

### Supplementary information

#### **Highly active and selective Ti-incorporated porous silica catalysts derived from grafting of titanium(IV) acetylacetonate**

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**Table S1.** Characteristics of Ti-MCM-41 catalysts synthesized using titanium isopropoxide and titanium butoxide as Ti source

	Si/Ti <sup>a</sup>	BET surface area <sup>b</sup> (m <sup>2</sup> ·g <sup>-1</sup> )	Mesopore volume <sup>c</sup> (cm <sup>3</sup> ·g <sup>-1</sup> )	Pore diameter <sup>c</sup> (nm)
Ti(isoPrO)-MCM-41	27	936	0.82	2.7
Ti(BuO)-MCM-41	38	925	0.83	2.8

<sup>a</sup> Calculated by energy dispersive X-ray spectrometry.

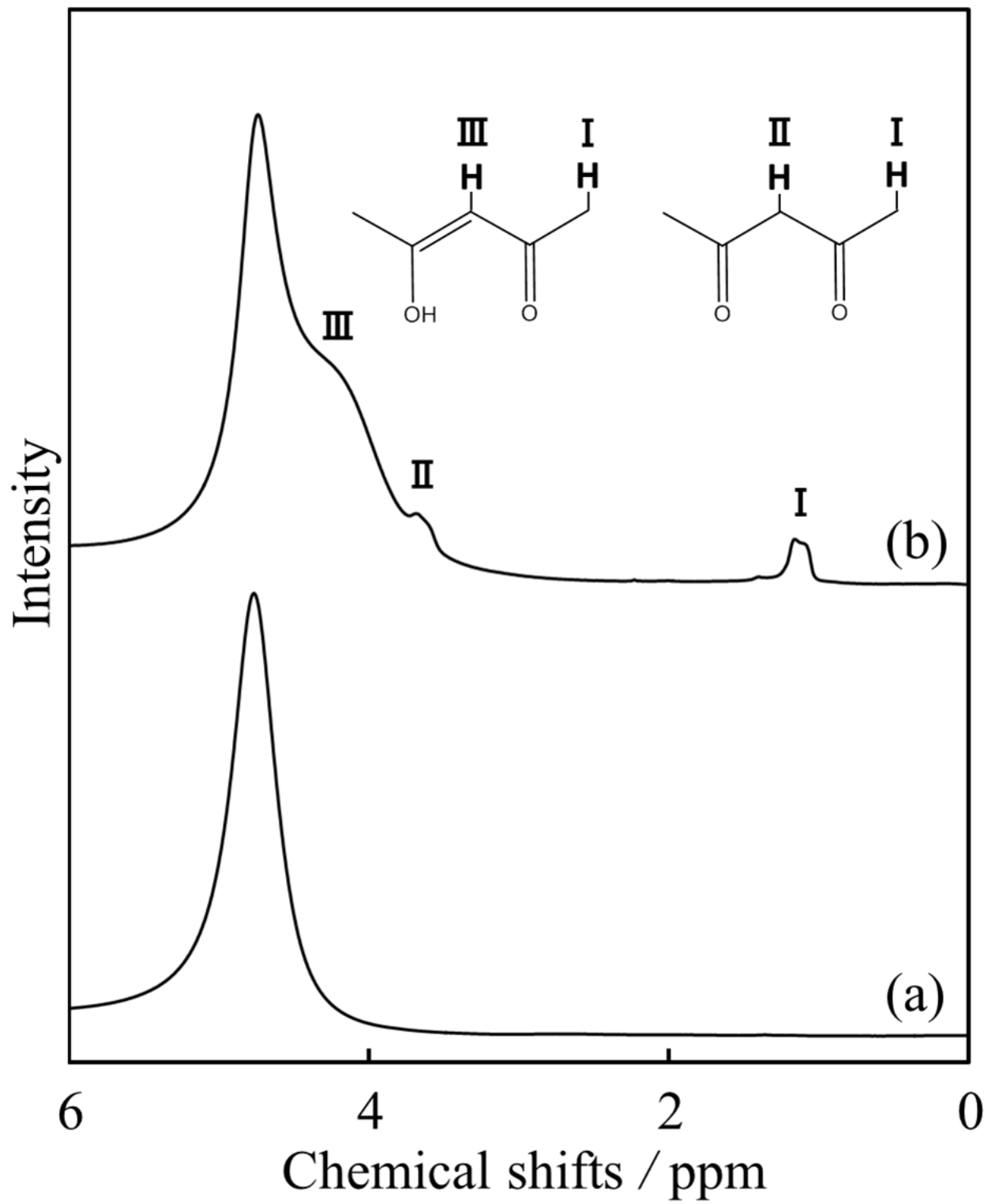
<sup>b</sup> Determined using the BET method.

<sup>c</sup> Determined using the BJH plot.

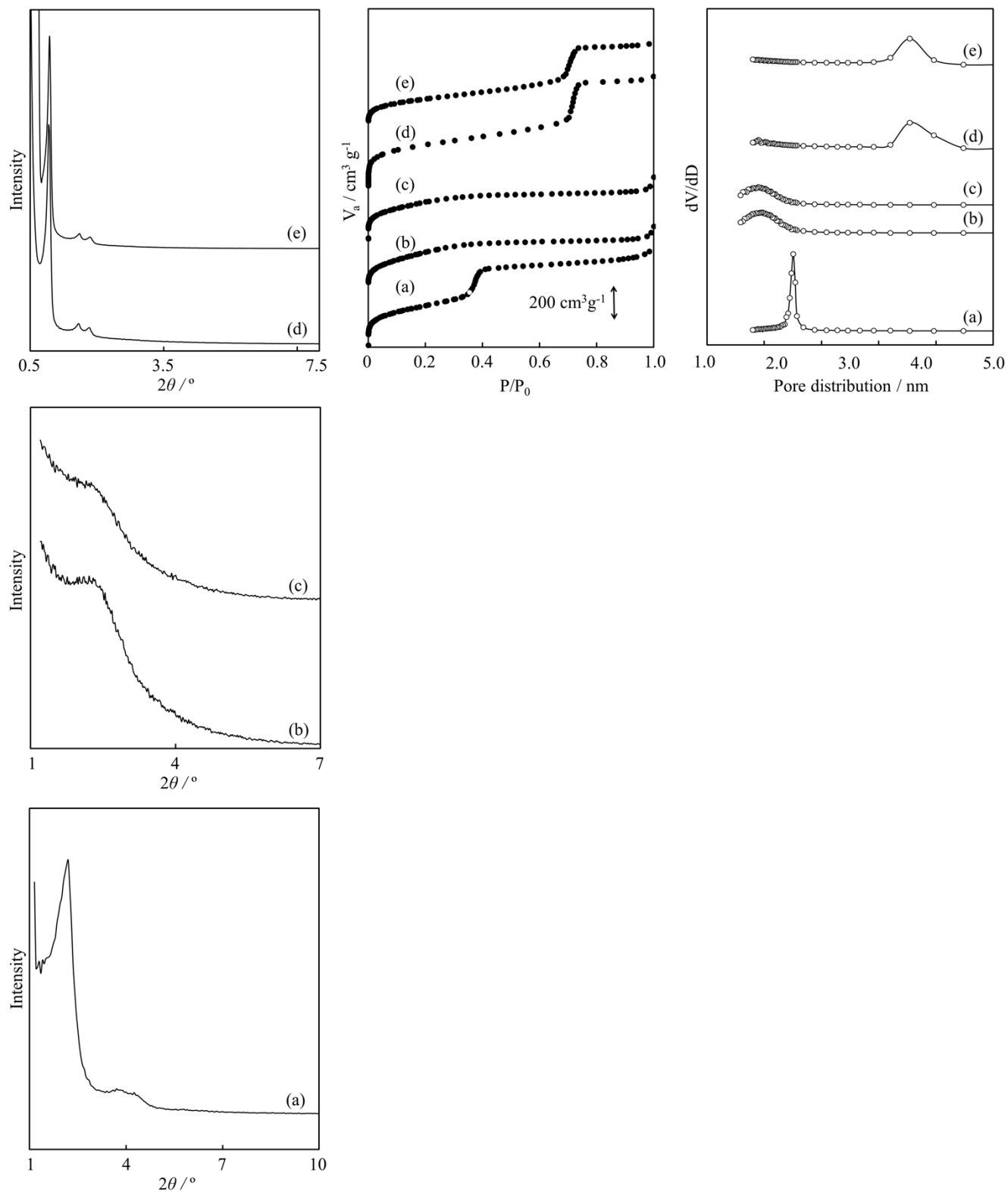
**Table S2.** Catalytic performances of Ti(isoPrO)-MCM-41 and Ti(BuO)-MCM-41 in the epoxidation of cyclohexene with *tert*-butyl hydroperoxide as an oxidant.<sup>a</sup>

	Conversion (%)	Epoxide yield (%)	Epoxide selectivity (%)	TOF (mol product <sub>cyclohexane</sub> oxide mol <sub>Ti</sub> <sup>-1</sup> ·h <sup>-1</sup> )
Ti(isoPrO)-MCM-41	3.7	1.8	49	15
Ti(BuO)-MCM-41	38.2	15.0	39	177

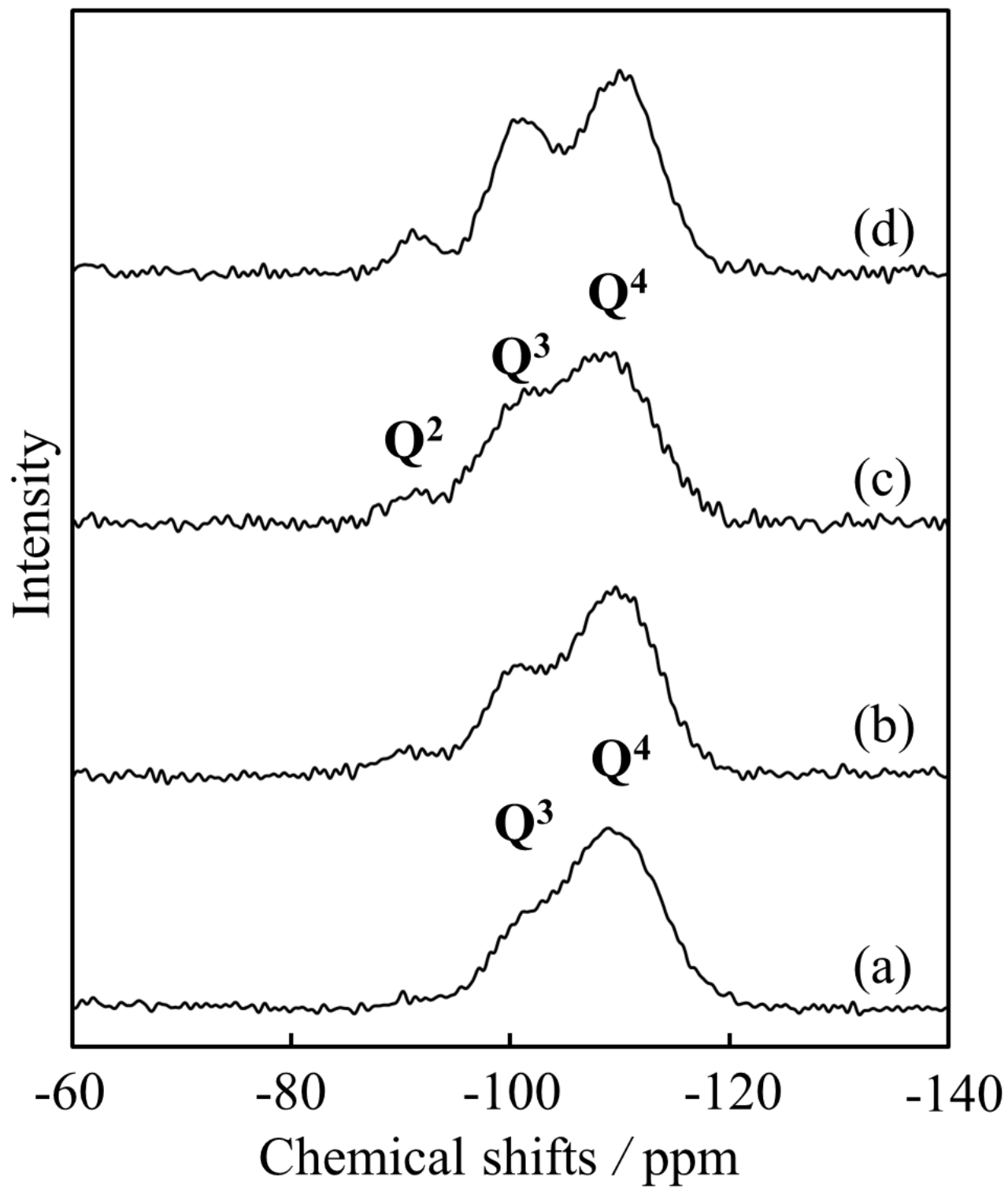
<sup>a</sup> Reaction conditions: catalyst, 10 mg; acetonitrile, 10 mL; cyclohexene, 10 mmol; *tert*-butyl hydroperoxide, 10 mmol; temp., 60 °C; time, 2 h.



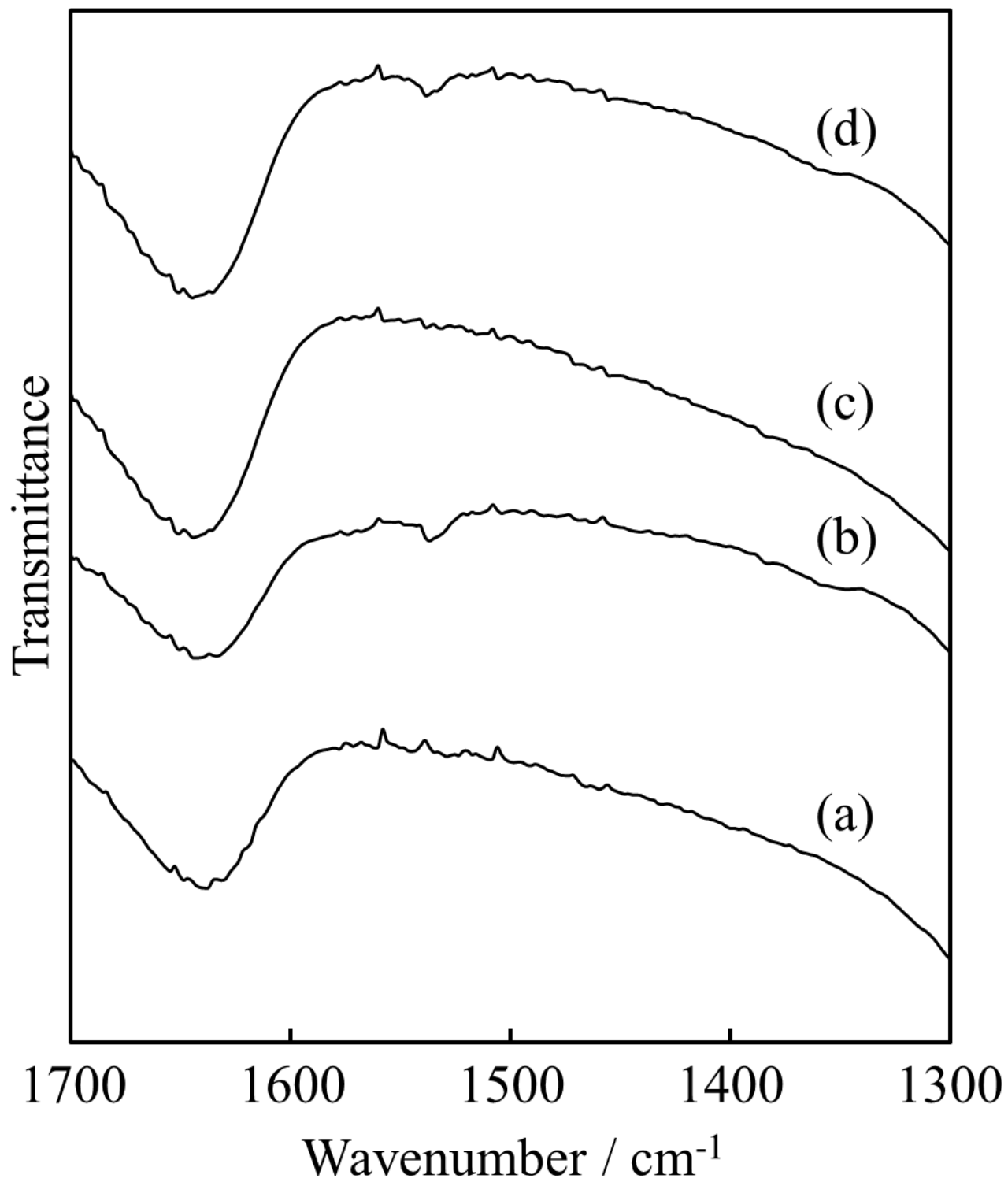
**Figure S1.**  $^1\text{H}$  MAS NMR spectra of (a) MCM-41 and (b) Ti(acac)-MCM-41.



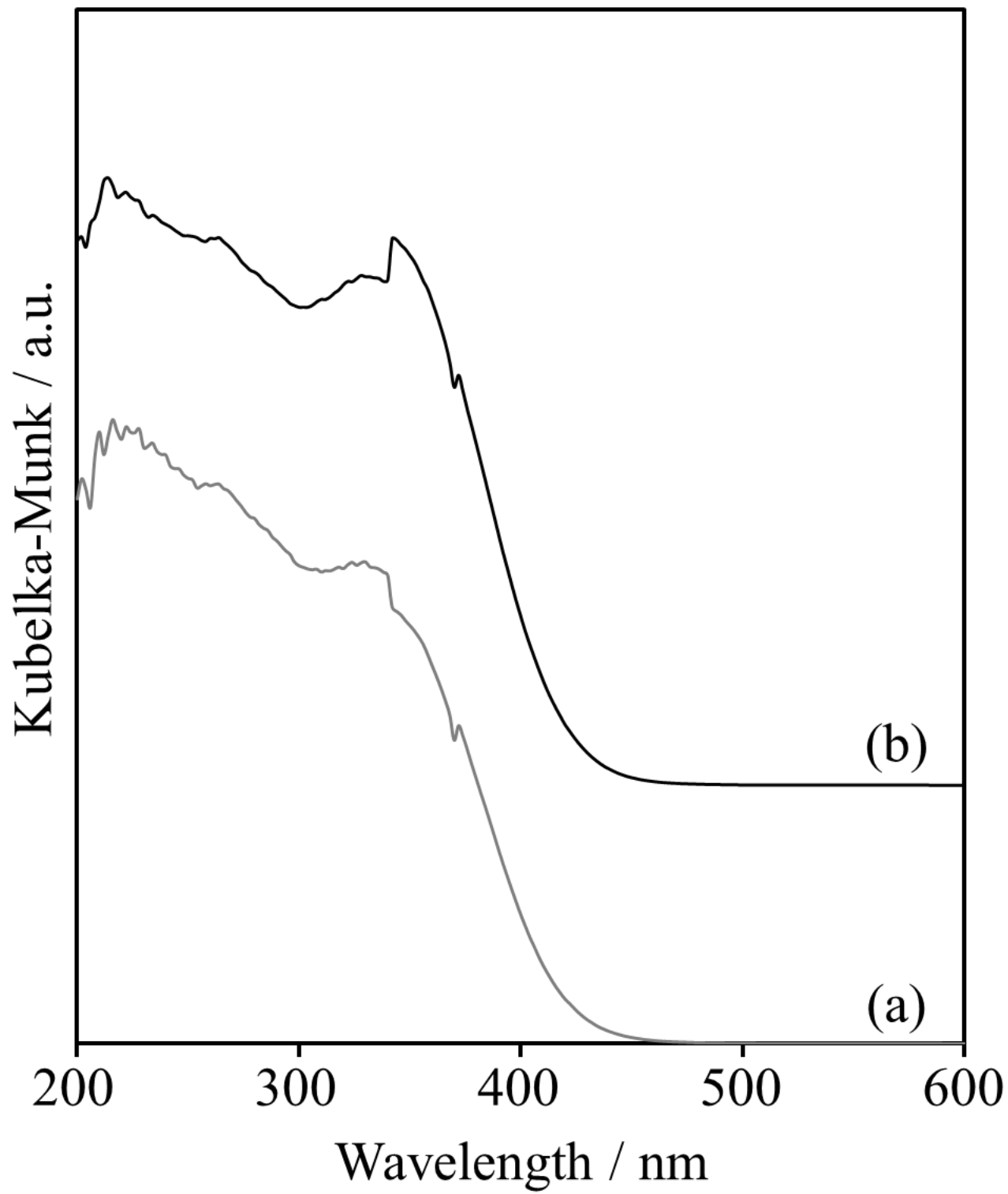
**Figure S2.** (left) XRD patterns, (center)  $N_2$  adsorption isotherms, and (right) BJH pore size distributions of (a) Ti-MCM-41(Ref.), (b) HUS-6, (c) Ti(acac)-HUS-6, (d) SBA-15, and (e) Ti(acac)-SBA-15.



**Figure S3.**  $^{29}\text{Si}$  MAS NMR spectra of (a) HUS-6, (b) Ti(acac)-HUS-6, (c) SBA-15, and (d) Ti(acac)-SBA-15.

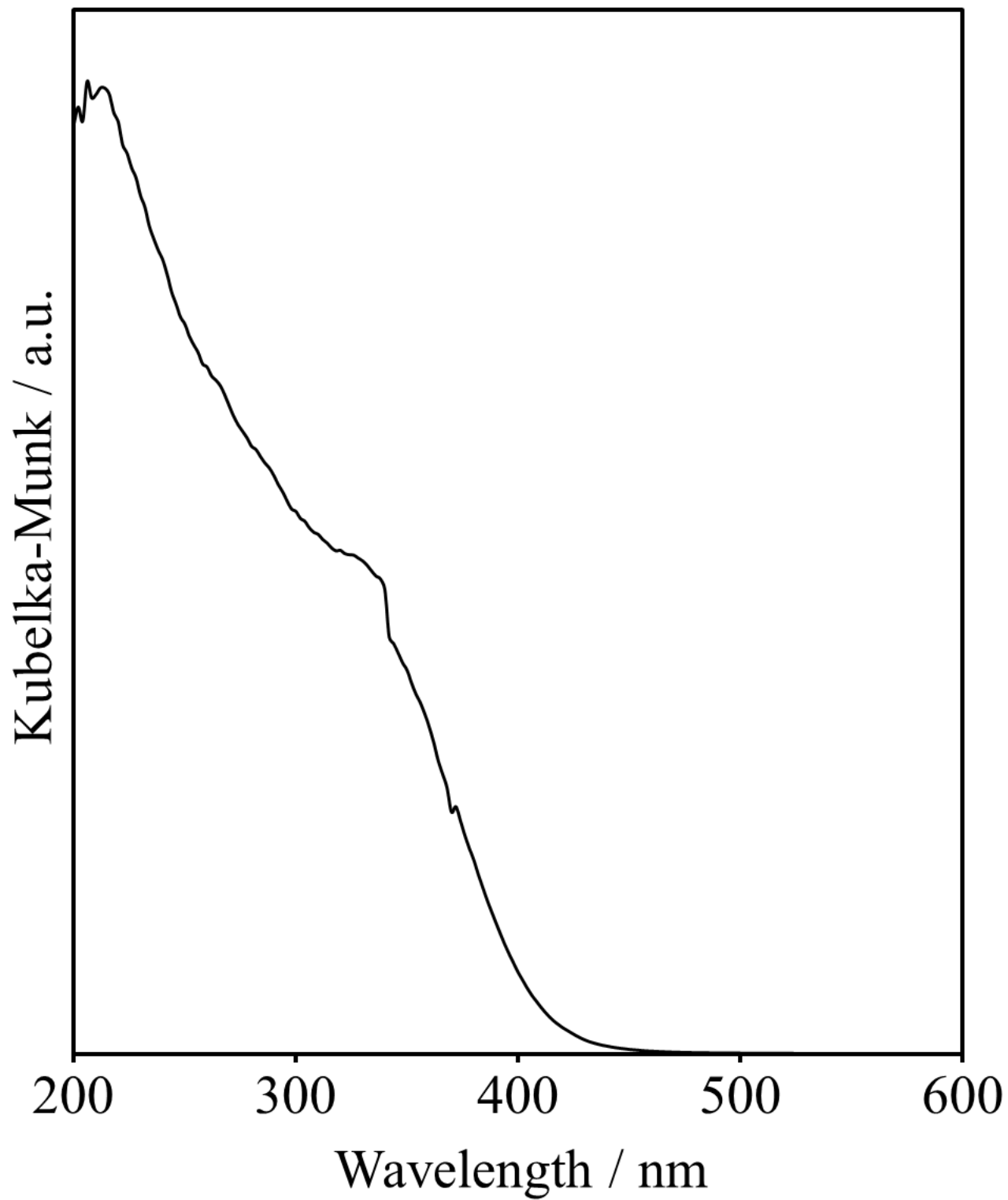


**Figure S4.** FT-IR spectra of (a) HUS-6, (b) Ti(acac)-HUS-6, (c) SBA-15, and (d) Ti(acac)-SBA-15.

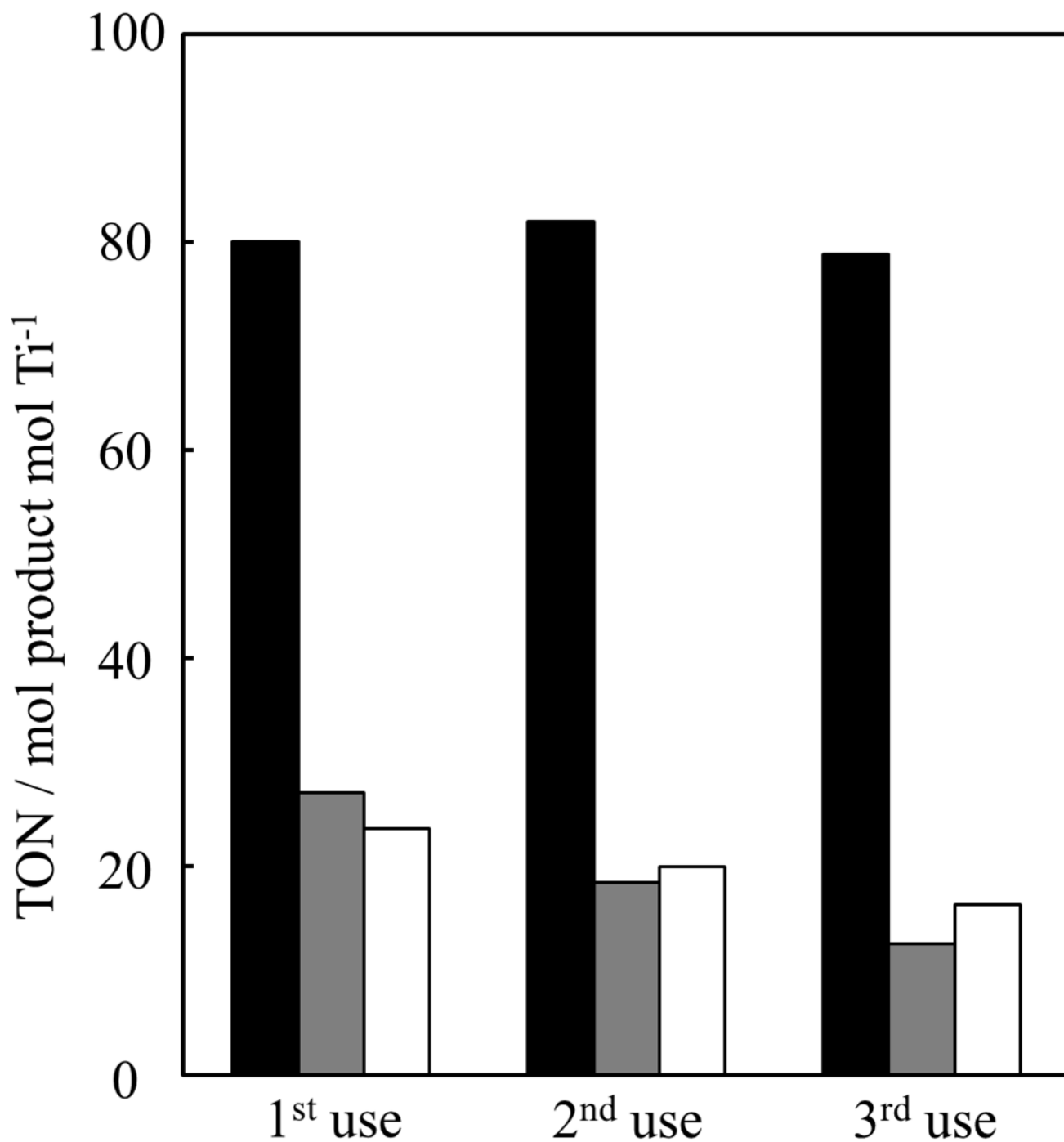


**Figure S5.** UV-vis spectra of (a) Ti(acac)-HUS-6 and (b) Ti(acac)-SBA-15.

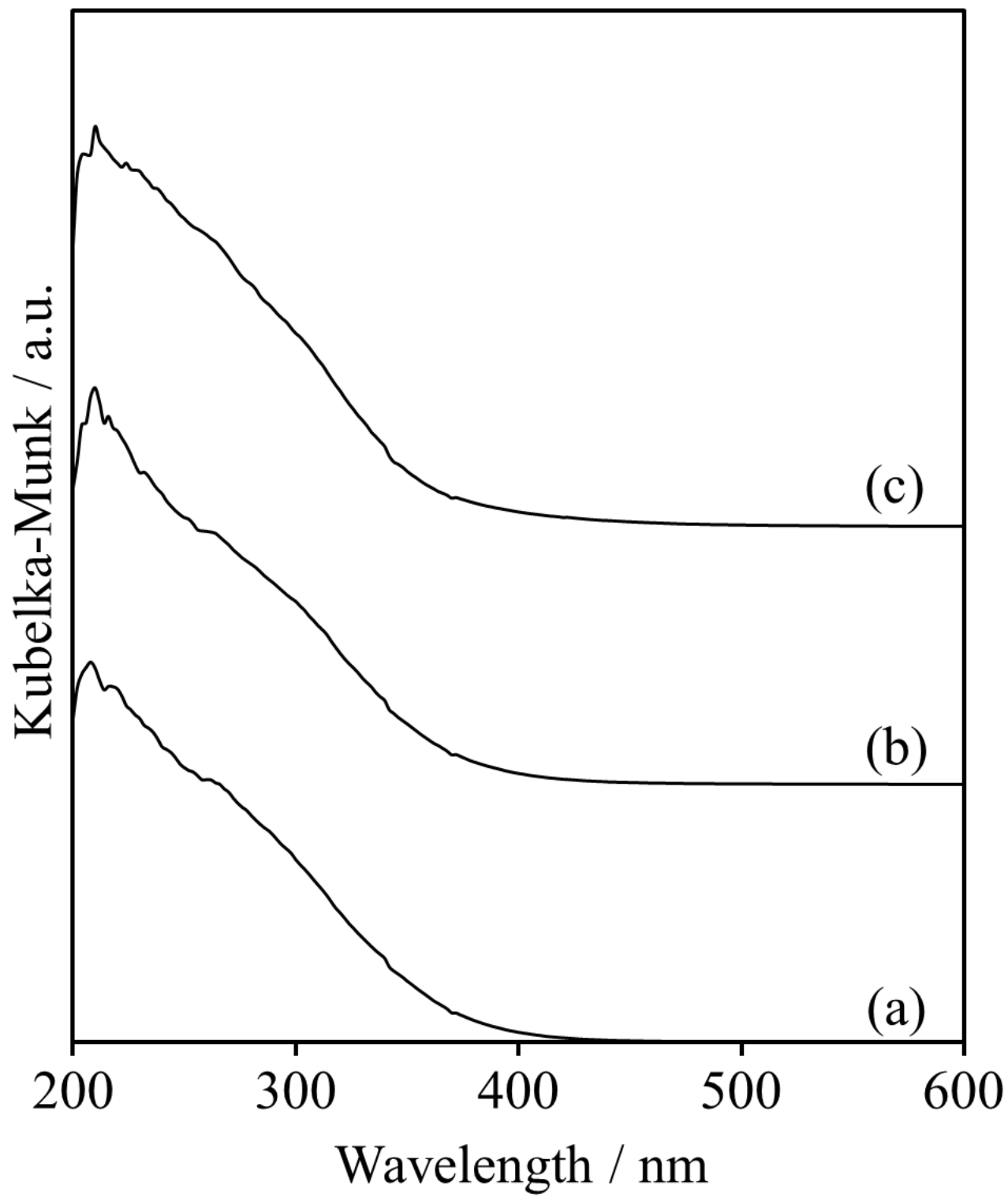




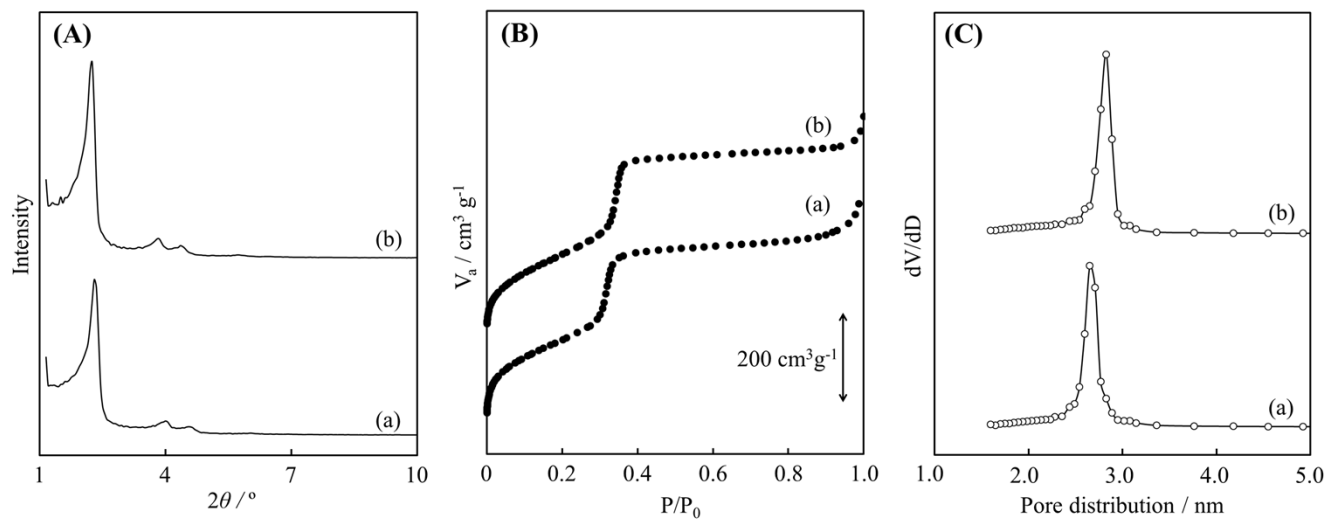
**Figure S6.** UV-vis spectrum of Ti(acac)-MCM-41 after reaction with large amount of acetylacetonone (acetylacetonone/Ti = 260).



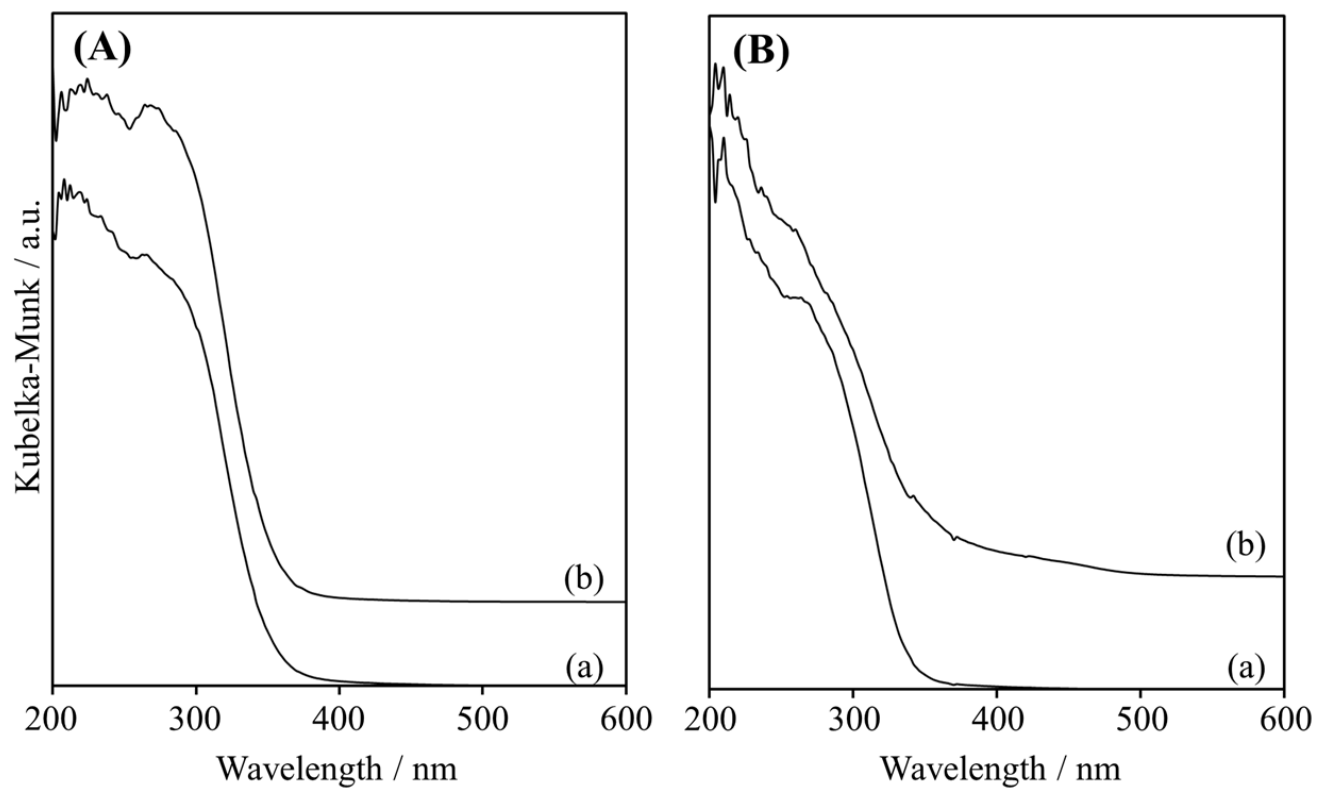
**Figure S7.** Catalytic reusability of (black) Ti(acac)-MCM-41, (grey) Ti(acac)-MCM-41cal, and (white) Ti-MCM-41(Ref.). Reaction conditions: catalyst, 50 mg; acetonitrile, 5 mL; cyclohexene, 5 mmol; *tert*-butyl hydroperoxide, 5 mmol; temp., 60 °C; time, 0.5 h.



**Figure S8.** UV-vis spectra of Ti(acac)-MCM-41 after epoxidation of cyclohexene: (a) 1<sup>st</sup> run, (b) 2<sup>nd</sup> run, and (c) 3<sup>rd</sup> run.



**Figure S9.** (A) XRD patterns, (B)  $N_2$  adsorption isotherms, and (C) BJH pore size distributions of (a) Ti(isoPrO)-MCM-41 and (b) Ti(BuO)-MCM-41.



**Figure S10.** UV-vis spectra of (A) Ti(isoPrO)-MCM-41 and (B) Ti(BuO)-MCM-41 (a) before and (b) after epoxidation reaction.

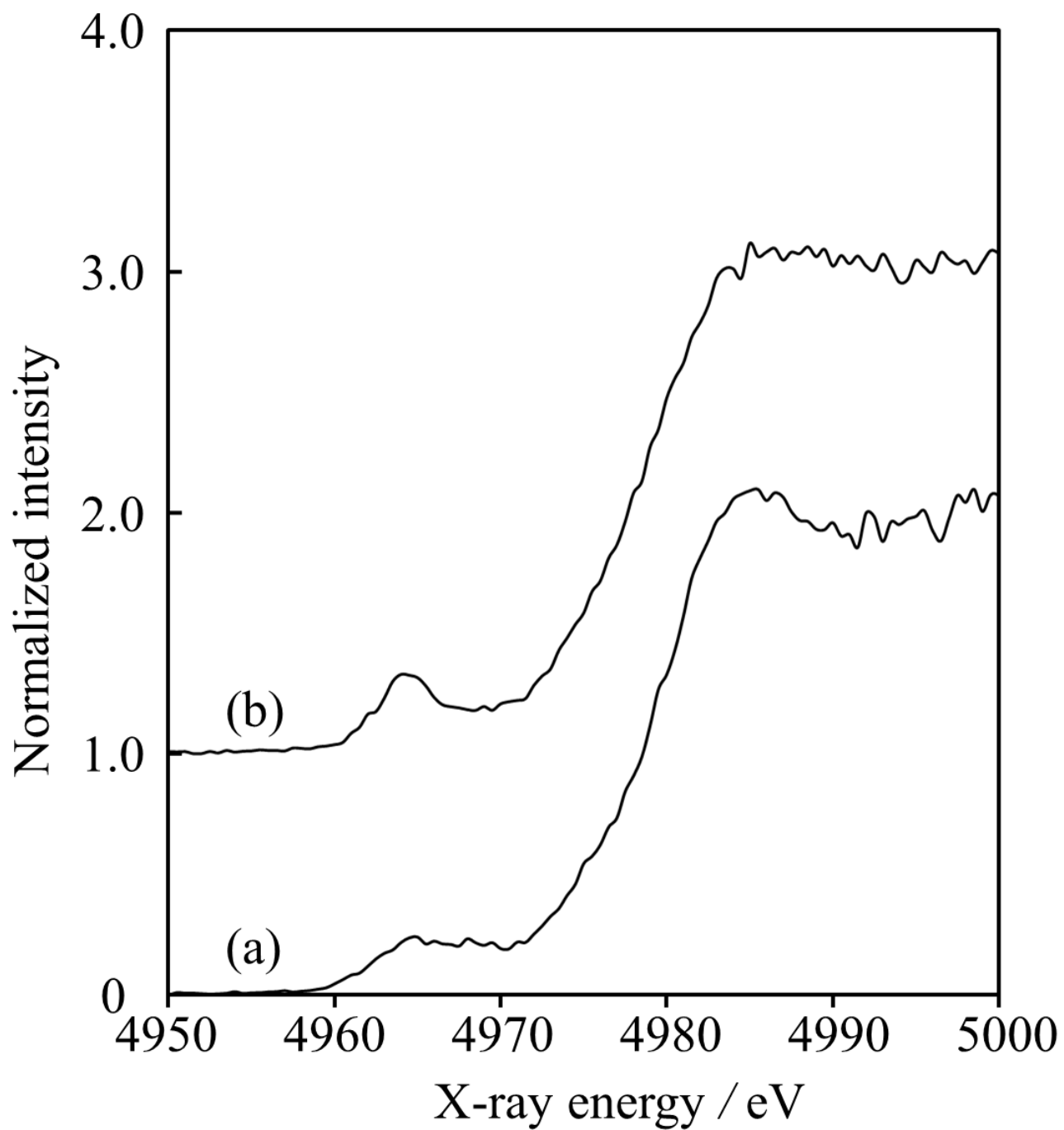


Figure S11. XANES spectra of (a) Ti(isoPrO)-MCM-41 and (b) Ti(BuO)-MCM-41.