

Journal of Cleaner Production

A Deconvolution Analysis Strategy on the Thermoreconstitution Process of Co/Fe Layered Double Hydroxides: Complementary Correlations between Physicochemical Variations and Thermo-kinetic Analyses

--Manuscript Draft--

Manuscript Number:	JCLEPRO-D-23-17573R3
Article Type:	Original article
Keywords:	Co/Fe layered double hydroxides; Thermoreconstitution process; Deconvolution analysis strategy; Thermokinetic modeling; correlation analysis
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Abstract:	A variety of physicochemical analyses were systematically conducted on the complex thermoreconstitution process of Co/Fe layered double hydroxides, and deconvolution analysis strategy was utilized in elucidating the reconstitution process. The thermal analysis of Co/Fe layered double hydroxides indicated that approximately 27.8 % weight loss, three weight loss peaks and two pronounced endothermic phenomena were detected via thermogravimetry, differential thermogravimetry, and differential scanning calorimetry, respectively. In the thermoreconstitution process of Co/Fe layered double hydroxides, scanning electron microscopy images indicated that the layered structure gradually collapsed, fractured into pieces, and partially melted. Meanwhile, significant X-ray diffraction peak broadening phenomena were detected and further confirmed by the d-spacing values in high-resolution transmission electron microscope images, which were mainly caused by the lattice expansion effect and the heterogeneous microstrain effect. Three reactions were deconvolved from the differential thermogravimetry curves, and the thermokinetic model of Reaction 2 indicated that volatile components in the form of H₂O and CO₂ escaped from the solid-state residuals via a one-dimensional diffusion reaction model. The major products in solid-state residuals were cubic Cobalt(III) oxide and Iron(II, III) oxide. The thermokinetic models played a complementary role in elucidating the physicochemical variations that occurred throughout the thermoreconstitution process of Co/Fe layered double hydroxides.
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Journal of Cleaner Production

April 9th, 2024

Dear Editor,

We are submitting a manuscript entitled: "**A Deconvolution Analysis Strategy on the Thermoreconstitution Process of Co/Fe Layered Double Hydroxides: Complementary Correlations between Physicochemical Variations and Thermokinetic Analyses**" for your consideration for publication in the **Journal of Cleaner Production**. We would like to thank you for giving us this precious opportunity to revise the paper and be grateful to the editor's comments. We have read all the comments and revised the manuscript carefully.

This work is original, has not been published elsewhere, is not under consideration by any other journal, and all the listed authors have approved the enclosed manuscript.

If you have any questions, please contact us at the above address.

Thank you very much for your consideration.

Sincerely yours,
Dr. Yuanfeng Qi;
Qingdao University of Technology
Dr. Kai He
Sun Yat-sen University

A Deconvolution Analysis Strategy on the Thermoreconstitution Process
of Co/Fe Layered Double Hydroxides: Complementary Correlations
between Physicochemical Variations and Thermokinetic Analyses

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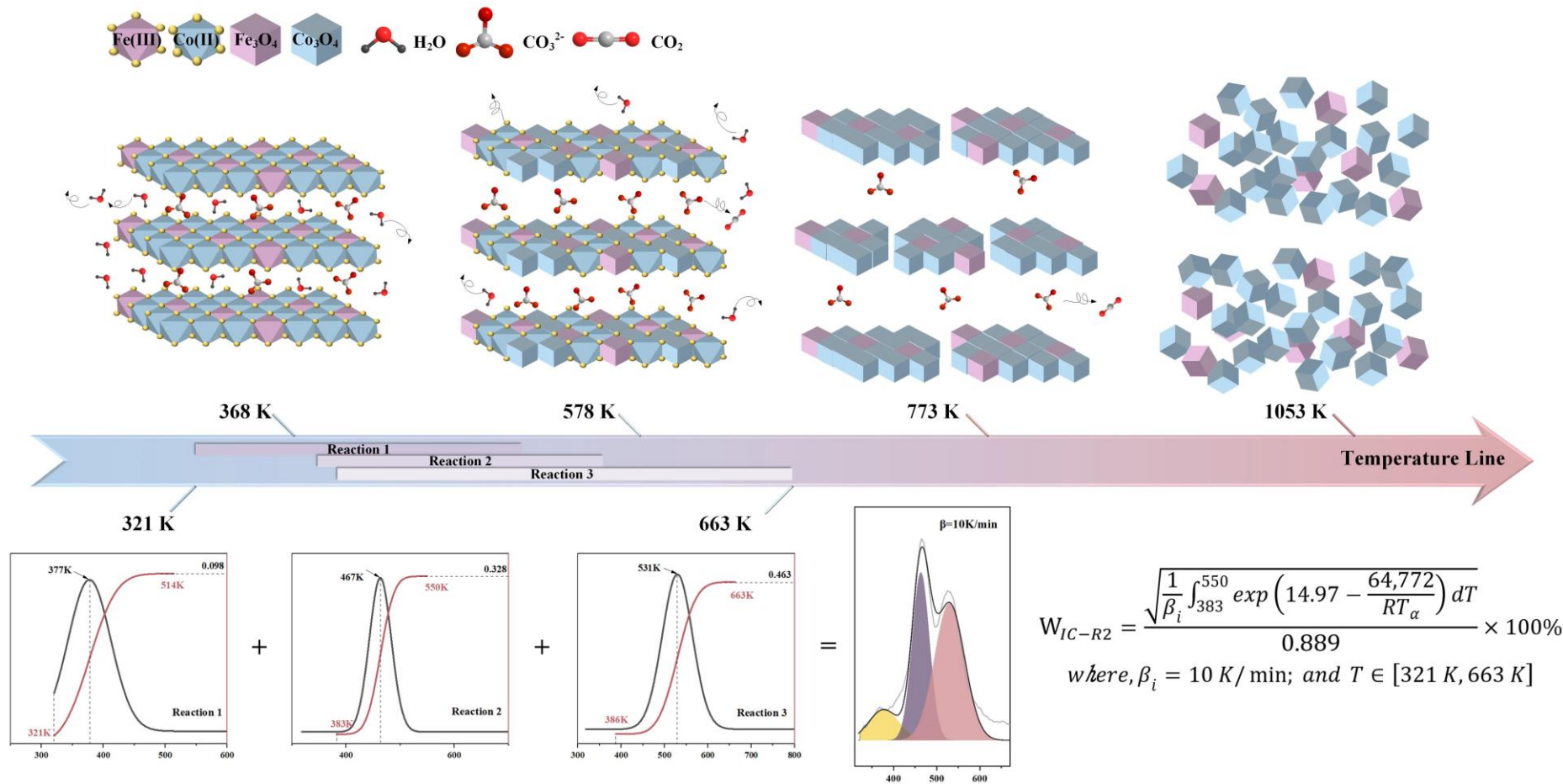
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Graphical Abstract



Highlights:

- A deconvolution analysis strategy was proposed.
- Physicochemical variations of Co/Fe-LDHs were scrutinized.
- Thermokinetic analyses were conducted.
- A complementary correlation was put forwarded.

Responses to editor and reviewers

Ms. Ref. No.: JCLEPRO-D-23-17573R2

Title:

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Dear editor:

We sincerely appreciate this valuable opportunity to refine our work. According to the comments from the editor, we have diligently revised our manuscript again.

In this document, the origin comments are denoted as “*Comment*”, and all responses are begun with “*Response:*”. The answer to the comment is denoted as “**Answer:**”, and the related revisions conducted in the revised manuscript are denoted as “**Action:**”.

All authors sincerely hope that our study will be accepted for publication in your prestigious international journal. We are honored to participate in this academic discourse. Should you have any questions or require further clarification, please do not hesitate to contact us.

Thank you once again for your comments and help throughout the submission process. Below, we have responded point-by-point to the editor's comments, as detailed:

Comments from Editor:

Comment 1:

1. Correct the citation of (Qi, Y. et al., 2021), (Zhang, W. et al., 2021). It should be (Qi et al., 2021), (Zhang et al., 2021).

Response:

Answer: In order to distinguish inaccurate citations, we removed the author's initials of the citation.

Action: The citations of (Qi, Y. et al., 2021), (Zhang, W. et al., 2021) has been corrected as (Qi et al., 2021a), (Zhang et al., 2021b).

Comment 2:

2. put the number of page(s) in reference of Muravyev et al., 2021.

Response:

Action: For the reference of Muravyev et al., 2021, the number of pages has been added.

“Muravyev, N.V., Luciano, G., Ornaghi, H.L., Jr., Svoboda, R., Vyazovkin, S., 2021. Artificial Neural Networks for Pyrolysis, Thermal Analysis, and Thermokinetic Studies: The Status Quo. *Molecules* 26(12).

<https://doi.org/10.3390/molecules26123727>.”

We are immensely grateful to the editor for the insightful comments and guidance. Wish the revised manuscript can satisfy the requirement of publication.

1 A Deconvolution Analysis Strategy on the Thermoreconstitution Process
2 of Co/Fe Layered Double Hydroxides: Complementary Correlations
3 between Physicochemical Variations and Thermokinetic Analyses

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13 **Abstract**

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Keywords: Co/Fe layered double hydroxides; Thermoreconstitution process; Deconvolution analysis strategy; Thermokinetic modeling; Correlation analysis

38 Terminologies

Abbreviations			
A_n	The Avrami-Erofeev reaction model	NCLs	Negatively charged layers
D_n	The Dimensional Diffusion reaction model	N_n	The N -th Order reaction model
DSC	Differential scanning calorimetry	PCLs	Positively charged layers
DTG	Differential thermogravimetry	P_n	Power Law reaction model
FWHM	Full Width at Half Maximum	R_c^2	Correlate coefficient
G-PDF	Gaussian probability distribution function	RMSE	The root-mean-square error
F-SF	Frazer-Suzuki function	R_n	The Phase-Boundary Controlled reaction model
ICTAC	International Confederation for Thermal Analysis and Calorimetry	TG	Thermogravimetry
JCPDS	Joint Committee Powder Diffraction Standards		
Symbols			
A	pre-exponential factor (s^{-1})	β	heating rate (K min^{-1})
E	activation energy (kJ mol^{-1})	ε_d	the elastic microstrain value (%)
R	gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$)	ε_v	the volume variation degree (%)

T	heating temperature (K)	θ	Bragg angle (rad)
W	weight of the residual (mg)	u	the independent variable of $P(u)$, $u = \frac{E_\alpha}{RT_\alpha}$
Subscripts			
α	conversion degree or rate	nor	normalized data
c	calculated value	ori	original data
con	conversed data	rep	the most representative reaction model
dec	deconvolved data	s	standard value
i	the i-th heating rate	t	reaction time
Functions			
$f(\alpha)$	the reaction model	$P(u)$	temperature integral function
$g(\alpha)$	the integral form of reaction model	W-H	Williamson-Hall equation

1 Introduction

Layered double hydroxides (LDHs) represent a broad and versatile class of anionic clays. Characterized by their unique sandwich-like 3D structures, LDHs exhibit the general formula of $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}]^{n-} \cdot mH_2O$ (Takehira, 2017), where M^{2+} (or M^{3+}) denotes divalent (or trivalent) metallic cations such as Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} (or Al^{3+} , Fe^{3+} , Co^{3+} and La^{3+}); A^{n-} are inorganic or organic (Wang et al., 2014) including OH^- , CO_3^{2-} , CH_3COO^- , glycine or even polyoxometalates (POMs) (Nikulshina et al., 2019), hetero polyacid (HPA) (Winoto et al., 2019) electronegative macromolecules. Under aqueous surroundings, LDHs are spontaneously generated from the cationic/anionic precursor by way of co-precipitation, which can be flexibly modulated by the participated ionic donors and modifications. Advantageous of this moderate method has been systematically reported in Wang and O'Hare's survey (Wang and O'Hare, 2012). LDHs are constructed by two types of anisotropic layers, which are the positively charged layers (PCLs) and negatively charged layers (NCLs). The divalent/trivalent metallic couples (M^{2+}/M^{3+}) are located in the edge-sharing octahedral cells of the PCLs; meanwhile, the NCLs are intercalated in the adjacent PCLs to maintain the electrical neutrality of the LDHs via electrostatic and van der Waals forces (Varoon et al., 2011). To date, a variety of LDHs have been prepared with distinct M^{2+}/M^{3+} couples, anions and synthetic strategies, which possess outstanding features such as self-recovery (colloquially described as the "memory effect") (Wang

et al., 2021), ion-exchangeability (Zhai et al., 2021), and selective absorption (Xie et al., 2023). Furthermore, as the transition element of Co or Fe (or both) is utilized as an M^{2+}/M^{3+} couple, extra magnetic properties are endowed to the derived LDHs, which are flexible for decoration or modification treatment. Specifically, Co/Fe-LDHs prepared with Co (II)/Fe (III) couples are intensively utilized in a variety of domains: as a matrix for the fabrication of energy-storage-oriented 2D films, hollow nanospheres and core-shell structured materials; as carriers or substrates for targeting drug delivery (Taviot-Guého et al., 2018); and mostly, as precursors in manufacturing specific high-performance catalysts for fine chemical engineering (Varoon et al., 2011) and environmental remedies (Nouaa et al., 2023).

Thermal treatment is effective in reconstructing Co/Fe-LDHs as di-metallic oxides via a complex thermoreconstitution process (Li et al., 2018). Under specific thermal conditions such as heating temperatures, rates, duration, and atmosphere, the reconstitution of Co/Fe-LDHs is thermally induced and accompanied by significant physicochemical changes in mineralogy (Wu et al., 2020), chemistry (Wang et al., 2021), and morphology (Vyazovkin et al., 2014). In most cases, those variations of the reconstituted Co/Fe-LDHs are intensively surveyed in elucidating the mechanisms underlying the catalytic (Peng et al., 2021), electrical (Feng et al., 2016), and magnetic (Takehira, 2017) performances. For instance, catalysts derived from thermally reconstituted Co/Fe-LDHs are utilized to activate oxidants such as ozone (O_3), persulfate (PS), and hydrogen peroxide (H_2O_2) for the degradation of contaminants

(Huang et al., 2021; Nosaka and Nosaka, 2017). Analogous studies can be found elsewhere (Guo et al., 2020; Sun et al., 2019; Xie et al., 2023). However, little attention has been given to the specific reactions responsible for the observed physicochemical changes in Co/Fe-LDHs, and the complex thermoreconstitution progress is seldom elucidated.

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee recommended (Vyazovkin et al., 2014) that thermal kinetic analysis is a reliable way of scrutinizing the thermal reaction progress (Koga et al., 2023; Vyazovkin et al., 2020) (i.e., single-step, multistep, or hybrid) of solid-state substances. Relying on the thermal mass- or energy-based data (Vyazovkin et al., 2011) obtained via thermogravimetry (TG), differential thermogravimetry (DTG), or differential scanning calorimetry (DSC) techniques, the thermokinetic model (Vyazovkin et al., 2020) established on the thermokinetic parameters is promising in depicting the specific reaction mechanism via precise mathematical functions (Koga et al., 2023). For an ideal single-step reaction process (Iwasaki et al., 2020; Vyazovkin et al., 2014), the parent function of the thermokinetic model is depicted in Eq. 1. Specifically, *Func. 1* and *Func. 2* of Eq. 1 are the differential and integral expression of the thermokinetic model for a single-step reaction, which are both established on the “kinetic triples” (Siddiqi et al., 2021), i.e., the activation energy (E), the preexponential factor (A), and the reaction model ($f(\alpha)$ or $g(\alpha)$). Employing a range of differential and integral calculation algorithms (Koga et al., 2023; Qi et al., 2021a), precise thermokinetic models can be

102 established. These models serve as powerful tools, enabling researchers to delve into
 103 the underlying reaction mechanisms and elucidate the physico-geometrical (Iwasaki et
 104 al., 2020), mineralogical, morphological (Qu et al., 2019), and chemical (Song et al.,
 105 2019) variations.

$$\begin{aligned}
 & \text{Func. 1} \quad \frac{d\alpha}{dt} = \beta_i \frac{d\alpha}{dT} = A_\alpha \exp\left(-\frac{E_\alpha}{RT_\alpha}\right) f(\alpha); \quad \beta_i = \frac{dT}{dt} \\
 & \text{where, } \alpha = \frac{W_i - W_t}{W_i - W_e} \times 100 \% \text{ or } \frac{1 - W_t/W_i}{1 - W_e/W_i} \times 100 \%; \quad \alpha \in [0, 1] \\
 & \text{Func. 2} \quad g(\alpha) = \int_0^1 \frac{d\alpha}{f(\alpha)} = \int_{T_0}^{T_e} \frac{A_\alpha}{\beta_i} \exp\left(-\frac{E_\alpha}{RT_\alpha}\right) dT \\
 & \quad \quad \quad = \frac{A_\alpha E_\alpha}{R\beta_i} p(u); \quad u = \frac{E_\alpha}{RT_\alpha} \\
 & \text{where, } P(u) = \int_\infty^u -\frac{e^{-u}}{u^2} du = \frac{e^{-u}}{u^2} \sum_{N=1}^{\infty} (-1)^{N-1} \frac{N!}{u^{N-1}}; \quad N \geq 1
 \end{aligned} \tag{1}$$

107 Where, α is the relative conversion ratio of the reactant in a specific reaction process,
 108 which could be calculated by the initial, instantaneous, and final weight of the residual
 109 (W_i , W_t , and W_e) in TG data, or could be obtained by the relative weight ratio (W_t/W_i)
 110 in the normalized TG data (within [0,1]); t is the reaction time; β_i is the i -th heating
 111 rate; R is the gas constant, 8.314 J/(mol·K); A_α , E_α and T_α denote the activation
 112 energy, the pre-exponential factor, and heating temperature at a certain α ; the $g(\alpha)$ is
 113 the integral form of reaction model- $f(\alpha)$; $P(u)$ is the temperature integral function,
 114 and the N value is the finite series level of $P(u)$.

115 Various thermal kinetic methodologies (Siddiqi et al., 2021; Zhang et al., 2014)
 116 have been developed to scrutinize complex reaction processes occurring under high-
 117 temperature conditions. These methods include the combustion, pyrolysis, gasification,

118 and decomposition (Song et al., 2019) processes of a variety of substances such as
119 biomass (Ali et al., 2017), solid waste sludge, coal, oily sludge, plastics (Zhang et al.,
120 2021b) and polymetallic oxide. Furthermore, in comparison with the convolutional
121 methodologies (Qi et al., 2021a) (for instance, the distributed activation energy
122 methodology, DAEM), the deconvolutional methodologies (Zhang et al., 2021a) are
123 effective in separating the complex reaction progresses, which are more reliable in
124 establishing the thermokinetic models in revealing the most likely reaction mechanisms
125 (Koga et al., 2023) of the physicochemical variations. For complex reaction that
126 deconvolved into finite sub-reactions, the ICTAC Kinetics Committee (Vyazovkin et
127 al., 2020) singles out two specific thermokinetic models that derived from those
128 statistical solution sets of "kinetic triples": the thermokinetic model with the highest
129 mathematical accuracy is called as mathematical deconvolution analysis, which is
130 beneficial in depicting the thermal curves; and the thermokinetic model established on
131 the most likely "kinetic triples" in elucidating the reaction mechanism is defined as
132 kinetic deconvolution analysis. To date, a variety of distribution function have been
133 utilized for the deconvolution of complex reaction progresses, and the Gaussian
134 probability distribution function (G-PDF) and Frazer-Suzuki function (F-SF) is wildly
135 applied in the domain of thermal kinetic analysis. Specifically, G-PDF is a type of
136 symmetric function with fewer independent variables and lower degree of freedom,
137 which is more convenient for the deconvolution treatment of the complex reaction
138 progress. On the contrary, F-SF is recommended as a more accurate asymmetric

function in deconvolving the complex reaction progresses than that of G-PDF (Vyazovkin et al., 2020). However, on the deconvolution treatment on the thermoreconstitution of Co/Fe-LDHs via G-PDF and F-SF is rarely reported. Meanwhile, the correlations between the physicochemical variations of Co/Fe-LDHs' thermoreconstitution process and thermo-reaction analyses in elucidating the thermoreconstitution mechanisms have not yet been established.

The heat surroundings trigger dramatic physicochemical variations in Co/Fe-LDHs via complex thermoreactions. The current reports on the thermoreconstitution process of Co/Fe-LDHs indicate an urgent need to correlate the physicochemical variations with reliable thermokinetic analyses. Furthermore, the precise models of the complex reconstitution reaction established via an accurate thermal kinetic analysis are a necessary step toward a deeper understanding of the various mechanisms of Co/Fe-LDHs thermoreconstitution. In this study, a systematic solution to unite physicochemical variations with thermokinetic analyses as a whole was proposed. Initially, a systematic analysis of the thermoreconstitution process of Co/Fe-LDHs was conducted across a wide range of thermal treatment temperatures under different heating rates. Then, deconvolution analysis strategy was proposed to distill the complex reconstitution process of Co/Fe-LDHs into a finite number of reactions, and the most likely kinetic models of the deconvolved reactions were optimized to elucidate the physicochemical variations. Eventually, a complementary correlation between the thermokinetic analyses and physicochemical variations was established.

2 Materials and Methods

The probe Co/Fe-LDHs utilized in this study were fabricated using a modified coprecipitation method. The thermo-analysis and the physicochemical characterization were conducted on the pristine Co/Fe-LDHs. The data processing was conducted in the authorized software without any data smoothing treatment.

2.1 Materials

The probe Co/Fe-LDHs was fabricated in lab-scale. The chemical reagents and synthesis procedure were detailed as follows:

2.1.1 Chemical Reagents

The chemicals used in this study include Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), Sodium hydroxide (NaOH), Sodium carbonate (Na_2CO_3), and Dilute hydrochloric acid (HCl , 1 mol/L). These reagents are all ACS reagent grade and require no additional purification. Synthetic air, composed of 99.99 % purity oxygen and 99.99 % purity nitrogen with a volume ratio of 21.5:78.5, was procured from Qingdao Specific Laboratory Gas Co., Ltd. for TG/DSC analysis. The Milli-Q ultrapure water (18.2 MU cm) was utilized for all experiments.

2.1.2 Synthesis of Co/Fe-LDHs

Co/Fe-LDHs were fabricated using a modified coprecipitation method (Sun et al., 2020). These layers are negatively charged due to the presence of carbonate and

hydroxyl ions (Song and Hu, 2014; Wang et al., 2014). The synthetic flowchart was depicted in Fig. S-1, and the procedure was detailed as follows: **(i)** Preparation of the acid metallic salt solution: 30 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (i.e., Co:Fe = 3:1) were codissolved in 100 ml of dilute hydrochloric acid solution (0.01 mol/L) in avoiding the hydrolysis of transition metallic salt (Nikulshina et al., 2019; Zhai et al., 2021); **(ii)** Coprecipitation: the acid metallic salt solution was dropwise added into 1 L of a basic solution (1 mol/L of NaOH and 0.1 mol/L of Na_2CO_3) which was vigorously stirred at 70 ± 2 °C, meanwhile, the pH of the basic solution was regulated at 12.3 ± 0.2 with 1 mol/L of NaOH solution throughout the reaction (Xie et al., 2023); **(iii)** Aging: After 100 ml of acid metallic salt solution was consumed, the basic solution was aged in a water bath under 80 °C for 24 h without stirring; **(iv)** Refinement: the light-pink sediments were centrifuged out and re-suspended in 1 L of Na_2CO_3 solution (1.5 mol/L, 80 °C) for another 24 h to substitute the Cl^- with CO_3^{2-} inside the negatively charged layers (Song and Hu, 2014); **(v)** Postprocessing of product: the refined sediments were washed three times, dried in a freeze dryer under -18 °C for 4 h, pulverized in a planet-type grinding mill (PM 100, Retsch, Germany), sealed and stored in a glass vial for further use.

2.2 Thermoreconstitution process of Co/Fe-LDHs and data processing

The mass/energy variation Co/Fe-LDHs thermoreconstitution was monitored in a high-precision thermoanalyzer with 0.1 µg of mass sensitivity and 0.001 °C of energy

sensitivity. The thermodata were directly recorded without any correction, and the data processing was corrected to two decimal places.

2.2.1 Thermoreconstitution process of Co/Fe-LDHs

Approximately 20 mg of the synthesized Co/Fe-LDHs was analyzed via an SDT Q600 thermoanalyzer (TA instrument, USA). The mass and energy variations of Co/Fe-LDHs from room temperature up to 1,053.15 K were recorded using the TG/DSC technique (Koga et al., 2023). The thermoreconstitution process of Co/Fe-LDHs was conducted under different heating rates, namely, lower heating rates ($\beta_i = 8$ and 10 K/min) and higher heating rates ($\beta_i = 16$ and 18 K/min). Each experiment was performed twice, and the TG/DSC data recorded were averaged.

2.2.2 Data processing for TG/DTG data conversion and deconvolution

The directly recorded TG data were first processed within the range of 0 to 100 %, which was denoted as the original TG data (TG_{ori}). Then, the TG_{ori} data were further normalized to a range between 0 and 1, which was labeled the normalized TG data (TG_{nor}). The TG_{ori} data were then converted to TG_{con} data (Eq. S-1 to Eq. S-3), which represents the conversion degree versus temperature, was further derived from the TG_{ori} data.

Mathematically, the DTG data are the first derivative of TG data versus temperature or time (Vyazovkin et al., 2011; Vyazovkin et al., 2014); hence, the original, normalized, and converted DTG data, i.e., DTG_{ori}, DTG_{nor}, and DTG_{con} are

derived from the TG_{ori} , TG_{nor} , and TG_{con} data, respectively. Additionally, the data processing methods between the six types of mass-natured data (namely TG_{ori}/DTG_{ori} , TG_{nor}/DTG_{nor} , and TG_{con}/DTG_{con}) are depicted in Eq. S-1 to Eq. S-7, which are detailed in S-1 and illustrated in Fig. S-2, respectively.

Based on the Gaussian probability distribution function (G-PDF) and the Frazer-Suzuki function (F-SF), three reactions that occurred during the thermoreconstitution process of Co/Fe-LDHs were deconvolved in response to three weight loss peaks of DTG_{con} curves (Perejon et al., 2011), respectively. The deconvolved curves for each reaction were denoted as DTG_{dec-1} , DTG_{dec-2} , and DTG_{dec-3} . These curves were integrated to obtain the corresponding TG_{dec} curves for each reaction. The data processing and deconvolution procedures were conducted with Origin Pro 2021 software, and the Levenberg–Marquardt (L-M) algorithm (Iwasaki et al., 2020; Muravyev et al., 2021; Naqvi et al., 2018) was utilized to optimize the nonlinear fitting of the deconvolution process.

2.3 Physicochemical Characterizations

Four samples, labeled Co/Fe@368K, Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K, were examined to assess the physicochemical changes during the thermoreconstitution process of Co/Fe-LDHs. These examinations included mineralogical analyses by X-ray diffraction (XRD, 7000X, Shimadzu Instruments, Japan); monitoring of chemical groups through Fourier transformed infrared

spectroscopy (FTIR, Thermo Scientific Nicolet iS5, Waltham, MA, USA) and Raman microscopy (Bruker Corporation, Raman, Italy); meanwhile, the chemical valence of Co and Fe elements was examined by X-ray photoelectron spectroscopy technique (XPS, EscaLab Xi+, Thermo Fisher Scientific, MA, USA); examination of the morphology by scanning electron microscopy (SEM, MIRA-LMS, Tescan Instruments, Czech Republic) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20, FEI, USA), and Co, Fe, and O element distributions of Co/Fe-LDHs before and after the thermoreconstitution process were compared via energy dispersive spectroscopy (EDS, BrukerS8 Tiger, Germany).

In addition, the operating conditions of the abovementioned instruments were detailed in S-2, and the calculation methods of *d*-spacing, lattice constants, the volume of the unit cell, and the value of microstrain for the major crystal phases (Rodenbough et al., 2016) detected from XRD patterns were introduced in S-3.

2.4 Procedure of the “deconvolution analysis strategy”

The “deconvolution analysis strategy” proposed for thermal kinetic analysis consists of four portions, i.e., 1) the deconvolutional separation of the DTG curve into three reactions, namely, Reaction 1, 2 and 3; 2) the scrutinization of "kinetic triples"; 3) the establishment of thermokinetic models; and 4) the construction of the corrections among the thermokinetic analyses and models to the physicochemical variations generated by the thermoreconstitution process of Co/Fe-LDHs. It should be noted that

thermokinetic models was only established for the Reaction 2.

Specifically, the "kinetic triples" are obtained as follows:

(i) The model-free iso-conversional method (Vyazovkin et al., 2011) is utilized to calculate the E values. On account of the integral and differential calculating algorithm are included in the model-free iso-conversional method for E values, in this study, the Flynn-Wall-Ozawa (FWO) algorithm (or Friedman algorithm) was adopted as the integral (or differential) calculating algorithm for E values, which was depicted in Eq. 2. In FWO algorithm, the specific E value at a certain α , i.e., E_α was the slope of a line plotted by $\ln \beta_i$ versus $\frac{1.052}{RT_{\alpha,i}}$, and the distribution of E_α versus α of each reaction was obtained (Qi et al., 2021a). The procedure of the Friedman algorithm in calculating the E values is detailed in S-4. As the E values are calculated under the FWO or Friedman algorithm, neither the specific reaction model nor the pre-exponential factor is required, which indicated E values calculated under the model-free method is relatively objective.

$$\begin{aligned} \text{FWO: } \ln \beta_i &= \ln \left[\frac{A_\alpha R}{E_\alpha g(\alpha)} \right] - 5.311 - 1.052 \frac{E_\alpha}{RT_{\alpha,i}} \\ \text{Friedman: } \ln \left[\beta_i \left(\frac{d\alpha}{dT} \right)_\alpha \right] &= \ln [A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \end{aligned} \quad (2)$$

(ii) The Kissinger peak algorithm (Eq. 3) is initially employed to calculate the proximate A_α value of Reaction 2. And then the "Compensation effect" (Eq. 4) is further utilized to refine the A_α value obtained via Eq. 3. Additionally, the mathematical reasoning process of the proximate calculation (Eq. 3) and the precise refinement (Eq. 4) of A_α values were elucidated in our previous studies (Qi et al.,

279 2021a; Qi et al., 2023). Because the proximate A_α value is initially calculated with the
 280 assumption of $f'(\alpha) = -1$, therefore, the A_α value is further calibrated as the most
 281 likely reaction model, $f(\alpha)$ or $g(\alpha)$ of Reaction 2 is certified (D_1 in this paper).
 282 Furthermore, an iterative computation process is conducted to calibrate and unify the
 283 A_α value with $f(\alpha)$ and $g(\alpha)$, which is detailed in S-5.

$$A_\alpha = -\frac{\beta_i E_\alpha}{RT_\alpha^2 f'(\alpha)} \exp \frac{E_\alpha}{RT_\alpha}$$

284 when $f'(\alpha) = -1$; $A_\alpha \cong \frac{\beta_i E_\alpha}{RT_\alpha^2} \exp \frac{E_\alpha}{RT_\alpha}$ (3)

$$\text{when } f'(\alpha) = -1/2\alpha^{-2}; A_\alpha = 2\alpha^2 \frac{\beta_i E_\alpha}{RT_\alpha^2} \exp \frac{E_\alpha}{RT_\alpha}$$

$$\ln A_\alpha = aE_\alpha + b \Rightarrow A_\alpha = \exp(aE_\alpha + b)$$

285 (4)

286 Where, $f'(\alpha)$ is the first derivation of $f(\alpha)$, for a first order reaction $f(\alpha) =$
 287 $1 - \alpha$ and $f'(\alpha) = -1$; for reaction model of D_1 , $f(\alpha) = 1/2\alpha^{-2}$ and $f'(\alpha) =$
 288 $-1/2\alpha^{-2}$; a and b are the slope and intercept of the fitted line.

289 (iii) The reaction-model-fitting method (Vyazovkin et al., 2011) is utilized to
 290 locate the most likely reaction model of Reaction 2. To rearrange *Func. 1* of Eq. 1 as
 291 Eq. 5, the mathematical expression of $f(\alpha)$ is obtained, and the profiles of $f(\alpha)$
 292 could be obtained with the A_α and E_α values as well as DTG_{dec} data. Meanwhile, to
 293 rewrite Eq. 2 as Eq. 6, the mathematical expression of $g(\alpha)$ via the FWO algorithm is
 294 gathered, and the curve of $g(\alpha)$ versus α for each deconvolved reaction could be
 295 directly plotted with precise A_α and E_α at each α .

$$f(\alpha) = \frac{\beta_i}{A_\alpha} \frac{d\alpha}{dT} \exp \left(\frac{E_\alpha}{RT_{\alpha,i}} \right)$$

296 (5)

$$g(\alpha) = 0.0049 \frac{A_{\alpha} R}{\beta_i E_{\alpha}} \exp\left(-1.052 \frac{E_{\alpha}}{RT_{\alpha,i}}\right) \quad (6)$$

Eventually, as the "kinetic triples" of Reaction 2 are certified, the thermokinetic model is constructed. More details were described in previous studies (Qi et al., 2021a; Qi et al., 2023)

3 Results and Discussion

The thermoreconstitution process of Co/Fe-LDHs is a complex procedure characterized by a range of physicochemical variations. This complexity is due to the interplay of a series of reactions that occur during the process, which is directly reflected on the mass/energy shifts. The thermal analyses on the mass/energy variations are powerful tools in elucidating the multifaceted physicochemical changes.

3.1 Thermoreconstitution process of Co/Fe-LDHs

Co/Fe-LDHs mass/energy variations under different heating rates ($\beta_i = 8, 10, 16$, and 18 K/min) throughout the thermoreconstitution process are shown in Fig. 1. Following the recommendations of the ICTAC Kinetics Committee (Vyazovkin et al., 2011; Vyazovkin et al., 2014), the beginning and ending temperatures were extrapolated from TG_{ori} curves. The TG_{ori} curves (Fig. 1-A) evidenced approximately 27.8 % weight loss, along with significant endothermic phenomena and overlapping weight loss peaks, respectively detected in the DSC curves (Fig. 1-B) and the DTG_{ori} curves (Fig. 1-C). Owing to the temperature hysteresis effect (Koga et al., 2023; Qi et

al., 2023; Vyazovkin et al., 2014), it is notable that the $TG_{ori}/DTG_{ori}/DSC$ curves were all right-shifted with increasing heating rates.

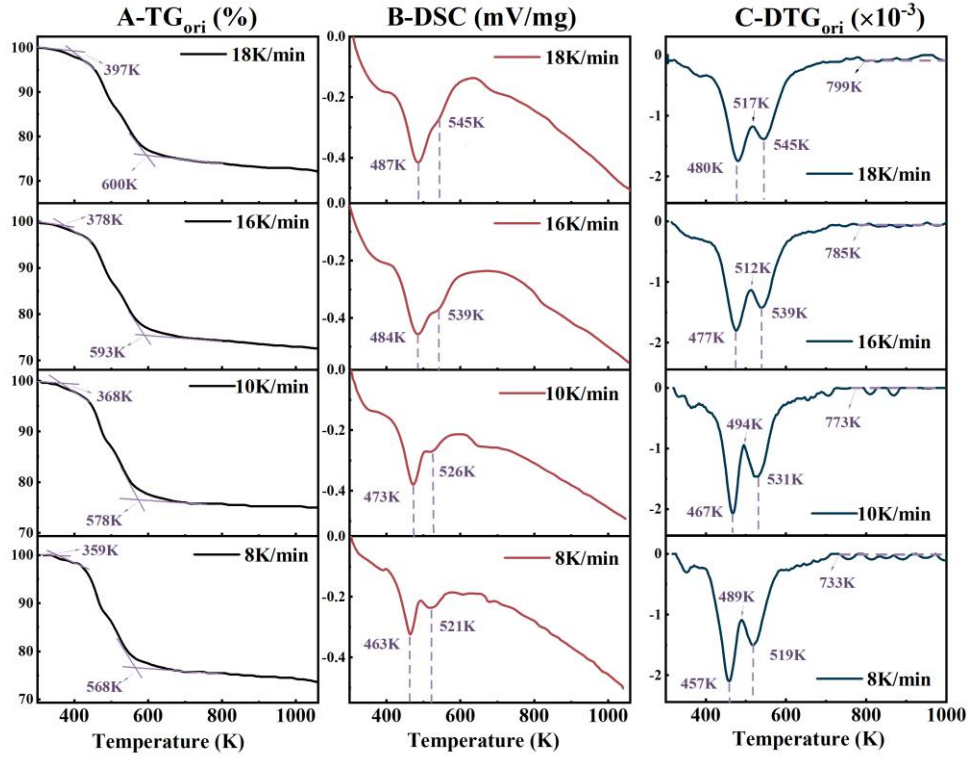


Fig. 1. Mass/energy variations of Co/Fe-LDHs throughout the

thermoreconstitution process distinct heating rates ($\beta_i = 8, 10, 16$, and 18 K/min) and thermal curves of TG_{ori} (A), DSC (B); and DTG_{ori} (C).

The thermoreconstitution process of Co/Fe-LDHs, derived from the three types of thermal curves, unfolded in three stages:

(i) Under 400 K, less than 2.5 % of weight loss in TG_{ori} (Fig. 1-A) surfaced alongside a weight loss peak in DTG_{ori} (Fig. 1-C). This stage, marked by a slight endothermic peak (Fig. 1-B), accounted for the evaporation of free absorbed water (Guo et al., 2020; Hu and Chen, 2014); this highlights the significant moisture-absorption capacity of Co/Fe-LDHs under ambient temperature (Palmer et al., 2009).

(ii) The primary thermoreconstitution phase of Co/Fe-LDHs ranged from 359-397 K to 568-600 K (Qi et al., 2021a; Qu et al., 2019), marked by a sharp weight loss (~22.5 % in Fig. 1-A). The DSC curves (Fig. 1-B) revealed dramatic endothermic reactions. It was noted that the two endothermic peaks, unified by a peak-shoulder under lower heating rates ($\beta_i = 8$ and 10 K/min), merged into an asymmetric endothermic peak under higher heating rates ($\beta_i = 16$ and 18 K/min). The two DTG_{ori} peaks (Fig. 1-C), joined by a peak-shoulder, corresponded to different types of dehydration reactions (i.e., the evaporation of crystal water (Sun et al., 2020) and dehydroxylation of -OH groups (Qi et al., 2020; Shinagawa et al., 2021)). Notably, the DTG_{ori} curves were not constant before 733-799 K, indicating that the reaction temperature of dehydration reactions ranged from 359-397 K to 733-799 K. When used for the preparation of catalysts (Peng et al., 2021) or carriers (Hou et al., 2022; Shinagawa et al., 2021), the temperature interval from 568-600 K (the extrapolated ending temperature of TG_{ori}) to 733-799 K (the constant temperature of DTG_{ori}) was critical due to significant physicochemical variations in Co/Fe-LDHs (further discussed in Section 3.2).

(iii) Beyond 733 K, the TG_{ori} curves (Fig. 1-A) showed a constant trend in weight loss along with a stationary value of DTG_{ori}. The decomposition of carbonate anions (Sun et al., 2020; Wang and O'Hare, 2012) in the negatively charged layers of Co/Fe-LDHs and the fusion of Co and Fe oxides were supported by FTIR spectra (Fig. 2-B) and SEM images (Fig. 4-A).

Under $\beta_i = 10$ K/min, four specimens at representative temperatures were chosen to examine the physicochemical changes of Co/Fe-LDHs throughout the thermoactivation process: first, Co/Fe-LDHs obtained at 368 K (Co/Fe@368K) illustrated the evaporation of free absorbed moisture; second, Co/Fe-LDHs obtained at 578 K (Co/Fe@578K) indicated the extrapolated ending temperature at the TG_{ori} curve; third, Co/Fe-LDHs obtained at 773 K (Co/Fe@773K) showed the constant temperature of the DTG_{ori} curve; and last, Co/Fe-LDHs obtained at 1,053 K (Co/Fe@1053K) represented the final product after the thermoreconstitution process.

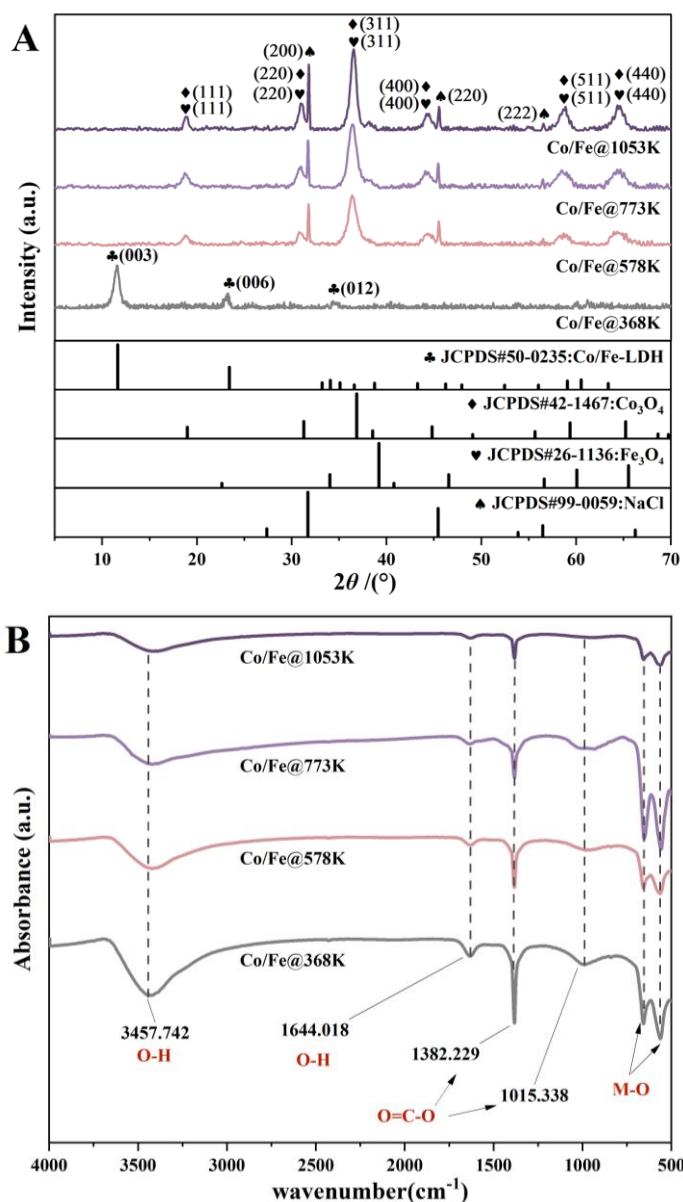
3.2 Physicochemical Variations of Co/Fe-LDHs Reconstitution

Physicochemical variations that occurred in the thermoreconstitution of Co/Fe-LDHs, including the mineralogy phases, chemical features and microscale/nanoscale morphologies, were systematically examined and analyzed.

3.2.1 Variations in Mineralogy phases

The XRD patterns of Co/Fe-LDHs throughout the thermoreconstitution process are presented in Fig. 2-A. The diffraction peaks of Co/Fe@368K at 11.5°, 23.2° and 34.3° corresponded to the (003), (006), and (012) planes of $Co_{5.84}Fe_{2.16}(OH)_{16}(CO_3)_{1.08} \cdot 0.32H_2O$ (referred to as $Co_{5.84}/Fe_{2.16}$ -LDHs). Co/Fe-LDHs in the form of $Co_{5.84}/Fe_{2.16}$ -LDHs held a hexagonal structure (Sun et al., 2020), as reflected in the SEM image (Fig. 4-A/a). The Co:Fe mole ratio in $Co_{5.84}/Fe_{2.16}$ -LDHs was 5.84:2.16 (i.e., 2.7:1) and was lower than that in the precursor metallic salt solution

369 (Co:Fe = 3:1), suggesting the generation of amorphous Co or Fe-based byproducts
 370 during the preparation of Co/Fe-LDHs. The water content of Co_{5.84}/Fe_{2.16}-LDHs was
 371 less than 0.71 %, implying that the weight loss in the first stage of the TG_{ori} curve (Fig.
 372 1-A) mainly originated from the evaporation of the absorbed water.



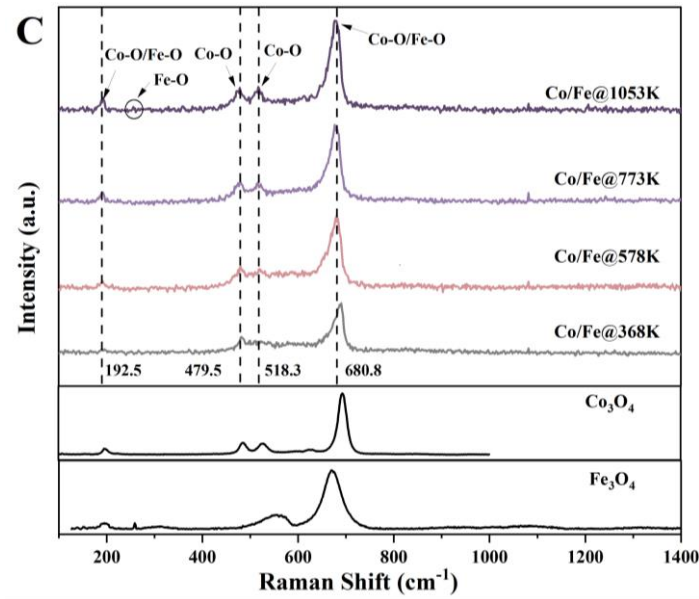


Fig. 2. XRD patterns (A), FTIR spectra (B), and Raman spectra (C) of Co/Fe-LDHs samples throughout the thermoreconstitution process ($\beta_i = 10$ K/min).

As the thermoreconstitution temperature exceeded 368 K, identical crystal phases in the XRD patterns were displayed in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K. Lattice planes assigned to (111), (220), (311), (400), (511), and (440) were well fitted to that of the cubic-structured Co_3O_4 and Fe_3O_4 crystals, which possessed analogous lattice parameters (Feng et al., 2016; Lu et al., 2019; Rodenbough et al., 2016). In addition, the calculated lattice parameters of the generated Co_3O_4 and Fe_3O_4 (hereafter, the generated Co_3O_4 and Fe_3O_4) and the standard Co_3O_4 and Fe_3O_4 crystals of JCPDS cards (hereafter, the standard Co_3O_4 and Fe_3O_4) are compared in Table S-1. With the thermoreconstitution temperature increased, the Bragg angles ($2\theta_{hkl}$) of Co_3O_4 and Fe_3O_4 detected in the XRD patterns were both inclined to that of the standard Co_3O_4 and Fe_3O_4 , correspondingly, the values of d -spacings calculated via the Bragg's Law (Eq. S-8) and lattice parameters calculated for the cubic-structured Co_3O_4

and Fe₃O₄ via Eq. S-14 were expanded. Specifically, the calculated lattice constants for the generated Co₃O₄ and Fe₃O₄ crystals of Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K were $a = b = c = 8.1581\text{-}8.1755\text{ \AA}$, $8.1712\text{-}8.1793\text{ \AA}$ and $8.1436\text{-}8.1636\text{ \AA}$, respectively, which were simultaneously expanded compared with those of the standard Co₃O₄ and Fe₃O₄ crystals (i.e., $a = b = c = 8.0835\text{-}8.0903\text{ \AA}$) (Rodenbough et al., 2016; Wang et al., 2011). Furthermore, the *d*-spacings of the adjacent crystal lattice planes (i.e., [111], [220], [311], [400], [511], and [440]) calculated for the generated Co₃O₄ and Fe₃O₄ were higher than those of the standard Co₃O₄ and Fe₃O₄. To take the [111] lattice planes of Co₃O₄ as an example, the *d*-spacings of the generated Co₃O₄ of Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K were 0.471 nm, 0.472 nm and 0.470 nm, respectively, which were both higher than that of the standard Co₃O₄ (*d*-spacing = 0.467 nm). Similarly, the volumes of the unit cells of the generated Co₃O₄ and Fe₃O₄ were $545.04\text{-}546.45\text{ \AA}^3$, $545.57\text{-}547.14\text{ \AA}^3$ and $540.08\text{-}544.41\text{ \AA}^3$ in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K, respectively, which were both higher than those of the Co₃O₄ and Fe₃O₄ standards ($528.20\text{-}529.50\text{ \AA}^3$). The collaboration of “lattice expansion effect” and “heterogeneous microstrain effect” triggered by the reconstitution temperature was the underlying cause in extending the values of *d*-spacings and lattice parameters, which was quantitatively evaluated in the following section.

3.2.2 Effect of the thermoreconstitution temperature on mineralogy

The XRD peaks of the generated Co₃O₄ and Fe₃O₄ in Co/Fe@578K, Co/Fe@773K,

and Co/Fe@1053K were significantly broadened, which was colloquially defined as the “XRD peak broadening phenomenon” (Rodenbough et al., 2016). Because the XRD peaks of the probe NaCl crystal were not expanded in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K (Fig. 2-A), it was reasonable that this broadening phenomenon was not attributed to the XRD instrument but was directly caused by the thermoreconstitution process. Universally, the “lattice expansion effect” (Rodenbough et al., 2016) caused by particle size variations, as well as the “heterogeneous microstrain effect” (Li et al., 2014) generated from crystal imperfection and distortion (Hou et al., 2022), were the two primary reasons for the broadening of the XRD peaks.

Quantitatively, the “lattice expansion effect” in expanding the XRD patterns of the generated Co₃O₄ and Fe₃O₄ could be evaluated via the volume variation degree of the unit cell, $\varepsilon_v(\%)$, which is depicted in Eq. 7. Meanwhile, the “heterogeneous microstrain effect” could be assessed via the “Williamson-Hall equation” (Hou et al., 2022; Li et al., 2014; Rodenbough et al., 2016), $\varepsilon_d(\%)$, which is displayed in Eq. 8.

$$\varepsilon_v(\%) = \frac{\Delta v}{v_s}(\%) = \frac{v_c - v_s}{v_s} \quad (7)$$

$$\varepsilon_d(\%) = \frac{\beta_{hkl} \cos \theta_{hkl}}{4 \sin \theta_{hkl}} = \frac{\beta_{hkl}}{4} \tan \theta_{hkl} \quad (8)$$

Where, $\varepsilon_v(\%)$ is the volume variation degree; v_c and v_s is the calculated and standard volume of a unit cell; $\varepsilon_d(\%)$ is the elastic microstrain value in radian of [hkl] direction; θ_{hkl} was the Bragg angle of the (hkl) plane; β_{hkl} is line broadening at FWHM of XRD peak detected at 2θ ;

The $\varepsilon_v(\%)$ and $\varepsilon_d(\%)$ values of the [111], [220], [311], [400], [511], and [440] directions of the generated Co_3O_4 and Fe_3O_4 in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K were calculated and are shown in Table S-1. The $\varepsilon_v(\%)$ values of the generated Co_3O_4 crystals were 3.09 % (Co/Fe@578K), 3.44 % (Co/Fe@773K) and 2.76 % (Co/Fe@1053K), while the $\varepsilon_v(\%)$ values of the generated Fe_3O_4 were 2.84 % (Co/Fe@578K), 3.19 % (Co/Fe@773K) and 2.51 % (Co/Fe@1053K). The positive $\varepsilon_v(\%)$ values of the generated Co_3O_4 and Fe_3O_4 crystals at 578 K, 773 K, and 1,053 K reflected the “lattice expansion effect” in broadening the XRD peaks. On the other hand, the $\varepsilon_d(\%)$ values of the generated Co_3O_4 and Fe_3O_4 were 1.12 %-2.03 % (Co/Fe@578K), 1.14 %-2.42 % (Co/Fe@773K) and 0.89 %-1.33 % (Co/Fe@1053K), respectively, which were lower than the corresponding $\varepsilon_v(\%)$ values of the generated Co_3O_4 and Fe_3O_4 in Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K. Hence, the “lattice expansion effect” was the superior reason for generating the XRD peak broadening phenomena throughout the Co/Fe-LDHs thermoreconstitution process.

To summarize the mineralogy aspect, the thermoreconstitution process of Co/Fe-LDHs resulted in (i) the formation of Co_3O_4 and Fe_3O_4 crystals through the breakdown of the Co/Fe-LDHs lattice, and (ii) the expansion of Co_3O_4 and Fe_3O_4 crystals via the lattice expansion effect.

3.2.3 Variations in Chemical Features

The FTIR spectra of Co/Fe-LDHs throughout the thermoreconstitution process are shown in Fig. 2-B. The chemical group at $3,457\text{ cm}^{-1}$ was assigned to the -OH (Hu and

Chen, 2014) of the free water absorbed onto the specimens from the ambient surroundings. The intensity of -OH at $3,457\text{ cm}^{-1}$ of Co/Fe@368K was significantly stronger than that of Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K, implying the decreasing hygroscopicity of the samples. The peak at $1,644\text{ cm}^{-1}$ (Taviot-Guého et al., 2018) was ascribed to -OH groups, which not only existed in the negatively charged layers (NCLs) to maintain the electrical neutrality of the LDH structure (Li et al., 2014) but also acted as a coordinate bond to Co^{2+} and Fe^{3+} in the positively charged layers (PCLs) (Wang and O'Hare, 2012). The intensity of -OH groups at $1,644\text{ cm}^{-1}$ declined as the thermoreconstitution temperature rose from 368 K to 1,053 K. Additionally, two types of dehydroxylation reactions stemmed from the elimination of -OH groups from NCLs and PCLs, leading to the significant weight loss depicted in the TG_{ori} curves in Fig. 1-A.

Moreover, wavenumbers at $1,382\text{ cm}^{-1}$ and $1,015\text{ cm}^{-1}$ were generated by the O=C-O group of CO_3^{2-} in the NCLs (Hou et al., 2022; Sun et al., 2020; Winoto et al., 2019). Both -OH and O=C-O notably declined as the thermoreconstitution temperature increased. Two FTIR spectra signals that appeared below 600 cm^{-1} were attributed to the vibration of the metal-oxygen bond (M-O) (Palmer et al., 2009; Seron and Delorme, 2008), which were further confirmed in Raman spectra (Fig. 2-C). In the Raman spectra of Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K, the signals detected at 192.5 cm^{-1} , 479.5 cm^{-1} , 518.3 cm^{-1} , and 680.8 cm^{-1} were characteristic of Co-O bonds in cubic-structured Co_3O_4 (Guo et al., 2020), and the signals detected at 192.5 cm^{-1} , 274.5 cm^{-1}

and 680.8 cm^{-1} were attributed to Fe-O bonds of cubic Fe_3O_4 (Rodenbough et al., 2016) crystals. The signal detected at 680.8 cm^{-1} in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K was the overlap of Co-O and Fe-O bonds. Interestingly, the strongest M-O bond in the Raman spectra of Co/Fe@368K slightly shifted from 680.8 cm^{-1} , implying that the Co-O and Fe-O bonds of $\text{Co}_{5.84}\text{Fe}_{2.16}$ -LDHs were distinct from those in the generated Co_3O_4 and Fe_3O_4 of Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K.

Chemical valence changes on the surface of Co/Fe-LDHs throughout the thermoreconstitution process were examined using the XPS technique, with the C1s calibrated to the binding energy of C-C of pollutant carbon at 248.8 eV (Qi et al., 2021b). The XPS survey spectra (Fig. 3-A) indicated an abundance of Co, Fe, and O on the surface of Co/Fe-LDHs. The relative atomic ratio of Co:Fe in Co/Fe@368K, Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K ranged between 2.95-2.98:1, which approximated that of the precursor metallic salt solution (Co:Fe = 3:1) but was higher than that in $\text{Co}_{5.84}\text{Fe}_{2.16}$ -LDHs (Co:Fe = 2.7:1). The discrepancy in Co:Fe ratios implied the generation of amorphous Co-based, Fe-based, or Co/Fe-based byproducts during the preparation of Co/Fe-LDHs.

XPS high-resolution spectra of C1s, Co2p, and Fe2p were further analyzed and compared in Fig. 3-B, C, and D, respectively. The bonding energies of C1s deconvoluted at 284.8 eV, 286.3 eV, and 288.6 eV were ascribed to the C-C of pollutant carbon, the C-O of the oxygen absorbed onto pollutant carbon, and the carbonate of CoCO_3 (Sun et al., 2019), respectively. Two peaks at Co 2p_{1/2} (797.5 eV) and Co 2p_{3/2}

494 (781.9 eV) in the four XPS spectra of Co 2p were consistent with the Co (II) of cobalt
 495 carbonate (Peng et al., 2021; Vyazovkin et al., 2014). Simultaneously, three peaks at
 496 Fe 2p_{1/2} (726.6 eV) and Fe 2p_{3/2} (714.3 eV and 718.1 eV) were assigned to Fe (III) of
 497 amorphous FeOOH and tetragonal wurtzite (β -FeOOH), respectively (Zhai et al., 2021).
 498 As the thermoreconstitution temperature rose to 578 K or above, peaks of Co 2p_{1/2} at
 499 795.7 eV/780.6 eV and Co 2p_{3/2} at 794.6 eV/779.6 eV were assigned to Co (II)/Co (III)
 500 of cubic-Co₃O₄ (Sun et al., 2020; Wang et al., 2010). Simultaneously, peaks of Fe 2p_{1/2}
 501 at 723.3 eV/709.8 eV and Fe 2p_{3/2} at 724.7 eV/711.4 eV were ascribed to Fe (II)/Fe (III)
 502 of cubic-Fe₃O₄ (Huang et al., 2021; Wu et al., 2020). Moreover, with the increase in
 503 the thermoreconstitution temperature from 578 K to 1,053 K, the atomic ratios of Co
 504 (II):Co (III) declined from 1.80:1 (Co/Fe@578K) to 1.62:1 (Co/Fe@773K) and 1.37:1
 505 (Co/Fe@1053K). Conversely, the Fe (III):Fe (II) atomic ratios increased from 2.71:1
 506 (Co/Fe@578K) to 2.83:1 (Co/Fe@773K) and 3.11:1 (Co/Fe@1053K). Therefore, the
 507 decrease in Co (II):Co (III) and the increase in Fe (III):Fe (II) suggested an
 508 accumulation of Co₃O₄ and Fe₃O₄ with the extension of the thermoreconstitution
 509 process, possibly due to the Co (II) and Fe (III) in Co_{5.84}/Fe_{2.16}-LDHs.

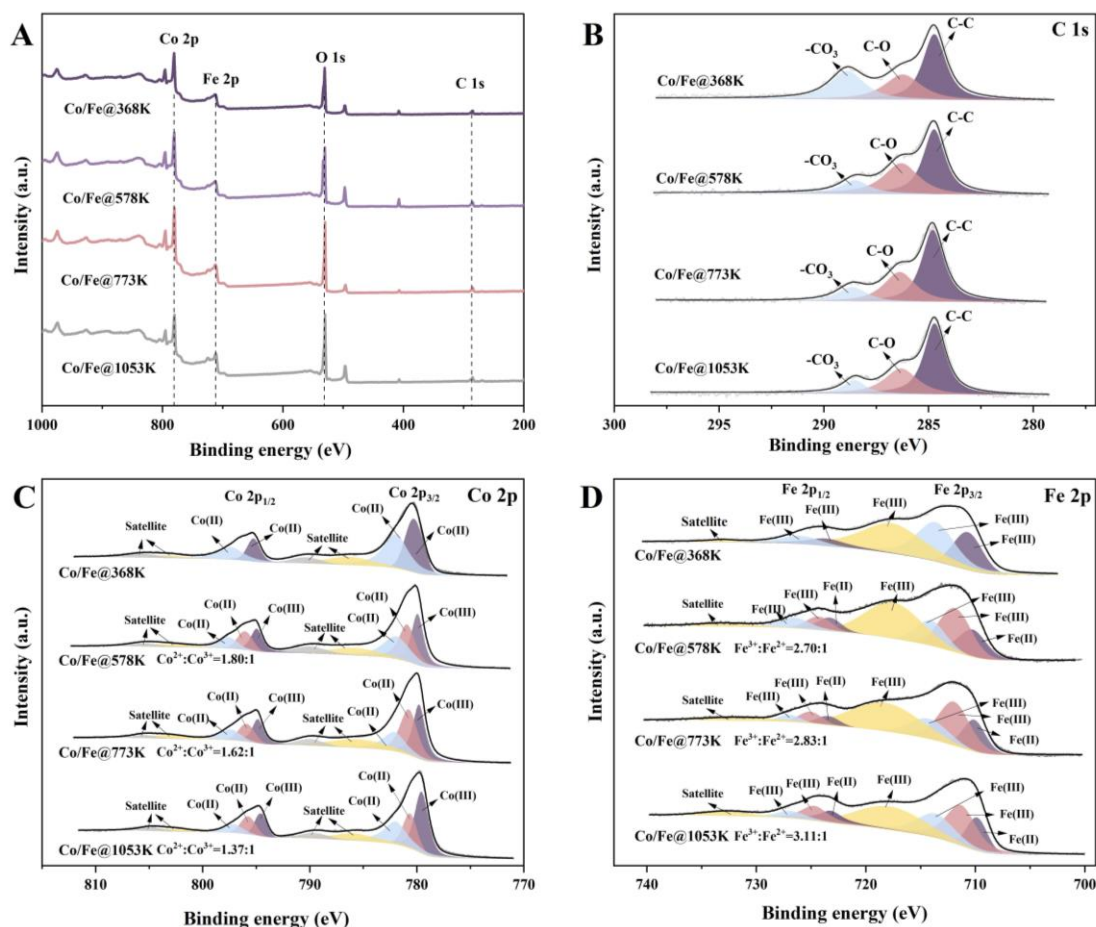


Fig. 3. XPS spectra of the full-range (A), C1s (B), Co 2p (C), and Fe 2p (D) on the surface of Co/Fe@368K, Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K.

3.2.4 Variations in Morphology

Co/Fe-LDHs exhibited microscale variations throughout the thermoreconstitution process, as observed via SEM (Fig. 4-A). The Co/Fe@368 surface structure, resembling oatmeal sheets (Fig. 4-A/a), gradually collapsed and overlapped onto Co/Fe@578 (Fig. 4-B/a) (Taviot-Guého et al., 2018; Vyazovkin et al., 2014; Zhai et al., 2021). As temperatures increased to 773 K (Fig. 4-C/a) and 1,053 K (Fig. 4-D/a), these structures were further fractured and partially melted on the surface of Co/Fe@1053K (Hou et al., 2022). EDX-mapping suggested negligible variation in the distribution of Co, Fe, and

521 O on the surfaces despite distinct appearances between Co/Fe@368K and
522 Co/Fe@1053K (Fig. S-3 A and B).

523 HRTEM images elucidated the nanoscale morphologies of Co/Fe at various
524 temperatures. The (012) lattice plane of Co_{5.84}Fe_{2.16}-LDHs in Co/Fe@368K (Fig. 4-A/c)
525 demonstrated a *d*-spacing of 0.251 nm, similar to the calculated *d*-spacing (0.259 nm,
526 Table S-1). The *d*-spacing values of 0.249 nm, 0.251 nm, and 0.248 nm in Co/Fe@578K,
527 Co/Fe@773K, and Co/Fe@1053K (Fig. 4-B/c, C/c, and Fig. 4-D/c) corresponded to
528 the (311) lattice plane of Co₃O₄ (or Fe₃O₄) crystals, aligning with calculated *d*-spacing
529 values (0.247 nm, Table S-1). These *d*-spacing values were consistent with those
530 calculated from XRD patterns (Table S-1). Diffraction patterns (Fast Fourier
531 Transform, FFT) indicated representative polycrystalline structures (Fig. 4-B/d, C/d,
532 and D/d) (Sun et al., 2019; Wang et al., 2021).

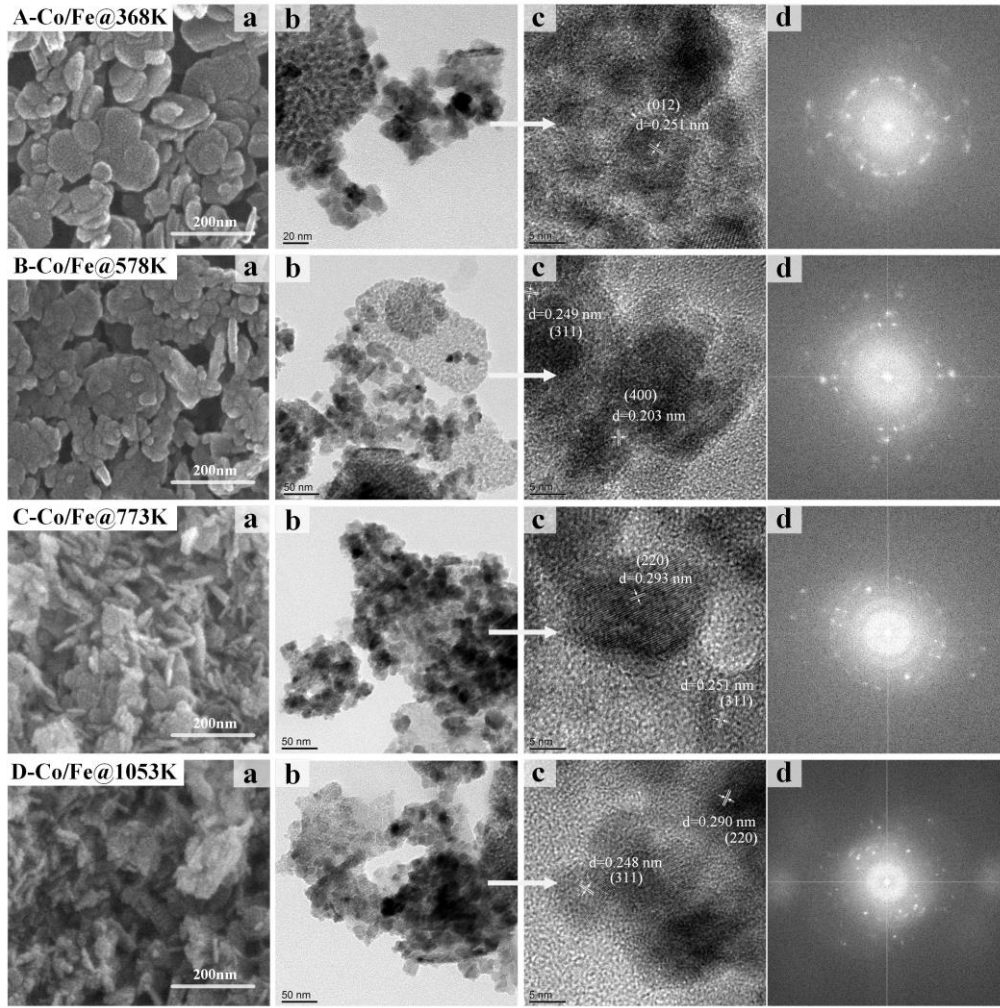


Fig. 4. SEM images (a), HRTEM images (b), Lattice structure (c) and FFT images (d) of Co/Fe-LDH at different temperatures (A-D).

3.3 Deconvolution of the Co/Fe-LDHs thermoreconstitution process

The normalized (TG_{nor}/DTG_{nor}) and converted (TG_{con}/DTG_{con}) TG/DTG curves, calculated from original TG data (TG_{ori}) under $\beta_i = 8, 10, 16$ and 18 K/min, are shown in Fig. 5-A. The starting and ending temperatures of the TG_{nor} and TG_{con} curves matched those of the TG_{ori} curve (Fig. 1-A), with DTG peaks aligning with those in the DTG_{ori} curve (Fig. 1-C). TG_{nor}/DTG_{nor} and TG_{con}/DTG_{con} curves differ in focus, with

the former examining solid-state residual variations and the latter concentrating on volatile matter decline (such as H₂O and CO₂) (Koga et al., 2023). The TG_{nor}/DTG_{nor} and TG_{con}/DTG_{con} curves presented opposite profiles, with the latter correlating with the $\alpha \frac{d\alpha}{dT}$ curves crucial for thermokinetic models established by Eq. 1 (Vyazovkin et al., 2011).

The G-PDF and F-SF both exhibit promising efficiency in deconvolving each DTG_{con} curve as three subcurves (Fig. 5-B and C). To take DTG_{con} curve under $\beta_i = 10$ K/min as an example (see Fig. 5-A/b, where peaks are respectively located at 377 K, 467 K, and 531 K), three overlapping subcurves are deconvolved by using three F-SFs with center points at 377 K, 467 K, and 531 K (Fig. 5-C/b). Similarly, the separation of the three overlapping subcurves are also achieved via three G-PDFs (Fig. 5-B/b). The correlate coefficient (R^2) of the cumulative fit peaks obtained via F-SF is superior than that gained from G-PDF, which indicated F-SF is more flexible and accurate in deconvolving the complex thermoreconstitution process. There are four independent variables, namely the asymmetry, width (or FWHM), center position, and altitude are included in the mathematical expression of F-SF, while asymmetry is absent in that of G-PDF. The higher degree of freedom of F-SF led to the superior R^2 of the cumulative fit peaks displayed in Fig. 5-C. However, it seems that the advantage of F-SF in deconvolving various DTG_{con} curves is not so significant as that demonstrated by G-PDF in this study. Because the R^2 values of the cumulative fit peaks are all higher than 0.96 in spite of the deconvolution processing is conducted via G-PDF or F-SF.

By using the mathematical expressions of G-PDF or F-SF (Dragoi et al., 2021; Qi et al., 2021a), subcurves deconvolved from DTG_{con} curve are presented as DTG_{dec-1} , DTG_{dec-2} , and DTG_{dec-3} . Meanwhile, subcurves integrated with respect to reaction temperature were denoted as TG_{dec-1} , TG_{dec-2} , and TG_{dec-3} . Hence the three reactions were thoroughly separated throughout the thermoreconstitution process. Under various of β_i , the TG_{dec} / DTG_{dec} curves of Reaction 1, 2 and 3 separated via G-PDF and F-SF were illustrated in Fig. S-4 and in Fig. S-5, respectively. On the one hand, the final TG_{dec} values of Reaction 1, 2 and 3 indicates the accumulated contributions (Dragoi et al., 2021; Muravyev et al., 2021) to the thermoreconstitution process of LDHs. To take Fig. S-4/B as an example, the final TG_{dec} values, 0.098 (Fig. S-4B/a), 0.328 (Fig. S-4B/b), and 0.463 (Fig. S-4B/c), represent the accumulated contributions of Reaction 1, 2, and 3 to the thermoreconstitution process as 9.8 %, 32.8 % and 46.3 %, which are strictly equal to the areas that covered by the corresponding DTG_{dec} curves depicted in Fig. 5-B/b. Because the peaks located in Area 1 and Area 2 (Fig. 5-B/b) were not deconvolved from the DTG_{con} curve, the total area covered by all three reactions is 0.889, indicating that 88.9 % of the thermoreconstitution process for Co/Fe-LDHs occurs below 663 K. Attributing to high values of final TG_{dec} , both Reactions 2 and 3 play a dominant role in the reconstitution of Co/Fe-LDHs to Co_3O_4 and Fe_3O_4 . Despite of the three reactions deconvolved via G-PDF or F-SF under various β_i , analogous relationships to Fig. 5-B (or Fig. 5-C) are obtained from Fig. S-4 (or Fig. S-5).

One the other hand, TG_{dec} value of each reaction at certain temperature represents the instantaneous contribution to the major weight loss of the Co/Fe-LDHs thermoreconstitution process. Continuing with the previous example as an illustration (Fig. S-4/B): for any certain temperature ($T_c \leq 663$ K), the values of TG_{dec-1} , TG_{dec-2} , TG_{dec-3} at T_c signify the instantaneous weight loss contributions of each reaction to the thermoreconstitution process of Co/Fe-LDHs extends to T_c , and the instantaneous contribution of Reaction 2 is depicted in Eq. 15. Additionally, we inferred the relative ratio, of the instantaneous contributions between Reactions 1, 2, and 3, can be utilized in predicting the instantaneous products that generated from the Co/Fe-LDHs' thermoreconstitution, which will be detailed in our subsequent study.

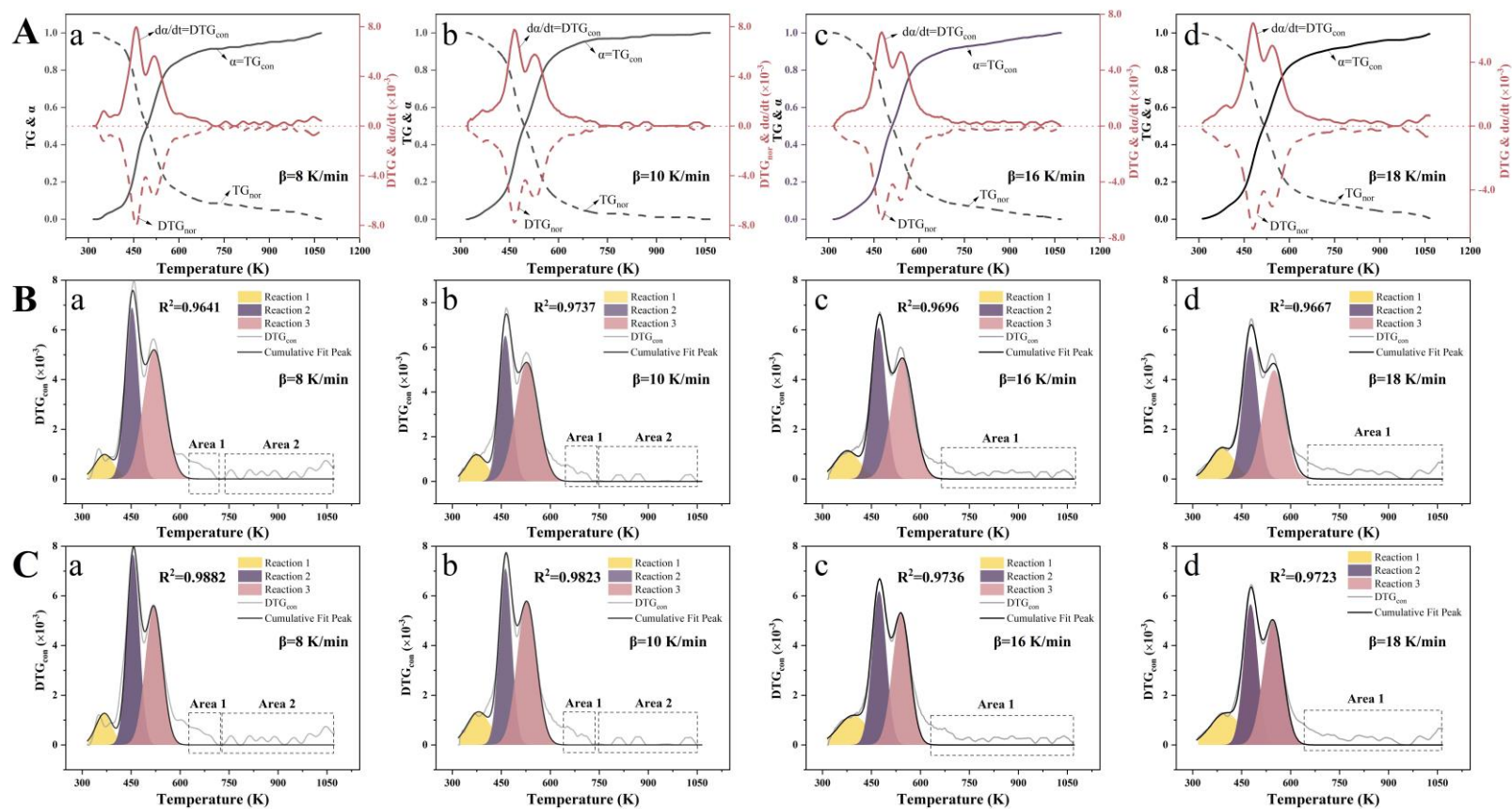


Fig. 5. TG_{nor}/DTG_{nor} and TG_{con}/DTG_{con} curves of Co/Fe-LDHs under various of β_i (A); the deconvolution of DTG_{con} ($\beta_i = 10$ K/min) into Reaction 1, Reaction 2 and Reaction 3 via Gaussian probability distribution function, G-PDF, (B) and Frazer-Suzuki function, F-SF, (C).

3.4 Thermokinetic analyses on the Co/Fe-LDHs thermoreconstitution process

Thermokinetic analyses are powerful tools for elucidating the specific reaction mechanism. Thermokinetic models is the mathematical expression of the thermokinetic analysis, which are constructed with "kinetic triples", namely the activation energy (E), the preexponential factor (A), and the reaction model ($f(\alpha)$ or $g(\alpha)$). However, mathematically, one may notice that there is no specific constant solution set but a statistical solution set of "kinetic triples" in constructing the thermokinetic model via Eq. 1. In this section, thermokinetic analyses throughout the Co/Fe-LDHs thermoreconstitution process was conducted, and the most likely "kinetic triples" of Reaction 2 is pursued to establish a reliable thermokinetic model in response to the physicochemical variations that detailed in second 3.2.

3.4.1 Scrutinization on E_α values

Activation energy, being the core of the "kinetic triples," is calculable via the model-free method (Chen et al., 2022; Liu et al., 2020; Mandapati and Ghodke, 2021) using the FWO and Friedman algorithm (Eq. 2), irrespective of the influence of the preexponential factor and the reaction model. The E_α values obtained under the FWO and Friedman algorithm throughout the Co/Fe-LDHs thermoreconstitution process are presented in Fig. 6-A and B, respectively. It should be emphasized that the specific " α " in Fig. 6-A and B (or Fig. 6-C and D) represents the relative conversion ratio of the Co/Fe-LDHs thermoreconstitution process (or Reaction 1, 2, or 3). Researchers (Koga

et al., 2023; Zhang et al., 2021b) recommended that more than 10 % of the E_{α} value fluctuation indicated that a complex multistep reaction occurred. Throughout the Co/Fe-LDH thermoreconstitution process, a complex multistep reaction is confirmed because the E_{α} values vigorously fluctuated. Furthermore, the E_{α} values obtained via the FWO algorithm decrease from 132 kJ/mol to 31.2 kJ/mol (Fig. 6-A), while the E_{α} values obtained via the Friedman algorithm fluctuate in the range of 37.5 kJ/mol to 121.8 kJ/mol (Fig. 6-B). One may observe that the E_{α} values calculated via the FWO algorithm possesses a smoother tendency and higher of accuracy (i.e., higher R^2) than those obtained from the Friedman algorithm, which indicated that integral-natured FWO algorithm is superior to the differential-natured Friedman algorithm in calculating the E_{α} values for the overall thermoreconstitution process.

For the deconvolved Reactions 1, 2 and 3 that separated by G-PDF and F-SF, the E_{α} values calculated under the FWO algorithm are illustrated in Fig. 6-C and D, respectively. Correspondingly, those E_{α} values obtained via the Friedman algorithm are illustrated in Fig. S-6/A and B, respectively. As the G-PDF is adopted for the deconvolution process (Fig. 6-C), the mean E_{α} values ($\overline{E_{\alpha}}$) of the three reactions are 47.09 kJ/mol, 64.77 kJ/mol and 74.85 kJ/mol, respectively. As the F-SF is utilized for deconvolution, those $\overline{E_{\alpha}}$ are 47.57 kJ/mol, 67.05 kJ/mol and 73.46 kJ/mol, respectively. For each reaction, the discrepancy of $\overline{E_{\alpha}}$ values calculated under FWO algorithm are not significant in spite of the deconvolution process is conduct through

G-PDF or F-SF. Identical findings are revealed by the E_{α} values obtained via the Friedman algorithm (Fig. S-6).

Furthermore, despite of the three curves is deconvolved via G-PDF or F-SF, the E_{α} values of each reaction calculated under FWO algorithm (Fig. 6-C and D) exhibit limited fluctuating tendency as that obtained under Friedman algorithm (Fig. S-6). However, E_{α} value variations in the three reactions are distinct. To take the three reactions deconvolved through G-PDF as an instance (Fig. 6-C), the E_{α} values in Reaction 1 (or 3) increase from 38.3 kJ/mol to 56.3 kJ/mol (or increase from 61.2 kJ/mol to 85.5 kJ/mol), with variation rates ($\Delta E_{\alpha}/\overline{E_{\alpha}}$) of 59.56 % (or 32.46 %), indicating that Reactions 1 and 3 are multistep reactions. In contrast, the E_{α} value variation in Reaction 2 is minimal, and the $\Delta E_{\alpha}/\overline{E_{\alpha}}$ value is 5.24 % (Fig. 6-C/b), implying that Reaction 2 is a single-step reaction. Identical findings are displayed by the E_{α} values obtained via the Friedman algorithm (Fig. S-6/A). Same occurrences are carried out as the three reactions deconvolved through F-SF, in spite of the E_{α} values are calculated under FWO algorithm (Fig. 6-B) or Friedman algorithm (Fig. S-6/B).

Complementing this with FTIR/XPS spectra (Fig. 2-B and Fig. 3-B), two reactions were presumed to be part of Reaction 1's multistep process: the evaporation of absorbed water and the removal of crystal water. The former reaction exhibited lower activation energies than the latter, contributing to the increasing trend of E_{α} values in Fig. 6-C/a and D/a. The dehydroxylation of -OH groups from Co/Fe-LDHs' PCLs primarily occurred in Reaction 2, which presented relatively constant E_{α} values, displaying a

658 single-step feature. For the multistep Reaction 3, decarbonization reactions from the
659 NCLs and CoCO_3 were evident, along with the dehydroxylation reactions in iron-based
660 byproducts such as amorphous FeOOH (Feng et al., 2016) and tetragonal wurtzite (β -
661 FeOOH) (Zhai et al., 2021), as confirmed by FTIR and XPS spectra (Fig. 2-B and Fig.
662 3-D).

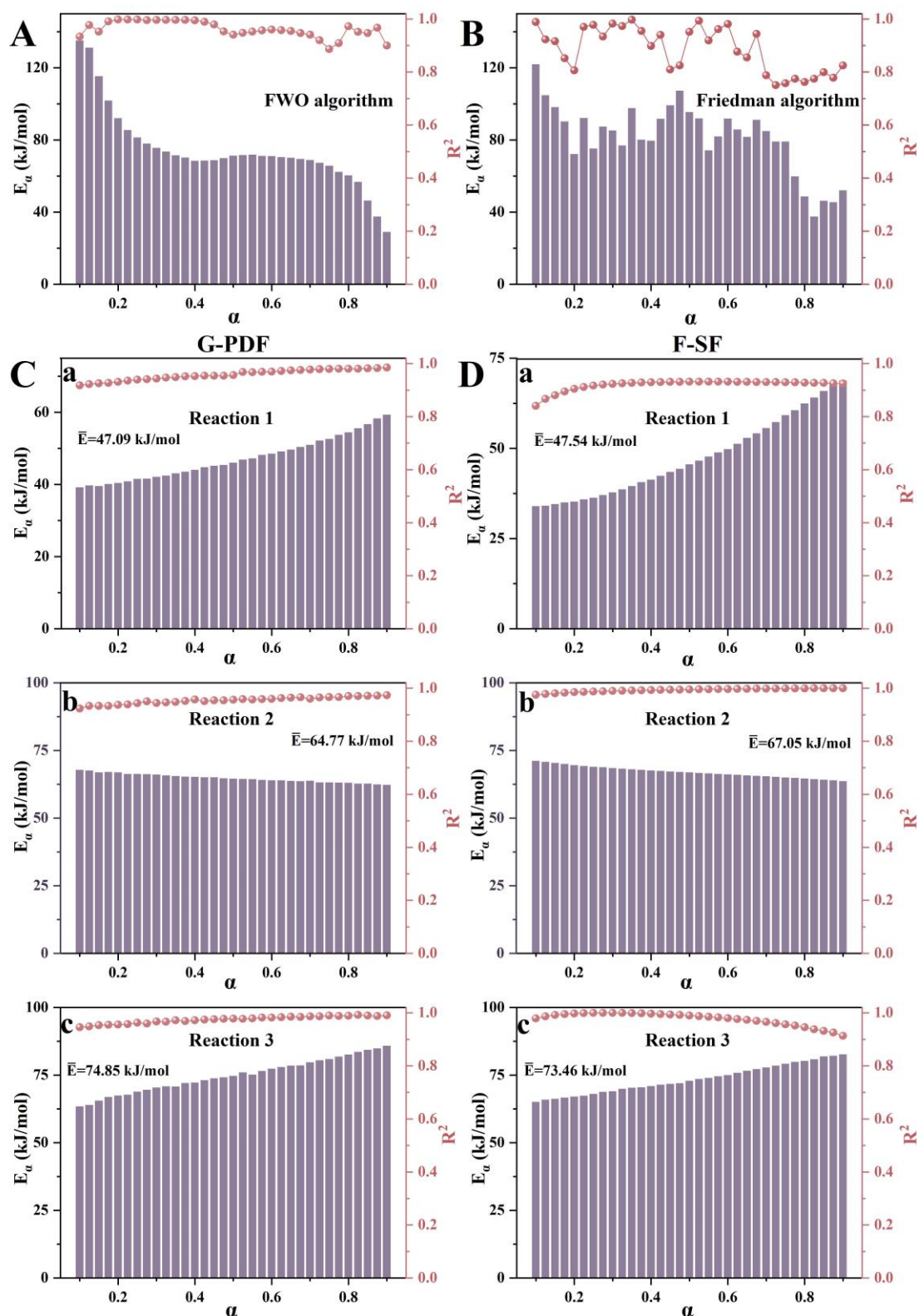


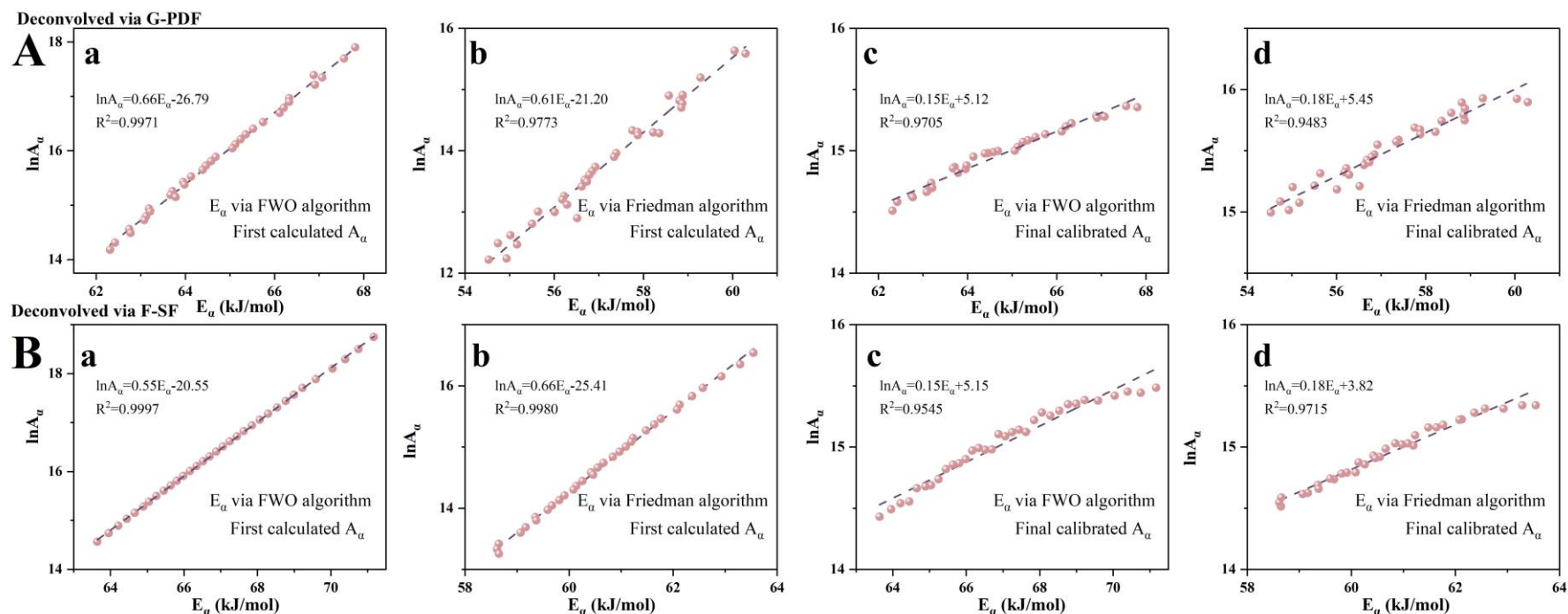
Fig. 6. E_α versus α throughout the Co/Fe-LDHs thermoreconstitution process with E_α values calculated through FWO algorithm(A) and Friedman algorithm (B);

666 The distribution of E_{α} values calculated via FWO algorithm in Reaction 1(a),
667 Reaction 2(b), and Reaction 3(c) separated with G-PDF (C) and F-SF (D). All
668 calculations were conducted as $\alpha \in (0.1, 0.9)$ with the stepping constant of α , i.e.,
669 $\Delta\alpha = 0.025$.

3.4.2 Optimization of A_α values for Reaction 2

As the target reaction is evidenced a single-step reaction ($\Delta E_\alpha / \overline{E}_\alpha \leq 10\%$), or a multistep reaction is dominated or limited by the rate of one step ($10\% \leq \Delta E_\alpha / \overline{E}_\alpha \leq 20\%$), the thermokinetic model could be established on Eq. 1 (Vyazovkin et al., 2020). More details and case studies were described in previous studies (Qi et al., 2021a; Qi et al., 2023). However, the $\Delta E_\alpha / \overline{E}_\alpha$ values of Reaction 1 and 3 are both higher than 30%, which indicate Eq. 1 is only suitable in constructing the thermokinetic models of Reaction 2. Furthermore, because limited DTG_{con} peaks are displayed in Fig. 5-A, neither Reaction 1 nor Reaction 3 can be further separated into series signal-step reactions. We inferred if the thermoreconstitution temperature ranges cover by Reaction 1 and Reaction 3 were monitored under relatively lower β_i , more DTG_{con} peaks might emerged. Reaction 1 or Reaction 3 could be further deconvolved into finite signal-step reactions through a second level of deconvolution process as it was depicted in section 3.3. And this inference will be further scrutinized in our further study.

The E_α values depicted in Fig. 6-C/b and D/b are utilized in calculating the precious A_α values of Reaction 2. When the reaction model is assumed as the 1st order reaction, the A_α values of Reaction 2 (both deconvolved via G-PDF and F-SF) are first calculated under Eq. 3, and the relationship of $\ln A_\alpha$ versus E_α values are depicted in Fig. 7. Furthermore, relying on the iterative computation process, the final calibrated A_α values of Reaction 2 versus E_α values are co-illustrated in Fig. 7.



690

691 Fig. 7. Relaying on the TG_{con}/DTG_{con} curves deconvolved through G-PDF (A) and F-SF (B), the “compensation effect” between $\ln A_\alpha$ and

692 E_α plotted with the first calculated A_α versus E_α , (a) and (b); the “compensation effect” between the final calibrated A_α versus E_α , (c) and

693

(d).

694 A strong linear relationship between $\ln A_\alpha$ and E_α is displayed in Fig. 7, which
 695 is constant in spite of whether A_α values are first calculated or final calibrated.
 696 Meanwhile, neither algorithms for calculating E_α values nor deconvolution functions
 697 exhibit hardly effect in varying the linear relationship between $\ln A_\alpha$ and E_α . Relying
 698 on the “compensation effect” and the iterative computation process conducted in Fig.
 699 7, the mathematical equation constructed for $\ln A_\alpha$ and E_α of the Reactions 2 are
 700 tabulated in Table 1, enabling direct calculation of the A_α value once the E_α value is
 701 certified. Furthermore, utilizing the average ($\overline{E_\alpha}$) values obtained through FWO or
 702 Friedman algorithm, the mean $\ln A_\alpha$ values ($\ln \overline{A_\alpha}$) of Reactions 2 were determined.

703 Table 1. linear equation constructed for $\ln A_\alpha$ versus E_α of Reaction 2

Deconvolved through G-PDF	Algorithms	$\ln A_\alpha = aE_\alpha + b$		$\overline{E_\alpha}$ (kJ/mol)	$\ln \overline{A_\alpha}$ (/min)	R^2
		a	b			
First calculated A_α	FWO	0.66	-26.79	64.77	15.89	0.9971
	Friedman	0.61	-21.20	59.15	15.10	0.9773
Final calibrated A_α	FWO	0.15	5.12	64.77	14.97	0.9705
	Friedman	0.18	5.45	59.15	15.86	0.9483
Deconvolved through F-SF	Algorithms	$\ln A_\alpha = aE_\alpha + b$		$\overline{E_\alpha}$ (kJ/mol)	$\ln \overline{A_\alpha}$ (/min)	R^2
		a	b			
First calculated A_α	FWO	0.55	-20.55	67.05	16.49	0.9997
	Friedman	0.66	-25.41	60.71	14.73	0.9980
Final calibrated A_α	FWO	0.15	5.15	67.05	15.03	0.9545
	Friedman	0.18	3.82	60.71	14.94	0.9715

704 Note: The final calibrated A_α values are in accordance with the most likely
 705 reaction model (D_1), where $f(\alpha) = \frac{1}{2}\alpha^{-1}$ and $f'(\alpha) = -\frac{1}{2}\alpha^{-2}$.

3.4.3 Determination of $f(\alpha)$ and $g(\alpha)$

Five groups of reaction models, namely the power law (P_n), the N -th order (N_n), the phase-boundary controlled (R_n), the Avrami-Erofeev (A_n) and the dimensional diffusion (D_n), have been widely employed to characterize the kinetics of thermorelated decomposition processes (Koga et al., 2023; Qu et al., 2019; Vyazovkin et al., 2011). Detailed descriptions of these models can be found in Vyazovkin's surveys (Sun et al., 2020; Vyazovkin et al., 2011). Correspondingly, twenty-one subdivided reaction models are summarized in Table 2, in both differential forms, $f(\alpha)$, and integral form, $g(\alpha)$, with their profiles illustrated in Fig. S-7/A and B, respectively.

The profiles of $g(\alpha)$ (in Fig. S-7/B) are more straightforward than those of $f(\alpha)$ (in Fig. S-7/A), providing a more convenient way to differentiate the reaction models of the three deconvolved reactions. Furthermore, based on the $g(\alpha)$ profiles (Fig. S-7/B), the twenty-one subdivided reaction models can be further categorized into three major types (Koga et al., 2023; Vyazovkin et al., 2014):

(i), the accelerating type, which includes thirteen subdivided reaction models, i.e., D_n ($n = 1, 2, 3$ and 4), R_n ($n = 1, 2$, and 3), N_n ($n = 1, 2$, and 3), $P_{2/3}$, and A_1 and $A_{0.5}$;

(ii), the deaccelerating type, which contains three subdivided reaction models of P_n ($n = 2, 3$, and 4);

and (iii), the sigmoidal type, which includes five subdivided reaction models of A_n ($n = 1.5, 2, 2.5, 3$, and 4).

726 Table 2. Five groups of representative reaction models utilized in the thermokinetic models (Koga et al., 2013; Koga et al., 2023; Qi et al.,
727 2021a; Vyazovkin et al., 2011; Vyazovkin et al., 2020; Vyazovkin et al., 2014)

Reaction model	Code	$f(\alpha)$	$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$
Power Law	P_n		
	$(n = \frac{2}{3}, 2, 3 \text{ or } 4)$	$n\alpha^{\frac{n-1}{n}}$	$\alpha^{\frac{1}{n}}$
N -th Order ^a	N_n	$(1-\alpha)$	$-\ln(1-\alpha)$
	$(n = 1, 2, \text{ or } 3)$	$(1-\alpha)^2$	$(1-\alpha)^{-1}$
		$(1-\alpha)^3$	$2(1-\alpha)^{-2}$
Phase-Boundary Controlled	R_n		
	$(n = 1, 2, \text{ or } 3)$	$n(1-\alpha)^{\frac{n-1}{n}}$	$1 - (1-\alpha)^{\frac{1}{n}}$
Avrami-Erofeev ^b	A_n		
	$(n = 0.5, 1, 1.5, 2, 2.5, 3 \text{ or } 4)$	$n(1-\alpha)[- \ln(1-\alpha)]^{\frac{n-1}{n}}$	$[- \ln(1-\alpha)]^{\frac{1}{n}}$
Dimensional Diffusion	D_n	D_1	α^2
		D_2	$(1-\alpha) \ln(1-\alpha) + \alpha$
		D_3	$\left[1 - (1-\alpha)^{\frac{1}{3}}\right]^2$
		D_4	$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}}$

728 Note: a, the reaction order, $n > 3$ is seldom in N -th order reaction; b, A_1 model possesses identical mathematical expressions as N_1 model.

By replacing the final calibrated A_α and E_α with their average values, $\overline{A_\alpha}$ and $\overline{E_\alpha}$ listed in Table 2, $g(\alpha)$ values for Reactions 2 under specific β_i can be directly calculated using Eq. 6. As an example, setting $\beta_i = 10$ K/min, the $g(\alpha)$ profiles of Reactions 2 are illustrated in Fig. 8. As a contrast, the $g(\alpha)$ profiles of Reactions 2 plotted under higher heating rate, $\beta_i = 18$ K/min, are illustrated in Fig. S-8.

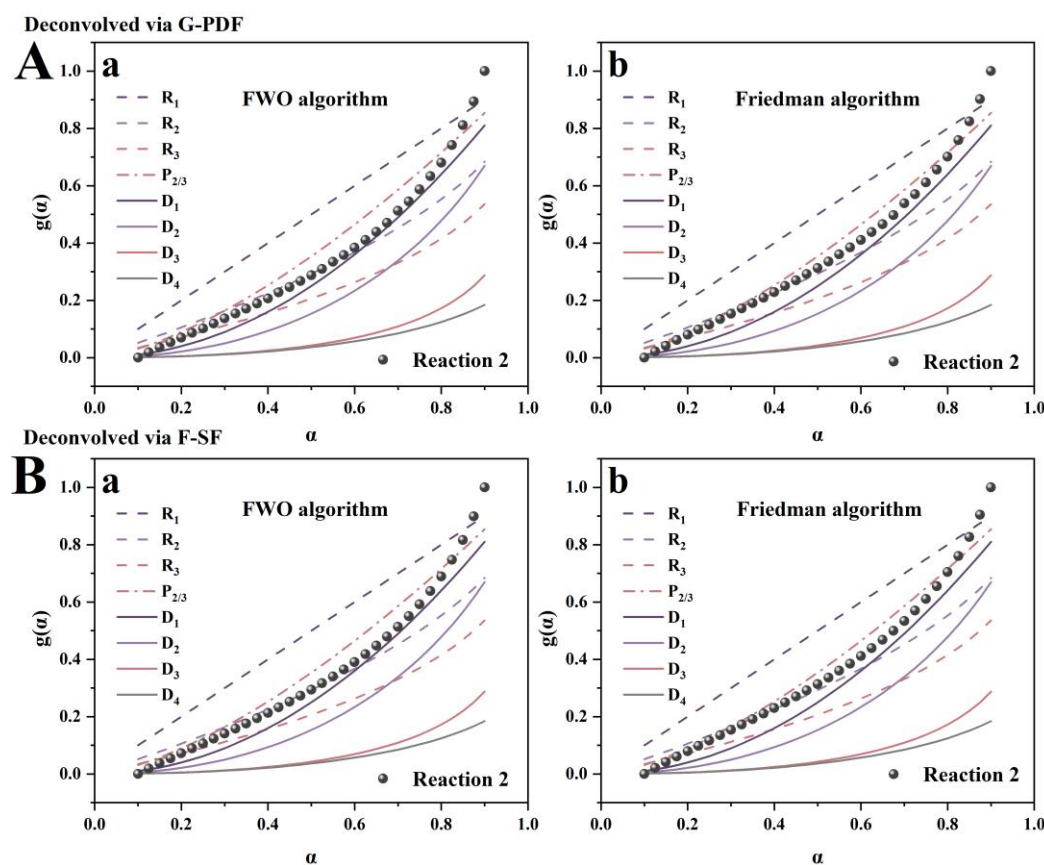


Fig. 8. the $g(\alpha)$ profiles of Reactions 2 deconvolved through G-PDF (A) and F-SF (B) and plotted with $\overline{E_\alpha}$ calculated under FWO algorithm (a) and Friedman algorithm (b), respectively. $\overline{A_\alpha}$ and $\overline{E_\alpha}$ values are listed in Table 1.

Despite of the heating rate β_i is set at lower or higher value (Fig. 8 or Fig. S-8), identical profiles of $g(\alpha)$ curves are displayed, which indicated that the reaction model of Reaction 2 is independent with heating rate. Meanwhile, Reaction 2 display

741 an accelerating profile, and $g(\alpha)$ curves are located in Phase diagram 2 (colored blue
 742 in Fig. S-7/B). This location suggests that D_n ($n = 1, 2, 3$ and 4), R_n ($n = 1, 2$, and 3)
 743 and $P_{2/3}$ are the potential options for the most likely reaction model (Zhang et al., 2021a).
 744 Mathematically, researchers have recommended that the correlate coefficient (R_c^2 ,
 745 depicted in Eq. 9) (Qu et al., 2019) and the root-mean-square error (RMSE, depicted in
 746 Eq. 10) (Muravyev et al., 2021) are beneficial in determining the most likely reaction
 747 models. Based on the $g(\alpha)$ profiles of Reactions 2 conducted under $\beta_i = 10$ K/min,
 748 the values of R_c^2 and RMSE of the potential options for the most likely reaction model
 749 are listed in Table 3.

$$750 \quad R_c^2 = 1 - \frac{\sum_{\alpha=0.1}^{\alpha=0.9} [g(\alpha)_{dec} - g(\alpha)_{rep}]^2}{\sum_{\alpha=0.1}^{\alpha=0.9} [g(\alpha)_{dec} - \overline{g(\alpha)_{rep}}]^2} \quad (9)$$

$$751 \quad RMSE = \sqrt{\frac{1}{N} \sum_{\alpha=0.1}^{\alpha=0.9} [g(\alpha)_{dec} - g(\alpha)_{rep}]^2} \quad (10)$$

752 Where, $g(\alpha)_{dec}$ was the value calculated via Eq. 6 under $\beta_i = 10$ K/min,
 753 $g(\alpha)_{rep}$ and $\overline{g(\alpha)_{rep}}$ was the value (or mean value) of representative reaction model
 754 i.e., D_n ($n = 1, 2, 3$, and 4), R_n ($n = 1, 2$, and 3) as well as $P_{2/3}$ located in Phase
 755 diagram 2 (colored in blue) of Fig. S-7/B; as $\alpha \in (0.1, 0.9)$ and the stepping constant
 756 of α , i.e., $\Delta\alpha = 0.025$, the value of N was 31.

757

Table 3. R_c^2 and RMSE calculated for the reaction models (D_n , R_n and $P_{2/3}$) of Reaction 2 under $\beta_i = 10$ K/min

$\beta_i = 10$ K/min			D_n				R_n			$P_{2/3}$
			D_1	D_2	D_3	D_4	R_1	R_2	R_3	
G-PDF	FWO	R^2	0.9512	0.5802	< 0.1	< 0.1	0.6486	0.7410	0.1337	0.9453
		RMSE	0.0545	0.1521	0.3334	0.3622	0.1674	0.0936	0.1710	0.0590
	Friedman	R^2	0.9485	0.5243	< 0.1	< 0.1	0.7052	0.7133	0.1135	0.9251
		RMSE	0.0604	0.1693	0.3495	0.3779	0.1482	0.1006	0.1844	0.0686
F-SF	FWO	R^2	0.9517	0.5650	< 0.1	< 0.1	0.6622	0.7332	0.1259	0.9452
		RMSE	0.0552	0.1565	0.3376	0.3663	0.1627	0.0954	0.1745	0.0580
	Friedman	R^2	0.9435	0.5220	< 0.1	< 0.1	0.7062	0.7105	0.1108	0.9239
		RMSE	0.0613	0.1700	0.3502	0.3785	0.1478	0.1012	0.7850	0.0691

758

Note: in this study, one iteration computation was conducted before the most likely reaction model was finally optimized to D_1 .

A relatively higher R_c^2 and a lower RMSE value indicated the most likely reaction model (Muravyev et al., 2021; Vyazovkin et al., 2020). As shown in Table 3, due to the highest R_c^2 and lowest RMSE value of D_1 , one-dimensional diffusion was the most likely reaction model of Reaction 2. The D_1 reaction model indicated that the volatile matter (Koga et al., 2013) (such as H_2O and CO_2) generated from the decomposition of Co/Fe-LDHs was directionally diffused from the higher concentrated region to the lower place. In addition, the $f'(\alpha)$ of the reaction model D_1 was $-1/2\alpha^{-2}$, which was utilized in calibrating the A_α values via the iterative computation process (S-5).

For a better understanding, the schematic diagrams of D_1 , D_2 , and D_3 are compared in Fig. S-9. Assuming the solid-state reactant (i.e., Co/Fe-LDHs) was reduced to a solid brick settled in a certain 3-D orthogonal space (x, y, z) (Iwasaki et al., 2020; Koga et al., 2013; Koga et al., 2023), the reaction advancement was perpendicularly conducted to the reaction interface of the solid products and reactant. When the reaction model followed D_1 , the solid products accumulated in the z-axis as the solid-state reactant was eliminated. Meanwhile, volatile matter diffused from the interface to the surroundings. This indicates that the direction of solid-state product accumulation was opposite to the diffusion direction of the volatile matter. Furthermore, on the cross-sections of z-x and z-y, one may observe that one pair of reaction interfaces of D_1 was parallel to the (x, y) plane, which indicated that the direction of the reaction was carried out along the z-axis and that the decomposition of Co/Fe-LDHs was carried

out layer by layer. Specifically, in Reaction 2, the water derived from the dehydroxylation of -OH groups of the PCLs escaped from the solid-state substances, which led to the generation of Co_3O_4 and Fe_3O_4 .

Moreover, the number of reaction interfaces in Fig. S-9 can be utilized to distinguish D_1 from D_2 and D_3 . In the schematic diagram of the D_2 reaction model, two pairs of reaction interfaces were exhibited in the (x, y) plane and the (z, y) plane. On the z-x and z-y cross-sections, one may observe that the reaction was not only carried out in the z-axis but also conducted in the x-axis, which indicated that two directions of reaction were processed in D_2 reaction model. Analogously, three pairs of interfaces were parallel to the (x, y), (x, z) and (y, z) planes in D_3 , suggesting that the solid products would accumulate in the z-, y- and x-axes.

3.4.4 Thermokinetic models of Reaction 2

Under $\beta_i = 10 \text{ K/min}$, substituting $\overline{A}_\alpha$, $\overline{E}_\alpha$, and $f(\alpha) = 1/2\alpha^{-1}$ into Eq. 5, the differential and integral formulas of thermokinetic models for Reaction 2, deconvolved from G-PDF with $\overline{E}_\alpha$ calculated via FWO algorithm or Friedman algorithm (denoted as G-PDF/FWO or G-PDF/ Friedman), are depicted in Eq. 11 and Eq. 12, respectively. And the thermokinetic models for Reaction 2, deconvolved from F-SF (denoted as F-SF/FWO or F-SF/ Friedman), are displayed in Eq. 13 and Eq. 14. Additionally, the reaction temperature interval of Reactions 2, $T \in [383 \text{ K}, 550 \text{ K}]$, is collected from the TG_{dec} curves in Fig. 5-C.

$$\begin{aligned}
& \frac{d\alpha}{dT} = \frac{\exp\left(14.97 - \frac{64,772}{RT_\alpha}\right)}{2\alpha\beta_i} \\
& \alpha = \sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(14.97 - \frac{64,772}{RT_\alpha}\right) dT}
\end{aligned}
\tag{11}$$

$$\begin{aligned}
& \frac{d\alpha}{dT} = \frac{\exp\left(15.86 - \frac{59,146}{RT_\alpha}\right)}{2\alpha\beta_i} \\
& \alpha = \sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(15.86 - \frac{59,146}{RT_\alpha}\right) dT}
\end{aligned}
\tag{12}$$

$$\begin{aligned}
& \frac{d\alpha}{dT} = \frac{\exp\left(15.03 - \frac{67,049}{RT_\alpha}\right)}{2\alpha\beta_i} \\
& \alpha = \sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(15.03 - \frac{67,049}{RT_\alpha}\right) dT}
\end{aligned}
\tag{13}$$

$$\begin{aligned}
& \frac{d\alpha}{dT} = \frac{\exp\left(14.94 - \frac{60,714}{RT_\alpha}\right)}{2\alpha\beta_i} \\
& \alpha = \sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(14.94 - \frac{60,714}{RT_\alpha}\right) dT}
\end{aligned}
\tag{14}$$

Where, $\beta_i = 10$ K/min, and $T \in [383 \text{ K}, 550 \text{ K}]$.

For the Co/Fe-LDHs, which were thermally reconstituted under $\beta_i = 10$ K/min (Fig. 5-B), the area covered by the DTG_{dec-1}, DTG_{dec-2}, and DTG_{dec-3} was contribution to the area covered by the DTG_{con} curve. Based on the integral formulas of thermokinetic models for Reaction 2, the instantaneous contribution of Reaction 2 to the major Co/Fe-LDHs thermoreconstitution process could be obtained (denoted as

810 W_{IC-R2}). As an example, the instantaneous contribution of Reaction 2 deconvolved
811 from G-PDF with $\overline{E_\alpha}$ calculated via FWO algorithm to the major weight loss of Co/Fe-
812 LDHs thermoreconstitution process conducted under $\beta_i = 10$ K/min is depicted in Eq.
813 15. It should be emphasized that the major weight loss of Co/Fe-LDHs
814 thermoreconstitution process conducted under $\beta_i = 10$ K/min is 0.889, which has been
815 obtained in Fig. 5-B/b.

$$816 \quad W_{IC-R2} = \frac{\sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(14.97 - \frac{64,772}{RT_\alpha}\right) dT}}{0.889} \times 100\% \quad (15)$$

817 *where, $\beta_i = 10$ K/min; and $T \in [321 \text{ K}, 663 \text{ K}]$*

817 3.5 Correlation analysis

818 Thermokinetic models, established on TG/DTG data and Eq. 1, primarily
819 concentrated on the variations in volatile matter (Zhang et al., 2014). These behaviors,
820 such as the generation (Koga et al., 2023) from Co/Fe-LDH decomposition and the
821 escape from the solid-state residual, are reflected in the reaction model of the
822 thermokinetic models. In contrast, the physicochemical variations in mineralogy (Fig.
823 2-A), chemistry (Fig. 2-B and C, Fig. 3), and morphology (Fig. 4) mainly focus on the
824 temporary or final solid-state residuals (Song et al., 2019). In combination with
825 deconvolution analysis and various examinations throughout the thermoreconstitution
826 of Co/Fe-LDHs, a complementary correlation among the thermokinetic analyses, the
827 most likely reaction model of Reaction 2, and physicochemical variations was proposed.
828 This correlation helps elucidate the thermoreconstitution process of Co/Fe-LDHs

conducted at $\beta_i = 10$ K/min. The scheme diagram is illustrated in Fig. 9.

First, as Co/Fe-LDHs were heated from the ambient temperature to 368 K (i.e., Co/Fe@368K), two types of dehydration processes were involved in Reaction 1. Specifically, the volatile matter was diffused in the form of water vapor, as denoted in Fig. 9. Meanwhile, the solid-state residuals were the Co/Fe-LDHs in the form of $\text{Co}_{5.84}\text{Fe}_{2.16}(\text{OH})_{16}(\text{CO}_3)_{1.08} \cdot 0.32\text{H}_2\text{O}$, detected by XRD in Fig. 2-A. These residuals displayed a typical layered morphology of Co/Fe@368K in SEM and HRTEM images, as shown in Fig. 4-A. The byproducts were mainly CoCO_3 , amorphous FeOOH , and tetragonal wurtzite (β - FeOOH), as certified by XPS spectra in Fig. 3-C and D.

Furthermore, as the heating temperature elevated to 578 K and 773 K (i.e., Co/Fe@578K and Co/Fe@773K), Reaction 2 and Reaction 3 both emerged, and the one-dimensional diffusion reaction model (D_1) were conducted in Reaction 2. However, distinct kinds of volatile matter were generated, as evident in the FTIR (Fig. 2-B) and revealed in the XPS spectra (Fig. 3). Specifically, the dehydroxylation of -OH groups on the PCLs, evident in the XRD patterns of Co/Fe@578K and Co/Fe@773K in Fig. 2-A, was responsible for Reaction 2. On the other hand, the elimination of two types of gaseous phases led to Reaction 3 with a multistep character. One of the gaseous phases was CO_2 escaped from NCLs (Fig. 2-B) and CoCO_3 (Fig. 4-C), and the other was vapor generated from amorphous FeOOH and tetragonal wurtzite (β - FeOOH). Reactions 2 and 3 played a key role in Co/Fe-LDH thermoreconstitution. The two reactions not only led to the decomposition of Co/Fe-LDHs as cubic- Co_3O_4 and Fe_3O_4 (Co/Fe@578K and

850 Co/Fe@773K in Fig. 2-A), but also triggered the collapse of the layered structure (Fig.
851 4-B and C).

852 Last, when the heating temperature increased to 773 K or more (Co/Fe@1053K),
853 the volatile matter was mainly CO₂ generated from deep decarbonization (as evidenced
854 by the FTIR spectra of Co/Fe@1053K in Fig. 2-B). In combination with Fig. 9 and Fig.
855 4-D, the solid-state residual of Co/Fe@1053K was in the form of cubic-Co₃O₄ and
856 Fe₃O₄, which had aggregated and partially melted (Fig. 4-D/a). However, due to the
857 absence of deconvolved curves in DTG_{con} (Fig. 5-B), this variation cannot be related to
858 a specific thermokinetic model. It could be inferred that if the thermoreconstitution
859 process was maintained at a higher temperature, the thermokinetic model established
860 on the energy-based data (for instance, the DSC data) might be a potential way to make
861 a deeper correlation with the physicochemical variations. This inference will be studied
862 in future reports.

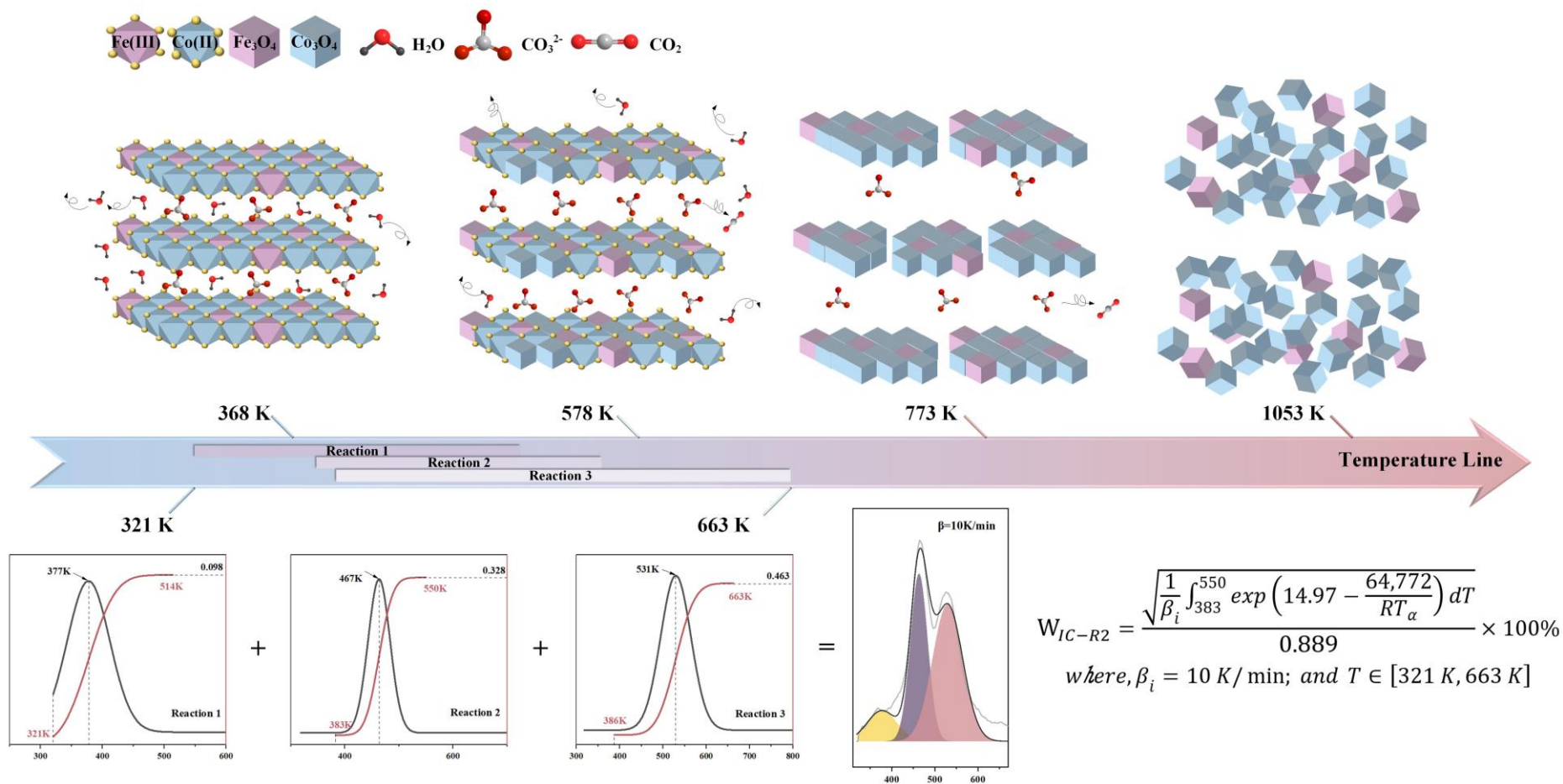


Fig. 9. The schematic diagram of the Co/Fe-LDHs thermoreconstitution process.

4. Conclusions

The thermoreconstitution of Co/Fe-LDHs involves a complex decomposition process accompanied by substantial physicochemical variations. This process was characterized by three distinct stages with ~27.8 % of weight loss and remarkable endothermic phenomenon, which were successfully separated into three reactions through G-PDF and F-SF. After the securitization on the most likely "kinetic triples", the thermokinetic model of the Reaction 2 was established on the one-dimensional diffusion model (D_1). The volatile substances, such as H_2O and CO_2 , were diffused directionally from the reconstitution interface of Co/Fe-LDHs, which triggered a progressive collapse of the layered structure. Correspondingly, the solid-state substances with the final products of cubic- Co_3O_4 and Fe_3O_4 , were fractured and partially melted in the SEM images, meanwhile, the XRD peak broadening phenomena were observed and were validated by measuring the d -spacing values in HRTEM images, which were primarily attributed to the lattice expansion and heterogeneous microstrain effects.

To interpret the thermoreconstitution process of Co/Fe-LDHs, the thermokinetic models, which were applied in depicting the behaviors of the volatile substances, and the physicochemical examinations, which were utilized in revealing the variations of the solid-state substances, were comprehensively combined with a complementary correlation.

Acknowledgment

This study is supported by the China Scholarship Council (No.202000810011), the Key Research and Development Program (Major technical innovation projects) of Shandong Province (No. 2020CXGC011204), the Guangdong Basic and Applied Basic Research Foundation (No. 2019B1515120052) and Guangdong Foundation for Program of Science and Technology Research (No. 2020B1212060053). Furthermore, all authors appreciate the kind help from Dr. Yang Bo of Kyoto University and the equipment support from Zhang Yunfei, the CEO of JM Filtec. Co.Ltd.

Supplementary materials

Documents of S-1 (including Eq. S-1 to Eq. S-7), S-2, S-3 (including Eq. S-8 to Eq. S-16), S-4 (including Eq. S-17), S-5; Table S-1, and Fig. S-1 to Fig. S-9 were proposed in supplementary materials.

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1 A Deconvolution Analysis Strategy on the Thermoreconstitution Process
2 of Co/Fe Layered Double Hydroxides: Complementary Correlations
3 between Physicochemical Variations and Thermokinetic Analyses

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13 **Abstract**

14 A variety of physicochemical analyses were systematically conducted on the
15 complex thermoreconstitution process of Co/Fe layered double hydroxides, and
16 deconvolution analysis strategy was utilized in elucidating the reconstitution process.
17 The thermal analysis of Co/Fe layered double hydroxides indicated that approximately
18 27.8 % weight loss, three weight loss peaks and two pronounced endothermic

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phenomena were detected via thermogravimetry, differential thermogravimetry, and differential scanning calorimetry, respectively. In the thermoreconstitution process of Co/Fe layered double hydroxides, scanning electron microscopy images indicated that the layered structure gradually collapsed, fractured into pieces, and partially melted. Meanwhile, significant X-ray diffraction peak broadening phenomena were detected and further confirmed by the *d*-spacing values in high-resolution transmission electron microscope images, which were mainly caused by the lattice expansion effect and the heterogeneous microstrain effect. Three reactions were deconvolved from the differential thermogravimetry curves, and the thermokinetic models of Reaction 2 indicated that volatile components in the form of H₂O and CO₂ escaped from the solid-state residuals via a one-dimensional diffusion reaction model. The major products in solid-state residuals were cubic Cobalt(III) oxide and Iron(II, III) oxide. The thermokinetic models played a complementary role in elucidating the physicochemical variations that occurred throughout the thermoreconstitution process of Co/Fe layered double hydroxides.

Keywords: Co/Fe layered double hydroxides; Thermoreconstitution process; Deconvolution analysis strategy; Thermokinetic modeling; Correlation analysis

38 Terminologies

Abbreviations			
A_n	The Avrami-Erofeev reaction model	NCLs	Negatively charged layers
D_n	The Dimensional Diffusion reaction model	N_n	The N -th Order reaction model
DSC	Differential scanning calorimetry	PCLs	Positively charged layers
DTG	Differential thermogravimetry	P_n	Power Law reaction model
FWHM	Full Width at Half Maximum	R_c^2	Correlate coefficient
G-PDF	Gaussian probability distribution function	RMSE	The root-mean-square error
F-SF	Frazer-Suzuki function	R_n	The Phase-Boundary Controlled reaction model
ICTAC	International Confederation for Thermal Analysis and Calorimetry	TG	Thermogravimetry
JCPDS	Joint Committee Powder Diffraction Standards		
Symbols			
A	pre-exponential factor (s^{-1})	β	heating rate (K min^{-1})
E	activation energy (kJ mol^{-1})	ε_d	the elastic microstrain value (%)
R	gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$)	ε_v	the volume variation degree (%)

T	heating temperature (K)	θ	Bragg angle (rad)
W	weight of the residual (mg)	u	the independent variable of $P(u)$, $u = \frac{E_{\alpha}}{RT_{\alpha}}$
Subscripts			
α	conversion degree or rate	nor	normalized data
c	calculated value	ori	original data
con	conversed data	rep	the most representative reaction model
dec	deconvolved data	s	standard value
i	the i-th heating rate	t	reaction time
Functions			
$f(\alpha)$	the reaction model	$P(u)$	temperature integral function
$g(\alpha)$	the integral form of reaction model	W-H	Williamson-Hall equation

1 Introduction

Layered double hydroxides (LDHs) represent a broad and versatile class of anionic clays. Characterized by their unique sandwich-like 3D structures, LDHs exhibit the general formula of $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}]^{n-} \cdot mH_2O$ (Takehira, 2017), where M^{2+} (or M^{3+}) denotes divalent (or trivalent) metallic cations such as Mg^{2+} , Ca^{2+} , Fe^{2+} , Co^{2+} , and Ni^{2+} (or Al^{3+} , Fe^{3+} , Co^{3+} and La^{3+}); A^{n-} are inorganic or organic (Wang et al., 2014) including OH^- , CO_3^{2-} , CH_3COO^- , glycine or even polyoxometalates (POMs) (Nikulshina et al., 2019), hetero polyacid (HPA) (Winoto et al., 2019) electronegative macromolecules. Under aqueous surroundings, LDHs are spontaneously generated from the cationic/anionic precursor by way of co-precipitation, which can be flexibly modulated by the participated ionic donors and modifications. Advantageous of this moderate method has been systematically reported in Wang and O'Hare's survey (Wang and O'Hare, 2012). LDHs are constructed by two types of anisotropic layers, which are the positively charged layers (PCLs) and negatively charged layers (NCLs). The divalent/trivalent metallic couples (M^{2+}/M^{3+}) are located in the edge-sharing octahedral cells of the PCLs; meanwhile, the NCLs are intercalated in the adjacent PCLs to maintain the electrical neutrality of the LDHs via electrostatic and van der Waals forces (Varoon et al., 2011). To date, a variety of LDHs have been prepared with distinct M^{2+}/M^{3+} couples, anions and synthetic strategies, which possess outstanding features such as self-recovery (colloquially described as the "memory effect") (Wang

et al., 2021), ion-exchangeability (Zhai et al., 2021), and selective absorption (Xie et al., 2023). Furthermore, as the transition element of Co or Fe (or both) is utilized as an M^{2+}/M^{3+} couple, extra magnetic properties are endowed to the derived LDHs, which are flexible for decoration or modification treatment. Specifically, Co/Fe-LDHs prepared with Co (II)/Fe (III) couples are intensively utilized in a variety of domains: as a matrix for the fabrication of energy-storage-oriented 2D films, hollow nanospheres and core-shell structured materials; as carriers or substrates for targeting drug delivery (Taviot-Guého et al., 2018); and mostly, as precursors in manufacturing specific high-performance catalysts for fine chemical engineering (Varoon et al., 2011) and environmental remedies (Nouaa et al., 2023).

Thermal treatment is effective in reconstructing Co/Fe-LDHs as di-metallic oxides via a complex thermoreconstitution process (Li et al., 2018). Under specific thermal conditions such as heating temperatures, rates, duration, and atmosphere, the reconstitution of Co/Fe-LDHs is thermally induced and accompanied by significant physicochemical changes in mineralogy (Wu et al., 2020), chemistry (Wang et al., 2021), and morphology (Vyazovkin et al., 2014). In most cases, those variations of the reconstituted Co/Fe-LDHs are intensively surveyed in elucidating the mechanisms underlying the catalytic (Peng et al., 2021), electrical (Feng et al., 2016), and magnetic (Takehira, 2017) performances. For instance, catalysts derived from thermally reconstituted Co/Fe-LDHs are utilized to activate oxidants such as ozone (O_3), persulfate (PS), and hydrogen peroxide (H_2O_2) for the degradation of contaminants

(Huang et al., 2021; Nosaka and Nosaka, 2017). Analogous studies can be found elsewhere (Guo et al., 2020; Sun et al., 2019; Xie et al., 2023). However, little attention has been given to the specific reactions responsible for the observed physicochemical changes in Co/Fe-LDHs, and the complex thermoreconstitution progress is seldom elucidated.

The International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee recommended (Vyazovkin et al., 2014) that thermal kinetic analysis is a reliable way of scrutinizing the thermal reaction progress (Koga et al., 2023; Vyazovkin et al., 2020) (i.e., single-step, multistep, or hybrid) of solid-state substances. Relying on the thermal mass- or energy-based data (Vyazovkin et al., 2011) obtained via thermogravimetry (TG), differential thermogravimetry (DTG), or differential scanning calorimetry (DSC) techniques, the thermokinetic model (Vyazovkin et al., 2020) established on the thermokinetic parameters is promising in depicting the specific reaction mechanism via precise mathematical functions (Koga et al., 2023). For an ideal single-step reaction process (Iwasaki et al., 2020; Vyazovkin et al., 2014), the parent function of the thermokinetic model is depicted in Eq. 1. Specifically, *Func. 1* and *Func. 2* of Eq. 1 are the differential and integral expression of the thermokinetic model for a single-step reaction, which are both established on the “kinetic triples” (Siddiqi et al., 2021), i.e., the activation energy (E), the preexponential factor (A), and the reaction model ($f(\alpha)$ or $g(\alpha)$). Employing a range of differential and integral calculation algorithms (Koga et al., 2023; Qi et al., 2021a), precise thermokinetic models can be

established. These models serve as powerful tools, enabling researchers to delve into the underlying reaction mechanisms and elucidate the physico-geometrical (Iwasaki et al., 2020), mineralogical, morphological (Qu et al., 2019), and chemical (Song et al., 2019) variations.

$$\begin{aligned}
 \text{Func. 1} \quad \frac{d\alpha}{dt} &= \beta_i \frac{d\alpha}{dT} = A_\alpha \exp\left(-\frac{E_\alpha}{RT_\alpha}\right) f(\alpha); \quad \beta_i = \frac{dT}{dt} \\
 \text{where, } \alpha &= \frac{W_i - W_t}{W_i - W_e} \times 100 \% \text{ or } \frac{1 - W_t/W_i}{1 - W_e/W_i} \times 100 \%; \quad \alpha \in [0, 1] \\
 \text{Func. 2} \quad g(\alpha) &= \int_0^1 \frac{d\alpha}{f(\alpha)} = \int_{T_0}^{T_e} \frac{A_\alpha}{\beta_i} \exp\left(-\frac{E_\alpha}{RT_\alpha}\right) dT \\
 &= \frac{A_\alpha E_\alpha}{R\beta_i} p(u); \quad u = \frac{E_\alpha}{RT_\alpha} \\
 \text{where, } P(u) &= \int_\infty^u -\frac{e^{-u}}{u^2} du = \frac{e^{-u}}{u^2} \sum_{N=1}^{\infty} (-1)^{N-1} \frac{N!}{u^{N-1}}; \quad N \geq 1
 \end{aligned} \tag{1}$$

Where, α is the relative conversion ratio of the reactant in a specific reaction process, which could be calculated by the initial, instantaneous, and final weight of the residual (W_i , W_t , and W_e) in TG data, or could be obtained by the relative weight ratio (W_t/W_i) in the normalized TG data (within [0,1]); t is the reaction time; β_i is the i -th heating rate; R is the gas constant, 8.314 J/(mol·K); A_α , E_α and T_α denote the activation energy, the pre-exponential factor, and heating temperature at a certain α ; the $g(\alpha)$ is the integral form of reaction model- $f(\alpha)$; $P(u)$ is the temperature integral function, and the N value is the finite series level of $P(u)$.

Various thermal kinetic methodologies (Siddiqi et al., 2021; Zhang et al., 2014) have been developed to scrutinize complex reaction processes occurring under high-temperature conditions. These methods include the combustion, pyrolysis, gasification,

1 118 and decomposition (Song et al., 2019) processes of a variety of substances such as
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4 119 biomass (Ali et al., 2017), solid waste sludge, coal, oily sludge, plastics (Zhang et al.,
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6 120 2021b) and polymetallic oxide. Furthermore, in comparison with the convolutional
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9 121 methodologies (Qi et al., 2021a) (for instance, the distributed activation energy
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12 122 methodology, DAEM), the deconvolutional methodologies (Zhang et al., 2021a) are
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15 123 effective in separating the complex reaction progresses, which are more reliable in
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18 124 establishing the thermokinetic models in revealing the most likely reaction mechanisms
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21 125 (Koga et al., 2023) of the physicochemical variations. For complex reaction that
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24 126 deconvolved into finite sub-reactions, the ICTAC Kinetics Committee (Vyazovkin et
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27 127 al., 2020) singles out two specific thermokinetic models that derived from those
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30 128 statistical solution sets of "kinetic triples": the thermokinetic model with the highest
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33 129 mathematical accuracy is called as mathematical deconvolution analysis, which is
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36 130 beneficial in depicting the thermal curves; and the thermokinetic model established on
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39 131 the most likely "kinetic triples" in elucidating the reaction mechanism is defined as
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42 132 kinetic deconvolution analysis. To date, a variety of distribution function have been
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45 133 utilized for the deconvolution of complex reaction progresses, and the Gaussian
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48 134 probability distribution function (G-PDF) and Frazer-Suzuki function (F-SF) is wildly
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51 135 applied in the domain of thermal kinetic analysis. Specifically, G-PDF is a type of
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54 136 symmetric function with fewer independent variables and lower degree of freedom,
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57 137 which is more convenient for the deconvolution treatment of the complex reaction
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60 138 progress. On the contrary, F-SF is recommended as a more accurate asymmetric
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1 139 function in deconvolving the complex reaction progresses than that of G-PDF
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4 140 (Vyazovkin et al., 2020). However, on the deconvolution treatment on the
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7 141 thermoreconstitution of Co/Fe-LDHs via G-PDF and F-SF is rarely reported.
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10 142 Meanwhile, the correlations between the physicochemical variations of Co/Fe-LDHs'
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12 143 thermoreconstitution process and thermo-reaction analyses in elucidating the
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15 144 thermoreconstitution mechanisms have not yet been established.

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18 145 The heat surroundings trigger dramatic physicochemical variations in Co/Fe-
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21 146 LDHs via complex thermoreactions. The current reports on the thermoreconstitution
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24 147 process of Co/Fe-LDHs indicate an urgent need to correlate the physicochemical
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27 148 variations with reliable thermokinetic analyses. Furthermore, the precise models of the
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30 149 complex reconstitution reaction established via an accurate thermal kinetic analysis are
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33 150 a necessary step toward a deeper understanding of the various mechanisms of Co/Fe-
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36 151 LDHs thermoreconstitution. In this study, a systematic solution to unite
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39 152 physicochemical variations with thermokinetic analyses as a whole was proposed.
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42 153 Initially, a systematic analysis of the thermoreconstitution process of Co/Fe-LDHs was
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45 154 conducted across a wide range of thermal treatment temperatures under different
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48 155 heating rates. Then, deconvolution analysis strategy was proposed to distill the complex
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51 156 reconstitution process of Co/Fe-LDHs into a finite number of reactions, and the most
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54 157 likely kinetic models of the deconvolved reactions were optimized to elucidate the
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57 158 physicochemical variations. Eventually, a complementary correlation between the
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60 159 thermokinetic analyses and physicochemical variations was established.

2 Materials and Methods

The probe Co/Fe-LDHs utilized in this study were fabricated using a modified coprecipitation method. The thermo-analysis and the physicochemical characterization were conducted on the pristine Co/Fe-LDHs. The data processing was conducted in the authorized software without any data smoothing treatment.

2.1 Materials

The probe Co/Fe-LDHs was fabricated in lab-scale. The chemical reagents and synthesis procedure were detailed as follows:

2.1.1 Chemical Reagents

The chemicals used in this study include Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), Sodium hydroxide (NaOH), Sodium carbonate (Na_2CO_3), and Dilute hydrochloric acid (HCl , 1 mol/L). These reagents are all ACS reagent grade and require no additional purification. Synthetic air, composed of 99.99 % purity oxygen and 99.99 % purity nitrogen with a volume ratio of 21.5:78.5, was procured from Qingdao Specific Laboratory Gas Co., Ltd. for TG/DSC analysis. The Milli-Q ultrapure water (18.2 MU cm) was utilized for all experiments.

2.1.2 Synthesis of Co/Fe-LDHs

Co/Fe-LDHs were fabricated using a modified coprecipitation method (Sun et al., 2020). These layers are negatively charged due to the presence of carbonate and

hydroxyl ions (Song and Hu, 2014; Wang et al., 2014). The synthetic flowchart was depicted in Fig. S-1, and the procedure was detailed as follows: **(i)** Preparation of the acid metallic salt solution: 30 mmol of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (i.e., Co:Fe = 3:1) were codissolved in 100 ml of dilute hydrochloric acid solution (0.01 mol/L) in avoiding the hydrolysis of transition metallic salt (Nikulshina et al., 2019; Zhai et al., 2021); **(ii)** Coprecipitation: the acid metallic salt solution was dropwise added into 1 L of a basic solution (1 mol/L of NaOH and 0.1 mol/L of Na_2CO_3) which was vigorously stirred at 70 ± 2 °C, meanwhile, the pH of the basic solution was regulated at 12.3 ± 0.2 with 1 mol/L of NaOH solution throughout the reaction (Xie et al., 2023); **(iii)** Aging: After 100 ml of acid metallic salt solution was consumed, the basic solution was aged in a water bath under 80 °C for 24 h without stirring; **(iv)** Refinement: the light-pink sediments were centrifuged out and re-suspended in 1 L of Na_2CO_3 solution (1.5 mol/L, 80 °C) for another 24 h to substitute the Cl^- with CO_3^{2-} inside the negatively charged layers (Song and Hu, 2014); **(v)** Postprocessing of product: the refined sediments were washed three times, dried in a freeze dryer under -18 °C for 4 h, pulverized in a planet-type grinding mill (PM 100, Retsch, Germany), sealed and stored in a glass vial for further use.

2.2 Thermoreconstitution process of Co/Fe-LDHs and data processing

The mass/energy variation Co/Fe-LDHs thermoreconstitution was monitored in a high-precision thermoanalyzer with 0.1 µg of mass sensitivity and 0.001 °C of energy

sensitivity. The thermodata were directly recorded without any correction, and the data processing was corrected to two decimal places.

2.2.1 Thermoreconstitution process of Co/Fe-LDHs

Approximately 20 mg of the synthesized Co/Fe-LDHs was analyzed via an SDT Q600 thermoanalyzer (TA instrument, USA). The mass and energy variations of Co/Fe-LDHs from room temperature up to 1,053.15 K were recorded using the TG/DSC technique (Koga et al., 2023). The thermoreconstitution process of Co/Fe-LDHs was conducted under different heating rates, namely, lower heating rates ($\beta_i = 8$ and 10 K/min) and higher heating rates ($\beta_i = 16$ and 18 K/min). Each experiment was performed twice, and the TG/DSC data recorded were averaged.

2.2.2 Data processing for TG/DTG data conversion and deconvolution

The directly recorded TG data were first processed within the range of 0 to 100 %, which was denoted as the original TG data (TG_{ori}). Then, the TG_{ori} data were further normalized to a range between 0 and 1, which was labeled the normalized TG data (TG_{nor}). The TG_{ori} data were then converted to TG_{con} data (Eq. S-1 to Eq. S-3), which represents the conversion degree versus temperature, was further derived from the TG_{ori} data.

Mathematically, the DTG data are the first derivative of TG data versus temperature or time (Vyazovkin et al., 2011; Vyazovkin et al., 2014); hence, the original, normalized, and converted DTG data, i.e., DTG_{ori}, DTG_{nor}, and DTG_{con} are

derived from the TG_{ori} , TG_{nor} , and TG_{con} data, respectively. Additionally, the data processing methods between the six types of mass-natured data (namely TG_{ori}/DTG_{ori} , TG_{nor}/DTG_{nor} , and TG_{con}/DTG_{con}) are depicted in Eq. S-1 to Eq. S-7, which are detailed in S-1 and illustrated in Fig. S-2, respectively.

Based on the Gaussian probability distribution function (G-PDF) and the Frazer-Suzuki function (F-SF), three reactions that occurred during the thermoreconstitution process of Co/Fe-LDHs were deconvolved in response to three weight loss peaks of DTG_{con} curves (Perejon et al., 2011), respectively. The deconvolved curves for each reaction were denoted as DTG_{dec-1} , DTG_{dec-2} , and DTG_{dec-3} . These curves were integrated to obtain the corresponding TG_{dec} curves for each reaction. The data processing and deconvolution procedures were conducted with Origin Pro 2021 software, and the Levenberg–Marquardt (L-M) algorithm (Iwasaki et al., 2020; Muravyev et al., 2021; Naqvi et al., 2018) was utilized to optimize the nonlinear fitting of the deconvolution process.

2.3 Physicochemical Characterizations

Four samples, labeled Co/Fe@368K, Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K, were examined to assess the physicochemical changes during the thermoreconstitution process of Co/Fe-LDHs. These examinations included mineralogical analyses by X-ray diffraction (XRD, 7000X, Shimadzu Instruments, Japan); monitoring of chemical groups through Fourier transformed infrared

spectroscopy (FTIR, Thermo Scientific Nicolet iS5, Waltham, MA, USA) and Raman microscopy (Bruker Corporation, Raman, Italy); meanwhile, the chemical valence of Co and Fe elements was examined by X-ray photoelectron spectroscopy technique (XPS, EscaLab Xi+, Thermo Fisher Scientific, MA, USA); examination of the morphology by scanning electron microscopy (SEM, MIRA-LMS, Tescan Instruments, Czech Republic) and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20, FEI, USA), and Co, Fe, and O element distributions of Co/Fe-LDHs before and after the thermoreconstitution process were compared via energy dispersive spectroscopy (EDS, BrukerS8 Tiger, Germany).

In addition, the operating conditions of the abovementioned instruments were detailed in S-2, and the calculation methods of *d*-spacing, lattice constants, the volume of the unit cell, and the value of microstrain for the major crystal phases (Rodenbough et al., 2016) detected from XRD patterns were introduced in S-3.

2.4 Procedure of the “deconvolution analysis strategy”

The “deconvolution analysis strategy” proposed for thermal kinetic analysis consists of four portions, i.e., 1) the deconvolutional separation of the DTG curve into three reactions, namely, Reaction 1, 2 and 3; 2) the scrutinization of "kinetic triples"; 3) the establishment of thermokinetic models; and 4) the construction of the corrections among the thermokinetic analyses and models to the physicochemical variations generated by the thermoreconstitution process of Co/Fe-LDHs. It should be noted that

thermokinetic models was only established for the Reaction 2.

Specifically, the "kinetic triples" are obtained as follows:

(i) The model-free iso-conversional method (Vyazovkin et al., 2011) is utilized to calculate the E values. On account of the integral and differential calculating algorithm are included in the model-free iso-conversional method for E values, in this study, the Flynn-Wall-Ozawa (FWO) algorithm (or Friedman algorithm) was adopted as the integral (or differential) calculating algorithm for E values, which was depicted in Eq. 2. In FWO algorithm, the specific E value at a certain α , i.e., E_α was the slope of a line plotted by $\ln \beta_i$ versus $\frac{1.052}{RT_{\alpha,i}}$, and the distribution of E_α versus α of each reaction was obtained (Qi et al., 2021a). The procedure of the Friedman algorithm in calculating the E values is detailed in S-4. As the E values are calculated under the FWO or Friedman algorithm, neither the specific reaction model nor the pre-exponential factor is required, which indicated E values calculated under the model-free method is relatively objective.

$$\begin{aligned} \text{FWO: } \ln \beta_i &= \ln \left[\frac{A_\alpha R}{E_\alpha g(\alpha)} \right] - 5.311 - 1.052 \frac{E_\alpha}{RT_{\alpha,i}} \\ \text{Friedman: } \ln \left[\beta_i \left(\frac{d\alpha}{dT} \right)_\alpha \right] &= \ln [A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \end{aligned} \quad (2)$$

(ii) The Kissinger peak algorithm (Eq. 3) is initially employed to calculate the proximate A_α value of Reaction 2. And then the "Compensation effect" (Eq. 4) is further utilized to refine the A_α value obtained via Eq. 3. Additionally, the mathematical reasoning process of the proximate calculation (Eq. 3) and the precise refinement (Eq. 4) of A_α values were elucidated in our previous studies (Qi et al.,

2021a; Qi et al., 2023). Because the proximate A_α value is initially calculated with the assumption of $f'(\alpha) = -1$, therefore, the A_α value is further calibrated as the most likely reaction model, $f(\alpha)$ or $g(\alpha)$ of Reaction 2 is certified (D_1 in this paper). Furthermore, an iterative computation process is conducted to calibrate and unify the A_α value with $f(\alpha)$ and $g(\alpha)$, which is detailed in S-5.

$$A_\alpha = -\frac{\beta_i E_\alpha}{RT_\alpha^2 f'(\alpha)} \exp \frac{E_\alpha}{RT_\alpha}$$

$$\text{when } f'(\alpha) = -1; A_\alpha \cong \frac{\beta_i E_\alpha}{RT_\alpha^2} \exp \frac{E_\alpha}{RT_\alpha} \quad (3)$$

$$\text{when } f'(\alpha) = -1/2\alpha^{-2}; A_\alpha = 2\alpha^2 \frac{\beta_i E_\alpha}{RT_\alpha^2} \exp \frac{E_\alpha}{RT_\alpha}$$

$$\ln A_\alpha = aE_\alpha + b \Rightarrow A_\alpha = \exp(aE_\alpha + b) \quad (4)$$

Where, $f'(\alpha)$ is the first derivation of $f(\alpha)$, for a first order reaction $f(\alpha) = 1 - \alpha$ and $f'(\alpha) = -1$; for reaction model of D_1 , $f(\alpha) = 1/2\alpha^{-2}$ and $f'(\alpha) = -1/2\alpha^{-2}$; a and b are the slope and intercept of the fitted line.

(iii) The reaction-model-fitting method (Vyazovkin et al., 2011) is utilized to locate the most likely reaction model of Reaction 2. To rearrange *Func. 1* of Eq. 1 as Eq. 5, the mathematical expression of $f(\alpha)$ is obtained, and the profiles of $f(\alpha)$ could be obtained with the A_α and E_α values as well as DTG_{dec} data. Meanwhile, to rewrite Eq. 2 as Eq. 6, the mathematical expression of $g(\alpha)$ via the FWO algorithm is gathered, and the curve of $g(\alpha)$ versus α for each deconvolved reaction could be directly plotted with precise A_α and E_α at each α .

$$f(\alpha) = \frac{\beta_i}{A_\alpha} \frac{d\alpha}{dT} \exp \left(\frac{E_\alpha}{RT_{\alpha,i}} \right) \quad (5)$$

$$g(\alpha) = 0.0049 \frac{A_{\alpha} R}{\beta_i E_{\alpha}} \exp(-1.052 \frac{E_{\alpha}}{RT_{\alpha,i}}) \quad (6)$$

Eventually, as the "kinetic triples" of Reaction 2 are certified, the thermokinetic model is constructed. More details were described in previous studies (Qi et al., 2021a; Qi et al., 2023)

3 Results and Discussion

The thermoreconstitution process of Co/Fe-LDHs is a complex procedure characterized by a range of physicochemical variations. This complexity is due to the interplay of a series of reactions that occur during the process, which is directly reflected on the mass/energy shifts. The thermal analyses on the mass/energy variations are powerful tools in elucidating the multifaceted physicochemical changes.

3.1 Thermoreconstitution process of Co/Fe-LDHs

Co/Fe-LDHs mass/energy variations under different heating rates ($\beta_i = 8, 10, 16,$ and 18 K/min) throughout the thermoreconstitution process are shown in Fig. 1. Following the recommendations of the ICTAC Kinetics Committee (Vyazovkin et al., 2011; Vyazovkin et al., 2014), the beginning and ending temperatures were extrapolated from TG_{ori} curves. The TG_{ori} curves (Fig. 1-A) evidenced approximately 27.8 % weight loss, along with significant endothermic phenomena and overlapping weight loss peaks, respectively detected in the DSC curves (Fig. 1-B) and the DTG_{ori} curves (Fig. 1-C). Owing to the temperature hysteresis effect (Koga et al., 2023; Qi et

al., 2023; Vyazovkin et al., 2014), it is notable that the $TG_{ori}/DTG_{ori}/DSC$ curves were all right-shifted with increasing heating rates.

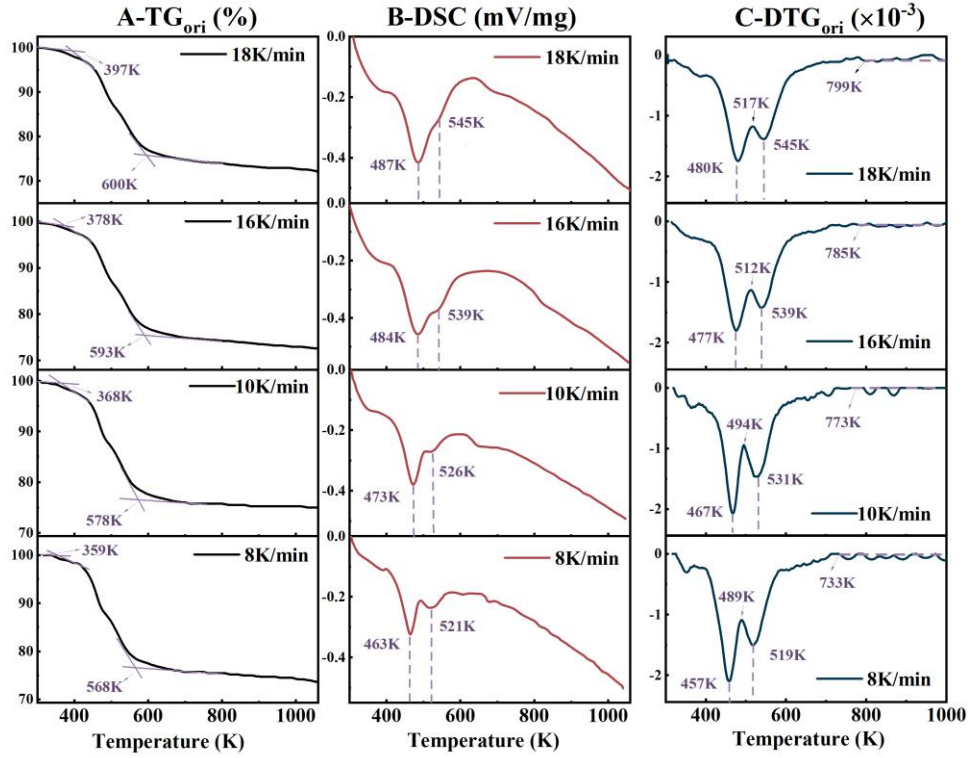


Fig. 1. Mass/energy variations of Co/Fe-LDHs throughout the

thermoreconstitution process distinct heating rates ($\beta_i = 8, 10, 16$, and 18 K/min) and

thermal curves of TG_{ori} (A), DSC (B); and DTG_{ori} (C).

The thermoreconstitution process of Co/Fe-LDHs, derived from the three types of thermal curves, unfolded in three stages:

(i) Under 400 K , less than 2.5% of weight loss in TG_{ori} (Fig. 1-A) surfaced alongside a weight loss peak in DTG_{ori} (Fig. 1-C). This stage, marked by a slight endothermic peak (Fig. 1-B), accounted for the evaporation of free absorbed water (Guo et al., 2020; Hu and Chen, 2014); this highlights the significant moisture-absorption capacity of Co/Fe-LDHs under ambient temperature (Palmer et al., 2009).

(ii) The primary thermoreconstitution phase of Co/Fe-LDHs ranged from 359-397 K to 568-600 K (Qi et al., 2021a; Qu et al., 2019), marked by a sharp weight loss (~22.5 % in Fig. 1-A). The DSC curves (Fig. 1-B) revealed dramatic endothermic reactions. It was noted that the two endothermic peaks, unified by a peak-shoulder under lower heating rates ($\beta_i = 8$ and 10 K/min), merged into an asymmetric endothermic peak under higher heating rates ($\beta_i = 16$ and 18 K/min). The two DTG_{ori} peaks (Fig. 1-C), joined by a peak-shoulder, corresponded to different types of dehydration reactions (i.e., the evaporation of crystal water (Sun et al., 2020) and dehydroxylation of -OH groups (Qi et al., 2020; Shinagawa et al., 2021)). Notably, the DTG_{ori} curves were not constant before 733-799 K, indicating that the reaction temperature of dehydration reactions ranged from 359-397 K to 733-799 K. When used for the preparation of catalysts (Peng et al., 2021) or carriers (Hou et al., 2022; Shinagawa et al., 2021), the temperature interval from 568-600 K (the extrapolated ending temperature of TG_{ori}) to 733-799 K (the constant temperature of DTG_{ori}) was critical due to significant physicochemical variations in Co/Fe-LDHs (further discussed in Section 3.2).

(iii) Beyond 733 K, the TG_{ori} curves (Fig. 1-A) showed a constant trend in weight loss along with a stationary value of DTG_{ori}. The decomposition of carbonate anions (Sun et al., 2020; Wang and O'Hare, 2012) in the negatively charged layers of Co/Fe-LDHs and the fusion of Co and Fe oxides were supported by FTIR spectra (Fig. 2-B) and SEM images (Fig. 4-A).

Under $\beta_i = 10$ K/min, four specimens at representative temperatures were chosen to examine the physicochemical changes of Co/Fe-LDHs throughout the thermoactivation process: first, Co/Fe-LDHs obtained at 368 K (Co/Fe@368K) illustrated the evaporation of free absorbed moisture; second, Co/Fe-LDHs obtained at 578 K (Co/Fe@578K) indicated the extrapolated ending temperature at the TG_{ori} curve; third, Co/Fe-LDHs obtained at 773 K (Co/Fe@773K) showed the constant temperature of the DTG_{ori} curve; and last, Co/Fe-LDHs obtained at 1,053 K (Co/Fe@1053K) represented the final product after the thermoreconstitution process.

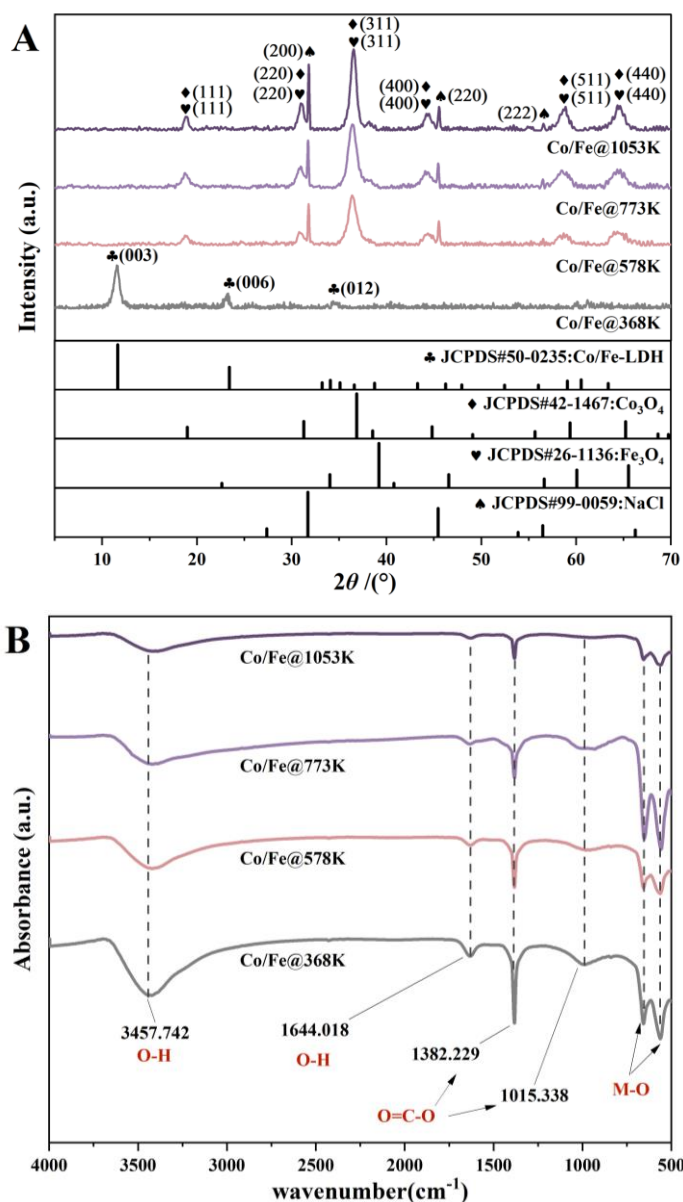
3.2 Physicochemical Variations of Co/Fe-LDHs Reconstitution

Physicochemical variations that occurred in the thermoreconstitution of Co/Fe-LDHs, including the mineralogy phases, chemical features and microscale/nanoscale morphologies, were systematically examined and analyzed.

3.2.1 Variations in Mineralogy phases

The XRD patterns of Co/Fe-LDHs throughout the thermoreconstitution process are presented in Fig. 2-A. The diffraction peaks of Co/Fe@368K at 11.5°, 23.2° and 34.3° corresponded to the (003), (006), and (012) planes of $Co_{5.84}Fe_{2.16}(OH)_{16}(CO_3)_{1.08} \cdot 0.32H_2O$ (referred to as $Co_{5.84}/Fe_{2.16}$ -LDHs). Co/Fe-LDHs in the form of $Co_{5.84}/Fe_{2.16}$ -LDHs held a hexagonal structure (Sun et al., 2020), as reflected in the SEM image (Fig. 4-A/a). The Co:Fe mole ratio in $Co_{5.84}/Fe_{2.16}$ -LDHs was 5.84:2.16 (i.e., 2.7:1) and was lower than that in the precursor metallic salt solution

(Co:Fe = 3:1), suggesting the generation of amorphous Co or Fe-based byproducts during the preparation of Co/Fe-LDHs. The water content of Co_{5.84}/Fe_{2.16}-LDHs was less than 0.71 %, implying that the weight loss in the first stage of the TG_{ori} curve (Fig. 1-A) mainly originated from the evaporation of the absorbed water.



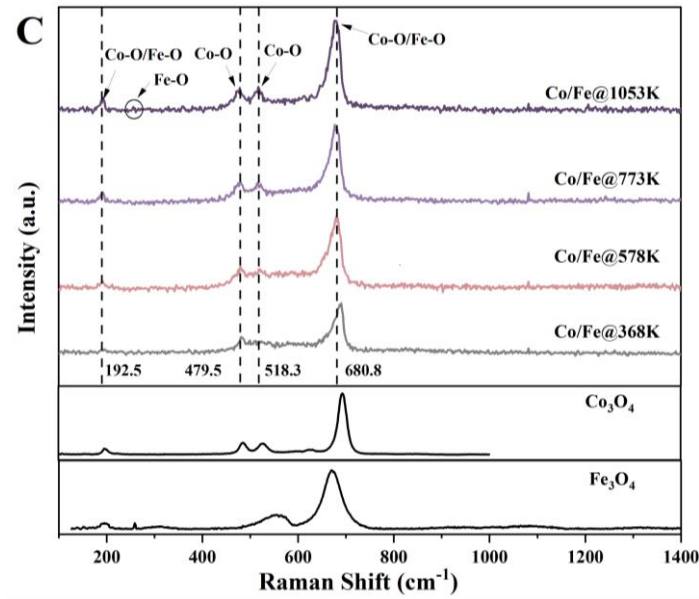


Fig. 2. XRD patterns (A), FTIR spectra (B), and Raman spectra (C) of Co/Fe-LDHs samples throughout the thermoreconstitution process ($\beta_i = 10$ K/min).

As the thermoreconstitution temperature exceeded 368 K, identical crystal phases in the XRD patterns were displayed in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K. Lattice planes assigned to (111), (220), (311), (400), (511), and (440) were well fitted to that of the cubic-structured Co_3O_4 and Fe_3O_4 crystals, which possessed analogous lattice parameters (Feng et al., 2016; Lu et al., 2019; Rodenbough et al., 2016). In addition, the calculated lattice parameters of the generated Co_3O_4 and Fe_3O_4 (hereafter, the generated Co_3O_4 and Fe_3O_4) and the standard Co_3O_4 and Fe_3O_4 crystals of JCPDS cards (hereafter, the standard Co_3O_4 and Fe_3O_4) are compared in Table S-1. With the thermoreconstitution temperature increased, the Bragg angles ($2\theta_{hkl}$) of Co_3O_4 and Fe_3O_4 detected in the XRD patterns were both inclined to that of the standard Co_3O_4 and Fe_3O_4 , correspondingly, the values of d -spacings calculated via the Bragg's Law (Eq. S-8) and lattice parameters calculated for the cubic-structured Co_3O_4

and Fe₃O₄ via Eq. S-14 were expanded. Specifically, the calculated lattice constants for the generated Co₃O₄ and Fe₃O₄ crystals of Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K were $a = b = c = 8.1581\text{--}8.1755\text{ \AA}$, $8.1712\text{--}8.1793\text{ \AA}$ and $8.1436\text{--}8.1636\text{ \AA}$, respectively, which were simultaneously expanded compared with those of the standard Co₃O₄ and Fe₃O₄ crystals (i.e., $a = b = c = 8.0835\text{--}8.0903\text{ \AA}$) (Rodenbough et al., 2016; Wang et al., 2011). Furthermore, the *d*-spacings of the adjacent crystal lattice planes (i.e., [111], [220], [311], [400], [511], and [440]) calculated for the generated Co₃O₄ and Fe₃O₄ were higher than those of the standard Co₃O₄ and Fe₃O₄. To take the [111] lattice planes of Co₃O₄ as an example, the *d*-spacings of the generated Co₃O₄ of Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K were 0.471 nm, 0.472 nm and 0.470 nm, respectively, which were both higher than that of the standard Co₃O₄ (*d*-spacing = 0.467 nm). Similarly, the volumes of the unit cells of the generated Co₃O₄ and Fe₃O₄ were $545.04\text{--}546.45\text{ \AA}^3$, $545.57\text{--}547.14\text{ \AA}^3$ and $540.08\text{--}544.41\text{ \AA}^3$ in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K, respectively, which were both higher than those of the Co₃O₄ and Fe₃O₄ standards ($528.20\text{--}529.50\text{ \AA}^3$). The collaboration of “lattice expansion effect” and “heterogeneous microstrain effect” triggered by the reconstitution temperature was the underlying cause in extending the values of *d*-spacings and lattice parameters, which was quantitatively evaluated in the following section.

3.2.2 Effect of the thermoreconstitution temperature on mineralogy

The XRD peaks of the generated Co₃O₄ and Fe₃O₄ in Co/Fe@578K, Co/Fe@773K,

and Co/Fe@1053K were significantly broadened, which was colloquially defined as the “XRD peak broadening phenomenon” (Rodenbough et al., 2016). Because the XRD peaks of the probe NaCl crystal were not expanded in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K (Fig. 2-A), it was reasonable that this broadening phenomenon was not attributed to the XRD instrument but was directly caused by the thermoreconstitution process. Universally, the “lattice expansion effect” (Rodenbough et al., 2016) caused by particle size variations, as well as the “heterogeneous microstrain effect” (Li et al., 2014) generated from crystal imperfection and distortion (Hou et al., 2022), were the two primary reasons for the broadening of the XRD peaks.

Quantitatively, the “lattice expansion effect” in expanding the XRD patterns of the generated Co₃O₄ and Fe₃O₄ could be evaluated via the volume variation degree of the unit cell, $\varepsilon_v(\%)$, which is depicted in Eq. 7. Meanwhile, the “heterogeneous microstrain effect” could be assessed via the “Williamson-Hall equation” (Hou et al., 2022; Li et al., 2014; Rodenbough et al., 2016), $\varepsilon_d(\%)$, which is displayed in Eq. 8.

$$\varepsilon_v(\%) = \frac{\Delta v}{v_s}(\%) = \frac{v_c - v_s}{v_s} \quad (7)$$

$$\varepsilon_d(\%) = \frac{\beta_{hkl} \cos \theta_{hkl}}{4 \sin \theta_{hkl}} = \frac{\beta_{hkl}}{4} \tan \theta_{hkl} \quad (8)$$

Where, $\varepsilon_v(\%)$ is the volume variation degree; v_c and v_s is the calculated and standard volume of a unit cell; $\varepsilon_d(\%)$ is the elastic microstrain value in radian of [hkl] direction; θ_{hkl} was the Bragg angle of the (hkl) plane; β_{hkl} is line broadening at FWHM of XRD peak detected at 2θ ;

The $\varepsilon_v(\%)$ and $\varepsilon_d(\%)$ values of the [111], [220], [311], [400], [511], and [440] directions of the generated Co_3O_4 and Fe_3O_4 in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K were calculated and are shown in Table S-1. The $\varepsilon_v(\%)$ values of the generated Co_3O_4 crystals were 3.09 % (Co/Fe@578K), 3.44 % (Co/Fe@773K) and 2.76 % (Co/Fe@1053K), while the $\varepsilon_v(\%)$ values of the generated Fe_3O_4 were 2.84 % (Co/Fe@578K), 3.19 % (Co/Fe@773K) and 2.51 % (Co/Fe@1053K). The positive $\varepsilon_v(\%)$ values of the generated Co_3O_4 and Fe_3O_4 crystals at 578 K, 773 K, and 1,053 K reflected the “lattice expansion effect” in broadening the XRD peaks. On the other hand, the $\varepsilon_d(\%)$ values of the generated Co_3O_4 and Fe_3O_4 were 1.12 %-2.03 % (Co/Fe@578K), 1.14 %-2.42 % (Co/Fe@773K) and 0.89 %-1.33 % (Co/Fe@1053K), respectively, which were lower than the corresponding $\varepsilon_v(\%)$ values of the generated Co_3O_4 and Fe_3O_4 in Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K. Hence, the “lattice expansion effect” was the superior reason for generating the XRD peak broadening phenomena throughout the Co/Fe-LDHs thermoreconstitution process.

To summarize the mineralogy aspect, the thermoreconstitution process of Co/Fe-LDHs resulted in (i) the formation of Co_3O_4 and Fe_3O_4 crystals through the breakdown of the Co/Fe-LDHs lattice, and (ii) the expansion of Co_3O_4 and Fe_3O_4 crystals via the lattice expansion effect.

3.2.3 Variations in Chemical Features

The FTIR spectra of Co/Fe-LDHs throughout the thermoreconstitution process are shown in Fig. 2-B. The chemical group at $3,457\text{ cm}^{-1}$ was assigned to the -OH (Hu and

Chen, 2014) of the free water absorbed onto the specimens from the ambient surroundings. The intensity of -OH at 3,457 cm⁻¹ of Co/Fe@368K was significantly stronger than that of Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K, implying the decreasing hygroscopicity of the samples. The peak at 1,644 cm⁻¹ (Taviot-Guého et al., 2018) was ascribed to -OH groups, which not only existed in the negatively charged layers (NCLs) to maintain the electrical neutrality of the LDH structure (Li et al., 2014) but also acted as a coordinate bond to Co²⁺ and Fe³⁺ in the positively charged layers (PCLs) (Wang and O'Hare, 2012). The intensity of -OH groups at 1,644 cm⁻¹ declined as the thermoreconstitution temperature rose from 368 K to 1,053 K. Additionally, two types of dehydroxylation reactions stemmed from the elimination of -OH groups from NCLs and PCLs, leading to the significant weight loss depicted in the TG_{ori} curves in Fig. 1-A.

Moreover, wavenumbers at 1,382 cm⁻¹ and 1,015 cm⁻¹ were generated by the O=C-O group of CO₃²⁻ in the NCLs (Hou et al., 2022; Sun et al., 2020; Winoto et al., 2019). Both -OH and O=C-O notably declined as the thermoreconstitution temperature increased. Two FTIR spectra signals that appeared below 600 cm⁻¹ were attributed to the vibration of the metal-oxygen bond (M-O) (Palmer et al., 2009; Seron and Delorme, 2008), which were further confirmed in Raman spectra (Fig. 2-C). In the Raman spectra of Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K, the signals detected at 192.5 cm⁻¹, 479.5 cm⁻¹, 518.3 cm⁻¹, and 680.8 cm⁻¹ were characteristic of Co-O bonds in cubic-structured Co₃O₄ (Guo et al., 2020), and the signals detected at 192.5 cm⁻¹, 274.5 cm⁻¹

and 680.8 cm^{-1} were attributed to Fe-O bonds of cubic Fe_3O_4 (Rodenbough et al., 2016) crystals. The signal detected at 680.8 cm^{-1} in Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K was the overlap of Co-O and Fe-O bonds. Interestingly, the strongest M-O bond in the Raman spectra of Co/Fe@368K slightly shifted from 680.8 cm^{-1} , implying that the Co-O and Fe-O bonds of $\text{Co}_{0.5,84}\text{Fe}_{2.16}$ -LDHs were distinct from those in the generated Co_3O_4 and Fe_3O_4 of Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K.

Chemical valence changes on the surface of Co/Fe-LDHs throughout the thermoreconstitution process were examined using the XPS technique, with the C1s calibrated to the binding energy of C-C of pollutant carbon at 248.8 eV (Qi et al., 2021b). The XPS survey spectra (Fig. 3-A) indicated an abundance of Co, Fe, and O on the surface of Co/Fe-LDHs. The relative atomic ratio of Co:Fe in Co/Fe@368K, Co/Fe@578K, Co/Fe@773K and Co/Fe@1053K ranged between 2.95-2.98:1, which approximated that of the precursor metallic salt solution (Co:Fe = 3:1) but was higher than that in $\text{Co}_{0.5,84}\text{Fe}_{2.16}$ -LDHs (Co:Fe = 2.7:1). The discrepancy in Co:Fe ratios implied the generation of amorphous Co-based, Fe-based, or Co/Fe-based byproducts during the preparation of Co/Fe-LDHs.

XPS high-resolution spectra of C1s, Co2p, and Fe2p were further analyzed and compared in Fig. 3-B, C, and D, respectively. The bonding energies of C1s deconvoluted at 284.8 eV, 286.3 eV, and 288.6 eV were ascribed to the C-C of pollutant carbon, the C-O of the oxygen absorbed onto pollutant carbon, and the carbonate of CoCO_3 (Sun et al., 2019), respectively. Two peaks at Co 2p_{1/2} (797.5 eV) and Co 2p_{3/2}

494 (781.9 eV) in the four XPS spectra of Co 2p were consistent with the Co (II) of cobalt
 495 carbonate (Peng et al., 2021; Vyazovkin et al., 2014). Simultaneously, three peaks at
 496 Fe 2p_{1/2} (726.6 eV) and Fe 2p_{3/2} (714.3 eV and 718.1 eV) were assigned to Fe (III) of
 497 amorphous FeOOH and tetragonal wurtzite (β -FeOOH), respectively (Zhai et al., 2021).
 498 As the thermoreconstitution temperature rose to 578 K or above, peaks of Co 2p_{1/2} at
 499 795.7 eV/780.6 eV and Co 2p_{3/2} at 794.6 eV/779.6 eV were assigned to Co (II)/Co (III)
 500 of cubic-Co₃O₄ (Sun et al., 2020; Wang et al., 2010). Simultaneously, peaks of Fe 2p_{1/2}
 501 at 723.3 eV/709.8 eV and Fe 2p_{3/2} at 724.7 eV/711.4 eV were ascribed to Fe (II)/Fe (III)
 502 of cubic-Fe₃O₄ (Huang et al., 2021; Wu et al., 2020). Moreover, with the increase in
 503 the thermoreconstitution temperature from 578 K to 1,053 K, the atomic ratios of Co
 504 (II):Co (III) declined from 1.80:1 (Co/Fe@578K) to 1.62:1 (Co/Fe@773K) and 1.37:1
 505 (Co/Fe@1053K). Conversely, the Fe (III):Fe (II) atomic ratios increased from 2.71:1
 506 (Co/Fe@578K) to 2.83:1 (Co/Fe@773K) and 3.11:1 (Co/Fe@1053K). Therefore, the
 507 decrease in Co (II):Co (III) and the increase in Fe (III):Fe (II) suggested an
 508 accumulation of Co₃O₄ and Fe₃O₄ with the extension of the thermoreconstitution
 509 process, possibly due to the Co (II) and Fe (III) in Co_{5.84}/Fe_{2.16}-LDHs.

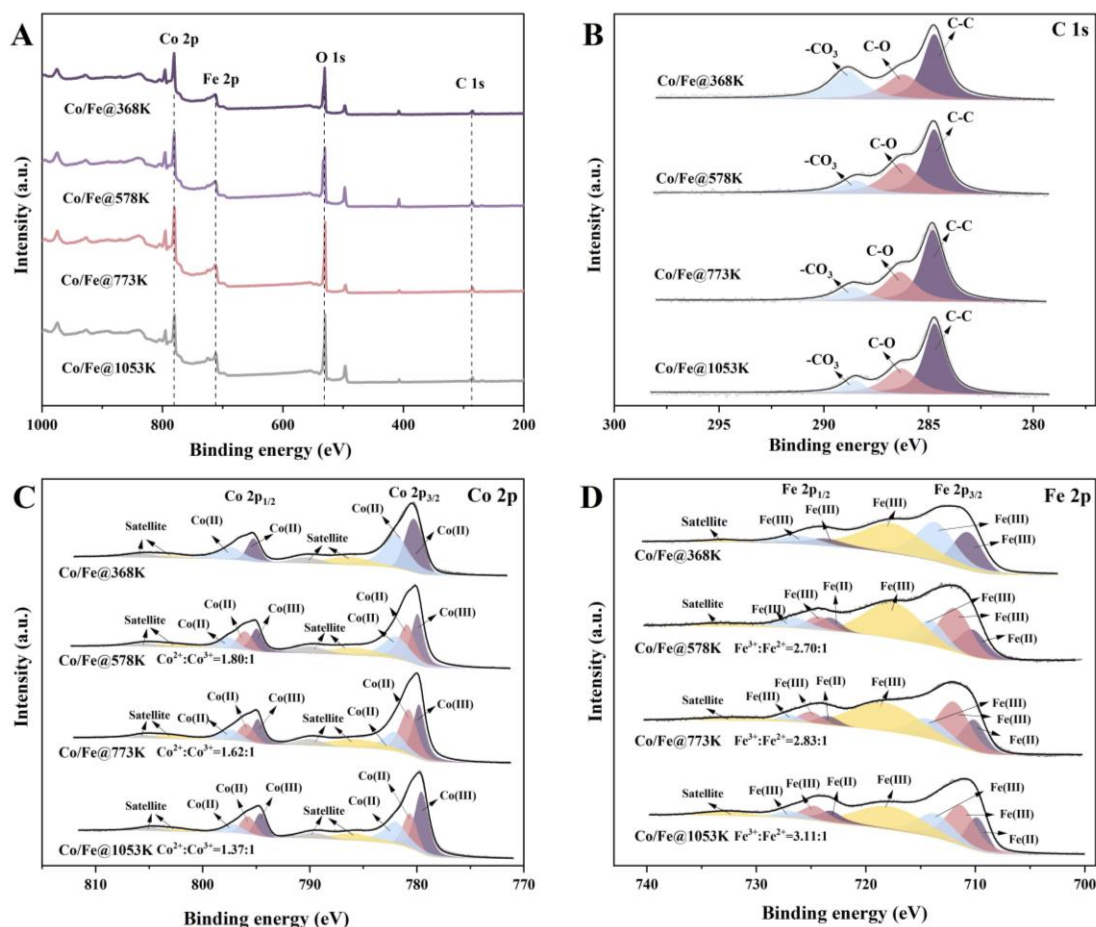


Fig. 3. XPS spectra of the full-range (A), C1s (B), Co 2p (C), and Fe 2p (D) on the surface of Co/Fe@368K, Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K.

3.2.4 Variations in Morphology

Co/Fe-LDHs exhibited microscale variations throughout the thermoreconstitution process, as observed via SEM (Fig. 4-A). The Co/Fe@368 surface structure, resembling oatmeal sheets (Fig. 4-A/a), gradually collapsed and overlapped onto Co/Fe@578 (Fig. 4-B/a) (Taviot-Guého et al., 2018; Vyazovkin et al., 2014; Zhai et al., 2021). As temperatures increased to 773 K (Fig. 4-C/a) and 1,053 K (Fig. 4-D/a), these structures were further fractured and partially melted on the surface of Co/Fe@1053K (Hou et al., 2022). EDX-mapping suggested negligible variation in the distribution of Co, Fe, and

1 521 O on the surfaces despite distinct appearances between Co/Fe@368K and
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4 522 Co/Fe@1053K (Fig. S-3 A and B).
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6 523 HRTEM images elucidated the nanoscale morphologies of Co/Fe at various
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9 524 temperatures. The (012) lattice plane of Co_{5.84}Fe_{2.16}-LDHs in Co/Fe@368K (Fig. 4-A/c)
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11
12 525 demonstrated a *d*-spacing of 0.251 nm, similar to the calculated *d*-spacing (0.259 nm,
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14
15 526 Table S-1). The *d*-spacing values of 0.249 nm, 0.251 nm, and 0.248 nm in Co/Fe@578K,
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18 527 Co/Fe@773K, and Co/Fe@1053K (Fig. 4-B/c, C/c, and Fig. 4-D/c) corresponded to
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21 528 the (311) lattice plane of Co₃O₄ (or Fe₃O₄) crystals, aligning with calculated *d*-spacing
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24 529 values (0.247 nm, Table S-1). These *d*-spacing values were consistent with those
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27 530 calculated from XRD patterns (Table S-1). Diffraction patterns (Fast Fourier
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30 531 Transform, FFT) indicated representative polycrystalline structures (Fig. 4-B/d, C/d,
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33 532 and D/d) (Sun et al., 2019; Wang et al., 2021).
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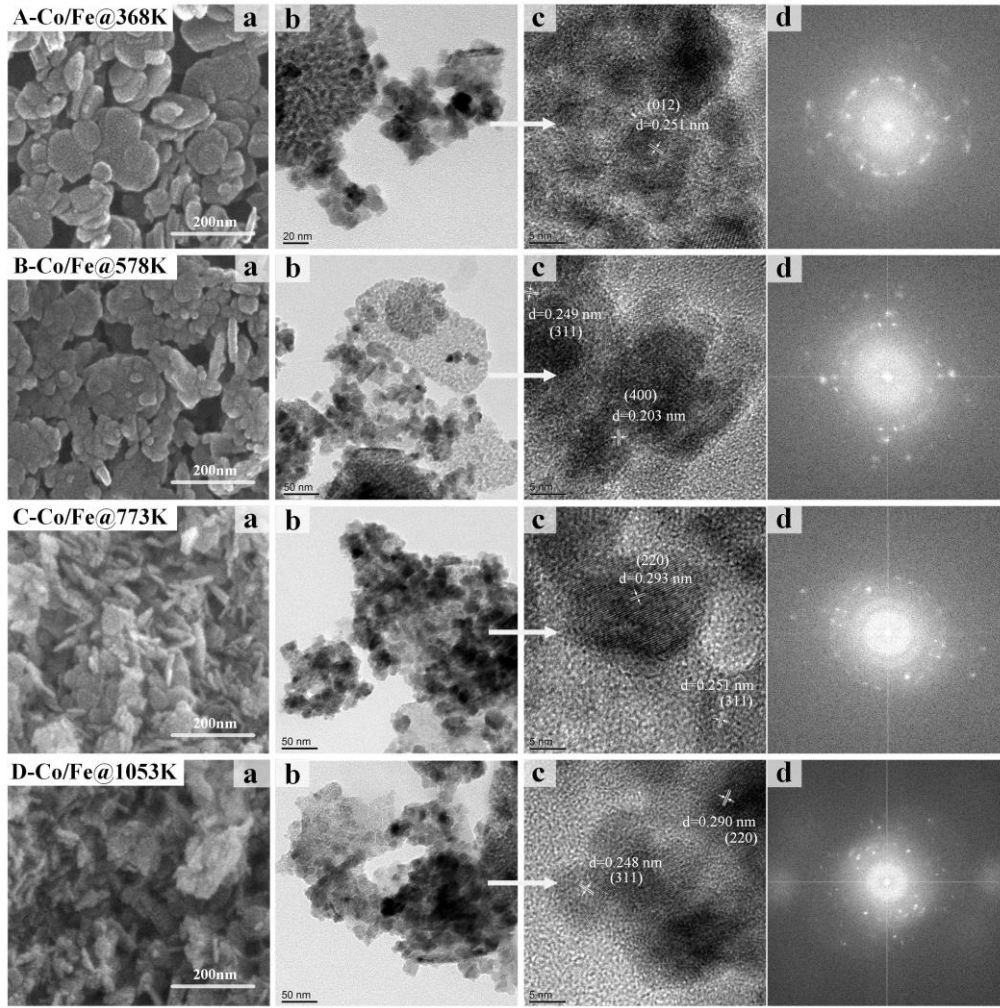


Fig. 4. SEM images (a), HRTEM images (b), Lattice structure (c) and FFT images (d) of Co/Fe-LDH at different temperatures (A-D).

3.3 Deconvolution of the Co/Fe-LDHs thermoreconstitution process

The normalized (TG_{nor}/DTG_{nor}) and converted (TG_{con}/DTG_{con}) TG/DTG curves, calculated from original TG data (TG_{ori}) under $\beta_i = 8, 10, 16$ and 18 K/min, are shown in Fig. 5-A. The starting and ending temperatures of the TG_{nor} and TG_{con} curves matched those of the TG_{ori} curve (Fig. 1-A), with DTG peaks aligning with those in the DTG_{ori} curve (Fig. 1-C). TG_{nor}/DTG_{nor} and TG_{con}/DTG_{con} curves differ in focus, with

the former examining solid-state residual variations and the latter concentrating on volatile matter decline (such as H₂O and CO₂) (Koga et al., 2023). The TG_{nor}/DTG_{nor} and TG_{con}/DTG_{con} curves presented opposite profiles, with the latter correlating with the $\alpha \frac{d\alpha}{dT}$ curves crucial for thermokinetic models established by Eq. 1 (Vyazovkin et al., 2011).

The G-PDF and F-SF both exhibit promising efficiency in deconvolving each DTG_{con} curve as three subcurves (Fig. 5-B and C). To take DTG_{con} curve under $\beta_i = 10$ K/min as an example (see Fig. 5-A/b, where peaks are respectively located at 377 K, 467 K, and 531 K), three overlapping subcurves are deconvolved by using three F-SFs with center points at 377 K, 467 K, and 531 K (Fig. 5-C/b). Similarly, the separation of the three overlapping subcurves are also achieved via three G-PDFs (Fig. 5-B/b). The correlate coefficient (R^2) of the cumulative fit peaks obtained via F-SF is superior than that gained from G-PDF, which indicated F-SF is more flexible and accurate in deconvolving the complex thermoreconstitution process. There are four independent variables, namely the asymmetry, width (or FWHM), center position, and altitude are included in the mathematical expression of F-SF, while asymmetry is absent in that of G-PDF. The higher degree of freedom of F-SF led to the superior R^2 of the cumulative fit peaks displayed in Fig. 5-C. However, it seems that the advantage of F-SF in deconvolving various DTG_{con} curves is not so significant as that demonstrated by G-PDF in this study. Because the R^2 values of the cumulative fit peaks are all higher than 0.96 in spite of the deconvolution processing is conducted via G-PDF or F-SF.

By using the mathematical expressions of G-PDF or F-SF (Dragoi et al., 2021; Qi et al., 2021a), subcurves deconvolved from DTG_{con} curve are presented as DTG_{dec-1} , DTG_{dec-2} , and DTG_{dec-3} . Meanwhile, subcurves integrated with respect to reaction temperature were denoted as TG_{dec-1} , TG_{dec-2} , and TG_{dec-3} . Hence the three reactions were thoroughly separated throughout the thermoreconstitution process. Under various of β_i , the TG_{dec} / DTG_{dec} curves of Reaction 1, 2 and 3 separated via G-PDF and F-SF were illustrated in Fig. S-4 and in Fig. S-5, respectively. On the one hand, the final TG_{dec} values of Reaction 1, 2 and 3 indicates the accumulated contributions (Dragoi et al., 2021; Muravyev et al., 2021) to the thermoreconstitution process of LDHs. To take Fig. S-4/B as an example, the final TG_{dec} values, 0.098 (Fig. S-4B/a), 0.328 (Fig. S-4B/b), and 0.463 (Fig. S-4B/c), represent the accumulated contributions of Reaction 1, 2, and 3 to the thermoreconstitution process as 9.8 %, 32.8 % and 46.3 %, which are strictly equal to the areas that covered by the corresponding DTG_{dec} curves depicted in Fig. 5-B/b. Because the peaks located in Area 1 and Area 2 (Fig. 5-B/b) were not deconvolved from the DTG_{con} curve, the total area covered by all three reactions is 0.889, indicating that 88.9 % of the thermoreconstitution process for Co/Fe-LDHs occurs below 663 K. Attributing to high values of final TG_{dec} , both Reactions 2 and 3 play a dominant role in the reconstitution of Co/Fe-LDHs to Co_3O_4 and Fe_3O_4 . Despite of the three reactions deconvolved via G-PDF or F-SF under various β_i , analogous relationships to Fig. 5-B (or Fig. 5-C) are obtained from Fig. S-4 (or Fig. S-5).

One the other hand, TG_{dec} value of each reaction at certain temperature represents the instantaneous contribution to the major weight loss of the Co/Fe-LDHs thermoreconstitution process. Continuing with the previous example as an illustration (Fig. S-4/B): for any certain temperature ($T_c \leq 663$ K), the values of TG_{dec-1} , TG_{dec-2} , TG_{dec-3} at T_c signify the instantaneous weight loss contributions of each reaction to the thermoreconstitution process of Co/Fe-LDHs extends to T_c , and the instantaneous contribution of Reaction 2 is depicted in Eq. 15. Additionally, we inferred the relative ratio, of the instantaneous contributions between Reactions 1, 2, and 3, can be utilized in predicting the instantaneous products that generated from the Co/Fe-LDHs' thermoreconstitution, which will be detailed in our subsequent study.

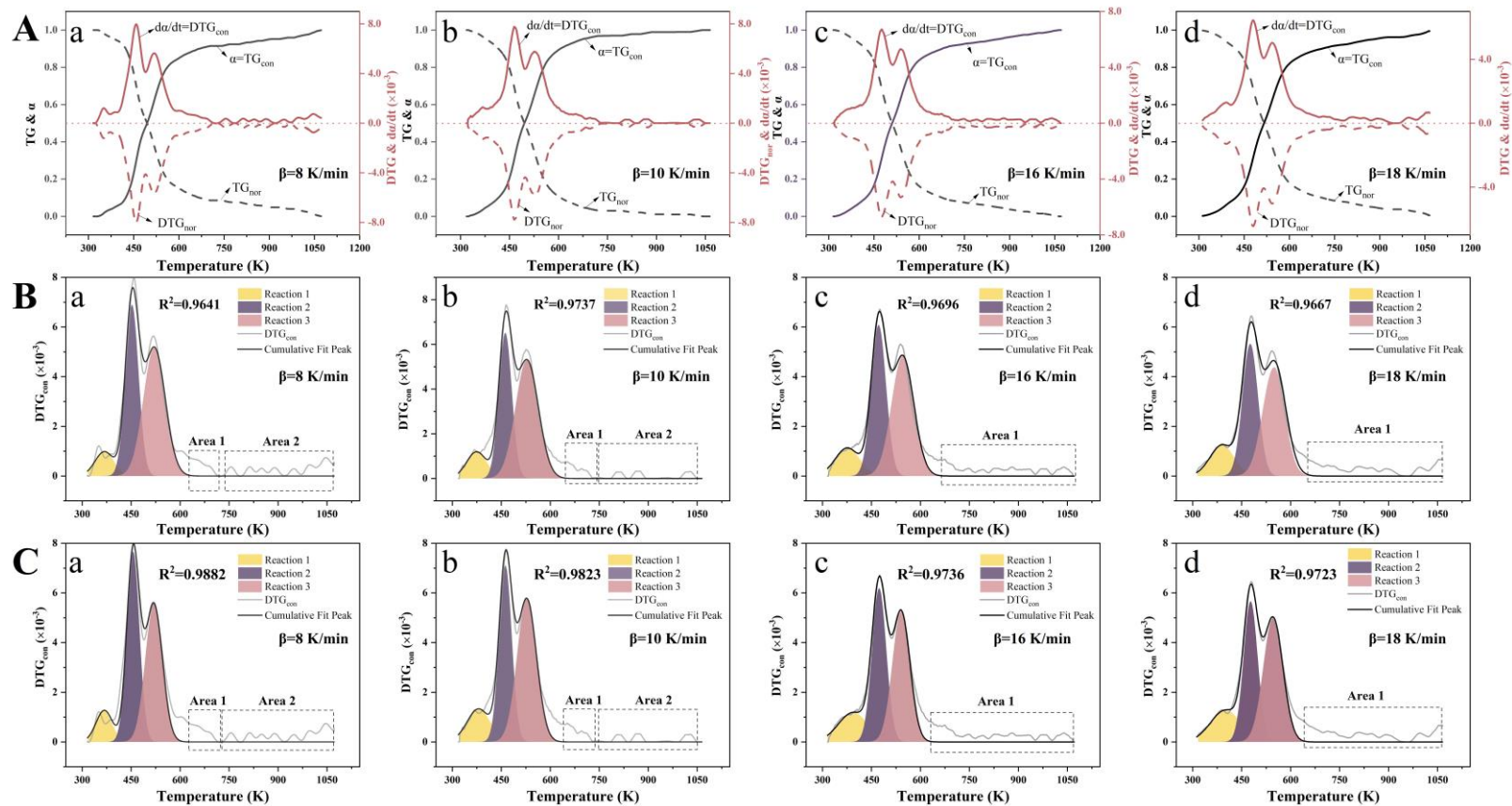


Fig. 5. TG_{nor}/DTG_{nor} and TG_{con}/DTG_{con} curves of Co/Fe-LDHs under various of β_i (A); the deconvolution of DTG_{con} ($\beta_i = 10$ K/min) into Reaction 1, Reaction 2 and Reaction 3 via Gaussian probability distribution function, G-PDF, (B) and Frazer-Suzuki function, F-SF, (C).

3.4 Thermokinetic analyses on the Co/Fe-LDHs thermoreconstitution process

Thermokinetic analyses are powerful tools for elucidating the specific reaction mechanism. Thermokinetic models is the mathematical expression of the thermokinetic analysis, which are constructed with "kinetic triples", namely the activation energy (E), the preexponential factor (A), and the reaction model ($f(\alpha)$ or $g(\alpha)$). However, mathematically, one may notice that there is no specific constant solution set but a statistical solution set of "kinetic triples" in constructing the thermokinetic model via Eq. 1. In this section, thermokinetic analyses throughout the Co/Fe-LDHs thermoreconstitution process was conducted, and the most likely "kinetic triples" of Reaction 2 is pursued to establish a reliable thermokinetic model in response to the physicochemical variations that detailed in second 3.2.

3.4.1 Scrutinization on E_α values

Activation energy, being the core of the "kinetic triples," is calculable via the model-free method (Chen et al., 2022; Liu et al., 2020; Mandapati and Ghodke, 2021) using the FWO and Friedman algorithm (Eq. 2), irrespective of the influence of the preexponential factor and the reaction model. The E_α values obtained under the FWO and Friedman algorithm throughout the Co/Fe-LDHs thermoreconstitution process are presented in Fig. 6-A and B, respectively. It should be emphasized that the specific " α " in Fig. 6-A and B (or Fig. 6-C and D) represents the relative conversion ratio of the Co/Fe-LDHs thermoreconstitution process (or Reaction 1, 2, or 3). Researchers (Koga

et al., 2023; Zhang et al., 2021b) recommended that more than 10 % of the E_{α} value fluctuation indicated that a complex multistep reaction occurred. Throughout the Co/Fe-LDH thermoreconstitution process, a complex multistep reaction is confirmed because the E_{α} values vigorously fluctuated. Furthermore, the E_{α} values obtained via the FWO algorithm decrease from 132 kJ/mol to 31.2 kJ/mol (Fig. 6-A), while the E_{α} values obtained via the Friedman algorithm fluctuate in the range of 37.5 kJ/mol to 121.8 kJ/mol (Fig. 6-B). One may observe that the E_{α} values calculated via the FWO algorithm possesses a smoother tendency and higher of accuracy (i.e., higher R^2) than those obtained from the Friedman algorithm, which indicated that integral-natured FWO algorithm is superior to the differential-natured Friedman algorithm in calculating the E_{α} values for the overall thermoreconstitution process.

For the deconvolved Reactions 1, 2 and 3 that separated by G-PDF and F-SF, the E_{α} values calculated under the FWO algorithm are illustrated in Fig. 6-C and D, respectively. Correspondingly, those E_{α} values obtained via the Friedman algorithm are illustrated in Fig. S-6/A and B, respectively. As the G-PDF is adopted for the deconvolution process (Fig. 6-C), the mean E_{α} values ($\overline{E_{\alpha}}$) of the three reactions are 47.09 kJ/mol, 64.77 kJ/mol and 74.85 kJ/mol, respectively. As the F-SF is utilized for deconvolution, those $\overline{E_{\alpha}}$ are 47.57 kJ/mol, 67.05 kJ/mol and 73.46 kJ/mol, respectively. For each reaction, the discrepancy of $\overline{E_{\alpha}}$ values calculated under FWO algorithm are not significant in spite of the deconvolution process is conduct through

1 637 G-PDF or F-SF. Identical findings are revealed by the E_{α} values obtained via the
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4 638 Friedman algorithm (Fig. S-6).
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6 639 Furthermore, despite of the three curves is deconvolved via G-PDF or F-SF, the
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9 640 E_{α} values of each reaction calculated under FWO algorithm (Fig. 6-C and D) exhibit
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12 641 limited fluctuating tendency as that obtained under Friedman algorithm (Fig. S-6).
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15 642 However, E_{α} value variations in the three reactions are distinct. To take the three
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18 643 reactions deconvolved through G-PDF as an instance (Fig. 6-C), the E_{α} values in
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21 644 Reaction 1 (or 3) increase from 38.3 kJ/mol to 56.3 kJ/mol (or increase from 61.2
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24 645 kJ/mol to 85.5 kJ/mol), with variation rates ($\Delta E_{\alpha}/\overline{E_{\alpha}}$) of 59.56 % (or 32.46 %),
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27 646 indicating that Reactions 1 and 3 are multistep reactions. In contrast, the E_{α} value
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30 647 variation in Reaction 2 is minimal, and the $\Delta E_{\alpha}/\overline{E_{\alpha}}$ value is 5.24 % (Fig. 6-C/b),
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33 648 implying that Reaction 2 is a single-step reaction. Identical findings are displayed by
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36 649 the E_{α} values obtained via the Friedman algorithm (Fig. S-6/A). Same occurrences are
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39 650 carried out as the three reactions deconvolved through F-SF, in spite of the E_{α} values
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42 651 are calculated under FWO algorithm (Fig. 6-B) or Friedman algorithm (Fig. S-6/B).
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44 652 Complementing this with FTIR/XPS spectra (Fig. 2-B and Fig. 3-B), two reactions
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47 653 were presumed to be part of Reaction 1's multistep process: the evaporation of absorbed
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50 654 water and the removal of crystal water. The former reaction exhibited lower activation
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53 655 energies than the latter, contributing to the increasing trend of E_{α} values in Fig. 6-C/a
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56 656 and D/a. The dehydroxylation of -OH groups from Co/Fe-LDHs' PCLs primarily
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59 657 occurred in Reaction 2, which presented relatively constant E_{α} values, displaying a
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1 658 single-step feature. For the multistep Reaction 3, decarbonization reactions from the
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4 659 NCLs and CoCO_3 were evident, along with the dehydroxylation reactions in iron-based
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6 660 byproducts such as amorphous FeOOH (Feng et al., 2016) and tetragonal wurtzite (β -
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9 661 FeOOH) (Zhai et al., 2021), as confirmed by FTIR and XPS spectra (Fig. 2-B and Fig.
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12 662 3-D).
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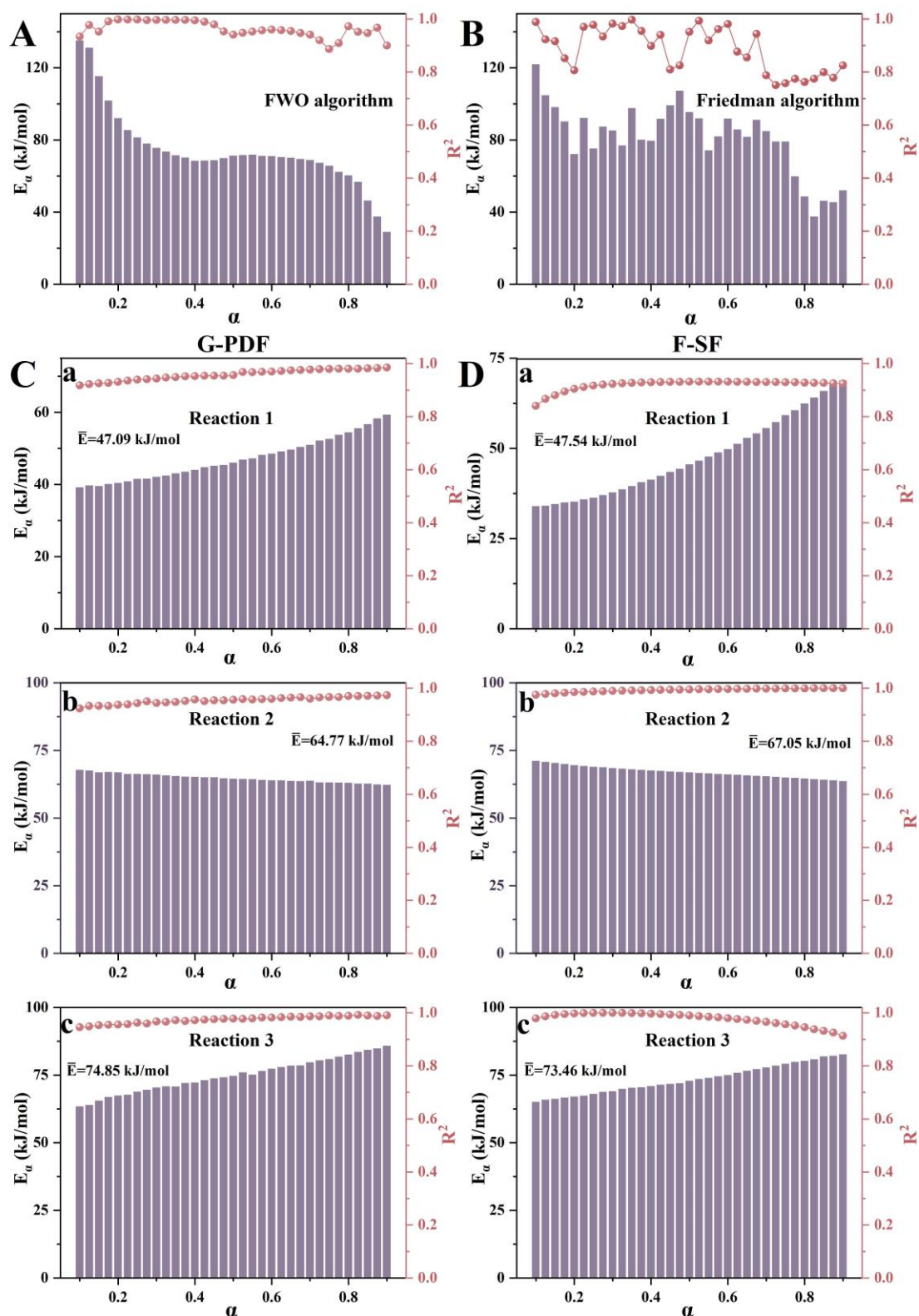


Fig. 6. E_{α} versus α throughout the Co/Fe-LDHs thermoreconstitution process with E_{α} values calculated through FWO algorithm(A) and Friedman algorithm (B);

1 666 The distribution of E_{α} values calculated via FWO algorithm in Reaction 1(a),
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4 667 Reaction 2(b), and Reaction 3(c) separated with G-PDF (C) and F-SF (D). All
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6 668 calculations were conducted as $\alpha \in (0.1, 0.9)$ with the stepping constant of α , i.e.,
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9 669 $\Delta\alpha = 0.025$.

3.4.2 Optimization of A_α values for Reaction 2

As the target reaction is evidenced a single-step reaction ($\Delta E_\alpha/\overline{E}_\alpha \leq 10\%$), or a multistep reaction is dominated or limited by the rate of one step ($10\% \leq \Delta E_\alpha/\overline{E}_\alpha \leq 20\%$), the thermokinetic model could be established on Eq. 1 (Vyazovkin et al., 2020). More details and case studies were described in previous studies (Qi et al., 2021a; Qi et al., 2023). However, the $\Delta E_\alpha/\overline{E}_\alpha$ values of Reaction 1 and 3 are both higher than 30%, which indicate Eq. 1 is only suitable in constructing the thermokinetic models of Reaction 2. Furthermore, because limited DTG_{con} peaks are displayed in Fig. 5-A, neither Reaction 1 nor Reaction 3 can be further separated into series signal-step reactions. We inferred if the thermoreconstitution temperature ranges cover by Reaction 1 and Reaction 3 were monitored under relatively lower β_i , more DTG_{con} peaks might emerged. Reaction 1 or Reaction 3 could be further deconvolved into finite signal-step reactions through a second level of deconvolution process as it was depicted in section 3.3. And this inference will be further scrutinized in our further study.

The E_α values depicted in Fig. 6-C/b and D/b are utilized in calculating the precious A_α values of Reaction 2. When the reaction model is assumed as the 1st order reaction, the A_α values of Reaction 2 (both deconvolved via G-PDF and F-SF) are first calculated under Eq. 3, and the relationship of $\ln A_\alpha$ versus E_α values are depicted in Fig. 7. Furthermore, relying on the iterative computation process, the final calibrated A_α values of Reaction 2 versus E_α values are co-illustrated in Fig. 7.

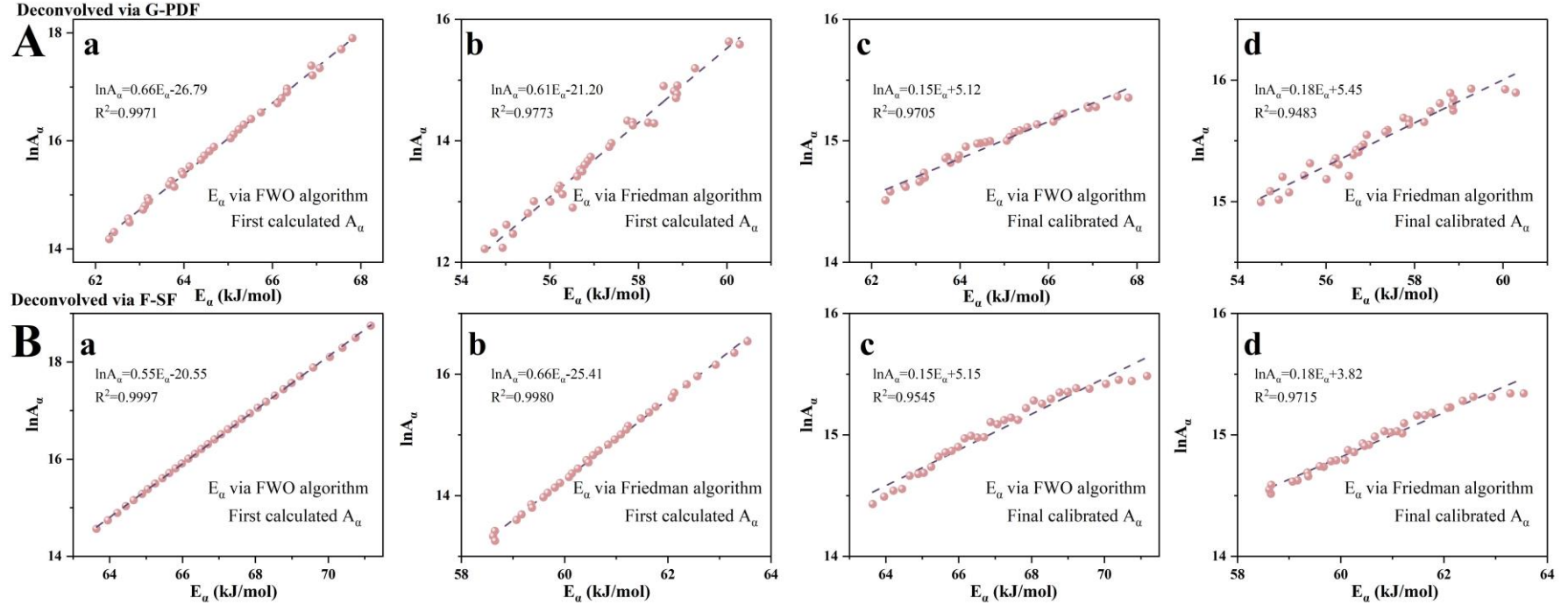


Fig. 7. Relaying on the TG_{con}/DTG_{con} curves deconvolved through G-PDF (A) and F-SF (B), the “compensation effect” between $\ln A_\alpha$ and E_α plotted with the first calculated A_α versus E_α , (a) and (b); the “compensation effect” between the final calibrated A_α versus E_α , (c) and (d).

A strong linear relationship between $\ln A_\alpha$ and E_α is displayed in Fig. 7, which is constant in spite of whether A_α values are first calculated or final calibrated. Meanwhile, neither algorithms for calculating E_α values nor deconvolution functions exhibit hardly effect in varying the linear relationship between $\ln A_\alpha$ and E_α . Relying on the “compensation effect” and the iterative computation process conducted in Fig. 7, the mathematical equation constructed for $\ln A_\alpha$ and E_α of the Reactions 2 are tabulated in Table 1, enabling direct calculation of the A_α value once the E_α value is certified. Furthermore, utilizing the average ($\bar{E}_\alpha$) values obtained through FWO or Friedman algorithm, the mean $\ln A_\alpha$ values ($\ln \bar{A}_\alpha$) of Reactions 2 were determined.

Table 1. linear equation constructed for $\ln A_\alpha$ versus E_α of Reaction 2

Deconvolved through G-PDF	Algorithms	$\ln A_\alpha = aE_\alpha + b$		$\bar{E}_\alpha$ (kJ/mol)	$\ln \bar{A}_\alpha$ (/min)	R^2
		a	b			
First calculated A_α	FWO	0.66	-26.79	64.77	15.89	0.9971
	Friedman	0.61	-21.20	59.15	15.10	0.9773
Final calibrated A_α	FWO	0.15	5.12	64.77	14.97	0.9705
	Friedman	0.18	5.45	59.15	15.86	0.9483
Deconvolved through F-SF	Algorithms	$\ln A_\alpha = aE_\alpha + b$		$\bar{E}_\alpha$ (kJ/mol)	$\ln \bar{A}_\alpha$ (/min)	R^2
		a	b			
First calculated A_α	FWO	0.55	-20.55	67.05	16.49	0.9997
	Friedman	0.66	-25.41	60.71	14.73	0.9980
Final calibrated A_α	FWO	0.15	5.15	67.05	15.03	0.9545
	Friedman	0.18	3.82	60.71	14.94	0.9715

Note: The final calibrated A_α values are in accordance with the most likely reaction model (D_1), where $f(\alpha) = \frac{1}{2}\alpha^{-1}$ and $f'(\alpha) = -\frac{1}{2}\alpha^{-2}$.

3.4.3 Determination of $f(\alpha)$ and $g(\alpha)$

Five groups of reaction models, namely the power law (P_n), the N -th order (N_n), the phase-boundary controlled (R_n), the Avrami-Erofeev (A_n) and the dimensional diffusion (D_n), have been widely employed to characterize the kinetics of thermorelated decomposition processes (Koga et al., 2023; Qu et al., 2019; Vyazovkin et al., 2011). Detailed descriptions of these models can be found in Vyazovkin's surveys (Sun et al., 2020; Vyazovkin et al., 2011). Correspondingly, twenty-one subdivided reaction models are summarized in Table 2, in both differential forms, $f(\alpha)$, and integral form, $g(\alpha)$, with their profiles illustrated in Fig. S-7/A and B, respectively.

The profiles of $g(\alpha)$ (in Fig. S-7/B) are more straightforward than those of $f(\alpha)$ (in Fig. S-7/A), providing a more convenient way to differentiate the reaction models of the three deconvolved reactions. Furthermore, based on the $g(\alpha)$ profiles (Fig. S-7/B), the twenty-one subdivided reaction models can be further categorized into three major types (Koga et al., 2023; Vyazovkin et al., 2014):

(i), the accelerating type, which includes thirteen subdivided reaction models, i.e., D_n ($n = 1, 2, 3$ and 4), R_n ($n = 1, 2$, and 3), N_n ($n = 1, 2$, and 3), $P_{2/3}$, and A_1 and $A_{0.5}$;

(ii), the deaccelerating type, which contains three subdivided reaction models of P_n ($n = 2, 3$, and 4);

and (iii), the sigmoidal type, which includes five subdivided reaction models of A_n ($n = 1.5, 2, 2.5, 3$, and 4).

Table 2. Five groups of representative reaction models utilized in the thermokinetic models (Koga et al., 2013; Koga et al., 2023; Qi et al., 2021a; Vyazovkin et al., 2011; Vyazovkin et al., 2020; Vyazovkin et al., 2014)

Reaction model	Code	$f(\alpha)$	$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$
Power Law	P_n		
	$(n = \frac{2}{3}, 2, 3 \text{ or } 4)$	$n\alpha^{\frac{n-1}{n}}$	$\alpha^{\frac{1}{n}}$
N -th Order ^a	N_n	$(1-\alpha)$	$-\ln(1-\alpha)$
	$(n = 1, 2, \text{ or } 3)$	$(1-\alpha)^2$	$(1-\alpha)^{-1}$
		$(1-\alpha)^3$	$2(1-\alpha)^{-2}$
Phase-Boundary Controlled	R_n $(n = 1, 2, \text{ or } 3)$	$n(1-\alpha)^{\frac{n-1}{n}}$	$1 - (1-\alpha)^{\frac{1}{n}}$
Avrami-Erofeev ^b	A_n $(n = 0.5, 1, 1.5, 2, 2.5, 3 \text{ or } 4)$	$n(1-\alpha)[- \ln(1-\alpha)]^{\frac{n-1}{n}}$	$[- \ln(1-\alpha)]^{\frac{1}{n}}$
Dimensional Diffusion	D_n	D_1	α^2
		D_2	$(1-\alpha) \ln(1-\alpha) + \alpha$
		D_3	$\left[1 - (1-\alpha)^{\frac{1}{3}}\right]^2$
		D_4	$1 - \frac{2}{3}\alpha - (1-\alpha)^{\frac{2}{3}}$

Note: a, the reaction order, $n > 3$ is seldom in N -th order reaction; b, A_1 model possesses identical mathematical expressions as N_1 model.

By replacing the final calibrated A_α and E_α with their average values, $\overline{A}_\alpha$ and $\overline{E}_\alpha$ listed in Table 2, $g(\alpha)$ values for Reactions 2 under specific β_i can be directly calculated using Eq. 6. As an example, setting $\beta_i = 10$ K/min, the $g(\alpha)$ profiles of Reactions 2 are illustrated in Fig. 8. As a contrast, the $g(\alpha)$ profiles of Reactions 2 plotted under higher heating rate, $\beta_i = 18$ K/min, are illustrated in Fig. S-8.

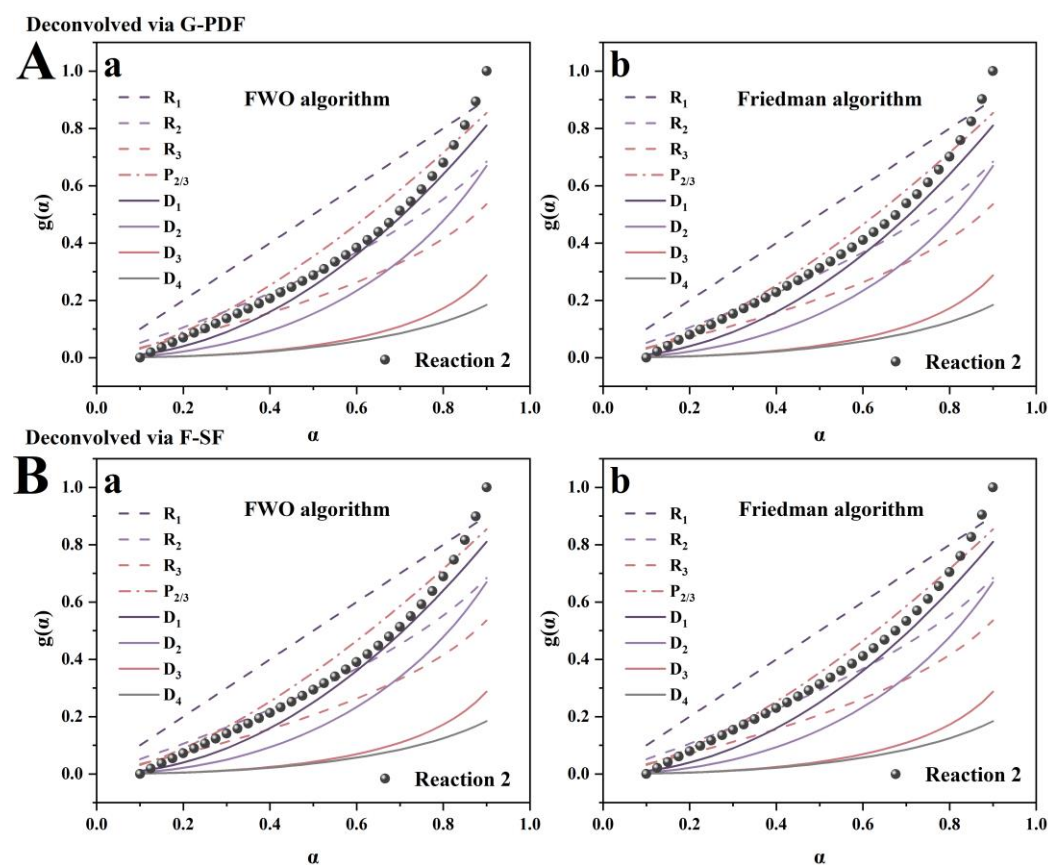


Fig. 8. the $g(\alpha)$ profiles of Reactions 2 deconvoluted through G-PDF (A) and F-SF (B) and plotted with $\overline{E}_\alpha$ calculated under FWO algorithm (a) and Friedman algorithm (b), respectively. $\overline{A}_\alpha$ and $\overline{E}_\alpha$ values are listed in Table 1.

Despite of the heating rate β_i is set at lower or higher value (Fig. 8 or Fig. S-8), identical profiles of $g(\alpha)$ curves are displayed, which indicated that the reaction model of Reaction 2 is independent with heating rate. Meanwhile, Reaction 2 display

an accelerating profile, and $g(\alpha)$ curves are located in Phase diagram 2 (colored blue in Fig. S-7/B). This location suggests that D_n ($n = 1, 2, 3$ and 4), R_n ($n = 1, 2$, and 3) and $P_{2/3}$ are the potential options for the most likely reaction model (Zhang et al., 2021a). Mathematically, researchers have recommended that the correlate coefficient (R_c^2 , depicted in Eq. 9) (Qu et al., 2019) and the root-mean-square error (RMSE, depicted in Eq. 10) (Muravyev et al., 2021) are beneficial in determining the most likely reaction models. Based on the $g(\alpha)$ profiles of Reactions 2 conducted under $\beta_i = 10$ K/min, the values of R_c^2 and RMSE of the potential options for the most likely reaction model are listed in Table 3.

$$R_c^2 = 1 - \frac{\sum_{\alpha=0.1}^{\alpha=0.9} [g(\alpha)_{dec} - g(\alpha)_{rep}]^2}{\sum_{\alpha=0.1}^{\alpha=0.9} [g(\alpha)_{dec} - \overline{g(\alpha)_{rep}}]^2} \quad (9)$$

$$RMSE = \sqrt{\frac{1}{N} \sum_{\alpha=0.1}^{\alpha=0.9} [g(\alpha)_{dec} - g(\alpha)_{rep}]^2} \quad (10)$$

Where, $g(\alpha)_{dec}$ was the value calculated via Eq. 6 under $\beta_i = 10$ K/min, $g(\alpha)_{rep}$ and $\overline{g(\alpha)_{rep}}$ was the value (or mean value) of representative reaction model i.e., D_n ($n = 1, 2, 3$, and 4), R_n ($n = 1, 2$, and 3) as well as $P_{2/3}$ located in Phase diagram 2 (colored in blue) of Fig. S-7/B; as $\alpha \in (0.1, 0.9)$ and the stepping constant of α , i.e., $\Delta\alpha = 0.025$, the value of N was 31.

Table 3. R_c^2 and RMSE calculated for the reaction models (D_n , R_n and $P_{2/3}$) of Reaction 2 under $\beta_i = 10$ K/min

$\beta_i = 10$ K/min			D_n				R_n			$P_{2/3}$
			D_1	D_2	D_3	D_4	R_1	R_2	R_3	
G-PDF	FWO	R^2	0.9512	0.5802	< 0.1	< 0.1	0.6486	0.7410	0.1337	0.9453
		RMSE	0.0545	0.1521	0.3334	0.3622	0.1674	0.0936	0.1710	0.0590
	Friedman	R^2	0.9485	0.5243	< 0.1	< 0.1	0.7052	0.7133	0.1135	0.9251
		RMSE	0.0604	0.1693	0.3495	0.3779	0.1482	0.1006	0.1844	0.0686
F-SF	FWO	R^2	0.9517	0.5650	< 0.1	< 0.1	0.6622	0.7332	0.1259	0.9452
		RMSE	0.0552	0.1565	0.3376	0.3663	0.1627	0.0954	0.1745	0.0580
	Friedman	R^2	0.9435	0.5220	< 0.1	< 0.1	0.7062	0.7105	0.1108	0.9239
		RMSE	0.0613	0.1700	0.3502	0.3785	0.1478	0.1012	0.7850	0.0691

Note: in this study, one iteration computation was conducted before the most likely reaction model was finally optimized to D_1 .

A relatively higher R_c^2 and a lower RMSE value indicated the most likely reaction model (Muravyev et al., 2021; Vyazovkin et al., 2020). As shown in Table 3, due to the highest R_c^2 and lowest RMSE value of D_1 , one-dimensional diffusion was the most likely reaction model of Reaction 2. The D_1 reaction model indicated that the volatile matter (Koga et al., 2013) (such as H_2O and CO_2) generated from the decomposition of Co/Fe-LDHs was directionally diffused from the higher concentrated region to the lower place. In addition, the $f'(\alpha)$ of the reaction model D_1 was $-1/2\alpha^{-2}$, which was utilized in calibrating the A_α values via the iterative computation process (S-5).

For a better understanding, the schematic diagrams of D_1 , D_2 , and D_3 are compared in Fig. S-9. Assuming the solid-state reactant (i.e., Co/Fe-LDHs) was reduced to a solid brick settled in a certain 3-D orthogonal space (x, y, z) (Iwasaki et al., 2020; Koga et al., 2013; Koga et al., 2023), the reaction advancement was perpendicularly conducted to the reaction interface of the solid products and reactant. When the reaction model followed D_1 , the solid products accumulated in the z-axis as the solid-state reactant was eliminated. Meanwhile, volatile matter diffused from the interface to the surroundings. This indicates that the direction of solid-state product accumulation was opposite to the diffusion direction of the volatile matter. Furthermore, on the cross-sections of z-x and z-y, one may observe that one pair of reaction interfaces of D_1 was parallel to the (x, y) plane, which indicated that the direction of the reaction was carried out along the z-axis and that the decomposition of Co/Fe-LDHs was carried

out layer by layer. Specifically, in Reaction 2, the water derived from the dehydroxylation of -OH groups of the PCLs escaped from the solid-state substances, which led to the generation of Co_3O_4 and Fe_3O_4 .

Moreover, the number of reaction interfaces in Fig. S-9 can be utilized to distinguish D_1 from D_2 and D_3 . In the schematic diagram of the D_2 reaction model, two pairs of reaction interfaces were exhibited in the (x, y) plane and the (z, y) plane. On the z-x and z-y cross-sections, one may observe that the reaction was not only carried out in the z-axis but also conducted in the x-axis, which indicated that two directions of reaction were processed in D_2 reaction model. Analogously, three pairs of interfaces were parallel to the (x, y), (x, z) and (y, z) planes in D_3 , suggesting that the solid products would accumulate in the z-, y- and x-axes.

3.4.4 Thermokinetic models of Reaction 2

Under $\beta_i = 10 \text{ K/min}$, substituting $\overline{A}_\alpha$, $\overline{E}_\alpha$, and $f(\alpha) = 1/2\alpha^{-1}$ into Eq. 5, the differential and integral formulas of thermokinetic models for Reaction 2, deconvolved from G-PDF with $\overline{E}_\alpha$ calculated via FWO algorithm or Friedman algorithm (denoted as G-PDF/FWO or G-PDF/ Friedman), are depicted in Eq. 11 and Eq. 12, respectively. And the thermokinetic models for Reaction 2, deconvolved from F-SF (denoted as F-SF/FWO or F-SF/ Friedman), are displayed in Eq. 13 and Eq. 14. Additionally, the reaction temperature interval of Reactions 2, $T \in [383 \text{ K}, 550 \text{ K}]$, is collected from the TG_{dec} curves in Fig. 5-C.

$$\begin{aligned}
& \frac{d\alpha}{dT} = \frac{\exp\left(14.97 - \frac{64,772}{RT_\alpha}\right)}{2\alpha\beta_i} \\
& \alpha = \sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(14.97 - \frac{64,772}{RT_\alpha}\right) dT}
\end{aligned}
\tag{11}$$

$$\begin{aligned}
& \frac{d\alpha}{dT} = \frac{\exp\left(15.86 - \frac{59,146}{RT_\alpha}\right)}{2\alpha\beta_i} \\
& \alpha = \sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(15.86 - \frac{59,146}{RT_\alpha}\right) dT}
\end{aligned}
\tag{12}$$

$$\begin{aligned}
& \frac{d\alpha}{dT} = \frac{\exp\left(15.03 - \frac{67,049}{RT_\alpha}\right)}{2\alpha\beta_i} \\
& \alpha = \sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(15.03 - \frac{67,049}{RT_\alpha}\right) dT}
\end{aligned}
\tag{13}$$

$$\begin{aligned}
& \frac{d\alpha}{dT} = \frac{\exp\left(14.94 - \frac{60,714}{RT_\alpha}\right)}{2\alpha\beta_i} \\
& \alpha = \sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(14.94 - \frac{60,714}{RT_\alpha}\right) dT}
\end{aligned}
\tag{14}$$

Where, $\beta_i = 10$ K/min, and $T \in [383 \text{ K}, 550 \text{ K}]$.

For the Co/Fe-LDHs, which were thermally reconstituted under $\beta_i = 10$ K/min (Fig. 5-B), the area covered by the DTG_{dec-1}, DTG_{dec-2}, and DTG_{dec-3} was contribution to the area covered by the DTG_{con} curve. Based on the integral formulas of thermokinetic models for Reaction 2, the instantaneous contribution of Reaction 2 to the major Co/Fe-LDHs thermoreconstitution process could be obtained (denoted as

810 W_{IC-R2}). As an example, the instantaneous contribution of Reaction 2 deconvolved
811 from G-PDF with $\overline{E_\alpha}$ calculated via FWO algorithm to the major weight loss of Co/Fe-
812 LDHs thermoreconstitution process conducted under $\beta_i = 10$ K/min is depicted in Eq.
813 15. It should be emphasized that the major weight loss of Co/Fe-LDHs
814 thermoreconstitution process conducted under $\beta_i = 10$ K/min is 0.889, which has been
815 obtained in Fig. 5-B/b.

$$W_{IC-R2} = \frac{\sqrt{\frac{1}{\beta_i} \int_{383}^{550} \exp\left(14.97 - \frac{64,772}{RT_\alpha}\right) dT}}{0.889} \times 100\% \quad (15)$$

where, $\beta_i = 10$ K/min; and $T \in [321 \text{ K}, 663 \text{ K}]$

3.5 Correlation analysis

818 Thermokinetic models, established on TG/DTG data and Eq. 1, primarily
819 concentrated on the variations in volatile matter (Zhang et al., 2014). These behaviors,
820 such as the generation (Koga et al., 2023) from Co/Fe-LDH decomposition and the
821 escape from the solid-state residual, are reflected in the reaction model of the
822 thermokinetic models. In contrast, the physicochemical variations in mineralogy (Fig.
823 2-A), chemistry (Fig. 2-B and C, Fig. 3), and morphology (Fig. 4) mainly focus on the
824 temporary or final solid-state residuals (Song et al., 2019). In combination with
825 deconvolution analysis and various examinations throughout the thermoreconstitution
826 of Co/Fe-LDHs, a complementary correlation among the thermokinetic analyses, the
827 most likely reaction model of Reaction 2, and physicochemical variations was proposed.
828 This correlation helps elucidate the thermoreconstitution process of Co/Fe-LDHs

conducted at $\beta_i = 10$ K/min. The scheme diagram is illustrated in Fig. 9.

First, as Co/Fe-LDHs were heated from the ambient temperature to 368 K (i.e., Co/Fe@368K), two types of dehydration processes were involved in Reaction 1. Specifically, the volatile matter was diffused in the form of water vapor, as denoted in Fig. 9. Meanwhile, the solid-state residuals were the Co/Fe-LDHs in the form of $\text{Co}_{5.84}\text{Fe}_{2.16}(\text{OH})_{16}(\text{CO}_3)_{1.08} \cdot 0.32\text{H}_2\text{O}$, detected by XRD in Fig. 2-A. These residuals displayed a typical layered morphology of Co/Fe@368K in SEM and HRTEM images, as shown in Fig. 4-A. The byproducts were mainly CoCO_3 , amorphous FeOOH, and tetragonal wurtzite (β -FeOOH), as certified by XPS spectra in Fig. 3-C and D.

Furthermore, as the heating temperature elevated to 578 K and 773 K (i.e., Co/Fe@578K and Co/Fe@773K), Reaction 2 and Reaction 3 both emerged, and the one-dimensional diffusion reaction model (D_1) were conducted in Reaction 2. However, distinct kinds of volatile matter were generated, as evident in the FTIR (Fig. 2-B) and revealed in the XPS spectra (Fig. 3). Specifically, the dehydroxylation of -OH groups on the PCLs, evident in the XRD patterns of Co/Fe@578K and Co/Fe@773K in Fig. 2-A, was responsible for Reaction 2. On the other hand, the elimination of two types of gaseous phases led to Reaction 3 with a multistep character. One of the gaseous phases was CO_2 escaped from NCLs (Fig. 2-B) and CoCO_3 (Fig. 4-C), and the other was vapor generated from amorphous FeOOH and tetragonal wurtzite (β -FeOOH). Reactions 2 and 3 played a key role in Co/Fe-LDH thermoreconstitution. The two reactions not only led to the decomposition of Co/Fe-LDHs as cubic- Co_3O_4 and Fe_3O_4 (Co/Fe@578K and

1 850 Co/Fe@773K in Fig. 2-A), but also triggered the collapse of the layered structure (Fig.
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4 851 4-B and C).

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6 852 Last, when the heating temperature increased to 773 K or more (Co/Fe@1053K),
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9 853 the volatile matter was mainly CO₂ generated from deep decarbonization (as evidenced
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12 854 by the FTIR spectra of Co/Fe@1053K in Fig. 2-B). In combination with Fig. 9 and Fig.
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15 855 4-D, the solid-state residual of Co/Fe@1053K was in the form of cubic-Co₃O₄ and
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18 856 Fe₃O₄, which had aggregated and partially melted (Fig. 4-D/a). However, due to the
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21 857 absence of deconvolved curves in DTG_{con} (Fig. 5-B), this variation cannot be related to
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23
24 858 a specific thermokinetic model. It could be inferred that if the thermoreconstitution
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27 859 process was maintained at a higher temperature, the thermokinetic model established
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30 860 on the energy-based data (for instance, the DSC data) might be a potential way to make
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33 861 a deeper correlation with the physicochemical variations. This inference will be studied
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36 862 in future reports.

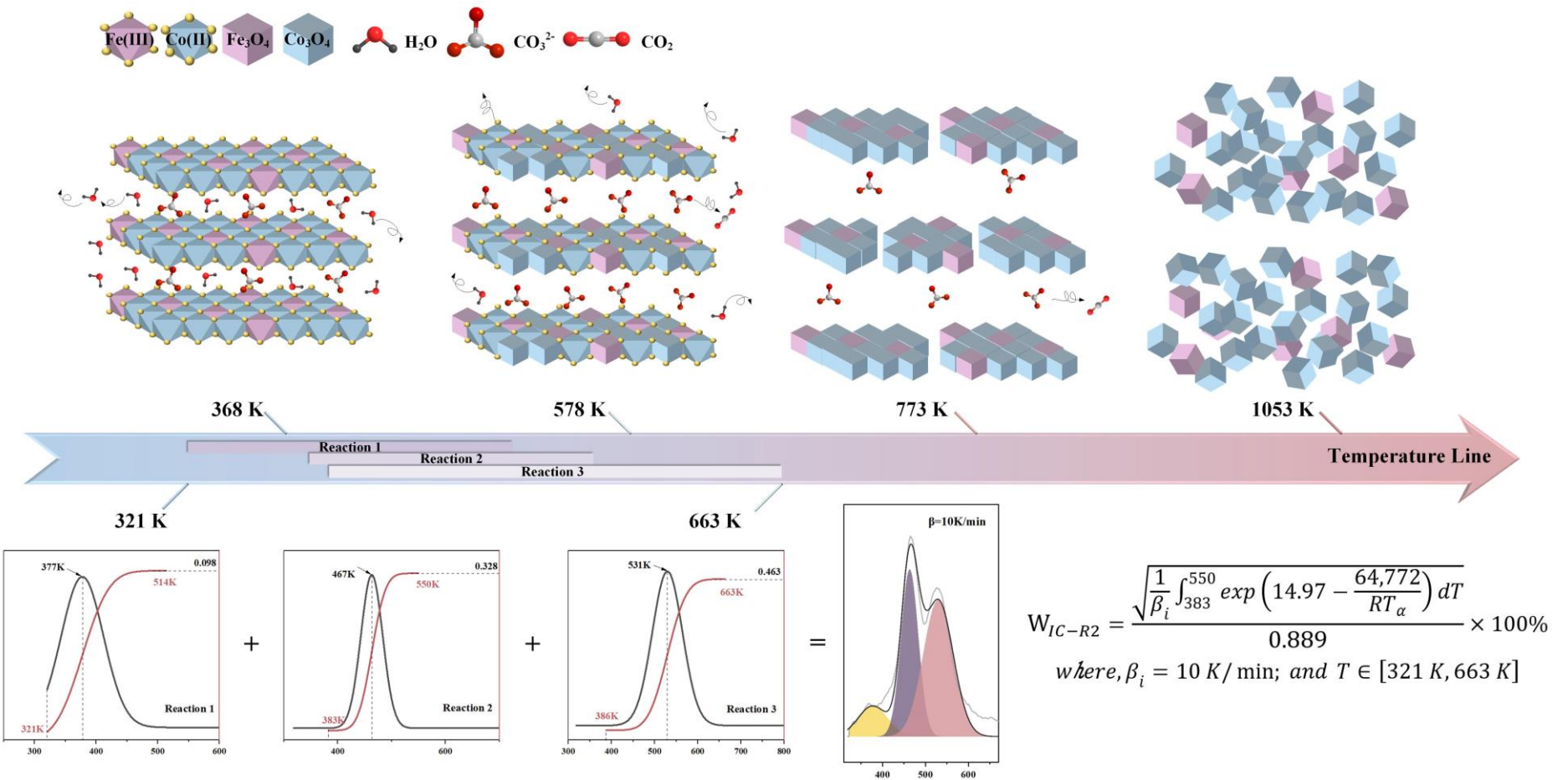


Fig. 9. The schematic diagram of the Co/Fe-LDHs thermoreconstitution process.

4. Conclusions

The thermoreconstitution of Co/Fe-LDHs involves a complex decomposition process accompanied by substantial physicochemical variations. This process was characterized by three distinct stages with ~27.8 % of weight loss and remarkable endothermic phenomenon, which were successfully separated into three reactions through G-PDF and F-SF. After the securitization on the most likely "kinetic triples", the thermokinetic model of the Reaction 2 was established on the one-dimensional diffusion model (D_1). The volatile substances, such as H₂O and CO₂, were diffused directionally from the reconstitution interface of Co/Fe-LDHs, which triggered a progressive collapse of the layered structure. Correspondingly, the solid-state substances with the final products of cubic-Co₃O₄ and Fe₃O₄, were fractured and partially melted in the SEM images, meanwhile, the XRD peak broadening phenomena were observed and were validated by measuring the d -spacing values in HRTEM images, which were primarily attributed to the lattice expansion and heterogeneous microstrain effects.

To interpret the thermoreconstitution process of Co/Fe-LDHs, the thermokinetic models, which were applied in depicting the behaviors of the volatile substances, and the physicochemical examinations, which were utilized in revealing the variations of the solid-state substances, were comprehensively combined with a complementary correlation.

Acknowledgment

This study is supported by the China Scholarship Council (No.202000810011), the Key Research and Development Program (Major technical innovation projects) of Shandong Province (No. 2020CXGC011204), the Guangdong Basic and Applied Basic Research Foundation (No. 2019B1515120052) and Guangdong Foundation for Program of Science and Technology Research (No. 2020B1212060053). Furthermore, all authors appreciate the kind help from Dr. Yang Bo of Kyoto University and the equipment support from Zhang Yunfei, the CEO of JM Filtec. Co.Ltd.

Supplementary materials

Documents of S-1 (including Eq. S-1 to Eq. S-7), S-2, S-3 (including Eq. S-8 to Eq. S-16), S-4 (including Eq. S-17), S-5; Table S-1, and Fig. S-1 to Fig. S-9 were proposed in supplementary materials.

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Tables:

Table 1. linear equation constructed for LnA_{α} versus E_{α} of Reaction 2

Deconvolved through G-PDF	Algorithms	$Ln A_{\alpha} = aE_{\alpha} + b$		$\overline{E_{\alpha}}$ (kJ/mol)	$Ln\overline{A_{\alpha}}$ (/min)	R^2
		a	b			
First calculated A_{α}	FWO	0.66	-26.79	64.77	15.89	0.9971
	Friedman	0.61	-21.20	59.15	15.10	0.9773
Final calibrated A_{α}	FWO	0.15	5.12	64.77	14.97	0.9705
	Friedman	0.18	5.45	59.15	15.86	0.9483

Deconvolved through F-SF	Algorithms	$Ln A_{\alpha} = aE_{\alpha} + b$		$\overline{E_{\alpha}}$ (kJ/mol)	$Ln\overline{A_{\alpha}}$ (/min)	R^2
		a	b			
First calculated A_{α}	FWO	0.55	-20.55	67.05	16.49	0.9997
	Friedman	0.66	-25.41	60.71	14.73	0.9980
Final calibrated A_{α}	FWO	0.15	5.15	67.05	15.03	0.9545
	Friedman	0.18	3.82	60.71	14.94	0.9715

Note: The final calibrated A_{α} values are in accordance with the most likely reaction model (D_1), where $f(\alpha) = \frac{1}{2}\alpha^{-1}$ and $f'(\alpha) = -\frac{1}{2}\alpha^{-2}$.

Table 2. Five groups of representative reaction models utilized in the thermokinetic models (Koga et al., 2013; Koga et al., 2023; Qi et al., 2021a; Vyazovkin et al., 2011; Vyazovkin et al., 2020; Vyazovkin et al., 2014)

Reaction model	Code	$f(\alpha)$	$g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$
Power Law	P_n		
	$(n = \frac{2}{3}, 2, 3 \text{ or } 4)$	$n\alpha^{\frac{n-1}{n}}$	$\alpha^{\frac{1}{n}}$
N -th Order ^a	N_n	$(1 - \alpha)$	$-\ln(1 - \alpha)$
	$(n = 1, 2, \text{ or } 3)$	$(1 - \alpha)^2$	$(1 - \alpha)^{-1}$
		$(1 - \alpha)^3$	$2(1 - \alpha)^{-2}$
Phase-Boundary Controlled	R_n $(n = 1, 2, \text{ or } 3)$	$n(1 - \alpha)^{\frac{n-1}{n}}$	$1 - (1 - \alpha)^{\frac{1}{n}}$
Avrami-Erofeev ^b	A_n $(n = 0.5, 1, 1.5, 2, 2.5, 3 \text{ or } 4)$	$n(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{n-1}{n}}$	$[- \ln(1 - \alpha)]^{\frac{1}{n}}$
Dimensional Diffusion	D_n	D_1	α^2
		D_2	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
		D_3	$\left[1 - (1 - \alpha)^{\frac{1}{3}}\right]^2$
		D_4	$1 - \frac{2}{3}\alpha - (1 - \alpha)^{\frac{2}{3}}$

Note: a, the reaction order, $n > 3$ is seldom in N -th order reaction; b, A_1 model possesses identical mathematical expressions as N_1 model.

Table 3. R_c^2 and RMSE calculated for the reaction models (D_n , R_n and $P_{2/3}$) of Reaction 2 under $\beta_i = 10$ K/min

$\beta_i = 10$ K/min			D_n				R_n			$P_{2/3}$
			D_1	D_2	D_3	D_4	R_1	R_2	R_3	
G-PDF	FWO	R^2	0.9512	0.5802	<0.1	<0.1	0.6486	0.7410	0.1337	0.9453
		RMSE	0.0545	0.1521	0.3334	0.3622	0.1674	0.0936	0.1710	0.0590
	Friedman	R^2	0.9485	0.5243	<0.1	<0.1	0.7052	0.7133	0.1135	0.9251
		RMSE	0.0604	0.1693	0.3495	0.3779	0.1482	0.1006	0.1844	0.0686
F-SF	FWO	R^2	0.9517	0.5650	<0.1	<0.1	0.6622	0.7332	0.1259	0.9452
		RMSE	0.0552	0.1565	0.3376	0.3663	0.1627	0.0954	0.1745	0.0580
	Friedman	R^2	0.9435	0.5220	<0.1	<0.1	0.7062	0.7105	0.1108	0.9239
		RMSE	0.0613	0.1700	0.3502	0.3785	0.1478	0.1012	0.7850	0.0691

Note: in this study, one iteration computation was conducted before the most likely reaction model was finally optimized to D_1 .

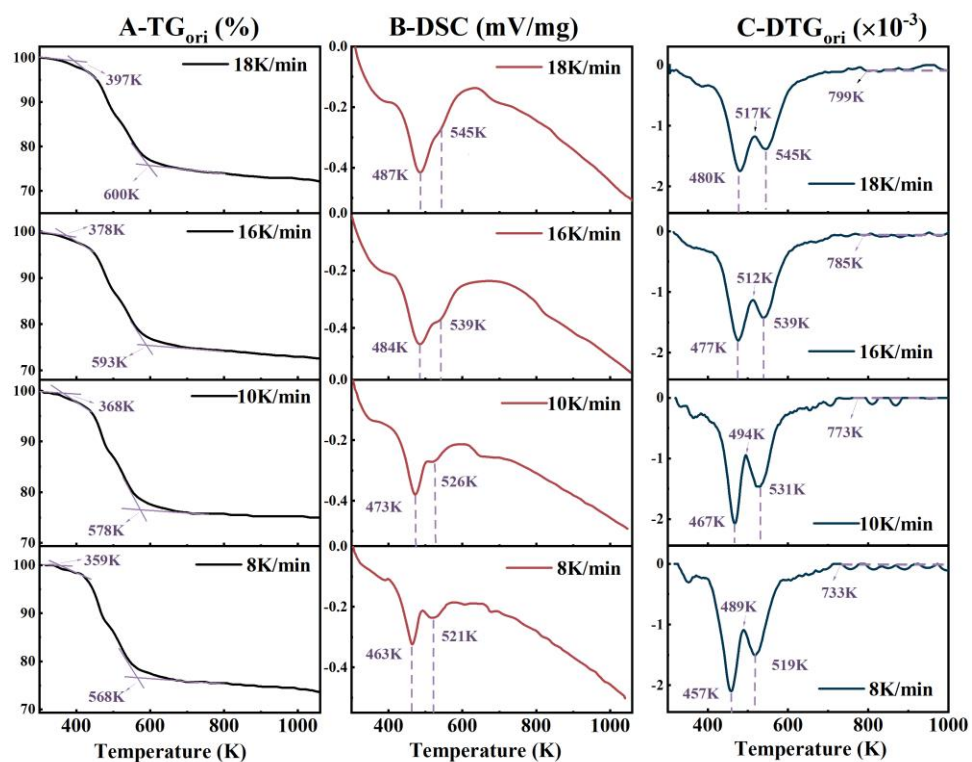
Figures:

Fig. 1. Mass/energy variations of Co/Fe-LDHs throughout the thermoreconstitution process distinct heating rates ($\beta_i = 8, 10, 16, \text{ and } 18 \text{ K/min}$) and thermal curves of TG_{ori} (A), DSC (B); and DTG_{ori} (C).

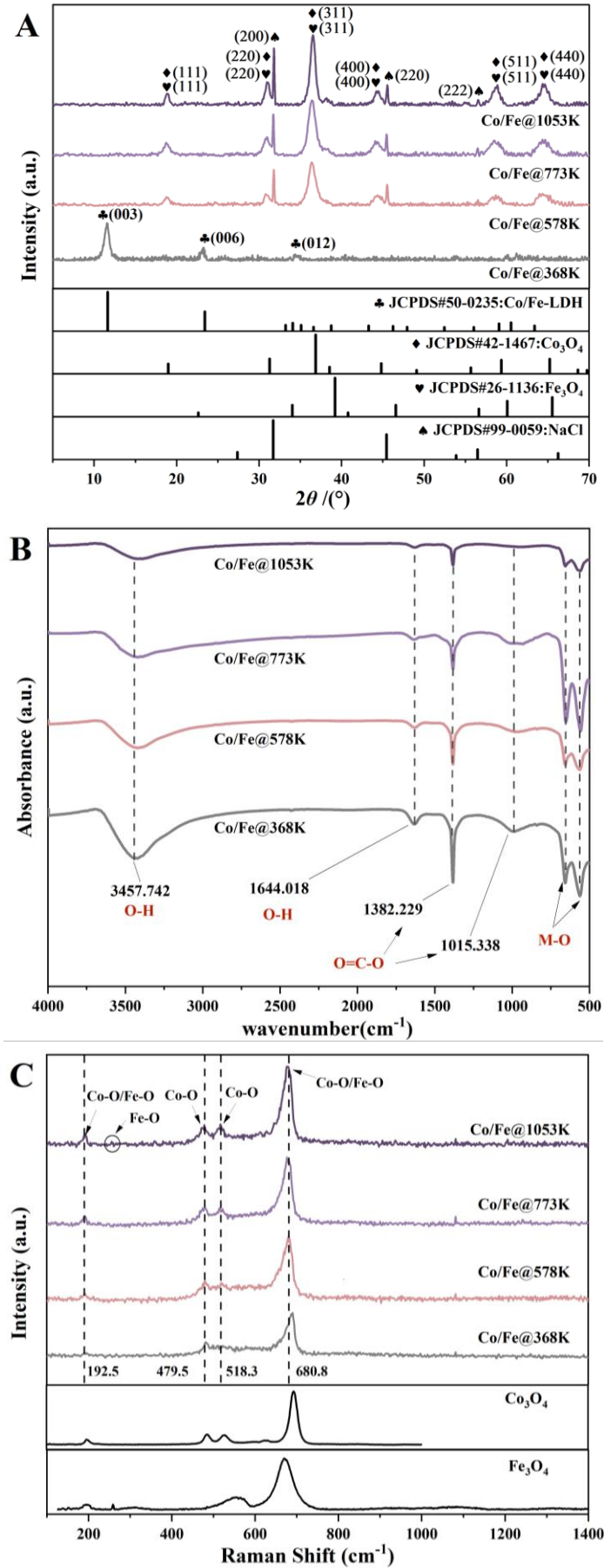


Fig. 2. XRD patterns (A), FTIR spectra (B), and Raman spectra (C) of Co/Fe-LDHs samples throughout the thermoreconstitution process ($\beta_i = 10$ K/min).

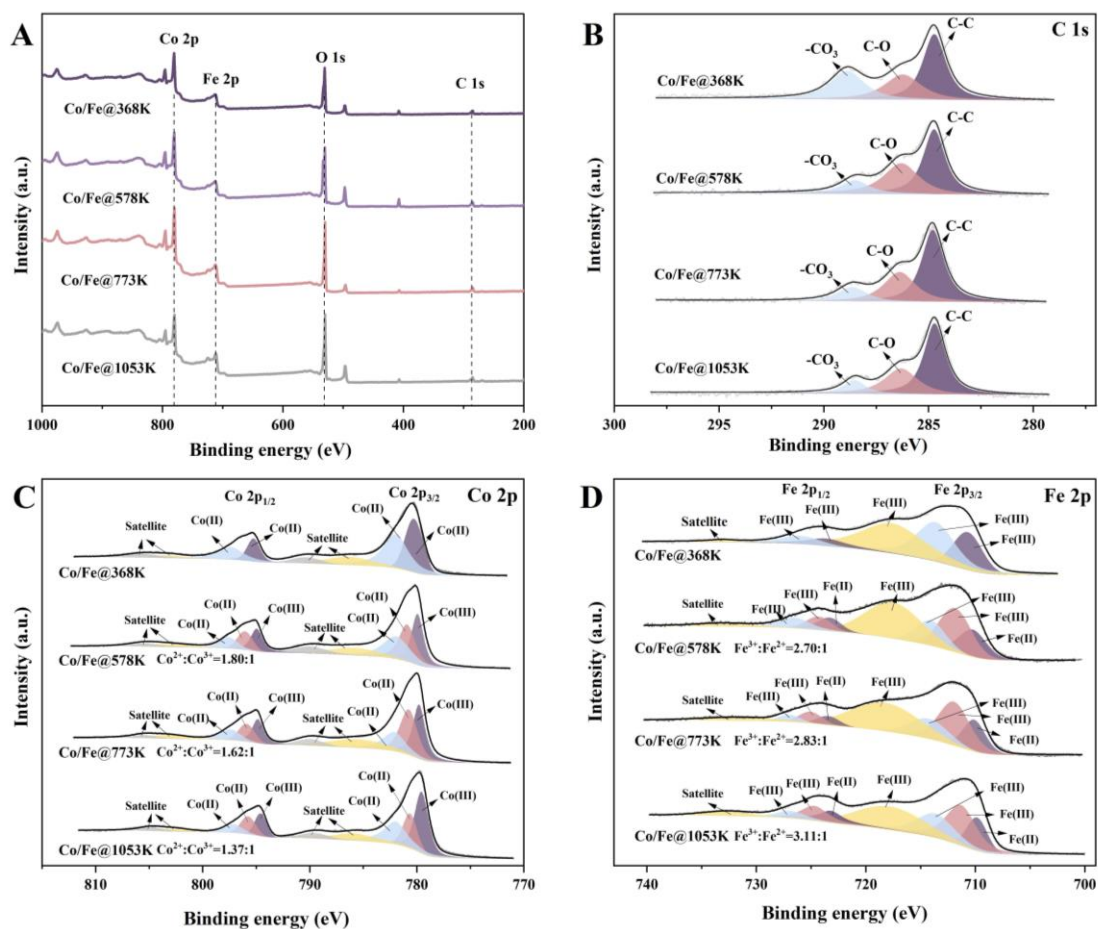


Fig. 3. XPS spectra of the full-range (A), C1s (B), Co 2p (C), and Fe 2p (D) on the surface of Co/Fe@368K, Co/Fe@578K, Co/Fe@773K, and Co/Fe@1053K.

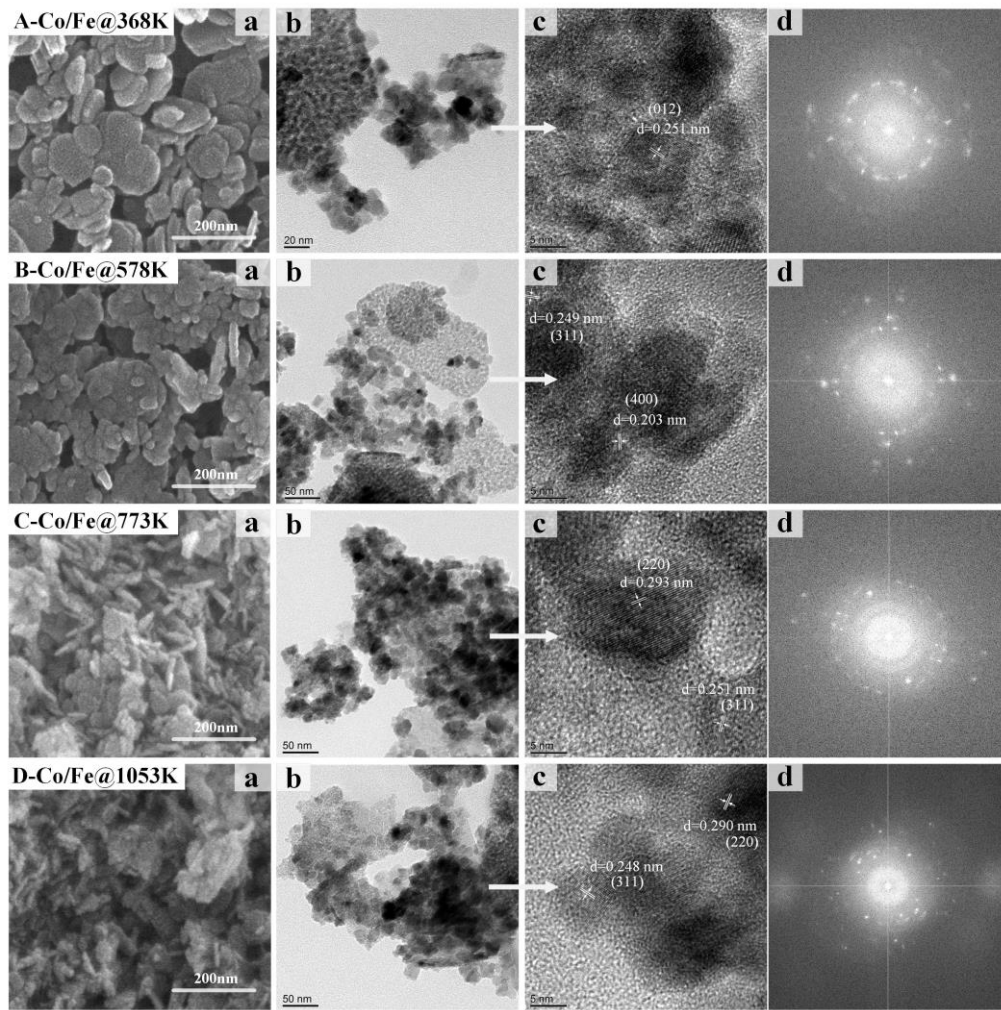


Fig. 4. SEM images (a), HRTEM images (b), Lattice structure (c) and FFT images (d) of Co/Fe-LDH at different temperatures (A-D).

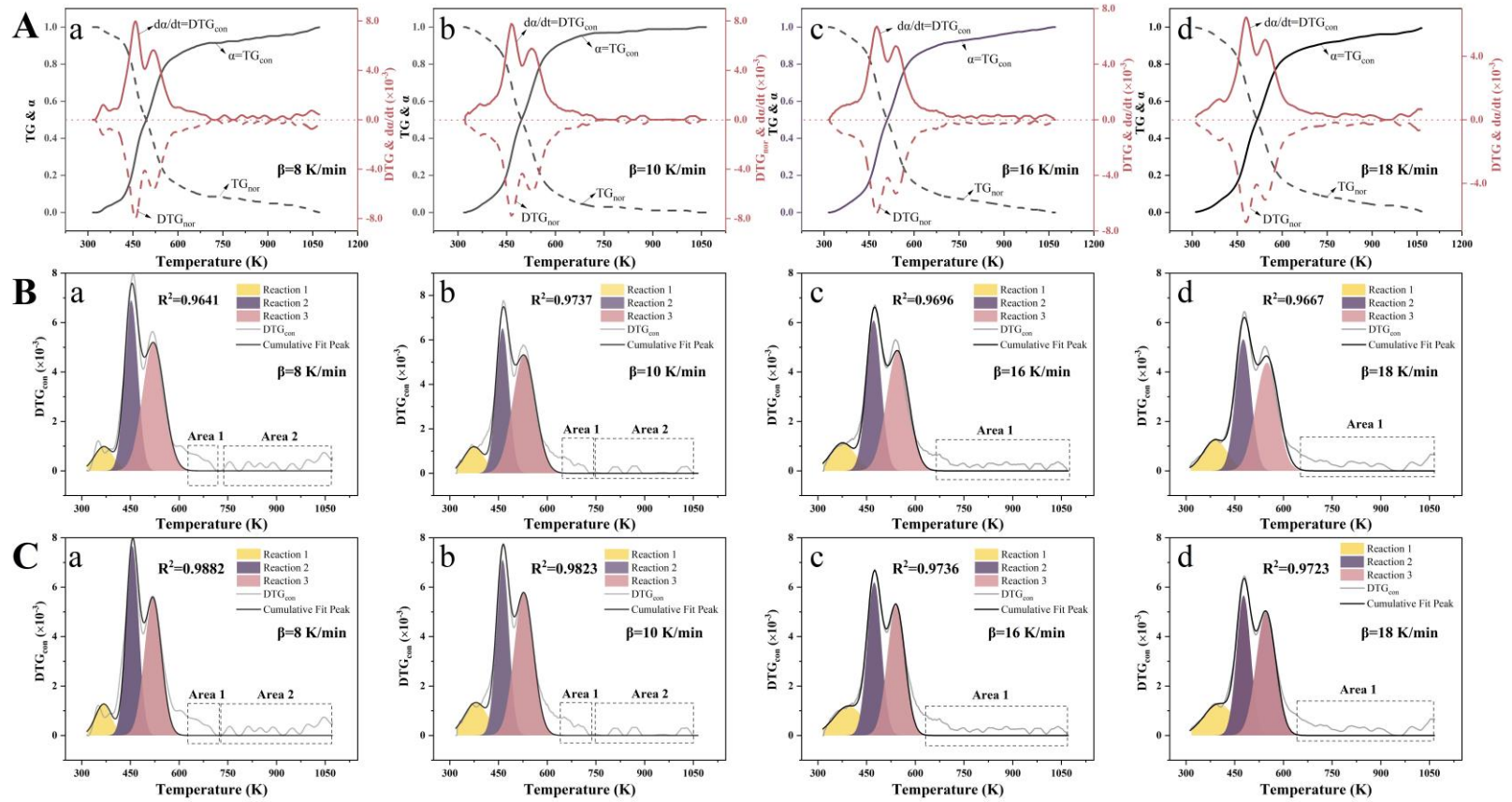


Fig. 5. TG_{nor}/DTG_{nor} and TG_{con}/DTG_{con} curves of Co/Fe-LDHs under various of β_i (A); the deconvolution of DTG_{con} ($\beta_i = 10$ K/min) into Reaction 1, Reaction 2 and Reaction 3 via Gaussian probability distribution function, G-PDF, (B) and Frazer-Suzuki function, F-SF, (C).

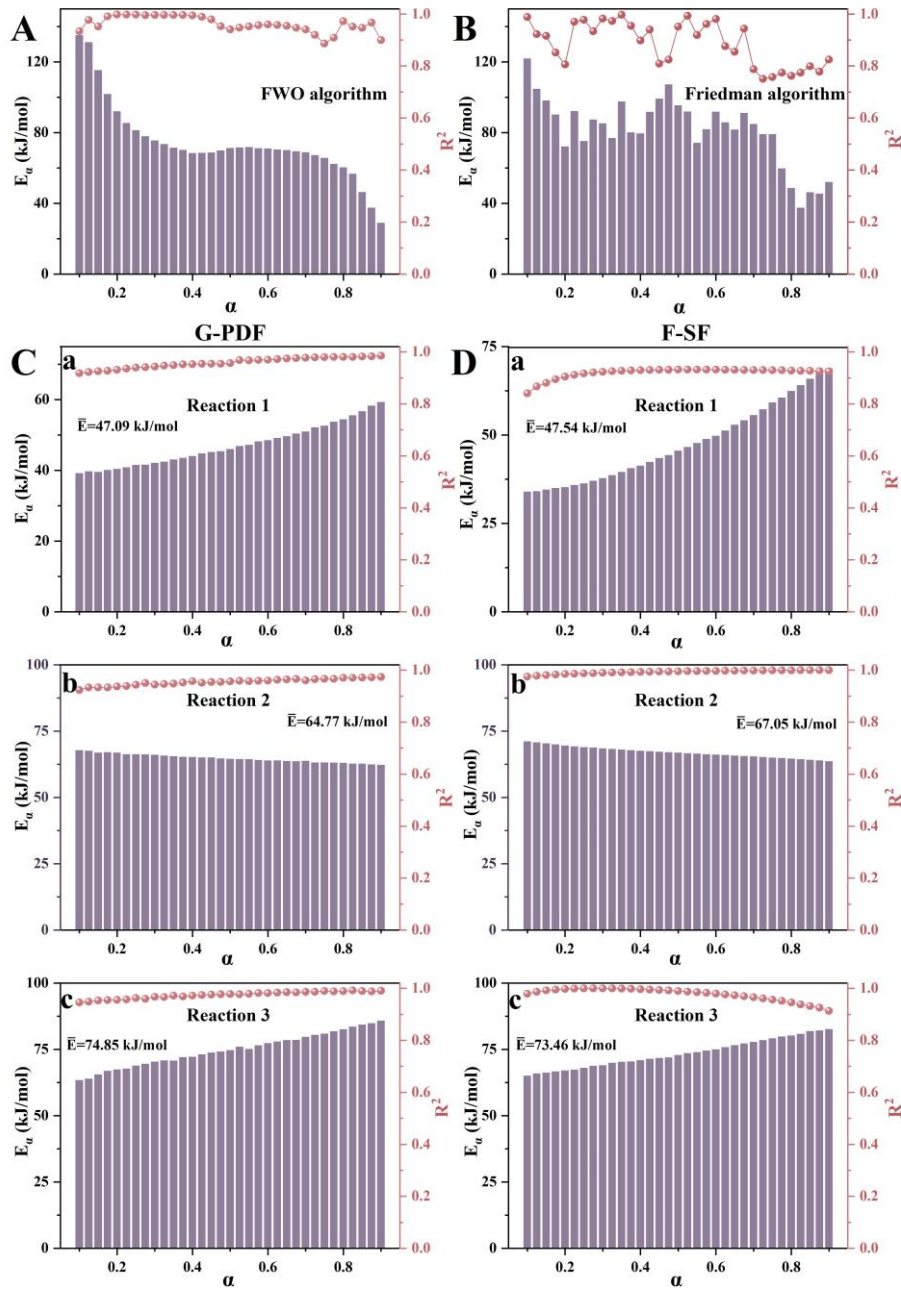


Fig. 6. E_α versus α throughout the Co/Fe-LDHs thermoreconstitution process with E_α values calculated through FWO algorithm(A) and Friedman algorithm (B);

The distribution of E_α values calculated via FWO algorithm in Reaction 1(a),

Reaction 2(b), and Reaction 3(c) separated with G-PDF (C) and F-SF (D). All

calculations were conducted as $\alpha \in (0.1, 0.9)$ with the stepping constant of α , i.e.,

$$\Delta\alpha = 0.025.$$

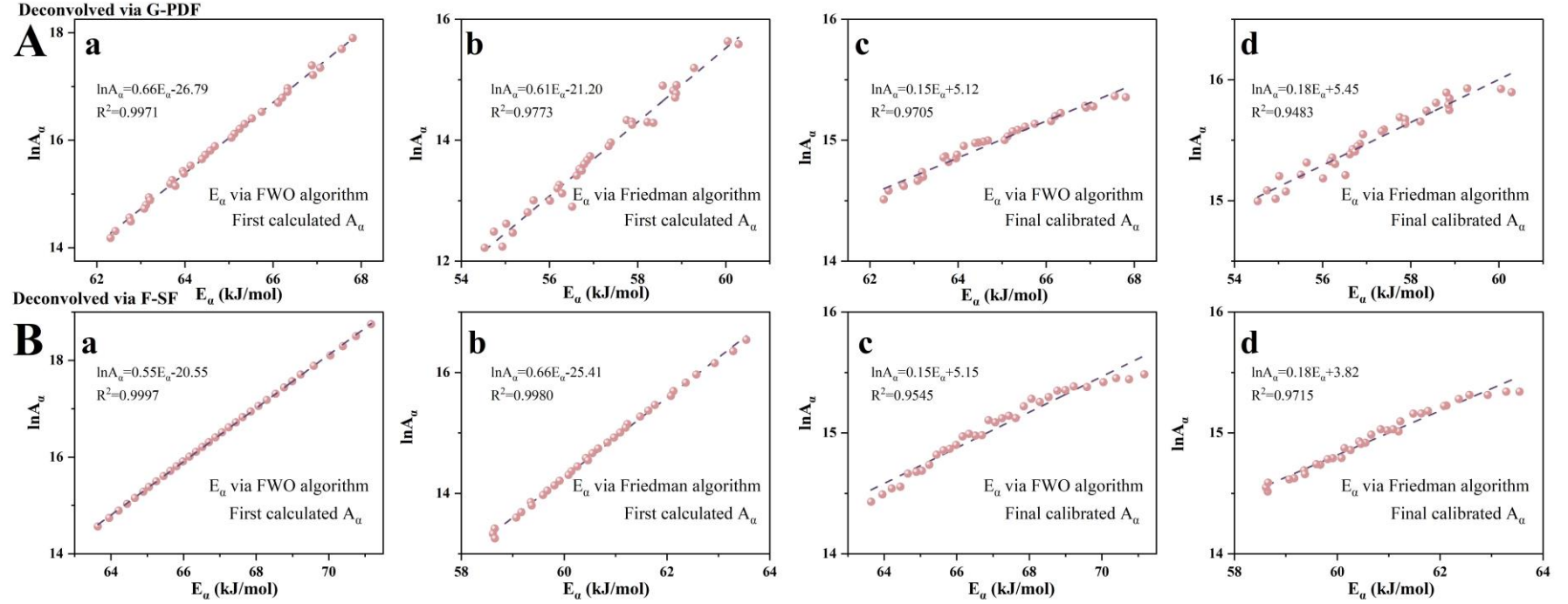


Fig. 7. Relaying on the TG_{con}/DTG_{con} curves deconvolved through G-PDF (A) and F-SF (B), the “compensation effect” between $\ln A_\alpha$ and E_α plotted with the first calculated A_α versus E_α , (a) and (b); the “compensation effect” between the final calibrated A_α versus E_α , (c) and (d).

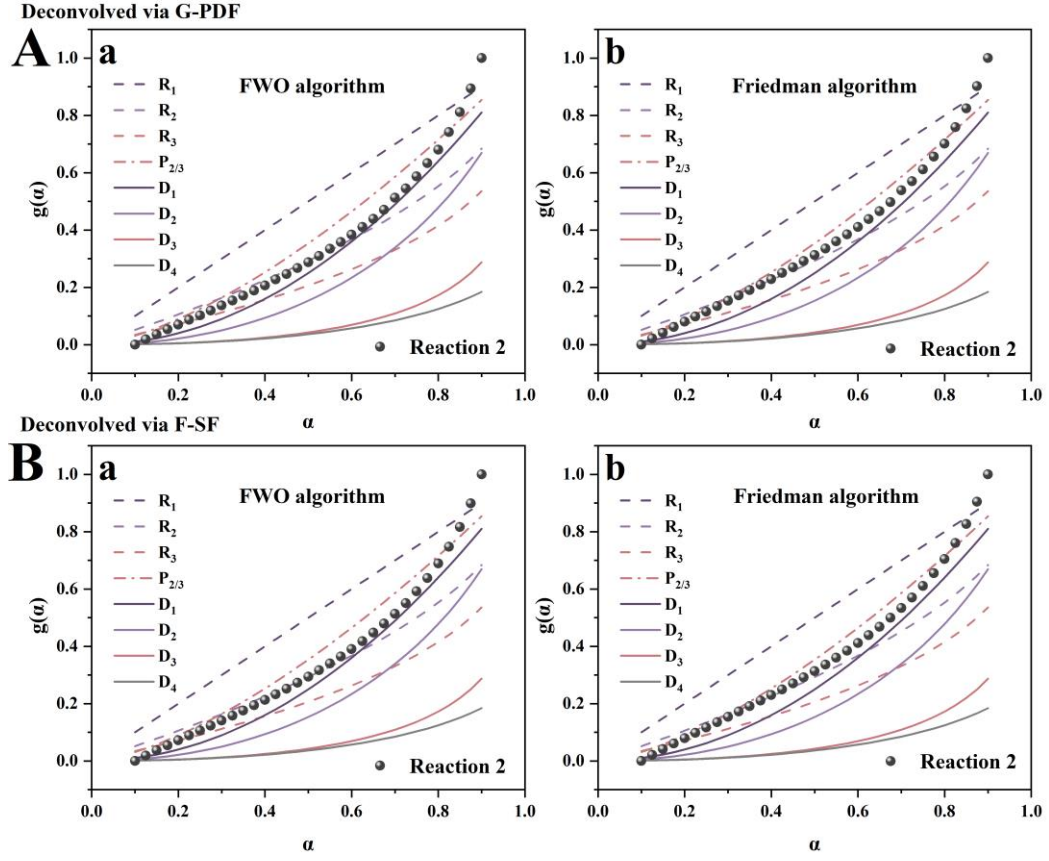


Fig. 8. the $g(\alpha)$ profiles of Reactions 2 deconvolved through G-PDF (A) and F-SF

(B) and plotted with $\overline{E_\alpha}$ calculated under FWO algorithm (a) and Friedman

algorithm (b), respectively. $\overline{A_\alpha}$ and $\overline{E_\alpha}$ values are listed in Table 1.

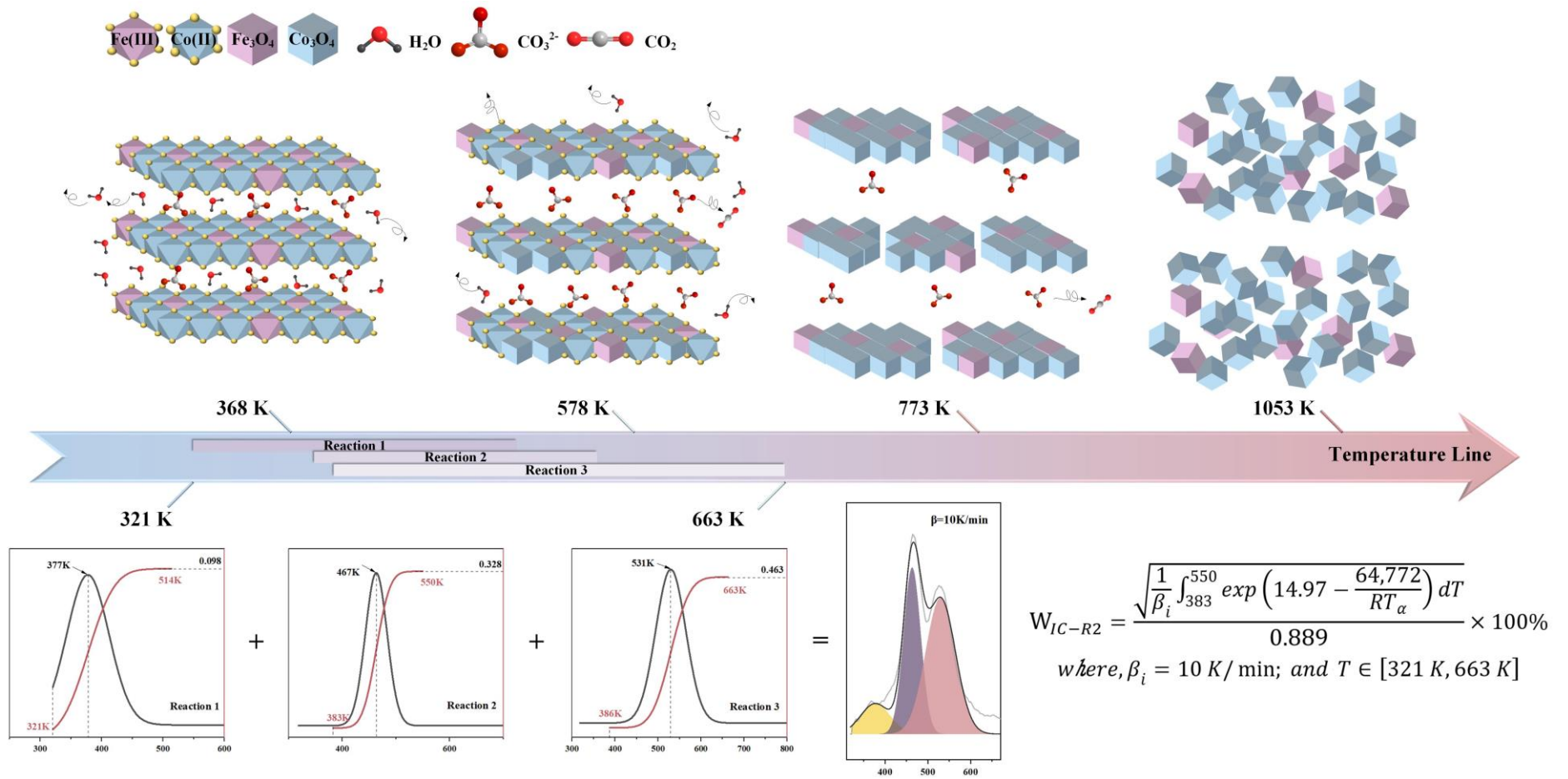
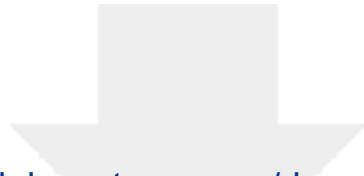


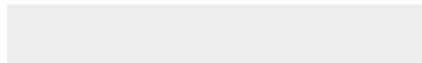
Fig. 9. The schematic diagram of the Co/Fe-LDHs thermoreconstitution process.



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Supplementary File

11- Supplementary Materials.docx



Declaration of interests

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

☒The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Yuanfeng Qi reports financial support was provided by China Scholarship Council. Yuanfeng Qi reports financial support was provided by the Key Research and Development Program (Major technical innovation projects) of Shandong Province. Kai He reports financial support was provided by the Guangdong Basic and Applied Basic Research Foundation. Kai He reports financial support was provided by Guangdong Foundation for Program of Science and Technology Research.

CRedit authorship contribution statement

Yuanfeng Qi: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. Resources

Xiao Quan: Methodology, Data curation, Investigation, Calculation, Visualization.

Toshimitsu Hata: Supervision, Writing –review & editing

Xiao Lu: Formal analysis, Visualization, Calculation, Writing - original draft.

Chang Xu: Conceptualization, Methodology, Writing –review.

BaoXin Ge: Investigation, Calculation, Visualization

Kai He: Resources, Calculation, Writing - review & editing, Supervision.