Experimental Details

The catalytic reactions were carried out in a stainless-steel catalytic reactor (100 ml, Parr) lined with Poly Ether Ether Ketone (PEEK). The substrates (primary, secondary, benzylic and unsaturated alcohols, cyclohexene, methyl cyclohexene and p-cymene), a suitable internal standard (adamantane) and the catalyst ($Mn^{III}AlPO-5$, $Cr^{VI}AlPO-5$) were then introduced into the reactor, which was subsequently sealed. The reactor and the inlet and outlet ports were purged thrice with dry nitrogen prior to reaction. The contents were stirred at 1200 rpm and the reactor was heated to the desired temperature under autogeneous pressure (N_2).

The solid oxidant (APB) used in our experiments was prepared according to procedures reported in US 5,462,692, and was shown[12] by titration studies to liberate 0.701 g of peroxyacetic acid (9.22 mmol) and 0.045g of hydrogen peroxide (1.32 mmol) immediately upon dissolution in double-distilled water. The oxidant (10.54 mmol) was dissolved in 20.5 g of double-distilled water and the resulting solution was fed slowly, over the course of the reaction, employing a syringe pump (Harvard "33") to the stirred contents of the reactor. (The slow addition of the oxidant to the catalyst/substrate mixture improves the overall selectivity and also helps minimize by-product formation. It also minimizes the contact time of the oxidant with the catalyst thereby enhancing the "peroxide efficiency" and restricting the rapid decompostion of the peroxide).

At the end of the reaction, the heating was turned off and the contents of the reactor were cooled (quenched). A mass-balance calculation was performed at this stage to check for handling and mass losses. (Where kinetic and rate effects were studied, a mini-robot liquid sampling valve was employed to remove small aliquots (0.1 µl) of the sample (aqueous and organic phases) during the course of the reaction).

The products were analyzed either online (using a robotically-controlled unit with an online computer-controlled system which is linked to a GC and/or LCMS) or offline by gas chromatography (GC, Varian, Model 3400 CX) employing a HP-1 capillary column (25 m × 0.32 mm) and flame ionisation detector using a variable ramp temperature program (from 65 °C to 220 °C). The identities of the products were first confirmed using authenticated standards and their individual response factors were determined using a suitable internal standard adamantane) by the calibration method. The overall yields were normalized with respect to the (GC) response factors obtained as above.

The conversions and selectivities were determined as defined by the following equations and the yields were normalised with respect to the response factors obtained as above:

[¥] Conv. % = [(moles of initial substrate – moles of residual substrate) / (moles of initial substrate)] x 100

[¥] Sel. % = [(moles of individual product) / (moles of total products)] x 100

For the internal standard GC method, the response factor (RF) and mol % of individual products were calculated using the following equations:

RF = (mol Product/mol Standard) × (Area Standard/Area Product)

Mol % Product = RF x Mol Standard × (Area Product/Area Standard) x 100/Mol Sample

In Tables 1 and 2, in addition to the actual conversions measured and calculated using the above equations, the oxidant efficiency is also included, as different substrate:oxidant mole ratios were employed with the various substrates tested. The oxidant efficiency and oxidant conversions were calculated using the following equations:

ζ Oxidant efficiency = 100 $\times$ (mmol oxidant utilized in product formation/mmol oxidant consumed)

ζ Oxidant conversion = 100 $\times$ (mmol oxidant consumed/mmol oxidant at the end of the reaction)

The identity of the products was further confirmed using LCMS (Shimadzu LCMS-QP8000), which was again employed either online or offline. Hot filtration experiments and ICP measurements of the aqueous and organic mixtures were independently (and regularly) carried out to rule out the possibility of leaching.

In most cases, the catalysts have been re-used 3 times without appreciable loss in catalytic activity or selectivity. Further, experiments analogous those reported earlier,[12,17] were carried out to rule out the possibility of leaching, and analysis of the resulting filtrate at the end of reaction by ICP and AAS revealed only trace amounts (< 5 ppb) of dissolved metal ions (Mn, Cr).