

Supplementary Information

Synthesis of Titanosilicate Nanoparticles with High Titanium Content from a Silsesquioxane-based Precursor for a Model Epoxidation Reaction

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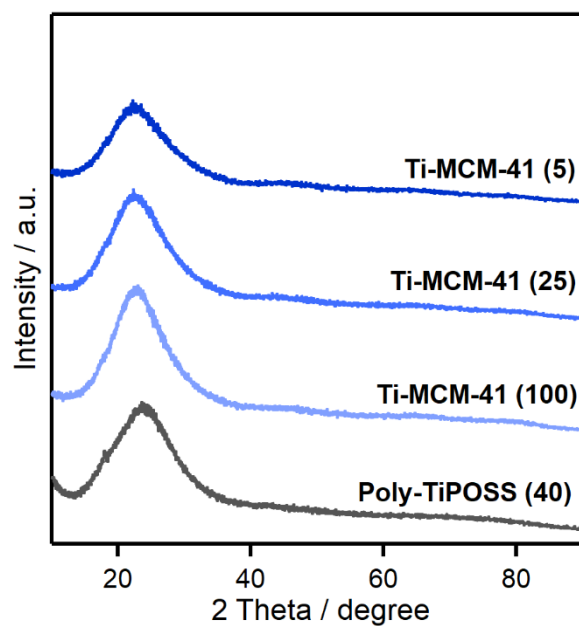


Figure S1-1. PXRD patterns of Ti-MCM-41(x) samples and **Poly-TiPOSS(40)** sample with the 2 theta range of 10° to 90°.

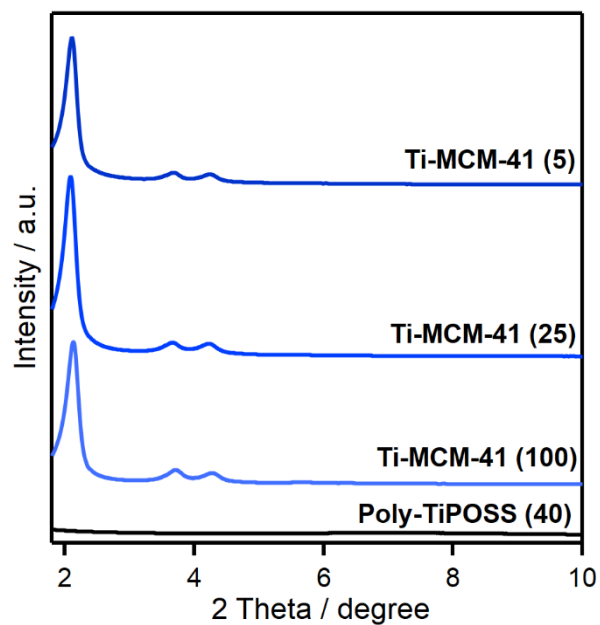


Figure S1-2. PXRD patterns of Ti-MCM-41(x) samples and **Poly-TiPOSS(40)** sample with the 2 theta range of 2° to 10°.

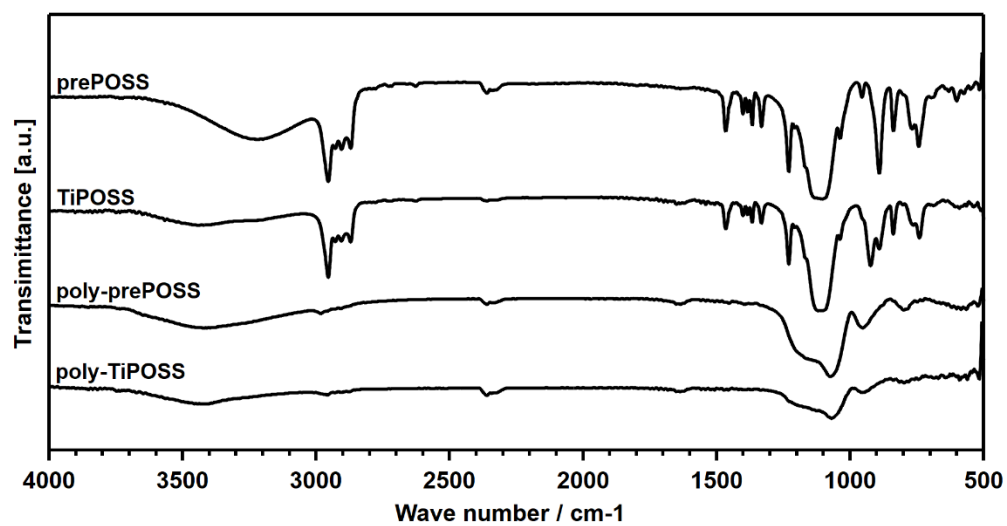


Figure S2. FTIR spectrum of **prePOSS**, **TiPOSS**, **Poly-prePOSS**, and **Poly-TiPOSS** samples.

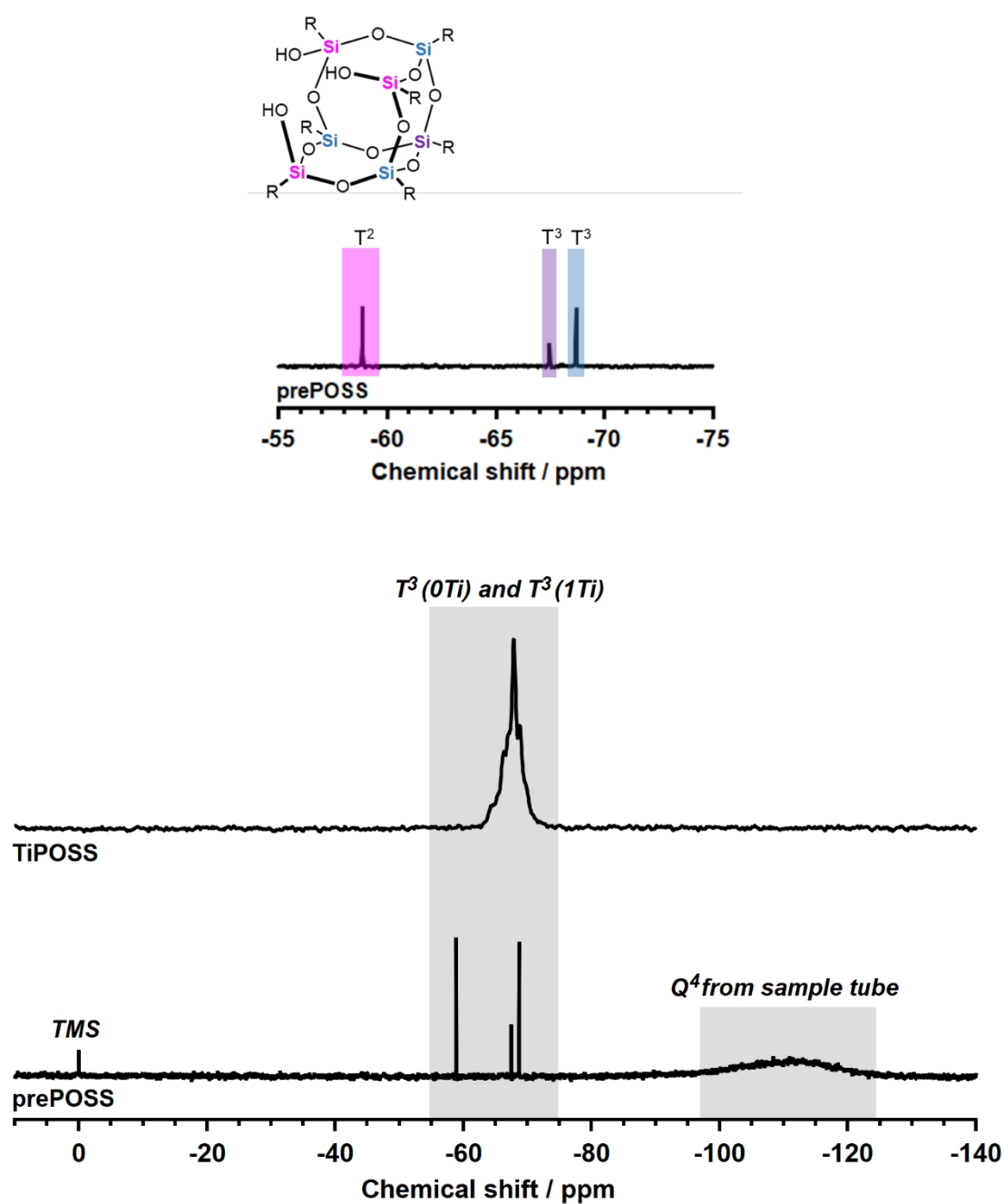


Figure S3. NMR spectrum of **prePOSS** sample and detailed signal assignment (top). And wide range NMR spectra of **prePOSS** and **TiPOSS** samples (bottom).

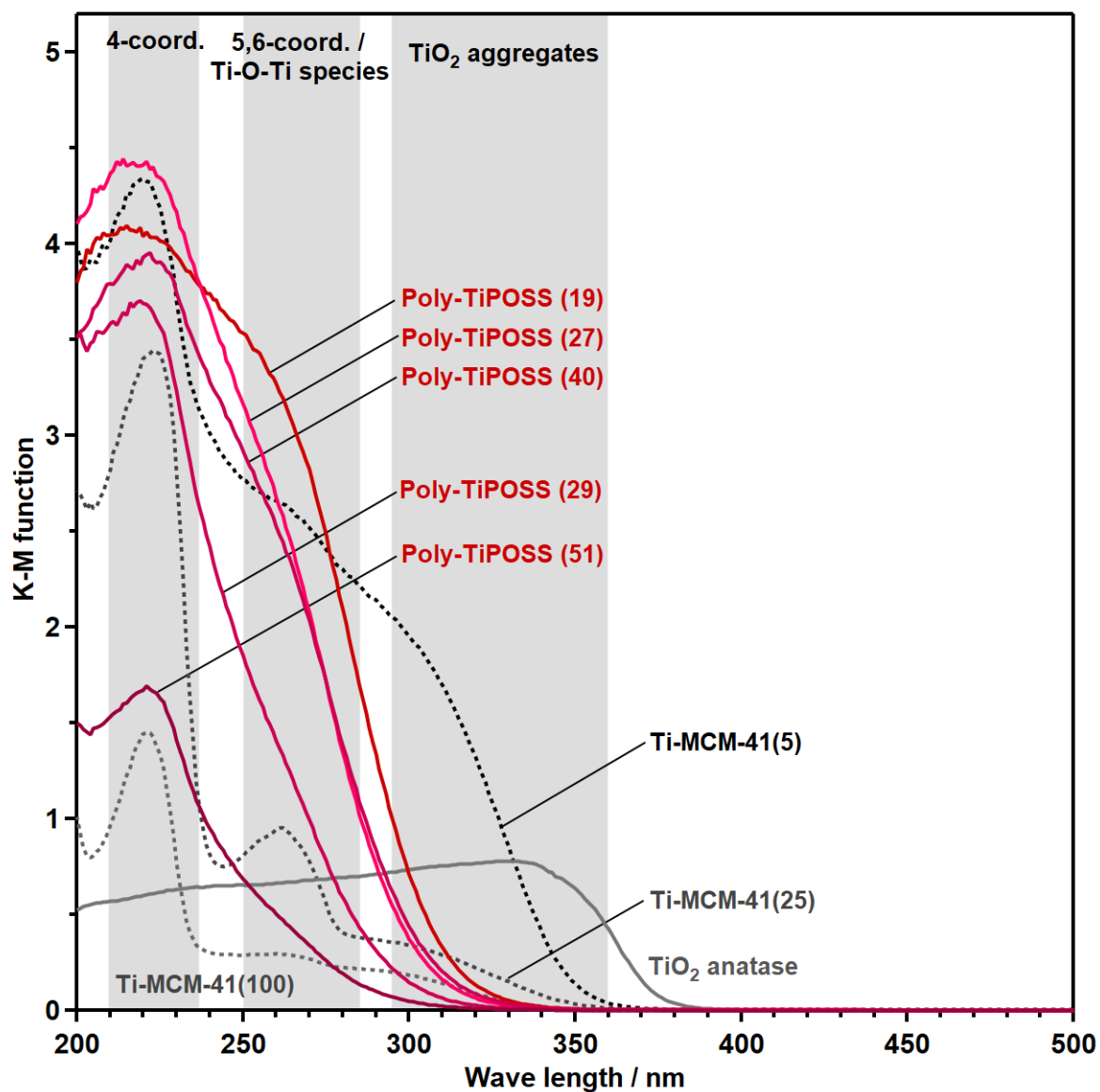


Figure S4. UV-Vis spectrum of **Poly-TiPOSS** samples with Si/Ti ratio range of 19 to 51, **Ti-MCM-41** materials with Si/Ti ratios of 5, 25, and 100, and **TiO₂ anatase** powder as a reference.

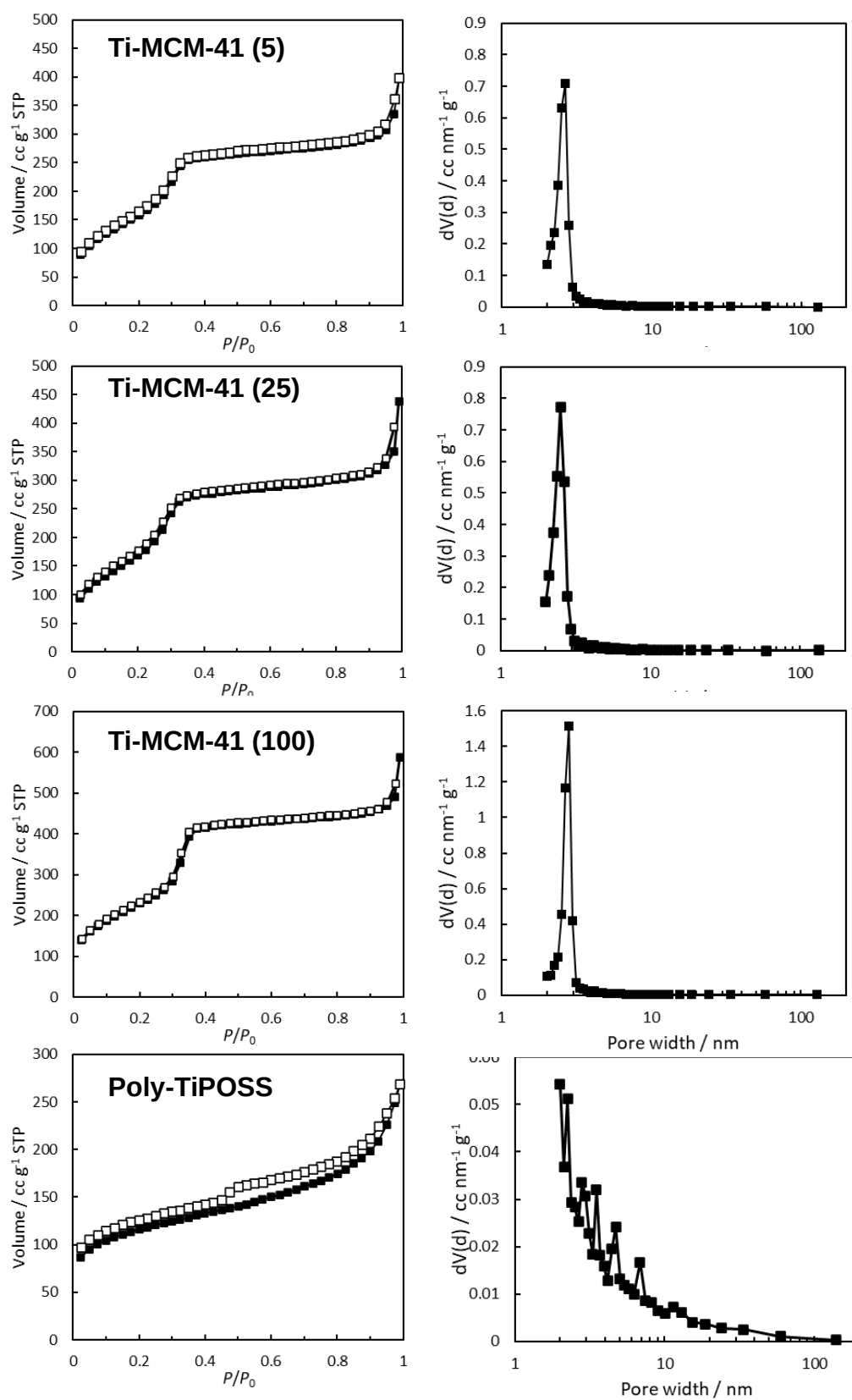


Figure S5. N_2 sorption isotherms and BJH pore distributions of Ti-MCM-41(x) samples and **Poly-TiPOSS** sample.

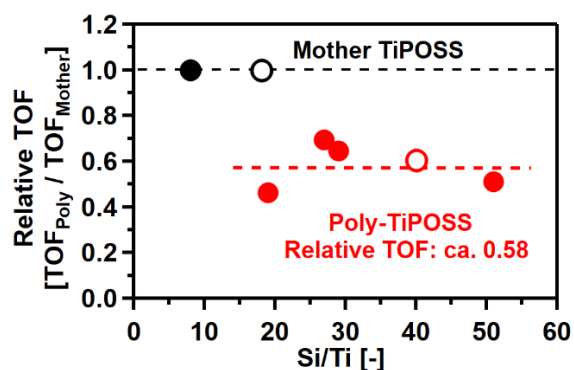


Figure S6. TOF values of Poly-TiPOSS (Si/Ti = 19–51) catalysts relative to those of mother TiPOSS catalysts (Si/Ti = 8 and 18) plotted along with Si/Ti ratio.

To estimate the number of active sites, the relative TOF of the reactant (cyclohexene) per Ti amount was compared with that of TiPOSS and Poly-TiPOSS (Figure 8). Two different TiPOSS samples with Si/Ti ratios of 8 and 18 (black filled and open circles in Figure 8) were polymerized to heterogeneous samples (red filled and open circles in Figure 8). The Si/Ti ratio of the polymerized sample was varied from 19 to 51 by controlling the amount of TEOS. The normalized TOF values of the Poly-TiPOSS samples were constant at around 0.58 relative to those of TiPOSS (Figure 8). The lower relative TOF value of Poly-TiPOSS can be explained by (1) a decrease in the number of accessible Ti sites due to the migration of the sites inside the silica nanoparticles and (2) a decrease in the catalytic activity owing to the neighboring silanol species hindering the attack of the hydrophobic reactant molecules. Although the former reason seems more critical, the modification of surface silanol groups could be a potential approach to increase the relative TOF, which will be investigated in future work.