Supporting Information

Formation and Characterisation of Mn-MIL-100

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Activation under vacuum at room temperature

Fig. S1: XRPD pattern of Mn-MIL-100 washed in ethanol and activated at 0.1 mbar at room temperature after the sorption experiment. The XRPD pattern was recorded using the STADI P Combi diffractometer equipped with and image plate detector (measurement time 3 min).

Fig. S2: Nitrogen sorption isotherm (measured at 77 K) of Mn-MIL-100 washed in ethanol and activated at 0.1 mbar at room temperature.
Fig. S3: IR-spectrum of as-synthesized Mn-MIL-100.

The IR-spectrum of Mn-MIL-100 exhibits a strong band around 3300 cm$^{-1}$, which is due to the hydrogen bonds of the occluded solvent molecules. Furthermore, the asymmetric CO$_2$-stretching band at 1620 cm$^{-1}$ belongs to the trimesate anions, while the shoulder at 1700 cm$^{-1}$ can be attributed to residual acid, which can be washed out by treatment with ethanol. Strong absorptions are also observed at 1350 cm$^{-1}$ and 713 cm$^{-1}$. The first is due to the symmetric CO$_2$-stretching of the carboxylate and the latter is the ring-out-of-plane vibration of the 1,3,5-substituted benzene core of the linker molecules.
Sharp-Hancock-Plots and Fits

Fig. S4: SH-Plot for the initial reaction stage at 125 °C.

Fig. S5: SH-Plot for the second reaction stage at 125 °C.
Fig. S6: SH-Plot for the initial reaction stage at 135 °C.

Fig. S7: SH-Plot for the second reaction stage at 135 °C.
Fig. S8: SH-Plot for the initial reaction stage at 145 °C.

Fig. S9: SH-Plot for the second reaction stage at 145 °C.
Fig. S10: Gualtieri-Fit for the reaction at 125 °C.

Fig. S11: Gualtieri-Fit for the reaction at 135 °C.
Fig. S12: Gualtieri-Fit for the reaction at 145 °C.

**Arrhenius Plots**

Fig. S13: Arrhenius-Plot for the initial reaction rate constant obtained from SH-Plot.
Fig. S14: Arrhenius-Plot for the second reaction rate constant obtained from SH-Plot.

Fig. S15: Arrhenius-Plot for the nucleation rate constant obtained from Gualtieri-Plot.
Fig. S16: Arrhenius-Plot for the growth rate constant obtained from Gualtieri-Plot.
Fig. S17: Pawley-Fit for Mn-MIL-100 as obtained using TOPAS.¹ The peak-shape was modelled using a Thompson-Cox-Hastings function and the number of background parameters was 10. The final $R_{wp}$ is 1.6%.
EPR- and UV/Vis-spectra

EPR spectra and UV/Vis spectra were recorded from a thoroughly washed sample (ethanol). The measured EPR spectrum is typical for the presence of Mn$^{2+}$ ions. Since the sensitivity for Mn$^{2+}$ ions is orders of magnitude larger than for Mn$^{3+}$ ions the signal is probably due to the presence of small amounts of Mn$^{2+}$ containing impurities in the pores.\textsuperscript{[2]} Thus, the oxidation states of the cations in the trimeric Mn-cluster can not be identified by means of EPR-spectroscopy.

![EPR spectrum](image1)

Fig. S18: X-band EPR-Spectrum of Mn-MIL-100 measured at 4 K. The signal can be clearly attributed to Mn$^{2+}$, which is highly EPR-sensitive.

![UV/Vis spectra](image2)

Fig. S19. UV/Vis-spectra of commercially available Mn(III) acetate (Aldrich, red line) and Mn-MIL-100 (black line). The similarity of the spectra with an inflection point at ~440 nm indicates that similar clusters are present in Mn-MIL-100 and manganese acetate. According to the literature [Mn(III)$_2$Mn(II)(µ$_3$-O)(O$_2$CCH$_3$)$_6$] are present in the so called Mn(III) acetate.\textsuperscript{3}

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