Electronic Supporting Information

Getting zeolite catalysts to play your tune: methyl carboxylate esters as switchable promoters for methanol dehydration to DME

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1. Reagents

Zeolite catalysts SSZ-13 SAR 24 (Product code ZD08028), ZSM-5 SAR 23 (Product code CBV2314), ZSM-5 SAR 50 (Product code CBV5524G), ZSM-5 SAR 80 (Product code CBV8014), beta SAR 25 (Product code CP814E) and mordenite SAR 20 (Product code CBV21A) were all obtained from Zeolyst International in the ammonium form. We thank Zeolyst International for supplying the SSZ-13 sample for research purposes. Zeolite catalyst ZSM-11 SAR 50 (Product code MZ110012) in its ammonium form was obtained from ACS Material. MCM-41 SAR 79 (Product code 643653) was obtained from Sigma-Aldrich. γ-Alumina was obtained from BASF (Product code SAS 200). The zeolite and MCM-41 catalysts were calcined in air at 500 °C before testing, see procedure below. Silicotungstic acid (STA) was obtained from Nipon Organic Chemicals. Carborundum (Product code C/3091/53, 80 grit) was obtained from Fisher Scientific. Silica (Davicat SP550-10013, G57) was obtained from Grace. Helium (CP grade, 99.999%) and nitrogen (oxygen free, 99.998%) gases were obtained from BOC. Table S1 below provides details of the organic chemicals used in the experiments.

Table S1

Chemical	**Supplier**	**Product Number**
Methanol	Honeywell	34860
Methyl formate	Sigma-Aldrich	291056
Methyl acetate	Alfa Aesar	L14475
Methyl propionate	Sigma-Aldrich	109258
Methyl n-butyrate	Sigma-Aldrich	246093
Methyl n-pentanoate	Sigma-Aldrich	148997
Methyl n-hexanoate	Sigma-Aldrich	W270806
n-Butyric acid	Acros Organics	10811-0010
Dimethyl malonate	Acros Organics	220702500
Dimethyl succinate	Acros Organics	150731000

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Dimethyl glutarate	Acros Organics	116231000
Dimethyl adipate	Sigma-Aldrich	186252
Dimethyl pimelate	Sigma-Aldrich	180068
Ethanol	VWR Chemicals	20821.300
Ethyl formate	Sigma-Aldrich	W243418

Prior to use all the liquid feeds were analysed for organic impurities. All the feeds used in the experiments contained less than 0.1 wt. % combined of ketones, aldehydes, ketals and acetals. The samples were also analysed for organic nitrogen-containing impurities by gas chromatography using nitrogen chemiluminescence detection. For all the liquid feeds used the total organic nitrogen content was < 0.2 ppm (mass) as nitrogen.

The methyl acetate supplied was found to contain ~200 ppm by mass of 1,1-dimethoxyethane. The methyl acetate was treated by taking 150 ml, adding 0.1 ml of deionised water and stirring the mixture at room temperature over 5g of H-mordenite for 1 hour. The zeolite was filtered off and the resultant solution was partially purified of the produced acetaldehyde (identified by GC) by distilling off about 30 ml of acetaldehyde enriched methyl acetate. The remaining solution used in catalyst testing contained less than 1 ppm of 1,1-dimethoxyethane and ~30 ppm of acetaldehyde.

2. Catalyst preparation

2.1 Silicotungstic acid supported on silica

30.1g of silica was added to a solution of 14.30g silicotungstic acid in 39.9g water. The silica/silicotungstic acid solution was left to stand for 30 minutes before being oven dried at a temperature of 120 °C for a period of 16 hours. The dried catalyst material was then cooled to 50 °C, with 40.93g of dried catalyst being recovered.

2.2 Catalyst calcination

The zeolite catalysts were converted from their ammonium-form into their H-form by calcination under air at 500 ºC by placing a shallow bed (< 1 cm depth) of the catalyst, typically 5 to 10 g, in a ceramic dish in a furnace (Carbolite, AAF 11/18). The furnace was heated using the following temperature programme:

- Room temperature to 90 °C over 20 minutes then hold for 120 minutes.
- 90 °C to 110 °C over 20 minutes then hold for 120 minutes.
- 110 °C to 500 °C over 80 minutes then hold for 240 minutes.
- Cool to < 90 ºC, after which the sample was transferred to a sealed vial.

The MCM-41 catalyst was also calcined using the above procedure.

2.3 Catalyst preparation for testing

Prior to testing the calcined zeolite and MCM-41 powders were pressed, crushed and sieved to the required size range (100 to 200 µm). A sample of the powder, typically 0.5 to 1.5 g, was compacted at 12 tonnes in a 32 mm die set using a pneumatic press. The sample was then gently ground using a pestle and mortar and sieved to a particle size fraction of 100 to 200 µm diameter. The silicotungstic acid/silica and γ-alumina catalysts were crushed and sieved to the same particle size fraction.

3. Catalyst testing, additional results and discussion

The methanol dehydration reactions were carried out using a 16-channel parallel fixed-bed reactor Flowrence™ system from Avantium N.V., using stainless steel reactors of 2mm internal diameter with a length of 300 mm. The liquid feed was introduced by a HPLC pump into a heated zone (493 K) along with inert gas feeds before feeding to the reactors. In a typical experiment fifteen of the reactors were packed with 25 ±0.5 mg of catalyst, having a particle size fraction of 100 to 200 µm diameter. The catalyst was loaded on top of a 6cm deep bed of an inert material, carborundum (silicon-carbide). The reactor volume above the catalyst was also packed with carborundum. The sixteenth reactor was packed with carborundum only. After a gas distribution test each reactor was heated, under a flow of inert gas (nitrogen mixed with helium at a volumetric ratio of 10:1 at 2.68 normal litres per hour per reactor), to a reaction temperature of 150°C (423 K) at a total pressure of 1100 kPa. After 1 hour at 423 K a gaseous feed comprising 10 mol% methanol and inert gas (nitrogen mixed with helium as an internal standard, with a volumetric ratio of 10:1) was then introduced into each reactor for a period of 24 hours. The total volumetric feed rate of the gases and vaporised liquid feed was 2.98 normal litres per hour per reactor. After 24 hours an additional organic component (e.g. a methyl mono-carboxylate ester) was added to the feed to achieve a gaseous feed comprising 10 mol% methanol and 5 mol% organic additive (relative to methanol), with the nitrogen flow being reduced to keep the total volumetric feed rate of the gases and vaporised liquid feed at 2.98 normal litres per hour per reactor. The effluent stream from each reactor was diluted with inert gas (nitrogen) and was periodically analysed by online gas chromatography to determine the yield of dimethyl ether (DME) product. Space time yields (STY) in grammes per kilogramme of catalyst per hour (g kg^{-1} h^{-1}) for making DME from methanol were determined between 18 and 24 hours after introducing the methanol only feed. Space time yields for making DME from methanol in the presence of an additional organic component were determined between 18 and 24 hours after introducing the organic additive. In some instances, data for the impact of more than one methyl ester co-feed was collected in the same experiment (for methyl formate and methyl n-hexanoate, and for methyl propionate and methyl n-butyrate) by flushing the reactors with methanol only for 24 hours after the first methyl ester co-feed was tested. This cleanly returned the catalysts to the performance originally observed at the end of the first period when it was tested with methanol only.

The DME STY for the zeolite catalysts tested with methanol only feed in Figure 1 are the average of two measurements taken towards the end of each period when methanol only was fed. The DME STY yield for H-ZSM-5 SAR 80 with the methanol only feed in Figures 2, 3 and S2 is the average of eleven measurements taken from different experiments, 405 ±47 g kg^{-1} h^{-1}. The DME STY data plotted in Figure 3 was collected in an additional four dedicated experiments in which the catalyst was conditioned with methanol only for a period of typically 24 hours and then different concentrations of ester feed were tested in sequence. The ester co-feed was fed for a period of between 9 and 44 hours until a steady state of DME make was observed. Longer periods were required to reach steady state when co-feeding the esters at very low concentrations, for example when switching from methanol only to methanol containing dimethyl adipate at 0.001 mol % relative to methanol. The DME STY measurement for each co-feed concentration was taken in the last 3 hours of its testing period, ensuring that the measurement was taken when a steady state of DME make was achieved.

The data in Figure 4 was all collected in the same experiment using an adaption of the typical reaction protocol described above, with the alcohol (methanol or ethanol) fed at 10 mol % relative to the total gaseous feed. In the first phase ethanol only was fed for 26 hours, before switching the feed to ethanol dosed with 5 mol % ethyl formate relative to ethanol for 23 hours and then back to ethanol only for 20 hours. In the second phase of the experiment methanol was then fed for 32 hours, followed by methanol dosed with 5 mol % methyl n-hexanoate relative to methanol for 26 hours and then back to methanol only for 39 hours.

The impact of co-feeding n-butyric acid along with methanol was determined for the H-ZSM-5 SAR 80 catalyst using an adaption of the typical reaction protocol described above, with the n-butyric acid fed at 5 mol % relative to the methanol. In the first phase methanol only was fed for 48 hours, before switching the feed to methanol dosed with 5 mol % n-butyric acid relative to methanol for 42 hours. The DME STY in the presence of 5 mol % n-butyric acid was 1119 g kg^{-1} h^{-1}, measured 24 hours after first introducing the n-butyric acid co-feed. GC analysis of the reactor effluent indicated that the n-butyric acid had been largely (> 90%) converted to methyl n-butyrate.

The impact of methanol partial pressure on DME STY was determined via an adaption of the typical reaction protocol described above, with the methanol mol % in the total feed being varied whilst keeping the total volumetric feed rate of the gases and vaporised liquid feed at a constant 2.98 normal litres per hour per reactor. The nitrogen flow was varied to keep the total volumetric feed rate of the gases and vaporised liquid feed constant. The results are presented in Figure S1.

The impact of co-feeding a homologous series of dimethyl di-carboxylate esters on DME STY was determined for H-ZSM-5 SAR 80 via an adaption of the reaction protocols described above. The di-esters were fed at 0.1 mol % (1000 ppm) relative to methanol and the results are presented in Figure S2.

The impact of homologous series of methyl carboxylate esters on Brønsted acid site turnover frequency to DME is compared in Figure S3 for H-ZSM-5 with a SAR of 50 and 80. These materials had different Brønsted acidities as determined by ammonia TPD (see Section 5) but very similar turn over frequencies to DME on a per Brønsted acid site basis across the entire range of esters tested in Figure S3. γ-Alumina, a catalyst containing Lewis acid and weak Brønsted acid sites, was also tested with methanol only and with methyl acetate, methyl propionate and methyl n-butyrate, each added at 5 mol % relative to methanol, using the standard protocol described above at 423 K. Under these conditions the DME STY was less than 5 g kg^{-1} h^{-1} in all cases, with only very weak signs of promotion when esters were co-fed. This data supports the view that Brønsted acid sites in the zeolites play a key role in the promotional chemistry. Of further note here is the observation that clear promotion by methyl esters is also seen with silicotungstic acid/silica, see Figure 4, which is a strong Brønsted acid catalyst.

All the methanol dehydration reactions conducted were observed to form DME with high selectivity, with negligible formation of hydrocarbons. A representative GC trace is shown in Figure S4 of the reactor effluent for a reaction which used 10 mol % methyl n-hexanoate as a promoter with H-ZSM-5 SAR 80 as the zeolite catalyst. The only significant by-product observed was trace amounts of dimethoxymethane, formed with a selectivity of 0.3% at a methanol conversion of 23%.

The impact of space velocity on methanol conversion and selectivity to DME was tested for H-ZSM-5 SAR 50 using methanol only and methanol plus 5 mol % methyl n-pentanoate by varying the amount of catalyst tested from 25 to 200 mg. The selectivity to DME was high across the entire conversion range observed and for the methyl n-pentanoate ester promoted reaction was greater than 99% for methanol conversions as high as 70%, Figure S5.

The apparent activation energy was determined for H-ZSM-5 SAR 80 with methanol and methanol plus 10 mol % methyl n-hexanoate using 25 mg of catalyst diluted with 50 mg of carborundum. The data was collected in a temperature range such that the methanol conversion was kept below 7%. An Arrhenius plot of the data collected is shown in Figure S6. The apparent activation energy for methanol only was determined to be 109 kJ mol^{-1}, whilst in the presence of the methyl n-hexanoate it was found to be lowered to 83 kJ mol^{-1}. Figure S6 also shows that methanol dehydration to DME is significantly promoted at temperatures as low as 383 K (110°C).

4. Additional Figures

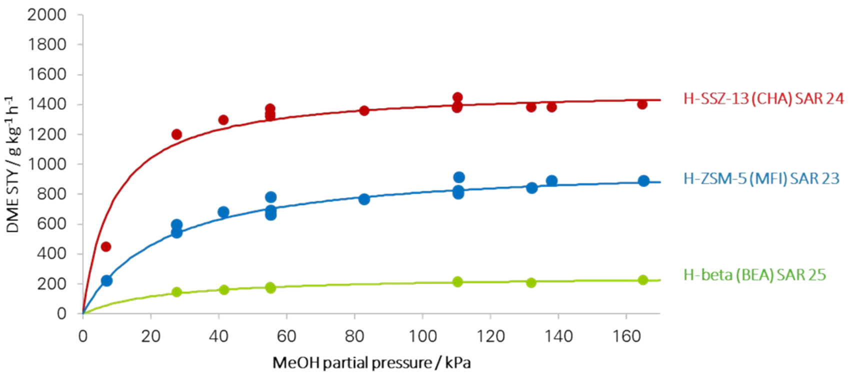

Fig. S1 Impact of methanol partial pressure in bar on DME STY for three different zeolites. Conditions: 423 K, methanol WHSV 1.07 to 25.1 h^{-1}, methanol partial pressure 7 to 165 kPa.

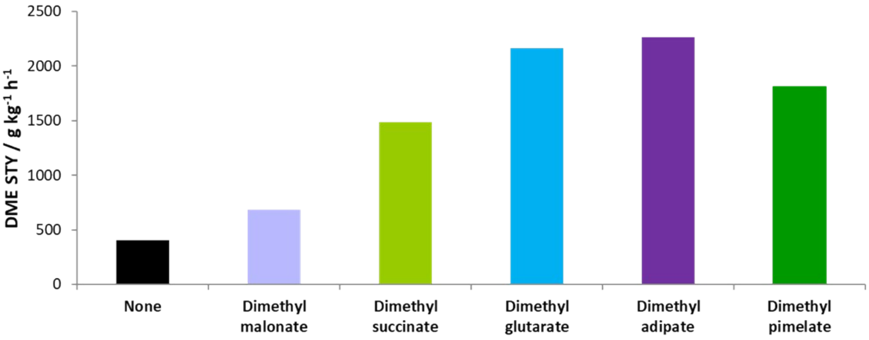

Fig. S2 Impact of co-feeding various dimethyl di-carboxylate esters, $[(CH_2)_n(CO_2Me)_2]$ n = 1 to 5, on DME STY for H-ZSM-5 SAR 80. Conditions: 423 K, methanol WHSV 17.1 h^{-1}, methanol partial pressure 110 kPa and di-ester partial pressure 0.11 kPa. Black bar methanol only data.

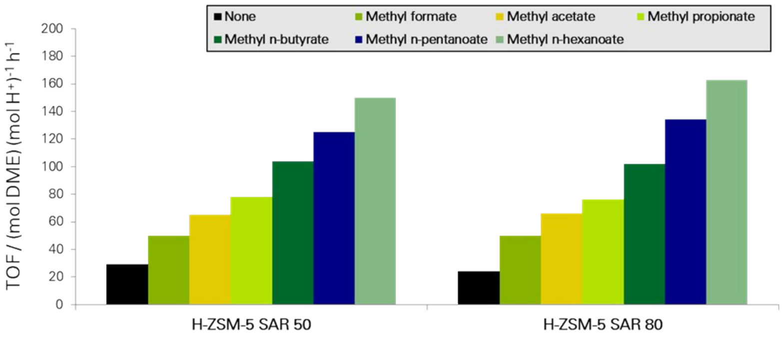

Fig. S3 Impact of co-feeding various methyl carboxylate esters on Brønsted acid site turnover frequency to DME for H-ZSM-5 SAR 50 and SAR 80. Conditions: 423 K, methanol WHSV 17.1 h^{-1}, methanol partial pressure 110 kPa and ester partial pressure 5.5 kPa. Black bar methanol only data.

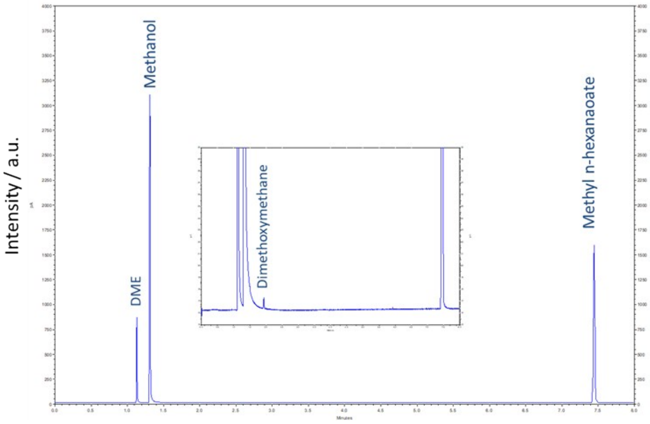

Fig. S4 GC chromatogram of products and by-products observed with H-ZSM-5 SAR 80 at a methanol conversion of ca. 23% as tested in Figure 3. Conditions: 423 K, methanol WHSV 17.1 h^{-1}, methanol partial pressure 110 kPa and methyl n-hexanoate partial pressure 11 kPa.

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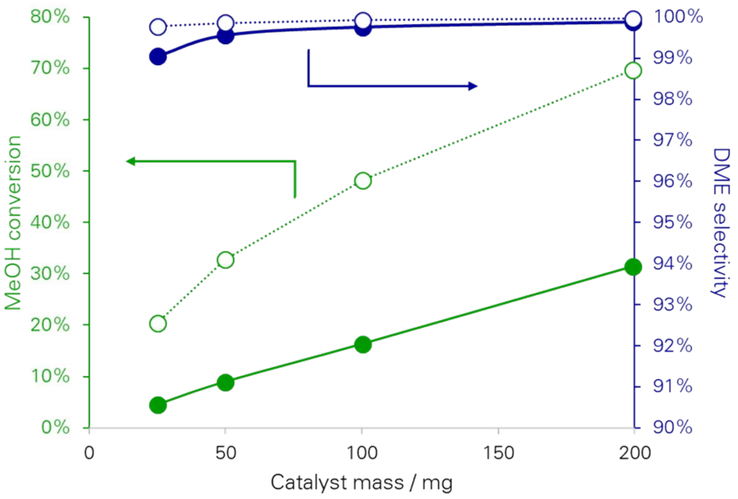

Fig. S5 Impact of feeding methanol only (filled circles) and methanol plus methyl n-pentanoate (hollow circles) on methanol conversion (green circles) and selectivity (blue circles) to DME for H-ZSM-5 SAR 50 tested with different amounts of catalyst. Conditions: 423 K, methanol WHSV 2.1 to 17.1 h^{-1}, methanol partial pressure 110 kPa and ester partial pressure 5.5 kPa.

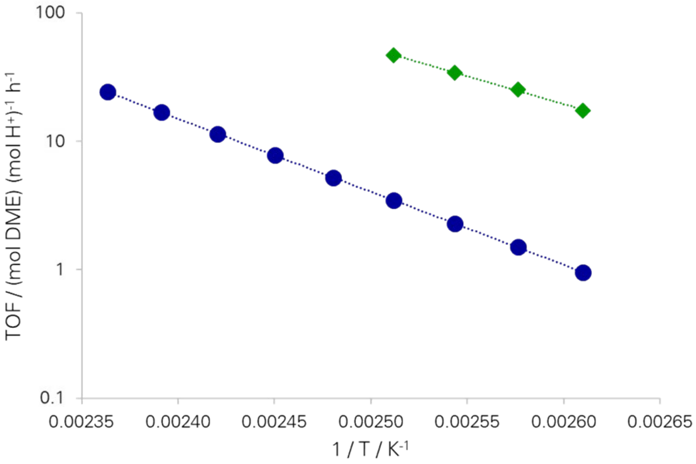

Fig. S6 Arrhenius plot for H-ZSM-5 SAR 80 with MeOH only feed (blue circles) and MeOH plus methyl n-hexanoate feed (green diamonds). Conditions: methanol WHSV 17.1 h^{-1}, methanol partial pressure 110 kPa and ester partial pressure 11 kPa, temperature range 383 to 423 K for methanol only feed and 383 to 398 K for ester containing feed.

5. Ammonia TPD

Ammonia temperature programmed desorption analysis was carried out using a fully automated Altamira AMI-200 Chemisorption Analyser. Approximately 50mg of sample was accurately weighed into a quartz U-shaped reactor tube. The reactor tube outlet was plugged using quartz wool that had been pre-treated in an oven at 120°C. The reactor tube was then placed in the AMI-200 unit and pre-treated in-situ under a flow of dry argon, heating from room temperature to 400°C at 10°C/min and dwelling for 60mins. Following drying, the sample was cooled to 100°C and NH_3 loading was carried out by flowing a 1% NH_3/Ar mix (30ml/min) for 60 minutes (or until saturation was reached). Whilst maintaining the bed temperature at 100°C, any physisorbed and other weakly adsorbed material was then purged from the surface by treating with water vapour for 60 minutes. Once physisorbed and other weakly adsorbed material had been removed, the sample was further treated with a flow of dry argon at 100°C for 60 minutes in order to remove any residual water from the sample bed. Finally, TPD analysis was carried out by heating the sample from 100°C to 800°C at a rate of 5°C/min under flowing argon (30ml/min). NH_3 desorption was continually monitored throughout using a Mettler Toledo T50 acid-base auto-titrator. This mode of detection utilises a Kjeldahl-style pH stat method whereby ammonia that desorbs from the sample is delivered to a dilute boric acid receiver solution. The pH of this solution is constantly maintained at 5 by adding a 0.02M HCl titrant. The volume of HCl required to sustain a constant pH can be used to calculate the amount of NH_3 that has desorbed from the sample. Results are expressed as µmoles of H^+ per gramme of catalyst based upon the NH_3 desorbed per loaded mass of sample and are given in Table S2 below for the zeolite and silicotungstic acid/silica catalysts tested in Figures 2 and S3.

Table S2

Catalyst	**Acidity / µmoles H^+ g^{-1}**
H-ZSM-5 SAR 80	346
H-ZSM-5 SAR 50	430
H-ZSM-11 SAR 40	440
STA/silica	426

6. Computational Methods

The optimized geometries and corresponding energies were calculated using VASP[1] package. A 400eV cut-off energy and PREC = Accurate were set for plane wave basis set, while consistent PAW potentials[2] were used for each atom. The optB86b-vdW DFT functional[3] was used to calculate the non-local exchange and correlation energies, as well as dispersion interaction contributions. A 1 x 1 x 1 Monkhorst-Pack was used to sample the Brillouin zone. All the geometries were converged until forces on all the atoms were below 0.05 eV/A, while the relaxation in electronic energy within the SCF loop was lower than 10^{-6}. The transition state geometry was firstly initiated using Nudged Elastic Band (NEB) method[4] and further refined using DIMER technique.[5]

The MFI crystallographic structure was retrieved from database of zeolites structures[6] and the Brønsted acid location was selected at zig-zag/straight pore intersection. Each adsorption energy was calculated as the energy difference between the zeolite with adsorbate, zeolite and adsorbate in the gas phase. The adsorption values reported here are associated with enthalpy contributions at 0 K, without any temperature corrections applied.

7. Additional molecular modelling data and discussion

Additional molecular modelling work was conducted using the methodology described in Section 6 to determine if methyl n-hexanoate would favourably adsorb on the Brønsted acid sites in the narrow pore zeolite H-SSZ-13 (CHA). These results show that methyl n-hexanoate can favourably adsorb on a Brønsted acid site in the zeolite, with the ester symmetrically orientated in the zeolite channels as shown in Figure S7 below. The adsorption energy for methyl n-hexanoate was determined to be -108 kJ mol^{-1}. The maximum width of methyl n-hexanoate viewed end on as shown in Figure S5 was found to be 3.57 Å by molecular modelling of the molecule in the gas phase. The maximum size of a sphere that can diffuse along the micropores of CHA is reported to be 3.72 Å by the IZA Structural Commission,[7] so even though the fit is quite tight in H-SSZ-13 (CHA) there is sufficient space for methyl n-hexanoate to diffuse along the 8-MR channels to the Brønsted acid sites at the entrance to the supercage. This is consistent with the promotional effect seen, which we attribute to Brønsted acid site catalysis, as seen with the other zeolites and indeed silicotungstic acid supported on silica. Due to its tight confines H-SSZ-13 is already quite a good methanol dehydration catalyst even in the absence of the promoter, which explains, at least in part, why the promotional effect is smaller with H-SZZ-13 than with the medium and wide pore zeolites tested.

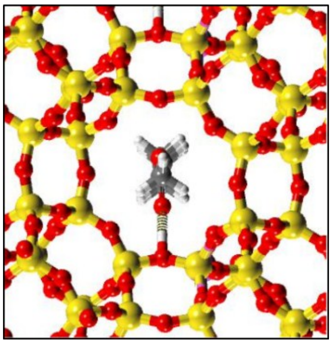

Fig. S7 Graphic showing the adsorption of methyl n-hexanoate on a BA site of H-SZZ-13 (CHA) with the pentyl chain aligned along the 8-MR interconnecting channel, with the pentyl group located predominantly in the supercage, and the carboxylate head-group at the entrance to the supercage.

8. References

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