

The selective catalytic oxidation of silanes to silanols with H₂O₂ activated by the Ti-beta zeolite

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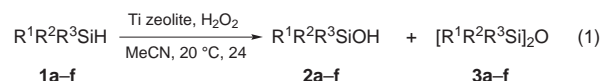
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Ti-beta catalyses the oxidation of small- and medium-sized silanes to the corresponding silanols by aqueous (30%) H₂O₂ as oxygen donor with high conversions and excellent selectivity (no disiloxane).

Although organosilanols have been of continual interest since their discovery,¹ only a limited number of methods for their selective preparation are available. Sterically exposed silanols are especially problematic as they readily dimerize with traces of acid or base to the disiloxanes. Therefore, the commonly used method, *i.e.* the hydrolysis of chlorosilanes,² is only applicable for sterically encumbered derivatives. Currently one of the best methods of making silanols is the oxidation of silanes with dioxiranes,³ but the disadvantage is that this reagent is used stoichiometrically. Catalytic Si–H insertions have also been reported for nickel, palladium, chromium, rhodium, and copper complexes,⁴ but these reactions are either limited to special substrates or produce disiloxanes in high amounts.

Recently we developed the first *selective* metal-catalysed Si–H insertion by using the methyltrioxorhenium/urea–H₂O₂ adduct (MTO/UHP) oxidant⁵ and proposed that the observed selectivity derives from oxidation in the urea channels (host–guest chemistry), which suppresses the subsequent dimerization of the silanol to the disiloxane. Since the redox molecular sieves TS-1 and Ti-beta are known to catalyse efficiently a variety of oxidations by H₂O₂,^{6–9} it was of interest to explore whether such Ti-doped zeolites could serve as catalyst as well as host for the selective oxyfunctionalisation of silanes without disiloxane

formation. Indeed, that this is the case is demonstrated herein for Ti-beta, which effectively catalyses the selective oxidation of silanes to silanols by H₂O₂. Most conveniently, our titanium zeolite-catalysed Si–H insertions [eqn. (1)] may be conducted at room temperature with H₂O₂, an environmentally benign oxygen source since its reduction product is water.



The Ti-beta samples used throughout this study were provided by Professor A. Corma, Valencia, Spain, with a Ti content of 2 wt% (as TiO₂) and an aluminium content of 0.29 wt%, and were cation-exchanged by 0.16 M aq. NaOAc. In a typical experiment, the substrate (*ca.* 330 μmol) was dissolved in 1 ml of MeCN, 1.1 equiv. of H₂O₂ (85% or 30% aq. solution) was added while stirring, followed by 30–50 mg of titanium catalyst. The slurry was stirred at ambient temperature (*ca.* 20 °C) for 24 h, subsequently the zeolite was removed by means of a membrane filter (millipore HV, 0.45 μm pore size) and washed three times with 2 ml of acetone. The product mixture was analysed by capillary gas chromatography (Fisons HRGC 5160 Mega Serie, 30-m HP-5 capillary column, FID) and the products were identified by comparing the GC retention times with authentic samples. Conversions and mass balances were calculated relative to an internal standard (Table 1).

Table 1 Conversions, mass balances and product selectivities of the oxidation of silanes **1** to silanols **2** by titanium catalysts

Entry	Substrate	Catalyst	Oxygen source	Conversion ^a (%)	Mass balance ^a (%)	Selectivity ^b 2:3
1	EtMe ₂ SiH 1a	Ti-beta	85% H ₂ O ₂	95	68	> 99:1
2	PrMe ₂ SiH 1b	Ti-beta	85% H ₂ O ₂	80	87	> 99:1
3	Bu ^t Me ₂ SiH 1c	Ti-beta	85% H ₂ O ₂	85	63	> 99:1
4	PhMe ₂ SiH 1d	TS-1	85% H ₂ O ₂	traces	86	> 99:1
5	PhMe ₂ SiH 1d	Ti-beta	85% H ₂ O ₂	58	> 99	> 99:1
6	PhMe ₂ SiH 1d	Ti-beta	30% H ₂ O ₂	61	> 99	> 99:1
7	PhMe ₂ SiH 1d	Ti-beta ^c	30% H ₂ O ₂	> 99	89	> 99:1
8	PhMe ₂ SiH 1d	Ti-beta (calc.)	85% H ₂ O ₂	48	72	59:41
9	PhMe ₂ SiH 1d	Ti-beta ^d	85% H ₂ O ₂	35	80	85:15
10	PhMe ₂ SiH 1d	Ti(OPr ⁱ) ₄ ^e	<i>t</i> BuOOH	38	74	39:61
11	Et ₃ SiH 1e	Ti-beta	85% H ₂ O ₂	74	71	> 99:1
12	Et ₃ SiH 1e	Ti-beta	30% H ₂ O ₂	75	74	> 99:1
13	(+)-Me(α-Np)PhSiH (<i>S</i>)- 1f	Ti-beta	85% H ₂ O ₂	—	> 99	—

^a Entries 1,2: determined by ¹H NMR spectroscopy directly on the crude reaction mixture, error ±5% of the stated values; entries 3–10: mass balances and conversions were determined by gas chromatography against an internal standard, error ±1% of the stated values; conditions for **2a**: 35 °C (8 min)→[30 °C min⁻¹]→100 °C (1 min)→[30 °C min⁻¹]→160 °C (2 min), flow 0.5 kg cm⁻², against toluene; for **2b**: 40 °C (7 min)→[30 °C min⁻¹]→100 °C (2 min)→[30 °C min⁻¹]→150 °C (5 min)→[30 °C min⁻¹]→240 °C (1 min), flow 0.5 kg cm⁻², against ethylbenzene; for **2c**: 35 °C (14 min)→[30 °C min⁻¹]→240 °C (5 min), flow 1.0 kg cm⁻², against toluene; for **2d**: 80 °C (4 min)→[30 °C min⁻¹]→130 °C (1 min)→[30 °C min⁻¹]→240 °C (1 min), flow 0.4 kg cm⁻², against *n*-hexadecane; for **2e**: 40 °C (3 min)→[30 °C min⁻¹]→100 °C (1 min)→[30 °C min⁻¹]→160 °C (1 min), flow 1.2 kg cm⁻², against *n*-dodecane; entry 13: determined by HPLC analysis with Chiralcel® OD-H column with *n*-hexane–PrⁱOH (9:1) as eluent and dimethyl isophthalate as internal standard, error ±2% of the stated value. ^b Selectivities were determined by gas chromatography under the conditions and with the internal standards specified in footnote *a*, error ±1% of the stated values. ^c Recycled catalyst. ^d Catalyst was stirred for 24 h with 1 equiv. H₂O₂ in MeCN and recycled as described. ^e In the presence of diethyl L-tartrate.

For our studies, two titanium-doped zeolites were used, namely TS-1 ($5.3 \times 5.6 \text{ \AA}$)¹⁰ and Ti-beta-Na ($6.4 \times 7.6 \text{ \AA}$).¹⁰ Control experiments showed that no reaction occurred in the absence of the titanium zeolite. This clearly indicates that the oxidative species requires the titanium metal for the activation of H₂O₂ and that direct oxidation of the silane by H₂O₂ does not take place. For comparison with a homogeneous Ti^{IV} catalyst, we employed the well-known Ti(OPrⁱ)₄/Bu^tOOH oxidant.

When Ti-beta was used as oxidation catalyst, good to excellent conversions of the silanes **1a–e** to the corresponding silanols **2a–e** were obtained (Table 1, entries 1–3, 5–7, 11, 12). In contrast, the conversion of the model substrate **1d** with the homogeneous system was lower by 20% (entry 10 compared to entries 5, 6). Notably, the silane **1f** is not oxidised because it is sterically too encumbered to enter the zeolite channels (entry 13). Steric hindrance is also the reason why the silane **1d** is not oxidised when the TS-1 zeolite is employed as catalyst (entry 4). The latter results provide unequivocal evidence that these oxidations take place inside the zeolite and not on the outer surface. In addition, if any oxidation of the silanes were to occur on the outer surface of the zeolite, significant amounts of the corresponding disiloxane products should have been formed, in analogy to the Si–H insertion in solution with Ti(OPrⁱ)₄/Bu^tOOH (entry 10).

A major advantage of the Ti-beta/oxidant system for the transformation of silanes to silanols is the fact that excellent product ratios of silanol *versus* disiloxane were obtained for all the silanes studied. This is in stark contrast to the silanol/disiloxane product distributions which have been observed in most previous studies.⁴ A further benefit is the fact that the 85% aq. H₂O₂ solution may be substituted by 35% aq. H₂O₂ solution without any loss of selectivity and reactivity (entry 5 *vs.* 6 and entry 11 *vs.* 12).

Since the inorganic framework of the zeolite is quite resistant to oxidative degradation, it was of interest to explore the possibility of catalyst recycling. Indeed, we found that the Ti-beta zeolite may be re-used several times by heating the filtered catalyst at 240 °C for several hours. Interestingly, the recycled catalyst showed even higher catalytic activity (entry 7). It is known that calcination reduces the coordination number of the lattice-bound titanium¹¹ from 5 or 6 to 4, and thus it seemed likely that the increase in activity is due to the loss of coordinated water; thus more activated sites for H₂O₂ are generated. However, an independently calcinated (*ca.* 500 °C) sample of Ti-beta did not show enhanced catalytic activity (entry 8); moreover, a lower silanol selectivity was observed (59:41). Furthermore, when a sample of Ti-beta was stirred in MeCN with 1 equiv. H₂O₂ for 24 h and recycled as described above, a moderate silanol selectivity (entry 9) was obtained. We propose that the increased catalytic activity is due to *in situ* silylation of free OH groups in the zeolite lattice. The beneficial effect of silylation on the enhancement of catalytic activity has previously been reported for Ti-MCM-41¹² and was assigned to a change to a less polar zeolite interior. The lower silanol selectivity in entries 8 and 9 might be caused by a higher zeolite acidity due to loss of coordination water on calcination, which would promote silanol dimerisation.

Recently, a peracid-type transition-state structure for the Ti-beta-catalysed epoxidation of chiral allylic alcohols with H₂O₂

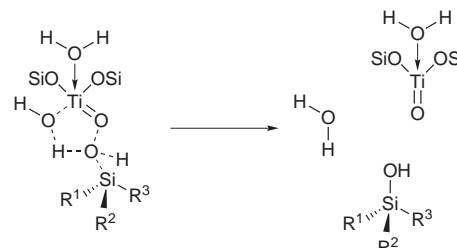


Fig. 1 Proposed transition-state structure for the titanium-catalysed Si–H oxidation.

has been assessed.⁸ In analogy, we propose also for the Si–H insertion a five-membered ring peracid-type geometry, as shown in Fig. 1.

In conclusion, the well-known Ti-beta/H₂O₂ oxidant is an excellent system for the catalytic conversion of silanes selectively into silanols. This catalytic oxidation takes place inside the zeolite channels and the observed selectivity (no disiloxane) is due to prevention of the dimerization of the silanol.

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