

Catalysis by hydrotalcite materials

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The search and exploitation of selective new catalytic material based on abundant materials in earth have been always interesting and also challenging. Hydrotalcites both natural and synthetic ones have been extensively examined in recent times as catalytic-materials for a variety of organic transformations. In all these reactions reported in literature, hydrotalcites have been precursors and active phases mostly resemble the conventional mixed oxides though they exhibit totally different catalytic property in terms of the Turn Over Number (TON) and also selectivity. Some of these catalysts derived from hydrotalcites promote typical base-catalyzed reactions. These systems also exhibit both acid and base sites adjacent to each other and thus responsible for the observed unusual selectivity.

Keywords: Hydrotalcites, Turn over number, Base-catalyzed reaction

Clays are one of the important natural materials, which have been examined for numerous catalytic applications. The search for alternate materials to be used as catalysts has been always continuing. The exploitation of natural resource materials for possible catalytic applications has been in practice for decades. Many synthetic catalytic systems have been modelled based on clay materials and these fall under the category of hydrotalcites. There are many reviews in recent times¹⁻⁸. Clays are characterized by a layered structure and hence they are slippery when wet. They are broadly classified as cationic or smectite type (having layer lattice structure in which two-dimensional oxyanions are separated by layers of hydrated cations) and anionic or brucite type (in which the charge on the layer and the gallery ion is reversed complimentary to smectite type). Anionic clays are rare in nature but they are relatively easy and inexpensive to prepare in the laboratory.

Hydrotalcite belongs to the class of anionic clays wherein the positively charged contiguous layers formed by the edge sharing of $Mg^*(OH)_6$ and $Al(OH)_6$ octahedra are separated by charge balancing anions and water, these occupying the interlayer spaces. A large variety of compounds with hydrotalcite like structure represented by the general formula⁹⁻¹¹.



Where x is $M(III)/(M(III)+M(II))$. These compounds are called layered double hydroxides (LDH) or hydrotalcite-like (HT) compounds, many of these compounds reported in literature are given in a previous review by Cavani *et al.*⁹

It is relevant here to discuss the implications of hydrotalcites being important catalyst precursors, though they themselves do not possess significant catalytic activity. After all the final catalytic phase obtained is a simple-oxide in some definite proportion. However, the generation of these systems from hydrotalcite phases appears to be efficient than simple mixed oxide system generated in any other means. The observations in literature show that the systems derived from hydrotalcites and in most cases efficient catalyst systems and this observation has to be recognized and accounted for.

The following questions may be of relevance in this context.

- (I) In what sense the mixed oxides generated from hydrotalcites are better systems as compared to other mixed oxides obtained by any other means since as per the composition one may not be able to find much of a difference since one can generate compositionally equivalent mixed oxide systems?
- (II) Is there any limitation to generation of mixed oxides from hydrotalcites precursors as compared to conventional methods of generating mixed oxide?

- (III) What is the specific role of the anions like hydroxide and carbonate ions in the hydrotalcites precursor and also on the new oxide compositions that are generated from hydrotalcites?
- (IV) In which chemical and surface properties, the catalyst systems generated from hydrotalcites, differ from the oxide systems generated from simple mixed oxides?
- (V) It is generally conceived that the acid/base property of the oxides derived from hydrotalcites are different from the other mixed oxide systems. Is there any specific reason for such an expectation?
- (VI) Can one primarily decide what will be the ultimate compositions of mixed oxides that can be generated from hydrotalcite precursors?
- (VII) Is there any specific relation between the ratios of the anions especially if the hydrotalcites are obtained from hydroxide/carbonate combination?
- (VIII) Is it possible to predict the variation of activity for a given catalytic reaction based on the composition of hydrotalcite precursor?
- (IX) Why does the mixed oxide grains formed from hydrotalcites behave differently from the grains formed from other mixed oxide preparations?
- (X) Are there any specific postulates to predict the direction and extent of property change, as a function of the composition of the hydrotalcite precursor?
- (XI) How the specific active sites are generated only in those systems which are generated from hydrotalcites but not in those which are generated otherwise?
- (XII) Hydrotalcites crystallize in layered structures with inter layer anions. How far the two-dimensional configuration of the precursor is responsible for the generation of active sites in the resultant catalytic system?

These are some simple but necessary questions to understand the behavior of hydrotalcite precursors and their catalytic activity.

Various combinations of M(II) and M(III) ions, many novel binary, ternary and quaternary hydrotalcite-like systems can be prepared. The burgeoning literature in this area in the recent past is indicative of the promising features of these layered compounds.

History

Hydrotalcite (HT) was first discovered in Sweden around 1842 as a naturally occurring foliated and contorted plates consisting of hydroxy carbonate of magnesium and aluminum. The molecular formulae of HT and other isomorphous material was presented by Manesse¹² who was also first to recognize that carbonate ions are essential for this type of structure. Aminoff and Broome¹³ also recognized the existence of two polytypes of hydrotalcites with rhombohedral and hexagonal symmetry by X-ray investigation. In 1942, Feitknecht¹⁴ synthesized a large number of compounds having HT structure, which he termed as doppelschichtstrukturen (double sheet structures)¹⁴. Taylor¹⁶ determined the structural features of these hydrotalcites and Allman¹⁵ based on the X-ray analysis of single crystals. They also concluded that both the cations (M^{2+} and M^{3+}) are localized in the same layer and only carbonate and water are in the interlayer. Miyata and co-workers^{17,18} have carried out extensive studies on the synthesis and physico-chemical properties of these materials especially on their anion exchange reactions. Research on use of HT materials as catalysts followed separate parallel routes until 1970 when the first patent was filed by BASF for using hydrotalcites as precursors for the hydrogenation catalysis¹⁹. The basic property of these materials were investigated by Nakatsuka *et al.*,²⁰ Reiche²¹ and Laylock *et al.*,²² for base catalyzed polymerization and aldol condensation reactions. The anion exchange property of these materials was efficiently utilized by Pinnavaia and co-workers²³ in their work on the intercalation of polyoxometallate anions as pillaring anions and their effect on the catalytic behaviour. Thermal calcination of these materials which resulted in the formation of non-stoichiometric mixed oxides, which are used as active catalysts for many catalytic transformations like steam reforming, methanol and synthesis of higher alcohols and methanation reactions.

Structural Features

The structure of HT materials can be visualized from the structure of brucite. Typical representation of this structure is shown in Fig. 1. In the brucite structure, Mg^{2+} ions are surrounded by six hydroxyl ions in an octahedral coordination and these through octahedral edge sharing form infinite sheets. These infinite sheets are stacked upon one another to give layered network held through hydrogen bonding.

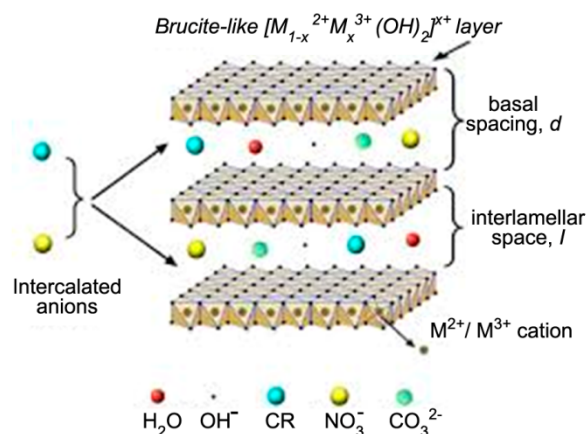


Fig. 1 — Typical structure of Brucite.

If one of the Mg^{2+} ions is substituted by a trivalent cation having a similar radius like Al^{3+} (in hydrotalcite), the positive charge density of the layer increases. To maintain electrical neutrality, the anions have to occupy the interlayer positions where water of crystallization also finds a place. The sheets containing both di- and tri-positive cations occupy randomly in the octahedral holes of the close-packed configuration of hydroxyl ions and the interlayer constituents namely the anion and water, are randomly located in this region and possess a high degree of mobility.

Each morphological work, later confirmed by X-ray unit cell determinations, showed that two sub-groups can be distinguished, which would be described as polytypes, differing only in their layer stacking sequences, namely, rhombohedral and hexagonal. If one were to call ABC (the three-fold axis of the hydroxyl groups), the stack may have the sequence BC-CA-AB-BC, thus constituting three sheets in the unit cell with rhombohedral symmetry or BC-CB-BC with two sheets in the unit cell having hexagonal symmetry. Pyroaurite (Mg-Fe hydroxy carbonate) and hydrotalcite crystallize in rhombohedral 3R symmetry the unit cell parameters being a and $c = 3c'$ (where c' is the thickness of one elementary layer constituted by a brucite-like sheet and one interlayer). Sjogrenite is the polytype form of pyroaurite and crystallizes with 2H symmetry, the parameters of the unit cell being a and $c=2c'$.

Between adjacent brucite-like layers there are the interlayers, which contain all the carbonate anions and water molecules. The most interesting feature of these materials is the way in which the oxygen atoms of both these groups are accommodated in a single set of sites. The main feature of the interlayer is groups of

oxygen sites distributed closely around the symmetry axis that pass through hydroxyl ions in adjacent brucite layers. Within each group, these sites are not near together that, at the most, only one of them can be occupied.

1H -NMR studies of powdered and oriented samples²⁴ of hydrotalcite with carbonate as counter ion showed that interlayer water possesses rotational freedom around C_2 axis and hence can take several orientations while the carbonate anions have their molecular plane parallel to the layered network. The existence of hydrogen bonding between oxygen atoms of the main layer and species in the interlayer has been identified. However, the symmetry axes of both water and carbonate are perpendicular to the layer.

The main criterion for the ions to enter the crystal lattice in the network structure is the ionic radius. There is practically no limitation on the anions that can be intercalated in to the interlamellar position of the HT like materials. The nature of the anions that can be intercalated are:

- i Inorganic anions like Cl^- , Br^- , CO_3^{2-} , SO_4^{2-}
- ii Heteropoly anions like $V_{10}O_{28}^{6-}$, $Mo_7O_{24}^{6-}$
- iii Complex anions, $Fe(CN)_6^{3-}$, $[IrCl_6]^{2-}$
- iv Organic acids like malonic, succinic and sabacic acids in their divalent anionic forms
- v Metallo-macrocyclic ligands like cobalt phthalocyanine.

This brings us to the concept of pillaring. The process of pillaring involves the propping up of the adjacent lamellae in the clay structure by exchanging the charge balancing ions in the inter-layer region with bulkier ones. This introduces two-dimensional channels into the layered structure, with the channel spacing, determined by the size of the pillaring agent and the density and homogeneity of its distribution.

Pillaring was first achieved in smectite clays with alkyl ammonium ions, bicyclic amine cations, and organometallic species. But all these pillaring agents, exhibited poor thermal stability²⁵. The use of polyhydroxy metal cations yields more thermally stable pillared clays but the number of species that can form such cations are limited – the aluminium hydroxy cations and the zirconium hydroxy cations being the most commonly used. Butruille and Pinnavaia²⁶ have carried out liquid phase alkylation of biphenyl with propene using aluminium hydroxy cation pillared montmorillonite.

Polyoxometallates offer a wide range of synthetically accessible molecular geometries, which

are stable towards both thermal and oxidative degradation. Hydrotalcite type anionic clays with positively charged lamellae are ideal hosts for these robust anions. There is growing interest in polyoxometallate catalyzed oxidations and the immobilisation of these species into the LDH galleries can provide a shape selective environment similar to that in zeolites.

Preparative Methods

Several factors have to be borne in mind for attempting the synthesis of pillared LDHs. Efficient pillaring can be achieved only by:

- (i) Careful selection of the exchanging anion
- (ii) Proper control of the pH of the solution and
- (iii) Maintaining an inert atmosphere throughout the process.

Mainly these strategies have been employed for the synthesis of polyoxometallate pillared LDHs. They are:

- (i) Simple exchange of the monovalent gallery anions like Cl^- , and NO_3^- by higher valent pillaring anions.
- (ii) Exchange via a synthetic mixture in a solution containing a swelling agent.
- (iii) Exchange via an organic anion pillared precursor.

The pillaring of LDHs with inorganic complexes like $\text{Fe}(\text{CN})_6^{4-}$, $\text{Co}(\text{CN})_6^{3-}$, $\text{Cr}_2\text{O}_7^{2-}$ and organic anions like dodecyl sulphate and p-toluene sulphonate are also reported in literature.

Kwon and Pinnavaia²⁷ have studied the intercalation of various Keggin-like anions of the type $[\text{XM}_{12}\text{O}_{40}]^{n-}$ into LDH galleries and have concluded that successful intercalation is achieved only with species having $n \geq 4$. Moreover, they have observed different intercalation properties for the α and β isomers of the same species $[\text{SiV}_3\text{W}_9\text{O}_{40}]^{7-}$, the β isomer being more difficult for exchange. This is explained on the basis of the enhanced host-guest interactions through hydrogen bonding, in case of the α isomer due to its favourable C_2 perpendicular orientation with respect to the host layers.

The various characterization technique employed to study the pillaring in LDH's have demonstrated how it is possible to follow the process in which the existing interlayer anions are replaced by the pillaring anions which diffuse into the interlayer region. With the intercalation of the bulkier anions, the basal spacing of the LDH increases according to the orientation of the pillars in the interlayer and the

crystal grows in the c direction. In many cases during direct exchange synthesis of pillared compounds a partial loss of crystallinity is observed as a result of pillaring. These features are well reflected in the X-ray diffraction patterns. Any structural distortion of the pillaring anion in the constrained environment of the interlayer region can be identified from NMR and FTIR spectral features of the compounds. The pillared LDH derivatives, the organic anion pillared LDHs in particular, show poor textural stability as compared to the pristine LDH compound. This behavior is attributed to either the combustion of the pillars (as in the case of organic anion pillars) or due to their sintering or enhanced interaction between pillared anions and the host layers.

Condensation Reactions

Carbon-carbon bond formation via base-catalyzed condensation involves the attack of a negatively polarized carbon, the carbanion on an electrophilic carbon like that in a carbonyl group. Heterogenous basic catalysts are interesting alternatives to their homogeneous analogues as they offer relatively easier work up procedure, recyclability and a more environmentally innocuous route.

Layered double hydroxides have been found to be efficient catalysts for a variety of base-catalyzed condensation reactions²⁸. The basicity of LDHs can be tuned up to the requirement of a particular reaction by the variation of M(II) and M(III) ions, the calcination temperature, the M(II)/M(III) ratio and the charge balancing anions²⁹.

Reichle³⁰ has studied the oligomerization of acetone over heat treated Cr-Zn, Ni-Al and Mg-Al LDHs and has observed that only the calcined CO_3^{2-} containing LDH is active towards the reaction. Both the uncalcined catalyst and the calcined sample which contains non-vapourisable anions like SO_4^{2-} , Cl^- and CrO_4^{2-} were found to be inactive. The condensation of benzaldehyde with acetone was investigated by Tichit *et al.*,³¹ who found that the rate determining step involves the attack of the carbanion to the carbonyl group of benzaldehyde. The aldol condensation between formaldehyde and acetone was carried out by Suzuki and Ono³² over mixed oxides derived from Mg^{2+} - Al^{3+} , Co^{2+} - Al^{3+} and Zn^{2+} - Cr^{3+} LDHs. The conversion of acetone was found to be highest with Mg^{2+} - Al^{3+} LDH with 96% selectivity towards methyl vinyl ketone (MVK). Maximum selectivity (100%) for MVK was

observed with $\text{Li}^+\text{-Al}^{3+}$ at an acetone conversion of 12%.

Corma *et al.*,³³ have investigated the one-step synthesis of citronil by the Knoevenagel condensation of ethyl cyano acetate and benzoyl acetone over Ca-Al, Zn-Al and Mg-Al LDHs with differing Al/(Al+Mg) ratios. Maximum activity on a unit weight basis was exhibited by Mg-Al LDH while the Ca-Al sample was found to be most active per unit surface area. On either basis Zn-Cr LDH showed the lowest activity. Among the various Mg-Al LDHs, the samples containing low aluminium content exhibited higher activity and the activity decreased steadily with increasing Al content. Moreover the catalytic activity was unaffected by changing the morphology of the LDHs by the variation of the crystallization temperature.

These observations suggest that both aldol and Knoevenagel condensation require only mild to moderately basic sites and the Bronsted basic ($\text{M}^{\text{n}+}\text{-OH}$) centres are considered to be the active sites for both the reactions. This is further established by the fact that these condensations require only low temperatures, the reactions work well in liquid phase and the rehydrated and even the uncalcined samples show good activity. Moreover, the Mg-Al LDH having carbonate as the gallery anion was found to be more active than that which contains the non-vapourisable anions like chloride and sulphate. Both these anions increased the Bronsted acidity of the LDH at the cost of Bronsted basicity.

Dumitriu *et al.*,³⁴ have carried out the vapour phase aldol condensation between formaldehyde and acetaldehyde over mixed oxides derived from Co-Al and Ni-Al hydroxy carbonates and Mg-Al LDH containing chloride or sulphate ions along with carbonate in the inter layers. The observed selectivity to acrolein was found to follow the decreasing order of basicity of the various LDHs as given Mg-Al > Co-AL > Ni-Al. Among the Mg-Al LDHs the order was found to be Mg-Al CO_3^{2-} > Mg-Al CO_3^{2-} , SO_4^{2-} > Mg-Al CO_3^{2-} , Cl^- .

Further the selectivity to acrolein was found to be higher on Mg-Al LDH than on MgO. This anomalous behaviour is explained by considering the acid-base cooperation. The basic sites facilitating the carbanion formation from acetaldehyde and the acidic sites increasing the electrophilicity of the carbonyl carbon. Such a cooperative behaviour is further established by the fact that the Mg-Al LDH calcined at 573 K, shows

higher activity as compared to the 673 K calcined sample. The sample calcined at 573 K has a higher surface Al content as compared to the sample calcined at 673 K. This behaviour is assumed to exist in many of the formaldehyde involved condensation.

Choudhary *et al.*,³⁵ have been successful in carrying out the aldol condensation reactions with uncalcined Mg-Al O TBu catalyst which gave excellent yield of aldols with no further dehydration at a temperature as low as 273 K.

Tichit *et al.*,³⁶ have investigated the Claisen-Schmidt condensation of benzaldehyde with acetone over Mg-Al carbonate LDH. The initial rate of the reaction was found to depend on the calcination temperature of the sample. Maximum rate was observed for the sample calcined at 823 K. The results obtained are in agreement with the observed decomposition patterns indicating the formation of high surface area mixed oxide and at higher temperatures, an MgAl_2O_4 spinel. However, the suggestion that the active sites for the reaction involve hydroxyl groups rather than O^{2-} species seems to be artificial.

The Claisen-Schmidt condensation of benzaldehyde with substituted acetophenones was carried out by Climent *et al.*,³⁷ over a series of basic catalysts like Cs exchanged zeolite and sepiolite and calcined hydrotalcites with varying Mg/Al ratio. Maximum activity was observed for Mg-Al LDH with Al/(Al+Mg) ratio between 0.25 and 0.30. The increase in Al content up to certain extent causes the segregation of Al on the surface resulting in the generation of cation defect sites and hence more low coordinated oxide ions. A further increase in Al content may result in lowering in strength of these sites due to Al Lewis acidity or in decrease in number of such sites due to the decrease in $\text{Al}_{\text{surface}}/\text{Al}_{\text{bulk}}$ ratio. Further, the crystallite size of the catalyst was also found to affect the activity. Samples with smaller crystallites were found to be more active. In such samples, a higher population of lower coordinated oxide ions is expected and hence these sites may be the active sites for the Claisen-Schmidt condensation. To our knowledge, the Cannizzaro reaction had not been successful with uncalcined or calcined LDHs, which indicate the requirement of stronger basic sites for the reaction.

Hydrogenation-Dehydrogenation Reactions

Hydrogenation reactions over solid bases are unique in several aspects including faster

hydrogenation of conjugated dienes as compared to mono-enes, preference for 1,4 addition over 1,2 addition and the retention of molecular identity of hydrogen atoms during the reaction. Mixed oxides derived from some transition metal-functionalized layered double hydroxides have been reported to be active in certain commercially significant hydrogenation reactions.

Cabello *et al.*,³⁸ have studied the influence of variables like catalyst composition, temperature and basicity of the catalysts on the nickel-catalyzed hydrogenation reaction. The higher basicity of the Mg-containing nickel catalyst {NiMgAl LDH} over the NiAl LDH was evidenced by the observed heat of adsorption of mono-ethylamine (MEA) data for the two catalysts and an optimum basicity at the Mg/(Mg+Al) ratio of 0.23 was found to be suitable for maximum MEA selectivity. Further, the number of by-products formed by the transamination reaction increased at higher temperatures and acetonitrile conversion. Moreover, maximum selectivity to MEA was observed at a calcination temperature of 623 K followed by the reduction of the Ni²⁺ in the catalysts to Ni with hydrogen at 723 K.

Castiglioni, Ferrari *et al.*,³⁹ have carried out the selective vapour phase hydrogenation of maleic anhydride to γ -butyrolactone with Cu/Zn/Al and Cu/Zn/Ga LDHs and not compared the activity with that of Cu/Zn/Cr catalysts. Better yields and conversion were obtained with the Al containing catalysts while the activities of Cu/Zn/Ga samples were only comparable with the Al containing samples.

LDH and their derived mixed oxides-supported metallic catalysts are also employed for the selective hydrogenation of unsaturated C=C and C=O bonds of biomass-derived substrates. A large amount of active metal sites for hydrogenation activity generated through the reduction treatment of LDH derived mixed oxides, and the reduced sample can be directly used as catalyst. Besides, the tunable interlayer spacing of LDH paves a more efficient route to convert potential biomass substrates to value added chemicals. Through controlling the synthetic protocol the surface acidic and basic properties, as well as homogeneous dispersion of metal cations in the brucite-like layers of LDH derived metal oxides can be rationally tuned. Nagpure *et al.*,⁴⁰ showed the Ru-containing HT catalysts were efficiently converted 5-hydroxymethylfurfural

(HMF) to 2,5-dimethylfuran (DMF) under H₂ atmosphere. They found that the incorporation of Ru in the layered HT structure by simple co-precipitation method offered a well dispersed Ru on the metal oxide support, consequently exhibited good catalytic activity. Yan *et al.*,⁴¹ have fabricated a series of Cu containing LDH derived materials for the selective reduction of furfural^{42,43}. The CuCr-LDH catalyst derived from LDH showed a high selectivity for the formation of furfuryl alcohol, whereas the LDH derived CuFe displays the best performance towards the synthesis of 2-methylfuran via hydrogenolysis. Authors demonstrated that the surface Cu²⁺ ions, spinel support stability, and the Cu²⁺-support interaction have crucial impact on the yield of product distribution. Furthermore, it also referred that CuCr-HT selectively hydrogenated the C=O bond, while CuFe-HT was beneficial for hydrogenolysis and complete reduction of furfural. Recently, Manikandan *et al.*,⁴⁴ reported Ni-based mixed oxide catalysts derived from NiMgAl-LDH was efficient for the selective hydrogenation of furfural to furfuryl alcohol. The reduced samples of HT derived NiMgAl mixed oxides display the best activity owing to the surface synergistic interaction between the metallic Ni sites and strong surface basic sites. Li *et al.*,⁴⁵ fabricated hierarchical three-dimensional Ni foam and used as a substrate for the NiZrAl-HT loading and employed for the hydrogenation of levulinic acid (LA). The mass transportation has been promoted by macroporous Ni foam, whereas the high dispersion and metal-support interaction enhanced through the *in-situ* growth of NiZrAl-LDH on the Ni foam. Furthermore, dissociation of hydrogen could be enhanced by abundant active centers on HT support, and the adsorption of the LA has been promoted by the nearby Lewis acid sites.

Heterogeneous basic catalysts are known to catalyze the dehydrogenation of alcohols in preference to dehydration, taking place over solid acid catalysts. Corma *et al.*,³³ have used the dehydrogenation of isopropanol as a model reaction to assess the acid-base properties of Mg-Al LDHs. They have investigated the influence of Al/(Al+Mg) ratio on the basic strength of the catalyst and found that the ratio of 0.25 was optimum for the basicity requirement of the reaction. Further they observed the presence of T_d-Al species in the calcined samples from the Al MAS NMR data. The presence of both T_d and O_h-Al species in mixed oxides formed on

calcination give rise to an unstable inverse spinel type structure. From the XRD patterns of the calcined samples, it is clear that the mixed oxides have a MgO type structure with isomorphous substitution of Al. This leads to the generation of Mg^{2+} and Al^{3+} defects in the frame work and thus forming coordinatively unsaturated oxide ions which act as strong basic sites (Fig. 2).

Liquid Phase Oxidations

Oxidation is one of the fundamental reactions in organic synthesis. Catalytic oxidations, especially the metal catalyzed oxidations using environmentally benign and economical oxidants like H_2O_2 have attracted considerable attention in the recent past and a number of homogeneous and heterogeneous catalytic systems have been reported.

Among these different catalysts the crystalline microporous titanium silicalite molecular sieves (TS-1 and TS-2) have figured prominently in the literature, mainly due to their heterogenous nature, transition state, size and shape selectivity and the possibility of incorporating various metal ions with redox characteristics as the active sites. These solid acid catalysts have been found to be active in the oxidation of a variety of organic compounds using aqueous hydrogen peroxide as the oxidant, under mild conditions⁴⁶. The relatively new class of heterogeneous basic catalysts called LDHs with wider scope of structural modifications and relatively easier preparation methods have recently been found to give excellent yield and selectivity comparable to or greater than TS-1 in many oxidative organic transformations⁴⁷.

Kaizheng Zhu *et al.*,⁴⁸ have carried out the liquid phase phenol hydroxylation using hydrogen peroxide

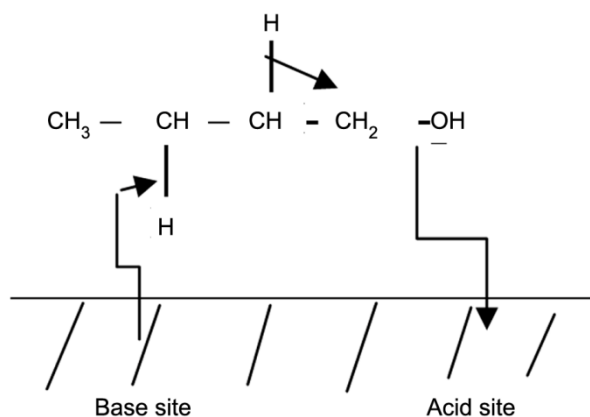


Fig. 2 — Schematic representation of push and pull mechanism on a substrate.

with various ternary LDH systems containing copper and have compared their activity with some binary analogues like Mg-Al, Zn-Al and Co-Al LDHs and also with TS-1. The results show highest phenol conversion (53.5%) and catechol selectivity (59%) with Cu-Al LDH. Under similar conditions, only 27% conversion of phenol with 53% catechol selectivity was observed with TS-1, while the Mg-Al, Zn-Al, Co-Al and Ni-Al LDHs exhibited little activity. Other, among the Cu-Al LDHs studied, the catalytic activity was found to increase with increase in Cu/Al ratio. Also, in the range of reaction conditions investigated, maximum activity was observed with water as the solvent and at 333 K and neutral pH. Based on these observations, Cu^{2+} centers in the lamellae are suggested to be the active sites for the reaction.

The higher activity observed in the case of copper containing LDH over TS-1 is presumably due to the lesser deactivation of the active sites in the course of the reaction. Such a deactivation has been reported with TS-1 catalyzed phenol hydroxylation reaction. However, this seems to be less significant in the LDH catalyzed reaction, especially at lower temperatures. This view is further substantiated by the fact that the Cu-containing LDHs show little activity in acetone, which is known to be the most efficient solvent for the dissolution of tar species.

The lower activity observed with the $CuM(II)AlCO_3^{2-}$ catalysts at low and high pH of the medium had been correlated with the dissolution of Cu^{2+} and the blocking of the Cu^{2+} centers by OH^- respectively. However, the catalyst is reported to show considerably lower activity after calcination. This observation coupled with the poor activity observed in the case of $CuSO_4$ catalyst indicate a possible participation of surface hydroxyl groups in the LDH catalyzed reaction. Moreover, the surface model of the $CuM(II)AlCO_3^{2-}$ catalyst showing coordinatively unsaturated Cu^{2+} as the active sites for the reaction, seems to be quite unlikely keeping in mind the preparation and pretreatment conditions reported. Further, the lower activity of the $CuM(II)AlCO_3^{2-}$ catalyst at high pH may be due to the loss of lamellar structure by the leaching out of Al^{3+} ions into the solution. Consequently, a mechanism for the reaction involving the participation of the surface OH groups seems to be more reliable for the reaction than the proposed radical mechanism. Yumin, Shetian *et al.*,⁴⁹ have studied the liquid phase oxidation of p-cresol to p-hydroxy benzaldehyde using cobalt containing LDH as the catalyst. The effect

of various metal ions in promoting the catalytic activity was studied and Cu^{2+} ion was found to showing the maximum promoting effect. The results were also compared with a mechanical mixture of Co_2O_3 , CuO and Al_2O_3 . The catalytic activities were found to follow the order $\text{CoCuAlCO}_3 > \text{CoFeCO}_3 > \text{CoAlCO}_3 > \text{mechanical mixture}$. Further, best results were obtained with a Co/Cu/Al ratio of 3:1:1 at the calcination and reaction temperatures of 723 K and 973 K. The decrease in surface area of the catalyst due to sintering and the deactivation of the active sites by tar formation are suggested to be the major reasons for the lower reactivities observed at higher calcination and reaction temperatures. Further, the uncalcined catalyst showed considerably lower activity for the reaction and hence the mixed oxide formed by calcination is supposed to be the catalytically active phase for the reaction.

The oxidation of allylic and benzylic alcohols to the corresponding aldehydes or ketones was achieved with Ru-Mg-Al LDH in the presence of molecular oxygen by Kaneda, Yamashita *et al.*⁵⁰ Excellent yields were obtained with the carbonate containing LDH. The conversion and yield were poor with the Mg-Al- CO_3 LDH. Moreover, the Ru-Mg-Al CO_3 showed higher heat of adsorption of benzoic acid as compared to the Mg-Al LDH catalyst, suggesting Ru-OH sites in the LDH lamellae to be the active centers for the reaction. The nature of the interlayer ions was found to affect the activity of LDH and the catalysts with bulkier gallery anions exhibited lesser activity.

A similar observation was made in the Baeyer Villager⁵¹ oxidation of various ketones using a combination of oxidant system of molecular O_2 and aldehydes. These observations indicate that the strongly basic external surface hydroxyl groups may be the active sites for these reactions and with increasing basal spacing a portion of the reactant molecules may diffuse into the interlayer spaces making themselves unavailable for the reaction. In the Baeyer Villiger oxidation of ketones, the yield of lactone was found to be influenced by the nature of the aldehyde used, the type of solvent and the ring size of the ketones. Better yields were obtained by using benzaldehyde as the aldehyde and CCl_4 as the solvent. Furthermore, cyclopentanone undergoes faster oxidation than cyclohexanone. The latter observation is in sharp contrast to the observed activity in the absence of LDH and also in organic per acid systems. Further, the authors have compared the

activity of the MgAlCO_3 LDH with its multimetallic analogues like Mg-Al-Fe CO_3 and Mg-Al-Cu- CO_3 . In these oxidations it was found that in most cases the multimetallic LDHs exhibited higher activities and in a few cases quantitative yield of the corresponding lactones was also obtained. In addition, the spent catalysts of these systems were reused without appreciable loss of activity. In comparison, the Mg-Al LDHs showed considerably lower recyclability. Further, the fact that MgAlCuCO_3 LDH was found to oxidize the bicyclic ketones more effectively than the monocyclic ones is again contrary to the behaviour shown by the homogeneous $\text{Cu}(\text{acetate})_2$ catalysts. With these observed features, a cooperative action of transition metal sites and the basic sites is envisaged in the Baeyer-Villiger oxidation, catalyzed by these multimetallic LDH catalysts and a tentative mechanism was suggested which involves the generation of perbenzoic acid by the auto-oxidation of benzaldehyde followed by base assisted oxygen transfer to ketones.

Fraile, Garcia *et al.*,⁵² have compared the epoxidation activities of the oxidant-catalyst systems TBHP-Ti/ SiO_2 , H_2O_2 -Mg-Al LDH and TBHP-KF/ Al_2O_3 towards a relatively stable substrate, α -isophorone. Although the TBHP-KF/ Al_2O_3 system yields better selectivity and higher conversions as compared to the H_2O_2 -Mg-Al LDH catalyst, the latter uses a more environment friendly and economical oxidant, which cannot be employed with the KF- Al_2O_3 system due to the solubility of KF. Moreover, the results are compared under varying experimental conditions due to which a definite conclusion on the relative activity of the catalysts seems to be unreliable.

Cativiela *et al.*,⁵³ have been successful in achieving the epoxidation of various unsaturated cyclic and acyclic ketones with Mg-Al LDH and H_2O_2 . While the open chain and the substituted and unsaturated compounds exhibit stereoselective epoxidations with good yield, the substituted cyclic compounds showed lower activity.

Ueno, Yamaguchi *et al.*,⁵⁴ have investigated the base-catalyzed epoxidations of linear and cyclic olefins with Mg-Al LDHs using hydrogen peroxide combination with PhCN. The addition of surfactants like dodecyl sulfate was found to enhance the activity considerably by increasing the contact area between the aqueous and organic phases. The epoxidation reaction is thought to be a two-step process proceeding through an initial base assisted generation

of peroxy carboximidic acid by the reaction between the nitrile and hydrogen peroxide and its subsequent oxygen transfer to the olefin to yield the corresponding epoxides.

The liquid phase oxidation of several benzylic hydrocarbons using Ni-Al, Mg-Al, Cu-Zn-Al and Zr-Cr LDHs have been reported by Chaudhary *et al.*,⁵⁵. The conversions to the corresponding ketones were only modest except with Zn-Cr LDH and in case of diphenyl methane and fluorene. As observed with many LDH catalyzed oxidations, the activity and selectivity were maintained to a considerable extent in the repeated cycles.

Bert Sels *et al.*,⁵⁶ have reported a novel biomimetic oxidative bromination route using tungstate exchanged layered double hydroxide in combination with NH_4Br and hydrogen peroxide as an alternative for the conventional bromination reaction which makes use of elemental bromine which is both, a pollutant and health hazard. The positively charged LDH lamellae is supposed to facilitate the approach of the bromide anions towards the negatively charged tungstate species. Both the specific activity and TOF (turn over frequency) for the tungstate exchanged MgAl LDH were found to be considerably higher than many solid acid heterogeneous oxidation catalysts like Ti-MCM-48, Ti-MCM-41 and TS-1, under similar reaction conditions. Moreover, using alkylated olefins as the substrates, excellent yields of epoxides were obtained via bromohydrin route.

Selective oxidation of HMF through the utilization of C=O and OH functional groups is one of the attractive applications in bio-refineries. Davis *et al.*,⁵⁷ investigated the oxidation reaction pathway of HMF to FDCA over TiO_2 supported Pt and Au catalysts. However, the utilization of noble metals and the difficulty in the recycling process in reported system revert to the further implications. To obtain a more eco-benign catalytic process, Ebitani *et al.*,^{58,59} developed a green process through a LDH-supported Ru catalyst for the selective oxidation of HMF. Authors further demonstrated that the surface basic sites of the LDH support greatly facilitates the abstraction of protons from alcoholic group of HMF even after the addition of metal nanoparticles. LDH derived mixed oxides often generated comparably high surface area and bountiful basic sites. These two important surface parameters play a vital role in their catalytic performance for the selective oxidation of HMF. Neațu *et al.*,⁶⁰ investigated the as fabricated MnCuAl-LDH and calcined MnCuAl- mixed oxides

in the selective oxidation of HMF into DFF, and found that the oxidation performances of LDH and their mixed oxides were correlated with the surface basic site density. Through comparison, it was conferred that Cu^{2+} existing as $\text{Cu}(\text{OH})_2$ in the LDH structure demonstrates relatively less activity than Cu^{2+} present in the mixed oxides after calcination. Gupta *et al.*,⁶¹ report a supported Au/HT catalyst for the oxidation of HMF to 2,5-furandicarboxylic acid using O_2 as an oxidant and water as a solvent. The authors demonstrated the robustness of the catalyst through the spent catalyst analysis using XANES and TEM, and found that there was no obvious change in the morphology, Au oxidation state and particle size after catalytic runs. Ebitani and co-workers⁶² employed Au on MgAl-LDH catalyst for the selective oxidation of glycerol with molecular oxygen in presence of water. It was notable to observe that Au supported on the non-calcined MgAl-LDH conferred no catalytic activity for the glycerol oxidation. However, catalysts thermally treated more than 373 K exhibited good glycerol conversion (>70%) with the 15% selectivity towards hydroxyacetic acid. Jin *et al.*,⁶³ reported the cost-effective Co nanoparticles supported on MgAl-LDH, were fabricated through a modified sol-gel method for the efficient oxidation of glycerol to tartaric acid with 64% selectivity. In their study, the authors differentiated the catalytic performance of catalysts prepared by conventional co-precipitation method and modified sol-gel method. The catalyst prepared by the modified sol-gel method exhibited better oxidation performance than the catalysts synthesized from the co-precipitation method. The difference in catalytic behavior of both preparation methods can be attributed that the co-precipitation process paves Co species incorporated and coordinated in the Mg_3AlO_x mixed oxide framework, while the sol-gel process renders Co species concentrated on the Mg_3AlO_x surface. Ebitani and co-workers⁶⁴ have fabricated Pt/Au alloy nanoparticles supported on LDH using starch as a green reducing agent and a stabilizing agent. The prepared Pt/Au nanoparticles exhibited excellent activity for the aerobic oxidation of 1,2-propanediol and glycerol. Owing to the distinct lattice parameters between Pt and Au, the modification of d-band structure has to happen when both metals were combined together and to form an alloy. The further characterization studies revealed that Pt atoms attained more electrons than that of Au atoms in Pt_xAu_y -starch/LDH catalyst system due to the transfers of electron from the starch

molecule to both Au and Pt atoms and further facilitated to the electron transfer from Au to Pt atoms. Furthermore, the efficient glycerol oxidation was significantly contributed from the ligand effect, strain effect and stabilizing effect on the LDH. Tongsakul *et al.*,⁶⁵ presented the Pt/LDH catalyst for the liquid phase oxidation of glycerol to glyceric acid. From the characterization results it was found that the Pt/LDH catalyst was a robust in the liquid phase oxidation of glycerol with no obvious change in the structure of Pt/LDH.

Selective oxidation of C5 and C6 carbohydrates is one of the fascinating routes in biomass conversion. Dhepe and co-workers⁶⁶ have differentiated the activity of Pt catalysts on an acidic (Al_2O_3) and a basic (MgAl-HT) supports for the oxidation of glucose and xylose. An appreciable gluconic acid yield up to 83% and a 57% yield of xylonic acid were observed over a homogeneous base free Pt/HT derived mixed oxide catalyst. The catalyst exists with high surface area of $200\text{--}500\text{ m}^2\text{ g}^{-1}$ and the support interaction would benefit a significant contribution to the better activity. Ebitani and co-workers⁶⁷ demonstrated that Au supported on MgAl-LDH is highly efficient for aqueous phase oxidation of diverse carbohydrates (e.g. ribose, mannose, xylose). Furthermore, the enhanced oxidation activity was facilitated from the surface basicity on LDH, which could efficiently promote the facile abstraction of proton from Au-alcoholate intermediate.

Oxidation on Hydrotalcite Supported Catalysts

Oxidation of variety of organic substrates has been carried out in variety of hydrotalcite based catalysts mostly on metal or active component supported on hydrotalcites. In these reactions, the surface properties of hydrotalcites play a definite role in activating the organic substrates. A number of oxidizing species like hydrogen peroxide, molecular oxygen and other organic oxidizing agents have been used for the oxidation of variety of organic aromatic or alkyl substituted substrates with high selectivity towards partial oxidized products.

Huyen *et al.*,⁶⁸ reported the Mg-Ni-Al- CO_3 hydrotalcite-like material synthesized by co-precipitation method at a certain pH. The Mg-Ni-Al- CO_3 catalyst has been tested for the oxidation of styrene with aqueous hydrogen peroxide solution and showed a good catalytic activity in the formation of benzaldehyde. Styrene conversion is in the range of 20–85% with the high selectivity to benzaldehyde at 50–80 °C for 4 h.

Thao and co-workers⁶⁹ have shown that Mg-Co-Al hydrotalcite like-catalysts for selective oxidation of styrene using air as oxidant and achieved 70–90% conversion of styrene with 92–99% selectivity of desired products. The partial substitution of Mg^{2+} by Co^{2+} in brucite layers has not significantly affected the layered double hydroxide structure, but plays a crucial role in the oxidation of styrene in presence of air. Both styrene conversion and desired product selectivity are strongly dependent on the content of cobalt. The intra-hydrotalcite lattice Co^{2+} ions are active sites for the epoxidation of styrene.

Thao *et al.*,⁷⁰ have also shown the Cu-doped Mg/Al based hydrotalcites are highly efficient for the oxidation of styrene to styrene oxide with 80–90% of selectivity. The partial substitution of Mg^{2+} by Co^{2+} in brucite layers has not significantly affected the layered double hydroxide structure, but plays a crucial role in the oxidation of styrene in presence of air. The intra-hydrotalcite lattice Co^{2+} ions are active sites for the epoxidation of styrene.

Gupta *et al.*,⁷¹ demonstrated hydrotalcite-supported Au-nanoparticles as a base-free catalyst for the aqueous oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid under atmospheric oxygen pressure without addition of homogeneous base.

Mitsudome *et al.*,⁷² reported a detailed study of hydrotalcite supported Au-nanoparticles as a highly efficient heterogeneous catalyst for the aerobic oxidation of alcohols under mild reaction conditions (40 °C, in air). This catalyst system does not require any additives and is applicable to a wide range of alcohols, including less reactive cyclohexanol derivatives. This Au/HT catalyst could also function in the oxidation of 1-phenylethanol under neat conditions; the turn over number (TON) and turn over frequency (TOF) reached 200,000 and $8,300\text{ h}^{-1}$, respectively. These values are among the highest values compared to those of other reported catalyst systems at high conversion. Moreover, the Au/HT can be recovered by simple filtration and reused without any loss of its activity and selectivity.

Choudary and co-workers⁷³ demonstrated the activation of molecular oxygen by Nickel in Ni-Al Hydrotalcite for developing the novel protocol for the selective oxidation of alcohols. NiO in association with aluminum oxide has been identified by temperature-programmed reduction as the active species in the Ni-Al hydrotalcite catalyst that oxidizes α -ketols as well as benzylic and allylic alcohols to their corresponding carbonyl

compounds in quantitative yields under mild reaction conditions.

Aguilera *et al.*,⁷⁴ showed the fabrication of hydrotalcites derived Cu-Mn and Co-Mn catalysts and found that the synthesized solids were active in the oxidation reaction of the VOCs, where the scale of difficulty to oxidize the different organic compounds evaluated was: butanol < ethanol < toluene. The authors confirmed that Co-Mn catalysts being the most active and the activity is associated to the generation of amorphous phases and redox cycles as a consequence of the cooperative effect among the metal.

Choudhary and co-workers⁷⁵ made comparison of various d group metals containing hydrotalcite materials for the evolution of the liquid phase oxidation of benzyl alcohol to benzaldehyde using molecular oxygen as an oxidizing agent in the solvent-free conditions. The Mn and Cu containing hydrotalcite-like solids show good catalytic activity in the oxidation and hence these are promising catalysts for the solvent-free oxidation reaction.

Zhu *et al.*,⁸⁰ reported the synthesis of CuM(II)AlCO₃-HTLcs, where M(II) = Co²⁺, Ni²⁺, Zn²⁺ and Fe²⁺ and studied their catalytic activity for the phenol hydroxylation by H₂O₂ in liquid phase. The catalyst CuAlCO₃-HTLcs having Cu/Al=3 efficiently oxidized phenol and gave high yields of the corresponding diphenols in appropriate reaction conditions.

Kaneda *et al.*,⁷⁷ showed heterogeneous oxidation of various Allylic and Benzylic Alcohols over Ru-Al-Mg Hydrotalcites in the presence of molecular oxygen and achieved good yield.

Pillai *et al.*,⁷⁸ have shown Sn-exchanged hydrotalcite catalysts for clean and selective Baeyer-Villiger oxidation of ketones using hydrogen peroxide as oxidant. The activity of the catalyst for the selective BV oxidation of ketones is attributed to the presence of active Sn sites in the interstitial position of hydrotalcite support. Sn sites activate the carbonyl group of ketones followed by a nucleophilic attack by the active peroxide species (peroxycarboximide acid by reaction of acetonitrile and H₂O₂) to form a Criegee adduct that rearranges to give the lactone.

Nishimura and co-workers⁷⁹ reported Palladium (II)-supported hydrotalcite as a catalyst for selective oxidation of alcohols using molecular oxygen. Palladium (II)-supported hydrotalcite acts as a reusable catalyst for the oxidation of alcohols to

aldehydes and ketones in the presence of pyridine under atmospheric pressure of oxygen.

Zhou *et al.*,⁸⁰ demonstrated the liquid phase catalytic oxidation of phenol carried out over Cu-Ni-Al hydrotalcite at ambient temperature and pressure using hydrogen peroxide as oxidant. It was found that the presence of inorganic chlorides promoted markedly the oxidation rate of phenol, probably due to the formation of intermediate products containing chlorine such as quinones and/or radicals.

Choudhary *et al.*,⁸¹ reported the MnO₄⁻ (0.4 mmol/g)-exchanged Mg-Al-hydrotalcite is an active and highly selective catalyst for the oxidation of benzyl alcohol to benzaldehyde by tert-butyl hydroperoxide under reflux condition in the absence of solvent. It was shown high activity for the oxidation of benzaldehyde to benzoic acid. The higher the Mg/Al ratio, higher is the catalytic activity (in both reactions) and basicity of the hydrotalcite catalyst.

Ebitani and co-workers⁸² showed interesting results for the highly efficient heterogeneous Catalysts for liquid-phase oxidation of alcohols with molecular oxygen over heterotrimetallic RuMnMn Species on a hydrotalcite Surface.

Tsuiji *et al.*,⁸³ reported hydrotalcite-supported platinum (Pt/HT) catalyst to be an active and selective heterogeneous catalyst for glycerol oxidation in pure water under atmospheric oxygen pressure. TEM measurements and titration analysis by using benzoic acid suggested that the solid basicity of hydrotalcite plays important roles in the precise control of platinum size and metal concentration as well as the initial promotion of alcohol oxidation.

Li *et al.*,⁸⁴ demonstrated a series of novel Pd/CoAlO catalysts derived from hydrotalcite-like compounds (HTLcs) have been prepared and investigated for total oxidation of toluene. It was found that the strong synergistic effect between Co₃O₄ and PdO, but not the amount of the surface palladium species which are generally believed to be the active sites, is the main factors determining the catalytic activity.

Kakiuchi *et al.*,⁸⁵ reported a heterogenized Pd catalyst, Pd (II)-hydrotalcite (palladium (II) acetate-pyridine complex supported by hydrotalcite) catalyzes the aerobic oxidation in toluene of a variety of primary and secondary alcohols into the corresponding aldehydes and ketones in high yields using atmospheric pressure of air as a sole oxidant under mild conditions.

Alejandre and co-workers⁸⁶ showed the systematic preparation and catalytic activity of Cu-Al mixed oxides derived from hydrotalcite-like precursors and evaluated for the oxidation of Phenol aqueous solutions.

Kawabata *et al.*,⁸⁷ demonstrated the preparation of Nickel (II) containing magnesium-aluminum (3/1) hydrotalcite (HT)-type anionic clays and tested as catalyst for liquid-phase oxidation of alcohols with molecular oxygen. The octahedrally coordinated Ni (II) cations incorporated inside the framework of hydrotalcite do not leach during the reaction and worked as a heterogeneous catalyst.

Gennequin *et al.*,⁸⁸ reported the preparation and catalytic studies of Co-Mg-Al Hydrotalcite precursors for catalytic total oxidation of volatile organic compounds. The comparison of the catalytic activities of the calcined hydrotalcites with those of calcined hydroxides showed the superiority of hydrotalcite based systems because of the higher specific surface area and more easily reducible particles.

Sanchidrián *et al.*,⁸⁹ reported various Mg/Al, Mg/Al/Sn and Mg/Al/Zr hydrotalcite-like compounds (HTs) for use as catalysts in the Baeyer-Villiger (BV) oxidation of cyclohexanone with H₂O₂/benzonitrile as oxidant and benzonitrile itself as solvent. The solids containing Mg/Al and Mg/Al/Sn and their calcination products (*viz.*, Mg/Al and Mg/Al/Sn mixed oxides) were found to be effective catalysts for the BV oxidation of cyclohexanone.

Nishimura *et al.*,⁹⁰ presented detailed study on the role of negatively charged Au states in aerobic oxidation of alcohols over hydrotalcite supported Au-Pd nanoclusters. Aerobic oxidations of 1-phenylethanol over the Au_xPd_y-PVP/HT catalysts showed that their catalytic activities were significantly affected by the Pd content. Correlations between charge transfer between Au and Pd and catalytic activity of the Au_xPd_y-PVP/HT catalysts were investigated with X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure (XANES), Michaelis-Menten kinetic studies for alcohol oxidation, and other analytical techniques. It was concluded that the electronic negativity of the Au 5d states controlled by the Pd content accelerated the rate-determining step in alcohol oxidation through highly active radical-like intermediates.

Kannan *et al.*,⁹¹ reported the synthesis of CuMgAl ternary hydrotalcites with a (Cu+Mg)/Al atomic ratio of 3.0 and a Cu/Mg atomic ratio of 5.0, 3.0, 1.0, 0.33

and 0.2 followed by systematic characterization. The fabricated solids were tested for the hydroxylation of phenol to catechol (CAT) and hydroquinone (HQ). The structure-activity relationship of these samples, obtained through scanning electron microscopy, N₂ adsorption measurements, X-ray photoelectron spectroscopy, and cyclic temperature-programmed reduction-oxidation measurements, corroborated such activity variations.

Su *et al.*,⁹² demonstrated the Ga-Al mixed-oxide supported Au-nanoparticles with enhanced activity for aerobic alcohol oxidation. The high activity for the aerobic oxidation of alcohols is achieved under base-free and ambient conditions by using gold catalysts supported on mesostructured γ -Ga₂O₃/Al₂O₃ solid solutions. The enhanced activity is attributed to the extraordinary alcohol-dehydrogenation activity of gallia-based mixed oxides.

Takagaki *et al.*,⁹³ showed the One-Pot Synthesis of 2,5-Diformylfuran from carbohydrate derivatives by sulfonated resin and hydrotalcite-supported ruthenium catalysts. A combination of hydrotalcite, Amberlyst-15, and Ru/HT catalysts successfully afforded direct synthesis of DFF from hexoses such as fructose and glucose via isomerization, dehydration, and successive selective oxidation in one pot. Stepwise addition of catalyst improved DFF yield up to 49% from fructose and 25% from glucose, respectively.

Rives *et al.*,⁹⁴ reported the hydroxylation of phenol over a series of CoNiAl ternary hydrotalcites (HTs) having a (Co + Ni)/Al atomic ratio close to 2.6 and a Co/Ni atomic ratios ranging from 1:0 to 0:1 using H₂O₂ as oxidant and water as solvent. It was found that probably an optimal configuration of sites involving cobalt, nickel, and Brønsted basic hydroxyl groups is necessary for promoting the reaction. Among the catalysts studied, catalyst with a Co/Ni atomic ratio of 1:5 showed maximum conversion of phenol (14.2%, substrate:oxidant=2:1, 65 °C) with a catechol/ hydroquinone ratio of 3.8. Heating of these samples even at slightly elevated temperatures (>120 °C in air for 5 h) led to complete loss in activity.

Jana *et al.*,⁹⁵ presented the NiAl hydrotalcites with Ni/Al molar ratios of 2–5 and prepared using, Cl⁻ or as a guest inorganic anion, were evaluated for the liquid-phase selective oxidation of a methylene group of ethylbenzene to carbonyl functionality with atmospheric pressure of oxygen as the sole oxidant under solvent-free and mild reaction conditions.

NiAl hydrotalcite prepared with a guest inorganic anion also showed very high acetophenone selectivity (>99%) compared with those prepared using Cl^- , or anions. compared with other transition metal-containing hydrotalcite-like solid catalysts (e.g., CuAl-, ZnAl-, CoAl-, MgFe-, MgCr-), with similar molar compositions and prepared in the presence of the anion, the catalytic activity of NiAl hydrotalcite was higher in the above oxidation reaction. The active NiAl hydrotalcite also exhibited good catalytic performance for the oxidation of a wide range of alkylaromatics to their corresponding benzylic ketones under similar experimental conditions.

Ueno and co-workers⁹⁶ elucidated the active sites in the heterogeneous Baeyer-Villiger oxidation of cyclopentanone by hydrotalcite catalysts. The active sites of hydrotalcites, A^nn^- ; CO_3^{2-} , Cl^- , etc., were studied in the heterogeneous Baeyer-Villiger oxidation of cyclopentanone to δ -valerolactone with a combination of oxidant system of molecular oxygen and benzaldehyde (O_2 /benzaldehyde) in a 1,2-dichloroethane solvent. Yields of δ -valerolactone were almost proportional to the basicities of hydrotalcites i.e., the heats of benzoic acid adsorption on hydrotalcites, which suggests that basic sites of hydrotalcites are active sites for the oxidation.

Xia *et al.*,⁹⁷ reported a detailed study of aerobic oxidation of 5-hydroxymethylfurfural to 2,5-difurancarboxylic acid over Pd-Au nanoparticles supported on Mg-Al hydrotalcite. The enhanced oxidation activity of HMF for the bimetallic catalysts is attributed to the synergistic effect between Au and Pd nanoparticles and the formation of smaller particle size that facilitates the oxidation of HMF to FDCA. Typical oxidation dehydrogenation reactions studied on hydrotalcite based catalysts are assembled in Table 1.

Hydrotalcites as Unique Catalysts

The important properties of hydrotalcites for use as catalysts are: High surface area, homogeneous inter-dispersion, basic properties, this is important property for a set of organic transformations and memory effect as it can regain its layered structure from changes due to calcination and other treatments.

Hydrotalcites can promote various reactions and their catalytic property can be generally classified as follows:

(i) Redox catalyst – Various hydrotalcites generally including copper or a heavy metal are known to function as oxidation or reduction catalysts.

(ii) Acid/base catalyst – Typical Mg/Al hydrotalcites have a unique and highly tunable structure with both acidic and basic properties. Hydrotalcites with their bi-functionality allow for the use of these materials as catalysts for various organic conversions.

(iii) Catalyst support – Hydrotalcites are known to be used as support for numerous catalytic species such as transition metals, alkali metals and even various anions.

Hydrotalcites have three important characteristics that make them useful for various applications:

(i) HTs have a good anion exchange capacity and are therefore used as ion exchangers, adsorbents or sensors

(ii) Hydrotalcites in most of the cases behave as solid bases and hence used as base catalysts for several reactions like self- condensation, cross-aldol condensation of aldehydes and ketones, Knoevenagel condensation, Claisen-Schmidt condensation Michael addition, trans-esterification and alkylation (Table 2). Detailed analysis is available in many reviews and also in the later part of this presentation.

In particular Mg-Al hydrotalcite and their calcination products are considered as models for base catalysis. Zn-Al hydrotalcites although less investigated could also be useful for this purpose.

(iii) Hydrotalcites can be prepared with several reducible bi-valent (Ni, Cu, Co) and trivalent (Fe, Cr) cations in the structure together with classical ones (Mg, Zn, Al) serving as precursors for the preparation of different mixed oxides active for oxidation and hydrogenation and dehydrogenation reactions.

Hydrotalcites can be used as such in their lamellar structure. In this case, their reactivity is mainly governed by the nature of the intercalated anion and by the amount of remaining water.

Highly homogeneous mixed oxides obtained from their decomposition can catalyze a wide range of reactions. In this case, the creation of M^{2+} - O^{2-} acid base pairs are the key parameter.

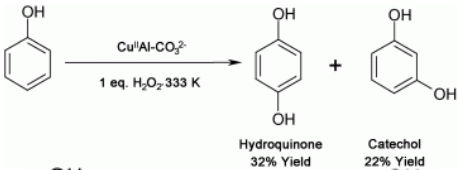
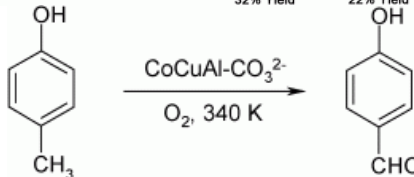
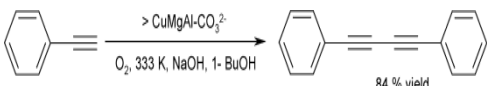
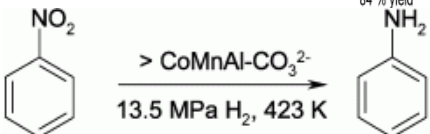
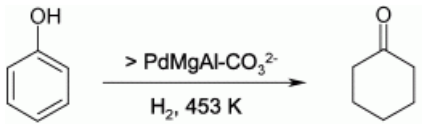
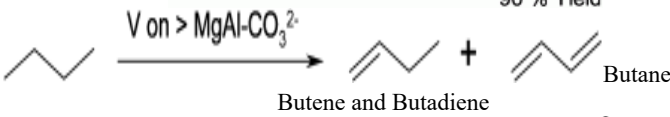
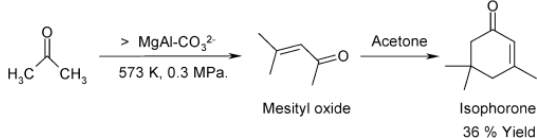
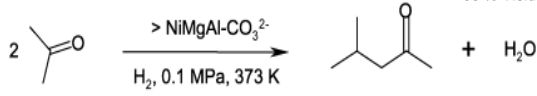
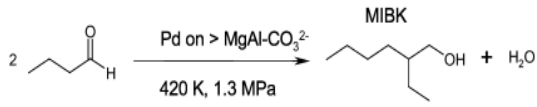
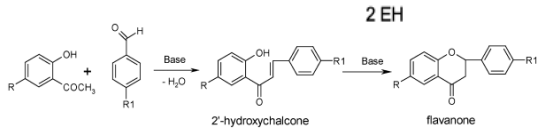
Reconstructed lamellar materials can be obtained from rehydration or calcined hydrotalcites which allows introducing almost any kind of compensating anions that can be used in the catalytic process.

Since the base property of hydrotalcites are often exploited in catalytic reactions, the various methods

Table 1 — Typical Oxidative dehydrogenation over hydrotalcites

S. No.	Title	Catalyst	Reaction Conditions	Results	Ref.
1	Oxidative dehydrogenation of ethyl benzene to styrene over hydrotalcite derived cerium containing mixed metal oxides	Mg/Al/Ce Mixed oxides	450 °C	49% conversion, 97% selectivity	132
2	V–Mg–Al catalyst from hydrotalcite for the oxidative dehydrogenation of propane	V–Mg–Al	400 °C	80% propene selectivity	133
3	Propane dehydrogenation over molybdenum hydrotalcite catalysts	Mo/Mg/Al	600 °C	80% propene selectivity	134
4	Vanadium oxides supported on hydrotalcite-type precursors – The effect of acid-base properties on the oxidation of isopropanol	VO _x /MgAl HT	250 °C	Conversion ~50% and propene selectivity 40%	135
5	Hydrotalcite-Supported Gold Catalyst for the Oxidant-Free Dehydrogenation of Benzyl Alcohol: Studies on Support and Gold Size Effects	Au-HT	393K	89% conversion and 99% selectivity	136
6	A Novel, Highly Efficient Catalyst for Propane Dehydrogenation	Pt-Sn/HT	600 °C	68% conversion	137
7	Performance of Ethane Dehydrogenation over PtSn Loaded onto a Calcined Mg(Al)O LDH with Three Mg:Al Molar Ratios Using a Novel Method	PtSn/ Mg(Al)O	550 °C	99% ethylene selectivity	138
8	Oxidant-Free Alcohol Dehydrogenation Using a Reusable Hydrotalcite-Supported Silver Nanoparticle Catalyst	Ag/HT	130 °C	99% conversion 99% selectivity	139
9	Gold nanoparticles on hydrotalcites as efficient catalysts for oxidant-free dehydrogenation of alcohols	Au/HT	120 °C	61% conversion and 99% selectivity	140
10	Copper nanoparticles on hydrotalcite as a heterogeneous catalyst for oxidant-free dehydrogenation of alcohols	Cu-HT	130–150 °C	99% selectivity	141
11	Oxidative dehydrogenation of short chain alkanes on supported vanadium oxide catalysts	VO _x /HT	550 °C	40% conversion ~50% selectivity	142
12	Oxidant-Free Dehydrogenation of Alcohols Heterogeneously Catalyzed by Cooperation of Silver Clusters and Acid–Base Sites on Alumina	Ag/Al ₂ O ₃	373K	100% conversion >90% yield Carbonyl to aldehyde	143
13	Influence of the Acid-Base Character of Supported Vanadium Catalysts on Their Catalytic Properties for the Oxidative Dehydrogenation of n-Butane	VO _x /HT	500–550 °C	26% conversion and 62% selectivity	144
14	Copper Nanoparticles from Copper Aluminum Hydrotalcite: An Efficient Catalyst for Acceptor- and Oxidant-Free Dehydrogenation of Amines and Alcohols	Cu(0)/Al ₂ O ₃	120 °C	100% conversion and 98% selectivity	145
15	Thermal decomposition of Mg/V hydrotalcites and catalytic performance of the products in oxidative dehydrogenation reactions	VO _x -MgO	600 °C		146

Table 2 — Some of the typical organic reactions promoted by hydrotalcites

No.	Catalyst	Reaction studied	Typical example	Ref.
1	MgAl HT	Epoxidation of alkenes with H ₂ O ₂		121
1	Cu(II)AlCO ₃ ²⁻	Hydroxylation of phenol with hydrogen peroxide	 <p>Phenol reacts with 1 eq. H₂O₂ at 333 K, catalyzed by Cu^{II}Al-CO₃²⁻, to produce Hydroquinone (32% Yield) and Catechol (22% Yield).</p>	119
2	CoCuAlCO ₃ ²⁻	Oxidation of para cresol	 <p>Para-cresol is oxidized to 4-hydroxybenzaldehyde using CoCuAl-CO₃²⁻ and O₂ at 340 K.</p>	120
3	RuCoAl-CO ₃ ²⁻	Oxidation of allylic and benzylic alcohols	Even Xanthene fluorene and alcohols containing thiophene group are oxidised	121
4	CuMgAlCO ₃ ²⁻	Oxidative coupling of alkynes	 <p>Phenylacetylene reacts with O₂ at 333 K in the presence of CuMgAl-CO₃²⁻ and NaOH in 1-BuOH to form diphenylacetylene (84% yield).</p>	121
5	CoMnAl-CO ₃ ²⁻	Reduction of nitrobenzene	 <p>Nitrobenzene is reduced to aniline using CoMnAl-CO₃²⁻ at 13.5 MPa H₂ and 423 K (66% Yield).</p>	121
6	Ni ²⁺ -based HT	Reduction of nitriles to primary amines	The basicity of HT that prevent acid catalyzed reaction	122
7	Pd ²⁺ -containing HTs	Reduction of phenol to cyclohexanone	 <p>Phenol is reduced to cyclohexanone using PdMgAl-CO₃²⁻ and H₂ at 453 K (90% Yield).</p>	123
8	HT as supports for V species	oxidative dehydrogenation	 <p>Butane is oxidatively dehydrogenated to Butene and Butadiene using V on >MgAl-CO₃²⁻.</p>	124
9	MgAlCO ₃ ²⁻ 573 K 0.3MPa	Aldol condensation	 <p>Acetone (H₃C-CO-CH₃) undergoes aldol condensation to form Mesityl oxide, which is further converted to Isophorone (36% Yield) in Acetone.</p>	125
10	NiMgAlCO ₃ ²⁻	synthesis of methyl isobutyl ketone from acetone	 <p>Acetone is converted to methyl isobutyl ketone using NiMgAl-CO₃²⁻ and H₂ at 0.1 MPa and 373 K.</p>	126
11	Pd/MgAlCO ₃ ²⁻	aldol condensation of n-butyraldehyde	 <p>n-Butyraldehyde is converted to MIBK (Methyl isobutyl ketone) using Pd on >MgAl-CO₃²⁻ at 420 K and 1.3 MPa.</p>	121
12	Claisen-Schmidt condensation - Mg(OtBu) ₂ and K ₂ CO ₃	substituted 2-hydroxyacetophenone and a substituted benzaldehyde	 <p>Claisen-Schmidt condensation of a substituted 2-hydroxyacetophenone and a substituted benzaldehyde using Mg(OtBu)₂ and K₂CO₃ yields 2-hydroxychalcone, which is further converted to flavanone.</p>	121

(Contd.)

Table 2 — Some of the typical organic reactions promoted by hydrotalcites (*Contd.*)

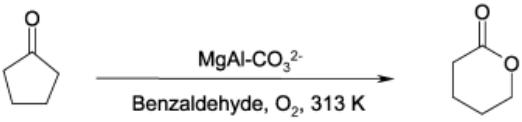
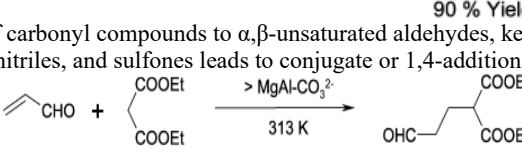
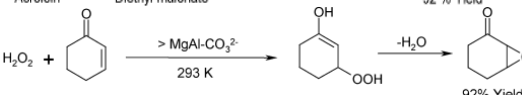
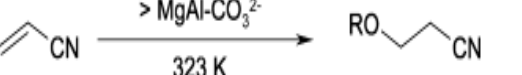
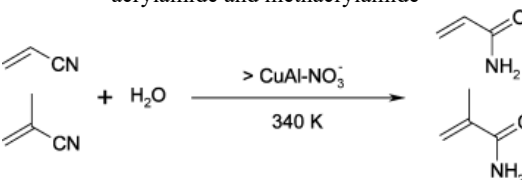
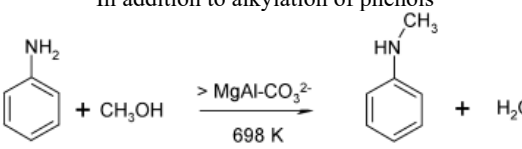
No.	Catalyst	Reaction studied	Typical example	Ref.
13	Rehydrated calcined HT	Knoevenagel Reaction	aromatic carbonyl compounds and aliphatic or cyclic ketones condensed with the active methylenic agents like malononitrile and ethyl cyanoacetate	127
14	MgAlCO_3^{2-}	Baeyer Villiger oxidation	oxidation of ketones into lactones and esters	128
				
15	MgAlCO_3^{2-} , 313 K	Michael addition	Exposure of carbonyl compounds to α,β -unsaturated aldehydes, ketones, esters, nitriles, and sulfones leads to conjugate or 1,4-additions.	129
				
16	$> \text{MgAlCO}_3^{2-}$	Weitz-Scheffer Epoxidation		130
				
17	$> \text{MgAlCO}_3^{2-}$	Cyanoethylation		131
				
18	$> \text{CuAlNO}_3^-$	Hydrolysis	Hydrolysis of acrylonitrile and methacrylonitrile is an attractive route to acrylamide and methacrylamide	121
				
19	$> \text{MgAlCO}_3^{2-}$	Alkylation	In addition to alkylation of phenols	121
				
20	HT solid bases	Acylation	Acylation of alcohols amines and imides by alkyl carbonate (dimethyl carbonate or ethyl carbonate)	121

Table 3 — Determination of basicity of hydrotalcites

Probe molecule/Reaction	Essential Results	Technique employed -characteristic values	Ref
Carbon dioxide	Several forms of carbonate species		98, 99
	Mono, bi dentate and bicarbonate	IR absorption in the range 1700–1300 cm^{-1} ; Thermal desorption usually around 320–550 K	98-101
	Monodentate on oxide ions	Strong basic sites 1510–1560 cm^{-1} and/or 1360–1400 cm^{-1} thermal desorption around 550 K Heat of adsorption above 80 kJ/mol	102, 103
	Bidentate species on acid-base pairs such as Mg^{2+} - O^{2-} or Al^{3+} - O^{2-}	Intermediate basic sites 1610–1830 cm^{-1} ; thermal desorption around 460 K; Heat of adsorption above 80 kJ/mol	103
	Bicarbonate require surface hydroxyl groups	Weak basic sites 1270, 1650, 1480 cm^{-1} ; thermal desorption around 320–400 K	99
Adsorption of deuterated chloroform	$^{13}\text{CO}_2/\text{CO}_2$ isotope exchange studies	A non-linear variation of rate with time shows the sites are heterogeneous	98
	The vibration modes of the C-D bond followed	Weak acidic probe suitable to get insights both on the amount and on the strength of basic sites	104

(Contd.)

Table 3 — Determination of basicity of hydrotalcites (<i>Contd.</i>)			
Probe molecule/Reaction	Essential Results	Technique employed -characteristic values	Ref
Sulphur dioxide	Adsorption calorimetry	190 kJ/mol strong basic sites	104
Trimethyl borate	IR spectra of adsorbed species	1360 and 1063 cm^{-1} assigned to B-O and C-O stretching modes. These bands are modified (split) upon interaction with surface basic sites	105
CH_3CN is an amphoteric probe	IR spectroscopy two regions need to be scanned	The 2360–2230 cm^{-1} range is characteristic of species formed on Lewis acidic sites. Vibration modes of the probe chemisorbed on basic O^{2-} sites fall in the range 2230–2050 cm^{-1} region	106
Benzoic acid	Styrene epoxidation	Reduction in the catalytic activity	107
Phenol and acrylic acid	Most of these probe molecules or transformations are site specific		108
Trichloroacetic acid in benzene;			103, 109, 110,
Beta-isophorone to alpha-isophorone			111, 112, 113, 114, 115
Diacetone alcohol (DAA) retroaldolisation			
Isomerisation of glucose into fructose			
Condensation of benzaldehyde with activated methylenic groups (ethyl cyanoacetate, ethyl malonate, ethyls bromoacetate)	Extent of the reaction is monitored		116
Base catalyzed disproportionation of 2-methyl-3-butyn-2-ol to acetylene and acetone	Reaction monitored		117,118
Binding energy of O 1s electrons	Lower the binding energy, the more basic surface		111

used to determine the basicity of solid catalysts derived from hydrotalcites are summarized in Table 3 for ready reference.

Conclusions

Hydrotalcites though promote various types of organic reactions as outlined in this presentation. The active phase is mostly a mixed-oxide of two or more cations present in the precursor of the hydrotalcites. The mixed oxides formed from the hydrotalcites precursor behave sometimes totally different from the mixed oxides prepared separately from the constituent oxides, this is due to the proximity of opposing sites present in the precursor (that is acid and basic sites) which can promote both push and pull action on the reactive molecule. A typical example is shown in Fig. 2

It may be necessary that one has to rationalize the generation of proximity of opposing sites on the system generated from the precursor hydrotalcites and also the strength and the number how do they vary when prepared from the precursor. This appears to be peculiar to catalyst systems generated from

hydrotalcites. It is rare to find two opposing type of sites are present in adjacent positions in a lattice. This appears to be possible in the case of hydrotalcite precursor, which can be due to various factors like the layer structure, the anion entrapment in the lattice and also the compositional variations that is possible in the precursor.

Secondly, how far these systems generated from precursor hydrotalcites, can be regarded as nascent and hence possess different active sites compared to the conventional mixed oxides prepared in a general manner from constituent oxides has to be established. This aspect has to be carefully examined from the point of view of active centers, since these active centers are not only function differently but also are capable of promoting unusual transformations not exhibited by mixed oxides.

There are variety of organic transformations promoted by variety of hydrotalcites and most of them are examples of base catalysis though there can be some promoted by the acid sites in hydrotalcites. In Table 2 some of the organic transformations carried using hydrotalcites are given.

It is seen from the limited examples shown in Table 2 that hydrotalcites are capable of promoting a variety of organic transformations and it can be expected that the list will grow in the near future and these systems can also be extensively employed for production of many organic end products in the near future. This is one of the areas that requires careful examination from time to time.

Typical oxidation dehydrogenation reactions studied on hydrotalcite based catalysts are assembled in Table 3. It is seen from the values given in Table 3 that high levels of conversion and fairly good selectivity is observed in dehydrogenation reaction.

It is possible in the coming years, hydrotalcites can become one of the important precursors for generating *in situ* catalysts with appropriate and suitable multiple functionalities (both acidic and basic sites in appropriate geometry) for many organic transformations which will result in the manufactured products.

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