Selective oxidation reactions are commonly required for the production of a wide variety of useful chemical compounds, such as highly functional resins and pharmaceuticals. From the view of green sustainable chemistry, hydrogen peroxide (H$_2$O$_2$) is well known as one of the most useful oxidants, although its oxidizability is not as strong as ozone (O$_3$) or peroxycarboxylic acids (i.e., peroxyacetic acid and m-chloroper oxybenzoic acid). A titanosilicate catalyst can activate H$_2$O$_2$ using selective oxidation to provide indispensable chemical resources.

A wide variety of microporous titanosilicates with isolated tetrahedral Ti species in the zeolitic framework have been developed as catalysts for selective oxidation with H$_2$O$_2$. For example, TS-1 with MFI topology having multi-dimensional 10-ring channels is an industrially useful titanosilicate that is an effective catalyst for phenol oxidation with H$_2$O$_2$ to hydroquinone (HQ), para-benzoquinone (p-BQ) and catechol (CL) (Scheme 1). Improvement of para-selectivity in phenol oxidation over the TS-1 catalyst has been achieved through post-synthetic modification of TS-1 (ref. 7 and 8) or with the aid of a solvent in the reaction system.$^{7-9}$

However, there are significant diffusion limitations for a phenol molecule within the 10-ring straight channel of TS-1 (0.51 × 0.55 nm)$^{10}$ although breathing of the pore window could make the aperture expand momentarily. More recently, we have succeeded in the first preparation of Ti-MCM-68 (ref. 11) with MSE-type framework as phenol oxidation catalysts with high activity and selectivity toward HQ. The 12-ring aperture (0.64 × 0.68 nm)$^{10}$ in Ti-MCM-68 (ref. 11–13) allowed a phenol molecule to diffuse and preferentially form para-isomers.

Although the MSE-type aluminosilicate is hydrothermally synthesized using $N,N',N''$-tetraethyl-bicyclo[2.2.2]oct-7-ene-2,3,5,6-dipyrrrolidinium diiodide, TEBOP$^{2+}$($I^-)_2$ (ref. 14–26) or dimethyl-dipropylammonium hydroxide as the organic structure-directing agent (OSDA), the direct crystallization of MSE containing framework heteroatoms such as Ti has remained difficult.$^{28}$ This is why we are focusing on the isomorphous substitution of Ti for Al in the aluminosilicates, which is a useful technique to introduce a sufficient amount of Ti into the framework.$^{29}$ Our first efficient successful way to the preparation of Ti-MCM-68 involved the dealumination by acid treatment followed by gas-phase Ti insertion using TiCl$_4$ at temperatures as high as 600 °C.$^{11,12}$ However, the intense reactivity of TiCl$_4$ with moisture, even at room temperature, is a serious issue during this Ti insertion treatment. Therefore, a gentle Ti modification process in the liquid phase at room temperature is desirable. Here we report the first successful preparation of Ti-MCM-68 through treatment at room temperature using an aqueous solution of Ti-source, and its excellent catalytic performance in the phenol oxidation with H$_2$O$_2$.

Al-MCM-68 was hydrothermally synthesized according to the known procedures$^{26-28}$ (see also ESI†). The crystallinity of MCM-68 samples prepared in this study remained unchanged during calcination, as confirmed by powder X-ray diffraction (Fig. S1†). According to FE-SEM images in Fig. S2,† the MCM-68 particle has a rectangular morphology with 50–80 nm in size. The dealumination treatment of the parent MCM-68 (Si/Al = 10)
using concentrated nitric acid solution (13.4 mol L\(^{-1}\)) under reflux condition gave highly dealuminated MCM-68 (Si/Al > 1000) without any loss of crystallinity. The dealuminated MCM-68 inevitably had site defects within the MSE framework due to dealumination from the framework (vide infra). To introduce Ti into the site defects (i.e., framework), commercially available “titanium(IV) chloride aqueous solution” (Wako Chemical) was used as a reagent. This is a clear yellowish and viscous solution that was prepared by reacting TiCl\(_4\) with excess water, and the analytical data were guaranteed as follows: Ti, 3.45 mmol g\(^{-1}\); Cl, 8.18–9.32 mmol g\(^{-1}\). The reaction of TiCl\(_4\) with excess H\(_2\)O ideally gives a solution with a Cl/Ti molar ratio of 4; however, analytical data showed a lower value of Cl/Ti = 2.37–2.70, which indicates that some HCl was evaporated before the final solution was obtained. This aqueous solution consists of H\(^+\), Cl\(^-\), and Ti\(^{4+}\) with various ligands such as H\(_2\)O (see next paragraph for more detailed discussion). The concentration of Ti\(^{4+}\) was defined; therefore, the aqueous solution was designated as Ti\(^{4+}/\)H\(_2\)O in this paper. Elemental analysis showed that a sufficient amount of Ti (0.20–0.22 mmol-Ti g\(^{-1}\)) was introduced into the dealuminated MCM-68 by treatment with the Ti\(^{4+}/\)H\(_2\)O. The as-prepared sample to which Ti was introduced at room temperature (16–20 °C) or at 30 °C was denoted as Ti-MCM-68_Ti\(^{4+}/\)H\(_2\)O_{rt} or Ti-MCM-68_Ti\(^{4+}/\)H\(_2\)O_{x}, respectively. The sample after further thermal treatment (=calcination) at 650 °C is represented by adding “cal” at the end of the sample name (e.g., Ti-MCM-68_Ti\(^{4+}/\)H\(_2\)O_{rt-cal}). Sorption experiments suggested no diminution in the microporosity or formation of mesopores for Ti-MCM-68_Ti\(^{4+}/\)H\(_2\)O_{rt-cal} (Fig. S3 and Table S1†).

Raman spectroscopy is one of the most informative techniques for evaluation of the coordination and conformation of Ti–ligand complexes.† Fig. 1 shows Raman spectra for the Ti\(^{4+}/\)H\(_2\)O, neat TiCl\(_4\), and TiCl\(_4\) dissolved in toluene (TiCl\(_4\)toluene). Fig. 1b shows that the TiCl\(_4\) molecule gives a sharp peak at 379 cm\(^{-1}\), which corresponds to the \(v_2\) (\(A_1\)) mode,\(^{26-31}\) accompanied by three peaks at 110 \((v_1(e))\), 131 \((v_4(f_2))\), and 477 cm\(^{-1}\) \((v_3(f_2))\).\(^{26-31}\) The Raman scattering of TiCl\(_4\)toluene (Fig. 1c) closely resembled a combination of the two scatterings for neat TiCl\(_4\) (Fig. 1b) and toluene (Fig. 1d), which indicates that TiCl\(_4\) molecules were intact in the toluene solution without dissociation. In contrast, the Raman peaks of Ti\(^{4+}/\)H\(_2\)O (Fig. 1a) were entirely different from that of neat TiCl\(_4\). A broad band at 650 cm\(^{-1}\) and weak broad bands at 150, 460, 790 and 934 cm\(^{-1}\) were assignable to [Ti(OH\(_2\))]\(^{4+}\) octahedra with considerable aggregation.\(^{35}\) In addition, very weak peaks at 248 and 340 cm\(^{-1}\) could correspond to the incorporation of chloride in the first coordination sphere of titanium; possibly, (TiCl\(_6\))\(^{2-}\) (\(O_x\)) and trans-[Ti(OH\(_2\))\(_2\)Cl\(_4\)]\(^{4-}\) (\(D_{4h}\)) complexes.\(^{35,36}\) During this process, it is reasonable to speculate that H\(_2\)O and framework oxygen behaves as ligands for Ti\(^{4+}\). The Ti\(^{4+}\) ions diffuse into the 12-ring channels with repetitive ligand exchange to fill in a site defect of the silicate framework. The possibility of TiCl\(_4\) molecule diffusion into the channels was excluded for the following reason. The diameter of the TiCl\(_4\) molecule is estimated to be ca. 7.4 nm, while that of the 12-ring pore-mouth of MCM-68 is 0.64 × 0.68 nm.\(^{38}\) It is at least obvious that the TiCl\(_4\) molecule cannot enter into the 12-ring channels at temperatures as low as 45 °C. The diffusion of the [Ti(OH\(_2\))]\(^{4+}\) octahedron itself into the 12-ring channels was also considered to be difficult for the same reason.

Fig. S4† shows DR/UV-vis spectra of various Ti-modified MCM-68 before and after thermal treatment at 650 °C. In the case of Ti\(^{4+}/\)H\(_2\)O, the as-prepared sample gave a clear peak at 210 nm, which corresponds to a 4-coordinated Ti species at closed sites, Ti(OSi)\(_4\), and a shoulder at 250 nm due to 4-coordinated Ti species at open sites, (OH)[Ti(OSi)]\(_3\),\(^{2,29}\) both of which are inside the framework. This reveals the successful incorporation of tetrahedral Ti into the silicate framework of dealuminated MCM-68 during the suitable treatment at room temperature. After thermal treatment, the UV-vis peak at 210 nm increased slightly, while the UV-vis band at 250 nm remained almost unchanged, which indicates that the dehydration condensation of 4-coordinated Ti with an open site into one of the closed sites with an adjacent silanol proceeded at temperatures as high as 650 °C. In contrast, the treatment of dealuminated MCM-68 using TiCl\(_4\)toluene gave different UV-vis bands. There were very broad peaks at 210, 260 and 300 nm, which were attributed to 4-coordinated Ti with the closed site, 5/6-coordinated Ti, and titanate oligomer, respectively.\(^{2,12,29}\) The UV-vis band was unchanged even during the thermal treatment at 650 °C, which indicates that TiCl\(_4\) molecules did not enter the 12-ring channels of MCM-68 as discussed earlier and may have resulted in partial polymerization on the external surface of dealuminated MCM-68 particles. When using Ti(OP\(_2\))\(_3\)/toluene for Ti-impregnation, the resultant sample, which has a large amount of Ti (0.62–0.64 mmol-Ti g\(^{-1}\); see also Table S2†), showed a broad band from 200 to 330 nm. This can be interpreted as the polymerization of titanate species on the external surface of the dealuminated MCM-68 particles. After thermal treatment, the UV-vis band became broader, probably due to the further polymerization of titanate species. Based on these data, only the use of Ti\(^{4+}/\)H\(_2\)O resulted in the successful introduction of Ti into the MSE framework, and the
resultant titanosilicates are potential catalysts for phenol oxidation and related reactions.

The Ti-modified MCM-68 samples were utilized as catalysts for phenol oxidation with H₂O₂ and the results are listed in Table S2.† The Ti-MCM-68 catalyst prepared using TiCl₄/toluene (runs 3 and 4) and Ti(OPr)₄/toluene (run 5) showed only low activity, with or without thermal treatment during the catalyst preparation by liquid-phase Ti-introduction. On the other hand, Ti-MCM-68_Ti⁴⁺/H₂O₂ (Table S2, run 1) exhibited a meaningful product yield (8.7%) with subtle para-selectivity (51.7%). This behavior clearly shows the potential of the preparation methodology with mild treatment conditions using Ti⁴⁺/H₂O₂ at room temperature, and strongly supports the spectroscopic results suggesting the incorporation of 4-coordinated Ti species into the MSE framework with such a mild treatment. The reaction over Ti-MCM-68_Ti⁴⁺/H₂O₂_cal obtained after thermal treatment at 650 °C (Table S2, run 2) gave significantly enhanced total yield (44.4%), turnover number (TON = 478) and para-selectivity (81.5%); the catalytic performance became much higher than that of a conventional catalyst, TS-1 (Table S2, run 6). The significant improvement in the catalytic performance via thermal treatment is consistent with the results in our previous reports on Ti-MCM-68 to which Ti was introduced by vapor-phase TiCl₄ treatment.¹⁰¹¹ Note that the remarkable effect of thermal treatment at 650 °C was also represented in Table 1, runs 1 and 2. Such a thermal treatment played some role to increase the hydrophobicity of the titanosilicate catalyst, as proven by the H₂O adsorption isotherm obtained at 25 °C (Fig. 2). The hydrophilic nature of as-prepared Ti-MCM-68_Ti⁴⁺/H₂O₂ could be mainly due to connectivity defects (a hydrolysed form of siloxane, ==Si–OH HO–Si==, not a silanol nest) in the zeolite framework. Conversely, the reverse process is the condensation of silanols (the reverse process of the siloxane condensation) to give the siloxane bond (==Si–O–Si==), and this is considered to be the main cause of hydrophobization during the thermal treatment. The decrease in the number of silanols during the thermal treatment is also supported by ²⁹Si MAS NMR (see Fig. S5†); the spectrum of thermally treated sample had a Q³ : Q⁴ ratio of 6.9 : 93.1, while that of as-prepared sample had a Q³ : Q⁴ ratio of 10.2 : 89.8 (Q³,H₂O : Q³,OSi; Q³,OSi). The enhanced hydrophobicity of Ti-MCM-68 caused an increase in the TON by allowing both phenol and H₂O₂ molecules to simultaneously move into the 12-ring channels.

The influence of the treatment temperature on the Ti modification was examined and the results are shown in Table 1, runs 2, 3, and 4. The temperature was precisely controlled using an oil bath. The Ti⁴⁺/H₂O₂ treatment at 25 °C enabled the effective formation of catalytic active sites in the 12-ring channels, and Ti-MCM-68_Ti⁴⁺/H₂O₂_25_cal (Table 1, run 2) exhibited a very high TON (832) and para-selectivity (76%). In the case of Ti-MCM-68_Ti⁴⁺/H₂O₂_40_cal and Ti-MCM-68_Ti⁴⁺/H₂O₂_60_cal, TON decreased slightly, probably due to the excess Ti species in the catalyst (Table 1, runs 3 and 4). Such a high-temperature treatment resulted in the polymerization of titinate species on the external surface, as confirmed by the appearance of a broad band at 210–300 nm in the UV-vis spectra (Fig. S6c and f), although the total yield and para-selectivity were still high, despite this negative effect.

The effect of the alcoholic cosolvent was examined, and a typical behaviour is demonstrated in Fig. S7.† The cosolvent here should be recognized as an additive rather than just

![Figure 2](https://example.com/figure2.png) Water adsorption isotherms obtained at 25 °C for (a) [Ti]-MCM-68_rt_Ti⁴⁺/H₂O₂, (b) [Ti]-MCM-68_rt_Ti⁴⁺/H₂O₂_cal, and (c) TS-1.

Table 1 Oxidation of phenol with H₂O₂ over various titanosilicates

| Run | Catalyst | Temperature for Ti-introduction/°C | Ti content/µmol g⁻¹ | Yield/% | TON | Total | HQ | p-BQ | para-Selectivity/% |
|-----|----------|-----------------------------------|----------------------|---------|-----|-------|-----|------|---------------------|
| 1   | Ti-MCM-68_Ti⁴⁺/H₂O₂_25 | 25 | 0.206 | 121 | 11.4 | 5.1 | 4.4 | 1.8 | 61.2 |
| 2   | Ti-MCM-68_Ti⁴⁺/H₂O₂_25_cal | 25 | 0.214 | 832 | 88.9 | 59.8 | 21.3 | 7.3 | 75.9 |
| 3   | Ti-MCM-68_Ti⁴⁺/H₂O₂_40_cal | 40 | 0.283 | 667 | 88.4 | 59.8 | 21.3 | 7.3 | 75.9 |
| 4   | Ti-MCM-68_Ti⁴⁺/H₂O₂_60_cal | 60 | 0.439 | 458 | 95.8 | 55.6 | 27.5 | 12.7 | 71.3 |
| 5   | Ti-MCM-68_cal⁴⁺ | 600 | 0.241 | 314 | 33.0 | 26.2 | 7.6 | 1.2 | 78.3 |

* Reaction conditions: catalyst, 20 mg; phenol, 21.25 mmol; H₂O₂, 4.25 mmol; H₂O, 17.9 mmol; temperature, 100 °C; time, 10 min. * The treatment with the liquid-phase titanium source was performed at predetermined temperature for 1 h. * The Ti content per a gram-catalyst was determined by ICP-AES analysis. * Turnover number = (moles of [HQ + CL + p-BQ] per mole of Ti site). * Product yields based on added H₂O₂. * Selectivity to para-isomers of dihydroxybenzenes and quinones (moles of [HQ + p-BQ]) per moles of [HQ + CL + p-BQ]). * The Ti-modification was performed using vapor-phase TiCl₄.
a solvent. In the current catalytic system, ethanol (EtOH) was the most suitable cosolvent, which remarkably enhanced para-selectivity up to 94%. The role of EtOH could be narrowing the space inside pores and deactivating the external active sites via hydrogen bonding between alcoholic OH and surface silanols.

It should be noted that the use of EtOH as a cosolvent inhibited the production of p-BQ, which could be due to the avoidance of radicalic active site formation for the interconversion between HQ and p-BQ.

In summary, we have developed a novel and convenient post-synthetic modification procedure for the preparation of Ti-MCM-68 as a highly efficient catalyst for the oxidation of phenol with H₂O₂ for the first time. In this procedure, the Ti⁴⁺/H₂O plays an important role to provide Ti⁴⁺ species to successfully incorporate Ti into the site defects at a temperature as low as room temperature. The improvement of the hydrophobic nature of the catalyst is the most likely factor for the enhanced catalytic performance. Addition of EtOH as a cosolvent to the reaction system realised extremely high selectivity toward HQ. This novel post-synthetic procedure that employs metal chloride aqueous solution under ambient conditions is applicable for the sustainable preparation of efficient catalysts with a wide variety of zeolitic framework.

Conflicts of interest

There are no conflicts to declare.

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