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Methanol-to-olefins process over zeolite catalysts with DDR topology: effect of composition and structural defects on catalytic performance†

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A systematic study of the effect of physicochemical properties affecting catalyst deactivation, overall olefin selectivity and ethylene/propylene ratio during the methanol-to-olefins (MTO) reaction is presented for two zeolites with the DDR topology, namely Sigma-1 and ZSM-58. Both catalysts show high selectivity towards light olefins and completely suppress the formation of hydrocarbons bigger than C₄, with selectivity to ethane not exceeding 1% and some traces of propane. By applying seeded growth approach, a series of Sigma-1 zeolites with tunable crystal size and acidity was synthesized. For this series the highest methanol throughput at 450 °C before deactivation was found for crystals 0.5 µm in size with an acidity corresponding to 0.5 Al atoms per zeolite cage, and a selectivity to ethylene and propylene reaching 90%. Comparison between ZSM-58 and Sigma-1 catalysts with similar morphologies and acidity under the same reaction conditions revealed a three times higher throughput of methanol in case of ZSM-58. The analysis of functional surface groups, assessed through FT-IR, revealed the presence of silanol defects in Sigma-1 responsible for faster catalyst deactivation. These silanol defects can be selectively removed (confirmed by FT-IR) from the zeolite framework by applying a mild treatment in presence of NaOH/CTAB, leading to an improved catalyst lifetime. Co-feeding experiments with short olefins and water show low reactivity of primary MTO products, which only react at the surface of the catalyst particles. These results demonstrate that migration of the reaction zone in case of DDR catalysts hardly affects catalyst stability, product composition and nature of deactivating species. The nature of these species depends mostly on reaction temperature: at low temperatures deactivation occurs mainly due to the formation of inert adamantane species, while at high temperatures poly-condensed aromatic hydrocarbons play the major role in deactivation.

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1. Introduction

Due to the growing demand for propylene and ethylene, the search for efficient alternative routes to the synthesis of light olefins is now at the forefront of industrial and academic research.¹ Among these routes, the methanol-to-hydrocarbons (MTH) conversion² has gained a lot of attention during the last few decades.

The reaction pathway includes conversion of methanol over acidic zeolites, with SAPO-34 (CHA) and ZSM-5 (MFI) being successfully implemented in industry.³ Several alternative

processes are commercially available, and most of these rely on zeolite ZSM-5 as catalyst. These include the Mobil Oil MTG process, the Topsøe integrated gasoline synthesis (TIGAS) process, and the Lurgi methanol-to-propylene (MTP) process.³ In the latter case, the selectivity is optimized towards propylene rather than C₅+ by tuning the reaction conditions (*i.e.*, high temperature and low pressure) and by recycling long chain hydrocarbons.⁴ In the Norsk Hydro/UOP methanol-to-olefins (MTO) process, mostly ethylene and propylene are produced using SAPO-34 as the catalyst material.⁵

However, there are still several drawbacks associated with the relatively low stability of SAPO-34 towards multiple regenerations due to the presence of phosphorus in its framework, and to the broad product distribution when using ZSM-5. Furthermore, for both catalytic materials, the energy intensive separation of the olefin/paraffin product mixtures is a major disadvantage.

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In this work we systematically study the effect of physico-chemical properties on catalyst deactivation, overall olefin selectivity and ethylene-to-propylene ratio using Sigma-1 and ZSM-58 zeolites with DDR topology as two case studies. All parameters were investigated independently, using always the same gel precursor composition, tuning zeolite morphology and acidity only by changing the amount of Al and by using as-synthesized material as seeds. By applying this approach,

A modified sample was obtained by treating calcined at 650 °C Sigma-1 with 20 ml of solution per gram of zeolite of 0.075 M NaOH and 0.5 M CTAB solution.³⁰ This modified

sample was further subjected to calcination at 550 °C to remove CTAB followed by ion-exchange as outlined above.

ZSM-58 crystals were synthesized as reported elsewhere using methyltropinium iodide (MTI) as template,⁹ keeping the SiO₂/Al₂O₃ ratio 110, and subjected to calcination and ion-exchange as described above.

MTI was prepared by adding drop-wise 25.1 g methyl iodide to a solution 25.0 g tropine in 100 g of ethanol at 0 °C. The resulted suspension was left for 3 days for stirring. After washing with 100 g of ethanol and filtering, the resulted powder was dried at 80 °C for 12 h.

2.2. Catalyst characterization

The XRD patterns of the powders are recorded in Bragg-Brentano geometry with a Bruker D8 Advance X-ray diffractometer equipped with a LynxEye position-sensitive detector. Measurements were performed at RT by using monochromatic CoK α (λ = 1.788970 Å) radiation between 2θ = 5° and 50°.

The Pawley fitting of the experimental data was performed using Reflex Plus module of the Accelrys Material Studio software package. The refinement of unit cell parameters giving values of $a = b = 13.8068(1)$ Å, $c = 40.8500(1)$ Å, $\beta = \alpha = 90^\circ$, $\gamma = 120^\circ$ suggested a close agreement with the one expected for DDR zeolite as reported in the Atlas of Zeolite Framework Types.³¹ Zero offset, the scale factor, six background terms and profile parameters were refined during Pawley fitting. The profiles have been modeled as a pseudo-Voigt function. Corresponding refinement results are summarized in Table S1† and plotted in Fig. S1.†

Images were recorded using a JEOL JSM-6010LA with a standard beam potential of 10 kV and an Everhart-Thornley detector. X-ray microanalysis (SEM/EDX) confirmed the elemental composition in the sample by scanning microscopy (SEM) coupled with a dispersive X-ray microanalysis system (EDX) with a Silicon-drift detector.

Elemental analysis was performed with PerkinElmer Optima 4300 DV instrument. The samples were first digested in an aqueous mixture of 1% HF and 1.25% H₂SO₄. After dilution, analysis was done by inductively coupled plasma optical emission spectrometry (ICP-OES).

N₂ adsorption was carried out using Tristar II 3020 Micromeritics sorptometer at 77 K. Prior to the experiment, samples were outgassed at 350 °C for 16 h.

Temperature-programmed NH₃ desorption (NH₃-TPD) was measured by AutoChem II chemisorption analyzer (Micromeritics). Approximately 0.2 g of the material was first degassed under He flow at 400 °C and then saturated with NH₃ at 200 °C during 1 h using a flow of 1.65% NH₃ in He. The gas mixture was then switched back to He and the sample was purged at 200 °C for about 1 h to remove weakly adsorbed NH₃ molecules. TPD was subsequently recorded under He flow, from 200 °C to 800 °C. All flow rates were adjusted to 25 mL min⁻¹, and the heating rates were 10 °C min⁻¹ during different stages of experiment.

Transmission FT-IR spectroscopy was performed using a Nicolet Nexus spectrometer at 4 cm⁻¹ resolution equipped with an extended KBr beam splitting and a mercury cadmium telluride (MCT) cryo-detector. The pellets were placed in an IR quartz cell equipped with CaF₂ windows. A movable sample holder allows the sample to be placed in the infrared beam for the measurements or into the furnace for thermal treatments. The cell is connected to a vacuum line for pretreatment. The specimen is activated in vacuum at 400 °C for 16 h to remove adsorbed species. After this step, the samples were cooled down to -130 °C and CO was dosed up to 30 mbar.

Thermogravimetric analysis (TGA) was performed by means of a Mettler Toledo TGA/SDTA851e on samples of 20 mg under flowing 100 mL min⁻¹ of air at a heating rate of 5 °C min⁻¹ up to 1000 °C. The amount of coke formed during the reaction was calculated from the weight loss between 150 °C and 800 °C for completely deactivated catalysts (after feeding at least 10 g methanol per g zeolite).

DRIFTS analysis was carried out in a Thermo Scientific Nicolet 8700 spectrometer, equipped with a high-temperature cell with CaF₂ windows (HVC Praying Mantis Harrick) and a DGTS detector. The spectra were collected after 128 scans and a resolution of 4 cm⁻¹, under 20 mL min⁻¹ He flow. KBr spectra (at given temperatures) are used as background. Before collecting the spectra, samples deactivated after 5 h of MTO reaction were preheated in a He flow at 120 °C for 60 min to remove water.

Hydrocarbons that were retained in the catalyst after testing were investigated by dissolution experiments. Typically, 15 mg of the spent catalyst was dissolved in 1 mL 50% HF in a Teflon container. The organic compounds were extracted from the water phase by the addition of three times 1 mL CH₂Cl₂. Analysis of the extracted phase was performed on a GCMS-QP2010Ultra GC/MS system, equipped with a Zoex ZX1 thermal modulator and an Agilent VF-5 ms and VF-17 ms column in series. Hereinafter, the term 'retained hydrocarbons' or 'coke' is used to describe all compounds that are detectable by this method.

2.3. Catalyst testing

Catalytic experiments were carried out in a Microactivity Reference unit (PID Eng&Tech) at 380–475 °C and ambient pressure. The catalyst (1.75 g, 250–420 μ m sieve fraction) was placed in a fixed-bed with internal diameter 9 mm. An HPLC pump (307 5-SC-type piston pump, Gilson) was used to feed methanol to the reactor system. The temperature was recorded by a thermocouple placed in the middle of the catalytic bed. A weight-hourly space velocity (WHSV) of 2 g_{MeOH} g_{cat}⁻¹ h⁻¹, a 1:1 molar feed composition of N₂ and MeOH and atmospheric pressure are applied and referred to as standard operating conditions at the different temperatures.

The product mixture was analyzed online with an Inter-science CompactGC equipped with a 15 m capillary RTX-1



(1% diphenyl-, 99% dimethylpolysiloxane) column and a flame ionization detector.

Conversion, selectivities and yields were calculated on a molar carbon basis. Thus, conversion was defined as the fraction of light oxygenates (methanol and dimethyl ether) consumed during the reaction:

$$X = \frac{n_{\text{C, MeOH}_{\text{in}}} - n_{\text{C, oxy}_{\text{out}}}}{n_{\text{C, MeOH}_{\text{in}}}} \cdot 100\% \quad (1)$$

the selectivity towards ethylene (2) and propylene (3) was calculated based on the carbon number as follows:

$$S_{\text{ethylene}} = \frac{2 \cdot n_{\text{C}_2\text{H}_4}}{n_{\text{C, MeOH}_{\text{in}}} - n_{\text{C, oxy}_{\text{out}}}} \cdot 100\% \quad (2)$$

$$S_{\text{propylene}} = \frac{3 \cdot n_{\text{C}_3\text{H}_6}}{n_{\text{C, MeOH}_{\text{in}}} - n_{\text{C, oxy}_{\text{out}}}} \cdot 100\% \quad (3)$$

and the yield of a component *i* was defined from its selectivity and methanol conversion:

$$Y_i = \frac{S_i \cdot X}{100} \quad (4)$$

Total molar flow rate at the outlet v_{out} was calculated based on the N_2 flow as an internal standard and its molar fraction in the outlet flow (eqn (5)). Since N_2 is an inert gas, its flow rate is equal to the inlet one.

$$y_{\text{N}_2} = \frac{v_{\text{N}_2}}{v_{\text{N}_2} + v_{\text{out}}} \quad (5)$$

Prior to each experiment, mixture containing N_2 and MeOH was bypassed through the reactor to GC to calculate response factors. In turn, response factors for individual products were obtained by calibration with a gas mixture containing all hydrocarbons up to C5.

Hence, the molar flowrate of a component *i* (v_i) could be calculated from the eqn (6):

$$v_i = y_i \cdot (v_{\text{N}_2} + v_{\text{out}}) \quad (6)$$

where y_i is the molar fraction of component *i* in the N_2 diluted gas phase and is directly obtained from GC analysis.³²

The performance results are presented in graphs as a function of the methanol throughput per amount of catalyst used ($\text{g}_{\text{MeOH}} \text{ g}_{\text{cat}}^{-1}$). The methanol conversion is an apparent one as it reflects the disappearance of this component, which can be due to chemical conversion or to retention on the catalyst. Parameters related to catalyst performance are summarized in Table 1.

Methanol throughput before deactivation (also referred to as MeOH uptake) is defined as overall MeOH throughput fed through the catalytic bed before the breakthrough of oxygenates ($X \approx 98\%$). Turnover numbers (TON) are defined as the total amount of MeOH converted per Brønsted acid site (BAS) before the conversion decreases below 98%. The amount of BAS was calculated from NH_3 -TPD. Ethylene/propylene (C2/C3) ratios (Table 1) are calculated for the experiments carried out at 450 °C taking into account integral selectivities.

Co-feeding experiments were performed keeping N_2 flowrates equal to the ones used in MTO experiments and adding ethylene, propylene and/or water flows to obtain the desired mixtures.

Typically, after testing a catalyst for 5 h to ensure almost complete deactivation, the MeOH flow was stopped and the catalyst was cooled down under N_2 flow. Later, the catalyst was transferred into a vial for further analysis of the trapped species.

3. Results

In this section the main properties and catalytic performance of the synthesized zeolites are described: (i) a series of Sigma-1 catalysts with different composition and particle size, (ii) a post-synthetically treated Sigma-1 catalyst and (iii) a series of ZSM-58 catalysts, produced with a different template.

Table 1 Catalytic properties of the zeolites with the DDR topology under the study

Sample	$\text{SiO}_2/\text{Al}_2\text{O}_3^a$ (mol mol ⁻¹)	$\text{SiO}_2/\text{Al}_2\text{O}_3^b$ (mol mol ⁻¹)	NH_3 capacity ^b (mmol NH_3 g ⁻¹)	Throughput before deactivation ($\text{g}_{\text{MeOH}} \text{ g}_{\text{cat}}^{-1}$)	TON ($\text{mol}_{\text{MeOH}}/\text{mol}_{\text{BAS}}^{-1}$)	$\text{C}2^=/\text{C}3^=^c$ (mol mol ⁻¹)	$\text{C}2^=/\text{C}2^c$ (mol mol ⁻¹)	$\text{C}3^=/\text{C}3^c$ (mol mol ⁻¹)	Coke ^d (wt%)
Sigma1-120-M	120	117	0.281	1.3	144	0.7	21	$\gg 10^3$	8.1
Sigma1-210-M	200	207	0.160	2.0	391	—	—	—	—
Sigma1-315-M	399	314	0.105	2.5	740	1.0	39	$\gg 10^3$	10.5
Sigma1-415-M	724	417	0.080	2.5	982	—	—	—	—
Sigma1-315-L	406	317	0.105	1.6	478	0.8	34	$\gg 10^3$	9.6
Sigma1-315-S	420	317	0.105	3.6	1076	1.1	52	$\gg 10^3$	11.7
Sigma1-315-S-m	404	317	0.104	6.5	1944	1.0	62	$\gg 10^3$	12.1
ZSM-58	110	111	0.296	4.5	476	—	—	—	11.8

^a Determined from ICP. ^b Determined from NH_3 -TPD. ^c Calculated from Table S2 based on integral selectivities. ^d From TGA measurements of spent catalysts used at 450 °C.



3.1. Synthesis and characterization of Sigma-1 zeolite

Powder XRD patterns shown in Fig. 1 together with reference peaks for DDR topology confirm that the synthesized catalysts consist only of pure DDR phase. SEM micrographs of zeolites synthesized with the same composition, but using different size of seeds are shown in Fig. 2. By using seeds with crystal sizes of 0.08, 0.5 and 2.5 μm , zeolites of 0.5, 2.5 and 4.6 μm with very narrow size distributions can be synthesized, respectively. The formed crystallites have a similar aspect ratio, with round slab shape. On the basis of their crystal size and NH_3 TPD results (Tables 1 and 2), the zeolites are denoted as Sigma1-*X*-*Y*, where *X* refers to the actual $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (120, 210, 315, 415), while *Y* is related to crystal size (S – 0.5 μm ; M – 2.5 μm ; L – 4.6 μm). On the basis of the same nomenclature, the modified sample is denoted as Sigma1-315-S-m.

When analyzing image of Sigma1-315-L (Fig. 2c), the observed intergrowth and aggregation infers an adhesive mechanism of growth, characteristic for the secondary growth mechanism taking place in the presence of seeds.³³

The acidic properties of the synthesized materials were assessed by NH_3 TPD (Fig. 3). For all samples, the desorption peak at high temperatures is assigned to the desorption of ammonia from Brønsted acid sites.⁹ Both the amount and the strength of acidity correlate well with the amount of Al in the zeolite, the more Al in the zeolite the more acid sites. Moreover, the maximum of the desorption peak shifts from

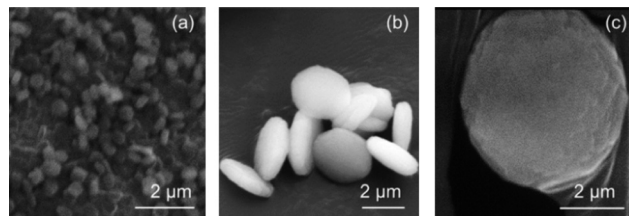


Fig. 2 SEM micrographs of (a) Sigma1-315-S (b) Sigma1-315-M (c) Sigma1-315-L with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 315$.

Table 2 Particle sizes and textural properties from N_2 adsorption of the zeolites with the DDR topology under the study

Sample	Particle size ^a (μm)	S_{meso}^b ($\text{m}^2 \text{g}^{-1}$)	S_{BET}^c ($\text{m}^2 \text{g}^{-1}$)
Sigma1-120-M	2.7	20	313
Sigma1-210-M	2.7	14	349
Sigma1-315-M	2.4	7	364
Sigma1-415-M	2.5	5	371
Sigma1-315-L	4.6	12	340
Sigma1-315-S	0.5	15	357
Sigma1-315-S-m	0.5	51	403
ZSM-58	0.6–1.8	22	372

^a Determined from SEM. ^b *t*-Plot method. ^c BET plot applied to the N_2 isotherm.

420 $^{\circ}\text{C}$ (Sigma1-120-M) to 375 $^{\circ}\text{C}$ (Sigma1-415-M), indicating the weakening of acid sites with decreasing Al content. Similar desorption temperatures for Sigma1-415-M, Sigma1-315-M and Sigma1-210-M indicate that their acid sites are isolated and possess a similar acid strength. The desorption peak of Sigma1-120-M is also characterized by a shoulder at 300 $^{\circ}\text{C}$, indicating the presence of weaker Lewis acidity. Comparison of acidic properties of zeolites with similar composition, but different crystal size does not reveal any changes either in the amount of acid sites or in their acid strength. The observed mismatch in the amount of Al calculated from NH_3 TPD and ICP for the high silica containing sample is associated to the small Al content, leading to a bigger error in the quantification.

Additionally, FT-IR spectroscopy of adsorbed CO (Fig. 4) was studied on Sigma1-120-M (*a*₁, *a*₂), ZSM-58 (*b*₁, *b*₂), Sigma1-315-S (*c*₁, *c*₂) and Sigma1-315-S-m (*d*₁, *d*₂) in order to assess surface groups and acid strength. The FT-IR spectra of pretreated samples show a complex absorption with a maximum at 3747–3745 cm^{-1} attributed to terminal Si–OH

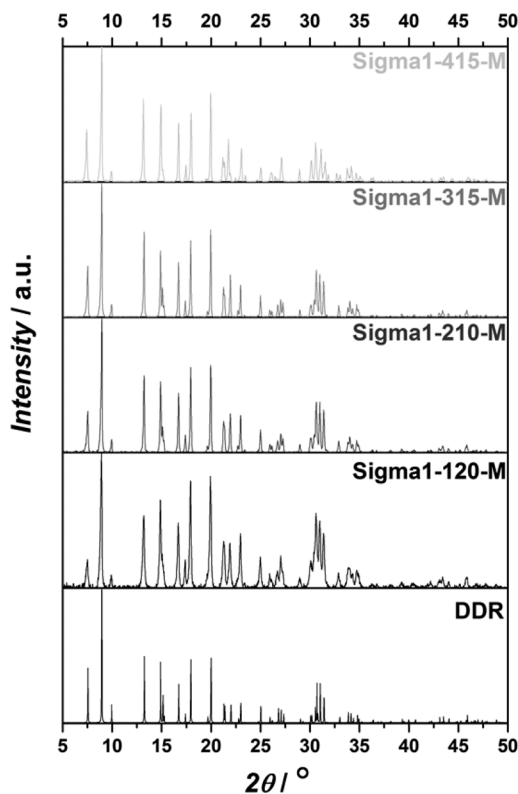


Fig. 1 XRD patterns of calcined Sigma-1 zeolites compared with the DDR powder patterns.

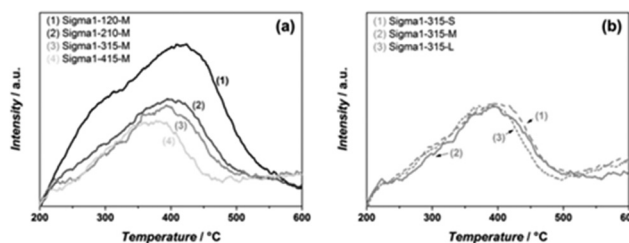


Fig. 3 NH_3 TPD profiles of Sigma-1 zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and medium crystal size (a), and of different crystal sizes with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 315 (b).



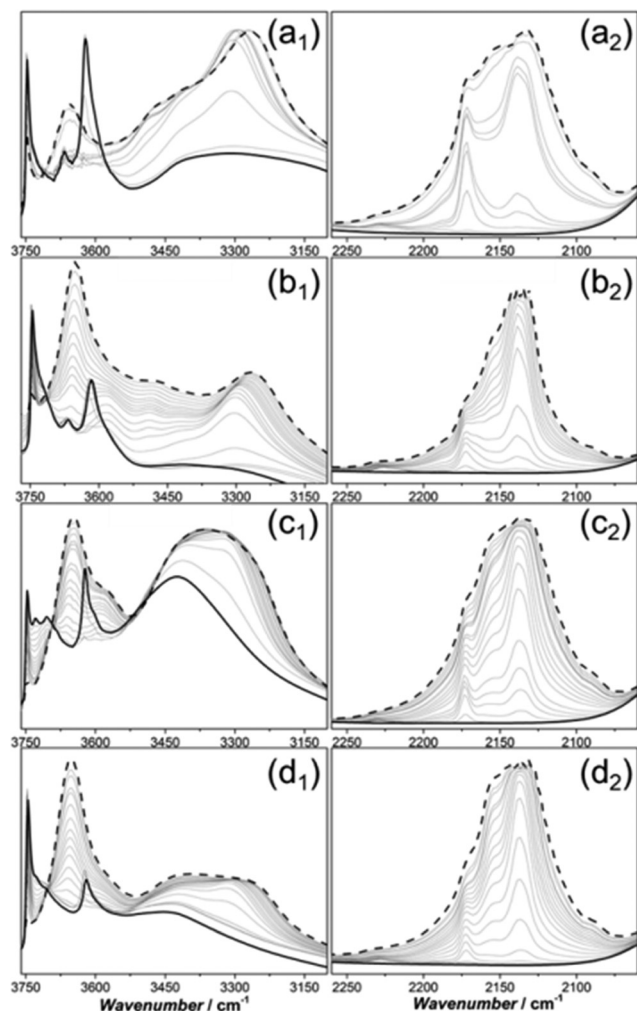


Fig. 4 FT-IR spectra measured at -130 °C after adding increasing dosages of CO on (a) Sigma1-120-M; (b) ZSM-58; (c) Sigma1-315-S; (d) Sigma1-315-S-m. Panels a_1 , b_1 , c_1 and d_1 report the spectra in the hydroxyl group range (3760 – 3100 cm^{-1}), while panels a_2 , b_2 , c_2 and d_2 report the CO vibrational mode region (2260 – 2060 cm^{-1}). The bold solid line represents pretreated catalysts in vacuum, while the dashed black curves represent spectra collected at 30 mbar CO equilibrium.

hydroxyl groups, located at the internal and external surface of the zeolite.³⁴ Sigma1-315-S is also characterized by the presence of a triplet with maxima at 3747 cm^{-1} (HF), 3729 cm^{-1} (LF) and 3706 cm^{-1} (LF). The latter two represent vicinal silanol groups where only oxygen participates in H-bonding and the proton is relatively mobile.³⁵ Further analysis reveals absorption bands around 3668 cm^{-1} for Sigma1-120-M and ZSM-58, pointing to the presence of extra-framework Al. An absorption band with a maximum at 3616 cm^{-1} is observed for all samples and represents Brønsted acidic OH groups. The broad band at about 3450 cm^{-1} , which is especially prominent for Sigma1-120-M (Fig. 4a₁) and Sigma1-315-S (Fig. 4c₁), suggests the presence of silanol nests originating from structural defects.³⁶ Upon interaction with CO, the bands associated with Brønsted acidity decrease at the same time as a band at ~ 3300 cm^{-1} develops. The exact position

of this band and shift in ν_{OH} is different for each sample: $\Delta\nu_{\text{OH}} = 355$ cm^{-1} (Sigma1-120-M), $\Delta\nu_{\text{OH}} = 351$ cm^{-1} (ZSM-58), $\Delta\nu_{\text{OH}} = 313$ cm^{-1} (Sigma1-315-S), $\Delta\nu_{\text{OH}} = 317$ cm^{-1} (Sigma1-315-S-m). The higher the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, the lower is the $\Delta\nu_{\text{OH}}$, indicating lower acid strength, in agreement with NH_3 TPD results.

In the CO stretching region (Fig. 4, panels a_2 , b_2 , c_2 , d_2), a band located at 2171 cm^{-1} appears at low CO coverage.¹⁷ This component arises from the interaction with strong Brønsted acid sites. At high CO coverage, the bands at about 2156 and 2138 cm^{-1} become more prominent, corresponding to CO interacting with silanol groups and liquid-like CO condensed in the zeolite pores, respectively. It should be also mentioned that the CO region is additionally characterized by the presence of components at 2227 cm^{-1} , protuberant for Sigma1-120-M and ZSM-58 (Fig. 4, panels a_2 , b_2). They are tentatively assigned to CO adsorbed on extraframework Al^{3+} .³⁷

3.2. Catalytic results

As also reported by Kumita *et al.*⁹ for DDR catalysts, no olefins bigger than C₅ are observed when Sigma-1 is used as catalyst, independent of the applied reaction conditions. In addition, the formation of paraffins is very low, with ethane yields lower than 1% and some traces of propane (Table 1). Formation of DME is only observed once MeOH conversion drops below 100% becoming the main product at the catalyst deactivation stage. The overall product distribution of catalysts is reported in ESI† (Table S2).

In the next paragraphs, the effect of reaction conditions on catalyst life-time and selectivity is extensively described.

3.2.1. Effect of temperature. Fig. 5 summarizes results obtained for Sigma1-315-M catalysts over the range of temperatures between 380 and 475 °C. The MeOH throughput before deactivation (Fig. 5a) increases with increasing reaction temperature, however without significant changes between 450 and 475 °C. As reported elsewhere,³⁸ higher temperatures favor ethylene formation (maximum yield 44%), while propylene is the main product at lower temperatures, with yields as high as 50%. The ethylene-to-propylene ratio varies from 0.5 to 1.6 when comparing results for 380 °C and 475 °C, while the maximum overall yield of ethylene and propylene together reaches 83% at 450 °C. The yield of butenes follows the same trend as propylene, reaching a maximum of 14% at 380 °C and not exceeding 5% at 475 °C. Based on these results and on additional experiments performed at varying the Si/Al ratio, 450 °C was chosen as the optimal reaction temperature and will be used as reference condition to compare the different Sigma-1 catalysts.

3.2.2. Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. In order to investigate the effect of the amount of acid sites and their strength on catalytic activity and selectivity, catalysts with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were synthesized while maintaining the mean crystal size. Fig. 6a compares catalytic performance at 450 °C for four Sigma-1 zeolites with different acidity, but the same crystal size. The methanol uptake is inversely related to the



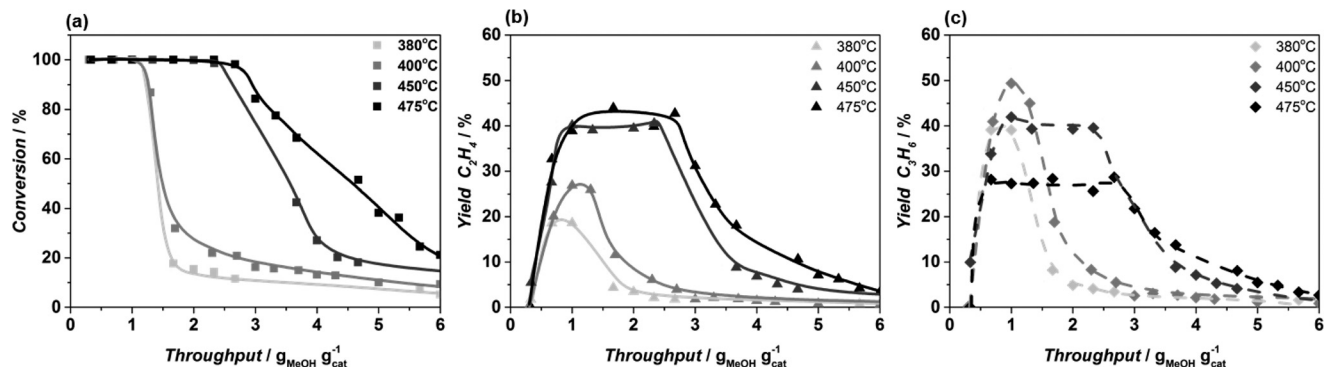


Fig. 5 Methanol conversion (a), yield of ethylene (b) and propylene at 380 °C (□, ▲, ◆), 400 °C (■, ▲, ◆), 450 °C (▨, ▲, ◆) and 475 °C (■, ▲, ◆) obtained in MTO reaction over Sigma1-315-M zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 315$ and crystal size of 2.5 μm at standard operation conditions.

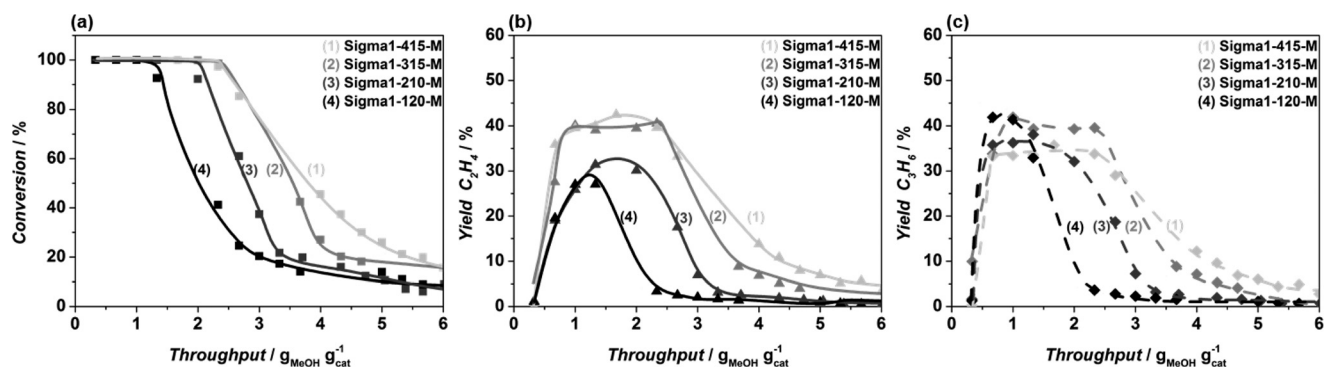


Fig. 6 Methanol conversion (a), yield of ethylene (b) and propylene at 450 °C, obtained in MTO reaction over Sigma1-415-M (□, ▲, ◆), Sigma1-315-M (■, ▲, ◆), Sigma1-210-M (▨, ▲, ◆), and Sigma1-120-M (■, ▲, ◆) zeolite at standard operation conditions.

amount of Al in the system, the difference in catalytic activity becoming less pronounced at high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. Thus, in both cases, for Sigma1-415-M and Sigma1-315-M, deactivation occurs after feeding 2.5 g of methanol per gram of catalyst. Based on the same catalytic activity of the abovementioned catalysts, a similar product distribution was expected, which is observed only for the yield towards ethylene. The maximum ethylene yield (Fig. 6b) increases from 28% (Sigma1-120-M) up to 43% (Sigma1-415-M), being the highest for the least acidic zeolite. The opposite trend is observed for the

propylene yield (Fig. 6c): the highest yield (43%) is monitored for Sigma1-120-M. To sum up, the C2/C3 ratio increases from 0.7 (Sigma1-120-M) to 1.3 (Sigma1-415) and the maximum overall yield (ethylene plus propylene) of 83% is observed for Sigma1-315-M. Therefore the effect of crystal size was further investigated using the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 315.

3.2.3 Effect of crystal size. Methanol conversion and yield to ethylene and propylene as a function of time on stream for zeolite Sigma1-315-M with crystal size 0.5, 2.5, and 4.6 μm are shown in Fig. 7. In line with previous reports,^{39,40} a

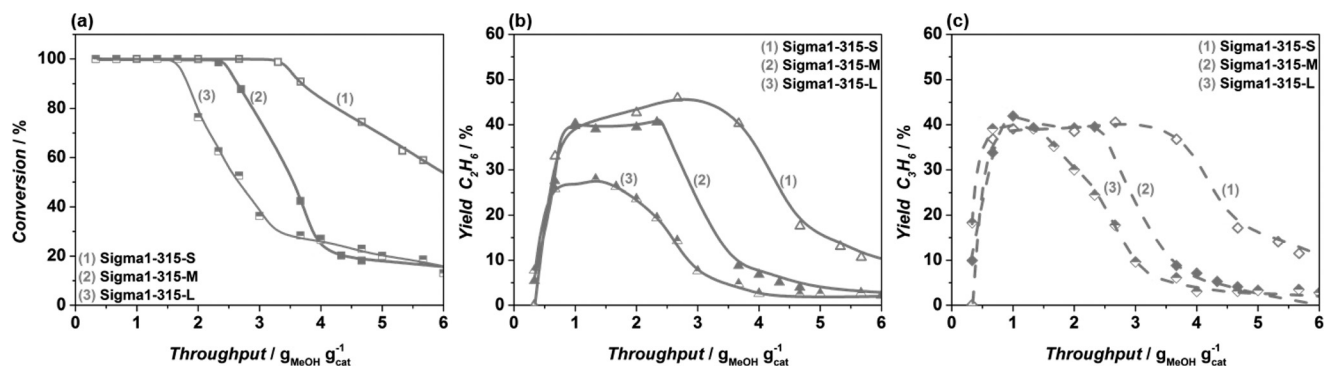
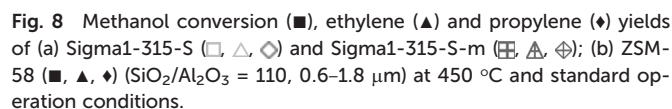


Fig. 7 Methanol conversion (a), yield of ethylene (b) and propylene at 450 °C, obtained in MTO reaction over Sigma1-315-S (□, ▲, ◆), Sigma1-315-M (■, ▲, ◆), Sigma1-315-L (◆, ▲, ■) zeolite at standard operation conditions.



This increase in propylene yield seems to be at the expense of ethylene formation. However, after having fed 2 g MeOH per gram of catalyst, the product distribution changes with decreasing propylene yield and increasing ethylene yield, becoming similar to the yields when only MeOH was

Finally, as the product mixture obtained from Sigma1-315-S tested at 450 °C consisted mainly of ethylene and propylene, also an experiment co-feeding ethylene, propylene and water was performed to mimic a situation where olefins can react with each other in absence of MeOH. Fig. 11 shows that although initially the product mixture contained equal molar amounts of ethylene and propylene, both decreased upon formation of butenes and some very small amounts of C5 and C6 products. Initially, ethylene was consumed more than propylene in this experiment, and their conversion gradually



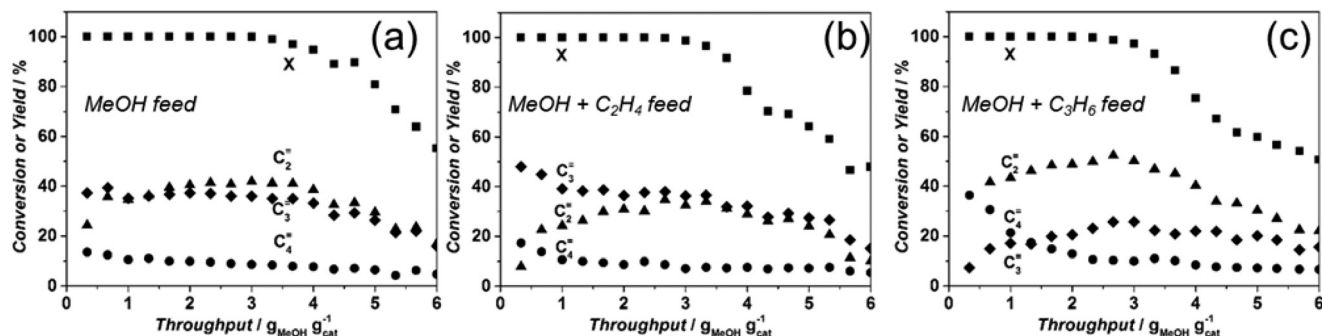


Fig. 9 Methanol conversion (■), ethylene (▲), propylene (♦) and butenes (●) yields obtained over Sigma1-315-S tested at 450 °C and standard operating conditions (a) 50% MeOH + 50% N₂; (b) 45% MeOH + 10% C₂H₄ + 45% N₂; (c) 45% MeOH + 10% C₃H₆ + 45% N₂.

declined until the composition returned to that of the feed mixture. The amount of butenes formed followed the ethylene and propylene conversion. Considering the converted amounts suggest only a minor participation of ethylene and propylene in consecutive reactions.

3.2.6. Coke formation. To characterize the coke species and elucidate their relation with catalyst selectivity, a DRIFT spectroscopic analysis was performed of the best catalytic system in terms of stability, Sigma1-315-S, after deactivation at four different temperatures and of the spent deactivated zeolites with different acidity and crystal size used at 450 °C. Fig. 12 summarizes the obtained results in the region of 2700–3100 cm⁻¹, characteristic of C–H bond vibrations. The spectra over the entire spectral range can be found in ESI† (Fig. S2).

Bands at around 2960 cm⁻¹, 2930 cm⁻¹ and 2870 cm⁻¹ are present in all deactivated samples. For spent catalyst used at 380 °C and 400 °C (Fig. 12a) the band at 2960 cm⁻¹ is more intense than the one at 2930 cm⁻¹. However, it steadily decreases with increasing reaction temperature and already at

450 °C the band at 2930 cm⁻¹ is dominant. Fig. 9b and c show that the ratio between the intensities of bands at 2930 cm⁻¹ and 2960 cm⁻¹ depend on acidity and crystal size. The latter band is more pronounced in samples with higher acidity (Sigma1-120-M) and large crystal size (Sigma1-315-L). The spectra obtained for the spent desilicated Sigma1-315-S-m are different from the non-modified samples: an additional band appears at 2856 cm⁻¹ and the band at 2960 cm⁻¹ shifts to 2958 cm⁻¹. Both bands at 2960 cm⁻¹ and 2930 cm⁻¹ are ascribed to the C–H stretching from methyl group in methylated benzenes and/or naphthalenes in the pores of the deactivated zeolites.⁴² The presence of bands in the region of 2960–2930 cm⁻¹ shows the presence of aromatics with different substituents indicating different formed species depending on the acidity and morphology of the catalyst as well as the testing conditions. The broad band at 2930–2925 cm⁻¹ is characteristic for highly alkylated benzenes, naphthalenes and phenanthrenes.⁴² The band at 2870 cm⁻¹ represents asymmetric stretching of the C–H bond from methyl group CH(CH₃),⁴³ while at 2855 cm⁻¹ C–H from methanol or DME.⁴⁴

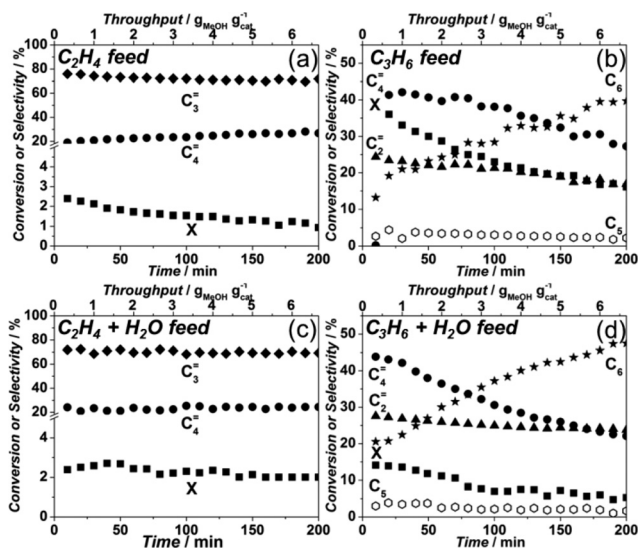


Fig. 10 Product distribution in co-feeding experiments performed over Sigma1-315-S at 450 °C (a) 10% C₂H₄ + 90% N₂; (b) 10% C₃H₆ + 90% N₂; (c) 45% H₂O + 10% C₂H₄ + 45% N₂; (d) 45% H₂O + 10% C₃H₆ + 45% N₂.

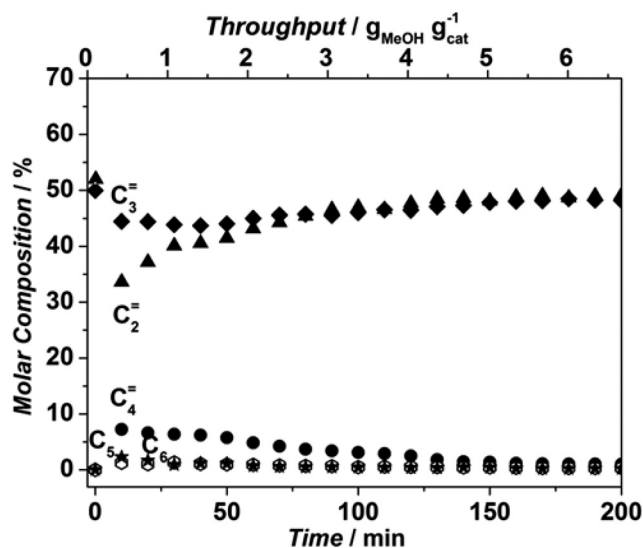


Fig. 11 Product distribution in co-feeding C₂H₄ and C₃H₆ in the presence of water over Sigma1-315-S at 450 °C.

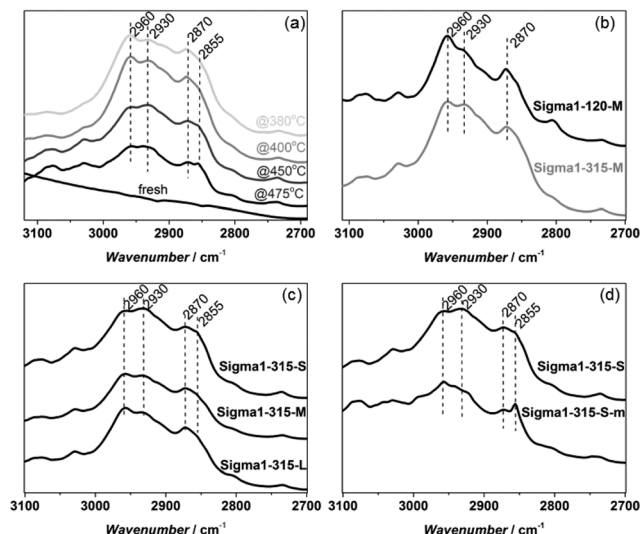


Fig. 12 DRIFT spectra of spent Sigma1-315-S catalyst used at different temperatures (a); Sigma1-120-M and Sigma1-315-M at 450 °C (b); Sigma1-315-S, Sigma1-315-M and Sigma1-315-L at 450 °C (c); Sigma1-315-S and desilicated Sigma1-315-S-m at 450 °C (d).

Additionally, a band at $\sim 3030\text{ cm}^{-1}$ could be identified in all catalysts, becoming more prominent in samples deactivated at temperatures higher than 400 °C. Bands in this region are attributed to aromatic C–H stretching vibrations, implying the presence of partially substituted aromatics.⁴⁵

The region at $1250\text{--}1700\text{ cm}^{-1}$ (Fig. S2 in ESI†) is characterized by bands (1600 and 1567 cm^{-1}) already described for deactivated DDR samples.⁹ In line with Kumita *et al.* observations, also a broad band at around 1600 cm^{-1} was observed, which is a combination of carbonaceous hydrogen deficient deposits⁴⁶ and aromatic $\nu(\text{C}=\text{C})$ modes.⁴⁷ The intensity of the band at 1567 cm^{-1} varies from sample to sample, being the highest for the one with the highest acidity (Sigma1-120-M) indicating a higher concentration of alkylnaphthalenes and phenanthrene and pyrene structures⁴⁸ trapped in the cages.

The spent catalysts chosen for DRIFTS were further analysed by dissolving the samples in HF, followed by extraction with CH_2Cl_2 and analysis of the extract with GC–MS. Fig. 13 shows that the nature of retained species is dependent on both reaction conditions and physicochemical

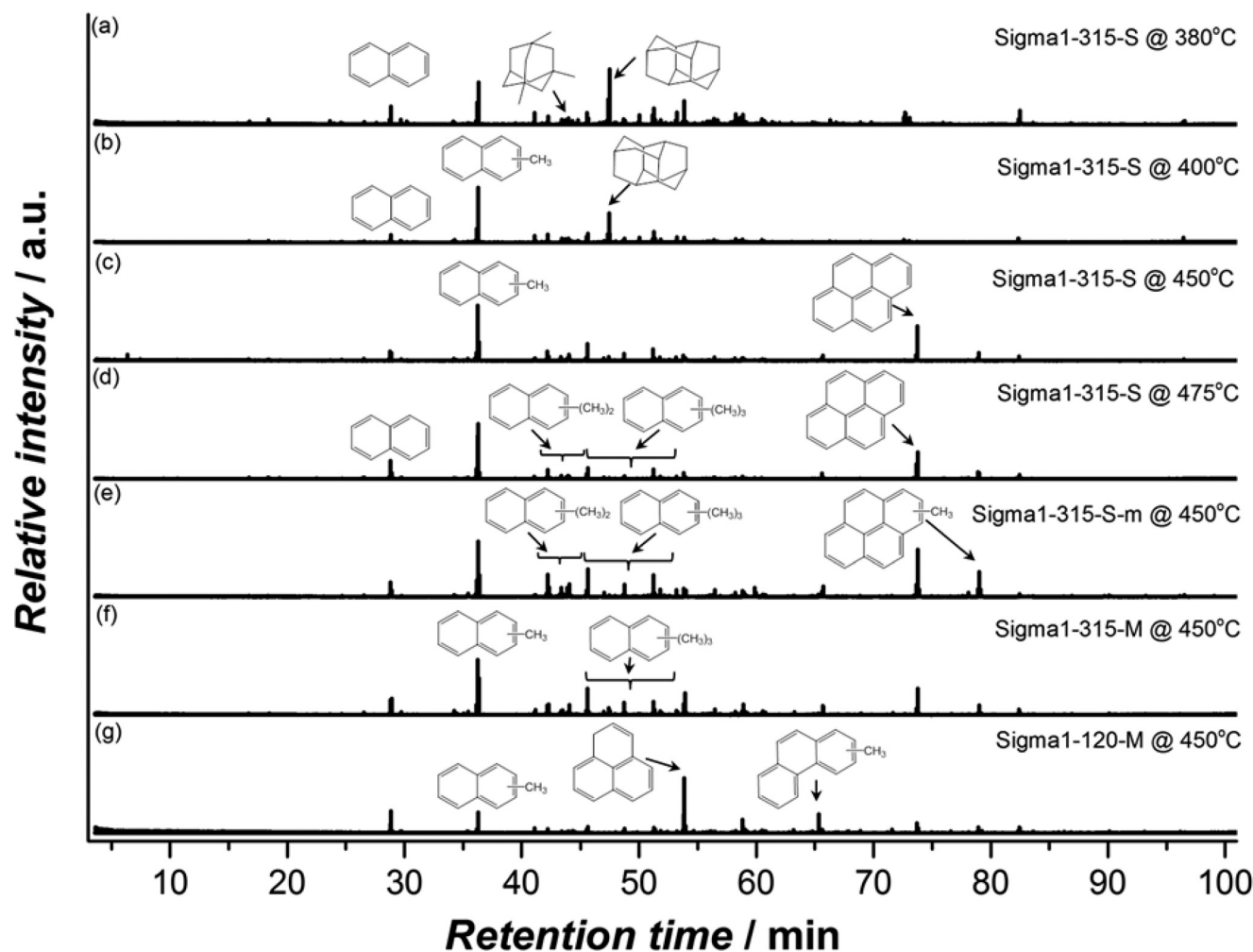


Fig. 13 GC–MS chromatograms of the hydrocarbon compounds retained in the various spent (deactivated) Sigma-1 zeolites used at different temperatures.



properties of the zeolites with naphthalenic species being dominant. The fraction of methylbenzenes was found to be negligibly small or even completely absent in some cases. Panels (a)–(d) show that the organic residue in the spent catalysts is characterized by mono-alkylated naphthalenes, being the main fraction for all samples except for Sigma1-315-S used at 380 °C, the lowest operation temperature. Interestingly, the main fraction of trapped species in this sample is represented by diadamantane, product of adamantane condensation. These species could also be found in all other deactivated samples, but their fraction significantly decreases with increasing reaction temperature. The formation of diamondoid hydrocarbons in cages of 8MR zeolites at lower temperatures was recently reported by Wei *et al.*⁴⁹ Chen *et al.*⁵⁰ also attributed the formation of adamantane hydrocarbons to spatial constraints imposed by the cage structure and attributed prompt deactivation at low temperatures to preferential formation of adamantanes over methylbenzenes. Further analysis of the organic residue in spent Sigma1-315-S reveals the formation of pyrene species, with an increased contribution at higher reaction temperatures.

In contrast with Sigma1-315-M, species trapped in Sigma1-120-M deactivated at 450 °C are mostly represented by phenalene and phenanthrenic species and almost no alkylated naphthalene derivatives. Comparison of zeolites with the same acidity but different crystal size (Sigma1-315-S vs. Sigma1-315-M) does not reveal any difference in the species found in the spent catalysts.

The total amount of retained organic material analyzed by TGA is observed to be dependent on the amount of acid sites and crystal size. The amount of coke retained in zeolite cages increases from 8.1 to 10.5 wt% for samples with SiO₂/Al₂O₃ = 120 and 400, respectively. Moreover, for samples with SiO₂/Al₂O₃ = 400 the coke content measured after use at 450 °C varies from 9.6 to 11.7 wt% for samples with crystal size 4.6 and 0.5 μm, respectively. However, the amount of coke linearly increases for catalysts having a MeOH throughput before deactivation of less than 4 g g^{−1}, reaching 12 wt% for materials that converted more than 4 g MeOH per gram catalyst, indicating that the catalytic improvement is due to the slowing down coke formation kinetics or due to the changing chemistry of the species itself (Fig. S3†).

4. Discussion

The MTO process is most probably among the most challenging catalytic processes from a fundamental perspective. In spite of the large number of investigations, still many questions regarding mechanism and reactivity are to be answered. One of the most striking observations is the difference in catalytic behavior among zeolite topologies. In case of 8MR zeolites, the carbon pool mechanism seems to dominate the formation of products.⁶ The nature of this mechanism, which proceeds *via* the formation of aromatics that obviously do not fit through small pore zeolites, makes catalyst testing rather challenging. Indeed, classical kinetic testing at low

conversion levels, in contrast to recent examples with ZSM-5,^{38,51,52} is not possible when 8MR zeolites are used. Inspired by these recent examples, we have performed experiments at varying space velocities. In every case, 100% conversion was reached and similar throughputs before deactivation, in clear contrast to what was observed in case of ZSM-5. These experiments point at a much higher reactivity of 8MR zeolites and to the fact that kinetic control cannot be achieved during catalyst testing. As a consequence, comparison between different catalysts has traditionally been done at 100% conversion, see for example the review article of Stöcker² about the comparison of different zeolites.

A logical consequence of catalyst testing at 100% conversion is the appearance of the so-called migrating reaction zone, first proposed by Schulz.⁴¹ Along this line, one can envisage the existence of at least two different zones in the catalytic bed, namely: the part of the bed where methanol is still present and the part of the bed where primary MTO products (short-chain olefins and water) participate in secondary reactions in the absence of methanol. This phenomenon might imply the dependence of the catalyst lifetime on the ratios of these zones in the catalytic bed and makes mechanistic discussions based on such testing conditions rather doubtful, as demonstrated for ZSM-5 over the last few years.^{38,51,52}

With this background, the assumption of a similar situation in case of 8MR zeolites is not straightforward. The migrating reaction zone considers that reaction products will diffuse into zeolite pores in the bottom part of the reactor and react further. This is indeed something feasible in case of 10MR or 12MR zeolites, where diffusivities of coefficients at reaction temperature for *i.e.* propylene have been estimated to be in the range of 10^{−8} m² s^{−1}. In contrast, for 8MR zeolites, such as CHA or DDR, diffusivities of at least two orders of magnitude smaller (10^{−10} m² s^{−1}) have been reported for propylene.^{53,54} When considering these numbers, one can anticipate that reaction of primary products in the bottom part of the reactor will be diffusion limited (*i.e.* to achieve half saturation capacity for propene of a 1 μm DDR crystal would take *circa* 20 minutes under reaction conditions, considering that there is no co-adsorption of other products like water). The co-feeding experiments confirm this hypothesis. On one hand, the presence of additional ethylene or propylene together with methanol does not alter the catalyst lifetime, pointing to a negligible interaction of formed olefins with coke precursors, which are of the same nature based on the results obtained from DRIFTS. Considering further the stage in the catalytic bed where the main products, ethylene, propylene and mixtures thereof, can undergo consecutive reactions in the presence of water, Fig. 10 indicates a negligible conversion of ethylene and a conversion of propylene with the production of butenes and C6 hydrocarbons. The appearance of longer hydrocarbons, which are not able to diffuse out of the DDR structure due to their big kinetic diameter,⁵⁵ indicates that they are formed on the outer surface of the crystals and that propylene reacts mostly at the surface of the particles as it does not have enough time to diffuse into the



pores of Sigma-1, while the less reactive ethylene passes through the reactor basically without being converted. Thus, on the outer surface of the crystals, propylene dimerization to C6 and cracking of C6 to C4 and C2 is taking place, both reactions being catalyzed by external acid sites.⁵⁶

These results demonstrate, that a mechanistic analysis, especially when referring to coke formation in small pore systems (8MR), can, with a large degree of confidence, be made based on results obtained at 100% conversion. Clearly, in order to fully assess selectivity to different products, co-feeding experiments should be performed.

Coming back to the catalyst itself, the Sigma-1 zeolite with DDR topology is a noteworthy nominee among 8MR zeolites displaying outstanding selectivities to light olefins (*i.e.*, propene) and hardly any formation of paraffins (Table 1), something highly relevant from the application perspective. Indeed, the selective formation of olefins means large savings as the separation of short olefin/paraffin mixtures is among the most energy intensive processes in chemical industry.⁵⁷

Despite the fact that the synthesis of Sigma-1 zeolite was patented in 1987 by Stewart,¹¹ the number of publications dealing with this material is rather low. This is probably due to the long synthesis and difficult reproducibility of materials with DDR topology, as extensively discussed by Gücüyener *et al.*¹⁴ However, the application of as-synthesized material as seeds does not only accelerate the synthesis¹³ but also leads to the pure phase with narrow crystal size distribution. The seed inductive effect described by Yu *et al.* for ZSM-5 (ref. 58) explains the role of seeds as a recognition effect, promoting nucleation of alike building units and acting as nuclei for the growth of zeolite crystals.

As already observed for ZSM-58,⁹ Sigma-1 displays up to 90% selectivity to ethylene and propylene almost without any propane being formed. The observed behavior lies in the unique structure of DDR cage and pore opening with dimensions of 4.4×3.6 Å, excluding molecules with kinetic diameter bigger than the window.^{15,55}

The ethylene-to-propylene ratio of the product mixture could be tuned by both varying reaction conditions and catalyst composition and morphology. As a general observation, the parameters leading to the highest selectivity to ethylene also lead to the lowest selectivity to propylene, already pointing at competing reaction pathways to form these molecules.

At lower temperatures, the formation of propylene is favored over ethylene, while the MeOH throughput before deactivation is two times smaller. According to the generally accepted dual-cycle mechanism for the MTO process,⁵⁹ the observed behavior is tentatively attributed to kinetic competition between the two cycles. First principle chemical kinetics calculations for the methylation of ethylene and propene show much higher activation energies for ethylene methylation pathway and hence methylation rates are one order magnitude higher when comparing ethylene and propylene.⁶⁰ Quick catalyst deactivation observed at lower temperatures could be ascribed to the formation of diamondoid species.

On the basis of literature evaluation^{49,50} and our own observations, one can suggest that at lower reaction temperatures 8MR zeolites with a cage-like structure promote formation of adamantane derivatives which are inert and lead to cage blocking. Their formation is probably favored due to the chemical and structural similarity to the SDAs (interaction of SDA with a cage is stable *a priori*) which points to the relatively low entropy contribution to the free energy barriers leading to high reaction rates.⁶¹ Higher reaction temperatures promote the cracking cycle together with elimination of ethylene from alkylated aromatics, but at this stage pyrene species (Fig. 13) start contributing to catalyst deactivation as these larger aromatic structures do not leave space for functionalization. The prevalence of dealkylation and/or cracking reactions at high temperatures was demonstrated by Qian *et al.*,⁶² who showed kinetic and mechanistic differences occurring in hydro-carbon pool at high and low temperatures by applying the combination of UV/Vis, confocal fluorescence, and synchrotron-based IR micro-spectroscopic techniques. It has to be mentioned as well that the presence of phenanthrene and pyrene species (Fig. 13) is surprising, as at most naphthalene derivatives fit in a DDR cage. This may indicate that polycyclic species should have been formed on the outer surfaces of the zeolite and/or in defects.¹⁷

The Si/Al ratio is another parameter that affects both MeOH throughput before deactivation of the catalyst and selectivity to light olefins. Application of zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 120$, which corresponds to one Al per cage of zeolite, leads to a fast deactivation, while the $\text{SiO}_2/\text{Al}_2\text{O}_3 = 315$ with 0.5 Al atoms per cage gives the best results, in terms of MeOH uptake and ethylene and propylene yields. NH_3 TPD results demonstrate that the Al content defines not only the amount but also the strength of acid sites. Application of zeolites with moderate acidity, characterized by an NH_3 desorption peak in the range of 375–385 °C significantly increases MeOH throughput before deactivation. Interestingly, FT-IR spectroscopy and dissolution experiments demonstrate that, depending on the strength of acidity, the formed ‘coke’ species are different, the presence of methylbenzenes/methylnaphthalenes being more prominent present in spent Sigma-415-S, the zeolite with the lowest acidity. Moreover, the maximum concentration of methylbenzenes and methylnaphthalenes coincides with the maximum yield of ethylene, confirming the hypothesis that ethylene originates from the aromatic cycle. Furthermore, analysis of coke species formed over more acidic Sigma1-120-M shows the lowest amount of methyl-substituted aromatics corresponds to the lowest yield of ethylene than comparing Sigma1-120-M with other samples.

The observed findings regarding the effect of Si/Al ratio are in contradiction with the ZSM-58 results, where the best catalytic performance was found for zeolites with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 110$ and a further decrease in acidity (higher ratios) led to an abrupt loss of activity.⁹ However, in case of ZSM-58 the decreasing acidity was accompanied by an increased particle size, distorting the effect of acidity by additional diffusional



An increased MeOH uptake for smaller particles is attributed to the shortening of the diffusion pathway of reactants and products and related to the accessibility of the crystals

Results reported by Barbera *et al.*, confirm our observations.²⁶ Recently, these authors showed that the deactivation of a series of ZSM-5 catalysts correlated with the relative intensities of silanols rather than with the amount of acid sites, suggesting possible “retention effects” of silanols on coke precursor that lead to a faster activity loss.

Secondary reactions of the olefinic products occurred hardly, and only at the outer surface of the zeolite crystals. These processes did not affect the activity for the MTO reaction.

The influence of internal framework defects on MTO performance has been shown to be of the utmost importance. The presence of a larger number of silanol nests in Sigma-1 resulted in a faster deactivation than in case of ZSM-58, where such defects were hardly observed. According to our results, the presence of structural defects leads to a faster coke formation kinetics and therefore to a rapid deactivation. Upon removal of silanol nests from Sigma-1, the catalytic performance becomes comparable to the one of ZSM-58. Indeed, the presence of structural defects has a much bigger importance than many other parameters usually studied and will certainly be key for the large scale implementation of MTO processes based on these materials, since both industrial catalyst production and continuous regeneration may lead to the formation of additional crystal defects that will eventually influence coke formation rate.

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The results here presented confirm the high selectivity of zeolites with the DDR topology for the formation of ethylene and propylene (up to a 90%) when used as catalysts in the MTO process. Such high selectivities are the result of an ideal combination between cage geometry and window size that allows only C2 and C3 olefins to leave the cages of this zeolite. From an application perspective, this size restriction is very important. Since pure C3 olefin is formed, the separation of products becomes much less energy intensive.

One of the crucial parameters for catalyst stability is the overall zeolite acidity and strength. It was found that decreasing acidity of the zeolite from $\text{SiO}_2/\text{Al}_2\text{O}_3 = 120$ to $\text{SiO}_2/\text{Al}_2\text{O}_3 = 315$ leads to a two-fold increase in methanol throughput before full deactivation occurs. Furthermore, a decrease in the crystal size of Sigma-1 zeolite with optimized acidity led to almost two times improved throughput, ascribed to an improved utilization of the 2D porosity of this material.

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