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Minireview

Layered double hydroxide and related catalysts for hydrogen production and a biorefinery

Wei Wang^{a,b}, Zhenxin Xu^a, Zhanglong Guo^{a,b}, Chengfa Jiang^a, Wei Chu^{a,b,*}^a Department of Chemical Engineering, Sichuan University, Chengdu 610065, Sichuan, China^b Sichuan Provincial Engineering Technology Center for Environmental Protection Catalytic Materials, Sichuan University, Chengdu 610064, Sichuan, China

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ABSTRACT

Layered double hydroxides (LDHs) have received much attention for their unique properties. As solid catalysts, LDHs and their derivatives have been widely studied and applied for their excellent catalytic performance. Several synthesis methods of LDHs were briefly introduced, and the applications of LDHs and related catalysts for hydrogen production and a biorefinery were emphasized in this article. The prospects for LDH related compounds in the synthesis of new materials and their catalytic application in green catalysis systems were also presented.

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1. Introduction

Layered double hydroxides (LDHs) are layered anionic clays also known as hydrotalcite-like compounds (HTLCs). They are new inorganic functional materials with positively charged brucite-like lamellas and charge-balancing anions and solvation molecules in the interlayer region. The lamellar structure is constructed with octahedrons by sharing their edges with divalent and trivalent metal cations in the center and six hydroxide ions at vertexes [1,2], as shown in Fig. 1.

LDHs have attracted considerable interest in recent years due to their unique structure and properties, including exchangeable lamellar anions, controllable basicity, tunable composition, and uniform deposition of the active metal [3,4]. Homogeneously dispersed mixed metal oxides can be obtained

by a controlled thermal decomposition of LDH precursors. These oxides have many special characteristics, such as high specific surface areas, basic character, high dispersion of the metallic phase, thermal stability against sintering, and capacity to regenerate the original layered structure [5,6]. Therefore, LDHs and their derivatives have been widely used as heterogeneous basic catalysts in many fields, such as clean energy and pollution control [7,8].

LDHs have received much attention for their properties and catalytic performance. Recent progress in the synthesis of LDHs is summarized with a special focus on the application of LDHs and derivatives as catalysts for H₂ production and a biorefinery in this work. We expect that more efforts will be devoted to the special layer structure and properties of LDHs, which are significant for the design of new materials [9,10].

*Corresponding author. Tel: +86-28-85403836; Fax: +86-28-85461108; E-mail: chuwei1965@scu.edu.cn, chuwei1965scu@163.com

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Fig. 1. Structure illustration of LDHs.

2. Synthesis methods of LDHs

The preparation methods of LDHs include co-precipitation method, urea hydrolysis process, anion exchange, and roasting recovery technique. The co-precipitation method is the most widely used process to prepare LDHs [11,12]. For this method, solution A and solution B are prepared first before co-precipitation. Solution A contains different metal nitrate hexahydrate with the proper molar ratio, and solution B is usually a mixture solution of Na_2CO_3 and NaOH . Then, solution A and solution B are simultaneously added dropwise to a vessel containing deionized water with vigorous stirring. During this process, the slurry is kept at a constant pH by controlling the dripping speed of the solution. After aging for a period of time, the precipitate obtained is separated from the mother solution, rinsed with deionized water, and appropriately dried to obtain the LDH [13,14]. Yan et al. [13] successfully synthesized a series of LDH precursors used for the dehydration of biomass-derived fructose into the platform chemical 5-hydroxymethylfurfural by this method. This technology includes the low supersaturation method and high supersaturation method [15]. Usually, the aging process is combined with a hydrothermal or microwave treatment [16,17]. The crystallinity of the LDHs can be improved, but the former is time consuming and the crystals always have a large particle size, while the latter is time saving and the crystals are relatively small with a uniform distribution.

The urea hydrolysis process usually employs urea as precipitant. By controlling the heating rate, the urea decomposition rate can be controlled, and the solution can be kept at a constant pH. Through this way, the sedimentation rate of the catalysts can be controlled [18]. In brief, solid urea is added to an aqueous solution containing metal nitrates with the desired molar ratio, until the urea to metal molar ratio reaches the desired value. The solution obtained is usually kept stirred at a certain temperature in a thermostatic reactor equipped with a coolant. The precipitates are filtered, washed, and then dried at the set temperature, and finally the LDH precursors are obtained [18,19]. Compared to the co-precipitation method, this procedure can be operated more easily and is time saving. Therefore, it has been widely used. In our previous works, Yu et al. [19] successfully synthesized the NiCuMgAl LDH precursors for ethanol steam reforming using this method. The XRD patterns of the $\text{Ni}_{0.5}\text{Mg}_{2.5-x}\text{Cu}_x\text{Al}$ precursors are shown in Fig. 2. This method is also combined with a hydrothermal or micro-

Fig. 2. XRD patterns of LDH precursors. (a) $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al}$; (b) $\text{Ni}_{0.5}\text{Cu}_{0.05}\text{Mg}_{2.45}\text{Al}$; (c) $\text{Ni}_{0.5}\text{Cu}_{0.1}\text{Mg}_{2.4}\text{Al}$; (d) $\text{Ni}_{0.5}\text{Cu}_{0.25}\text{Mg}_{2.25}\text{Al}$. Reproduced from Ref. [19] with kind permission from Springer Science and Business Media.

wave treatment to improve the morphology of the LDHs [20,21]. Recently, Deng et al. [22] synthesized a series of LDH precursors using urea as precipitating agent combined with a microwave-hydrothermal treatment. The resulting material had a narrow particle size distribution. Scanning electron microscopy images of LDH and calcined LDH are shown in Fig. 3.

The anion exchange technique takes advantage of the exchangeability of the interlayer anions to realize the exchange of the interlayer anions with other desired anions. Usually, LDH precursors synthesized by the methods given above are suspended in a solution containing the desired anions under mild conditions. A few hours later, LDHs with the desired anion can be obtained [18,23]. Recently, a binary system of SbIII, an important alternative for Leishmaniasis chemotherapy, was prepared by Menezes et al. [24] using MgAl LDHs as a nanocarrier via ion exchange. The roasting recovery method makes full use of the “memory effect” of LDHs. When the mixed oxides, calcined LDHs, are put back into a solution containing the required anions with a certain pH, they can reconstruct the original lamellar structure after a period of time [25,26]. Álvarez et al. [5] found that the rehydrated LDHs had many basic Brönsted sites. Therefore, they showed excellent catalytic activity for the transesterification of glycerol. Meanwhile, Sun et al. [26] reported that F^- modified CuNiAl LDHs synthesized by this method had high activity for the selective oxidation of toluene to benzyl alcohol.

Fig. 3. SEM images of LDH (a) and calcined LDH at 773 K for 6 h (b). Reprinted with permission from Ref. [22]. Copyright 2011 Elsevier.

In addition, some unconventional preparation methods have also been reported, such as the reverse microemulsion method [27] and the sol-gel method [28].

3. Catalytic applications of LDHs and related catalysts

3.1. Catalysis for H_2 production

Hydrogen, a clean energy, has attracted attention for its development and utilization in the field of clean energy [29,30]. Due to their high hydrogen content, methane and low carbon alcohols, such as methanol and ethanol, have been widely investigated for their catalytic reforming or oxidation for H_2 production.

3.1.1. Methane reforming or methane oxidation

Steam reforming of methane is an economic way to produce hydrogen. It is generally accepted that methane and steam are first catalytically reformed into CO and H_2 (Eq. (1)). Usually, the water-gas shift reaction is introduced to further convert CO into CO_2 (Eq. (2)). However, the methane conversion and hydrogen productivity are limited by the thermodynamic equilibrium of the reverse methanation (Eqs. (1) and (3)) and water-gas shift reactions (Eq. (2)) [31,32].

To solve this problem, sorption-enhanced steam methane reforming (SE-SMR) based on the idea of shifting the thermodynamic equilibrium of the reactions towards the hydrogen product direction by selectively adsorbing CO_2 on an effective adsorbent was proposed in recent years. Broda et al. [31] investigated SE-SMR over a mixture catalyst containing a Ni-LDH-derived catalyst and a synthetic, calcium aluminate supported Ca-based carbon dioxide adsorbent. The combination of Ni-LDH-derived catalyst and the synthetic CO_2 adsorbent produced high purity H_2 . Equilibrium conversion of me-

thane was achieved with the purity of hydrogen up to 99 vol% (dry and without the inert component) at a reaction temperature of 550 °C and a steam to methane ratio of 4. Ca-based pellets showed excellent performance in the reaction, which was attributed to their stable nanostructured morphology, as shown in Fig. 4. The homogeneously dispersed mayenite substantially retarded the thermal sintering of CaO grains. At almost the same time, Chanburanasiri et al. [32] reported that K_2CO_3 -promoted LDHs with in situ CO_2 capture were also an efficient catalyst for SE-SMR. They noted that the CO_2 adsorption type was diverse among the different LDHs, which resulted in different sorption-enhanced characteristics. Under optimized conditions, high purity H_2 production was also obtained.

Compared to the conventional methane steam reforming process, autothermal reforming (ATR) of methane has also received much attention for higher energy efficiency and lower energy requirements [33,34]. Ni-based catalysts prepared from LDH precursors showed high catalytic activity. However, they are susceptible to carbon deposition and may be oxidized at low temperatures. It has been reported that the doping of a small amount of noble metals can significantly improve catalyst stability and activity [33]. Nagaoka et al. [33] found that NiRh alloy particles were formed in a NiRh/MgAl catalyst and Rh enhanced the dispersion of Ni nano-particles on the surface of the NiRh alloy, which were critical for the catalytic activity. Due to the H_2 spillover effect from Rh on the NiRh alloy, the stability of the NiRh/MgAl catalyst against oxidation was enhanced. Takehira et al. [35] investigated the structure-activity relationship of the Ni/MgAl catalysts for ATR of methane. Catalysts with a high surface area of 150 m^2/g_{cat} were successfully prepared by the co-precipitation method followed by thermal decomposition and H_2 reduction. The dispersion of Ni was repeatedly enhanced, which was attributed to the formation of a Mg-O-Ni solid solution. Highly dispersed Ni active centers with a small particle size about 8 nm were obtained after H_2 reduction, and the catalyst showed relatively high stability compared with the catalysts prepared by the conventional impregnation

Fig. 4. HR-SEM and TEM images of unreacted and cycled (10 cycles) materials. (a,b) Ca-based pellets; (c,d) Rheinkalk limestone; (e,f) Ni-based catalyst. Reprinted with permission from Ref. [31]. Copyright 2013 American Chemical Society.

Fig. 5. Dynamic profiles of effluent CH₄ conversion and H₂ yield obtained in ATR and SE-ATR. Reprinted with permission from Ref. [34]. Copyright 2011 Elsevier.

method. Recently, Halabi et al. [34] for the first time combined the sorption-enhanced concept together with the ATR of methane at low temperature and a relatively low pressure. They investigated the SE-ATR using K-promoted LDHs as sorbent combined with a conventional Ni/MgO catalyst. The SE-ATR showed advantages over the ATR process (Fig. 5). The CH₄ conversion and H₂ purity were up to 85% and 96%, respectively, with a low level of CO + CO₂ impurities less than 0.03% at the experiment conditions in the SE-ATR process. However, compared with lithium zirconate, the low adsorption capacity of LDHs was still a limiting factor in the reaction.

On the other hand, methane partial oxidation (Eq. (4)) is also a promising technology which shows high conversion and selectivity and works with short contact times [36]. Cesar et al. [36] studied the catalytic performance of NiMgAl and RhNiMgAl catalysts in the partial oxidation of methane. The results indicated that the reducibility of Ni can be improved by Rh and its stability was increased against carbon deposition, which was consistent with the result reported before [33]. As mentioned above, the preparation procedure always influenced the interactions between the metal and the support, which play an important role on the catalyst properties. Basile et al. [37] found that the catalytic performance can be improved by a microwave-hydrothermal treatment (MWHT) compared with the conventional co-precipitation method (Fig. 6). They revealed that the MWHT not only improved the crystallinity of the LDHs precursor, but also modified the catalyst properties. A smaller oxide and spinel crystallite size were obtained for the MW-aged sample compared with those obtained by the conventional co-precipitation method after calcination. Furthermore, due to the better dispersion of the active metal in the oxide matrix, the stability of Ni against reduction was enhanced. Meanwhile, Tanasoi et al. [38] observed that mesoporous CuMgAl mixed oxide with high surface area derived from LDH precursors was active for the total oxidation of methane (Eq. (5)). CuO and CuAl₂O₄ phases were present in the calcined

Fig. 6. Methane conversion for the Ni₁₀Mg₆₁Al₂₉ catalysts prepared using the conventional co-precipitation method and MWHT during the tests by feeding diluted conditions at $T_{\text{oven}} = 500$ °C. Reprinted with permission from Ref. [37]. Copyright 2010 Elsevier.

catalysts, which increased the dispersion of CuO. The total conversion of methane can be achieved at 525 °C below, and no CO was detected at the exhaust under all the experimental conditions.

3.1.2. Low carbon alcohol reforming

Steam reforming of alcohols, mainly methanol and ethanol vapor reforming, is considered a favorable process for H₂ production. The major challenge for alcohol reforming is to produce high purity H₂ with ppm level of CO content. The overall reaction of steam reforming of methanol can be written as

Catalysts derived from LDH precursors were extensively studied because the homogeneous stable oxide composite inhibited the surface active phase from sintering and, as a consequence, long term stability with high activity was achieved. Cu-based catalysts are frequently studied for the steam reforming of alcohols due to their high selectivity and activity [39,40]. Tang et al. [40] found that the catalyst derived from a CuZnAl LDH provided excellent activity and stability for methanol steam reforming, which was attributed to the formation of the CuAl₂O₄ spinel phase during the decomposition of CuZnAl LDH. They revealed that the spinel phase played a key role in isolating and stabilizing the Cu particles on the catalyst surface. A CuZnAl catalyst prepared from metal acetates showed the best catalytic activity and stability, and converted a H₂O/CH₃OH (1.3/1, mol/mol) mixture into H₂ with a CO concentration as low as 0.05% at 250 °C or 0.005% at 210 °C and maintained its activity (>98%) with a CO concentration of 0.03%–0.05% in the dry product gas for the entire 100-h test at 250 °C. Meanwhile, they observed that catalysts synthesized using sulfates and chlorides as Cu and Zn sources were inactive due to the toxic effect of S and Cl residues.

Ethanol steam reforming was also widely studied because of the potentially high yield to hydrogen. Eq. (7) represents the steam reforming of ethanol.

Ni is commonly employed as the active phase for ethanol steam reforming for its low cost and high activity, but it also favors the methanation reaction (Eq. (1)), which limits the H_2 yield. Previous studies found that Cu can limit the latter reaction by suppressing CO dissociation on Ni [19,41]. In our previous works, Yu et al. [19] successfully synthesized NiCuMgAl catalysts derived from the corresponding LDH precursors by the urea hydrolysis method. The addition of small amounts of Cu increased surface Ni species and the reducibility of Ni^{2+} (Fig. 7). The $\text{Ni}_{0.5}\text{Cu}_{0.1}\text{Mg}_{2.4}\text{Al}$ catalyst exhibited strong resistance to coke formation and sintering of Ni particles, and showed high activity and stability with no apparent deactivation during 20 h on stream at 700 °C. Recently, the sorption-enhanced reaction process has also been extensively studied. Cunha et al. [42] investigated the steam reforming and sorption enhanced steam reforming of ethanol over Cu, Zn, Al materials. The CuZnAl catalyst derived from LDH precursor showed the highest activity and selectivity with satisfying stability among all the samples. Due to good interaction of CO_2 and the presence of a ZnO phase, a sorption enhanced steam reforming of ethanol phenomena was observed. After that, they successfully synthesized a new multifunctional K-Ni-Cu-HTLC hybrid material for H_2 production [43]. A desired sorption-enhanced reaction process was achieved using a K promoter together with the hydrotalcite-like material for CO_2 adsorption. They reported that Cu was favored for the ethanol dehydrogenation (Eq. (8)) and the water-gas shift (Eq. (2)) reaction, while Ni was suitable for acetaldehyde decomposition (Eq. (9)) and steam reforming of methane (Eq. (1)). At 773 K, using the water to ethanol molar ratio of 10, a high purity hydrogen stream (99.8 mol% on dry basis) was obtained during the prebreakthrough period.

Ethanol autothermal reforming was also widely studied [44,45]. Huang et al. [45] investigated the catalytic performance

Fig. 7. TPR patterns of the layered double hydroxide precursors. (a) $\text{Ni}_{0.5}\text{Mg}_{2.5}\text{Al}$; (b) $\text{Ni}_{0.5}\text{Cu}_{0.05}\text{Mg}_{2.45}\text{Al}$; (c) $\text{Ni}_{0.5}\text{Cu}_{0.1}\text{Mg}_{2.4}\text{Al}$; (d) $\text{Ni}_{0.5}\text{Cu}_{0.25}\text{Mg}_{2.25}\text{Al}$. Reproduced from Ref. [19] with kind permission from Springer Science and Business Media.

of $\text{Co}_{0.3}\text{Mg}_{2.7}\text{Al}_{1-x}\text{Fe}_x\text{O}_{4.5\pm\delta}$ in autothermal reforming of bio-ethanol for H_2 production. Due to the synergism of Co and Fe, the $\text{Co}_{0.3}\text{Mg}_{2.7}\text{Al}_{0.9}\text{Fe}_{0.1}\text{O}_{4.5\pm\delta}$ catalyst showed better performance compared with the iron-free catalyst with the conversion of ethanol being nearly 100% and the H_2 yield above 3.2 mol H_2 /mol $\text{C}_2\text{H}_5\text{OH}$ throughout the 30-h test.

3.2. Catalysts for a biorefinery

A biorefinery provides a possible solution to the challenges from the diminution of oil and the increase of CO_2 emission, while it opens a new way to the sustainable production of fuels and chemicals from vast renewable biomasses [46]. LDHs and their derivatives show good application prospects in the catalysis in a biorefinery because of important advantages, such as suitable basicity, high surface area, and pore volume, improved selectivity under mild conditions and easy separation from the reaction mixtures.

Biodiesel, a mixture of long chain fatty acid methyl esters (FAME), is a diesel fuel that could solve environmental concerns and the limited resources of fossil fuels. At present, biodiesel is mainly produced by the transesterification of renewable biological triglyceride sources (plant oils and animal fats) with alcohols (methanol or ethanol) using homogeneous basic catalysts (Scheme 1) [47]. However, this homogeneous process has severe pollution and corrosion problems. Recently, LDHs and their derivatives have been widely used as solid basic catalyst for biodiesel production. Quite good results have been obtained. It has been reported that the catalytic activity is associated with the catalyst basicity. With the increase of the Mg molar ratio, the basicity of the catalyst can be enhanced [48–50]. Silva et al. [48] systematically evaluated the effect of the Mg/Al ratio on the basicity and catalytic activity for the methanolysis of soybean oil. They indicated that the LDH catalyst with a Al/(Mg+Al) molar ratio of 0.33 contained many medium strength basic sites, which were preferred for the reaction. The conversion of soybean oil was up to 90% when the reaction was carried out at 230 °C with a methanol to oil molar ratio of 13, a catalyst loading 5 wt%, and 1-h reaction time. This differed from that observed by Martins et al. [49]. They found that an LDH prepared by the co-precipitation method with a Mg/Al molar ratio of 3 and calcined at 450 °C had numerous moderately basic sites, as displayed in Fig. 8. The highest intensity peak indicated the presence of numerous moderately basic sites. The results showed that the highest FAME conversion of about 94.8% was achieved using a methanol to oil molar ratio of 20, and 5 wt% catalyst for 10-h. Recently, Liu et al. [51] indicated that during the thermal decomposition of LDHs, the basic sites of LDHs changed from the OH groups to $\text{M}^{n+}\text{-O}^{2-}$ ($\text{M} = \text{Zn}$

Scheme 1. Triglycerides transesterification reaction with methanol.

Fig. 8. CO₂-TPD profile for the hydrotalcite after calcination at 450 °C (Mg/Al = 3). Reprinted with permission from Ref. [49]. Copyright 2013 AIDIC Servizi S.r.l.

or Al) pairs and isolated O²⁻ ions. Therefore, the basicity of the catalyst was enhanced, which benefited the transesterification. At the same time, Helwani et al. [52] pointed out that an LDH calcined at 850 °C possessed a higher surface area (124.30 m²/g), suitable pore diameter and more medium strength basic sites than that calcined at a low temperature. This sample favored the chemical reaction due to the high electronegativity. The highest conversion of jatropha curcas oil was up to 75.2% under the experimental conditions. They revealed that it was not the leachability of Mg²⁺ and Al³⁺ in the liquid products but the heterogeneity of the surface basicity that was a major concern, possibly due to the weakened Lewis basic sites (O²⁻).

LDHs containing transition metals as a solid base catalyst for this reaction have also been reported [53,54]. The addition of transition metals enhanced the formation of Mg²⁺-O²⁻ and Al³⁺-O²⁻ pairs, which decreased the surface area of the catalyst but increased the basicity, as listed in Table 1. Meanwhile, the pore size of the catalysts was also increased, for instance, the pore size increased from 8 to 10 nm for the catalysts containing Ni²⁺ [54]. However, due to the loss of active metal ions, the reusability and stability of these catalysts were low [53]. It is worth mentioning that Liu et al. [51] indicated that a dehydrated ZnAl LDH obtained at 200 °C was active for the methanolysis of soybean oil. It exhibited high activity with a biodiesel yield of approximately 76%, and after about 150 h the catalyst showed no deactivation, as shown in Fig. 9.

On the other hand, a more recent investigation demonstrated that structured catalysts had good potential for improving the synthesis of biodiesel by transesterification. Gao et al. [55] used KF/Ca-Al LDH as the basic catalyst for the transesterification of methanol with palm oil to produce biodiesel. The fatty acid methyl esters yield reached 99.74% and 97.14% under the optimal conditions and only needed 3 and 1 h, re-

Fig. 9. Stability of ZnAl_{473K} catalyst for transesterification. Reaction conditions: WHSV = 1.0 h⁻¹, 140 °C, 1.7 MPa, feed volume ratio of methanol to soybean oil 1:1. Reproduced from Ref. [51] with permission of The Royal Society of Chemistry.

spectively. Meanwhile, metallic monoliths based on MgAl LDHs were synthesized for the methanolysis of sunflower oil by Reyero et al. [56]. This catalyst gave 62%–77% oil conversion after 10 h under mild conditions.

The growing production of biodiesel generates a large surplus of glycerol as a major byproduct. Therefore, the catalytic conversion of glycerol to high value-added products has been widely studied. The transesterification of glycerol with dimethyl carbonate to produce glycerol carbonate under mild conditions is an attractive way (Scheme 2) [50,57]. Zheng et al. [50] found that Mg-Al layered double hydroxides with a Mg/Al molar ratio of 2, after it was calcined at 400 °C for 4 h, had a large surface area (158.5 m²/g), mid-range density of basic sites (1.10 μmol/m²), and large pore channels, which were suitable for this reaction. The catalyst exhibited high activity with 66.9% of glycerol conversion and 97.1% of selectivity of glycerol carbonate at 70 °C for 3 h. Meanwhile, this catalyst showed good reusability (Fig. 10). The calcined LDHs can be reconstructed back to the original layer structure due to their “memory effect”. The reconstruction of the LDHs by exposing the decomposed sample to water under a CO₂ free atmosphere generated many Brønsted base sites in the interlayer, which favored the transesterification reaction [58,59]. This has been confirmed by Álvarez et al. [5,59]. Recently, Liu et al. [60] reported that transition metal doping enhanced the base strength of the catalyst, which improved the catalytic performance. On the other hand, the catalytic oxidation of glycerol to glyceric acid and dihydroxyacetone and hydrogenolysis of glycerol to propanediols are other important ways to convert glycerol into value-added products. Tongsakul et al. [61] investigated the catalytic oxidation of glycerol in a base-free aqueous solution under ambient conditions over bimetallic Pt_xAu_y-starch/HTLC catalysts. The Pt₆₀Au₄₀-starch/HTLC was efficient for the selec-

Table 1

Textural properties of the materials.

Sample	Surface area (m ² /g)	CO ₂ adsorption (mmol/g)	Ref.
Mg ₃ Al	185.0	0.16	[53]
MgAlFe ₆	124.5	0.18	[53]
MgAlFe ₁₅	100.1	0.24	[53]
MgAlNi ₄	105.5	0.19	[54]
MgAlNi ₁₆	91.6	0.25	[54]

Scheme 2. Glycerol transesterification reaction with dimethyl carbonate.

Fig. 10. Recycling of the catalyst (Mg/Al = 2) in the transesterification of glycerol [50]. Reaction conditions: catalyst 0.45 g, glycerol 43.8 mmol dimethyl carbonate 135 mmol, CH₃OH 7 mL, 70 °C, 3 h.

tive aerobic oxidation of glycerol using molecular oxygen and showed 73% glycerol conversion with 57% glyceric acid yield (Fig. 11). Xia et al. [14] reported that the addition of Ru or Re enhanced the adsorption and activation of H₂ on the surface of the catalysts, which resulted in excellent performance for the hydrogenolysis of biomass-derived glycerol under mild conditions.

Even though much effort has been given to improve the catalyst activity for transesterification, the reusability of the catalyst is generally low. The deactivation of the catalysts during the transesterification reaction may be attributed to the loss of basic sites on the surface of the catalyst and the adsorption of products, which makes catalyst regeneration hard. Structured catalysts with a suitable pore size and reusability should be paid more attention.

Many other catalytic applications for LDHs and their derivatives have also been widely reported in recent years, such as catalysis for the aerobic oxidation of alcohols [62,63], catalytic aldol condensation [64,65], and as catalysts for biomass utilization [66,67] and decomposition of pollutants [68,69].

4. Conclusions and perspectives

We briefly introduced the synthesis methods of LDHs with focus on their catalytic applications for hydrogen production and a biorefinery. The several important observations made are summarized as follows.

LDHs have a unique lamellae structure and special properties. Therefore, they can be widely applied in many fields. The investigation of their structure and the relationship between their morphology and catalytic performance is significant for the design of new materials.

LDHs and their derivatives exhibited excellent catalytic performance for hydrogen production and a biorefinery, which was attributed to their special structure with high dispersion of active centers, medium basicity, and suitable pore size. Meanwhile, there are many factors that affect the structure-activity relationship of the catalyst. Therefore, more efforts should be given to this field.

Fig. 11. Glycerol conversion, product yield, and glyceric acid (GA) selectivity versus time on stream. Glycerol conversion (■), GA yield (●), tartronic acid yield (Δ), glycolic acid yield (▽), oxalic acid yield (☆), and GA selectivity (◇). Reaction conditions: Glycerol 0.5 mmol, H₂O 2 mL, catalyst 20 mg, oxygen flow 10 mL/min, 25 °C. Reprinted with permission from Ref. [61]. Copyright 2013 American Chemical Society.

As heterogeneous basic catalysts, LDHs and their derivatives demonstrated special advantages compared to conventional homogeneous catalysts, which have severe pollution and corrosion problems. However, the reusability and stability of LDH related catalysts need to be further improved. The design of LDHs with one or two active components including a transition metal or noble metal has been widely studied. However, there are less comprehensive studies on the synergistic interaction of the active components and the synergistic catalytic mechanism, which effectively promote the catalytic activity and are significant for the rational design of new catalysts with special structure and active components. In the future, more efforts should be given to the synthesis and application of LDH related catalysts with multiple components and high activity in the green chemical industry.

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Graphical Abstract

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Layered double hydroxide and related catalysts for hydrogen production and a biorefinery

Wei Wang, Zhenxin Xu, Zhanglong Guo, Chengfa Jiang, Wei Chu*
Sichuan University

Homogeneously dispersed nano-metal oxides can be obtained by the controlled thermal decomposition of layered double hydroxide precursors. These catalysts have many advantages, such as high specific surface areas, basic character, high dispersion of the active centers and thermal stability against sintering. They exhibit excellent catalytic activity for hydrogen production.

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水滑石类催化剂催化制氢及生物炼制

王伟^{a,b}, 徐振新^a, 郭章龙^{a,b}, 江成发^a, 储伟^{a,b,*}

^a四川大学化学工程学院, 四川成都610065

^b四川大学四川省环境保护催化与材料工程研究中心, 四川成都610064

摘要: 近年来, 水滑石由于其独特的性质受到越来越多的关注. 作为非均相固体催化剂, 水滑石及其衍生物具有优良的催化性能, 因此得到了广泛研究和应用. 本文简述了水滑石的几种合成方法, 重点介绍了水滑石类催化剂在催化制氢和生物炼制方面的应用, 并预测了水滑石类材料在新材料合成及环境友好催化体系中的应用前景.

关键词: 水滑石; 非均相催化剂; 水蒸气重整; 制氢; 生物炼制; 酯交换反应

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*通讯联系人. 电话: (028)85403836; 传真: (028)85461108; 电子邮箱: chuwei1965@scu.edu.cn, chuwei1965scu@163.com

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