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## ARTICLE



# Efficient aerobic oxidation of alcohols catalyzed by NiGa hydrotalcites in the absence of any additives

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The aerobic oxidation of alcohol catalyzed by NiGa hydrotalcites in the absence of any additives has been detailedly studied. The research results revealed that the surface basicity significantly affected the catalytic performance. Moreover, the Brønsted OH basic site on Ni-containing hydrotalcites was suggested to be the key active site and accelerated the oxidation. The catalytic system had good tolerance for varied alcohols, and excellent selectivity of aldehyde could be obtained for the oxidation of primary alcohol. A probable non-radical reaction path for the transformation has been proposed according to the catalytic results, isotope labelling experiments and Hammett experiments.

#### 1. Introduction

Developing high-efficiency catalytic system for the transformation of alcohol to corresponding carbonyl compound using molecular oxygen without any additives is particularly attractive in synthetic and industrial chemistry. Evident progress has been made with the noble metals, for example, Ru [1,2], Au [3–5], Pt [6], and Pd [7–9], etc. However, only a few catalytic systems originated from nonnoble metals could be found in literatures, including OMS-2 (cryptomelane octahedral molecular sieve) [10,11], Mn-Ca oxide [12], NiAl hydrotalcite-like anionic clay [13,14], and VSB-5 phosphates molecular sieve treated with NaOH [15]. Developing economical and easy-manufactured catalysts for the oxidative transformation is still highly desirable from the perspective of application.

Layered double hydroxides (LDHs) with the hydrotalcite structure is a typical basic material, consisted of M<sup>2+</sup> and M<sup>3+</sup> cations in the brucite layer, and anions in the interlayer [16,17]. These components can be adjusted through certain methods to tune the physicochemical properties of the material. These features make the hydrotalcite an ideal material of catalyst or the support of catalyst. Actually, the hydrotalcite-like compounds have been investigated in varied reactions, and efficient catalytic performances have been observed [18]. To the best of our knowledge, only two types of Ni-containing materials have been found effective in the oxidation of alcohol via molecular oxygen [13,14], and the catalytic efficiency were not satisfactory. To find more efficient catalyst for the transformation, we have studied the relation between Ni-containing hydrotalcites structure and the

catalytic property in detail in case of NiMgAl hydrotalcites [19]. The results indicated that the reaction was not through a radical path and the surface basicity had significantly effect on the catalytic activity.

On the basis of the obtained results, we speculated that enhancing the basicity of catalyst might be a breakthrough point to design more efficient catalyst. The hydrotalcites' basicity is mainly affected by the composition, including cations in the brucite layers and anions in the interlayers. Recently we have communicated a result of alcohol oxidation/ Knoevenagel condensation tandem reaction over NiGa hydrotalcites [20]. Excellent catalytic activity for the NiGa LDHs in the tandem reaction has been observed. In the present research, the catalytic behavior of NiGa LDHs in the alcohol oxidation and the probable mechanism were investigated in detail.

#### 2. Experimental Section

#### 2.1. Materials and methods

The preparation method for  $CO_3^{2^-}$ -Ni<sub>x</sub>Ga-LDHs (x = 2, 3, 4 and 5) samples can be found in the literature [20]. Ni<sub>3</sub>Ga-LDO-200 and Ni<sub>3</sub>Ga-LDO-400 were obtained by calcining  $CO_3^{2^-}$ -Ni<sub>3</sub>Ga-LDH under 200 °C or 400 °C for 5 h, respectively.

#### 2.2. Catalysts characterization

The Powder X-ray diffraction (XRD) was recorded in a Rigaku D/max 2500 PC X-ray diffractometer. The element chemical analysis was performed by ICP-OES in a Varian Vista-AX device. N<sub>2</sub>-adsorption/desorption isotherms of the catalysts were collected on a Micromeritics ASAP 2010C instrument at liquid N<sub>2</sub> temperature. Titration was used to analyze the surface basicity of the samples using 0.025 M benzoic acid solution as the titrant and phenolphthalein as the indicator [21].

#### 2.3. Catalytic oxidation of alcohol

In a typical procedure, the oxidation of alcohol was performed in a carousel reaction tube under molecular oxygen. A mixture of toluene (5 mL), benzyl alcohol (108 mg, 1 mmol), chlorobenzene (0.5 mmol) and catalyst (0.5 g) at 80 °C was magnetically stirring

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under oxygen. The products were analyzed through a GC (Shimadzu GC-2010AF) and GC-MS (Shimadzu GCMS-2010). When the reaction finished, the catalyst was filtered and washed with solvent, and then dried at 120 °C before being recycled. The TOF (turnover frequency) values were obtained on the basis of the total Ni in the catalysts.

#### 2.4. Procedure for Hammett study

Benzyl alcohol (10 mmol) and *para*-(X)-substituted benzyl alcohol (10 mmol, X =  $-OCH_3$ ,  $-CH_3$ , -CI, and  $-NO_2$ ), chlorobenzene (10 mmol, internal standard),  $CO_3^{2^-}$ -Ni<sub>3</sub>Ga-LDH (0.25 g), and toluene (5 mL) was mixed and stirred at 80 °C under oxygen. The reaction mixture was regularly sampled and analyzed. The equation  $k_x/k_H = C_xX_i/C_HH_i$  ( $C_x$  and  $C_H$  are the conversions of the two substrates, and  $X_i$  and  $H_i$  are the initial concentrations) was applied to determine the relative reactivities of the substituted substrates.

#### 2.5. <sup>18</sup>O-labeled experiments

<sup>18</sup>O-labeled benzylalcohol (93% <sup>18</sup>O enriched, prepared according to reported method [22], 110 mg, 1 mmol),  $CO_3^{2-}$ -Ni<sub>3</sub>Ga-LDH (0.5 g), and toluene (8 mL) was mixed and stirred under oxygen at 80 °C. The reaction mixture was sampled and analyzed through GC-MS. The <sup>16</sup>O and <sup>18</sup>O compositions in benzaldehyde were calculated according to the relative abundance of mass peaks at m/z = 106 for <sup>16</sup>O and m/z = 108 for <sup>18</sup>O.

#### 3. Results and discussion

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#### 3.1. Catalyst characterization studies

The characterization of  $CO_3^{2^-}$ -Ni<sub>x</sub>Ga-LDHs samples, including XRD, FTIR, DR UV-vis, TG-DTG and SEM, can be found in our previous reported literature [20]. And the results indicated that the hydrotalcite structure formed for all the samples and the cations were well dispersed. The data of ICP analysis in Table 1 shows that the Ni/Ga ratios are very close to the theoretical value. Nitrogen sorption measurement was also performed to explore the textural parameters of the NiGa hydrotalcites (Table 1). The analysis results show that the BET surface area of these NiGa LDHs change irregularly, while the pore volumes and the average pore diameter of these NiGa hydrotalcites with different Ni/Ga ratio are close to each other. Upon replacing Al by Ga in hydrotalcites, the average pore diameter increases, which may be ascribed to the change of the microscopic morphology for the introduction of Ga<sup>3+</sup> cations in



**Fig. 1** N<sub>2</sub> adsorption/desorption isotherms and pore size distribution (inserted picture) of CO<sub>3</sub><sup>2–</sup>-Ni<sub>x</sub>Ga-LDHs.

the brucite layer [23,24].

According to the IUPAC classification, the N<sub>2</sub> adsorptiondesorption isotherm depicted in Fig. 1 indicate that all the NiGa LDHs exhibit type IV isotherm, suggesting the mesoporosity of the materials. Concerning the hysteresis loops, the NiGa LDHs samples with Ni/Ga ratios of 2 and 3 show H2-type hysteresis. In contrast, broad H3 type hysteresis loops can be observed for the  $CO_3^{2^-}$ -Ni<sub>4</sub>Ga-LDH and  $CO_3^{2^-}$ -Ni<sub>5</sub>Ga-LDH, suggesting plate-like particles aggregated during the synthesis [25,26]. These phenomena imply that the different composition of the brucite layer results in the diverse types of pore shapes.

To elucidate the probable significant influence of basicity on the catalytic activity, the surface basicity of these prepared samples should be analyzed. The method of Hammett indicator instead of  $CO_2$ -TPD analysis was applied to determine the amount of the basic sites. Because the structure of LDHs samples must be destroyed during the pretreatment process (high temperature is needed) in the  $CO_2$ -TPD analysis. The results presented in Table 1 indicate that both of the basic strength and the total amount of basic sites are significantly affected by the Ga content, and  $CO_3^{2^-}$ -Ni<sub>3</sub>Ga-LDH exhibits the strongest basicity and the largest number of basic sites. The enhancement of the basicity in comparision with NiAl hydrotalcite suggests that substituting the Al by Ga is an efficient

Table 1         Sample notation and chemical compositions of CO <sub>3</sub> <sup>2-</sup> -Ni <sub>x</sub> Ga-LDHs								
Sample	Weight content (%)			Saure	Porevolume	Average pore		Basicity at H -
	Ni	Ga	Ni : Ga	$(m^2/g)$	(cm <sup>3</sup> /g)	diameter (nm)	рН <sup>а</sup>	7.6~10.0 (mmol/g) <sup>b</sup>
CO3 <sup>2-</sup> -Ni2Ga-LDH	32.2	17.6	2.2:1	122	0.32	8.7	7.78	0.16
CO3 <sup>2-</sup> -Ni3Ga -LDH	35.5	13.8	3.1 : 1	109	0.28	8.8	8.36	0.20
CO3 <sup>2-</sup> -Ni4Ga -LDH	40.1	11.2	4.3 : 1	133	0.28	6.7	7.82	0.16
CO <sub>3</sub> <sup>2−</sup> -Ni₅Ga -LDH	41.9	9.3	5.4 : 1	151	0.32	7.5	7.77	0.13
CO3 <sup>2-</sup> -Ni <sub>2</sub> Al-LDH	33.6	7.92	2.0 : 1	109	0.15	3.8	7.94	0.02
Ni₃Ga-LDO-200	34.6	12.4	3.3 : 1	51	0.10	7.8	9.14	0.23
Ni <sub>2</sub> Ga-LDO-400	42.4	16.1	31:1	100	0.23	9.2	9 72	_

 $^{a}$  Suspension of 0.3 g hydrotalcite in 20 mL deionized water.  $^{b}$  0.1 g hydrotalcite, suspended in 2 mL phenolphthalein indicator solution, is titrated with 0.025 M benzoic acid.

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#### way to enhance the basicity of these samples. 3.2. Catalytic activity of CO<sub>3</sub><sup>2-</sup>-Ni<sub>x</sub>Ga-LDHs

In the course of benzyl alcohol oxidation under the  $CO_3^{2-}-Ni_xGa-$ LDHs with molecular oxygen as the sole oxidant, no byproduct was observed under the optimized conditions. The time-plots of the conversion for these hydrotalcites catalysts with different Ni/Ga ratio are illustrated in Fig. 2. The CO32--Ni3Ga-LDH exhibits the highest catalytic activity, which should be due to its highest content of basic site [20]. And the higher activity of  $CO_3^{2-}$ -Ni<sub>5</sub>Ga-LDHs than  $\text{CO}_3^{\ 2\text{-}}\text{-Ni}_2\text{Ga-LDHs}$  and  $\text{CO}_3^{\ 2\text{-}}\text{-Ni}_4\text{Ga-LDHs}$  may be ascribed to the higher Ni content of the sample.

Further, some representative heterogeneous catalytic systems have been collected in Table 2 for comparision. It can be seen that CO<sub>3</sub><sup>2-</sup>-Ni<sub>3</sub>Ga-LDH provided the excellent catalytic results for the



Fig. 2 Catalytic oxidation of benzyl alcohol over different Ni<sub>x</sub>Ga hydrotalcites. Reaction conditions: benzyl alcohol 1 mmol; toluene 5 mL; catalyst 0.5 g; oxidant oxygen; reaction temperature 80 °C

Table 2 Some typical results of heterogeneous catalytic systems for the oxidation of benzyl alcohol using O<sub>2</sub> as the sole oxidant.<sup>a</sup>

Entry	Catalyst	C <sup>b</sup> (%)	S <sup>c</sup> (%)	TOF <sup>d</sup> (×10 <sup>-3</sup> s <sup>-1</sup> )	Ref.
1	CO <sub>3</sub> <sup>2-</sup> -Ni <sub>3</sub> Ga-LDH	97	>99	20.6	This work
2	$Ca_{0.16}MnO_2{\cdot}2H_2O$	100	82 <sup>e</sup>	0.6	12
3	VSB-5 nickel phosphate	93	99.9	-	15
4	Mg <sub>2.5</sub> Ni <sub>0.5</sub> Al-HT	51.8	97.8 <sup>e</sup>	-	14
5	Ni <sub>2</sub> Al-HT	33	1 <sup><i>f</i></sup>	-	13
6	H-K-OMS-2	97	100	-	11
7	Pd-(VO) <sub>4</sub> P <sub>2</sub> W <sub>18</sub> / <i>m</i> APO	68.6	99	-	9
8	Au/Cr <sub>4</sub> -HT	7	6	844.4	27
9	Au/CuO	85.7	99	1.8	28
10	Au nanoparticles	99	€,	-	29
11	NAP-Mg-Pd(0)	100	99	2.9	1
13	Au@8Pd/SiO₂	91	87 <sup>g</sup>	7666.7	8
14	Au/MgCr-HT	7	6	522.2	2

<sup>a</sup> See the reference for the detailed structure of catalyst. <sup>b</sup> Conversion of benzyl alcohol. <sup>c</sup> Selectivity of benzaldehyde. <sup>d</sup> Based on the observed reaction rate.<sup>e</sup> The by-product is benzoic acid.<sup>f</sup> Yield of benzaldehyde.<sup>g</sup> The other products are toluene (4.6%), benzoic acid (4.3%) and benzyl benzoate (3.7%).

oxidation, comparable to the best results reported in the literatures. The TOF of the reaction was also calculated the the study to make the comparision more precise. Three Au-containing catalysts exhibit evidently high catalytic activity in the reaction (entries 8 and 9), but the present catalytic system provides higher selectivity. The TOF of CO<sub>3</sub><sup>2-</sup>-Ni<sub>3</sub>Ga-LDH in the oxidation is higher than the previous reported catalysts based on non-noble metals.

With this optimization in hand, the applicability of  $CO_3^{2-}$ -Ni<sub>3</sub>Ga-LDH was tested in the oxidation of a range of representative substrates (Table 3). In general, oxidation of the benzyl alcohol and its analogs efficiently proceeded to give the corresponding aldehydes (entries 1-8) without the formation of any byproducts, significantly better than some reported results [13,14]. The reaction times required for the complete conversion of the benzyl alcohol analogues were varied, obviously indicating that electronic effect existed during the oxidation. Interestingly, both electron-donating substituents (entries 1, 5 and 6) and electron-withdrawing substituents (entries 2-4) enhanced the reactivity. However, although excellent yields were also obtained in cases of 4tertbutylbenzyl alcohol and 1-naphthalenemethanol (entries 7 and 8), the reactivity decreased concerning the reaction time, which was likely to be due to the steric effect. An exceptional case was found that CO<sub>3</sub><sup>2-</sup>-Ni<sub>3</sub>Ga-LDH could not catalyze the transformation of the 4-hydroxybenzyl alcohol (entry 9).

Delightedly, excellent yields (entries 10-14) of the corresponding ketone have also been obtained for the secondary alcohol. 1-phenyl ethanol and the analogues could be smoothly transformed to the corresponding products under the catalytic system, significantly better than the NaOH treated VBS-5 [15]. The lower activity might be due to the smaller pore size of the VBS-5 (1.0 nm), while the data for NiGa hydrotalcites has a widened distribution (Table 1), and these bulky substrates can easily approach the active site. Further, steric effect was also observed in the catalytic transformation, because different reaction times were required for the substrates with various size.

Table 3 Catalytic oxidation of varied alcohols under CO<sub>3</sub><sup>2-</sup>-Ni<sub>3</sub>Ga-

LDH.				
Entry	Substrate	Product	Conv. (%)	time (h)
1	Н3С ОН	H <sub>3</sub> C O	>99	0.75
2	O2N OH	O <sub>2</sub> N O	>99	1.5
3	СІ	CI	>99	3
4	F <sub>3</sub> C OH	F <sub>3</sub> C O	>99	0.5
5	ОН		>99	0.5
6	ОН		>99	0.5



 $^a$  Reaction conditions:  $\rm CO_3^{2^-}-Ni_3Ga-LDH$  0.5 g, substrate 1 mmol, 80 °C, toluene 8 mL, O\_z. The selectivities of the corresponding carbonyl products for these substrates were all >99%.  $^b$  Selectivity.  $^c$  Under the catalysis of  $\rm CO_3^{2^-}-Ni_2Al-LDH.$ 

Allylic alcohol such as cinnamyl alcohol produces cinnamaldehye selectively without formation of any epoxide product (entry 15). Additionally, geranial and perilla aldehyde are important fragrances and organic synthetic intermediates and always produced by oxidation of the corresponding 30 condes of the present catalytic system can also provide excellent yields (entries 16 and 17), significantly better than commercial results and some reported results [30–32].

Moreover, the present catalytic system was also effective in the aerobic oxidation of some heterocyclic alcohols. Excellent yields were obtained for 3-thienylmethanol and 3-pyridinemethanol (entries 18 and 19), although 24 h was needed for the complete conversion of 3-pyridinemethanol. Good yield for the diol (entry 21) was also obtained under the catalytic system.

Moreover, the aliphatic alcohols (entries 22–23) have also been tested under the catalytic system, although these substrates are very challenging and have not been studied under the Nicontaining catalytic systems [13–15]. Although the NiGa catalyst only gave a moderate yield of 2-pentanone, the observation was very interesting.

#### 3.3. Discussion of the mechanism

The radical scavenger experiments have excluded the formation of radical intermediate [20]. In addition, benzyl alcohol together with  $\alpha$ -phenethyl alcohol with same amount was introduced into the reaction and the results could be found in Fig. 3. The reaction rate of primary alcohol was faster than that of secondary substrate, suggesting that an alcoholate species between the catalyst and the alcohol formed in the oxidation [2,33,34].

In the oxidative transformation of benzyl alcohol to benzaldehyde, the cleavage of O–H and  $\alpha$ -C–H bonds [4,5,8,9,27] are generally involved. For the cleavage of O–H, only the basic sites located in the catalysts were suggested to be effective by the controlled experiments [20]. To further unravel the effect of the type of basic site,  $CO_3^{2-}$ -Ni<sub>3</sub>Ga-LDH was calcined at 200 and 400 °C in air for 5 h, respectively, and the corresponding samples (Ni<sub>3</sub>Ga-LDO-200 and Ni<sub>3</sub>Ga-LDO-400) were obtained (XRD patterns are displayed in Fig. 4A) [35,36]. Hammett method was also used to analyze the surface basicity of the LDO samples. The results in Table 1 show that the basic strength markedly increased after the calcination, whereas it was difficult to analyze the total basic sites



**Fig. 3.** Comparision of the conversions of benzyl alcohol and  $\alpha$ -phenethyl alcohol. Reaction conditions: catalyst 0.5 g, benzyl alcohol 0.5 mmol,  $\alpha$ -phenethyl alcohol 0.5 mmol, toluene 8 mL, 80  ${}^{\circ}$ C, O<sub>2</sub>.

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Fig. 4 XRD patterns of the calcined samples and their catalytic performance. Reaction conditions: benzyl alcohol 1 mmol; toluene 5 mL; catalyst 0.5 g; oxidant oxygen; reaction temperature 80 ºC.

for the black of color Ni<sub>3</sub>Ga-LDO-400. In addition, the basic site probably changed from Brønsted OH groups to metal-oxygen pairs, namely Ni–O and Ga–O, and low-coordinated oxygen atoms  $(O_2^{-1})$ ions) [37,38]. Surprisingly, an even reduced catalytic activity was observed for these calcined samples (Fig. 4B), especially for the Ni<sub>3</sub>Ga-LDO-400, suggesting that OH groups as Brønsted basic sites in the prepared hydrotalcite were necessity for accelerating the oxidation. These observations implied that the reaction was affected by both of the basic strength and the type of the basic site of the catalyst. Moreover, the compared experiment of calcined samples suggested that Brønsted basic OH groups presented in HTlike lattice were particularly important for the oxidation of alcohol by molecular oxygen.

In prior to the Hammett experiment, the existence of pore diffusion limitations inside the catalysts was examined. And a Weisz-Prater criterion (expressed in eqn (1)) has been introduced in the catalytic system [39-41].

$$\phi_{\rm WP} = \frac{r_{\rm a}R_{\rm p}^2}{C_{\rm s}D_{\rm eff}}$$
(1)

The calculation was performed according to ref. 40 for its similar liquid-phase reaction (see SI for the detailed calculation procedure). The value of  $P_{WP}$  for each reactant ( $P_{WP|O_2} = 1.0 \times 10^{-3}$ ,  $P_{WP|benzyl alcohol} = 2.6 \times 10^{-4}$ ) is less than 0.3, which excludes the presence of significant pore diffusional limitations during the reaction under the selected conditions [40].

Then, Hammett experiment was performed to elucidate the cleavage  $\alpha$ -C–H bonds [15]. In the present study, the competitive oxidations of para-substituted benzyl alcohols were conducted by CO<sub>3</sub><sup>2-</sup>-Ni<sub>3</sub>Ga-LDH to explain the effect of substituents on the transformation. To ensure that the reaction proceeded in a zero grade mode during the Hammett reaction, excess amount of substrates were introduced. The relative rates were calculated based on the conversions of substrate when the values are <5%. Interestingly, the Hammett plots depicted in Fig. 5 indicate that both electron-donating and electron-withdrawing substituents can accelerate the oxidation, different from the reported catalytic systems [42]. Concerning the electron-donating substituents such as the -OCH<sub>3</sub> and -CH<sub>3</sub>, the results suggest the formation of the carbocation-type transition state via the hydride abstraction. The enhancement of the  $-NO_2$  and -CI substituted benzyl alcohol might be due to the increase of the substrates' acidity in the situation, because the strong acidity of the alcohol benefited for the first acid-base reaction step. The catalytic



Fig. 5 Hammett plot of p-substituted benzyl alcohols. Reaction conditions: 5 mmol p-X-benzyl alcohol (X = CH<sub>3</sub>O, CH<sub>3</sub>, H, Cl, NO<sub>2</sub>), 5 mmol benzyl alcohol, CO<sub>3</sub><sup>2-</sup>-Ni<sub>3</sub>Ga-LDH 0.5 g, toluene 8 mL, 1 mmol chlorobenzene, 60 °C, O<sub>2</sub>.

behavior was quite different from that we previous reported NiMgAl samples [19]. We speculated that the phenomenon might be due to the different basicity of the two catalysts. Under the catalysis of NiGa samples, the relative reaction rates of the O-H and  $\alpha$ -C–H bond cleavages were depended on the substrate. For the benzyl alcohols with electron-donating substituents, the  $\alpha$ -C–H bond cleavage was the rate-controlled step, while the O-H bond cleavage was slower for the electron-withdrawing groups substituted benzyl alcohols. These results suggest that both O-H and  $\alpha$ -C–H bond cleavages might be kinetically-relevant steps in transformation catalyzed by NiGa hydrotalcites.

Further, isotope labelling experiments were conducted by using <sup>18</sup>O labelled benzyl alcohol as the substrate. The results in Table 4 indicate that only about 5.7% of the produced benzaldehyde was labelled by <sup>18</sup>O after 5 min and 60 min, which was quite strange. If the oxygen in benzaldehyde was not from benzyl alcohol, there should be no <sup>18</sup>O labelled product was observed; on the other hand, if the oxygen originated from benzyl alcohol, the observed content of the <sup>18</sup>O labelled benzaldehyde was obviously too low. We speculated that the low content of the <sup>18</sup>O labelled benzaldehyde might be due to the fast exchange of the oxygen atom between benzaldehyde and H<sub>2</sub>O formed in the reaction. To check the speculation, excess H<sub>2</sub><sup>16</sup>O was added into the reaction after 5 min, and only 1.1% of <sup>18</sup>O labelled benzaldehyde was remained after 5 min, indicating that the exchange reaction existed and the equilibrium was established rapidly. Further, we investigated the exchange reaction of oxygen atom between benzaldehyde consisted of  ${}^{16}O$  and  $H_2{}^{18}O$  under the similar reaction conditions. The results in Table 4 indicate that the  $CO_3^{2-}$ -Ni<sub>3</sub>Ga-LDH certainly can accelerate the exchange reaction (a possible reaction path for the oxygen exchange between benzaldehyde and water is shown in Scheme 1). These results show that the <sup>18</sup>O labelled benzaldehyde was formed by the oxidation of <sup>18</sup>O labelled benzyl alcohol in the present catalytic system. However, because the fast exchange reaction of oxygen atom between benzaldehyde and H<sub>2</sub>O produced in the oxidation under the catalytic system, only a part of the <sup>18</sup>O labelled benzaldehyde was detected.

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Table 4 The	results of	isotope-label	experiments. <sup>a</sup>

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Entry	C. hatasha	A .   .   1   1	Content of <sup>18</sup> O-
	Substrate	Additive	benzaldehyde /%
1	<sup>18</sup> O - benzyl alcohol	-	5.7 (5.8) <sup>c</sup>
2	<sup>18</sup> O - benzyl alcohol	$H_2^{16}O$	1.1
3 <sup>b</sup>	<sup>16</sup> O - benzaldehyde	H <sub>2</sub> <sup>18</sup> O	1.1(2.7) <sup>c</sup>
4	<sup>16</sup> O - benzaldehyde	$H_2^{18}O$	17.5 (18.8) <sup>c</sup>

<sup>a</sup> Reaction conditions: substrate 0.5 mmol,  $H_2^{16}O$  or  $H_2^{16}O$  10 mmol,  $CO_3^{2-}$ -Ni<sub>3</sub>Ga-LDH 0.5 g, toluene 8 mL, 1 mmol chlorobenzene, 60 °C,  $O_2$ , reaction 5 min. <sup>b</sup> Without catalyst. <sup>c</sup> The data in bracket was analyzed after 60 min.



**Scheme 1** A possible reaction path for the oxygen exchange between benzaldehyde and water.

On the basis of the obtained and reported results [13,14,15,19,20], a possible reaction mechanism for the catalytic alcohol oxidation was proposed in Scheme 3. The reactant alcohol firstly reacts with Brønsted basic OH group linked to the Ga<sup>3+</sup> (step 1) in NiGa hydrotalcite to form alcoholate species. Then the  $\alpha$ - H of the alcoholate transfers to the neighboring Ni atom (step 2), and the carbonyl product simultaneously forms as well as the nickel hydride species (step 3). The species then react with adsorbed  $O_2$  to generate OOH group (step 4), and the catalytic cycle finished after releasing of  $1/2O_2$  (step 5). According to the reaction path, the low reactivity of 4-hydroxybenzyl alcohol should be attributed to the stronger acidity of phenolic hydroxyl, which reacted with Brønsted basic OH group faster than alcohol hydroxyl. The high selectivity of aldehyde can also be explained by the proposed mechanism, because the produced carbonyl compounds cannot be activated by the catalyst for the further oxidation under the reaction conditions.



**Scheme 2** The proposed mechanism of the oxidation of alcohol catalyzed by NiGa hydrotalcite.

#### 4. Conclusions

#### DOI: 10.1039/C7NJ03895J Developing efficient heterogeneous catalysts originated from nonnoble metals for the aerobic oxidation of alcohols in the absence of any additives has been a highly research attractive topic. In the present work, the catalytic oxidation of alcohol by molecular oxygen under NiGa hydrotalcites has been studied in detail. The results suggested that the enhanced catalytic activity in the transformation is associated with the surface basicity of the NiGa hydrotalcites, including both of the type of basic sites and the strength. Further, the controlled experiments implied that the Brønsted OH basic site plays the key role in the results suggested that both O–H and $\alpha$ -C–H bond cleavages are kinetically-relevant steps in the aerobic oxidation of alcohol. According to the obtained results, a probable mechanism has been proposed.

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#### **Conflicts of interest**

There are no conflicts to declare.

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The surface Brønsted OH basic site on NiGa hydrotalcites was suggested to be the key active site for the oxidation.