# Trimethylsilylation of ordered and disordered titanosilicates: improvements in epoxidation with aqueous $H_2O_2$ from micro- to meso-pores and beyond†

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**A novel method for trimethylsylilation of micro- and mesoporous titanosilcates using BSTFA [N,O-bis(trimethylsilyl-)trifluoroacetamide] renders Ti-MCM-41 and $SiO_2/TiO_2$ aerogels active for olefin epoxidation with aqueous $H_2O_2$, and even improves the activity of TS-1.**

The importance of hydrophobicity for titanosilicate catalyzed oxidation reactions with aqueous $H_2O_2$ has been the subject of much recent research. The hydrophobicity of the interior pores of titanosilicalite (TS-1) and Al-free Ti-beta renders them active for aqueous $H_2O_2$ oxidation of alkanes and alkenes.[1,2] By comparison, Al containing Ti-beta is less efficient, mainly because of framework Al induced hydrophilicity.[3] Because of their mesoporous nature (25–100 Å pores) Ti-MCM types[4,5] would be useful as oxidation catalysts for larger, higher value molecules. However, Corma and coworkers[5] observed that because of its hydrophilic nature, Ti-MCM-41 was much less effective for oxidation with aqueous $H_2O_2$ than even Al-Ti-beta. Therefore it is not surprising that efforts to render Ti-MCM's hydrophobic and hence, more active, were undertaken: Tatsumi *et al.*[6] trimethylsilylated Ti-MCM-41 and Ti-MCM-48 using trimethylsilyl chloride and hexamethyldisiloxane and observed increased oxidation activity.[4] Amorphous silica/titanias with even wider pores present opportunity for further increasing the range of oxidation substrates. Recently non-catalytic and hydrophilic amorphous silica/titanias have been made hydrophobic and catalytic by substituting alkoxy groups in the silica precursors with alkyl or phenyl groups during the sol–gel synthesis.[7,8]

Herein we report a simple and effective technique for trimethylsilylation of microporous crystalline TS-1, mesoporous Ti-MCM-41(Ti-MCM), and $SiO_2/TiO_2$ aerogels (Ti-Agel). The resultant materials are hydrophobic and have enhanced activity for olefin epoxidation with aqueous $H_2O_2$.

TS-1 was synthesized by the method of Thangaraj and Sivasanker.[9] Corma's method[5] for the preparation of Ti-MCM-41 was modified by using a single precursor for titanium and silicon: Gelest diethoxysiloxane–ethyltitanate copolymer (no. in Gelest catalogue = PSITI-019), $[(EtO)_2SiO][(EtO)_2TiO]$, Si : Ti ≈ 15. The general method for the preparation of aerogel catalysts was that of Dutoit *et al.*,[10] with acetylacetone-modified titanium isopropoxide. The sol–gel was continuously extracted with supercritical $CO_2$ at 40 °C at 24.2 MPa for 5 h. The resulting fluffy yellow powder was calcined at 400 °C for 1 h in $N_2$ followed by 600 °C for 5 h in air.

A typical procedure for the trimethylsilylation of catalysts is as follows: a mixture of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide $[CF_3COSiMe_3)_3]$=$NSiMe_3$ or BSTFA] (1.0 g) and toluene (8 g) was added to the catalyst (0.5 g). The mixture was stirred for 2 h at room temperature, filtered, and the solids washed with toluene and air dried. The dried materials' hydrophobicity was evidenced by their floating on water. In addition, using a TGA method derived from Anderson and Klinowski[17] we obtained the following hydrophobicities (mg water adsorbed silylated/ mg water adsorbed non-silylated at 50 °C) for TS-1, Ti-MCM, and TiAgel respectively: 1.04, 0.41, 0.68. As expected, the ratio for trimethylsilylated TS-1 was near unity because trimethylsilylation is not expected to affect the interior pore system. However, for the mesoporous materials the ratio is less than unity consistent with trimethylsilylation of the accessible surface. Other trimethylsilylating agents such as trimethylsilyl chloride and hexamethydisilazane were also used successfully. However, these required more severe conditions and, in the case of the chloride, resulted in loss of Ti from the aerogels. While BSTFA has been used to derivatize organics and end group cap chromatographic columns,[11] there is no reference to using it to modify catalysts. Characterization data for the catalysts are given in Table 1.

BSTFA treatment of TS-1 introduces IR bands consistent with trimethylsilylation. Because of the strong asymmetric stretch of the silicate lattice at *ca.* 1225–1230 $cm^{-1}$, we are unable to detect the diagnostic symmetric methyl deformation in the 1250–1260 $cm^{-1}$ region.[12] We do see the antisymmetric methyl deformation at *ca.* 1400 $cm^{-1}$, as well as bands at *ca.* 725 and 700 $cm^{-1}$ that may be assigned to the antisymmetric Si–C and the symmetric Si–C stretching modes, respectively.

**Table 1** Characterization data for TS-1, Ti-MCM and Ti-Agel[a]

$$CF_3C(OSiMe_3){=}NSiMe_3 + 2\,[O_3Si{-}OH]_s \rightarrow CF_3CONH_2 + 2\,[O_3Si{-}O{-}SiMe_3]_s$$

| Sample name | XRD[b] | IR[c]/$cm^{-1}$ | $I_{960}/I_{1090}$ | $A_1$, $A_2$ (UV–VIS/nm) | $A_1/A_2$ (UV–VIS/nm) | Si/Ti ICP | $N_2$ adsorption SA | PV | APD |
|---|---|---|---|---|---|---|---|---|---|
| TS-1 | MFI | 962 | 0.10 | 215, 258[d] | 1.34 | 26 | 485 | 0.11 | 52 |
| TS-1-syl | MFI | 972 | 0.05 | 207, 260 | 1.45 | — | 453 | 0.14 | 74 |
| Ti-MCM | MCM-41 | 960 | 0.37 | 216, 268 | 0.97 | 8[e] | 810 | 0.12 | 27 |
| Ti-MCM-syl | — | 950 | 0.23 | 214, 269 | 0.99 | — | 727 | 0.14 | 24 |
| Ti-Agel | Amorphous | 959 | 0.34 | 214, 255 | 1.21 | 12 | 493 | 1.50 | 148 |
| Ti-Agel-syl | — | 955 | 0.32 | 214, 260 | 1.15 | — | 318 | 1.33 | 166 |

[a] Elemental analysis by inductively coupled plasma spectroscopy (ICP): MCM: Ti-MCM-41, Ti-Agel: $SiO_2/TiO_2$ Aerogel, syl: trimethylsilylated $I_{960}$: assumed to be $\nu$(Si–O–Ti):[10] $I_{1090}$: $\nu$(Si–O–Si).[10] $A_1$: absorbance of band due to isolated Ti. $A_2$: absorbance of band due to $(Ti–O)_n$ oligomers. SA: BET $N_2$ surface area/$m^2\ g^{-1}$. PV: BJH $N_2$ pore volume ml $g^{-1}$. APD: BJH $N_2$ av. pore diameter/Å. [b] No $TiO_2$ phases observed by XRD in any of the samples. [c] Position of 960 band, KBr pellet technique. [d] Si/Ti charged = 15. [e] Shoulder at ≈320 nm indicates anatase.

Bands near 1680 and 1750 cm$^{-1}$ are assigned to the amide group of trifluoroacetamide (the silylation byproduct) and residual BSTFA, respectively. The IR spectrum of Ti-Agel is very similar to that of Ti-MCM, which is to be expected since the latter is composed of amorphous walls. For both Ti-MCM and Ti-Agel, silylation added bands to the IR spectra that can be attributed to $SiMe_3$ groups, especially the very distinctive band at 1250–1260 cm$^{-1}$, and the $CH_3$ rocking modes at *ca*. 840 and 755 cm$^{-1}$.[12]

The IR band at *ca*. 960 cm$^{-1}$ (the 960 band) has been attributed to Si–O–Ti bonds as a fingerprint for tetrahedral Ti substitution in silicate lattices,[10] or to Si–OH groups.[13, 14] We hypothesize that for our TS-1 loss of silanol groups after trimethylsilylation results in a decrease in the 960 band intensity. The intensity of the 960 band of Ti-MCM decreased on silylation, in agreement with Tatsumi *et al*.[6] However, the 960 band of Ti-Agel decreases only slightly upon trimethylsilylation, consistent with a smaller fraction of silanols available to the silylating agent compared to MCM. Based upon the pronounced hydrophobic nature of the silylated material these must be the ones which confer hydrophilicity to the base aerogel.

Analysis of the UV–VIS data[15] for all of the base materials indicates the presence of isolated Ti and oligomeric $(Ti–O)_n$ species; in addition, TS-1 and Ti-MCM are contaminated by anatase. The non-isolated Ti-species may have a detrimental effect on the epoxidation reaction, since they have been reported to decompose $H_2O_2$ homolytically.[16] Ti-isolation, as measured roughly by the ratio of the absorbance of band due to isolated Ti to the band due to $(Ti–O)_n$ oligomers, $(A_1/A_2)$, is better for Ti-Agel compared with Ti-MCM. This may be ascribed to the acac modification performed on the Ti-precursor for Ti-Agel, which slows down the condensation rate of the hydrolyzed Ti species.[10] The effect of trimethylsilylation on the UV–VIS spectra of the samples is not great, indicating that the silylation procedure probably did not result in reaction with the isolated Ti sites or $H_2O_2$ destroying sites.

$N_2$ adsorption measurements on Ti-MCM confirmed that surface area and pore size decrease on trimethylsilylation.[6] Our Ti-MCM contains microporosity, probably related to the titania or silica/titania impurities resulting from the high Ti-concentration in the synthesis gel. For Ti-Agel, trimethylsilylation decreases surface area and mesopore volume as expected. Because of limitations in the $N_2$ adsorption techniques, the effect of trimethylsilylation on the microporosity of TS-1 could not be determined.

Trimethylsilylation of the available surfaces of TS-1, Ti-MCM, and Ti-Agel increased the efficiency of olefin epoxidation reactions with dilute aqueous hydrogen peroxide (Table 2). Especially striking were the results with Ti-MCM and the aerogels where epoxidation yields were dramatically increased after the treatment. Rendering the catalyst surfaces hydrophobic has either improved access of the olefin to the active sites or has diminished the inhibitory effect of water.[1] Either scenario should result in increased catalytic activity.

In the case of the TS-1 the improved activity after trimethylsilylation may be attributed to better wetting of the microcrystallite surface with the olefin. While it is possible that the increase in activity is related to loss of oligomeric $(Ti-O)_n$ $H_2O_2$ decomposition sites after trimethylsilylation, lack of changes in the UV–VIS and the probably very low concentration of reaction sites for silylation argue against this.

It is important to note that the trimethylsilylation technique described in this communication results in nearly equivalent epoxidation activity for any of the titanosilicates studied, the only requirement being the presence of isolated, tetrahedral Ti sites. Especially striking is the treatment of normally inert aerogel; we believe this to be the first report of *post synthesis* activation of this material. In addition the expectation of epoxidizing molecules too large to fit in the pores of TS-1 has been realized for the Ti-aerogel after the silylation treatment. *cis*-Cyclooctene is epoxidized readily by Ti-Agel-syl compared to almost no reaction with either TS-1 or TS-1-syl.

**Table 2** Effect of trimethylsilylation on the epoxidation activity of Ti-Agel, Ti-MCM, and TS-1 titanosilicates[a]

| Catalyst | $\%H_2O_2$ | Olefin[b] | Epoxide yield[c] |
|---|---|---|---|
| Ti-Agel | 10 | 1-Oct | 0.2 |
| Ti-Agel | 10 | COT | 0.5 |
| Ti-Agel-syl | 10 | 1-Oct | 6 |
| Ti-Agel-syl | 10 | COT | 32 |
| Ti-MCM | 3 | 1-Oct | 0.5 |
| Ti-MCM-syl | 3 | 1-Oct | 23.6 |
| TS-1 | 10 | 1-Oct | 2.4 |
| TS-1 | 10 | COT | 0 |
| TS-1-syl | 10 | 1-Oct | 12.9 |
| TS-1-syl | 10 | COT | 0.5 |

[a] *Reaction conditions*: olefin (3 ml), aq. $H_2O_2$ (1 ml), catalyst (50–100 mg)[d] stirred at room temperature for 24 h. [b] 1-Oct: oct-1-ene, COT: *cis*-cyclooctene. [c] Yield of the corresponding epoxide was based on initial $H_2O_2$ concentration. The only significant byproduct with oct-1-ene was octan-1-al (5–10%); with cyclooctene no byproducts were observed. [d] 100 mg with Ti-Agel and TS-1, 50 mg with Ti-MCM.

In summary we have demonstrated a general method for significantly increasing the activity of titanosilicate oxidation catalysts using aqueous hydrogen peroxide by rendering their surfaces hydrophobic by treatment with the trimethylsilylating agent BSTFA.

## Notes and references

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