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# Magnetic nickel ferrite nanoparticles as highly durable catalyst for catalytic transfer hydrogenation of bio-based aldehydes

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**Abstract**: Magnetic nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>) nanoparticles were exploited as stable and easily separable heterogeneous catalyst for catalytic transfer hydrogenation (CTH) of furfural to furfuryl alcohol with 2-propanol as both hydrogen source and solvent providing 94% product yield at 180 °C after 6 h of reaction. The magnetic property of the catalyst provided facile recovery by an external magnet after reaction allowing it to be reused in five reaction cycles without loss of catalytic performance. Importantly, the NiFe<sub>2</sub>O<sub>4</sub> nanoparticles was also applicable to CTH of other alkenyl/allyl/aromatic aldehydes affording over 94% selectivity towards the targeted alcohol products, thus being attractive as a highly universal catalyst for CTH of aldehydes.

**Keywords**: Furfural; catalytic transfer hydrogenation; magnetic catalyst; biomass valorization; Meerwein-Ponndorf-Verley reduction.

# **1** Introduction

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Upgrading of biomass-derived platform chemicals to bio-fuels and value-added chemicals has received extensive interest as a mean to link biomass to a renewable chemical industry where the dependence on our fossil resources can be reduced [1-4]. Furfural (FF) is generated from the dehydration of biomass-based C5-carbohydrates via acid catalysis, and is hailed as one of the most versatile and promising building block chemicals for the synthesis of liquid bio-fuels and fine chemicals [5,6]. Hydrogenation of FF is an interesting route for FF upgrading since many of the attainable products are important intermediate and specialty chemicals, including furfuryl alcohol (FAOL), tetrahydrofurfuryl alcohol, 2-methylfuran and 2-methyltetrahydrofuran (Scheme 1) [7,8]. Particularly, the selectivity hydrogenation of FF to FAOL is of great significance because FAOL not only widely apply in the manufacture of resins, lubricants, adhesives and synthetic fibers, but also bridge the gap between biomass-based C5-carbohydrates and downstream furanic products and important platform molecule (e.g., levulinic acid and  $\gamma$ -valerolactone) (Scheme 1) [9-11].



**Scheme 1**. Tandem production of FAOL from biomass-derived carbohydrates and upgrading of FAOL to other platform chemicals.

Lately, several strategies have been explored and significant advances achieved for efficient catalytic hydrogenation of FF to FAOL using hydrogen gas as H-donor [12-18]. Nevertheless, some drawbacks persist such as high cost base (e.g., noble

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metal catalysts, special facilities for storage and transportation of  $H_2$ ), handling complexity (e.g., elimination of air and inflation of H<sub>2</sub> to reactor) and safety-related issues associated to the flammable and explosive nature of  $H_2$  [19,20] making it less applicable for smaller-scale processes in particular. Furthermore, it is challenging to selectivity hydrogenate FF to FAOL with H<sub>2</sub> owing to its multi-functionalities, which often results in byproduct formation from further hydrogenation of FAOL under the typically applied reaction conditions [21]. Catalytic transfer hydrogenation (CTH) is an alternative hydrogenation strategy where formic acid, alcohols or hydrazine hydrate are employed instead of H<sub>2</sub> as H-donor. CTH is attractive since it allows circumventing most of the described shortcomings resulting from handling  $H_2$  gas [19]. The CTH process with alcohols rely on Meerwein-Ponndorf-Verley (MPV) reduction, where carbonyl compounds are selectivity reduced to the corresponding hydroxyl compounds [22]. The dual role of the alcohol as solvent and H-donor, combined with the abundant, inexpensive and easily storable properties of alcohols, has encouraged the use of CTH with biomass-derived molecules [23-29]. Although, an excessive use of alcohol is necessary in CTH, the solvent (un-oxidized alcohol) and the formed carbonyl products may be separated by distillation and reused [22].

Heterogeneous catalysts are generally preferred compared to homogeneous catalysts in liquid-phase reactions due to their ease of separation and durability. In this context, catalysts with magnetic properties are especially interesting, since an external magnet easily separates them from a reaction mixture. For applied use, this operation is timesaving and energy-efficient compared to conventional centrifugation and filtration techniques often applied in heterogeneous catalysis [30-32]. Moreover, magnetic separation caters economical, efficient, practical and environmental-friendly features, which are significant factors for large-scale production [33]. Despite the potential, exploitation of magnetic catalysts for CTH of FF is only very recently reported [34].

Ferrites with the general formula  $M^{II}Fe^{III}{}_{2}O_{4}$  (M = Fe, Co and Ni) are common, magnetically and structurally stabile materials that are well-known in heterogeneous catalysis [35]. Typically, the materials are used as catalyst carriers in the form of nanoparticles and not as the catalytic entity themselves [36-38], however some pioneering work has been done with Fe<sub>3</sub>O<sub>4</sub> nanoparticles in organic synthesis for the coupling of aldehydes, alkynes and amines [39] and for synthesis of xanthene derivatives [40]. Utilization of magnetic nanoparticles as magnetically recoverable catalyst has, to the best of our knowledge, not been reported for CTH of biomass-derived FF. Hence, in continuation of our research work with CTH of biomass-derived molecules we here report that CTH of FF to FAOL with commercial nanoparticle ferrites (Fe<sub>3</sub>O<sub>4</sub>, CoFe<sub>2</sub>O<sub>4</sub> and NiFe<sub>2</sub>O<sub>4</sub>) proceed with high selectivity (> 90%). Moreover, we demonstrate for the first time that NiFe<sub>2</sub>O<sub>4</sub> nanoparticles provide very high catalytic activity in the CTH of FF to FAOL, and that the excellent performance applies to other aldehyde substrates as well. Combined with the great potential of ferrites in industrial application, we anticipate that the results open new possibilities for exploring practical, environmental, recoverable and durable materials catering to commercial exploitation in biomass valorization.

# 2 Experimental

#### 2.1 Materials

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Furfuryl alcohol (98%, FAOL), 5-methylfurfural (99%), 2-propanol (99.5%), methanol ( $\geq 99.8\%$ ), ethanol (99.5%), 1-butanol ( $\geq 99.5\%$ ), acetone ( $\geq 99\%$ ), naphthalene (>99%, internal standard), benzaldehyde (>99%), benzyl alcohol ( $\geq$ 99%), 4-methoxybenzaldehyde (98%), 4-methoxybenzyl (98%), alcohol 3,4-dimethoxybenzaldehyde (99%), 3,4-dimethoxybenzyl alcohol (96%), heptanal  $(\geq 95\%)$ ,  $\beta$ -citronellol (95%), cinnamic alcohol (98%), 2,4,6-trimethylbenzaldehyde (98%), 2,4,6,-trimethylbenzyl alcohol (99%), Fe<sub>3</sub>O<sub>4</sub> ( $\geq$ 98%, <50 nm particle size (TEM)), NiFe<sub>2</sub>O<sub>4</sub> ( $\geq$ 98%, <50 nm particle size (APS)) and CoFe<sub>2</sub>O<sub>4</sub> ( $\geq$ 99%, ~30 nm particle size (TEM)) were purchased from Sigma-Aldrich. Furfural ( $\geq$ 99%), *n*-propanol ( $\geq$ 99.5%), 2-butanol ( $\geq$ 99.5%), *tert*-butyl alcohol ( $\geq$ 99.7%), butenal (>99%), 2-buten-1-ol  $(\geq 95\%)$ , *n*-heptanol (>99%) and  $(\pm)$  citronellal (90%) were purchased from Fluka. 5-Methylfuran-2-methanol (295%) was procured from

Bepharm Ltd and cinnamaldehyde (>98%) was provided by Merck. All chemicals were used as received.

#### 2.2 Characterization

X-ray diffraction (XRD) patterns in the range of  $2\theta = 5-80^{\circ}$  were collected using a Huber G670 diffractometer with Cu K $\alpha$  radiation. Nitrogen adsorption/desorption measurements were conducted at -196 °C using a Micromeritics ASAP 2020 porosity analyzer. The samples were heated at 200 °C for 4 h under vacuum before the N<sub>2</sub> physisorption measurements. Thermogravimetric (TG) analysis were performed on a Mettler Toledo thermal analyzer under air flow (30 mL/min) from 25-600 °C (heating rate 10 °C/min). Temperature-programmed desorption (TPD) of NH<sub>3</sub> and CO<sub>2</sub> were carried out on a Micromeritics AutoChem II 2920 apparatus to evaluate the total acid/base amount of catalysts. Initially, the samples were dried at 300 °C for 1 h under helium flow (25 mL/min), then cooled to 50 °C followed by subjecting to a gas flow (15 mL/min) of NH<sub>3</sub>/He or CO<sub>2</sub>/He (v/v = 1/9). Subsequently, the redundant and physically adsorbed NH<sub>3</sub> or CO<sub>2</sub> were removed by purging with a He flow (25 mL/min). Afterward, the temperature was raised to 600 °C (heating rate 10 °C/min) to record the chemically adsorbed NH<sub>3</sub> or CO<sub>2</sub>. The magnetic property of the ferrites was evaluated using a Quantum-Design MPMS-XL SQUID magnetometer at 17 °C.

#### 2.3 Catalytic transfer hydrogenation (CTH)

CTH of aldehydes was performed in a 50 mL stainless steel autoclave with magnetic stirring (900 rpm). In a typical run, 0.1922 g (2 mmol) FF, 0.06 g (0.26 mmol, based on metal) catalyst and 0.04 g naphthalene (internal standard) were mixed in 10 mL 2-propanol in the autoclave. The reactor was then heated to a specified temperature (120-180 °C) for a desired reaction time (0.5-8 h) without inter gas purging establishing an autogenic pressure of about 3.5, 9 and 16 bar at 140, 160 and 180 °C, respectively. After reaction, the reactor was immersed into ice-cold water to quench the reaction. For recycling experiments, the catalyst was collected by virtue of using an external magnet, washed twice (2 × 5 mL) with ethanol and acetone, dried at 80 °C

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for 2 h and subsequently used for the next reaction run.

The products in the reaction mixture was identified and quantified by GC-MS (Agilent 6850-5975C) and GC (Agilent 6890N equipped with a FID detector), respectively, using HP-5MS capillary columns (30.0 m  $\times$  250  $\mu$ m  $\times$  0.25  $\mu$ m) in both apparatus. The FF conversion and FAOL yields were calculated on basis of standard curves of reference compounds with naphthalene as internal reference. The CTH protocol with other aldehydes was the same as for FF except that 1 mmol reactant was used instead.

### **3 Results and Discussion**

#### 3.1 Catalytic performance of different ferrites

Table 1 compiles the catalytic performances measured of different ferrites nanoparticles in the CTH of FF to FAOL using 2-propanol as H-donor. Auto-hydrogenation of FF at 180 °C without catalyst gave a negligible yield of FAOL with a low FAOL selectivity of 17% after 4 h of reaction (entry 1, Table 1). In contrast, all the ferrites afforded high FAOL selectivity (>91%) at 180 °C demonstrating that the materials were efficient catalysts for CTH of FF to FAOL at this temperature. Notably, NiFe<sub>2</sub>O<sub>4</sub> revealed high FF conversion (95%) as well as high FAOL yield (90%) at 180 °C after 4 h of reaction (entry 13, Table 1) in contrast to Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> under the same conditions (entries 5 and 9, Table 1). For NiFe<sub>2</sub>O<sub>4</sub> this corresponded to a high initial formation rate of FAOL (456  $\mu$ mol g<sup>-1</sup> min<sup>-1</sup>) as well as a first-order reaction rate constant  $(11.5 \cdot 10^{-3} \text{ min}^{-1})$  that was 3.9 and 2.7 times higher than the corresponding rate constants of Fe<sub>3</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub>, respectively (Table 1, Table S1 and Figure S1). Notably, a similar reactivity trend was also reported for Raney Ni and Co in CTH of aromatic alcohols using 2-propanol as H-donor [41]. Raney Ni are known to be an efficient catalyst for CTH reactions in 2-propanol [42,43], however the active sites of Ni(0) are easily oxidized in air making the catalyst inconvenient to use compared to Ni-ferrite. The excellent performance of NiFe<sub>2</sub>O<sub>4</sub> was probably attributed to it high acid and base amount (Table 1 and Figure S2), as it

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is well known that acid-base sites are crucial for the CTH reaction based on MPV reduction [44-46]. Based on the interesting initial results the catalytic behavior of NiFe<sub>2</sub>O<sub>4</sub> was hereafter more systematically investigated.

Entry	Catalyst	Time	FF	FAOL	Sel.	Acid/base	FAOL initial	Reaction
		(h)	conv.	yield	(%)	amount	formation rate	rate const.
			(%)	(%)		$(\text{mmol/g})^{b}$	(µmolg <sup>-1</sup> min <sup>-1</sup> ) <sup>c</sup>	$(\min^{-1})^d$
1	-	4	24	4	17	-	-	-
2	Fe <sub>3</sub> O <sub>4</sub>	0.5	21	19	91	0.215/0.047	211	$2.9 \cdot 10^{-3}$
3		1	29	28	97			
4		2	44	41	93			
5		4	57	54	95			
6	CoFe <sub>2</sub> O <sub>4</sub>	0.5	33	31	94	0.380/0.074	344	4.3·10 <sup>-3</sup>
7		1	42	41	98			
8		2	60	57	95			
9		4	73	71	97			
10	NiFe <sub>2</sub> O <sub>4</sub>	0.5	43	41	95	0.501/0.109	456	11.5·×10 <sup>-3</sup>
11		1	60	56	93			
12		2	74	71	96			
13		4	95	90	95			

 Table 1. The catalytic performance of different ferrites in the CTH of FF<sup>a</sup>

<sup>a</sup> Reaction conditions: 2 mmol FF, 10 mL 2-propanol, 0.06 g catalyst, 180 °C. <sup>b</sup> Evaluated by NH<sub>3</sub>/CO<sub>2</sub>-TPD. <sup>c</sup> Calculated from the FAOL yield obtained after 0.5 h. <sup>d</sup> Calculated assuming first order reaction kinetics:  $-\ln(1-X) = kt + C$ , where X = FF conversion and t = 30, 60, 120 and 240 min.

#### 3.2 Effect of reaction temperature and time

Figure 1 displays the influence of reaction temperature and reaction time on the CTH of FF to FAOL in 2-propanol over NiFe<sub>2</sub>O<sub>4</sub> nanoparticles (0.06 g). In general, NiFe<sub>2</sub>O<sub>4</sub> yielded excellent selectivity of about 90% at all examined temperatures (*i.e.*, 120, 140, 160 and 180 °C), implying that NiFe<sub>2</sub>O<sub>4</sub> was a highly selectivity catalyst for the formation of FAOL, whereas the activity was very temperature dependent. Thus, at 120 °C the FF conversion and FAOL yield increased only moderately with reaction time reaching 51 and 49%, respectively, after a reaction time of 8 h (Figure 1a). In contrast, near quantitative FF conversion of 99% and FAOL yield of 94% was obtained after 6 h at 180 °C (Figure 1d). Throughout the experiments, minute amount of 2-(diisopropoxymethyl)furan and 2-isopropoxyfuran were observed as revealed

from GC-MS analysis, which resulted from acetalization of furfural with 2-propanol and etherification of furfuryl alcohol with 2-propanol, respectively. Reaction rate constants (k) at the different temperatures was obtained by plotting  $-\ln(1-X)$  versus reaction time assuming that the FF conversion was a pseudo-first-order reaction (Figure 2a and Table S2). From these values the activation energy ( $E_a$ ) of CTH of FF to FAOL over NiFe<sub>2</sub>O<sub>4</sub> in 2-propanol was evaluated from an Arrhenius plot (Figure 2b) to be 48.2 kJ/mol (Table S2). This value was close or slightly lower than values reported in literature for CTH of FF with other catalyst systems (Table S1) [26,28,34], confirming the remarkable catalytic activity of NiFe<sub>2</sub>O<sub>4</sub>.

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**Figure 1**. Synthesis of FAOL from FF over NiFe<sub>2</sub>O<sub>4</sub> at (a) 120 °C, (b) 140 °C, (c) 160 °C and (d) 180 °C from 0.5-8 h of reaction. Reaction conditions: FF (2 mmol), NiFe<sub>2</sub>O<sub>4</sub> (0.06 g), 2-propanol (10 mL).

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**Figure 2**. (a)  $-\ln(1-X)$  vs. reaction time and (b)  $\ln(k)$  vs. reciprocal of reaction temperature in CTH of FF over NiFe<sub>2</sub>O<sub>4</sub>. Reaction conditions: FF (2 mmol), catalyst (0.06 g), 2-propanol (10 mL), t = 0.5-4 h.

#### 3.3 Effect of various alcohols as H-donors

The catalytic performances obtained with NiFe<sub>2</sub>O<sub>4</sub> for CTH of FF to FAOL in different C2-C4 alcohols are summarized in Table 2. Notably, above 93% FAOL selectivity was obtained in both primary (entries 1-3, Table 2) and secondary alcohols (entries 4-5, Table 2), whereas almost no FAOL was formed in the case of tertiary alcohol (entry 6, Table 2). The latter result was not surprising considering that

*tert*-butanol has no hydrogen atom on the carbon atom with the hydroxyl group available to form a six-membered ring intermediate from FF and *tert*-butanol on the surface of the catalyst, which is a key step in the hydrogen-transfer process of the MPV reduction [24,44-46]. Moreover, the secondary alcohols gave better FF conversion than the primary alcohols, which is associated to the lower reduction potential of secondary alcohols compared to primary alcohols as also demonstrated in earlier studies [47,48].

Entry	Alcohol	Conversion (%)	Yield (%)	Selectivity (%)
1	Ethanol	67	64	96
2	1-Propanol	48	45	94
3	1-Butanol	51	48	94
4	2-Propanol	99	94	95
5	2-Butanol	96	91	95
6	tert-Butanol	8	2	25

Table 2 CTH of FF to FAOL over NiFe<sub>2</sub>O<sub>4</sub> using various alcohols as H-donors<sup>a</sup>

<sup>a</sup> Reaction conditions: FF (2 mmol), NiFe<sub>2</sub>O<sub>4</sub> (0.06 g), solvent (10 mL), 180 °C, 6 h.

#### 3.4 Effect of catalyst dosage and hot filtration experiment

As depicted in Figure 3a, the FAOL yield obtained from CTH of FF at 180 °C after 6 h of reaction was almost negligible without added NiFe<sub>2</sub>O<sub>4</sub> catalyst. In contrast, a small amount of NiFe<sub>2</sub>O<sub>4</sub> (*i.e.*, 0.02 g) gave 80% FF conversion along with 72% FAOL yield. When the catalyst amount was further increased to 0.06 g the FF conversion reached 99% and the FAOL yield 94%, while only a marginal variation in FAOL yield was observed with more catalyst added, suggesting that the optimal catalyst dosage under the examined conditions were 0.06 g in terms of FAOL yield. In addition, the effect of stirring speed on the CTH of FF to FAOL over the magnetic NiFe<sub>2</sub>O<sub>4</sub> catalyst was also evaluated (Table S4). Only slightly lower FF conversion and FAOL yield were observed when the stirring speed was decreased to 600 rpm, while a considerable decrease in FAOL yield was detected when the stirring speed was increased to 1200 rpm, indicating that too high stirring speed was not advantageous with the magnetic catalyst. The heterogeneity of NiFe<sub>2</sub>O<sub>4</sub> during the CTH process was rationalized by conducting a hot filtration experiment, wherein the catalyst was removed from the reaction mixture via an external magnet after the reaction had proceeded at 180 °C for 1 h. Afterwards, the reaction mixture was allowed to react for another 7 h under the same conditions. The data in Figure 3b clearly shows that the FAOL yield remained unchanged around 56% after the catalyst removal, indicating that the NiFe<sub>2</sub>O<sub>4</sub> was stable with no active species leaching from the catalyst during the reaction.



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**Figure 3**. Influence of catalyst dosage on the CTH of FF to yield FAOL (a) and time-yield plots after catalyst removal after 1 h (b). Reaction conditions: FF (2 mmol), NiFe<sub>2</sub>O<sub>4</sub> (0.06 g), 2-propanol (10 mL), 180 °C.

#### 3.5 Catalyst reusability

The reusability of NiFe<sub>2</sub>O<sub>4</sub> in CTH of FF was examined under reaction conditions resulting in both low FF conversion (180 °C, 1 h; Figure 4a) and high conversion at optimal reaction conditions (180 °C, 6 h; Figure 4b). As exhibited in Figure 4, no significant decline in FF conversion or FAOL yield occurred during five consecutive reaction cycles at both of the examined conditions, thus demonstrating NiFe<sub>2</sub>O<sub>4</sub> to form an apparently highly durable CTH catalyst system. To verify durability of the catalyst, the NiFe<sub>2</sub>O<sub>4</sub> recovered after CTH at 180 °C for 6 h was further characterized by XRD, TG, N<sub>2</sub>-physisorption and SQUID analysis. The XRD analysis (Figure 5a) revealed no crystallographic change of the spent catalyst compared to the fresh catalyst. Similarly, the saturation magnetization of the spent and fresh catalyst was almost identical (Figure 5c). A slight increment of 2.3% in total weight loss (Figure 5b) and a small decline  $\sim 8.1 \text{ m}^2/\text{g}$  (Figure S3) in surface area was, however observed for the spent catalyst compared to the fresh catalyst. These observations confirm that NiFe<sub>2</sub>O<sub>4</sub> indeed was a highly durability catalyst with only traces of carbon residue deposited on the surface. The high resistance for carbon residue deposition could arise from the magnetism of the material as previously suggested [49].





**Figure 4**. Recycling tests of NiFe<sub>2</sub>O<sub>4</sub> in the CTH of FF to FAOL at 180 °C for (a) 1 h and (b) 6 h. Reaction conditions: FF (2 mmol), NiFe<sub>2</sub>O<sub>4</sub> (0.06 g), 2-propanol (10 mL).





**Figure 5**. XRD pattern (a), TG curve (b) and magnetization curve (c) of fresh and spent NiFe<sub>2</sub>O<sub>4</sub> catalyst.

#### 3.6 Substrate scope

The substrate scope of the CTH reaction system with NiFe<sub>2</sub>O<sub>4</sub> was extended from FF to several alternative aldehydes to demonstrate the versatility of the system towards substrates contained in, *e.g.* biomass-derived bio-oils [50] (Table 3). Interestingly, NiFe<sub>2</sub>O<sub>4</sub> proved also to be a very efficient CTH catalyst forming the targeted products with all of the alternative aldehydes in above 94% selectivity, and – importantly - over 90% conversion was achieved with both saturated and unsaturated (*i.e.*, alkenyl, allyl or aromatic) aldehydes (entries 1-4, 6 and 8, Table 3) under optimized reaction

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conditions. However, in the case of 2,4,6-trimethylbenzaldehyde (entry 5, Table 3) and citronella (entry 7, Table 3) low to moderate conversion was observed even at high temperature (*i.e.*, 200 °C), which was probably attributed to the steric bulkiness of the substrates hampering the reaction at the surface of the NiFe<sub>2</sub>O<sub>4</sub> particles. Hence, good universality for CTH of many aldehydes combined with excellent product selectivity and ease of recyclability makes the NiFe<sub>2</sub>O<sub>4</sub> nanoparticle catalyst system attractive for further exploration.

Entry	Substrata	Product	Temperature	Time	Conversion	Yield	Selectivity
Entry	Substrate		(°C)	(h)	(%)	(%)	(%)
1		OH OH	180	6	92	88	96
2		ОН	180	2	99	96	97
3	Н3СО-	нзсо-	180	3	95	93	98
4		ОН	180	6	91	89	98
5		ОН	200	6	27	26	96
6	$//_4$	<u> </u>	180	6	94	91	97
7		ОН	200	6	76	74	97
8		ОН	180	3	92	87	95

Table 3 CTH of other aldehydes over NiFe<sub>2</sub>O<sub>4</sub> catalyst<sup>a</sup>

<sup>a</sup> Reaction conditions: Substrate (1 mmol), NiFe<sub>2</sub>O<sub>4</sub> (0.06 g), 2-propanol (10 mL).

# 4 Conclusions

Commercial available NiFe<sub>2</sub>O<sub>4</sub> nanoparticles are demonstrated to be a highly efficient catalyst in the CTH of FF to FAOL using 2-propanol as H-donor and solvent, affording 99% FF conversion with 95% FAOL selectivity at 180 °C with a reaction time of 6 h. The excellent CTH performance was associated to a relatively low activation energy (~48.2 kJ/mol) as calculated from the Arrhenius equation assuming

first-order kinetics. Moreover, the NiFe<sub>2</sub>O<sub>4</sub> nanoparticle catalyst was stable and durable under the applied CTH reaction conditions with FF as revealed from a hot filtration experiment and reuse in five consecutive reactions with facile separation of the magnetic NiFe<sub>2</sub>O<sub>4</sub> nanoparticles by an external magnet. Importantly, the versatility of the NiFe<sub>2</sub>O<sub>4</sub> nanoparticles for CTH was further verified with other aromatic/allyl/alkenyl aldehydes in 2-propanol, which all yielded high selectivity (>94%) for the targeted alcohol products. In perspective, it is anticipated that NiFe<sub>2</sub>O<sub>4</sub> nanoparticles could be established as a prominent catalyst not only for CTH of FF to FAOL, but also exploited as a highly efficient heterogeneous catalyst for CTH of biomass-derived molecules in general.

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# **Graphical abstract**



**Effective use of magnetic nanoparticles**: Commercial nickel ferrite (NiFe<sub>2</sub>O<sub>4</sub>) nanoparticles are efficient, durable and magnetically recoverable heterogeneous catalysts for catalytic transfer hydrogenation of biomass-derived furfural as well as other aldehydes with 2-propanol as H-donor forming furfuryl alcohol and various aromatic/allyl/alkenyl alcohols, respectively, which are precursors for bio-fuels and fine chemicals.