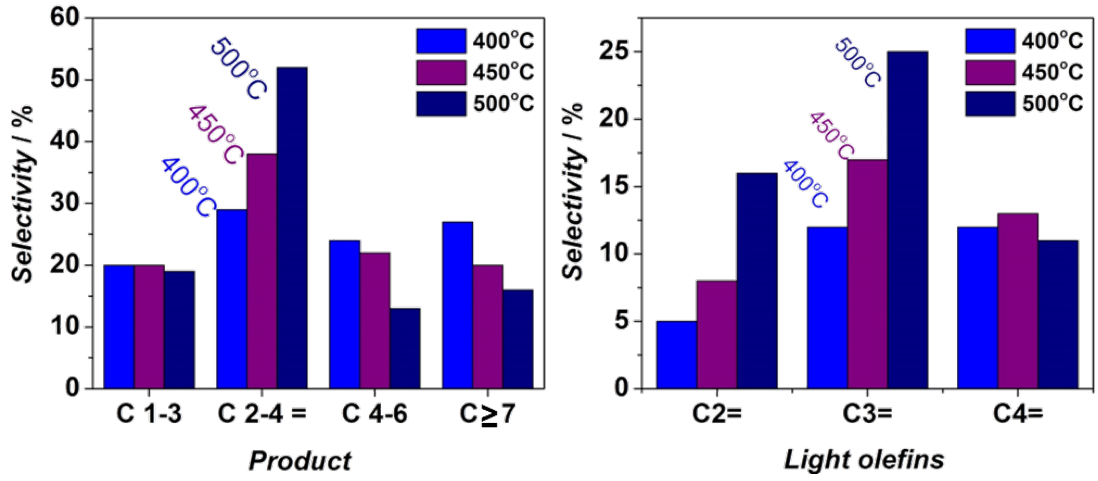

Figure S2. (*Left*) Product selectivities obtained over ZSM-5 tested at different temperatures. (*Right*) Light olefins selectivities obtained over ZSM-5 tested at different temperatures. Values are integral selectivities over the experiment duration.

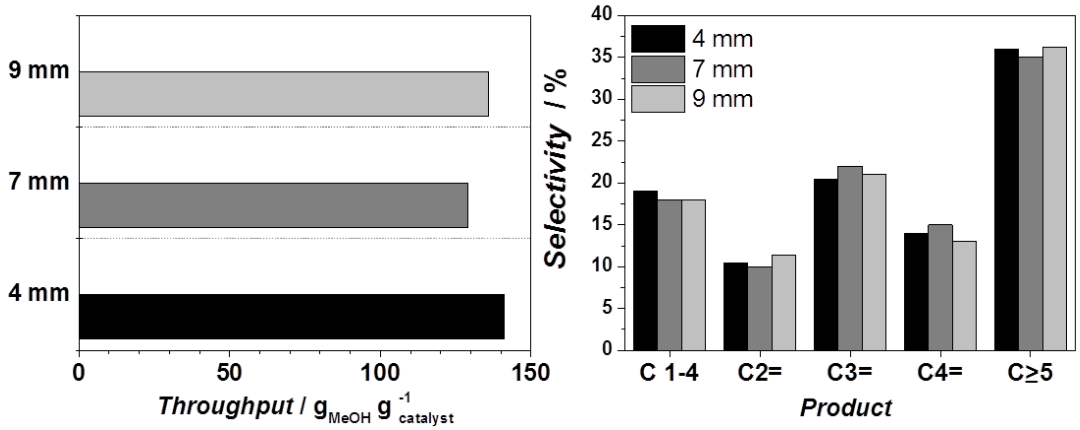

Figure S3. (*Left*) Catalyst lifetime (throughput) obtained over undiluted ZSM-5 tested in reactors with different i.d. (4, 7, 9 mm) at 470 °C. L_{bed} = 5 cm, *WHSV* = 4 h^{-1}, MeOH:N_2=1:1. (*Right*) Corresponding integral product selectivities.

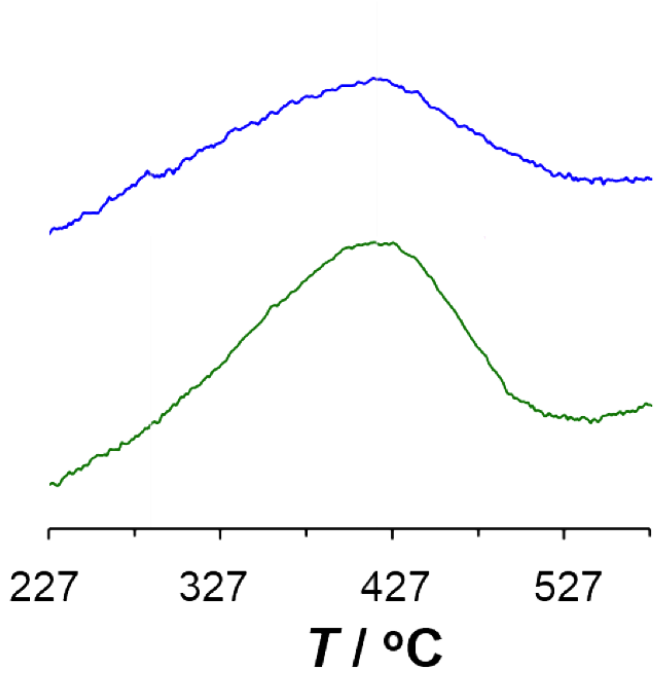

Figure S4. NH_3 TPD profiles of parent ZSM-5 (*green*) and desilicated and acid washed ZSM-5 (*blue*).

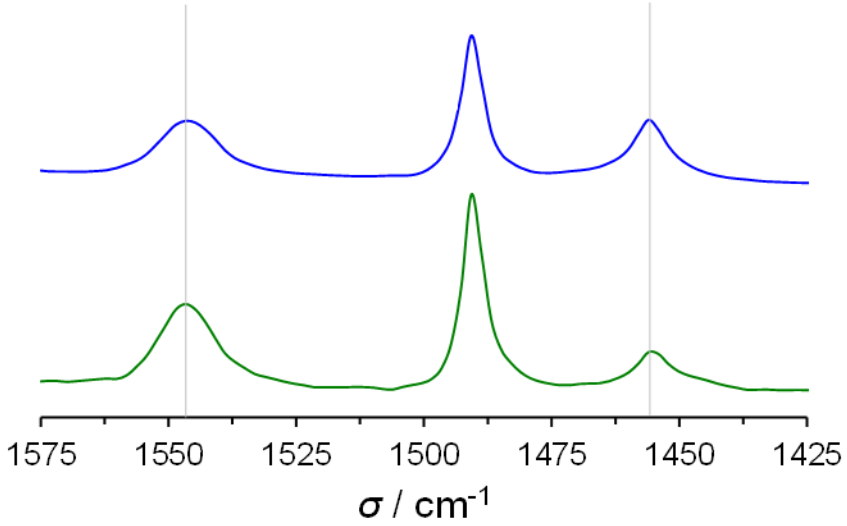

Figure S5. IR spectra of parent ZSM-5 (*green*) and desilicated and acid washed ZSM-5 (*blue*) upon pyridine adsorption.

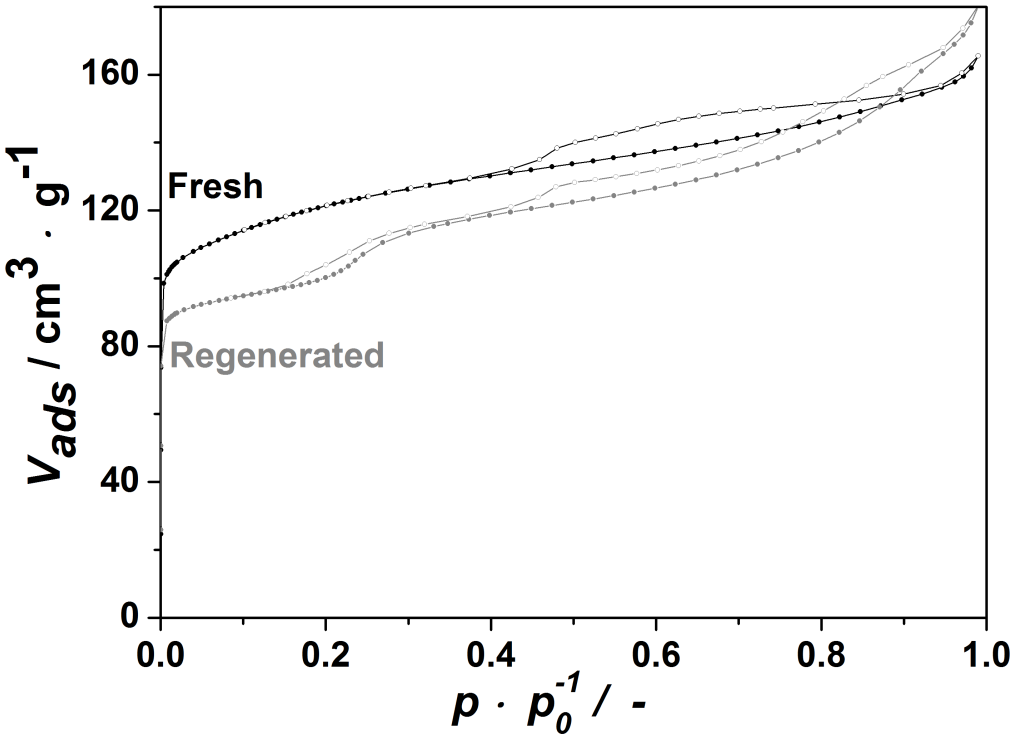

Figure S6. N_2 physisorption isotherms at 77 K of fresh ZSM-5 and regenerated sample after three catalytic runs.