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H-SAPO-5 as methanol-to-olefins (MTO) model catalyst: Towards elucidating the effects of acid strength

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ABSTRACT

The methanol-to-hydrocarbons (MTH) reaction was studied over a moderately acidic zeotype material, H-SAPO-5, at 350–450 °C and with WHSV = 0.3-5 h⁻¹. C_3-C_5 alkenes were the main products of reaction, followed by C_{6+} aliphatics. Conversion-selectivity plots from experiments conducted at various contact times revealed that coking did not influence product selectivity significantly. Steady-state isotope transient experiments (12 CH₃OH// 13 CH₃OH) were performed at 450 °C. 13 C incorporation was more rapid in the alkene products than in the polymethylated benzene molecules that were retained inside the catalyst after testing, suggesting that polymethylbenzenes contribute only to a minor extent to alkene formation in H-SAPO-5. Co-feed studies of methanol and benzene at 350 °C revealed that benzene shifts the product selectivity towards ethene and aromatic products. Co-feeding 13 CH₃OH and benzene at 250 °C, giving <2% conversion of both reactants, indicated that polymethylbenzenes, when present in excessive amounts, may contribute to ethene and propene, but not to C_{4+} alkene, formation. Furthermore, the isotopic label-ling pattern of ethene provided the first direct experimental evidence for ethene formation by a paring-type reaction from polymethylated benzene intermediates. Overall, the results obtained in this study suggest that a lower acid strength promotes an alkene-mediated MTH reaction mechanism, and that acid strength is therefore an important design parameter for selectivity optimisation in zeotype catalysis.

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1. Introduction

As world oil reserves are becoming increasingly difficult to extract, the interest in utilisation of alternative feedstocks, such as natural gas and biomass, for production of petrochemicals, is increasing. The conversion of methanol-to-hydrocarbons (MTH) represents a family of flexible processes for production of either light alkenes or gasoline, depending on catalyst used and conditions employed. As methanol production from a variety of sources is well established, commercial interest in methanol conversion processes is on the rise [1]. Several technologies are being commercialised, such as the UOP/Hydro methanol-to-olefins (MTO) process, Lurgi's methanol-to-propene (MTP) process, Mobil's methanol-to-gasoline (MTG) process and the Topsøe TIGAS process [1].

The MTH reaction is carried out over zeolite or zeotype catalysts, which are Brønsted-acidic, crystalline materials with internal pores and cavities of molecular dimensions. A key issue in MTH is product selectivity. A complex network of reactions is in operation during the conversion of methanol into the observed products. Generally speaking, apart from the simple dehydration to form dimethyl ether, three main product groups can be obtained. These are light alkenes such as ethene and propene, higher alkenes (C_4-C_8) and mixtures of aromatic and alkane products. Which product groups are favoured depend strongly on the catalyst used, as changes in the available internal channel space influence both which intermediates can be formed, and which products are able to diffuse out of the structure [2]. Tuning the reaction so that only a select group of products is produced is highly desirable, but requires a high degree of insight into both the fundamental reaction mechanisms and their interplay with the sterical limitations of the employed catalysts.

The MTH reaction has been known for more than 30 years. It was first published by Chang and Silvestri [3], and mechanistic studies have been a core research topic for many years. As an example, more than 20 mechanisms have been proposed for the direct formation of carbon–carbon bonds from methanol [4], even though it now appears as if such direct coupling of C–C bonds is not an important part of the reaction under steady-state conditions [5,6]. A major breakthrough in mechanistic understanding was the proposal by Dahl and Kolboe [7–9] that alkene formation proceeds by sequential methylation and elimination from an initially undefined hydrocarbon pool. Later studies revealed that multiply methylated aromatics play an important role as hydrocarbon pool species in the catalysts H-SAPO-34 [10–12] and H-Beta [13,14].



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Hexamethylbenzene and its further methylated cation, the heptamethylbenzenium cation (heptaMB⁺), are believed to be particularly important intermediates for alkene formation in these catalysts.

While the studies that led to the acceptance of the hydrocarbon pool mechanism and the focus on aromatic intermediates were performed using catalysts with large pores or internal voids, some later studies have focused on zeolites where the internal volumes are too small to allow dealkylation reactions of the largest polymethylbenzenes (polyMBs). In H-ZSM-5, which consists of 3D 10-ring pores, isotope transient experiments showed that lighter polyMBs (Xylene, TriMB and TetraMB in particular) were the main intermediates in the polyMB-based, or arene, cycle [15,16], leading mainly to ethene formation. In addition, those experiments revealed that C₃₊ alkenes were the dominating reaction intermediates for C_{3+} formation, by a methylation – cracking cycle [15,16]. Overall, the observed reaction mechanism, where alkenes and arenes function side by side as reaction intermediates, and are conthrough hydride transfer reactions leading nected to transformation of alkenes into aromatics and alkanes, was called the dual-cycle mechanism [15-17].

Recently, it has been demonstrated that the arene cycle can be further suppressed by using narrow pored 1D 10-ring catalysts such as H-ZSM-22 to produce product streams rich in higher alkenes and poor in aromatics, alkanes and ethene [18,19]. On the other extreme, a thorough investigation into three large-pore zeolites revealed similar behaviour and reactivity of the polyMBs as in H-Beta [20]. Yet other studies showed that it is possible to alter the mechanistic pathway in large-pore zeolites towards the alkene cycle when operating at very low temperature and high pressure [21,22].

The zeotype catalyst used in commercial MTO plants [1], H-SAPO-34 (CHA topology), has a significantly lower acid strength than conventional zeolites such as H-ZSM-5 (MFI topology). The difference in acid strength has been demonstrated by FTIR experiments using CO as probe molecule at -196 °C, showing a weaker interaction in the case of H-SAPO-34 than of H-ZSM-5 $(\Delta v_{OH} = -270 \text{ cm}^{-1} \text{ [23] and } > -300 \text{ cm}^{-1} \text{ [24], respectively). A}$ long-standing, but not yet fully resolved issue, is the influence of acid strength on the MTH performance of the catalyst. This issue was first addressed by Yuen et al. [25], who compared aluminosilicate and silicoaluminophosphate versions of both AFI (H-SAPO-5 versus H-SSZ-24) and CHA (H-SAPO-34 versus H-SSZ-13) structured catalysts. They compared the materials under conditions giving full initial methanol conversion and observed a more rapid breakthrough of methanol over the zeolite catalysts compared to their silicoaluminophosphate analogues. More recently, a detailed comparison between H-SAPO-34 and H-SSZ-13 was published [26]. The study included a series of tests performed at less than full conversion at different temperatures, as well as characterisation of retained hydrocarbons after testing. As expected, the more acidic H-SSZ-13 had a higher activity, and deactivated faster, than the less acidic H-SAPO-34. However, it was surprisingly found that at one test temperature, the methanol conversion capacity (i.e. the cumulative methanol production before full deactivation) was higher over H-SSZ-13 than over H-SAPO-34. Further mechanistic insight proved difficult due to the severe diffusional constraints in the CHA structure leading to a high degree of product shape selectivity [27].

The present work employs a zeotype catalyst of similar acid strength as H-SAPO-34, namely H-SAPO-5 (AFI structure). H-SAPO-5 features a one-dimensional pore system of tubular channels that, while similar in diameter to the H-SAPO-34 cavities, are open to the exterior and allows bulky compounds to diffuse in and out of the structure. Importantly, H-SAPO-5 can thus be employed as a model system in which the hydrocarbon pool is easily moni-

tored and can be manipulated through co-reaction experiments. By employing a combination of co-feeding and isotopic labelling experiments, this work provides detailed mechanistic insight for the MTH reaction over H-SAPO-5.

2. Experimental

2.1. Catalyst synthesis and characterisation

H-SAPO-5 was synthesised hydrothermally from water, triethylamine (TEA) (Fluka, 99.5%), orthophosphoric acid (Merck, 85%), Cab-O-Sil M5 (Riedel-de Haën) and Catapal B (Vista). A mixture with the composition 50 H₂O:1 Al₂O₃:1 P₂O₅:0.1 SiO₂:3.9 TEA was prepared and crystallised for 4 h at 200 °C in a rotating Teflon-lined steel autoclave. Removal of the structure directing agent (TEA) was performed by calcination in air at 600 °C for 2 h. Calcined samples were characterised by powder XRD, SEM, N₂ adsorption, NH₃ TPA and FT-IR.

For powder XRD measurements, a Siemens D-500 with primary Ge monochromator and Bragg–Brentano geometry using Cu K α radiation (λ = 1.5406 Å) was employed. SEM was performed with a FEI Quanta 200 FEG-ESEM. N₂ adsorption isotherms were measured at –196 °C, using a BELSORP-mini II instrument. The sample was outgassed in vacuum for 1 h at 80 °C and 3 h at 300 °C. Specific surface area was calculated using the BET equation based on p/p_0 data in the range 0.01–0.15. FT-IR measurements were performed in transmission mode on a Vertex 80 instrument with MCT detector. Before measurement, the sample was deposited on a silicon wafer and was pretreated under vacuum by heating to 120 °C for 1 h, 300 °C for 1 h and 450 °C for 1 h.

Temperature programmed adsorption of NH₃ was performed in a TGA setup, using a Mettler Toledo TGA/SDTA851e. Samples were heated to 500 °C under a flow of N₂ at a rate of 10 °C min⁻¹ and held there for 15 min before switching to a flow of 2% NH₃ in N₂. After a further 40 min, the temperature was decreased to 400 °C (10 °C min⁻¹). This temperature was again held for 40 min before decreasing to 300 °C, which was held for another 40 min before decreasing to 200 °C. The weight gain after each temperature decrease was logged and used for calculating the amount of adsorbed NH₃ per gram catalyst.

2.2. Catalytic tests

All catalytic tests were performed in a fixed-bed glass reactor of 8 mm inner diameter. The catalyst powder was pressed and sieved to obtain particles between 0.25 and 0.42 mm. Prior to the introduction of reactants, for all experiments, the pressed and sieved catalyst was calcined in situ at 550 °C under a flow of oxygen for 1 h before cooling to reaction temperature. Reactants used were ¹²C methanol (VWR, 99.8%), ¹³C methanol (Cambridge Isotope Laboratories, 99%) and benzene (Riedel-de Haën, 99.5%).

Three types of experiments were performed as part of this study:

- 1. Ordinary methanol reactions, where ¹²C methanol was reacted over H-SAPO-5 at 350 or 450 °C. 100 mg of catalyst was used, and methanol was fed by passing a stream of helium through a methanol saturator at 0 °C (methanol partial pressure of 40 mbar). Gas flows were varied in order to obtain WHSV between 0.31 and 5.0 h⁻¹, and the effluent was analysed by on-line GC during the reaction.
- 2. Steady-state isotope transient experiments, where ¹²C methanol was reacted over 50 mg of catalyst at 450 °C for 18 min before switching to a feed of ¹³C labelled methanol. Two identical lines with methanol partial pressures of 40 mbar and WHSV

 $0.93 h^{-1}$ were used for this purpose. After the feed to the reactor was rapidly changed, the isotopic compositions of both effluent and compounds retained inside the catalyst were monitored.

3. Co-reactions of methanol and benzene over 100 mg of catalyst were performed with feed partial pressures of 40 mbar and 13 mbar, respectively (saturator temperatures of 4 °C and 10 °C for the two lines), for experiments with unlabelled reactants (WHSV 1.5 and 1.2 h⁻¹). The experiment was carried out at 350 °C. When ¹³C methanol and ¹²C benzene were used, partial pressures were 76 mbar and 25 mbar, respectively (saturator temperatures of 20 °C and 10 °C, WHSV 1.0 and 0.8 h⁻¹). These experiments were carried out at 250 and 275 °C.

The reactor effluent was analysed quantitatively by online GC analysis (Agilent 7890 with flame ionisation detector) on a Restek Rtx[®]-DHA-150 column (150 m, 0.25 mm i.d., stationary phase thickness 1 μ m). Hydrogen (purity 6.0) was used as carrier gas. For isotope analysis of effluent in the benzene/methanol co-feed experiments, the same GC and conditions were used, but the effluent was routed to an Agilent 5975C MS detector. The isotopic composition of the gas-phase effluent from transient experiments was analysed by injection into a HP6890 GC with a GS GasPro column (30 m, 0.32 mm i.d.) and HP 5973 MS detector running on helium (purity 5.0) carrier gas.

In order to analyse aromatic compounds trapped inside the zeolite voids, catalyst samples quenched at predetermined times were dissolved in 15% hydrofluoric acid. The aromatics were then extracted using CH_2Cl_2 (Merck, 99.9%) and subsequently analysed by an Agilent 6890 GC equipped with an Agilent 5973 MS detector. The column used was a HP-5ms (60 m, 0.25 mm i.d., 0.25 µm stationary phase), and carrier gas was helium (purity 5.0).

3. Results and discussion

3.1. Physical characteristics of the catalyst

Fig. 1 displays the powder XRD pattern and a representative SEM micrograph of the sample. The diffractogram corresponds to that of a pure highly crystalline AFI structure. SEM revealed hexagonal crystals, mostly around 1 μ m in diameter, with lengths of the crystals varying between 1 and 2 μ m.

FT-IR spectra of the activated sample exposed to increasing dosages of CO at -196 °C are shown in Fig. 2. The clean sample displays two absorptions in the O–H stretching region (Fig. 2a): one at 3626 cm⁻¹ and another at 3530 cm⁻¹. These absorptions



Fig. 1. Powder XRD diffractogram (top) and SEM micrograph (bottom) of the employed H-SAPO-5 sample.



Fig. 2. FT-IR spectra of increasing dosages of CO on H-SAPO-5 at -196 °C. In (a), the OH stretching region is shown, while (b) shows the CO stretching region (background subtracted). The black bold curves correspond to the clean sample, while the grey bold curves correspond to the spectrum of highest CO loading.

correspond well with observations from previous studies of H-SAPO-5 and have been assigned to Si-OH-Al hydroxyls located in the 12- and 6-rings of the structure, respectively [28]. The hydroxyls in the 6-rings are reported to be inaccessible to weakly basic probe molecules at low temperatures, but will react with stronger bases and/or at elevated temperatures [28,29]. Thus, they are not expected to interact with CO at -196 °C, and, indeed, no interaction is observed here. However, the broad absorption for hydroxyls in the 12-rings (centred around 3626 cm⁻¹) erodes upon CO adsorption, mirroring the growth of two bands at lower wavenumbers (3460 cm⁻¹ and 3358 cm⁻¹). These two bands may represent different types of acid sites, as previously suggested [30]. Alternatively, the two bands may be caused by a similar fermi resonance effect as that proposed by Chakarova and Hadjiivanov [24] when adsorbing CO on H-ZSM-5. Regardless of the nature of this other absorption band, the largest observed red-shift (Δv_{OH} = -268 cm^{-1}) is comparable to what has been found in similar experiments for H-SAPO-34 ($\Delta v_{OH} = -270 \text{ cm}^{-1}$ [23]). Thus, a similar acid strength is also inferred. In addition, this value is significantly lower than the shifts $\Delta v_{OH} > -300 \text{ cm}^{-1}$ commonly measured for high-silica zeolites [24]. The other Δv_{OH} value (-196 cm^{-1}) is much lower, suggesting a weakly acidic site. The CO stretching region of the spectra (Fig. 2b) suggests similar conclusions, as the observed absorptions at 2138 cm⁻¹ (free, liquidlike CO molecules) and 2173 cm⁻¹ (CO interacting with Brønsted sites) correspond well with spectra of H-SAPO-34 [23]. In addition, an absorption is observed between these two possibly indicative of CO interacting with a weaker acid site. None of the absorptions normally assigned to Si-OH, Al-OH or P-OH hydroxyls were observed for this sample, implying that it contains few defects.

Acid site density of the material was determined by NH_3 TPA. Uptake of ammonia per gram catalyst corresponded to an (Al + P)/Si ratio of 43. The BET surface area of the sample was found to be 341 m² g⁻¹, which is in the upper range of values reported in literature [31–35].

3.2. Methanol conversion over H-SAPO-5

Methanol was reacted over the H-SAPO-5 sample at temperatures of 350 °C and 450 °C, within a range of WHSVs between 0.3 and 4.9 h^{-1} . Table 1 lists representative product selectivities at 65% and 20% methanol conversion for the two temperatures studied. HTI values listed are hydrogen transfer indexes: the ratios between the yield of alkanes and the yield of alkenes and alkanes combined. Iso values represent the fraction of branched versus linear hydrocarbons (alkanes and alkenes). Details on methanol conversion, deactivation and product yields can be found in the Supplementary information (Figs. S1 and S2).

Overall, the dominant products of methanol conversion over the H-SAPO-5 catalyst are C_3-C_5 hydrocarbons (Table 1), mainly in the

Table 1

Selectivity of H-SAPO-5 samples at 20% and 65% methanol conversion for temperatures 350 °C and 450 °C. HTI refers to hydrogen transfer indexes: yield of alkanes/ (yield of alkenes + alkanes). Iso refers to the fraction of branched hydrocarbons, covering both alkanes and alkenes.

| Compounds | 350 ℃ | 450 °C | 350 ℃ | 450 ℃ |
|----------------------|-------|--------|-------|-------|
| | 20% | 20% | 65% | 65% |
| Methane | 0.2 | 3.2 | 0.2 | 2.6 |
| C_2 | 1.3 | 1.5 | 2.7 | 1.7 |
| C_3 | 12.0 | 19.1 | 21.2 | 28.4 |
| C_4 | 51.5 | 43.1 | 38.1 | 37.4 |
| C_5 | 15.7 | 17.0 | 11.9 | 13.9 |
| C_{6^+} aliphatics | 14.0 | 13.6 | 10.6 | 11.1 |
| Aromatics | 5.3 | 2.6 | 15.4 | 4 9 |
| C_4 HTI | 0.07 | 0.03 | 0.27 | 0.03 |
| C_5 HTI | 0.14 | 0.06 | 0.40 | 0.07 |
| C_4 iso | 0.77 | 0.67 | 0.73 | 0.59 |
| C_5 iso | 0.80 | 0.71 | 0.84 | 0.69 |

form of alkenes. However, the aromatics fraction becomes significant at high conversions (65% versus 20% in Table 1) and low reaction temperature and is accompanied by an increasing alkane fraction; shown in Table 1 as an increasing HTI. Branched hydrocarbons are found in higher abundance than linear ones across all product fractions, especially at low conversion levels (Table 1). Among the main products, the ratio between C₄ and C₃ hydrocarbons decreases sharply as methanol conversion increases. A higher selectivity to C₃ than C₄ products is obtained at higher conversions than those listed here (at 450 °C), while at lower conversion levels, isobutene becomes increasingly dominant. Conversely, the ratio between C₄ and C₅ hydrocarbons appears largely unaffected by changes in conversion level, remaining nearly unchanged over the entire conversion range studied. C₄ hydrocarbons are favoured over both C_3 and C_5 hydrocarbons when the temperature is decreased from 450 °C to 350 °C.

The selectivity versus conversion data shown in Supplementary information (Figs. S1 and S2) indicate that product selectivities depend mainly on reaction temperature and the degree of methanol conversion, while being mostly independent of both the feed rate and the degree of deactivation. This observation corresponds well with the proposal by Janssens [36] that deactivation is nonselective and can be viewed simply as the loss of active sites, without any influence on the product selectivity. An exception to this general trend is observed for severely deactivated samples, where the selectivity to methane becomes higher than if the same conversion levels were obtained over a fresh catalyst.

3.3. Steady-state methanol isotope transient experiments

Steady-state isotope transient experiments are commonly used in catalysis research to distinguish between reaction intermediates and spectator molecules. In general, an active intermediate will incorporate the labelled component more rapidly than, or equally fast as, the product molecules. On the other hand, a spectator molecule will incorporate the labelled component more slowly than the products. In the MTH process, two main classes of possible intermediates are commonly considered, that is, alkenes and arenes, respectively (see Section 1).

In this study, a steady-state switch from unlabelled to ¹³C-labelled methanol was performed after 18 min on stream. This test duration should allow unlabelled hydrocarbon pool species to be built up before the switch. At the time of the switch, the conversion of methanol was 75%.

The evolution of ¹³C content with time after isotopic switch for light alkenes in the effluent as well as retained polyMBs in the

H-SAPO-5 sample is displayed in Fig. 3. One minute after the switch, the 13 C content of the alkene fraction was 70–85%, while it was only 4–30% in the retained aromatics fraction. With increasing time after the switch (2 min), the 13 C content of both fractions increased, to 85–95% in the alkene fraction and 10–50% in the retained aromatics fraction. The hydrocarbon pool mechanism is far too complex to allow for quantitative determination of individual reaction rates from the transient experiment. However, the much slower incorporation of 13 C in the aromatic compounds compared to the alkenes, as seen in Fig. 3, clearly suggests that polyMBs are not major reaction intermediates for alkene formation in the H-SAPO-5 catalyst under the given conditions.

A comparison of the fraction of ¹³C in the retained polyMBs and light alkene effluent after 18 min of ¹²C methanol feed and 2 min of ¹³C methanol over H-SAPO-5 and previously reported similar experiments over the catalysts H-Beta, H-ZSM-5 and H-ZSM-22 is included in the Supplementary information (Fig. S3). Starting from the sample with the narrowest pore size, H-ZSM-22 (4.6×5.7 Å, no intersections), via the sample with intermediate pore size, H-ZSM-5 (5.3×5.6 Å for the largest pores, with 3D intersections) to the sample with largest pore size, H-Beta $(7.7 \times 6.6 \text{ Å} \text{ for the})$ largest pores, with 3D intersections), a clear trend is observed: In H-ZSM-22, ¹³C incorporation is rapid in the light alkene fraction, while it is very slow in the retained polyMB fraction, thus suggesting that the polyMB fraction does not contribute to alkene formation in this structure [18]. In H-ZSM-5, ¹³C incorporation is significantly more rapid in the C₃₊ alkenes compared to the retained polyMBs, but the polyMBs are significantly more active than in H-ZSM-22. Furthermore, the incorporation of ¹³C in ethene is very similar to that of the polyMBs, which led to the conclusion that ethene is formed from polyMB intermediates, while C₃₊ alkenes are formed mainly from alkene intermediates in H-ZSM-5 [15,16]. Finally, in H-Beta zeolite, the ¹³C incorporation with time after switch is very similar in the alkene fraction and the aromatics fraction, suggesting that polyMBs are even more important reaction intermediates in this structure [17,37]. In conclusion. the comparison shows a clear trend with respect to an increasing importance of PolyMB intermediates with an increasing pore/ cavity size.

Another prominent feature when comparing H-Beta zeolite with H-ZSM-5 (Fig. S3) is that ¹³C is more rapidly incorporated in hexamethylbenzene among the polyMBs in H-Beta zeolite (in agreement with a higher alkene formation rate with increasing



Fig. 3. Evolution of ¹³C in effluent and retained aromatics after switching from ¹²C to ¹³C methanol. The experiment was performed at 450 °C and WHSV 0.93 h⁻¹, and the isotopic switch executed after 18 min on stream.

number of methyl substituents on the benzene ring, as reported by Sassi et al. [13]), while it is more rapidly incorporated in xylene and trimethylbenzene in H-ZSM-5. This observation suggests that the pores and intersections of H-ZSM-5 are too narrow to promote dealkylation of the heavier polyMBs [16]. Now, when turning to H-SAPO-5, which has pore dimensions similar to H-Beta (7.3×7.3 Å) but with no intersections, the ¹³C incorporation pattern among the polyMBs follows the expected reactivity trend, where ¹³C incorporation is fastest in the heaviest polyMBs. This observation demonstrates that the available space in the pores of H-SAPO-5 is larger than in H-ZSM-5. In spite of this, the ¹³C incorporation in the polyMBs is much slower in H-SAPO-5 than in both H-Beta and H-ZSM-5, while the ¹³C content observed for the alkene fraction is similar in all three materials.

The large difference in ¹³C incorporation between polyMBs and alkenes in H-SAPO-5 suggests that the reaction mechanism is shifted in the direction of an alkene-mediated mechanism in H-SAPO-5, compared to a higher importance of the arene-mediated mechanism in H-Beta and H-ZSM-5. Taking into account that the pore size of H-SAPO-5 is larger than of H-ZSM-5 and similar to H-Beta, the comparison strongly suggest that the shift is due to the lower acid strength of H-SAPO-5 compared to H-ZSM-5 and H-Beta.

While these experiments strongly suggest that methylbenzenes do not contribute significantly to alkene formation in H-SAPO-5 under the conditions tested, some indications that methylbenzenes could still be active hydrocarbon pool species are found. In particular, the ¹³C incorporation is not as low as in narrow-pore zeolites such as H-ZSM-22 ([18] and comparison in Supplementary information Fig. S3). Furthermore, in the effluent, ethene displays a lower incorporation of ¹³C than propene and isobutene. This observation may indicate a mechanistically separate pathway to ethene formation, possibly more closely linked with polyMB intermediates than formation of the heavier alkenes, as previously suggested for H-ZSM-5 [15,16].

3.4. Effects of benzene as co-reactant

The low ¹³C incorporation rate observed for retained polyMBs compared to alkenes in H-SAPO-5 (Section 3.3) could either mean that H-SAPO-5 is not able to catalyse the dealkylation of polyMBs, or that the rate of polyMB dealkylation is slow compared to alkene methylation and cracking. A low rate of polyMB dealkylation could either be due to a low abundance of these products, or to a low reaction rate, compared to what is observed in the more acidic zeolites. To elucidate whether polyMB dealkylation is feasible in H-SAPO-5, several methanol and benzene co-feed experiments were carried out.

Product selectivities obtained for methanol feed alone and for methanol - benzene co-feed (molar ratio 3:1, partial pressures 40 and 13 mbar, respectively) at 350 °C are shown in Fig. 4. The conversion was approximately 18.5% in both experiments. It is apparent from Fig. 4 that the addition of benzene to the feed increases the relative selectivity towards C₂ and C₃ hydrocarbons at the expense of C₄ selectivity. This is especially apparent for the ethene selectivity, which is very low (1.3%) when methanol is reacted alone but increases almost fivefold (to 5.7%) when benzene is added to the feed. Previous mechanistic studies of the MTH reaction over H-ZSM-5 indicated that ethene is predominantly formed from dealkylation of polyMBs (Section 3.3), while C₃₊ alkenes are more easily formed via an alkene methylation - cracking mechanism [16–18]. The observed change in product distribution upon benzene co-feed over H-SAPO-5, and in particular the increase in ethene selectivity, suggests that H-SAPO-5 is indeed able to catalyse polyMB dealkylation.



Fig. 4. Comparison of the distribution within the aliphatic products range during co-reaction of benzene and methanol (WHSV 1.2 h^{-1} and 1.5 h^{-1} , respectively) and for pure methanol feed (WHSV 0.6 h^{-1}) at 350 °C. The comparison has been made at approximately 18.5% conversion of either methanol alone, or methanol and benzene combined. The total selectivity to aliphatics was 40% and 95%, respectively, for the two experiments.

3.5. Selective labelling of aromatic intermediates

In order to reveal mechanistic information on the polyMB-mediated reaction cycle, ¹³CH₃OH was co-fed with ¹²C-benzene at 250 °C and WHSV 1.0 h⁻¹ and 0.8 h⁻¹ for methanol and benzene, respectively (molar ratio 3:1). Under these conditions, the conversion was low (1.8% of methanol and benzene combined), and reactions other than (methyl)benzene methylation and subsequent dealkylation were suppressed. This was verified both by the low selectivity to aliphatic products (8%) and by the observation that the polyMBs contained predominantly the same number of ¹³C atoms as methyl groups, with only a small degree of scrambling observed in the most highly methylated compounds (see Supplementary information, Fig. S4). While these conditions are somewhat removed from conventional methanol conversion conditions, they were necessary in order to avoid formation of methylbenzenes from methanol alone, which would render the alkene labelling patterns unintelligible. The effluent was analysed after 2 min on stream and labelling patterns of the light alkenes are shown in Fig. 5.

From this figure, some interesting differences between the products are immediately apparent. While the majority of the ethene and propene molecules contain one ¹²C atom, the isobutene and isopentene (2-methyl-2-butene) molecules display an excess of all ¹³C molecules. The most natural assumption from these results is that the two groups of alkenes are formed via different reaction pathways. To elaborate further on this difference, it is necessary to recapitulate the current understanding of polyMB dealkylation mechanisms.

The mechanisms of alkene elimination from polyMBs in the MTH reaction have been a subject of debate for many years. The two main mechanistic proposals are the paring reaction and the exocyclic methylation mechanism. A simplified scheme of these two reaction pathways is presented in Fig. 6. The latter mechanism was first proposed by Mole et al. [38,39] and later refined by Haw et al. [2] and involves deprotonation of HeptaMB⁺ to form a neutral compound with an exocyclic double bond. This double bond can then be methylated once or twice to form an ethyl or isopropyl side-chain, which is subsequently eliminated. On the other hand, the paring reaction, first proposed by Sullivan et al. [40], involves the rearrangement of HeptaMB⁺ to a five-membered ring with an alkyl substituent. This smaller ring can then either split off propene directly or reorganise further to eliminate isobutene before deprotonation and expansion back to a six-ring. In Fig. 6, stars signify ¹³C-labelled carbon atoms, that is, the carbons originally present as methyl groups. Since only the paring reaction involves



Fig. 5. Distribution of ¹³C atoms in ethene (left), propene (middle left), isobutene (middle right) and isopentene (right) after 2 min of co-reacting methanol with benzene (molar ratio 3:1) at 250 °C. Total ¹³C content was 53% in ethene and 67% in propene, while it was nearly 90% in both isobutene and isopentene. The molecules above the graphs are drawn with stars signifying labelled carbon atoms representative of the most abundant isotopologues.



Fig. 6. Expected labelling patterns when propene is split off from a selectively labelled heptaMB⁺ via paring or exocyclic mechanisms, respectively. Stars signify labelled carbon atoms.

scrambling of the benzene ring carbons into the alkene products (and methyl group carbons into the aromatic ring), the labelling patterns of the alkene products may be used to distinguish between the two mechanisms. While the scheme in Fig. 6 depicts HeptaMB⁺ as the main intermediate, similar mechanisms are assumed to exist for polymethylbenzenium cations with fewer methyl groups, and the labelling patterns are also expected to be similar if the elimination products are ethene or isobutene instead of propene (i.e. one unlabelled carbon should be observed in both alkenes if the paring mechanism dominates).

Now, when returning to the data in Fig. 5, we observe that for ethene and propene, the labelling patterns are consistent with a paring mechanism. While a similar labelling pattern has previously been observed for propene [14], this is, to the best of our knowledge, the first reported evidence of ethene formation via the paring reaction in any acid catalyst. However, ethene loss from poly MBs via paring-type mechanisms has been studied by mass spectrometric methods by Uggerud et al. [41,42].

It is interesting to note that the C_{4+} alkenes show a different labelling pattern and are dominated by all-¹³C compounds. Such a labelling pattern could either be an indication of a shift in the polyMB dealkylation mechanism towards exocyclic methylation for higher alkenes, or it could indicate that the C_4 alkenes are not formed via polyMB intermediates, but rather via an alkene methylation-cracking cycle. Looking closely at the exocyclic methylation cycle in Fig. 6, it is observed that elimination of isobutene (or isopentene) from this cycle would necessitate, first, deprotonation of the ethyl side-chain, followed by another methylation to form an isopropyl group, which would again need to be deprotonated before finally being methylated to an isobutyl group (or twice to an isopentyl group). It is not likely that such a sequence of steps would lead selectively to isobutene and isopentene formation, while giving insignificant amounts of ethene and propene. It is therefore concluded that the dominating all-¹³C isobutene labelling pattern shown in Fig. 5 signifies that isobutene and isopentene are mainly formed via an 'all-methanol' cycle in the co-feed experiments, that is, by the alkene methylation – cracking cycle, where the abundance of ¹³C (from methylation of C₃₊ by methanol) increases with each cycle when originally starting with ¹²C¹³C₂propene.

The results of this experiment reveal again some interesting differences to the results previously obtained by Biørgen et al. [14] over H-Beta zeolite. A comparison of the results obtained by cofeeding ¹³C-methanol and ¹²C-benzene over H-Beta zeolite in [14] with those obtained for H-SAPO-5 in this study is shown in the Supplementary information, Fig. S5. The most striking difference is observed for isobutene/isobutane, where H-SAPO-5 gives predominantly all-13C-isobutene at both temperatures, while H-Beta zeolite gives predominantly isobutane with one ¹²C. The more acidic H-Beta zeolite thereby seems to favour the arenebased mechanism, where $iso-C_4$ is formed by a paring-type reaction, and where the hydrogen transfer index (HTI) is high due to significant formation of aromatic products (and coke). The less acidic H-SAPO-5, on the other hand, favours the alkene-based mechanism, in which isobutene is formed by cracking of higher alkenes, and the HTI is low, in agreement with a lower selectivity to aromatic products over this catalyst. It should be noted that the labelling pattern of isobutane in H-SAPO-5 was similar to that of isobutene, but could not be accurately determined due to the almost negligible selectivity to isobutane.

Turning to the propene labelling pattern, which was only reported at 275 °C for H-Beta zeolite, propene with one ¹²C dominates for H-SAPO-5 at 250 °C, strongly indicating formation by a paring-type dealkylation of polyMBs. At 275 °C, however, where the total methanol and benzene conversion was 6.9% (compared to 1.8% at 250 °C), the all-¹³C propene compound dominated, suggesting a stronger contribution from the alkene methylation-cracking cycle in propene formation at this temperature. In H-beta zeolite, on the other hand, propene with one ¹²C dominates even at 270 °C, at 6.9% conversion, suggesting that the arene-based cycle still dominates propene formation at this temperature. Finally, in the ethene fraction, which was not reported for H-Beta zeolite, the monolabelled compound dominated in H-SAPO-5 at both temperatures, suggesting that ethene is formed predominantly via a paring-type reaction of polyMB intermediates.

Together, the data reported in Sections 3.2–3.5 give the following key information about the methanol-to-hydrocarbons reaction over H-SAPO-5:

- 1. H-SAPO-5 gives a high selectivity to non-aromatic products, predominantly C_3 - C_5 alkenes, at 350–450 °C.
- Steady-state isotope transient experiment with ¹²CH₃OH// ¹³CH₃OH feed at 350 °C reveals a more rapid incorporation of ¹³C in alkene products than in retained polyMBs, indicating that alkene formation proceeds mainly via an alkene methylationcracking cycle in this catalyst.
- 3. Co-feed studies of methanol and benzene at 350 °C give a shift in product distribution towards C_2 and C_3 alkenes compared to methanol only feed, suggesting that arenes (when present in sufficient amounts) may act as intermediates for light alkene formation in H-SAPO-5.
- 4. Co-feed studies of ¹³C-methanol and ¹²C-benzene at conditions giving low conversions, and high concentrations of polyMBs in the catalyst, at 250–275 °C give isotope labelling patterns in the C_2-C_5 products which suggest that ethene and propene could be formed by an arene cycle, via a paring-type dealkylation of polyMBs when PolyMBs are present in sufficient amounts, while isobutene and isopentene (and partly propene) are formed mainly via an alkene cycle, via methylation and cracking of alkenes.

Together, these observations lead to the suggestion of a reaction scheme, which is presented in Fig. 7. Here, an arene cycle is assumed to account for production of the lightest alkenes (ethene and, partly, propene), while an alkene cycle produces the heavier alkenes. Such a 'dual-cycle mechanism' is similar to the proposed mechanism for H-ZSM-5 [15,16]. However, due to the increased available space inside the channels of H-SAPO-5 relative to H-ZSM-5, both the proposed alkene and arene cycles consist of larger compounds in H-SAPO-5 than in H-ZSM-5. Note also that interconversion between the two cycles would account for many of the observed minor products, such as cyclic compounds, polyunsaturated hydrocarbons and alkanes.

In the alkene cycle of Fig. 7, 2,3,3-trimethyl-2-butene has been drawn as the end product. While other homologues and isomers certainly exist, this proposal is in accordance with recent reports by Bercaw et al. [43] and Iglesia et al. [21,22] for similar systems.

Furthermore, C_8 alkenes are the largest alkenes observed in the effluent of H-SAPO-5 in this study. Finally, the observation that the ratio between C_4 and C_5 hydrocarbons formed does not vary significantly when conditions are changed (apart from temperature) corresponds well with their formation primarily from a common intermediate. If this common intermediate is an alkene, it would be expected to consist of at least eight carbons, since smaller species would be unable to crack into a C_5 compound without the involvement of primary carbocations or elimination of ethene (which is produced in very small amounts over H-SAPO-5).

In the arene cycle of Fig. 7, ethene and propene are formed from polyMBs. In line with the observed and previously reported [13], correlation between reactivity and increasing number of methyl groups, the largest observed polyMB, hexamethylbenzene, is drawn as the key intermediate in the figure. The light alkenes are assumed to be formed in a paring-type mechanism since the strong preference for incorporation of one aromatic-ring carbon into ethene and propene cannot be explained by an exocyclic methylation pathway. More recent theoretical work also favours the paring reaction over the exocyclic methylation reaction mechanism in zeolite H-ZSM-5 [44].

This study provides, as far as we know, the first experimental evidence reported for ethene formed by a paring-type reaction from polyMBs. It is worth mentioning that, according to theoretical work by Arstad et al. [45,46], formation of ethyl chains cannot proceed via a ring contraction. On the other hand, the same studies also concluded that it may proceed with the involvement of a ring-expansion step. The expansion to tropylium-type ions before alkene elimination has been studied by mass spectrometry [41,42]. Either way, similar incorporation of ring carbons into the eliminated alkenes may occur in mechanisms, involving ring expansion and ring contraction. For this reason, it appears prudent to refer to the mechanism involved simply as 'paring-type' or carbocation-based, without stating whether contraction or expansion is involved.

Perhaps the most interesting observation of this mechanistic investigation is the uncovered mechanistic differences from previously studied medium- and large-pore zeolites; that is, the relatively higher ¹³C incorporation in alkene products than in retained PolyMBs in H-SAPO-5, compared to previously studied zeolites, after a methanol isotope transient (Fig. S3), as well as the clear difference in labelling pattern of the isobutene/isobutane fraction in ¹³C-methanol-¹²C-benzene co-feed experiments performed over H-SAPO-5 in this study, and over H-Beta zeolite in a



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Fig. 7. Scheme of the proposed dual-cycle mechanism in operation during methanol-to-hydrocarbons catalysis over H-SAPO-5.

previous study (Fig. S5). Together, these observations suggest that the lower acid strength of the H-SAPO-5 catalyst compared to the previously studied zeolites induces a shift in reaction mechanism from predominantly arene-based in wide pore zeolites, to mainly alkene-based in wide pore H-SAPO-5. However, an influence of the differences in framework structure among the samples cannot be ruled out without direct comparisons of isostructural catalysts with different acid strength. Indeed, as a closing comment on topology influence, it should be noted that the conditions employed in the co-feed experiments in this study probably lead to a hydrocarbon pool composition more similar to that obtained in H-SAPO-34, because its cavity-window structure leads to trapping and accumulation of aromatic compounds, in favour of an arenebased mechanism for light alkene formation [10,11,27,47]. This observation further underlines that MTH catalyst optimisation is indeed a multiparameter task.

4. Conclusions

A combination of conventional, co-feed and labelling experiments has been performed for methanol conversion over the weakly acidic catalyst H-SAPO-5. Together, the experiments have led to the proposal of a mechanistic scheme where both polymethylbenzenes (polyMBs) and higher alkenes operate as hydrocarbon pool species. While the existence of the dual-cycle mechanism is known in other catalyst systems as well, it is here revealed that the alkene cycle is significantly more important for product formation in H-SAPO-5 than in previously studied large-pore catalysts of higher acid strength. This is mainly based on two observed differences from previous experiments on H-Beta: The slower incorporation of ¹³C into the retained aromatics in H-SAPO-5 during transient experiments, and the negligible abundance of isobutene formation from polyMB intermediates in H-SAPO-5. Although not confirmed to be the sole cause, we propose that the observed differences are related to the low acid strength of H-SAPO-5 as compared to H-Beta.

Furthermore, the co-reactions of benzene with ¹³C methanol performed in this work provide us with mechanistic details for the dealkylation of polyMB intermediates. The observed labelling patterns show that ethene and propene can be formed by a mechanism involving ring contraction or expansion of the intermediates, the so-called paring mechanism.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jcat.2012.11.004.

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