



# Groups IV, V and VI metal oxide-containing hydrotalcite catalysts: state of the art on their catalytic applications

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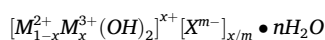
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## ABSTRACT

The present contribution is a review paper that summarizes the structure, properties and catalytic applications of hydrotalcite based materials when they are modified by the incorporation of oxide metals from groups 4, 5 and 6. The unique properties of hydrotalcites, with a double layer structure able to host ions in the interlayer space and its basicity, together with the properties of transition metal oxides from groups 4, 5 and 6, leads to materials highly promising as catalysts. The incorporation can form dispersed species of those oxides on the hydrotalcite-like structure, which acts as support, or by the incorporation of those elements into the hydrotalcite structure. The structure and properties of these materials have been reviewed and analyzed, in order to give a detailed description of the main factors that affect the catalytic properties of these interesting materials.

## 1. Introduction

Hydrotalcites (HT) are doubled-layered lamellar clays with a structure similar to the natural mineral brucite,  $Mg(OH)_2$ , in which magnesium is octahedrally surrounded by six oxygen atoms in the form of hydroxide, with the octahedral units extending to form infinite sheets through edge-sharing. The positive charge of the octahedral layers that results from the substitution is balanced by anions (di-metallic ( $M^{II}$ ) and tri-metallic ( $M^{III}$ )) as well as  $H_2O$  molecules, arranged in layers alternating with the octahedral ones [1–3]. The general formula of the hydrotalcites is:



Where  $M$  represents a metal cation and  $X$  represents an anion.  $M^{2+}$  could be  $Mg^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Ni^{2+}$  or  $Zn^{2+}$ ,  $M^{3+}$  could be  $Al^{3+}$ ,  $Cr^{3+}$  or  $Fe^{3+}$  and  $X^{m-}$  is the interlayer anion such as  $CO_3^{2-}$ ,  $Cl^-$ ,  $NO_3^-$ ,  $OH^-$ ,  $SO_4^{2-}$ , vanadates, molybdates, tungstates, or heteropolyoxometalates, among others [1–6]. Co-precipitation is the most frequently employed method to prepare hydrotalcite materials due to its simplicity, time, low cost, and mild conditions [7,8]. Thermal treatment of hydrotalcite materials generates stoichiometric and non-stoichiometric mixed metal oxides exhibiting unique characteristics, due to the layered structure and charge compensating interlayer anions [9,10]. In addition, the

thermal evolution of such structure yields basic solids with catalytic applications. In this line, Melián-Cabrera and coworkers [11] demonstrated with experimental and DFT calculations how during thermal treatment the carbonates in the interlayer have able to form well dispersed metal phases such as Cu or Zn oxides in the final structure of the solid, preventing the growth of the oxide crystals. By this way, a high surface area solid with well dispersed oxide active phases are obtained.

Due to this unique structure and properties, hydrotalcite and hydrotalcite-like based materials, serve as catalysts for various catalytic reactions such as: alcohol and aldol coupling reaction [12–15], hydrogenolysis [16], steam reforming [17], dry reforming [18], oxidation of ammonia [19], transesterification [20,21], hydrogenation reactions including methanol synthesis [7,11,22–24], or glycerol etherification [25], among others.

Transition metals are widely used in catalysis, and especially those of groups 4, 5 and 6 with the advantage that the surface chemistry, and subsequently the catalytic properties, can be reasonably predicted and modulated for both bulk mixed metal oxides as well as for supported metal oxides [25]. In this sense, Titanium, and Zirconium have attracted a lot of interest in catalysis [26–28]. Titania is used as support for various applications in catalysis and photocatalysis, e.g.: dehydration [29], hydrogenation [30,31], dehydrogenation [25] and oxidation reactions [32,33]. Moreover, zirconia has been reported as an acidic catalyst and support for  $CO_2$  reforming [34], esterification [35,36],

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transesterification [36,37], NO<sub>x</sub> reduction [38,39], biomass conversion to biofuels [40] etc. Additionally, Hafnium's catalytic potential is not as extensively explored as some other transition metals, however, it has been used as a support for metal nanoparticle catalysts due to its high thermal and chemical stability for some reactions: hydrogenation [41] and dehydration reactions [42].

Group V based catalysts also have also probed be effective for catalyzing several reactions at a commercial scale [43–48]. Vanadium oxide has multiple oxidation states that can be interconverted under reaction conditions, making this element useful in catalysis and electrocatalysis applications, and specially for partial oxidation and oxidative dehydrogenation reactions [43–58]. Besides, Nb also possesses multiple oxidation states (from +5 to +3) and acid properties [59,60], which makes it useful in catalysis as support, active site or as a dopant for several processes such as: biomass conversion [61,62], ethanol reforming [63], esterification [64], partial oxidation [65], dehydration [66] and hydrogenation reactions [67]. Tantalum catalysts, on the other hand, have not been as widely explored as some other transition metals; nevertheless, tantalum-based catalysts display catalytic activity in some essential reactions, especially those that need redox properties materials [68–73].

Following this line, Chromium, Molybdenum and Tungsten, from Group VI, are also widely used in various catalytic processes such as oxidation, hydrogenation, dehydrogenation, dehydration, and polymerization reactions. Cr oxides are used for ethylene polymerization [74], Guerbet reaction [75], CO oxidation [76], and oxidative dehydrogenation [77–79], dehydrogenation [80] and hydrogenation reactions [81]. Also, molybdenum oxides represent a great alternative as a heterogeneous catalyst for a variety of chemical reactions: epoxidation of alkenes [82], synthesis of ammonia [83], methanol oxidation [84], partial oxidation and ammoxidation of propane [85–87], dehydrogenation [88,89] and oxidation reactions for removal of pollutants [90, 91]. Tungsten oxide (WO<sub>3</sub>) exhibits catalytic activity especially to undergo redox reactions [92,93]: epoxidation of alkynes [94], propylene oxidation [95] and electro-oxidation of methanol [96].

These examples show the wide number of catalytic applications in which elements from groups 4, 5 and 6 are efficient catalysts. Prof. Wachs and coworkers [25] studied these metal oxides using methanol as probe molecule, to analyze the surface chemistry. They found that for unsupported oxides, the number of active surface sites depend on the morphology, and, among the unsupported, Cr<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> have the most active redox sites, whereas WO<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> have the most acid ones. For supported oxides, the activity can be modulated with a combination of the supported oxide sites and of the support ones [25].

The most common hydrotalcite is made from Mg and Al. When alkali and alkaline earth atoms are incorporated to oxide catalysts, they form strong ionic bonds that modified the catalytic properties, and specially the reducibility and the number of basic sites [97–107], allowing the modulation of the redox properties of the materials. In addition to other properties of hydrotalcites such as their morphology, high surface area, low cost, and the ease of composition adjustment [108–112], this makes hydrotalcite materials useful as catalytic support. Thus, the incorporation of metals from groups IV, V, and VI to hydrotalcite materials renders supported catalysts useful for a high number of processes, but it is necessary to analyze the relationships between the structure (coverage, surface sites, dispersion) of them and the relationships with the catalytic activity, as well as the keys for modulating the effect of Mg. For this reason, it is the aim of present paper to critically analyze the literature on metals of groups IV, V, and VI to give a detailed description of the main factors that affect the catalytic properties of these interesting materials.

## 2. Overview of the main applications of hydrotalcite based catalysts

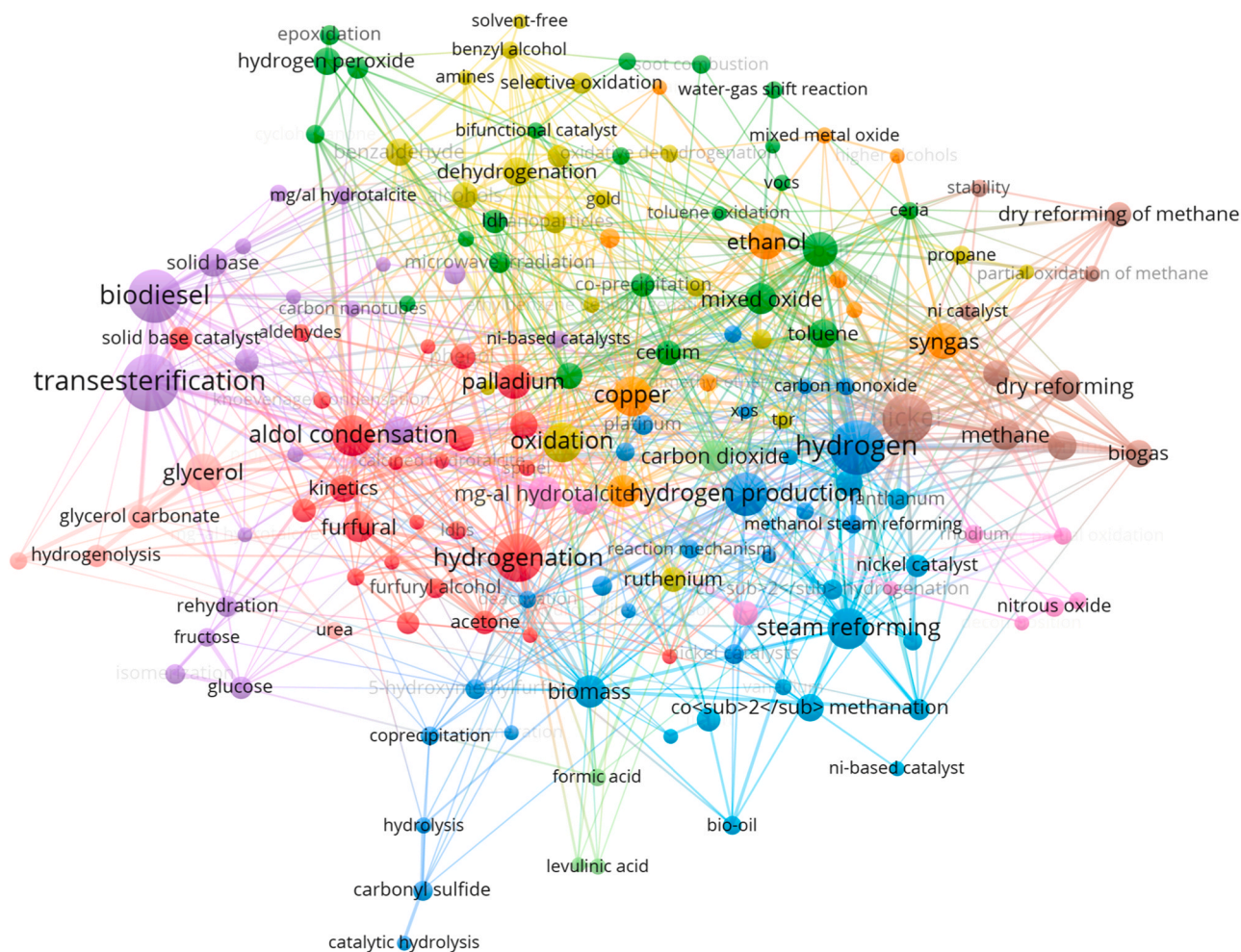
A bibliometric map of the most cited articles with the authors'

keywords in Scopus indexed for hydrotalcite and catalysts is shown in Fig. 1. This map is useful to give an idea about the main applications in catalysis investigated during the last years. There are several circles in the figure that clearly indicates the main topics of interest. The purple node includes the key words related with the production of biodiesel by transesterification by solid base catalysts. In these studies, it has been shown that  $[Mg_{(1-x)}Al_x(OH)_2]^{x+}(CO_3^{2-})_{x/n}$  hydrotalcite materials with compositions over the range  $x = 0.25\text{--}0.55$  are effective for catalyzing the oil transesterification reaction with methanol for the production of biodiesel [113,114]. It was observed how the activity of the hydrotalcites increases with Mg content, being the hydrotalcite one order of magnitude more active than MgO oxide [115], indicating that the catalytic performance is not only related with the catalysts basicity, but also with its structural texture [115]. These studies demonstrated that hydrotalcite and hydrotalcite related materials are efficient heterogeneous base catalysts, useful for biodiesel production as well as for other reaction such as the synthesis of glycerol carbonate [116–121], illustrated as the light pink node in Fig. 1, or aldol condensation, whose studies appears in the strong pink node. Glycerol transformations are of paramount interest since it is the main by-product in the biodiesel production and in other processes concerning biomass as raw material, being a platform molecule at the biorefinery [122]. Glycerol carbonate is an intermediate in the production of glycerol, which is used in chemical synthesis, pharmaceuticals, surface coatings, among other important applications, thus, the transformation of glycerol into glycerol carbonate is quite interesting from a commercial point of view. Corma and coworkers [123] studied the synthesis of glycerol carbonate by transesterification and carbonylation with urea using hydrotalcites derived oxides. They found that the number of Lewis basic sites can be increased by substituting the Mg by Li, improving the catalytic properties during the transesterification reaction. They also described how modified hydrotalcite materials with balanced bifunctional acid-base sites (pairs) are efficient for the carbonylation of glycerol with urea.

Other authors have also described how the acid-base properties of hydrotalcite materials can be tuned by heat treatment and rehydration processes, due to the memory effects of hydrotalcite materials. The structure of hydrotalcites may change from layered double hydroxide to mixed metal oxide, and subsequently to a spinel structure during heat treatment, and returned from mixed metal oxide to a layered double hydroxide structure by rehydration [124]. Due to this versatility of hydrotalcites, they are useful catalysts for several glycerol transformation such as hydrogenolysis, reforming and selective oxidation [125–129], illustrated in the bibliographic map (Fig. 1) for all the connections with the “glycerol” light pink circle.

Fig. 1 clearly illustrates that another important issue is the hydrogen production reactions (blue circles), that are connected with steam (blue) and dry reforming (brown). Fig. 1 shows that steam reforming circle is connected with ethanol, methanol, methane, glycerol, and biomass, indicative that several research groups have investigated the use of hydrotalcites as catalysts for the steam reforming process using all these starting materials [130–134]. It is also connected to nickel, which has a significant circle diameter, indicative that most of the catalytic systems used for the steam reforming reaction, are modified with Ni. The studies show that the basic sites of the hydrotalcites are key for decreasing the coke production [135,136]. Dry (carbon dioxide) reforming circle relates to nickel, cobalt, and Ce, indicative that hydrotalcites have been used as support for those metals and/or oxides for preparing catalytic materials for the dry reforming reaction. These studies [137] show that hydrotalcite materials show high activity and stability at relatively high temperatures, although the deactivation is still a problem to be solved [137,138]. However, hydrotalcites as support perform better than other materials due to the basic sites, and to the structure that allows high dispersion and reducibility of metal nanoparticles [138–140].

Fig. 1 underlines that another important node is related to hydrogenation (yellow), that includes keywords such as aldol condensation, furyl alcohol, aldol condensation, and copper. These studies confirm



**Fig. 1.** Bibliometric map showing the main applications of hydrotalcite-based catalysts. All the papers that had hydrotalcite and catalysts within the authors keywords were included. Scopus (February 2024) was used. The software (VOSviewer) assigns colors to keywords that are related and positions them in close proximity, being the circle and font size proportional to the number of hits. The lines represent the citation links.

that Cu-hydrotalcite-catalysts are efficient for the selective hydrogenation of biomass-derived molecules such as furfural or levulinic acid, among other alcohols [141–144], as well as for the hydrogenation of carbon dioxide for production of fuels and platform molecules [145, 146]. The activity of hydrotalcites in CO<sub>2</sub> transformation is directly connected with its basic sites [145–148], being also useful hydrotalcites as CO<sub>2</sub> adsorbent materials [149–151]. The bibliographic map (Fig. 1) shows other minor nodes related with other applications of hydrotalcite materials such as epoxidation reactions [152,153].

This brief graphic resume of literature on the applications of hydrotalcites in catalysis (Fig. 1) illustrates the possibilities of these materials as catalytic support and as a solid basic material. During the last decades, solid basic catalytic materials have been developed in order to replace corrosive acids and basic homogeneous catalysis for the synthesis of several organics and fine chemicals thought condensation, transesterification and epoxidation reactions [154] and hydrotalcites are playing a key role in this important step forward in order to develop green catalytic processes. Hydrotalcites possess basic sites, that can be modulated during the synthesis and heat treatments whereas the morphology of the double layered material provides a unique and useful structure for the dispersion of oxide and metals.

### 3. Group IV elements hydrotalcite supported catalysts

Wachs group studied the surface chemistry and reactivity of ZrO<sub>2</sub> and TiO<sub>2</sub> supported and unsupported oxides [25] by methanol-TPSR,

since methanol reaction can be used as a smart probe since redox sites form HCHO, HCOOCH<sub>3</sub> and CH<sub>2</sub>(OCH<sub>3</sub>)<sub>2</sub>, basic sites CO and CO<sub>2</sub>, and acid sites CH<sub>3</sub>OCH<sub>3</sub> [155]. These studies showed that bulk TiO<sub>2</sub> only presented acid character whereas bulk ZrO<sub>2</sub> was mainly dominated by acid sites, but also contained some redox sites [25]. When these oxides are incorporated to another one, such as a hydrotalcite, the supported metal oxide consist of a two-dimensional surface of TiOx or ZrOx phases dispersed on the support. The supported oxide structures are formed by anchoring to the surface hydroxyls or defects. Depending on the coverage (number of TiOx or ZrOx units per surface unit of the support) different structures can be formed [45].

There are not many studies of TiOx and/or ZrOx species supported on hydrotalcites, although some examples can be found. For example, Bellato et al. [156] deposited anatase titanium dioxide and iron on hydrotalcite support samples with different amount of titanium, with the objective to confer to the hydrotalcite photoactivity and magnetic properties. There are several studies that demonstrate that the performance of TiO<sub>2</sub> is improved when its particle size is at the nanoscale [157–159]. But these small sizes would create several disadvantages, such as the presence of suspended nanoparticles when the photocatalyst has been used in a liquid effluent. In this line, Bellato et. Al. [156] used the hydrotalcite to stabilize the TiOx nanoparticles, in addition to the magnetic properties for facilitating the recovering of the material after use. They optimized the amount of TiOx to be supported on the hydrotalcite material and probed the effectivity of the material during the degradation of several organic molecules during several cycles. A



similar approach was followed by Zhang and coworkers [160], that prepared hydrotalcite materials loaded with  $\text{TiO}_x$  species and used several dopants such as Fe, obtaining also good photoactivity for the  $\text{TiO}_x$  supported material. They established that the incorporation of  $\text{TiO}_2$  in hydrotalcite catalyst improved the surface density of  $\text{OH}^\bullet$  and  $h^+$  where the aromatic rings of tetracycline are attacked and subsequently degraded [160]. Xu and coworkers [161] prepared hydrotalcite-like compounds (type  $\text{Co}_{1.5}\text{M}_{1.5}/\text{Ti}_x\text{Al}_{1-x}$  with  $\text{M} = \text{Co}, \text{Ca}$  and  $x = 0, 0.1$ ) whereas Ti was introduced during the synthesis for achieving a partial substitution of Al atoms by Ti. They studied these materials for the NO decomposition and reported that the Ti incorporation destabilizes the adsorbed  $\text{NO}_x$  species on the catalyst surface, favoring the NO decomposition reaction.

Zr-mixed oxides, such as Zr-Ce-O, are included in several catalytic systems such as automotive three-way catalyst (TWC) to promote oxygen storage capacity due to its redox properties [162]. There are also effective for catalyzing  $\text{CO}_2$  reforming processes [137]. For this reaction, some studies use Mg-hydrotalcite materials and other Al-containing hydrotalcite-like material, in order to modulate the basicity of the surface. Debek and coworkers [163,164] prepared  $\text{Mg}(\text{Ni},\text{Al})\text{O}$  hydrotalcite materials with Zr species incorporated by coprecipitation. They found that the incorporation of Zr species in the framework of the hydrotalcite-like (with Al) structure exhibited high resistance to coking due to the rearrangement of metal particles upon  $\text{CO}_2$  methane reforming reaction. There are other studies that show how Al-hydrotalcites-like materials are able to disperse and stabilize Zr species [165], and that describe how these materials possess a high basicity, stability, and sorption capacity, concluding that the strong basic sites of the hydrotalcite-like material facilitated the activation of  $\text{CO}_2$  and consequently promoted the activity. Although most of the works for  $\text{CO}_2$  reactions use Al containing hydrotalcite like materials, some studies can be found that use Mg materials [166,167], that incorporated Zr atoms to Mg-containing hydrotalcite material. They described how the basicity of these materials inhibited coke formation and undesired reactions. Both with Al or Mg containing hydrotalcite structure, the results show how the basic sites can be modulated, in order to obtain active and selective catalysts for the transformation of  $\text{CO}_2$ .

Zr-doped Mg-Al hydrotalcites have been also used as basic catalysts for the transesterification process [168–170]. The results show that the Zr incorporated hydrotalcites have larger pore diameter and stronger base-strength due to the incorporation of  $\text{Zr}^{4+}$  species into the brucite-like structure of hydrotalcites [171], enhancing basicity of the catalytic materials, which correlates well with the increase in catalytic activity observed for these catalysts. The incorporation of Zr species to the hydrotalcite support confers redox functionality to the material, and subsequently, some oxidation catalysts can be prepared following this approach. For example, Zr based hydrotalcite-like compounds are effective for VOCs combustion [172].

#### 4. Group V elements hydrotalcite supported catalysts

Temperature Programmed Surface Reaction (TPSR) Methanol characterization [25] for group V elements indicated that unsupported  $\text{V}_2\text{O}_5$  oxide has basic and redox surface sites, whereas acid and, in a minor extent redox, are present in  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  oxides. The properties of vanadium mixed-oxides in which V species present different oxidation states that can be interconverted under reaction conditions, make V-based catalysts adequate during partial oxidation, oxidative dehydrogenation (ODH), and hydrogenation reactions. Fig. 2 [45] shows how the structure of the supported VOx is affected by the total coverage on the support. For low coverages, dispersed and polymeric species can be found, in addition to exposed support. At monolayer coverage  $\text{V}_2\text{O}_5$  nanoparticles may form.

Alkane oxidodehydrogenation (ODH) and partial oxidation processes are relevant for the production of olefins, oxygenates, and other important chemical intermediates, being V based catalysts active and selective for most of these processes [173–175], and commercially used for some of them, as for the butane transformation into maleic anhydride [176]. Hydrotalcites are useful materials for the incorporation of vanadium species, since Mg and V can form several vanadates, with different stoichiometries and oxidation states of V (such as  $\text{Mg}_3(\text{VO}_4)_2$ ,  $\text{Mg}_2\text{V}_2\text{O}_7$  or  $\text{Mg}_3(\text{VO}_4)_2$ ) [177]. Volta and coworkers [178] attributed the catalyst activity to the presence of  $\text{Mg}_2\text{V}_2\text{O}_7$ , that possess a  $\text{V}=\text{O}$  short bond able to initiate the H abstraction, and a bridging V-O-V involved in the ODH mechanism, being a catalytic dynamic model in which the structure of V species should change from  $\text{V}_2\text{O}_4^{2+}$  units to  $\text{MgVO}_3$  ones [178].

These structural and redox reversible cycles of the Vanadium active species under reaction conditions that facilitate the partial oxidation and oxidative dehydrogenation reactions have been pointed out as responsible of the activity of vanadium-based as catalysts [179]. Due to that, Kooli and coworkers [180] investigated the influence of layer-doping versus interlayer-doping with V species on the catalytic properties of layered double hydroxide-derived vanadium catalysts for oxidative dehydrogenation of propane. They concluded that the catalytic performance depended on the manner of incorporation of vanadium species to the double layer structure, since pyrovanadate was formed in the case of interlayer- and ortho-vanadate in the case of layer-doping. The results showed that catalysts obtained from interlayer-doped ( $\text{Mg-Al-V}$ ) precursors were more active and selective than mixed oxides obtained from layer-doped ( $\text{Mg-V}$ ), underlining the importance of Mg and Al sites, as have been also shown when hydrotalcites are used as support for other catalytic systems. A similar approach was followed by Palacio and coworkers [181], that successfully incorporated decavanadate anions between the layers of the hydrotalcite support, identifying Mg-Al-V-O structures, and obtaining promising results for these catalytic materials for the propane ODH reaction. These catalysts have been also studied for the oxidative dehydrogenation of n-butane [182–186], concluding that the acid/basic sites ratio determines the total selectivity, being the total selectivity for the dehydrogenated products higher on the highly basic

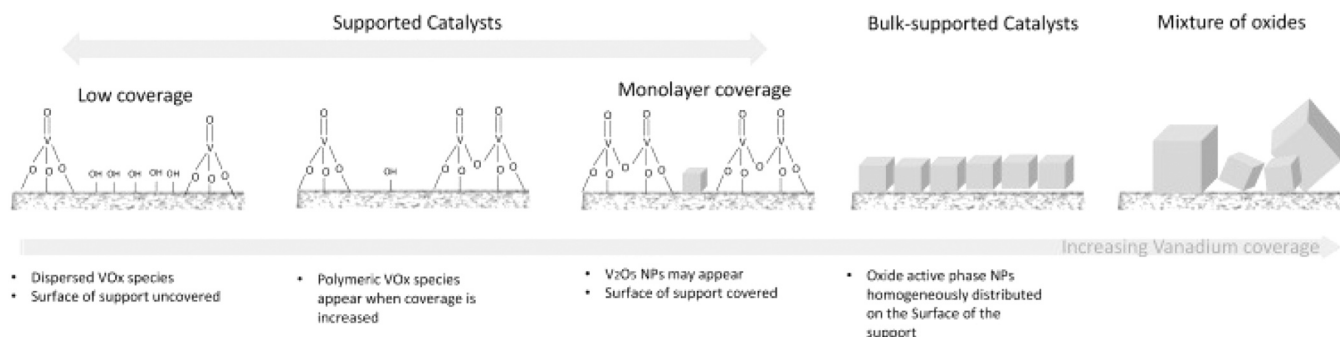


Fig. 2. Effect of coverage on the structure of VOx supported catalysts. Reproduced from [45] with permission from Elsevier.

catalysts. This is in line with the Electron Spin Resonance (ESR) investigations performed by Serwicka et al. [187] that concluded that the presence of Al sites leads to the formation of  $V^{4+}$  species that possess weak vanadyl bonds, active during the alkane oxidative dehydrogenation. Rabello de Castro and coworkers [188,189] identified hydrotalcite-like compound containing  $V^{3+}$  in the layers and vanadate (V) species in the interlayers.

The discussed studies have demonstrated that Mg-Al-V-O structures can be formed in the interlayer and that present useful catalytic properties. In addition, hydrotalcite based materials can serve as support for vanadium oxide dispersed species, that are useful catalysts for environmental applications [190], as well as for partial oxidation and dehydrogenation reactions as have been discussed [191]. Da Costa and coworkers studied the effect of vanadium as promoter of Ni based hydrotalcite catalysts during the CO methanation reaction [192] and described that vanadium species can enhance the interaction between Ni and the hydrotalcite support.

When hydrotalcite oxides are modified with Nb, acid sites are incorporated, as a result, acid-base pairs are obtained in the Nb/hydrotalcite material, which can be beneficial in several reactions. In this line, Oliveira et al. [193] modified hydrotalcite with Nb as catalysts for the glycerol conversion into oxygenates such as diglycerol, ethers and ketone, useful as fuel additives. Fig. 3 shows a diagram of the catalysts synthesis procedure [193]. The authors found that mixed oxide obtained from hydrotalcite modified with Nb (5 %) (MgAlNb oxide) exhibits high catalytic activity in the conversion of glycerol to allyl alcohol and cyclic ethers. In fact, they state that this catalyst is more active than others reported in the literature, reaching glycerol conversions of almost 80 % at 6 h (shorter times than reported at that time) due to an increase in its acidic nature and oxidizing species [193]. Krasno-baeva et al. [194] proposed a series of Nb-hydrotalcite catalysts for the oxydehydrogenation of alkanes and alcohols. Catalysts that contain Nb–Mg–Al showed a conversion of ethane of 12 % and a yield to ethylene of 11 % at 500 °C, however, the incorporation of Mo (Nb–Mo–Mg–Al) to the catalyst improved the activity and yield (conversion of 17 % and yield of 16 %). Additionally, a more complex catalyst that contains Nb–V–Mo–Mg–Al was tested for the oxidative conversion of ethylbenzene, *n*-octane and sec-butanol at 500 °C showing high conversions and selectivities to styrene, ethylbenzene and ketone,

respectively, showing a great synergetic effect of Group V metals (Nb and V) and Group VI metal (Mo) with Mg–Al hydrotalcite catalysts [194] and the capacity of the double layer hydrotalcite oxides to act as support for multioxide catalysts.

Padula et al. [195] obtained NbMgAl mixed oxide catalysts by ion exchange using MgAl hydrotalcite as precursor, obtaining a high surface area composite MgAl material with segregated  $Nb_2O_5$  nanoparticles, as was demonstrated by the XRD characterization (Fig. 4). They observed how the incorporation of Nb preserved the hydrotalcite structure, that is lost after thermal treatment at 600°C. Fig. 4 shows how the pattern of niobium oxide ( $Nb_2O_5$ ) is in the composite material. Characterization of the structure by electron energy-loss spectroscopy (EELS), as it is shown in Fig. 4, to determine the lattice parameters, indicated a contraction of the HT structure, reducing the interlayer space, upon Nb incorporation. That changed the HT surface from smooth to rough, indicative that Nb oligomers are deposited over the HT surface rather than in the interlayer space (Fig. 4). This indicated that the  $Nb^{5+}$  cations can replace the  $Mg^{2+}$  ones in the HT structure, since they have similar radii, in line with structural studies [196,197]. These catalytic materials were efficient for the glycerol transformation into oxygenates with commercial applications such as formic acid, diglycerol and dioxanes.

In catalysis, Nb is commonly used as dopant of several catalytic systems [65], due to its ability to modulate both redox and acid sites, and to incorporate to the lattice several structures forming defects, that usually enhance the catalytic properties of the undoped catalysts. Following this line, Nb was incorporated to Cu/HT catalysts, to improve their performance for the ethanol condensation into *n*-butanol [198]. The results indicated the effective incorporation of Nb into the Cu/HT structure and its ability to improve both activity and selectivity to butanol. Similar results have been reported when using Nb as additive of Ni/HT catalysts for reforming reactions [199].

## 5. Group VI elements hydrotalcite supported catalysts

TPSR Methanol characterization [25] for group VI elements indicated that unsupported  $MoO_3$  only showed redox character,  $WO_3$  only acidic, and  $CrO_3$  was dominated by basic and redox sites, with a minor amount of acid sites [200]. Although Cr is highly pollutant, its unique characteristics made that some relevant applications in catalysis have

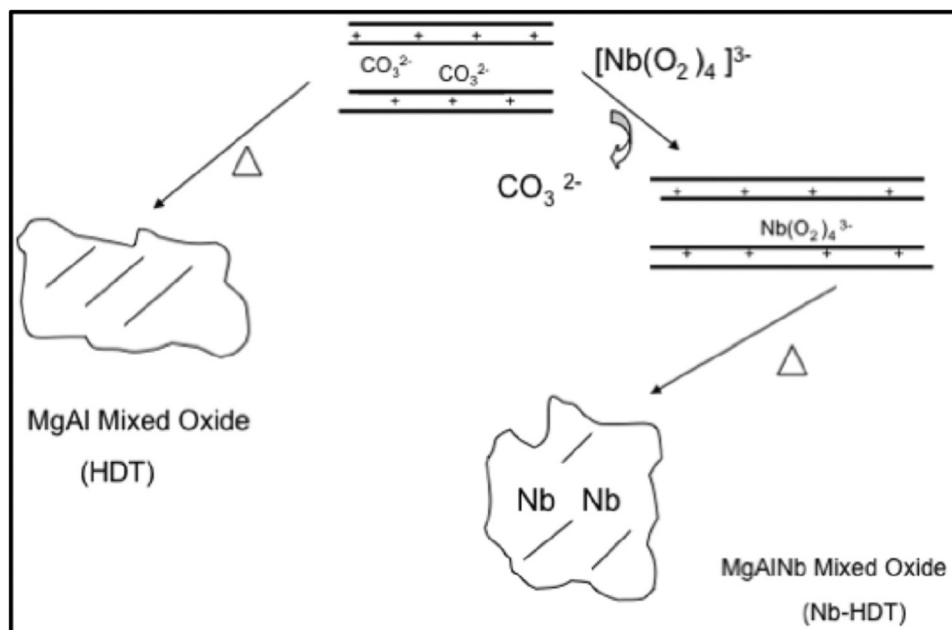
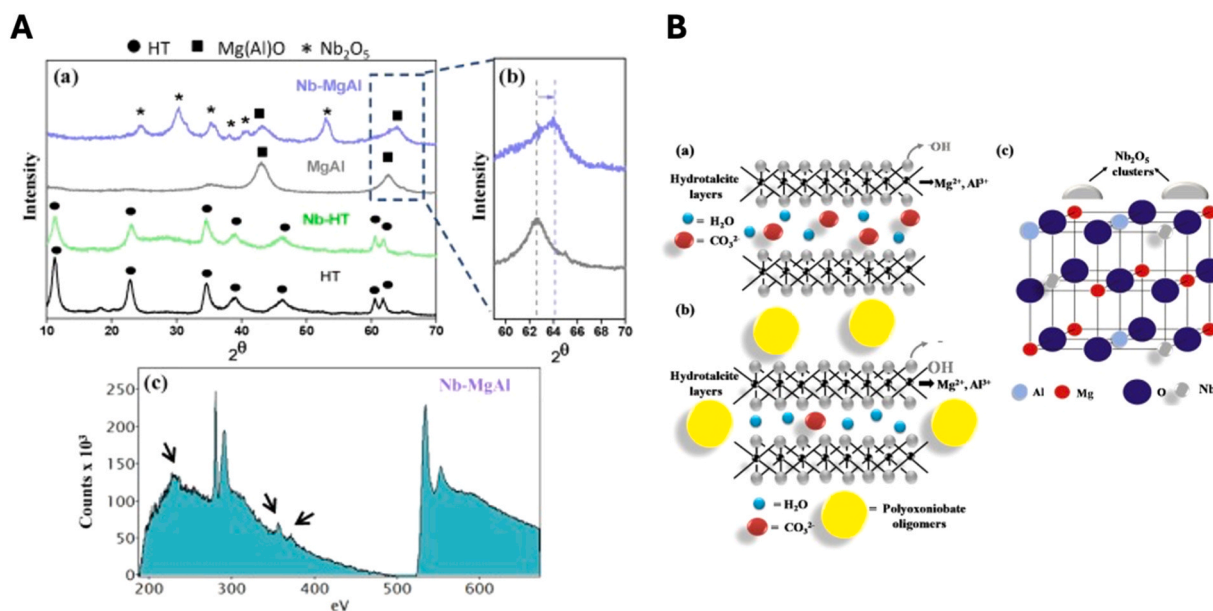


Fig. 3. Diagram of Nb-modified MgAl mixed oxide preparation. (a) Reproduced from [193] with permission from Elsevier.



**Fig. 4.** (A) XRD patterns of the hydrotalcite and Nb containing catalysts (a), magnification (b) and EELS spectrum of NbMgAl (c). (B) Scheme of the proposed structure for hydrotalcite: (a) after anion exchange process with peroxyoniobate species, and (b) after calcination at 600°C during 2 h. Reproduced from [195] with permission from Elsevier.

been described. In this line, Rao et al. [201] prepared a series of hydrotalcite materials composed of Mg–Al, Mg–Cr and Zn–Al for the *tert*-butylation of phenol with isobutanol. The results showed that all the hydrotalcite-type catalysts are more active for the *tert*-butylation than MgO and Al<sub>2</sub>O<sub>3</sub> oxides. The Cr<sup>3+</sup> substitution of Al<sup>3+</sup> caused a decrease in the acidity sites that modulated the selectivity in several reactions, such as the formation of *tert*-butyl phenyl ether and *o*-*tert*-butyl phenol [201], during the alkylation of phenol [202], dehydration [203], and for isomerization reactions [204]. It was described how Cr<sup>3+</sup> species in octahedral coordination can occupy a similar position to that of aluminum in layered double hydroxides [205,206]. Wei et al. have described that these octahedral Cr<sup>3+</sup> sites into the hydrotalcite structure are responsible of d-d transitions and subsequently these materials are potentially visible-light responsive photocatalysts [207].

Another model for these structures in which chromate and molybdate are formed in the interlayer space of the hydrotalcite structure was studied by Frost and coworkers [208]. They described how these anions are not polymerized and proposed a model of bonding with two types of anions, hydrated and hydroxyl surface bonded. Thus, these molybdate structures in the interlayer space confer redox sites to the hydrotalcite structure and subsequently these materials are efficient catalysts for several oxidation reactions, as have been studied by several research groups [209–213]. Following this approach, Sakthivel and coworkers [214] studied molybdate species intercalated in Fe-doped hydrotalcite materials as catalysts for olefin epoxidation, demonstrating the successful intercalation of molybdate ions in a high valent oxidation state in the interlayer space and the stabilization of the layered structure. In the same line, Shan et al. [215] incorporated Ni whereas Coelho and coworkers [213] used Co. In both cases, efficient doped molybdenum intercalated catalysts were synthesized, active and selective for methane decomposition and HDS (hydrodesulfuration) respectively. These examples illustrate the possibilities of doped molybdate interlayered materials as catalysts.

Jones and coworkers [216] studied MoS<sub>2</sub> catalysts supported on hydrotalcite materials and demonstrated their efficiency for catalyzing alcohol synthesis from syngas reactions. These MoS<sub>2</sub> on hydrotalcite derived materials can be also promoted with K [217] with the aim of preparing dispersed MoS<sub>2</sub> domains for higher alcohol synthesis. The addition of K allowed them to modulate the acidity, by this way, the

sample with the lowest K loading, presented some acid sites that enhance ethane selectivity via ethanol hydrogenation and dehydration, whereas the samples with higher K content yielded only a low number of higher hydrocarbons, including ethane. By this way, they prepared efficient catalysts for the synthesis of higher alcohol from syngas [217]. With a similar approach and using K promoter for modulating basicity, Okoye and coworkers [218] prepared efficient catalysts for glycerol carbonate synthesis. In the same manner, also tungstate species can be interlayer in the hydrotalcites [219,220], having been described as active catalysts for oxidation reactions [221]. In addition, MoS<sub>2</sub> introduced into layered oxides have been studied as electrocatalysts since the layered structure presents plenty of OER (Oxygen Evolution Reaction) sites [222].

## 6. Outlook

This review demonstrates that hydrotalcites, in combination with oxides from elements 4, 5, 6, are promising materials that found many applications in catalysis. Only the main, or most used, of these applications are collected in Table 1, as a brief outlook of the main uses of

**Table 1**  
Main application of hydrotalcite supported oxides of groups 4, 5 and 6.

Ti	V	Cr-Mo-V
Hydrotalcite is able to stabilize and disperse TiO <sub>2</sub> nanoparticles, resulting in active photocatalytic materials.	Decavanadates and Mg-Al-V-O species form in the interlayer space of the hydrotalcite, being active for alkane dehydrogenation reactions.	Chromates, molybdates and tungstates may form in the hydrotalcite interlayer structure, resulting in catalysts and photocatalysts useful for some oxidation reactions.
Zr Zr and Zr based oxides such as Ce-Zr-O structures can be stabilized and dispersed in the hydrotalcite structure, forming redox catalysts with basic sites, useful for CO <sub>2</sub> hydrogenation reactions	Nb Nb/hydrotalcite material poses acid-basic pairs, able to catalyze several reactions.	

these catalytic materials. There are several factors that determine the structure and properties of the final catalytic material and, subsequently, the catalytic performance. Hydrotalcites are usually prepared by coprecipitation, being important factors the temperature and the pH during this process, this is followed by a thermal treatment at moderate temperatures, most usually in the 400 – 500 °C range. After calcination, the material usually returns to the hydrotalcite structure due to a rehydration and reconstruction transformation that is usually called as “memory effect” [223,224]. The final material has a double layer unique structure with anions and water molecules in the interlayer space that, as have been exposed, can be replaced by different structures based on groups 4, 5 and 6 oxides, as has been exposed along the manuscript. These structures can be nanoparticles, isolated cations with octahedral structure, anions, or as polyoxides.

Basic sites are important in catalysis since they are able to catalyze several processes such as transesterification of oils to obtain biodiesel, and for several organic processes such as condensations. Thus, hydrotalcite based materials, as possess basic sites that can be modulated by the Mg/Al, among other parameters, are solid basic materials that, as have been described, are useful for many catalytic processes and that can replace homogeneous catalysis that involves the use of highly corrosive strong basic solutions. When hydrotalcites are modified by the incorporation of additional groups 4–5–6 metal oxides, redox and acid functionalities are also incorporated, obtaining effective catalytic materials for a wide range of applications, as have been described.

#### CRedit authorship contribution statement

**M. Olga Guerrero-Pérez:** Writing – review & editing, Writing – original draft, Validation, Supervision, Investigation, Formal analysis, Conceptualization. **Daniel A. Valdivieso-Vera:** Investigation.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

No data was used for the research described in the article.

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