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Supplementary information to

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The intricacies of the "steady-state" regime in methanol-to-hydrocarbons experimentation over H-ZSM-5

Marie-Elisabeth M.L. Lissens, Pedro S.F. Mendes, Tingjun Lei, Maarten K. Sabbe,
Joris W. Thybaut*

Laboratory for Chemical Technology, Ghent University, Technologiepark 125, B-9052 Ghent, Belgium

*Corresponding author: Joris.Thybaut@UGent.be

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S1. Materials

To obtain the protonic form, the zeolite was calcined under static atmospheric air via a stepwise temperature procedure as shown in the following graph[1].

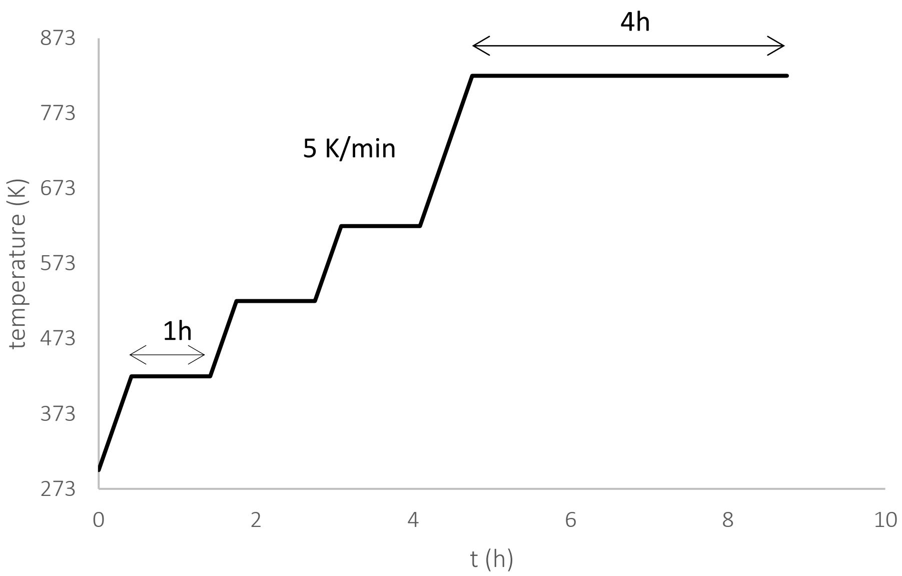

Figure 1: Temperature profile for calcination of NH_4-ZSM-5 catalyst into its protonic form.

S2. Characterisation

The bulk elemental chemical composition (sodium, aluminium and silicon) of the uncalcined and calcined catalyst was determined by inductively coupled plasma optical emission spectrometry (IRIS Intrepid II XSP from Thermo Scientific) and is shown in Table 1.

The Si/Al ratio obtained by ICP has a slight deviation to the information provided by Zeolyst International.

Table 1: Si, Al and Na content in the zeolite H-ZSM-5 determined by ICP OES.

%mol	Si	Al	Na_2O_3	Si/Al
NH_4-ZSM-5(40)	97.6	2.4	< 0.01	41.3
H-ZSM-5(40)	97.6	2.5	0.02	38.6

N_2-adsorption experiments were performed at 77 K in a Tristar Micromeritics set-up. The samples were first degassed to remove adsorbates from the surface. The total porous volume V_{tot} was calculated via the adsorbed nitrogen volume for a relative pressure P/P° of 0.97, while the micropore volume V_{micro} and the external surface area S_{ext} of the catalyst was determined using the t-plot method[1, 2]. The mesoporous volume V_{meso} was calculated as the difference between V_{tot} and V_{micro}.

The results were as expected[3] and are shown in Table 2.

Table 2: Porous volumes measured by N_2-adsorption-desorption measurements for H-ZSM-5 and NH_4-ZSM-5 (Si/Al=40)

	NH_4-ZSM-5	**H-ZSM-5**
Total pore volume (cm^3/g)	0.25	0.25
Micropore volume (cm^3/g)	0.12	0.12
Mesopore volume (cm^3/g)	0.13	0.13
BET Surface Area (m^2/g)	383	400
t-Plot Micropore Area (m^2/g)	252	234
External Surface Area (m^2/g)	130	162

The crystalline structure of the uncalcined and calcined zeolites was determined using powder X-ray diffraction (XRD) with a Bruker D8-AXS Discover setup and a linear Vantec detector, and a CuK_α X-ray source (λ = 1.54 Å) under continuous scan mode. The XRD pattern was compared to literature patterns and show good correspondence[4-6], as shown in Figure 2 .

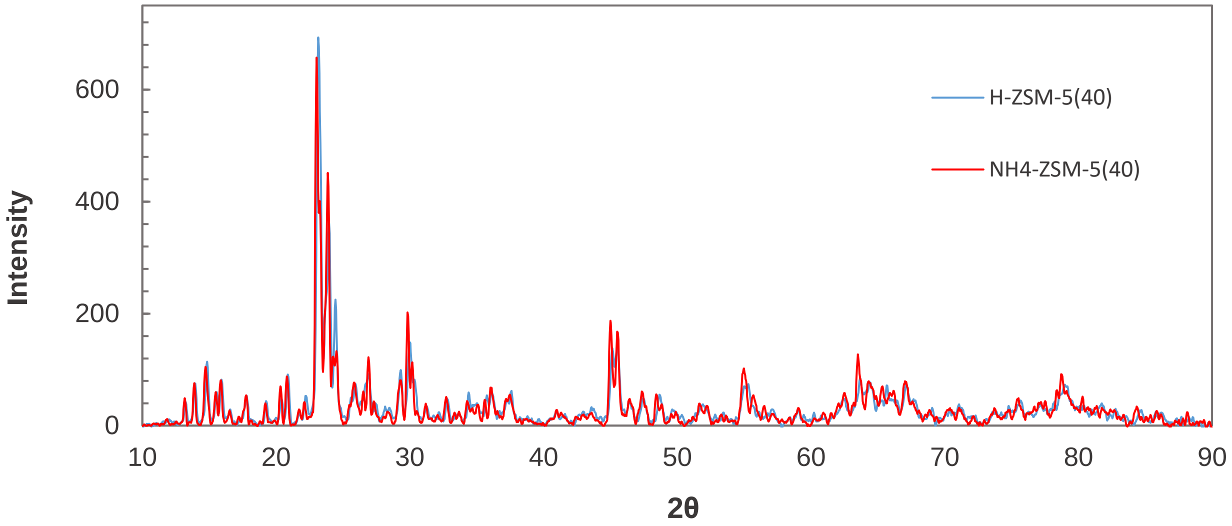

Figure 2: XRD patterns of ZSM-5 (Si/Al=40), of the calcined and uncalcined sample

S3. Spent catalyst characterization procedure

The procedure consisted of five consecutive steps. First, 20 mg of the spent catalyst sample was treated with HF (Chem-lab, 40%) with 0.5 ml in a polypropylene cup for 1h at room temperature. This was followed by adding 0.5 ml of dichloromethane (Sigma–Aldrich, 99.8%) which was mixed for 2 min. Subsequently, the organic and aqueous phases were separated using a centrifuge to remove the aqueous phase. Next, 0.5 ml demineralized water was added, mixed with the organic phase, separated using a centrifuge and removed three times to ensure the absence of HF. Finally, the organic phase was analysed by a Agilent Technologies 6850 series II gas chromatograph equipped with an FID detector and HP-PONA column. The relative amount of components from different catalyst samples was determined based on the peak areas of the aromatic fraction versus the solvent in the chromatogram.

S4. Catalytic testing

S4.1. Component identification

Table 3: Components (paraffinic, olefinic, aromatic and oxygenates) identified by GCxGC-MS after methanol conversion over ZSM-5 by increasing carbon number (from top to bottom and left to right).

methane
MeOH
ethane+ethylene
propane+propylene
DME
isobutane
isobutene + 1-butene
n-butane
trans-2-butene
cis-2-butene
2-methyl-1-butene (cis)
3-methyl-2-butene
iso-pentane
3methylbutane
1-pentene
2-methyl-1-butene
n-pentane
trans-2-pentene
cis-2-pentene
2-methyl-2-butene
3methyl1pentene
3methyl2pentene (cis)
2-methyl-pentane
3-methyl-pentane
2-methyl-pentene
3hexene (cis)
3 hexene (trans)
2hexene (cis)
3hexene (trans)
4methyl2pentene (cis)
3methyl2pentene (trans)
methylcyclopentane
4methyl2pentene (trans)
benzene
cyclohexane
C7-
C7=
cyclic C7
toluene
dimethylcyclopentene
cyclohexene
C8-
C8=
cyclic C8
ethylbenzene
ethylbenzene
p-xylene
m-xylene
o-xylene
n-propylbenzene
1-methyl-4-ethylbenzene
1-methyl-3-ethylbenzene
1,3,5-trimethylbenzene
1-methyl-2-ethylbenzene
1,2,4-trimethyl-benzene
1,3,5-tri-methyl-benzene
n-propyl-benzene
1,2,3-tri-methyl-benzene
1,2-dimethyl-4-ethylbenzene
1,4-diethyl-benzene
1,3-di-methyl-4-ethyl-benzene
1,4-di-methyl-2-ethyl-benzene
1,3-dimethyl-5-ethyl-benzene
1,3-di-ethyl-benzene
1,3-di-methyl-2-ethyl-benzene
1,2-dimethyl-3-ethyl-benzene
1,2,3,4-tetra-methyl-benzene
1,2,3,5-tetra-methyl-benzene
1,2,4,5-tetra-methyl-benzene

S4.2. Deactivation regime

As indicated in Figure 5 of the manuscript, the deactivation regime starts immediately at elevated temperatures (> 425 °C). At lower temperatures, long periods of stability (> 20h) are observed.

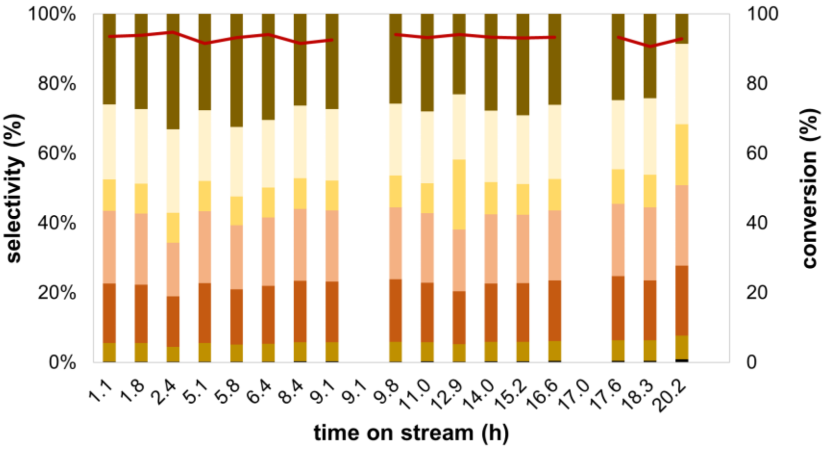

Figure 3: Oxygenate conversion (red line) and hydrocarbon selectivity of alkanes, light olefins and aromatics with TOS for H-ZSM-5 (Si/Al = 40) at 40 kPa, 375 °C and 15.5 kg_{cat} *s* mol_{MeOH}^{-1}*, with (■) methane, (■) ethylene, (■) propylene, (■)* C_4*-*C_5 *olefins, (■)* C_{6+} *olefins, (■) alkanes, (■) aromatics.*

S5. Intrinsic regime determination

Plug flow conditions, avoiding were evaluated using correlations from Mears et al.[7, 8]. The pressure drop (Δp) over the catalyst bed was evaluated with the Ergun equation[9] and should not exceed 20% of the total operating pressure for first order reactions. Radial isothermicity is verified by a criterion derived by Mears et al.[8] and axial temperature gradients were reduced by diluting the bed with inert α-Al_2O_3. To avoid invalid catalyst distribution affection the conversion, the bed dilution should remain limited[10].

In the catalyst pellet scale, the external mass transfer limitation over the gas around the catalyst pellet can be expressed with Carberry's number (Ca)[8], using Wakao's correlation for the mass transfer coefficient between pellet and bulk gas phase[11]. The intrapellet mass transfer limitation is evaluated by the Weisz-Prater criterion (ϕ)[12, 13]. The external and intrapellet mass transfer limitations were experimentally assessed by varying the catalyst particle diameter. The occurrence of intraparticle and external temperature gradients were assessed by criteria by Mears et al[8].

Table 4: Experimental conditions ensuring intrinsic kinetic data

Temperature (°C)	**325**	**350**	**375**	**400**	**450**
Catalyst particle size (µm) d_p	150-300	150-250	150-200	100-150	50-75
Inert:catalyst ratio (g/g)	2.5	2.5-4	5	5-7	10
Catalyst mass (g)	1.0	0.7-1.0	0.5	0.3	0.1
Bed length (L_b) (cm)	5	5	4	2-3.5	1.15
Pressure drop (Δp) (bar)	0.16	0.16	0.17	0.17	0.18
Carberry's number (Ca)	10^{-4} - 10^{-3}				
Weisz modulus(φ)	0.01-0.05				
Peclet number (-)	8.6-8.7				
Nusselt number (-)	2.6-4.0				
Reactor tube diamter (d_t) (cm)	1.1				

S6. Product distribution

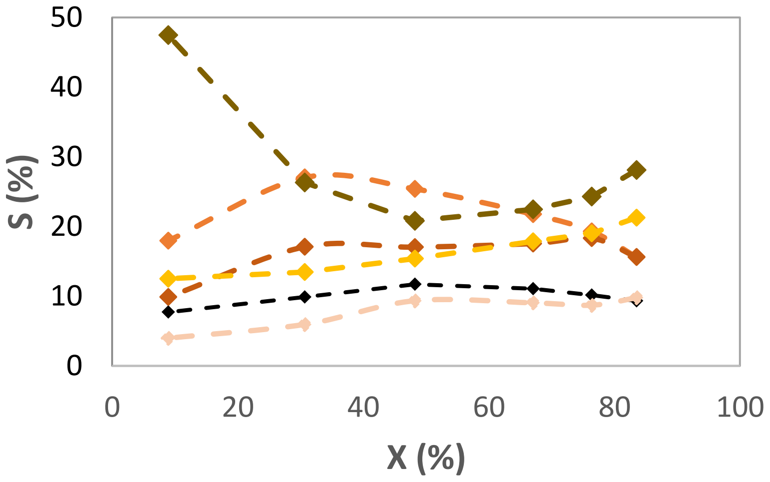

Figure 4: Hydrocarbon selectivity of alkanes, light olefins and aromatics with oxygenate conversion for H-ZSM-5 (Si/Al = 40) at 40 kPa p_{MeOH} and 350 °C and space times from 1.4 to 8.7 kg s mol^{-1}, with (■) methane, (■) ethylene, (■) propylene, (■) C_4-C_5 olefins, (■) C_{6+} olefins, (■) alkanes, (■) aromatics.

S7. References

1. F. M. Mota, PhD KU Leuven, 2013.
2. G. Leofanti, M. Padovan, G. Tozzola and B. Venturelli, *Catalysis Today*, 1998, **41**, 207-219.
3. J. Zhang, Z. Huang, P. Li, X. Zhang, X. Zhang, Y. Yuan and L. Xu, *Catalysis Science & Technology*, 2017, **7**, 2194-2203.
4. S. Ilias, R. Khare, A. Malek and A. Bhan, *Journal of Catalysis*, 2013, **303**, 135-140.
5. D. Serrano, G. Calleja, J. A. Botas and F. J. Gutiérrez, *Separation and Purification Technology*, 2007, **54**, 1-9.
6. A. S. Al-Dughaither and H. de Lasa, *Industrial & Engineering Chemistry Research*, 2014, **53**, 15303-15316.
7. D. E. Mears, *Chemical Engineering Science*, 1971, **26**, 1361-1366.
8. D. E. Mears, *Journal of Catalysis*, 1971, **20**, 127-131.
9. S. Ergun and A. A. Orning, *Industrial & Engineering Chemistry*, 1949, **41**, 1179-1184.
10. C. M. Van Den Bleek, K. Van Der Wiele and P. J. Van Den Berg, *Chemical Engineering Science*, 1969, **24**, 681-694.
11. N. Wakao, S. Kaguei and T. Funazkri, *Chemical Engineering Science*, 1979, **34**, 325-336.
12. P. B. Weisz and C. D. Prater, in *Advances in Catalysis*, eds. W. G. Frankenburg, V. I. Komarewsky and E. K. Rideal, Academic Press, 1954, vol. 6, pp. 143-196.
13. G. F. Froment, *Industrial & Engineering Chemistry*, 1967, **59**, 18-27.