Intraparticle Ripening Creating Hierarchically Porous Ti-MOF Single Crystals for Deep Oxidative Desulfurization

Shen Yu,‡[ab] Zhan Liu,‡[abc] Jia-Min Lyu,[a] Chun-Mu Guo,[a] Yi-Long Wang,[d] Zhi-Yi Hu,[ac] Yu Li[a], Ming-Hui Sun,[a] Li-Hua Chen, *[a] and Bao-Lian Su*[ae]

* To whom correspondence should be addressed: Li-Hua Chen (chenlihua@whut.edu.cn); Bao-Lian Su (bao-lian.su@unamur.be)

[a] Laboratory of Living Materials at the State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 122 Luoshi Road, Wuhan, 430070, Hubei, China

[b] International School of Materials Science and Engineering, Wuhan University of Technology,

Wuhan, 430070, Hubei, China

[c] Nanostructure Research Center, Wuhan University of Technology, Wuhan, 430070, Hubei, China

[d] School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, Wuhan, 430070, Hubei, China

[e] Laboratory of Inorganic Materials Chemistry, University of Namur, 61 rue de Bruxelles, B-5000 Namur, Belgium

‡ These authors contributed equally

Supporting Figures and Tables

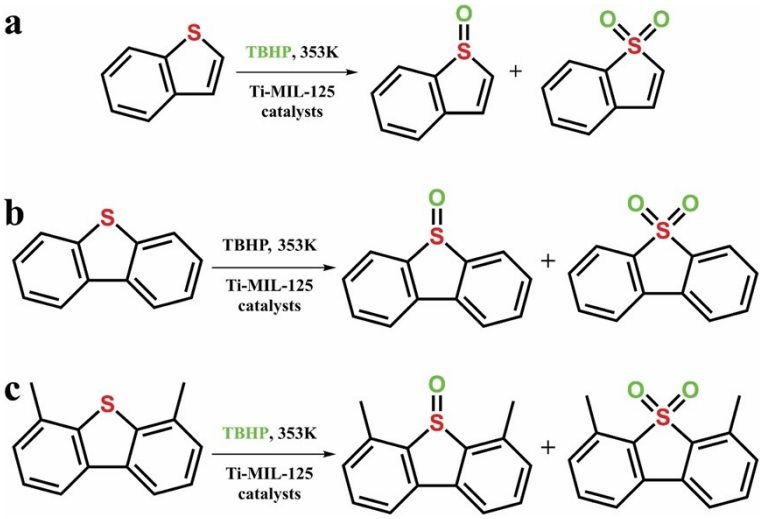

Figure S1. Reaction equations of catalytic oxidative desulfurization of (a) BT, (b) DBT, and (c) DMDBT into their oxidative products.

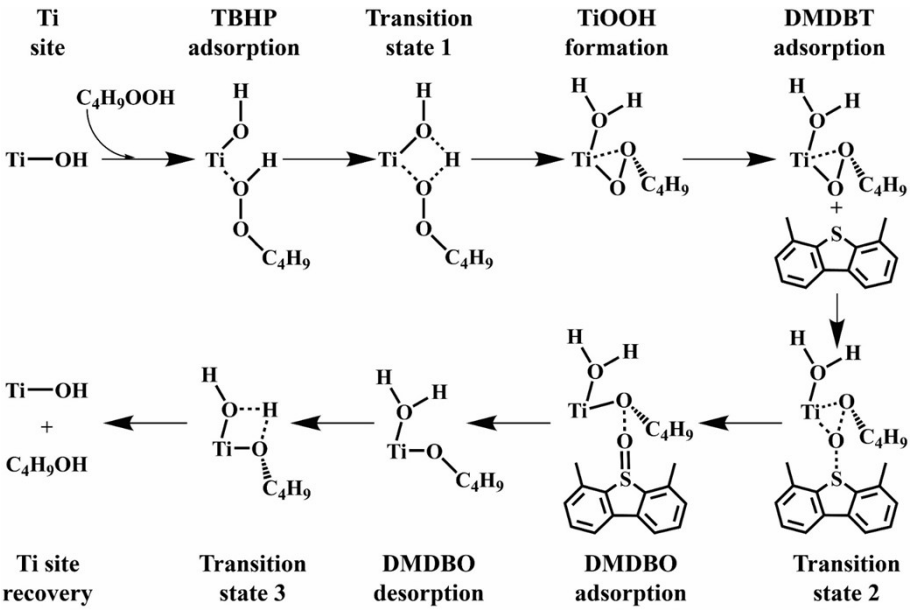

Figure S2. Proposed ODS reaction pathway over Ti site of Ti-MIL-125.

Taking the ODS of 4,6-dimethyldibenzothiophene (DMDBT) into 4,6-dimethyldibenzothiophene oxide (DMDBO) for an example (**Figure S2**), **Ti site** adsorbs an oxidation (tert-butyl hydroperoxide, TBHP, C_4H_9OOH) to form **TBHP adsorption**, which turns into a transition state (**Transition state 1**) for the formation of reaction intermediate TiOOH (**TiOOH formation**). By adsorption of a reactant DMDBT (**DMDBT adsorption**), it transforms into another transition state (**Transition state 2**) and produce a product DMDBO (**DMDBO adsorption**). After the desorption of DMDBO (**DMDBO desorption**), transition state 3 happens (**Transition state 3**). Finally, Ti site recoveries (**Ti site recovery**) after the formation and desorption of product tert-Butanol (TBO).

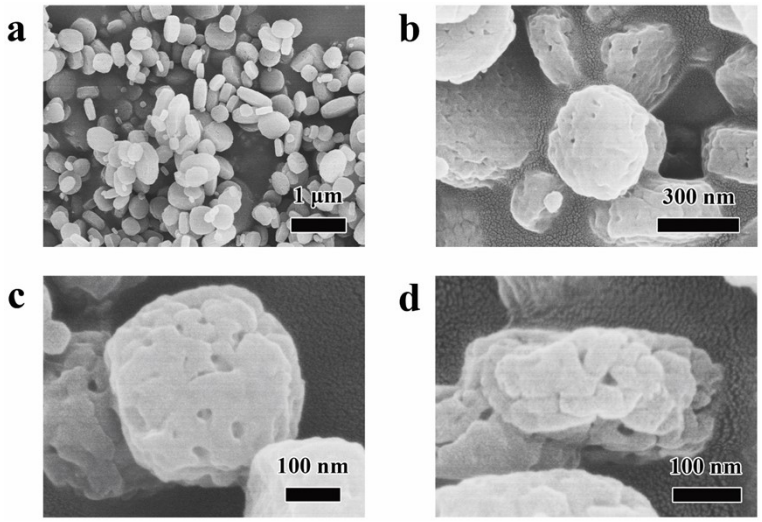

Figure S3. SEM images of the Meso-Ti-MIL-125-120C with a crystallization time of 18 h.

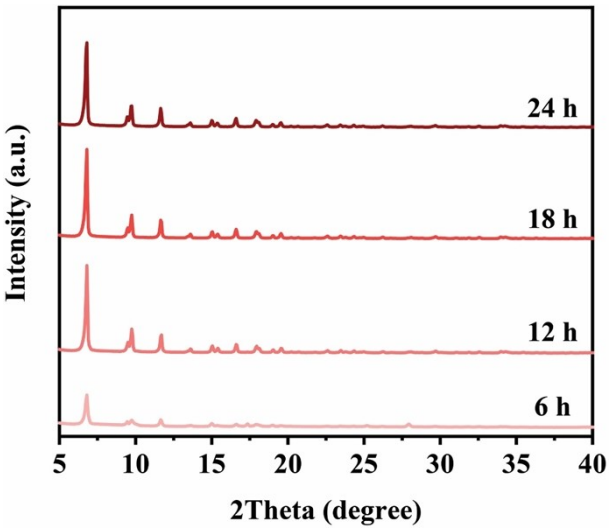

Figure S4. XRD patterns of the Meso-Ti-MIL-125-120C obtained with a crystallization time from 6 h to 24 h.

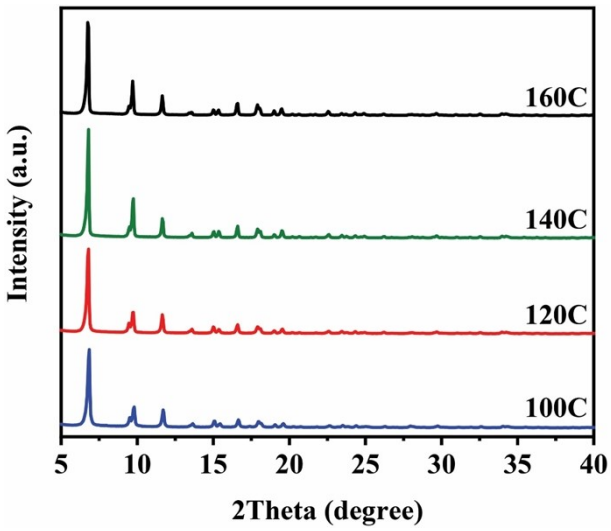

Figure S5. XRD patterns of the Meso-Ti-MIL-125 samples obtained under a crystallization temperature from 100℃ to 160℃.

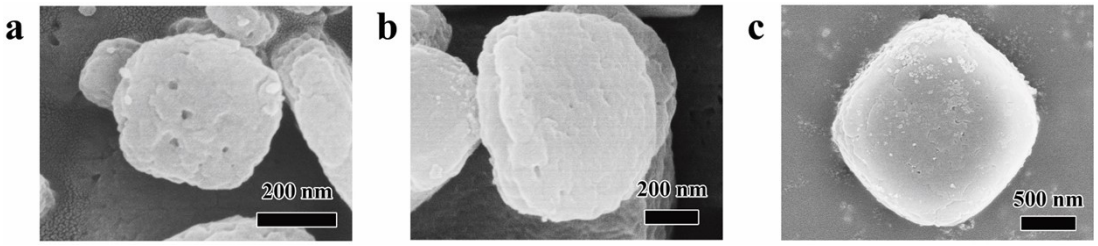

Figure S6. SEM images showing the single crystal morphology of the (a) Meso-Ti-MIL-125-100C, (b) Meso-Ti-MIL-125-140C, and (c) Meso-Ti-MIL-125-160C.

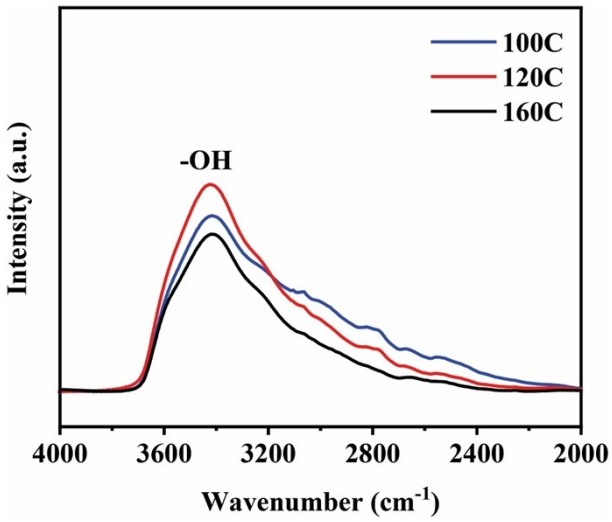

Figure S7. FT-IR spectra of the Meso-Ti-MIL-125-*100–160C* in the range from 4000–2000 cm^{-1}.

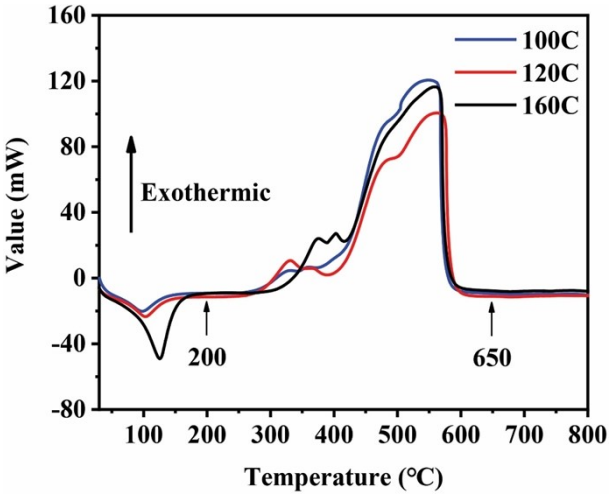

Figure S8. DSC curves of the Meso-Ti-MIL-125-*100–120C* in the air.

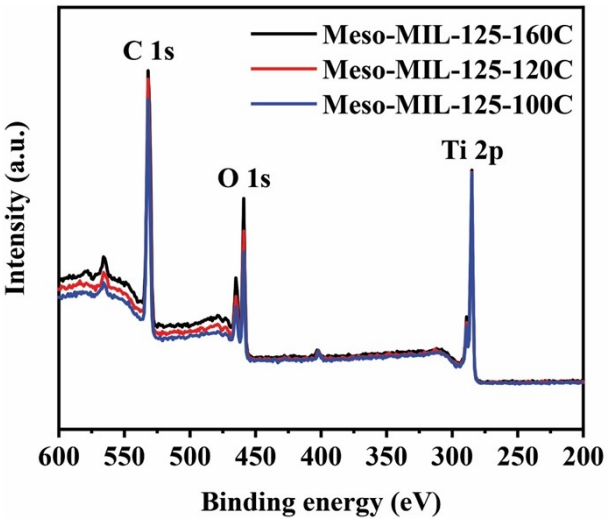

Figure S9. XPS results of the Meso-Ti-MIL-125-100–120C showing the signals of C 1s, O 1s, and Ti 2p.

Table S1. Textural properties of the Ti-MIL-125 samples

Sample	*Surface Ti/O*	S_{BET} (m^2g^{-1})	S_{micro} (m^2g^{-1})	S_{exter} (m^2g^{-1})	V_{tol} (cm^3g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})
Meso-MIL-125-100C	0.18	1181	1116	65	0.59	0.47	0.12
Meso-MIL-125-120C	0.20	1401	1325	76	0.71	0.56	0.15
Meso-MIL-125-160C	0.22	1158	1109	49	0.56	0.47	0.09

Surface Ti/O ratio: determined by XPS results, S_{BET}: BET surface area, S_{micro}: micropore surface area, S_{exter}: external surface area, V_{total}: total pore volume, V_{micro}: micropore volume, V_{meso}: mesoporous pore volume obtained by analysis of N_2 adsorption–desorption data. The micropore and external surface area were determined from N_2 adsorption using the Brunauer-Emmett-Teller method. Micropore size was calculated by a Horvath-Kawazoe method. Mesopore volume and mesopore size were determined by the desorption branches of N_2 isotherms, using the Barret-Joyner-Halenda model. Total pore volumes were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.99.

Table S2. Catalytic oxidative desulfurization performance of different Meso-MIL-125

catalysts

	BT (%)		DBT (%)		DMDBT (%)	
	1st cycle	**5th cycle**	**1st cycle**	**5th cycle**	**1st cycle**	**5th cycle**
Meso-MIL-125-100C	89	\	100	\	73	\
Meso-MIL-125-120C	100	100	100	100	100	100
Meso-MIL-125-160C	42	\	66	\	15	\