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Oxidation of Benzene to Phenol

Direct Oxidation of Benzene to Phenol with Hydrogen Peroxide over a Modified Titanium Silicalite

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Phenol is one of the most important intermediates of the chemical industry. Nearly all its current production is based upon the cumene process, which also represents the most important route to acetone, coproduced in 1:1 molar ratio with respect to phenol. However, as the expected market growth is quite different for phenol and acetone, much effort is currently being devoted to decouple their productions. In this context, a long-standing goal is the development of an effective process for the direct oxidation of benzene to phenol with hydrogen peroxide. This reaction, however, is often affected by a poor selectivity, due to the lack of kinetic control. Indeed, phenol is more reactive toward oxidation than benzene itself, and substantial formation of over-oxygenated by-products (catechol, hydroquinone, benzoquinones, and tars) usually occurs.[1]

In our continuing effort aimed at discovering new processes for a one-step, by-product-free synthesis of phenol,[2] we report herein that by combining a suitable solvent and a modified titanium silicalite catalyst (TS-1B), satisfactory selectivities and yields can be achieved in the direct oxidation of benzene to phenol with hydrogen peroxide.

In the first stage of this study, the hydroxylation of benzene was investigated by 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 alkenes epoxidation,[4] alkanes oxidation,[5] alcohol oxidation,[6] cyclohexanone ammoximation,[7] and phenol hydroxylation.[8] The reactions were carried out with different cosolvents to homogenize the hydrophobic substrate and the aqueous hydrogen peroxide in the liquid phase.

As expected, the selectivity to phenol (expressed as moles of produced phenol/moles of reacted benzene × 100) rapidly dropped when with conventional solvents such as acetone, acetonitrile, and *tert*-butanol, even at low benzene conversion (Figure 1). With these solvents, under the reaction conditions described in Table 1 (H_2O_2/benzene molar ratio = 0.1), the selectivity based on benzene was lower than 50% with a selectivity based on hydrogen peroxide (expressed as moles of produced phenol/moles of reacted $H_2O_2 \times 100$) lower than

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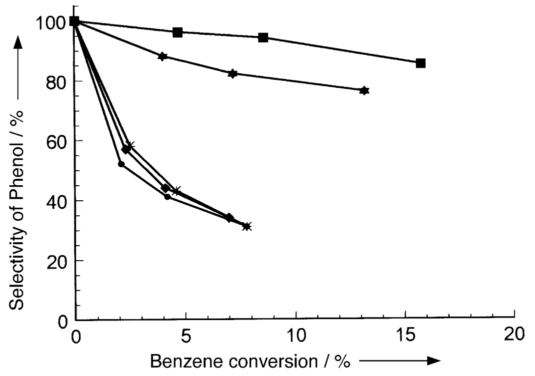


Figure 1. Effect of the solvent on benzene oxidation. (●) acetone, (*) acetonitrile, (◆) *tert*-butanol, (✱) sulfolane, (■) sulfolane/TS-1B. Reaction conditions: benzene/solvent = 2/8 w/w, TS-1/benzene = 0.1 w/w, temperature = 100 °C. An aqueous solution of H_2O_2 (30% w/w) was gradually added in 2 h up to a hydrogen peroxide/benzene molar ratio = 0.2.

Table 1: Effect of the solvent and the catalyst treatment on benzene oxidation.

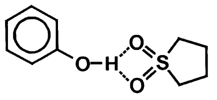
	Solvent[a]	Benzene	H_2O_2	Selectivity to phenol	
		Conversion [%]	Conversion [%]	based on benzene[b]	based on H_2O_2[c]
1	acetone	4.2	90	41	19
2	acetonitrile	4.6	93	43	21
3	*tert*-butanol	4.1	90	44	20
4	sulfolane	7.8	97	83	67
5	sulfolane/ TS-1B[d]	8.6	97	94	83

[a] Reaction conditions: benzene/solvent = 2:8 w/w, H_2O_2/benzene molar ratio = 0.1, TS-1/benzene = 0.1:1 w/w, temperature = 100 °C. [b] Moles of phenol/moles of reacted benzene × 100. [c] Moles of phenol/moles of reacted H_2O_2 × 100. [d] Reaction carried out using the TS-1B (TS-1 modified with NH_4HF_2 and H_2O_2).

20%, mainly owing to the formation of dioxygenated products and tars. Even worse results were obtained with methanol and 2-propanol, which were oxidized in competition with benzene to give formaldehyde dimethyl acetal and acetone, respectively, or with nitrogen-containing solvents (dimethylformamide and *N*-methylpyrrolidone) the reaction afforded only negligible yields of phenol.

Conversely, as shown in Figure 1, a dramatic improvement of selectivity was observed by using tetrametilene sulfone (sulfolane) as a cosolvent, which allowed a conversion of benzene close to 8% with a selectivity of phenol higher than 80% (Table 1, entry 4). In this case the detected by-products were catechol (7%), hydroquinone (4%), 1,4-benzoquinone (1%), and tars (5%).

Sulfolane is a solvent with high dipole moment (4.81 debye) and dielectric constant (43.26), thus having the peculiar property of being able to form complexes with phenolic compounds. These complexes are not stable enough to be isolated but were identified in solution by IR spectroscopy.[9] In the case of phenol, the formation of the complex **1** was reported.[10]



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The increased selectivity observed by performing the benzene oxidation in sulfolane may be due to the formation of this sterically hindered species, which can not enter the titanium silicalite pores, thus allowing phenol to remain relatively protected towards further oxidation.[11] This effect was confirmed by calculating the 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), by using the program Sorption,[15] which turned out to be 13.6 for phenol and 0.8 for the phenol–sulfolane complex.

The protective effect exerted by sulfolane can be also evaluated by measuring the reaction rate, expressed as turnover 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 cosolvents. In the case of acetone, the phenol oxidation rate (TOF = 190) was ten times faster with respect to that measured for benzene (TOF = 19), conversely, when the reaction was performed in sulfolane the rate measured for phenol (TOF = 51) was only 1.6 times faster than that measured for benzene (TOF = 31), according to the higher value of the observed selectivity. However, 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, which differ in reactivity and shape-selectivity and some of these are accessible to sterically hindered catechol and hydroquinone. It was 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 four preferential positions[12] which, in principle, might display different catalytic properties.

With the aim to remove the less selective catalytic sites, we studied a new post-synthesis treatment of TS-1. What we found was a method that can remove selectively a fraction of titanium atoms leaving unchanged the crystalline structure of the zeolite. The treatment was carried out at 80 °C in an aqueous solution of NH_4HF_2 and H_2O_2 with a F/Ti molar ratios = 7 and a H_2O_2/Ti molar ratios = 30. In these conditions up to 75% of titanium was removed as $(NH_4)_3TiF_5O_2$, as confirmed by UV/Vis, IR, and Raman spectroscopy. Only a negligible fraction of silica (1%) was removed as $(NH_4)_2SiF_6$. As shown in Figure 2, both the catalytic activity and the selectivity of the modified catalyst increased at lower residual titanium concentration. After removal of 75% of the initial titanium, the TOF of the residual metal, measured for the oxidation of benzene, increased from 31 to 80, while the selectivity to phenol was raised from 83 to 94% (Table 1, entry 5), with formation of catechol (4%), and hydroquinone (2%) as the only by-products, without any evidence of further oxidation reactions.

A preliminary characterization of the modified catalyst (residual titanium = 29%), carried out by UV/Vis spectroscopy[13] (Figure 3), showed: a) the titanium atoms that had a tetrahedral coordination environment, $[Ti(OSi)_4]$, and absorbed at 48000–50000 cm^{-1} (as the majority of atoms present in the starting TS-1), were almost completely removed; b) the

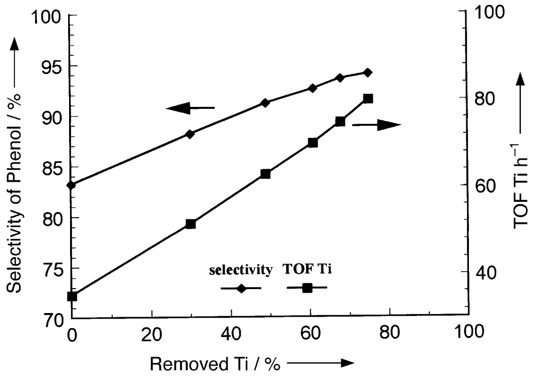

Figure 2. Effect titanium removal on the catalyst activity and selectivity. (◆) Selectivity to phenol = moles of phenol/moles of reacted benzene × 100 (■) TOF Ti = moles of reacted benzene/moles of Ti × hour. The reactions were carried out as previously described in Figure 1.

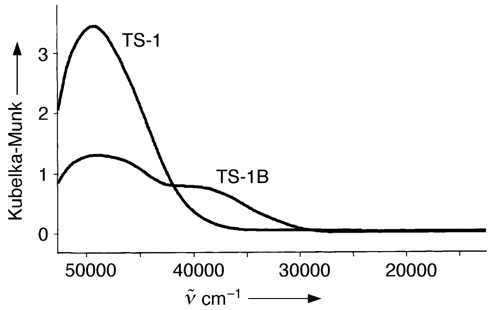

Figure 3. UV/Vis DRS (Diffuse Reflectance Spectroscopy) of TS-1 and TS-1 B. Spectra were recorded starting from on a TS-1 sample containing 2.8% w/w of TiO_2, totally free of amorphous extraframework titanium. After the treatment, the TiO_2 content of the resulting TS-1 B was reduced to 0.8%.

formation of amorphous extraframework titanium species (TiO_2) that absorbed at 30000–35000 cm^{-1} was not observed; c) a new titanium species that absorbed at 40000 cm^{-1} was generated by the treatment.

After the treatment, titanium atoms in tetrahedral coordination decreased by 87%, as quantitatively determined by IR spectroscopy (960 cm^{-1} band):[14] 71% of them were removed and the remaining 16% transformed in the new species. The formation of this new species, the characterization of which is currently in progress, makes the treated catalyst a completely new material, now named TS-1 B, with respect to the starting TS-1, and can explain the different catalytic properties, such as the increased activity, that cannot be a consequence of the simple removal of the titanium sites with low shape selectivity.

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

In conclusion, the simplicity of this one-step process, the high selectivity value achieved, and the demonstrated possibility of a continuous operation process in CSTR reactors, make this methodology particularly attractive for a possible industrial development.

Experimental Section

Titanium silicalite containing 3.6% (w/w) of TiO_2 was synthesised according to a literature procedure.[3] All other chemicals (Aldrich) were used as purchased.

Postsynthesis modification of titanium silicalite: Titanium silicalite (10 g, containing 4.5 mmol of Ti, corresponding to 3.6% w/w of TiO_2) was suspended in an aqueous solution (300 mL) containing NH_4HF_2 (0.9 g, 15.8 mmol) at 80 °C. A 30% (w/w) aqueous solution of hydrogen peroxide (15.4 g, 135.5 mmol) was added and the suspension was mechanically stirred for 4 h. 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 calcinated in air at 550 °C for 4 h. The TiO_2 content of the modified titanium silicalite (TS-1B) was 0.9% (w/w) determined by XRF and ICP analysis.

Benzene oxidation (general procedure): Titanium silicalite (either TS-1 or TS-1 B, 5 g) was suspended in a solution of benzene (40 g, 512.8 mmol) and one of a cosolvent (acetone, acetonitrile, *tert*-butanol, sulfolane; 160 g). The suspension was added into a stainless steel autoclave, and pressurised 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 one hour under mechanical stirring, while the reaction was kept at 100 °C. At the end of the reaction, the hydrogen peroxide concentration in the aqueous phase was determined by titration with potassium permanganate and the oxidation products concentration in both the aqueous and organic phases was determined by HPLC analysis.

TOF determination: The initial turn over frequency of the titanium was expressed as moles of reacted substrate/(moles of Ti × hour). The TOF were determined carrying out the oxidation reactions as described above, but the total amount of hydrogen peroxide was added at the beginning of the reaction and the reaction was stopped (by filtering off the catalyst and fast cooling) at an oxidant conversion lower that 20%.

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