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# $Fe/FeO_x$ embedded in LDH catalyzing C-C bond forming reactions of furfural with alcohols in the absence of a homogeneous base

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#### ARTICLE INFO ABSTRACT Keywords: Fe/FeO<sub>x</sub> embedded in LDH was prepared by reducing the pre-synthesized $[Fe(C_2O_4)_3]^{3-}$ anions intercalated Heterogeneous catalysis LDH and used as a multi-functional catalyst for synthesis of C7-C9 compound via transfer hydrogenation between Furfural furfural (C5) and short-chain alcohols (C2-C4) and a subsequent aldol reaction of furfural with intermediate Biomass conversion short-chain aldehydes in the absence of a homogeneous base with furfuryl alcohol as a byproduct. Screening Layered double hydroxides reaction conditions, evaluation and improvement of the cyclic catalytic performance, and determination of C-C bond forming catalytically active components were performed, and the results demonstrated that both high conversion and high selectivity to the C-C bond forming product can be obtained under a non-oxidizing atmosphere of Ar or H<sub>2</sub>/Ar mixed gas, a reaction temperature of 140 °C and a reaction time of 4 h; the catalyst was easily deactivated during the cycle experiments, however, its catalytic stability can be effectively improved by depositing Ni with weak reducibility on the surface of Fe nanoparticles at the cost of reducing partial catalytic activity. $Fe/FeO_x$ together with LDH as a whole proved to be effective in catalyzing the transfer hydrogenation reaction and the support LDH imparted basic catalytic function to the composite realizing the aldol reaction in the absence of a homogeneous base.

# Introduction

Developing renewable biomass fuels instead of fossil fuels is an effective path to address the growing energy demands and environmental problems. [1,2] Furfural is a renewable biomass platform molecule derived from wasted corncob, bagasse, straw, *etc.*, and can be industrially produced on a large scale. [3–5] With the active aldehyde group, furfural containing 5 carbon atoms is an ideal platform molecule for production of biofuel precursors (Fig. 1) with various carbon chain lengths by self-condensation or co-condensation with other renewable carbon sources, *e.g.* methyl furan [6], acetone [7–9], levulinic acid [10], and short-chain alcohols (C2-C4) [11,12].

Short chain alcohols, such as ethanol, propanol and butanol, also can be obtained from converting renewable biomass resources by chemical catalysis or biological fermentation [13–16], and used as hydrogen donors in transfer hydrogenation reaction and C2-C4 building blocks for the synthesis of compounds with longer carbon chains [12]. Several recent studies have shown that short-chain alcohols (C2-C4) can react with furfural (C5) to produce furfural derivatives (C7-C9) by a C–C bond forming reaction with the aid of catalysts and using  $O_2$  for synchronously oxidizing the byproduct furfuryl alcohol to reactant furfural. [17] Specifically, Tong's group have developed several highefficiency catalytic systems, such as  $Co_xO_y - N@K-10 - Cs_2CO_3$  [18], Au/Fe<sub>x</sub>O<sub>y</sub>/hydroxyapatite-K<sub>2</sub>CO<sub>3</sub> [19], Au/CeO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub> [20], Co-MOF-Cs<sub>2</sub>CO<sub>3</sub> [17], CuO/CeO<sub>2</sub>-K<sub>2</sub>CO<sub>3</sub> [21], Pt/HTc-K<sub>2</sub>CO<sub>3</sub> [11] and Fe/C-K<sub>2</sub>CO<sub>3</sub> [12] for synthesis of furfural derivatives (C<sub>7</sub>-C<sub>9</sub>) *via* an one-pot two-step reaction, *i.e.*, transfer hydrogenation of furfural with shortchain alcohols to produce short-chain aldehydes and furfuryl alcohol followed by an aldol reaction of furfural with intermediate short-chain aldehydes. In the above pioneering works, homogeneous bases such as K<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub> were used to catalyze the aldol reaction. However, as many other homogeneous catalysts, the separation and recovery of homogeneous base catalysts requires additional tedious steps, and their high basicity also places high requirements on the equipment. To avoid these issues, homogeneous-base-free catalytic systems for the C–C forming reaction of furfural with alcohols are expected.

Layered double hydroxides (LDHs) are an anionic clay composed of positively charged mixed bivalent and trivalent metal hydroxide layers and negatively charged interlayer anions and bound water [22–26], and have been used as both a solid base catalyst and a carrier where metal nanoparticles can be easily deposited on the surface or intercalated in the interlayer galleries [27–29]. Fe, a rich and environmentally friendly element in the crust, has proven to be an efficient catalytic component for transfer hydrogenation reaction in forms

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Fig. 1. Furfural derivatives synthesized through the C-C bond forming reaction of furfural with itself and other renewable biomass platform molecules. [6-12].

of free element or oxides together with carriers or other oxides or alkali additives such as (Fe/C-K<sub>2</sub>CO<sub>3</sub>) [12], Fe<sub>3</sub>O<sub>4</sub>@C [30] and y-Fe<sub>2</sub>O<sub>3</sub>@HAP [31]. In this work, amorphous Fe nanoparticles with a surface oxide passivation layer consisting of oxidized iron species of Fe(II) and Fe(III) (abbreviated as FeOx) embedded in LDH (Fe/FeOx@LDH) was constructed by reduction of pre-prepared [Fe(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>3-</sup> intercalated LDH obtained via an ion exchange method and used as a homogeneous-basefree catalytic system for the C-C forming reactions of furfural with alcohols (C2-C4) to produce furan-2-acrolein (C7), 3-(furan-2-yl-)-2-methylacrylaldehyde (C8) and 3-(furan-2-yl-)-2-ethylacrylaldehyde (C9) which can be further hydrogenated to obtain C7-C9 alkanes as biofuels [32,33]. The textural properties of Fe/FeOx@LDH were characterized by TEM, XRD, ICP, N2 adsorption-desorption isotherms, XPS and CO2-TPD. The catalytic properties of Fe/FeOx@LDH were valuated under different atmosphere (Ar, O2 and Ar/H2 mixed gas), pressures, temperatures and reaction time using the sole LDH and Fe/FeO<sub>x</sub> as contrast. Evaluation and improvement of the cyclic catalytic performance was explored, and determination of catalytically active components for transfer hydrogenation and the aldol reaction was carried out through conducting contrast experiments and analysis of the reaction products.

#### Experimental

### Materials

Magnesium nitrate hexahydrate, aluminum nitrate nonahydrate, nickel nitrate hexahydrate, sodium borohydride, sodium hydroxide, sodium oxalate, ethanol, *n*-propanol, *n*-butanol, furfural, furfuryl alcohol, *n*-propanal and furan-2-acrolein were all of analytical grade and purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). *o*-xylene (> 98.0 %, GC) was purchased from TCI (Tokyo, Japan). Potassium tris (oxalato)ferrate(III) trihydrate (N/A) was produced by strem chemicals inc. (Massachusetts, America).

#### Catalyst preparation

 $Fe/FeO_x@LDH$  was prepared by reduction of pre-synthesized complex anion tris(oxalato)ferrate(III) intercalated LDH. In detail, 40 mL of

0.2 M NaOH solution was quickly added to 50 mL of mixed solution of magnesium nitrate, aluminum nitrate and potassium tris(oxalato)ferrate(III) trihydrate (0.1 M/0.05 M/0.022 M), followed by adjusting the pH of the obtained suspension to 9.5. After hydrothermal treatment at 70 °C for 24 h, the obtained product was concentrated by centrifugation, decanted and washed twice with deionized water, and re-dispersed in 40 mL of deionized water containing 0.026 mol of sodium borohydride, and after stirring for 2 h, the final product Fe/FeOx@LDH was obtained by centrifugation, decanted and washed five times with deionized water. The contrast sample Fe/FeO<sub>x</sub> were synthesized by the same method as Fe/FeOx@LDH except using potassium tris(oxalato) ferrate(III) trihydrate instead of coordination anion tris(oxalato)ferrate (III) intercalated LDH. The contrast sample LDH was synthesized by the same method as coordination anion tris(oxalato)ferrate(III) intercalated LDH excepted using the mixed solution of magnesium nitrate and aluminum nitrate (0.1 M/0.05 M) instead of the mixed solution of magnesium nitrate, aluminum nitrate and potassium tris(oxalato)ferrate(III) trihydrate (0.1 M/0.05 M/0.022 M).

### Catalyst characterization

High-resolution and low-resolution TEM images were taken on a JEOL JEM-2100 and a JEOL JEM-1011 transmission electron microscope, respectively. SEM images were obtained by a JEOL JSM-6360LV scanning electron microscope. N<sub>2</sub> adsorption–desorption isotherms were obtained on a Micromeritics ASAP TriStar II 3020 pore analyzer, and the samples were outgassed at 150 °C for 8 h before measurements. XRD patterns were collected using a Rigaku D/Max-2200 PC X-ray diffractometer.  $CO_2$ -TPD tests were performed on a Quantachrome ChemBET Pulsar equipment. The contents of Mg, Al and Fe in catalysts were determined by ICP-AES (Leeman Prodigy XP ICP-AES spectrometer). The contents of C, N and H in catalysts were determined by elemental analyzer (EA3000, Euro vector). The surface element contents of Mg, Al, Fe, C and N in catalysts were given by a X-ray Photoelectron Spectroscopy (PH1500C, ULVAC).

#### Catalytic tests

The reactions of furfural with short-chain alcohols were carried out on a 50 mL of high-pressure aerated stainless steel reactor equipped with an explosion-proof valve, a gas inlet, a gas outlet, a pressure gauge, a digital heating device and an autosampler. Firstly, a certain amount of catalyst, furfural, alcohol and internal standard o-xylene, and a magnetic stir bar were placed into the reactor, then Ar ( $O_2$  or 5%H<sub>2</sub>/ 95 %Ar) gas was filled and discharged several times to exhaust the air in the reactor, and after the gas pressure was set and the given reaction temperature was reached, the reaction started. After stirring at 600 rpm at a given temperature for a certain period of time, the reaction was stopped by natural cooling. The solid catalyst was separated from the reaction product by centrifugation. The reaction products were analyzed by a Shimadzu GC2010 gas chromatograph equipped with a FID detector and a capillary column (Rtx-5). The conversion of furfural, and the selectivity to the byproduct furfuryl alcohol SFFA (base on the amount of furfural) are calculated by an internal standard method. The selectivity to the main product 3-(furan-2-yl-)-2-methylacrylaldehyde (base on the amount of furfural) is approximately equal to  $(1-S_{FFA})$  due to that other products are very few and were not detected in the reaction batches. The yield of 3-(furan-2-yl-)-2-methylacrylaldehyde is equal to the product of the conversion of furfural and the selectivity to 3-(furan-2-yl-)-2-methylacrylaldehyde.

#### **Results and discussion**

# Textural properties of Fe/FeO<sub>x</sub>@LDH, Fe/FeO<sub>x</sub> and LDH

The morphology of the synthesized Fe/FeO<sub>x</sub>@LDH is shown in the high-resolution (Fig. 2a,b) and low-resolution (Fig. S1a) TEM images, and irregularly shaped Fe/FeOx NPs with diameters less than 10 nm (marked with blue circles) are embedded in the disc-shaped LDH. At a magnification of 400,000, no lattice streaks of iron species were found (Fig. S2), indicating their amorphous structure, in accordance with the results of the XRD analysis (Fig. 2c) where no crystalline phase of Fe was found in Fe/FeO<sub>x</sub>@LDH, which is probably due to the presence of oxalate derived from Fe precursor inhibiting the orderly arrangement of Fe atoms by strong complexation. The typical XRD peaks of LDH in Fe/ FeO<sub>x</sub>@LDH all shifted to low 20 values compared with those of the contrast LDH, and the calculated interlayer distance of LDH in Fe/ FeO<sub>x</sub>@LDH is ~1.0 nm based on the Bragg Equation ( $2d\sin\theta = n\lambda$ ), which is larger than that of normal LDH intercalated with NO3<sup>-</sup>, demonstrating the intercalating of  $C_2O_4^{-2-}$  into the galleries of LDH. Meanwhile, Fe/FeO<sub>x</sub>@LDH possesses all the infrared characteristic bands (Fig. 2d) of the single Fe/FeOx and LDH (Fig. S1b-d) prepared under the same conditions, further indicating Fe/FeO<sub>x</sub>@LDH consists of Fe/FeO<sub>x</sub> and LDH. The IR peaks in both Fe/FeO<sub>x</sub> and Fe/FeO<sub>x</sub>@LDH similar to those for ferric oxalate [34] appeared at 1638 cm<sup>-1</sup>, 1328 cm<sup>-1</sup> <sup>1</sup>, 777 cm<sup>-1</sup> and 511 cm<sup>-1</sup> can be attributed to the complexation of the oxalate derived from the precursor of iron (potassium tris(oxalato)ferrate(III) trihydrate) with the coordination-unsaturated ferric iron at the surface of Fe/FeO<sub>x</sub>. The XPS of Fe 2p for Fe/FeO<sub>x</sub>@LDH shows a Fe 2p<sub>3/</sub>  $_2$  peak at 710.5 eV, a Fe  $2p_{1/2}$  peak at 724.2 eV and a shake-up satellite  $(2p_{3/2} \text{ and } 2p_{1/2})$  peak at 719.4 eV (Fig. 2f), indicating that oxidized iron species of Fe(II) and Fe(III), such as Fe<sub>2</sub>O<sub>3</sub>, FeOOH and Fe<sub>3</sub>O<sub>4</sub> [35], formed on the surface of Fe NPs, which is consistent with the XPS results of the reported zero-valent iron materials [36-39] for which the oxide passivation layer will inevitably form on the surface. The XPS peak of Fe° (at about 706.0 eV) was not found, which is probably caused by two reasons: low XPS detection depth  $(1 \sim 3 \text{ nm})$  which may not exceed the thickness of the surface passivation layer and the low Fe content in Fe/FeO<sub>x</sub>@LDH (4.7 %). The color of Fe/FeO<sub>x</sub>@LDH is black gray (insert in Fig. 2b), rather than yellow and reddish brown of ferric iron, which indirectly indicates that the main body of Fe species in Fe/ FeO<sub>x</sub>@LDH exists in form of Fe° [40], which locates under the surface oxide passivation layer [36,37]. The results of ICP and XPS analysis (Table 1) showed the entire Fe content and the surface Fe content in Fe/FeO<sub>x</sub>@LDH are 5.4 % and 1.6 %, respectively, indicating the Fe element is mainly in the interior of the composite. 2012b).

The presence of 2.5 % carbon in Fe/FeO<sub>x</sub>@LDH is most likely derived from the oxalate in the interlayer of LDH or complexed with Fe/FeO<sub>x</sub> NPs. The BET surface area of Fe/FeO<sub>x</sub>@LDH calculated from N<sub>2</sub> adsorption-desorption isotherms is  $35.6 \text{ m}^2 \text{ g}^{-1}$ , indicating the small particle size and loose structure of Fe/FeO<sub>x</sub>@LDH.

The basic strength distributions of Fe/FeO<sub>x</sub>@LDH and the contrast LDH were measured *via* a CO<sub>2</sub>-TPD test and are showed in Fig. 2h. For CO<sub>2</sub>-TPD, the basic sites in the high desorption temperature range are usually designated as strong basic sites, and *vice versa*. It can be seen that Fe/FeO<sub>x</sub>@LDH exhibited a more border band than LDH, demonstrating more kinds of basic sites are introduced into the former when being compounded with Fe/FeO<sub>x</sub> NPs. The total peak area of CO<sub>2</sub>-TPD signals is linearly proportional to the amount of CO<sub>2</sub> adsorbed and can thus be used as a semi-quantitative parameter for assessing the number of basic sites of the catalysts. It thereby can be concluded that the basic site number of Fe/FeO<sub>x</sub>@LDH is roughly equal to that of LDH based on their close peak areas (Fig. 2h).

### Catalytic performance of Fe/FeO<sub>x</sub>@LDH

The catalytic properties of Fe/FeOx@LDH were investigated by a one-pot reaction of furfural 1 with n-propanol (n-PrOH) to produce 3-(furan-2-yl-)-2-methylacrylaldehyde 3, under homogeneous alkali-free conditions with furfuryl alcohol 2, which has huge demand in foundry resins and agrochemical manufacture, [41] as a by-product (Fig. 3). The effect of oxidative, inert and reductive reaction atmosphere on the catalytic properties was examined by filling the reactor with 0.5 MPa of O<sub>2</sub>, Ar and a mixture gas of Ar (95 %) and H<sub>2</sub> (5%), respectively. As shown in Fig. 3a, the conversions of furfural (71.3 % and 71.4 %) under the atmosphere of Ar and H<sub>2</sub>/Ar mixed gases are much higher than that (20.8 %) under the  $O_2$  atmosphere, which is probably due to the fact that Fe/FeO<sub>x</sub> is easy to be oxidized and unstable in the O<sub>2</sub> atmosphere and then loses their catalytic activity of transfer hydrogenation. Then, the catalytic performance of Fe/FeO<sub>x</sub>@LDH under the Ar atmosphere of 0.1 MPa, 0.25 MPa, 0.5 MPa, 1.7 MPa and 3 MPa was evaluated, and the best performance was obtained under a pressure of 0.5 MPa (Fig. 3b). The effect of the reaction temperature on the catalytic performance was also investigated, and from 100 °C to 160 °C, the conversions increased with the incremental temperatures, but when the temperature increased to 180 °C, the conversion no longer increased (Fig. 3c). However, the selectivities to the main product 3 gradually decreased with the increasing temperatures, which revealed that the reaction path has changed significantly at the high temperatures, compared with that at the low temperatures. The reaction kinetics showed that the conversions increased with increasing reaction time, and after 24 h, the highest conversion of 96.4 % appeared (Fig. 3d). However, the selectivity to the main product 3 has no obvious regularity over time, and the highest selectivity is 87.1 % at 4 h. To examine the applicable scope of Fe/FeOx@LDH, the reactions of other alcohols such as ethanol (EtOH) and *n*-butanol (*n*-BuOH) with furfural were also performed, and the conversions are 89.3 % and 71.2 %, respectively (Fig. 3e), under the same reaction conditions except the pressure of the reaction of furfural with ethanol set at 0.65 MPa (above 0.5 MPa) to maintain the liquid reaction medium temperature at 140 °C. Since the pressure of the inert gas (Ar) has a small influence on the catalytic performance of Fe/ FeO<sub>x</sub>@LDH (Fig. 3b), it can be concluded that the catalytic performance decreased with incremental carbon chain lengths of alcohols, consistent with the reported results of other catalytic systems [18,21], which may be attributed to the reason that the transfer hydrogenation rate of furfural with alcohols decreases with the increased carbon chain lengths of alcohols [18,21].

In order to examine the catalytic stability of Fe/FeOx@LDH,



**Fig. 2.** TEM images (a, b), XRD patterns (c), IR spectrum (d), XPS spectrum (e, f),  $N_2$  adsorption-desorption isotherms (g) and CO<sub>2</sub>-TPD (h) of Fe/FeO<sub>x</sub>@LDH, LDH and/or Fe/FeO<sub>x</sub>; The insert in Fig. 2b is a digital photo of Fe/FeO<sub>x</sub>@LDH powder.

#### Table 1

Textual	l properties	of the	pristine a	and used	Fe/FeO <sub>x</sub> @	LDH, and	the contrast	samples	of sole Fe/FeO	<sub>x</sub> and LDH.
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Samples	Fe (%) <sup>a</sup>	Mg (%) <sup>a</sup>	Al (%) <sup>a</sup>	N (%) <sup>b</sup>	C(%) <sup>b</sup>	H(%) <sup>b</sup>	Surf. Fe (%)	Surf. Mg (%)	Surf. Al (%)	Surf. O (%)	Surf. C (%)	$S_{BET}(m^2 g^{-1})^d$
Fe/FeO <sub>x</sub> @LDH Used Fe/FeO <sub>x</sub> @LDH	4.7 5.4	9.6 11.3	5.1 5.9	0 0	2.5 15.8	3.2 2.7	1.5° 1.6°	12.5° 8.3°	6.0 <sup>c</sup> 6.1 <sup>c</sup>	55.2° 38.4°	12.2 <sup>c</sup> 29.2 <sup>c</sup>	35.6 -
Fe/FeO <sub>x</sub> LDH	75.6 0	0 21.4	0 10.9	0 3.4	3.5 1.2	0.3 3.5	-	-	-	-	-	8.4 53.8

<sup>a</sup> Obtained by ICP test.

<sup>b</sup> Measured by elemental analyzer (EA).

<sup>c</sup> The surface element content given by XPS analysis (Fig. 2e, f and Fig. S3).

 $^{\rm d}\,$  Calculated from  $N_2$  adsorption-desorption isotherms (Fig. 2g).

recycling experiments were carried out. After the catalyst completed a batch of reaction, it was then centrifuged, dried and weighed for the next reaction, and the results showed that the conversion was only *ca* 1% for the 2nd cycle (Fig. 3f, **left**). By analyzing the surface of the used

catalyst by a XPS test, it was found that the element C content on the catalyst surface increased significantly (Table 1 and Fig. S2), indicating that the reaction reactants and products might be adsorbed on the surface of the catalyst. Therefore, oxalate with strong complexation was



**Fig. 3.** The effect of the atmosphere of  $O_2$ , Ar and 5% H<sub>2</sub>+95 %Ar (a), pressure of Ar (b), reaction temperature (c), reaction time (d), short-chain alcohol species (e) on the catalytic properties of Fe/FeO<sub>x</sub>@LDH; (f) Cyclic catalytic experiments over Fe/FeO<sub>x</sub>@LDH with a simple drying process (left) or being washed with oxalate solution (middle) after each cycle, or surface treatment by Ni(NO<sub>3</sub>)<sub>2</sub> solution before the first cycle (right). Unstated reaction conditions: catalyst: 50 mg, furfural: 1 mmol, *n*-PrOH (alcohols): 5 mL, *o*-xylene (internal standard): 45  $\mu$ L, 140 °C, 4 h, Ar (0.5 MPa). The reaction of EtOH with furfural in Fig. 3e was performed at 0.65 MPa (Ar).



Fig. 4. Possible reaction routes using  $Fe/FeO_x@LDH$ ,  $Fe/FeO_x@LDH$  and LDH as catalysts, respectively.

used to remove the organic matter adsorbed on the used catalyst by washing with sodium oxalate solution, and after this treatment, the conversion of the second cycle increased to 9%, also a very low value (Fig. 3f, middle). Considering that Fe/FeO<sub>x</sub> NPs are easily oxidized during the drying process, which may be the main reason for catalyst deactivation, the fresh Fe/FeO<sub>x</sub>@LDH was treated with nickel salt to increase the antioxidant performance of Fe/FeO<sub>x</sub>@LDH by depositing Ni with weak reducibility on the surface of Fe/FeO<sub>x</sub> [42,43], and then used for the cyclic catalytic experiments. Although the conversion (48.4 %) of the first cycle was significantly lower than that (71.3 %) before the treatment, the cyclic catalytic stability of the catalyst was greatly improved as showed in the second cycle (26.9 %) and the third cycle (28 %) (Fig. 3f, right).

#### Catalytic active components and possible reaction route

In the serial reactions of furfural with *n*-PrOH, *n*-propanal and furfuryl alcohol were detected, demonstrating a reaction route of transfer hydrogenation of furfural with *n*-PrOH to produce *n*-propanal and furfuryl alcohol followed by an aldol reaction of furfural with intermediate *n*-propanal (Fig. 4) as proposed by Tong' group [19,21]. So as to determinate the catalytically active components in Fe/FeO<sub>x</sub>@LDH, the sole Fe/FeO<sub>x</sub> and LDH were used for catalyzing the reaction of furfural with *n*-PrOH, and the results revealed that no main product 3-(furan-2yl-)-2-methylacrylaldehyde **3**, and intermediates *n*-propanal and furfuryl alcohol **2** were produced (Table 2, Entry 2, 3) and the only product was furfuryl dipropyl acetal (product **4** in Fig. 4),

demonstrating an acetal reaction catalyzed by the Lewis acidic sites of the sole Fe/FeO<sub>x</sub> and LDH and that the catalytically active components for transfer hydrogenation of furfural with *n*-PrOH is the composite Fe/ FeO<sub>x</sub>@LDH rather than the sole Fe/FeO<sub>x</sub> and LDH. For transfer hydrogenation of furfural with alcohols, a cyclic transition state formed with the aid of specific acid and/or base sites is the key to the transfer of hydrogen from alcohols to furfural [30,44]. In this catalytic system, neither Fe nor LDH alone can effectively catalyze the reaction, indicating the two are synergistic in activating the transfer hydrogenation reaction. Therefore, a possible activation mechanism, where the surface coordination-unsaturated Fe<sup>2+</sup> and Fe<sup>3+</sup> of Fe/FeO<sub>x</sub>@LDH was used as acidic sites to coordinate with the oxygen in alcohols and aldehydes and the surface low-coordinated  $O^{2-}$  from LDH used as basic sites to activate the hydrogen on the hydroxyl group of alcohols, leading to the formation of the six-membered cyclic transition state (bottom of Fig. 4) and the subsequent formation of furfuryl alcohol and propionaldehyde, was given. The aldol reaction of intermediate *n*-propanal with furfural over LDH using n-propanal as both a reactant and a solvent was also performed to identify whether LDH is the catalytically active components in Fe/FeOx@LDH for the aldol reaction, and as expected the main product 3-(furan-2-yl-)-2-methylacrylaldehyde 3 with a yield of 44.3 % was obtained (Table 2, Entry 4). The self-condensation products of the solvent *n*-propanal were also found, which might interfere the aldol condensation reaction of furfural with n-propanal, resulting in reduced conversion of furfural. However, in the absence of oxygen, furfuryl alcohol as a by-product cannot enter the reaction cycles by being oxidized to the reactant furfural. The esterification reaction of by-product furfuryl alcohol and n-PrOH easily occurs in the presence of acidic catalysts [45,46]. However, no etherification products are detected in this catalytic reaction system ("GC and GC-MS patterns" section in the supporting formation), indicating that etherification reaction is not a preferred path, probably due to the lack of Brønsted acid sites in Fe/ FeO<sub>x</sub>@LDH [45,46]. As showed in Fig. 4, the theoretical yield of furfuryl alcohol 2 should be equivalent to (or higher) than that of 3-(furan-2-yl-)-2-methylacrylaldehyde 3, if the second-step aldol reaction is completed thoroughly (or partially), but in fact, the yields of furfuryl alcohol were lower (or much lower) than those of the main product 3 in part of the reaction batches (Fig. 3), thus, it can be speculated that other unknown reaction paths are involved in this catalytic system. The performance comparison of Fe/FeOx@LDH with other catalytic systems in the reaction of furfural with *n*-PrOH is shown in Table 3. Compared with the reported heterogeneous catalyst/homogeneous base catalytic systems, Fe/FeO<sub>x</sub>@LDH realized the C-C bond forming reactions in a non-oxidizing atmosphere with slightly lower conversion and selectivity in the absence of homogeneous base. However, the catalytic performance of Fe/FeOx@LDH in oxygen atmosphere and its cycle stability was poor, and the yield of by-product furfural was much lower than the theoretical yield (Fig. 3a-f) according to the assumed reaction path (Fig. 4), which still need further improvement and exploration.

# Conclusion

Fe/FeO<sub>x</sub> nanoparticles embedded in LDH was successfully constructed through the reduction of the pre-synthesized  $\left[Fe(C_2O_4)_3\right]^{3-}$ 

Table 2

Contrast experiments using single Fe/FeO<sub>x</sub> and LDH as contrast and using the intermediate *n*-propanal instead of *n*- PrOH as both a reactant and a solvent <sup>a</sup>.

Entry	Catalysts	Reactants	Conv.of 1(%)	Sel. to 2(%)	Sel. to 3(%)	Sel. to 4(%)
1	Fe/FeO <sub>x</sub> @LDH	Furfural + n-PrOH	71.3	12.9	87.1	0
2 <sup>b</sup>	Fe/FeO <sub>x</sub>	Furfural + n-PrOH	38.9	0	0	100
3 <sup>b</sup>	LDH	Furfural + n-PrOH	24.8	0	0	100
4 <sup>c</sup>	LDH	Furfural + n-propanal	44.3	0	100	0

<sup>a</sup> Reaction conditions: catalyst: 50 mg, furfural: 1 mmol, n-PrOH (n-propanal): 5 mL, o-xylene (internal standard): 45 µL, 140 °C, 4 h, Ar (0.5 MPa).

 $^{\rm b}\,$  Reaction temperature: 100 °C, reaction time: 6 h.

<sup>c</sup> 5 mL of *n*-propanal instead of *n*-PrOH as both a reactant and a solvent.

Table 3

Comparison of catalytic performance of Fe/FeO<sub>x</sub>@LDH with other catalytic systems containing homogeneous base in reaction of furfural with *n*-PrOH.<sup>a</sup>.

Entry	Catalysts Reaction conditions		Conv.(%)	Sel.(%)	Ref.
1	Fe/FeO <sub>x</sub> @LDH	Catalyst: 50 mg; furfural: 1 mmol, <i>n</i> -PrOH: 5 mL, 140 °C, 4 h, 5 MPa (Ar).	71.3	87.1	This work
2	Fe/FeO <sub>x</sub> @LDH	Catalyst: 50 mg; furfural: 1 mmol, <i>n</i> -PrOH: 5 mL, 140 $^{\circ}$ C, 4 h, 5 MPa (O <sub>2</sub> ).	20.8	99.8	This work
3	$Pt/FH + K_2CO_3$	Catalyst: 50 mg; furfural: 0.2 g, <i>n</i> -PrOH: 15 mL, 140 °C, 4 h, 0.3 MPa (O <sub>2</sub> ), K <sub>2</sub> CO <sub>3</sub> : 50 mg.	90.1	90	[11]
4	$Fe@C + K_2CO_3$	_ a	86.7	96.2	[12]
5	$[Co(tia)(H_2O)_2]_n + Cs_2CO_3$	Catalyst: 25 mg; furfural: 0.1 g, n-PrOH: 15 mL, 140 °C, 4 h, 0.3 MPa (O <sub>2</sub> ), Cs <sub>2</sub> CO <sub>3</sub> : 25 mg.	84.9	99.7	[17]
6	Co <sub>x</sub> O <sub>y</sub> -N@K-10+Cs <sub>2</sub> CO <sub>3</sub>	Catalyst: 50 mg; furfural: 0.2 g, <i>n</i> -PrOH: 15 mL, 140 °C, 4 h, 0.3 MPa (O <sub>2</sub> ), Cs <sub>2</sub> CO <sub>3</sub> : 50 mg.	75.1	92.8	[18]
7	$Au/FH + K_2CO_3$	_ a	94	97	[19]
8	$CuO-CeO_2 + K_2CO_3$	_ a	85.4	95.3	[21]

<sup>a</sup> The reaction conditions are the same as in Entry 3.

anion intercalated LDH for catalyzing the one-pot two-step C-C band forming reaction of furfural with *n*-propanol in the absence of a homogeneous base. The irregularly shaped Fe/FeO<sub>x</sub> NPs (a passivation layer of oxidized iron species of  $Fe^{2+}$  and  $Fe^{3+}$  on the surface of Fe NPs) with diameters less than 10 nm together with the support LDH as a whole proved to be effective in catalyzing the transfer hydrogenation of furfural with n-propanol to prepare furfuryl alcohol and n-propanal, while only acetal reaction occurred when using the sole Fe nanoparticles and the sole LDH as catalysts; the support LDH imparted basic catalytic function to the composite realizing the second-step aldol reaction of furfural with the intermediate *n*-propanal to produce the main product 3-(furan-2-yl-)-2-methylacrylaldehyde (C8). Both high conversion of furfural and high selectivity to the main product (C8) can be obtained in a non-oxidizing atmosphere of Ar or H<sub>2</sub>/Ar mixed gas, reaction temperature of 140 °C and reaction time of 4 h. This catalyst is also applicable for the C-C bond forming reaction of other short-chain alcohols such as ethanol and *n*-Butanol with furfural to prepare the corresponding C7 and C9 products. The catalyst was easily deactivated during cycle experiments, probably due to the oxidation of Fe/FeO<sub>x</sub> in the used catalyst during the drying process. By soaking Fe/FeOx@LDH in a solution of nickel nitrate, the cyclic catalytic stability of the catalyst can be effectively improved, but at the cost of reducing partial catalytic activity. In addition, in some batches of reactions, the yields of the byproduct furfuryl alcohol were lower (or much lower) than those of the main product 3-(furan-2-yl-)-2-methylacrylaldehyde, indicating other unknown reaction paths are involved in this catalytic system, which needs to be explored further in the following research.

#### CRediT authorship contribution statement

Yang Zhong: Conceptualization, Methodology, Investigation, Writing - original draft. **Bo Zhou:** Investigation, Methodology. **Lijun Wang:** Conceptualization, Resources, Writing – review & editing, Supervision.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2020.111056.

# References

- [1] X. Qi, R. Zhou, H.-J. Ai, X.-F. Wu, HMF and furfural: Promising platform molecules in rhodium-catalyzed carbonylation reactions for the synthesis of furfuryl esters and tertiary amides, J. Catal. 381 (2020) 215–221, https://doi.org/10.1016/j.jcat.2019. 11.008.
- [2] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sadaba, M.L. Granados, Furfural: a renewable and versatile platform molecule for the synthesis of chemicals and fuels, Energy Environ. Sci. 9 (2016) 1144–1189, https://doi.org/10.1039/c5ee02666k.
- [3] A. Bohre, S. Dutta, B. Saha, M.M. Abu-Omar, Upgrading furfurals to drop-in biofuels: an overview, ACS Sustain. Chem. Eng. 3 (2015) 1263–1277, https://doi.org/ 10.1021/acssuschemeng.5b00271.
- [4] M. Li, J. Wei, G. Yan, H. Liu, X. Tang, Y. Sun, X. Zeng, T. Lei, L. Lin, Cascade conversion of furfural to fuel bioadditive ethyl levulinate over bifunctional zirconium-based catalysts, Renew. Energ. 147 (2020) 916–923, https://doi.org/10. 1016/j.renene.2019.09.064.
- [5] K. Yan, G. Wu, T. Lafleur, C. Jarvis, Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals, Renewable and Sustainable Energ. Rev. 38 (2014) 663–676, https://doi.org/10.1016/j.rser.2014. 07.003.
- [6] S. Li, N. Li, G. Li, L. Li, A. Wang, Y. Cong, X. Wang, T. Zhang, Lignosulfonate-based acidic resin for the synthesis of renewable diesel and jet fuel range alkanes with 2methylfuran and furfural, Green Chem. 17 (2015) 3644–3652, https://doi.org/10. 1039/C5GC00372E.
- [7] Q. Xia, Y. Xia, J. Xi, X. Liu, Y. Wang, Energy-efficient production of 1-octanol from biomass-derived furfural-acetone in water, Green Chem. 17 (2015) 4411–4417, https://doi.org/10.1039/c5gc01119a.
- [8] L. Hora, V. Kelbichová, O. Kikhtyanin, O. Bortnovskiy, D. Kubička, Aldol condensation of furfural and acetone over MgAl layered double hydroxides and mixed oxides, Catal. Today 223 (2014) 138–147, https://doi.org/10.1016/j.cattod.2013. 09.022.
- [9] M. Xu, S. Célérier, J.-D. Comparot, J. Rousseau, M. Corbet, F. Richard, J.-M. Clacens, Upgrading of furfural to biofuel precursors via aldol condensation with acetone over magnesium hydroxide fluorides MgF<sub>2-x</sub>(OH)<sub>x</sub>, Catal. Sci. Technol. 9 (2019) 5793–5802, https://doi.org/10.1039/C9CY01259A.
- [10] G. Liang, A. Wang, X. Zhao, N. Lei, T. Zhang, Selective aldol condensation of biomass-derived levulinic acid and furfural in aqueous-phase over MgO and ZnO, Green Chem. 18 (2016) 3430–3438, https://doi.org/10.1039/C6GC00118A.
- [11] Z. Liu, X. Tong, J. Liu, S. Xue, A smart catalyst system for the valorization of renewable furfural in aliphatic alcohols, Catal. Sci. Technol. 6 (2016) 1214–1221, https://doi.org/10.1039/c5cy01195g.
- [12] Z. Zhang, X. Tong, H. Zhang, Y. Li, Versatile catalysis of iron: tunable and selective transformation of biomass-derived furfural in aliphatic alcohol, Green Chem. 20 (2018) 3092–3100, https://doi.org/10.1039/c8gc00852c.
- [13] M. Tarrsini, Y.P. Teoh, S.H. Shuit, Z.X. Ooi, Q.H. Ng, B. Kunasundari, Evolution toward the utilization of mango leaves as lignocellulosic material in bioethanol production: A review of process parameter and integrated technologies, Environ. Prog. Sustain. Energ. 38 (2019) e13233, https://doi.org/10.1002/ep.13233.
- [14] H.B. Aditiya, T.M.I. Mahlia, W.T. Chong, H. Nur, A.H. Sebayang, Second generation bioethanol production: a critical review, Renew. Sustain. Energ. Rev. 66 (2016) 631–653, https://doi.org/10.1016/j.rser.2016.07.015.
- [15] X. Cao, Z. Chen, L. Liang, L. Guo, Z. Jiang, F. Tang, Y. Yun, Y. Wang, Co-valorization of paper mill sludge and corn steep liquor for enhanced n-butanol production with Clostridium tyrobutyricum Δcat1::adhE2, Bioresour. Technol. 296 (2020) 122347, , https://doi.org/10.1016/j.biortech.2019.122347.
- [16] Y. Deng, S.S. Fong, Metabolic engineering of Thermobifida fusca for direct aerobic bioconversion of untreated lignocellulosic biomass to 1-propanol, Metab. Eng. 13 (2011) 570–577, https://doi.org/10.1016/j.ymben.2011.06.007.
- [17] L. Ning, S. Liao, X. Liu, L. Yu, X. Zhuang, X. Tong, Selective transformation of renewable furfural catalyzed by diverse active species derived from 2D co-based metal-organic frameworks, J. Catal. 352 (2017) 480–490, https://doi.org/10.1016/ j.jcat.2017.06.017.
- [18] L. Yu, S. Liao, L. Ning, S. Xue, Z. Liu, X. Tong, Sustainable and cost-effective protocol for cascade oxidative condensation of furfural with aliphatic alcohols, ACS Sustain. Chem. Eng. 4 (2016) 1894–1898, https://doi.org/10.1021/acssuschemeng. 6b00002.
- [19] X. Tong, Z. Liu, L. Yu, Y. Li, A tunable process: catalytic transformation of renewable furfural with aliphatic alcohols in the presence of molecular oxygen, Chem.

Commun. (Camb.) 51 (2015) 3674-3677, https://doi.org/10.1039/c4cc09562f.

- [20] X. Tong, Z. Liu, J. Hu, S. Liao, Au-catalyzed oxidative condensation of renewable furfural and ethanol to produce furan-2-acrolein in the presence of molecular oxygen, Appl. Catal. A-Gen. 510 (2016) 196–203, https://doi.org/10.1016/j. apcata.2015.11.025.
- [21] X. Tong, L. Yu, X. Luo, X. Zhuang, S. Liao, S. Xue, Efficient and selective transformation of biomass-derived furfural with aliphatic alcohols catalyzed by a binary Cu-Ce oxide, Catal. Today 298 (2017) 175–180, https://doi.org/10.1016/j.cattod. 2017.04.057.
- [22] Q. Wang, D. O'Hare, Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets, Chem. Rev. 112 (2012) 4124–4155, https:// doi.org/10.1021/cr200434v.
- [23] G. Varga, V. Kozma, V.J. Kolcsár, Á. Kukovecz, Z. Kónya, P. Sipos, I. Pálinkó, G. Szöllősi, β-Isocupreidinate–CaAl-layered double hydroxide composites—heterogenized catalysts for asymmetric Michael addition, Mol. Catal. 482 (2020) 110675, https://doi.org/10.1016/j.mcat.2019.110675.
- [24] Y. Cao, H. Zhang, J. Dong, Y. Ma, H. Sun, L. Niu, X. Lan, L. Cao, G. Bai, A stable nickel-based catalyst derived from layered double hydroxide for selective hydrogenation of benzonitrile, Mol. Catal. 475 (2019) 110452, https://doi.org/10. 1016/j.mcat.2019.110452.
- [25] J. Qin, H. Zhang, H. Sun, Y. Wang, L. Niu, X. Lan, G. Bai, In situ fabrication of nickel-based layered double hydroxides catalysts with carboxymethyl chitosan as biomass template for hydrogenation, Mol. Catal. 478 (2019) 110561, https://doi. org/10.1016/j.mcat.2019.110561.
- [26] H. Wang, Q. Fan, Z. Yang, S. Tang, J. Chen, Y. Wu, A novel pre-sulfided hydrotreating catalyst derived from thiomolybdate intercalated NiAl LDHs, Mol. Catal. 468 (2019) 1–8, https://doi.org/10.1016/j.mcat.2019.01.027.
- [27] B.M. Choudary, S. Madhi, N.S. Chowdari, M.L. Kantam, B. Sreedhar, Layered double hydroxide supported nanopalladium catalyst for Heck-, Suzuki-, Sonogashira-, and Stille-type coupling reactions of chloroarenes, J. Am. Chem. Soc. 124 (2002) 14127–14136, https://doi.org/10.1021/ja026975w.
- [28] A.H. Chowdhury, P. Bhanja, N. Salam, A. Bhaumik, S.M. Islam, Magnesium oxide as an efficient catalyst for CO<sub>2</sub> fixation and N-formylation reactions under ambient conditions, Mol. Catal. 450 (2018) 46–54, https://doi.org/10.1016/j.mcat.2018.03. 003.
- [29] S. Said, M. Elhossieny, M. Riad, S. Mikhail, Pristine Cu (Co)/Fe layered double hydroxides (Co(Cu)/Fe-LDH) as active catalysts for the transalkylation of toluene to trimethylbenzenes, Mol. Catal. 445 (2018) 213–222, https://doi.org/10.1016/j. mcat.2017.11.038.
- [30] F. Li, S. Jiang, J. Huang, Y. Wang, S. Lu, C. Li, Catalytic transfer hydrogenation of furfural to furfuryl alcohol over a magnetic Fe<sub>3</sub>O<sub>4</sub>@C catalyst, New J. Chem. 44 (2020) 478–486, https://doi.org/10.1039/C9NJ04698D.
- [31] F. Wang, Z. Zhang, Catalytic transfer hydrogenation of furfural into furfuryl alcohol over magnetic γ-Fe<sub>2</sub>O<sub>3</sub>@HAP catalyst, ACS Sustain. Chem. Eng. 5 (2017) 942–947, https://doi.org/10.1021/acssuschemeng.6b02272.
- [32] M.J. Sheppard, A.M. Kunjapur, K.L.J. Prather, Modular and selective biosynthesis of gasoline-range alkanes, Metab. Eng. 33 (2016) 28–40, https://doi.org/10.1016/j. ymben.2015.10.010.

- [33] K. Li, F. Zhou, X. Liu, H. Ma, J. Deng, G. Xu, Y. Zhang, Hydrodeoxygenation of lignocellulose-derived oxygenates to diesel or jet fuel range alkanes under mild conditions, Catal. Sci. Technol. 10 (2020) 1151–1160, https://doi.org/10.1039/ c9cy02367d.
- [34] M.C. D'Antonio, A. Wladimirsky, D. Palacios, L. Coggiolaa, A.C. González-Baró, E.J. Baran, R.C. Mercader, Spectroscopic investigations of iron(II) and iron(III) oxalates, J. Braz. Chem. Soc. 20 (2009) 445–450.
- [35] M. Fan, T. Li, J. Hu, R. Cao, X. Wei, X. Shi, W. Ruan, Artificial neural network modeling and genetic algorithm optimization for cadmium removal from aqueous solutions by reduced graphene oxide-supported nanoscale zero-valent Iron (nZVI/ rGO) composites, Materials 10 (2017), https://doi.org/10.3390/ma10050544.
- [36] S. Bae, R.N. Collins, T.D. Waite, K. Hanna, Advances in surface passivation of nanoscale zerovalent Iron: a critical review, Environ. Sci. Technol. 52 (2018) 12010–12025, https://doi.org/10.1021/acs.est.8b01734.
- [37] Y. Mu, F. Jia, Z. Ai, L. Zhang, Iron oxide shell mediated environmental remediation properties of nano zero-valent iron, Environ. Sci-Nano 4 (2017) 27–45, https://doi. org/10.1039/c6en00398b.
- [38] J. Kašlík, J. Kolařík, J. Filip, I. Medřík, O. Tomanec, M. Petr, O. Malina, R. Zbořil, P.G. Tratnyek, Nanoarchitecture of advanced core-shell zero-valent iron particles with controlled reactivity for contaminant removal, Chem. Eng. J. 354 (2018) 335–345, https://doi.org/10.1016/j.cej.2018.08.015.
- [39] Y. Feng, J. Zhong, L. Zhang, Y. Fan, Z. Yang, K. Shih, H. Li, D. Wu, B. Yan, Activation of peroxymonosulfate by Fe<sup>°</sup>@Fe<sub>3</sub>O<sub>4</sub> core-shell nanowires for sulfate radical generation: electron transfer and transformation products, Sep. Purif. Technol. 247 (2020) 116942, https://doi.org/10.1016/j.seppur.2020.116942.
- [40] N. Horzum, M.M. Demir, M. Nairat, T. Shahwan, Chitosan fiber-supported zerovalent iron nanoparticles as a novel sorbent for sequestration of inorganic arsenic, RSC Adv. 3 (2013) 7828–7837, https://doi.org/10.1039/c3ra23454a.
- [41] C.P. Jiménez-Gómez, J.A. Cecilia, D. Durán-Martín, R. Moreno-Tost, J. Santamaría-González, J. Mérida-Robles, R. Mariscal, P. Maireles-Torres, Gas-phase hydrogenation of furfural to furfuryl alcohol over Cu/ZnO catalysts, J. Catal. 336 (2016) 107–115, https://doi.org/10.1016/j.jcat.2016.01.012.
- [42] Z. Li, H. Dong, Y. Zhang, J. Li, Y. Li, Enhanced removal of Ni(II) by nanoscale zero valent iron supported on Na-saturated bentonite, J. Colloid Interface Sci. 497 (2017) 43–49, https://doi.org/10.1016/j.jcis.2017.02.058.
- [43] Y. Li, X.Q. Li, D.H. Han, W.L. Huang, C. Yang, New insights into the role of Ni loading on the surface structure and the reactivity of nZVI toward tetrabromo- and tetrachlorobisphenol A, Chem. Eng. J. 311 (2017) 173–182, https://doi.org/10. 1016/j.cej.2016.11.084.
- [44] R. Radhakrishan, D.M. Do, S. Jaenicke, Y. Sasson, G.-K. Chuah, Potassium phosphate as a solid base catalyst for the catalytic transfer hydrogenation of aldehydes and ketones, ACS Catal. 1 (2011) 1631–1636, https://doi.org/10.1021/cs200299v.
- [45] T.A. Natsir, T. Hara, N. Ichikuni, S. Shimazu, Kaolinite catalyst for the production of a biodiesel-based compound from biomass-derived furfuryl alcohol, ACS Appl. Energ. Mater. 1 (2018) 2460–2463, https://doi.org/10.1021/acsaem.8b00694.
- [46] T.A. Natsir, S. Shimazu, Fuels and fuel additives from furfural derivatives via etherification and formation of methylfurans, Fuel Process. Technol. 200 (2020) 106308, https://doi.org/10.1016/j.fuproc.2019.106308.