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New and ecofriendly options for the production of speciality and fine chemicals

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Abstract

Earlier research efforts in the area of catalysis have focused on large volume, low value products of petroleum and petrochemical industry since the benefits of catalytic processes are enormous in terms of simplification of process technology, atom economy, effluents and finally economy. Fine and specialty chemicals industry with its massive profits realized through huge value addition had endeavored on product innovation. The emerging global competitiveness and public outcry against large amounts of effluents prompted to translate the knowledge of catalytic processes to the fine chemicals industries.

In this article, multidirectional efforts towards atom economy, zero emission of effluents and simplification of the processes in the oxidation of olefins, alkenes, alcohols and amines are discussed. Various options encompassing both homogeneous and heterogeneous systems have been explored in the said reactions. The application of microporous and mesoporous heterogeneous catalysts for various oxidations seems to be ideal. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic process; Heterogeneous catalyst; Chemicals; Homogeneous catalyst; Ecofriendly

1. Introduction

Chemicals are broadly classified as commodities, fine and performance chemicals. Petrochemicals, basic chemicals, organic chemicals (large-volume), monomers, commodity fibers and plastics belong to the class of commodities, while advanced intermediates, building blocks, bulk drugs and bulk pesticides, active ingredients, bulk vitamins and flavor and fragrance chemicals are listed under fine chemicals. Performance chemicals encompass adhesives, diagnostics, disinfectants, electrochemicals, food additives, mining chemicals, pesticides, pharmaceuticals, photographic chemicals, specialty polymers and water treatment chemicals.

In view of the shorter life cycles of fine and performance chemicals as compared to commodities, product innovation, which requires enormous resources, is highly knowledge based. The growth of the fine chemicals business is mainly fostered by the introduction of new pharmaceuticals, agrochemicals, engineering plastics and other specialties requiring high value organic intermediates. Fine and specialty chemicals are generally considered chemicals that are manufactured to high and well-defined standards of purity compatible to the desired performance as opposed to heavy chemicals made in large amounts to technical levels of purity.

Catalytic science and technology were largely confined to petroleum and petrochemical industry until the seventies. Fine and specialty chemical industry had focused its attention mainly on product innovation and less on process development until recently. Consequently, every kg of product obtained in

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multistep process generates 15–20 kg waste causing pollution in alarming levels that prompted strident public pressure on many of the governments to lay increasingly stringent environmental legislation. This has led to the adoption of clean technology in the fine and performance chemical industry. Chemical industry at the same time has focused its attention on development of cutting edge technologies to meet global competitiveness and zero emission of effluents. To meet these challenges, the industry requires innovative catalytic technologies that offer high space–time yield, improved yield of the desired product, high regio- and enantioselectivity for the market driven isomer, low water requirement and non-corrosivity of the reacting chemicals. Established chemical processes that are often based on technology developed in the first half of the 20th century may no longer be acceptable in these environmentally conscious days. Therefore, enviro-economics will become the driving force behind the development of new processes for existing and new products [1–3]. Earlier, it was the commodity industry which utilized catalytic processes, but now the above-mentioned constraints have forced the fine chemical industries to prefer catalytic processes thus cutting down the expenditure significantly, while keeping in stride with the environmental regulations laid out. The use of heterogeneous catalysts, in particular zeolites and clays, has significantly contributed to the development of new methodologies in organic synthesis targeted to dispense the conventional and waste generating reagents and achieve high atom economy to be applied in fine chemical sector [4,5].

2. Epoxidation

Epoxides are versatile intermediates for laboratory and industrial chemicals such as epoxy resins, surfactants, paints, adhesives, and surface coating agents, in addition to a range of bioactive substances. The paramount reason for the synthetic importance of the epoxide moiety is the existence of regio- and stereoselective methods both for constructing it and for controlling its subsequent reactions. Terminal epoxides are particularly important, while the more substituted epoxides are used for the synthesis of structurally more elaborate fine chemicals. Although olefin epoxidation is thought to be a matured chemistry, a truly ecofriendly method still remains elusive. Direct epoxidation of olefins with oxygen is a more desirable process.

The most commonly used oxidants are peroxyacids and *tert*-butyl hydroperoxide either in alkaline solutions [6] or in the presence of transition metal compounds of Ti, V, Cr, Mo and W [7–12]. Metal complexes ranging from monomeric to clusters and heterogeneous catalysts in the form impregnated/anchored on solid supports comprising silica, zeolites and polymers, metal zeolites have been employed for various epoxidations.

Molybdenyl(VI) acetylacetonate catalyzes the conversion of various cholesterol esters into the corresponding β-epoxides in good yields with the in situ formed peracid from the interaction of molecular oxygen and isobutyraldehyde at room temperature [13].

Ishii and coworkers [14] carried out the epoxidation of olefins with aldehyde and $(NH_4)_5H_4$–$PMo_6V_6O_{40}$ catalyst in the presence of oxygen at 25°C and arrived at high selectivities of 81–100%. Noyori and coworkers [12] developed a catalytic system of sodium tungstate dihydrate, (aminomethyl)phosphonic acid, and methyltrioctyl-ammonium hydrogen sulfate which effected the epoxidation of olefins using 30% hydrogen peroxide with a substrate: catalyst molar ratio of 50–500.

In the area of heterogeneous catalysis, Shell used Ti^{IV}/SiO_2 catalysts for the epoxidation of propylene with ethylbenzene hydroperoxide [15,16]. Baiker and coworkers [17] have carried out the epoxidation of bulky olefins with TBHP employing the titania–silica aerogels and found them to be quite active.

2.1. Selectivity

Mayoral and coworkers [18] reported a $Ti(OPr^i)_4$–silica derivative for the epoxidation of alkenes with TBHP. The higher rate of reactions observed in the epoxidation of cyclic over acyclic alkenes, disubstituted double bonds over monosubstituted double bonds and Z-double bonds over E-double bonds with this catalyst allows the selective epoxidation of compounds with double bonds of different types. (*R*)-limonene is preferentially oxidized at the cyclic double bond with high selectivity (Fig. 1).

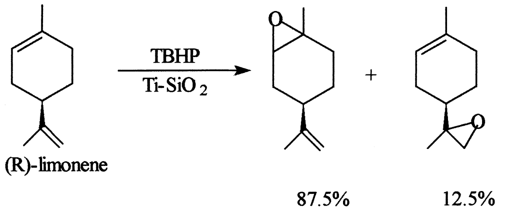


Fig. 1. Selective oxidation of (*R*)-limonene by Ti–SiO_2.

2.2. Shape selectivity

While using microporous to mesoporous catalysts, shape selectivities conspicuously manifest in the epoxidation reactions. A number of articles on the catalytic potential of Ti catalysts (TS-1 and TS-2) in the epoxidation of smaller alkenes, e.g., propylene and allyl chloride using H_2O_2 have appeared [17–25]. If the alkenes and the oxidants are larger than pores of these micropore zeolites, the epoxidation is not possible. Only very recently, work on the catalytic applicability of the aluminum-free titanium containing zeolite beta in oxygenation reactions has appeared [26–29] in which 90–100% selectivities for the oxidation of alkenes in acetonitrile have been reported. The presence of aluminium in Ti,Al-beta causes Brönsted acidity, which leads to acid-consecutive ring opening reactions [20,30]. Though selectivities in the epoxidation of bulky alkenes like norbornene, substituted cyclohexenes, cyclic terpenes and moderately bulky allylic alcohols [30] catalyzed by large-pore zeolite Ti-beta are high, the yields are less than 13%. With the mesoporous zeolite Ti–MCM-41, improved yield (30%) and high selectivity were observed [31,32] in the epoxidation of the bulky norbornene with H_2O_2 or TBHP.

Smectite clays acquire a high thermal stability and structural rigidity required for molecular sieving by pillaring with polycationic complexes of Al, Zr, Cr, Ti, etc., in the interlayers via the process of cation exchange [33]. Hitherto, the evaluation of the pillared clays has been focused mainly on shape selective studies of vapor phase reactions and very few reports discuss liquid phase reactions. We designed and synthesized a novel vanadium pillared clay by covalently cross-linking the interlayers of montmorillonite K10 with vanadia. Natural layered montmorillonite is transformed into a mesoporous montmorillonite commercially known as K10 montmorillonite on treatment with concentrated mineral acid. The acid treatment partially disrupts the fine stacks of layered montmorillonite into several broken pieces and the interaction with oligomers provides pillaring in the intact layered structure and exchange in the fractured structures. This type of pillared catalysts exhibit superior activity in comparison with the pillared clays developed with natural montmorillonite due to easy accessibility of the oligomers to the substrate.

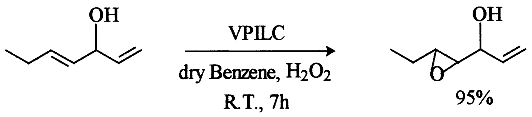
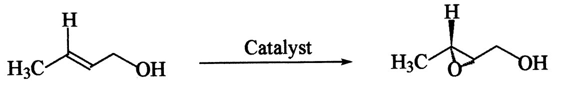


Fig. 2. VPILC catalyzed oxidation of allylic alcohols.

Vanadium-pillared montmorillonite (VPILC) was reported to catalyze the regioselective epoxidation of allyl alcohols with TBHP [34]. Unusual regioselectivity towards internal allylic double bonds in preference to terminal allylic double bonds was displayed by the VPILC (Fig. 2).

Asymmetric epoxides are building blocks for many natural products such as β-blockers, pheromones, etc. The successful combination of a titanium alkoxide (metal template), an alkyl hydroperoxide (oxidizing agent), diethyl tartrate (chiral auxillary) and molecular sieves (water scavenger) was developed by Sharpless and coworkers [35] for asymmetric epoxidation of allylic alcohols with high ee. The use of heterogeneous catalysts in place of homogeneous ones in any reaction affords easy separation of the catalyst without destroying the catalyst. Therefore, we chose pillared clays as catalysts by choosing a suitable metal template as pillaring material to perform enantioselective organic reactions with the aid of external chiral auxiliary. The use of oligomeric transition metal oxy or hydroxy pillared clay catalysts offer more approachable metal sites than the conventional surface dispersed heterogeneous catalysts which are expected to exhibit high reactivity, possibly with a different reaction pathway as directed and imposed by the support.

The oxidation of unsaturated alcohols over a chirally modified TiPILC gave the optically active epoxides [36] with enantiomeric excesses as good as those obtained using the homogeneous Sharpless catalyst



Catalyst	Yield %	ee %
$Ti(O\text{-}iPr)_4$	70	91
TiPILC	91	95

Fig. 3. Asymmetric epoxidation of unsaturated alcohols by $Ti(O–iPr)_4$/TiPILC.

(Fig. 3), $Ti(OPr^i)_4$ with molecular sieves [35]. The present system is catalytic without the use of molecular sieves and does not require a low concentration of substrate as in the case of homogeneous conditions to avoid side reactions. The use of TiPILC provides easy separation by simple filtration without tedious experimental work-up.

Of the two procedures, one from titanium isopropoxide and the other from titanium tetrachloride, adopted for the preparation of TiPILC catalysts, the latter is more useful as it is reproducible [37,38]. The catalyst should be dried in hot air or nitrogen to remove the moisture embedded in the catalyst just before the reaction. The filtrate obtained with the interaction of TBHP and TiPILC afforded negligible yield of the epoxide. This establishes the heterogeneous nature of the catalyst.

2.3. Base catalyzed epoxidations

In some instances, a base catalyst has been employed for the epoxidation. Bases such as NaOH and KOH reportedly induce the epoxidation of olefins using hydrogen peroxide in the presence of nitriles, a sacrificial reagent to produce amides in stoichiometric quantities [39,40]. However, the use of soluble base contributes to the generation of total dissolved salts (TDS) as effluents consequent to neutralization at the end of reaction. Hence, the need to replace soluble bases with solid base to eliminate the generation of the TDS is strongly felt and the research efforts towards this direction are accounted in this article.

2.3.1. Hydrotalcites

Hydrotalcite (HT), $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$ is one of the naturally occurring anionic clay minerals, which contains positively charged brucite-like $[MgAl(OH)_2]$ layers. The interlayer space is filled with carbonate ions and water molecules [41]. Hydrotalcite-like compounds (HTLcs) are structurally similar to HT, but cations other than Mg^{2+} and Al^{3+} may occur. They can be synthesized by coprecipitation [42] from aqueous solutions of corresponding metal salts. The general formula of HTLcs is $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n}\cdot zH_2O$, where $M^{II}=$ Mg, Zn, Co, Ni, Cu, Fe and $M^{III}=$ Al, Cr, Fe. A stands for an interlayer exchangeable anion, and $x=0.17$–0.40. In $Mg_6Al_2(OH)_{16}CO_3\cdot 4H_2O$ when Mg^{2+} and Al^{3+} are replaced wholly or partially with M^{2+} (M = Zn, Co, Ni, Cu, Fe) and M^{3+} (M = Cr, Fe), respectively, crystalline materials of the hydrotalcite type can be obtained, as is evident from X-ray powder patterns. Recently a new class of expanded anionic pillared clays prepared by introducing complex anions of organic and organometallic [43], large inorganic anions [44], silicate [45] and polyoxometalate [46,47] in the layers of HT/HTLcs.

Kaneda and coworkers [48] reported a base catalyst, $Mg_{10}Al_2(OH)_{24}CO_3$ hydrotalcite for the epoxidation of various alkenes using H_2O_2 in the presence of benzonitrile and with MeOH as solvent. Addition of sodium dodecyl sulfate and sodium dodecylbenzoate sulfate to the above system markedly increased the rates of the epoxidation [49]. The main drawback of this reaction is the formation of stoichiometric amounts of amides from the benzonitrile. Although shape selective epoxidation in the presence of H_2O_2 reported by Tatsumi et al. [50] was clean in the case of polyoxometalate-intercalated hydrotalcites, diols and oxolanes were formed to some extent by successive cleavage of the epoxides [50–53].

We have developed a methodology much superior to the existing methodologies employing modified hydrotalcites, Mg–Al–O–*t*-Bu–HT for the epoxidation of unfunctionalized olefins and α,β-unsaturated ketones using hydrogen peroxide as an oxidant [54] (Fig. 4). The scope of this reaction is under progress.

While the earlier methods required 6–24 h, the Mg–Al–O–*t*-Bu–HT effected the reactions in just 5–45 min with excellent yields. Mg–Al–O–*t*-Bu–HT displayed an amazing 720-fold activity over simple calcined hydrotalcite in the epoxidation of chalcone. The epoxidation of terminal olefins to racemic epoxides in the presence of nitrile in excellent yields is noteworthy and assumes further significance since value added optically pure epoxides and 1,2-diols

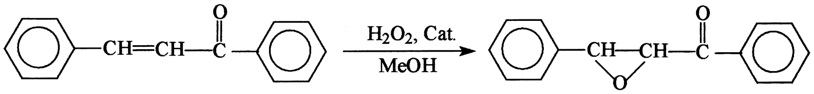


Fig. 4. Epoxidation of electron-deficient alkenes by Mg–Al–O-*t*-Bu–HT.

could be easily obtained from the racemic epoxides through kinetic resolution [55]. The amazing activity of Mg–Al–O–*t*-Bu–HT catalyst in the epoxidation of various olefins is ascribed to the anion O–*t*-Bu paired with Mg and Al of the main frame hydrotalcite since the reaction was practically very slow with potassium *t*-butoxide and a mechanical mixture of potassium *t*-butoxide and Mg–Al–NO_3 hydrotalcite. Thus, our catalyst can be a potential candidate to offer environmentally benign chemical technologies.

3. Wacker oxidation

The Wacker process for oxidation of ethylene to acetaldehyde and subsequent extension to terminal olefins to give methyl ketones involves $PdCl_2$–$CuCl_2$ homogeneous system [56]. Formation of chlorinated products, aldehydes and internal ketones as by-products, corrosion, precipitation of metallic palladium and the environmental hazards are major drawbacks inherently present in the above systems [57]. Hydrogen peroxide, organic peroxides [58] and *p*-benzoquinones [59] have been used in place of $CuCl_2$ as the reoxidant to overcome the problems stated above, but have met with only partial success.

The two-component redox system comprising Pd(II) as catalyst and heteropoly acid (HPA-*n*), $PMo_{10}V_2O_{40}^{-5}$ as co-oxidant has been employed successfully for oxidation of alkenes [60,61].

Matveev [62] proposed the use of HPA-*n* as chloride-free oxidant in the Wacker reaction and the rate of reaction is very slow. Catalytica [62] has recently developed a new ecofriendly technology for the Wacker oxidation of ethylene and higher olefins with the use of HPA-*n* + Pd(II). This process employs Cl^- ions at a very low concentration to enhance the rate of the reaction. Production of the chlorinated by-products is decreased from 15% to less than 0.01% yield on ethylene.

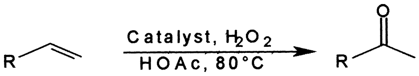


Fig. 5. Oxidation of olefins by montmorillonite silylpropylethylenediamine palladium(II) complex.

The heterogeneous system using the solid HPA-*n* + Pd(II) [61] as such and molecular oxygen in the oxidation of butene to methyl ethyl ketone is deactivated. In contrast, $PdCl_2 + Mn^{2+}$ + HPA-*n* supported on silica [63] was stable in the oxidation with the selectivity of 98%.

A true heterogeneous Wacker catalyst Pd–Cu system encapsulated in zeolite supercages via exchange of Cu^{2+} and Pd^{2+} for oxidation of ethylene to acetaldehyde is reported [64]. These catalysts are used for the heterogeneous gas phase Wacker oxidation of C_2–C_4 alkenes with dioxygen. However, the reaction was not conducted in liquid phase conditions.

Selective oxidation of terminal olefins to methyl ketones in quantitative yields using a montmorillonite silylpropylethylenediamine palladium(II) complex and hydrogen peroxide as reoxidant is described [65] (Fig. 5). Another special feature is the display of tenfold increased activity by the heterogenized catalyst when compared with the analogous palladium acetate–hydrogen peroxide under identical conditions. Hydrogen peroxide is an ideal oxidant; it may only be used for substrates for which molecular oxygen could give by-products in large quantities. This catalyst exhibited high turnover number (4300) and high activity as against (TON, 46) the homogeneous system of $PdSO_4$ and O_2 mediated by cyclodextrin [66].

4. Oxidative cleavage of olefins to aldehydes

The transition metal peroxo complexes can play an important role in catalytic oxidation of hydrocarbons by hydrogen peroxide. With the discovery of bromo peroxidase, vanadium containing enzyme isolated

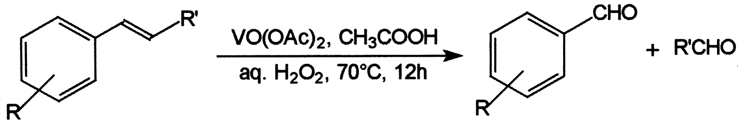


Fig. 6. Selective oxidation of aralkenes to benzaldehydes by $VO(OAc)_2$.

primarily from marine algae is known to catalyze the oxidation of halides by H_2O_2 [67,68], the oxidation chemistry of vanadium chemistry received increased attention. Selective oxidation of olefins to aldehydes is an important transformation in synthetic organic chemistry. Oxidations of olefins to yield either epoxides or cleavage products selectively failed due to various non-selective radical reactions leading to a large diversity of unidentified products [69–71]. Earlier attempts to achieve stoichiometric oxidation of olefins selectively to aldehydes by vanadium(V) peroxo picolinate complexes [72] resulted in the formation of a mixture of epoxide and oxidative cleavage products. We have reported the unusual reactivity of peroxo vanadium complex for catalytic oxidation of aralkenes to benzaldehydes selectively (99%) in conjunction with aqueous H_2O_2 as an oxidant [73] (Fig. 6). A notable feature is the non-oxidation of the aromatic aldehydes formed to the corresponding acids. The newly designed peroxo vanadium complex bearing acidic ligands, i.e., acetates are probably playing dual role, on one hand preventing the catalyst from decomposing to dimer, and on the other enhancing the activity of the catalyst to form aldehydes.

5. Benzylic oxidations

Benzylic oxidation is an important transformation in organic synthesis. Benzylic oxidations are generally carried by stoichiometric amounts of chromium(VI) reagents [74]. Tedious work-up and voluminous amounts of environmentally hazardous chromium residues formed as a result of the use of large excess of chromium reagents are the main disadvantages. In spite of its importance very little attention has been focused on the development of a catalytic method for benzylic oxidations. Muzart [75,76], a pioneer in chromium catalyzed oxidations, developed a method for benzylic transformations using soluble 2,4-dimethylpentane-2,4-diol cyclic chromate or CrO_3 in combination with TBHP, affording moderate yields.

We have reported on CrPILC as an efficient catalyst for the oxidation of benzylic compounds to the corresponding carbonyl compounds in good to excellent yields in conjunction with TBHP (Fig. 7) [77]. The selectivity observed for the production of mono carbonyl compounds from substrates in which more than one benzylic methylene group is present is due to steric effects.

Arylglyoxylic acids are important biosynthetic and synthetic precursors for several biologically active compounds such as α-amino acids and α-hydroxy acids [78,79]. Although the synthesis of arylglyoxylic acid is realized either by adopting the retrosynthetic route of the oxidation of α-amino acids [80] and α-hydroxy acids [81] or the palladium complex catalyzed double carbonylation of iodobenzene [82], there is no direct methodology to obtain arylglyoxylic acids by the oxidation of arylacetic acids. We presented a simple and convenient method for direct oxidation of cheap and readily available arylacetic esters to arylglyoxylic esters in excellent yields by VPILC with *tert*-butylhydroperoxide (TBHP) as an oxidant [83].

Acyl cyanides are versatile synthetic intermediates [84–86] and gained importance as building blocks of heterocycles or herbicides. Generally, they are prepared by the reaction of acid halides with metal

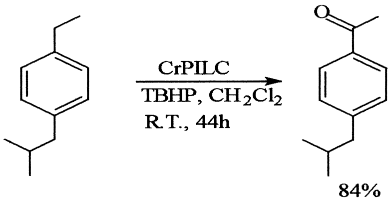


Fig. 7. Selective oxidation of *para*-isopropylethylbenzene by CrPILC/TBHP.

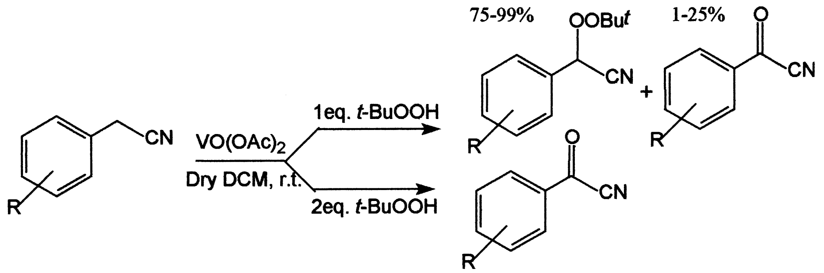


Fig. 8. Oxidation of benzyl cyanides by $VO(OAc)_2$.

cyanides [87–89], trimethylsilyl cyanides [90,91] or by the oxidation of cyanohydrins [84–86,92–97]. Alkyl peroxovanadium complexes oxidize the methylene group in benzyl cyanides to afford peroxo nitriles or aroyloxy cyanides selectively depending on the molar quantities of oxidant *t*-butyl hydroperoxide used [98] (Fig. 8).

We have developed an improved process for the production of benzaldehyde with 40–50% selectivity by catalytic liquid phase air oxidation of toluene which produces benzaldehyde (40–50%), benzyl alcohol (5–10%) and benzoic acid (40–50%) without any trace amounts of benzyl bromide. This is achieved due to the low loading of the catalyst and use of small amounts of carboxylic acids. The novelty of our process with respect to prior art is the realization of the high selectivity of benzaldehyde and benzyl alcohols in the air oxidation of toluene, with a turnover number of 350–700. The process is environmentally safe since there is no effluent disposal problem associated with it. This process is currently carried out on a 100 kg/day pilot plant scale set up to realize data for a commercial plant envisaged 15 000 tpa. The process is being patented in India and abroad [99].

Yumin et al. [100,101] used $CoCuAlCO_3$–HTLc for the air oxidation of *p*-cresol to *p*-hydroxybenzaldehyde in an alkali MeOH medium which gave a yield of 89.6% of *p*-hydroxybenzaldehyde at 93.5% conversion of *p*-cresol. It is noteworthy to observe that there is no subsequent Dakin type reaction to afford hydroquinone as end product. This interesting reaction provides access to the intermediates of several fine and performance chemicals.

6. Allylic oxidations

The oxidation of an olefin to an α,β-unsaturated ketone has been utilized in the synthesis and in the transformation of natural products. Allylic oxidation is promoted by CrPILC catalysts with good yields of the α,β-unsaturated ketones under mild reaction conditions [102] (Fig. 9).

7. Oxidation of alcohols

Selective oxidation of alcohols to the carbonyl compounds is of continued interest. Transition metal catalysts, both homogeneous and heterogeneous systems, in conjunction with a variety of reagents such as iodobenzene and nitrobenzaldehyde acting as hydrogen acceptors, have been successfully employed for the oxidation of alcohols to carbonyl compounds. Since the reagents required are more than stoichiometric amounts of alcohols subjected for oxidation, it

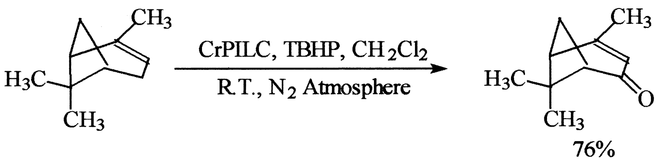


Fig. 9. Oxidation of α-pinene by CrPILC.

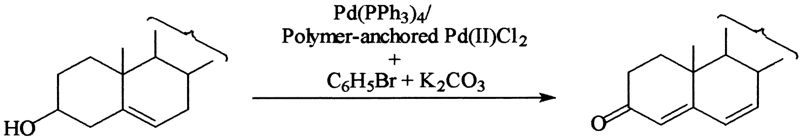


Fig. 10. Selective oxidation of Δ^5-sterols to $\Delta^{4,6}$-dien-3-ones.

is desirable to accomplish reactions with cheaper or renewable reagents.

7.1. Hydrogen transfer reactions

Hydrogen transfer reactions are known to be catalyzed homogeneously by ruthenium [103], iridium [104], and rhodium complexes [105]. We have reported a solid–liquid phase transfer catalytic system for the oxidation of primary and secondary alcohols via hydrogen transfer in good yields at room temperature and atmospheric pressure using palladium acetate as catalyst, tetrabutylammonium chloride as phase transfer agent and sodium hydrogen carbonate as base and iodobenzene as hydrogen acceptor [106]. This is a Heck type reaction used for oxidation of alcohols in which iodobenzene is transformed to benzene after acceptance of hydrogen source. The yields were found to be dependent on the nature and concentration of the phase transfer reagent.

Akamanchi and Chaudhari [107] reported an efficient oxidation of secondary alcohols to ketones at room temperature in high yields using diisopropoxyaluminium trifluoroacetate as catalyst and 4-nitrobenzaldehyde as a hydride acceptor.

Steroidal ketones are used extensively in the synthesis of steroid hormones and biologically important compounds. Steroidal 4,6-dien-3-ones are synthesized by the oxidation of 5-sterols with stoichiometric amounts of MnO_2 [108] or aluminium isopropoxide [109] which generates solid waste. However, the yields are poor. We have reported hydrogen transfer reactions using polymer anchored palladium(II) chloride, homogeneous $Pd(PPh_3)_4$ and $Pd(PPh_3)_2Cl_2$ (Fig. 10) [110]. However, the yields are very low with homogeneous $Pd(PPh_3)_2Cl_2$ compared with the analogous polymer anchored complex. This may be because reduced palladium in homogeneous $Pd(PPh_3)_2Cl_2$ has a tendency to agglomerate to form larger metallic particles in the absence of excess triphenylphosphine, while the reduction of Pd(II) in polymer anchored complex gives either Pd(0) or palladium metal which does not agglomerate due to a trapping effect in the polymer [111].

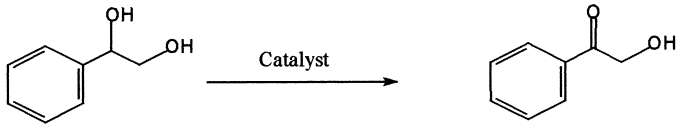
7.1.1. Peroxides as oxidants

Oxidations of primary, secondary and benzylic alcohols were performed with zirconium alkoxides [112] as the catalysts and hydroperoxides such as TBHP or cumene hydroperoxide as the oxidant, but the results were not attractive. Esters or acids could be the by-products in the case of primary alcohols. Secondary alcohols, if not severely hindered, are usually converted quantitatively to the corresponding ketones. Several catalytic systems such as $RuCl_2(PPh_3)_3$ [113], $PdCl_2$ [114], CrO_3–PTC [115], $CuCl_2$–PTC [116] and Cr–AlPO-5 [117–121] have been developed for the selective oxidations of benzylic alcohols to the corresponding carbonyl compounds.

Sasson and co-workers [122] reported oxidation of allylic and benzylic alcohols to ketones by TBHP in the presence of copper salts under phase-transfer conditions. This dehydrogenation was found to proceed via a heterolytic mechanism. $CuCl_2$, CuCl, and even copper powder were equally facile as catalysts, as they were all transformed in situ into Cu(OH)Cl which was extracted into the organic phase by the phase-transfer catalyst, tetrabutyl ammonium bromide.

VPILC catalyzes the oxidation of primary benzylic alcohols to the acids with TBHP and exhibits shape selectivity in that *para*-substituted benzylic alcohols are oxidized, while the *ortho*- and *meta*-substituted species are essentially inert [123].

Sheldon et al. [117,124] found that chromium-substituted aluminophosphate-5 (CrAPO-5) was an active and very selective catalyst for the oxidation of secondary alcohols using either molecular oxygen or TBHP as the oxidant. Sheldon [125] later clarified that the reaction really occurred with the chromium leached from the catalyst. This was confirmed by the



Catalyst	conversion	selectivity
CrAPO-5	54%	73%
CrPILC	100%	92%

Fig. 11. Selective oxidation of secondary alcohols by Cr catalysts.

experiment in which CrAPO-5 was incubated with TBHP. After filtration of the catalyst the reaction was performed by addition of the substrate and the reaction progressed at the same rate.

Following the same protocol, the reaction was performed with the filtrate of chromium pillared catalyst after incubation with TBHP, there was no reaction with the filtrate. Apart from this, the catalyst displayed consistent activity for number of recycles. This clearly indicates the heterogeneity of the chromium pillared catalyst. Although secondary alcohols are selectively oxidized in the presence of a primary hydroxy group of a diol to give keto alcohols in excellent yields catalyzed by both the catalysts CrPILC and CrAPO-5, CrPILC affords higher selectivity and conversion [126] (Fig. 11).

In contrast to the lack of selectivity observed in the TS-1 catalyzed oxidation of 3-penten-2-ol, the oxidation with TBHP over CrPILC gave the unsaturated ketone in 82% yield [126], while the oxidation over a VPILC gave the epoxy alcohol in 94% yield [34] (Fig. 12).

7.1.2. Molecular oxygen as oxidant

Molecular oxygen is vital for the life processes both in plant and animal kingdom. With inherent advantages such as ready availability, low price and innocuous gas that produces water as byproduct, molecular oxygen plays a pivotal role in synthetic chemistry. However, the application of molecular oxygen in chemical reactions is confined to only limited examples employing high temperatures or pressures. Hence the development of efficient oxygenation reactions envisaging the direct use of molecular oxygen under mild conditions is of topical interest.

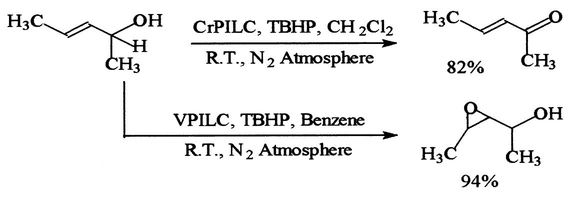


Fig. 12. Oxidation of 3-penten-2-ol over CrPILC/VPILC.

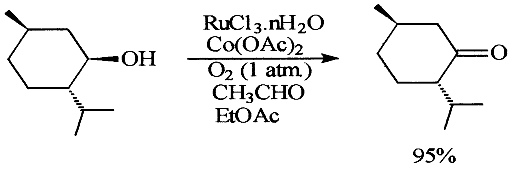


Fig. 13. $RuCl_3$–$Co(OAc)_2$ catalyzed oxidation of alcohols with molecular oxygen.

The oxidation of alcohols was performed at room temperature with molecular oxygen (1 atm) in the presence of an aldehyde and $RuCl_3$–$Co(OAc)_2$ bimetallic catalyst [127] (Fig. 13).

Various aliphatic and aromatic secondary alcohols can be oxidized at room temperature under O_2 atmosphere (1 atm). Kaneda et al. [128] and we reported an efficient oxidation system consisting of molecular oxygen, and an aldehyde devoid of any metal catalyst for epoxidation of olefins and oxidation of secondary alcohols [129]. This is possible because of in situ generation of stoichiometric production of peracid from a system of molecular oxygen and benzaldehyde and catalytic amounts of HCl from the aging of peracid with dichloroethane used as solvent to trigger the above reactions. This establishes that the oxidation of alcohols can be carried out in the presence of aldehydes without metal complexes.

The use of O_2 as the sole reoxidant of palladium in the oxidation of alcohols was first reported by Blackburn and Schwartz [130]. A catalytic system consisting of 1 mol% $PdCl_2$ and 0.5 equiv. of NaOAc in ethylene carbonate at 38°C with an O_2 atmosphere led to the efficient oxidation of saturated primary and secondary alcohols. An attempt to oxidize an olefinic alcohol failed. This was reported to be due to strong complexation of palladium by the olefin. Echavarren and co-workers [131] reported that the oxidation of allylic alcohols using a catalyst system consisting of 10 mol% $Pd(PPh_3)_4$ in toluene in the presence or absence of both NH_4PF_6 and K_2CO_3 at 100°C under an O_2 atmosphere gave moderate to good yields of the corresponding α,β-unsaturated carbonyl compounds. This system was only applied to allylic substrates. Larock et al. [132,133] and a few other groups [134–136] have suggested that a catalyst consisting of 5 mol% $Pd(OAc)_2$ in DMSO with an O_2 atmosphere leads to high turnovers of the palladium(II) catalyst. The same catalyst proved to be effective for the oxidation of allylic and benzylic alcohols [137]. Kaneda et al. [138] reported the selective oxidations of allylic alcohols with molecular oxygen using metal cluster complex catalysts.

Catalytic oxidations of alcohols using O_2 as the ultimate stoichiometric oxidant have not been limited to palladium chemistry. Many procedures using a variety of metals such as Ru, Co, Cu, Pt and Rh [139–147] catalysts in presence of oxygen with/without co-oxidants have been reported. There were several reports on aerobic oxidation of benzylic alcohols mediated by copper-amine complexes [116,148,149]. This method, however expedient, requires 2 equivalents of copper complex per equivalent of alcohol. Moreover, it is severely limited in scope to some benzylic alcohol substrates. Marko et al. [142] developed an efficient, aerobic system for the transformation of alcohols into carbonyl compounds under mild conditions. Under the conditions of 5% CuCl, 5% phenanthroline, 5% *tert*-butyl analogue of diethylazodicarboxylate hydrazine ($DBADH_2$), 2 equiv. K_2CO_3, O_2 or air, toluene, 70–90°C, a wide range of primary, secondary, allylic, and benzylic alcohols can be smoothly oxidized to the corresponding aldehydes or ketones in good to excellent yields. This catalytic system utilizes oxygen or air as the ultimate stoichiometric oxidant to regenerate azo compound from the hydrazine, producing water as the only by-product (Fig. 14). In the absence of air, stoichiometric amount of azo compound should be employed to accomplish the reaction.

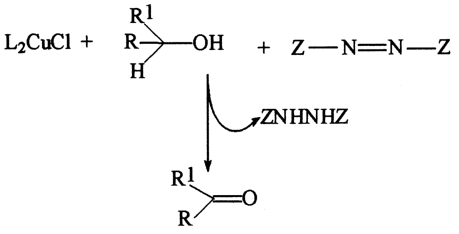


Fig. 14. Aerobic oxidation of alcohols to ketones by CuCl.

Kaneda et al. [150] have performed the oxidation of allylic and benzylic alcohols employing Ru–Mg–Al–CO_3 hydrotalcite (Fig. 15). The advantage of this heterogeneous catalyst over the other homogeneous oxidizing reagents is not only the use of molecular oxygen but also of a simple work-up procedure compared to the other homogeneous oxidizing agents.

Kaneda and co-workers [151] also developed Ru–Co–Al–CO_3–HT catalyst in which substitution of Mg ion with cobalt ion in the brucite layer of Ru–Mg–Al–CO_3 enhanced catalytic activity phenomenally in the oxidation of allyl alcohols in the presence of molecular oxygen. This higher activity is ascribed to synergetic effect arising due to interaction of Ru and Co ions.

8. Oxidation of amines

An efficient ruthenium-catalyzed oxidation of secondary amines to imines [152] and tertiary amines

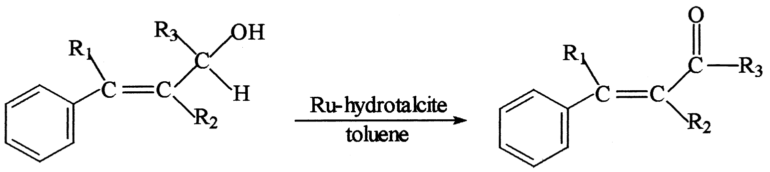


Fig. 15. Ru–Mg–Al–CO_3 hydrotalcite catalyzed oxidation of alcohols.

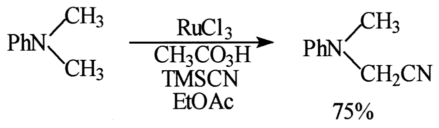


Fig. 16. Ruthenium catalyzed oxidation of amines.

to the corresponding α-(*t*-butyldioxyalkyl)amines [153] in presence of tetra-butyl hydroperoxide is reported. The ruthenium-catalyzed oxidation of amines and amides with peracetic acid in the presence of trimethylsilyl cyanide gives the corresponding α-cyano derivatives efficiently [154] (Fig. 16). The direct oxidative cyanation of tertiary amines opens a new and efficient approach to the synthesis of *N*,*N*-dialkyl-α-amino acid derivatives upon subsequent hydrolysis reactions.

TS-1 has been successful for the execution of oxidation of primary [155] (Fig. 17) and secondary amines [156] to oximes and hydroxylamines, respectively. The isopropyl amine was oxidized with somewhat higher selectivity over the larger pore TS-2 catalyst [155].

The MEL–Cr silicalite (a ZSM-11 type) catalyzed oxidation of arylamines with electron-withdrawing substituents like COOH, NO_2 and CN to the corresponding nitroarenes is remarkable because these compounds are difficult to obtain by conventional nitration methods. For the aliphatic amines, no prototopic rearrangement to oximes was observed, whereas benzylamine gives benzaldoxime only [157].

Titanium silicalites in combination with H_2O_2 exhibit remarkable activities and selectivities in the oxidation of anilines to symmetrical azoxybenzenes [158]. The selectivity for the formation of 3,3-dichloroazoxybenzene by oxidation of 3-chloroaniline was found to be 95% (2.5 h) over Ti–MCM-41 [15,16].

The oxidation of piperidine by TS-1 in the presence of ethyl vinyl ether allows the synthesis of isooxazoline with 65% selectivity in a single step without isolation of the intermediate nitrone [159] (Fig. 18).

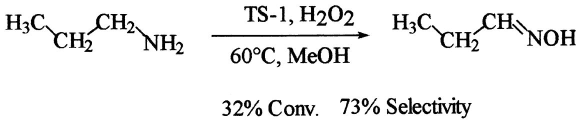


Fig. 17. TS-1 catalyzed oxidation of primary amines.

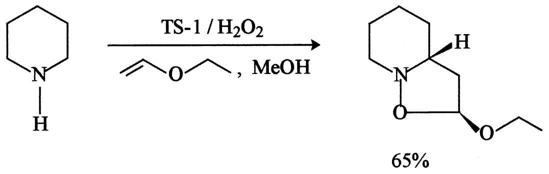


Fig. 18. Oxidation of piperidine to isoxazolidine.

8.1. ZnCrCO3–HTLc

Pyridyl ketones are found to be highly useful as intermediates in the synthesis of natural products and drugs. Various methodologies are used for the preparation of pyridyl ketones [160–163] but a universal methodology for the preparation of both acyl and benzoyl pyridines is lacking. Alkyl and benzyl pyridines are oxidized selectively to the corresponding ketones using catalytic amounts of calcined $ZnCrCO_3$–HTLc in conjunction with TBHP in dry *t*-BuOH at reflux conditions under nitrogen atmosphere giving excellent yields of ketones [164] (Fig. 19). There is no formation of by-products such as N-oxides. The catalyst is heterogeneous and easily recovered and reused with consistent activity and selectivity. The oxidation of alkyl and benzyl pyridines is realized by the use of basic catalysts as they show very weak complexation with the nitrogen of the pyridines.

The transition metal catalyzed oxidation of benzyl amines led to the formation of benzamides, benzyl cyanides and Schiff bases [152]. Benzyl amines, both primary and secondary benzyl amines are oxidized to the corresponding Schiff bases using catalytic amounts of calcined $ZnCrCO_3$–HTLc in the presence of anhydrous TBHP using dry DCM as solvent at room temperature under inert atmosphere in good yields without formation of by-products resulting from the aldol condensation products [165].

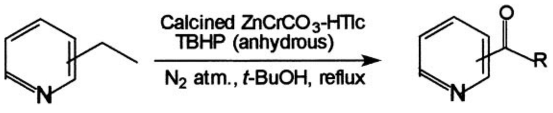


Fig. 19. Oxidation of benzyl pyridines by $ZnCrO_3$–HTLc.

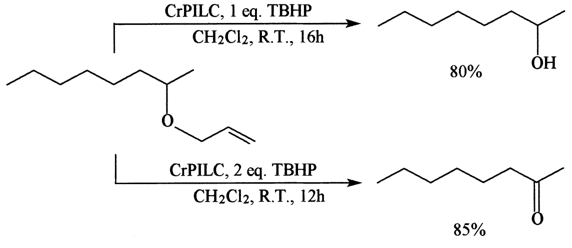


Fig. 20. CrPILC catalyzed oxidation of ethers in different quantities of TBHP.

9. Deprotection reactions

Oxidative deprotection of O- and N-benzyl groups using reagents developed for benzylic oxidation has not been well exploited. Earlier reports for the oxidative deprotection of the benzylic group with a few reagents such as CrO_3/AcOH [166], $Ce(SO_4)_2$/AcOH [167], etc., possess drawbacks such as the use of large excess of reagents, drastic conditions [168] and an insufficient selectivity towards the products. The treatment of allyl or benzyl ethers with one equivalent of TBHP in the presence of CrPILC at room temperature resulted in the oxidative cleavage of the allyl- or benzyl-oxygen bond to give the alcohol but when two equivalents of TBHP were used, the alcohol was oxidized further to the aldehyde or ketone [77] (Fig. 20).

Oxidation of allyl amines resulted in the cleavage of the allyl-nitrogen bond to give the des-allyl amine [102] but the benzyl amines were oxidized to the benzamides [77]. The catalyst displayed consistent activity and selectivity for four recycles.

Molybdenyl acetylacetonate is an effective catalyst for the deprotection of acetals into the corresponding aldehydes and ketones in good yields [169].

10. Oxidative coupling reaction

The synthesis of binaphthols by oxidative coupling of 2-naphthols has been of great synthetic interest since binaphthol and its derivatives for example BINOL and BINAP have wide applicability as chiral ligands in organic chemistry. Earlier, the oxidative coupling of 2-naphthols has been carried out with stoichiometric reagents such as $FeCl_3$ [170,171], K_3FeCN_6 [172], $Mn(acac)_3$ [173,174], copper amine complexes [175–177]. Apart from the disadvantage of being stoichiometric, these methods suffer from difficulties in separation of organic and inorganic products and low yields of the desired products. A clear improvement has been the introduction of heterogeneous catalysis using oxidation by air or oxygen. We have reported a simple and inexpensive oxidative coupling of 2-naphthols catalyzed by copper exchanged montmorillonite (Cu-mont) under aerated conditions in good yields [178] (Fig. 21). In fact, this methodology, which is the first catalytic methodology with the facile reuse of catalyst without any further reactivation, is being adapted by a Japanese industry for bulk production. Cu-mont is the most efficient heterogeneous catalyst giving nearly quantitative yields. The catalyst can be recycled several times with success. The high activity is attributed to the easy accessibility of catalytic sites. We have also executed the oxidative coupling of 2-naphthols by iron supported either on a pure montmorillonite clay (Fe pillared clay) or Fe-K10, an acid treated mesoporous clay [179].

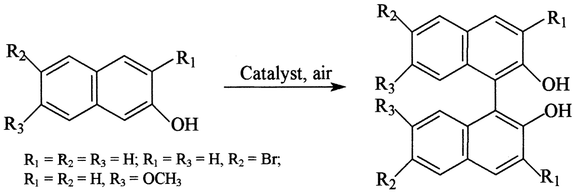


Fig. 21. Oxidative coupling of binaphthols by Cu-exchanged montmorillonite.

11. Concluding remarks and future prospects

The work in this review articulates the multifaceted efforts made in several laboratories towards achieving atom economy, zero-emission of effluents and the technological simplification of processes, the key factors for future advances in the field of selective oxidation applicable for fine and specialty chemicals. The use of molecular oxygen or air for safety reasons in place of other expensive oxidants for the oxidation reactions, the dream of chemists, will certainly bring down the cost of end products. However, this is a difficult task set for chemists for realization, particularly for epoxidation reactions. The selective oxidation of the specific functional group in the presence of other identical functionalities in the same molecule is a great challenge. Design of the catalysts that include active species as well as support is a critical parameter to achieve the targets enumerated as above. Studies in homogeneous catalytic reactions provide better understanding that helps identification of the active species. Understanding at molecular level to fix the active species in the heterogeneous systems, an essential ingredient is now possible with the advent of several solid probes such as ESCA, EXAFS, CP/MAS, NMR, FT-IR, and thermal studies. It is equally important to choose a suitable support for the active species compatible with the specific transformation for a targeted substrate. The industrial handling of oxidation reactions that are highly exothermic requires high level of expertize in chemical engineering aspects involving entropy, enthalpy, heat transfer, and safety. Therefore, the field of selective oxidation is by no means a mature area of research. But the exploration of new ideas and possibilities discussed above on oxidation lays a strong path for exponential growth.

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