

Electronic Supplementary Information

Monitoring and controlling zeolite synthesis via reactor-based solutions: A Fed-batch strategy

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1. Chemicals

Tetraethyl orthosilicate or TEOS [$\text{Si}(\text{OC}_2\text{H}_5)_4$, Fischer Scientific, $\geq 99\%$]

Tetrapropylammonium hydroxide or TPAOH [$(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{N}(\text{OH})$, Sachem, 40 wt%]

Tin chloride pentahydrate [$\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, Sigma-Aldrich, 98%]

Tin acetate [$\text{Sn}(\text{OAc})_4$, Fisher scientific, 98%]

Zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Fisher scientific, 98%]

Zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, Fischer Scientific, $\geq 97\%$]

Zinc chloride [ZnCl_2 , Alfa Aesar, $>98\%$]

Zinc hydroxide [$\text{Zn}(\text{OH})_2$, Fluorochem, 98%]

Barium sulfate [BaSO_4 , Fisher scientific, 98%]

Lithium metaborate [LiBO_2 , Sigma-Aldrich, 99.9%]

Milli-Q water ($18.2 \text{ M}\Omega \cdot \text{cm}^{-1}$)

2. Zeolite synthesis

2.1. Zeolite synthesis in FB reactor (Time-mapping)

Silicalite-1 zeolites (MFI topology) were prepared by hydrothermal synthesis according to the following procedure. The molar composition of the synthesis mixture was 1 SiO₂: 0.5 TPAOH: x H₂O (where x is 20 or 32). Typically, the appropriate amount of TPAOH was added to deionized H₂O. Then, TEOS was added slowly under continuous stirring, and the mixture was then stirred for 12 h at room temperature until full hydrolysis of TEOS and obtaining of a homogeneous single-phase system. Then, it was then transferred into the FB reactor and heated at 90 or 160 °C under constant stirring (70 rpm) for 24 or 72 hours. The FB reactor was filled about 80% of whole volume (144 ml). During synthesis procedure, intermediate samples were extracted by sampling valve for further analysis. Solid part of samples was recovered by centrifuge (6000 rpm, ≥5 min, Thermo Fisher Scientific SL16), washed several times with deionized water (18.2 MΩ·cm⁻¹) until the pH value of the decanted water reached 9 and lastly with acetone, and then dried overnight at 100 °C. If required, dry samples were calcined to remove the organic template in a muffle furnace under airflow at 580 °C for about 9 h with a ramping time of 6 h (1 °C/min heating rate).

2.2. Zeolite synthesis in FB reactor (Batch mode)

Stannosilicate (MFI topology) syntheses were prepared by hydrothermal synthesis according to the following procedure. The starting molar composition of the synthesis mixture was 1 SiO₂: 0.5 TPAOH: X Sn⁻¹: 28 H₂O (where x is 41 or 100). Typically, the appropriate amount of TPAOH was added to deionized H₂O (18.2 MΩ·cm⁻¹). Then, TEOS was added slowly under continuous stirring. Prior the hydrolysis stage, an aqueous solution of metal salt (tin chloride pentahydrate) was added, and the mixture was stirred for 12 h at room temperature to evaporate ethanol arising from hydrolysis of TEOS. Then it was then transferred into the FB reactor and heated at 90 °C under constant stirring (70 rpm) for 72 hours. During the synthesis procedure, intermediate samples were extracted by sampling valve for yield calculation and to investigate the metal impact on the zeolite formation. Finally, the resultant solid was recovered and treated as described in ESI 2.1.

2.3. Zeolite synthesis in FB reactor (Timed-addition)

Stannosilicate and zincosilicate (MFI topology) syntheses were carried out through timed-addition approach in the FB reactor. The starting molar composition of the synthesis mixture was 1 SiO₂: 0.5 TPAOH: 20 H₂O. The synthesis mixture was prepared and transferred into the FB reactor according to the Time-mapping procedure (ESI 2.1). The reactor was filled about 50% of whole volume (90 ml). In different time intervals (specified in the manuscript text), an aqueous solution of metal salt was pumped (with different feeding rates from 20-310 μl.min⁻¹, and, therefore, different concentrations of 0.02-0.06 g/ml, for keeping molar ratios constant) into the reactor while at temperature and under autogenous pressure. Finally, the resultant solid was recovered and treated as described in ESI 2.1.

Final composition after feeding: 1 SiO₂: 0.5 TPAOH: $\frac{1}{41}$ Me: 28 H₂O (Me represents metal salts: tin chloride pentahydrate, zinc nitrate hexahydrate, zinc acetate dihydrate, or zinc chloride)

2.4. Zeolite synthesis in classic batch reactor

The Sn-MFI and Zn-MFI zeolites were prepared by hydrothermal synthesis according to the same procedure as section 2.2. The molar composition of the synthesis mixture was 1 SiO₂: 0.5 TPAOH: $\frac{1}{41}$ Me: 28 H₂O (Me represents metal salts: tin chloride pentahydrate, zinc nitrate hexahydrate, zinc acetate dihydrate, or zinc chloride). The clear gel was then transferred into the stainless-steel batch autoclaves and heated in a mechanical convection oven (Heratherm, Thermo Scientific) under 600 rpm internal stirring at 90 or 160°C. After hydrothermal treatment, autoclaves were taken out, cooled and the resultant solid was recovered and treated as described in ESI 2.1.

2.5. Checking the impact of metal addition on pH

To check the impact of adding metals precursor salts on the pH value, three conventional batches were prepared with similar starting molar compositions: 1 SiO₂: 0.5 TPAOH: 20 H₂O. After adding TEOS, TPAOH, and deionized water, the mixture was stirred to evaporate ethanol. pH of the starting gel (after the hydrolysis stage) was 13.08. Subsequently, deionized H₂O (A) or metal precursors (aqueous solution of tin chloride pentahydrate (B) or zinc nitrate

hexahydrate (C)) were added rapidly to the batches to obtain the final molar composition, and pH was measured instantly after the addition:

Synthesis solution A: 1 SiO₂: 0.5 TPAOH: 28 H₂O, with a pH of 13.02

Synthesis solution B: 1 SiO₂: 0.5 TPAOH: $\frac{1}{41}$ Sn: 28 H₂O, with a pH of 12.69

Synthesis solution C: 1 SiO₂: 0.5 TPAOH: $\frac{1}{41}$ Zn: 28 H₂O, with a pH of 12.59

3.Characterization methods

3.1. X-ray Powder Diffraction (PXRD)

The structure and crystallinity of the zeolites were confirmed by X-ray powder diffraction (PXRD) on a high-throughput STOE STADI P Combi diffractometer in transmission mode with focusing Ge (111) monochromatic X-ray inlet beams ($\lambda = 1.5406 \text{ \AA}$, Cu K α source). For each sample, a beam time of 10 min was used.

3.2. Nitrogen Physisorption

Porosity was measured by nitrogen physisorption (Tristar II 3020, Micromeritics) at $-196 \text{ }^\circ\text{C}$ on calcined samples. The relative nitrogen pressure was varied between 0.01 and 0.99 (p/p_0). The surface area and micropore volume of the materials are reported using BET and t-plot methods, respectively.

3.3. Scanning Electron Microscopy (SEM)

SEM was performed on the JEOL JSM-6010LV microscope at an acceleration voltage of 15 or 20 kV. Zeolite samples were attached to a piece of carbon tape. Subsequently, a thin Pd/Au (60/40 ratio) layer was deposited on top of the samples to achieve sufficient conductivity.

3.4. ICP–AES

ICP–AES analyses were conducted on a PerkinElmer Optima 3300 DV. Samples for the analysis of stannosilicates were prepared via the “oven method”.¹ Before an ICP–AES measurement (important as silicon tends to sediment from an acidic solution), 50 mg of samples was mixed with 250 mg of lithium metaborate. Next, the mixture was placed in a graphite crucible and held inside a muffle oven for 10 min at $1000 \text{ }^\circ\text{C}$. Then, the formed still hot droplet was transferred to 10 wt % HCl solution in water and stirred for 10 min. After an additional 2 hours, samples were diluted using the HCl solution of the same concentration by a factor of 5.

Samples for the analysis of zincosilicates were prepared via the “HF method”. Before an ICP–AES measurement, 50 mg of samples was dissolved using 2 ml of HF and 0.5 ml of aqua regia. After 3 h, they were neutralized using 33 ml of boric acid solution (30 g/l) and diluted with milli-Q water. After an additional 2 h, samples were diluted using 0.42 M HNO₃ in water by a factor of 26.

3.5. pH

Off-line or ex-situ pH was measured with a Mettler Toledo SevenCompact pH meter with a polymeric InLab Expert Pro-ISM pH electrode. It should be noted that pH measurements were carried out after reaching the extracted samples at room temperature. After each measurement, the electrode was rinsed with Milli-Q water. Subsequently, the pH was measured, and the electrode was stored afterward in KCl storage solution (3.8 M).

On-line or in-situ pH was measured with a Mettler Toledo SevenCompact pH meter with a glass body Sigma-Aldrich micro pH combination electrode (3.5 mm diameter with a refillable Ag/AgCl reference half-cell). The pH probe should be stored in KCl solution (3.8 M) and fully calibrated within the operating pH range before each experiment. For both methods, the calibration solutions are technical buffers with pH of 11, 9.21, and 7 from Mettler Toledo.

3.6. Diffuse Reflectance Spectroscopy

Diffuse reflectance spectroscopy in the UV–vis–NIR energy range (UV-vis-NIR) was performed with a Varian Cary 5000 UV-vis-NIR spectrophotometer equipped with the internal DRA 2500 accessory at ambient atmosphere and room temperature against BaSO₄ in the 4000–57000 cm⁻¹ energy range.

4. Supplementary Text

Several metal sources (Sn and Zn) were evaluated for use in the FB platform. However, only those that are highly soluble in water demonstrated compatibility with the feeding process in the FB reactor. Metal sources such as tin acetate (Sn(OAc)₄) and zinc hydroxide (Zn(OH)₂) exhibited relatively low solubility in water, posing a risk of blockage in the feeding line (see Fig.S10). Additionally, switching the carrier solvent from water to other solvents (such as Isopropanol or diethyl ether) would elevate pressure upon addition and complicate our system, which we aimed to avoid.

5. Figures and tables

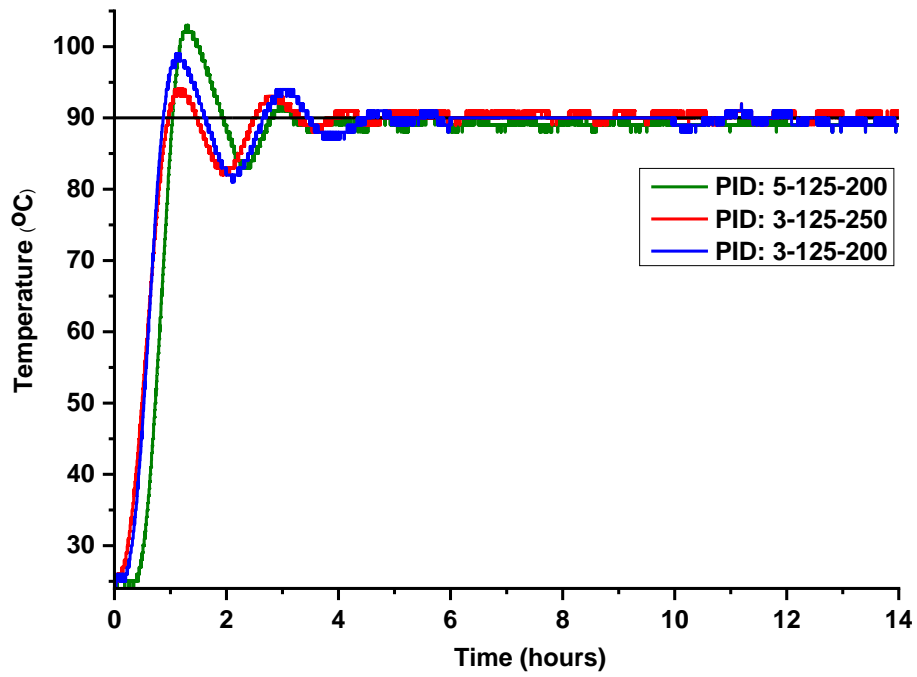


Fig.S1. Temperature profile of FB reactor based on different PID (Proportional–Integral–Derivative) parameters.

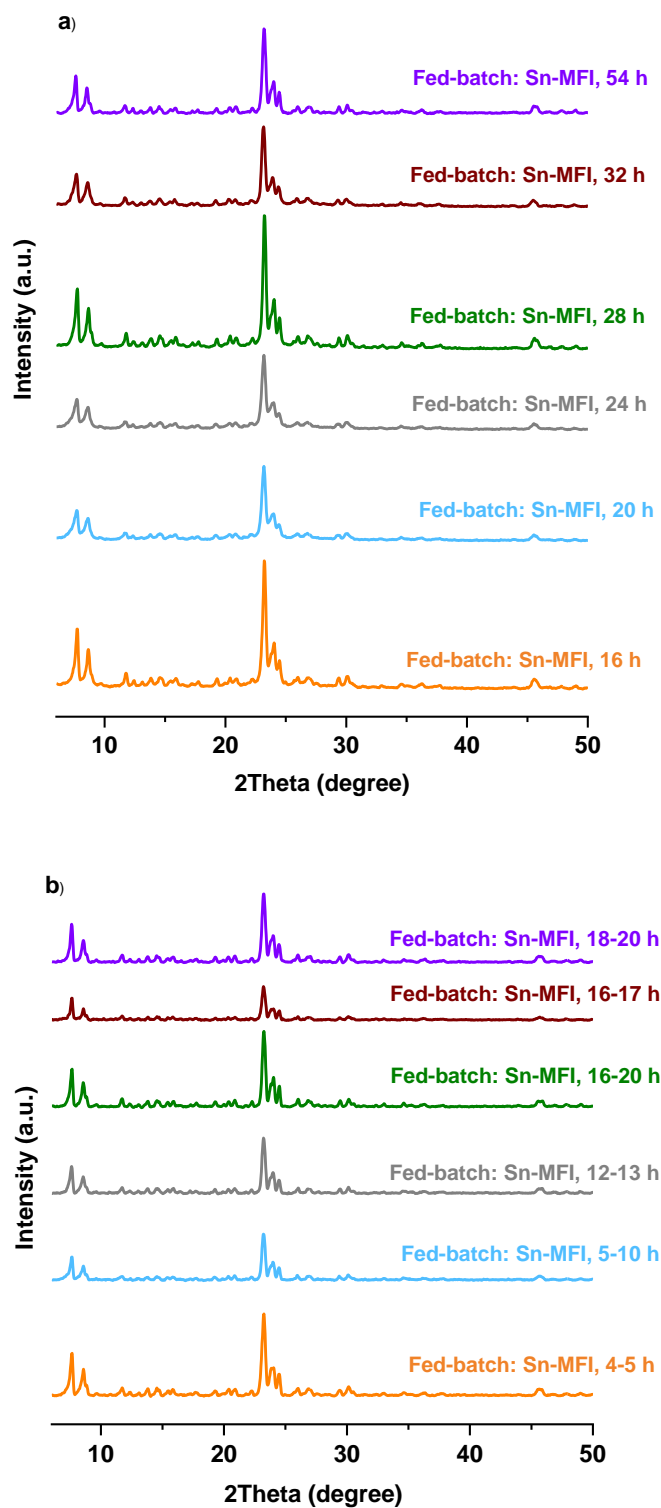


Fig.S2. PXR D spectra of Sn-MFI samples synthesized (a) at 90 °C and (b) 160 °C in FB. The curves are offset to provide better clarity.

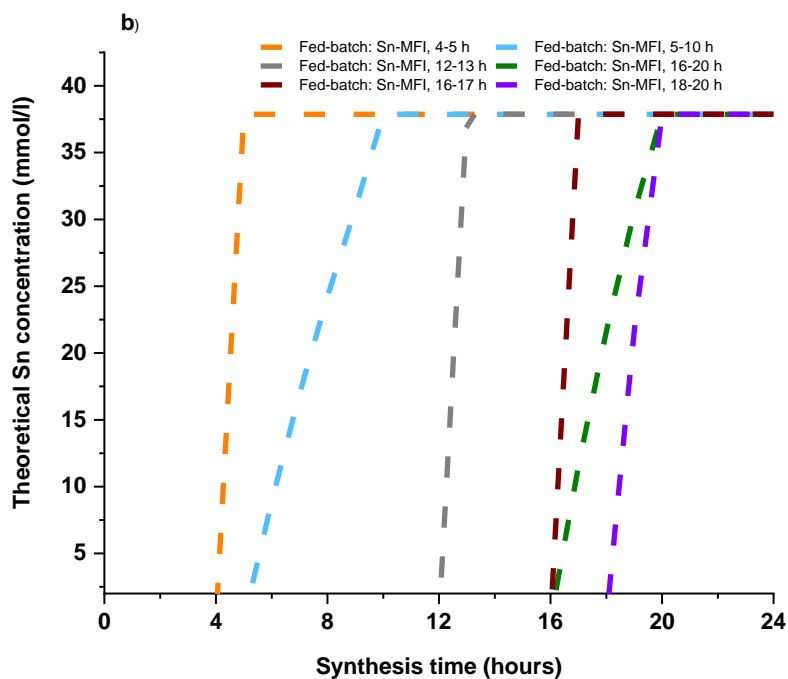
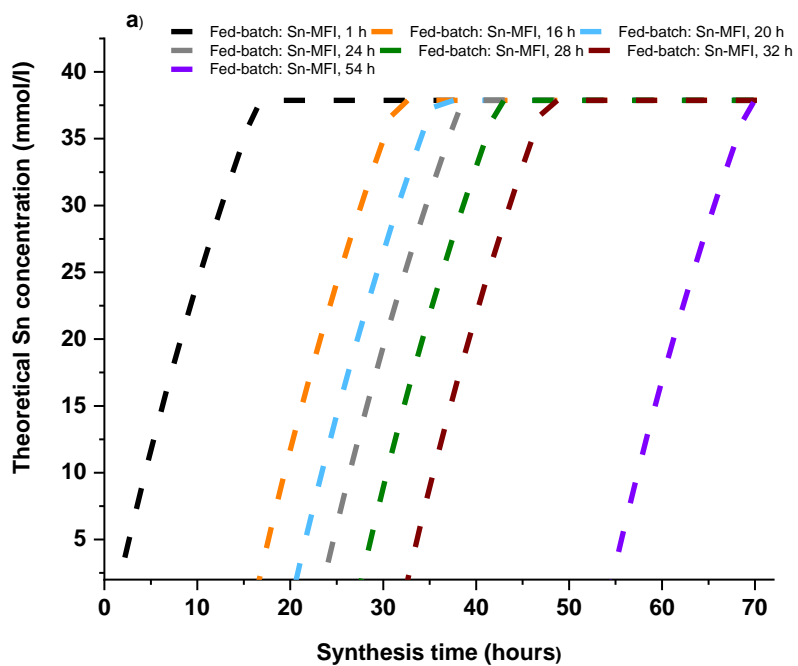


Fig.S3. Theoretical profile of tin concentration inside FB reactor based on the synthesis time in (a) 90°C and (b) 160°C experiments.

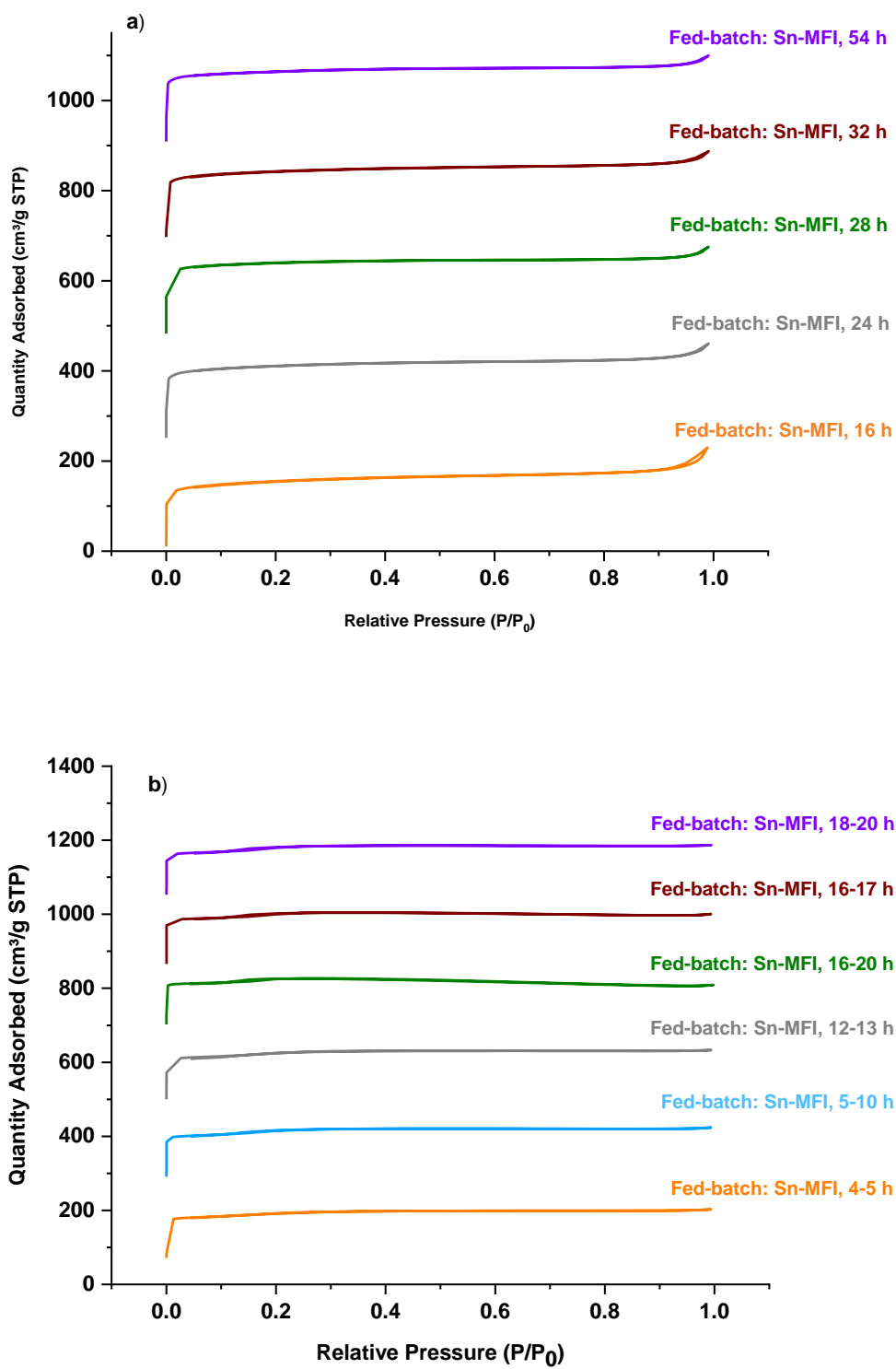


Fig.S4. N₂ adsorption/desorption isotherms of Sn-MFI samples synthesized (a) at 90°C and (b) 160°C in FB. The curves are offset to provide better clarity.

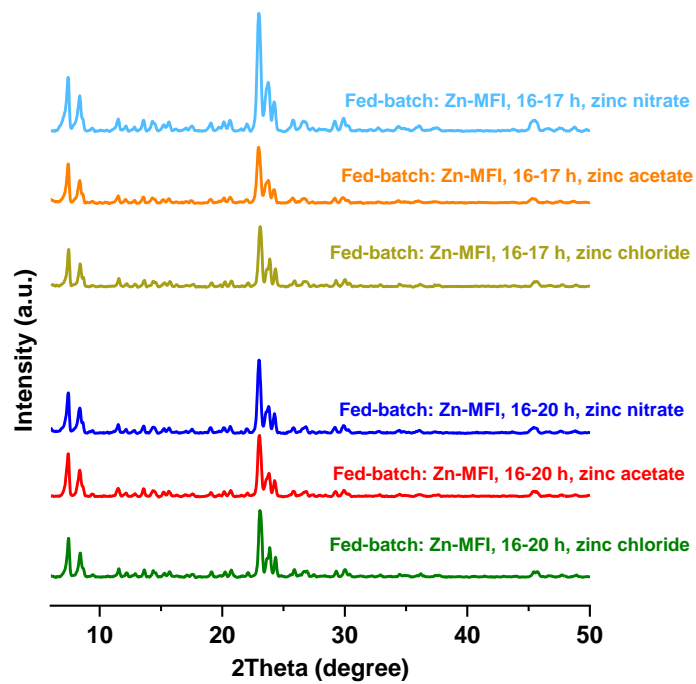


Fig.S5. PXRD spectra of Zn-MFI samples synthesized at 160 °C in FB. The curves are offset to provide better clarity.

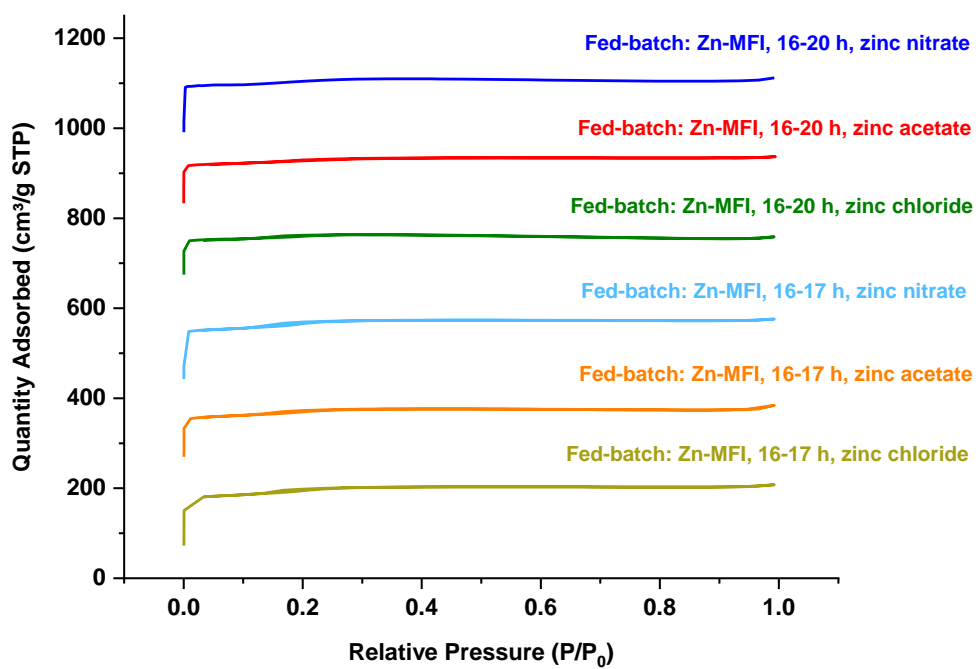
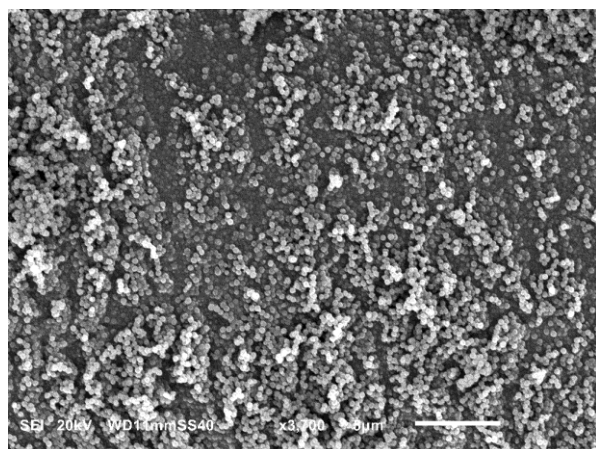
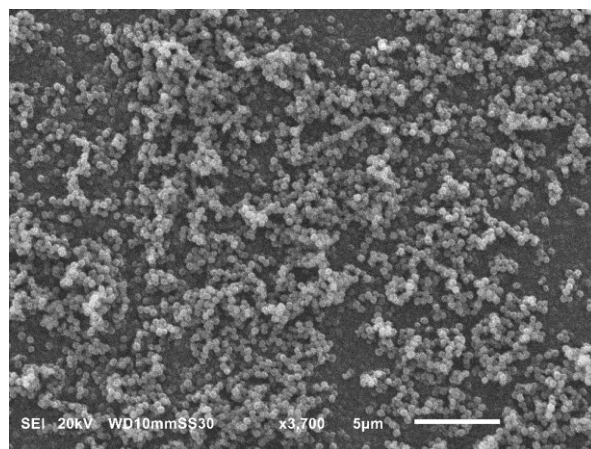


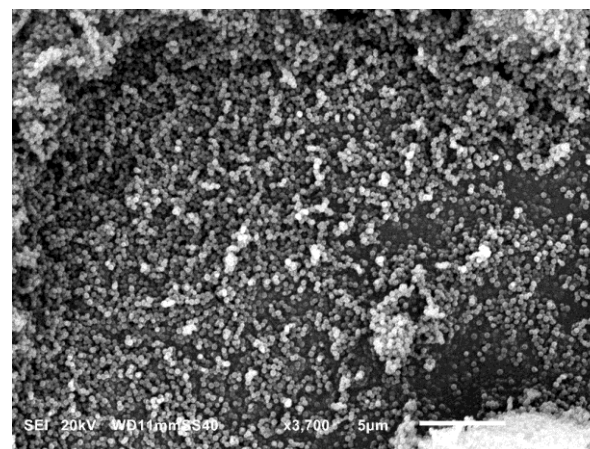
Fig.S6. N₂ adsorption/desorption isotherms of Zn-MFI samples synthesized at 160 °C in FB. The curves are offset to provide better clarity.



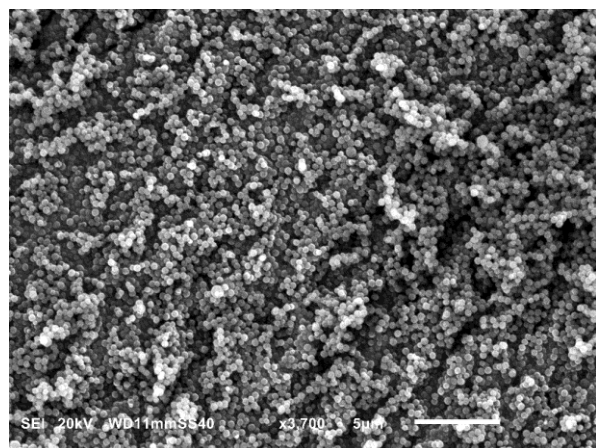
Fed-batch: Sn-MFI, 16 h



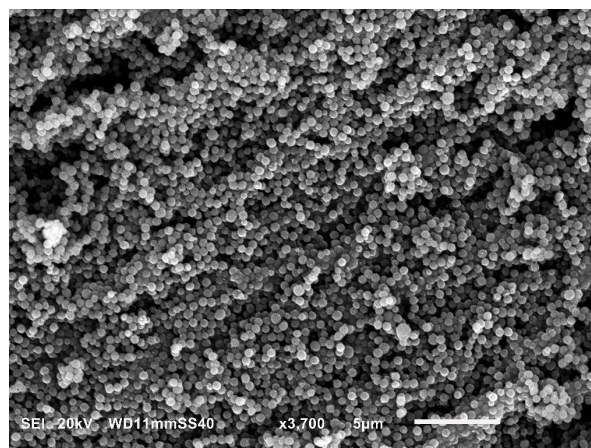
Fed-batch: Sn-MFI, 20 h



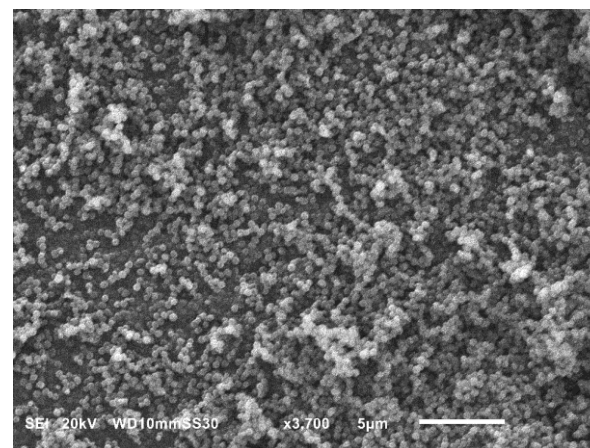
Fed-batch: Sn-MFI, 24 h



Fed-batch: Sn-MFI, 28 h

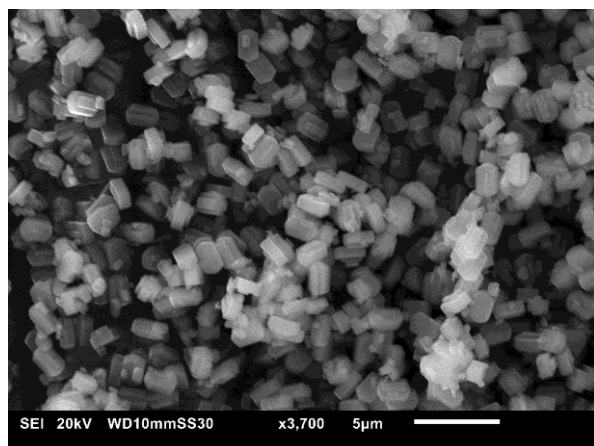


Fed-batch: Sn-MFI, 32 h

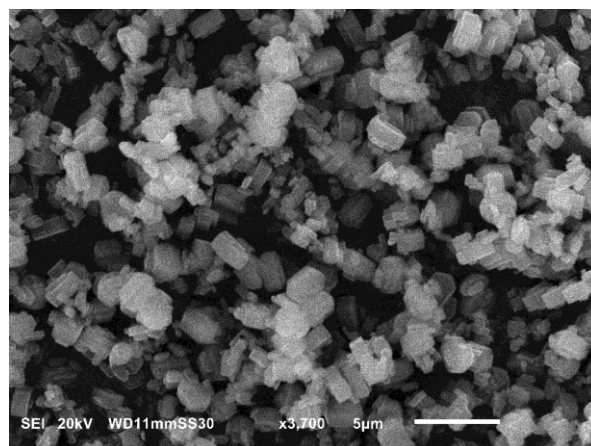


Fed-batch: Sn-MFI, 54 h

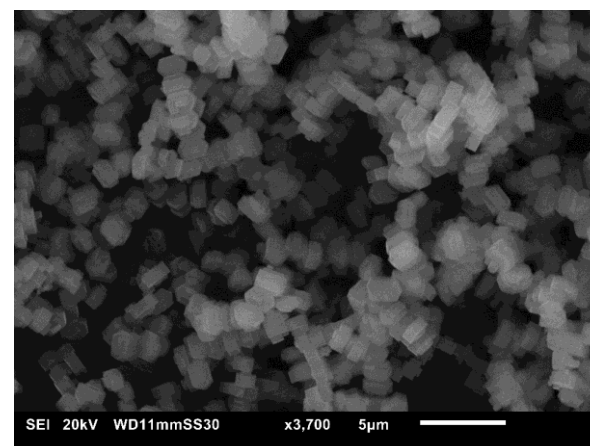
Fig.S7. SEM images of Sn-MFI samples synthesized at 90°C in FB. Images are shown at magnification of 5 μm.



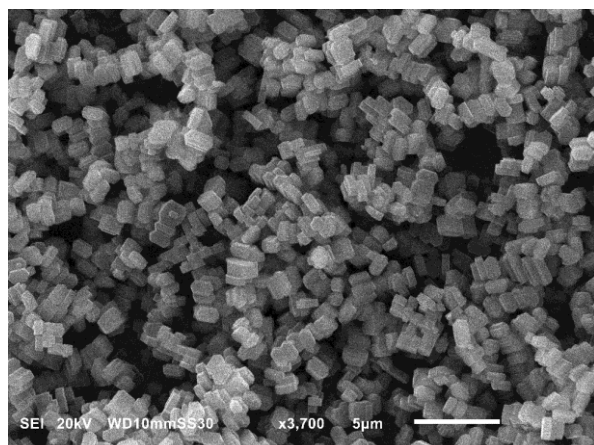
Fed-batch: Sn-MFI, 4-5 h



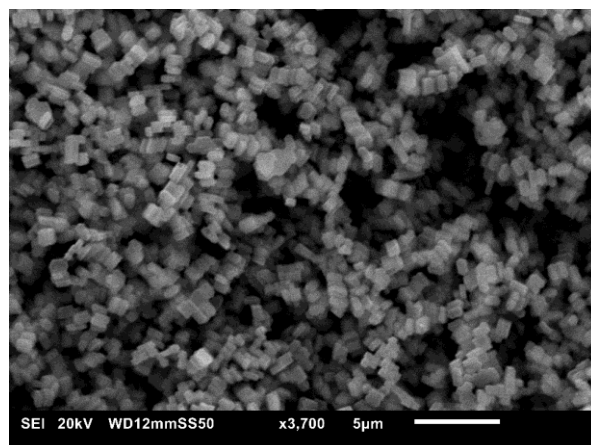
Fed-batch: Sn-MFI, 5-10 h



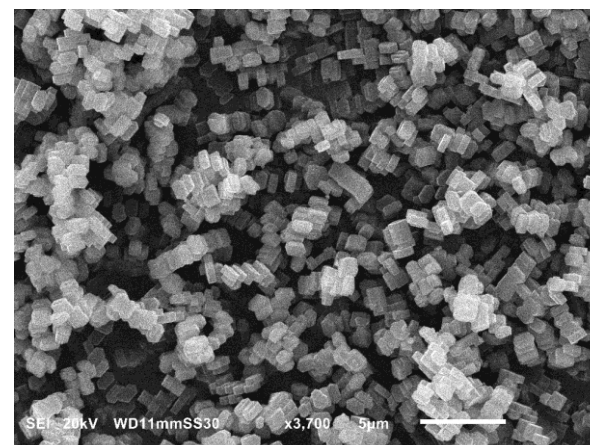
Fed-batch: Sn-MFI, 12-13 h



Fed-batch: Sn-MFI, 16-20 h

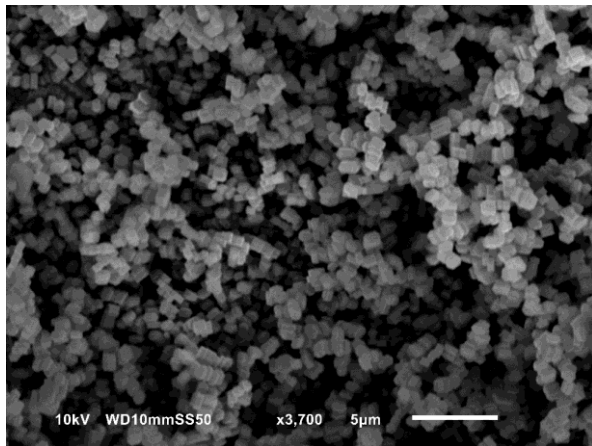


Fed-batch: Sn-MFI, 16-17 h

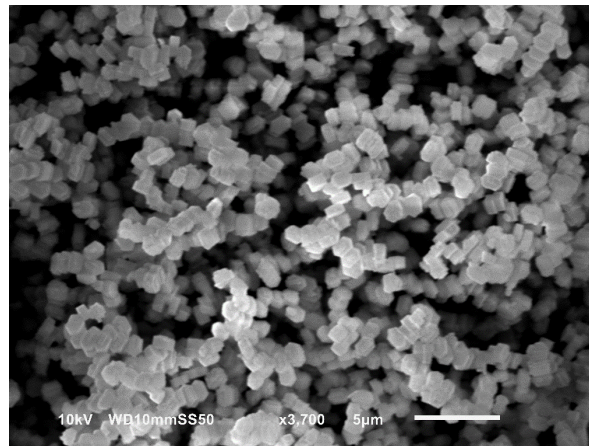


Fed-batch: Sn-MFI, 18-20 h

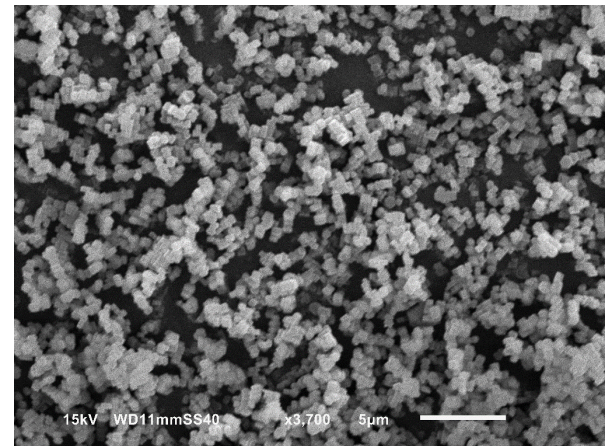
Fig.S8. SEM images of Sn-MFI samples synthesized at 160°C in FB. Images are shown at magnification of 5 µm.



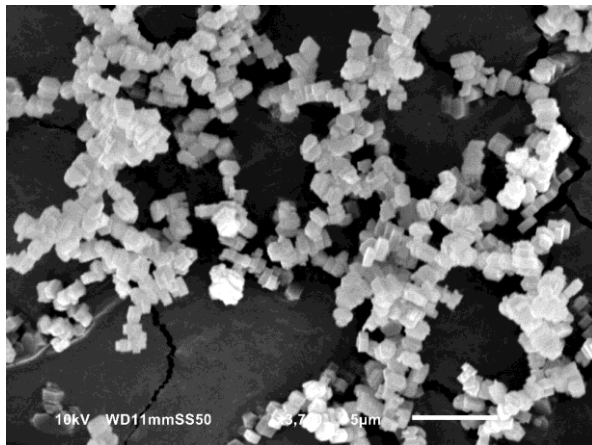
Fed-batch: Zn-MFI, 16-20 h, zinc nitrate



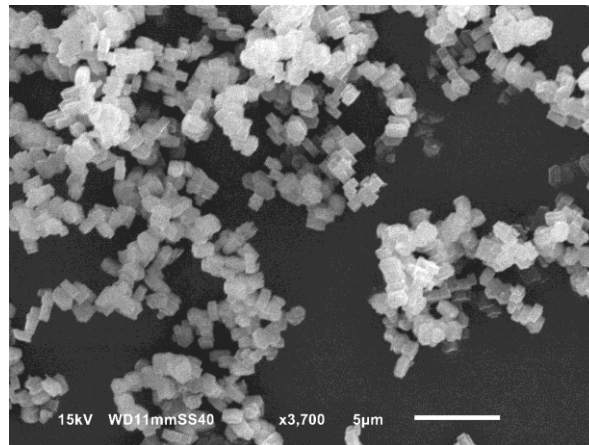
Fed-batch: Zn-MFI, 16-20 h, zinc acetate



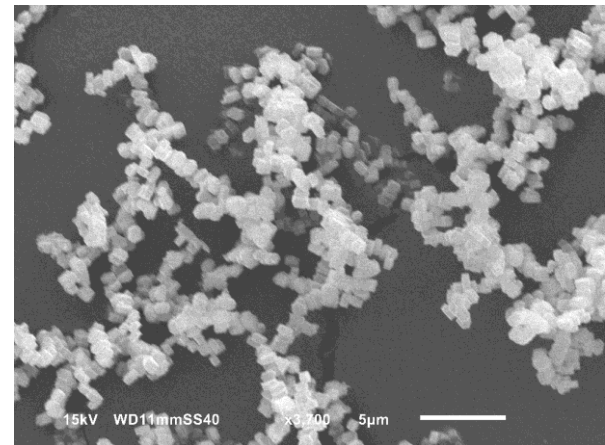
Fed-batch: Zn-MFI, 16-20 h, zinc chloride



Fed-batch: Zn-MFI, 16-17 h, zinc nitrate



Fed-batch: Zn-MFI, 16-17 h, zinc acetate



Fed-batch: Zn-MFI, 16-17 h, zinc chloride

Fig.S9. SEM images of Zn-MFI samples synthesized in FB. Images are shown at magnification of 5 µm.

Residual species inside the Feeding tube

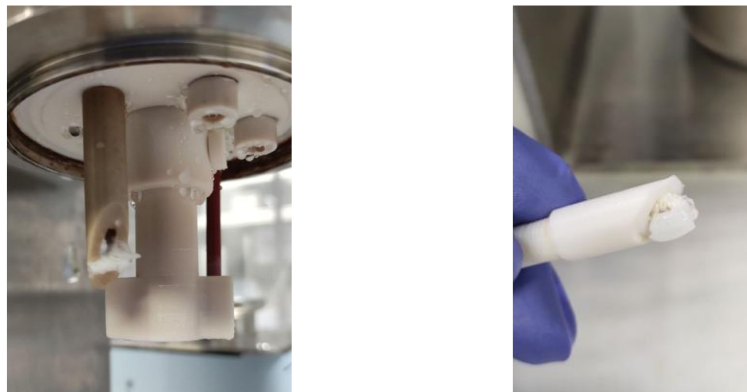


Fig.S10. Blockage in the feeding line of FB platform due to accumulation of insoluble metal salts.

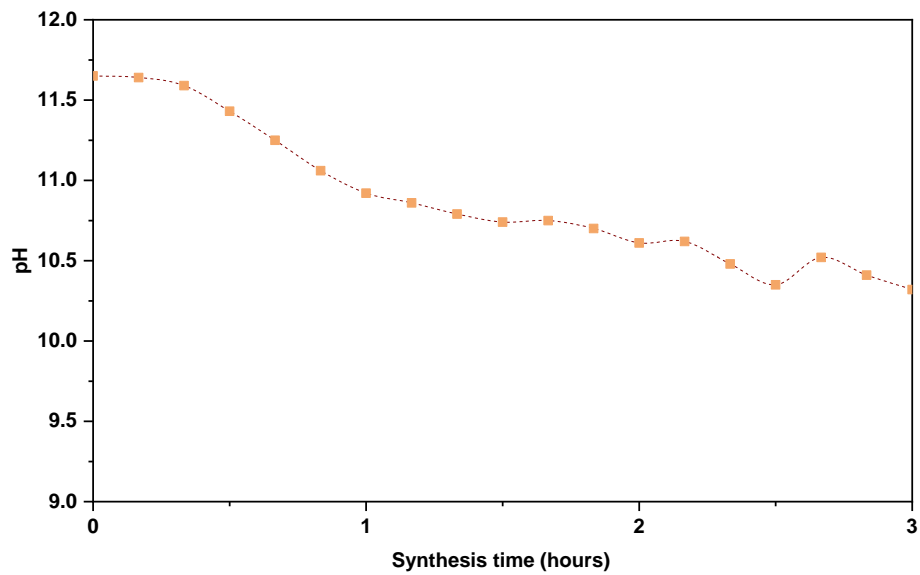


Fig.S11. On-line pH profile of early stage of MFI synthesis in FB reactor. Molar composition of the synthesis mixtures: 1 SiO₂: 0.5 TPAOH: 32 H₂O.

Table S1. Experimental data and characterization of Sn-MFI and Zn-MFI zeolites.

Synthesis temperature (°C)	Synthesis time (hours)	Sample	Metal source	Starting time of addition (hour)	Feeding duration (hours)	Feeding rate (μl/min)	Specific surface area ^a (m ² /g)	Micropore volume ^b (cm ³ /g)	Theoretical Si/Me ^c ratio	Actual (final) Si/Me ratio ^d	Synthesis yield (%)
90	216	Batch: Sn-MFI	SnCl ₄ ·5H ₂ O	-	-	-	543	0.11	41	450	22
90	72	Fed-batch: Sn-MFI, 54 h		54	15	20	589	0.17		1792	47
		Fed-batch: Sn-MFI, 32 h		32	15	20	572	0.14		93	35
		Fed-batch: Sn-MFI, 28 h		28	15	20	605	0.17		257	43
		Fed-batch: Sn-MFI, 24 h		24	15	20	625	0.17		886	42
		Fed-batch: Sn-MFI, 20 h		20	15	20	-*	-*		595	15
		Fed-batch: Sn-MFI, 16 h		16	15	20	595	0.14		949	28
160	24	Batch: Sn-MFI	SnCl ₄ ·5H ₂ O	-	-	-	469	0.14	41	114	18
		Fed-batch: Sn-MFI, 18-20 h		18	2	158	454	0.14		775	59
		Fed-batch: Sn-MFI, 16-17 h		16	1	310	440	0.15		567	66
		Fed-batch: Sn-MFI, 16-20 h		16	4	79	459	0.15		305	67
		Fed-batch: Sn-MFI, 12-13 h		12	1	310	454	0.14		530	56
		Fed-batch: Sn-MFI, 5-10 h		5	5	60	445	0.13		599	58
		Fed-batch: Sn-MFI, 4-5 h		4	1	310	440	0.13		519	55
160	24	Batch: Zn-MFI, zinc nitrate	Zn(NO ₃) ₂	-	-	-	468	0.12	41	30	57
		Batch: Zn-MFI, zinc acetate	(H ₃ CCOO) ₂ Zn	-	-	-	506	0.14		35	62
		Batch: Zn-MFI, zinc chloride	ZnCl ₂	-	-	-	451	0.11		28	54
		Fed-batch: Zn-MFI, 16-20 h, zinc nitrate	Zn(NO ₃) ₂	16	4	79	485	0.13		47	65
		Fed-batch: Zn-MFI, 16-20 h, zinc acetate	(H ₃ CCOO) ₂ Zn	16	4	79	351	0.11		209	44

		Fed-batch: Zn-MFI, 16-20 h, zinc chloride	ZnCl ₂	16	4	79	360	0.12		474	42
		Fed-batch: Zn-MFI, 16-17 h, zinc nitrate	Zn(NO ₃) ₂	16	1	310	459	0.14		296	66
		Fed-batch: Zn-MFI, 16-17 h, zinc acetate	(H ₃ CCOO) ₂ Zn	16	1	310	419	0.12		89	60
		Fed-batch: Zn-MFI, 16-17 h, zinc chloride	ZnCl ₂	16	1	310	464	0.14		84	64

^a Based on nitrogen physisorption, BET method.

^b Based on nitrogen physisorption, t-plot method.

^c Me refers to Sn and Zn in stannosilicate and zincosilicate synthesis, respectively.

^d Based on elemental analysis.

*N₂ physisorption was not performed on this sample due to low synthesis yield.

References

- 1 G. Ivanushkin and M. Dusselier, *Chem. Mater.*, 2023, **35**, 5049–5058.