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Basic solids in the oxidation of organic compounds

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Abstract

Solids with basic properties have been used in a variety of oxidation reactions and play three main roles. In some cases basic alumina has been used as a support for the oxidant and acts to control the acidity of the oxidant. More important is their role as a base for the activation of either the substrate or the oxidant, giving rise to different types of attack, i.e. electrophilic attack on carbanions or nucleophilic attack with peroxoanions. The third role is that of a support for the catalytic species and this mainly involves hydrotalcites. The catalytic centres can be included as part of the structure of the solid or, alternatively, be incorporated in between the sheets by anion exchange. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Basic solids; Oxidation reactions; Epoxidation

1. Introduction

The use of basic heterogeneous catalysts is an area of growing interest given that it is far less developed than that of acid catalysis. For this reason, considerable effort has been focused on the use of basic solids in organic reactions, either as catalysts or as supports. Given the great importance of oxidation reactions in organic synthesis, the application of solid catalysts is always a subject of current interest and the use of basic solids is not an exception. This review offers a general perspective of the different roles played by basic solids in oxidation reactions, with special emphasis on fine chemicals synthesis.

2. Basic solid as a support for the oxidant

The first role of solids in the oxidation of organic compounds was undoubtedly that of the support for the oxidant. Several different solids have been used, such as silica, alumina or clays [1,2], irrespective of their acid–base properties. The ease of handling, increased stability of the oxidant and the simple work-up procedures are the main advantages of this type of system.

However, basic alumina shows better performance in certain cases than its acidic counterpart, and this has been attributed to the control of the acidic character of the oxidant. In this way side reactions are minimised and the yield of desired product is higher. The oxidation of alcohols has been used as the standard test reaction for this kind of oxidant.

Pyridinium chlorochromate (PCC) on basic alumina [3] oxidises secondary alcohols to ketones and primary allylic alcohols to α,β-unsaturated aldehydes. The yields obtained were greater than 95% and the systems studied include some terpenes and cholesterol. The same supported oxidant was used in one step in the preparation of an intermediate in prostaglandin synthesis. This step involved the oxidation of 1-hydroxy-12-[(tetrahydro-2H-pyran-2-yl)-oxy]dodecan-4-one to the corresponding aldehyde

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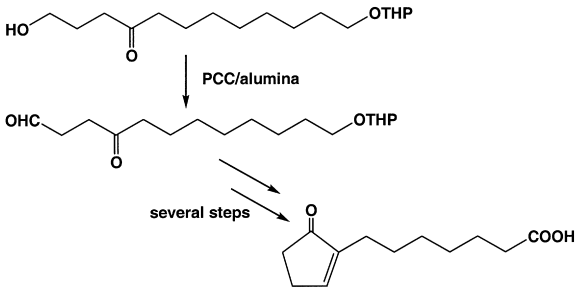


Scheme 1.

(Scheme 1) while preserving the protection of the alcohol in position 12 [4].

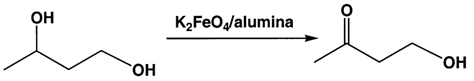
Another oxidant supported on basic alumina is potassium ferrate (K_2FeO_4) in combination with hydrated copper sulphate [5]. In this case primary aliphatic alcohols are oxidised in very low yields, which enables the system to be used for the oxidation of secondary alcohols in molecules that also contain primary alcohol groups. This is the situation in 1,3-butanediol, which is oxidised to 4-hydroxy-2-butanone (Scheme 2). The role of basic alumina is not clear in this case, but it was found that the use of silica leads to lower yields.

More recently, another kind of supporting system for the oxidant has been described. The anion exchange capacity of hydrotalcites (HT) has been used to support the permanganate anion [6]. Primary benzylic alcohols are oxidised with this supported permanganate to the corresponding benzaldehydes, whereas primary aliphatic alcohols lead to carboxylic acids.

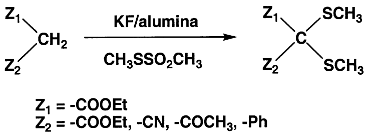
3. Activation of the reagents by proton abstraction

The abstraction of a proton by the solid base, either from the substrate or the oxidant, changes the nature of the oxidation reaction, and leads to either electrophilic or nucleophilic attack of the oxidant, respectively.

In the case in which the proton is abstracted from the substrate, the generation of a carbanion allows electrophilic attack of the oxidant at this position. Villemin et al. have explored this possibility using KF on alumina (KF/alumina) as a base. In the work described in their first paper [7], substrates with two electron-withdrawing groups were oxidised with a thiosulfonic ester, S-methyl methane sulfothioate, and such conditions led to thioketals (Scheme 3). The reaction is greatly accelerated by microwave irradiation and yields in the range 85–94% were obtained in only 2 min. On using a less acidic substrate, such as methyl phenylacetate, a lower yield was obtained (70%).



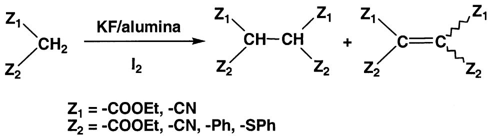
Scheme 2.



Scheme 3.

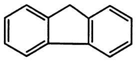
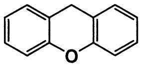
A second paper [8] deals with oxidative coupling of the same kind of substrates in the presence of iodine (Scheme 4). The reaction leads to alkanes or alkenes depending on the amount of iodine and the nature of the substrate. The reaction is not selective to alkanes but is synthetically useful for alkenes on using 1 equiv. of iodine. In the proposed mechanism the carbanion donates an electron to iodine, leading to a free radical and an iodide ion. The coupling takes place between two radicals, yielding the alkane or the alkene in the absence or in the presence of another molecule of iodine, respectively. The yields are in the range 60–90% and are noticeably increased by the use of ultrasound activation. As an example, diethyl malonate leads to 86% yield with ultrasound activation as opposed to the 65% obtained without ultrasound.

In a third paper, the oxidation of weakly acidic compounds to ketones with molecular oxygen in the presence of KF/alumina is described [9]. Compounds with a pK_a as high as 34 are oxidised, although the yield is strongly dependent on the pK_a values (Table 1). When the reaction is carried out at room temperature



Scheme 4.

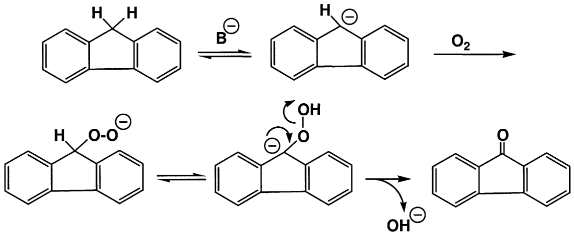
Table 1
Oxidation of weakly acid compounds with molecular oxygen in the presence of KF/alumina

Substrate	pK_a	Solvent	T (°C)	Yield (%)
 fluorene	23	Acetonitrile	25	92
 xanthene	30	Acetonitrile	25	35
Diphenylmethane	34	Acetonitrile	25	15
Fluorene	23	–	150	100
Xanthene	30	–	200	95
Diphenylmethane	34	–	200	92

in acetonitrile, fluorene (pK_a=23) leads to a high yield (92%) whereas the yield with diphenylmethane, the less acidic substrate (pK_a=34), is the lowest (15%). The reaction can be also carried out at higher temperature in the absence of a solvent. Under these conditions high yields (>90%) are always obtained, but the pK_a value dictates the reaction temperature. In the proposed mechanism (Scheme 5) the carbanion that is formed attacks molecular oxygen to give an alkylperoxide anion, which subsequently loses a hydroxide anion to give the corresponding ketone. This mechanism explains why more acidic substrates that contain only a single benzylic hydrogen, such as triphenylmethane, do not react under these conditions.

When a proton is abstracted from the oxidant by the base, the character of the oxidant becomes nucleophilic and its reactivity changes.

The most important oxidation reaction with nucleophilic oxidants is probably the epoxidation of electron-deficient alkenes, and this process occurs through conjugate addition of the oxidant and subsequent intramolecular substitution (Scheme 6).



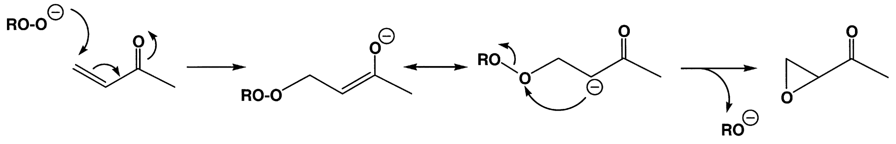
Scheme 5.

The first example of this kind of epoxidation to be described involves the system formed by KF/alumina as a base and *tert*-butyl hydroperoxide (TBHP) as an oxidant [10,11]. This system is able to epoxidise α,β-unsaturated ketones, although the yield depends on the structural features of the substrate. With acyclic ketones that contain aromatic substituents, such as chalcone, the reaction is very fast and a quantitative yield is obtained in only 10 min. With cyclic ketones (Table 2) the substitution pattern of the C–C double bond is the factor affecting the reactivity. The epoxidation of 2-cyclohexenone is fast and efficient, but the introduction of a substituent in the α-position (methyl) decreases the reactivity, as shown by the result obtained with carvone. Substitution in the β-position has a more dramatic effect and this is demonstrated by the epoxidation of 3-methyl-2-cyclopentenone and 3-methyl-2-cyclohexenone. The presence of substituents in other positions also has an influence on the reactivity, as demonstrated by the case of isophorone, which does not react under the conditions described. The conditions used included the use of acetonitrile as a solvent, although some solvent effect is also described. The use of benzene, hexane and THF lead to better results in the epoxidation of carvone, whereas the use of diglyme was completely ineffective. This solvent effect was further demonstrated in the epoxidation of isophorone, a reaction that does not take place in acetonitrile but does proceed in high yield on using toluene as the solvent [12].

α,β-Unsaturated esters, such as methyl cinnamate, do not react with the system TBHP+KF/alumina unless two electron-withdrawing groups are conjugated to the C–C double bond, as in dimethyl benzylidenemalonate.

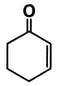
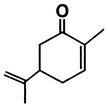
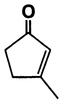
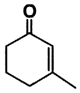
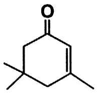
An alternative for this kind of epoxidation is the use of hydrogen peroxide as the oxidant and HT as the base [13]. Although the results with cyclic ketones (Table 2) are not as good as those described with TBHP+KF/alumina, the use of hydrogen peroxide introduces an additional advantage from a practical point of view. A similar structural dependence of the yield is observed and isophorone, for example, is slowly epoxidised.

One significant difference with the other system is the behaviour of aliphatic acyclic ketones. In all cases in which H_2O_2/HT is used, another product appears that is different from the epoxide.



Scheme 6.

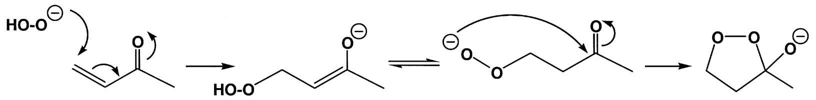
Table 2
Epoxidation of cyclic α,β-unsaturated ketones

Ketone	TBHP+KF/alumina[a]		H_2O_2+hydrotalcite[b]	
	Time (h)	Yield (%)	Time (h)	Yield (%)
 2-cyclohexenone	1	85	6	92
 carvone	10	85	24	70
 3-methyl-2-cyclopentenone	20	65	–	–
 3-methyl-2-cyclohexenone	20	40	–	–
 isophorone	20	0	72	66

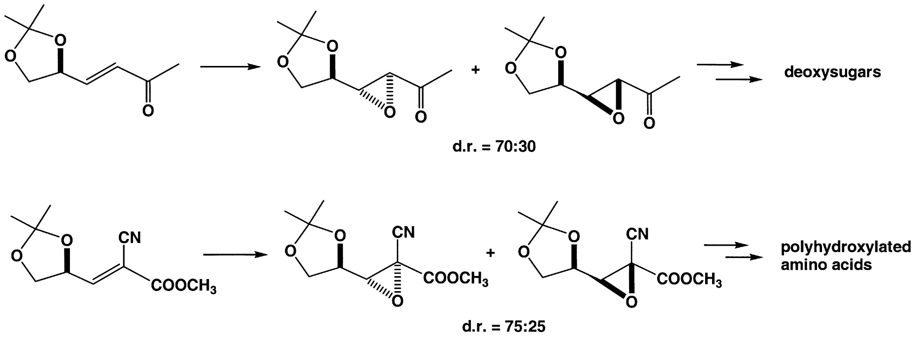
[a] [11].
[b] [13].

This product was identified as the corresponding 3-hydroxy-1,2-dioxolane. The mechanism (Scheme 7) to account for the formation of this product should be similar to that of the epoxidation reaction. However, the intermediate enolate can abstract the proton from the hydroperoxide moiety to create a nucleophilic species, which in turn attacks the carbonyl carbon. In order for this situation to arise the presence of a hydrogen atom bonded to the peroxide moiety is necessary and, in the case of the reaction with TBHP, this behaviour cannot occur. The appearance of these 1,2-dioxolanes with HT but not with NaOH may be due to the different basic strength.

The system H_2O_2/HT is not able to epoxidise cinnamonitrile or methyl cinnamate, but the nitrile and the ester groups are hydrolised. However, the presence



Scheme 7.



Scheme 8.

of both groups in methyl 2-cyanocinnamate makes the C–C double bond sufficiently electrophilic to react with the hydroperoxide anion.

The performance of this system has recently been improved by anion-exchange of the *tert*-butoxide anion, which increases the basicity of the solid [14]. In this way high yields (86–100%) after only short reaction times (5–30 min) are obtained with cyclic ketones and chalcones. Unfortunately, the effect of this modification on the selectivity to 1,2-dioxolanes is not described.

It is important to note that both systems are complementary, given that KF/alumina cannot be used in aqueous media or that hydrotalcite is unable to activate TBHP.

The application of both systems to the diastereoselective synthesis of epoxides has been studied very recently [15]. A chiral ketone and a cyanoester derived from D-glyceraldehyde (Scheme 8) have been epoxidised in fairly good yields. As happened with simple substrates, the use of H_2O_2/HT leads to some by-products, due to hydrolysis of the nitrile group, together with lower diastereoselectivities. By contrast, the system TBHP+KF/alumina leads to the desired products with total conversion and diastereomeric excesses ranging from 40 to 50%.

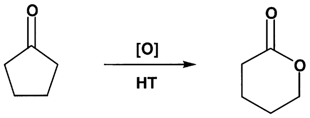
4. Support of the catalytic centres

4.1. Catalytic centres as a part of the solid structure

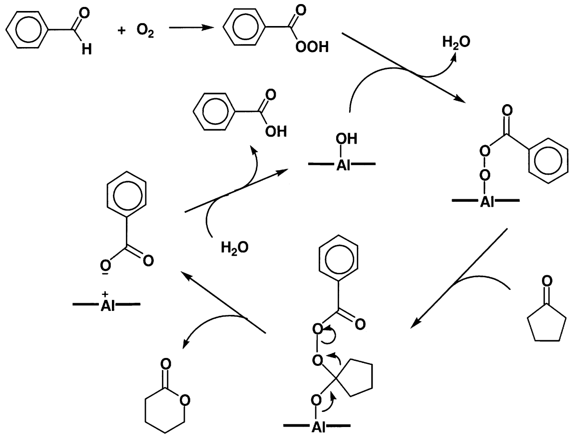
Hydrotalcites and hydrotalcite-like compounds (HTlc), i.e. layered double-metal hydroxides (LDH) with a HT structure in which magnesium and aluminium are replaced by transition metals, are able to catalyse oxidation reactions through catalytic centres included in the solid structure.

Kaneda and co-workers have thoroughly studied this ability in different oxidation reactions. Their first work in this field concerned the Baeyer–Villiger oxidation of cyclopentanone (Scheme 9) using a combination oxidant system of molecular oxygen and benzaldehyde in the presence of HT bearing different Mg/Al ratios (from 1:1 to 6:1) and different anions (CO_3^{2-}, Cl^- and *p*-toluenesulfonate) [16]. The best results were obtained with the HTs $Mg_{10}Al_2(OH)_{24}CO_3$ and $Mg_5Al(OH)_{12}Cl$. In the case of the first solid, the study was extended to a series of cyclic and aromatic ketones. The best results (conversions and yields over 90%) were obtained with five-membered ring ketones and *p*-methoxyacetophenone. On the other hand, cyclohexanones gave rise to conversions that were similar or lower to those obtained in the absence of a catalyst.

A complete mechanistic study of this oxidation system was described in a further publication [17]. In this study, a series of HTs with different numbers and strengths of basic sites was used in the Baeyer–Villiger oxidation of cyclopentanone with benzaldehyde/O_2. The comparison between the different results showed



Scheme 9.



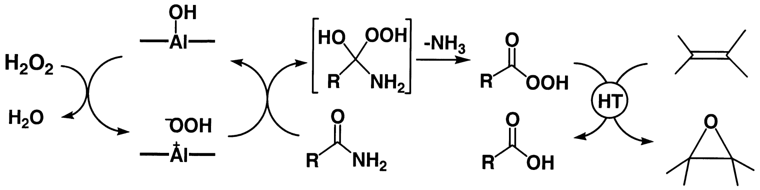
Scheme 10.

that both the number and the strength of basic sites are important for the reaction to progress. The postulated mechanism for this reaction consists of two steps. Firstly, the benzaldehyde undergoes an autoxidation to give perbenzoic acid, which subsequently transfers an oxygen atom to the ketone. The same reaction was studied using *m*-chloro perbenzoic acid (MCPBA) as the oxidant, in the presence of the same HT, and the results obtained were similar to those observed with the oxidant system benzaldehyde/O_2. The production of perbenzoic acid from benzaldehyde and O_2 was also studied in the presence and in the absence of HT, and in this case no particular influence of the basic solid was observed. Thus, the mechanism proposed for this reaction can be summarised as shown in Scheme 10. It can be seen that the HT not only acts as a base, but also participates in the oxygen transfer step, and it can therefore be concluded that the aluminium centres of the HT do play a catalytic role.

This situation is shown clearly in the case of HT functionalised with transition metals. Kaneda and co-workers [18] prepared several HTs with the general formula $Mg_3AlM_{0.3}CO_3$ (M=Fe, Cu). It was demonstrated that these solids are better catalysts than the parent HT in the Baeyer–Villiger oxidation of ketones with benzaldehyde/O_2. The Fe-HT gives good results in most cases and leads to almost quantitative yields. On the other hand, the Cu-HT shows better behaviour with bicyclic and acyclic ketones and gives yields of over 90%. Comparison of these results with those obtained in the homogeneous phase using $Cu(acac)_2$ as a catalyst showed that the behaviour of the heterogeneous catalyst is different from that of the homogeneous one, and that this behaviour can even be complementary in some cases. Furthermore, all the solids used could be recovered and reused successfully. Similarly, the same research group also showed that HT functionalised with Ni and Cu, as well as HTs themselves, could act as catalysts in the Baeyer–Villiger oxidation of ketones with MCPBA [19]. In this case, the presence of transition metals led to an improvement in the results obtained with simple HT in the oxidation of pivalaldehyde.

The strategy of immobilising an active metal species in the HT structure has been used by Kaneda and co-workers to promote the oxidation of allylic and benzylic alcohols with molecular oxygen [20]. Thus, the HT $Mg_6Al_2Ru_{0.5}(OH)_{16}CO_3$ was able to catalyse the complete oxidation of cinnamic alcohol to cinnamaldehyde in 24 h. Furthermore, the catalyst was recovered and reused three times without loss of activity. Other solids, in which Fe, Ni, Mn, V, or Cr are used instead of Ru, led to worse results, as did the use of anions other than CO_3^{2-}. The study was extended to the oxidation, catalysed by the Ru-HT, of a series of allylic and benzylic alcohols. In all cases, conversions of over 95% and almost quantitative yields were obtained, with the exception of benzylic alcohols bearing electron-withdrawing groups.

HTlcs have been also used as catalysts in the oxidation of allylic and benzylic alcohols, as well as aromatic compounds with benzylic positions, with molecular oxygen [21]. Thus, Kaneda and co-workers prepared a series of HTlcs in which Mg is replaced by other divalent ions, such as Co, Mn, Fe or Zn, with the Ru maintained in their structures ($Ru:M^{II}:Al=0.3:3:1$). These solids were studied in the benchmark reaction of oxidation of cinnamic alcohol to cinnamaldehyde. The replacement of Mg by Co or Mn gave rise to a spectacular increase in the catalytic activity, with total conversions obtained after reaction times of only 40 min. The CoRu-HTlc was subsequently used in the oxidation of a series of alcohols, including a number of heterocyclic systems. In all cases, excellent results were obtained, even for aliphatic allylic alcohols. This solid is also active in the oxidation of the benzylic position of aromatic compounds such as xanthene, fluorene or diphenylmethane, with yields over 95%. As far as the catalytic



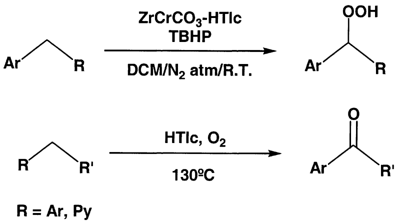
Scheme 11.

mechanism is concerned, the Co-HTlc, without Ru in its structure, was not able to catalyse these reactions, and the activity of the CoRu-HTlc was far superior to that of the physical mixture of Ru-HT and Co-HTlc. This superiority demonstrates the existence of a synergetic effect of Ru and Co. XPS experiments revealed the presence of Ru atoms in high oxidation states (Ru^{IV} or Ru^{V}), which is probably favoured by the close proximity of Co.

The epoxidation of alkenes has also been catalysed by HT using different oxidant systems. Thus, a combination of benzonitrile and hydrogen peroxide was used, in the presence of HTs with different Mg/Al ratios and interlayer anions, in the benchmark reaction of epoxidation of cyclohexene [22]. The presence of the nitrile is essential for the epoxidation reaction to take place. The best result (complete conversion of cyclohexene and quantitative yield in epoxide) was obtained with the most basic solid, $Mg_{10}Al_2(OH)_{24}CO_3$. The use of a liquid base, such as NaOH, gave rise to high conversions but much lower yields in epoxide. This HT was subsequently employed for the epoxidation of a series of alkenes, giving rise in all cases to yields in epoxide of over 90%. It is important to note that neither other oxidation products nor epoxide ring-opening products were observed. Another interesting point is that the epoxidation rate noticeably increases with the use of anionic surfactants, such as sodium dodecylsulfate (SDS), probably due to an increase in the extent of surface contact between the organic (alkene, nitrile) and the aqueous (H_2O_2) phases. The mechanism proposed starts with the reaction of the nitrile with hydrogen peroxide to give a peroxycarboxymidic acid, which is the actual epoxidation agent.

The methodology described in a further report by this group is very similar to that described above [23]. In this case, the oxidant system consists of isobutyramide/H_2O_2 in the presence of HT and anionic surfactants. This system is able to epoxidise alkenes without leading to other by-products. In most cases, a stoichiometric amount of isobutyramide is sufficient to promote the reaction. However, in some cases, such as 1-octene, an excess of the amide is required. The stereospecificity and regioselectivity observed in the epoxidations suggested that they take place through peracid intermediates. Since it had been demonstrated that HTs are able to catalyse epoxidation reactions with MCPBA, it is suggested that the HT activity takes place at two different stages of the reaction: formation of the hydroperoxide anions, HOO^-, and oxygen transfer from the peracid to the alkene double bond (Scheme 11). Finally, the solids can be recovered and reused at least three times without loss of activity.

$ZnCrCO_3$-HTlc has been used by Choudary and co-workers [24] in the mild and selective hydroperoxidation of arylalkanes with *tert*-butyl hydroperoxide (TBHP) (Scheme 12). The calcined catalyst led to optimal selectivity and yield when compared to the uncalcined one. Indeed, yields between 40–60% of hydroperoxide were obtained with a series of aromatic compounds with free benzylic positions. In a further study [25], the same authors used similar systems to obtain ketones from this kind of aromatic compound by oxidation with molecular oxygen (Scheme 12). The reactions were carried out at 130°C, a temperature that was found to provide a good compromise



Scheme 12.

between conversion and selectivity in ketone. Different solids were tested as catalysts ($ZnCrCO_3$, $NiAlCO_3$, $CuZnCO_3$, and $MgAlCO_3$), but the best results were obtained with the former. These solids are considered by the authors as highly dispersed mixed oxides, and the presence of a metal with oxidative ability is mandatory, since $MgAlCO_3$ (HT) does not display any catalytic activity. Calcined solids have better catalytic activity, and these solids can be efficiently recovered and reused without loss of catalytic activity or metal leaching.

A similar reaction, in which $ZnCrCO_3$-HTlc has also been used, is the oxidation with TBHP of alkyl and benzylpyridines to the corresponding ketones (Scheme 12) [26]. The reactions give better results with benzyl (45–87% yields) than with alkylpyridines (15–50% yields), and yields are higher when the benzylic carbon to be oxidised is linked to the 4-position of the pyridine ring.

Another similar reaction is the oxidation of *p*-cresol to *p*-hydroxybenzaldehyde with molecular oxygen, and this system was studied by Wu and co-workers [27]. These authors used several HTlcs as catalysts, $CoAlMCO_3$ (M=Cu, Ni, Mn, Cr, Fe), in which the ratios between the different metals were changed. All the solids were characterised by different physical techniques (XRD, IR, CO_2-TPD, BET surface areas). The XRD study showed that the HTlc structure changes when the calcination temperature increases, with the HT structure gradually becoming spinel in structure. Catalytic studies were carried out in order to find the best experimental conditions. It was found that calcined HTlcs display much higher catalytic activity than mechanically mixed oxides (Co_2O_3, CuO, Al_2O_3), the best results being obtained with $CoAlCuCO_3$. The best reaction conditions were 5 h at 70°C (98.4% yield). Higher reaction temperatures result in the production of a tarry mass and subsequent deactivation of catalyst. Finally, the best catalyst was recycled ten times and maintained the same activity and selectivity. XRD experiments on the recovered solid showed that the spinel structure is maintained after ten catalytic runs.

The reaction mechanism proposed for this process indicates that both Co^{2+} and Co^{3+} are able to act as catalysts. It is suggested on this basis that the simultaneous presence of both oxidation states of Co in the spinel structure of the solid could be responsible for the high catalytic efficiency observed.

The same authors have studied the hydroxylation of phenol with hydrogen peroxide, catalysed by several HTlcs $CuAlMCO_3$ (M=Co, Ni, Cu, Zn, Fe) [28]. The presence of Cu^{2+} in the structure is essential for the catalytic activity of these solids and so it is assumed that this is the true catalytic centre of the HTlc, whereas the other divalent metal in the structure does not play any catalytic role. The catalytic activity of these solids favourably compares with that of TS1. A thorough study was carried out on the different aspects of the reaction. In this case, calcined HTlcs lead to worse results than uncalcined ones, and the catalytic activity increases with the Cu/Al ratio. It should be noted, however, that it is not possible to prepare HTlcs with arbitrarily high Cu/Al ratios. Reaction does not take place in organic solvents and water is the only solvent of use, the best results being obtained at pH 7 (for a studied range of 2–11).

The proposed mechanism involves the formation of Cu^{3+} in the H_2O_2 decomposition step. These Cu^{3+} ions participate in the oxidative step of the biphenol formation. The strong solvent and pH dependence observed are explained on the basis of this mechanism.

4.2. Supported catalytic species

Layered double hydroxides (including both HTs and HTlcs) have also been used as supports for oxidation catalysts. Depending on the nature of the hosted system, it is possible to establish a division between LDH intercalated with oxometalates and LDH intercalated with anionic complexes. An excellent review dealing with the synthesis, properties and applications of this kind of material has recently been published [29].

4.2.1. Layered double hydroxides intercalated with oxometalates

In one of the pioneering works, Twu and Dutta [30] intercalated vanadate ions into $LiAl_2(OH)_6{}^+$ by ion exchange. Complete chloride exchange was observed at pH 5–11, with an increase in the gallery height from 3 to 6 Å. The layer structure of $LiAl_2(OH)_6$–V_2O_7 begins to disappear at temperatures beyond 300°C (gallery height 1.8 Å) along with the formation of polymeric O–$(VO_2)_n$–O species. The material obtained upon heating to 300–400°C was tested in the air oxidation of *o*-xylene at 350°C. Although the conversion to product is relatively poor, the material does, to some extent, promote the selective oxidation to *o*-tolualdehyde. $LiAl_2(OH)_6Cl$ that had been thermally decomposed under the same conditions did not show any catalytic activity, which confirms the participation of the vanadium centres.

Kwun and Pinnavaia [31] have prepared Zn_2Al-LDH derivatives pillared by $[XM_{12}O_{40}]^{n-}$ Keggin ions by ion exchange of $[Zn_2Al(OH)_6]NO_3 \cdot xH_2O$. Under the conditions used is not possible to intercalate ions with $n \leq 4$. However, it is possible to achieve complete intercalation with $n \geq 6$. The gallery height is close to 10 Å. Some of these LDH intercalated anions were investigated in the photocatalytic oxidation of isopropanol to acetone. The turnover number was found to depend on the nature of the polyoxometalate and thus, in air, $Zn_2Al[BV^{IV}W_{11}O_{40}]^{7-}$ gives a turnover number of 3.9, $ZnAl_2[SiV_3W_8O_{40}]^{7-}$ of 8.0, and $ZnAl_2[H_2W_{12}O_{40}]^{7-}$ of 10.3.

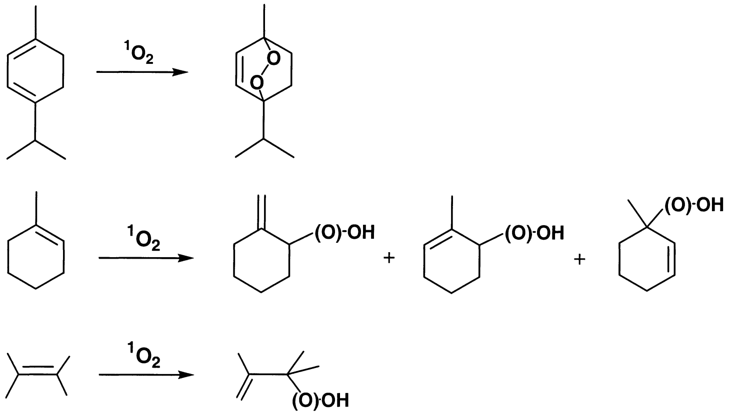
Tatsumi and co-workers have described [32,33] the use of molybdate- and tungstate-intercalated LDH as catalysts for alkene epoxidation with H_2O_2 in tributylphosphate. With the molybdate-pillared hydrotalcite, the epoxidation of 2-hexene proceeded faster than that of cyclohexene, whereas the opposite is true when free heptamolybdate was used as a catalyst. This behaviour was attributed to a hampered accessibility of cyclohexene to the catalytic sites. This effect was less marked for the tungstate-pillared solid, which is in agreement with its wider basal spacing (12.2 vs. 9.9 Å).

The faster epoxidation of *cis*-2-hexene in comparison with the *trans*-isomer was also attributed to the constraint imposed by the interstitial environment. The epoxidation of cyclohexene promoted by these catalysts was inhibited by triethylamine but not by triphenylamine, which was explained in terms of shape-selective poisoning. Another effect of intercalation was a higher epoxide/diol selectivity, which might be related to the basic nature of the brucite layers, in contrast to the slightly acidic properties of polyoxometalates.

The same solids, together with the related Zn_2Al-LDH-polyoxometalate systems, have been studied by Gardner and Pinnavaia [34] as catalysts for the epoxidation of cyclohexene under the same conditions. The LDH intercalates showed lower catalytic activities than the unsupported catalysts. The epoxide/diol selectivity also changed from the unsupported to the intercalated catalysts, but also from Zn_2Al-LDH to Mg_2Al-LDH systems. This result is in agreement with the influence of the acid–base properties of the catalyst. It was pointed out in this work that $Mg_2Al–Mo_7O_{24}{}^{6-}$ and $Mg_2Al–W_7O_{24}{}^{6-}$ decompose at the temperature used to dry the catalysts prior to the reaction. The origin of the previously described substrate selectivity cannot be attributed to molecular sieving. Even the structurally stable $Zn_2Al–H_2W_{12}O_{40}{}^{6-}$ LDH lacks of the microporosity necessary to allow access of reagents to the solvated gallery anions under the reaction conditions. XRD results showed the presence of salt-like impurity phases, which can have a significant influence on the catalytic properties of these solids.

LDH-supported tungstates have been used as catalysts in the H_2O_2 epoxidation of several olefins [35,36]. The polarity of the environment of the catalytic centres was modulated by means of the modification of the anion population of the LDH. A hydrophilic system, (Cl^-, $WO_4{}^{2-}$) (Mg, Al)-LDH, and a hydrophobic system, (*p*-Tos$^-$, $WO_4{}^{2-}$) (Mg, Al)-LDH, were obtained by anion exchange in such a way that tungstate takes 10–15% of the anion-exchange capacity and the rest is occupied by the co-anion. Reaction of $WO_4{}^{2-}$ with H_2O_2 produces peroxocomplexes. The hydrophilic catalyst is active in the epoxidation of a variety of olefins, particularly allylic alcohols. The alkaline nature of the catalysts seems to prevent solvolysis reactions, and selectivities in epoxide are, in general, satisfactory. However, for some substrates, allylic hydroperoxidation is a competing reaction. The epoxidation of apolar olefins proceeds more conveniently with the hydrophobic catalyst, and the epoxide selectivities are clearly superior. The *p*-tosylate increases the hydrophobicity of the micro-environment, although formation of heteronuclear S-W peroxoclusters may also contribute to the improved selectivity. In fact, the use of ($SO_4{}^{2-}$, $WO_4{}^{2-}$) (Mg, Al)-LDH, which has a polarity similar to the Cl^- exchanged LDH, leads to better selectivities.

As expected, the oxidations are stereospecific with both catalysts. However, the stereo- and regio-selectivities are affected by the nature of



Scheme 13.

the catalyst. For instance, in the epoxidation of 2-cyclohexenol, the *cis*/*trans* ratio changes from the hydrophilic (90:10) to the hydrophobic (69:31) LDH. Tungstate catalysts show a preference for the double bond at the α-position to the hydroxyl group in geraniol over the distal one (98:2), whereas this regioselectivity is reversed (15:85) with the hydrophobic catalyst.

30% H_2O_2 has been used in the oxidation of benzaldehyde to benzoic acid catalysed by $ZnAl[SiW_{11}O_{39}]^{8-}$ and $ZnAl[SiW_{11}O_{39}Z(H_2O)]^{6-}$ ($Z=Co^{2+}$, Ni^{2+}, Cu^{2+}) [37]. The highest catalytic activity corresponds to the Co catalysts and this was attributed to the easy variation of the oxidation number of cobalt, with a tentative mechanism based on the oxidation of Co^{2+} to Co^{3+} by H_2O_2, followed by oxidation of benzaldehyde by Co^{3+}.

Guo et al. have studied the oxidation of cyclohexene by O_2 with LDH-intercalated $XW_{11}Z(H_2O)O_{39}{}^{n-}$ (where X=P, Si, and $Z=Mn^{2+}$, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) [38]. Catalysts were prepared by ion exchange reaction of $Mg_3Al(OH)_8NO_3{\cdot}xH_2O$ with aqueous solutions of the polyoxometalates. Allylic oxidation is the main reaction, with 2-cyclohexenol and 2-cyclohexenone being the major products, whereas cyclohexene oxide and *trans*-1,2-cyclohexane diol are obtained in smaller amounts.

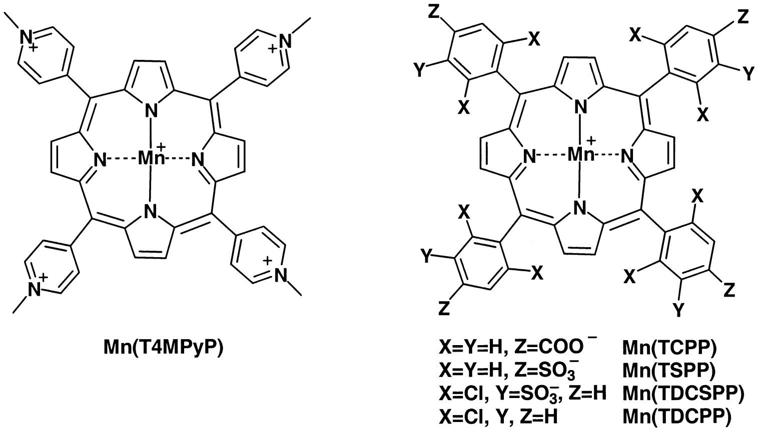
The LDH-intercalated polyoxometalates are more active than the nitrate form of the hydrotalcite and than the alkaline salts of the polyoxometalates. The Z-ions in the polyoxometalates had a noticeable influence on the catalytic activity. Thus, whereas Mn, Cu and Co systems showed high activities with conversions higher than 80%, with Ni and Fe the conversions reached only ca. 10%. Consequently, adjusting the type and number of transition metal cations could modify the catalytic activities.

Jacobs and co-workers have described molybdate immobilised on Mg, Al-LDH as an active catalyst able to generate singlet molecular oxygen from H_2O_2 [39]. When the catalyst is exposed to hydrogen peroxide in dioxane, polyperoxomolybdate species are formed that smoothly release $^1O_2$. This behaviour is in agreement with the basic nature of the LDHs. The released $^1O_2$ was used in $[4\pi+2\pi]$ cycloadditions and in ene-type reactions (Scheme 13). Epoxides are also formed as minor products (<20%). When the occupancy of the anion exchange capacity by $[MoO_4{}^{2-}]$ is lowered from 37.5 to 12.5%, the yield almost doubles. Apparently, a slower release of $^1O_2$ from the diluted active centres ensures an optimal capture by the organic substrate. The elemental composition of the LDH is also important, with a decrease in the Al content leading to a decrease in the epoxide formation and to a increase in the peroxidation yield.

4.2.2. Layered double hydroxides intercalated with anionic complexes

Tetracationic and tetraanionic Mn-porphyrins have been supported on a diverse range of organic and inorganic materials [40] (Scheme 14).

The catalytic activity of the materials obtained was first tested in the epoxidation of cyclooctene with

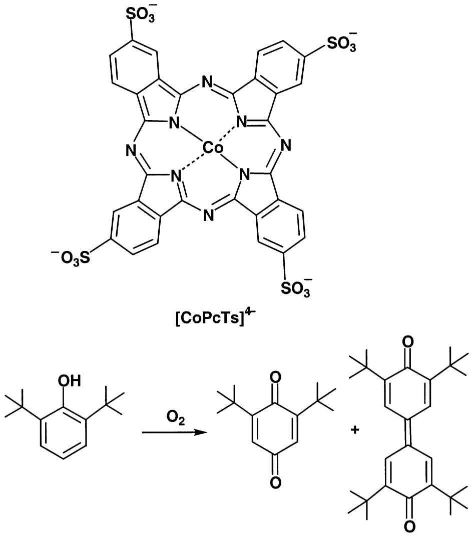


Scheme 14.

PhIO. Although all of the materials studied exhibited catalytic activity, the behaviour was remarkable for Mn(T_4MPyP) on SiO_2 and on KSF clay, and for Mn(TDCSPP) on Al_2O_3 or MgAl-LDH. These catalysts led to excellent yields (86–92%) in less than 2 h.

Some of these catalysts were very efficient in the hydroxylation of the poorly reactive heptane. Whereas Mn(T_4MpyP) gave very low yields, the same complex supported on SiO_2 or KSF clay led to yields of up to 49%, which are similar or even better than those obtained with the best homogeneous system, Mn(TDCPP). Mn(PDSPP) supported on Al_2O_3 is also a good catalyst and led to 46% yield. Some of these solids were shown to be efficient catalysts in the hydroxylation of other alkanes.

Pinnavaia and co-workers have tested Co(II)-tetrasulfophthalocyanines, intercalated in LDHs, as catalysts in the dioxygen oxidation of 2,6-di-*tert*-butylphenol [41,42] (Scheme 15).



Scheme 15.

The intercalation in Mg_2Al- and Mg_4Al-LDH increased the catalytic activity and longevity in relation to the homogeneous complex, and this is probably due to the inhibition of the deactivating dimerisation and self-oxidation. In contrast, $[CoT_4MPyP]^{4+}$ intercalated in fluorohectorite is less active than the homogeneous system. This behaviour was related to the different orientation of the complex within the galleries. The vertical orientation in LDH optimises accessibility to the catalytic centres near the edge sites of the crystallites. The improved accessibility may also be responsible for the greater activity of the lower charge density host Mg_4Al-LDH in comparison with Mg_2Al-LDH.

The same LDH-intercalated complex showed increased stability, in comparison with the homogeneous catalyst, in the oxidation of 1-decanethiol with O_2 [43].

$[CoPcTs]^{4-}$ immobilised on ZnAl-LDH has been studied as catalyst for the PhIO oxidation of cyclohexene [44] and gives rise to a low turnover frequency and a distribution of products 2-cyclohexenol:2-cyclohexenone:cyclohexene

$$4\,RS^- + O_2 + 2H_2O \longrightarrow 2RSSR + 4HO^-$$

Scheme 16.

oxide=53:44:3. The behaviour of the catalyst was monitored in situ by EXAFS and XRD, and the results obtained suggest that only sites on the surface are accessible to the reactants.

$[CoPcTs]^{4-}$, both in neat form and intercalated in MgAl-LDH, was shown to promote the H_2O_2 oxidation of cyclohexanol to cyclohexanone [45]. In both cases the final conversions were high, but the intercalated catalyst is five times more active, which was primarily attributed to site isolation.

Complexes of Co(II)-phthalocyanine tetracarboxylic and tetrasulfonic acid, intercalated into the interlayer space of Mg_5Al_2-LDH, have been used by Iliev et al. [46] as catalysts for the oxidation of ethanethiol with O_2 (Scheme 16).

For the range of concentrations studied, the rate was found to be higher in the homogeneous phase. The effectiveness of the catalyst in both the homogeneous and heterogeneous phases decreased as the concentration of the complex increased. This effect was attributed to aggregation and crystallisation of the phthalocyanine complexes. Intercalation compounds with high concentrations of cobalt phthalocyanine complexes increase the possibility of formation of less active μ-peroxocompounds between neighbouring molecules.

Immobilised Zn-phthalocyanine complexes catalyse the photooxidation of ethanothiol to the corresponding sulfonic acid [47]. The catalytic activity is promoted by monomeric distribution and it is higher when supports with well-defined microcrystalline cavities, such as layered double hydroxides and NaX zeolite, are used. The co-adsorption of water retards the diffusion of the reagents towards the catalytic centres, which in turn reduces the catalytic activity, but also the degree of photodestruction of the complexes. Hydrophobic modification by the use of dodecylsulfate in the case of LDH, or tetrabutylammonium in the case of the zeolite, increased both the catalytic activity and the degree of photocatalyic destruction of the complex.

$\{Mo^{VI}O_2\text{-}[O_2CC(S)Ph_2]_2\}^{2-}$ was the first dioxomolybdenum(VI) complex described as being capable of oxidising aliphatic thiols under homogeneous conditions [48,49]. During the oxidation the Mo(VI) complex is reduced to monomeric $Mo^{V}O$ species via an intermediate $Mo^{IV}O$ species [50] (Scheme 17). Given the difficulty of reoxidising Mo(V) to Mo(VI), the formation of this species prevents the use of common oxidants, such as DMSO, in the design of catalytic cycles.

When the complex is intercalated into ZnAl-LDH [51–54], site isolation and steric hindrance prevent the comproportionation reaction, and the $Mo^{IV}O$ species can be reoxidised to close the catalytic cycle. This process allowed the oxidation of ethanethiol with DMSO in air, although the reactions were found to be too slow. Better results were obtained using molecular oxygen as the oxidant.

5. Concluding remarks

Basic solids can play different roles in oxidation reactions. On the one hand, their basic character can be used to activate the oxidant or the substrate. On the other, the catalytic centres can be introduced into the structure in different ways. In any case, the basic character can be advantageous when organic substances with acid-sensitive functional groups are involved in the oxidation process. In general, although basic solids are promising for the synthesis of fine chemicals and specialities, most of work has been carried out with benchmark reactions and deeper studies are needed to know the chemo-, regio- and stereo-selectivity of the different oxidation reactions and the comparison with the homogeneous bases most commonly used.

The role of LDH materials as precursors for mixed oxides containing active metals, such as Fe, Co or Cu, is another interesting point which needs a deeper study. Their use in Baeyer–Villiger and alcohol oxidation is

$$\{Mo^{VI}O_2[O_2CC(S)Ph_2]_2\}^{2-} + RSH \rightleftharpoons \{Mo^{IV}O[O_2CC(S)Ph_2]_2\}^{2-} + RSSR + H_2O$$

$$\{Mo^{IV}O[O_2CC(S)Ph_2]_2\}^{2-} + \{Mo^{VI}O_2[O_2CC(S)Ph_2]_2\}^{2-} + 2H^+ \rightleftharpoons 2\{Mo^{V}O\ [O_2CC(S)Ph_2]_2\}^{-} + H_2O$$

Scheme 17.

quite well documented but a complete screening in other important oxidation reactions, allylic oxidation or epoxidation for example, seems to be necessary.

The intercalation of anionic species into LDH is an interesting alternative for the inmobilisation of catalytic complexes. The changes in catalytic performance due to the different environment of the catalytic species are difficult to predict. So more studies are needed to rationalise this effect. Moreover, the intercalation of complexes with anionic ligands may be the starting point for the preparation of chiral heterogeneous catalysts, one of the most important goals in the field of fine chemical synthesis.

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