11	Insight into the effects of confined hydrocarbon species on the lifetime of
12	methanol conversion catalysts
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25 26 27 28 29 30 31 32 33 34 35 36 37 38	Abstract : The methanol-to-hydrocarbons (MTH) reaction refers collectively to a series of important industrial catalytic processes to produce either olefins (MTO) or gasoline (MTG). Mechanistically, methanol conversion proceeds via a 'pool' of hydrocarbon species. For MTO, these can broadly be delineated into 'desired' lighter olefins and 'undesired' heavier fractions causing deactivation in a matter of hours. The crux in further catalyst optimization is the ability to follow the formation of carbonaceous species during operation. Herein, we report the combined results of an <i>operando</i> Kerr-Gated Raman Spectroscopy study with state-of-the-art <i>operando</i> molecular simulations, which allowed to follow the formation of hydrocarbon species at various stages of methanol conversion. Polyenes are identified as crucial intermediates towards formation of polycyclic aromatic hydrocarbons, with their fate being largely determined by the zeolite topology. Notably, we provide the missing link between active and deactivating species, which allows us to propose potential design rules for future generation catalysts.
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47	Small olefins are highly important platform chemicals, derived from their significance as

'building blocks' for the global polymer and plastic market, giving a propylene market worth 48 of \$90b p.a.¹ Steam cracking of light hydrocarbons or naphtha typically produces ethylene, 49 whereas fluid catalytic cracking of naphtha produces propylene. Alternative, sustainable 50 routes to olefin production are necessary to omit crude oil as a source, requiring new process 51 technologies and catalytic materials. Alternative sources for olefins production include coal 52 and natural gas, and sustainable options, i.e. second-generation biomass, which can be 53 realized at a large scale through a multi-step process involving methanol synthesis from 54 syngas, followed by the methanol-to-hydrocarbon (MTH) process using zeolites.^{2–4} MTH has 55 been commercialized in many variants and remains a vital technology for the production of 56 57 chemicals and fuels, especially under a variable window of operation in terms of feed or product distribution. The scope to influence MTH products by altering parameters such as 58 reaction conditions (temperature and flow) and zeolite properties (topology and acidity) is 59 particularly attractive. These variables sway product selectivity between the extremities of 60 gasoline (methanol-to-gasoline or MTG) and light olefins (MTO).^{2,3} Catalyst stability is 61 perhaps the major challenge for the widespread use of this technology, specifically the fast 62 formation of carbon deposits during operation severely compromises process efficacy.^{2,5–7} For 63 small-pore zeolites, deactivation occurs in a matter of hours. Despite intensive research 64 efforts, a comprehensive molecular insight into deactivation phenomena is still absent yet 65 necessary to improve process efficiency. The presence of many intermediate species and 66 need to track them under reaction conditions renders this very challenging.^{2,3,5} 67

To set the scene, the MTH reaction has been shown to proceed through an indirect 68 hydrocarbon pool (HP) mechanism, wherein organic molecules confined within zeolite 69 micropores act as reaction centres to which methanol is added and olefins are split off via 70 dealkylation/cracking steps (Fig. 1a).^{2,8,9} There is a consensus that methylated benzenes and 71 olefins are key HP species in both CHA and MFI zeolite topologies, whereas polycyclic 72 aromatic hydrocarbons (PAH) are related to catalyst deactivation, blocking zeolite pores and 73 forming carbon deposits.^{2,5,8-12} Recent studies have shown that altering the catalyst structure 74 and/or acidity, as well as co-feeding of H₂ can improve lifetime,^{4,13,14} nevertheless, it is 75 unclear how the plethora of adsorbed species affects this. Most mechanistic insight has been 76 gleaned from NMR,¹⁵⁻¹⁸ Raman,¹⁹⁻²¹ IR,^{10,22,23} and UV-vis spectroscopic studies,²³⁻²⁵ some of 77 which were employed under in situ/operando conditions, as well as theoretical 78 calculations.^{11,26} Studies that can truly discriminate between essential and deactivating species 79 in the catalytic process are very limited;^{15,20,21,23-25,27} with time/temperature-resolved studies 80

most suited to unravel this complexity. To further progress in controlling catalytic performance, a deep mechanistic understanding into the formation and evolution of the HP species under operating conditions is needed.

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Figure 1. Illustration of the different stages of the MTO reaction and the Kerr-Gate Raman setup. a. Illustration of different stages of the MTO reaction on CHA-type zeolite materials, with the corresponding adsorbed intermediates and outlet products. b. Representation of the Kerr-Gate blocking fluorescence from the detector. This technique makes use of the difference between fluorescence and Raman temporal behavior (i.e. Raman process is instant and limited by the laser pulse while fluorescence occurs on longer time scale of 10^{-6} to 10^{-9} s) to temporally reject fluorescence (see Supporting Information for further details).

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Herein we combine *operando* Kerr-Gated Raman studies with advanced simulation tools to
follow carbonaceous species formation during methanol conversion. Raman spectroscopy is a
powerful technique for characterizing carbon species under reaction conditions, but its
application to zeolite catalysts is often hindered by inherent and incidental fluorescence from
the sample.²⁸ To some extent using differing excitation wavelengths can circumvent this,
though at the expense of either weaker Raman signal (IR source) or higher energy load on the

sample (UV) which can cause photodegradation.^{28,29} An interesting alternative is to use a 92 visible excitation source combined with a Kerr-Gated spectrometer, which discriminates 93 between the Raman signal and fluorescence based on the temporal differences of the two 94 processes (Fig. 1b and S1).^{30,31} Furthermore since many key molecular 'protagonists' in the 95 reaction pathway are colored^{23,24} the phenomenon of resonance enhancement of Raman (up to 96 10^8 signal enhancement) allows us to detect species not normally observable in this 97 reaction.^{28,29} The benefit of performing Kerr-Gated Raman spectroscopy vs. conventional 98 Raman is clearly demonstrated in Fig. S2. Operando molecular simulations identified reaction 99 100 intermediates and determined their mobility within the zeolite host. The combined 101 experimental/theoretical approach allowed the hydrocarbon evolution to be pieced together within two of the most well-studied zeolite topologies: CHA and MFI. As a major finding, we 102 103 identified the crucial role of polyenes and show that their fate is dependent on the zeolite topology. Within the CHA topology, they are precursors for deactivating PAH species. 104

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106 Early stages of the MTO reaction: pre-equilibrium stage and initiation of the induction period (100 to 260 °C). The evolution of hydrocarbon species formed during MTO on SSZ-107 108 13 was examined by operando Kerr-Gated Raman Spectroscopy combined with real-time 109 product analysis using a mass spectrometer (MS) (see Methods and Table S1 for further details). Data recorded up to 300 °C are given in Fig. 2 and S3-4. Between 100 and 240 °C, a 110 gradual drop in the Raman bands of methanol (2954 and 2855 (C-H v_{as} and v_s), 1455 (CH_{3 δ}), 111 and 1006 cm⁻¹ (C-O v)) was observed (Fig. S3-4), with dimethyl ether (DME) and water 112 detected by MS in the reactor outlet stream (Fig. S4). These products are characteristic of the 113 pre-equilibrium stage of the reaction (Fig. 1)³² wherein methanol is dehydrated into a mixture 114 115 of methanol, DME and water. Note that methanol bands in the experimental spectra are in 116 agreement with the simulations (see Supporting Information, Fig. S5-S6, Table S2 and Fig. S7-S8). At 240 – 260 °C the bands of methanol were barely observed (Fig. 2a), and a new 117 weak signal was detected at 1600 - 1625 cm⁻¹ that according to previous work^{33,34} and our 118 simulations (Fig. 3a and S9-11), can be assigned to stretching modes of isolated C=C bonds, 119 indicating the onset of alkene formation and possibly, small polyenes. These observations are 120 consistent with the formation of the first hydrocarbons,¹⁶ representing the beginning of the 121 induction period and the build-up of HP species within zeolite micropores (Fig. 1). 122



Figure. 2. Operando Kerr-Gated Raman of SSZ-13 zeolite during the MTO reaction – Formation of HP intermediates and onset of deactivation. a. Kerr-Gated Raman spectra of SSZ-13 zeolite during the MTO reaction between 250 and 300 °C. Measurements performed at increasing reaction temperatures (heating rate 1°C.min⁻¹; WHSV of 1.6 $g_{MeOH}.g_{cat}^{-1}.h^{-1}$). Excitation wavelength 400 nm. Raman bands are observed at 1608 (C=C v_s), 1551 (conjugated π -system C=C v), 1519 (C=C v_{as}), 1375 (CH₂/CH₃ δ ; ring breathing mode), 1265 (C-H rock), 1182 (C-C v), 576 (C-C δ) and 480 cm⁻¹ (zeolite T-O bend vibration). **b.** Mass traces of methanol and the reaction products.

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125 Identification of HP intermediates (270 to 280 °C). Further temperature increase led to 126 significantly increased methanol conversion – with a maximum at 283 °C, along with the 127 formation of C₂-C₄ products (Fig. 2b), characteristic of the autocatalytic stage (Fig. 1). In 128 accordance, intense Raman bands observed in the spectra at 270 – 280 °C, attributed to 129 various HP species. Previous work in conjunction with our simulations (Fig. 3 and S12),^{19,33,34} 130 identified bands at ca. 1608 and 1519 (C=C v_s and v_{as}), 1375 (CH_{3 δ}), 1265 (C-H rock), 1182 131 (aromatic C-C v modes), 576 cm⁻¹ (alkyl aromatic ring C-C _δ); the origin of these bands we attribute to methylated-benzenium ions which are now readily observable due to resonance
enhancement.^{17,24} We note the excellent correspondence between our experiments and
theoretical simulations (Fig. 3b and S12).

135 Besides alkenes, small polyenes and methylated-benzenium ions, our simulations identified contributions from additional species. Specifically, Raman bands around 550 $\text{cm}^{\text{-1}}$ (C-C $_{\delta}$) and 136 between $1250 - 1400 \text{ cm}^{-1}$ (C-H rock and CH₂ and CH_{3 δ}) characteristic of dienylic cations 137 (Fig. 3 and S9), formed from dienes by protonation and subsequent hydride abstraction or the 138 139 reaction of monoenyl carbocations and olefins. The identification of (methylated-)naphthalene(s) is more challenging. We note that the width and height of the 1375 cm⁻¹ band 140 is sufficiently broad to contain multiple contributions including, as predicted by theory (Fig. 3 141 and S12) and identified in previous works,³³ a ring-breathing mode of naphthalenes along 142 with CH_{3 δ} modes. From these observations, methylated-benzenium ions, along with alkenes, 143 144 small polyenes, dienylic cations and possibly (methylated-)naphthalene(s) are concluded to be the HP species formed on SSZ-13 during the induction period and present in the autocatalytic 145 146 stage of the reaction.



Figure. 3. Comparison of experimental and simulated Raman spectra. a. Simulated Raman spectra of SSZ-13 zeolite loaded with model alkenes and small polyenes (red, blue and green traces) vs. experimental Raman spectrum (orange trace) acquired during the MTO reaction at 260 °C. b. Simulated Raman spectra of SSZ-13 zeolite loaded with model dienyl, benzene and naphthalene species (red, blue and green traces) vs. experimental Raman spectrum (orange trace) acquired during the MTO reaction at 280 °C. c. Simulated Raman spectrum (orange trace) acquired during the MTO reaction at 280 °C. c. Simulated Raman spectra of SSZ-13 zeolite loaded with model polyenes (red, blue and green traces) vs. experimental Raman spectrum (orange trace) acquired during the MTO reaction at 300 °C. Protonated structures are indicated with a + sign. Full assignments are provided in the ESI, along with the simulated spectra of additional model alkenes, polyenes and aromatic

species.

Confined hydrocarbon species at the onset of deactivation (290 to 300 °C). Coincident 148 with decreasing methanol conversion at 290 °C, a new intense band at 1551 cm⁻¹ emerged in 149 the C=C stretch region of conjugated olefins (Fig. 2). Bands in this region were previously 150 observed during conversion of methanol, DME and light olefins, and tentatively assigned to 151 polyene-type species.^{19,22,33} However, their high reactivity has prevented the study of zeolite 152 adsorbed polyenes, preventing their unambiguous identification. To gain definitive insight 153 154 into the species present, vibrational signatures of a number of polyene species were calculated (Fig. 3c and Figs. S9-11, S13-19). For linear polyenes with either straight or curled 155 topologies, four characteristic vibrations were identified, including the stretching mode of the 156 conjugated π -system (1520-1580 cm⁻¹), which red-shifted with increasing chain length. 157 Branched polyenes showed an additional feature at 850-1000 cm⁻¹, due to the out-of-plane 158 wagging of C-H bonds. The absence of this mode in the experimental spectrum, along with 159 160 the stretching frequency of the conjugated π -system identifies extended polyenes with no or 161 small branches (Fig. 3c and Figs. S9-11),

As the reaction progresses, at 300 °C, significant growth of the 1551 cm⁻¹ band was observed. No additional features were detected in the 850-1000 cm⁻¹ region (Fig. 3). The intensification of the 1551 cm⁻¹ band accompanied an important decrease in methanol conversion (Fig. 2b), revealing a direct correlation between extended polyenes formation and the onset of catalyst deactivation, likely associated with confinement-induced effects on the mobility of these large molecules.

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Mobility of hydrocarbon species formed during onset of activation and deactivation. So 169 far, it remains unclear whether the carbonaceous species detected block the zeolite pore 170 system or remain mobile. First principle molecular dynamics simulations (MD) allowed the 171 examination of the mobility of detected hydrocarbons within the zeolite pores (Fig. S20-33). 172 We followed the path of the centres of mass (COMs) of the carbon atoms during MD runs of 173 40 ps at 350 °C, projecting the COMs onto the different channels as the reaction intermediates 174 are expected to move along channels in the zeolite. The resulting mobility plots are visualized 175 through a dark orange line in a 2D-plot (Fig. 4 and Fig. S21, S25, S28, S30 and S31) and the 176 177 projections of all carbon atom positions on the channel are visualized in light orange. Marked 178 differences in mobility for the various HP species were observed. With small alkenes, simulations indicated no obvious impediments to their mobility, although a lack of preferred 179

propagation direction reduces their probability of traveling through the pores via the 8-ring 180 (Figs. 4a and S25). It is well known that primary product diffusion is hindered through 8-181 rings.^{6,35} Small, branched polyenes (i.e. isoprene and vinylpentadiene) in contrast showed 182 reduced mobility, particularly once they become branched (Fig. S25). Interestingly, medium-183 length linear structures, such as heptatriene, exhibited the largest mobility along the channels, 184 characterised by the displacement of its COM, some ~15 Å along the channel (Fig. 4b and 185 S22). The large mobility along a certain direction is the result of the linearity of the molecule. 186 187 The length of heptatriene approaches the size of the cell, while still fitting through the 8-rings. 188 The molecule aligned itself with the channel (Fig. S23) probably due to the presence of 189 Brønsted sites, that facilitate their propagation along the channel. A COM displacement of ~ 5 Å for octatetraene suggested that this molecule is becoming too long to travel through the 190 pores, whereas decapentaene showed almost no mobility (Fig. 4c and S24), curling around an 191 8-ring, becoming ensconced between two neighbouring cells, inhibiting further diffusion. 192 Consistent with Kerr-Gated Raman, the limited mobility observed for extended polyenes 193 indicate their key role in catalyst deactivation. 194

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Figure 4. Mobility of polyene species formed at the onset of deactivation. Position of the centre of mass of the intermediate (dark orange) and the positions of the carbon atoms (light orange) projected on one of the 8-ring channels (horizontal axis) and a direction perpendicular to it (vertical axis). The amount of time the centre of mass resides at a certain position is illustrated by histogram plots. **a.** Propene. **b.** Heptatriene. **c.** Decapentaene. Protonated structures are indicated with a + sign.

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Formation of polycyclic aromatic hydrocarbons (310 to 450 °C). Further increase in temperature (Fig. 5a) saw the evolution of clear, distinctive low-frequency bands (629 to 1100 cm⁻¹) and more subtle changes in the intensities of bands between 1250 and 1608 cm⁻¹. Based on our simulations, these features are consistent with the formation of PAH (Fig. 5b and S12). The decreased relative intensity of the 1608 cm⁻¹ (v_s C=C) shoulder is likely due to consumption of small alkenes/polyenes and/or methylated-benzenium ions. While PAH also present a band around this frequency (Fig. 5b), these are less resonant than the species being consumed leading to a decrease in signal intensity. Additionally, a drop in the zeolite bands, essentially vanishing by 360 °C, indicates significant hydrocarbon accumulation, due to increased absorption (gradual sample darkening) of the incident excitation beam.³⁶

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Our mobility studies revealed that branched polyenes block the CHA pore system. We 208 observed during a regular MD run at 350 °C of an exemplar branched polyene (3,4-209 210 divinylhexa-1,3,5-triene) spontaneous intramolecular cyclisation, forming a new ring type 211 species (in this case 3,4-diethyl-2-methylcyclopentenium ion). This observation establishes for the first time a clear link between the presence of polyenes and the eventual formation of 212 PAHs (Fig. S13). To assess whether this propensity toward cyclisation is intrinsic to all 213 polyenes irrespective of their degree of branching, we performed additional MD simulations 214 215 on the non-branched, 6-protonated 1,3,5-heptatriene at 350°C. When starting from a cis configuration for the C1-C2 and C2-C3 bonds, we observed spontaneous cyclisation in all 216 simulations (Fig. S34a), confirming that intramolecular cyclisation from the cis, cis 217 218 conformation is basically barrierless. Steric hindrance between the C1 and the C5 hydrogens 219 explains the high reactivity of the *cis, cis* conformation, preventing the π -system being fully coplanar and significantly reducing the delocalization of the positive charge (Fig. S34b). 220 However, linear, non-branched polyenes must overcome an energetic penalty to isomerize the 221 C_1 - C_2 and C_2 - C_3 bonds from the stable *trans, trans* to the reactive *cis, cis* conformation. For 222 non-branched polyenes, this barrier equals 55 kJ/mol, whereas highly branched polyenes have 223 no energetic barrier to form the pre-reactive complex for intramolecular cyclisation (Figs. 224 225 \$35-36). We conclude that branched polyenes formed in the zeolite pores immediately 226 cyclize, whereas linear polyenes survive longer due to the energetic penalty to form the 227 reactive cis, cis isomers.

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Besides intramolecular cyclisation, other ring-forming routes from extended polyenes comprise: electrophilic aromatic substitution of single-ring aromatics or Diels-Alder reaction between polyenes and alkenes, both followed by intramolecular rearrangement steps (Figure S37). In view of the concomitant consumption of small alkenes/polyenes and methylatedbenzenium ions during this temperature range (cause of the decreased band intensity at 1608 cm⁻¹), it is likely these other processes also occur. Once extended PAHs form, they block the CHA cage, as supported by a mobility analysis (Fig. S28-29). *Operando* Kerr-Gated Raman is
able therefore to identify initial polyene formation, track their consumption and consequent
transformation into PAH. This is seen both under variable-temperature (Fig. 2) and isothermal
conditions (Fig. S38). We propose therefore that deactivation of CHA materials occurs via
cage blocking first by extended polyenes and subsequently as these react, PAH species.

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Figure. 5. *Operando* Kerr-Gated Raman of SSZ-13 zeolite during the MTO reaction– Formation of polycylic aromatic hydrocarbons and comparison with ZSM-5 and SAPO-34- archetypal MTH catalysts. a. Kerr-Gated Raman spectra of SSZ-13 zeolite during the MTO reaction between 320 and 450 C. Measurements performed at increasing reaction temperatures (heating rate 1°C.min⁻¹; WHSV of 1.6 $g_{MeOH}.g_{cat}^{-1}.h^{-1}$). Excitation wavelength 400 nm. Raman bands are observed at 1608 (C=C v_s), 1562 (conjugated π -system C=C v), 1377 (CH₂/CH₃ δ ; ring breathing mode), 1265 (C-H rock), 1100-629 (ring-opening vibrations) and 480 cm⁻¹ (zeolite T-O bend vibration). b. Simulated Raman spectra of SSZ-13 zeolite loaded with a model polycyclic aromatic (anthracene, blue trace) and its precursor (red trace) vs. experimental Raman spectrum acquired during the MTO reaction at 450 °C (orange trace). Protonated structures are indicated with a + sign. Full assignments are provided in the ESI, along with the simulated spectra of additional model alkenes, polyenes and aromatic

species. **c.** Kerr-Gated Raman spectra of SSZ-13, SAPO-34 and ZSM-5 catalysts recorded at room temperature after quenching the reaction at 450 C.

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244 Effect of zeolite topology on intermediates formation. Similar results were obtained during MTH over ZSM-5, although formation of HP species occurs at higher temperatures (i.e. 300 245 °C; Fig. S39a). Above 300 °C, features at 1605, 1522, 1383, 1265, 1179 and 564 cm⁻¹ were 246 observed, assigned to methylated-benzenium ions, dienyl carbocations and possibly 247 248 (methylated-)naphthalene(s). Simultaneously, the MS showed a gradual increase in methanol conversion, olefins and aromatics formation (Fig. S39b). At 330 °C, polyenes are formed (i.e. 249 1552 cm⁻¹) without any effect on activity. Also contrasting to SSZ-13, the lower relative 250 intensity of this band to 1605 cm⁻¹ (C=C v_s) suggests that among the species detected, 251 methylated-benzenium ions dominate. Importantly, further heating to 450 °C (Fig. S39c) did 252 not induce PAH formation - consistent with previous reports that PAHs do not build-up 253 significantly within ZSM-5 micropores at this stage,37 and no drop in methanol 254 255 conversion/product formation was observed by MS. We propose that in larger-channelled ZSM-5, linear polyenes diffuse relatively unimpeded, preventing catalyst deactivation 256 through blocking. Considering the larger void volume of the chabazite cage compared with 257 the ZSM-5 channel intersections,³⁸ steric constraints may also play a role, inhibiting polyene 258 cyclization on the MFI topology and preventing PAH formation. The zeolite band at 360 cm⁻¹ 259 also did not drop, indicating a diminished accumulation of hydrocarbons compared to SSZ-260 13. Note however, that due to the increased lifetime of this material,³⁷ we cannot rule out that 261 at longer reaction times, polyenes might contribute to deactivation. 262

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Spent catalysts. At 450 °C, the reactions were quenched to record several scans at room 264 265 temperature (Fig. 5c). Again, no clear features of PAH were seen for ZSM-5 - supporting the idea that, if present, just little amounts of PAH are formed on this catalyst, probably on the 266 external zeolite surface.³⁹, while SSZ-13 showed a number of intense low-frequency peaks, 267 attributable to PAH. For comparison, data are also given for (CHA) SAPO-34, considered the 268 archetypal system for industrial MTO.² The final spectra for SAPO-34 and SSZ-13 are almost 269 identical, confirming that the mechanistic insight is applicable to CHA topologies in general. 270 271 The only noticeable difference between these catalysts is the temperature of HP species 272 formation (270 °C for SSZ-13 vs. 300 °C for SAPO-34), arising from the weaker acidity of the silicoaluminophosphate, as previously reported.^{24,40} For completeness, the Kerr-Gated
Raman data for MTO on SAPO-34 are given in Fig. S40, with additional characterization on
the spent SSZ-13 (Figs. S41-42).

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Figure. 6. Hydrocarbon species evolution taking place during the MTO reaction on small-pore catalyst materials. Different hydrocarbon pool species are formed during the induction period of the MTO reaction, including alkenes, small polyenes, dienylic cations, methylated-benzenium ions and possibly, (methylated-)naphthalene(s), which are responsible for the formation of C_2 - C_4 alkenes in the period of maximum methanol conversion. The formation of polyenes with no or small branches (e.g. decapentaene) - which show almost no mobility and curl around the 8-ring of the zeolite framework, leads to an important decrease in activity, likely related to a reduced diffusivity of both reactant and products. Subsequently, PAH start to accumulate on the catalyst surface, formed from polyenes (possibly) via intramolecular cyclisation.

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Outlook. The unique combination of Kerr-Gated Raman Spectroscopy with molecular 278 simulations allowed the formation of hydrocarbon species at various stages of methanol 279 conversion to be followed (Fig. 6). Our results conclude the CHA topology rapidly 280 deactivates due to the tendency of extended polyenes to block the zeolite pores, eventually 281 undergoing cyclisation within the large chabazite cage and leading to the formation of PAH. 282 We note that polyenes have been previously proposed to provide the precursors to PAH that 283 lead to deactivation.^{33,41} However, for the first time we provide mechanistic insight into how 284 and why this occurs and propose that this does not happen in the MFI structure due to steric 285 286 constraints inhibiting the cyclisation of polyenes and PAHs within the pores and channel 287 intersections leading to enhanced catalyst lifetime (Fig. 6). Previous studies demonstrated that SAPO-34 deactivation may start before significant amounts of PAH form, possibly arising 288 from bulky products trapped in the large framework cavities.⁶ Our findings evidence that it is 289 the extended polyenes with no or small branches that are the crucial deactivating species 290 291 causing the onset of deactivation. As polyenes are typically produced through H-transfer 292 reactions, higher reaction temperatures and/or diminished acid site densities should be

beneficial, by favouring reactions such as cracking or reducing the rate of H-transfer.
Nonetheless, to ultimately design a stable catalyst, steric effects also need to be fully
considered.

Based on our findings, optimal MTO catalysts must present topological characteristics similar 296 to chabazite (i.e. 8-ring three-dimensional channels to retain shape-selectivity, maximising 297 light olefins production while enabling diffusion), ideally with smaller cavities approaching 298 the size of MFI channel intersections, to inhibit intramolecular polyene cyclisation. Materials 299 300 which combine small cavities to prevent cyclisation reactions and tailored acid sites to 301 decrease H-transfer rate will be less prone to deactivation via extended polyene formation and more competitive for MTO. An examination of the zeolite database suggests that there is 302 perhaps only one 8-ring three dimensional zeolite (MER) with the cage size/aspect ratio 303 304 required to inhibit polyene cyclisation. A combination of this topology only being available with a low Si:Al and the comparatively narrow pore openings will likely affect the olefin 305 product distribution however.³⁸ Nowadays, hypothetical databases exist that contain a huge 306 numbers of structures for exploration; an examination of one database reveals already a few a 307 interesting 3-dimensional, 8-ring containing candidate structures that potentially combine 308 restricted cage size with accessibility similar to CHA (3.8 Å) (Fig. S43).^{42,43} The challenge 309 310 though is to make such structures, although we note that our results indicate how insight derived from reaction mechanisms can provide a basis for targeted zeolite design (an 311 approach recently advocated by Corma et al.¹³) which, when combined with potential 312 hypothetical structures, could allow for the realization of a solution to this 'polyene problem'. 313 314 Understanding a reaction mechanism lies at the heart of improving a catalyst's performance 315 suggesting that this approach could prove very powerful for revealing the 'mechanistic secrets' behind a range of catalytic reactions. The technique is not limited to catalysis 316 317 however and could easily be applied to study a range of functional materials.

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319 **References**

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321 1. Available at: https://www.transparencymarketresearch.com/ethylene-and-propylene.html.

Olsbye, U. *et al.* Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size
 Controls Product Selectivity. *Angew. Chemie Int. Ed.* 51, 5810–5831 (2012).

 Yarulina, I., Chowdhury, A. D., Meirer, F., Weckhuysen, B. M. & Gascon, J. Recent trends and fundamental insights in the methanol-to-hydrocarbons process. *Nat. Catal.* 1, 398–411 (2018).

- 327 4. Yarulina, I. *et al.* Structure–performance descriptors and the role of Lewis acidity in the
 328 methanol-to-propylene process. *Nat. Chem.* 10, 804–812 (2018).
- 329 5. Olsbye, U. *et al.* The formation and degradation of active species during methanol conversion
 330 over protonated zeotype catalysts. *Chem. Soc. Rev.* 44, 7155–7176 (2015).
- Hereijgers, B. P. C. *et al.* Product shape selectivity dominates the Methanol-to-Olefins (MTO)
 reaction over H-SAPO-34 catalysts. *J. Catal.* 264, 77–87 (2009).
- Bleken, F. *et al.* The Effect of Acid Strength on the Conversion of Methanol to Olefins Over
 Acidic Microporous Catalysts with the CHA Topology. *Top. Catal.* 52, 218–228 (2009).
- Bahl, I. M. & Kolboe, S. On the Reaction Mechanism for Hydrocarbon Formation from Methanol over SAPO-34: I. Isotopic Labeling Studies of the Co-Reaction of Ethene and Methanol. J. Catal. 149, 458–464 (1994).
- 338 9. Dahl, I. M. & Kolboe, S. On the Reaction Mechanism for Hydrocarbon Formation from
 339 Methanol over SAPO-34: 2. Isotopic Labeling Studies of the Co-reaction of Propene and
 340 Methanol. J. Catal. 161, 304–309 (1996).
- Bjørgen, M. *et al.* Spectroscopic Evidence for a Persistent Benzenium Cation in Zeolite HBeta. J. Am. Chem. Soc. 125, 15863-15868 (2003).
- McCann, D. M. *et al.* A Complete Catalytic Cycle for Supramolecular Methanol to Olefins
 Conversion by Linking Theory with Experiment. *Angew. Chemie Int. Ed.* 47, 5179–5182
 (2008).
- Fu, H., Song, W. & Haw, J. F. Polycyclic Aromatics Formation in HSAPO-34 During
 Methanol-to-Olefin Catalysis: Ex Situ Characterization After Cryogenic Grinding. *Catal. Letters* 76, 89–94 (2001).
- Li, C. *et al.* Synthesis of reaction adapted zeolites as methanol-to-olefins catalysts with
 mimics of reaction intermediates as organic structure directing agents. *Nat. Catal.* 1, 547–554
 (2018).
- Arora, S. S., Nieskens, D. L. S., Malek, A. & Bhan, A. Lifetime improvement in methanol-toolefins catalysis over chabazite materials by high-pressure H2 co-feeds. *Nat. Catal.* 1, 666–672
 (2018).
- Hunger, M., Seiler, M. & Buchholz, A. In situ MAS NMR spectroscopic investigation of the
 conversion of methanol to olefins on silicoaluminophosphates SAPO-34 and SAPO-18 under
 continuous flow conditions. *Catal. Letters* 74, 61–68 (2001).
- Wang, W., Buchholz, A., Seiler, M. & Hunger, M. Evidence for an Initiation of the Methanolto-Olefin Process by Reactive Surface Methoxy Groups on Acidic Zeolite Catalysts. *J. Am. Chem. Soc.* 125, 15260–15267 (2003).
- 361 17. Dai, W. *et al.* Understanding the Early Stages of the Methanol-to-Olefin Conversion on H362 SAPO-34. ACS Catal. 5, 317–326 (2015).
- 363 18. Wang, C. *et al.* Experimental Evidence on the Formation of Ethene through Carbocations in
 364 Methanol Conversion over H-ZSM-5 Zeolite. *Chem. A Eur. J.* 21, 12061–12068 (2015).
- Chua, Y. T. & Stair, P. C. An ultraviolet Raman spectroscopic study of coke formation in methanol to hydrocarbons conversion over zeolite H-MFI. *J. Catal.* 213, 39–46 (2003).
- Beato, P., Schachtl, E., Barbera, K., Bonino, F. & Bordiga, S. Operando Raman spectroscopy
 applying novel fluidized bed micro-reactor technology. *Catal. Today* 205, 128–133 (2013).
- 369 21. Signorile, M. *et al.* Topology-dependent hydrocarbon transformations in the methanol-to 370 hydrocarbons reaction studied by *operando* UV-Raman spectroscopy. *Phys. Chem. Chem.*

- 371 *Phys.* **20**, 26580–26590 (2018).
- Howe, R. F. *et al.* Reactions of Dimethylether in Single Crystals of the Silicoaluminophosphate
 STA-7 Studied via Operando Synchrotron Infrared Microspectroscopy. *Top. Catal.* 61, 199–
 212 (2018).
- Qian, Q. *et al.* Combined Operando UV/Vis/IR Spectroscopy Reveals the Role of Methoxy and Aromatic Species during the Methanol-to-Olefins Reaction over H-SAPO-34. *ChemCatChem*377
 6, 3396–3408 (2014).
- Borodina, E. *et al.* Influence of the Reaction Temperature on the Nature of the Active and
 Deactivating Species during Methanol to Olefins Conversion over H-SSZ-13. *ACS Catal.* 5,
 992–1003 (2015).
- 381 25. Goetze, J. *et al.* Insights into the Activity and Deactivation of the Methanol-to-Olefins Process
 382 over Different Small-Pore Zeolites As Studied with Operando UV–vis Spectroscopy. *ACS* 383 *Catal.* 7, 4033–4046 (2017).
- Lesthaeghe, D., Horré, A., Waroquier, M., Marin, G. B. & Van Speybroeck, V. Theoretical
 Insights on Methylbenzene Side-Chain Growth in ZSM-5 Zeolites for Methanol-to-Olefin
 Conversion. *Chem. A Eur. J.* 15, 10803–10808 (2009).
- 387 27. Forester, T. R. & Howe, R. F. In situ FTIR studies of methanol and dimethyl ether in ZSM-5.
 388 *J. Am. Chem. Soc.* 109, 5076–5082 (1987).
- 389 28. Stair, P. C. The Application of UV Raman Spectroscopy for the Characterization of Catalysts
 390 and Catalytic Reactions. *Adv. Catal.* 51, 75–98 (2007).
- Kim, H., Kosuda, K. M., Van Duyne, R. P. & Stair, P. C. Resonance Raman and surface- and
 tip-enhanced Raman spectroscopy methods to study solid catalysts and heterogeneous catalytic
 reactions. *Chem. Soc. Rev.* 39, 4820-4844 (2010).
- 30. Stanley, A., Parker, A. W., Towrie, M. & Matousek, P. Efficient Rejection of Fluorescence
 from Raman Spectra Using Picosecond Kerr Gating. *Appl. Spectrosc.* 53, 1485–1489 (1999).
- 396 31. Matousek, P., Towrie, M. & Parker, A. W. Fluorescence background suppression in Raman
 397 spectroscopy using combined Kerr gated and shifted excitation Raman difference techniques. J.
 398 Raman Spectrosc. 33, 238–242 (2002).
- 399 32. Blaszkowski, S. R. & van Santen, R. A. The Mechanism of Dimethyl Ether Formation from
 400 Methanol Catalyzed by Zeolitic Protons. *J. Am. Chem. Soc.* 118, 5152-5253 (1996).
- Allotta, P. M. & Stair, P. C. Time-Resolved Studies of Ethylene and Propylene Reactions in
 Zeolite H-MFI by In-Situ Fast IR Heating and UV Raman Spectroscopy. *ACS Catal.* 2, 2424–
 2432 (2012).
- 40434.Socrates, G. Infrared and Raman Characteristic Group Frequencies. (John Wiley & Sons, Ltd,4052001).
- 406 35. Ghysels, A. *et al.* Shape-Selective Diffusion of Olefins in 8-Ring Solid Acid Microporous
 407 Zeolites. J. Phys. Chem. C 119, 23721–23734 (2015).
- Tinnemans, S. J., Kox, M. H. F., Nijhuis, T. A., Visser, T. & Weckhuysen, B. M. Real time
 quantitative Raman spectroscopy of supported metal oxide catalysts without the need of an
 internal standard. *Phys. Chem. Chem. Phys.* 7, 211-216 (2005).
- 411 37. Bjørgen, M. *et al.* Conversion of methanol to hydrocarbons over zeolite H-ZSM-5: On the origin of the olefinic species. *J. Catal.* 249, 195–207 (2007).
- 413 38. Database of Zeolite Structures. Available at: http://www.iza-structure.org/databases/.

414 415 416	39.	Mores, D. <i>et al.</i> Space- and Time-Resolved In-situ Spectroscopy on the Coke Formation in Molecular Sieves: Methanol-to-Olefin Conversion over H-ZSM-5 and H-SAPO-34. <i>Chem A</i> <i>Eur. J.</i> 14, 11320–11327 (2008).
417 418 419	40.	Borodina, E. <i>et al.</i> Influence of the Reaction Temperature on the Nature of the Active and Deactivating Species During Methanol-to-Olefins Conversion over H-SAPO-34. <i>ACS Catal.</i> 7 , 5268–5281 (2017).
420 421 422	41.	Hwang, A., Kumar, M., Rimer, J. D. & Bhan, A. Implications of methanol disproportionation on catalyst lifetime for methanol-to-olefins conversion by HSSZ-13. <i>J. Catal.</i> 346 , 154–160 (2017).
423 424	42.	Li, Y., Yu, J., Xu, R. Criteria for zeolite frameworks realizable for target synthesis. <i>Angew. Chem.</i> 52 , 1673-1677 (2013).
425 426	43.	Li, Y. & Yu, J. New stories of zeolite structures: Their descriptions, determinations, predictions, and evaluations. <i>Chemical Reviews</i> 114 , 7268–7316 (2014).
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444

445 Author Contributions

446 I.L.G and A.M.B. conceived and coordinated the project, in close collaboration with V.V.S.,

447 M.T. and I.V.S. I.L.G. performed the operando Kerr-Gated Raman experiments with support

- 448 from E.C., M.A.A., E.K.G., A.G. and I.V.S. The molecular simulations were performed by
- 449 A.E.J.H., M.B., K.D.W. and V.V.S. I.L.G, E.C., A.E.J.H., V.V.S., K.D.W., A.M.B, M.T. and

- 450 I.V.S. contributed to the data analysis and discussion. The manuscript was written by I.L.G.,
- 451 E.C., A.E.J.H., V.V.S. and A.M.B, with input from all authors.
- 452

453 **Competing Interests**

- 454 The authors declare no competing interests.
- 455

456 Methods

457 Catalyst synthesis

ZSM-5 zeolite (Si/Al=15) was supplied by Zeolyst International in the ammonium form
(CBV3024E), and the H-form of the zeolite material was obtained by calcination in air at 550
°C (2 °C.min⁻¹ to 120 °C, held for 30 min; and 5 °C.min⁻¹ to 550 °C, and 12 h at this
temperature). SAPO-34 material is commercially available (ACS Material).

462 SSZ-13 zeolite (Si/Al=15) was synthesized as described previously,⁴⁴ but using static 463 conditions. The sample was calcined in air (with the following temperature program: 1 464 °C.min⁻¹ to 120 °C, held for 2.5 h; 2.2 °C.min⁻¹ to 350 °C, and 3 h at this temperature; and 465 finally 0.8 °C.min⁻¹ to 580 °C, and held for 3 h). Identity and purity of the zeolite were 466 verified by XRD. Further characterization of the material (i.e. XRD, chemical analysis, ²⁷Al 467 NMR, NH₃-TPD, SEM and FT-IR) is reported in a previous study⁴⁵ and not repeated herein.

468 Operando Kerr-Gated Raman

The Kerr-Gated Raman Spectrometer was used at the ULTRA Facility of the Central Laser 469 Facility at the Rutherford Appleton Laboratory³²⁻³³. The laser source is a titanium sapphire 470 laser which emits at 800 nm. The beam is frequency doubled to 400 nm to produce the Raman 471 probe beam. About 10 mW average power was delivered to samples in pulses of 3 ps at 10 472 kHz repetitions. The spot size of the beam at the sample is 100 μ m and the sample was 473 474 rastered to minimize sample damage caused by the beam. CS₂ was used as a Kerr medium, 475 activated by the fundamental 800 nm beam of the laser. The arrival time of the excitation 476 pulse at the sample is adjustable with respect to the gating pulse. Several time delays are 477 measured at each acquisition to ensure that the optimal Raman signal is measured. Details on 478 the ULTRA laser system and the Kerr-Gate setup are provided in the ESI.

The reaction was performed in a commercially available CCR1000 stage by Linkam Scientific. The cell consists of a ceramic cup, which holds the solid catalyst on top of a ceramic fabric filter. This is placed inside the cell with quartz windows, where an inner heating element controls the temperature of the catalyst. The outer surface of the cell is cooled by a water cooling system. Gases enter the cell flowing down the catalyst bed. Gases enter a chamber in the cell where they flow upwards and then down over the catalyst bed. The cell outlet is carried to a Pfeiffer OmniStar MS to analyze the reaction products.

486 50 mg of catalyst was used in the experiments. Prior to the reaction, the catalyst was activated 487 at 550 °C (5 °C min⁻¹) under a 20% O_2 /He flow for 1 hour. He was flushed through the system to remove all O₂, and the catalyst cooled to 100 °C. He was used as a carrier gas at a

- flow of 30 ml min⁻¹. Methanol was injected into the system by use of a HPLC pump set to 1.7
- 490 μ l min⁻¹ corresponding to a WHSV of 1.6 h⁻¹, and flows allowed to equilibrate by monitoring
- the signals from the MS. Subsequently, the catalyst was heated up to 450 °C with a rate of 1
- 492 °C min⁻¹. After the experiment, the zeolite catalyst was cooled rapidly to 30 °C by the cooling
- 493 system of the cell, to quench the reaction.
- 494 Prior to beginning the reaction, Raman spectra of the calcined catalyst samples were 495 measured, using 5 accumulations of 20 seconds exposure to give a total 100 s exposure time. 496 During the reaction, 1 accumulation of 20 seconds exposure was used per measurement. This 497 allows time resolution of 20 seconds, to allow real-time investigation of the HP intermediates. 498 During temperature ramp experiments, measurements were taken every 10 °C.

499 Theoretical calculations

MD simulations were carried out with the CP2K simulation package (version 3.0)⁴⁶ at a Density Functional Theory (DFT) level of theory combined with a Gaussian and plane wave basis set (GPW).⁴⁷ The revPBE-D3 functional⁴⁸ with a DZVP-GTH basis set and pseudopotentials were selected,⁴⁹ as done previously,⁵⁰ with a plane wave cutoff of 400 Ry. All simulations were performed in a periodic zeolite unit cell representing the CHA topology containing 36 T-sites and two Brønsted acid sites, corresponding to a Si/Al ratio of 17 -which is close to the experimental value of 15.

- 507 A large set of MD simulations were performed encompassing the empty zeolite, a methanol loaded zeolite and a broad variety of alkene, polyene and aromatic adsorbates (Fig. S5). For 508 each guest molecule, cell parameters were obtained by computing time-averaged values from 509 a 50 ps NPT MD simulation at 350 °C and atmospheric pressure. The temperature and 510 pressure were controlled via a chain of 5 Nosé-Hoover thermostats and an MTK barostat, 511 respectively.⁵¹ An integration time step of 0.5 fs was applied. Production MD runs used as 512 input for the Raman spectra and mobility analysis were carried out in the NVT ensemble at 513 350 °C for 40 ps, with the unit cell parameters as listed in Table S2, preceded by an 514 equilibration of 2.5 ps. 515
- 516 Theoretical Raman spectra were obtained via Fourier transforms of the autocorrelation
- 517 functions of the polarizability tensor.⁵² Therefore, the polarizability tensor was derived every
- 2 fs through a finite difference approach.⁵³ For more details we refer to the ESI.
- 519

520 Data Availability

521 Source data for Figs. 1-6, S3-S4, S38-42 are provided with the paper. Example CP2K input 522 files and processing scripts are available from the public GitHub online repository at 523 <u>https://github.com/AlexanderHoffman/supporting-info</u>. Due to the size of the MD trajectories

- and CP2K output files, they are available upon author request.
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- 44. Moliner, M., Franch, C., Palomares, E., Grill, M. & Corma, A. Cu–SSZ-39, an active and hydrothermally stable catalyst for the selective catalytic reduction of NOx. *Chem. Commun.*48, 8264-8266 (2012).
- 45. Lezcano-Gonzalez, I. *et al.* Determining the storage, availability and reactivity of NH ₃ within
 Cu-Chabazite-based Ammonia Selective Catalytic Reduction systems. *Phys. Chem. Chem. Phys.* 16, 1639–1650 (2014).
- Hutter, J., Iannuzzi, M., Schiffmann, F. & VandeVondele, J. cp2k: atomistic simulations of
 condensed matter systems. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 4, 15–25 (2014).
- Lippert, G., Hutter, J. & Parrinello, M. The Gaussian and augmented-plane-wave density
 functional method for ab initio molecular dynamics simulations. *Theor. Chem. Accounts Theory, Comput. Model. (Theoretica Chim. Acta)* 103, 124–140 (1999).
- 48. Yang, K., Zheng, J., Zhao, Y. & Truhlar, D. G. Tests of the RPBE, revPBE, τ-HCTHhyb,
 wB97X-D, and MOHLYP density functional approximations and 29 others against
 representative databases for diverse bond energies and barrier heights in catalysis. *J. Chem. Phys.* 132, 164117 (2010).
- 542 49. Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* 54, 1703–1710 (1996).
- 544 50. Cnudde, P. *et al.* How Chain Length and Branching Influence the Alkene Cracking Reactivity
 545 on H-ZSM-5. *ACS Catal.* 8, 9579–9595 (2018).
- 546 51. Frenkel, D. & Smit, B. Understanding Molecular Simulation. (Academic Press: San Diego, 2002).
- 548 52. Luber, S., Iannuzzi, M. & Hutter, J. Raman spectra from *ab initio* molecular dynamics and its application to liquid *S*-methyloxirane. *J. Chem. Phys.* 141, 094503 (2014).
- 53. Thomas, M., Brehm, M., Fligg, R., Vöhringer, P. & Kirchner, B. Computing vibrational
 spectra from ab initio molecular dynamics. *Phys. Chem. Chem. Phys.* 15, 6608-6622 (2013).