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Article

Geometric effect promoted hydrotalcites catalysts towards aldol condensation reaction

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ABSTRACT

In solid basic catalysis field, how to achieve optimized activity and desired stability through elaborate control over basic site properties remains a challenge. In this work, taking advantage of the structure memory effect of layered double hydroxides (LDHs), rehydrated $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x\text{-LDHs}$ and $\text{Ca}_4\text{Al}_{1-x}\text{In}_x\text{-LDHs}$ catalysts were prepared and applied in aldol condensation reaction that isobutyraldehyde (IBD) reacts with formaldehyde (FA) to obtain hydroxypivalaldehyde (HPA). Notably, the resulting re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}\text{-LDHs}$ exhibits an extraordinarily-high catalytic activity (HPA yield: 72%), which is to our best knowledge the highest level in this reaction. The weak Brønsted basic site, 7-coordinated Ca–OH group, which serves as an active site, catalyzes the condensation process and promotes the product desorption. Studies on structure-property correlations demonstrate that Ga as a structural promoter induces a moderate expansion of the laminate lattice, which results in a significant increase in the concentration of weak basic sites in re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}\text{-LDHs}$, accounting for its high catalytic activity. This work illuminates that geometric structure of basic active sites can be tuned *via* introducing catalyst additive, which leads to a largely improved performance of hydrotalcite solid basic catalysts towards aldol condensation reaction.

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1. Introduction

Serving as a critical aspect of synthetic chemistry applied in numerous industrial processes, base-catalyzed aldol condensation reactions have caused considerable attention so as to produce various value-added chemicals with all kinds of industrial applications [1–4]. Among these condensation processes, the

reaction of isobutyraldehyde (IBD) with formaldehyde (FA) serves as a crucial process to produce hydroxypivalaldehyde (HPA), which is an important intermediate for production of neopentyl glycol (NPG) widely used in the manufacturing of polyesters, lubricants, plasticizers, and synthetic resin coatings [5,6]. Generally, homogeneous catalysts such as triethylamine, NaOH and KOH have been widely used in this reaction due to

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cost effectiveness and high activity; whereas, they show disadvantages in separation and recovery, and are unable to meet the increasingly stringent requirements for environmental benignity and sustainability [7–9]. Based on the idea of environmentally friendly catalysis, solid basic catalysts such as metal oxides, metal nitrides and perovskites are extremely desirable in these condensation processes with facile separation and depressed pollution [10–12]. However, compared with homogeneous catalysts (the highest level of HPA yield: 73.5%), the HPA yield of solid basic catalysts is not satisfied (only 4.3%–50%), and the catalytic activity needs to be further improved [10]. Therefore, it is essential to explore and develop solid basic catalysts with high catalytic performance.

Layered double hydroxides (LDHs), owing to their large amount of surface hydroxyl and structural memory effects, have been used in this aldol condensation reaction as solid basic catalysts in our previous work [13,14]. The prepared rehydrated Ca_4Al -LDHs displays a superior activity (HPA yield: 60%) to those of conventional solid basic catalysts (HPA yield: 22%–50%). Moreover, it has been verified that the weak Brönsted basic site (7-coordinated Ca-OH group) acts as an active site of the aldol condensation reaction and promotes the production desorption [13,15]. Despite advances in re- Ca_4Al -LDHs catalyst, gaps remain in catalytic activity compared to liquid basic catalysts, which inspires us to take measures to further enhance catalytic performance. Geometric effects by introducing cations with different ionic radius into LDHs laminar lattice play an crucial role on the regulation of the microstructure of active center [16–19]. For instance, geometric effects would impose active-site isolation, distort geometry structure and change adsorption modes, leading to an enhanced activity or selectivity of heterogeneous catalysts [20–24]. Some metal ions as a structural promoter have been investigated in redox, hydrogenation and condensation reactions, such as transition metals (Mn, Zr, etc.) and rare earth elements (La, Y, Ce, etc.) [25–28]. Herein, we hypothesized that a positive geometric effect by insertion of cation with appropriate ionic radius in Ca_4Al -LDHs catalyst will further improve the catalytic performance.

Inspired by the above idea, a series of rehydrated $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -LDHs and $\text{Ca}_4\text{Al}_{1-x}\text{In}_x$ -LDHs ($x = 0, 0.05, 0.10, 0.15$) catalysts were prepared and used in the reaction of FA with IBD to produce HPA. Among these samples, the re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs catalyst displays the best catalytic performance with a 91% IBD conversion and 72% HPA yield, which is significantly exceeding the re- Ca_4Al -LDHs catalyst (conversion: 80%; yield: 60%) and even close to the catalytic properties of liquid base catalysts (conversion: 97%; yield: 73.5%). According to our previous work, the weak basic site (7-coordinated Ca-OH group) in re- Ca_4Al -LDHs has been demonstrated to serve as an active site of aldol condensation reaction, which facilitates the desorption of product molecules accompanied with the increment of HPA selectivity. Herein, as a combination study including *in situ* XANES, CDCl_3 -FTIR characterization and structure-property correlation study demonstrated, re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs with incorporation of Ga into hydrotalcite laminates gives rise to a moderate lattice expan-

sion and thus increases the concentration of weak basic sites, accounting for an extraordinary catalytic performance; whereas, re- $\text{Ca}_4\text{Al}_{0.90}\text{In}_{0.10}$ -LDHs possess abundant highly coordinated In-OH group, leads to a decreased 7-coordinated Ca-OH group and poor catalytic properties. Thus, we came to the conclusion that Ca_4Al -LDHs is a structure-sensitive catalyst, whose performance can be optimized by introducing promoter cation with appropriate ionic radius. This work investigates geometry effects on the structure of Ca-based hydrotalcites, and provides a way to attain high performance solid basic catalyst with refined regulation on the structure toward aldol condensation reaction.

2. Experimental

2.1. Chemicals

$\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{In}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, FA (37% aqueous solution), IBD, NaOH, 1,4-dioxane, cetyltrimethylammonium bromide (CTAB) and HPA were purchased from Sigma-Aldrich. Notably, all the reagents were used without further purification. In the total experimental processes, decarbonated and deionized water was also used.

2.2. Preparation of catalysts

$\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -LDHs precursors with various $\text{Ga}^{3+}/\text{M}^{3+}$ atomic ratios were synthesized by the co-precipitation method. Solution A (a mixture solution) was prepared by dissolving $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ga}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with various $\text{Ga}^{3+}/\text{M}^{3+}$ atomic ratios (0, 0.05, 0.10, 0.15) in 100 mL of decarbonated and deionized water. 2.96 g of NaOH was dissolved in the same volume of water to obtain a base solution (solution B). Both solution A and B were simultaneously dropped into a round-bottom flask with three neck under the protection of N_2 stream. Afterwards, the obtained precipitate was stirred vigorously for 10 h; moreover, the product was separated and washed thoroughly, and finally dried at 60 °C for another 20 h. Subsequently, the precursors were activated *via* a two-step approach. Firstly, the LDHs precursor sample was calcined at 500 °C for 5 h in a N_2 atmosphere with a heating rate of 5 °C min^{-1} . After cooling to room temperature, the sample was dispersed and stirred in NaOH solution for 3 h. Then the obtained sample was washed thoroughly with deionized water and ethanol; finally, the sample was dried in a vacuum oven at 65 °C for 24 h (denoted as re- $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -LDHs). Rehydrated $\text{Ca}_4\text{Al}_{1-x}\text{In}_x$ -LDHs samples were prepared through a similar process and denoted as re- $\text{Ca}_4\text{Al}_{1-x}\text{In}_x$ -LDHs.

2.3. Catalytic activity testing

The condensation reaction was performed on a cylindrical glass tube (batch-type reactor, 50 mL). Dioxane serving as internal standard (0.2 g) and CTAB (a phase transfer catalyst: 0.1 g) were added to FA (6 mL, 37% aqueous solution) and IBD (5 mL), then the catalyst $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -LDHs (0.2 g) or

re-Ca₄Al_{1-x}In_x-LDHs was dispersed into the mixture solution and heated to 70 °C for 8 h in a N₂ atmosphere while stirring. When the reaction started, aliquots were taken every 30 min. Product analysis was carried out using a Shimadzu GC-2014 with an Rtx-5 capillary column (diameter: 0.25 mm; length: 30 m). A flame ionization detector (FID) was used to analyze all the products. GC-MS was used to identify the product composition. Conversion and selectivity were calculated based on the integrated gas-phase peak area of IBD and HPA.

2.4. Characterization

Powder XRD measurements were performed on the diffractometer (Rigaku XRD-6000) by using Cu K α radiation (λ = 0.1542 nm, 40 kV, 40 mA; scanning rate: 10 °C min⁻¹; 2 θ angle: 3° to 70°). Scanning electron microscopy (Zeiss Supra 55) was executed to investigate the morphology of the catalyst (accelerating voltage: 20 kV). Low-temperature N₂ adsorption-desorption isotherms of the samples were determined on a Quantachrome Autosorb-1C-VP analyzer and the total specific surface area and pore volume were obtained by the Brunauer-Emmett-Teller (BET) measurement. Elemental composition was obtained with the Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectrometer (ICP-AES).

X-ray photoelectron spectra (XPS) were obtained by using a Thermo VG Escalab X-ray photoelectron spectrometer (pressure, 2×10^{-9} Pa), using Al K α X-rays as the excitation source. EXAFS measurements were carried out at the 4B7A of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). Additionally, the typical energy (2.2G eV) of the storage ring (maximum current: 100 mA) was used with the Si(111) double crystal monochromator. The data analysis and fitting was conducted on the IFFEFIT (1.2.11) data analysis package including Athena, Arctis, Artemis, and FEFF6.

Fourier-transform infrared spectroscopy (FTIR) was carried out with transmission mode in a Bruker Equinox 55 spectrometer in the range of 4000 and 400 cm⁻¹ (resolution: 4 cm⁻¹; per spectrum: 600 scans). FTIR spectroscopy was performed with absorption mode on an instrument spectrophotometer of Nicolet 380. The adsorbed deuterated chloroform CDCl₃-FTIR spectroscopy was used to characterize microstructure of the basic site. The operational processes were obtained according to our previous work [13]. According to the adsorption of CDCl₃, the strength of basic site can be measured *via* the following equation:

$$\log \Delta\nu_{\text{CD}} = 0.0066 \text{ PA} - 4.36 \quad (1)$$

where $\Delta\nu_{\text{CD}}$ represents the shift of ν_{CD} (cm⁻¹) while PA represents the proton affinity [kJ mol⁻¹].

2.5. Computational methods

DFT calculations were performed using the Vienna Ab-initio Simulation Package (VASP) code [29,30]. Spin-polarized Perdew-Burke-Ernzerhof (PBE) functional was employed to solve the Kohn-Sham equation, and the Grimme's DFT-D3 method was used to consider the effect of van der Waals inter-

action [31,32]. The core electrons were performed by the projector augmented wave (PAW) method [33]. A $3 \times 3 \times 1$ *k*-points was taken in the geometry optimization and a $6 \times 6 \times 1$ *k*-points was taken in the Bader charge calculations. The convergence criteria was 1.0×10^{-4} eV for the electronic self-consistent iteration and 0.05 eV/Å for force. Ca₄Al-Cl-LDHs was constructed based on a 3×3 supercell of Mg(OH)₂. Ga/In-doped LDHs model was built by replacing one Al atom with one Ga or In atom at (001) surface. Two chloride ions were added in the unit cell of the studied LDHs to keep the charge neutral. A 15 Å vacuum was added to avoid the interaction between the slabs. 7-coordinated Ca was built by adding one OH group on the Ca at (001) surface. HPA desorption energy is calculated as follows:

$$E_{\text{des}} = E_{\text{HPA}} + E_{\text{surf}} - E_{\text{HPA/surf}} \quad (2)$$

where E_{surf} is the energy of the Ca₄Al-Cl-LDHs (001) surface, E_{HPA} is the energy of HPA in gas phase, and $E_{\text{HPA/surf}}$ is the energy of HPA adsorbs on the LDHs (001) surface.

3. Results and discussion

3.1. Structural and morphological studies on various catalysts

The XRD patterns of Ca₄Al_{1-x}Ga_x-LDHs and Ca₄Al_{1-x}In_x-LDHs precursors (Fig. 1A) display a series of characteristic reflections at 10.5°, 20.8°, 31.4°, 37.8°, and 55.6°, which are indexed to Ca₄Al-LDHs with interlayer NO₃⁻ anions [34,35]. The position of the (003) reflection shifts to lower angle after the incorporation of Ga and In compared with Ca₄Al-LDHs, indicating that Ga or In is successfully introduced into the hydroxide laminate (Fig. S1). After calcination at 500 °C for 4 h, the Ca₄Al_{1-x}Ga_x-LDHs and Ca₄Al_{1-x}In_x-LDHs precursors transform to a mixed oxide phase, which are denoted as Ca₄Al_{1-x}Ga_x-MMOs and Ca₄Al_{1-x}In_x-MMOs, as shown in Fig. 1B. The diffraction peaks at 37.6°, 43.7°, and 63.8° are indexed to a cubic CaO phase; moreover, the presence of Ga₂O₃ or In₂O₃ phases was not detected, implying a high dispersion with tiny particle size in Ca₄Al-LDHs materials. Afterwards, the reconstructed Ca₄Al_{1-x}Ga_x-LDHs and Ca₄Al_{1-x}In_x-LDHs can be obtained through the rehydration process of MMOs samples in an aqueous NaOH. The results (Fig. 1C) show that the rehydrated samples re-express characteristic feature of an LDHs phase and the (003) reflection shifts from 10.5° to 11.5° (2 θ) relative to the NO₃⁻-containing LDHs precursor, indicating a replacement of NO₃⁻ by OH⁻ groups in the interlayer region. SEM measurement was performed to explore the morphology of these rehydrated samples (Fig. 2A–2G), from which laminar microcrystals (a lateral diameter: ~2 μ m) are observed for all these samples. Nitrogen adsorption-desorption isotherms were performed to study the specific surface area and pore-size distribution of all these rehydrated samples. As summarized in Table 1, with the increase in the amount of Ga or In, the surface area shows an increase trend from 15.1 m²/g to 40.9 m²/g with an average pore diameter ranging in 21.3 nm to 24.9 nm. Furthermore, the molar ratios of Ga³⁺/M³⁺ and In³⁺/M³⁺ determined by ICP-AES are close to nominal values, indicating that Ga or In is successfully introduced into re-Ca₄Al-LDHs.

Fig. 1. XRD patterns of (A) LDHs, (B) MMOs, and (C) re-LDHs. (a) Ca_4Al , (b) $\text{Ca}_4\text{Al}_{0.95}\text{Ga}_{0.05}$, (c) $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$, (d) $\text{Ca}_4\text{Al}_{0.85}\text{Ga}_{0.15}$, (e) $\text{Ca}_4\text{Al}_{0.95}\text{In}_{0.05}$, (f) $\text{Ca}_4\text{Al}_{0.90}\text{In}_{0.10}$, (g) $\text{Ca}_4\text{Al}_{0.85}\text{In}_{0.15}$.

3.2. Catalytic performance of samples

The catalytic performance of these $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -LDHs and re- $\text{Ca}_4\text{Al}_{1-x}\text{In}_x$ -LDHs samples towards the aldol condensation of FA with IBD to produce HPA was studied. Generally, a low temperature could not meet the requirement of activation of aldol condensation; while a high temperature leads to undesired side reactions [36]. The reaction temperature was studied and the corresponding performances of catalysts are listed in Table S1. The selectivity of HPA in the presence of re- $\text{Ca}_4\text{Al}_{0.95}\text{Ga}_{0.05}$ -LDHs shows an obvious change flowing the increase of reaction temperature: it rises from 55.2% (at 65 °C) to the maximal value of 79.3% (at 70 °C), followed by a sharp drop to 58.4% (at 75 °C). Therefore, a reaction temperature of 70 °C was chosen. Figure S2 shows the HPA yield over these rehydrated LDHs samples along with reaction time. It is observed that all these catalysts reach reaction equilibrium at 8 h, and the performance of re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs is far superior to re- Ca_4Al -LDHs and re- $\text{Ca}_4\text{Al}_{1-x}\text{In}_x$ -LDHs. Additionally, the catalytic performance results evaluated under optimal conditions are shown in Fig. 3A. For re- $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -LDHs catalysts, with the improve of $\text{Ga}^{3+}/\text{M}^{3+}$ atomic ratios from 0 to 0.15, the equilibrium conversion enhances obviously at first and then decreases slightly. For the HPA selectivity, a similar trend is found, and the maximal value (conversion: 90%; selectivity: 80.5%) is obtained on the re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs catalyst with the highest yield of 72%. In the case of re- $\text{Ca}_4\text{Al}_{1-x}\text{In}_x$ -LDHs catalysts, both the conversion and selectivity are below those of re- $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -LDHs samples. In addition, the initial formation

rate of HPA at 2% IBD conversion that reflects the intrinsic catalytic property is listed in Table 2. The results show that the formation rate of HPA follows a similar change tendency and re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs sample exhibits the maximal value (104 $\text{mmol g}^{-1}\text{h}^{-1}$). A comparison study for the catalytic performances of control samples including conventional solid base (e.g., $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -LDHs, $\text{Ca}_4\text{Al}_{1-x}\text{In}_x$ -LDHs, $\text{Ca}_4\text{Al}_{1-x}\text{Ga}_x$ -MMOs, $\text{Ca}_4\text{Al}_{1-x}\text{In}_x$ -MMOs), and liquid alkali catalysts for this reaction were explored (Table S2). The results reveal that re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs catalyst exhibits a significantly improved HPA yield (72%) than that of LDHs precursors (45%) and conventional solid base catalysts (55%), even close to the level of liquid basic catalysts (73.5%). In addition, the stability test of re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs catalyst shows a decrease by 10% for conversion and selectivity within five cycles and then remains stable in the sixth cycle (Fig. 3B). XRD pattern of the used catalyst gives the presence of CaCO_3 phase (Fig. S3), which is the reason of partial deactivation.

3.3. Studies on structure-property correlations

To identify the nature of basic site, *in situ* DRIFTS spectra, with a suitable probe molecule (CDCl_3 , a weak acid molecule) under mild conditions, were performed over these rehydrated samples [37]. As shown in Fig. 4, a wide FTIR band can be ob-

Fig. 2. SEM images of (A) re- Ca_4Al -LDHs, (B) re- $\text{Ca}_4\text{Al}_{0.95}\text{Ga}_{0.05}$ -LDHs, (C) re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs, (D) re- $\text{Ca}_4\text{Al}_{0.85}\text{Ga}_{0.15}$ -LDHs, (E) re- $\text{Ca}_4\text{Al}_{0.95}\text{In}_{0.05}$ -LDHs, (F) re- $\text{Ca}_4\text{Al}_{0.90}\text{In}_{0.10}$ -LDHs and (G) re- $\text{Ca}_4\text{Al}_{0.85}\text{In}_{0.15}$ -LDHs.

Table 1
Structure properties of rehydrated LDHs samples.

Sample	$\text{Ga}^{3+}/\text{or In}^{3+}/\text{M}^{3+}$ molar ratio ^a	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore diameter (nm)	a (Å) ^b	c (Å) ^c
re- Ca_4Al -LDHs	0	15.1	26.4	3.30	22.59
re- $\text{Ca}_4\text{Al}_{0.95}\text{Ga}_{0.05}$ -LDHs	0.048	22.2	21.4	3.30	22.62
re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs	0.102	24.3	21.1	3.31	22.63
re- $\text{Ca}_4\text{Al}_{0.85}\text{Ga}_{0.15}$ -LDHs	0.148	35.2	21.5	3.18	22.62
re- $\text{Ca}_4\text{Al}_{0.95}\text{In}_{0.05}$ -LDHs	0.042	15.3	27.6	3.32	22.62
re- $\text{Ca}_4\text{Al}_{0.90}\text{In}_{0.10}$ -LDHs	0.094	40.9	26.1	3.31	22.64
re- $\text{Ca}_4\text{Al}_{0.85}\text{In}_{0.15}$ -LDHs	0.140	39.5	20.9	3.32	22.62

^a $\text{Ga}^{3+}/\text{M}^{3+}$ or $\text{In}^{3+}/\text{M}^{3+}$ molar ratio was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). ^b Lattice parameter a was determined by the formula $a = 2d_{110}$, which is related to the average cation-cation distance in the brucite-like sheets. ^c Lattice parameter c was determined by the formula $c = 3d_{003}$, which is indicative of interlayer distance.

Fig. 3. (A) The conversion and selectivity of IBD as well as HPA yield over re-Ca₄Al_{1-x}Ga_x-LDHs catalysts and re-Ca₄Al_{1-x}In_x-LDHs catalysts; (B) Catalytic performance of re-Ca₄Al_{0.90}Ga_{0.10}-LDHs toward the aldol condensation reaction of IBD with FA (six consecutive cycles). Reaction conditions: catalyst (0.2 g), IBD (5 mL), FA (6 mL), CTAB (0.1 g), 70 °C, 6 h, N₂.

Table 2

Catalytic performance of various samples toward the aldol condensation of isobutyraldehyde with formaldehyde.

Sample	Proton affinity ^a (kJ mol ⁻¹)	B _W /B _W +B _M ^b (area g ⁻¹)	B _M /B _W +B _M ^b (area g ⁻¹)	IBD conversion (%)	HPA selectivity (%)	HPA yield (%)	Formation rate ^c (mmol g ⁻¹ h ⁻¹)
re-Ca ₄ Al	838	0.55	0.44	80.3	75.0	60.5	57.1
re-Ca ₄ Al _{0.95} Ga _{0.05}	830	0.58	0.42	82.3	76.1	62.4	73.3
re-Ca ₄ Al _{0.90} Ga _{0.10}	827	0.63	0.36	91.0	79.0	71.8	104
re-Ca ₄ Al _{0.85} Ga _{0.15}	828	0.59	0.41	88.5	77.1	68.1	88.0
re-Ca ₄ Al _{0.95} In _{0.05}	842	0.30	0.65	77.0	75.5	58.1	34.5
re-Ca ₄ Al _{0.90} In _{0.10}	843	0.20	0.79	70.5	71.0	50.0	24.9
re-Ca ₄ Al _{0.85} In _{0.15}	845	0.05	0.95	68.0	71.5	48.6	16.7

^aThe proton affinity is estimated based on the equation 1. ^bB_W and B_M are calculated based on the integral intensity of absorption bands of CDCl₃ on weak and medium basic sites divided by the sample quantity, respectively. ^cFormation rate of HPA is calculated on the basis of the tangent slope of the yield-reaction time plot at the 2% yield of HPA.

served in the range 2180–2300 cm⁻¹, and further deconvoluted to two peaks by a Gaussian peak fitting approach in order to obtain the distribution of basic strength and semi-quantitative data. The two bands, with maximum at 2254 and 2214 cm⁻¹, are defined as the C–D stretching vibration of CDCl₃ adsorbed on the weak and medium basic sites, respectively. In addition, in Ca₄Al_{0.85}Ga_{0.15}-LDHs, the wide FTIR band can deconvoluted to four peaks by a Gaussian peak fitting approach, the two peaks at relatively high wavenumber (2275 and 2264 cm⁻¹) are assigned to the C–D stretching vibration of CDCl₃ gas and physically adsorbed CDCl₃, respectively. With the increase of Ga³⁺/M³⁺ atomic ratios from 0 to 0.15, the peak area of ν_{C-D} on weak alkaline sites enhances obviously and re-Ca₄Al_{0.90}Ga_{0.10}-LDHs catalyst gives the maximum value. This indicates that the incorporation of Ga element enhances the concentration of 7-coordinated Ca–OH group (weak basic site). However, in the case of re-Ca₄Al_{1-x}In_x-LDHs catalysts, the normalized peak area of weak basic site decreases significantly along with the increase of In content. Moreover, compared with the re-Ca₄Al-LDHs sample, no obvious band shift is observed for re-Ca₄Al_{1-x}Ga_x and re-Ca₄Al_{1-x}Ga_x system, indicating that the strength of alkaline sites remains unchanged with the introduction of Ga or In. On the other hand, the desorption energies of HPA from three kinds of samples were studied (Fig. S4) by DFT

calculations. The results show that HPA desorption energy from re-Ca₄Al-LDHs (1.10 eV) is close to re-Ca₄Al_{1-x}Ga_x-LDHs (0.94 eV) and re-Ca₄Al_{1-x}In_x-LDHs (1.19 eV), in accordance with their close catalytic selectivity towards HPA. Our previous work has demonstrated that the weak basic site is assigned to the active 7-coordinated Ca–OH group and the medium basic site is

Fig. 4. Fourier-transform infrared spectra (FTIR) of (a) re-Ca₄Al-LDHs, (b) re-Ca₄Al_{0.95}Ga_{0.05}-LDHs, (c) re-Ca₄Al_{0.90}Ga_{0.10}-LDHs, (d) re-Ca₄Al_{0.85}Ga_{0.15}-LDHs, (e) re-Ca₄Al_{0.95}In_{0.05}-LDHs, (f) re-Ca₄Al_{0.90}In_{0.10}-LDHs and (g) re-Ca₄Al_{0.85}In_{0.15}-LDHs recorded at 2180–2300 cm⁻¹ with transmission mode after CDCl₃ adsorption at 25 °C.

Fig. 5. Formation rate of HPA as a function of the normalized FTIR peak area assigned to weak (A) and medium basic sites (B) over (a) re-Ca₄Al-LDHs, (b) re-Ca₄Al_{0.95}Ga_{0.05}-LDHs, (c) re-Ca₄Al_{0.90}Ga_{0.10}-LDHs, (d) re-Ca₄Al_{0.85}Ga_{0.15}-LDHs, (e) re-Ca₄Al_{0.95}In_{0.05}-LDHs, (f) re-Ca₄Al_{0.90}In_{0.10}-LDHs and (g) re-Ca₄Al_{0.85}In_{0.15}-LDHs.

considered as the physically-adsorbed surface OH⁻ group in the re-Ca₄Al-LDHs catalyst [13]. To give a deep insight into the relationship between the catalytic performance and the quantity of basic sites for these rehydrated samples, the initial formation rate of HPA vs. the relative concentration of weak or medium basic site is represented in Fig. 5A and 5B, respectively. A positive correlation between formation rate of HPA and the relative concentration of weak basic site is obtained, demonstrating that 7-coordinated Ca–OH site performs as active site for this reaction. In general, the incorporation of Ga leads to an increase in weak basic site in re-Ca₄Al-LDHs, accounting for its high catalytic activity. In contrast, the propor-

tion of active site in re-Ca₄Al_{1-x}In_x-LDHs decreases significantly, resulting in the activity decline toward aldol condensation.

XANES (Fig. 6A) and EXAFS spectroscopy (Fig. 6B) were used to study the detailed structure of these samples. We selected re-Ca₄Al_{0.90}Ga_{0.10}-LDHs, which showed the best performance, as the optimal catalyst; while re-Ca₄Al-LDHs and re-Ca₄Al_{0.90}In_{0.10}-LDHs were chosen as reference samples catalysts. As shown in Fig. 6A, compared with Ca(OH)₂ sample, these three catalysts manifest the pre-peak observed at 4043 eV corresponding to transition state (1s to 3d), indicating a distorted 7-coordinated Ca²⁺–OH with a low structural symmetry existing in Ca-based LDHs [13,38]. Moreover, according to the

Fig. 6. (A) Normalized Ca K-edge XANES spectra and (B) Fourier-transform Ca K-edge EXAFS spectra for different samples. (C) In L-edge for re-Ca₄Al_{0.90}In_{0.10}-LDHs and In(OH)₃ samples. (D) XPS O 1s of (a) re-Ca₄Al-LDHs, (b) re-Ca₄Al_{0.90}Ga_{0.10}-LDHs and (c) re-Ca₄Al_{0.90}In_{0.10}-LDHs.

Ca K-edge EXAFS spectra (Fig. 6B), the bond length of Ca–O of re-Ca₄Al-LDHs increases from 1.719 Å to 1.769 Å for re-Ca₄Al_{0.90}Ga_{0.10}-LDHs and 1.781 Å for re-Ca₄Al_{0.90}In_{0.10}-LDHs, respectively, indicating a lattice expansion of re-Ca₄Al-LDHs with the incorporation of Ga or In. It is interesting that the Ca–O shell coordination number in re-Ca₄Al_{0.90}Ga_{0.10}-LDHs is larger than that of re-Ca₄Al sample; in contrast, the Ca–O shell coordination number in re-Ca₄Al_{0.90}In_{0.10}-LDHs is smaller than that of re-Ca₄Al sample. In order to explore this unusual phenomenon, we used In(OH)₃ as a reference sample to investigate the coordination number of In–O shell in re-Ca₄Al_{0.90}In_{0.10}-LDHs catalyst by using In L-edge EXAFS (Fig. 6C) and In 3d XPS characterization. Figure 6C shows that the coordination number of In–O shell increases obviously compared with In(OH)₃, suggesting the existence of highly coordinated In–OH group in re-Ca₄Al_{0.90}In_{0.10}-LDHs [39,40]. Moreover, the binding energy of In in the XPS spectrum (Fig. S5) moves toward high energy relative to In(OH)₃ sample, indicating the existence of electron transfer in re-Ca₄Al_{0.90}In_{0.10}-LDHs catalyst. Therefore, according to results of EXAFS spectra and catalytic evaluation, Ga as a structural promoter introduced into the laminate causes a moderate lattice expansion, which results in a certain degree of distortion of the hydrotalcite laminates with more exposed active sites. This is in accordance with the results of FTIR, in which the introduction of Ga induces an increase in quantity of weak active sites (7-coordinated Ca–OH) and largely promoted IBD conversion. On the contrary, for re-Ca₄Al_{0.90}In_{0.10}-LDHs system, the IBD conversion decreases remarkably. Based on the Ca K-edge and In L-edge EXAFS analysis, the introduction of In with a large ionic radius prefers to induce a significant expansion of the lattice framework, which leads to a high In–OH coordination and a decreased number of 7-coordinated Ca–OH group. Therefore, a depressed catalytic activity is obtained in the re-Ca₄Al_{1-x}In_x-LDHs system, which is consistent with the CDCl₃-FTIR and catalytic evaluation results.

X-ray photoelectron spectroscopy (XPS) was carried out to investigate the electronic structure of O species. For all samples, the broad asymmetric O 1s peak can be deconvoluted into three peaks by the Gaussian peak fitting approach at 532.4, 531.4 and 530.4 eV, which are attributed to the surface OH[−] in 7-coordinated Ca–OH group, lattice oxygen species of Ca–O–Al in Ca(OH)₆ octahedron, and defective O^{2−} species with low coordination, respectively [41,42]. Figures 6D and S6 show that the binding energy of OH[−] oxygen species in these samples gives inconspicuous change (between 532.5 eV and 532.3 eV), indicating that the incorporation of Ga or In has little impact on the electron density of oxygen in LDHs catalysts. Moreover, Bader charge analysis by DFT calculation shows that 7-coordinated OH[−] in three samples possesses close electron density (Fig. S7: Ca₄Al-LDHs, 1.45 eV; re-Ca₄Al_{1-x}Ga_x-LDHs, 1.41 eV; re-Ca₄Al_{1-x}In_x-LDHs, 1.47 eV), which is in agreement with the results obtained from XPS. This does not induce significant change in the strength of basic sites, consistent with the CDCl₃-FTIR result.

To further understand the geometric effect of Ga or In on rehydrated Ca₄Al-LDHs catalysts, DFT calculations were performed to investigate detailed structural information of these

three samples, and the lattice parameters of crystals are listed in Table S3. According to the geometric optimized results, the Ca–O bond length in Ca–O–Ga octahedron for Ca₄Al_{0.90}Ga_{0.10}-LDHs (Fig. 7A₂) is 2.348 Å while that in Ca–O–In system (Fig. 7A₃) is 2.417 Å, both of which are larger than that in Ca–O–Al structure (Fig. 7A₁, 2.315 Å) for re-Ca₄Al-LDHs. This indicates that Ga or In atoms introduced into Ca₄Al-LDHs laminate cause a lattice expansion, which is consistent with Ca K-edge EXAFS results. From CDCl₃-FTIR spectra, we concluded that adding metal elements with different ionic radius has different effects on the quantity of active sites. Figure 7B₁ shows the normal Ca–Al hydrotalcites model with a 7-coordinated Ca–OH group (weak active basic site). Interestingly, with the incorporation of Ga into the Ca–Al hydrotalcites, the number of 7-coordinated Ca–OH group increases, as shown in Fig. 7B₂ (*i.e.*, more weak basic sites are formed with the insertion of Ga atoms), which is agreement with the FTIR results. However, with the incorporation of In atoms, the number of 7-coordinated Ca–OH group decreases accompanied with the formation of a new highly coordinated In–OH group (Fig. 7B₃). According to the result of EXAFS and FTIR, a reasonable explanation is proposed. The incorporation of Ga or In atoms with larger ion radius induces a lattice expansion of hydrotalcites laminates, which is attributed to geometric effect. A moderate lattice expansion with the introduction of Ga atoms with appropriate ion radius (0.47 Å) results in an enhancement of weak basic sites, accounting for the improved catalytic activity. However, the incorporation of In (ion radius: 0.79 Å) causes an excessive lattice expansion by a stronger geometric effect, accompanied with the formation of undesirable In–OH with medium basic sites. Therefore, the introduction of a cation as a structure promoter with appropriate ionic radius is essential to achieve optimized catalytic performance towards aldol condensation between IBD and FA.

4. Conclusions

In summary, rehydrated Ca₄Al_{1-x}Ga_x-LDHs and Ca₄Al_{1-x}In_x-LDHs were fabricated by virtue of the structural topotactic transformation and memory effect of LDHs precursors. The obtained re-Ca₄Al_{0.90}Ga_{0.10}-LDHs exhibits the best catalytic activity toward the aldol condensation reaction that isobutyraldehyde (IBD) reacts with formaldehyde (FA) to produce hydroxypivalaldehyde (HPA) (HPA yield: 72%), which is

Fig. 7. Top (A) and side (B) views of geometry structure of (1) Ca–O–Al, (2) Ca–O–Ga, and (3) Ca–O–In systems based on DFT calculations.

comparable to the level of liquid basic catalysts (HPA yield: 73.5%). A combination study including *in situ* XANES and CDCl_3 -FTIR spectra reveals that incorporation of Ga with moderate ionic radii leads to the lattice expansion of hydrotalcite laminates (geometric effect), which significantly influences the concentration of weak basic sites. Studies on the structure-property correlation indicate that the optimal re- $\text{Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}$ -LDHs catalyst possesses the most abundant 7-coordinated Ca–OH group (weak basic site), accounting for its excellent catalytic activity. This work systematically investigates the geometric effects of doping elements with different ionic radii on the structure of Ca-based hydrotalcites, which can be used as a prospective candidate in green catalysis of aldol condensation reactions.

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Graphical Abstract

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Geometric effect promoted hydrotalcites catalysts towards aldol condensation reaction

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Ga as a structural promoter induces a moderate expansion of the laminate lattice, which results in a significant increase in the concentration of active sites in CaAlGa hydrotalcites, accounting for its high catalytic activity.

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几何效应促进水滑石催化剂实现对羟醛缩合反应性能提升

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摘要: 近年来, 绿色发展观念深入人心. 与液体碱相比, 固体碱催化剂由于其环境友好、腐蚀性小、易于回收等优点引起了科研工作者的广泛关注. 但是, 在固体碱催化领域, 如何对碱性位点进行调控从而使羟醛缩合反应获得优异性能仍然是一个很大挑战. 甲醛和异丁醛反应生成的产物羟基新戊醛是精细化工合成中一类非常重要的有机中间体, 广泛应用于药物、润滑油、聚酯树脂等化工产品生产. 目前, 应用于该反应的固体碱催化剂催化活性较低, 性能有待进一步提升. 因此, 设计一类结构可调、性能优异的固体碱催化剂材料迫在眉睫.

本文利用水滑石材料结构特有的记忆效应制备了一系列掺杂镓、铟的钙铝水滑石催化剂, 并将其应用于甲醛与异丁醛缩合生成羟基新戊醛反应, 并探讨了不同离子半径的元素掺杂对钙铝水滑石结构产生的影响和作用. 结果表明, 复原后的 $\text{re-Ca}_4\text{Al}_{0.90}\text{Ga}_{0.10}\text{-LDH}$ 对羟基新戊醛的生成表现出优异的性能(HPA产率为72%), 达到固体碱催化剂催化该反应的最高水平, 甚至与液体碱催化剂水平相当. 通过氘代氯仿原位红外光谱对催化剂的活性位点进行表征, 结果证明掺入镓之后使弱碱性位点的相对浓度增加, 而掺入铟后使弱碱性位点的相对浓度减小. 进而将弱碱性位点的数量和中强碱性位点的数量与催化性能结果进行构效关联, 证明了该反应中的活性中心为弱碱性位点(7配位Ca-OH). 该弱碱性位点不仅促进了产物羟基新戊醛的脱附, 还提高了反应的活性和选择性, 使得羟基新戊醛的产率大大提升. 通过EXAFS手段对催化剂的精细结构进行表征, 证明了掺入镓和铟后, 钙铝水滑石晶格发生了膨胀, Ca-O键长增加. 其中, 掺杂铟元素使得铟与水滑石层间羟基形成额外的In-OH化学键, 从而使七配位的Ca-OH位点浓度降低. 通过XPS和DFT计算证明了掺入镓和铟后催化剂的碱性强度没有发生变化, 说明镓和铟的掺入只改变了碱性位点数量而对碱性位点强度没有明显影响. 最后, 对催化剂结构和性能进行了关联, 证明了镓作为结构助剂掺入到水滑石层板中产生的几何效应使得晶格发生膨胀从而暴露了更多的活性位点, 实现了催化反应活性的极大提升. 该工作揭示了不同离子半径元素的掺杂所产生的几何效应对催化活性位点的有效调控作用, 从而大大提升了羟醛缩合反应性能, 为制备新型优异的固体碱催化剂提供了思路和依据.

关键词: 固体碱催化剂; 几何结构; 结构助剂; 羟醛缩合; 复原水滑石

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