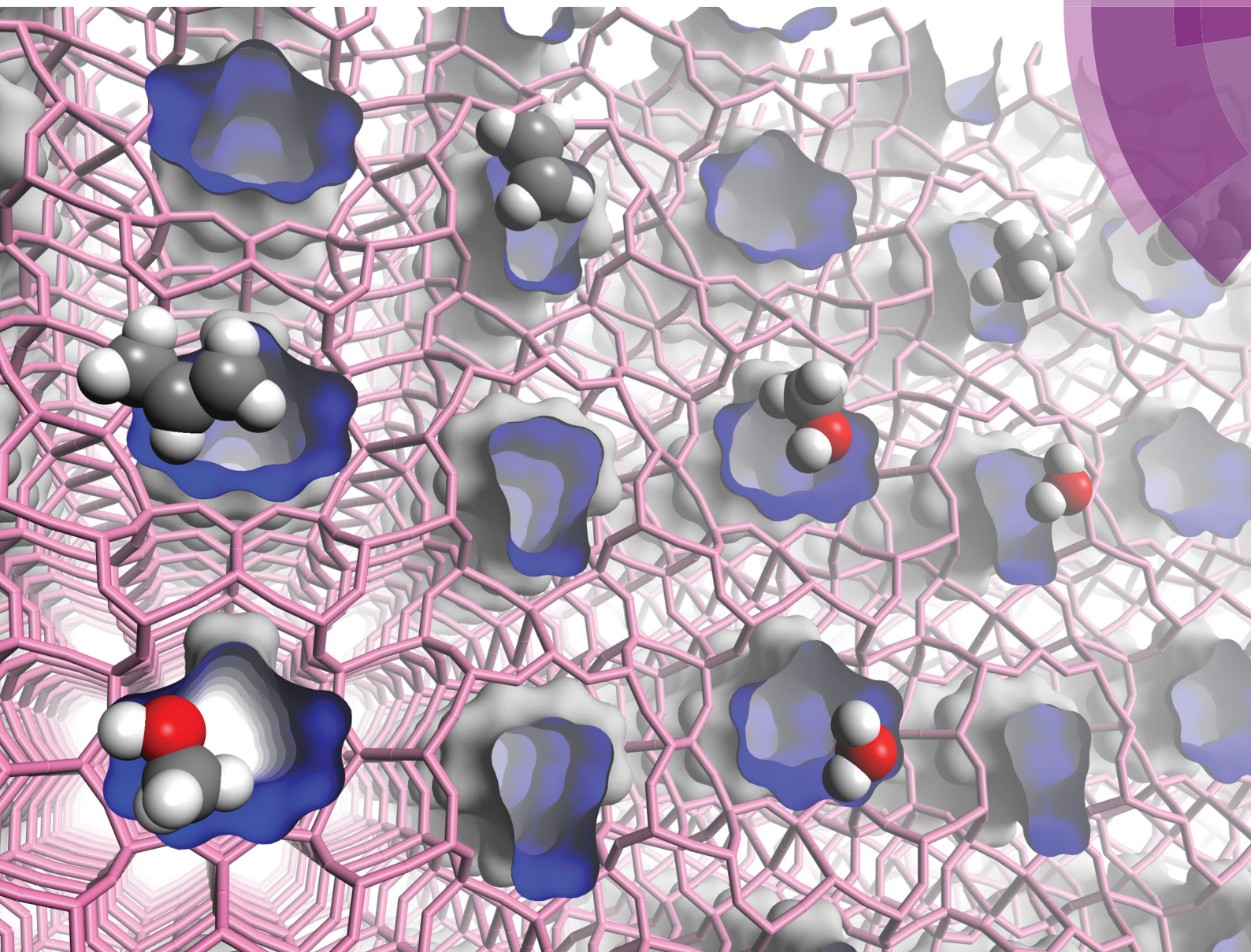


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S. Svelle, P. Beato *et al.*

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Conversion of methanol to hydrocarbons over zeolite ZSM-23 (MTT): exceptional effects of particle size on catalyst lifetime†

A. Molino,^a K. A. Łukaszuk,^a D. Rojo-Gama,^{ab} K. P. Lillerud,^a U. Olsbye,^{ab} S. Bordiga,^{ab} S. Svelle^{*a} and P. Beato^{ib} ^{*c}

A variety of synthetic procedures have been used to obtain zeolite ZSM-23 (MTT) catalysts with crystallite sizes ranging from the micrometer to nanometer scale. When the acidic zeolite is used as a catalyst for the methanol to hydrocarbon (MTH) reaction, the catalytic lifetime is dramatically influenced by the crystallite shape and size.

The methanol to hydrocarbon reaction is an important process in a chain of processes to convert carbon-rich feedstocks such as coal, natural gas, or biomass into hydrocarbon species such as light alkenes or gasoline fuel over porous acidic zeolite and zeotype catalysts. Because the reaction occurs within pores of molecular dimensions, the product selectivity is highly sensitive to the size and arrangement of the channel system; this is known as shape selectivity. Of particular interest are medium pore zeolites (pore circumference defined by 10 T atoms), such as the commercially employed ZSM-5 catalyst (10-ring intersecting channels that form a three-dimensional porous network). This catalyst is used in the Mobil Methanol to Gasoline (MTG)¹ and Topsøe Improved Gasoline Synthesis (TIGAS)² processes and shows a high selectivity towards an aromatics rich gasoline-range C₅–C₆₊ product.

Recently, it has been demonstrated that some 10-ring zeolites with non-intersecting, one-dimensional channels, such as ZSM-22 (TON) and ZSM-23 (MTT), also show a high selectivity towards C₅–C₆₊, but with a very low amount of aromatics.³ Such a product could be used as “clean gasoline”, similar to alkylate⁴ and isomerate.⁵ In the absence of channel intersections, aromatics

formation, and especially reactivity, is limited,⁶ but rapid deactivation caused by pore blocking is an issue because of the one-dimensional pore system. However, the role of the catalysis at the pore mouth for both ZSM-22 and ZSM-23 is still being argued.^{6,7} The one-dimensional medium pore zeolite ZSM-23 was first synthesized by Rubin.⁸ It is a high silica framework, belonging to the MTT topology. As many other unidirectional materials, ZSM-23 tends to grow with a needle-like shape morphology³ with a high aspect ratio, where the channel direction is parallel to the longest dimension of the needle.⁹ It is known that the zeolite crystallite size may influence the activity and selectivity of the catalysts, and in particular the catalyst lifetime. For example, the conversion of methanol,¹⁰ ethanol, and 2-propanol¹¹ to hydrocarbons has been studied on the SAPO-34 and SAPO-35¹² zeotype catalysts, and an increase of one order of magnitude in the catalytic lifetime¹³ was seen for the nano-sized SAPO-34. Moreover, for ZSM-5 a similar trend was observed¹³ for the MTH reaction. Khare *et al.*¹⁴ have highlighted how increasing the particle size may lead to a higher selectivity towards light alkenes due to a longer intra-crystalline residence time of key intermediates in the MTH reaction over ZSM-5. Of particular relevance to this study is the work of Wang *et al.*¹⁵ who employed ball milling to produce nano-sized ZSM-22 with a substantially improved MTH lifetime.

In this work, a series of zeolite ZSM-23 (MTT) catalysts with different particle sizes and morphologies have been prepared using direct synthesis and applied as catalysts for the conversion of methanol into hydrocarbons. A profound effect of the particle size on lifetime is demonstrated. The best catalyst produces nearly two orders of magnitude more turnovers compared to those of previous reports for the same and comparable topologies. This might pave the way for commercial (fixed bed) applications, which previously was unrealistic due to short lifetimes. ZSM-23 catalysts with different crystallite sizes were prepared by modifying the synthetic procedures described in the literature. The reported gel compositions were adjusted to obtain products with similar Si/Al ratios, in the range of 14–39. Key information is presented in Table 1 and the exact details of the synthesis procedures are presented in the ESI.†

^a Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway.
E-mail: stian.svelle@kjemi.uio.no

^b Department of Chemistry, NIS and INSTM Reference Centers, University of Turin, via Quarello 15, I-10135 Turin, Italy

^c Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark.
E-mail: pabb@topsoe.com

† Electronic supplementary information (ESI) available: Detailed description of the synthesis procedure, testing, N₂ isotherms, NH₃-TPD and refined powder XRD. See DOI: 10.1039/c6cc10118f

Table 1 Precursor gel molar batch composition of the different samples of ZSM-23

Catalyst	SiO ₂	Al ₂ O ₃	H ₂ O	Na ₂ O	SDA	Si source	Al source	SDA type	Time (h)	T (°C)
ZSM-23 DMF	1	0.014	29.5	0.36	0.55	Colloidal SiO ₂	Al ₂ (SO ₄) ₃	DMF	94	185
ZSM-23 Pyrr	1	0.03	45.5	0.20	0.45	Fumed SiO ₂	Al(NO ₃) ₃	Pyrrolidine	66	180
ZSM-23 iPA	1	0.012	26.7	0.046	2	Fumed SiO ₂	NaAlO ₂	Isopropylamine	92	160
ZSM-23 H/TMPD	1	0.025	31	0.06	1	Colloidal SiO ₂	NaAlO ₂	30% HMPD/70% TMPD	160	160
ZSM-23 C7 diquat	1	0.03	40	0.16	0.15	Fumed SiO ₂	Al(NO ₃) ₃	Heptamethoniumbromide	335	160

The catalysts are labelled according to the structure directing agent (SDA) employed:

ZSM-23 DMF for *N,N*-dimethylformamide,^{16,17} ZSM-23 Pyrr for pyrrolidine,⁹ ZSM-23 iPA for isopropylamine,⁹ ZSM-23 H/TMPD for a molar mixture of 70% *N*¹,*N*¹,*N*³,*N*³-tetramethylpropane-1,3-diamine (TMPD) and 30% *N*¹,*N*¹,*N*³,*N*³,2,2-hexamethylpropane-1,3-diamine (HMPD),¹⁸ and ZSM-23 C7 diquat as heptamethonium bromide.^{19–22} Characterization data are presented in Fig. 1 (SEM and XRD) and Table 2.

As is evident from these data, by using different structure directing agents, it has been possible to synthesize a series of

ZSM-23 catalysts with different particle sizes and morphologies but with similar acid site densities. The Si/Al ratios are all in the range of 14–39 (the values measured by TPD-NH₃ are consistently higher compared to the ICP data, probably as a result of the accuracy of the method). It has previously been demonstrated that the MTT channels strongly prefer to be aligned with the longest direction of the crystals.⁹ This has also been verified using electron imaging and diffraction for some of the samples studied here (not shown). Thus, we are particularly interested in the longest particle dimension, as this can reasonably be related to the catalyst performance in a unidirectional system.^{6,15}

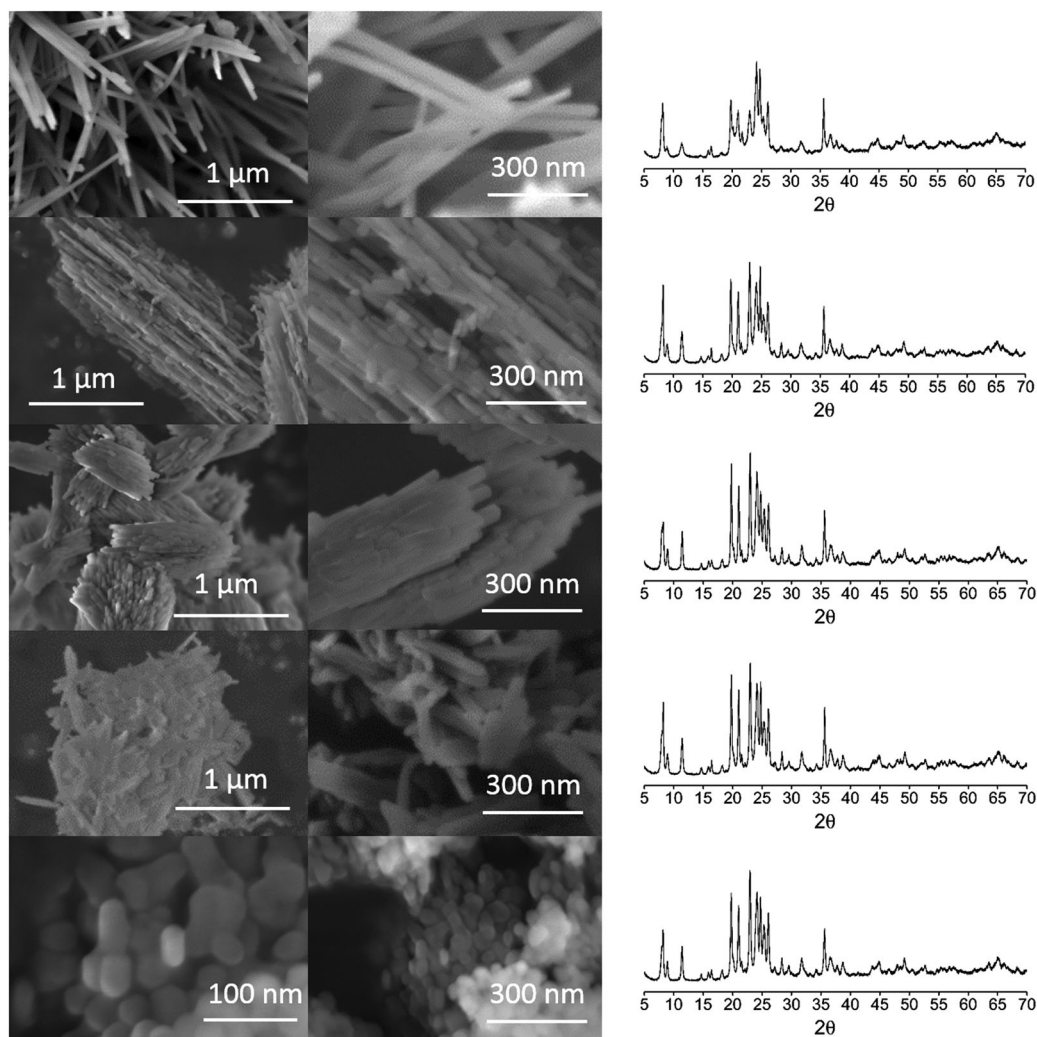


Fig. 1 Low-resolution and high-resolution scanning electron images and powder X-ray diffractograms for five ZSM-23 catalysts. From top to bottom: ZSM-23 DMF, ZSM-23 Pyrr, ZSM-23 H/TMPD, ZSM-23 iPA, and ZSM-23 C7 diquat.

Table 2 Characterization of the ZSM-23 samples

Catalyst	Si/Al mol ratio (ICP)	Si/Al mol ratio (NH ₃ -TPD)	BET surface area (m ² g ⁻¹)	t-Plot micropores surface area (m ² g ⁻¹)	Crystal length in nm (SEM)	Conversion capacity (g _{MeOH} g _{cat} ⁻¹)
ZSM-23 DMF	36.5	45.5	150	134	300–1000	1.1
ZSM-23 Pyr	32.4	42	271	251	120	12
ZSM-23 iPA	39.3	47	264	246	180	5.7
ZSM-23 H/TMPD	14	31	281	219	160	7.7
ZSM-23 C7 diquat	25.4	31.5	276	251	50	70

This information has been extracted from SEM and is summarized in Table 2, and the catalysts may be ranked by size accordingly: ZSM-23 DMF > ZSM-23 iPA > ZSM-23 Pyr > ZSM-23 H/TMPD >> ZSM-23 C7 diquat.

The LeBail refined powder X-ray diffractograms (see ESI†) show that the use of isopropylamine, the mixed templating agent H/TMPD, or the diquatary templating agent gives a highly crystalline pure phase of ZSM-23 (MTT). The use of DMF and pyrrolidine gives less sharp reflections around 22°. This might be due to the presence of an amorphous siliceous phase (in particular for the DMF sample, which displays a low surface area; Table 2). Alternatively, the broader reflections might be caused by the presence of a high number of stacking faults, which can generate an intergrowth phase MTT/TON (SSZ-54), which has been described for the synthesis of high aluminium containing phases in the presence of dimethylamine.^{23,24} Obviously, dimethylamine will be produced by the hydrolysis of DMF under the basic conditions used here.

Many aspects influence the outcome of these synthesis protocols, and it is not straightforward to produce materials with similar compositions. Ernst *et al.*²² have studied the crystallization of ZSM-23 and suggested that a higher concentration of Al in the synthesis gel gives a slower crystal growth, which in turn leads to smaller particles. Liu²⁵ and co-workers have shown that both the concentration of SDA and the alkalinity are important parameters that can influence the phase purity and morphology of ZSM-23.

The ZSM-23 zeolite is a high silica framework²⁶ and the Al content can only be adjusted in a narrow range of compositions while using the same pH and concentration. Moving outside

this range leads to the formation of siliceous amorphous species or other crystalline phases that can be formed without the presence of an organic SDA, such as ZSM-5,^{17,22,25} mordenite,¹⁷ and cristobalite.¹⁶ It should be emphasized that the use of the diquatary templating agent has the advantage of giving high selectivity for ZSM-23, since the flexible alkane chain fits well into the one-dimensional channels and the distance between the two terminal nitrogen atoms gives the selectivity for a specific channel system,²⁰ which means that a lower concentration of the templating agent is permissible and that a much broader range of Si/Al compositions can be achieved.²²

The catalyst performance of the 5 materials highlighted here was investigated in the conversion of methanol to hydrocarbons at atmospheric pressure and 400 °C, with a weight hourly space velocity (WHSV) of 2 g_{MeOH} g_{catalyst}⁻¹ h⁻¹ (Fig. 2). Previous investigations have shown that higher feed rates, or shorter residence times, do not allow sufficient time for the all-important hydrocarbon pool species to accumulate within the pores.²⁷ Clearly, there is a huge difference in stability and lifetime among the catalysts.

This difference is quantified further by the total conversion capacities, defined as the total amount of methanol converted into hydrocarbons until complete deactivation, which are listed in Table 2. Importantly, it seems clear that the lifetime is linked to the particle dimension, and in particular the dimension in the direction of the channel system. By selecting the appropriate catalyst preparation procedure, the lifetime can be extended by orders of magnitude. For the material prepared using DMF, the conversion capacity is so small that it might be more appropriate to discuss this as a stoichiometric process between methanol and acid sites. On the other hand, catalysts prepared using the C7 diquatary SDA always leads to superior catalysts.

We have prepared a large number of catalysts using this SDA, and the conversion capacity ranges from 60 up to 170 g_{MeOH} g_{catalyst}⁻¹. However, as the particles become extremely small, reproducibility becomes a major issue, as one might reasonably imagine. Therefore, we have decided to only report data which can be routinely reproduced. Previous investigations of ZSM-23 (and the structurally related ZSM-22) reported conversion capacities not higher than 16 g_{MeOH} g_{catalyst}⁻¹ at 400 °C and slightly higher at 450 °C.³ Thus, it is clear that the data presented here represent a very significant improvement. For SAPO-34, the archetype MTO catalyst, conversion capacities are typically around 25 g g⁻¹ for commercially relevant catalysts.^{28,29} For ZSM-5, the MTG catalyst, on the other hand, values as high as 1000 g_{MeOH} g_{catalyst}⁻¹ have been reported.³⁰ Nevertheless, the data presented here constitute a significant step towards the stability required

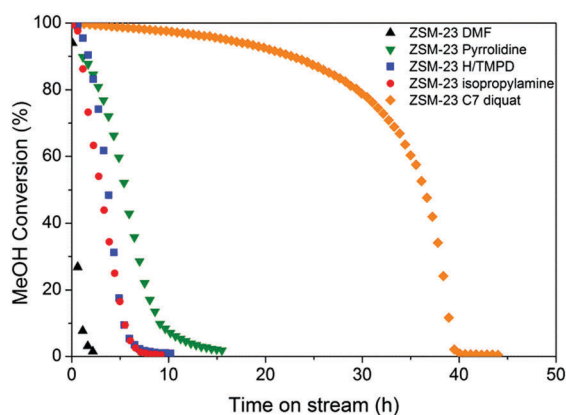


Fig. 2 MeOH conversion over ZSM-23 catalysts at 400 °C, 1 atm and WHSV of 2 g_{MeOH} g_{catalyst}⁻¹ h⁻¹.

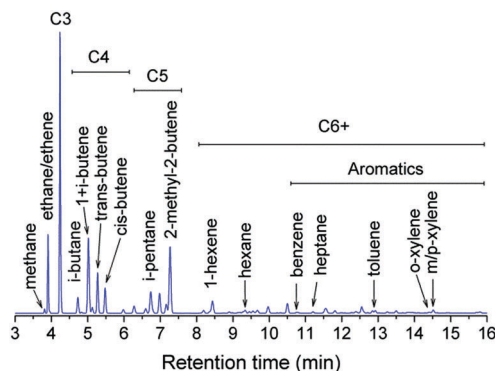


Fig. 3 Gas chromatogram recorded at essentially full methanol conversion for the ZSM-23 C7 diquat. Note the near absence of product peaks in the aromatics region of the chromatogram.

for potential fixed bed application of ZSM-23 in the conversion of methanol to hydrocarbons. A GC-FID chromatogram of the product distribution at 100% MeOH conversion using the ZSM-23 C7 diquaternary as the catalyst is presented in Fig. 3. As previously reported,³ the quantity of aromatics produced is negligible. Initial data indicate only very subtle differences in product selectivities among the catalysts tested here. Work is currently underway to verify and to elucidate the origin of these effects.

Zeolite ZSM-23 catalysts with similar acid densities but with widely different particle sizes have been prepared by changing the synthetic parameters and the structure directing agent.

Synthesis with pyrrolidine and isopropylamine gives micrometer-sized crystals with short lifetime, while the synthesis in the presence of an alkyl diammonium salt provides access to very small crystallites, for which the catalytic lifetime is increased by at least one order of magnitude. The results indicate that the catalyst lifetime can be explained by the length of the unidirectional channels, which tend to be parallel to the longest crystal dimension, leading to long diffusion pathways and rapid coke accumulation for large crystals.

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