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

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Hierarchically porous Ti-SBA-2 with high framework Ti content (up to 5 wt%) was firstly synthesized by employing organic mesomorphous complexes of cationic surfactant (CTAB) and anionic polyelectrolyte (PAA) as template. The material exhibited excellent performance in oxidative desulfurization of diesel fuel at low temperature (40 °C or 25 °C) due to the unique hierarchically porous structure and high framework Ti content.

Ultra-deep desulfurization of diesel is a matter of major focus not only for effectively controlling the environmental pollution caused by the S-content in fuel oils, but also for fuel cell applications.[1] The traditional industrial process is hydrodesulfurization (HDS), which is effective for non-thiophenic S-compounds, but less effective for the desulfurization of thiophene (Th), benzothiophene (BT), dibenzothiophene (DBT) and their derivatives,[2] which can be oxidized under mild reaction conditions.[3] Generally, oxidative desulfurization (ODS) combined with extraction or adsorption is considered to be one of the most promising processes to obtain ultra-low sulfur fuels.[3c,4]

Titanium-containing mesoporous materials have attracted considerable attention because of their excellent catalytic activity and selectivity in organic oxidation reactions in the presence of aqueous H_2O_2 or t-butyl hydroperoxide (TBHP), including epoxidation of alkenes and esters,[5] selective oxidation of 2,3,6-trimethylphenol (TMP),[6] and oxidative desulfurization (ODS) of diesel fuel.[1a,1b,3a] Chica et al synthesized well-designed Ti-MCM-41, which could fully oxidize sulfur compounds (such as DBT, 4,6-DMDBT) at 80 °C by using organic peroxide (e.g., TBHP) as oxidant.[1a] Cho et al performed the ODS reaction for refractory sulfur compounds by using Ti-grafted SBA-15 as catalyst at 80 °C.[3a] Chamack and his co-workers completely desulfurized model oil

within 80 min at 60 °C by using cesium salts of tungsten-substituted molybdophosphoric acid supported on platelet SBA-15 as catalyst. In industrial process, low temperature or even room temperature is more favourable for low energy consumption and easy operation. However, it remains still a challenge to develop effective heterogeneous catalysts for low temperature ODS reaction.

Though Titanium-containing mesoporous materials have been widely reported, it is still difficult to achieve high framework Ti content by common hydrothermal synthetic method. Corma et al synthesized Ti-MCM-41 with titanium ethoxide as Ti source,[5a] and the final TiO_2 content was 2.3 wt%, corresponding to Ti content of about 1.4 wt%. Trukhan and his co-workers reported that the well-organized Ti-MMM were effective catalysts for TMP oxidation.[6] The Ti-MMM catalyst actually was a mixture of microporous Ti-silicate and mesoporous MCM-41. Although the Ti content in Ti-MMM was up to 4.32 wt%, the experiment results indicated that the catalysts with titanium loading of 1.5~2.0 wt% exhibited the highest activity and selectivity. Ji et al successfully prepared Ti-incorporated SBA-1 with Ti content up to 2.5 wt% (Si/Ti = 30) under strongly acidic condition by hydrothermal synthetic method.[5] As far as we know, there is no report on the synthesis of Ti-containing ordered mesoporous materials with the framework Ti content more than 5 wt%.[5b,6b,8]

The catalytic performance is affected not only by the framework Ti content but also by the accessibility of the active sites in titanium-containing silicate materials.[5c,9] Three-dimensional interconnected pore structures are generally expected to be superior to 2-D hexagonal structured materials (with one dimensional channels), especially in reactions involved bulky molecules. Mesoporous silica SBA-2 exhibits hexagonal close-packed (hcp) array (space group *P6₃/mmc*) of spherical cavities connected by cylindrical channels.[10] Such well interconnected pore structure makes SBA-2 of interest for applications in adsorption and catalysis.[11] Hierarchically porous structured mesoporous materials are more favourable for the accessibility of the active sites as well as the diffusion of reactants and products.[12] Though there are several reports focused on the preparation of meso-macroporous titania-silica materials, the mesoporous structure of the obtained

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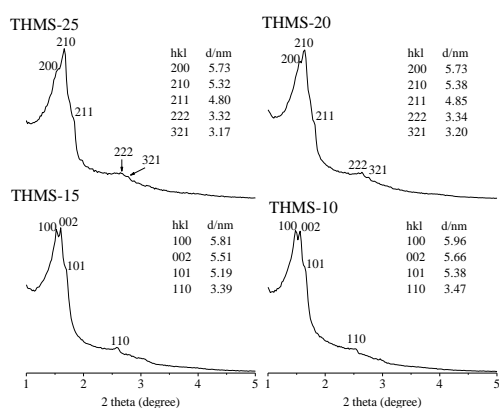
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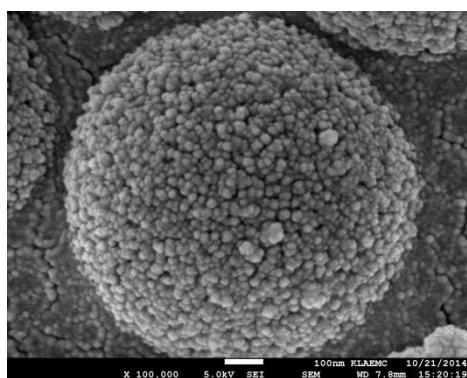
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materials were either disordered or in 2-D hexagonal structure.[5c,12d,12e].

Herein, we successfully synthesized Ti-containing hierarchically mesoporous silica (THMS) single crystals by using cationic surfactant CTAB and anionic polyelectrolyte PAA as co-templates and $TiOSO_4$ as titanium source. The obtained Ti-containing silica materials have highly ordered 3-D cubic (*Pm-3n*) or 3-D hexagonal (*P6₃/mmc*) mesostruture, larger secondary mesoporores and high Ti content (up to 5 wt%) of framework Ti species. It is the first report of hierarchically mesoporous Ti-SBA-2 single crystals, which also exhibited excellent activities in ODS reaction at low temperature (40 °C or 25 °C).

Fig. 1 showed the small-angle XRD patterns of Ti-containing mesoporous silicas with different titanium content. The label was THMS-x, where x indicated the molar ratio of Si/Ti in the initial synthesis solution. The calcined samples THMS-25 and THMS-20 displayed five-well resolved diffraction peaks in the small-angle range, which were indexed to the (200), (210), (211), (222) and (321) characteristic diffractions of the cubic *Pm-3n* mesostructure (Fig. 3a, b). With increasing the content of titanium in silica, we could obtain Ti-containing mesoporous silica materials with 3-D hexagonal close-packed mesostructure (hcp) with *P6₃/mmc* symmetry, which displayed four character diffractions (100), (002), (101) and (110) (Fig. 1c, d). The unit cell parameters of the calcined THMS-15 were a = 6.71 nm, c = 11.02 nm, and the c/a ratio was 1.642, which was very close to the ideal c/a ratio (1.633) of the hexagonal close-packed structure.

SEM images (Fig. S1, ESI†) showed that all the calcined samples were generally nanospheres with diameter of 500~1000 nm. From the enlarged SEM image of the sample THMS-15 (Fig. 2), it could be seen that the surface of the nanosphere was not smooth and there were a variety of interstitial pores on the surface of the whole sphere.

TEM images of the calcined samples (Fig. 3) showed different contrast inside the nanospheres, implying the presence of interstitial pores (as was seen in SEM image and proved by nitrogen adsorption discussed below). What amazing was that the secondary mesopores did not destroy the ordered mesostructure and the whole particle was still a mesostructured single crystal. In the TEM images the orientation of the mesopores remained identical through the whole particle and the Fourier diffractograms were collected from the area of several hundreds of nanometers. The Si/Ti ratios of THMS materials detected by TEM-EDX measurement on different positions, and the values were consistent with the initial Si/Ti ratios of the precursors (Table S1, ESI†). The weight percent of titanium was 3.82% in THMS-20, 5.52% in THMS-15 in ICP analysis, which were consistent with the results detected by TEM-EDX measurements. EELS (electron energy loss spectroscopy) images (Fig. S2, ESI†) and the EDX pattern (Fig. S3, ESI†) of THMS-15 revealed the presence of Si, Ti and O elements in the ordered domains of the hierarchically porous nanospheres. Titanium element was uniformly distributed in the whole particle.
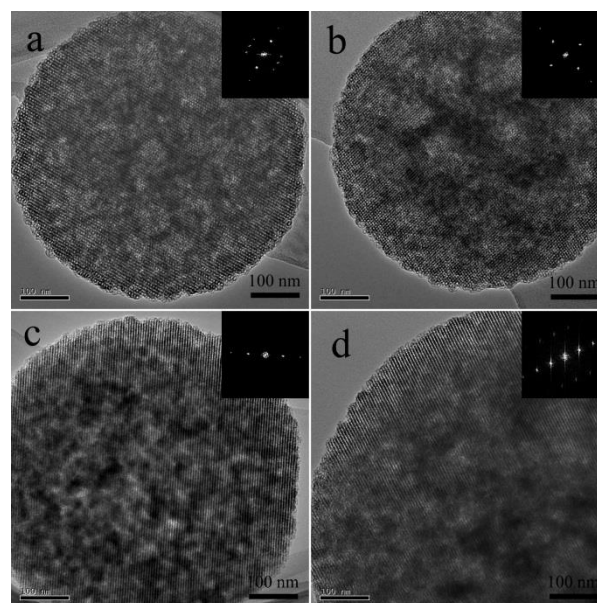

Fig. 1 Small-angle XRD patterns of the calcined samples with different Ti content.

**Fig. 2** High resolution SEM image of one nanosphere of calcined THMS-15.

Fig. 3 TEM images and their Fourier diffractograms (insets) of the calcined samples: (a) THMS-25, (b) THMS-20, (c) THMS-15, (d) THMS-10.
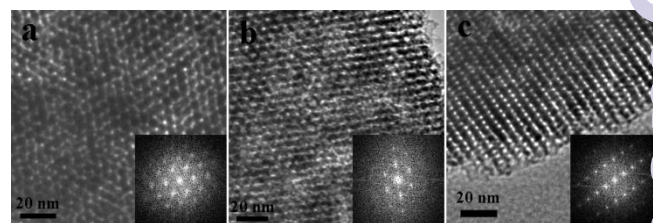
Fig. 4 TEM images and their Fourier diffractograms (insets) of the calcined THMS-15. The TEM images were recorded along different directions.

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HRTEM images of THMS-15 and the corresponding Fourier diffractograms (Fig. 4) were taken along different directions. As shown in Fig. 4a, a hexagonal close-packed layer was formed by the arrangement of uniform mesocages. In Fig. 4c, the mesopores kept well long-range order within the whole particle along the [100] direction in spite of the presence of interstitial mesopores.

It has been reported that the formation of mesostructure was affected by surfactants, drying, solvents/co-solvents, cations/anions, acidity and so on.[13] In our synthesis system, the samples THMS-25 and THMS-20 exhibited cubic *Pm-3n* mesostructure. With increasing the content of titanium, THMS-15 and THMS-10 tuned to 3-D hexagonal close-packed mesostructure (hcp) with *P6₃/mmc* symmetry. The synthesis conditions (such as surfactants, drying, solvents/co-solvents, cations/anions) of the obtained materials are all the same, except for the amount of peroxo titanic acid. Che et al. reported that in synthesis of mesoporous silica, different counteranion would result in change of the packing parameter of surfactant micelles to induce transformation of mesophases. Particularly, addition of H_2SO_4 led to formation of the 3D-hexagonal *P6₃/mmc* mesophase. [13a] Here in our case the peroxo titanic acid was synthesized with $TiOSO_4 \cdot nH_2O$, and with the increase of the Ti source in the synthesis, more sulfate anions were introduced, and the transformation of mesophase could occur due to the superabundant sulfate anions.
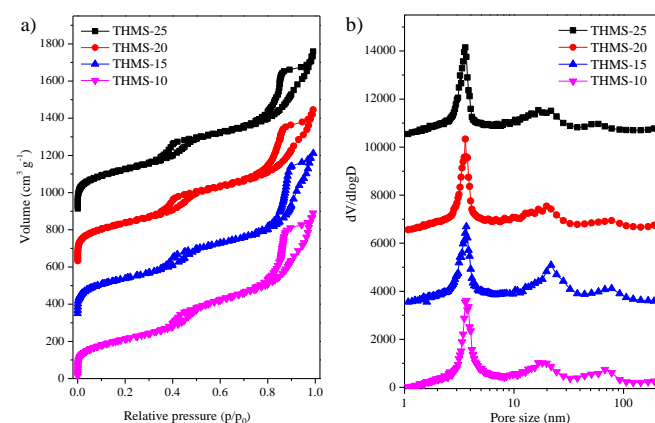
Fig. 5 (a) Nitrogen adsorption-desorption isotherms and (b) PSD curves of the calcined samples with different Ti content. The lines were shifted upward for clarity.

The nitrogen adsorption-desorption isotherms of the calcined Ti-containing hierarchically mesoporous silica materials were shown in Fig. 5. The calcined samples exhibited type IV isotherms with two distinct adsorption steps at the relative pressure of 0.35–0.60 and 0.80–0.98, respectively. The first step corresponded to the relatively narrow peak at about 3.6 nm in the pore size distribution curve, indicating the ordered mesopores (as were seen in the TEM images). The second adsorption step gave rise to two broad pore size distributions centring at ~20 nm and 50~100 nm. The mesopores centring at ~20 nm corresponded to the secondary interstitial mesopores as observed in the SEM and TEM images. The third broad pore size distribution could be due to the voids of the aggregated nanospheres and probably some larger secondary pores inside the single-crystal nanospheres.

For the samples THMS-25 and THMS-20, there was only one signal at 210 nm can be observed in the UV-vis spectra (Fig. 6a), corresponding to the presence of tetrahedral coordinated Ti species in silicates. With the increase of Ti content (for THMS-15 and -10), there appeared a small shoulder-signal at around 260 nm, corresponding to six-coordinated Ti species in the titanium-silicates. FT-IR spectra of the samples were shown in Fig. 6b, in which there appeared the band at 960 cm^{-1}. It has been reported that the band at ca. 960 cm^{-1} could be associated with Si-OH or framework Si-O- if the DRIFT spectra were recorded at the ambient condition. Indeed in the FT-IR spectrum of pure silica HMS sample there was a weak band ca. 960 cm^{-1}, however its intensity was much weaker in compared with that of THMS-15 (Fig. S4, ESI†), and the band at 960 cm^{-1} could mainly be assigned to framework Si-O-Ti.
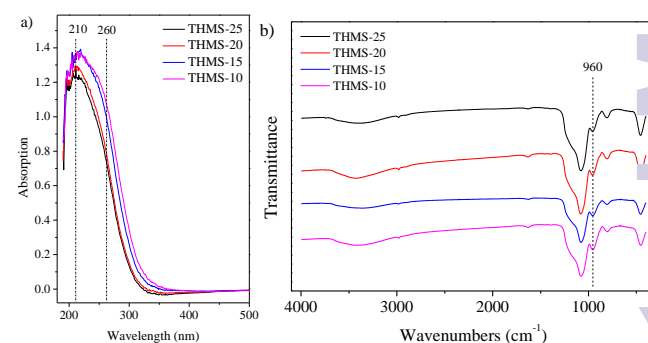

Fig. 6 (a) UV-vis spectra and (b) FT-IR spectra of the calcined samples. The lines of FT-IR spectra were shifted upward for clarity.

All above the characterizations well illustrated that with $TiOSO_4$ as titanium sources, we successfully synthesized Ti-containing hierarchically mesoporous silica materials. Moreover, hierarchically Ti-SBA-2 single crystals were reported for the first time, which had highly ordered 3-D hexagonal mesostruture, larger secondary mesopores and high content of framework Ti species.

The catalytic activity of the THMS samples was studied in oxidative desulfurization with DBT as model sulfur compound. From Fig. 7, we could see that the model fuel (containing 500 ppm DBT) was completely desulfurized within 30 min by using Ti-containing hierarchically mesoporous silica materials as catalysts at 40 °C. Without the addition of TBHP no conversion was detected, and this indicated that the desulfurization was due to catalytic oxidation instead of adsorption. With THMS-15 as catalyst, DBT could be completely oxidized within 20 min at 40 °C, and the initial TOF value of THMS-15 was 48.6 h^{-1} based on the conversion at 2 min reaction time. Even at 25 °C, oxidative desulfurization could be completely achieved within 80 min, and this is of great significance for the industrialization of oxidative desulfurization.

Oxidative desulfurization reactions with commercial P25 and TS-1 (Si/Ti ratio 26) as catalysts were carried out for comparison. The UV-vis spectra of TS-1 and P25 were shown in Fig. S5 (see ESI†). Commercial P25 exhibited no activity in oxidative of DBT. The micropore in TS-1 could be too small for diffusion of DBT, and thus exhibited no oxidative activity either, similar with the result in literature.[3e]
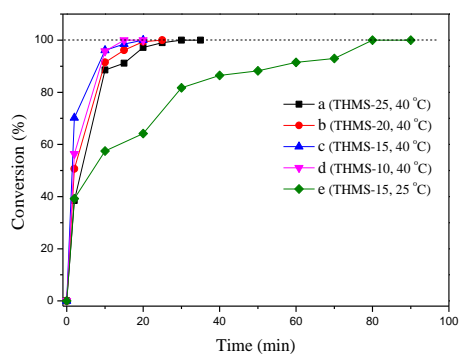
Fig. 7 The reaction of oxidative desulfurization (500 ppm DBT) using Ti-containing mesoporous silica materials as catalysts.
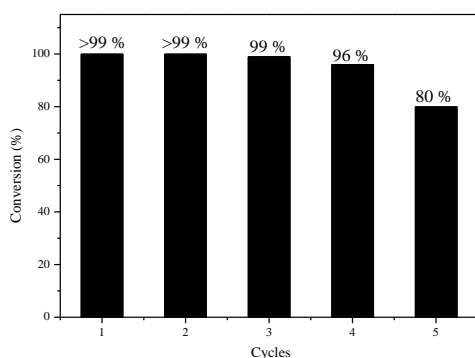
Fig. 8 The conversion of DBT at 20 min of reaction time with THMS-15 as catalyst in recycled runs (reaction temperature 40 ^{o}C).

In order to characterize the durability of the THMS materials, the recycled use of catalyst were carried out. The conversions of DBT at 20 min in different recycle runs were shown in Fig 8. Both XRD pattern (Fig. S6, ESI†) and HRTEM image (Fig. S7, ESI†) of THMS-15 after ODS reaction at 40 ^{o}C for five runs indicated that the mesostructure remained well. This is reasonable because the reaction condition is very mild. The Si/Ti ratio detected by TEM-EDX measurement of was about 14.9, indicating almost no leaching of titanium during the reaction. The reason of deactivation could be due to the adsorption of the oxidation product, which could cover some active centers of the catalyst. The deactivated THMS-15 was regenerated by ethanol extraction (see ESI†) and re-used as catalyst. After 20 min of reaction the conversion of DBT was 98%, and this indicates that the catalytic activity can be greatly recovered by ethanol extraction of the adsorbed oxidation product.

In summary, hierarchically mesoporous Ti-SBA-2 with high framework Ti content was successfully synthesized by using TiOSO$_4$ as titanium sources. The Ti-SBA-2 nanospheres were mesostructured single-crystals, with both ordered mesopores and larger secondary mesopores. Ti-SBA-2 exhibited excellent oxidative activity at low temperature (40 ^{o}C or 25 ^{o}C). The sources of titanium, the synthesized procedure and the ODS reaction temperature are all favorable for the industrial process. The obtained catalyst has great significance for ultra-deep oxidative desulfurization of diesel fuel.

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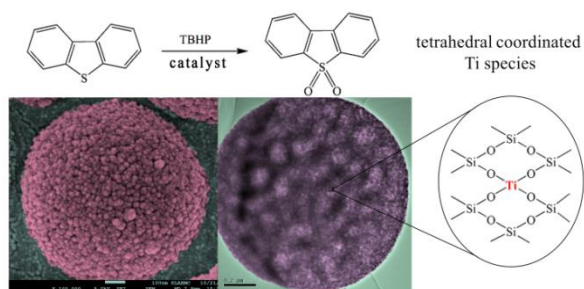
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