

Insights on Active Sites of CaAl-Hydrotalcite as a High-Performance Solid Base Catalyst toward Aldol Condensation

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Supporting Information

ABSTRACT: Solid base catalysts are highly demanded in many heterogeneous catalysis processes, but insights on active sites and structure-property correlation have rarely been revealed and remain a challenge. Herein, activated MrAllayered double hydroxides (denoted as re- M_x Al-LDH, M = Ca, Mg), as solid base catalysts toward the aldol condensation reaction, were prepared via a two-step procedure: calcination of the M,Al-LDH precursor to produce M,Al-mixed metal oxide (M,Al-MMO), followed by a further rehydration treatment. Structural characterizations confirm that re-Ca,Al-LDH and re-Mg_xAl-LDH show similar morphology, particle size, specific surface area, and pore size distribution. However, a combination study including XPS, EXAFS, CDCl₃-FTIR,



and DFT calculations verifies that the host layer of re-Ca_xAl-LDH contains a distorted Ca(OH)₆ octahedron with an additional Ca-OH coordination that provides weak Brønsted basic site; in contrast, re-Mg,Al-LDH consists of a Mg(OH)₆ octahedron structure accompanied by surface adsorbed hydroxyl group via noncovalent interaction, resulting in a medium Brønsted basic site. For the re-Ca,Al-LDH samples, the concentration of weak Brønsted basic sites can be enhanced by tuning the Ca/Al molar ratio in the LDH precursor. The optimized re-Ca,Al-LDH catalyst (re-Ca₄Al-LDH) exhibits prominent catalytic performance toward the condensation of isobutyraldehyde (IBD) and formaldehyde (FA) to produce hydroxypivaldehyde (HPA), with a HPA yield of 61.5%. This is much higher than that of re-Mg_xAl-LDH (12.2%) and conventional solid base catalysts (4-33%), and even comparable to the level of liquid alkali (55-72%). Studies on the structure-property correlation reveal that the weak Brønsted basic site serves as active center to catalyze the aldol condensation, which accelerates the product desorption and largely promotes the HPA selectivity.

KEYWORDS: CaAl-hydrotalcite, solid basic catalysts, aldol condensation, hydroxypivaldehyde, structure-activity correlation

1. INTRODUCTION

The base-catalyzed aldol condensation is an important facet of synthetic chemistry used in many industrial processes, which produces a variety of value-added chemicals with versatile commercial applications (e.g., polymers, pharmaceuticals, and agricultural chemicals).¹⁻³ At present, the liquid alkali as a homogeneous catalyst (e.g., aqueous NaOH, KOH, and triethylamine) has been commonly used in aldol reactions due to high activity and cost effectiveness.^{4,5} However, several problems remain unsolved: the generation of large amounts of waste liquid, environmental pollution, and equipment corrosion; moreover, the product separation from liquid alkali catalyst is a big conundrum, which results in further polycondensation of the product.^{6,7} Recently, solid base materials such as heterogeneous catalysts (e.g., metal hydroxides, hydrotalcite-like compounds) are considered as a substitutional candidate to resolve the above problems encountered in the application of liquid alkali. $^{8-11}$ Many previous studies have been focused on solid base catalysts via synthesis exploration on category, particle size, morphology, specific surface area, *etc.*¹²⁻¹⁴ To date, although much progress has been made, their catalytic performances in aldol condensation (catalytic activity and product selectivity) are far from satisfactory and still need improvement. As is wellknown, the catalytic behavior is in principle determined by the structure/property of alkaline sites on the surface (geometric

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and electronic structure).^{15,16} However, detailed knowledge concerning the influence of alkaline site structure on catalytic performance is rather lacking, and how to achieve largely improved catalytic performances *via* tuning the microstructure of alkaline species remains a challenge.

Layered double hydroxides (LDHs) are a class of twodimensional anion-intercalated materials that are also known as hydrotalcite-like compounds. LDHs can be represented by the general formula $[M_{1-x}^{2+}M_x^{3+}(OH)_2](A^{n-})_{x/n} \cdot mH_2O$, where M²⁺ and M³⁺ are divalent and trivalent metal cations distributed at an atomic level in the hydroxide layers with an edge-sharing $M(OH)_6$ octahedron, and A^{n-} is charge-balance interlayer anion.¹⁷ Recently, LDH materials have received increasing attention in solid base catalysts, owing to their versatility in chemical composition and structural architecture. It has been recognized that the alkaline site structure and catalytic performance of LDH-based catalysts are strongly related to the activation pretreatment.^{10,18} By a controlled thermal decomposition process, LDHs convert into mixed metal oxide (MMOs), and a following rehydration of MMO in the liquid phase (e.g., aqueous NaOH), due to its so-called memory effect, yields the reconstructed LDHs with enhanced alkaline property.¹⁹ Moreover, the nature and strength of basic sites can be modulated by changing chemical composition and structure of rehydrated LDHs (e.g., types of metal cations or exchangeable anions, the molar ratio of M^{2+}/M^{3+}).^{19,20} By virtue of these advantages, LDH materials provide a viable program for the design and preparation of solid basic catalysts with tunable alkaline site structure and corresponding desired catalytic performance.

In this work, M, Al-layered double hydroxides (M, Al-LDH, M = Ca, Mg) were prepared by a coprecipitation method reported by our group.¹³ By means of calcination and subsequently rehydration, activated M₂Al-LDH solid base catalysts (denoted as re-M.Al-LDH) with tunable Brønsted basic sites were obtained and used in aldol condensation of isobutyraldehyde (IBD) with formaldehyde (FA) to produce hydroxypivalaldehyde (HPA). Surprisingly, we found the re-Ca,Al-LDH as a unique catalyst, in comparison with commonly studied LDH materials (e.g., re-Mg,Al-LDH sample). The resulting re-Ca₄Al-LDH sample shows an excellent catalytic performance with a HPA yield of 61.5%, significantly higher than conventional solid base catalysts and even comparable to liquid alkali catalysts. Structural studies reveal no obvious difference between these two catalysts, but a combination investigation based on XPS, EXAFS, and DFT calculations verifies that the host layer of re-Ca,Al-LDH contains an isolated Ca-OH coordination in addition to the distorted $Ca(OH)_6$ octahedron (Scheme 1), which provides a weak Brønsted basic site confirmed by deuterated chloroform-FTIR spectra. In contrast, re-Mg_xAl-LDH involves a $Mg(OH)_6$ octahedron structure with a physically adsorbed surface hydroxyl group, giving rise to a medium Brønsted basic site. By establishing the correlation between catalytic performance and alkaline site structure, it is found that weak a Brønsted basic site as an active center facilitates the product desorption and inhibits further polycondensation, accounting for the significantly enhanced HPA yield over re-Ca_xAl-LDH. This work demonstrates a successful paradigm for the exploration of LDH-based solid base catalysts via a detailed insight on structure-property correlation, which can be potentially used as a promising candidate in heterogeneous aldol condensation reactions.





2. RESULTS AND DISCUSSION

2.1. Structural and Morphological Characterizations. The Ca,Al-LDH precursors with various Ca/Al ratios (4:1, 3:1, and 2:1) were prepared via a facile coprecipitation method reported by our group.¹³ Their XRD patterns (Figure 1A) show a series of diffraction peaks at 2θ of 10.5° , 20.8° , 31.4° , 37.8° , and 55.6°, which can be indexed to a characteristic feature of the layered Ca_xAl-NO₃⁻-LDH phase.²¹ Moreover, weak peaks at 18.3° and 34.4° are observed with the increase of Ca/Al ratio, attributed to the presence of a small amount of $Ca(OH)_2$ phase. Subsequently, Ca.Al-LDH precursors converted to Ca/ Al mixed metal oxide (Ca_xAl-MMO) via calcination at 450 °C for 4 h, followed by a rehydration process in an aqueous NaOH to obtain the reconstructed CarAl-LDH material (see Experimental Section). Figure 1B gives the XRD patterns of Ca,Al-MMO, in which three strong reflections (centered at $\sim 37.6^{\circ}$, $\sim 43.7^{\circ}$, and $\sim 63.8^{\circ}$) attributed to a CaO-periclase phase are observed. However, no reflection of Al₂O₃ is observed, indicating an amorphous phase. As shown in Figure 1C, the rehydrated Ca,Al-LDH materials display characteristic peaks of an LDH phase, with the (003) reflection shifting to a higher 2θ relative to the Ca, Al-NO₃⁻-LDH precursor (11.5° vs 10.5°). This indicates the reconstruction of a layered structure with OH⁻ as an interlayer anion. Correspondingly, the cell parameters of re-Ca, Al-LDH (listed in Table 1) are calculated based on (003) and (110) reflection as $c = \sim 22.50$ Å and a = \sim 3.30 Å, respectively, which are in accordance with the characteristics of OH⁻ intercalated Ca_xAl-LDH.

The activated Mg_xAl-LDH samples with OH⁻ as an intercalated anion (re-Mg_xAl-LDH) were also obtained by a similar calcination and rehydration procedure (Figure S1 and Table 1). It should be noted that the parameter *a* value of re-Mg, Al-LDH ($a = \sim 3.04$ Å) is significantly smaller than that of re-Ca,Al-LDH ($a = \sim 3.30$ Å), which is attributed to the bigger ionic radius of Ca²⁺ and the increased cation-cation distance in the host layer of re-Ca,Al-LDH. In addition, the Al coordination in re-Ca_xAl-LDH and re-Mg_xAl-LDH samples was also investigated by ²⁷Al MAS NMR spectroscopy, so as to confirm the reconstruction of the layered structure.¹⁸ The NMR spectra of both re-Ca_xAl-LDH and re-Mg_xAl-LDH (Figure 2) show one single resonance peak with a narrow and symmetric signal at a chemical shift of ~ 11 ppm, corresponding to octahedrally coordinated Al. This suggests that the layered structure is well reconstructed after the calcination and rehydration process, in agreement with the XRD results. SEM was used to study the morphology of rehydrated LDH samples. Both re-Ca_xAl-LDH (Figure 3A-C) and re-Mg_xAl-LDH (Figure 3D-F) samples show plate-like



Figure 1. XRD patterns of (A) Ca_xAl-LDH, (B) Ca_xAl-MMOs, and (C) re-Ca_xAl-LDH, where a, b, and c represent a Ca/Al ratio of 4:1, 3:1, and 2:1 samples, respectively.

	Table	e 1.	. Ph	vsicoche	emical	Pro	perties	of	Various	Reh	vdrated	LDH	sam	ple
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sample	M ²⁺ /Al ³⁺ molar ratio ^a	BET surface area $(m^2 g^{-1})$	pore diameter (nm)	total pore volume($cm^3 g^{-1}$)	с (Å) ^ь	a (Å) ^c
re-Ca ₂ Al-LDH	2.18	26.4	7.1	0.0887	22.59	3.30
re-Ca ₃ Al-LDH	3.36	29.6	6.9	0.0878	22.56	3.30
re-Ca ₄ Al-LDH	4.28	20.3	7.4	0.0798	22.44	3.32
re-Mg ₂ Al-LDH	1.92	21.3	7.0	0.0919	22.56	3.04
re-Mg ₃ Al-LDH	2.86	23.9	7.9	0.0937	22.47	3.04
re-Mg ₄ Al-LDH	3.95	29.1	7.7	0.0954	22.89	3.04

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



Figure 2. ²⁷Al MAS NMR spectra of re-Ca_xAl-LDH and re-Mg_xAl-LDH samples.



Figure 3. SEM images of (A-C) the three re-Ca_xAl-LDH samples, (D-F) the three re-Mg_xAl-LDH samples.

microcrystals with a lateral diameter distribution of $1.0-2.0 \mu m$. Moreover, the nitrogen adsorption–desorption isotherms of re-Ca_xAl-LDH and re-Mg_xAl-LDH samples display a comparable specific surface, average pore size, and total pore volume (Table 1). Moreover, the molar ratios of M^{2+}/Al^{3+} determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES) are also summarized in Table 1, which are close to the nominal values.

EXAFS spectroscopy (Figure 4) was performed to reveal the detailed structure of re-Ca_xAl-LDH samples, and the



Figure 4. (A) Normalized XANES spectra at Ca K-edge for (a) re- Ca_2Al -LDH, (b) re- Ca_3Al -LDH, (c) re- Ca_4Al -LDH, and (d) calcium hydroxide. (B) Fourier-transform EXAFS spectra at Ca K-edge for (a) re- Ca_2Al -LDH, (b) re- Ca_3Al -LDH, (c) re- Ca_4Al -LDH, and (d) calcium hydroxide (the solid line, experimental data; the dashed line, fitting curve).

normalized Ca K-edge XANES spectra for the three re-Ca_xAl-LDH samples and calcium hydroxide reference are shown in Figure 4A. The pre-edge feature in XANES spectra gives important electronic and structural information, especially structural symmetry.²² For the three re-Ca_xAl-LDH samples, a weak pre-edge feature, originating from transitions from a 1s to 3d state, is observed at ~4043 eV. This indicates a geometrically distorted Ca–OH octahedron (with a low structural symmetry) existing in the host layer of re-Ca_xAl-LDH samples, according to selection rules for electric dipole transitions. In contrast, except for a shoulder peak of white line

(at \sim 4047 eV) observed in the XANES region, this pre-edge feature disappears completely for the reference sample of calcium hydroxide with a symmetric octahedron. Furthermore, this phenomenon has also been observed in M_r Al-LDHs (M = Mg, Zn, Ni, etc.) consisting of a typical M-OH octahedron, ^{16,23,24} since a 1s to 3d transition is forbidden in the octahedrally symmetrical Ca-OH coordination structure. The Ca²⁺ cation in the host layer of re-Ca_xAl-LDH is prone to coordinate with surface hydroxyl to form an additional/isolated Ca-OH bond (the so-called 7-fold coordinated Ca-OH), due to its big ionic radius and high s-orbital exposure. This thus leads to a remarkable decrease in the symmetry of the Ca-OH octahedron and the corresponding occurrence of the pre-edge feature (1s \rightarrow 3d transition). In previous studies, the additional/ isolated Ca-OH coordination in Ca-based hydrotalcites has already been reported by using theoretical calculation or structure simulation. $^{25-28}$ This work provides clear experimental evidence for the 7-fold coordination of Ca²⁺ in hydrotalcites. In addition, the white line peak of re-Ca_xAl-LDH (4052.1 eV) is 1.2 eV lower than that of the calcium hydroxide reference (4053.3 eV), which suggests a decreased average oxidation state of Ca²⁺ in re-Ca,Al-LDH samples. This is possibly attributed to an increase in average electron density of Ca²⁺, resulting from the formation of additional/isolated Ca-OH coordination and concomitantly strengthened Ca²⁺/ OH⁻ interaction (OH⁻ group as an electron donor).

For the three re-Ca_xAl-LDH samples and calcium hydroxide reference, the FT k³-weighted EXAFS spectra at the Ca K-edge (the R-space plot) and corresponding curve-fitting results are obtained (Figure 4B). The R-space plots of all samples exhibit two major peaks at ~1.83 Å and ~3.08 Å, respectively, corresponding to the first Ca–O shell and the second Ca–Ca shell (i.e., Ca–O–Ca bond). Notably, the R-space plots (Figure 4B) are not phase corrected and thus do not represent the true bond distances. The fitting results including coordination number, bond distance, and Debye–Waller factor are listed in Table 2. The first Ca–O shell distance of re-Ca_xAl-

Table 2. EXAFS Fitting Parameters at the Ca K-Edge for Various Samples

	first Ca–O shell			second Ca–Ca shell			
sample	R (Å) ^a	N ^b	$\sigma^2 (\text{\AA}^2 \times 10^3)^c$	R (Å) ^a	N ^b	$\sigma^2 (\text{\AA}^2 \times 10^3)^c$	
calcium hydroxide reference	2.35	6.00	0.006	3.58	6.00	0.006	
re-Ca ₂ Al-LDH	2.38	7.49	0.010	3.51	1.88	0.003	
re-Ca ₃ Al-LDH	2.39	7.56	0.010	3.50	2.52	0.005	
re-Ca ₄ Al-LDH	2.38	7.64	0.009	3.52	2.96	0.004	
	$S_0^2 = 0$.71		$S_0^2 = 0.77$			

^{*a*}*R*: bond distance. ^{*b*}*N*: coordination number. ^{*c*} σ^2 : Debye–Waller factor. S_0^2 was obtained from the experimental EXAFS fitting over Ca(OH)₂ reference with known crystallographic value, which was then used for all the samples.

LDH samples (~2.38 Å) is slightly larger than that of calcium hydroxide reference (2.35 Å), and the Debye–Waller factors of the first Ca–O shell also give the same trend. This accords with a distorted Ca–OH octahedron associated with an additional/ isolated Ca–OH coordination. Moreover, it should be noted that coordination number of the first Ca–O shell for re-Ca_xAl-LDH samples is ~7.5, much larger than that of calcium hydroxide reference (~6.0). This further substantiates the

existence of additional/isolated Ca–OH coordination, which results in a distorted Ca–OH octahedron in re-Ca_xAl-LDH samples. In addition, DFT calculations were performed as a supplementary method to experimental studies, which also verified the existence of 7-fold Ca–OH coordination structure in re-Ca_xAl-LDH materials (see details in Figures S2 and S3).

XPS spectra in O 1s regions for re-Mg_xAl-LDH and re-Ca_xAl-LDH samples were further investigated, so as to explore the electronic structure of O species. Figure 5A shows a broad O 1s



Figure 5. (A) XPS O 1s of (a) re-Mg₂Al-LDH, (b) re-Mg₃Al-LDH, (c) re-Mg₄Al-LDH, (d) re-Ca₂Al-LDH, (e) re-Ca₃Al-LDH, and (f) re-Ca₄Al-LDH. Schematic octahedral unit cell of (B) re-Mg₃Al-LDH and (C) re-Ca₂Al-LDH.

spectrum within 528.8-535.2 eV, which can be deconvoluted to three peaks by a Gaussian peak fitting method for these rehydrated LDH samples. For the three re-Mg,Al-LDH samples (Figure 5A, curves a-c), the two peaks at ~530.9 eV and ~ 531.8 eV are assigned to the defective O²⁻ species with low-coordination and lattice oxygen species in brucite-like layers of an edge-sharing $M(OH)_6$ octahedron, while the peak at ~532.7 eV is attributed to the physically adsorbed surface hydroxyl via a noncovalent interaction (Figure 5B).^{29,30} In the case of re-Ca_xAl-LDH samples (Figure 5A, curves d-f), interestingly, the deconvoluted peak (at ~533.1 eV) due to the surface hydroxyl shifts to higher binding energy relative to re-Mg_xAl-LDH samples, implying a decrease in average electron density of surface hydroxyl species. This is related to the existence of additional/isolated Ca-OH coordination (Figure 5C): the empty s orbitals of Ca^{2+} in the Ca–OH octahedron bond with valence electrons provided by the surface hydroxyl (as an electron donor) to form additional/isolated Ca-OH coordination, resulting in an increased electron density of Ca²⁺ but a decreased electron density at the oxygen in the hydroxyl group. This is in line with the results of Ca K-edge XANES spectra. In contrast, the physically adsorbed surface hydroxyl on re-Mg, Al-LDH cannot induce such an electron excursion effect.

2.2. Surface Basic Properties of re-M_xAl-LDH (M = Ca, Mg) Samples. Fourier-transform infrared spectroscopy (FTIR), with a suitable probe molecule under mild conditions, has been employed as a powerful and accurate method to study basic properties of solid materials.^{31,32} CO₂ as a probe molecule is normally used in FTIR experiments, but its relatively strong acid would induce a reaction with OH⁻ of LDHs to bicarbonate and carbonate species.³³ In this work, therefore, deuterated

chloroform (CDCl₃, a weak acid) was chosen as a molecule probe to identify basic properties of rehydrated LDH samples. For re-Mg_xAl-LDH and re-Ca_xAl-LDH samples, a broad FTIR band located in the range 2180–2290 cm⁻¹ is observed (Figure 6), corresponding to C–D stretching vibration (ν_{CD}).^{18,34} To



Figure 6. (A) FTIR transmission spectra of (a) re-Mg₂Al-LDH, (b) re-Mg₃Al-LDH, and (c) re-Mg₄Al-LDH recorded in 2170–2300 cm⁻¹ after CDCl₃ chemiadsorption at 25 °C. (B) FTIR transmission spectra of (a) re-Ca₂Al-LDH, (b) re-Ca₃Al-LDH, and (c) re-Ca₄Al-LDH recorded in 2185–2300 cm⁻¹ after CDCl₃ chemiadsorption at 25 °C.

obtain the distribution of basic strength and semiquantitative data, the FTIR spectrum is further deconvoluted to four peaks via a Gaussian peak fitting method, and the normalized FTIR peak areas of the C–D stretching vibration are listed in Table 3. The two peaks at a relatively high wavenumber (~ 2275 cm⁻¹ and $\sim 2265 \text{ cm}^{-1}$) are assigned to the C–D stretching vibration of CDCl₃ gas and physically adsorbed CDCl₃.^{18,34} A red-shift magnitude relative to the CDCl₃ gas peak (~ 2275 cm⁻¹) and the resulting proton affinities (calculated by eq 1) are related to the Brønsted basic strength.^{18,34} The deconvoluted FTIR spectra of all these samples display two bathochromic peaks with a maximum in the regions 2252-2255 cm⁻¹ and 2211-2214 cm⁻¹, which are identified as the C-D stretching vibration of CDCl₃ adsorbed on a weak basic site and on a medium basic site, respectively.³⁴ For re-Mg_xAl-LDH samples, the FTIR peak (at 2214 cm⁻¹) assigned to the medium basic site (with proton affinity of ~ 925 kJ mol⁻¹) is dominant (Figure 6A), with the existence of surface hydroxyl adsorbed on brucite-like layers. However, in the case of re-Ca,Al-LDH samples, the FTIR peak (at 2252 cm^{-1}) corresponding to the weak basic site (with a proton affinity of ~854 kJ mol⁻¹) is predominant, in the presence of additional/isolated Ca-OH coordination. Moreover, the normalized peak area of the weak basic site shows a linear increase along with the increment of Ca²⁺ content (*i.e.*, Ca²⁺/Al³⁺ molar ratio; Figure S4), which indicates that the weak basic site originates from additional/ isolated Ca–OH coordination. The formation of 7-fold Ca–OH coordination (as confirmed by EXAFS and XPS) causes valence electron excursion of hydroxyl oxygen within this Ca–OH bond, resulting in a weakened interaction between the hydroxyl oxygen and hydrogen proton (proton affinity of ~854 kJ mol⁻¹) and the relatively weak Brønsted basic site. In contrast, for re-Mg_xAl-LDH, the physically adsorbed surface hydroxyl oxygen and more active outer shell electrons, leading to an enhanced O–H interaction (proton affinity of ~925 kJ mol⁻¹) and a medium Brønsted basic site.

2.3. Catalytic Evaluations and Structure–Property Correlation. The aldol condensation of isobutyraldehyde (IBD) with formaldehyde (FA) to produce hydroxypivaldehyde (HPA, an intermediate in the production of neopentyl glycol) is a base-catalyzed reaction with great industrial importance.³⁵ An efficient and "green" route is highly desirable. In this work, the aldol condensation of IBD with FA was performed over

the aldol condensation of IBD with FA was performed over these LDH solid basic catalysts, and the catalytic evaluation data are shown in Figure 7A and Table 3. For the re-Mg_xAl-



Figure 7. (A) IBD conversion, HPA selectivity, and HPA yield over pure Ca(OH)₂, re-Mg_xAl-LDH, and re-Ca_xAl-LDH catalysts, respectively. (B) Catalytic behavior of re-Ca₄Al-LDH for six consecutive cycles. Reaction conditions: IBD (0.55 mmol), FA (0.80 mmol, 37% aqueous solution), cetyltrimethylammonium bromide (CTAB 0.1 g), dioxane (0.2 g), catalyst (0.2 g), 70 °C, 6 h, Ar atomosphere.

LDH catalysts, as the Mg²⁺/Al³⁺ molar ratio rises from 2 to 4, the equilibrium conversion and selectivity at 6 h increase gradually, and the selectivity remains at a low level (8–16%), resulting in a poor HPA yield (5–12%). In the case of re-Ca_xAl-LDH catalysts, however, with the increment of Ca²⁺/Al³⁺ from 2 to 4, the equilibrium conversion remains at ~80%, while the selectivity increases markedly and reaches the maximal value (75.6%) over the re-Ca₄Al-LDH catalyst with a maximal yield

Table 3. Catalytic Performances of Various Samples toward Aldol Condensation of Isobutyraldehyde with Formaldehyde^a

sample	B _W ^𝔥 (area g ^{−1})	${\rm B_M}^b$ (area g ⁻¹)	IBD conversion (%)	HPA selectivity (%)	HPA yield (%)	formation rate $c \pmod{g^{-1} h^{-1}}$
re-Ca ₄ Al ₁ -LDH	46.7	11.5	81.4	75.6	61.5	52.5
re-Ca ₃ Al ₁ -LDH	34.1	11.1	78.3	46.1	36.1	37.4
re-Ca ₂ Al ₁ -LDH	23.4	8.2	76.2	32.5	24.8	28.7
re-Mg ₄ Al ₁ -LDH	18.3	61.8	74.5	16.4	12.2	10.7
re-Mg ₃ Al ₁ -LDH	11.1	73.1	62.9	12.8	8.1	6.5
re-Mg ₂ Al ₁ -LDH	4.5	43.3	56.6	8.6	4.9	4.1

^{*a*}Reaction conditions: isobutyraldehyde (0.55 mol), formaldehyde (0.80 mol), cetyltrimethylammonium bromide (0.1 g), dioxane (0.2 g), catalyst (0.2 g), 70 °C, 6 h, Ar atomosphere. ^{*b*}B_W and B_M are the normalized FTIR peak area assigned to the weak basic site and medium basic site, respectively, which are calculated based on each integral area divided by sample quantity. ^{*c*}Formation rate of hydroxypivaldehyde (HPA) is calculated on the basis of the tangent slope of the yield-reaction time plot at the 2% yield of HPA.

of 61.5%. Meanwhile, some byproducts from the Cannizzaro reaction or deep condensation are detected by HPLC-MS, including major neopentyl glycol, 3-hydroxy-2,2,4-trimethylpentanal, and polymerization products. Moreover, it should be noted that a small amount of $Ca(OH)_2$ impurity coexists with re-Ca_xAl-LDH catalysts. In order to investigate the influence of $Ca(OH)_2$ in re-Ca,Al-LDH catalysts, we performed the aldol reaction over pure $Ca(OH)_2$ as a catalyst (Figure 7A). The selectivity and yield of HPA are 42.6% and 32.8%, respectively, significantly lower than those of the re-Ca₄Al-LDH catalyst (selectivity, 75.6%; yield, 61.5%). This indicates that a small amount of $Ca(OH)_2$ is not responsible for the prominent catalytic performance of re-Ca₄Al-LDH. For a comparison study, the catalytic performances of M_xAl-LDH precursors, conventional solid base, and liquid alkali toward this reaction were investigated and are listed in Table S1. The results show that the re-Ca₄Al-LDH catalyst exhibits much superior performances to those of LDH materials (conversion, 40-66%; selectivity, 10–48%) and conventional solid base catalysts (conversion, 50-64%; selectivity, 9-35%). More importantly, its selectivity is even comparable to that of liquid alkali catalysts (75.6% vs 56-76%), despite a lower conversion (81.4% vs 95-99%). A comparison study between re-Ca₄Al-LDH and previously reported catalysts toward the synthesis of HPA is performed, and the results show the largest HPA yield demonstrated in this work (Table S2). When the re-Ca₄Al-LDH catalyst was reused for six consecutive cycles, both the conversion and yield decreased by $\sim 10\%$ after the first four consecutive cycles and then remained at a stable level within five to six cycles (Figure 7B). We found that the used catalyst was contaminated by sticky organic species, resulting in its activity loss in the subsequent reaction cycle. To remove this surface contamination, we performed a regeneration treatment after each employment: the used catalyst was separated from the reaction mixture, washed, and dried, followed by calcination at 450 °C for 4 h and final rehydration in a NaOH solution (1.1 M) for 2 h. In addition, aldol condensation reactions of various aldehydes with acetone are investigated, and the results are summarized in Table S3. The re-Ca₄Al-LDH displays satisfactory catalytic performances toward one-step aldol condensation.

In order to determine the active site of re-LDH solid basic catalysts, the yield of HPA vs reaction time and initial formation rate at 2% IBD conversion that reflects the intrinsic catalytic property are shown in Figure 8A and Figure S5, respectively. For all these samples, HPA yield increases gradually along with reaction time and reaches the equilibrium maximum at 6 h. The largest yield is present in the sample of re-Ca₄Al-LDH (61.5%). In addition, the formation rate of the product (Figure S5) also shows a big difference: the three re-Mg_xAl-LDH catalysts give a rather low level (4–11 mmol $g^{-1} h^{-1}$), while re-Ca_xAl-LDH catalysts exhibit satisfactory behavior $(28-53 \text{ mmol g}^{-1} \text{ h}^{-1})$. It has been reported that the byproducts of aldol condensation normally come from a deep condensation of the hydroxyaldehyde product (*e.g.*, aldolization, hemiacetal reaction, and polycondensation);^{36,37} therefore, timely desorption of alcohol aldehyde from the active site without further polycondensation is the key step determining the selectivity toward the aldol condensation product. In the base-catalyzed aldol condensation, the property of alkaline sites (strength, concentration) imposes a crucial influence on the product desorption and selectivity. Recently, the surface acid-base properties and structure-property correlation of solid catalysts used in aldol



Figure 8. (A) Profiles of HPA yield vs reaction time: (a) re-Mg₂Al-LDH, (b) re-Mg₃Al-LDH, (c) re-Mg₄Al-LDH, (d) re-Ca₂Al-LDH, (e) re-Ca₃Al-LDH, and (f) re-Ca₄Al-LDH. (B, C) Formation rate of HPA as a function of the normalized FTIR peak areas assigned to the weak basic site (B_W) and medium basic site (B_M) over re-Ca₄Al-LDH, respectively. (D, E) Desorption energy of HPA on the surface of re-Ca₄Al-LDH and re-Mg₄Al-LDH based on DFT calculations. Ca, Mg, Al, O, C, and H atom are represented as green, yellow, pink, red, gray, and white spheres, respectively.

condensation were studied by calorimetry and the CO2-TPD technique.^{10,38,39} Herein, to further study the fine structure of basic sites and establish a structure-property correlation, the initial formation rate of product vs the relative concentration of the two kinds of base sites (weak B_W and medium B_M) based on the normalized FTIR peak area (listed in Table 3) for re-Ca_xAl-LDH catalysts are displayed in Figure 8B and C, respectively. A linear correlation between initial formation rate and B_w concentration is observed, but no relationship is found between initial formation rate and B_M concentration. Similar results are also obtained over re-Mg,Al-LDH catalysts (Figure S6A and B). This manifests that the B_W site (additional/isolated Ca²⁺-OH) serving as the active center plays a leading role in the aldol condensation reaction, other than the B_M site (physically adsorbed hydroxyl). The IBD molecule is adsorbed and deprotonated to carbanion on the basic site of the catalyst and then attacks the carbonyl group of FA to produce deprotonated HPA. In the case of re-Mg_xAl-LDH, H^+ strongly adsorbs on the B_M site without mobility, which would inhibit its combination with deprotonated HPA. This results in a side-reaction (Cannizzaro reaction or deep condensation) of deprotonated HPA and thus a low HPA yield (Figure 7A). In contrast, the 7-fold Ca²⁺-OH coordination with a weak basic site (B_W) is inclined to release and transfer the absorbed $\boldsymbol{H}^{\scriptscriptstyle +}$ to attack the deprotonated HPA that is adsorbed on the adjacent acid site. This therefore facilitates the

formation and desorption of HPA (Scheme 2), which is responsible for the largely enhanced HPA selectivity of the re-

Scheme 2. Schematic Reaction Mechanism for the Aldol Condensation of IBD and FA over re-CaAl-LDH Catalyst



Ca₄Al-LDH catalyst. To further confirm this conclusion, the desorption behavior of HPA from these two catalysts was also studied by DFT calculations (Figure 8D and E). The results show that the proton adsorbed on the Brønsted basic site (7-fold Ca–OH or physically adsorbed surface hydroxyl group) attacks the intermediate species (large carbanion) to produce HPA. In view of the desorption of HPA (the selectivity-determining step), its desorption energy from re-Ca_xAl-LDH (weak alkaline site) is significantly lower than that from re-Mg_xAl-LDH (medium alkaline site; 0.320 eV vs 0.615 eV), in agreement with the catalytic selectivity.

On the basis of the structural characterizations and catalytic evaluations in this work, as well as the results of previous studies,^{40,41} a possible mechanism considering a surface weak Brønsted base site for aldol condensation of IBD and FA over re-CaAl-LDH catalysts is proposed (Scheme 2). Initially, as an acidic species, the α -C-H of the aldehyde group in the isobutyraldehyde molecule is absorbed at the oxygen of the hydroxyl group with 7-fold Ca-OH coordination, accompanied by adsorption of the formaldehyde on an adjacent acid site (hydrogen in hydroxyl of host layer). In the second step, the cleavage of the adsorbed α -C-H bond produces a water molecule and deprotonated isobutyraldehyde, which transforms to an enolate anion *via* keto-enol tautomerism. Subsequently, the enolate anion reacts with formaldehyde to form large carbanion adsorbed on the surface hydroxyl of LDH (as confirmed by DFT calculation), which then accepts protolysis from the neighboring Brønsted basic site (7-fold Ca-OH) to produce HPA. Most importantly, the weak alkaline site is prone to release and transfer H⁺ to the larger carbanion, which activates the desorption of HPA and thus inhibits deep polycondensation.

3. CONCLUSION

In summary, activated Ca–Al layered double hydroxides (LDHs) as a heterogeneous basic catalyst were prepared

based on the structural topotactic transformation and rehydration of LDH precursors. The resulting re-Ca₄Al-LDH exhibits a largely enhanced catalytic performance (HPA yield of 61.5% and product formation rate of 52.5 mmol $g^{-1}h^{-1}$) toward aldol condensation of isobutyraldehyde with formaldehyde, comparable to the level of liquid alkali catalysts. A combination study including XPS, EXAFS, deuterated chloroform-FTIR spectra, and DFT calculation verifies that the host layer of re-Ca, Al-LDH contains a distorted Ca(OH)₆ octahedron with an additional Ca-OH coordination that provides a weak Brønsted basic site. Studies on the structure-property correlation and desorption energy of the product reveal that the weak Brønsted basic site serves as an active center to adsorb the α -C–H of the aldehyde group and accelerate the product desorption, accounting for the largely promoted HPA selectivity. This work provides a facile and cost-effective approach for the preparation of LDH-based solid basic catalysts, which can be used as a promising candidate in green catalysis of aldol condensation reactions.

4. EXPERIMENTAL SECTION

4.1. Materials. $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, isobutyraldehyde (IBD), formaldehyde (FA, 37% aqueous solution), dioxane, hydroxypivaldehyde (HPA), and cetyltrimethylammonium bromide (CTAB) were purchased and used without further purification. Decarbonated deionized water was used in all the experimental processes.

4.2. Catalysts Preparation. $Ca_xAl-LDH$ precursors with varying Ca/Al molar ratios were prepared by the coprecipitation method as follows. Solution A was a mixture of $Ca(NO_3)_2$. $4H_2O$ and $Al(NO_3)_3$. $9H_2O$ ($[Ca^{2+}] + [Al^{3+}] = 0.48$ M) with various Ca/Al molar ratios (from 2 to 4) dissolved in 50 mL of deionized and decarbonated water (purged with N₂ to remove carbonate). Solution B was obtained by dissolving NaOH in the same volume of deionized water with [NaOH] = 1.1 M. Both solutions were added rapidly and simultaneously to a three-neck round-bottom flask in a N₂ atomosphere. The precipitate was stirred vigorously at room temperature for 6 h, followed by separation, washing thoroughly, and drying at 80 °C for 24 h. Mg_xAl-LDH samples were synthesized by a similar method but with an additional crystallization process (at 110 °C for 12 h).

The catalysts were activated in a two-step procedure. Typically, 0.5 g of the as-synthesized LDH sample was heated in flowing N₂ (100 mL min⁻¹) for 4 h, at a heating rate of 2 °C min⁻¹, up to 450 °C. Afterward, the sample was cooled down to room temperature, followed by dispersion and stirring in a NaOH solution (100 mL, 1.1 M) for 2 h. The product was filtered, washed thoroughly with water and ethanol, finally dried in an air-circulating oven at 80 °C for 12 h, and labeled as re-Ca_xAl-LDH and re-Mg_xAl-LDH, (x = 2, 3, and 4).

4.3. Catalytic Evaluation toward Aldol Condensation of IBD with FA. The aldol condensation reaction was performed with a batch-type reactor (cylindrical glass tube). Typically, the freshly activated catalyst (0.2 g) was dispersed into a mixture of IBD (0.55 mol), FA (0.80 mol, 37% aqueous solution), dioxane (0.2 g, as internal standard), and CTAB (0.1 g). Herein, CTAB is used as a phase transfer catalyst, which can facilitate the migration of IBD from the oil phase into the water phase to accelerate the reaction, so as to obtain a high conversion and inhibit byproducts in the oil–water two-phase reaction system. After vacuuming and inletting argon gas, the solution was magnetically stirred in an oil bath at 70 °C. The

power and rotating rate of the magnetic stirrer were also studied to reduce the influence of mass transfer, and an optimized stirring condition (15 W, 600 r/min) was applied in this reaction. Once the reaction started, aliquots were periodically taken from the reaction mixture, filtered, and analyzed on a gas chromatograph (GC-2014) equipped with a flame ionization detector (FID) and an Rtx-5 capillary column (0.25 mm in diameter, 30 m in length). Conversion was calculated based on the decrease in isobutyraldehyde concentration.

4.4. Characterization. X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer, using Cu K α radiation (λ = 0.1542 nm) at 40 kV and 30 mA. X-ray photoelectron spectra (XPS) were recorded on a Thermo VG Escalab 250 X-ray photoelectron spectrometer at a pressure of $\sim 2 \times 10^{-9}$ Pa with Al K α X-rays as the excitation source. The morphology was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV. The specific surface area was obtained by the Brunauer-Emmett-Teller (BET) method with the use of a Quantachrome Autosorb-IC-VP analyzer. Thermogravimetry (TG) curves were obtained on a Beifen PCT-IA instrument in the temperature range 30-900 °C. Elemental analyses were carried out by using a Shimadzu ICPS-7500 inductively coupled plasma atomic emission spectrometer (ICP-AES). The single pulse solid-state ²⁷Al MAS NMR spectra were acquired under MAS conditions on a Bruker 400WB Avance III spectrometer, at 9.4 T. In the determination, 100 mg of finely powdered and dried LDH sample was used. The spinning speed of samples was 10 kHz, and at least 5000 scans were performed.

Deuterated chloroform was used as a basicity probe molecule for the measurement of FTIR transmission spectroscopy, which was carried out in a Bruker Equinox 55 spectrometer, between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹ after 600 scans per spectrum. Fourier-transformed infrared absorption spectroscopy was also carried out using a Nicolet 380 instrument spectrophotometer. The nature of the basic site was characterized by the FTIR spectroscopy of adsorbed deuterated chloroform (CDCl₃-IR). About 18 mg of the sample was pressed into a wafer with a diameter of 1.3 cm, which was then installed in an IR cell with CaF2 windows, reduced at 150 °C for 0.5 h, followed by an evacuation treatment at this temperature. Subsequently, the sample was cooled to 50 °C for recording the background spectrum. With the introduction of deuterated chloroform into the cell for 1 h, another evacuation was performed to remove physisorbed deuterated chloroform; afterward, the spectrum was recorded with a step of 4 cm⁻¹ and an accumulation of 32 sans. The strength of base site involved in the adsorption of CDCl₃ was estimated based on the following equation:

$$\log \Delta \nu_{\rm CD} = 0.0066 \text{PA} - 4.36 \tag{1}$$

where $\Delta \nu_{CD}$ is the shift of ν_{CD} (cm⁻¹) and PA is the proton affinity (kJ mol⁻¹).

The Ca XAFS measurements were performed at beamline 4B7A of the Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics (IHEP), Chinese Academy of Sciences (CAS). Extended X-ray absorption fine structure spectra (EXAFS) were recorded at ambient temperature in total electron yield mode. The typical energy of the storage ring was 2.2 GeV with a maximum current of 100 mA; the Si (111) double crystal monochromator was used. The IFFEFIT 1.2.11 data analysis package (Athena, Artemis, Atoms, and FEFF6) was used for the data analysis and fitting.

4.5. Computational Methods. The density functional theory calculations were performed with the Vienna Ab-initio Simulation Package (VASP) in slab models. The model of CaAl-OH-LDH was constructed according to the crystal data of these LDHs reported previously. The space group of LDHs was r3m, with unit cell parameters $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$. The other three unit cell parameters, *a*, *b*, and *c*, are referred to the powder X-ray diffraction data of these LDHs. The supercell of bulk CaAl-LDH is set to be $3 \times 3 \times 1$ in the *a*, *b*, and *c* directions with the accustomed molar ratio of Ca/Al = 2. Three hydroxyl ions were placed into the interlayer gallery of bulk Ca₂Al-LDH to keep the charge neutral. The exchangecorrelation potential was described by the Perdew-Burke-Ernzerhof (PBE) in the generalized gradient approach (GGA). The structure optimizations were based on the following points: (1) an energy tolerance of 1.0×10^{-4} eV per atom, (2) a maximum force tolerance of 0.2 eV, and (3) the k-points were set to be $3 \times 3 \times 1$ in calculating the electronic structure.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b03022.

Figures S1-S6 and Tables S1-S3 (PDF)

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