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Defect-less, layered organo-titanosilicate with superhydrophobicity and its catalytic activity in room-temperature olefin epoxidation[†]

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A new type of defect-less, layered organo-titanosilicate is synthesized using a simple, template-free, evaporation-induced self-assembly process. The obtained layered material has super-hydrophobicity and exhibits promising catalytic activity in the epoxidation of olefins using $30\%~H_2O_2$ aqueous solution as oxidant at room temperature.

Layered organic–inorganic hybrid materials have attracted much attention because of their emerging applications in ion exchange, adsorption and catalysis.^{1,2} These novel materials provide an ordered array of organic moieties with a stable and robust inorganic matrix. Tailoring of the organic components and inorganic matrix is very important to optimize their performance in a particular application. Many research efforts have focussed on the modification of these layered nanocomposites by altering the organic groups or inserting another sheet of inorganic cations (*e.g.* Ca, Mg, Sn, Al)^{2,3} into the organosilicate layers. However, the partial substitution of silicon atoms with other functional metal cations such as Ti⁴⁺ has been rarely reported.

The unique reduction/oxidation properties of titaniumcontaining silica-based materials (TS) make them particularly attractive for heterogeneous catalysis in selective oxidation.4-8 One of the most important findings in this field is that the catalytic activity is not only related to well-dispersed isolated tetrahedral Ti(IV) but also to the location of Ti in hydrophobic/ hydrophilic channels or cavities in the structure.9,10 It has been proven that hydrophobicity can prevent poisoning of the active site by water as well as unproductive decomposition of H₂O₂ and then leads to a high catalytic performance.11 Two main strategies have been developed to synthesize hydrophobic TS materials via: (1) grafting hydrophobic organic groups onto the surface;^{12,13} (2) directly incorporating them into the frameworks.^{9,14} However, the restricted incorporation of organic content and large portion of uncondensed silanol groups resulted in a limited enhancement of hydrophobicity.15-17 To the best of our knowledge,

a superhydrophobic TS material has not been successfully prepared.

Here, we report a defect-less, layered organo-titanosilicate (denoted as LOTS) with covalently linked phenyl groups through a simple and template-free synthetic route. Comparing with other TS catalysts, LOTS displays superhydrophobicity, and exhibits superior catalytic activity in epoxidation of olefins using 30% H₂O₂ as oxidant at room temperature.

LOTS is synthesized *via* a facile one-step method as illustrated in Fig. 1a. In a typical synthesis, 10 mmol phenyltrimethoxysilane (PTMS) and 0.7 mmol titanium *n*-butoxide (TBOT) were mixed in a acidic ethanol solution with a PTMS : TBOT : HCl : HAc : EtOH : H₂O molar ratio of 1.0 : 0.07 : 1.2 : 4.0 : 53 : 4.1. The mixture was stirred vigorously for 2 h at room temperature. A transparent viscous liquid was formed after the ethanol solvent was completely evaporated. The liquid sample was further aged at elevated temperature to ensure full condensation of titanosilicate frameworks. The final LOTS sample is obtained in the form of a solid powder after grinding.

The layered structure of the LOTS materials is verified by a complementary combination of X-ray diffraction (XRD) and transmission electron microscopy (TEM) analysis. The XRD pattern of LOTS displays two distinct peaks at $2\theta = 6.72$, 19.39° corresponding to (001) and (020)/(110) reflections, which are characteristic for layered inorganic–organic nanocomposites



Fig. 1 (a) Scheme of synthetic procedure for LOTS, (b) TEM image (XRD pattern as inset) and (c) HRTEM image of LOTS aged at 250 °C.

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(Fig. 1b, inset). The sharp diffraction peak at $2\theta = 6.72^{\circ}$ ($d_{001} = 1.3$ nm) can be attributed to a bilayer structure with a linear arrangement of two phenyl groups. The interlayer spacing *d* of LOTS is about 1.3 nm from TEM measurement (Fig. 1b), in good agreement with XRD characterization. This value is much larger than that of a layered organosilicate containing covalently linked phenylene groups (0.76 nm) and is similar to that with biphenylene groups (1.19 nm),¹⁸ suggesting the existence of a bilayer structural motif of the phenyl groups in LOTS.

The intense and broad peak centred at $2\theta = 19.39^{\circ}$ (d = 0.46 nm) is assigned to the uniform spacing between phenyl groups (in-plane), which is consistent with the spacing of alkyl chains (d = 0.47 nm) of the *n*-alkyltrialkoxysilane monolayer as revealed by grazing incidence X-ray diffraction.^{3,19} Molecular structure simulation also suggested that the spacing of covalently linked phenylene in an ordered mesoporous benzene-silica hybrid is about 0.44 nm.²⁰ Here, we first observed the spacing between phenyl groups of LOTS by HRTEM analysis. As shown in Fig. 1c, many lattice fringes with a uniform spacing of 0.46 nm were observed, which directly confirmed the existence of molecular-scale periodicity within the titano-silicate sheets.

The covalently linked phenyl groups of LOTS were confirmed by solid-state ²⁹Si, ¹³C MAS NMR spectra and FTIR spectroscopy. ²⁹Si MAS NMR for LOTS aged at 250 °C exhibits a strong peak around -78.5 ppm and a weak peak around at -72.2 ppm, which are assigned to T³ [RSi(OSi)₃] and T² [RSi(OH)(OSi)₂], respectively.²¹ It is noted that the proportion of T³ is >90% (Fig. 2a), which is much higher than in previous reports (40–65%) for ordered mesoporous organosilica and layered hybrid silica,^{21,22} suggesting nearly completely condensed organo-titanosilicate frameworks have been formed. The ¹³C NMR spectrum also confirms the presence of phenyl groups in LOTS (Fig. 2b). FTIR spectroscopy not only indicates the characteristic peaks of phenyl groups (1431, 1384, 738, 696 cm⁻¹), but also confirms that the Si–C bond (1134 cm⁻¹)²³ of phenyl organosilane remained intact during the synthesis and aging process (Fig. 2c).

The homogeneous incorporation of titanium into the silica sheets is revealed by energy dispersive X-ray (EDX) element



Fig. 2 (a) Solid-state 29 Si, (b) 13 C MAS NMR spectra and (c) FTIR spectrum for LOTS aged at 250 °C; (d) TG analysis and CA (insets) for LOTS aged at 250 and 500 °C.

mapping and FTIR spectra. A detailed EDX element mapping measurement of LOTS at a resolution of ~ 10 nm shows the uniform X-ray intensity of Ti, Si and C signals throughout the particles (Fig. S1, ESI⁺), revealing that Ti atoms are homogeneously distributed within the organo-silicate frameworks. A vibration band at \sim 960–970 cm⁻¹ in FTIR is the characteristic peak of Ti-O-Si for Ti containing silica zeolites²⁴ and related materials.²⁵ For LOTS samples, there is a new absorption band at 926 cm⁻¹ (Fig. 2c, Fig. S2, ESI⁺), which is much lower in intensity than that at \sim 960–970 cm⁻¹ for Ti-containing zeolites and related materials, due to the organic groups covalently attached to silicon, and can be assigned to the Ti-O-Si heterolinkages.^{26,27} The XPS spectrum of LOTS is shown in Fig. S3 (ESI^{\ddagger}). The binding energy for Ti $2p_{3/2}$ of the sample is centered at 459.5 eV, well above the typical value of 458.5 eV for anatase TiO_{2} ,^{27,28} is also taken as a proof of Ti incorporation into the organo-silica framework in a tetrahedral environment.

LOTS has been confirmed to be superhydrophobic owing to the nature of large portion of incorporated organic moieties and highly condensed organo-titanosilicate frameworks. Contact angle (CA) measurement is usually used to characterize the hydrophobic/hydrophilic properties of materials.²⁹ The CA of LOTS aged at 250 °C is $153 \pm 0.5^{\circ}$ (Fig. 2d), suggesting that a superhydrophobic material has been obtained. The materials changed from superhydrophobic to hydrophilic after calcination at 500 °C due to the loss of phenyl groups as confirmed by thermogravimetric analysis (TGA, Fig. 2d). A ~ 51% weight loss occurs in the temperature range of 300–700 °C corresponding to the phenyl functional groups of LOTS. This value is close to the starting organic species concentration in as-synthesized LOTS (51.3%), indicating that the phenyl groups can be fully retained after aging at 250 °C.

Epoxidation of olefins is one of fundamental reactions for organic chemistry and is of great importance for laboratory and commercial processes.^{30,31} In this work, we investigated the catalytic performance of LOTS in the epoxidation of cyclohexene and compared it with microporous titanosilicate TS-1 and mesoporous titanosilicate (m-TS). The detailed characterizations of TS-1 and m-TS are shown in Fig. S4 and S5, respectively (ESI⁺). The catalytic reaction was performed at room temperature by using 30% H₂O₂ aqueous solution as oxidant and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) as solvent. The results of catalytic tests are shown in Fig. 3a and b and Table S1 (ESI⁺). LOTS aged at 250 °C exhibits an exceptionally high activity as compared to other TS catalysts. The conversion of cyclohexene reaches 98.8% in 2 h with a selectivity of 98% to the epoxide at room temperature. The turnover number (TON) for LOTS is about 5-10 times as high as that of m-TS (calcined at 450 °C) or commercial TS-1, indicating that LOTS showed the highest activity among these titanosilicates. The LOTS material can be easily recycled and exhibits an almost constant catalytic performance. After four repeated reaction runs with regeneration, the cyclohexene conversion slightly decreased from 98.8 to 93.0%, showing that the prepared organotitanosilicate is a relatively stable catalyst (Table S1 and Fig. S6, ESI[†]). It is noteworthy that the surface area of LOTS is only 6.8 m² g⁻¹, which is 50–60 fold less than that of m-TS $(423 \text{ m}^2 \text{ g}^{-1})$ or TS-1 $(339 \text{ m}^2 \text{ g}^{-1})$. This implies that the genuine activity of accessible Ti⁴⁺ sites of LOTS may be two



Fig. 3 (a) Catalytic activity of LOTS (aged at 250 °C) in epoxidation of cyclohexene; (b) yield of epoxycyclohexane *vs.* reaction time using m-TS, TS-1 and LOTS as catalysts.

orders of magnitude higher than those of other TS catalysts. LOTS also shows good catalytic performance in methanol or acetonitrile and its catalytic activity can compete with those of layered alkoxysilylated Ti-containing silicates³² under the same reaction condition despite of its much lower surface area value (Table S2, ESI†). Besides, the better catalytic activity for LOTS in methanol than that in acetonitrile further confirmed that LOTS is hydrophobic.^{33–35} The exceptional catalytic activity is probably attributable to the superhydrophobicity resulting from high phenyl group content (Si : phenyl = 1 : 1) and the fully condensed titanosilicate frameworks.

In summary, we have described a green, simple and templatefree synthetic route for the synthesis of defect-less, organic-inserted layered titanosilicates. The layered hybrid materials provide a superhydrophobic surface and well-dispersed titanium species. They have high thermal stability and display outstanding catalytic activity in the epoxidation of olefins at room temperature. The materials are expected to provide new opportunities for applying superhydrophobic materials in industrial catalytic applications.

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