

Hydrotalcites as Versatile Functional Materials for Renewable Feedstock Upgrading to Value-added Chemicals

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Abstract: Hydrotalcites are inorganic layered materials which have been used in a wide spectrum of applications from catalysis and adsorption to heavy metals immobilization and polymer stabilization. Apart from this, they can act as drug carriers or acid scavengers. More recently, due to the urgent need for developing functional materials required in the production of renewable fuels and chemicals, hydrotalcites have been increasingly noticed as versatile compounds. For instance, they are applicable in biofuel synthesis, biomass upgrading, plastics degradation, hydrogen storage and so forth. In addition, they are cost-efficient materials and thus beneficial for the realization of the above-mentioned applications on the industrial scale. It is noteworthy that for further development of novel hydrotalcites, validation of their performance and their stability are essential. To elucidate these aspects, the major significance of these materials and their capability for application in various catalytic fields are discussed in this survey. Particular focus is given to their most recent utilization in sustainable and green applications.

Keywords: Hydrotalcite; Co-precipitation; Spinel; Plastics degradation; Organic carbonates; Energy transition; Biofuels synthesis; Biomass upgrading; CO₂ upgrading

1. Introduction

Clays are a subset of inorganic materials which are classified as layered oxides or oxyhydroxides^[1]. These inorganic materials

with either natural or synthetic origins display attractive physicochemical features resulting from their atomic level structure^[1,2]. They commonly consist of lamellar sheets built by stacking two-dimensional layers which



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can be electrically neutral, negative or positive^[2]. In practice, the natural layered minerals contain several mixed phases as well as impurities, while the synthetic ones can be obtained in a highly pure state^[3]. The positively charged and brucite-like layered clays are called hydrotalcites, in which the positive charges are balanced with anions such as carbonate. Accordingly, hydrotalcites are representative of anionic clays which embed anions in their interlayer or basal spaces^[1]. This class of inorganics also covers hydrotalcite-like materials (i.e., layered double hydroxides and mixed oxides) with the same layered structure but with different chemical compositions^[4]. From a synthesis point of view, artificial hydrotalcites can be obtained by several techniques, such as co-precipitation, hydrothermal synthesis, sol-gel synthesis, combustion, microwave irradiation, urea hydrolysis, solvothermal synthesis and so forth^[5-7]. For the synthesis of hydrotalcites, inorganic and organic salts can be utilized to assist the formation of lamellar structures as they can release anions. Nevertheless, the crystallization of hydrotalcites does not necessarily require the presence of organic salts such as those used in many zeolites (e.g., alkyl ammonium salts or hydroxides) and so they can be obtained with less complicated synthesis procedures under milder reaction conditions compared to zeolites^[8,9]. In addition, they are commonly inexpensive and benign solid base materials. Since they are a prime alternative for homogeneous base catalysts (e.g., hydroxides) with the advantage of eliminating waste liquid streams and ease of separation from reaction media, they can open vast avenues for the synthesis of green chemicals^[10-12]. Hydrotalcites are also known as inorganic materials with a “*memory effect*” due to their reversible reconstruction/recrystallization properties stemming from their alterable hydration level^[13,14]. Regarding their layered structure, ion-exchange ability and unique characteristics, they have demonstrated a versatile role in energy sectors such as water-gas shift reaction, CO₂ capture/utilization (CCU), gas separation, H₂ production, pollutant elimination and energy storage^[3,15-20], and together with the simplicity of synthesis, the interest in the application of these materials has been increased, recently^[21]. Furthermore, they have demonstrated good adaptation with novel synthesis approaches such as soft templating technique for textural and morphological improvement^[22].

Hydrotalcites are compositionally flexible and possess adjustable properties by which, different metals can be grafted into their structure to create synergistic acidic-basic effects^[23]. They display tunable basicity due to having memory effect. Furthermore, their basicity can be optimized through modifying hydroxyl groups or doping alkalinity through the introduction of alkali metals (Na, K, Li). These features bring about hybrid assets for hydrotalcites to be employed as functional materials in a variety of applications (e.g., heterogeneous catalysts and adsorbents)^[24-26]. Their capability for synthesis of fine chemicals^[27], upgrading of biomass^[28], catalyzing base reactions^[29], as well as enzyme-like reactions^[30], are just a few examples of dozens of applications^[31]. By screening the huge number of articles and patents which have been published on the synthesis methodology and application of hydrotalcites, we obtain an indication about several industries (e.g., steel, cement, biogas and biofuels plants) which are potential end users for seeking cutting-edge hydrotalcite functional material for their needs^[32]. The motive of unveiling the state-of-the-art knowledge and future perspective of hydrotalcite materials regarding the increasing demands in coming years, urged authors to prepare this review with more pronounced details on the utilization of hydrotalcites in the sustainable synthesis of value-added chemicals with bio- and renewable origins.

2. Structural Properties, Modifications and Applications

Hydrotalcites have two-dimensional and positively charged layers with anionic species and water molecules accommodated in the interlayer spaces (**Figure 1**)^[29]. The co-precipitation reaction is the common method for hydrotalcite synthesis in which pH of the reaction is an important parameter and depends on the point where all precipitation curves of the cationic metals cross there^[33]. In hydrotalcite materials, the atoms which form the layers such as Mg and Al are strongly connected to oxygen atoms by ionic-covalent bounds, whereas the anions located in the interlayers weakly interact with atoms of layers and, thus, the lamellar structure is formed due to the nature of these interactions^[34]. Other key synthetic parameters such as the type of metals, metals molar ratio, type of starting precursors, aging time, drying method,

rehydration and heating techniques (e.g., calcination, microwave irradiation, *etc.*) are also determinative for the development of target hydrotalcites, and the correct adjustment of these parameters are crucial. The undesired variations in the above-stated parameters may cause textural, compositional and morphological changes such as phase transformation, segregation, or changes in crystallites size^[35-39]. The surface basicity/acidity can be adjusted by changing the M^{2+}/M^{3+} molar ratio, the type of intercalated anions, and by thermal activation as well^[40]. The so-called memory effect of

hydrotalcite materials indicates their reversible route of formation and recrystallization. Owing to this intrinsic property, hydrotalcite materials are able to recover their original lamellar structure using a rehydration step in the presence of liquid water and also by steaming^[41]. Hydrotalcites are also known as hydroxyl rich materials^[42]. Due to the presence of anions in the basal spaces (interlayers), they have high ion-exchange ability and can act as appropriate candidates for heavy metals adsorption from wastewater streams^[42].

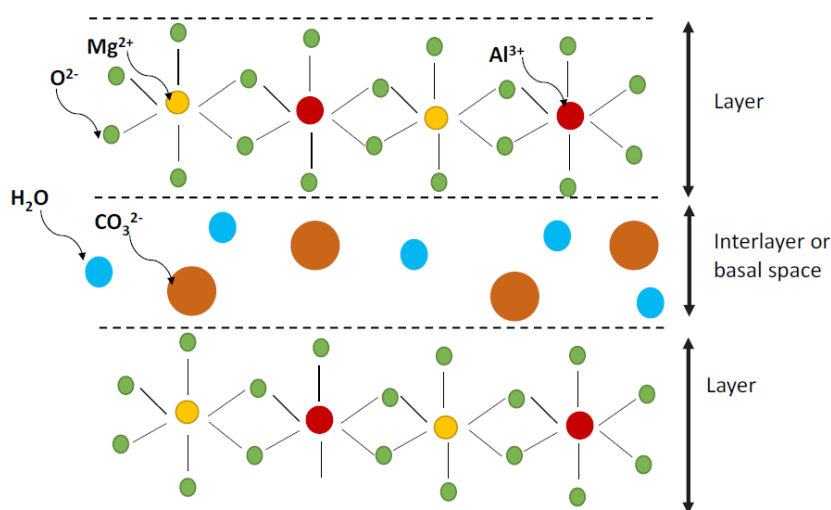


Figure 1. Schematic illustration of the hydrotalcite layered structure (the yellow and red circles are representative of di- and trivalent cations (e.g., Mg^{2+} and Al^{3+}), and the brown circle is representative of a type of anion (CO_3^{2-}))

In general, calcined hydrotalcites display lower basicity compared to uncalcined samples owing to gradual loss of crystalline water and carbonate anions, which latter one is released as CO_2 at elevated temperatures^[43]. No morphological or structural alteration occurs in hydrotalcite after such thermal treatment up to certain temperatures. However, the Brønsted basicity of hydrotalcite is decreased by calcination and such samples possess mainly Lewis basicity^[29,44]. It is noteworthy that the diversity in hydrotalcites synthesis methods with the possibility of

the selection of several di- and trivalent metals as well as different interlayer anions grant them a wide range of physicochemical properties, allowing us to architect their textural properties such as porosities and surface area^[45-47]. Thanks to the above-mentioned intrinsic assets and compatibility with alteration, they have been explored in different types of catalytic reactions (**Figure 2**). In the following sections, hydrotalcite applications as heterogeneous catalysts for green applications is thematically represented regarding the most recent studies.

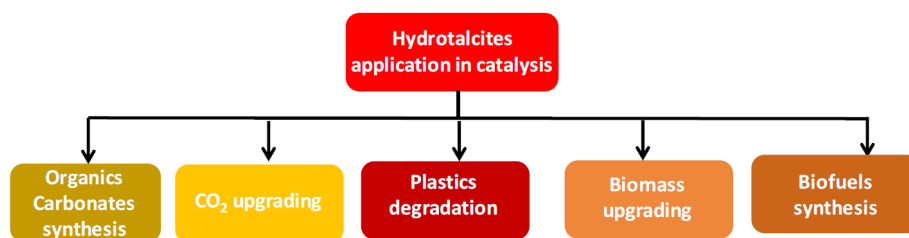


Figure 2. A schematic illustration of different catalytic reactions in which hydrotalcites are applied as heterogeneous catalyst

3. Synthesis of Organic Carbonates

Hydrotalcites have been frequently used as heterogeneous catalysts in the synthesis of organic carbonate because they are basic in essence with catalytic stability and reusability^[48]. Several catalytic materials such as Mg-Al hydrotalcite, Mg-Al hydrotalcite doped with Ni²⁺ and Ca-Al-derived hydrotalcite have been tested for the synthesis of organic carbonates for which well-dispersivity of different metallic phases, the strength of basic sites and fine particle size of doped metals have been reported as very important parameters^[47,49-52]. One way

to synthesize cyclic carbonates is the fixation of CO₂ which is desired in many aspects such as demonstrating sustainable and circular values.

3.1 Synthesis of Cyclic Carbonates by CO₂ Upgrading

Cyclic carbonates (**Figure 3**) are a type of organic carbonates with desired properties. They can be served as precursors for polymers synthesis and also directly as green solvents^[53,54]. The synthesis of cyclic carbonates by CO₂ fixation is one of the several catalytic reactions for utilizing CO₂ with the possibility of 100% carbon efficiency (i.e., no side-product, no waste)^[55].

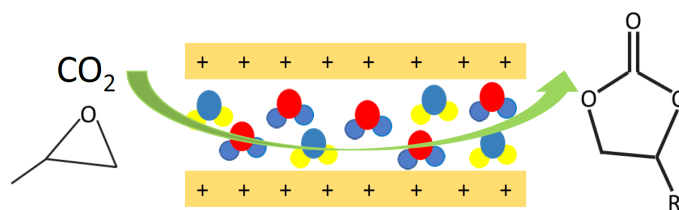


Figure 3. Catalytic conversion of CO₂ to cyclic carbonates by means of hydrotalcite materials

Although the synthesis of cyclic carbonates from CO₂ does not have a major impact on reducing the emission of CO₂, it cannot be excluded because CO₂ is a renewable, earth abundant and inexpensive C1 feedstock. Thus CO₂ application as carbon source provides a green path for the synthesis of chemicals and helps for further implementation of the circular carbon economy. Considering all these aspects, this catalytic reaction is in line with the goal of net-zero emission of greenhouse gases. In addition, obtaining organic carbonates by fixation of CO₂ in fully renewable biomass-derived compounds, aligns us with the right indicator for sustainable CO₂ conversion^[56]. However, the scale up of such a catalytic reaction is yet a milestone, since various relevant steps should be verified, such as design of catalytic system which is affordable and scalable to further envision the maturation of such catalytic route for the “mass production” step. In this context, hydrotalcite is demonstrating an increasing trend in academic research with the potential of being used for large-scale purposes. Hydrotalcite-derived materials as base catalysts have displayed high activity in such reactions with the advantage of stability and reusability. For instance, a trimetallic hydrotalcite-derived catalyst consisting of Mg, Al and Zn with optimized molar ratios between metallic constituents was obtained by co-precipitation method and showed high activity in

cycloaddition reaction of propylene oxide and CO₂. By employing this catalyst, propylene carbonate was obtained under relatively mild reaction conditions (130 °C, 1.5 bar, 8 h)^[57]. Furthermore, the catalyst was modified by potassium iodide (KI) prior to the reaction. This alteration strengthened the catalyst both structurally and compositionally through generating high degrees of nucleophilicity. Besides, the high activity of modified hydrotalcite was ascribed to high surface area after calcination at 450 °C, optimal molar composition and good dispersion of metals^[57]. Hydrotalcites have also been served as support for grafting corrosive homogeneous bases such as sodium aluminate (NaAlO₂). By this approach, the corrosivity issue can be alleviated and the activity of the final catalyst is augmented via promoting effects of NaAlO₂. For instance, a type of mixed oxides obtained by calcination of NaAlO₂/Mg-Al hydrotalcite, demonstrated high activity in the synthesis of glycerol carbonate at 90 °C^[58]. The key factors for high activity are attributed to the high basicity of the catalyst and morphological alteration caused by either mixing hydrotalcite and NaAlO₂ or by subsequent calcination^[58].

3.2 Synthesis of Organic Carbonates by Transesterification Reaction

Cyclic carbonates can also be obtained by transesterification reactions^[59]. One of the cyclic

carbonates with wide usage as protic solvent is glycerol carbonate, which is applicable as intermediate for the synthesis of polycarbonates and polyesters as well^[60]. A remarkable activity has been reported by the application of uncalcined hydrotalcite- hydromagnesite composite in the transesterification of glycol and dialkyl carbonates to give glycerol carbonate^[61]. The high catalytic activity has been attributed to the cooperative effects of hydrotalcite and hydromagnesite on enhancing the surface area and adsorption sites, simultaneously^[61]. In this regard, several catalysts such as Mg-Al hydrotalcite, Ca-Mg-Al hydrotalcite modified by 5 wt.% KF, rare earth-containing Mg-Al hydrotalcites (e.g., La³⁺, Ce³⁺, Pr³⁺, Sm³⁺, Y³⁺) and Zr-containing Mg-Al hydrotalcites have been tested as featured hydrotalcites for conducting this reaction and showed to be active catalysts^[62-65]. The diversity of hydrotalcites for cyclic carbonate synthesis highlights their efficiency in catalyzing this class of catalytic reactions. This is also beneficial because we can apply them as greener catalysts instead of homogenous catalysts. The preparation method is also pivotal and can significantly influence the performance of hydrotalcites in cyclic carbonates synthesis^[66]. A systematic study using Ca-Al-hydrotalcite has disclosed that higher basicity notably favors the cyclic carbonates formation. High alkalinity can be created by calcination at elevated temperature (750 °C) which helps to ensure that a high quantity of basic CaO is formed inside hydrotalcite after calcination^[66]. To conclude, parameters such as the type of metallic elements and the procedure for thermal treatment play significant roles in the final performance of hydrotalcite

in cyclic carbonate synthesis, although the catalytic performance is not only limited to these factors.

Likewise cyclic carbonates, polycarbonate can be synthesized using hydrotalcites through transesterification reaction. Polycarbonates are versatile materials with several applications (**Figure 4**) and thus, the catalytic route for their synthesis is an attractive research subject where hydrotalcites materials have shown good performance. For example, a type of calcined hydrotalcite optimized by doping Ni²⁺ has displayed high activity in the synthesis of polycarbonate diols for which dimethyl carbonate and 1,4-butanediol were used as precursors^[67]. Here, adjusting the quantity of Ni²⁺ and calcination temperature are key factors for increasing the activity of the catalyst. Accordingly, the sample grafted by 0.7 mmol Ni²⁺ per each gram of hydrotalcite and calcined at higher temperature (i.e., 773 K) resulted in an optimum amount of basicity for conducting the reaction. Despite the lower intensity in the XRD pattern and smaller lattice parameters, Ni-containing hydrotalcite displayed all the characteristic peaks of hydrotalcite. In addition, both surface area and pore volume increased after calcination^[67]. As stated before, the general rule for boosting the catalyst activity in organic carbonates synthesis is the application of higher calcination temperatures to enhance the amounts of basicity in the presence of transition metals^[68]. By this approach, the formation of mixed oxides with open metallic structures is favored because they potentially serve as OH nests and, therefore, enhance the catalyst alkalinity as the characteristic asset for the synthesis of organic carbonates^[68].

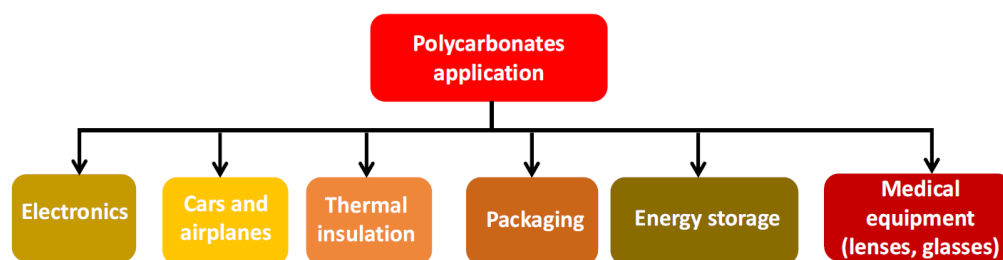


Figure 4. Polycarbonates application in different industries

In this regard, Mg-Fe-Ti-containing hydrotalcites, Ce-containing hydrotalcite as well as Mg-Al hydrotalcite have been optimized and applied for polycarbonates synthesis^[52,69-71]. In addition of basicity, the structure of the hydrotalcite is also important for

catalyzing reactions for organic carbonates formation. For such aim, smaller pore size and moderate to high surface area are desired^[72]. Nevertheless, with respect to the reaction condition and hydrotalcite preparation method, such properties should be properly optimized

for a given reaction^[73].

4. Synthesis of Heterocyclic Organics

Hydrotalcites have demonstrated a good ability for catalyzing multi component reactions resulting in the formation of organic heterocycles (**Figure 5**). Heterocyclic organics are known as important intermediates for the synthesis of fine chemicals, specialties and pharmaceutical products^[74,75]. Using hydrotalcites, the reaction can be carried out in a

solvent-free medium which provides greener synthesis route for generating these molecules. Application of hydrotalcites as catalyst in this class of reactions is also advantageous because the need for utilization of environmentally hazardous solvents can be removed^[76]. In addition, the physicochemical properties of hydrotalcites can be preserved under the reaction condition. High catalytic activity and reusability have been reported after consecutive runs^[77].

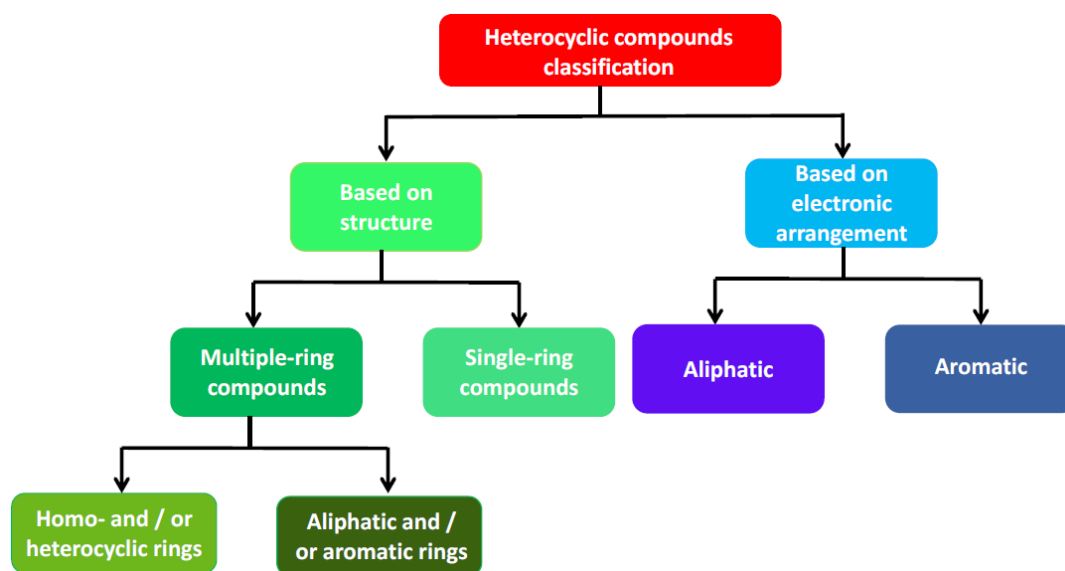


Figure 5. Classification of heterocyclic organics

For instance, a type of tri-functional hydrotalcite has been synthesized and applied for the synthesis of chiral diols in the presence of H_2O_2 as the oxidant^[78]. This catalyst included three anionic species (i.e., PdCl_4^{2-} , OsO_4^{2-} , and WO_4^{2-}) which were obtained by co-precipitation technique and embedded in the basal spaces of hydrotalcite. Nobel metals such as Ru, Pd and Au nanoparticles supported on hydrotalcites have been used for one-pot synthesis of multiple catalytic reactions such as quinolines, α -alkylated nitriles and Flavones^[79]. The application of hydrotalcite as catalyst or catalytic support makes the catalytic system simpler. Furthermore, it is advantageous from time, energy, reusability, and affordability point of view for such reactions with the possibility of inserting different types of anions between interlayer spaces, simultaneously.

5. CO_2 Upgrading

Due to the shortage of fossil fuels in coming decades

as well as net-zero emission plans to overcome global warming issues, CO_2 is considered as C_1 feedstock which is renewable and its utilization by upgrading to value added compounds can further develop a circular economy^[80]. One of the upgrading routes is CO_2 reforming and hydrotalcite-derived compounds have displayed good ability to catalyze this reaction, resulting in the formation of syn-gas (i.e., a mixture of CO and H_2). This catalytic reaction is a conducive solution to manage the greenhouse gas emissions by consuming two major emitted gases (i.e., CO_2 and CH_4). However, there are some major barriers to the scale up of CO_2 catalytic reforming (also known as CO_2 methanation) such as high endothermic condition, low catalytic stability, and formation of high amount of coke species^[81]. Generally, transition metals are active sites for CO_2 methanation. However, such catalysts suffer from fast deactivation^[82]. On the other hand, noble metals such as Ru are more stable due

to the formation of lower degrees of coke, but they are expensive and rare^[83]. To find appropriate support to embed the catalytic active centers, hydrotalcite-derived materials have received high attention as they have special layered structure and alterable chemical composition with the possibility of grafting various di- and trivalent metals, which can consequently, modify their basicity and redox properties^[84]. In this regard, Ni-based hydrotalcites have been reported as promising catalysts to conduct CO₂ reforming reaction (**Figure 6**)^[85]. In addition, the combination of Zn and Ni has displayed synergistic effects as they form a Zn-Ni alloy. Doping 3 wt.% Zinc in Ni-MgAl-hydrotalcite using co-precipitation technique can minimize the coke formation by reducing the metallic particles size and, thus improving the metal/support interaction as well as raising the basicity of the catalyst^[86]. Since Ni is an active species in reforming different types of molecules (CO₂ is one of those molecules), Ni insertion in hydrotalcites has also been studied by different synthesis methods for producing efficient catalysts. Here, the type of method used for the synthesis is influential in the final catalytic performance. Among different techniques (e.g., co-precipitation, urea

hydrolysis and impregnation), Ni-Mg-Al hydrotalcite prepared by urea hydrolysis showed to be more stable and active than other catalysts in CO₂ methanation^[87]. The higher activity is attributed to the higher surface area, Ni nano-size particles and catalyst high basicity. Adjustment of temperature and aging time can further improve that catalytic activity in this case^[87]. For instance, Ni-Mg-Al promoted by loading 2 wt.% vanadium has been designed for CO₂ methanation, in which the presence of vanadium as promoter enhances the interaction between Ni particles and the surface of hydrotalcite. The higher interaction leads in uniform dispersion of fine particles of Ni⁰ which, in turn, increases the basicity of the catalyst^[88]. Another example of CO₂ methanation is Co-Al hydrotalcite-like catalyst which was able to work at atmospheric pressure^[89]. In total, the Co/Al molar ratio equal to 1, which gave a high content of Co⁰, higher surface area and higher basicity were determined as the most important factors for the catalytic activity^[89]. Moreover, the cobalt content has an impact on the morphology of the catalyst, in which Co/Al = 1 displayed plate-like nanosheets^[89].

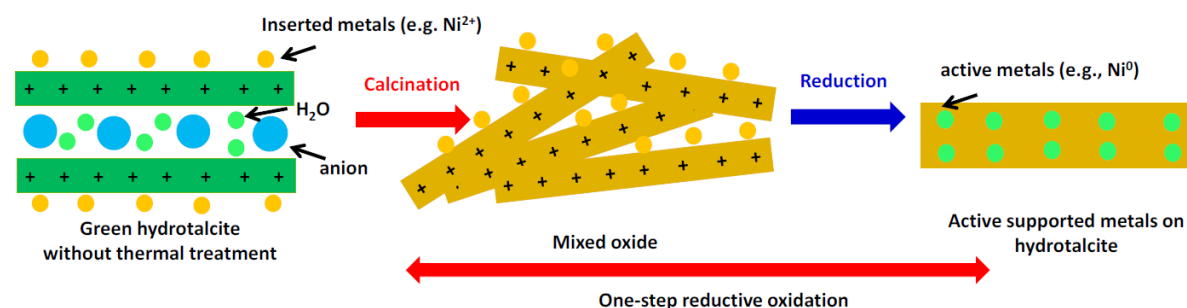


Figure 6. Schematic illustration of Ni-based catalyst preparation route for CO₂ methanation

Indeed, a catalyst which can conduct CO₂ methanation at lower temperatures is more desired and for this aim, hydrotalcite containing metals of group VIII (e.g., Ru, Rh, Pd, Ni, Co, Fe) have been examined in this reaction^[90-91]. By means of in situ spectroscopic studies on Ni-Fe-containing hydrotalcite, it was found that higher activity of catalysts is related to the higher surface area, good metal dispersion and optimal basicity, as frequently reported to be important factors^[92]. Ni-containing hydrotalcite with high ability to work at low temperatures (< 300 °C) has been obtained by co-precipitation technique under mild

temperature and, by means of one-step reduction calcination (see **Figure 6**). In this study, catalytic activity was directly related to the amount of Ni⁰^[93]. Hydrotalcites are also applicable for reforming organic biomass-derived compounds such as toluene. For instance, a Ni-Fe-Ce-containing hydrotalcite supported on monolithic wood has been developed with higher activity due to the presence of Ce in the structure plus the application of hydrotalcite as support rather than activated carbon. This catalytic system is cost-effective and diffusion- and coke-resistant^[94].

CO₂ upgrading to methanol is another catalytic

pathway for which several types of hydrotalcites, such as Pd-Zn-Al hydrotalcite supported on mesoporous silica (MCM-48), Cu-based hydrotalcite and Cu-Zn-Al/Zr containing hydrotalcite-like material have been used^[95-98]. In this context, Zr has shown promoting effects on Cu interaction and its dispersion on the surface of hydrotalcite. The optimum amount of Zr for Cu-Zn-Al/Zr mixed oxides obtained after co-precipitation and calcination step, has been reported based on $Zr^{4+}/(Zr^{4+}+Al^{3+})$ atomic ratio equal to 0.3 for which the catalytic activity and methanol selectivity were the highest^[98]. In this reaction, methanol selectivity is directly related to the basicity of the catalyst, and which can be maximized at the above-mentioned ratio (i.e., 0.3)^[98].

In the field of CO₂ release management, hydrotalcites are also applicable as catalysts. Recently, hydrogen storage from CO₂ capturing process has become an attractive technical subject, for which unsaturated molecules are considered as good carriers^[99]. For instance, molecules for storing liquid organic hydrogen are mainly double or triple bond aromatic components (e.g., N-ethylcarbazole) which can react with hydrogen in the presence of hydrotalcites, by which their unsaturated carbon bonds are converted to saturated bonds^[100]. In fact, these carriers are organic tools which can adsorb hydrogen released from CO₂ capturing, and therefore, can be served as the storage medium for hydrogen^[101,102]. The lack of adequate materials as affordable catalysts for this reaction, has drawn attention to hydrotalcites as all-purpose catalysts with adjustable properties for this need. In this regard, ultrafine Ru particles supported on Ni/Al hydrotalcite-derived oxides have shown promising results in relatively mild conditions^[103]. In line with the goal of hydrogen storage, one of the directions for hydrogen production is NO_x Selective Catalytic Reduction (SCR) to NH₃ and next, NH₃ decomposition to hydrogen^[104]. NH₃ is also considered as one of the H₂-carrier compounds which has the potential to be converted to hydrogen either in situ or ex situ by means of hydrotalcite (e.g., Ni-containing hydrotalcites)^[105,106]. In particular, NH₃ in situ decompositions can supply the released H₂ as power resource for downstream processes which also removes the need for hydrogen storage in tanks, and obstacles related to it such as further transportation management or pipeline construction^[107]. A spinel-like Ni₂-Mg₃-Al₂

hydrotalcite prepared with co-precipitation technique and calcination at 600 °C, exhibited high activity in H₂ production^[108].

Hydrotalcite-derived materials are applicable for NO_x reduction using CO (carbon monoxide) for which hydrotalcite-based Co-Cu-Al mixed oxides has been used and the high specific surface area was the key factor for catalyst activity^[109]. This reaction is important as the purity of captured CO₂ is an essential specification for its utilization in downstream process and CO and NO_x are two major impurities generated by combustion units^[109]. Hydrotalcites are also applicable for NO_x removal from exhausted gases, for which their layered structures and flexible physicochemical properties grant them good selectivity for NO_x elimination. For such reactions, several chemical compositions have been developed based on hydrotalcite structure, which can be found in cited references^[110-112]. Co-containing Mg-Al hydrotalcite has exhibited remarkable efficiency for NO_x removal after calcination at higher temperatures (e.g., 700 °C) because of the formation of spinel phases. This catalyst was further promoted by calcination at 800 °C and next, by potassium insertion via incipient wetness impregnation using an aqueous solution of KNO₃^[113].

6. Plastics Degradation

Currently, plastics are considered as one of the major water and soil pollutants. The most abundant types of plastic pollutions are generated by disposal of polyethylene, polypropylene, polystyrene, polyvinyl chloride, nylon, polyurethane and so forth. Furthermore, microplastics with dimensions below 5 nm are severely troublesome for the environment. The hydrotalcites family has demonstrated good ability for decomposition of plastics^[114,115]. For instance, polyethylene has been degraded using Ni-doped spinel (NiAl₂O₄) via photocatalytic reaction^[116]. Ni-spinels can be produced with both hydrothermal and co-precipitation protocols, which enables us to degrade both low- and high-density grade polyethylene (LDPE and HDPE, respectively). The key factor, here, is the degree of dispersion and attachment of nickel particles on the surface of support so that the catalyst is active and stable and efficiently resists against the sintering, coking and fast deactivation^[116]. Fe-Mg-Al and Ca-Mg-Al mixed oxide have been used as catalysts

for degradation of PVC with the minimum amount of residue^[117]. These examples reflect the potential capability of hydrotalcites for plastics degradation, which are one of the major environmental threats.

7. Biomass Upgrading

Several platform molecules (e.g., furfural, glycerol, 5-hydroxymethyl furfural, levulinic acid, lactic acid, *etc.*, **Figure 7**) can be derived from biomass (i.e., cellulose, hemicellulose, and lignin). Furanic-based molecules are one of the main derivatives of biomass and can be upgraded by means of hydrogenation reaction^[118]. A type of Ni-Mg-Al hydrotalcite obtained by urea hydrolysis and doped with Ru as promoter has been examined in furfural selective reduction to furfural alcohol. The presence of bimetallic Ni-Ru alloy with 15 wt.% Ni and 2 wt.% Ru content demonstrated synergetic metal effects and enhanced the catalytic activity compared with monometallic catalysts under selected reaction condition (150 °C and 10 bar H₂ pressure demonstrating 100% furfural conversion and 86% furfural alcohol selectivity). In addition, catalyst preserved stability after 6 reaction runs, which

can be a good indication of the catalyst's ability to work at longer reaction times^[119]. In another study, the effect of highly dispersed Ru on mixed oxides derived from Mg/Al hydrotalcite was investigated in phenol hydrogenation^[120]. A series of catalysts with different Si/Al ratios (1, 2, 3, 4) with 2 wt.% Ru was prepared and tested in this reaction. Among them, the catalyst containing the lowest Mg/Al ratio (Mg/Al = 1) displayed the highest activity attributed to the complete transformation of hydrotalcite material to corresponding oxides after thermal treatment but no spinel phase (MgAl₂O₄) was found. Furthermore, high surface area, large amounts of uniformly-dispersed Ru and the optimal acidic to basic ratio were further promoted the catalytic activity^[121]. The effect of Fe has been also investigated for furfural hydrogenation to furfural alcohol and the catalytic results disclosed that Mg₂-Al_{0.5}-Fe_{0.5}-hydrotalcite possesses the optimal ratio of acidic and basic sites evaluated by pyridine probing. This finding indicated that the basic sites have a more pronounced role than acidic sites for conducting hydrogenation of furfural^[121].

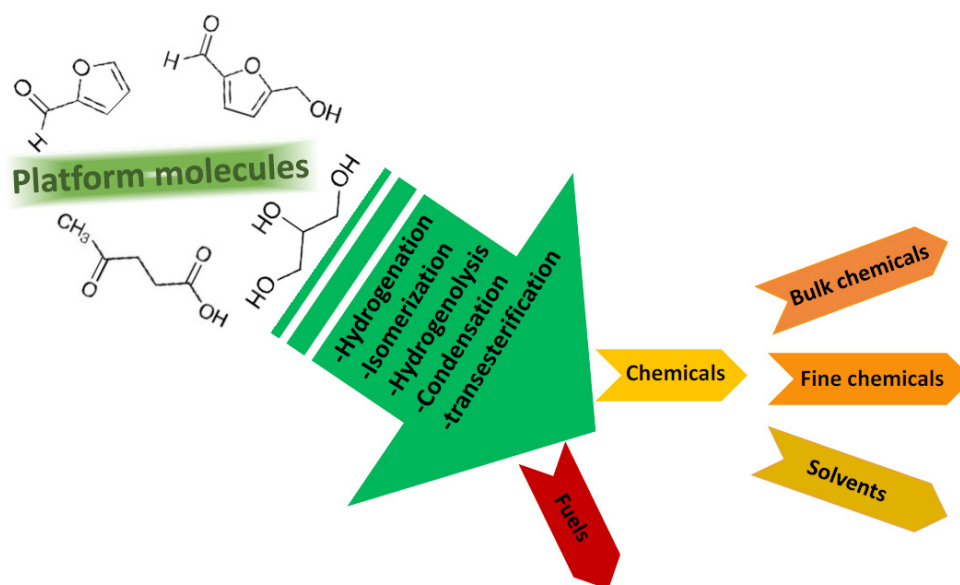


Figure 7. Schematic illustration of main platform molecules derived from biomass as building blocks for the formation of value-added chemicals

The selective hydrogenation of 5-hydroxymethylfurfural (5-HMF) to 2,5-Bis(hydroxymethyl)furan (2,5-BHMF) has been performed using well-dispersed Cu-hydrotalcite^[122]. The catalyst was obtained using the co-precipitation technique whereby atomic copper

species were dispersed on the surface of hydrotalcite and this phenomenon was proved by X-ray absorption spectroscopy as well as other analyzing methods. This material in its reduced form excellently catalyzed 5-HMF hydrogenation to 2,5-BHMF, which is attributed to the

fine nature and uniform distribution of Cu-active sites and, therefore, provisioning a level of accessibility to the active sites^[122].

The catalytic performance of hydrotalcite including Ni-Pt alloy has been studied in glucose hydrogenation to polyols^[123]. A novel microwave heating technique was employed and allowed for fine-tuning of metals with particle diameter equal to 2.7 nm on the surface of the hydrotalcite in a highly dispersed mode. The Pt and Ni contribute as a dipole-like alloy ($\text{Pt}^{\delta-}-\text{Ni}^{\delta+}$) for H_2 activation and adsorption of glucose aldehyde branch. On the other hand, the inherent basic feature of hydrotalcite performs the glucose isomerization as well as retro-aldol step in water. The material consisted of lamellar nanosheets with slit-like pores and demonstrated stability and reusability within 5 consecutive runs^[123]. Glycerol is another important platform molecule obtained as the main by-product (10 wt.%) during biodiesel manufacturing and can be upgraded by hydrogenolysis over hydrotalcite^[124]. Hydrogenolysis is involved with the collapse of the glycerol C-C bonds for which Fe, Ni, Zn and Cu supported hydrotalcite have been developed by co-precipitation technique^[124]. The Cu-containing hydrotalcite showed the highest activity for both pure and crude glycerol. The high activity of the catalyst has been ascribed to the positive effect of large pore volume, since the isotherm curve displayed a hysteresis loop for the calcined materials at higher pressures indicating the presence of many slot-like channels. Furthermore, the high basicity of the material enhances the catalytic activity^[124]. Cu-Ca-Al hydrotalcite-derived material has been synthesized using co-precipitation technique and used for glycerol hydrogenolysis by which the 1,2-propanediol was selectively formed while the former one (Cu-based catalyst) was selective toward 1,3-propanediol^[125]. In agreement with this finding, Zn-containing hydrotalcite possessing large macropores in the range of 1 μm to 10 μm as well as low amounts of acidic sites selectively produced 1,2-propanediol^[126]. Glycerol oligomerization is another pathway for transforming it into more value-added chemicals for which hydrotalcites are applicable. The selective hydrogenation reaction over hydrotalcites has been applied for furfural conversion to furfuryl alcohol in the aqueous medium under mild reaction conditions (303 K and 1.5 MPa H_2 pressure)^[127]. Due

to the presence of a wide range of unsaturated groups, maximizing the yield of the target product is not an easy task in this reaction. An active catalyst should be able to conduct H_2 dissociative and furfural selective adsorption from the aldehyde side. Afterwards, hydrogen should be transferred inside the intermediate species (i.e., hydrogenation step) and after surface and water mediation, the product should be desorbed from the catalyst surface. A type of Pt-containing hydrotalcite has been designed for this target reaction and obviously performed better than Pt supported on Al_2O_3 , MgO and Al_2O_3 -MgO mixed oxides. This outperformance of the material is attributed to the hydrotalcite-like structure which allows for better dispersion of Pt and for an efficient reduction of Pt precursor to Pt^0 ^[127].

Another catalytic route for biomass upgrading is isomerization reaction, for which hydrotalcite materials are applicable as catalysts. For instance, isomerization of glucose-derived hydrolysate using Mg-Al containing hydrotalcite (Mg/Al = 3) was conducted in different reaction condition and the effect of pH of reaction mixture, temperature, residence time and catalyst mass were investigated on the efficiency of catalyst^[128]. The outcome of this study demonstrated that hydrotalcite has the highest activity at neutral pH in aqueous reaction medium, for which 25% fructose yield at 38% glucose conversion was obtained. In contrast, catalytic activity decreases at acidic pH with 16% yield vs. 32% conversion because of the alteration in both textural and chemical composition of the catalyst. This finding highlights the importance of neutralization of acidic hydrolysate for improving hydrotalcite catalytic performance in catalyzing glucose-derived hydrolysate isomerization^[128]. Furthermore, Ca-Al containing hydrotalcite, and conventional Mg/Al hydrotalcite have been applied for isomerization of glucose and other sugars and exhibited high activity by achieving moderate to good selectivity and yield of target products. More details can be found elsewhere^[129-130]. A composite material consisting of Mg-Al hydrotalcite and carbon nanotubes was developed and used for aqueous isomerization of glucose to fructose^[131]. This combination of the above-mentioned materials allowed to alter the physicochemical properties of the final catalyst composite. Interestingly, the carbon nanotubes contribute to the alteration of morphology and the modification of surface electronic properties

whereby the aggregation of active sites is avoided^[131]. Dehydration of xylose to furfural with Cr-Mg hydrotalcite has been reported recently, as a catalytic route carried out by both Lewis acidity (Cr^{+3}) and Brønsted basicity (Mg^{+2})^[132]. The effect of calcination was also investigated and it was disclosed that the material obtained after calcination possesses higher surface area and mesopores with the average size of ca. 14 nm, which is beneficial for catalytic reaction compared with non-thermally treated sample^[132].

Esterification of biomass such as levulinic acid is another example of a catalytic reaction for which hydrotalcite has been applied. A series of molybdate intercalated hydrotalcite-like material were tested in this reaction^[133]. Prior to molybdate insertion, hydrotalcite materials (i.e., Mg-Fe, Mg-Al, Mg-Cr) were obtained by hydrothermal treatment. Among all catalytic materials, the Mo-Mg/Fe catalyst showed to be the most active one at selected reaction condition (120 °C, 4 h) with 43% conversion of Levulinic acid to butyl levulinate (95% selectivity). This catalytic activity stems from the generation of Lewis acidic site by introducing Mo as proved by pyridine FTIR^[133]. Other examples of hydrotalcite utilization in esterification can be found in cited literature^[134-135].

Aldol condensation is another example of important organic reactions for biomass upgrading, in particular, to fuels^[136]. Recently, a greener synthesis route by employing the impregnation technique instead of the common co-precipitation technique has been used for the synthesis of hydrotalcite and resulted in an efficient catalytic system with adequate Brønsted acidity for aldol condensation reaction of furfural with acetone^[137]. Glycerol steam reforming is an alternative catalytic route for upgrading biomass-derived glycerol. At first, the co-precipitation method was used for the synthesis of Mg-Al-La hydrotalcite. After calcination, 5 wt.% Ni was incorporated into the hydrotalcite structure using impregnation and both characterization results and catalytic outcome showed that lanthanum has promoting effects on the catalytic performance, since it improves the basicity of the catalyst, the metal-support interaction and dispersibility of Ni. Although this catalyst was active, it was not coke-resistant, which is a drawback^[138].

The catalytic conversion of biomass derived ethanol into butanol and other bulk chemicals through

the Guerbet coupling process has been extensively investigated over hydrotalcite materials. Different types of mixed oxides (Fe-, Ni-, Cu- and Zn-Mg containing oxides) were synthesized from hydrotalcites precursors and used in this reaction which was conducted in a fixed bed reactor^[139]. Among different catalysts, Zn-Mg mixed oxides with 20 wt.% Zn content displayed the best activity regarding ethanol conversion and the formation of Guerbet products^[139]. A series of Cu-Mg_xAlO_y mixed oxides with different Cu loading (0.1-1.5 wt.%) has been examined in ethanol oligomerization for synthesis distillate-range molecules. Based on the results, the catalyst was selective to linear C₄⁺ alcohols and C₆⁺ esters up to 0.6 wt.% Cu loading. However, higher Cu loading (> 1.2 wt.%) decreased this ratio as selectivity shifted toward ethyl acetate and acetone. This finding disclosed that higher surface area of the catalyst and lower Cu content favors alcohols formation while high basicity and higher Cu loading enhance the formation of esters^[140]. In another study, the conversion of bioethanol to n-butanol was explored using Cu/Ni-based mixed oxides in a continuous flow system and the results revealed that Cu/NiAlO_x was selective to butanol and stable at reaction condition (280 °C, 110 h), while Cu/NiFeO_x and Cu/NiCoO_x deactivated rapidly^[141].

Regarding the challenges that exist for biomass upgrading such as control over selectivity of target products and the need for acid-base bifunctional catalyst, hydrotalcite-based materials have been frequently used for the target catalytic reaction of platform molecules. For instance, Toluene can be synthesized using hydrodeoxygenation of anisole over a Ru-Containing Ni-Fe hydrotalcite-like catalyst^[142]. The Ni-Fe hydrotalcite prepared by co-precipitation technique with Ni/Fe molar ratio = 2 and doped with 4 wt.% ruthenium, demonstrated high activity with 98% anisole conversion toward toluene as the main product of this reaction. This result has been rationalized by the highly crystalline structure of Ni-Fe hydrotalcite, which is able to accommodate uniformly Ru centers. The TPR analysis was evident that Ru/Ni alloy with synergistic effects is formed^[142]. Following on from the above-stated reactions, phenol hydrogenation using Ru-Mg-Al hydrotalcite-derived mixed oxides^[120], lignin depolymerization using Co-containing hydrotalcite (Co-MgAl₂O₄)^[143], glycerol oligomerization using

Fluoride-containing hydrotalcite^[144] have been also explored, but the applications are not limited to these examples.

8. Synthesis of Biofuels

Various edible or non-edible oils such as sunflower, soybean, palm oils and rape seeds can be utilized as feedstock for biodiesel production^[144-149]. The catalytic reaction is one of the several synthesis routes for biodiesel formation (**Figure 8A**), which is involved with the replacement of alkyl groups of vegetable oils with methyl or ethyl alcohol groups to produce biodiesel (alkyl esters)^[150]. As stated above, glycerol is the main by-product of the esterification reaction^[151].

Different heterogeneous catalysts, including acid, base and acid/base catalysts have been used for biodiesel synthesis, such as metal oxides (e.g., alkaline earth oxides, transition metal oxides), mesoporous silicas, resins, zeolites and hydrotalcites^[149,152-155]. Among them, Mg-Al hydrotalcites have demonstrated to be efficient heterogeneous catalysts owing to possessing basic properties, stability, reusability, and capability of producing high quality biodiesel by transesterification reaction (**Figure 8B**)^[156-161]. The high activity is related to their special layer structure constructed by positively charged metal hydroxide and interlayer anionic species which balance the lattice total charge along with a high degree of basicity^[162]. Although applying calcination at elevated temperatures increases the activity and the stability of hydrotalcites for biodiesel synthesis^[12,163], to further increase their activity, other metals such as Ni, Fe, Zn and Ce have been inserted into the structure of Mg-Al hydrotalcite^[159,164,165]. For instance, a study of the deactivation process in the presence of cerium in the hydrotalcite structure disclosed that this metal can facilitate the rehydration and reconstruction of hydrotalcite, thus it has promoting effects on the catalyst performance in soybean oil methanolysis. Furthermore, it has been theorized that Ce can alter the reaction pathway. It was further confirmed by different adsorbed species detected using post-reaction measurements on the catalytic samples with different Ce loading^[165]. The strength of basicity is crucial for the final performance, where stronger basic sites can conduct the reaction at lower temperatures^[166]. Apart from basicity, the performance of hydrotalcite in

biodiesel synthesis is correlated to its textural porosity, where the presence of larger mesopores can favor better the catalysis of bulky triglyceride^[166]. In this context, templated Mg-Al hydrotalcite, which was shaped by macroporous polystyrene beads, showed high activity in transesterification of long-chain triglyceride (up to C₁₈) into biodiesel. This high activity is stemming from reduced diffusion limitations^[167]. Furthermore and in order to change the textural properties of hydrotalcite, hybrid structures such as ternary Mg-Al-Zn hydrotalcite/SBA-15 have been synthesized and used in transesterification of vegetable oils^[168]. Here, Zn has a promoting effect on the catalyzing process and introducing hydrotalcite in mesoporous silica SBA-15 channels enhances the catalytic efficiency by maximizing the accessibility to the active sites and increasing catalytic stability and lifetime^[168].

Another example of a developed hydrotalcite-based catalyst is the composite of hydrotalcite dispersed in a polymer solution (poly(vinyl alcohol)) which forms a type of basic catalyst for the synthesis of biodiesel. By tuning the degree of hydrophilicity, the catalytic results can be improved^[169]. In addition, the composite of hydrotalcite-hydroxyapatite has been developed and tested in conversion of vegetable oil deodorization distillate into biodiesel^[170]. For this catalyst, the optimized calcination temperature was shown to be crucial factor in increasing the accessibility to the active sites as well as preventing the formation of secondary crystalline phase as well as promoting the generation of densely packed particles^[170]. Potassium has shown promoting effects on the hydrotalcite's performance in biodiesel formation. A type of Mg-Al hydrotalcite impregnated with 1.5% potassium acetate was highly active in palm oil transesterification using methanol with 86.6% yield of biodiesel^[171]. A similar result was observed in the conversion of *Jatropha curcas* oil using potassium-promoted Mg-Al hydrotalcite^[172]. The K-loaded hydrotalcite was prepared by physical mixing of 50 wt.% K₂CO₃ and hydrotalcite in the presence of water and dried under a very mild condition (65 °C). Thereafter, the calcination was carried out at 600 °C to obtain the final catalyst. This catalyst gave a high yield of biodiesel (97%)^[172]. K₂CO₃ has shown the same promoting effects on the other hydrotalcite-like materials properties such as Al-Ca-hydrotalcite^[173]. Impregnation of calcined hydrotalcite using K₂CO₃

is also beneficial due to the presence of CO_3^{2-} ions which can help for recrystallization of the hydrotalcite layered structure after calcination^[174]. In order to boost the properties of hydrotalcite in biodiesel synthesis, rehydration after calcination has also been explored indicating the supportive role of the rehydrating step in enhancing the basicity and activity of calcined hydrotalcite^[175]. The higher activity is emanating from the generation of strong basicity by the presence of hydroxide ions which can replace the carbonate ions located in the interlayer spaces, as well as higher

hydrophilicity of the catalyst which allows better interaction of methanol with the catalytic surface^[175]. A type of novel trimetallic hydrotalcite containing Ba, Sn and Al with a high specific surface area and relatively stable structure was used for rice bran oil conversion, yielding 97% biodiesel production^[176]. As a guideline, the efficiency of hydrotalcite materials as promising catalysts in biodiesel manufacturing depends on the optimal calcination temperature, chemical composition of hydrotalcite such as Mg/Al ratio and selected reaction conditions^[177].

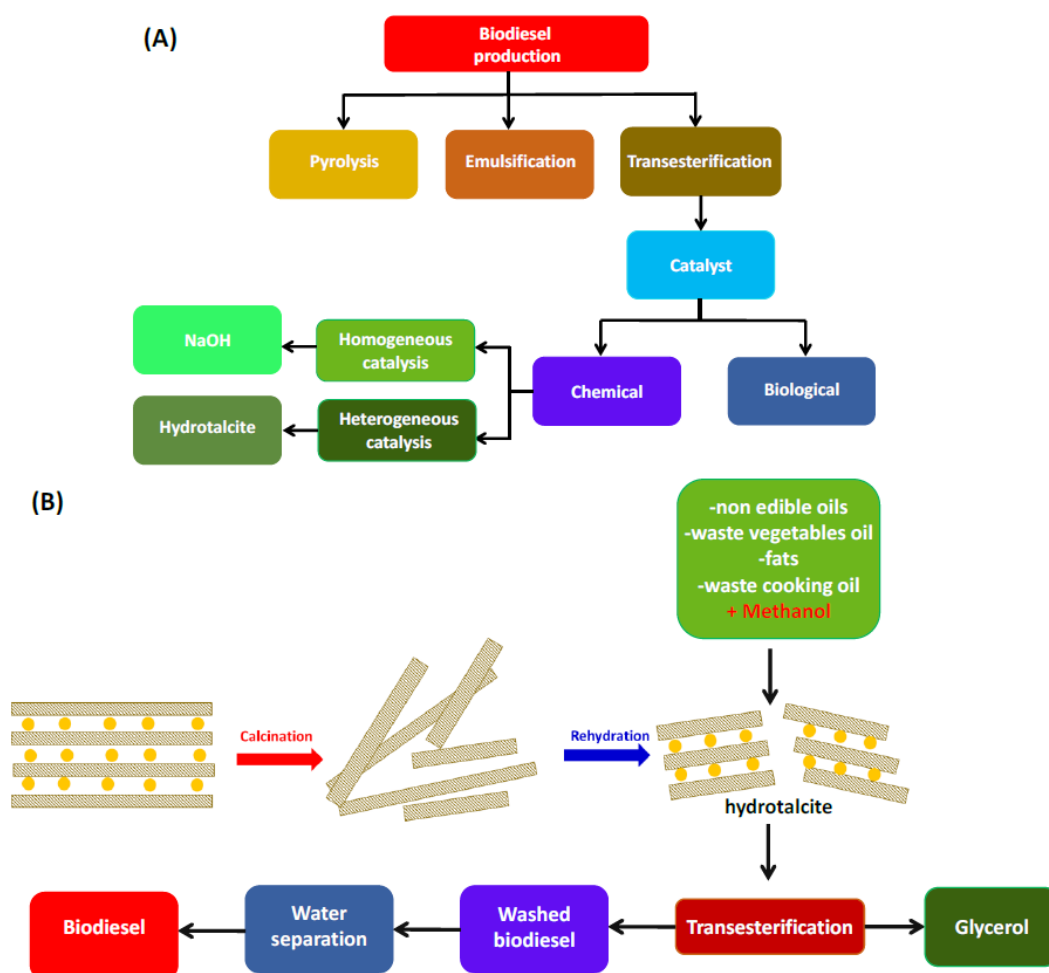


Figure 8. (A) Different pathways for biodiesel production, (B) Schematic illustration of biodiesel synthesis using biomass or waste materials through catalytic route over rehydrated hydrotalcite

9. Conclusions and Future Application Perspective

This study provides a review about the sustainable synthesis of value-added chemicals by means of hydrotalcite as heterogeneous catalysts. Aside from hydrotalcites' principal role in base catalysis, such as the transesterification reaction, they can also

serve as support materials for embedding active catalytic centers. Since they are conformable to green synthesis constraints, they can be exploited for further development of "green" functional materials. These assets signify the importance of this class of inorganics and materials derived from them as versatile materials in different catalysis fields. One example

is enzyme immobilization by means of hydrotalcites, which has the advantage of donating larger spaces to enzyme catalysis under harsher reaction conditions. On the other hand, some obstacles, such as tuning of basicity, reproducibility, and hygroscopicity, should be deliberated and evaluated properly. This awareness is crucial for crafting new hydrotalcites and for preserving the essential properties of as-synthesized ones regarding their vulnerable features. Their reusability, acid-base cooperative catalysis, tunable surface properties, and promising compatibility with conducting a broad range of chemical reactions rank them as a superior class of functional materials and act as a major incentive to prompt scientists to apply them in many research subjects to get better insights, either in their synthetic or structural properties or in widening their applications to new fields. According to all main points stated above, a promising perspective on hydrotalcites application in several green fields can be envisioned.

Ethics Statement

Not applicable.

Consent for publication

Not applicable.

Availability of Supporting Data

Not applicable.

Conflict of Interest

The authors declare no conflict of interest.

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