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Polymer Supported VO^{2+} Schiff Base Catalyst for Hydroxylation of Benzene

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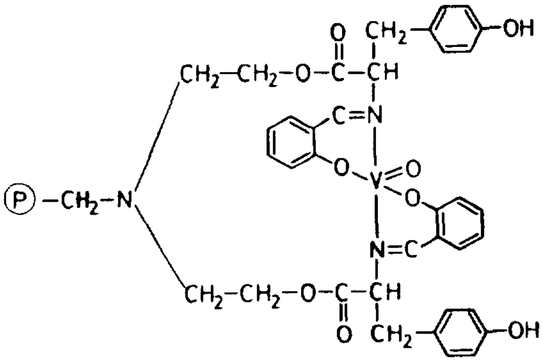
Abstracts: Polymer support VO^{2+} having schiff base functional group involving L-tyrosine was prepared from which the metal leaching did not occur. Using this recyclable catalyst, the hydroxylation of benzene by H_2O_2 was carried out at 65°C.

Direct formation of phenol from benzene is of great commercial importance1) and the use of H_2O_2 (as oxidant) is preferred because it minimizes the pollution. In the past, several transition metal complexes have been used for this purpose2) but these reactions are mostly carried out in molar ratios and the complexes can not be recycled. It has been shown, for example, that vanadium(V) oxo peroxo complex, $VO(O_2)(pic)(H_2O)_2$ (picH = picolinic acid) can hydroxylate benzene in acetonitrile solvent;3) however, this system suffers from parallel decomposition of the complex by the solvent during the hydroxylation of benzene.3,4) In our laboratory we have developed a polystyrene bound schiff base resin involving L-tyrosine which complexes readily with VO^{2+} ion. Here we report the preparation of a new polymer bound schiff base which can hold vanadyl ion effectively and we also report a new method for the direct synthesis of phenol from benzene and H_2O_2 catalyzed by this recyclable polymer supported vanadyl (VO^{2+}) group (as heterogeneous catalyst).

Macroporous Styrene-divinyl benzene copolymer (78:22) was produced by suspension polymerization technique5) which gave porous beads (10 m^2/g, measured using Pulse Chemisorb 2700 from Micromeritics) on which chloromethylation was performed using the technique given in the literature.6) The extent of chloromethylation was found to be 5% and was determined by boiling it with NaOH solution and then using $AgNO_3$ solution. These porous beads were subsequently reacted with diethanolamine and then with L-tyrosine (other amino acids gave poor results) followed by salicylaldehyde resulting in the formation of schiff base ligand environment with O N donors in the polymer resin. The vanadyl ion (VO^{2+}) was then fixed onto this insoluble polymer by refluxing $VO(acac)_2$ (acac = acetyl acetonate) and the polymer bound schiff base in MeCN for 48 hr to give the following (**A**) metal site on it.



A

The vanadyl loaded polymer catalyst⁷⁾ exhibits a strong green color which is indicative of the presence of V^{4+} ion and shows its characteristic EPR spectrum at room temperature. These vanadyl loaded polymer beads catalyze the hydroxylation of benzene to form phenol by H_2O_2 to selectively in 30% yield.

In a typical experiment, we have taken 225 mmol of benzene and 225 mmol H_2O_2 (30% aqueous H_2O_2) and added 65 ml acetonitrile to it to get a single phase. Then 6 gm (2.22 mmol vanadium, 1 mol%) of the vanadyl loaded beads were added to the reaction mixture. This was then stirred at 65°C for 6 h. A gas chromatographic analysis of the reaction mixture showed that 30% of benzene was converted to phenol (and later confirmed by isolating the product by distillation) with no side products formed. The polymer catalyst was removed by filtration, washed with acetonitrile and then recycled. Finally the mixture containing phenol, benzene, water and acetonitrile was distilled at 100°C and pure phenol was obtained with little amount of water which was further checked by gas chromatograph and ^1H NMR. After the reaction, the separated polymer catalyst beads were ground and subjected to IR studies, this way revealing that the phenyl residues of the polymer did not get hydroxylated.

No reaction is detected in the absence of the catalyst. During the course of the reaction, we observe that the green color of the polymer beads change within five minutes to yellow-orange. We confirmed that all VO^{2+} species (green colored, EPR active species, d^1 system) are oxidized to V^{5+} oxo-peroxo species (yellow-orange colored) by H_2O_2 because the latter do not give any EPR spectrum (V^{5+} species, d^0 system). The presence of vanadium- oxo and -peroxo groups in the yellow-orange beads has been shown by the IR spectrum7) and Vanadium(V)-peroxo species seems to be responsible for the conversion of benzene to phenol. Earlier work of Mimoun *et al*[3] on the use of $VO(O_2)(pic)(H_2O)_2$ complex for conversion of benzene to phenol stipulated that the transferred oxygen atom is of a peroxidic nature.

In conclusion, the direct synthesis of phenol from benzene and H_2O_2 is promising and can be adopted industrially. In this unique catalytic system there is no leaching of the metal and the particles do not break due to stirring. The insoluble beads of the catalyst can be quantitatively separated from the reaction mixture and recycled (checked for ten times after which the catalyst starts breaking). Furthur study on the kinetics and mechanism and the scope of this hydroxylation to other systems, such as heptane, cyclohexane and naphthalene are currently in progress. The details will be reported elsewhere in the near future.

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References and Notes.

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7. The infrared spectrum of the green vanadyl loaded polymer support exhibits bands in the 900-970 cm^{-1} range associated with ν(V=O). The infrared spectrum of the H_2O_2 treated yellow-orange beads show bands in the 900-970 cm^{-1} for ν(V=O) and bands in the 850-870 cm^{-1} range for ν(O-O). One gram of the polymer catalyst contains 0.019 gram of vanadium.

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