

Experimental Methods

1. Bromination Methods

1.1 Bromination method based on H₂O₂/HBr

An efficient method of bromination of aromatic amines, hydrocarbons and naphthols was selected in our study (*P.V. Vyas et al., Tetrahedron Letters 44 (2003) 4085-4088*). The bromination procedure basically consists in an oxidation of hydrobromic acid by hydrogen peroxide without the use of any transition metal catalyst.

We have optimized the bromination method of a commercial resin LK2621, yielding a reproducible bromination degree in different lots and different scales. The optimal bromination conditions are the following:

1. The resin was washed three times with methanol, using equal volumes of solvent and resin..
2. Solid was dried (60 °C) under vacuum for 1 h.
3. 3 g of resin were kept in suspension in a solution of hydrobromic acid (2.43 g of a 48 wt. % aq. solution) in 50 mL of methanol.
4. Hydrogen peroxide (1.06 g of a 47 wt. % aq. solution) was slowly added (drop by drop) for a period of 15 min at 10-15 °C over the suspension
5. The mixture was refluxed for 72 h.
6. The solid was filtered and washed several times with methanol.
7. Finally, resin was dried under vacuum at 60 °C for 1 h.

1.2 Bromination of Lewatit LK2621 with Br₂

The second family of bromide containing resins is prepared by the direct addition of Br₂ catalyzed by a Lewis acid. We have optimized the synthesis conditions to yield a high incorporation of Br without presence of small amounts of catalysts.

The best results have been obtained using an aprotic solvent (CH_2Cl_2) and dry AlCl_3 catalyst.

The optimum bromide incorporation is the following:

1. The resin was washed three times with CH_2Cl_2 , using equal volumes of solvent and resin.

2. Solid was dried ($60\text{ }^\circ\text{C}$) under vacuum for 1 h.

3. 10 g of resin was mixed with 100 mL of CH_2Cl_2 , then 84 mL of a bromine solution (3.07 g Br_2) of the same solvent was added and the glass flask was covered with aluminum foil to avoid exposure to light.

4. After 30 min of stirring, a solution of dry AlCl_3 (0.13 g in 84 mL CH_2Cl_2) was added to the polymer suspension.

5. The mixture was refluxed for 72 h

6. The solid was filtered and washed several times with CH_2Cl_2 to remove completely the red-orange color of bromine.

7. To be sure that the resin is in the acidic form, the washed solid was ion exchanged with a solution of H_2SO_4 (0.5 M) three times, one hour each.

8. The solid is washed with acetone three times, one hour each in order to remove completely the aluminum present in the resin.

9. The solid was dried ($60\text{ }^\circ\text{C}$) under vacuum for 1 h. This procedure is quite reproducible.

1.3 Catalyst Preparation

All three supports (commercial silica and Br-modified resins) were employed in the preparation of catalysts by adding palladium. A suspension of the support (10 g) in acetone (125 mL) was prepared and maintained under stirring for 1 h at room temperature. A Pd (II) acetate solution in 50 mL of acetone was added dropwise to the

suspension. After 1 h of contact at RT, the solid was filtered off, washed with acetone and dried at 60 °C for 1 h.

1.4 Catalyst Characterization

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a Mg K α (h ν = 1253.6 eV) non-monochromatic X-ray source. The fresh samples were degassed in the pretreatment chamber at room temperature for 1 h prior to being transferred into the instrument's ultra-high vacuum analysis chamber. The Si 2p, O 1s, S 2p, Br 1s and C 1s signals were scanned several times at pass energy of 20 eV to obtain good signal-to-noise ratios and good resolution. The binding energies (BE) were referenced to the BE of the C1s line at 284.9 eV. The invariance of the peak shapes and widths at the beginning and end of the analyses indicated constant charge throughout the measurements. Peaks were fitted by a non-linear least squares fitting routine using a properly weighted sum of the Lorentzian and Gaussian component curves after background subtraction.

1.5 Hydrogen Peroxide direct synthesis

Palladium catalysts were tested in the direct synthesis of hydrogen peroxide. In a typical run, the amount of catalyst necessary to load a reactor was 0.062 g of Pd was placed in a high-pressure stirred reactor (Autoclave Engineers) working in semi-batch conditions mode. In the system, the liquid was kept inside the reactor for whole experiment while a continuous gas flow was fed; the pressure in the reactor was kept constant with a pressure controller on the autoclave. Then 320 g of methanol were added to the reactor and the system was then pressurized under N₂ flow at the reaction pressure (5.0 MPa) and heated at 60 °C. Then, the flows of oxygen and hydrogen were added successively without stirring to avoid the reaction. The total gas flow was 5300 mL(STP)·min⁻¹, with a molar concentration of gases; 3.6 % H₂: 46.4 % O₂: 50.0 % N (outside flammability limits). When the system was stable, the reaction was started by stirring the mixture (1500 rpm). On-line GC (Varian CP-4900 microGC) device was used to determine the consumption of hydrogen. The H₂O₂ was

determined by a standard titration with potassium permanganate in 2N sulfuric acid solutions (reduction of permanganate with H_2O_2 in acidic solutions), and water concentrations were determined by a volumetric Karl Fisher titration. Selectivity was calculated on the basis of the concentration of H_2O_2 and water formed during the reaction.

1.6 Hydrogen Peroxide decomposition

The decomposition was performed mixing high purity 30 wt.% H_2O_2 solution in water (25.52 g, supplied by Solvay) and 53.48 g of methanol. were mixed. This solution was heated in open glass reactor at a temperature of 40 °C under stirring. Then, the catalyst was added and samples were taken every 30 min over a period of 180 min. The amount of catalyst was selected to add the same amount of palladium to the mixture (0.062 g of Pd), for this reason the amount of catalyst were adjusted to reach this objective. The decomposition experiments were performed at atmospheric pressure in an open glass reactor, without addition of any gas.