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# Oxidation of Benzene to Phenol with Hydrogen Peroxide Catalyzed by a Modified Titanium Silicalite (TS-1B)

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**Abstract:** The hydroxylation of benzene to phenol with hydrogen peroxide was investigated using different solvents and a series of catalysts, obtained by modification of titanium silicalite (TS-1). The best results were obtained after post-synthesis treatment of TS-1 with $NH_4HF_2$ and $H_2O_2$. The new catalyst (TS-1B), used in the presence of a particular co-solvent (sulfolane) is able to protect the produced phenol from over-oxidation and dramatically enhanced the selectivity of the reaction.

**Keywords:** hydrogen peroxide; hydroxylation; phenols; solvent effects; titanium; zeolites

## Introduction

Phenol is one of the most important intermediates of the chemical industry with a global production estimated at around 8 Mt/year, almost completely based upon the cumene process which also co-produces acetone. Since the expected market growth is much larger for phenol than for acetone, the development of a process based on the direct oxidation of benzene to phenol is an important goal in industrial organic chemistry. Unfortunately, the oxidation of benzene is usually affected by a poor selectivity due to the lack of kinetic control: indeed, phenol is more easily oxidized than benzene itself and substantial amounts of over-oxygenated by-products (catechol, hydroquinone, benzoquinones, and tars) also form. Moreover, only few oxidants are environmentally acceptable, the most promising among them appearing to be nitrous oxide (exploited in the Solutia process, based on catalysis by iron containing zeolites)[1] and hydrogen peroxide.

With the latter oxidant, remarkable results have been recently obtained by combining the use of a peculiar solvent (sulfolane) and a modified titanium silicalite (TS-1B) as the catalyst.[2] We now report full details about this new, acetone-free route to phenol and about the synthesis and the performance of the new catalyst.

## Results and Discussion

The aim of this work was the development of a selective method for the oxidation of benzene to phenol with hydrogen peroxide. In the first stage of the study, the hydroxylation of benzene was investigated using titanium silicalite (TS-1)[3] as the catalyst, on the basis of its well established efficiency in a series of oxidation processes with hydrogen peroxide, such as alkene epoxidation ,[4] alkane oxidation,[5] alcohol oxidation,[6] cyclohexanone ammoximation,[7] and phenol hydroxylation.[8]

The reactions were carried out either in a solvent-free medium (benzene/water),[9,10] or using different co-solvents in order to homogenize the hydrophobic substrate and the aqueous hydrogen peroxide in the liquid phase.

As shown in Table 1, the selectivity of the reaction was strongly affected by the nature of the solvent. In our hands, the selectivity of the reaction observed operating under the biphasic, solvent-free conditions was sensibly lower than that reported in the literature.[9] Namely, the selectivity to phenol (expressed as moles of produced phenol/moles of reacted benzene × 100) measured for 4.5 % and 15.1 % benzene conversions were 42 % and 24 %, respectively.

In the case of the most commonly used co-solvents (acetone, acetonitrile, methanol, *tert*-butyl alcohol and acetic acid) the selectivity to phenol (expressed as moles of produced phenol/moles of reacted benzene × 100) was lower than 50 % even at a benzene conver-

**Table 1.** Effect of the co-solvent on benzene oxidation.

| Co-solvent[a] | $H_2O_2$ conv. [%] | $H_2O_2$ sel. [%][b] | Benzene conv. [%] | Product selectivity [%][c] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | PH | CA | HY | BQ | TAR |
| none[d] | 100 | 20 | 4.5 | 42 | 14 | 17 | - | 27 |
| acetone | 90 | 19 | 4.2 | 41 | 13 | 12 | 4 | 30 |
| acetonitrile | 93 | 21 | 4.5 | 43 | 16 | 12 | 3 | 26 |
| methanol | 98 | 19 | 4.7 | 40 | 15 | 15 | 4 | 26 |
| *tert*-butyl alcohol | 90 | 20 | 4.1 | 44 | 8 | 10 | 3 | 35 |
| acetic acid | 85 | 30 | 5.1 | 50 | 16 | 11 | 11 | 12 |
| dimethylformamide | 100 | 3 | 0.3 | >99 | 0 | 0 | 0 | 0 |
| *N*-methylpyrrolidone | 12 | 6 | 0.1 | >99 | 0 | 0 | 0 | 0 |
| dimethylsulfone | 94 | 62 | 7.3 | 80 | 7 | 5 | 1 | 7 |
| sulfolane | 97 | 67 | 7.8 | 83 | 7 | 4 | 1 | 5 |

[a] *Reaction conditions:* benzene/co-solvent = 2/8 w/w, $H_2O_2$/benzene molar ratio = 0.1, TS-1/benzene = 0.1 w/w, temperature = 100 °C. PH = phenol, CA = catechol, HY = hydroquinone, BQ = benzoquinone.

[b] Moles of phenol/moles of reacted $H_2O_2 \times 100$.

[c] Moles of product/moles of reacted benzene × 100.

[d] *Reaction conditions:* benzene/water = 1/5 w/w, $H_2O_2$/benzene molar ratio = 0.1, TS-1/benzene = 0.15 w/w, temperature = 60 °C.[9]

sion lower than 5%, mainly due to the formation of dioxygenated products and tars.

Even worse results were obtained using nitrogen-containing solvents, such as dimethylformamide, that promotes the unproductive decomposition of hydrogen peroxide, and *N*-methylpyrrolidone, that depresses the catalytic activity of TS-1, affording only negligible yields to phenol.

Conversely, a dramatic improvement of selectivity was observed using co-solvents bearing a sulfone group, such as dimethyl sulfone and tetramethylene sulfone (sulfolane), which allowed a conversion of benzene close to 8% with a selectivity to phenol higher than 80%. In the case of sulfolane, the detected by-products were catechol (7%), hydroquinone (4%), 1,4-benzoquinone (1%), and only a small amount of tars (5%).

Sulfolane is a solvent with high dipole moment (4.81 Debye) and dielectric constant (43.26), showing the peculiar property of forming complexes with phenolic compounds.[11] These complexes are not stable enough to be isolated but have been identified in solution by IR spectroscopy.[12]

The increased selectivity observed running the benzene oxidation in sulfolane may be due to the formation of a sterically hindered species (Figure 1) which cannot enter the titanium silicalite pores, thus allowing phenol to remain relatively protected towards further oxidation.

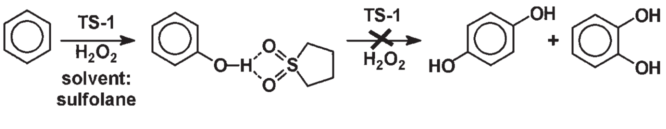

**Figure 1.** Protecting effect of sulfolane.

This effect was confirmed by the estimated loading of the free phenol molecule and the phenol-sulfolane complex (expressed as number of loaded molecules in a crystal elementary unit of TS-1), which turned out to be 13.6 and 0.8, respectively, calculated using the software 'Sorption' (Accelrys Inc., San Diego).

Additional evidence for the protective effect exerted by sulfolane was obtained by measuring the reaction rate, expressed as turn-over frequency (TOF: moles of reacted substrate/moles of Ti × hour) for the oxidation of benzene and phenol, carried out separately in acetone and sulfolane as co-solvents. As shown in Figure 2, in the case of acetone, the phenol oxidation rate (TOF = 190 hour$^{-1}$) was 10 times faster

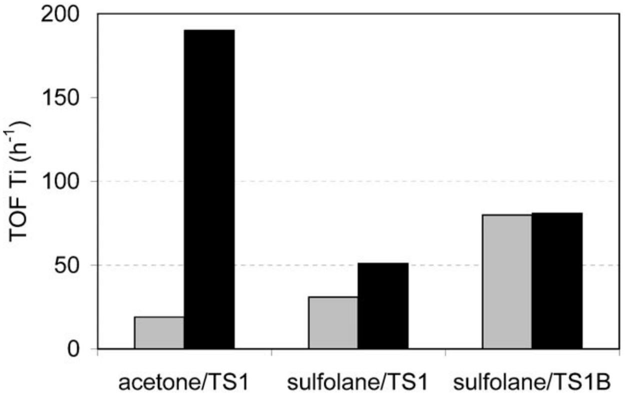

**Figure 2.** Oxidation rate of benzene and phenol. The oxidations of benzene and phenol were carried out separately using acetone and sulfolane as co-solvents and TS-1 ($TiO_2$ = 3.6% by weight) or TS-1B ($TiO_2$ = 0.9%, obtained from TS-1 by post-treatment with $(NH_4)HF_2$ and $H_2O_2$). (▨) TOF of Ti measured on benzene (moles of reacted benzene/moles of Ti × hour); (■) TOF of Ti measured on phenol (moles of reacted phenol/moles of Ti × hour)

with respect to that measured for benzene (TOF = 19 hour$^{-1}$). Conversely, operating in sulfolane the rate measured for phenol (TOF = 51 hour$^{-1}$) was only 1.6 time faster than that measured for benzene (TOF = 31 hour$^{-1}$), in agreement with the higher value of the observed selectivity.

Despite the improvement of the selectivity obtained by the solvent engineering, the overall performance of the reaction was still not suitable for the development of a new process for phenol production, mainly due to the low productivity and the conspicuous amount of by-products.

In particular, the formation of over-oxidation by-products, such as 1,4-benzoquinone and tars, suggests the possible presence of a heterogeneous population of catalytic sites on TS-1, differing in reactivity and selectivity.

In order to remove the less selective catalytic sites, a catalyst engineering study, based on post-synthesis treatments, was carried out on TS-1.

It has been reported that titanium atoms are not equally distributed in the 12 crystallographically independent sites of the MFI framework of TS-1, but are hosted in 4 preferential positions,[13] which, in principle, might display different catalytic properties.

Different titanium species can also have different structural properties, therefore they could be extracted from the zeolite framework at different rates. As listed in Table 2, several post-synthesis treatments of the catalyst were carried out in water suspension at 80 °C, using different methods.

The simple treatment with ammonium acetate, currently used to clean-up the catalyst,[14] did not promote any titanium leaching, with negligible change of the catalytic activity of TS-1, tested on benzene oxidation. Conversely, using ammonium bifluoride, the extraction of a small amount of titanium was detected, but, also in this case, with only a minor effect on the selectivity of the catalyst.

Further treatments were carried out under acidic conditions, in presence of hydrogen peroxide, in order to promote the extraction of titanium as a soluble peroxide species. The efficiency of the titanium removal was strongly dependent on the acid used for the treatment. The extraction was negligible (2%) with phosphoric acid, moderate (10%) with sulfuric acid and massive (close to 50%) with hydrofluoric acid.

In the case of sulfuric acid, some titanium was solubilized but no significant effects were observed on the performances of the resulting catalyst.

Conversely, using hydrofluoric acid, the modified TS-1 turned out to be a less selective catalyst than the starting material, with a drop of the selectivity based on hydrogen peroxide from 67 to 56%. This was probably due to a severe damage of the crystalline structure of the zeolite, after the aspecific removal of a consistent fraction of both silicon and titanium atoms, under the strong treatment conditions.

Operating under milder conditions, using ammonium fluoride as the fluorine source and hydrogen peroxide, the extraction of titanium was equally effective (46%), but, in this case, a dramatic enhancement of selectivity was observed. Even better results were obtained using ammonium bifluoride and hydrogen peroxide, with the selectivity based on benzene rising from 83 to 91% and that based on hydrogen peroxide from 67 to 80%.

The treatment carried out with ammonium bifluoride and hydrogen peroxide (F/Ti molar ratio = 7 and a $H_2O_2$/Ti molar ratio = 30) was highly selective in the removal of titanium atoms, leaving unchanged the crystalline structure of the zeolite. Up to 75% of titanium was extracted as $(NH_4)_3Ti(O_2)F_5$, as confirmed by UV-Vis, IR and Raman spectroscopy, in comparison with an authentic sample prepared as reported in the literature.[15] Only a negligible molar fraction of silica (1%) was removed as $(NH_4)_2SiF_6$.

**Table 2.** Post-synthesis modification of TS-1.

| Treatment[a] | $H_2O_2$ conv. [%][b] | $H_2O_2$ sel. [%][c] | Benzene conv. [%] | Product selectivity [%][d] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | PH | CA | HY | BQ | TAR |
| none | 97 | 67 | 7.8 | 83 | 7 | 4 | 1 | 5 |
| $(NH_4)OAc$ | 94 | 64 | 7.3 | 82 | 7 | 4 | 1 | 6 |
| $(NH_4)HF_2$ | 95 | 65 | 7.6 | 81 | 8 | 5 | 1 | 5 |
| $H_3PO_4/H_2O_2$ | 95 | 69 | 7.8 | 84 | 7 | 4 | 1 | 4 |
| $H_2SO_4/H_2O_2$ | 95 | 65 | 7.4 | 84 | 5 | 3 | 2 | 6 |
| $HF/H_2O_2$ | 96 | 56 | 6.7 | 80 | 6 | 3 | 4 | 7 |
| $(NH_4)F/H_2O_2$ | 98 | 77 | 8.4 | 90 | 6 | 3 | 0 | 1 |
| $(NH_4)HF_2/H_2O_2$ | 98 | 80 | 8.6 | 91 | 5 | 3 | 0 | 1 |

[a] The post-synthesis treatments of TS-1 were carried out as described in the experimental section.

[b] *Reaction conditions:* benzene/sulfolane = 2/8 w/w, $H_2O_2$/benzene molar ratio = 0.1, TS-1 (or modified TS-1)/benzene = 0,1 w/w, temperature = 100 °C. PH = phenol, CA = catechol, HY = hydroquinone, BQ = benzoquinone.

[c] Moles of phenol/moles of reacted $H_2O_2 \times 100$.

[d] Moles of product/moles of reacted benzene × 100.

As reported in Figure 3 the extent of titanium extraction in the treatment was tuned using different F/Ti molar ratios (moles of fluoride, added as ammonium bifluoride, versus moles of titanium present in the given sample).

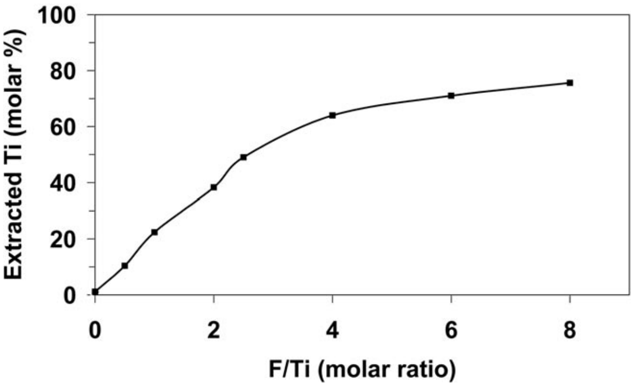

**Figure 3.** Post-synthesis modification of TS-1: extraction of titanium. The treatment of TS-1 ($TiO_2=3.6\%$ by weight) was carried out in aqueous solution using $(NH_4)HF_2$ (F/Ti molar ratio ranging from 0.5 to 8) and $H_2O_2$ ($H_2O_2$/Ti molar ratio = 30) at 80°C for 4 h. The F/Ti ratio is expressed as moles of fluoride, added as ammonium bifluoride, versus moles of titanium present in the given sample.

As reported in Figure 4, the selectivity of the catalyst modified with ammonium bifluoride and hydrogen peroxide, now named TS-1B, increased at lower residual titanium concentrations. After removal of 75% of the initial titanium, the selectivity to phenol raised up to 94%, with formation of catechol (4%), and hydroquinone (2%) as the only by-products, without any evidence for further oxidation reactions.

The activity of the catalyst was also affected by the treatment, and the TOF of the residual metal in the oxidation of benzene increased from 31 to 80 hour$^{-1}$, as shown in Figure 2.

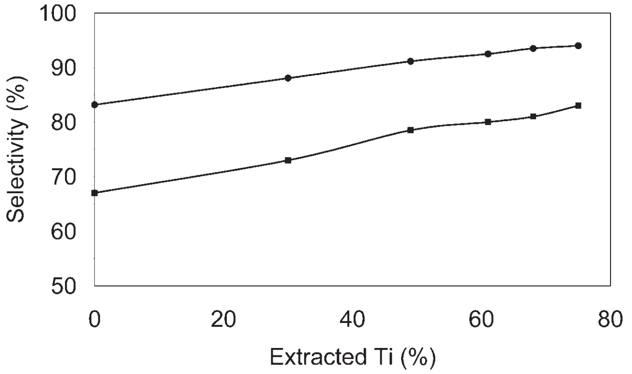

**Figure 4.** Effect titanium removal on the catalyst selectivity. (■) Selectivity based on $H_2O_2$; (●) selectivity based on benzene. The reactions were carried out as previously described in Table 2.

The TOF measured for the oxidation of phenol also increased, but to a lesser extent, from 51 to 81 hour$^{-1}$, according to the higher selectivity observed in the reaction.

The catalyst performances were strongly dependent on the temperature at which the treatment was carried out. As shown in Figure 5, a mild and selective removal of titanium, was achieved up to 80°C, conversely, at 90°C, the titanium sites were severely damaged and a sharp decrease of the catalytic activity was observed.

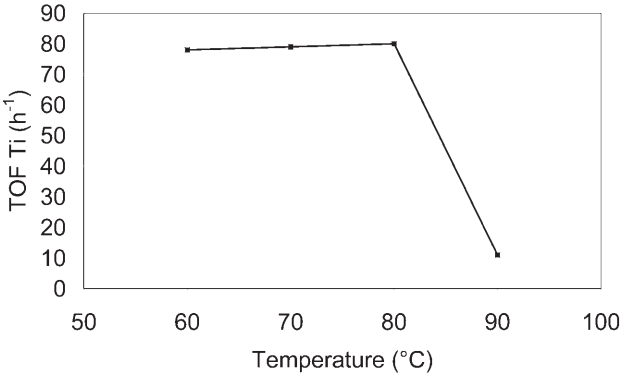

**Figure 5.** Effect of the post-synthesis treatment temperature on the catalytic performances of TS-1B. The treatment of TS-1 (initial Ti/Si molar ratio = 0.028) was carried out in aqueous solution using $(NH_4)HF_2$ and $H_2O_2$ (F/Ti molar ratio = 7 and $H_2O_2$/Ti molar ratio = 30) at different temperature. All the samples showed a similar extent of titanium leaching (75%) after 4 h, as determined by XRF analysis.

The catalytic properties of TS-1B ($TiO_2=0.97\%$) were compared with those of the starting TS-1 ($TiO_2=3.60\%$) and of an untreated TS-1 preparation with a similar titanium content ($TiO_2=0.93\%$). As shown in Figure 6, the reaction profiles obtained for

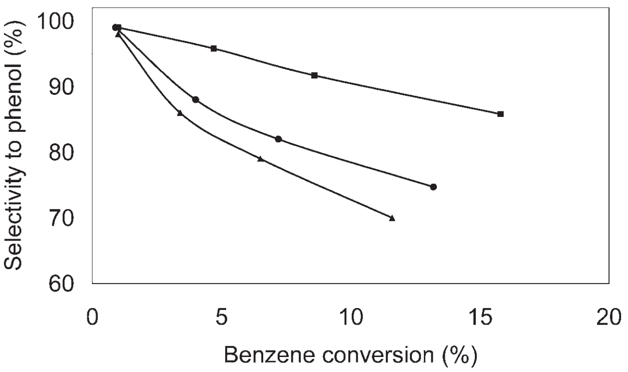

**Figure 6.** Effect of the catalyst modification on benzene oxidation. Reaction conditions for benzene oxidation: benzene/sulfolane = 2/8 w/w, catalyst/benzene = 0.1 w/w, temperature = 100°C. An aqueous solution of $H_2O_2$ (30% w/w) was gradually added. Catalysts: (●) TS-1 ($TiO_2=3.60\%$), (▲) TS-1 ($TiO_2=0.93\%$), (■) TS-1B ($TiO_2=0.97\%$).

benzene oxidation clearly demonstrate the superior performances of TS-1B in terms of selectivity, which became even more evident at higher benzene conversion.

The selectivity of the oxidation was not affected by the temperature, in the range from 80 to 100 °C while it started to decrease above 110 °C due to the unproductive decomposition of hydrogen peroxide to oxygen and water. Conversely, the catalytic activity of TS-1B sharply increased with the temperature, the TOF measured in the oxidation of benzene rising from 15 to 80 $h^{-1}$ on operating at 80 and 100 °C, respectively.

Some effort has been devoted to characterize the new catalyst, TS-1B, in comparison with samples of the parent TS-1, with different titanium loadings. The characterization studies were carried out using as starting material a well crystallized TS-1 sample with a lower titanium content with respect to the industrial catalyst (2.8 % *vs.* 3.6 %) bearing all the titanium atoms in the tetrahedral form.

The parent TS-1, with 2.8 % $TiO_2$, has been treated with ammonium bifluoride and hydrogen peroxide, stopping the reaction at different extents of titanium extraction, in order to obtain samples of TS-1B containing 2.4, 1.7, 1.4, 1.0, 0.9 and 0.8 % of residual $TiO_2$, respectively.

TS-1 and TS-1B samples have been characterized by *i*) DRS UV-Vis; *ii*) FT-IR; and *iii*) argon adsorption.

It is well known that the UV-Vis spectrum of TS-1 shows two important features.[16] One is the band near 50,000 $cm^{-1}$ ascribed to LMCT (ligand to metal charge transfer) of the tetrahedral Ti(IV) center and the other, which occurs at 30,000 $cm^{-1}$, is evidence of an impurity due to a colloidal or crystalline anatase $TiO_2$ phase.

In Figure 7 the spectra of a pure TS-1 (2.8 % $TiO_2$) and those of two samples of TS-1B with different residual titanium levels are compared. The treated samples show a new feature centered near 40,000 $cm^{-1}$ and evident erosion of the tetrahedral Ti(IV) absorption. The new species is consistent with a Ti center having an enlarged coordination sphere[17,18] but probably still isolated in the silicalite matrix while no aggregated $TiO_2$ species seem to be formed upon the treatment.

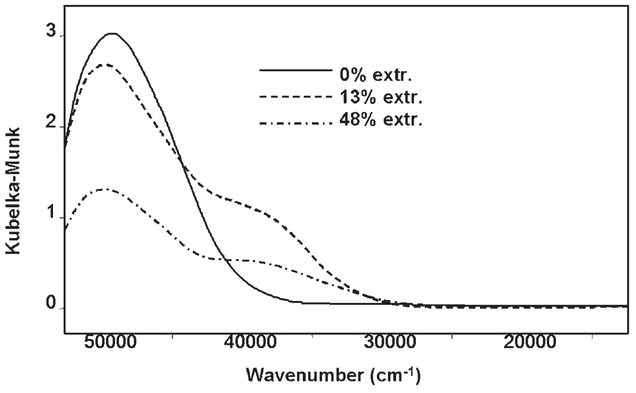

**Figure 7.** DRS UV-VIS spectra of TS-1 and TS-1B. TS-1 (Full line); TS-1B after extraction of 13 % of $TiO_2$ (dashed line); TS-1B after extraction of 48 % of $TiO_2$ (dot-dashed line).

The intensity of the 960 $cm^{-1}$ band in the FT-IR spectrum allows the quantitative estimation of the tetrahedral Ti sites by means of a suitable titration curve.[19] In Figure 8 we report the FT-IR spectra, in the range 1000–700 $cm^{-1}$, of the above mentioned samples of TS-1B at different extents of extraction together with the parent untreated sample. The label reported in the Figure identifies each sample according to the decreasing of the 960 $cm^{-1}$ band. All the spectra have been normalized on overtone absorption in the 1500–2100 $cm^{-1}$ range (not shown); the reliability of the normalization procedure is confirmed by the good superimposition of the 800 $cm^{-1}$ band which does not change its intensity and shape upon the treatment (although a minor emerging of a fine complex structure upon increasing the extent of extraction is visible).

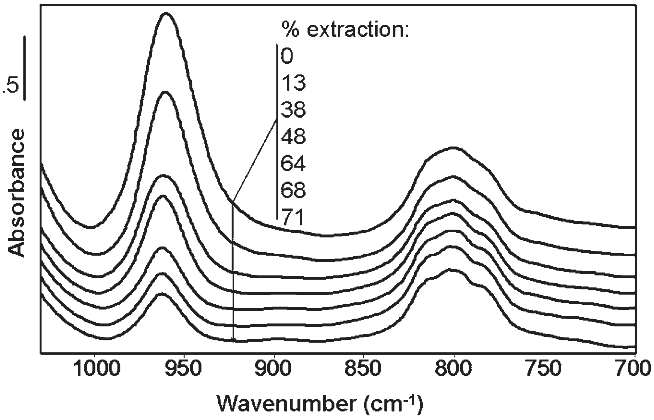

**Figure 8.** IR spectra of TS-1 and TS-1B. Ti extracted fraction increases from top to bottom. All spectra have been normalized on overtone absorption in the 1500–2100 $cm^{-1}$ range.

In Figure 9 we plot the results of the 960 $cm^{-1}$ band measurements of the TS-1B treated samples *vs.* titanium content (by XRF analysis) together with a series of samples of TS-1 at different Ti loadings (directly from synthesis) taken as reference. The two series fit two good straight line correlations but even if for the unextracted series (including the parent sample) the straight line passes through the origin, this is not the case for the line fitting the TS-1B extracted samples.

Figure 9 shows that, for the treated samples, the 960 $cm^{-1}$ band does not account for all analytical titanium. Therefore, a new species of titanium, which

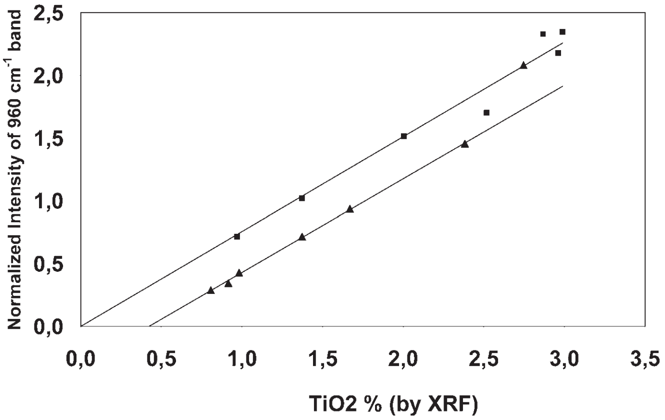

**Figure 9.** Estimation of tetrahedral Ti site concentration. IR 960 cm$^{-1}$ band measurement *vs.* analytical (XRF) Ti content for (■) samples at different Ti loading directly from the synthesis and (▲) TS-1B at different Ti residual concentration.

does not contribute to the intensity of the 960 cm$^{-1}$ band, and which may be tentatively associated to that found in UV-Vis spectra, must be present. Surprisingly, the two straight lines in Figure 8 run quite parallel indicating that the amount of the new species does not increase with the Ti extraction.

It is known that, in as-synthesized TS-1, the number of internal defects decreases upon increasing the titanium loading.[13] Conversely, in the case of TS-1B samples the number of silanols decreases with residual titanium content. In Figure 10 we report the same normalized spectra of Figure 8 plotting the OH stretching range from 3800 to 3000 cm$^{-1}$ in which both isolated and defective silanols (titanols) are known to absorb. A quantitative determination of defect concentration is not straightforward but it is evident from reported spectra that both isolated (3800–3650 cm$^{-1}$) and hydrogen bonded (3650–3000 cm$^{-1}$) defects decrease with increasing extent of extraction.

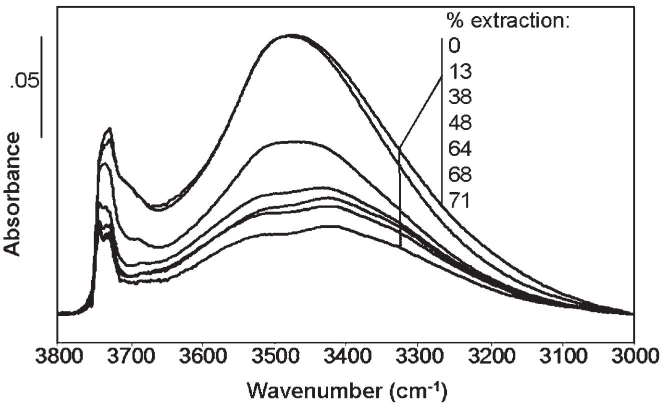

**Figure 10.** IR spectra in the OH stretching range. From top to bottom: Ti content as well as silanols defects decrease upon strengthening of the treatment.

In this way a low concentration of active sites is obtained in a structure with a very low concentration of defects, the latter being a property commonly associated with a high hydrophobic character of the catalytic materials.[20]

The low defects and titanium concentration reflect a very regular and highly ordered MFI structure. Despite the hydrolyzing treatment, leading to extraction of up to 70% of Ti atoms, the crystalline structure does not suffer any evident damage according to XRD and TEM characterization (XRD patterns and micrographs not shown for the sake of brevity). Moreover, an overall increase in surface homogeneity arises as a consequence of the treatment. In Ar adsorption isotherms (see Figure 11), a substep in the micropores filling region becomes more and more evident as a higher fraction of titanium is extracted. The parent TS-1 does not show this substep at all, the transition being masked by a broadening of the step along p/p$^0$. The treatment initially leads to a slight decrease in the adsorbed volume, probably reflecting a minor smoothing of the external surface (a decrease of micropore volume being unlikely). Then the substep appears and moves towards higher partial pressures as the strength of the treatment increases.

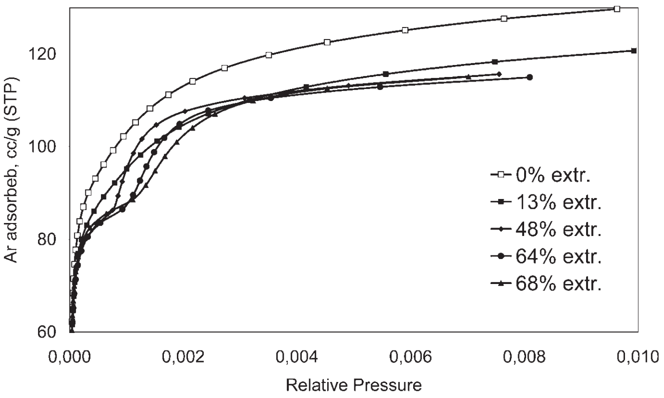

**Figure 11.** Ar adsorption at 87 K. Isotherms in the relative pressure range 0–1 × 10$^{-2}$ are reported for clarity, being the further adsorption up to p/p$^0$ = 1 almost negligible.

This is reminiscent of a well known effect,[21,22] typical of MFI structure. The features reported are very similar to those observed for ZSM5 at different Al content (Si/Al molar ratio from 20 to 10,000) and for dealuminated ZSM5. During the step, argon adsorbed in micropores undergoes a *fluid to crystalline-like* phase transition with a consequent density increase. The presence and the sharpness of the transition step reflect a high homogeneity of the surface which, in turn, points to a very low concentration of preferential and highly energetic adsorption sites.

In summary, we observed the appearance of a new titanium species, other than the former tetrahedral one, upon the treatment of TS-1 with ammonium bifluoride and hydrogen peroxide. This species is characterized by a larger coordination sphere and seems not to contribute to the characteristic vibrational feature at 960 cm$^{-1}$ in the IR spectrum of the TS-1. We do not know the actual role of this species as catalytic site but it cannot be excluded that it contributes, together with the modified surface property (lower defectivity and the consequent enhanced hydrophobicity), to the improved catalytic performances reported for TS-1B.

## Conclusions

The selective oxidation of benzene to phenol with hydrogen peroxide was achieved by using a peculiar cosolvent (sulfolane) and an improved zeolite catalyst (TS-1B), obtained by modification of titanium silicalite with $NH_4HF_2$ and $H_2O_2$.

In a further development study, the reaction was carried out under continuous operation, by using a continuous stirred-tank reactor (CSTR) equipped with filter, to maintain the catalyst inside the vessel. Running the process at 100 °C, only a negligible loss of catalytic activity was observed after 100 h of continuous operation.

The simplicity of this one-step process, the high selectivity achieved, and the demonstrated possibility of a continuous operation process in CSTR reactors, make this technology particularly attractive for industrial application.

## Experimental Section

### General Remarks

Titanium silicalites, with different titanium contents (3.60, 3.00, 2.80, 2.55, 2,00, 1,40 and 0.93 % w/w of $TiO_2$) were synthesized according to a literature procedure.[3] All other chemicals (Aldrich) were used as purchased.

The loading of the free phenol molecule and the complex phenol-sulfolane in the crystal elementary unit of TS-1 was calculated using the software 'Sorption' (Cerius 2, Accelrys Inc., San Diego).

FT-IR spectra have been recorded with a System 2000 Perkin–Elmer equipped with an MCT detector cooled at 77 K with liquid nitrogen on samples pressed in self supported pellets, and outgassed at room temperature up to $10^{-5}$ Torr. Ar adsorption measurements at 87 K have been carried out on an ASAP 2010 Micromeritics. DRS UV-Vis spectra have been recorded with a Lambda 5 Perkin–Elmer spectrophotometer equipped with reflectance sphere on powder samples previously outgassed at 100 °C up to $10^{-5}$ Torr.

HPLC analysis of the oxidation products were carried out using an RP-18 column (250 × 4 mm, from Merck) and a mixture of acetonitrile and 0.5 mM aqueous trifluoroacetic acid (46/54 v/v) as the eluent, with a flow rate of 1 mL min$^{-1}$. The UV detector was set at 212 nm (for phenol, catechol and hydroquinone) and 260 nm (for 1,4-benzoquinone).

### Preparation of TS-1B

Titanium silicalite TS-1 (10 g, containing 4.5 mmol of Ti, corresponding to 3.60 % w/w of $TiO_2$) was suspended in an aqueous solution (300 mL) containing $NH_4HF_2$ (0.9 g, 15.8 mmol, corresponding to a F/Ti molar ratio = 7) at 80 °C. A 30 % (w/w) aqueous solution of hydrogen peroxide (15.4 g, 135.5 mmol) was added in a single step and the suspension was mechanically stirred for 4 h, keeping the temperature at 80 °C. The mixture was then cooled at 25 °C and the catalyst filtered off and washed with 100 mL of water. The wet catalyst was dried at 100 °C and calcined in air at 550 °C for 4 h. The $TiO_2$ content of the modified titanium silicalite (TS-1B) was 0.9 % (w/w) as determined by XRF and ICP analysis, both the techniques giving fully comparable results.

### Preparation of TS-1B with Different Titanium Contents

Titanium silicalite TS-1 (10 g, containing 4.5 mmol of Ti, corresponding to 3.60 % w/w of $TiO_2$) was suspended in an aqueous solution (300 mL) containing different amounts of $NH_4HF_2$, ranging from 0.06 g, (1.13 mmol) to 1.0 g (18 mmol) corresponding to an F/Ti molar ratio from 0.5 to 8. A 30 % (w/w) aqueous solution of hydrogen peroxide (15.4 g, 135.5 mmol) was added in a single step and the suspension was mechanically stirred for 4 h, keeping the temperature at 80 °C. The samples were isolated and analyzed for the titanium content as described above. The titanium content of the resulting catalysts (expressed as % of $TiO_2$ by weight) is reported in brackets for each F/Ti ratio used in the treatment: F/Ti = 0.5 ($TiO_2$ = 3.2 %, corresponding to 10 % extraction), F/Ti = 1 ($TiO_2$ = 2.8 %, corresponding to 22 % extraction), F/Ti = 2 ($TiO_2$ = 2.2 %, corresponding to 38 % extraction), F/Ti = 2.5 ($TiO_2$ = 1.8 %, corresponding to 49 % extraction), F/Ti = 4 ($TiO_2$ = 1.3 %, corresponding to 64 % extraction), F/Ti = 6 ($TiO_2$ = 1.0 %, corresponding to 71 % extraction), F/Ti = 7 ($TiO_2$ = 0.9 %, corresponding to 75 % extraction).

### Other Post-Synthesis Modifications of Titanium Silicalite

Using the same procedure above described, TS-1 was treated at 80 °C for 4 h with the following methods:

*a) $(NH_4)OAc$ (18 mmol):* The resulting $TiO_2$ content of the modified catalyst was 3.60 % (w/w).

*b) (NH4)HF2 (18 mmol):* The resulting $TiO_2$ content of the modified catalyst was 3.20 % (w/w).

*c) $H_3PO_4$ (18 mmol) and $H_2O_2$ (67.5 mmol):* The resulting $TiO_2$ content of the modified catalyst was 3.53 % (w/w).

*d) $H_2SO_4$ (18 mmol) and $H_2O_2$ (67.5 mmol):* The resulting $TiO_2$ content of the modified catalyst was 3.24 % (w/w).

*e) HF (13.5 mmol) and $H_2O_2$ (67.5 mmol):* The resulting $TiO_2$ content of the modified catalyst was 1.87% (w/w).

*f) $(NH_4)F$ (13.5 mmol) and $H_2O_2$ (67.5 mmol):* The resulting $TiO_2$ content of the modified catalyst was 2.02% (w/w).

*g) $(NH_4)HF_2$ (13.5 mmol) and $H_2O_2$ (67.5 mmol):* The resulting $TiO_2$ content of the modified catalyst was 1.84% (w/w).

### Benzene Oxidation (Solvent Free)

Titanium silicalite (TS-1, 6 g) was suspended in a mixture of benzene (40 g, 512.8 mmol) and water (200 g) in a glass reactor at 60°C. Then, an aqueous solution of 30% w/w hydrogen peroxide (5.8 g, 51.3 mmol or 19.2 g, 170 mmol) was fed stepwise within 1 hour and the suspension stirred for an additional hour keeping the temperature at 60°C. At the end of the reaction, the hydrogen peroxide concentration was determined by titration with potassium permanganate and the oxidation products concentration was determined by HPLC analysis. The amount of tars was determined after separation of the products by silica gel chromatography, first eluting phenol, catechol and hydroquinone with ethyl acetate, then the tars with methanol.

### Benzene Oxidation (Co-solvent)

Titanium silicalite (either TS-1 or TS-1B, 5 g) was suspended in a solution of benzene (40 g, 512.8 mmol) and one of a co-solvent: acetone, acetonitrile, methanol, *tert*-butyl alcohol, acetic acid, dimethylformamide, *N*-methylpyrrolidone, dimethylsulfone or sulfolane (160 g). The suspension was charged into a stainless steel autoclave, and pressurized at 5 bar with nitrogen. Then, an aqueous solution of 30% w/w hydrogen peroxide (5.8 g, 51.3 mmol) was fed stepwise within 1 hour and the suspension stirred for an additional hour keeping the temperature at 100°C. At the end of the reaction, the hydrogen peroxide concentration was determined by titration with potassium permanganate and the oxidation products concentration was determined by HPLC analysis. The amount of tars was determined after separation of the products by silica gel chromatography, first eluting phenol, catechol and hydroquinone with ethyl acetate, then the tars with methanol.

### Turn-Over Frequency (TOF) Determination

The turn over frequency of the titanium was expressed as moles of reacted substrate/(moles of Ti × hour).

The TOFs were determined by carrying out the oxidation reactions as described above, but adding the total amount of hydrogen peroxide at the beginning of the reaction and stopping it (by filtering off the catalyst and fast cooling) at an oxidant conversion lower than 20%.

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