#### ARTICLE



## Catalytic transfer hydrogenation of furfural into furfuryl alcohol over Ni-Fe-layered double hydroxide catalysts

Tao Wang<sup>1</sup> | Aiyun Hu<sup>1</sup> | Haijun Wang<sup>1</sup> | Yongmei Xia<sup>2</sup>

Revised: 6 March 2019

<sup>1</sup>Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi, China <sup>2</sup>State Key Laboratory of Food Science & Technology, Jiangnan University, Wuxi, China

#### Correspondence

Haijun Wang, Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Jiangsu, Wuxi 214122, China. Email: wanghj329@outlook.com

#### **Funding information**

Ministry of Education of the People's Republic of China & SAFEA for the 111 Project, Grant/Award Number: B13025; SAFEA; MOE, Grant/Award Number: B13025

#### 1 | INTRODUCTION

The development of the global economy has led to the excessive depletion of fossil resources and the further deterioration of the environment, which has been paid much attention by the world.<sup>[1]</sup> In the last few years, lignocellulosic biomass has attracted strong interest due to its abundant, renewable, and easily obtainable properties.<sup>[2]</sup> Consequently, the production of biofuels and chemicals from lignocellulosic biomass becomes an effective way to alleviate the energy crisis and improve environmental issues.<sup>[3-5]</sup> Furfural (FF) can be produced from the lignocellulosic biomass through multistep acid-catalyzed reactions, and has also been deemed as one of the most significant biomass-derived platform molecules for the synthesis of fine chemicals and liquids fuels.<sup>[6–8]</sup> Hydrogenation of FF is a very interesting exploration idea because many of its downstream products are value-added chemicals, such furfuryl alcohol (FAOL), as 

Layered double hydroxides (LDHs) and their derivatives have been reported to be widely used as heterogeneous catalysts in various reactions. Herein, Ni-Fe LDHs with the controlled Ni/Fe molar ratios (2:1, 3:1, 4:1) were synthesized via an easy hydrothermal method, which were used to catalyze the selective reduction of biomass-derived furfural into furfuryl alcohol using 2-propanol as a H-donor under autogenous pressure and characterized using FT-IR, XRD, TGA, BET, SEM, NH<sub>3</sub>-TPD, and CO<sub>2</sub>-TPD. It was found that the LDH with a Ni/Fe molar ratio of 3:1 demonstrated the best catalytic activity among the LDHs with different Ni/Fe molar ratios, which showed 97.0% conversion of furfural and 90.2% yield of furfuryl alcohol at 140°C for 5 hr. This was attributable to the synergistic effect of acidic sites and basic sites of the catalyst.

#### **KEYWORDS**

2-propanol, catalytic transfer hydrogenation, furfural, furfuryl alcohol, Ni-Fe (3/1) LDH

tetrahydrofurfural, tetrahydrofurfuryl alcohol, 2-methylfuran, and 2-methyltetrahydrofuran.<sup>[9–13]</sup> Among these compounds, FAOL is viewed as a very important compound, which has wide applications in the manufacture of resins, lubricants, adhesives, and synthetic fibers.<sup>[14]</sup>

With respect to the production of FAOL, it is normally generated through chemoselective reduction of FF over various homogeneous or heterogeneous catalysts. The industrialized production of FAOL is mainly carried out from the hydrogenation of furfural over copper chromate at high hydrogen pressure.<sup>[8,15]</sup> It is clear that this catalyst is costly and has carcinogenic chromium causing serious environmental pollution. What is more, the high cost of hydrogen transport and storage and its easy burning and explosiveness are the key factors that must be considered in practical applications. Most of the production of FF occurs in China, which provides cheap raw materials for downstream furanbased products. With the rapid development of China's

© 2019 The Chemical Society Located in Taipei & Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

2

economy, the amount of furan-based compounds increases rapidly, and the market price of these substances is much higher than that of FF. Therefore, it is very desirable to improve the deep processing technology of FF to achieve higher economic benefit.

Recently, catalytic transfer hydrogenation (CTH) of FF to FAOL is of great interest to researchers. This process employs inexpensive and abundant alcohol to avoid the large number of problems caused by the use of hydrogen. For example, in recent years, the application of Zr- and Hf-based catalysts to CTH reaction has always been the focus, including Li-Zr-BEA,<sup>[16]</sup> Hf-BEA,<sup>[17]</sup> PhP-Hf,<sup>[18]</sup> Zr-Has,<sup>[19]</sup> Zr-PhyA,<sup>[20]</sup> ZrPN.<sup>[21]</sup> and Zr-FDCA-T<sup>[22]</sup> etc., which demonstrated good catalytic performance. In addition, various metal oxides have been discovered to catalyze the reduction of FF by hydrogen transfer, such as MgAlO<sub>1</sub>, [23] La<sub>2</sub>O<sub>3</sub>, [24] and Al<sub>2</sub>O<sub>3</sub>. [25]Although much effort has been devoted to this aspect of the study, some disadvantages including low catalyst reactivity and harsh reaction conditions remain. Based on the industrial demand, it is very meaningful to develop cheap and efficient catalysts in the conversion of FF to FAOL.

Since the last few years, the Zr- and Hf-based catalysts have been widely reported for the reduction of the carbonyl group, but the reports of other metals were few. Recently, a series of Ni-based and Fe-based catalysts, such as NiO,<sup>[26]</sup> Co/SBA-15,<sup>[27]</sup>  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>@HAP,<sup>[28]</sup> NiFe<sub>2</sub>O<sub>4</sub>,<sup>[29]</sup> Fe-L1/C-800,<sup>[30]</sup> Fe(NiFe)O<sub>4</sub>-SiO<sub>2</sub>,<sup>[31]</sup> and NiFe/SiO<sub>2</sub>,<sup>[32]</sup> have been applied to CTH of FF into FAOL. The catalysts prepared by these metals with abundant reserves on the earth are of great application value. Based on the above reports, we have stimulated our enthusiasm for exploring non-noble-metal-based catalyst systems.

In this work, Ni-Fe LDHs with variable Ni/Fe molar ratios were synthesized using a simple hydrothermal method. LDHs have the general formula  $[M_{1-x}^{2+}M_{x}^{3+} (OH)_{2}]^{x+} (A^{n-})_{x/n}$ mH<sub>2</sub>O, where x ranges from 0.20 to 0.33 and  $M^{2+}$  and  $M^{3+}$ usually stand for divalent (Co, Ca, Mg, Cu, Ni, and Mn) and trivalent (Fe, Al, and Cr) metallic cations, respectively.<sup>[33]</sup> A is the interlayer anion of charge n, including  $CO_3^{2-}$ ,  $SO_4^{2-}$ , Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup>, etc.<sup>[34]</sup> Meanwhile, monometallic hydroxide catalysts (Ni(OH)<sub>2</sub> and Fe(OH)<sub>3</sub>) were obtained by means of sedimentation. It was found that Ni-Fe LDHs with a Ni/Fe molar ratio of 3:1 exhibited better catalytic activity for the synthesis of FAOL through CTH reaction compared with the other catalysts. The reasons for the different catalytic effects were discussed in detail. The effects of reaction temperature, reaction time, and the amount of catalysts on the conversion of FF to FAOL were also investigated. Finally, the characterization of fresh and used catalysts was carried out, and the possible reaction mechanism was proposed.

**FIGURE 1** FT-IR spectra of LDHs with different Ni/Fe molar ratios

## 2 | RESULTS AND DISCUSSION

#### 2.1 | Characterization of catalysts

Catalyst characterization methods can be seen in the Support Information. The Fourier transform-infrared (FT-IR) spectra in the 400–4,000 cm<sup>-1</sup> range of the as-prepared catalysts are included in Figure 1. A broad absorption band at around 3,460 cm<sup>-1</sup> was attributed to the stretching vibration of the – OH groups. The band at 1,625 cm<sup>-1</sup> was assigned to the bending motion of interlayer water.<sup>[35]</sup> The absorption bands appearing at 1,363 cm<sup>-1</sup> and 834 cm<sup>-1</sup> were assignable to the asymmetric stretching mode and out-of-plane deformation vibration of interlayer carbonate species.<sup>[36]</sup> The peaks at 800–400 cm<sup>-1</sup> were due to metal oxygen vibrational modes



**FIGURE 2** XRD patterns of LDHs with different Ni/Fe molar ratios



implying Ni–O, Fe–O, and Ni–O–Fe bonds in brucite-type  ${\rm layers}^{[37,38]}$ 

The powder XRD patterns of as-synthesized LDHs with different Ni/Fe molar ratios are depicted in Figure 2, which demonstrated clearly the characteristic diffraction peaks corresponding to the hydrotalcite-like LDH family, that is, (003), (006), (012), (015), (018), (110), and (113) at 20 values 11.26, 22.76, 34.28, 38.64, 45.84, 59.76, and 61.02°, respectively. This value is consistent with the data reported in other literature.<sup>[39]</sup> The layer spacings of the (003), (006), and (012) crystal planes were 0.80, 0.40, and 0.27 nm, respectively, and the multiple relationship of the lattice spacing also shows that the hydrotalcites have a well-developed layered structure. In addition, these crystal faces were sharp, indicating that the hydrotalcite had a complete structure and good crystallinity. It can be seen that impurity peaks of the Ni-Fe (3/1) LDH were relatively less, indicating that its crystallinity was better than others.

From Figure 3, it was shown that all the samples had similar thermal decomposition processes. Firstly, a small decrease in the sample quantity of about  $65^{\circ}$ C should be because of the removal of residual ethanol in the layered structure. Then, the second stage of weight loss in the temperature range from 100 to 200°C was due to the loss of physically absorbed and interlayer water. In the end, the decomposition stage occurred in the range of 250–600°C, which was attributed to the further loss of water in the interlayer structure, the removal of interlayer carbonate anions, and the dehydroxylation of the Ni–Fe LDHs.<sup>[40]</sup> This process results in the destruction of the layered structure and the formation of bimetallic composite oxides when heated to  $600^{\circ}$ C. It proved that the Ni–Fe LDH catalysts had pronounced stability at the reaction temperatures (below  $160^{\circ}$ C).

SEM was conducted to investigate the morphology of the surface of Ni–Fe LDHs, and the images are presented in Figure 4. SEM indicated that the Ni–Fe LDHs had a distinct layered structure. It can be observed that the Ni–Fe (3/1) LDH had better lamellar structures among the LDHs with different Ni/Fe molar ratios. It was also found that the fine granular aggregates were dispersed well on the nanoplates of the Ni–Fe (3/1) LDH.

The porous properties of the Ni–Fe LDHs were analyzed using the N<sub>2</sub> adsorption–desorption method. As shown in Figure 5, the N<sub>2</sub> adsorption–desorption isotherms of the Ni–Fe LDHs belong to type III according to the IUPAC classification, indicating that the macroporous structure of the materials existed. The results of the Brunauer–Emmett–Teller (BET) surface area, pore volume, and average pore size are included in Table 1. By comparison with the others, the Ni–Fe (3/1) LDH has a larger pore volume and average pore diameter, which is conducive to more sufficient contact between reactants and the active center of the catalyst.<sup>[41]</sup>



**FIGURE 3** Thermogravimetric curves of (a) Ni–Fe (2/1) LDH, (b) Ni–Fe (3/1) LDH, and (c) Ni–Fe (4/1) LDH

According to previous reports,  $^{[42-44]}$  acidic sites and basic sites play synergistic catalytic roles in the CTH of carbonyl compounds. Therefore, the acidity and basicity of catalysts were characterized by CO<sub>2</sub>-TPD and NH<sub>3</sub>-TPD (Figure 6), respectively. Compared with others, it can be seen that Ni–Fe (3/1) LDH had higher acidity and basicity. First, the acidic sites (stemming from Ni<sup>2+</sup> and Fe<sup>3+</sup>) and the basic sites (originating from –OH) assist in the





**FIGURE 4** Representative SEM images of (a) Ni–Fe (2/1) LDH, (b) Ni–Fe (3/1) LDH, and (c) Ni–Fe (4/1) LDH

adsorption of 2-propanol onto Ni–Fe LDHs, resulting in the formation of isopropoxide and hydride by dissociation.<sup>[40]</sup> Furthermore, the carbonyl groups in the substrate molecules were activated by acidic Ni<sup>2+</sup> and Fe<sup>3+</sup> species and are able to generate a transition state with six links to accomplish the



**FIGURE 5** Nitrogen adsorption–desorption curves and the corresponding pore size distribution of (a) Ni–Fe (2/1) LDH, (b) Ni–Fe (3/1) LDH, and (c) Ni–Fe (4/1) LDH

hydrogen transfer route to yield corresponding alcohol compounds and acetone.<sup>[26]</sup> From the above discussion it was clear that the higher catalytic performance of Ni–Fe (3/1) LDH was probably due to its high acid and base amount.

Entry	LDH material	Surface area (m²/g)	Pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
1	Ni-Fe (2/1)	188	0.70	3.4
2	Ni–Fe (3/1)	164	0.74	5.6
3	Ni-Fe (4/1)	179	0.62	4.9



**FIGURE 6** NH<sub>3</sub>-TPD spectra (a) and CO<sub>2</sub>-TPD spectra (b) of Ni–Fe LDHs

**TABLE 2** The catalytic performance of various catalysts in the CTH of  $FF^a$ 

Entry	Catalysts	Conversion (%)	Yield (%)	Selectivity (%)
1	None	0	0	0
2	Ni(OH) <sub>2</sub>	6.7	3.2	47.8
3	Fe(OH) <sub>3</sub>	70.2	40.6	57.8
4	Ni-Fe (2/1) LDH	73.2	61.1	83.5
5	Ni-Fe (3/1) LDH	77.0	70.8	91.9
6	Ni-Fe (4/1) LDH	74.3	63.7	85.7

<sup>a</sup>Reaction conditions: catalyst amount: 0.10 g; FF: 1 mmol; 2-propanol: 5 mL; temperature: 140°C; time: 5 hr.

# **2.2** | Conversion of FF to FAOL by various catalysts

To select the most active catalyst, a series of catalysts were applied in the CTH of FF to FAOL using 2-propanol as a hydrogen donor, and the results are listed in Table 2. It showed that the reaction did not proceed in the absence of any catalyst (Table 2, entry 1). The conversion of FF was negligible in the presence of Ni(OH)<sub>2</sub> probably due to its weak basicity (Table 2, entry 2).<sup>[42]</sup> Although Fe(OH)<sub>3</sub> produced 70.2% conversion of FF, it had low selectivity to FAOL (Table 2, entry 3). However, it was observed that the LDH with a Ni/Fe molar ratio of 3:1 showed the best catalytic activity among the LDHs with three different Ni/Fe molar ratios, which revealed 77.0% conversion of FF and 70.8% yield of FAOL at 140°C for 5 hr (Table 2, entries

4, 5, and 6) and accorded well with the results of acidity and basicity analysis.

# **2.3** | Conversion of FF to FAOL by Ni–Fe (3/1) LDH

From what has been discussed above, Ni–Fe (3/1) LDH showed the best catalytic performance in converting FF into FAOL. Thus, it was used to study the conversion of FF into FAOL. Furthermore, the influence of reaction parameters on the conversion of FF to FAOL was also discussed.

# **2.4** | Effects of reaction temperature and reaction time

The effects of reaction temperature and reaction time on the synthesis of FAOL from FF were studied by varying the temperature in the range between 120 and 150°C and the time in the range between 1 and 6 hr, and the results are shown in Figure 7. It can be seen that the reaction temperature and reaction time had a dramatic influence on the CTH reaction of FF. For instance, only 26.7% of FAOL yield was achieved at 120°C with a reaction time of 1 hr. However, 90.2% yield of FAOL was obtained when the reaction was carried out at 140°C after 5 hr, which indicated that high reaction temperature and long reaction time were beneficial to the production of FAOL from FF at the beginning. During the experiments, traces of side-product (2-[diisopropoxymethyl]furan) were observed, which were generated by acetalization of FF and 2-propanol. Although increasing the reaction temperature to 150°C or extending the reaction time to 6 hr can further promote conversion of FF, the yield of FAOL was almost constant and the selectivity of FAOL was slightly lowered. This was possibly due to the formation of a new by-product (2-[isopropoxy]methyl furan) at higher reaction temperature with a longer reaction time, which could be formed by etherification between FAOL and 2-propanol. Considering the energy input in the reaction, 140°C and 5 hr were thus selected as the most appropriate reaction parameters under our reaction conditions.



**FIGURE 7** Effect of reaction temperature and time on the FF conversion and FAOL yield. Reaction conditions: Catalyst amount: 0.20 g, FF: 1 mmol, 2-propanol: 5 mL



**FIGURE 8** Effect of catalyst amount. Reaction conditions: FF: 1 mmol, 2-propanol: 5 mL, temperature: 140°C, and time: 5 hr

TABLE 3 Effect of different solvents in the CTH of FF<sup>a</sup>

Entry	Solvent	FF conversion (%)	FAOL yield (%)
1	Methanol	32.8	3.6
2	Ethanol	67.8	49.4
3	2-propanol	97.0	90.2
4	2-butanol	94.5	87.7
5	tert-butanol	0.7	0

<sup>a</sup>Reaction conditions: catalyst amount: 0.20 g; FF: 1 mmol; 2-propanol: 5 mL; temperature: 140°C; and time: 5 hr.

## 2.5 | Effects of the catalyst amount

Figure 8 displays the influence of the Ni-Fe (3/1) LDH dosage on the conversion of FF to FAOL in 2-propanol at 140°C in 5 hr. It was observed that the conversion of FF and the yield of FAOL significantly increased when the amount of catalyst increased from 0.05 to 0.20 g, which could be due to more available catalytic sites. With an increment of catalyst dosage from 0.20 to 0.25 g, the conversion of FF increased, while the FAOL yield changes almost nothing,

which may be principally attributed to more catalytic sites promoting the generation of more by-products including 2-(isopropoxy)methyl furan and 2-(diisopropoxymethyl) furan. Thus, the optimum catalyst amount of 0.20 g in this work was used in subsequent research

## 2.6 | Effects of the solvent

We also studied the catalytic performance of the prepared Ni-Fe (3/1) LDH for CTH of FF to FAOL in different solvents, and the results are summarized in Table 3. It can be seen that the structure of solvents plays a key role in the conversion of FF and the yield of FAOL. No FAOL was obtained when tert-Butanol was employed as the hydrogen donor, which was ascribed to difficult form of the sixmembered ring structure in the MPV reaction process without hydrogen atoms on the carbon atom (Table 3, entry 5). It was clear that the primary alcohols, including methanol and ethanol, gave poor yield of FAOL (Table 3, entries 1 and 2). In contrast, 90.2% FAOL yield was obtained using 2-PrOH as the solvent, and 87.7% FAOL yield was achieved using 2-BuOH as the solvent (Table 3, entries 3 and 4). It can be seen that the secondary alcohols achieved better conversion of FF and yield of FAOL than the primary alcohols, mainly because the dehydrogenation of secondary alcohols is easier than that of primary alcohols shown in previous studies.<sup>[45]</sup>

## 2.7 | Effects of various substrates

The versatility of the Ni–Fe (3/1) LDH catalyst was investigated by CTH of several carbonyl compounds with various structures, and the results are shown in Table 4. Compared with other compounds, FF showed a higher activity owing to a weaker steric effect (Table 4, entry 1). It is exciting that the Ni–Fe (3/1) LDH catalyst has been proved to have a higher than 90% selectivity of the target products. It can also been seen that that the reaction of aldehydes is easier than that of ketones, because of the steric effect and the electron giving effect of alkyl in ketones<sup>[19,29]</sup>

TABLE 4 Catalytic transfer hydrogenation of different carbonyl compounds over Ni-Fe (3/1) LDH<sup>a</sup>

Entry	Substrate	Product	T (hr)	Conv. (%)	Yield (%)	Sel. (%)
1	$\sim$	но	5	97.0	90.2	93.0
2		ноУ	8	80.2	73.2	91.3
3		NO	10	78.1	72.2	92.4
4	$\sim$	NO	8	84.3	78.8	93.5
5	$\rightarrow \bigcirc$		8	70.2	63.4	90.3

Note. T: time; Con.: conversion: Sel: selectivity.

<sup>a</sup>Reaction conditions: catalyst amount: 0.20 g; 2-propanol: 5 mL; temperature: 140°C.



**FIGURE 9** Reusability of the catalyst. Reaction conditions: Catalyst amount: 0.20 g, FF: 1 mmol, 2-propanol: 5 mL, and temperature: 140°C, time: 5 hr

#### 2.8 | Reusability and leaching of the catalyst

To examine the reusability of the Ni–Fe (3/1) LDH catalyst, the catalyst was separated by centrifugation, washed with isopropanol ( $3 \times 10$  mL) and dried in a vacuum oven at  $80^{\circ}$ C for 6 hr before reuse. The catalytic activity of the used catalyst was examined under the identical conditions. It was found that the Ni–Fe (3/1) LDH catalyst could be repeatedly used up to five cycles without any distinct loss in its catalytic performance (Figure 9). Moreover, the leaching property of the Ni–Fe (3/1) LDH catalyst was studied via filtering the catalyst from the system after the reaction proceeded for 3 hr at 140°C, and no reaction took place even after another 3 hr (Figure 10). Meanwhile, the used Ni–Fe (3/1) LDH catalyst after five runs was characterized using



**FIGURE 10** Leaching of the catalyst. Reaction conditions: Catalyst amount: 0.20 g, FF: 1 mmol, 2-propanol: 5 mL, and temperature: 140°C



JOURNAL OF THE CHINESE

**FIGURE 11** TG curves (a), XRD pattern (b), FT-IR spectrum (c), and SEM image (d) of Ni–Fe (3/1) LDH after five cycles



**SCHEME 1** Possible reaction mechanism for the CTH of FF to FAOL over Ni–Fe (3/1) LDH using 2-propanol as a hydrogen donor

TG, XRD, FT-IR, and SEM (Figure 11). The results suggested that the structure and properties of the Ni–Fe (3/1) LDH catalyst went through slight change after being reused for five cycles. Therefore, the as-synthesized catalyst Ni–Fe (3/1) LDH was stable under the studied reaction conditions.

## 2.9 | Reaction mechanism

On the basis of the above discussion, we put forward a plausible reaction mechanism for the CTH of FF to FAOL over Ni–Fe (3/1) LDH (Scheme 1), which is consistent with previous studies.<sup>[18,22,26,29]</sup> We considered the synergistic effect of acidic sites (resulting from Ni<sup>2+</sup> and Fe<sup>3+</sup>) and basic sites (originating from –OH) of Ni–Fe (3/1) LDH in CTH of FF to FAOL. First, 2-propanol was adsorbed on the Ni–Fe (3/1) LDH and interacted with the acidic sites (Ni<sup>2+</sup> and Fe<sup>3+</sup>) and basic sites (–OH) on the catalyst, causing it to dissociate into the corresponding alkoxide and protons.<sup>[18,22]</sup> Subsequently, the carbonyl group of furfural may be activated by the acidic site to form a transitional state with six links.<sup>[26,29]</sup> Finally, the system can obtain free furfural alcohol and acetone by hydrogen transfer. During the reactions, some by-products including 2-(isopropoxy)methyl furan and 2-(diisopropoxymethyl)furan could be generated by the etherification of FAOL with 2-propanol and the acetalization of FF with 2-propanol, respectively.

#### **3** | EXPERIMENTAL

#### 3.1 | Materials

Furfuryl alcohol was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Nickel nitrate hexahydrate, iron nitrate hydrate, urea, ammonia water, furfural, 2-propanol, and other chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All reagents were of analytical grade and used without further purification. Deionized water was produced by using a laboratory waterpurification system (RO DI Digital plus).

#### 3.2 | Preparation of Ni–Fe LDHs

The Ni-Fe-LDHs with different Ni/Fe molar ratios were synthesized using the hydrothermal method based on previous literature,<sup>[45,47]</sup> although some changes have been made here. Briefly, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (6, 9, and 12 mmol) and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (3 mmol) and a certain amount of urea were dissolved in 160 mL deionized water, in which the amount of urea is 3.3 times that of the total metal ion concentration. The mixture was magnetically stirred at room temperature for 1 hr and transferred to a 180 mL Teflon-lined stainlesssteel autoclave for hydrothermal reaction at 140°C for 20 hr under autogenous pressure. The reactor was then naturally cooled down to room temperature. The product was washed with deionized water and anhydrous ethanol several times by suction filtration, and dried in a vacuum oven at 60°C overnight to obtain a Ni-Fe-LDHs composite, which was ground and put into a desiccator for use. The prepared materials were denoted as Ni-Fe (2/1) LDH, Ni-Fe (3/1) LDH, and Ni-Fe (4/1) LDH.

#### 3.3 | Preparation of Fe(OH)<sub>3</sub> and Ni(OH)<sub>2</sub>

In a general synthetic run, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was dissolved in deionized water to prepare a 0.25 M solution. Ammonia water (25–28 wt%) was slowly added to adjust the solution pH value around 9 with vigorous stirring, and then the resulted suspension was aged at room temperature for 24 hr. Finally, the precipitate was isolated by centrifugation, washed with deionized water several times, and dried overnight at 80°C. The same process was used in the preparation of Ni(OH)<sub>2</sub>.

#### 3.4 | Catalytic reactions

Catalyst characterization methods can be seen in the Support Information. The activity of the synthesized catalyst was detected by catalytic transfer hydrogenation of furfural. In a typical run, furfural (1 mmol), catalyst (0.2 g), and isopropanol (5 mL) were introduced into the 25 mL Teflon lined stainless steel autoclave. The reaction was carried out using magnetic stirring and heating at suitable temperatures for a desired time. After cooling the reactor to room temperature, the resulting liquid samples were collected and analyzed quantitatively by gas chromatography (GC 9790II) using naphthalene as the internal standard, and the identification of the products was done by GC–MS (GCMS-QP2010Ultra). The yield of FAOL, the conversion of FF, and the selectivity to FAOL were calculated based on the following formula

Yield of FAOL(%) = 
$$\frac{\text{Final moles of FAOL}}{\text{Initial moles of FF}} \times 100$$
(1)

Conversion of FF(%)  
= 
$$\frac{\text{Initial moles of FF} - \text{Final moles of FF}}{\text{Initial moles of FF}} \times 100$$
 (2)

Selectivity to FAOL(%)  
= 
$$\frac{\text{Final moles of FAOL}}{\text{Initial moles of FF} - \text{Final moles of FF}} \times 100$$
 (3)

## 4 | CONCLUSIONS

In summary, the Ni–Fe (3/1) LDH catalysts were synthesized using a simple hydrothermal method and were employed in catalytic transfer hydrogenation of FF to FAOL using isopropanol as a H-donor. The catalysts could be reused for up to five consecutive runs without a distinct loss in catalytic activity. The remarkable catalytic performance was attributed to the synergistic effect of acidic sites (Ni<sup>2+</sup> and Fe<sup>3+</sup>) and basic sites (–OH) of the catalyst. What is more, the Ni–Fe (3/1) LDH catalysts could be applied to the catalytic transfer hydrogenation of other aldehydes and ketones.

#### ACKNOWLEDGMENTS

This work was financial supported by the Ministry of Education of the People's Republic of China & SAFEA for the 111 Project (B13025).

9

#### ORCID

Haijun Wang b https://orcid.org/0000-0003-2857-5861

#### REFERENCES

- H. Z. Tian, L. Lu, J. M. Hao, J. J. Gao, K. Cheng, K. Y. Liu, P. P. Qiu, C. Y. Zhu, *Energy Fuel* **2013**, *27*, 601.
- [2] P. Gallezot, Chem. Soc. Rev. 2012, 41, 1538.
- [3] C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, *Science* 2012, 337, 695.
- [4] M. Besson, P. Gallezot, C. Pinel, Chem. Rev. 2014, 114, 1827.
- [5] G. Kumar, S. Shobana, W. H. Chen, Q. V. Bach, H. K. Sang, A. E. Atabani, J. S. Chang, *Green Chem.* 2016, 19, 44.
- [6] K. Yan, G. Wu, T. Lafleur, C. Jarvis, *Renew. Sust. Energ. Rev.* 2014, 38, 663.
- [7] P. Zhou, Z. H. Zhang, Cat. Sci. Technol. 2016, 6, 3694.
- [8] R. Mariscal, P. Mairelestorres, M. Ojeda, I. Sádaba, M. L. Granados, *Energy Environ. Sci.* 2016, 9, 1144.
- [9] H. Chen, H. H. Ruan, X. L. Lu, J. Fu, T. Langrish, X. Y. Lu, *Mol. Catal.* 2018, 445, 94.
- [10] R. J. Huang, Q. Q. Cui, Q. Q. Yuan, H. H. Wu, Y. J. Guan, P. Wu, ACS Sustain. Chem. Eng. 2018, 6, 6957.
- [11] Y. L. Yang, J. P. Ma, X. Q. Jia, Z. T. Du, Y. Duan, J. Xu, *RSC Adv.* 2016, 6, 51221.
- [12] N. S. Date, A. Hengne, K. W. Huang, R. C. Chikate, C. V. Rode, *Green Chem.* 2018, 20, 2027.
- [13] X. Chang, A. F. Liu, B. Cai, J. Y. Luo, H. Pan, Y. B. Huang, *ChemSusChem* 2016, 9, 1.
- [14] Y. Nakagawa, M. Tamura, K. Tomishige, ACS Catal. 2013, 3, 2655.
- [15] D. Liu, D. Zemlyanov, T. Wu, R. J. Lobo-Lapidus, J. A. Dumesic, J. T. Miller, C. L. Marshall, *J. Catal.* 2013, 299, 336.
- [16] A. Prasertsab, T. Maihom, M. Probst, C. Wattanakit, J. Limtrakul, *Inorg. Chem.* 2018, 13, 6.
- [17] Y. Injongkol, T. Maihom, P. Treesukul, J. Sirijaraensre,
   B. Boekfa, J. Limtrakul, *Phys. Chem. Chem. Phys.* 2017, 19(35), 24042.
- [18] H. Li, Y. Li, Z. Fang, R. L. Smith, Catal. Today 2019, 319, 84.
- [19] Y. F. Sha, Z. H. Xiao, H. C. Zhou, K. L. Yang, Y. M. Song, N. Li, R. X. He, K. D. Zhi, Q. S. Liu, *Green Chem.* **2017**, *19*, 4829.
- [20] J. L. Song, B. W. Zhou, H. C. Zhou, L. Q. Wu, Q. L. Meng, Z. M. Liu, B. X. Han, Angew. Chem. Int. Ed. 2015, 54, 9399.
- [21] H. Li, J. He, A. Riisager, S. Saravanamurugan, B. A. Song, S. Yang, ACS Catal. 2016, 6, 7722.
- [22] H. Li, X. F. Liu, T. T. Yang, W. F. Zhao, S. Saravanamurugan, S. Yang, *ChemSusChem* **2017**, *10*, 1761.
- [23] J. R. Ruiz, C. Jiménez-Sanchidrián, J. M. Hidalgo, J. M. Marinas, J. Mol. Catal. A-Chem. 2006, 246, 190.
- [24] T. A. Natsir, T. Hara, N. Ichikuni, S. Shimazu, Bull. Chem. Soc. Jpn. 2018, 91, 1561.
- [25] R. López-Asensio, J. A. Cecilia, C. P. Jiménez-Gómez, C. García-Sancho, R. Moreno-Tost, P. Maireles-Torres, *Appl. Catal. A Gen.* 2018, 556, 1.

- [26] J. He, L. Schill, S. Yang, A. Riisager, ACS Sustain. Chem. Eng. 2018, 6, 17220.
- [27] M. Audemar, C. Ciotonea, K. D. O. Vigier, S. Royer, A. Ungureanu, B. Dragoi, E. Dumitriu, F. Jérôme, *ChemSusChem* 2015, 8, 1885.
- [28] F. Wang, Z. H. Zhang, ACS Sustain. Chem. Eng. 2017, 5, 942.
- [29] J. He, S. Yang, A. Riisager, Cat. Sci. Technol. 2018, 8, 790.
- [30] J. Li, J. L. Liu, H. J. Zhou, Y. Fu, ChemSusChem 2016, 9, 1339.
- [31] A. Halilu, T. H. Ali, A. Y. Atta, P. Sudarsanam, S. K. Bhargava, S. B. A. Hamid, *Energy Fuel* **2016**, *30*, 2216.
- [32] P. Jia, X. Lan, X. Li, T. Wang ACS Sustain. Chem. Eng. 2018, 6, 13287.
- [33] C. Jaubertie, M. J. Holgado, M. S. S. Román, V. Rives, *Chem. Mater.* 2006, 18, 3114.
- [34] L. Zhao, X. Y. Li, X. Quan, G. H. Chen, *Environ. Sci. Technol.* 2011, 45, 5373.
- [35] J. Graus, C. J. Bueno-Alejo, J. L. Hueso, Catalysts 2018, 8, 354.
- [36] Z. X. Yan, Z. H. Xu, L. Yue, L. Shi, L. Y. Huang, *Chin. J. Catal.* 2018, 39, 1919.
- [37] S. Kannan, A. Narayanan, C. S. Swamy, J. Mater. Sci. 1996, 31, 2353.
- [38] P. H. Holgado, M. J. Holgado, M. S. S. Román, V. Rives, *Mater. Chem. Phys.* 2015, 151, 140.
- [39] S. Chitravathi, S. Kumar, N. Munichandraiah, RSC Adv. 2016, 6, 103106.
- [40] F. B. Saiah, B. L. Su, N. Bettahar, J. Hazard. Mater. 2009, 165, 206.
- [41] Y. D. Xie, F. Li, J. J. Wang, R. Y. Wang, H. J. Wang, X. Liu, Y. M. Xia, *Mol. Catal.* 2017, 442, 107.
- [42] X. Tang, H. W. Chen, L. Hu, W. W. Hao, Y. Sun, X. H. Zeng, L. Lin, S. J. Liu, *Appl. Catal. B Environ.* 2014, 47, 827.
- [43] J. J. Wang, R. Y. Wang, H. M. Zi, H. J. Wang, Y. M. Xia, X. Liu, J. Chin. Chem. Soc. 2018, 65, 750.
- [44] R. Y. Wang, J. J. Wang, H. M. Zi, H. J. Wang, Y. M. Xia, X. Liu, J. Chin. Chem. Soc. 2018, 65, 1398.
- [45] F. K. Li, L. J. France, Z. P. Cai, Y. W. Li, S. J. Liu, H. M. Lou, J. X. Long, X. H. Li, *Appl. Catal. B Environ.* 2017, 214, 67.
- [46] A. Yasir, K. Shukla, V. C. Srivastava, *Energy Fuel* 2017, 31, 9890.
- [47] Y. Arai, M. Ogawa, Appl. Clay Sci. 2009, 42, 601.

## SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Wang T, Hu A, Wang H, Xia Y. Catalytic transfer hydrogenation of furfural into furfuryl alcohol over Ni–Fe-layered double hydroxide catalysts. *J Chin Chem Soc*. 2019;1–9. https://doi.org/10.1002/jccs.201800477