



Recent advances for layered double hydroxides (LDHs) materials as catalysts applied in green aqueous media



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ABSTRACT

Water as a green solvent has attracted considerable research interests in many important organic reactions. Development of effective and recyclable water-tolerant catalysts, especially heterogeneous catalysts, is the main challenge for the catalytic reactions in aqueous medium. Layered double hydroxides (LDHs) are a class of anion clays consisting of brucite-like host layers and interlayer anions, with versatility in composition, morphology and architecture. By virtue of the hydrophilicity of the hydroxyl-riched host layers as well as the 2D confined region of interlayer gallery, LDHs display great potential as supports to immobilize catalytically-active species so as to obtain water-compatible heterogeneous catalysts, in which catalytic sites can be preferentially orientated, highly dispersed, and firmly stabilized to afford excellent catalytic performance and recyclability in aqueous medium. Moreover, LDHs can be used as precursors for the preparation of hydrophilic metal or metal oxides catalysts based on the unique topotactic process transformation. In this *Overview Article*, we will summarize the latest developments in the design and preparation of LDHs-based heterogeneous catalysts in green aqueous media.

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1. Introduction

In recent decade, water as a solvent has attracted considerable research interests among the synthesis community toward many important organic reactions (e.g., Diels–Alder reactions, aldol reactions, Claisen-rearrangements, allylation reactions, oxidations, hydrogenations and ring-opening reactions), in terms of the green chemistry perspective [1–14]. Water is a safe, harmless and environmentally benign solvent in comparison with a large number of deleterious organic solvents; the unique physicochemical properties of water (e.g., high dielectric constant and cohesive energy density vs. organic solvents) can even accelerate some reactions [3,13]. Moreover, from practical and synthetic standpoints, it is not necessary to dry solvents and substrates for reactions in aqueous media. Despite of all these advantages of water as solvent/additive, it has long been deemed a seriously damaging contaminant in organic synthesis, as a result of the instability of many intermediates as well as catalysts in water. Therefore, the development of water-tolerant catalysts that allow organic reactions to be carried

out in aqueous medium is one challenging goal in the field of green catalysis.

The homogeneous catalysts are most commonly used for the organic reactions in aqueous medium. They show great merits in the accessibility of catalytic sites, tunability in chemo-, regio- and enantioselectivity of catalysts, and the resulting high catalytic activity and selectivity [15–17]. However, the employment of expensive and toxic organic metallic reagents as well as the difficulty in catalytic separation/recyclability would create great economic and environmental barriers, which restrict commercial applications of homogeneous catalysts. To overcome these problems, chemists and engineers have made extensive explorations, for instance, the use of a solid state catalyst conducted under heterogeneous conditions would be an attractive solution owing to the facile separation, recycling and adoptability in large-scale production [18]. Therefore, how to develop efficient heterogeneous catalysts in aqueous media instead of their homogeneous counterparts is one of main tendencies in catalysis chemistry.

Layered double hydroxides (LDHs), also known as hydrotalcite-like materials, are a class of two-dimensional (2D) anionic clays consisting of positively-charged host layers and exchangeable interlayer anions, which can be expressed by the formula $[M^{2+}_{1-x}M^{3+x}(OH)_2](A^{n-})_{x/n} \cdot mH_2O$ (M^{2+} and M^{3+} are divalent and trivalent metals, respectively; A^{n-} is the interlayer anion) [19–23]. Owing to the specific structure, versatility in composition,

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morphology and particle size, LDHs materials have been widely studied and used in the fields of catalysis [24–27], biology [28], magnetic [29] and optical functional materials [30,31]. Especially, the hydrophilicity of hydroxyl groups guarantees LDHs materials with a high water affinity and compatibility, so as to achieve a green catalysis in aqueous medium [32,33]. The intercalation capability of LDHs can ensure the immobilization and dispersion of catalysts in the interlayer region via the electrostatic host–guest interactions [34,35], providing an effective strategy to heterogenize the conventional homogeneous catalysts [36,37]. Moreover, LDH microcrystals can be exfoliated into positively-charged 2D nanosheets, which serve as building blocks to stabilize various catalytically active anions [38]. In addition, LDHs can be used as precursors for the preparation of hydrophilic metal or metal oxides catalysts based on the topotactic transformation of LDH materials upon calcination [39,40]. By virtue of these attractive structure features and synthetic strategies, LDHs materials can serve as promising water-compatible heterogeneous catalysts/precursors in green aqueous media.

In this *Overview Article*, we comprehensively summarize recent progress in the design and preparation of heterogeneous catalysts based on LDHs materials, which have been applied in catalytic reactions in water medium. The unique structure features of LDHs (e.g., intercalation, delamination, topotactic transformation) as well as their applications in green catalysis (as catalysts, catalyst precursors, supports) are reviewed in detail. In the final section, current challenges and future strategies are discussed from the viewpoint of catalyst design and practical applications. It is anticipated that this *Overview Article* will attract more attention toward LDHs-based green catalysts and encourage future work to push forward the advancement of this exciting area.

2. LDHs-based heterogeneous catalyst in aqueous media reactions

2.1. Catalytically-active species intercalated in LDHs gallery

Taking advantage of the anion-exchange property of LDHs materials, a variety of catalytically-active species (e.g., inorganic anions, organic acid/base and organic complexes) can be intercalated in the LDHs gallery by the method of coprecipitation or ion exchange. This feature gives the chance to obtain LDHs-based heterogeneous catalysts for organic reactions in aqueous media, which will overcome the drawbacks of their homogeneous counterparts (e.g., short lifetime, low thermal stability, and difficulties in separation and purification). Moreover, LDHs themselves offer a number of advantages as hosts: the electrostatic interactions between LDH layers and catalytically-active anions can induce an ordered arrangement of interlayer species and tailor the orientation of active sites; the distribution of active sites can be controlled by modulating the charge density of host layers (which depends on the ratio of M^{II} to M^{III} cation); the host–guest interaction between LDH layers and catalytically-active anions would also lead to an increase in the stability of the latter.

In the last decade, it has been demonstrated that the intercalation of active species into LDHs is capable of improving their catalytic activity, selectivity and stability in aqueous media, compared with the homogeneous counterparts. A typical example is the peroxidative oxidation of hydrocarbon using aqueous hydrogen peroxide instead of O_2 /organic mixture as oxidant [24], in which the water-compatible heterogeneous catalysts are necessary from the perspective of green catalysis. Sels et al. [41] reported a heterogeneous catalyst containing MoO_4^{2-} (Mo-LDHs) for the oxidation of unsaturated organics in aqueous H_2O_2 . The oxidation kinetics was studied in detail to compare the oxidation process

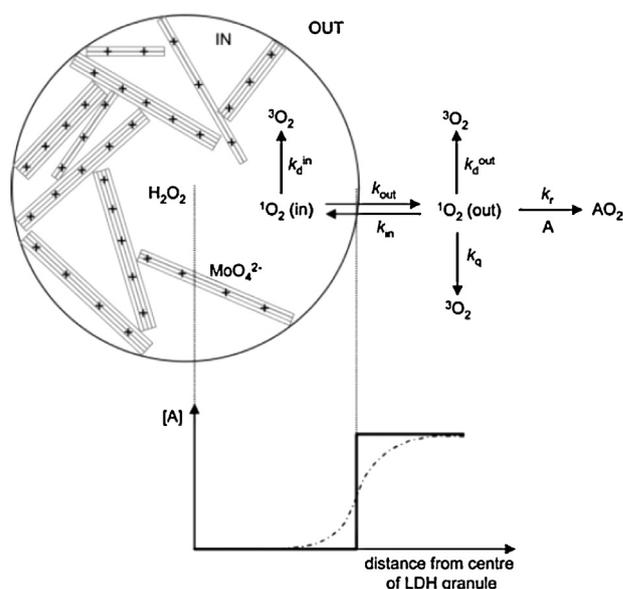


Fig. 1. Schematic representation for the kinetic model of the solid–liquid system used to peroxidize organic substrates over MoO_4^{2-} intercalated in LDHs with H_2O_2 as the oxidant. Reproduced with permission from Ref. [41].

between the heterogeneous catalyst and the corresponding homogeneous molybdate. The results demonstrated that although the yield over the heterogeneous Mo-LDHs catalyst is somewhat lower in comparison with soluble molybdate, a higher productivity was obtained as a result of the improved disproportionation rates. A general kinetic model was proposed to describe the yields for olefin peroxidation in the heterogeneous catalytic system as illustrated in Fig. 1. The kinetics of oxygenation by singlet oxygen is well-known for homogeneous media but less for heterogeneous systems. This work is the first detailed kinetic study on the oxidation of organics by 1O_2 generated from a heterogeneous catalyst, which gives a deep insight for further research in epoxidation systems. Recently, organometallic complexes intercalated LDHs (e.g., Ti(IV)-Schiff [42], Cu(II)-AHBD [43]) are also developed as excellent heterogeneous catalysts toward oxidation of hydrocarbons in aqueous media. Parida et al. [42] further reported a novel heterogeneous catalyst by immobilizing a Ti(IV)-Schiff base complex in ZnAl-LDH by an ion-exchange method as shown in Fig. 2. The catalytic evaluation of the stabilized catalyst for the epoxidation of cyclohexane was carried out under organic solvent-free conditions with aqueous hydrogen peroxide as oxidant; a 95% conversion of cyclohexene and 84% selectivity toward cyclohexene oxide were obtained, significantly superior to the homogeneous catalyst (62% and 74%, respectively). The stability of the immobilized catalyst was also demonstrated by conducting three successive runs without appreciable loss of reactivity.

The chiral catalysis in aqueous media has also attracted much interest, especially in the case of LDHs-based materials as heterogeneous chiral metal complex catalysts in the presence of water. In addition to the increase in reaction yield, in many cases intercalation of a chiral catalyst into an LDH host affords increase in enantioselectivity [44–46], which has been attributed to the controlled orientation and/or dispersion degree of the intercalated active species. He's group [47,48] reported the intercalation of chiral Sharpless titanium tartrate catalysts in MgAl-LDH hosts. A high dispersion of Ti active sites was confirmed by the dark-field TEM image. Through tailoring the charge density of the brucite-like layers, the loading of interlayer titanium tartrate anions could be reliably tuned, giving an interdigitated bilayer arrangement. Being used as a catalyst for the heterogeneous sulfoxidation of prochiral

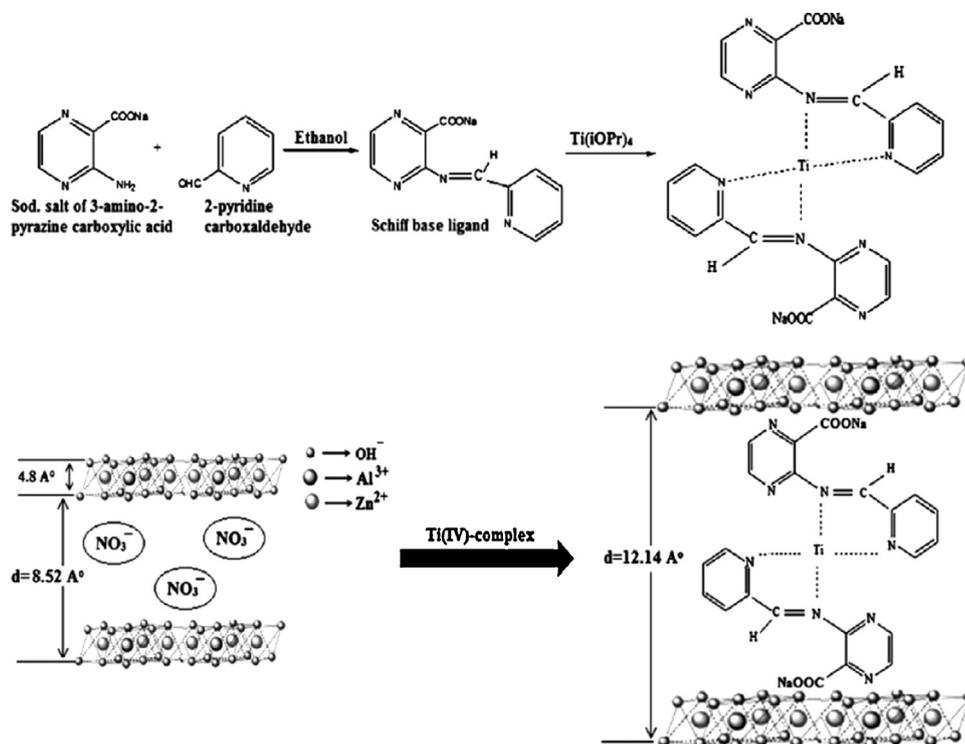


Fig. 2. Preparation pathway for the Ti(IV)-complex intercalated LDHs catalyst toward epoxidation of cyclohexane in aqueous media. Reproduced with permission from Ref. [42].

methyl phenyl sulfide, the *ee* value was boosted from the negligible value over homogeneous counterpart to 50% [47]. The 2D interlayer space can be swollen by addition of various organic solvents (e.g., CH₃CN or MeOH/CH₂Cl₂) during the reaction process, and therefore accommodates the reactants in the LDHs gallery. However, it was found that the *ee* value decreased with the increase of the inter-layer spacing. This verifies the role of confinement effect of LDHs materials on enhancing the catalytic properties of an intercalated species [48]. He's group [49,50] further developed heterogeneous titanium tartrate intercalated LDHs by *in situ* coordination of the pre-intercalated L-tartrate anions as chiral ligands to the Ti(IV) center within the LDH galleries. The tartrate ligands were tuned to adopt a perpendicular- or horizontal-orientation to further control the coordination mode toward the Ti(IV) center. It was found that the catalytic sites with the tartrate ligand in the perpendicular-standing orientation display a higher catalytic activity (93%) and better chiral induction (58%) in the asymmetric sulfoxidation than in the corresponding horizontal-orientation. A catalytic mechanism was also proposed, as illustrated in Fig. 3. Although the organic solvents were also used in these cases, the increased stability of organo-metallic catalysts derived from the confinement effect can facilitate these reactions to proceed with good recyclability in the presence of water (using aqueous H₂O₂ as oxidant).

Besides the catalytically-active anions intercalated in the LDH gallery, the metal cations in LDH host layers (e.g., Ru³⁺, Rh³⁺, Co²⁺, Cu²⁺) also act as active species for catalytic oxidation reactions [51–54]. As a typical example, Asefa et al. [55] demonstrated the synthesis of ZnCo-LDHs and their efficient catalytic performances toward water and alcohol oxidation, respectively (Fig. 4). The Co cations in LDH layers provide active sites for catalytic oxidation process; while the presence of Zn species imposes an essential synergistic effect to improve the catalytic behavior. The resulting LDHs catalysts exhibited excellent catalytic activity toward water electrooxidation, with the turnover frequency (TOF) per Co atom more than 10 times higher than the counterparts (e.g., Co(OH)₂

and Co₃O₄) toward water electrooxidation at the same applied potential.

Owing to the active sites on the LDH layers, the host layers themselves not only act as a support for catalytically-active anions, but also play the role of cocatalyst for organic reactions. Polyoxometallate (POM) has been intercalated in LDHs as an efficient

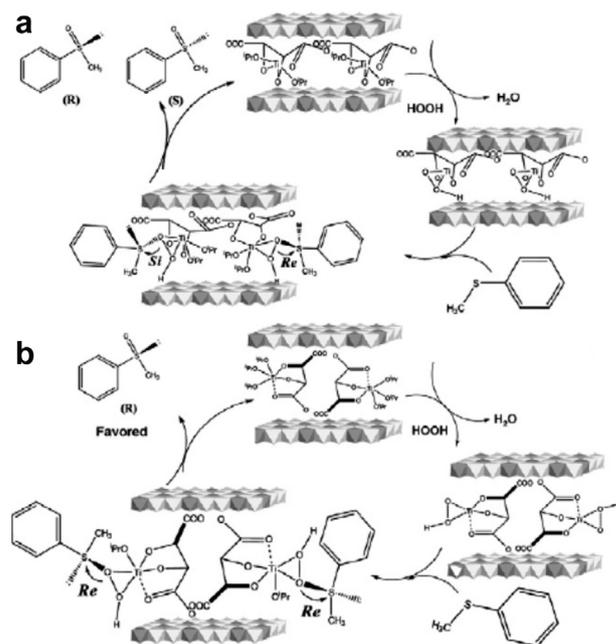


Fig. 3. The heterogeneous catalytic mechanism for the asymmetric sulfoxidation by a Ti(IV) tartrate complex intercalated in an LDH host, in which the tartrate ligand exists in (a) horizontal- and (b) perpendicular-orientation in the pre-intercalation process, respectively. Reproduced with permission from Ref. [49].



Fig. 4. The synthesis of ZnCo-LDHs catalyst as an efficient electrocatalyst and catalyst for water and alcohol oxidation, respectively. Reproduced with permission from Ref. [55].

oxidation catalyst in aqueous medium [24,32,33]. Li et al. [56,57] reported that a series of polyoxometalate (POM) intercalated LDHs catalysts exhibit base-synergistic catalysis toward epoxidation of allylic alcohols without using organic solvent. The cooperation between the POM guest and LDH host achieves excellent catalytic behavior (selectivity of epoxide: 99%; H_2O_2 efficiency: 95%; TOF: $37,200 \text{ h}^{-1}$) without the need of base additives and pH controlling; the LDH–POM catalysts can be readily recycled with no apparent loss of catalytic performance. The extremely higher epoxide selectivity of the heterogeneous LDH–POM catalysts than the corresponding homogeneous Na–POM ones is attributed to the beneficial effect of basic LDH host on the suppression of the acid-catalyzed epoxide hydrolysis. Recently, Song et al. [58,59] further developed the sandwich-type polyoxometalates (POMs) of $\text{K}_{11}\text{WM}_3(\text{H}_2\text{O})_2\text{O}[\text{ZnW}_9\text{O}_{34}]_2 \cdot 44\text{H}_2\text{O}$ ($\text{K}-\text{Zn}_2\text{M}^{\text{III}}_3\text{WO}$; $\text{M}^{\text{III}} = \text{Fe}^{3+}$, Mn^{3+}) intercalated LDHs, which catalyzed the oxidation of aromatic aldehydes by aqueous H_2O_2 without any organic solvents (Fig. 5). The $\text{Zn}_3\text{Al}-\text{Zn}_2\text{Mn}^{\text{III}}_3\text{WO}$ heterogeneous catalyst exhibits a much higher selectivity (85%) than the homogeneous counterpart (55%). It was also proposed that the synergistic interaction between the LDH host and intercalated POM anions plays a key role in the high oxime selectivity.

2.2. Catalytically-active species immobilized on the exfoliated LDHs nanosheets

Great progresses have been made for the intercalation of catalytically-active anions in LDHs as excellent heterogeneous catalysts in aqueous media. However, many active species cannot be intercalated into LDHs owing to their large size or low charge

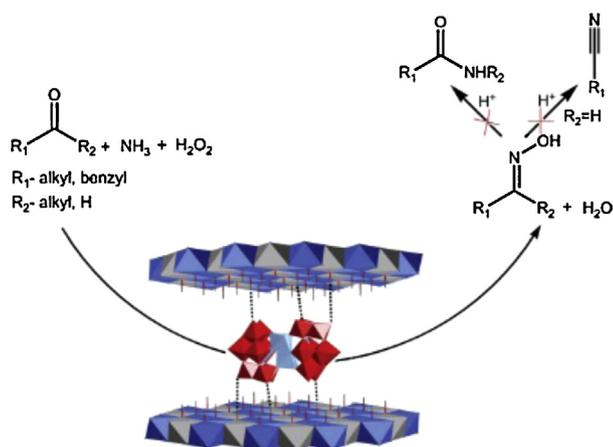


Fig. 5. Sandwich polyoxometalate intercalated LDHs catalyst toward highly selective oximation reaction. Reproduced with permission from Ref. [58].

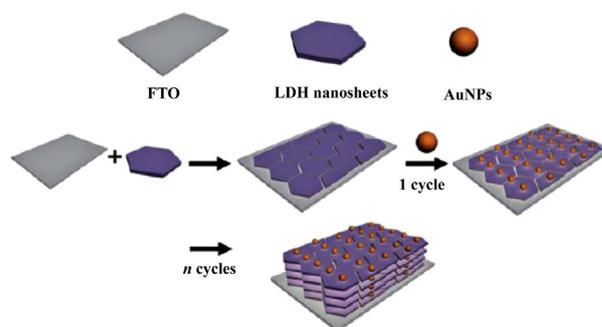


Fig. 6. Schematic representation for the assembly process of the (LDH/Au NPs)_n UTFs used as an excellent electrocatalyst toward the oxidation of glucose in aqueous medium. Reproduced with permission from Ref. [65].

density [60]. Moreover, the interlayer reaction kinetics is generally unsatisfactory in terms of large reactants due to the diffusion resistance. Concerning these problems, the LDHs microcrystals can be exfoliated to obtain ultra-thin nanosheets that serve as supports for the immobilization of catalytically-active species [61]. Recently, Wang et al. [62] reviewed various synthesis methods to obtain positively-charged dispersion of LDH nanosheets. By taking advantage of the electrostatic forces and/or hydrogen bonding between LDHs nanosheets and oppositely-charged species, nanocatalysts can be fabricated in a simple manner either *via* layer-by-layer (LBL) assembly [63], or *via* immobilization of active compounds on the exfoliated LDH nanosheets [64]. These approaches largely increase the scope and efficiency of LDHs-based heterogeneous catalysts in aqueous media.

By using LBL assembly of LDH nanosheets with large catalytically-active anions, Song et al. [63] reported well-ordered, ultra-thin films (UTFs) fabricated *via* self-assembly of $\text{Na}_9[\text{EuW}_{10}\text{O}_{36}] \cdot 32\text{H}_2\text{O}$ (denoted as EuW_{10}) and exfoliated MgAl-LDH monolayers. The UTFs exhibit a periodic, long-range ordered structure, and the resulting LDH monolayers provide EuW_{10} with a confined and protective microenvironment to give a high dispersion. Moreover, these assembled film materials have been used as excellent electrocatalysts in aqueous media. Wei et al. [65] fabricated LBL multilayers of Au nanoparticles (Au NPs) and LDH nanosheets on fluorine-doped tin oxide (FTO) substrates (Fig. 6). Structural and morphological studies indicated that the (LDH/Au NPs)_n UTFs exhibit a long-range stacking order, in which the Au NPs are highly dispersed and immobilized with a monolayer arrangement in the LDH gallery. The resulting (LDH/Au NPs)_n UTFs display excellent electron transfer kinetics and electrocatalytic activity toward the oxidation of glucose with good long-term electrocatalytic stability in aqueous medium.

Alternately, directly immobilization of catalytically-active species on the exfoliated LDHs nanosheets is another effective strategy for the maximum utilization of active center, which was described as the so-called “pseudo-homogeneous catalyst”. An example of the approach, involving the immobilization of amino acids as chiral ligands in the vanadium(V)-catalyzed asymmetric epoxidation of allylic alcohols with *tert*-butyl hydroperoxide (BuOOH), is shown in Fig. 7. He et al. [66–68] compared the catalytic performance of a homogeneous vanadium(V) complex, intercalated in a ZnAl-LDH host, and immobilized on LDHs nanosheets. It was found that the intercalation of amino acid ligands leads to a significant increase in the enantiomeric selectivity but with a low reaction rate compared with the homogeneous catalyst. This can be attributed to the access of reactant molecules to the active sites being restricted and/or directed by the rigid inorganic layers. Immobilization of the vanadium(V) complex on LDHs nanosheets allows the catalytic reaction occurring under

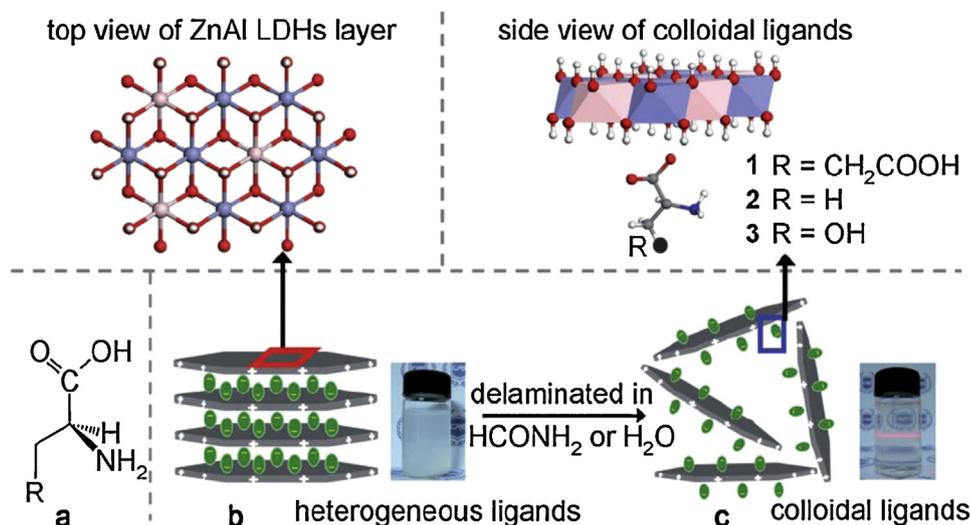


Fig. 7. Intercalation of α -amino acids (1) L-glutamic acid; (2) L-alanine; (3) L-serine (a) in an LDH host gives a heterogeneous catalyst precursor (b), whilst immobilization on delaminated LDH nanosheets gives a pseudo-homogeneous catalyst precursor (c). The materials obtained by treating (a)–(c) with VO(OPri)₃ were used as catalysts for the asymmetric epoxidation of allylic alcohols with ButOOH. Reproduced with permission from Ref. [66].

pseudo-homogeneous conditions, thereby significantly increasing the reaction rate while maintaining a high enantioselectivity. Most notably, the pseudo-homogeneous catalyst has also been used in water medium with excellent activity, and the colloidal catalyst was more easily separated from the products by simple liquid/liquid separation than in organic solvents. The catalysts can be recycled and reused with no obvious loss of catalytic activity and enantioselectivity.

2.3. Supported metal or metal oxide nanocatalysts derived from LDHs

Nanoparticles have emerged as sustainable alternatives to conventional materials, as robust, high surface area heterogeneous catalysts and catalyst supports [17]. The nano-sized particles exhibit fascinating physical and chemical properties (e.g., surface effect/size effect) [69–71], thereby dramatically enhancing the contact between reactants and active center, which build a bridge between homogeneous and heterogeneous catalysis. Development of metal and metal oxide nanocatalysts instead of noxious and costly organometallic complexes is another trend for organic chemistry in water. The LDHs materials themselves are very excellent hydrophilic supports for metal/metal oxide nanocatalysts. Moreover, the supported metal or metal oxide nanocatalysts can be obtained through a topotactic transformation process of LDHs precursors upon calcination in hydrogen/air conditions. These structure features endow LDHs materials with great potential to fabricate nanocatalysts in aqueous media.

Recently, studies in the field of nanocatalysts such as Au, Ag and Pd in synthetic organic chemistry have gained much attention [72–74]. A remarkable advantage for these noble metal nanocatalysts is their chemical stability in water and can be applied in aqueous media. Choudary et al. [75] reported nanopalladium particles supported on LDHs by a simple ion-exchange technique followed by reduction, which show excellent yields and high TOF values in Heck-, Suzuki-, Sonogashira-, and Stille-type coupling reactions of chloroarenes, even deactivated chloroarenes. Low yields were obtained with nonpolar solvents such as toluene and *o*-xylene, while polar solvents such as THF, 1,4-dioxane and 1,4-dioxane/water (5:1) give good yields. Specially, the water-containing solvents show higher activity compared with those of organic polar solvents. Zhang et al. [76] demonstrated the

preferential deposition of gold nanoparticles (Au NPs) with a narrow size distribution (2–3 nm) on the lateral (1 0 $\bar{1}$ 0) facets of LDH platelets by a homogeneous deposition–precipitation (HDP) technique (Fig. 8). The crystal face features of LDH platelets impose a crucial effect on the location and particle size of Au NPs. The lateral (1 0 $\bar{1}$ 0) facet with high density of dangling bonds may have relatively active chemical characteristics, resulting in the preferential deposition of Au NPs; the strong metal-support interaction prevents the aggregation of Au particles. The crystal-face-selective Au NPs on LDHs can efficiently catalyze the epoxidation of styrene with aqueous ButOOH as the oxidant; the TOF value for styrene oxide production reaches to 970 h⁻¹. In addition, several other metal or metal oxide nanocatalysts supported on LDHs have also been developed for catalysis in aqueous media, e.g., the chemoselective hydrogenation of olefinic bonds over Pd/LDHs [77], coupling reactions of alcohols and nitriles or oxidation of alcohols over bimetallic Au-Pd/LDHs [78,79], hydration of nitriles to amides over

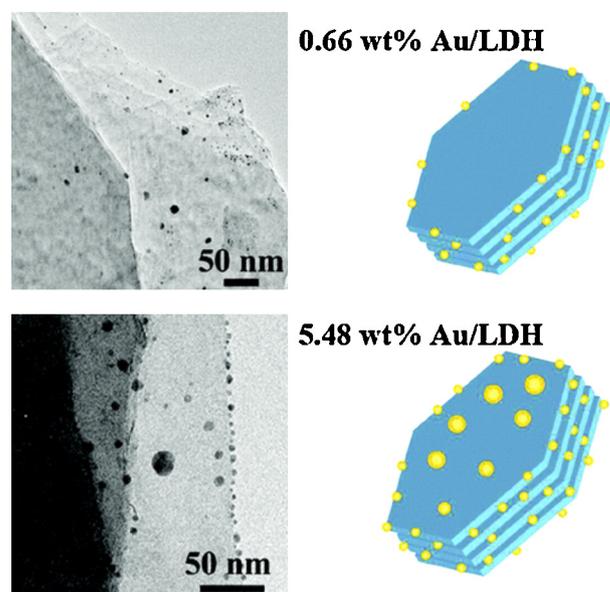


Fig. 8. The fabrication of Au/LDHs catalyst by a homogeneous deposition–precipitation (HDP) technique for catalytic epoxidation of styrene with aqueous ButOOH as the oxidant. Reproduced with permission from Ref. [76].

Ni/LDHs [80], and aerobic oxidation of 5-hydroxymethylfurfural over ruthenium hydroxide/LDHs [81]. In some cases, the synergistic effect between the metal nanocatalyst and the basicity of LDH support can produce a further enhancement in catalytic activity, and avoid the addition of extra alkaline additive as well [75,76,81].

The topotactic transformation of LDH materials upon calcination in hydrogen/air atmosphere provides a facile approach for the fabrication of supported metal/metal oxide nanocatalysts with high dispersion and stability. Wei et al. [82–85] reported a series of monometallic or bimetal supported nanocatalysts derived from the reduction process of LDHs in hydrogen, which display excellent catalytic activity/selectivity and stability. The obtained metal nanocatalysts also exhibit good catalytic performance in aqueous media. Shen et al. [86] reported a Co nanocatalyst obtained from a ternary CoZnAl-LDH precursor, with high activity, stability and recyclability toward the hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) in aqueous media. The supported Co catalyst (16 nm) gives the best glycerol conversion of 70.6% and the 1,2-PDO selectivity of 57.8%. Moreover, calcination of LDHs in air results in supported oxide or spinel catalysts for aldol condensation or phenol oxidation [87,88]. Medina et al. [88] reported well-dispersed metal oxide and spinel-like phases obtained by calcining CuNiAl-LDHs with various M^{2+}/M^{3+} ratios in the temperatures range 373–1173 K, which serve as excellent catalysts toward wet air oxidation of phenol aqueous solutions. The pristine LDHs precursors are practically inactive for this reaction, but the calcination catalysts exhibit significantly increased activity (>90 and >70% of phenol conversion over CuO- and NiO-based catalyst, respectively). In addition, the spinel phases obtained from LDHs precursors by calcination at 1023 K also show good conversions (among 40–75%), without obvious loss in activity after a continuous working run of 15 days using a trickle-bed reactor.

As an extension of this idea, the LDHs materials themselves [26,89–93] or composite nanomaterials [94–101] derived from LDHs can serve as excellent photocatalysts in water medium owing to the semiconductor feature of LDHs-based materials. A unique feature of LDHs as photocatalytic materials is the high dispersion of some photo-active transitional metal octahedron (e.g., CrO_6 in ZnCr-LDHs) in the LDHs matrix [102–104], which may facilitate the electron transfer and avoid the electron–hole recombination, and thus increase the photocatalytic efficiency. Tanaka et al. [105] reported the photocatalytic conversion of CO_2 in water in the presence of various LDHs such as Mg–Al hydrotalcite. They concluded that the high water tolerance of LDHs base sites facilitates the adsorption and activation of CO_2 on the surface of LDHs, accounting for the superior activity toward the photocatalytic conversion of CO_2 into CO in water. In addition, LDHs-based composite nanomaterials fabricated by loading metal [106] or metal oxide [107] can further improve the photocatalytic activity. As a typical example, Wei et al. [108] reported ZnO nanoplatelets with a high exposure of (0001) facet embedded on a hierarchical flowerlike matrix, which were achieved via the *in situ* topotactic transformation process of a ZnAl-LDH precursor (Fig. 9). A topotactic transformation based on the hexagonal structure of LDH is believed to occur, resulting in the formation of hexagonal ZnO nanoplatelets embedded on the Al_2O_3 matrix. The hexagonal crystals of ZnAl-LDH nanoflakes serve as both a ZnO source and a rigid template, which restrains the fast growth rate of ZnO along the *c*-axis and induces the preferred growth of the nanoplatelets along the $[1\ 0\bar{1}\ 0]$ direction. The resulting ZnO/ Al_2O_3 nanocatalyst displays superior visible-light photocatalytic activity toward the degradation of Rhodamine-B in aqueous solution, whose behavior can be attributed to the enhanced separation efficiency of electron–hole pairs resulting from the oxygen defect-riched ZnO nanoplatelets. Furthermore, the anchoring effect of LDHs precursor

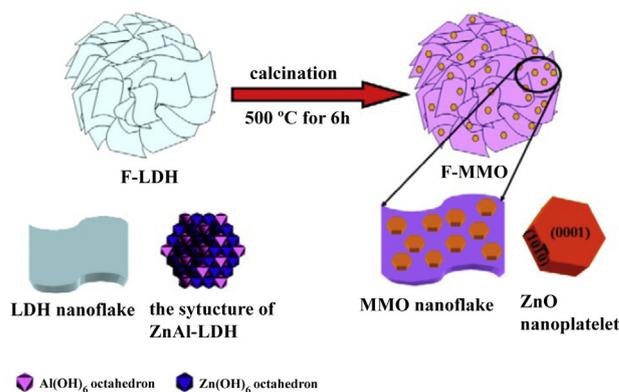


Fig. 9. Schematic illustration for the formation of supported ZnO nanoplatelets with a high exposure of (0001) facet via the *in situ* topotactic transformation of hierarchical flowerlike ZnAl-LDHs. Reproduced with permission from Ref. [108].

affords excellent stability and recyclability of this oriented ZnO photocatalyst.

3. Conclusion

This Overview Article summarizes the recent progress in the design and preparation of LDHs-based materials as heterogeneous catalysts in green aqueous media, including intercalation of active species in LDH hosts, immobilization of active species on the exfoliated LDHs nanosheets, loading of metal/metal oxide nanoparticles on LDHs supports or matrixes. By virtue of the versatility of LDHs in chemical composition, size and morphology, a great number of water-tolerant heterogeneous catalysts with preferential orientation, high dispersion and good stability have been fabricated, exhibiting excellent catalytic performance and recyclability toward organic reactions in water. However, there are still great challenges in the design and application of the LDHs-based catalysts in green aqueous media: (i) generally speaking, only anions or a few neutral molecules with appropriate size can be intercalated into LDH hosts, which restricts the incorporation of many water-tolerated catalytic active species (e.g., carboniums); (ii) although the exfoliated LDH nanosheets can immobilize large active species, this system can only be stabilized in a small number of solvents (e.g., aqueous methanamide) that may be poison for many organic catalytic reactions; (iii) except for oxidation reactions, other important organic reactions such as Diels–Alder reactions or Claisen-rearrangements in aqueous medium are scarcely exploited by LDHs materials as catalysts; (iv) the effect of water on organic reactions over heterogeneous LDHs catalysts may be another interesting research topic in the further, which is always ignored in the current stage. How to employ positively-charged active species as well as to stabilize exfoliated LDH nanosheets remain a great challenge in the LDHs-based green catalysis. In order to overcome these problems, more sophisticated material design and new fabrication methods/techniques should be developed; a deep insight into the catalytic mechanism over LDHs-based materials in green aqueous media is necessary to make further progress of this fast-growing field.

Acknowledgments

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