



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



Changming Li, Min Wei\*, David G. Evans, Xue Duan

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

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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,

\* Corresponding author. Tel.: +86 10 64412131/+86 10 6442 5385; fax: +86 10 64425385.

E-mail address: [weimin@mail.buct.edu.cn](mailto:weimin@mail.buct.edu.cn) (M. Wei).

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.

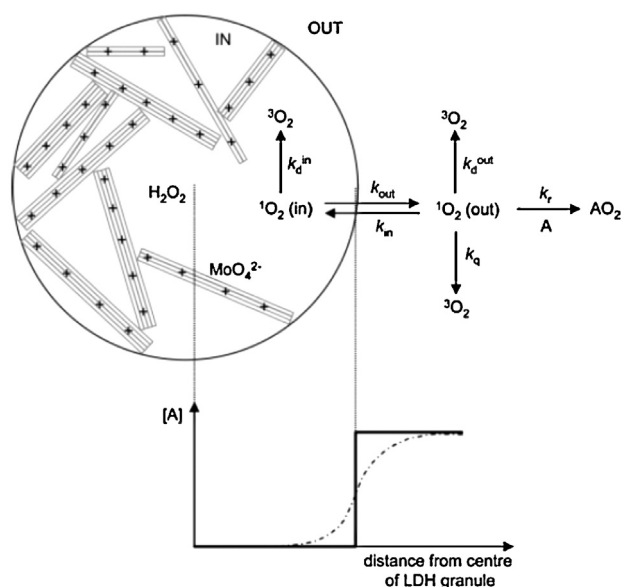
In this *Overview Article*, we comprehensively summarize recent progress in the design and preparation of heterogeneous catalysts based on LDHs materials, which have been applied in catalytic reactions in water medium. The unique structure features of LDHs (e.g., intercalation, delamination, topotactic 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

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