

Prominent role of mesopore surface area and external acid sites for the synthesis of polyoxymethylene dimethyl ethers (OME) on a hierarchical H-ZSM-5 zeolite

Supplementary information

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1. Equilibrium constant calculation

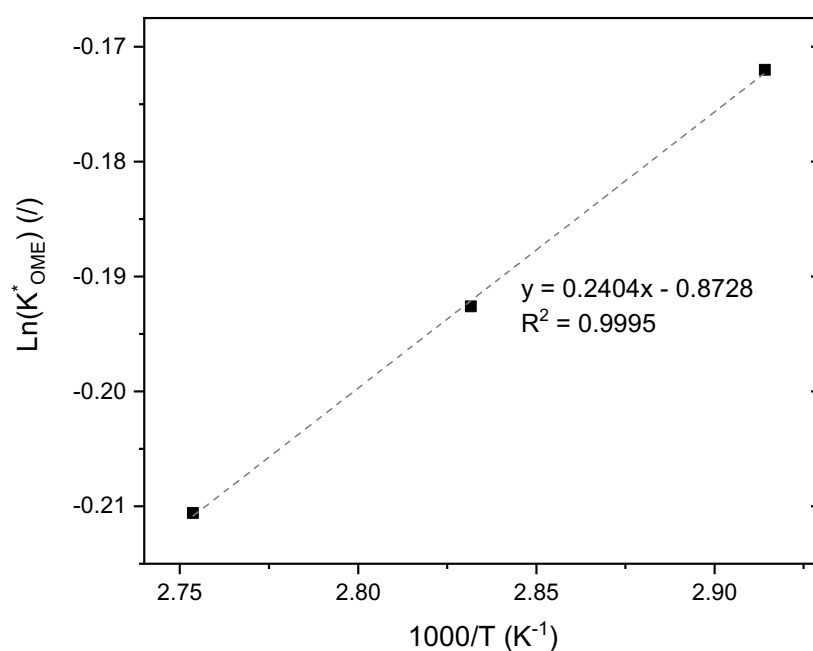


Figure S1. Van 't Hoff plot of the experimental values of K_{OME}^* . The model is indicated by a dashed line. The OME synthesis process was performed with an OME₁/TRI ratio of 3.3 and 0.5 wt % of catalyst. Reaction was stopped after 90, 180 and 360 min respectively for the synthesis at 90, 80 and 70 °C.

2. XRD pattern

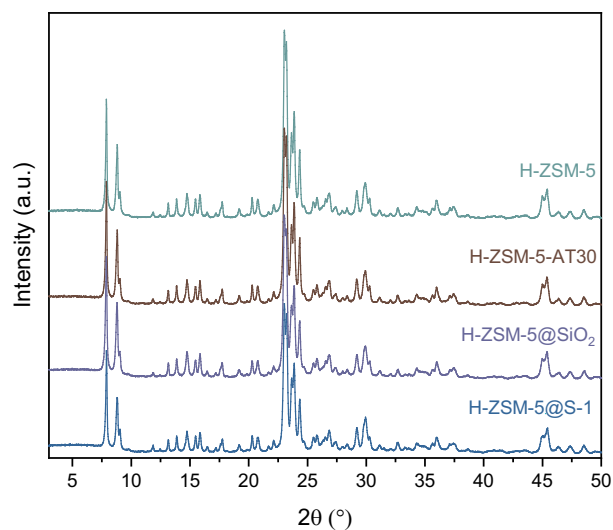


Figure S2. XRD diffractogram of H-ZSM-5 zeolites.

3. ²⁷Al NMR of mesoporous and untreated zeolites

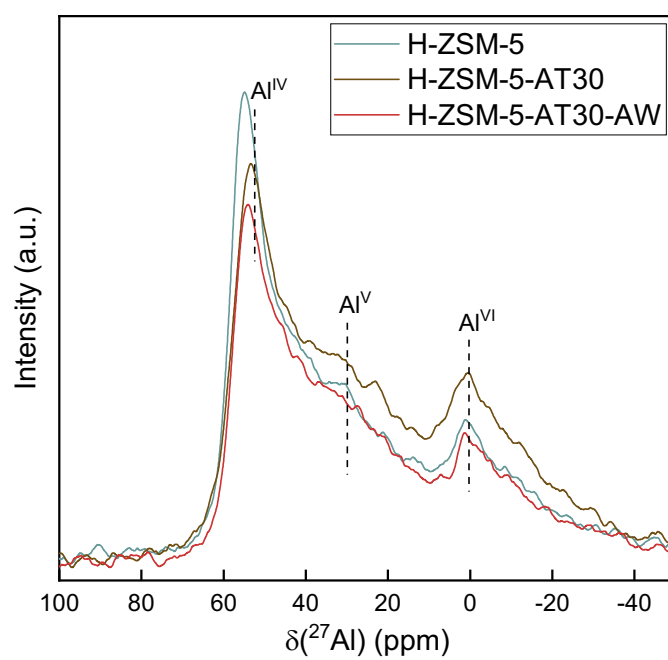


Figure S3. ²⁷Al NMR of untreated and mesoporous H-ZSM-5.

4. FTIR of the silanol region

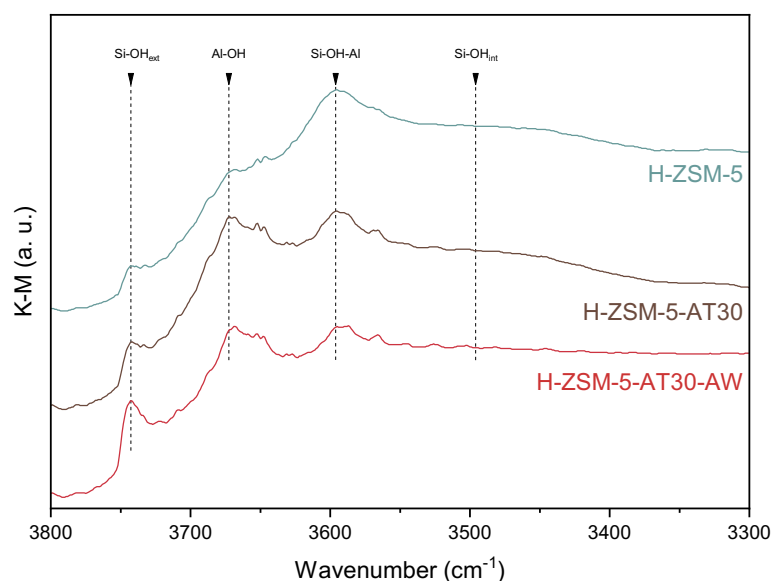


Figure S4. DRIFT spectra in the silanol region of untreated and mesoporous H-ZSM-5.

5. ICP-OES

Table S1. ICP results of untreated, mesoporous and passivated H-ZSM-5 zeolites.

Sample	Si (wt %)	Al (wt %)	Si/Al (mol/mol)
H-ZSM5	39	3.3	11.3
H-ZSM-5-AT30	39.6	3.5	10.9
H-ZSM-5-AT30-AW	39.5	3.12	12.7
H-ZSM-5@SiO ₂	39.2	2.6	14.3
H-ZSM-5@S-1	40.3	3.3	11.7

6. Textural properties

Table S2. Textural parameters of untreated, mesoporous and passivated H-ZSM-5 zeolites.

Sample	S _{BET} (m ² .g ⁻¹)	S _{micro} ^a (m ² .g ⁻¹)	S _{meso} ^b (m ² .g ⁻¹)	S _{ext} (m ² .g ⁻¹)	V _{micro} ^a (cm ³ .g ⁻¹)	V _{meso} ^b (cm ³ .g ⁻¹)
H-ZSM-5	379	294	54	85	0.124	0.052
H-ZSM-5-AT30	388	280	80	108	0.116	0.110
H-ZSM-5-AT30 _{0.4M}	389	273	94	116	0.118	0.168
H-ZSM-5-AT30 _{0.6M}	329	177	131	152	0.076	0.512
H-ZSM-5-AT30 _{0.8M}	376	173	179	203	0.075	0.545
H-ZSM-5-AT30 _{1.0M}	43	25	14	17	0.011	0.032
H-ZSM-5-AT30-AW	414	287	99	127	0.122	0.127
H-ZSM-5-AT30 _{0.4M} -AW	445	311	104	134	0.129	0.165
H-ZSM-5-AT30 _{0.5M} -AW	468	320	111	147	0.136	0.208
H-ZSM-5-AT30 _{0.6M} -AW	450	294	119	156	0.125	0.237
H-ZSM-5@SiO ₂	336	272	47	64	0.116	0.050
H-ZSM-5@S1	414	345	43	69	0.144	0.060

^a microporous surface and volume are determined by the t-plot method, ^b Mesoporous volume and surface are determined BJH method on the adsorption branch.

7. ^{29}Si NMR of untreated and passivated zeolites

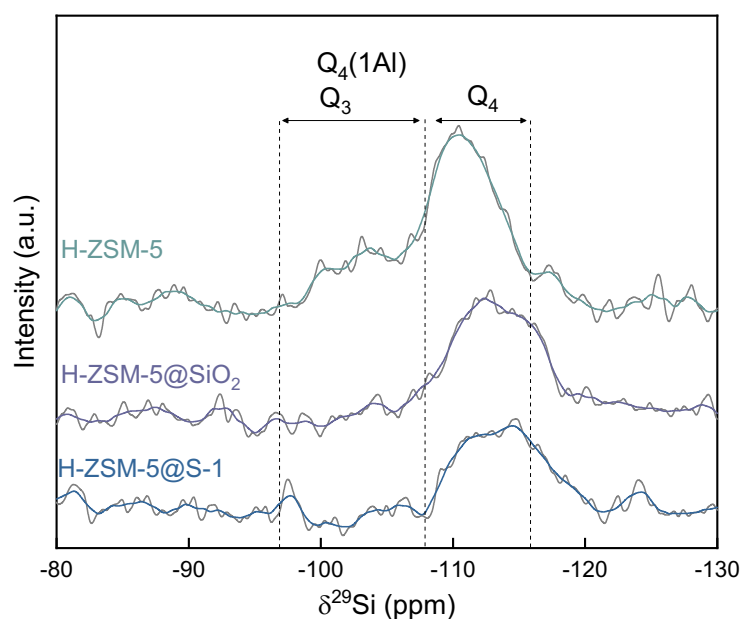


Figure S5. ^{29}Si ssNMR of untreated and passivated H-ZSM-5. A smoothing of the signal (adjacent-averaging, 20 points) is displayed for clarity.

8. NH_3 -TPD

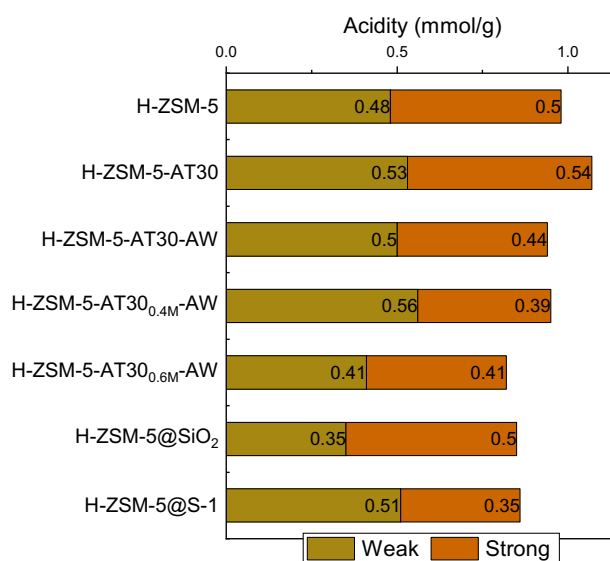


Figure S6. Weak and strong acidity concentrations resulting from the deconvolution of desorption peaks in NH_3 -TPD with the H-ZSM-5 zeolites.

Table S3. NH_3 -TPD of untreated, mesoporous and passivated H-ZSM-5 zeolites.

Sample	Total acidity (mmol/g)	Weak (100-200 °C) (mmol/g)	Strong (200-500 °C) (mmol/g)
H-ZSM-5	0.98	0.48	0.50
H-ZSM-5-AT30	1.07	0.53	0.54
H-ZSM-5-AT30-AW	0.94	0.50	0.44
H-ZSM-5-AT30_{0.4M}-AW	0.95	0.56	0.39
H-ZSM-5-AT30_{0.6M}-AW	0.82	0.41	0.41
H-ZSM-5@SiO₂	0.86	0.35	0.50
H-ZSM-5@S-1	0.86	0.51	0.35

9. DTBPy-TPD

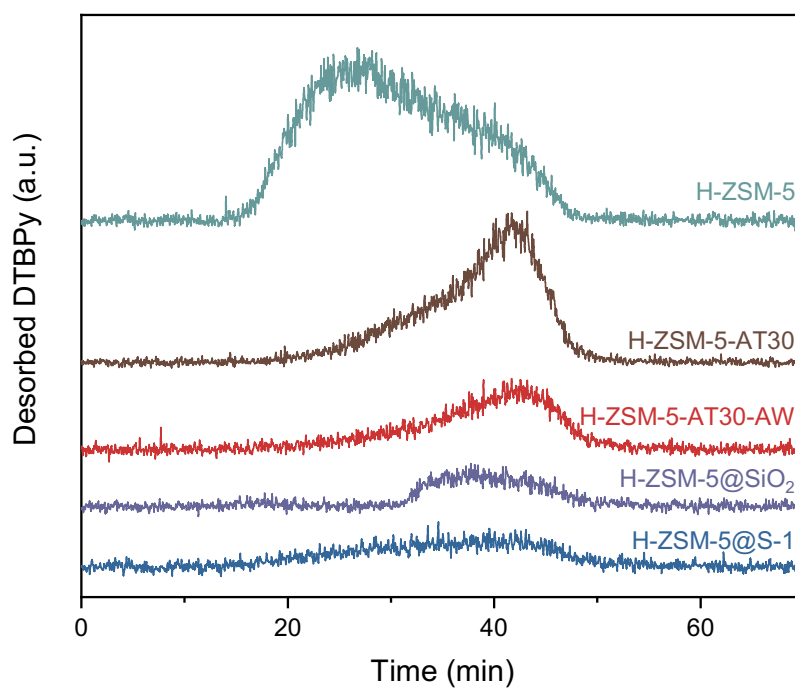


Figure S7. DTBPy-TPD for untreated, mesoporous and passivated zeolites.

10. MF production for the untreated, mesoporous and passivated H-ZSM-5 zeolites

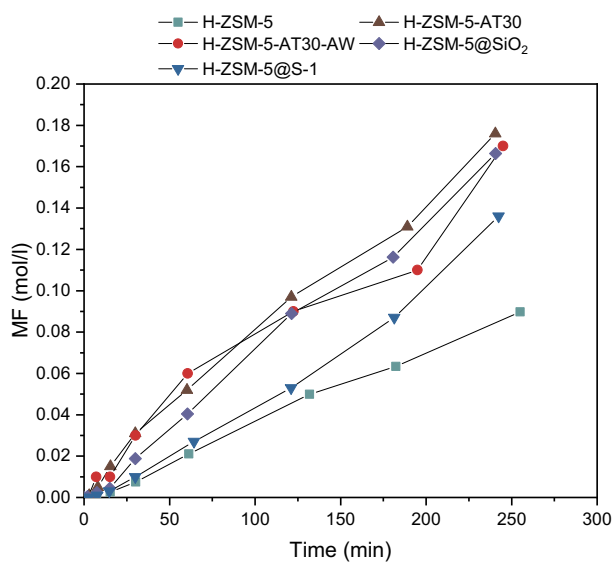


Figure S8. Production of methyl formate (MF) versus time in the batch reactor (OME₁/TRI: 3.3; 0.5 wt % catalyst; 70 °C) obtained with untreated, mesoporous and passivated H-ZSM-5 zeolites.

11. Performance of the alkaline-treated and acid-washed samples

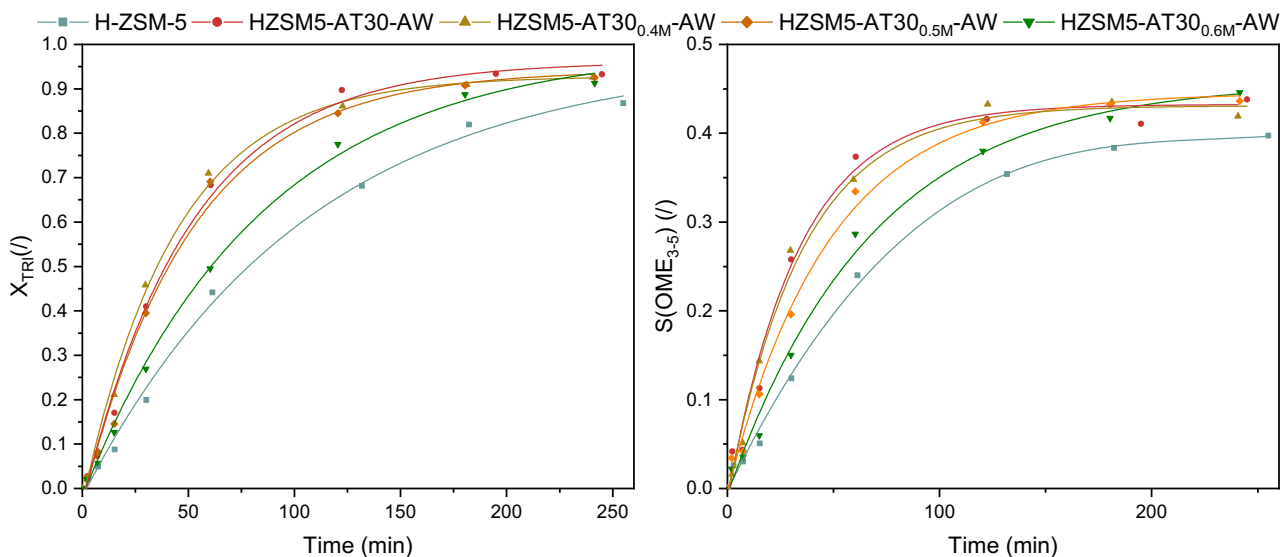


Figure S9. Performance comparison of untreated, mesoporous and passivated H-ZSM-5 zeolites with (a) TRI conversion and (b) $S(OME_{3-5})$ (OME_1/TRI : 3.3; 0.5 wt % catalyst; 70 °C).

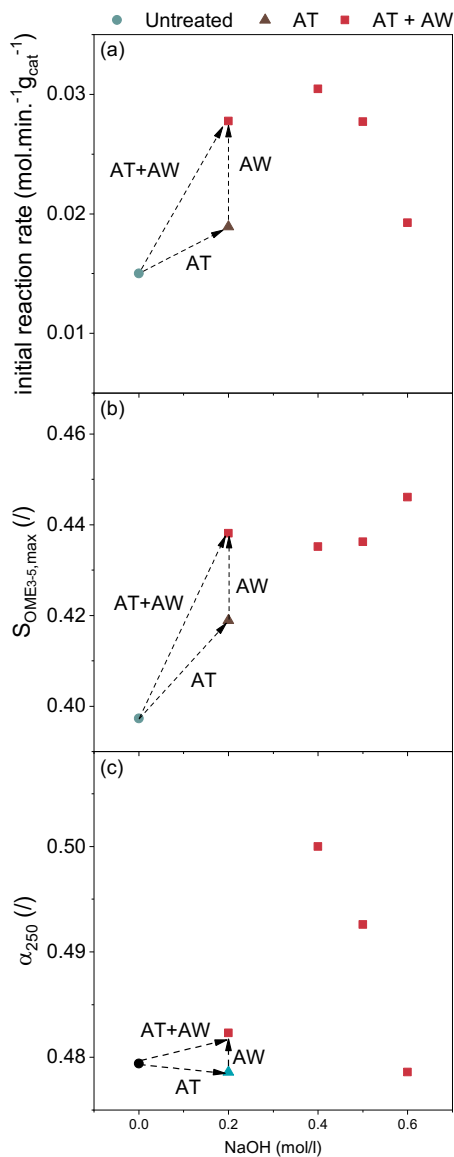


Figure S10. Influence of pre-treatment of H-ZSM-5 on the catalytic performance during OME synthesis (OME_1/TRI : 3.3; 0.5 wt % catalyst; 70 °C). (a) initial reaction rate, (b) maximum selectivity $S(OME_{3-5}, \text{max})$ reached during the run and (c) growth probability after 250 min.

12. Kinetic study results and model outputs

Table S4. Results of the kinetic model for the kinetic study on the various catalysts.

Number	Catalyst	Temperature (°C)	RMSE (/)	$k_{\text{OME},f}$ (L.mol ⁻¹ .min ⁻¹)
K1	H-ZSM-5	70	0.60	0.0304
K2	H-ZSM-5	80	0.65	0.110
K3	H-ZSM-5	90	0.64	0.292
K4	H-ZSM-5@S-1	70	0.57	0.00695
K5	H-ZSM-5@S-1	80	0.58	0.0148
K6	H-ZSM-5@S-1	90	0.62	0.0318
K7	H-ZSM-5-AT30 _{0.4M} -AW	70	0.65	0.0659
K8	H-ZSM-5-AT30 _{0.4M} -AW	80	0.61	0.142
K9	H-ZSM-5-AT30 _{0.4M} -AW	90	0.51	0.424

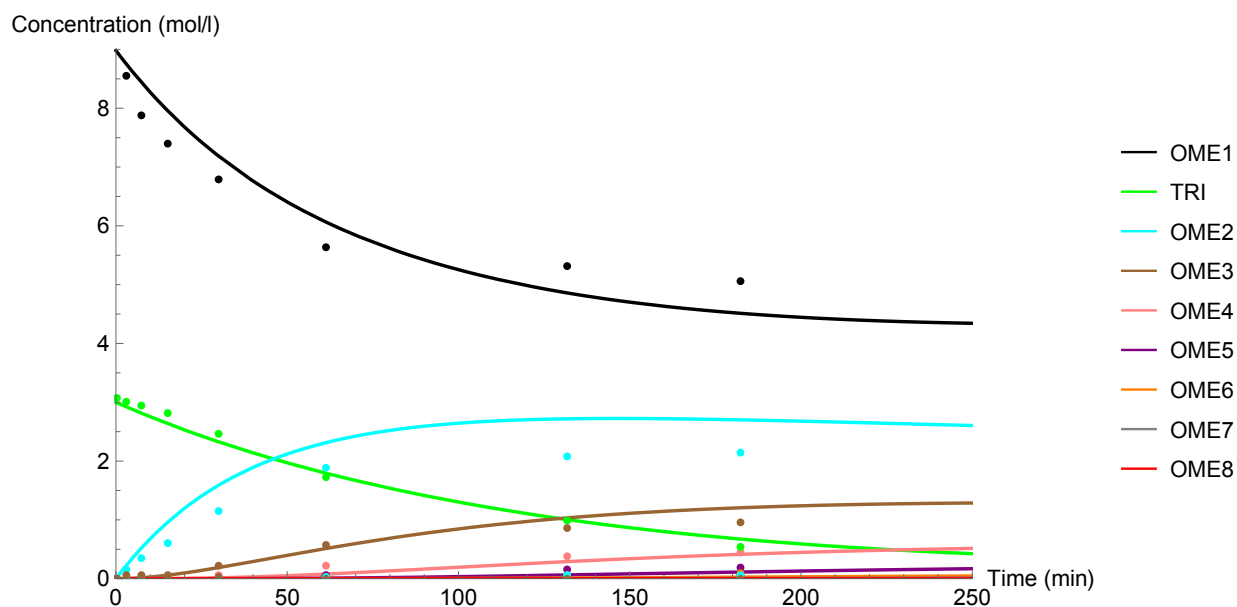


Figure S11. Concentration of the various components versus time for experiment K1 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5; 70 °C). The model output is given by the solid lines.

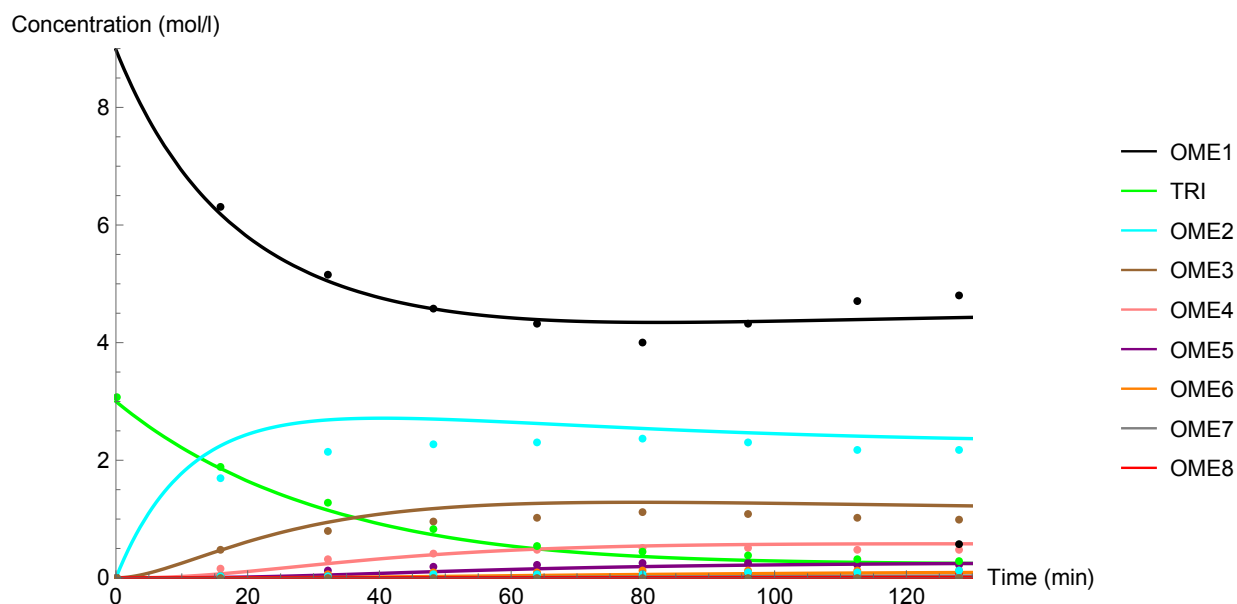


Figure S12. Concentration of the various components versus time for experiment K2 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5; 80 °C). The model output is given by the solid lines.

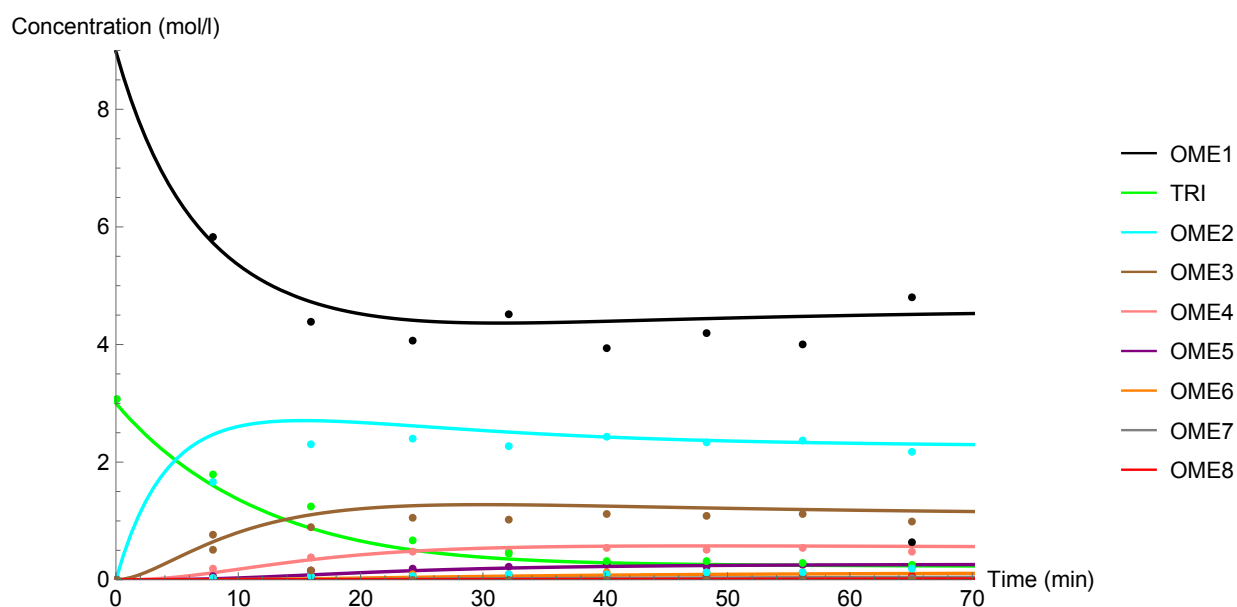


Figure S13. Concentration of the various components versus time for experiment K3 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5; 90 °C). The model output is given by the solid lines.

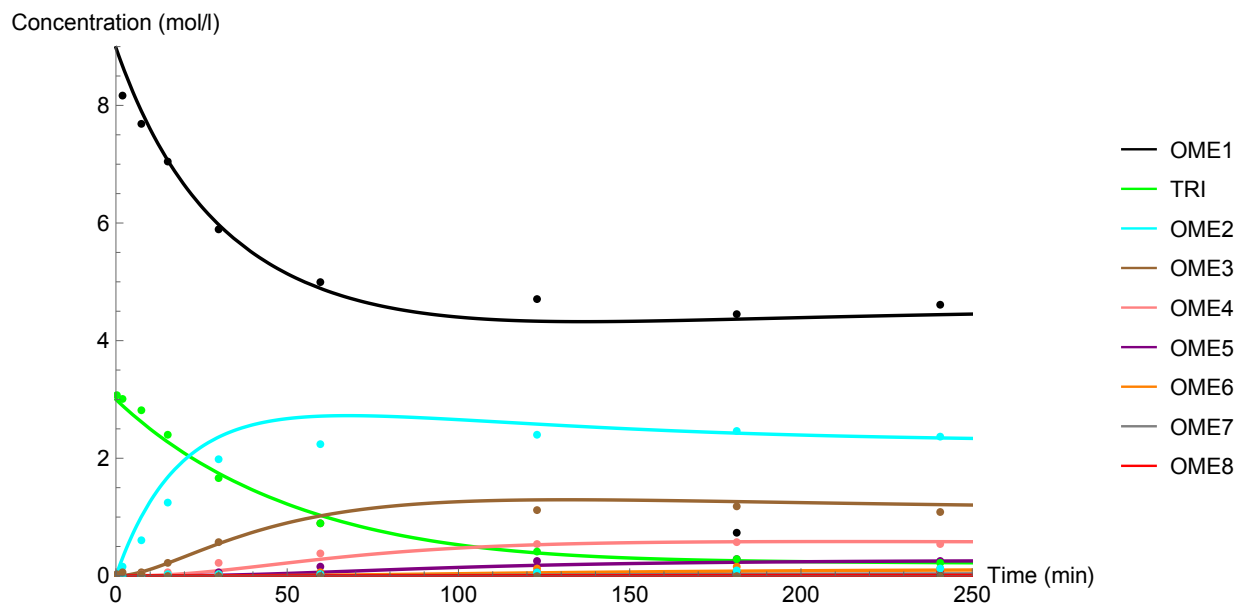


Figure S14. Concentration of the various components versus time for experiment K4 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5-AT30_{0.4M}-AW; 70 °C). The model output is given by the solid lines.

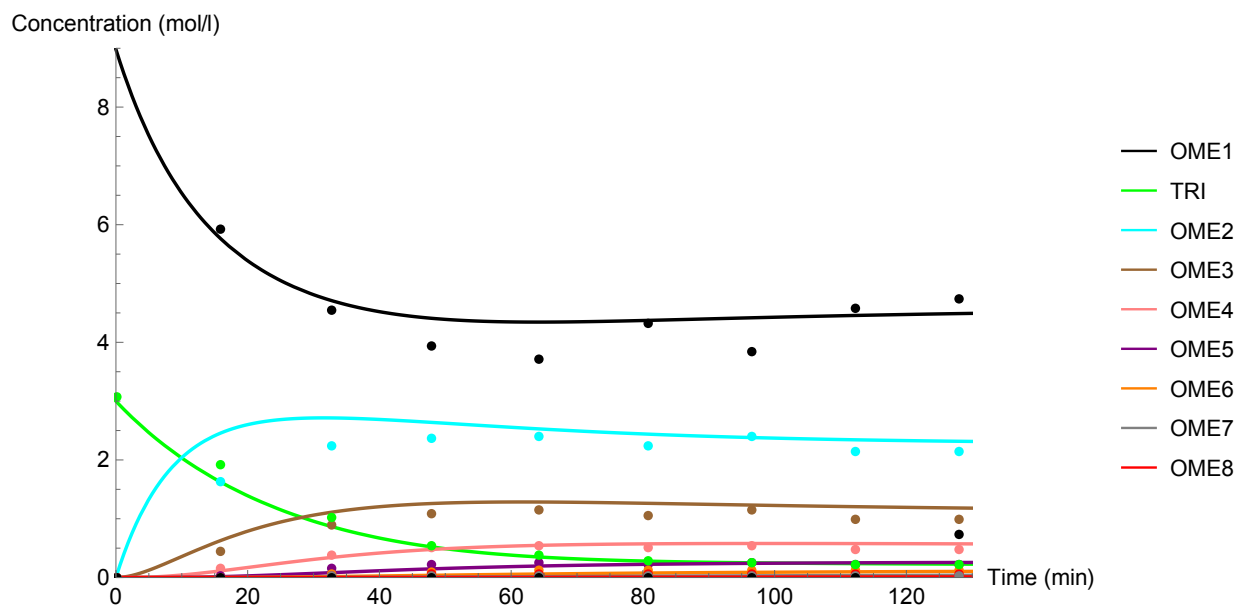


Figure S15. Concentration of the various components versus time for experiment K5 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5-AT30_{0.4M}-AW; 80 °C). The model output is given by the solid lines.

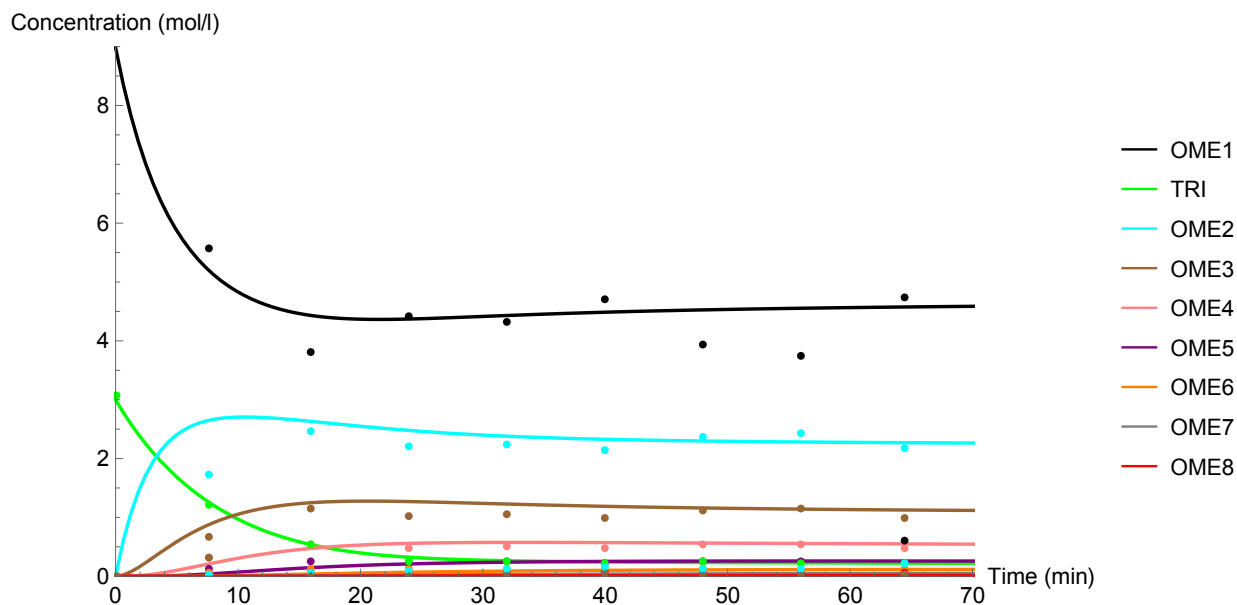


Figure S16. Concentration of the various components versus time for experiment K6 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5-AT30_{0.4M}-AW; 90 °C). The model output is given by the solid lines.

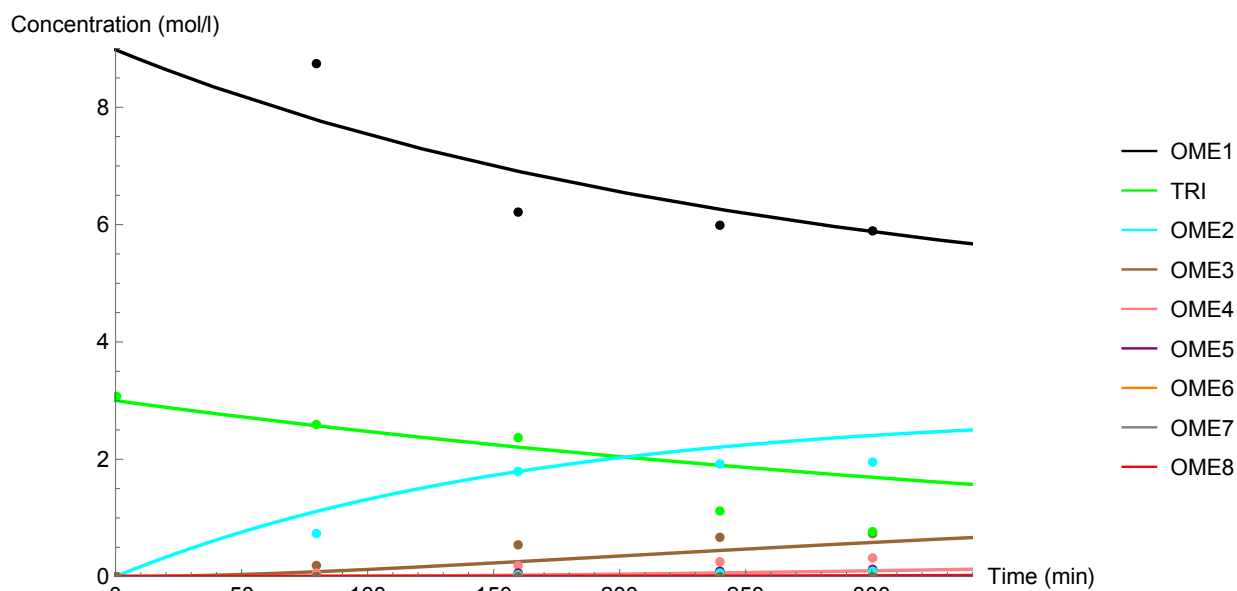


Figure S17. Concentration of the various components versus time for experiment K7 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5@S-1; 70 °C). The model output is given by the solid lines.

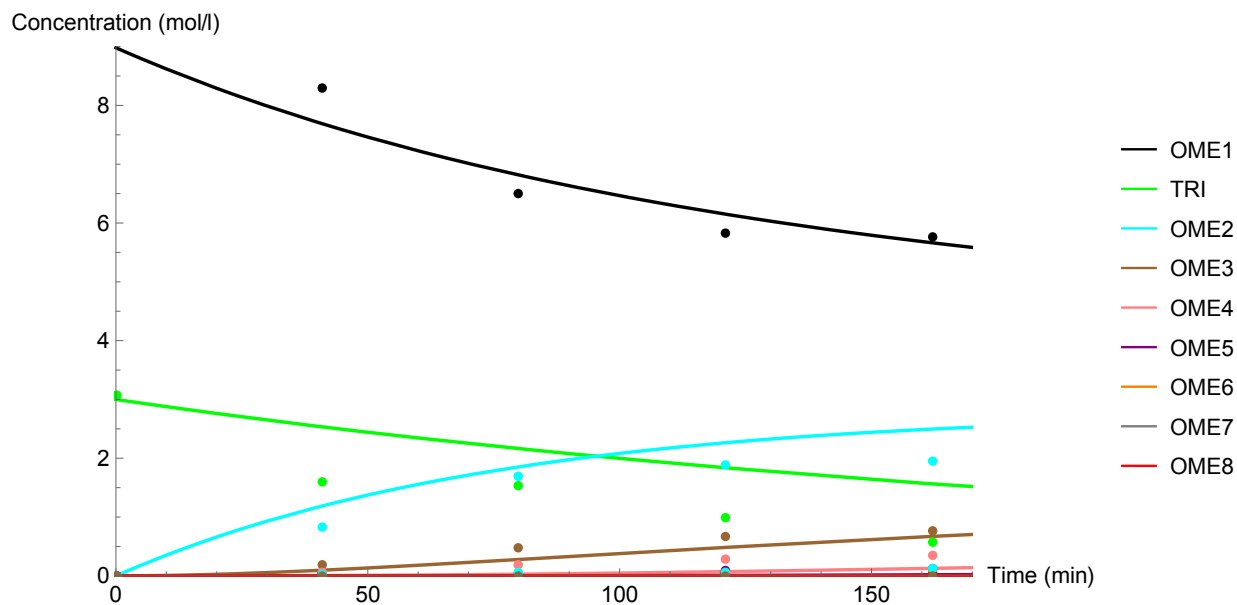


Figure S18. Concentration of the various components versus time for experiment K8 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5@S-1; 80 °C). The model output is given by the solid lines.

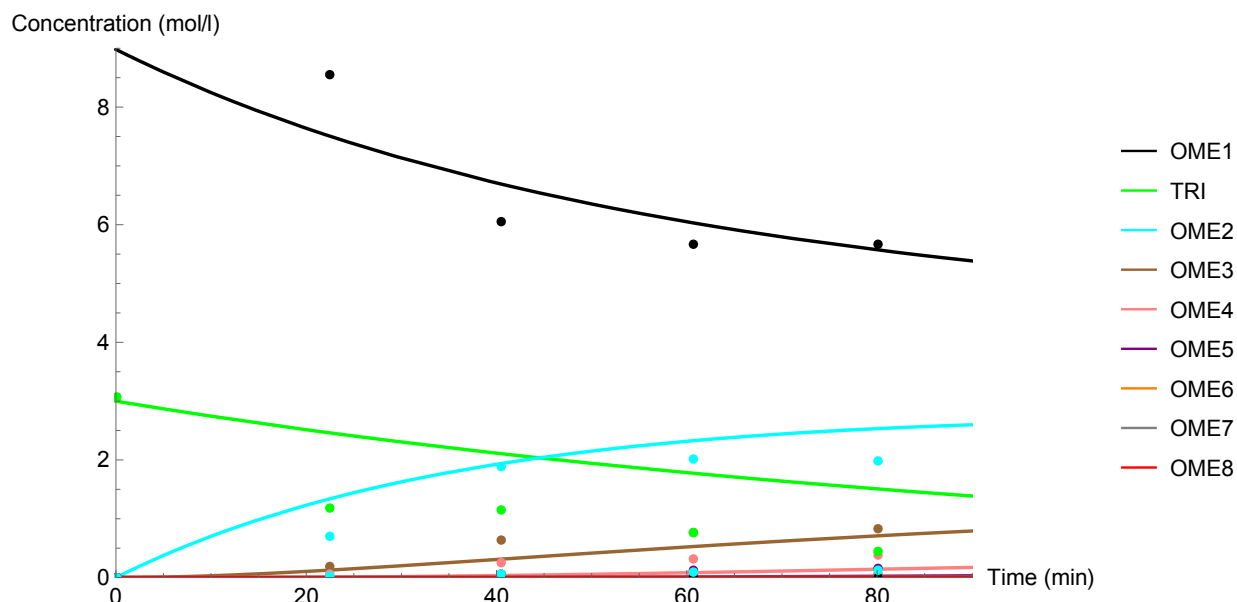


Figure S19. Concentration of the various components versus time for experiment K9 (OME₁/TRI: 3.3; 0.5 wt % H-ZSM-5@S-1; 90 °C). The model output is given by the solid lines.