

Ti Coordination in Titanium Silicalite-1

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The coordination states of heteroatoms (e.g., B, Al, P, Ti, V, Fe, and Ga) acting as active sites within molecular sieve catalysts must be known to fully comprehend catalyst activity and reaction mechanisms. Titanium Silicalite-1 (TS-1), with MFI framework structure, is a highly important industrial catalyst for selectively oxidizing organic compounds (e.g., secondary alcohols to ketones, olefin epoxidation) under mild conditions using aqueous H₂O₂ as oxidizing agent.¹ Numerous studies of the TS-1 structure and reaction mechanisms have been made recently,^{2–12} yet the Ti coordination states of the various catalytic forms still remain controversial.

Unambiguous experimental evidence is presented here that incorporation of Ti^{IV} within the structure of silicalite-1 is accompanied by the introduction of one formal negative charge per Ti atom, consistent with the formation of Ti sites with five covalent bonds to oxygen. At the outset, a combination of crystal structure, ¹H and ²⁹Si MAS NMR data confirmed that there are three H-bonded silanol protons per siloxy anion (SiO⁻) in as-synthesized silicalite-1. This result was then used, along with ¹H MAS NMR, to quantify for the first time the siloxy defect sites in a series of as-synthesized catalysts with increasing amounts of Ti or B atoms. In general, the methodology described can be applied to crystalline molecular sieves to reveal the formal charges of atoms isomorphically incorporated within the framework, often not amenable to other approaches.

As-synthesized zeolite catalysts, which still retain the organic structural directing agent (SDA), are of interest because they represent the initial state of the catalyst before activation by calcination. The heteroatom distribution is already fixed in this form. Conceivably, the SDA could “direct” its distribution in addition to the framework structure.¹³

Unlike calcined TS-1, with its TiO₄ sites in nonadsorbate form, few workers have expressed interest in as-synthesized TS-1. IR studies suggested five- or six-coordinate Ti,¹⁰ while XANES analysis concluded mainly six-coordinate.¹¹ However, these studies might have been influenced by impurities (e.g., anatase). Structural changes caused by template removal from as-synthesized TS-1 were studied by in situ XRPD,¹² but without any information on the Ti coordination. Our laboratories recently prepared as-synthesized Ti- and B-containing MFI zeolites with increasing amounts of heteroatom content. These samples were crystallized from alkali-free gels using tetrapropylammonium (TPA⁺) as SDA and characterized by synchrotron XRPD, thermal and elemental analyses⁸ (Supporting Information). The Ti sites in these “pre-catalysts” are examined here by NMR spectroscopy.

A survey of direct spectroscopic methods lent little hope of clearly distinguishing Ti types in TS-1. Solid-state ^{47,49}Ti NMR spectroscopy has allowed identification of Ti coordination states in some pure titanium oxides and related minerals at high applied magnetic fields.¹⁴ However, the low Ti content in TS-1, combined with the low intrinsic NMR sensitivities of ^{47,49}Ti, deferred this analysis. ²⁹Si MAS NMR spectra cannot resolve Si–O–Ti sites in

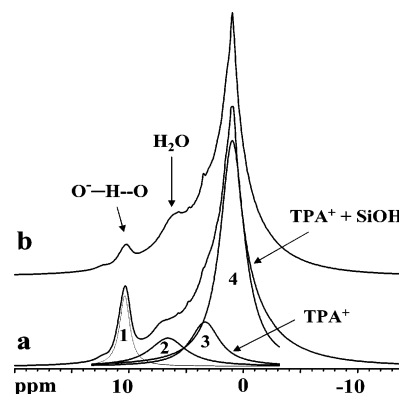


Figure 1. (a) ¹H MAS NMR spectrum (central region), decomposed into four peaks, of as-synthesized silicalite-1 dried at 90 °C for 15 h followed by storage over activated silica gel for 3 days. H-bonded protons gave two signals: peak 1 and small shoulder near 12 ppm. (b) Spectrum for TS-1 with highest Ti content (2.14 Ti per unit cell). Bruker ASX-300 spectrometer collected spectra of powder (80 mg) in 4 mm rotor spinning at 14 kHz using 2 μs (60°) pulses, 5 s delay, and 200 scans. Longest longitudinal relaxation time was 0.6 s. Shifts referenced externally to water (4.8 ppm). Full spectrum is in Supporting Information.

Table 1. Relative Amounts of Atoms, Molecules, or Molecular Groups Found for As-Synthesized Silicalite-1

| atom, molecule | amount (per unit cell) | method |
|----------------------------|---------------------------|---|
| Si | 96 | crystal structure ⁸ |
| TPA ⁺ | 4.4 | elemental analysis ⁸ |
| O···H···O | 11.8 | ¹ H MAS NMR |
| SiO ⁻ + SiOH | 25 | ²⁹ Si MAS NMR |
| SiOH isolated | 9 | ²⁹ Si MAS NMR, calcined form |
| SiO ⁻ | 4 | presume [SiO ⁻] = [TPA ⁺] |
| SiOH near SiO ⁻ | 12 | by difference (25–9–4 =) |

titanosilicalites.⁹ Although not intuitive, ¹H MAS NMR spectroscopy is actually ideally suited, provided that the H-bonded protons are easily resolved and a fixed number of these silanol protons stabilize the “defective” SiO⁻ sites charge-compensating the occluded SDA cations.

As-synthesized silicalite-1, with known unit cell composition (Table 1), gave the ¹H MAS NMR spectrum shown in Figure 1. Four TPA⁺ molecules maximum fit within the MFI structure. Thermogravimetric analysis was consistent with a 0.4 molecule surplus residing on the external crystal surface.⁸ The ¹H spectral area of peak 1 was related to molar amounts (Table 1 and Supporting Information) using peaks 3 and 4, which arise from known amounts of protons: 28 from each TPA⁺ and 9 “isolated” or “external” SiOH protons (from ²⁹Si MAS NMR spectra) per unit cell.¹⁵

Spectral areas from Figure 1a yielded a total of 11.8 H-bonded protons per unit cell. Of the 96 Si atoms making up the unit cell, 25 are not completely condensed within the framework (i.e., they contain a siloxy or silanol group) being located at “defect sites” or

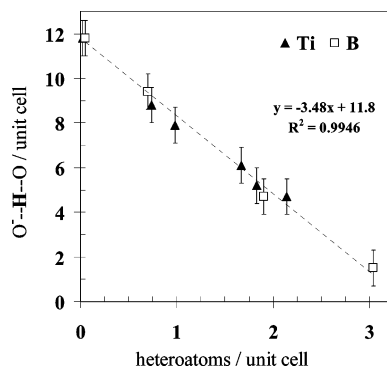


Figure 2. Quantities of silanol protons H-bonded to siloxy oxygens at defect sites (near TPA^+) in as-synthesized silicates as a function of Si atom substitution by Ti or B. Error bars reflect $\pm 8\%$ estimated uncertainty in protons amounts, calculated from ^1H MAS NMR spectra as for Figure 1. Dotted line shows the best fit of linear regression.

at the external surface (isolated silanols, Table 1). The latter were estimated to be 9 Si from ^{29}Si NMR spectra.¹⁵ Given that 4 Si within the unit cell must be siloxy (to charge-balance TPA^+), there remain 12 Si atoms with “nonisolated” silanols. These are silanol-containing Si, near a siloxy, that will condense during template removal. Thus, both NMR approaches yield three $\text{O}^-\cdots\text{H}\cdots\text{O}$ protons per siloxy group, in accord with the exhaustive multiple-quantum ^1H MAS NMR work of Shantz et al.¹⁶

The fixed ratio of three H-bonded protons per siloxy group provides a convenient indirect means for monitoring the siloxy concentration. As shown in Figure 2, isomorphic incorporation of Ti^{IV} or B^{III} , for Si in silicalite-1, caused a progressive decrease in the H-bonded proton signal area. Addition of Al^{III} , to give AlO_4 sites, also caused siloxy disappearance.¹⁶ The linear reduction in siloxy content on introducing a heteroatom means that the incorporated atom contains a negative charge; otherwise, TPA^+ is not charge-balanced.

The negatively charged Ti^{IV} species, obviously due to a TiO_5 site, is assigned to $[\text{Ti}(\text{OSi})_4\text{OH}]^-$.¹⁷ It is the preferred counterion for TPA^+ , excluding siloxy formation up to the maximum Ti occupancy. Thus, this work reveals that Ti behaves as other incorporated heteroatoms, bearing a negative charge; it substitutes Si atoms at “defective” (siloxy) sites near the SDA. Furthermore, since Ti must be proximal to the N of TPA^+ , its position within the framework is not expected to be random. In fact, recent powder neutron diffraction studies concluded that Ti distribution in TS-1 is nonrandom^{5–7} and revealed a striking correspondence between sites preferentially hosting Ti atoms and Si vacancies.⁷ Direct association between framework heteroatoms (B, Al) and the charged center of mono-quaternary SDAs, to give charge-induced ordering, has been evidenced by modern solid-state NMR experiments.¹⁸

Supporting Information Available: Complete citation for ref 3d, chemical compositions, and ^1H MAS NMR data for all samples, example calculation of proton amounts, and two representative full ^1H

MAS NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (15) From comparison of ^{29}Si MAS NMR signal areas near -103 ppm, due to $(\text{SiO})_3\text{SiOX}$ groups before ($X = \text{H}$ and O^-) and after ($X = \text{H}$) calcination at 550°C for 4 h (see Supporting Information). Spectra were collected with ASX-300 for samples in 7 mm zirconia rotors spinning at 5 kHz using $4\ \mu\text{s}$ (70°) pulses, 120 s delay, ^1H decoupling, and 600 scans. Shifts referenced externally to tetrakis(trimethylsilyl)silane at -9.8 and -135.2 ppm.
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- (17) Our observations do not allow exclusion of a six-coordinate species having one neutral ligand, such as $[\text{Ti}(\text{OSi})_4(\text{H}_2\text{O})\text{OH}]^-$, although the proximity of TPA^+ to Ti seems to disfavor a sixth ligand. Other negatively charged Ti species were excluded: (1) titanoxo, such as $[\text{Ti}(\text{OSi})_3\text{O}]^-$, $[\text{Ti}(\text{OSi})_3(\text{H}_2\text{O})\text{O}]^-$, and $[\text{Ti}(\text{OSi})_3(\text{H}_2\text{O})_2\text{O}]^-$, since there would be accompanying H-bonded protons; (2) $[\text{Ti}(\text{OSi})_5]^-$, based on steric considerations; and (3) bonding to a molecular oxygen radical $[\text{Ti}(\text{OSi})_4(\text{O}_2)]^-$, as ESR found typical amounts ($\leq 10^{-3}$ O_2^- per unit cell) resulting from air exposure to trace Ti^{III} formed during synthesis.
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