Supporting Information

Bridging the Gap between the Direct and Hydrocarbon Pool Mechanisms of the Methanol-to-Hydrocarbons Process

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S I. Experimental: Materials and Methods

All reactions and sample treatments were carried out under nitrogen atmosphere, unless specified otherwise. The H-SAPO-34 and $^{12}$C-methyl acetate ($\geq$98%, W267600 Aldrich, CAS: 79-20-9; N.B.: impurity is methanol. For consultation, $^1$H and $^{13}$C NMR spectra are available at: https://www.sigmaaldrich.com/spectra/fnmr/FNMR002387.PDF) / 1,2-$^{13}$C$_2$-methyl acetate ($\geq$98%, $\geq$99 $^{13}$C -atom%, 900536 Aldrich; N.B.: CAS number of this product is not mentioned, as it is not a commercially available material. ‘This product can be packaged on demand’ from Sigma-Aldrich) were purchased from ACS material and Sigma Aldrich, respectively. The characterization details of the H-SAPO-34 material under study were included in our previous publication.[1] Although this commercially available H-SAPO-34 material is already detemplated, an additional calcination/pre-treatment has always been performed prior to the reaction according to the following procedure under O$_2$ environment (flow rate of 20 mL/min): heating to 623 K at 15 K/min and keeping the sample at this temperature for the next 10 min, then heating the sample to 823 K at a rate of 5 K/min and hold there the sample for the next 90 min. Finally, the sample was cooled down to 673 K with a rate of 10 K/min under a flow of N$_2$ gas (rate of 20 mL/min). All reactions were performed using a Linkam cell (THMS600) equipped with a temperature controller (Linkam TMS94) and its lid is equipped with a quartz window. Details of the set-up can be found in previous publications from our group.[1,2] The UV-vis diffuse reflectance spectroscopy (DRS) measurements were performed with a CRAIC 20/30 PV™ UV-vis-NIR micro-spectrophotometer using a 15X objective. A 75 W Xenon lamp was used for illumination. The on-line gas phase product analyses were performed by a Pfeiffer OmniStar GSD 320 O3 (1-300 amu) mass spectrometer (MS), which was directly connected to the outlet of the Linkam cell. The mass spectrometry database from the National Institute of Standards and Technology (NIST) was consulted for referencing purposes (Figure S4).

For solid-state NMR measurements, post-reacted sample was transferred to a 3.2 mm rotor. All experiments were performed on a Bruker 700 MHz standard-bore magnet with an AVANCE-III console and equipped with a 3.2 mm triple channel Efree HCN probe. All experiments were performed at room temperature (set temp.: 290 K; effective temp.: 295-298K) and a MAS frequency of 12, 15 or 18 kHz. Note that an effective sample temperature is slightly higher (5-10 degrees) here due to the frictional heating. Referencing of $^1$H and $^{13}$C chemical shifts was done externally to adamantane. $^1$H and $^{13}$C pulses were applied with field strength of 71.5 and 50 kHz, respectively. 71.5kHz SPINAL64$^{[3]}$ $^1$H decoupling was applied during acquisition for the 1D and 2D $^{13}$C detected spectra. The 1D $^1$H-$^{13}$C cross-polarisation (CP) spectrum was recorded using a 2 s recycle delay, 11 ms acquisition time and an accumulation of 4096 scans. Cross-polarization was achieved using a 40
kHz $^{13}$C field and 67 kHz 70-100% ramped $^1$H field during 1ms. The 1D $^{13}$C direct excitation (DE) spectrum was recorded using a 4 s recycle delay, 11 ms acquisition time and an accumulation of 4096 scans. The 1D $^1$H-$^{13}$C insensitive nuclei enhanced by polarization transfer (INEPT)\cite{4} spectrum was recorded using a 1.5 s recycle delay, 11 ms acquisition time and an accumulation of 8192 scans. 1D CP and DE spectra were processed using 10Hz line-broadening and 50Hz line-broadening was used for the INEPT spectrum. 2D $^{13}$C-$^{13}$C spectra were recorded using a 2 s recycle delay, 11 ms (CP) or 10.8 ms (DE) (F2) and 4ms (CP) or 5.7ms (DE) (F1) acquisition time and an accumulation of 112 (both CP and DE) scans. $^{13}$C-$^{13}$C mixing was achieved through proton-driven spin-diffusion using Phase-alternated-recoupling-irradiation-schemes (PARIS) for 120ms and 200ms.\cite{5} The 2D CP and DE $^{13}$C-$^{13}$C spectra were processed using a 0.5 $\pi$ shifted sine squared window function in both dimensions. 2D $^1$H-$^{13}$C spectrum was recorded using a 1.5 s recycle delay, 10.4ms (F2) or 10.7 ms (F1) acquisition time and an accumulation of 128 scans. 145 Hz for J was used in the INEPT delay. Prior to Fourier transformation, a window function corresponding to a 0.5 $\pi$ shifted sine squared function was applied to both dimensions. 2D $^{13}$C-$^{13}$C TOBSY was recorded using a mixing time of 4.3 ms, a 1.5 s recycle delay and 15ms (F2) or 5.7 ms (F1) acquisition time using 128 scans.\cite{6} The spectrum was recorded using 145 Hz for J in the INEPT delay and processed using a 0.33 $\pi$ shifted sine squared window function in both dimensions. For all J based spectra, 10kHz WALTZ $^1$H decoupling was used during detection.\cite{7} All NMR spectra were processed with Bruker Topspin3.5 and analysed using SPARKY.\cite{8} Assignments of the identified spin-systems in the NMR spectra are summarised in Table S1. Additional spin-systems identified in the 2D spectra that could not be definitively assigned to a molecular structure are listed in the Table S2.

The methyl acetate-to-hydrocarbon (MATH) reactions were performed without any pressing and sieving of the H-SAPO-34 material. *Operando* UV-vis diffuse reflectance spectroscopy (DRS) reactions were performed using ~30 mg of the catalyst material. Initially it was placed on the heating stage of Linkam cell, which was further connected to water cooler. The inlet of the reactor was connected to the N$_2$ gas line, *via* a methyl acetate saturator, whereas outlet is either connected to the Pfeiffer mass spectrometer or vented out. The lid of the Linkam cell is equipped with a quartz window to monitor the reaction by UV-vis DRS. Prior to each UV-vis DRS, the H-SAPO-34 material was further pre-treated/calcined according to the procedure described above. The sample was then cooled down to 673 K (the reaction temperature) with a rate of 10 K/min under a flow of N$_2$ gas. Finally, a N$_2$ flow of 20 mL/min was introduced at 673 K to a saturator with methyl acetate. The UV-vis DRS were recorded every 30 s interval during the MATH experiment, which typically took
30 min. Finally, the reaction was quenched by rapid cooling of the Linkam cell, by using a Linkam TMS94 temperature controller.

SII. Extended Supplementary Discussion

Solid-state NMR spectroscopic studies indicated 1, 2, 4, 5-tetramethylbenzene as possibly the highest methylated aromatic species present in the arene cycle of the dual-cycle based hydrocarbon-pool (HCP) mechanism during H-SAPO-34 catalyzed MATH reaction (Figure 2, Scheme 2). This observation is very similar to that proposed by Wang et al., where they have theoretically proven that 1, 2, 4, 5-tetramethylbenzene is the primary component of arene cycle within the CHA-framework zeolites during the methanol-to-hydrocarbon (MTH) process. An absence of the methanol (the actual reactant/alkylating agent of the MTH process) under our present experimental condition restricted arene species to form fully methylated benzenes (e.g. hexa-/hepta-methylbenzene) during the MATH reaction. This interpretation is also consistent with earlier literature reports.\[^{1,10}\] Such highly methylated benzene species is widely-acknowledged as the most influential/governing HCP species during CHA-zeolite catalyzed MTH process.\[^{1,10–13}\] Therefore, further oligomerization or methylation is not possible in absence of an alkylating agent (i.e. methanol) under our current MATH reaction condition. It fundamentally allowed us to detect only those HCP species, which were exclusively derived from the ‘direct C-C bond containing’ acetyl group of the methyl acetate.\[^{1}\] Although clearly detected in the mass spectrometry, it is also worth mentioning that the lack of NMR response for alkoxy (55-70 ppm) and acetal (90-100 ppm) groups was due to the non-isotope enrichment of methoxy-carbon of methyl acetate in the present study (Scheme 1 & Figure S1).
Scheme S1. Plausible reaction routes to the formation of olefins from ketene, via alkylation-decarbonylation pathway, as theoretically postulated by Plessow and Studt.\textsuperscript{[14,15]} CO of ketene is neither consumed nor incorporated itself in the HCP species.\textsuperscript{[16]} Thus, CO should also be regarded as one of the co-catalysts in the zeolite-catalyzed methanol-to-hydrocarbon process.
**Figure S1.** *Operando* UV-vis diffuse reflectance spectra of H-SAPO-34 being exposed for (a) 0-5 min and (b) 5-30 min to the methyl acetate at 673 K. (c) 3D plot of the UV-vis diffuse reflectance
spectra and (d) change of the absorbance as a function of reaction time.\textsuperscript{[1]} The observed bands at ~297, 350, 419, and 624 nm could be attributed to the neutral methylated benzenes, dienylic carbocationic/methylbenzenium ions, trienylic/highly methylated arenium ions, and methylated poly-arenium ions/highly conjugated polyenes, respectively.\textsuperscript{[1]} Spectral features during the first 5 min of reaction (in a), as absorption bands at ~297, 350, 419, and 624 nm increase in intensity as a function of reaction time (in b-d).\textsuperscript{[1]} A decrease in intensity was observed only in the case of the 624 nm band, which could be attributed to the existence of intra-molecular transformation within the zeolite framework. The time-dependent mass-spectral profiles for (e) methane, methanol, dimethyl ether (DME), dimethoxymethane (DMM), ethylene and propylene as major products and (f) butylene, and tetramethylethylene (TME)/a structural isomer of C\textsubscript{6}H\textsubscript{12} as minor products in the effluent gas-stream.\textsuperscript{[1]} Interestingly, a substantial quantity of DMM was observed from methyl acetate, whereas only traces of DMM were detected previously during the H-SAPO-34 catalyzed methanol-to-hydrocarbon reaction.\textsuperscript{[1]} It is implying that the dominant existence of Koch-carbonylation reaction in the present case due to the presence of a carbonylated substrate.
**Figure S2.** 2D $^{13}$C-$^{13}$C MAS solid-state NMR spectra of rigid molecules measured at 290 K, 12 kHz, 700 MHz. a) Polarization of $^{13}$C atoms was achieved through cross-polarization (CP, purple, on the left) or direct-excitation (DE, blue, on the right) and a 120 ms PARIS mixing period was used. Grey boxes indicate spinning side bands. b) Zoom from the overlay of 2D $^{13}$C-$^{13}$C CP and DE MAS spectra, showing the broadening of the signal of the carbonyl resonances and aromatic/olefinic signals in the CP-based spin diffusion spectrum compared to the DE-based spectrum.
Figure S3. 2D $^{13}$C-$^{13}$C MAS solid-state NMR spectra measured at 290 K, 12 kHz, 700 MHz. The polarization of $^{13}$C atoms was achieved through direct-excitation (DE) and a 200ms PARIS mixing period was used. Grey boxes indicate spinning side bands. The $^{13}$C-$^{13}$C correlations in the carbonyl region (zoomed section in this figure) could be attributed to the surface acetate type moieties (Species C in the Scheme 2 of the manuscript).\cite{1}
**Figure S4.** The mass spectrometry profile of H-SAPO-34 being exposed to the methyl acetate at 673 K for 30 min under operando condition. (a) Two representatives full range mass-spectrum at the beginning (5 min, in black) and end (30 min, in red) of the reaction. The time-dependent mass-spectral profiles of products of interest could be found in the Figure S1e,f. The mass spectrometry database from the National Institute of Standards and Technology (NIST) was consulted for referencing purposes. The full spectrum is overwhelmed by the carrier gas, nitrogen (N$_2$: 28, 14 amu) and the unreacted reactant, methyl acetate (MA: 75, 43 amu). (b) Zoom of 10-45 amu region, illustrating nitrogen (N$_2$: 28, 14 amu), methane (CH$_4$: 16 amu), water (H$_2$O: 18 amu), ethylene (C$_2$H$_4$: 26 amu), methanol (CH$_3$OH: 31, 32 amu), propylene (C$_3$H$_6$: 41 & 39 amu), methyl acetate (MA: 43 amu) and dimethyl ether (DME: 45 amu). It should be noted that m/z=26 amu belongs to the secondary peak of ethylene, while its 100% relative abundance peak at m/z=28 amu is
overlapping with a peak originating from the carrier gas, nitrogen. (c) Zoom of 50-85 amu region, illustrating butylene (C₄H₈: 56, 55 amu), methyl acetate/acetic acid (MA/AA: 60 amu), methyl acetate (MA: 74 amu), dimethoxymethane (DMM: 75 amu), and tetramethylethylene (TME: 84 amu). It should be noted that m/z=75 amu was considered for DMM as its secondary peak, while its 100% relative abundance peak at m/z=45 amu is overlapping with a peak originating from DME.
SV. Supplementary Tables

*Table S1.* Overview of the assigned solid-state NMR spin-systems from the reaction intermediates observed in this work. Atoms, as observed in our solid-state NMR experiments along with their assigned chemical shifts (in ppm), are given in this table only. Due to the overlap of signals, even in the 2D spectra, some signals could not be assigned to a specific atom.

| Structure | Chemical Shifts |
|-----------|-----------------|
| Zeolite   |                 |
|           | 127.8 (Ca)      |
|           | 131.6 (Cb)      |
|           | 140.9 (Cc)      |
|           | 22.8 (Cd)       |
|           | 132.6 (Cb)      |
|           | 136.4 (Cc)      |
|           | 21.2 (Cd)       |
|           | 131.7 (Cb)      |
|           | 138.0 (Cc)      |
|           | 22.8 (Cd)       |
|           | 32.6 (Ca)       |
|           | 23.9 (Cb)       |
|           | 1.31 (Ha)       |
|           | 0.79 (Hb)       |
|           | 27.0 (Ca)       |
|           | 14.8 (Cb)       |
|           | 1.16 (Ha)       |
|           | 0.77 (Hb)       |
|           | 18.6 (Ca)       |
|           | 18.0 (Cb)       |
|           | 1.20 (Ha)       |
|           | 0.79 (Hb)       |
|           | 7.71 (Ca)       |
|           | 0.7 (Ha)        |
**Table S2.** Remaining spin-systems unassigned in solid-state NMR. Data for rigid (denoted as CP, observed in CP $^{13}$C-$^{13}$C correlation spectrum), restricted mobile (denoted as DE, observed in DE $^{13}$C-$^{13}$C correlation spectrum) and purely mobile (denoted as M, observed in INEPT-TOBSY $^{13}$C-$^{13}$C correlation spectrum) molecules/fragments.

| Name  | $^{13}$C$_a$ | $^{13}$C$_b$ | $^{13}$C$_c$ | $^1$H$_a$ | $^1$H$_b$ | $^1$H$_c$ |
|-------|-------------|-------------|-------------|-----------|-----------|-----------|
| DE6   | 182.2       | -           | 23.2        | -         | -         | -         |
| DE6’  | -           | -           | 23.3        | -         | -         | 2.19      |
| DE7   | 180.8       | 22.4        | -           | -         | -         | -         |
| DE8   | 179.9       | -           | 20.6        | -         | -         | -         |
| DE9   | 184.9       | 24.0        | 23.9        | -         | -         | -         |
| CP20  | 42.3        | 22.9        | -           | -         | -         | -         |
| CP21  | 49.8        | 35.3        | -           | -         | -         | -         |
| M32   | 26.5        | -           | -           | 0.78      | -         | -         |
| M35   | 13.0        | -           | -           | 0.74      | -         | -         |
| M37   | -           | 130.7       | -           | -         | 7.26      | -         |
SVI. Supplementary References

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