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## COMMUNICATION

## Construction of Unique Six-Coordinated Titanium Species with an Organic Amine Ligand in Titanosilicate and Their Unprecedented High Efficiency for Alkenes Epoxidation

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**A novel organic-inorganic layered titanosilicate consisting of Ti-containing MWW-type nanosheets and piperidine ligands was constructed and exhibited an unprecedented high catalytic activity and recyclability in the alkenes epoxidation.**

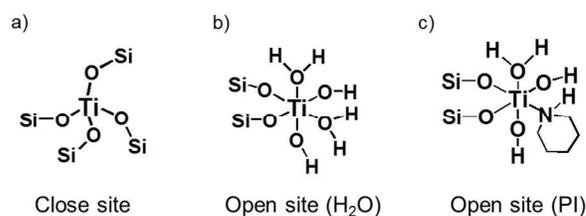
Zeolites are crystalline aluminosilicates with the Si and Al ions tetrahedrally coordinated by the oxygen bridges in the framework.<sup>1-3</sup> Titanosilicates, with the tetrahedral Ti ions isomorphously substituted for the Al or Si in zeolite framework, turn to be selective oxidation catalysts, which open the door for the revolution in clean synthesis.<sup>4</sup> Since the first discovered titanosilicate (well known as TS-1), capable of catalysing the oxidation of a number of organic compounds with H<sub>2</sub>O<sub>2</sub> oxidant, tremendous successes have been achieved in petrochemical industry.<sup>5</sup>

It is commonly acceptable that the isolated Ti ion is tetrahedrally located in the silicate lattice as a perfect “close” site, Ti(OSi)<sub>4</sub> (Fig. 1a), or as a defective “open” site, Ti(OSi)<sub>3</sub>(OH). In addition, the Ti ions in other coordinated states (usually six) are also observed in non-framework positions.<sup>6</sup> The Ti species in tetrahedral coordination are assumed to be the active sites for activating H<sub>2</sub>O<sub>2</sub>, forming the Ti-peroxo intermediates for catalysing the selective oxidations. However, previous researches indicate that the Ti sites with other coordination styles such as located near Si vacancies and in octahedral coordination could also be responsible for the high catalytic performances of titanosilicates.<sup>7-9</sup> These studies unravel the importance of coordination environment of Ti sites on the selective oxidation.

Hence, tuning the Ti coordination states of titanosilicates by chemical modification has attracted considerable scientific and technological interests.

Herein, we communicate the chemical construction of a novel organic-inorganic hybrid titanosilicate (Re-Ti-MWW-PI) with a two dimensional (2D) layered structure by structural rearrangement. Characterizations with UV-Raman, UV-Vis and XPS spectroscopies verified that it contained unusual six-coordinated Ti active species. The newly generated Ti species bearing an amine molecule as ligand exhibited an unprecedented high catalytic activity and recyclability in alkenes epoxidation. This specie never determined elsewhere could be responsible for the great enhancement for catalytic behaviour. Moreover, the presence of piperidine (PI) ligand suppressed the acidity of hydroxyl groups, which then enhanced the peroxide selectivity.

The 2D organic-inorganic hybrid Re-Ti-MWW-PI material was synthesized from Ti-MWW with the 3D structure by PI treatment.<sup>10</sup> The hydrothermal treatment with PI aqueous solution converted Ti-MWW into corresponding lamellar precursor (Re-Ti-MWW-PI), which was characteristic of layer-related [001] and [002] diffractions in the 2θ range of 3-7° (Fig. S1A, ESI†). It was converted reversibly into the MWW structure (Re-Ti-MWW-cal) by further calcination. These reversible struc-



**Fig. 1** Proposed titanium active sites: a) close site, b) open site (H<sub>2</sub>O), c) open site (PI).

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**Table 1** The catalytic activity of the epoxidation of alkenes with different molecular size over titanasilicates.<sup>a</sup>

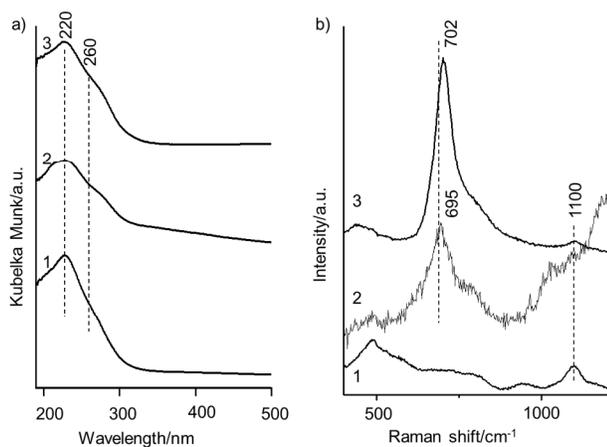
No.	Catalyst	Si/Ti	SA /m <sup>2</sup> g <sup>-1</sup>	Alkene epoxidation <sup>b</sup>							
				1-hexene		cyclopentene		cyclohexene		cycloheptene	
				conv. /%	TON	conv. /%	TON	conv. /%	TON	conv. /%	TON
1	Ti-MWW	49	536	48.8	293	11.9	71	1.3	8	2.5	15
2	Re-Ti-MWW-PI	51	61	92.8	680	96.8	710	6.9	51	2.2	16
3	Re-Ti-MWW-cal	51	557	60.3	384	12.9	82	5.6	36	3.5	22

<sup>a</sup> Reaction conditions: cat., 50 mg; alkene, 10 mmol; H<sub>2</sub>O<sub>2</sub> (30 wt.%), 10 mmol; CH<sub>3</sub>CN, 10 mL; temp., 333 K; time, 2 h. <sup>b</sup> TON in mol (mol Ti)<sup>-1</sup>. The oxide product selectivity was over 99 % for all the reactions, which is thus omitted for clarity.

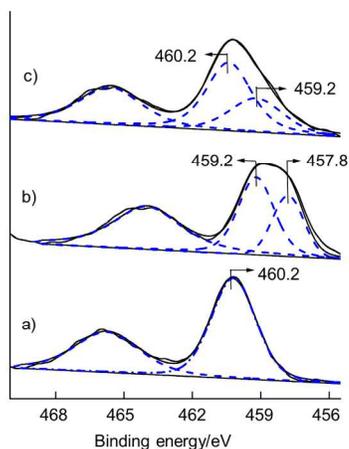
tural changes occurred as a result of PI insertion into interlayer spaces and interlayer condensation in turn (Fig. S1B, ESI<sup>†</sup>). This transformation was also evidenced by <sup>29</sup>Si MAS NMR spectra (Fig. S2, ESI<sup>†</sup>). Re-Ti-MWW-PI showed very similar resonances due to Q<sup>4</sup> sites but a much intensive resonance of Q<sup>3</sup> site (-94.5, -97.9 ppm) and an additional Q<sup>2</sup> site (-90.4 ppm), indicating more hydroxyl groups generated. After calcination, a portion of defect sites disappeared, and the resonance of Q<sup>3</sup> sites decreased obviously in intensity. The crystal morphology remained unchanged during the whole processes (Fig. S3, ESI<sup>†</sup>). Element analysis and <sup>13</sup>C MAS NMR spectra of Re-Ti-MWW-PI indicated that the PI molecules were incorporated and remained intact without decomposition (Table S1, Fig. S4, ESI<sup>†</sup>). Re-Ti-MWW-PI showed two stages of weight loss in TG curve. The weight loss above 573 K were attributed to the PI molecules in the intralayer sinusoidal 10-ring channels of MWW sheets (7.5 wt.%), whereas the loss below 573 K belonged to those PI molecules located between layers (7.4 wt.%) (Table S1<sup>†</sup>, Fig. S5<sup>†</sup>). The PI treatment affected negligibly the Ti amount but made Ti-MWW deboronated slightly (Table S1, ESI<sup>†</sup>). Re-Ti-MWW-PI possessed extremely low specific surface area (61 m<sup>2</sup> g<sup>-1</sup>) and micropore volume (0.001 cm<sup>3</sup> g<sup>-1</sup>) because of pore-blocking effect by PI molecules. A further calcination reopened the pores, making the textural properties of Re-Ti-MWW-cal comparable to those of Ti-MWW.

Firstly, we applied three catalysts (Ti-MWW, Re-Ti-MWW-PI, Re-Ti-MWW-cal) to the epoxidation of alkenes with different molecular dimensions. The epoxide selectivity reached 99 % for the reactions in an inert solvent of acetonitrile, and the presence of PI in Re-Ti-MWW-PI did not have a negative influence on the product selectivity. Re-Ti-MWW-PI showed a much higher conversion for the epoxidation of alkenes with small dimensions, such as 1-hexene and cyclopentene, in comparison to Ti-MWW (Table 1). The outstanding example is that the PI post-treatment enhanced the specific catalytic activity, turnover number (TON), by 10 times for cyclopentene epoxidation. The further calcined sample, Re-Ti-MWW-cal, was also more active than Ti-MWW, but much less active than Re-Ti-MWW-PI. The catalytic activity in the epoxidation of cycloalkenes (cyclohexene and cycloheptene) with bulky dimension decreased sharply. This is due to a serious steric constraint of zeolite pores, which made diffusion of the bulky substrate molecules difficult within the channels or even impossible into the channels.<sup>11</sup> Therefore, these reactions needing an open reaction space are considered to be catalyzed mainly by the Ti species within the side pockets on the crystal surface. As a result, the PI treatment gave rise to an extremely active catalyst for alkenes epoxidation. Considering the fact that the channels of Re-Ti-MWW-PI were heavily blocked by the PI molecules as mentioned above, the greatly improved catalytic activity observed for Re-Ti-MWW-PI is thus hardly ascribed to an easy molecular diffusion of its 2D layer structure. Moreover, Re-Ti-MWW-HMI catalyst containing hexamethylenimine (HMI) also exhibited efficient catalytic behaviour in alkenes epoxidation (Table S2, ESI<sup>†</sup>). Thus, it is of scientific interests to understand the role of organic molecules in the catalytic epoxidation.

Therefore, we focused our attention on the coordination environments of the Ti sites in three catalysts. Both the UV-Visible spectra of Re-Ti-MWW-PI and Re-Ti-MWW-cal showed a new broad absorbance band around 260 nm, while the band at 210 nm of Re-Ti-MWW-PI was somewhat weakened and its intensity recovered to certain extent after removal of PI molecules (Fig. 2a). In addition, the broad and weak absorbance band over 310 nm was due to the organic molecules. Generally, the 210 nm band is assigned to framework Ti species, while the 260 nm band is believed to be associated with multiple (five or six) coordinated Ti species.<sup>12</sup> Therefore, it could be deduced that the Ti species in Ti-MWW were mainly in tetrahedrally coordinated state and the PI treatment induced the



**Fig. 2** a) UV-Visible spectra and b) UV resonance Raman spectra excited at 266 nm of 1) Ti-MWW, 2) Re-Ti-MWW-PI, and 3) Re-Ti-MWW-cal.



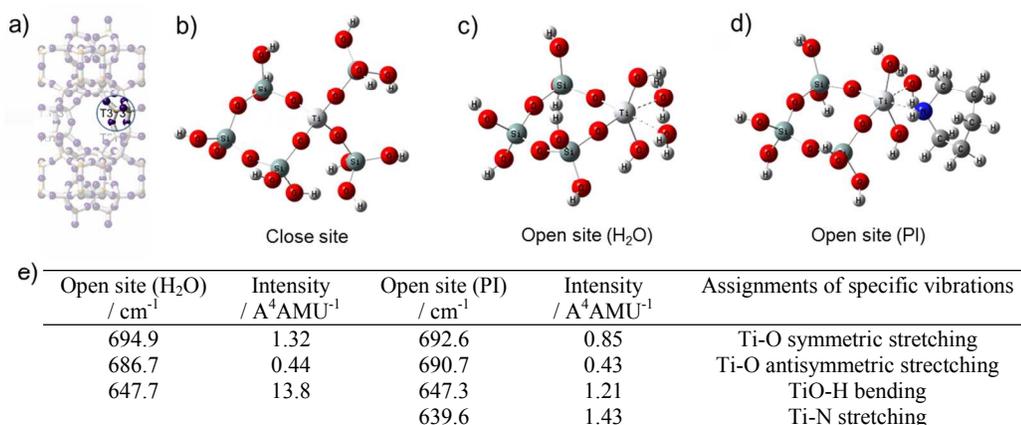
**Fig. 3** Ti 2p XPS spectra of a) Ti-MWW, b) Re-Ti-MWW-PI, and c) Re-Ti-MWW-cal.

transformation of a part of tetrahedral Ti species to multi-coordinated species.

UV Resonance Raman spectroscopy excited at 266 nm was employed to further identify the newly formed Ti species with the feature UV-Vis absorption band at 260 nm (Fig. 2b). The spectra of the Ti-MWW and Re-Ti-MWW-cal gave the same Raman band at  $1100\text{ cm}^{-1}$ . A similar Raman band around  $1125\text{ cm}^{-1}$  has been well reported for titanosilicates in the literature, and it is assigned to the tetrahedrally coordinated framework  $\text{TiO}_4$  units.<sup>13-15</sup> Although the Raman features of Re-Ti-MWW-PI around this position were blurred by the background signal from the carbon species in PI molecules, the UV Resonance Raman spectra excited at 220 nm further confirmed the presence of framework  $\text{TiO}_4$  units in all of the three samples (Fig. S6, ESI†). It is worth notifying that a new Raman band was observed for Re-Ti-MWW-PI at  $695\text{ cm}^{-1}$  and Re-Ti-MWW-cal at  $702\text{ cm}^{-1}$ , when the excitation line was at 266 nm. This band was absent in the Raman spectrum of Ti-MWW. The Raman band at  $695\text{ cm}^{-1}$

developed by the exciting at 266 nm was previously assigned to the Ti species in octahedral coordination (Fig. 1b).<sup>9</sup> The results imply that both Re-Ti-MWW-PI and Re-Ti-MWW-cal samples possessed the Ti species in octahedral coordination while the Ti species in Ti-MWW was mainly in tetrahedral coordination. Moreover, the feature Raman bands around  $700\text{ cm}^{-1}$  showed a frequency difference by  $7\text{ cm}^{-1}$  between Re-Ti-MWW-PI and Re-Ti-MWW-cal, revealing possible different micro-environments in these two materials.

Moreover, the X-ray photoelectron spectroscopy (XPS) was employed to study the state of Ti species (Fig. 3). XPS is a surface-sensitive technique for the analysis of elements and their oxidation states. The bonding energy (BE) has a close relationship with the estimated charges on the central atom.<sup>16</sup> The PI treatment downgraded the BE of Ti  $2p_{3/2}$  from 460.2 eV for Ti-MWW to 459.2 eV and 457.8 eV for Re-Ti-MWW-PI, indicating that the charge distribution of Ti ions in Re-Ti-MWW-PI became more negative. The Ti species in tetrahedral coordinated state of Ti-MWW may be transformed into two different Ti coordination states with more negatively charged. Further calcination caused the BE shift back to 460.2 eV with a shoulder at 459.2 eV for Re-Ti-MWW-cal, and the peak at 457.8 eV in Re-Ti-MWW-PI disappeared with the decomposition of organics. It seems that the more negative Ti active sites attributed to the peak at 457.8 eV in Re-Ti-MWW-PI were related to the presence of PI molecules. Based on the above results, we assume that a part of PI molecules may be coordinated directly to the Ti active sites, forming a new six-coordinated Ti species with a PI molecule ligand (open site (PI), Fig. 1c), while the peak at 459.2 eV was associated with another six-coordinated Ti species with two water ligands (open site ( $\text{H}_2\text{O}$ ), Fig. 1b). The close Ti species in Ti-MWW turned to open Ti (PI) species together with open Ti ( $\text{H}_2\text{O}$ ) species in Re-Ti-MWW-PI, and thereafter the organic ligand was replaced by a water molecule in Re-Ti-MWW-cal. Meanwhile, a part of open sites transformed back to close ones during calcination.



**Fig. 4** a)  $\text{Ti}^{4+}$  species at T3 site in the MWW zeolite; b) the optimized structures of titanium active sites for close site; c) open site ( $\text{H}_2\text{O}$ ); d) open site (PI); e) the calculated Raman bands for the open site ( $\text{H}_2\text{O}$ ) and open site (PI) with B3LYP.

In order to demonstrate the Ti octahedron configurations in Re-Ti-MWW-PI and Re-Ti-MWW-cal, the Raman spectra of titanium species in open Ti (PI) and open Ti ( $\text{H}_2\text{O}$ ) were calculated using the density functional theory (DFT) method. It has been reported that T3 sites might be the most preferable site for the  $\text{Ti}^{4+}$  species in MWW framework.<sup>17</sup> Therefore, the cluster models mainly involving the T3 sites were constructed by truncating

the Si-O bonds in the crystal structure of Ti-MWW (Fig. 4a). The calculated frequency of the specific Ti-O symmetric stretching vibrations for open site (PI) and open site (H<sub>2</sub>O) are 692.6 and 694.9 cm<sup>-1</sup> respectively (Fig. 4e), which were in good agreement with the observed experimental values of 695 and 702 cm<sup>-1</sup> in Fig. 2b. Taking into consideration that the Ti-O symmetric stretching vibrations of open Ti sites with two water ligands in TS-1 is at 695 cm<sup>-1</sup>,<sup>9</sup> it is credible to assign the Raman band around 695-702 cm<sup>-1</sup> to the Ti-O symmetric stretching vibrations. Additionally, the charges of Ti ions in close site, open site (PI) and open site (H<sub>2</sub>O) were calculated to be 2.37, 2.16 and 2.35, respectively (Fig. 4b-d). These results indicated that the charge distribution of Ti ions decreased in the order of close site, open Ti sites (H<sub>2</sub>O), open Ti sites (PI), which also had a good accordance with the XPS results.

The apparent activation energies of these three samples were estimated by fitting the Arrhenius equation in 1-hexene epoxidation (Fig. S7a, ESI†). They were 21.03, 19.28 and 15.71 kJ mol<sup>-1</sup> for Ti-MWW, Re-Ti-MWW-cal and Re-Ti-MWW-PI, respectively. Obviously, the appearance of the newly formed Ti species with a PI ligand significantly lowered the apparent activation energy when compared with other two samples.

It was concerned that the epoxide selectivity may be influenced by the acidic property of hydroxyl groups in open Ti sites. The propylene epoxidation was carried out using methanol as solvent (Table S3, ESI†). It has been reported the best solvent for Ti-MWW in alkenes epoxidation is acetonitrile,<sup>11</sup> in which the epoxide selectivity maintain over 99 %. The epoxide undergoes easily ring-opening solvolysis reaction in a protic solvent like methanol, yielding byproducts of alcohol ethers. Re-Ti-MWW-PI, however, showed a much higher propylene oxide (PO) selectivity of 97.8 % than the other catalysts. Although more hydroxyl groups were generated during hydrothermal treatment, the presence of amine ligand with basic property in Ti micro-environment neutralized the acidity of the hydroxyl groups, then improved the PO selectivity. Therefore, the presence of PI in Ti octahedron configurations not only enhanced the catalytic activity but also suppressed the acidity of titanasilicate. The open Ti (PI) site in Re-Ti-MWW-PI was assumed to react with H<sub>2</sub>O<sub>2</sub> solution, forming a cyclic intermediate species with a five-membered ring through the coordination and hydrogen-bonding of a protic molecule to the Ti-hydroperoxo complex. Then, the C=C double bond in alkenes is expected to interact with more electrophilic O as the active oxygen-donating species (Fig. S8, ESI†). The Re-Ti-MWW-cal possessing open Ti sites (H<sub>2</sub>O) exhibited the lowest PO selectivity (49.8 %) owing to a higher acidity. The result is very similar to that observed on TS-1.<sup>9</sup>

The stability of the Re-Ti-MWW-PI was checked in 1-hexene epoxidation (Fig. S7b, ESI†). There was no significant decrease in 1-hexene conversion after reuse for three times. The yield then decreased gradually with increasing the number of recycle, probably owing to the leaching of PI molecules. After the catalyst was reused for five times, it was regenerated by PI treatment again. The regenerated catalyst showed almost restored

activity in the sixth run. The result confirmed that the Ti sites attached PI ligand was advantageous to the selective oxidation.

Taking advantage of these novel Ti species in catalysis, we further checked the catalytic performance of these catalysts in continuous epoxidation of 1-hexene in a fixed-bed reactor (Fig. S9, ESI†). Starting from extruded Ti-MWW catalyst, the shaped Re-Ti-MWW-PI and Re-Ti-MWW-cal catalysts were prepared by PI treatment and subsequent calcination, respectively. In shaped form, Re-Ti-MWW-PI also showed a higher catalytic activity and a lower deactivation rate than the other two catalysts. The results indicated that developing active six-coordinated Ti sites is a potentially useful technology for practical processes.

In summary, this study communicates the postsynthesis of a novel organic-inorganic hybrid titanasilicate containing unique Ti active sites through incorporating an organic ligand that coordinate to the framework Ti species. With well-tuned coordination micro-environment of titanium species, the catalyst exhibited an unprecedented high catalytic activity and recyclability in alkenes epoxidation. This is the first example that six-coordinated titanium active sites with organic ligand, which would open the door for controlling the coordination environment of Ti species by suitable modifications. Moreover, this technique is promising for designing practically usable catalysts for clean epoxidation processes.

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