



Marco Ricci
Eni SpA
Divisione Refining & Marketing
Centro Ricerche Novara
"Istituto Guido Donegani"

SELECTIVE OXIDATION AN INDUSTRIAL PERSPECTIVE

Selective oxidations of organic functional groups are basic to preparative organic chemistry. They find widespread use both in research laboratories and in the industrial manufacture of fine chemicals and large-volume petrochemicals.

During the development of an oxidation reaction in view of its possible industrial application, a number of issues should be kept in mind which are often neglected when working on the laboratory scale. They include: the availability of both the oxidant and the raw material; pros and cons of heterogeneous and homogeneous catalysis; and issues such as conversion, selectivity, and productivity. Recent efforts towards the development of an industrial process for the direct oxidation of benzene to phenol provide a perfect frame to show the importance of several of these topics.

Phenol is one of the most important intermediates of the chemical industry. Its current production, around 8×10^6 t/y, is almost completely based upon the cumene process, which also represents

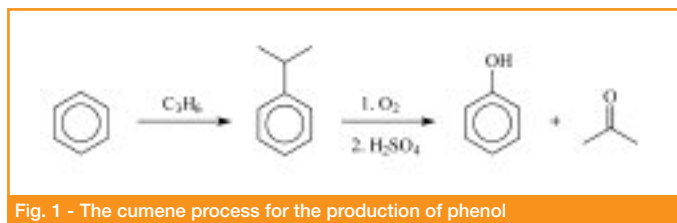


Fig. 1 - The cumene process for the production of phenol

the most important route to acetone, co-produced in 1:1 molar ratio with respect to phenol. 1:1 molar ratio means, in this case, that 0,6 t of acetone are coproduced per each t of phenol (Fig. 1). However, the expected market growth is quite different for phenol and acetone. This forecast is mainly based on two facts:

- on one side, all volatile organic compounds (including acetone) are subjected to a strong environmental pressure urging for their substitution in the medium term;
- on the other side, the main current use of phenol is in polycarbonate synthesis, which does not actually require phenol itself but rather Bisphenol A. Now, to produce Bisphenol A, you need both phenol and acetone but just one mole of acetone is required per two moles of phenol so that, again, there is a disequilibrium between their consumption.

For these reasons, much effort is currently being devoted to decouple phenol and acetone productions and, particularly, to develop an effective process for the direct oxidation of benzene to phenol.

A first answer to this problem is the Solutia process, discovered by Panov and coworkers at the Boreskov Institute of Catalysis in Novosibirsk and then developed in close cooperation with Monsanto. In this process, the oxidant is nitrous oxide, N_2O , while an iron-containing zeolite is used as the catalyst (Fig. 2).

The reaction is run at 350 °C and, at 27% of benzene conversion, selectivity on phenol can attain an astonishing 98%. Nevertheless, it seems unlikely that this process can become a major source of phenol, since nitrous oxide availability is quite limited and its production on-purpose (for instance, by pyrolysis of ammonium nitrate or by selective oxidation of ammonia) would result too expensive. So, the only reasonable scenario to exploit the Solutia process is its implementation close to adipic acid plants, where nitrous oxide is co-produced by the nitric oxidation of cyclohexanol/cyclohexanone mixtures and where it could be used to produce phenol instead of being disposed off.

A promising alternative to nitrous oxide is provided by hydrogen peroxide, which is finding more and more success due to the lack of environmental impact of its use and to its easy storage and handling. This is why Polimeri Europa started, several years ago, a long term project aimed at developing the use of hydro-

gen peroxide in the direct oxidation of benzene to phenol with both homogeneous and heterogeneous catalysts (Fig. 3).

In the first case, soluble iron complexes were used under biphasic conditions, whereas titanium-containing zeolites were selected as heterogeneous catalysts.

A biphasic Fenton reagent

The direct oxidation of benzene to phenol is often affected by a poor selectivity, due to the lack of kinetic control. Indeed, phenol is more reactive toward oxidation than benzene itself, so that consecutive reactions occur with substantial formation of over-oxidised products like catechol, hydroquinone, benzoquinones, and tars.

Similar over-oxidation problems are efficiently solved in biological systems by segregating catalysts and products into different environments. So, for instance, the active sites of several oxygenases are deeply buried into hydrophobic pockets where lipophilic substrates are readily oxidised, while the more hydrophilic reaction products are promptly released into the surrounding aqueous environment and do not have further access to the catalytic site.

So, we wondered whether a simple biphasic system could mimic these important feature of biological systems and looked for a reaction medium formed by an aqueous phase containing the catalyst and an organic one able to dissolve most of the produced phenol.

We started our experiments with a conventional Fenton catalyst such as iron sulphate. As expected, the use of an aqueous/organic reaction medium dramatically affected the selectivity of the reaction and, particularly, a remarkable enhancement was obtained using a biphasic system generated by water and acetonitrile (volume ratio = 1:1) in the presence of benzene. With this particular medium the concentration of benzene in the aqueous phase raised from 0.18% (solubility of benzene in water) to 0.76% and the produced phenol was extracted for the most part (85%) in the organic phase. In this way, the biphasic operation minimises the over-oxidation reactions by reducing the contact between the phenol and the catalyst, which is soluble in the aqueous phase.

To improve the performances of the catalytic systems, however, it

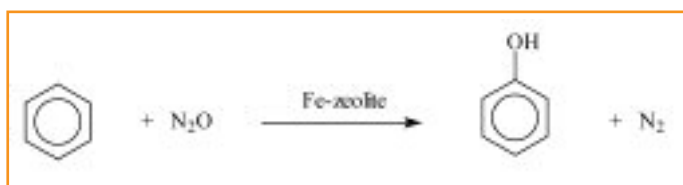


Fig. 2 - The Solutia process

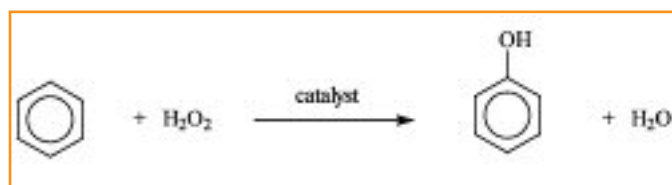


Fig. 3 - Direct oxidation of benzene to phenol with hydrogen peroxide

was necessary to add a ligand. Again, we tried a large number of them and, eventually, we got the best results with a couple of derivatives of pyrazinecarboxylic acid. Particularly, 2-methylpyrazine-5-carboxylic acid N-oxide, but also the corresponding ligand without the methyl group (pyrazine-3-carboxylic acid N-oxide), turned out to be the most efficient catalyst precursors (Fig. 4).

Using FeSO_4 , the selected ligand and trifluoroacetic acid, in the water/acetonitrile/benzene biphasic system, after the optimization of the reaction conditions, it was possible to achieve a benzene conversion of 8.6% with selectivities of 97% (based on benzene) and 88% (based on H_2O_2). These values are definitely higher than those described in literature for a classical Fenton system, whereas iron complexes with pyridine-2-carboxylic acid derivatives are reported to be completely ineffective in the oxidation of benzene under the Gif reaction conditions.

The attained conversion is a very low value, but it must be compared with the current benzene conversion in the cumene process, which is a two-steps process. In the first reaction, benzene is reacted with propylene to get cumene which, in the second step, is oxidised with oxygen to get both phenol and acetone. In the first reaction, usual conversion is 15% in order to avoid polyalkylation and, in the oxidation reaction, conversion is not higher than 37% in order to keep a safe concentration of the intermediate cumene hydroperoxide. So, benzene conversion is never higher than 8,5% and, most often, is around 6%, a value which is, indeed, lower than those obtained in the direct oxidation.

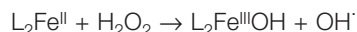
It must be noted that toluene (and ethylbenzene and tert-butylbenzene as well) turned out to be less reactive than benzene, which is not consistent with the expected order in electrophilic aromatic substitutions. And there are other differences with respect to the classic Fenton reagent. As already stated, under biphasic conditions the reaction is definitely more selective than a classic Fenton system: although comparisons are difficult due to the huge amount of data, sometimes inconsistent, on the Fenton system, with most of the data obtained with the iron used in stoichiometric amounts, it seems that selectivities close to those observed under biphasic conditions are only attained at conversion around 1%.

Furthermore, in the biphasic system, only a negligible amount (<1%) of biphenyl was detected among secondary products whereas, in the classic Fenton oxidation, this compound is formed by radical dimerization of

hydroxycyclohexadienyl radicals with typical yields of 8 to 39%.

So, should we need to think that a different mechanism is operative under biphasic conditions?

Although detailed mechanistic information is not currently available, the reaction is likely to start with the oxidation of Fe(II) to Fe(III) :



Thus, it is also likely that hydroxyl radicals are present in the reaction mixture where they probably act as oxidizing agents according to the overwhelmingly established Fenton radical mechanism and differences could simply arise due to the peculiar biphasic system (for instance, toluene is less soluble than benzene in the aqueous phase, in which the reaction takes place, and this could help to explain its lower reaction rate). Alternatively, these differences might be the result of a competition with a second mechanism. Following a number of recent suggestions, the new mechanism could be triggered by the formation of a Fe(III) hydroperoxo species which could undergo heterolytic cleavage to afford an electrophilic, high-valent iron-oxo complex, stabilized by the ligand, able to oxidize aromatic hydrocarbons to phenols.

Heterogeneous catalysis by titanium silicalite

The process based on the soluble iron-based catalyst is affected by a low volume productivity, measured as the amount of produced phenol in a fixed time per liter of reactor volume. This is a common weakness of homogeneous catalysts versus heterogeneous ones. So, we turned our attention towards a more promising heterogeneous catalyst: titanium silicalite, or TS-1, discovered in 1979 in the laboratories of the Eni group in San Donato Milanese (the relevant patent was filled on December 21, 1979). TS-1 is a synthetic zeolite with the MFI structure, the same of the better known ZSM 5 zeolite and of the natural counterpart of these synthetic zeolites: mutinaite, from the latin name of Modena, the ancient Mùtina, a nice Italian city in with an excellent research tradition about zeolites. It should be noted that mutinaite was discovered in Antarctica, only 20 years after the first synthesis of TS-1.

Soon after its discovery, TS-1 (with its channels with a diameter of 5.6 Å) was recognised to be a valuable catalyst for many oxidations by hydrogen peroxide, including alkanes oxidation, olefins epoxidation, alcohol oxidation, phenol hydroxylation, and cyclohexanone ammoxidation.

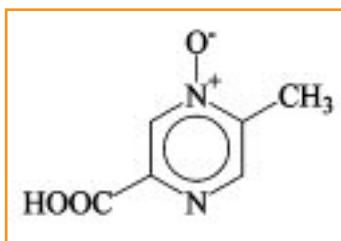


Fig. 4 - 2-Methylpyrazine-5 carboxylic acid N-oxide

So, we decided to explore its potential as a benzene oxidation catalyst. We started our research looking for co-solvents able to

homogenize the hydrophobic substrate and the aqueous hydrogen peroxide. As expected, with conventional solvents such as acetone, acetonitrile and tert-butanol, the selectivity to phenol rapidly dropped, even at low benzene conversion, mainly due to the formation of dioxygenated products and tars. Even worse results were obtained using methanol, which was oxidized in competition with benzene to give formaldehyde dimethyl acetal. Conversely, a dramatic improvement of selectivity was observed using sulfolane as a co-solvent, which allowed a conversion of benzene close to 8% with a selectivity to phenol higher than 80%. In this case the detected byproducts were catechol (7%), hydroquinone (4%), 1,4-benzoquinone (1%), and tars (5%). Why sulfolane, and only sulfolane, is so effective in improving selectivities?

Already in 1963, Drago suggested that sulfolane forms, via hydrogen bond, complexes with phenol. These complexes are not stable enough to be isolated but their occurrence was inferred by the IR spectra of the solutions. DFT ab initio method confirm the Drago finding that sulfolane and phenol should form a complex, and that its possible structure is exactly that imagined by Drago. So, the improved selectivity observed running the benzene oxidation in sulfolane may be due to the formation of this large species, which can not enter the titanium-silicalite pores, thus allowing

phenol to remain relatively protected towards further oxidation. The selectivity, still relatively low, exhibited by the TS-1 may suggest the presence of a heterogeneous population of catalytic sites. With the hope to remove some poorly selective catalytic sites, a number of post-synthesis treatments of TS-1 have been evaluated, but just one of them turned out to be effective. So, treating TS-1 with both hydrogen peroxide and ammonium hydrogen fluoride, a substantial amount of titanium (up to 75% of the initial value) is removed. Nevertheless, the crystalline structure of the zeolite remains unchanged and the catalytic activity does not decrease. On the contrary, it actually increases since the turn-over frequency of residual titanium atoms rises from 31 to 80 h⁻¹. Even more important, the selectivities, both on benzene and on hydrogen peroxide, also increase from 83 to 94%, with formation of catechol (4%), and hydroquinone (2%) as the only byproducts, without any evidence of further oxidation reactions.

A preliminary characterization of TS-1 B (residual titanium = 29%) showed that it has a peculiar UV-vis spectrum. Particularly, absorption at 48,000-50,000 cm⁻¹ (typical of pure TS-1) was strongly reduced and a new titanium species, absorbing at 40,000 cm⁻¹, was generated by the treatment. The formation of amorphous extraframework titanium species (TiO₂), absorbing at 30,000-35,000 cm⁻¹, was not observed.

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