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Ordered mesoporous titanosilicates with catalytically stable and active four-coordinated titanium sites†

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The stable ordered mesoporous titanosilicate (Ti-JLU-20) has been successfully synthesized from an assembly of mixed surfactants (fluorocarbon and triblock copolymer surfactants) with preformed titanosilicate zeolite precursors at high temperature (180–220 °C), and catalytic tests show that Ti-JLU-20 has highly stable and active four-coordinated titanium sites in oxidations.

Microporous crystals such as TS-1 show remarkable catalytic properties in a series of oxidations by H_2O_2.[1,2] However, one disadvantage of these titanosilicate catalysts is that their pores are too small for access by bulky reactants in the fine chemical and pharmaceutical industries. Recent progress in this area has been the incorporation of titanium ions into the framework sites of mesoporous materials and the grafting of a titanocene complex onto mesoporous silica.[3–5] These ordered mesoporous titanosilicates have pore diameters of 2–8 nm and exhibit catalytic properties for the oxidation of bulky reactants under mild conditions, but unfortunately, when compared with TS-1, the catalytic activity is relatively low, *e.g.* of Ti-MCM-41, which can be assigned to the difference in the titanium coordination environment (amorphous nature of the mesoporous walls).[6]

Recently, we have reported that the assembly of preformed titanosilicate zeolite precursors with triblock copolymers can lead to an ordered mesoporous titanosilicate (MTS-9), which is hydrothermally stable. Catalytic tests show that MTS-9 is very active for the oxidation of small molecules such as phenol and styrene and also of the bulky molecule trimethylphenol.[7] However, calcination of MTS-9 leads to significant reduction of catalytic activities towards both small and bulky molecules, which is due to the relatively low stability of catalytically active four-coordinated titanium sites in MTS-9, compared with that of TS-1.[8] Therefore, ordered mesoporous titanosilicates with both active and stable four-coordinated titanium species are very desirable.

The relatively low stability of titanium species in catalysis may be related to imperfectly condensed mesoporous walls. Possibly, the level of condensation for mesoporous walls will be enhanced by increasing the crystallization temperature.[9,10] More recently, we have reported that high-temperature synthesis (180–220 °C) of mesoporous silica materials templated by a fluorocarbon and triblock copolymer mixture, results in more condensed mesoporous walls, leading to excellent thermal and hydrothermal stability for these materials.[10] We demonstrate here that highly ordered mesoporous titanosilicates with catalytically both active and stable four-coordinated Ti species, designated Ti-JLU-20, are successfully assembled from preformed TS-1 nanoclusters at high temperature (180–220 °C).

In a typical synthesis, the preformed TS-1 nanoclusters were prepared from $Ti(OC_4H_9)_4$, TEOS, TPAOH, C_2H_5OH and H_2O, with molar ratio of $TiO_2/SiO_2/TPAOH/C_2H_5OH/H_2O$ at 1.0/30/8/120/1500. Ti-JLU-20 was synthesized at 180 °C for 40 h by assembly of preformed TS-1 nanoclusters with a fluorocarbon (FC-4)/copolymer (P123) mixture (FC-4/P123 = 3/1, wt%).

The small-angle X-ray diffraction pattern for a typical as-synthesized Ti-JLU-20 (Fig. 1(A)) shows well-resolved peaks that can be indexed as (100), (110) and (200) reflections associated with the hexagonal symmetry. Notably, after calcination in air at 550 °C for 5 h (Fig. 1(B)) or treatment in boiling water for 200 h (Fig. 1(C)), Ti-JLU-20 still exhibits its characteristic peaks, confirming that mesostructure of Ti-JLU-20 is thermally and hydrothermally stable, compared with JLU-20 (Fig. 1(F)),[10] MTS-9 (Fig. 1(H))[7] and Ti-SBA-15 (Fig. 1(J)).[5] Furthermore, the TEM image of Ti-JLU-20 exhibits ordered hexagonal arrays of mesopores with uniform pore size (Fig. 2). The corresponding ED

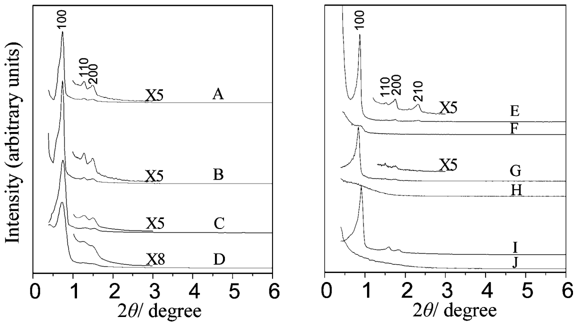

Fig. 1 XRD patterns of as-synthesized Ti-JLU-20 (A), calcined Ti-JLU-20 (B), Ti-JLU-20 treated in boiling water for 200 h (C), 300 h (D), calcined JLU-20 (E), JLU-20 treated in boiling water for 120 h (F), calcined MTS-9 (G), MTS-9 treated in boiling water for 200 h (H), calcined Ti-SBA-15 (I), and Ti-SBA-15 treated in boiling water for 100 h (J). The XRD patterns were obtained with a Siemens D5005 diffractometer using Cu-Kα radiation.

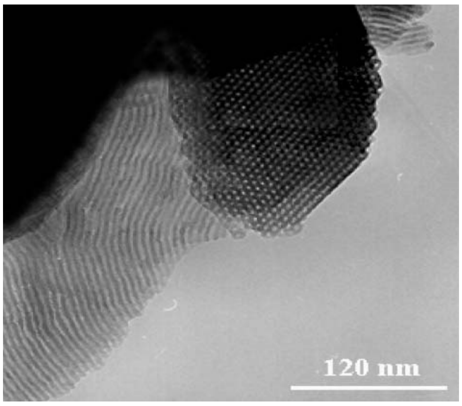

Fig. 2 TEM images of calcined Ti-JLU-20 taken in the (100) and (110) directions. TEM image of calcined Ti-JLU-20 taken in the [100] and [110] direction. The TEM image was taken using a JEOL JEM-3010 instrument (operated at 300 kV).

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† Electronic supplementary information (ESI) available: Fig. S1: N_2 isotherms and pore size distributions. Fig. S2: IR spectra. Fig. S3: ^{29}Si NMR spectrum. Table S1: Properties of the samples before and after hydrothermal treatment. See http://www.rsc.org/suppdata/cc/b4/b410305j/

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Table 1 Catalytic activities of MTS-9, Ti-JLU-20 and Ti-MCM-41 for the hydroxylation of phenol and 2,3,6-trimethylphenol by H_2O_2

Sample	Conv. (%)	TOF/h^{-1}	Si/Ti ratio	Product selectivity (%)		
				P1	P2	P3
MTS-9^b	26.3	6.8	40	59.5	39.8	0.7
MTS-9^b	14.5	4.0	41	53.2	45.7	1.3
MTS-9^c	18.8	7.4	40	66.7	21.1	12.2
Ti-JLU-20^b	20.8	10.6	79	60.5	38.7	0.8
Ti-JLU-20^b	20.1	9.7	75	57.5	40.8	1.7
Ti-JLU-20^c	16.5	12.8	79	58.5	40.5	1.0
Ti-MCM-41^b	2.5	0.5	31	60.1	38.0	1.9
Ti-MCM-41^c	4.1	1.4	31	25.5	69.8	4.6

^{a} Sample was washed with H_2O and ethanol. ^{b} phenol/H_2O_2 = 3/1. The products are catechol (P1), hydroquinone (P2), and benzoquinone (P3). ^{c} Trimethylphenol/H_2O_2 = 3/1. The products are trimethylhydroquinone (P1), trimethylbenzoquinone (P2), others (P3). ^{d} Samples were calcined at 550 °C for 5 h. ^{e} Samples were treated in boiling water for 100 h.

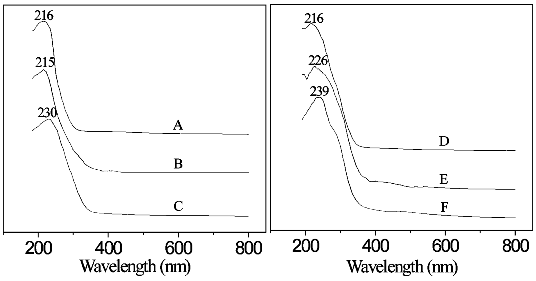

Fig. 3 UV-vis spectra of as-synthesized Ti-JLU-20 (A), as-synthesized MTS-9 (B), as-synthesized Ti-SBA-15 (C), calcined Ti-JLU-20 (D), calcined MTS-9 (E) and calcined Ti-SBA-15 (F). UV-vis spectra were measured with a PE Lambda 20 spectrometer and $BaSO_4$ was the internal standard sample.

pattern also shows reflections consistent with hexagonal symmetry. The adsorption isotherm of Ti-JLU-20 (Fig. S1 and Table S1, ESI†) shows a typical adsorption curve of type-IV, giving BET surface area and pore size of 398 m^2 g^{-1} and 7.8 nm, respectively.

Table 1 presents catalytic activities of MTS-9, Ti-JLU-20 and Ti-MCM-41 for hydroxylation of phenol and 2,3,6-trimethylphenol by H_2O_2. Obviously, both MTS-9 and Ti-JLU-20 are very active for the catalytic conversion of phenol and trimethylphenol. However, the active sites of Ti species in Ti-JLU-20 are much more stable than those in MTS-9 during calcination and hydrothermal treatments. For example, the calcined MTS-9 exhibits activity at 14.5% in phenol hydroxylation whereas calcined Ti-JLU-20 gives conversion at 20.8%. Apparently, stable and active Ti species in ordered mesoporous titanosilicates are very important in recycling of titanosilicate catalysts in oxidations.

The catalytically stable and active four-coordinated titanium sites in Ti-JLU-20 have been also confirmed by UV-vis spectroscopy. The UV-vis spectra of as-synthesized Ti-JLU-20 and as-synthesized MTS-9 have adsorption bands at near 215 nm, indicating four-coordinated Ti species in Ti-JLU-20 and MTS-9 (Fig. 3(A) and (B)), in good agreement with that in TS-1. In contrast, Ti-SBA-15 shows a peak at near 230 nm, which is been assigned to titanium species with a coordination number between four and six.[8] Interestingly, the calcined Ti-JLU-20 still shows a band at near 215 nm (Fig. 3(D)), demonstrating retention of the four-coordinated Ti species. In contrast, the calcined MTS-9 exhibits a band at 226 nm (Fig. 3(E)), indicating that the Ti species in MTS-9 are partially transformed.[8]

We attribute the high catalytic activities of Ti-JLU-20 as due to the TS-1-like environment of the Ti species in Ti-JLU-20. One evidence for this is provided by IR spectroscopy of Ti-JLU-20 which shows a band at 557 cm^{-1}, (Fig. S2, ESI†) which is characteristic of 5-ring subunits in TS-1 zeolite.[1] Additionally, Ti-JLU-20 exhibits a UV-vis band at 215 nm, which is almost the same as that of TS-1. Similar phenomena have been observed in characterization of MTS-9.[7] Possibly, during the preparation of Ti-JLU-20, the titanium sites are fixed in the framework of the TS-1 nanoclusters in the first step and are introduced into the mesoporous structure when the nanoclusters self-assemble with the template in the second step.

The high stability of both the mesostructure and four-coordinated titanium species in Ti-JLU-20 is reasonably attributed to the high degree of condensation of the mesoporous walls. This is confirmed by ^{29}Si NMR (Fig. S3, ESI†). As-synthesized Ti-JLU-20 (Si/Ti = 59) shows a large peak of fully condensed Q^4 silica units (−112 ppm, $Si(OSi)_4$) and a small contribution at −102 ppm (Q^3 species) assigned to both $Si(OSi)_3OH$ and $Si(OSi)_3OTi$, giving a very high Q^4/Q^3 ratio of 4.8, which is much higher than that of MTS-9 ($Q^4/(Q^3 + Q^2) = 1.9$) and Ti-SBA-15 ($Q^4/(Q^3 + Q^2) = 1.2$) with the same Si/Ti ratio.[10–12] Possibly, the high degree of silica condensation for mesoporous walls prevents the transformation of four- to five- or six-coordinated titanium species.[12]

In summary, catalytically stable and active ordered mesoporous titanosilicates are synthesized from the assembly of preformed titanosilicate precursors with a surfactant mixture at high temperature of 180–220 °C. More importantly, although thermally and hydrothermally mesostructured stability of mesoporous materials is enhanced significantly, the improved stability of catalytically active sites in mesoporous materials, in particular for titanium species in mesoporous titanosilicates, is reported rarely.

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