

Electronic Supplementary Information

Low Temperature Oxidative Desulfurization with Hierarchically Mesoporous Titaniumsilicate Ti-SBA-2 Single Crystals

*Chengxiang Shi, Wenxuan Wang, Ni Liu, Xueyan Xu, Danhong Wang, Minghui Zhang, Pingchuan Sun, and Tiejong Chen**

College of Chemistry, School of Materials Science and Engineering, Institute of New Catalytic Materials Science, Key Laboratory of Advanced Energy Materials Chemistry (MOE), Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, PR China

1. Experimental

1.1 Chemicals

Cetyltrimethylammonium bromide (CTAB) and ammonia (25 wt% aqueous solution) were purchased from Guangfu Chemical Reagent Company, China; poly (acrylic acid) (PAA) (average molecular weight 240,000, 25 wt % solution in water) was from Alfa Aesar; tetraethyl orthosilicate (TEOS), titanium oxysulfate hydrate ($\text{TiOSO}_4 \cdot n\text{H}_2\text{O}$) and hydrogen peroxide solution (H_2O_2 , 30 wt%) were purchased from Aladdin, China. Decalin and tert-butyl hydroperoxide (TBHP) were purchased from the China National Pharmaceutical Group (Sinopharm). Dibenzothiophene (DBT) was purchased from Acros Organics. All the chemical agents were used without further purification.

1.2 Synthesis of peroxy titanate acid solution

In a typical synthesis, 0.01 mol titanium oxysulfate hydrate ($\text{TiOSO}_4 \cdot n\text{H}_2\text{O}$) was completely dissolved in 25 mL distilled water under stirring at room temperature, then the solution was transferred to a water bath with ice cube (the temperature of the ice water mixture was around 2 °C), after stirring for 30 min, 0.04 mol hydrogen peroxide solution (H_2O_2 ,

30 wt%) was slowly added under stirring, the solution was continued to stir for 2 hours to obtain the stable peroxy titanate solution.

1.3 Synthesis of Ti-containing hierarchically mesoporous silica (THMS)

In a typical reaction, 0.55 g CTAB was completely dissolved in 25.0 mL of deionized water under stirring, and 3.0 g 25 wt% PAA aqueous solution was added at room temperature to obtain a clear solution. And then, 2.0 g ammonia (25 wt% aqueous solution) was added under stirring, immediately the solution became a milky suspension.¹ After further stirring for 30 min, the emulsion was transferred to water bath with ice cubes (around 2 °C), after stirring for 10 min, 2.08 g of tetraethyl orthosilicate (TEOS) and a certain amount of peroxy titanate solution (with the Si/Ti molar ratio of 25, 20, 15, 10 and 5) were added under stationary state. After being stirred for 60 min at ambient temperatures, the mixture was transferred into an autoclave, which was left in an oven at 80 °C for 48 h. The final product was centrifuged, dried and calcined. The samples were denoted as THMS-x, where x indicates the molar ratio of Si/Ti in the initial solution.

1.4 Oxidative desulfurization of DBT as model sulfur compound

Oxidative desulfurization of DBT was carried out in a glass batch reactor. A simulated model diesel (500 ppm DBT) was prepared as follows: 0.05 g of DBT was dissolved in 99.95 g of decalin to obtain a solution containing 500 mg/g of DBT. Tert-butyl hydroperoxide is used as the oxidant in this reaction and the molar ratio of TBHP/DBT (O/S) equals 3. A typical ODS process in a batch reactor is as follows: in a 50 ml round bottom flask, 30 ml simulated diesel (500 ppm DBT) was heated to a desired temperature with stirring, then 0.03 g catalyst was added. After stirring for 10 min, 0.0338 g 65% TBHP was added, the oxidation reaction last for about 1.5 h. The oxidation products were analyzed by gas chromatograph (GC-FID) at different reaction time. The detecting limit of GC for DBT solution is 3 ppm. The TOF value was calculated from mole of converted DBT per mole of titanium in THMS materials per hour.

1.5 Catalyst deactivation and regeneration

Oxidative desulfurization with high concentration DBT (5000 ppm) was carried out with the sample THMS-15 as catalyst. 30 ml simulated diesel (5000 ppm DBT) was heated to 40 °C with stirring, then 0.03 g THMS-15 was added. After stirring for 10 min, 0.338 g 65% TBHP was added, the oxidation reaction was repeated until no further conversion of DBT was detected.

The deactivated THMS-15 was regenerated by ethanol extraction. Typically, 1 g catalyst was extracted with 100 mL ethanol under stirring for about 12 h at room temperature, and then centrifuged. The process was repeated 3 times, and the final catalyst was dried at 80 °C for 12 h.

1.6 Characterization

X-ray powder diffraction (XRD) patterns were taken on a Rigaku D/max-2500 diffractometer, with Cu K α Radiation at 40 kV and 100 mA ($\lambda = 0.15418$ nm). SEM images were obtained with a JEOL JSM7500F instrument and a Shimadzu Model SS-550 instrument. Transmission TEM observations and elemental analysis for Si/Ti ratios were performed on a Philips Tecnai F20 microscope, working at 200 kV. All samples subjected to TEM measurements were dispersed in ethanol ultrasonically and were dropped on copper grids. Nitrogen adsorption and desorption isotherms were measured on a BELSORP-mini II sorption analyzer at 77 K. Before measurements, the samples were degassed in nitrogen flow at 350 °C at least 6 h. Specific surface area and total pore volume (obtained at p/p_0 equals to 0.98) were calculated by BET (Brunauer-Emmett-Teller) method, the pore-size distribution was calculated from the adsorption branch using BJH (Barrett-Joyner-Halenda) method. UV-vis spectra were measured on a Shimadzu 2450 spectrometer, using barium sulfate as the reference. FT-IR) spectroscopy was measured on a Bruker Tensor 27 spectrometer. Oxidation products were analyzed by gas chromatograph (GC-FID), which was equipped with a SE-54 capillary column, 0.25 mm in diameter and 30 m in length. The products were identified by checking

the retention time with standard materials.

Reference

- 1 J. Wang, H. Zhou, P. Sun, D. Ding and T. Chen, *Chem. Mater.*, 2010, **22**, 3829-3831.

Table S1 Physical and textual properties of the calcined Ti-containing mesoporous silica materials.

Sample	Mesostructure	Si/Ti ^a	Ti ^b /wt%	S _{BET} ^c (m ² ·g ⁻¹)	V _{meso.} ^d (cm ³ ·g ⁻¹)	Mesopore Size /nm	Secondary Mesopore Size /nm
THMS-25	<i>Pm-3n</i>	22.0/23.0	--	837	1.23	3.6	c.a. 20
THMS-20	<i>Pm-3n</i>	20.1/20.1	3.82	801	1.20	3.6	c.a. 20
THMS-15	<i>P6₃/mmc</i>	14.7/15.3	5.52	790	1.20	3.7	c.a. 22
THMS-10	<i>P6₃/mmc</i>	9.6/10.1	--	782	1.30	3.7	c.a. 18

^a The Si/Ti molar ratios estimated from the TEM-EDX analysis on different positions;

^b Ti content detected by ICP measurement;

^c BET surface area detected by nitrogen adsorption-desorption measurements;

^d calculated from p/p₀=0.98 by BET method.

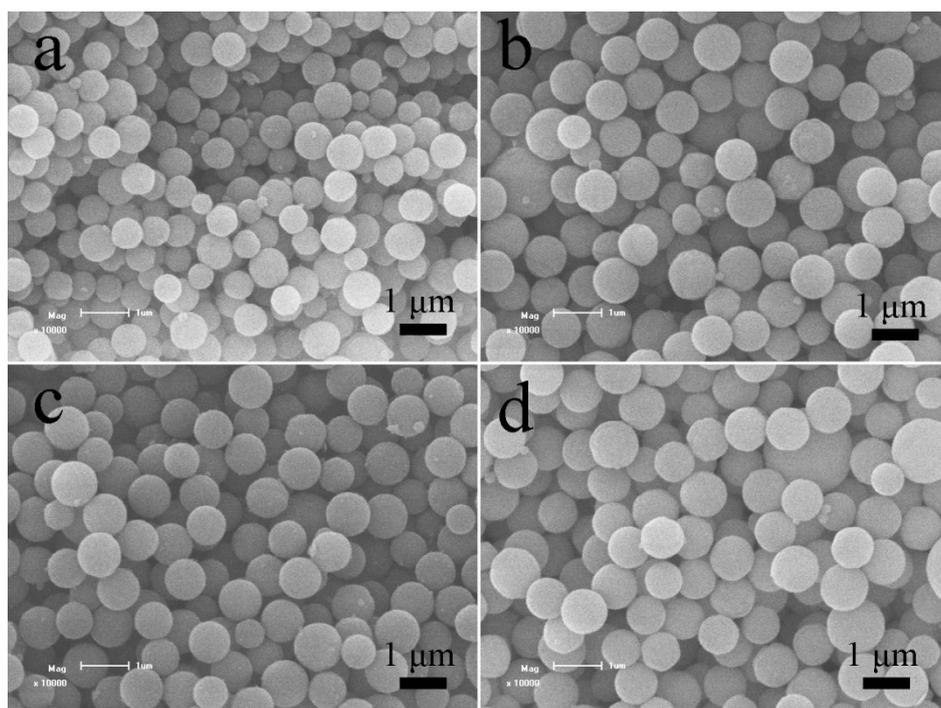


Fig. S1 SEM images of the calcined samples: (a) THMS-25, (b) THMS-20, (c) THMS-15, (d) THMS-10.

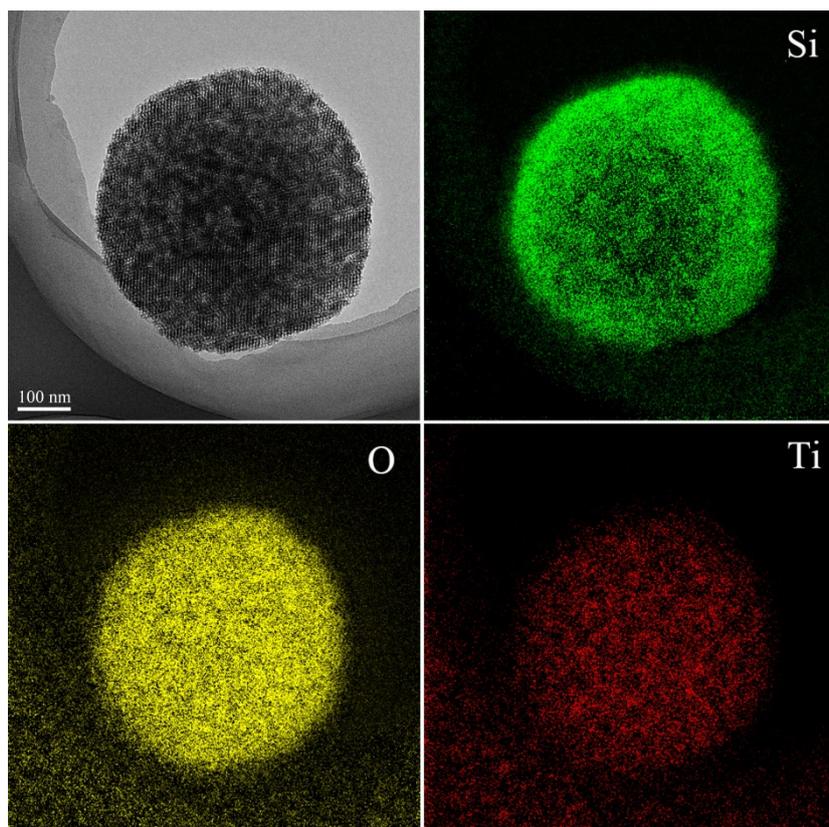


Fig. S2 EELS (electron energy loss spectroscopy) images of the calcined THMS-15.

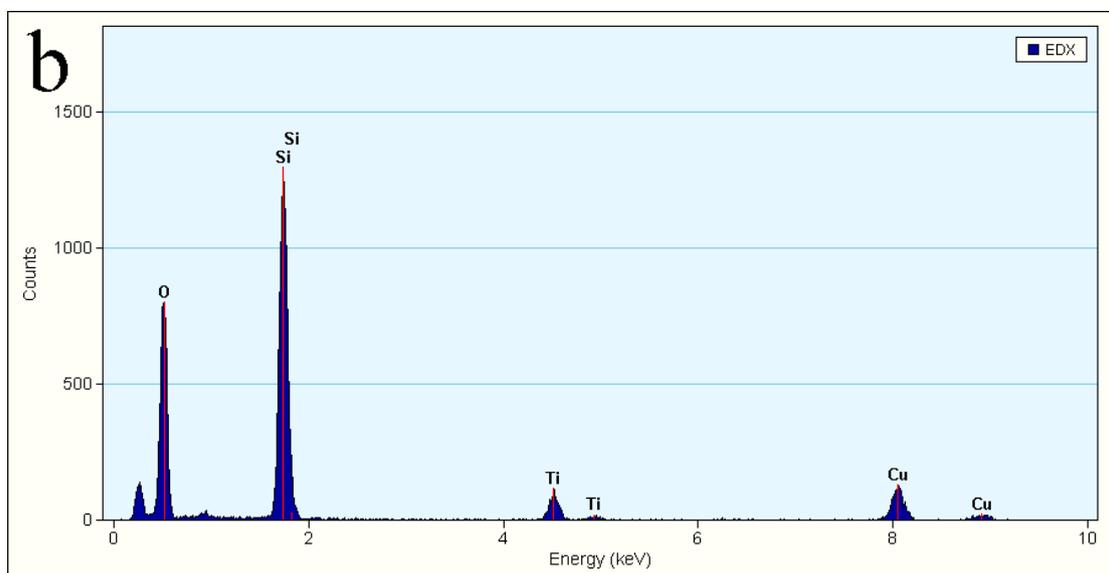
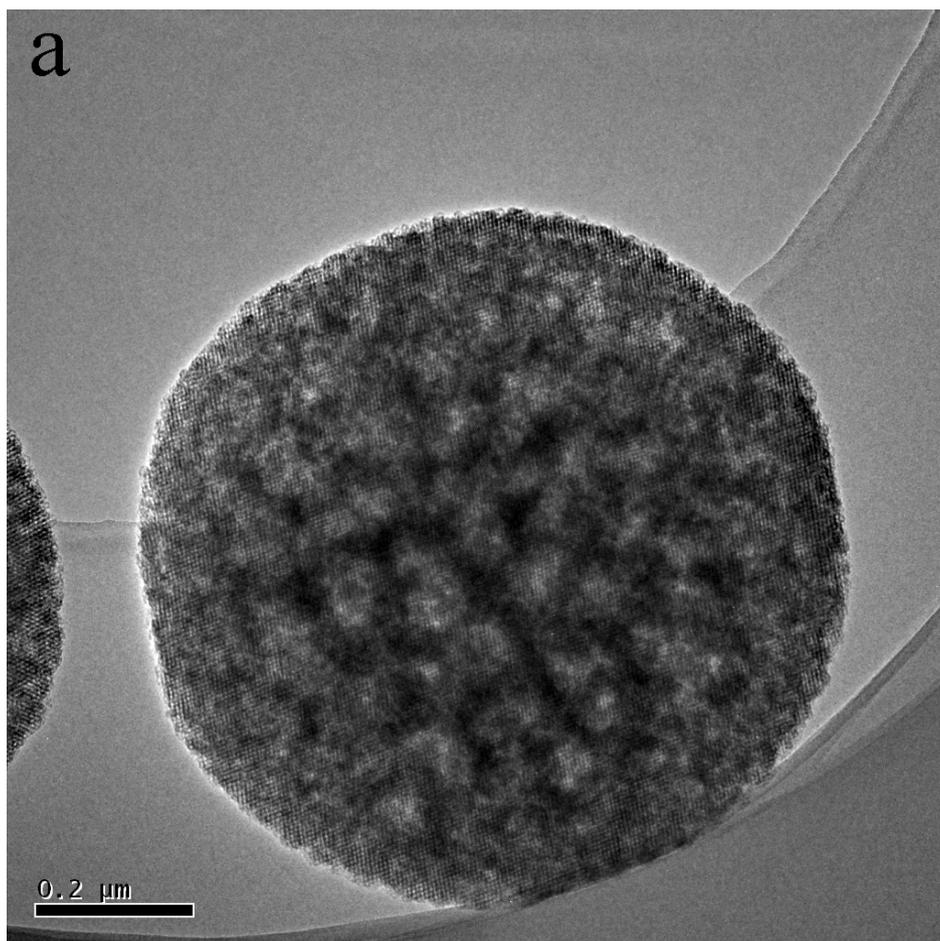


Fig. S3 TEM image (a) and its corresponding EDX pattern (b) of the calcined THMS-15.

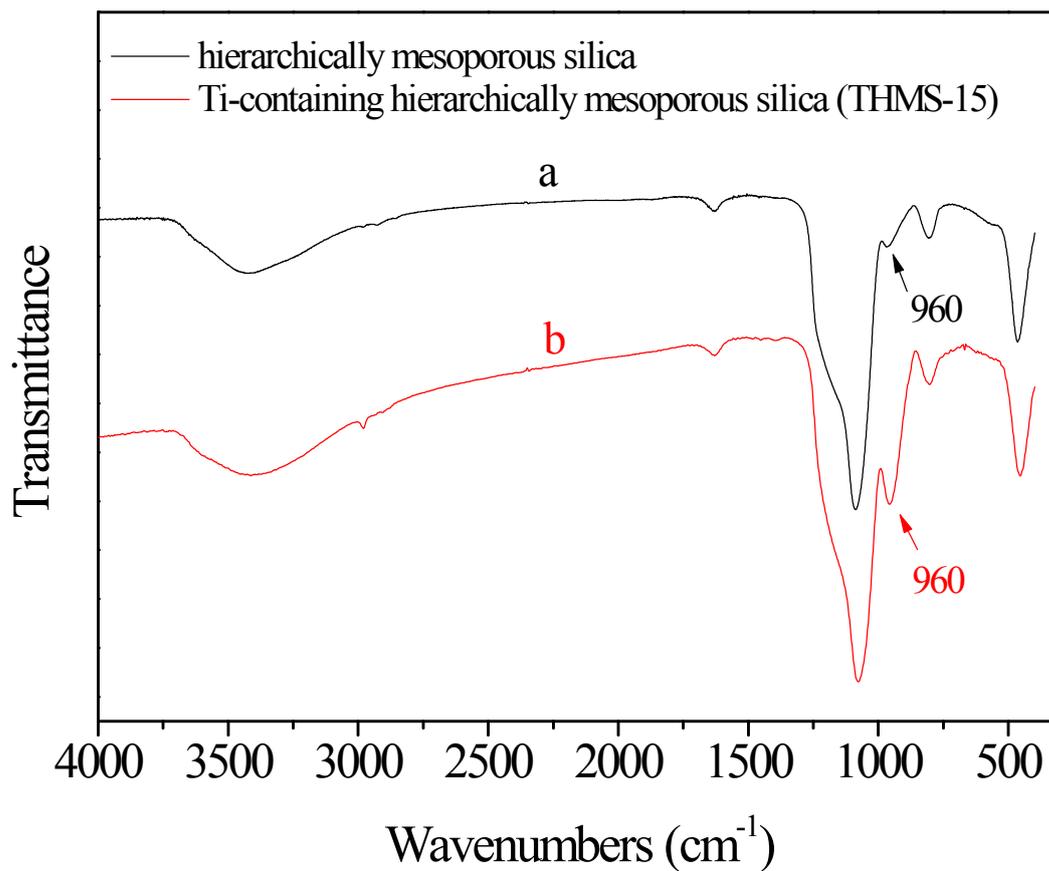


Fig. S4 FT-IR spectra of the calcined samples: (a) hierarchically mesoporous silica (pure HMS), (b) THMS-15. The lines of FT-IR spectra were shifted upward for clarity.

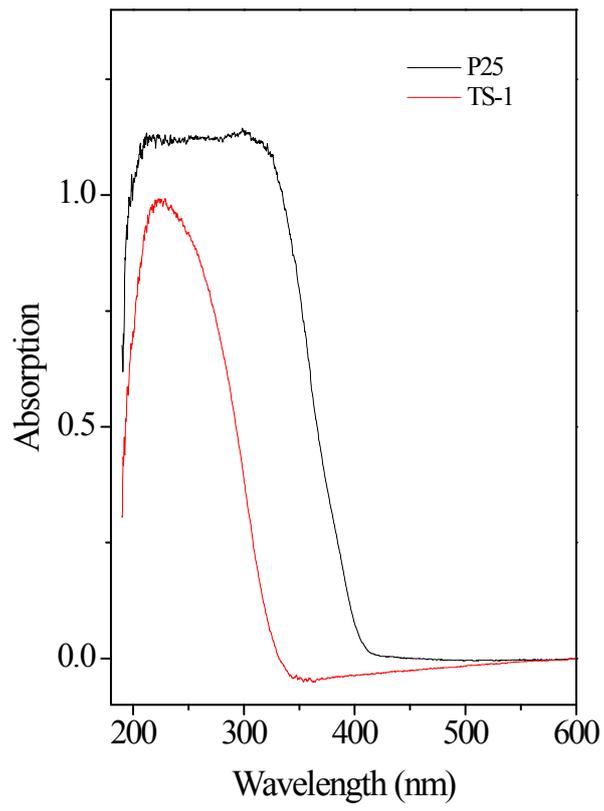


Fig. S5 UV-vis spectra of the calcined samples: P25 and TS-1.

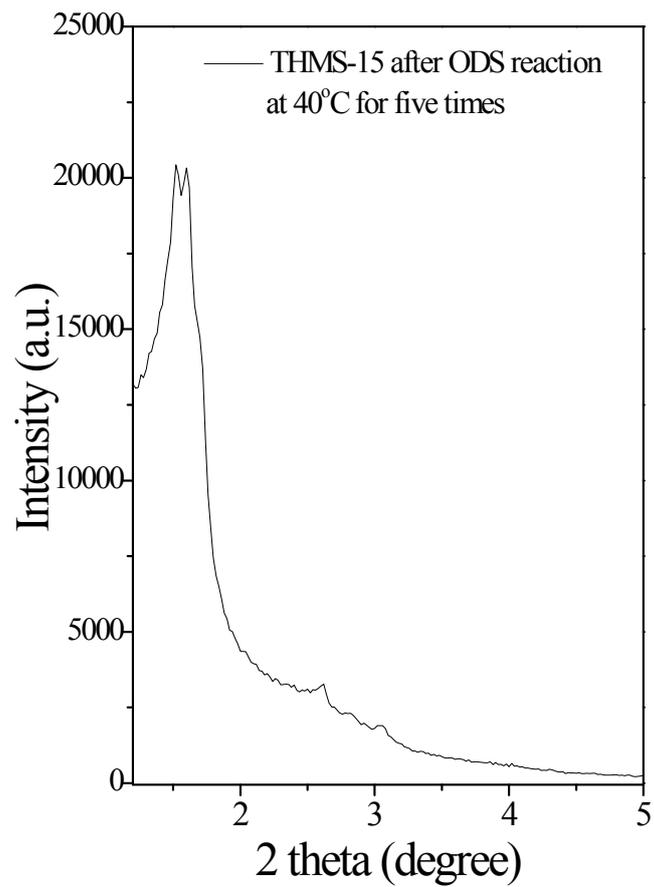


Fig. S6 XRD pattern of THMS-15 after ODS reaction at 40 °C for five runs

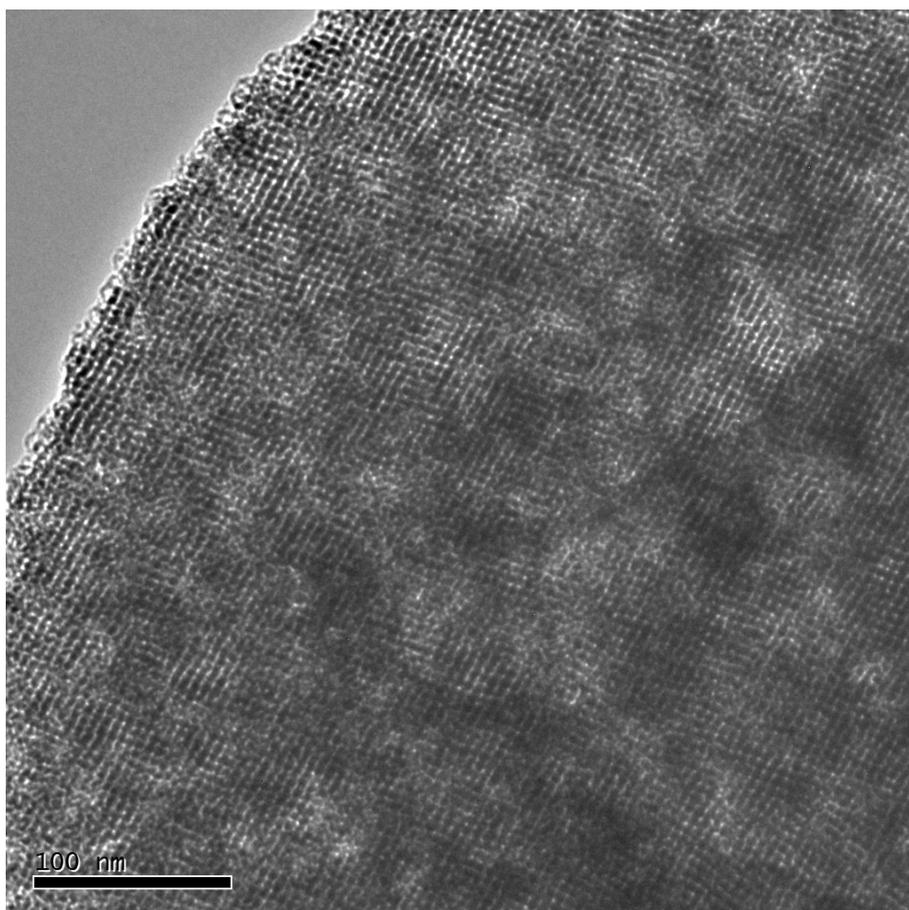


Fig. S7 HRTEM of THMS-15 after ODS reaction at 40 °C after five runs.