

## NOTE

# Formation of Phenol from Benzene Catalyzed by Polymer-Bound Vanadyl Acetylacetonate

Industrially, phenol is produced by a multistep cumene process (1) and it is desired to develop its direct synthesis from benzene where the oxidation occurs either by  $\text{H}_2\text{O}_2$  or by molecular oxygen (2). In the past, the latter using  $\text{H}_2\text{O}_2$  as oxidant has been catalyzed using several transition metal complexes and transition metal salts (3–10) but is mostly carried out in molar ratios and the metal cannot be recycled. Recently, titanium silicalite has been reported to be an effective hydroxylation catalyst for benzene as well as phenol (11). Previously, vanadium complex with picolinic acid ligand has been shown to hydroxylate benzene in moderate yield (12). However, this complex is unstable and cannot be stored as it decomposes in air at room temperature. In view of this, we wished to develop other vanadium complexes which are stable. Here, we report on a polymer-supported  $\text{VO}(\text{acac})_2$  (acac, acetylacetonate) catalyst which is useful in the direct synthesis of phenol from benzene in acetic acid medium using  $\text{H}_2\text{O}_2$  as the oxidant.

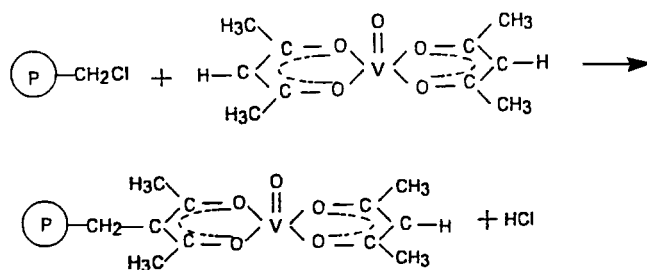
The complex  $\text{VO}(\text{acac})_2$  has been prepared by the procedure given in the literature (13). We have prepared polymer-anchored vanadyl acetylacetonate catalyst by a simpler procedure different from the one reported (14, 15). Macroporous divinylbenzene cross-linked polystyrene beads (copolymer ratio, 22 : 78) having a high surface area ( $6 \text{ m}^2/\text{g}$ , measured using a Pulse Chemisorb 2700 instrument from Micromeritics) and average pore size as  $560 \text{ \AA}$  (measured by mercury porosimeter) were first chloromethylated (16). These chloromethylated beads (5% chloromethylation, determined by refluxing beads in  $\text{NaOH}$  then reacting with  $\text{AgNO}_3$ ) are subsequently refluxed with  $\text{VO}(\text{acac})_2$  dissolved in acetonitrile for 24 h to give greenish-blue polymer-supported vanadyl acetylacetonate. The fixation of vanadyl acetylacetonate on to chloromethylated beads is shown schematically in Scheme 1.

It is likely that not all the chloromethyl groups are available for this reaction because of diffusion restriction in the polymer, making some of them inaccessible for the reaction, but we have no way to confirm this.

The characteristic EPR spectrum of  $\text{V}^{4+}$  ( $d^1$  system) ion bound on polymer beads is shown in Fig. 1. Estimation of vanadium was done by energy dispersive spectroscopy (EDS) (JEOL JSM 840A scanning electron microscope) and it gave 0.004 g of vanadium per gram of beads.

The typical procedure for hydroxylation of benzene consisted of the following: 10.0 g of benzene (128 mmol) was added to 16.32 g (1.28 mmol as metal ion) of the vanadyl acetylacetonate loaded polymer bead catalyst in 40 ml of acetic acid. Subsequently 14.5 g (128 mmol) of  $\text{H}_2\text{O}_2$  (30% aqueous  $\text{H}_2\text{O}_2$ ) was added to this. The reaction mixture was maintained under stirring at  $70^\circ\text{C}$  for 4 h. A gas chromatographic analysis of the reaction mixture showed that 10% of benzene was converted to phenol with no appreciable side products formed. The polymer catalyst was then removed by filtration, washed with acetonitrile, dried, and then recycled. The amount of unreacted  $\text{H}_2\text{O}_2$  was estimated at the end of each run and it was found that most of the peroxide was decomposed due to autolysis during the course of reaction. To confirm that the phenyl groups of the polymer beads are not becoming hydroxylated, we have taken the FTIR spectrum of them after the reaction and this does not show characteristic hydroxyl peaks.

No appreciable reaction is observed in the absence of the catalyst. During the course of the reaction, on addition of  $\text{H}_2\text{O}_2$  the colour of the beads changes from greenish-blue to yellow-orange. We confirm through EPR studies that all green colored beads with  $\text{V}^{4+}$  species ( $d^1$  species, EPR active) are oxidized to yellow orange  $\text{V}^{5+}$  species ( $d^0$  system, EPR silent). The infrared spectrum of the  $\text{H}_2\text{O}_2$  treated orange-yellow beads shows bands in the range  $900\text{--}970 \text{ cm}^{-1}$  for  $\nu(\text{V}=\text{O})$  and bands in the  $850\text{--}870 \text{ cm}^{-1}$  range for  $\nu(\text{O}-\text{O})$ . This  $\text{V}(\text{V})$ -peroxo species may be responsible for the conversion of benzene to phenol. Mimoun *et al.* (12) reported that the vanadium complex  $[\text{V}^{\text{V}}\text{O}(\text{O}_2)(\text{pic})(\text{H}_2\text{O})_2]$  (picH, picolinic acid) reacts with benzene to produce



SCHEME 1

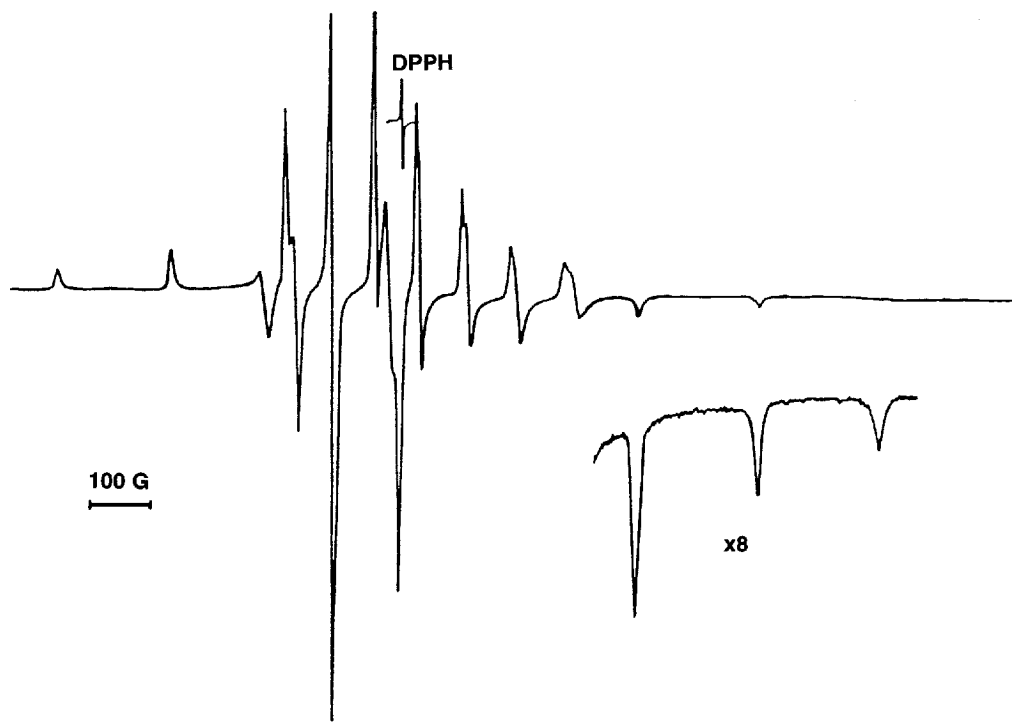
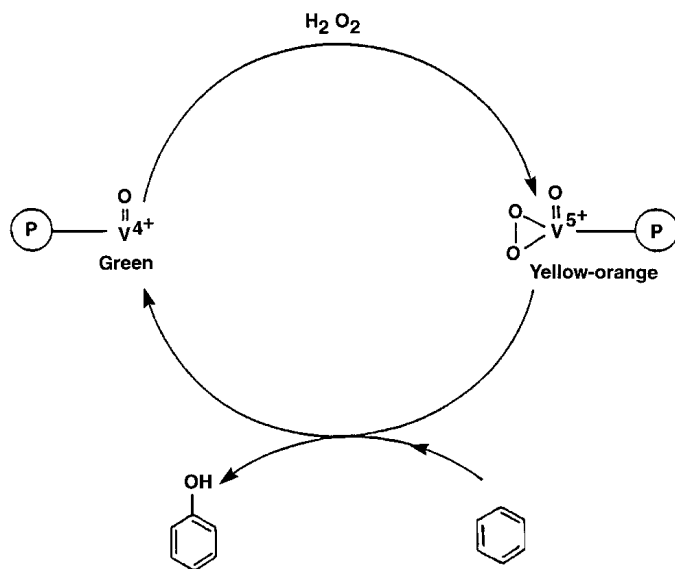


FIG. 1. Room temperature EPR spectrum of vanadyl-loaded polymer catalyst.

phenol, where it was argued that peroxy group is the active site which interacts with benzene. Our experimental work also supports this and the formation of phenol from benzene can be schematically described as shown in Scheme 2.

After four runs, the metal content of the catalyst was measured by energy dispersive spectroscopy and the loss of metal (because of the acetic acid) ion was found to reduce



SCHEME 2

from 0.004 to 0.003 g of vanadium per gram of catalyst. After the catalyst has been used for 6 times, the particles become brittle and start breaking up. The variation of the yield of phenol with the number of runs was 10.0%, 9.0%, 8.5%, and 8.0% for the first four runs, respectively.

In the literature titanium silicalite has been reported to give higher conversion, but it also hydrolyzes phenol further (11) and in this regard it is less specific. Since there is metal leaching, it may be argued that the reaction may be catalyzed by dissolved vanadium complex. To show that there is no free metal in the reaction mass, we measured the atomic absorption spectrum of the reaction mass and found it gave a negative result.

We conclude that the direct preparation of phenol from benzene and  $\text{H}_2\text{O}_2$  is promising. The vanadium-loaded beads are quite stable in acetic acid and the insoluble beads can be easily separated from the reaction mixture by filtration and then can be recycled.

#### ACKNOWLEDGMENT

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