Supplementary Information

The influence of precursors on the induction period and transitionregime of dimethyl ether conversion to hydrocarbons over ZSM-5 catalysts

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S1. TAP reactor

The TAP reactor consists of three chambers connected in series: the reactor chamber, the differential chamber, and the detector chamber. The reactor chamber contains a fixed-bed reactor, 6 mm O.D. (4 mm I.D.) and 40 mm long. The reactor chamber has a cone-shaped inset for uniform radial distribution. The differential chamber acts as a cryogenic trap to eliminate scattered molecules reaching the detector chamber where the quadrupole mass spectrometer is housed. The differential chamber works as a molecular beam. Gases are introduced either through two continuous feed valves or two pulse valves into the reactor inlet. A baking procedure was carried before and in-between experiments to remove residual water or organics in the TAP reactor.

S2. Blank experiments



Figure S1: A normalised step response of 5 vol% DME (balance argon) over ZSM-5 (25) and over an inert quartz bed, both at 450 °C.

S3. Characterisation

The zeolite samples were studied by X-ray diffraction (XRD) with a Bruker D5005 diffractometer using Cu K_a radiation equipped with standard Bragg-Brentano geometry and a diffracted beam graphite monochromator. The morphology was characterized using a Carl Zeiss sigma series Field Emission Scanning Electron Microscope (FE-SEM) at an accelerated voltage of 20 kV. The crystal size distribution was obtained from an image analysis software. Nitrogen physisorption studies were carried out on a Micromeritics 2020 unit. The samples were degassed by heating to 400 °C under vacuum (10⁻⁶ mbar) for 12 h prior to measurements. Figure S2.1 below gives the XRD patterns of ZSM-5 (11.5) and ZSM-5 (25) used in this study.



Figure S2.1: XRD patterns of ZSM-5 (11.5), ZSM-5 (25) and a reference highly crystalline ZSM-5 sample (standard) obtained from the database of the International Zeolite Association ¹. "Reprinted in part with permission from ². Copyright 2017. The author(s)".



(b) ZSM-5 (25)

Figure S2.2: (a) SEM image of the ZSM-5 (11.5) and (b) SEM image of ZSM-5 (25). "Reprinted in part with permission from ². Copyright 2017. The author(s)".

Thermogravimetric analysis (TGA) of the ZSM-5 (25) and ZSM-5 (11.5) catalyst powder was carried out in a Setsys Evolution TGA 16/18 instrument (SETARAM). Before each experiment, 12 mg of sample was placed into an alumina crucible held in a TGA chamber that was purged with air at 20 °C at 200 mL min⁻¹ for 8 min. All gas flow rates refer to normal temperature and pressure. The experiments were performed under air flowing at 20 mL min⁻¹ at a heating rate of 5 °C min⁻¹ to the temperature of 600 °C.



Figure S2.3: TGA of ZSM-5 catalysts of Si/Al ratios of 11.5 and 25.

S4. Quantification

To ascertain what to quantify, the full gaseous product release during the step response cycles was obtained (Figure S3). This quantification method has been used before³. The quantification was performed in the following sequence: (1) Ion fragmentation patterns determined from calibration experiments done over a quartz bed of equal bed length and diameter to the ZSM-5 bed were obtained. Calibration experiments were conducted by passing each specie listed in Table S1 as well as argon through an inert bed consisting of quartz wool/quartz beads/quartz wool. The major m/e value was obtained in accordance with the NIST chemical database. Argon was used as internal standard for quantification, (2) Ion current intensities were taken relative to the inert standard, (3) Molar flow rates were obtained from the molar flow rate of the inert standard, the sensitivity coefficients, and the relative ion current intensities. A recursive deconvolution methodology was used: throughout all calculations, ion current intensities were taken relative to that of the chosen inert standard at the chosen m/e value:

$$I_{a(i),m(j)}^{*} = \frac{I_{a(i),m(j)}}{I_{S,m(S)}}$$

Where $I_{a(i),m(j)}$ is the ion current intensity of specie i and m/z ratio of j. $I_{s,m(s)}$ is the ion current intensity of argon at m/z=40. Next, the sensitivity coefficient was calculated from calibration experiments where the partial pressures, respective mole fractions or molar flows are known:

$$Sens_{a(i),m(j)} = I_{a(i),m(j)}^* \cdot \frac{n_S}{n_{a(i)}} = \frac{I_{a(i),m(j)}}{I_{S,m(S)}} \cdot \frac{n_S}{n_{a(i)}}$$

Where n_s is the molar flow rate of argon and $n_{a(i)}$ is the molar flow rate of specie i. Sens_{a(i),m(j)} is the sensitivity coefficient of specie i at m/z ratio of j. To exploit an analysis by the mass spectrometer, the equation defining the sensitivity coefficient is rearranged, yielding an expression for the partial pressure, mole fraction or flow of the probe molecule as a function of the respective partial pressure, molar fraction or flow of the inert standard.

$$n_{a(i)} = I_{a(i),m(j)}^{*} \cdot \frac{n_{S}}{Sens_{a(i),m(j)}} = \frac{I_{a(i),m(j)}}{I_{S,m(S)}} \cdot \frac{n_{S}}{Sens_{a(i),m(j)}}$$

A (recursive) deconvolution (unfolding of the different compound contributions to the ion current intensity at a given m/e value) can be accomplished if the ion current intensity of interfering compounds is known at other m/e values without overlap.

$$I_{a(i),m(j)}^{*} = I_{common,m(j)}^{*} - \frac{Sens_{a(l),m(j)}}{Sens_{a(l),m(n)}} \cdot I_{a(l),m(n)}^{*} = \frac{I_{common,m(j)}}{I_{S,m(S)}} - \frac{Sens_{a(l),m(j)}}{Sens_{a(l),m(n)}} \cdot \frac{I_{a(l),m(n)}}{I_{S,m(S)}} + \frac{I_{a(l)$$

Where $I_{common,m(j)}^{*}$ is the overall contribution of specie i at m/z ratio of j. Sens_{a(l),m(j)} is the sensitivity coefficient of an overlapping fragment at m/z ratio of j. Sens_{a(l),m(n)} is the sensitivity

coefficient of an overlapping fragment at its own non-interfering m/z ratio of n. $I_{a(l),m(n)}$ is the ion current intensity of an overlapping fragment at its own non-interfering m/z ratio of n. Ar was monitored at m/e = 40, CH₃OH at m/e = 31, DME at m/e = 45, H₂O at m/e = 18, C₂H₄ at m/e = 27 and C₃H₆ at m/e = 41.

Subsequent deconvolution allowed for the subtraction of minor fragments from main species. The original data was subjected to noise reduction (a smoothing function (moving average of 5) to the curves to smoothen out irregularities due to noise in the signal) before presentation in the manuscript, except in Figure 3 where a moving average of 3 was used.

Table S1 below gives an overview of the major gaseous components and most interfering components that were detected in this study.

Table S1

Species present in the effluent, m/e values for measurement and the most important interfering components

Specie	m/e value	Interfering components
CH₃OH	31	DME
DME	45	
H ₂ O	18	
C ₂ H ₄	27	C ₃ H ₆
C ₃ H ₆	41	

S5. Full spectrum of species



Figure S3: Full spectrum of species formed at steady-state after a step response of 5 vol% DME (balance argon) over ZSM-5 (25) catalysts at 300 °C. Argon signals at m/z=20 and 40 have been removed for better clarity. "Reprinted with permission from ⁴. Copyright 2019. John Wiley & Sons."





Figure S4: TPD of the working ZSM-5 (25) catalyst from 300 °C to 470 °C at 15 °C min⁻¹ after a step response of 5 vol% DME at 300 °C.

S7. Temperature programmed desorption of dimethoxymethane and 1,5-hexadiene



Figure S5a: TPD of DMM (m/z=75) and its decomposition products over ZSM-5 at 15 °C min⁻¹ up to 470 °C.



Temperature, °C

Figure S5b: TPD of 1,5-hexadiene (m/z=67) over ZSM-5 at 15 °C min⁻¹ up to 470 °C showing temperatures of desorption.



S8. Consecutive step response methodology



Figure S6: Consecutive step response profiles of (a) dimethoxymethane, (b) 1,5-hexadiene at 300 °C over ZSM-5 (11.5) catalysts followed by TPD at 15 °C min⁻¹.

S9. Transmission FTIR experiments of hydrocarbon-occluded ZSM-5, and dimethoxymethane and 1,5-hexadiene on ZSM-5 catalysts

S9.1. Ex-situ zeolite characterisation

S9.1.1. Sample preparation

157 mg of fresh NH₄-ZSM-5 (11.5) catalysts were decomposed under vacuum conditions at 15 °C min⁻¹ up to 450 °C and holding for 30 min. Afterwards, a step response of 5 vol% DME was passed over ZSM-5 (11.5) catalysts at 370 °C. A first series of experiments involved a minimum of two cycles of a step response of 5 vol% DME followed by cooling in argon. This sample is called sample A. Sample B was obtained after 10 min of introducing a step response of 5 vol% DME over ZSM-5 (11.5). It was observed that at 10 min, the zeolite was effectively in its induction period (Figure S7.1). Sample C was obtained after decomposing the ammonium form of the zeolite in the TAP reactor. Sample D was the initial ammonium form of the ZSM-5 (11.5) catalyst. These extracted samples were characterised by FTIR spectroscopy as described in section S9.1.2 below.



Figure S7.1: Step response of 5 vol% DME over 157 mg of ZSM-5 (11.5) showing various stages of sample extraction for FTIR studies.

S9.1.2. FTIR study

FTIR studies were carried out in the following instances: (1) over samples A, B, C and D described above activated at temperatures between 250 and 450 °C; (2) pyridine adsorbed on sample D and (3) DMM or 1,5-hexadiene adsorbed on sample D.

Prior to the separate pyridine, DMM or 1,5-hexadiene FTIR studies, the ZSM-5 catalyst was pressed into self-supporting discs (~9-12 mg, 13 mm in diameter) and pre-treated in an *in-situ* IR cell at 450 °C under vacuum (10^{-3} Pa) for 5 h. The adsorption experiments with different probe molecules were monitored by Thermo Nicolet iS10 FTIR spectrometer equipped with a deuterated triglycine sulfate detector, at a spectral resolution of 4 cm⁻¹ collecting 64 scans. An excess of probe molecules (pyridine, 1,5-hexadiene and DMM) was admitted by injection of 2.0 µL liquid into the IR cell. Physisorbed molecules were subsequently removed by evacuation at the adsorption temperature. Adsorption of 1,5-hexadiene and DMM was performed at room temperature. Pyridine (C₅H₅N, Acros Organics, 99.5%) was adsorbed at 150 °C. Desorption profiles were obtained by evacuating the sample at increasing temperatures in 50 °C steps for pyridine and 100 °C for DMM and 1,5-hexadiene. The obtained spectra were analysed (including integration, subtraction and determination of peak positions) using the OMNIC 9 software. All the spectra presented in this work were normalised to 10 mg sample mass.

S9.2. FTIR study of ZSM-5 (11.5) catalysts

FTIR experiments were carried out over ZSM-5 (11.5) catalyst with increased hydrocarbon loading. Figure S7-2 gives IR of the ZSM-5 (11.5) catalyst and the pyridine IR study. FTIR spectrum of sample D which is the ammonium form of ZSM-5 (11.5) shows two major peaks (Figure S7-2a): (1) 3744 cm⁻¹ with a shoulder at 3735 cm⁻¹ which are attributed to external and internal silanol groups (Si-OH), respectively and (2) 3610 cm⁻¹ which is assigned to acidic bridging Si-OH-AI groups.⁵ In the range of 1400 – 1700 cm⁻¹ (Figure S7-2b), chemisorbed pyridine is revealed with the two pyridinium ion bands at 1546 cm⁻¹ and 1637 cm⁻¹ ⁶, two bands assigned to pyridine coordinated to Lewis acid sites at 1455 cm⁻¹ and 1622 cm⁻¹ ^{5,7} and the superposition of signals of Lewis and Brønsted acid sites at 1490 cm⁻¹ ⁶.







Figure S7-2: (a) Infrared spectra of the hydroxyl region of ZSM-5 (11.5) and ZSM-5 (25), activated at 450 °C; **(b)** Infrared spectra of the pyridine region following pyridine adsorption on ZSM-5 (11.5) and ZSM-5 (25); **(c)** Infrared spectra of sample A following activation at different temperatures





Figure S7-3: (a) Infrared spectra of sample B and C activated at 300 °C. Sample C is the TAPdecomposed ZSM-5 zeolite while sample B is sample C subjected to 10 min of a step response cycle of 5 vol% DME at 370 °C, (b) Infrared spectra of sample A and B activated at 350 °C; (c) Difference spectrum of sample A activated at 350 °C minus sample B activated at 350 °C. Sample A is sample C subjected to multiple step response cycles of 5 vol% DME at 370 °C while sample B is sample C subjected to 10 min of a step response cycle of 5 vol% DME at 370 °C.

Figure S7-3a shows that at very short time on stream, only the 1470 cm⁻¹ can be readily distinguished. This corresponds to the beginning of the induction period and could be associated with the formation of the first C-C bond. Figure S7-3b compares spectra of samples A and B activated at 350 °C. The difference spectrum (Figure S7-3c) shows the growth of major adsorbed species at 1483 and 1470 cm⁻¹. A decrease in intensity of bridging Si-OH-AI groups is observed. The band at 1620 cm⁻¹ is due to OH deformation vibrations probably due to methanol⁸. The appearance of a 1470 cm⁻¹ band with a 1480 cm⁻¹ shoulder has been previously attributed to alkenyl carbenium ion adsorption over ZSM-5 catalysts which could be attributed to the adsorption of methanol, propylene or butadiene.⁹ These bands are all persistent up until 450 °C as shown in Figure S7-2c and are in accordance with the desorption profiles shown in Figure S4. The 2900 and 2440 cm⁻¹ bands refer to antisymmetric and symmetric stretching OH vibrations of protonated methanol molecules.⁸ As shown in ref.² and section 3.5, methanol desorbs at lower temperatures and propylene desorbs at temperatures lower than 350 °C.¹⁰ Thus, the adsorbed specie could be a diene as its conversion is also followed by the formation of alkenyl cations on ZSM-5 catalysts.⁹ The difference spectrum of sample A and B activated at 350 °C corresponds to the difference between the start of the induction period and a fully established working catalyst. The data suggest that dienes could be prominent in this region.

Literature provides evidence for dimethoxymethane and 1,5-hexadiene as intermediates during the induction period.¹¹⁻¹⁴ Further investigations on the IR spectrum of DMM and hexadiene were carried out separately.



Figure S7-4: (a) Infrared spectra of sample D after activating at 450 °C before and after adsorption of 1,5-hexadiene at 370 °C; (b) Infrared spectra of sample D after activating at 450 °C and sample D adsorbed with DMM at 370 °C; (c) Difference spectra between sample D adsorbed with 1,5-hexadiene and pure sample D at 370 °C and between sample D adsorbed with DMM and pure sample D at 370 °C. Sample D is the ammonium-form of ZSM-5 (11.5).

Figure S7-4 shows the infrared spectra of sample D after heating at 450 °C and sample D with adsorbed 1,5-hexadiene (Figure S7-4a) and DMM (Figure S7-4b). A comparison of Figure S7-3c to Figure S7-4c shows that the IR spectra are comparable in the region of persistent occluded species in the ZSM-5 (1470 – 1490 cm⁻¹) as the zeolite transitions through the induction period to its working state.

Figure S7-3c shows the IR spectrum of sample A minus sample B at 350 °C. This difference spectrum shows the change in adsorbed species as the zeolite transforms from during the induction period to its working state. The hydrocarbon pool components can be obtained by the analysis of this spectrum. The IR spectrum of the spent zeolite (Figure S7-3c) within the 1400 – 1500 cm⁻¹ region is comparable to the IR spectrum of adsorbed 1,5-hexadiene (Figure S7-4a) or DMM (Figure S7-4b) on a fresh ZSM-5 catalyst. This indicates that either 1,5-hexadiene or DMM forms propylene in similar steps with DME. This is also confirmed with TPD experiments in Figures S5a and S5b. As a result, no differentiation can be made based on FTIR alone.

S10. References

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