

Aromatics processing and zeolite catalysis: the phenol production case

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Introduction of zeolite catalysts in the industrial treatment/productions of aromatics is a very nice example of Energy/Raw material/Emissions saves by improved and efficient technologies.

Aromatic alkylation, transalkylation and disproportionation are key processes for Refinery and Petrochemistry that has been strongly improved in the last decades, in term of yield - catalyst life - byproducts - etc., by using zeolite based catalysts and materials in their acido/base configuration.

In recent years processes for aromatic valorization are looking to take advantages from Zeolite/Zeotype materials by using redox approaches.

Phenol industrial production is a very intriguing example useful to high light the fascinating world of zeolite based catalysis, red-ox and acido-base.

Phenol, an intermediate product used in several industrial sectors such as production of phenolic resins - fibres - detergents, etc., is produced, on an industrial scale, through a multi-step process which starts from benzene and propylene, by alkylation with acid catalysts, and leads, via cumene hydroperoxyde (CHP), to the co-formation of phenol and acetone (1:1 mol.).

Benzene alkylation to cumene industrial process has been improved, in term of yield - catalyst life - byproducts - etc., at the end of last century, by changing the catalyst from older SPA (phosphoric acid on silica) to zeolite based ones¹. Cumene product purity higher than 99.9%wt, no acid leaching, negligible bromine index (no clay treatments for finished cumene), less maintenance costs, no spent SPA acid disposal are only few improvement of zeolite based catalyst (e.g PBE-1) respect to the use of classic SPA catalyst².

At least in the short term is forecasted that acetone will have to continue to make positive contributions to the phenol product chain. Anyway it's important to consider that Cumene to phenol process, via CHP, which accounts for more than 90% of worldwide phenol (about 8 million tons), and leads to the co-production of acetone, is expected to suffer an economic drawback due to acetone slower market growth, with respect to phenol, in the medium-long term. Researches are therefore being actively carried out for an alternative commercial process.

Production of phenol using co-produced acetone, from propylene via dehydration of intermediate isopropanol, via propanol alkylation or using acetone with reducing and alkylating catalysts, are under industrial development³.

Use of zeolites in R&D approaches, not involving new pathways but improvements of existing industrial route, can be considered in CHP acid cleavage stage (zeolites seems to be active catalysts for the reaction, however some doubt are concerning their selectivity)⁴ and tar/heavies cracking (sometimes introduced to further yields increase by recovery of phenol, AMS and cumene).

From the redox side a mention is due for processes based on N₂O and H₂O₂.

In a very elegant one step gas-phase process (Alphox) originally proposed by Panov et al.⁵, phenol is directly produced from benzene and nitrous oxide N₂O on an Iron containing zeolite catalyst.

Oxidation of benzene to phenol by hydrogen peroxide, was made possible using suitable Titanium containing zeolite-like based catalytic systems (e.g. TS-1)⁶.

Direct oxidation of benzene to phenol still remains a major research target as a potential technological advancement that could redefine the landscape of phenol production.

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