SUPPORTING INFORMATION FOR

New insights in catalyst deactivation and product distribution of zeolites in the Methanol-To-Hydrocarbons (MTH) reaction with methanol and dimethyl ether feeds

Juan S. Martinez-Espin[1,2], Magnus Mortén[1], Ton V. W. Janssens[2], Stian Svelle[1], Pablo Beato[,2], Unni Olsbye[*,1]*

[1] Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

[2] Haldor Topsøe A/S, Haldor Topsøes Allé 1, DK-2800 Kgs. Lyngby, Denmark

*Corresponding authors: unni.olsbye@kjemi.uio.no, pabb@topsoe.dk

S1. Additional MTH stability tests with MeOH and DME/Water feeds

Additional MTH stability tests were run over H-ZSM-5 with MeOH and DME/W feeds at 350 °C to corroborate that the experimental carbon conversion capacities determined depended solely on the selected feed, and were independent of the contact time applied, as shown in previous works from the group with MeOH feed [1, 2]. **Figure S1** shows the results, where different contact times applied led to similar conversion capacities.

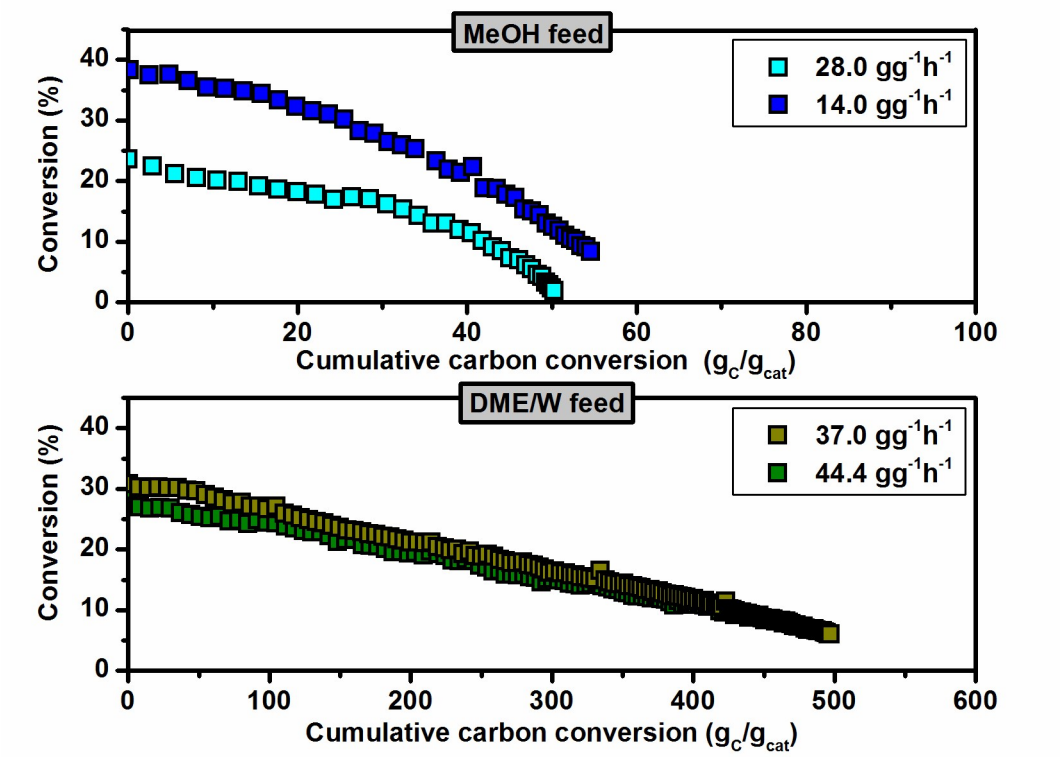

Figure S1. Cumulative carbon conversion capacity plots as g_{carbon} converted per $g_{catalyst}$ into hydrocarbons over H-ZSM-5 at 350°C with 60 mbar of MeOH (14.0 $gMeOHg_{catalyst}^{-1}h^{-1}$), 120 mbar MeOH (28.0 $gMeOHg_{catalyst}^{-1}h^{-1}$), 60:60 mbar DME/W (37.0 $gDMEg_{catalyst}^{-1}h^{-1}$) and 60:60 mbar DME/W (44.4 $gDMEg_{catalyst}^{-1}h^{-1}$).

S2. MTH activity over H-SAPO-5 and H-SSZ-24 at 350°C

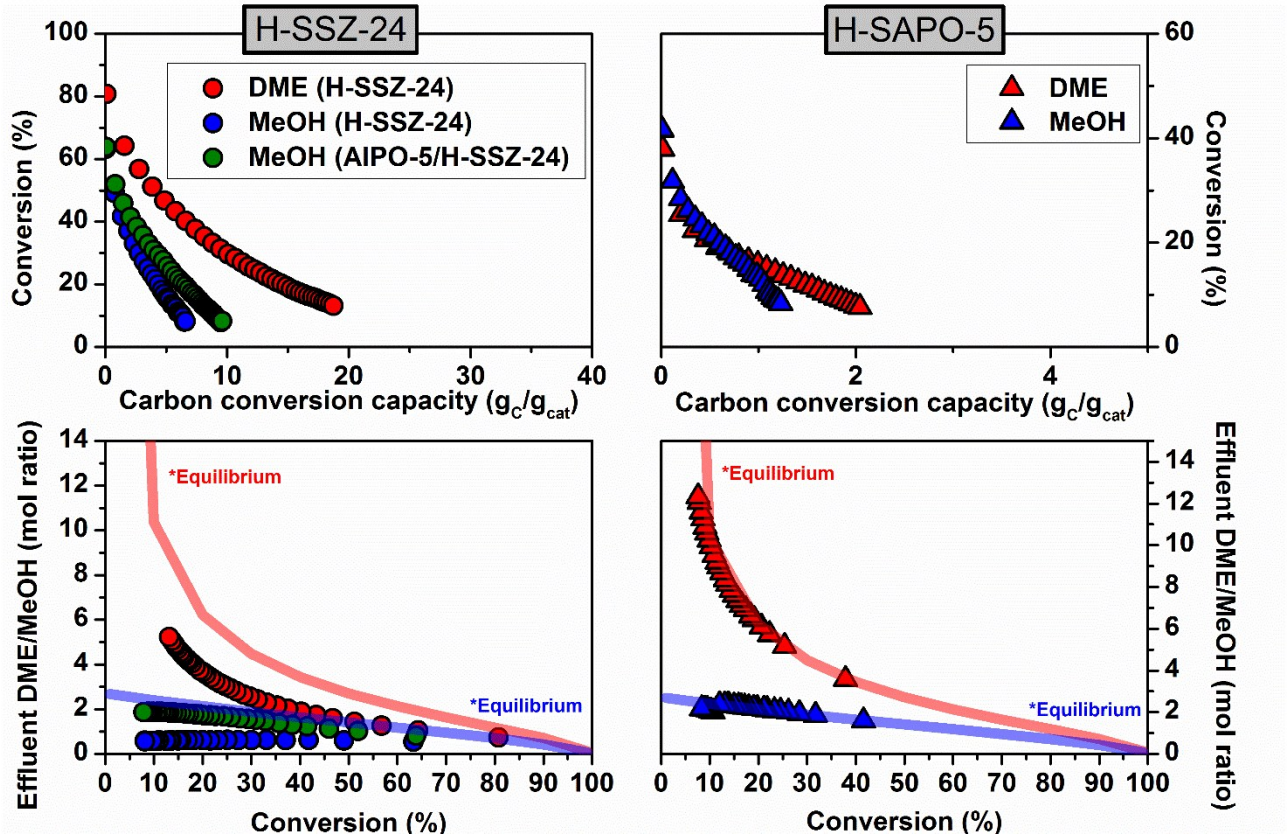

Figure S2. Cumulative carbon conversion capacity (top) and effluent DME/MeOH molar ratio as a function of conversion (bottom) during MTH reaction over H-SSZ-24 and H-SAPO-5 at 350 °C with DME and MeOH feeds.

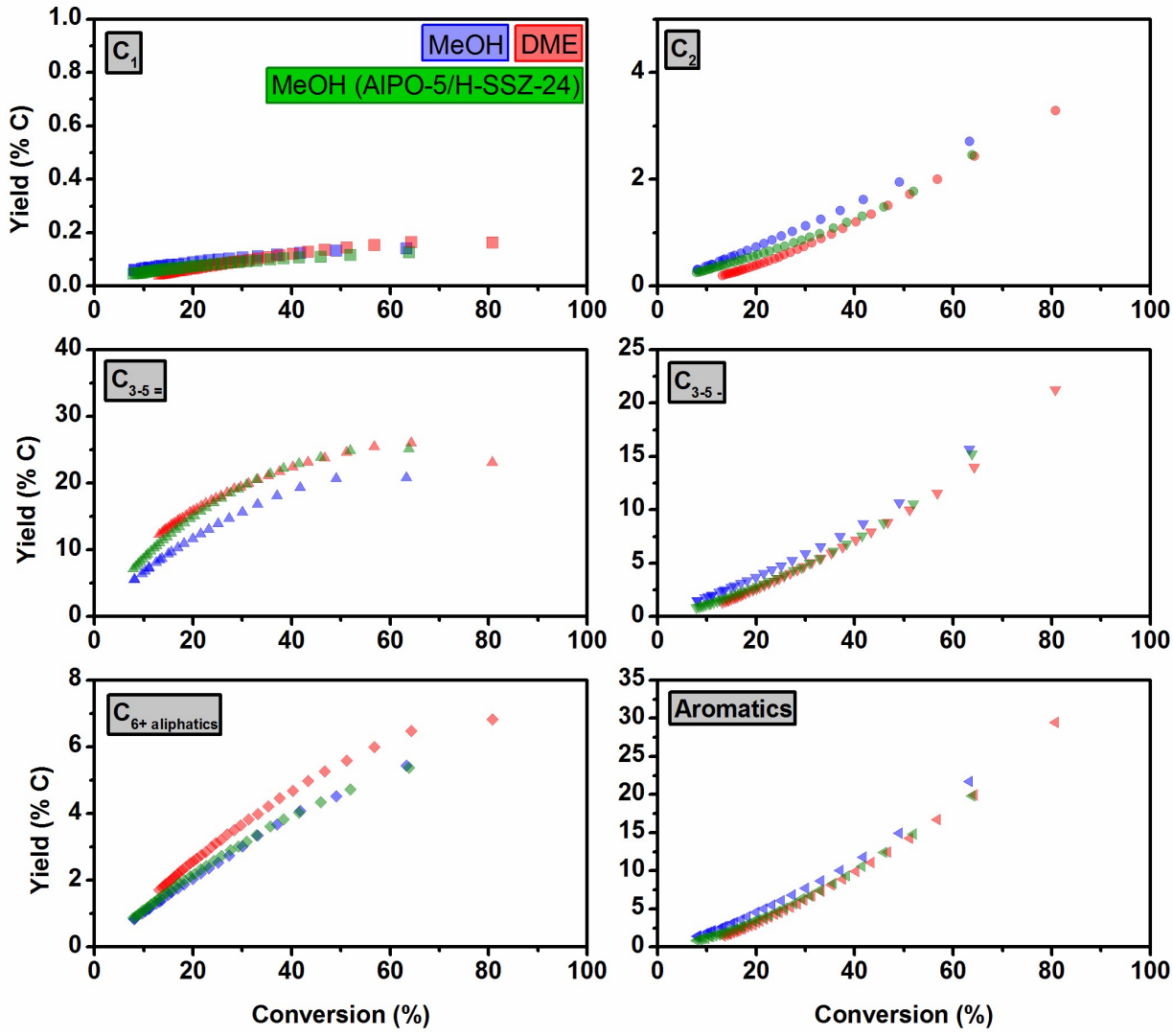

Figure S3. Yields of hydrocarbons fractions versus conversion during MTH over H-SSZ-24/H-SSZ-24+AlPO-5 at 350 °C by feeding DME (red) and MeOH (blue and green).

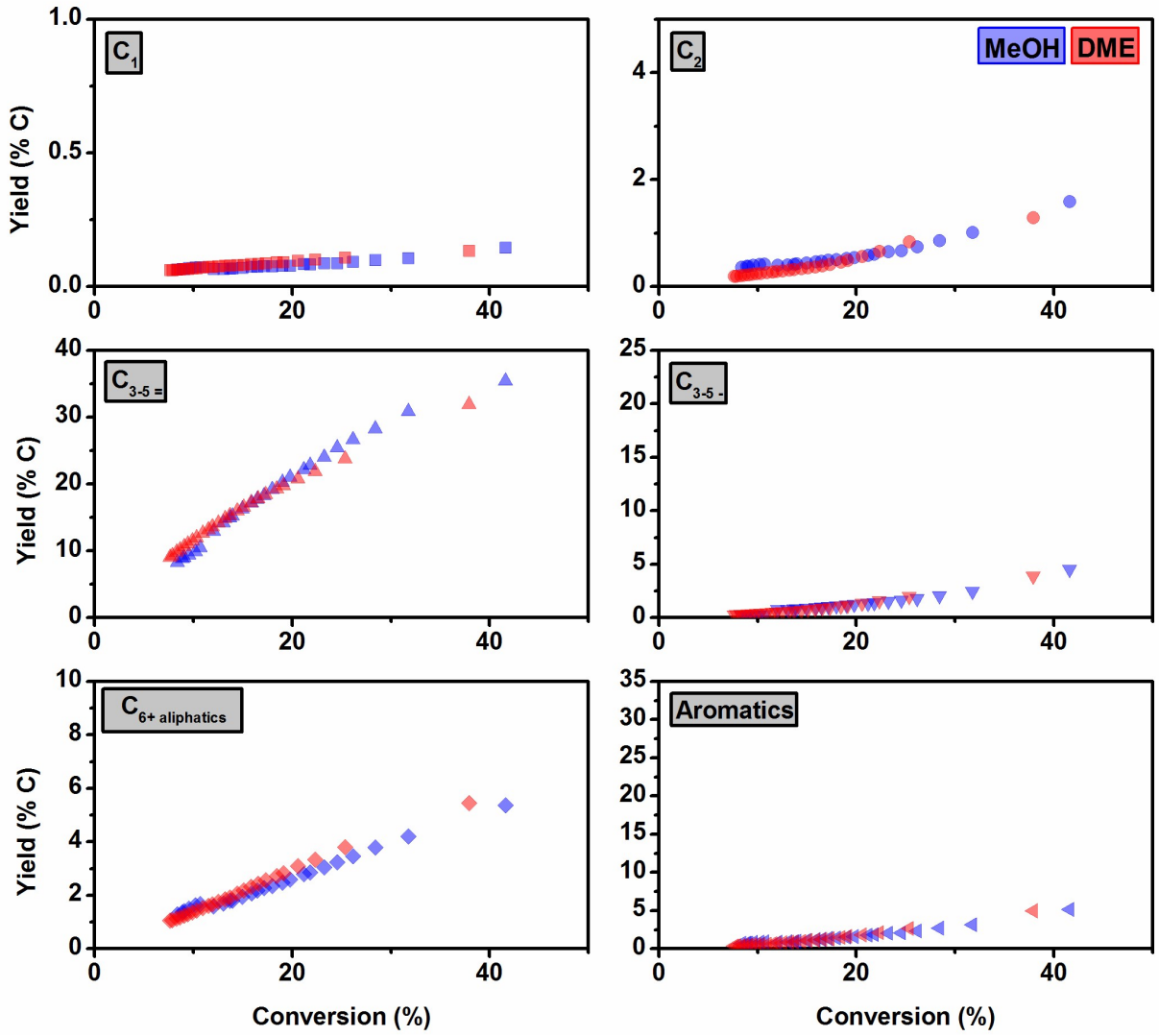

Figure S4. Yields of hydrocarbons fractions versus conversion during MTH over H-SAPO-5 at 350 °C by feeding DME (red) and MeOH (blue).

S3. Evaluation of MeOH dehydration capacity of AlPO-5 at 350 and 450 °C

The dehydration capacity of AlPO-5 was tested at 350 and 450 °C before using this catalyst in combination with H-SSZ-24 in order to assure a good dehydration capacity under desired WHSV. A 2.8 g_{MeOH}/g_{cat}*h was targeted, and **Figure S5** corroborated that DME and MeOH co-existed under thermodynamic equilibrium conditions at the mentioned WHSV.

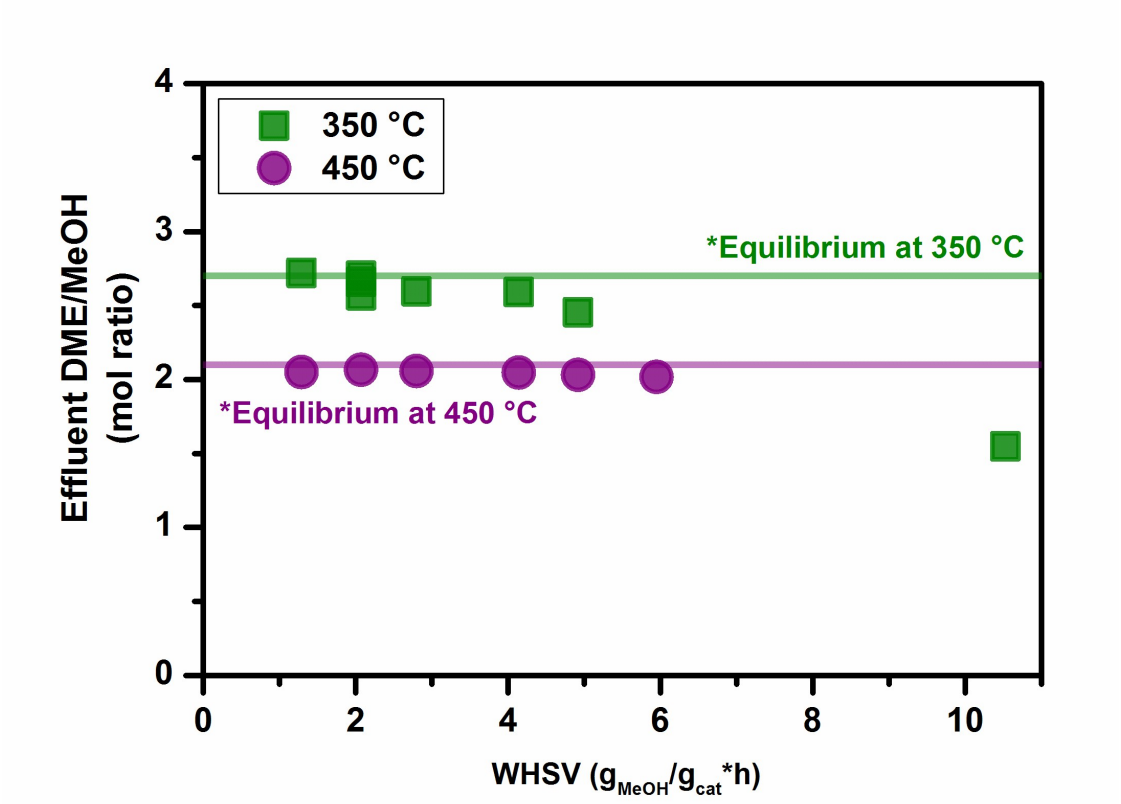

Figure S5. Molar ratios DME/MeOH in the effluent as a function of WHSV when feeding 40 mbar MeOH over AlPO-5 at 350 and 450 °C. *Lines represent the thermodynamic ratios expected at both temperatures, considering that the only reaction occurring is MeOH dehydration.

S4. Deactivation model application over H-SAPO-5 and H-ZSM-5

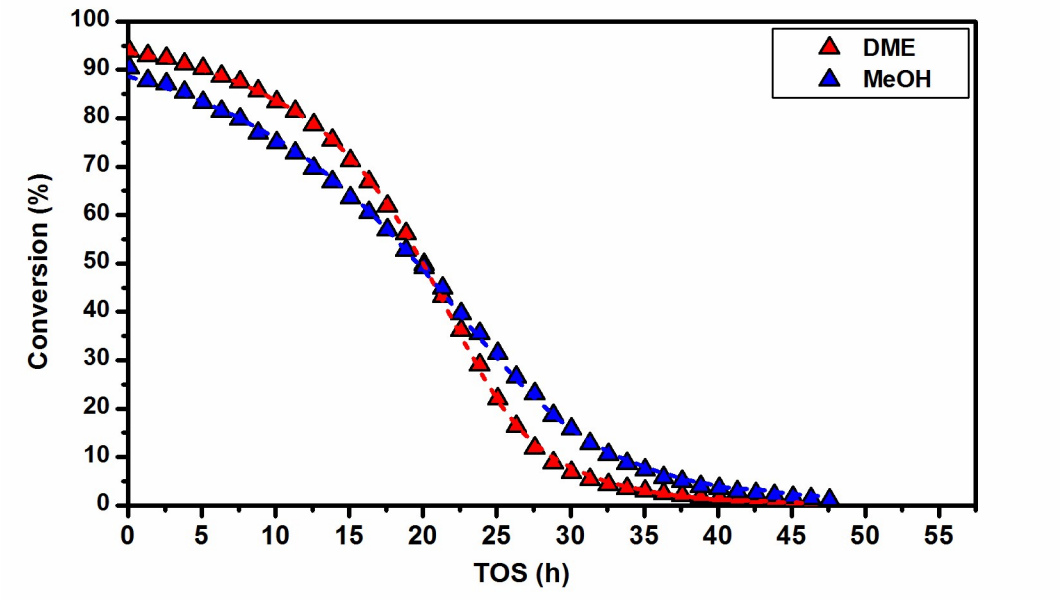

Figure S6. Deactivation profiles based on oxygenates conversion versus time-on-stream at 450 °C over H-SAPO-5. Symbols illustrate experimental data, while the simulated model conversion curve is represented by dashed lines.

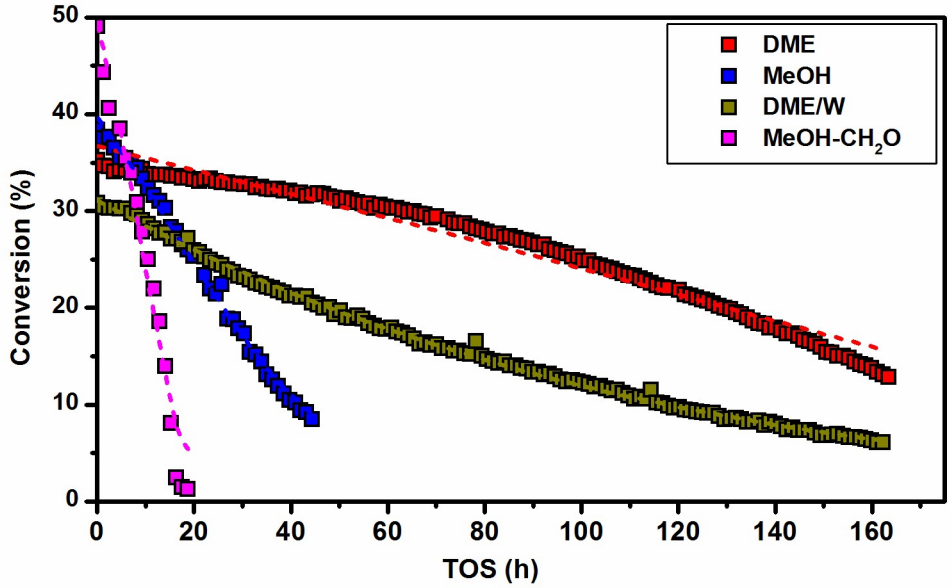

Figure S7. Deactivation profiles based on oxygenates conversion versus time-on-stream at 350 °C over H-ZSM-5. Symbols illustrate experimental data, while the simulated model conversion curve is represented by dashed lines.

S5. HTI of C_4 aliphatics fraction over H-ZSM-5, H-SSZ-24, H-SAPO-5

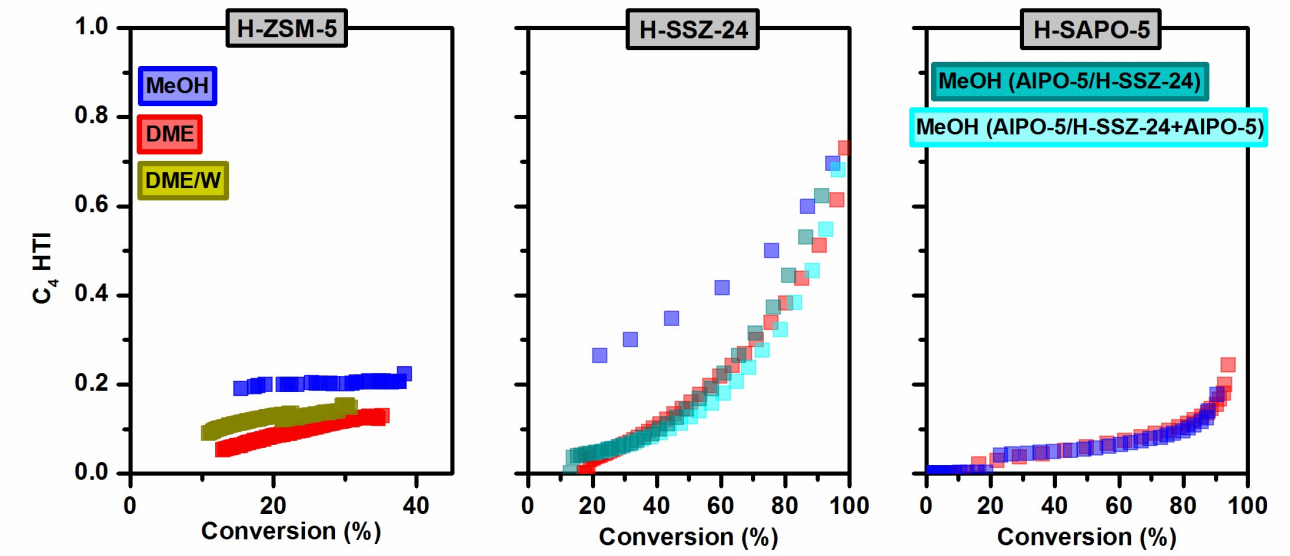

Figure S8. Evolution of the HTI for the hydrocarbon products fractions C_4 (■), as a function of conversion over H-ZSM-5 (350 °C), H-SSZ-24 and H-SAPO-5 (450 °C) with MeOH, DME and DME/W feeds.

S6. Calculation of thermodynamic DME/MeOH concentration curves in the effluent

The thermodynamic equilibrium concentrations of DME and MeOH in the gas phase at each oxygenate conversion level were calculated assuming that the rate of the DME-MeOH interconversion reaction, Reaction (1) in the manuscript, is much faster than the reaction rates of DME and MeOH with hydrocarbons to form new hydrocarbons, Reactions (2a) and (2b) in the manuscript. Adding Reactions (2a) and (2b), Reaction (2c) is obtained. Since the two sides of Reaction (1) are equimolar, the equilibrium is independent of pressure; and hydrocarbon production only influences it by altering the water concentration. Furthermore, due to the equimolarity of Reaction (1), we can ignore the volume change incurred by hydrocarbon formation.

$2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$ (1)

$CH_3OH + RH \rightarrow RCH_3 + H_2O$ (2a)

$CH_3OCH_3 + RH \rightarrow RCH_3 + CH_3OH$ (2b)

$CH_3O\ CH_3 + 2\ RH \rightarrow 2\ RCH_3 + H_2O$ (2c)

In the following,

M = The sum of C atoms in the methanol molecules present

D = The sum of C atoms in the DME molecules present

X = The sum of C atoms in the hydrocarbon molecules present

Starting from MeOH and setting the initial MeOH concentration to 100, it follows that X also represents the percentage conversion of oxygenates to hydrocarbons. By combining Reaction (1) and Reaction (2a) we obtain:

$M = 100 – D – X$

and:

$[MeOH] = 100 – D - X$

$[DME] = D/2$

$[H_2O] = D/2 + X$

$K_{eq,f} = [DME] \times [H_2O] / [MeOH]^2 = (D/2) \times (D/2 + X) / (100 – D – X)^2$

For each level of conversion, X, D was determined by regression analysis, leading to the corresponding concentrations of MeOH, DME and water, and thereby, the [DME]/[MeOH] ratio.

Starting from DME, the initial DME concentration was set to 50. Hence, the initial number of C atoms in DME molecules was set to 100, in order to ensure that X also in this case would represent the oxygenate conversion level. Combining the reverse Reaction (1) and Reaction (2c), it follows that:

$CH_3OCH_3 + H_2O \leftarrow 2\ CH_3OH$ (-1)

$CH_3O\ CH_3 + 2\ RH \rightarrow 2\ RCH_3 + H_2O$ (2c)

$D = 100 – M – X$

and:

$[DME] = (100 – M – X)/2$

$[MeOH] = M$

$[H_2O] = (X - M)/2$

$K_{eq,b} = M^2 /[(X - M)/2]*[(100 – M – X)/2]$

Again, for each level of conversion, X, M was determined by regression analysis, leading to the corresponding concentrations of MeOH, DME and water, and thereby, the [DME]/[MeOH] ratio.

S7. Product selectivities with MeOH, DME and DME/water feeds over H-ZSM-5 at 350 °C

As MTH tests with MeOH, DME and DME/water feeds over H-ZSM-5 were performed under relatively low conversion levels, we stress the differences observed in product distribution by adding the product selectivity differences in **Figure S.9**. Reproducibility tests are also included for the 3 feeds and are consistent with the highlighted differences. Interestingly, MeOH feed gives the most stable selectivities within the conversion range measured in line with constant effluent DME/MeOH ratios (**Figure 3**). Conversely, DME and DME/water feeds give selectivity curves that change with conversion level. With decreasing conversion, the effluent DME/MeOH ratio increased (**Figure 3**) in line with increased selectivity to $C_{6+\ aliphatics}$ and decreased in selectivity to ethylene, alkanes and aromatics.

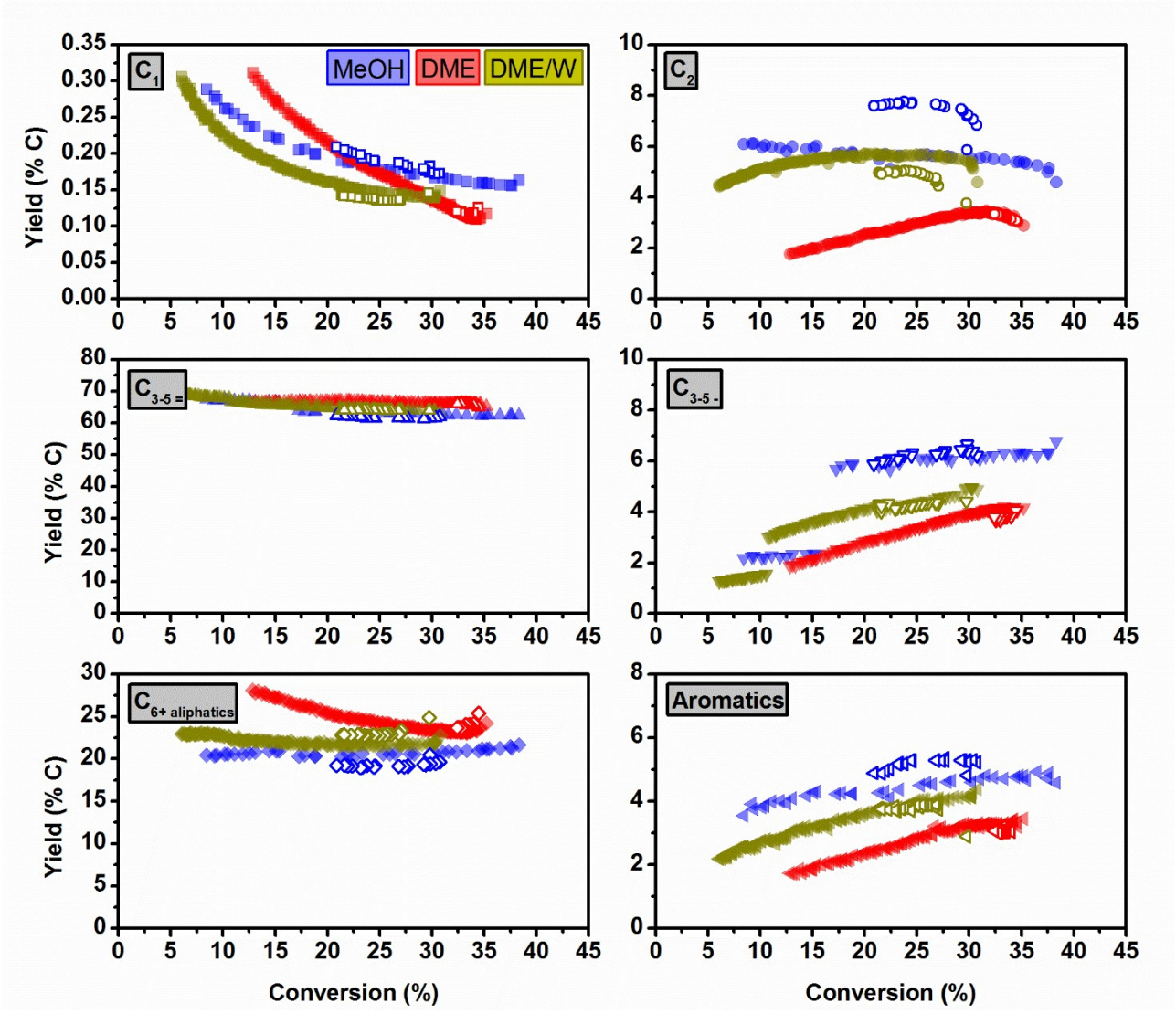

Figure S.9. Selectivities of hydrocarbon fractions versus conversion during MTH over H-ZSM-5 at 350 °C by feeding DME (red), MeOH (blue) and DME/W (green). Empty symbols refer to reproducibility experiments. *Small deviations in C_{3-5} alkanes at low conversions are due to overlapping isobutane/MeOH signals under high MeOH concentrations.

S8. References

[1] F.L. Bleken, T.V.W. Janssens, S. Svelle, U. Olsbye, Product yield in methanol conversion over ZSM-5 is predominantly independent of coke content, Microporous Mesoporous Mater., 164 (2012) 190-198.
[2] D. Rojo-Gama, S. Etemadi, E. Kirby, K.P. Lillerud, P. Beato, S. Svelle, U. Olsbye, Time- and space-resolved study of the methanol to hydrocarbons (MTH) reaction - influence of zeolite topology on axial deactivation patterns, Faraday Discuss., (2017. DOI: 10.1039/C6FD00187D).