Supporting Information Thermal Dehydration of Lithium Sulfate Monohydrate Revisited with Universal Kinetic Description over Different Temperatures and Atmospheric Water Vapor Pressures

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S1. Literature Survey

Table S1 summarizes the previous studies for the thermal dehydration of LSM, which report the kinetic parameters of E_a and $\ln A$.^{S1-S23} Before 1990, Vasil'ev and Ershova, ^{S1} Okhotnikov et al., ^{S2-S5} and Koga and Tanaka^{S6, S7} had reported their kinetic results. Okhotonikov et al. used a quartz crystal microbalance to study the linear advancement of the reaction interface for the reactions of single crystal and pellet samples. Koga and Tanaka used simultaneous TG-DSC instrument and investigated the reactions of single crystal and crushed crystals with different particle size fractions in N₂ flow under isothermal and nonisothermal conditions. They also employed polarizing microscopy for observing the reaction geometry and the morphology of the reaction interface. Based on these studies, the ICTAC kinetics committee (chairman: J.H. Flynn at that time) proposed a project for establishing the kinetic analysis procedures using thermal analysis as exemplified by the thermal dehvdration of LSM.^{S24} With responding to the proposal, many researchers concentrated to the kinetic study of the thermal dehydration of LSM focusing on various experimental and calculational factors that influence on the kinetics and kinetic results during 1990-1993.^{S9-S16, S18, S25} Further detailed studies mainly focused on the physico-geometrical reaction mechanisms^{\$20, \$21, \$26, \$27} and the effect of water vapor^{\$17, \$28-\$30} were continued up until today.

Figure S1 shows the mutual dependence of the reported E_a and $\ln A$ values. Although two statistically significant linear correlations are observed in parallel, majority of the reported kinetic data is on the line drawn for the kinetic parameters reported by Koga and Tanaka.^{S7} The other line is drawn for the kinetic parameters reported by Huang and Gallagher.^{S13} They calculated E_a and $\ln A$ values using Ozawa method without considering kinetic model function; thus, the reported $\ln A$ values are the intercept of the Ozawa plot, which is the approximation of $\ln A$ value and the cause of the parallel shift from the line drawn for the data of Koga and Tanaka. The linear correlation of the experimentally determined kinetic parameters, known as the kinetic compensation effect, ^{S31-S38} is one of the problems that remain to be solved in the formal kinetic analysis of the reactions using thermal analysis.



Figure S1. An apparent mutual dependence between E_a and $\ln A$ observed for the previously reported kinetic parameters for the thermal dehydration of LSM.

Ref.	Sample	Particle Size	Technique	Condition	Atmosphere	Sample	Calculation	Kinetic	Kinetic P	arameters
						Mass	method	Model	$E_{ m a}$ / kJ mol $^{-1}$	$\ln (A / s^{-1})$
S1	Powder	0.315±0.100 mm	Quartz- spiral micro- balance	Isothermal (<i>T</i> = 351– 401 K)	Air (2, 100, and 760 mmHg)	10 mg	isothermal	A(<i>m</i>)	60–74	
S2	Single crystal	$0.5 \times 0.3 \times 0.03$ cm parallelepiped	Quartz- crystal micro- balance		Vacuum condition (residual pressure within 4×10^{-5} Pa)				87	33
S3	Single crystal	0.1 cm thickness	Quartz- crystal	Isothermal $(T = 343 \text{ K})$	Vacuum condition (residual pressure				85	12.8
	Pellets		micro- balance		within 4×10^{-5} Pa)				79	10.6

Table S1. A brief summary of the kinetic results reported previously for the thermal dehydration of LSM

continue

Ref.	Sample	Particle Size	Technique	Condition	Atmosphere	Sample	Calculation	Kinetic	Kinetic P	arameters
						Mass	method	Model	$E_{\rm a}$ / kJ mol $^{-1}$	$\ln (A / s^{-1})$
S6	Powder	-170+200 mesh	TG–DSC	Isothermal $(T = 368 - 376 \text{ K})$	N_2 flow (50 cm ³ min ⁻¹)	20 mg	Isothermal	R(n) or $A(m)$	123	32
				Nonisothermal $(\beta = 0.55 - 2.41 \text{ K min}^{-1})$			Coats & Redfern (CR)		91–165	23–45
S7	Single crystal		TG–DSC	Isothermal $(T = 386 - 526 \text{ K})$	N_2 flow (30 cm ³ min ⁻¹)	15 mg	Isothermal	R(n) or $A(m)$	104–115	24–27
				Nonisothermal $(\beta = 0.47 - 8.04 \text{ K min}^{-1})$			CR Ozawa + Master plot (MP)	R(n) or $A(m)$	82–105	17–25
	Powder	-100+170 mesh		Isothermal $(T = 358 - 372 \text{ K})$			Isothermal	R(n) or $A(m)$	89–93	22–23
				Nonisothermal			CR	R(<i>n</i>) or	103-126	26–34
		-48+100 mesh		$(\beta = 0.45 - 7.67 \text{ K min}^{-1})$			Ozawa + MP	A(<i>m</i>)	103–128	25–34
	~ 1 1	-170+200 mesh						R(2.44)	108	27
S8	Crushed single	-100+170 mesh	TG–DSC	Nonisothermal $(\beta = 0.45 - 7.58 \text{ K min}^{-1})$	N_2 flow (30 cm ³ min ⁻¹)	15 mg	Ozawa + MP	R(n) or $A(m)$	103–125	26–33
	crystal		TG–DTA	Nonisothermal $(\beta = 0.45 - 7.66 \text{ K min}^{-1})$					112–136	28–37
S9	Single crystal		EGD	Isothermal $(T = 360-400 \text{ K})$	$p(H_2O): < 10^{-4}$ Torr	20–40 mg	Isothermal	R(n) or $A(m)$	73–87	14–18
	Crushed single crystal	-100+200 mesh	Isotherr $(T = 349-3)$	Isothermal (<i>T</i> = 349–377 K)		30 mg		R_{n} or D_{4} or F_{1}	71–103	16–23
	Rehydrated crystal			Isothermal $(T = 367 - 397 \text{ K})$		20–40 mg		R(n) or $A(m)$	65–66	14–15
S10	Single crystal		TG–DSC	Nonisothermal ($\beta = 0.47 - 8.04 \text{ K min}^{-1}$)	N ₂ flow		CR Ozawa + MP	R(3) or A(1)	78–272	15–76
	Crushed single crystal	-48+100 mesh -100+170 mesh -170+200 mesh	TG–DSC	Nonisothermal $(\beta = 0.5 - 8.0 \text{ K min}^{-1})$	N ₂ flow		Friedman + MP	$\begin{array}{c} \mathbf{R}(n) \text{ or} \\ \mathbf{A}(m) \end{array}$	103–154	25-43
	Crushed single crystal	-100+170 mesh	TG–DSC	Nonisothermal $(\beta = 0.5 - 8.0 \text{ K min}^{-1})$	N ₂ flow	10–25 mg		A(<i>m</i>)	90–103	22–26
S11	Crushed single crystal	-100+170 mesh	TG	Isothermal $(T = 352 - 373 \text{ K})$	N ₂ flow (30 cm ³ min ⁻¹)	2.5–25 mg	Isothermal	R(1)	98	26

continue

Ref.	Sample	Particle Size	Technique	Condition Atmosphere		Sample	Calculation	Kinetic	Kinetic Pa	arameters
						Mass	method	Model	$E_{\rm a}$ / kJ mol ⁻¹	$\ln (A / s^{-1})$
S13	Powder		TG	Nonisothermal	N_2 flow (20 cm ³ min ⁻¹)	36–38 mg	Ozawa		86-220	26-70
				$(\beta = 0.5 - 10 \text{ K min}^{-1})$	$p(H_2O) (35 \text{ cm}^3 \text{ min}^{-1})$				80-114	24–36
			DSC	Nonisothermal	N ₂ flow (20 cc min ⁻¹)				73-85	23–27
				$(\beta = 0.5 - 10 \text{ K min}^{-1})$						
	Pellet	$2 \times 2 \times 1 \text{ mm}$	TG	Nonisothermal	N_2 flow (20 cm ³ min ⁻¹)				61–94	19–29
				$(\beta = 0.5 - 10 \text{ K min}^{-1})$	$p({\rm H_2O}) (35 \text{ cm}^3 \text{ min}^{-1})$				71–96	21–29
			DSC	Nonisothermal	N ₂ flow (20 cc min ^{-1})				51-72	16–23
				$(\beta = 0.5 - 10 \text{ K min}^{-1})$						
	Crystals	Cubic	TG	Nonisothermal	N_2 flow (20 cm ³ min ⁻¹)				71-88	20–26
				$(\beta = 0.5 - 10 \text{ K min}^{-1})$	$p({ m H_2O}) (35 \ { m cm^3 \ min^{-1}})$				74–108	21–32
			DSC	Nonisothermal	N_2 flow (20 cm ³ min ⁻¹)				70–78	20–24
				$(\beta = 0.5 - 10 \text{ K min}^{-1})$						
	Single	Plate: 0.1–0.3	TG	Nonisothermal	N_2 flow (20 cm ³ min ⁻¹)				74–105	21–32
	crystals	mm thickness		$(\beta = 0.5 - 10 \text{ K min}^{-1})$	$p({\rm H}_2{\rm O})$ (35 cm ³ min ⁻¹)				81–117	23–35
			DSC	Nonisothermal	N_2 flow (20 cm ³ min ⁻¹)				66–84	19–26
				$(\beta = 0.5 - 10 \text{ K min}^{-1})$						
S14	Single		EGD	Isothermal	<i>p</i> (H ₂ O): 0–10 Torr	30–44 mg	Isothermal	R(n) or $A(1)$	105–110	24–27
	crystal(A)	1.50		(T = 362 - 402 K)		14.00			05.00	20.24
	Crushed	Crushed $< 150 \mu m$ Is	Isothermal $(T - 222, 2(2, K))$		14–22 mg		R(n) or $A(1)$	85–92	20–24	
	single			(I = 323 - 303 K)						
\$15	Crushed	< 150 um	DSC	Isothermol	Na flow		Isothermol		66 70	14.20
515	single	< 150 µm	DSC	isotiletillai	1N2 110 W		isotileitilai		00-79	14-20
	crystal(A)			Nonisothermal		2.6 mg	Borchardt and		120-121	32-33
	orystat(11)			$(\beta = 2 - 20 \text{ K min}^{-1})$		2.0 mg	Daniels (BD)		120 121	52 55
	Single		EGD	(p 2 20 R mm)			Isothermal	R(n) or $A(1)$	101	22-24
	crystal(B)		DSC	Isothermal	N ₂ flow	15.7 mg	Isothermal	R(n) or $A(1)$	95	25
	5 ()			(T = 363 - 413 K)				(-)		
				Nonisothermal		9.3 mg	BD		98	20
				$(\beta = 5 \text{ K min}^{-1})$		U				
			TG	Isothermal			Isothermal	A(1)	60-84	11–22
				(T = 323 - 393 K)						
				Nonisothermal			BD		93	20
				$(\beta = 5 \text{ K min}^{-1})$						
S16	Powder	-100+150 mesh	TG	Isothermal	Vacuum condition: $5 \times$	5 mg	Isothermal	A(2) or R(2)	22–29	1–2
				(T = 343 - 408 K)	10 ⁻⁴ Torr					

continue

Ref.	Sample	Particle Size	Technique	Condition	Atmosphere	Sample	Calculation	Kinetic	Kinetic P	arameters
						Mass	method	Model	$E_{ m a}$ / kJ mol $^{-1}$	$\ln (A / s^{-1})$
S17	Powder	-100+150 mesh	TG–DTA	Isothermal $(T = 363 - 393 \text{ K})$	$p(H_2O) = 280 \text{ Pa} (60 \text{ cm}^3 \text{ min}^{-1})$	6 mg	Isothermal	A(2) or R(2)	110	29
					$p(H_2O) = 1.3 \text{ kPa} (60 \text{ cm}^3 \text{ min}^{-1})$				118	31
					$p(H_2O) = 2.7 \text{ kPa} (60 \text{ cm}^3 \text{ min}^{-1})$				141	38
S18	Single crystal		TG	CRTA (C = 0.03 h ⁻¹)	Vacuum condition: 8 × 10^{-3} mbar	19 mg	MP + differential	A(3)	60	9
	Powder			CRTA ($C = 0.02 \text{ h}^{-1}$)		24 mg	single run	A(2) or A(3)	38–41	3
				CRTA ($C = 0.3 \text{ h}^{-1}$)	Vacuum condition: 5 × 10^{-5} mbar	275.6 mg		R(<i>n</i>) or A(1)	30–64	9–10
S19	Powder	100 mesh	DSC	Nonisothermal $(\beta = 6-10 \text{ K min}^{-1})$	Static air	5.0 mg	Integral isoconversional	A(<i>m</i>)	65	14
S20	Single crystal	plate	microscope	Isothermal $(T = 373-413 \text{ K})$	Humidified air: 13 mbar (230 cm ³ min ⁻¹)		Isothermal		Nucleation: 240 Growth in the bulk: 88	Nucleation: 78 Growth in the bulk: 29
S22	Reagent	ACROS Organics	DSC	Nonisothermal $(\beta = 0.05-20 \text{ K min}^{-1})$	N ₂ flow (80 cm ³ min ⁻¹)	~7.2 mg	Isoconversional Vyazovkin		70–150	17–40
S23	Reagent		DSC	Nonisothermal $(\beta = 2-10 \text{ K min}^{-1})$	$N_2 \text{ flow} = 0.1 \text{ MPa} (200 \text{ cm}^3 \text{ min}^{-1})$	3.6 mg			85–130	20–34
					$N_2 \text{ flow} = 7 \text{ MPa} (200 \text{ cm}^3 \text{ min}^{-1})$				60–135	12–35

S2. Sample Characterization

(1) Microscopic observation: Appearance of the collected single crystals were observed using a stereomicroscope (SZX7, Olympus). The single crystals are hexagonal plates with well-developed crystal faces and optically transparent (Figure S2). Each single crystal has a size charaterized by length of the long axis in an approximate range from 1.0 to 2.0 mm and the thickness in a range from 0.2 to 0.4 mm.



Figure S2. Appearance of the LSM crystals.

(2) XRD: The single crystals were ground using an agate mortar and pestle to obtain powders. The powdered sample was pressfitted on a platinum sample holder for XRD measurement. The XRD pattern of the sample was recoreded using a diffractometer (RINT 2200V, Rigaku) in the 2θ range from 5 to 60° scanned at a rate of 4° min⁻¹ in steps of 0.01° by radiating X-ray (monochrome Cu-K_a, 40 kV, 20 mA). The XRD pattern of the powdered sample (Figure S3) perfectly corresponded to that reported for LSM (monoclinic, S.G.: $P2_1(4)$, a = 5.4500, b = 4.8720, c = 8.1640, $\beta = 107.310$, ICDD 01-084-0647).^{S39, S40}

(3) FT-IR: The FT-IR spectrum of the powered sample was recorded using a spectrometer (FT-IR 8400S, Shimadzu) by the diffuse reflectance method after diluting the sample with KBr. The IR spectrum (Figure S4) shows typical IR absorption peaks reported previously for LSM.^{S41} The O–H streching and H–O–H bending bands are observed at 3487 and 1612 cm⁻¹, respectively. Th absorption peaks at 1176 and 1119 cm⁻¹ are attributed to v_3 mode of SO₄^{2–}. The peaks at 1013, 640, and 474 cm⁻¹ are identified as the v_1 , v_4 , and v_3 modes of SO₄^{2–}, respectively. The H₂O libration and Li–OH₂ streaching vibrations appear at 573 and 444 cm⁻¹, respectively.

(4) TG–DTA: Approximately 5 mg of the single crystals were weighed into a platinum cell (5 mm in diameter and 2.5 mm in height). The sample was heated in a TG–DTA instrument (TG-8121, Thermoplus Evo2, Rigaku) at a β of 5 K min⁻¹ in flowing dry N₂ gas (flowrate: 300 cm³ min⁻¹). The TG–DTA curves (Figure S5) indicated the smooth mass-loss curve that

start at approximately 373 K and accompanied DTA endothermic peak. The observed mass-loss value agreed with that calculated for the thermal dehydration of LSM (Eq. (2)).



Figure S3. XRD pattern of the LSM crystals.



Figure S4. FT-IR spectrum of the LSM crystals.



Figure S5. TG–DTA curves for the thermal dehydration of the LSM crystals ($m_0 = 5.129 \text{ mg}$), recorded at a β of 5 K min⁻¹ in flowing dry N₂ (flowrate: 300 cm³ min⁻¹).

(5) High temperature XRD: The changes in the XRD pattern of the sample in the temperature range corresponding to the mass-loss process were traced using the aforementioned XRD instrument by equipping a heating chamber with the temperature controller (PTC-20A, Rigaku). The powdered sample, fitted to the platinum plate, was heated at a β of 2 K min⁻¹ from room temperature to 423 K in flowing dry N_2 gas (flowrate: 300 cm³ min⁻¹). During heating the sample, the sample temperature was held at various temperatures from 323 to 423 K in steps of 10 K for each 15 min interval. The XRD measurements were performed during the isothermal holding periods (Figure S6(a)), in corresponding with the temperature range of the mass-loss observed by the TG-DTA measurement (Figure S5). The XRD pattern of the product solid (Figure S6(b)) perfectly agrees with that reported for Li₂SO₄ (monoclinic, S.G.: $P2_1(4)$, a = $8.250, b = 4.950, c = 8.440, \beta = 107.900, ICDD 01-075-$ 0929).

S3. Instrumental

Both of the TG–DTA instruments (TG-8120 and TG-8121, Rigaku) are constructed by a horizontally arranged differential balance and electric furnace (PtPR13%). TG-8121 used for the measurements of TG–DTA curves in flowing N₂ gas is equipped with the flow rate controller. Figure S7 shows the configuration of the instrument for the measurements in flowing wet N₂ gas with various controlled $p(H_2O)$ values. The measurement system (HUM-TG, Thermoplus 2, Rigaku) is composed of TG-8120, humidity controller (HUM-1, Rigaku), temperature-controlled water circulator (F-24, Julabo), and temperature-controlled transfer tube that transfer wet N₂ gas from the humidity controller to TG-8120.



Figure S6. Change in the XRD pattern on heating the LSM crystals: (a) XRD patterns at different temperatures and (b) XRD pattern of the dehydration product at 423 K.



Figure S7. Schematic illustration of the humidity control TG–DTA system (HUM-TG, Thermoplus 2, Rigaku).

Previously to the measurements, calibration for the measured sample temperature and mass-change value were performed using standard methods under the atmospheric conditions that apply to the sample measurements, i.e., in flowing dry N₂ gas (300 cm³ min⁻¹) for TG-8121 and in flowing wet N₂ gas (400 cm³ min⁻¹) with the controlled $p(H_2O)$ value of approximately 5 kPa for TG-8120. Sample temperature was calibrated via the DTA measurements of melting point of various pure metals (Ga, In, Sn, Pb, Zn, Al, and

Ag; > 99.99%, Nilaco) at a β of 5 K min⁻¹. The masschange value was initially calibrated bv addition/removal of a standard weight of a 10 mg to/from the sample holder at ambient conditions by opening the furnace. Subsequently, the TG-DTA curves for the thermal decomposition of CaC_2O_4 ·H₂O (>99.9985%, Alfa Aesar) at a β of 5 K min⁻¹ under the respective atmospheric conditions for TG-8121 and TG-8120. The recorded mass-loss values for the three thermal decomposition steps were compared with those calculated values to confirm the reliability of the measured mass-loss value by TG.

For the TG-DTA measurements in flowing N₂ using TG-8121, approximately 5.0 mg of Al₂O₃ weighed into a Pt sample pan was used as the reference material for the DTA and the counter balance. In the TG measurements in flowing wet N2 gas with controlled $p(H_2O)$ values using TG-8120, only Pt pan was used for the counter balance for avoiding the absorption of water vapor on the reference material. For the measurements in flowing wet N2 gas using the system shown in Figure S7, the reaction chamber of the TG-8120 and the gas transfer tube were preliminary heated at a temperature higher by approximately 15 K than the drew point of respective $p(H_2O)$ values applied to the measurements. At the same time, balance system was continuously purged by flowing dry N2 gas (flowrate: 50 cm³ min⁻¹) for avoiding possible inflow of wet N_2 gas. Figure S8 shows typical records of TG measurements in flowing wet N2 gas under isothermal (Figure S8(a)) and linear nonisothermal (Figure S8(b)) conditions. The measurements started in flowing dry N2 gas (flowrate: 400 cm³ min⁻¹) and the sample was heated at a β of 5 K min⁻¹ to a temperature higher by



Figure S9. Conventional Arrhenius plots for the IP of the thermal dehydration of LSM at each $p(H_2O)$ value.

approximately 15 K than the drew point of the $p(H_2O)$ value lately applied to the measurement. Immediately after the sample temperature achieved the programmed temperature, the atmosphere in the furnace tube was switched to that in flowing wet N₂ gas (flowrate: 400 $cm^3 min^{-1}$) with the controlled $p(H_2O)$ value and the measurement system was stabilized for 30 min by holding the sample temperature at constant. Then, the sample was heated according to various temperature programs to record TG curves.



Figure S8. Typical mass-change records for the thermal dehydration of LSM in flowing wet N2 gas with $p(H_2O) = 8.63$ kPa under (a)isothermal (T = 394 K, m_0 = 5.495 mg) and (b) linear nonisothermal (β = 2 K min^{-1} , $m_0 = 5.018$ mg) conditions.

 Table S2. Apparent Arrhenius parameters for the IP of
 the thermal dehydration of LSM at each $p(H_2O)$ value, as determined by the conventional Arrhenius plot without considering the influence of $p(H_2O)$ value.

	υ	1 (=	/
p(H ₂ O) /kPa	$E_{ m a,IP}$ /kJ mol $^{-1}$	$\ln[A_{\rm IP}f(\alpha_{\rm IP})/{\rm s}^{-1}]$	$-\gamma^{a}$
0.26	152 ± 6	45.3 ± 1.7	0.9940
0.81	248 ± 27	74.2 ± 8.8	0.9771
3.65	256 ± 16	74.1 ± 5.0	0.9888
8.63	277 ± 15	79.0 ± 4.4	0.9897

^aCorrelation coefficient of the linear regression analysis.

S4. Formal Kinetic Analysis for the Induction Period



Figure S10. Schematic illustration of the assumed process of surface nucleation for the thermal dehydration of LSM.



Figure S11. Arrhenius plot for the IP of the thermal dehydration of LSM, modified by introducing the AF in Eq. (7) with (a, b) = (0, 1).

Table S3. Apparent Arrhenius parameters for the IP of the thermal dehydration of LSM at each $p(H_2O)$ value, as determined by the Arrhenius plot modified by introducing the AF in Eq. (7) with (a, b) = (0, 1).

$p(H_2O)$	$E_{\mathrm{a,IP}}$	$\ln[4mf(\alpha_{\rm TD})/s^{-1}]$	$-\gamma^{a}$	
/ kPa	/kJ mol ⁻¹	m[//lp/(alp)/s]	-γ	
0.26	151 ± 6	44.8 ± 1.7	0.9939	
0.81	245 ± 28	73.4 ± 8.8	0.9764	
3.65	248 ± 16	71.7 ± 5.0	0.9881	
8.63	264 ± 14	75.2 ± 4.3	0.9891	

^a Correlation coefficient of the linear regression analysis.



Figure S12. Arrhenius plot modified by the AF in Eq. (7) with the restriction of a = b, applied to the IP of the thermal decomposition of LSM in (a) the entire temperature range and (b) two separated temperature regions above and below 371 K.

Table S4. Kinetic parameters for the IP of the thermal dehydration of LSM, determined through the Arrhenius plots modified by introducing the AF in Eq. (7) with the restriction of a = b

Temperature range	а	b	$E_{\rm a,IP}$ / kJ mol ⁻¹	$\ln[A_{\rm IP}f(\alpha_{\rm IP})/s^{-1}]$	$-\gamma^{a}$
<i>T</i> < 371 K	2.25	2.25	151.9 ± 4.2	31.8 ± 1.4	0.9948
<i>T</i> > 371 K	1.93	1.93	260.8 ± 7.0	69.3 ± 2.2	0.9933

^a Correlation coefficient of the linear regression analysis.



Figure S13. The P_{eq} values at various temperatures and the $p(H_2O)$ values applied to the measurements of the kinetic data.

S5. Formal Kinetic Analysis for the Mass-Loss Process



Figure S14. Mass-loss curves for the thermal dehydration of LSM recorded under CRTA conditions in flowing wet N₂ gas with $p(H_2O) = 0.26$ kPa: (a) typical CRTA record ($m_0 = 4.980$ mg) and (b) temperature profiles during the mass-loss process recorded at different *C* values ($m_0 = 5.305 \pm 0.265$ mg).



Figure S15. Conventional Friedman plots at different α values for the mass-loss process of the thermal dehydration of LSM at each $p(H_2O)$ values: $p(H_2O) = (a) 0.26$, (b) 0.81, (c) 3.65, and (d) 8.71 kPa.

Table S5. Average E_a values for the mass-loss process of the thermal dehydration of LSM evaluated by the conventional Friedman plot at different $p(H_2O)$ values

$p(\mathrm{H_2O}) / \mathrm{kPa}$	α range	$E_{\rm a}$ / kJ mol ⁻¹
0.26	0.1 - 0.9	86.4 ± 2.0
0.81	0.2 - 0.9	108.3 ± 3.0
3.65	0.3 - 0.9	132.9 ± 2.8
8.71	0.4 - 0.9	163.3 ± 9.2



Figure S16. The experimental master plot for the thermal dehydration of LSM at $p(H_2O) = 0.26$ kPa, together with fitting curves using R(n) model.



Figure S17. Schematic illustration of the assumed process of interface reaction for the thermal dehydration of LSM.



Figure S18. Modified Friedman plots with the AF in Eq. (7) ($a \neq b$) applied to all the data points in the overall range of measured temperatures: (a)–(i) are at various α values from 0.1 to 0.9 in steps of 0.1, respectively.



Figure S19. Results of the modified Friedman plots $(a \neq b)$ applied to all the data points in the overall range of measured temperatures: (a) (a, b) values at various α values and (b) E_a values at various α values.



Figure S20. Modified Friedman plots with the AF in Eq. (7) (a = b) applied to all the data points in the overall range of measured temperatures: (a)–(i) are at various α values from 0.1 to 0.9 in steps of 0.1, respectively.



Figure S21. Results of the modified Friedman plots (a = b) applied to all the data points in the overall range of measured temperatures: (a) a (= b) values at various α values and (b) E_a values at various α values.



Figure S22. Modified Friedman plots with the AF in Eq. (7) ($a \neq b$) applied separately to the temperature ranges above and below 371 K: (a)–(i) are at various α values from 0.1 to 0.9 in steps of 0.1, respectively.



Figure S23. Modified Friedman plots with the AF in Eq. (7) (a = b) applied separately to the temperature ranges above and below 371 K: (a)–(i) are at various α values from 0.1 to 0.9 in steps of 0.1, respectively.



Figure S24. Results of the modified Friedman plots (a = b) applied to the individual temperature ranges above and below 371 K: (a) a (= b) values for the reaction at temperatures lower than 371 K at various α values, (b) a (= b) values for the reaction at temperatures higher than 371 K at various α values , and (c) comparison of E_a variations with α for the reactions in two temperature ranges.

S6. Kinetic Analysis Based on the Physico-Geometrical Consecutive Reaction Model

Table S6. Differential kinetic equations of the IP–SR–PBR(*n*) models

n	Condition	Kinetic equation
1	$t - t_{\mathrm{IP}} \le 1/k_{\mathrm{PBR}}$	$k_{\mathrm{PBR}} [1 - \exp(-k_{\mathrm{SR}}(t - t_{\mathrm{IP}}))]$
	$t - t_{\rm IP} \ge 1/k_{\rm PBR}$	$k_{\mathrm{PBR}} \mathrm{exp} \left(-k_{\mathrm{SR}} (t - t_{\mathrm{IP}}) \right) \left[\mathrm{exp} \left(\frac{k_{\mathrm{SR}}}{k_{\mathrm{PBR}}} \right) - 1 \right]$
2	$t - t_{\mathrm{IP}} \le 1/k_{\mathrm{PBR}}$	$-2k_{\rm PBR}\left[\left(1+\frac{k_{\rm PBR}}{k_{\rm SR}}\right)\exp\left(-k_{\rm SR}(t-t_{\rm IP})\right)+k_{\rm PBR}(t-t_{\rm IP})-\left(1+\frac{k_{\rm PBR}}{k_{\rm SR}}\right)\right]$
	$t - t_{\rm IP} \ge 1/k_{\rm PBR}$	$-2k_{\rm PBR}\exp\left(-k_{\rm SR}(t-t_{\rm IP})\right)\left[1+\frac{k_{\rm PBR}}{k_{\rm SR}}-\frac{k_{\rm PBR}}{k_{\rm SR}}\exp\left(\frac{k_{\rm SR}}{k_{\rm PBR}}\right)\right]$
3	$t - t_{\mathrm{IP}} \le 1/k_{\mathrm{PBR}}$	$-3k_{\rm PBR}\left[\left(1+2\frac{k_{\rm PBR}}{k_{\rm SR}}+2\left(\frac{k_{\rm PBR}}{k_{\rm SR}}\right)^{2}\right)\exp\left(-k_{\rm SR}(t-t_{\rm IP})\right)-\left(k_{\rm PBR}(t-t_{\rm IP})\right)^{2}+2k_{\rm PBR}\left(\frac{k_{\rm PBR}}{k_{\rm SR}}+1\right)(t-t_{\rm IP})-\left(1+2\frac{k_{\rm PBR}}{k_{\rm SR}}+2\left(\frac{k_{\rm PBR}}{k_{\rm SR}}\right)^{2}\right)\right]$
	$t - t_{\rm IP} \ge 1/k_{\rm PBR}$	$3k_{\rm PBR} \exp\left(-k_{\rm SR}(t-t_{\rm IP})\right) \left[2\left(\frac{k_{\rm PBR}}{k_{\rm SR}}\right)^2 \left(\exp\left(\frac{k_{\rm SR}}{k_{\rm PBR}}\right) - 1\right) - \left(1 + 2\frac{k_{\rm PBR}}{k_{\rm SR}}\right)\right]$

$p(\mathbf{H},\mathbf{O})/\mathbf{h}\mathbf{D}_{\mathbf{O}}$	T / V	$k_{ m IP}$	$k_{ m SR}$	$k_{\rm PBR(2)}$	R ^{2,a}		
$p(H_2O) / kPa$	<i>I /</i> K	$/ 10^{-4} \mathrm{s}^{-1}$	$/ 10^{-4} \mathrm{s}^{-1}$	/ 10 ⁻⁴ s ⁻¹	differential	integral	
0.81	363.4	4.87	0.84	1.18	0.9952	0.9988	
	367.0	7.12	1.44	2.89	0.9985	0.9989	
	369.5	10.64	1.92	4.94	0.9963	0.9954	
	373.1	32.26	2.90	6.90	0.9991	0.9976	
	375.8	45.05	4.44	12.81	0.9990	0.9983	
	378.6	68.97	5.42	14.31	0.9956	0.9952	
3.65	373.5	2.68	0.61	0.67	0.9918	0.9992	
	376.7	6.34	1.00	1.82	0.9939	0.9992	
	379.4	10.20	1.54	2.07	0.9968	0.9993	
	382.0	13.07	2.16	3.26	0.9961	0.9991	
	384.4	25.25	3.05	6.14	0.9986	0.9989	
	387.7	34.36	5.49	7.90	0.9991	0.9980	
	389.3	79.37	6.00	22.87	0.9480	0.9917	
8.63	382.1	2.32	0.76	0.50	0.9696	0.9960	
	384.6	4.25	0.63	1.70	0.9665	0.9868	
	387.7	11.24	1.63	3.00	0.9680	0.9753	
	390.5	16.53	1.91	4.88	0.9913	0.9969	
	394.4	31.75	3.66	6.43	0.9872	0.9933	

Table S7. Rate constants for the respective reaction steps optimized on the basis of the IP-SR-PBR(2) model

^a Determination coefficient of the nonlinear squares analysis.

Table S8. Rate constants for the respective reaction steps optimized on the basis of the IP-SR-PBR(3) model

$p(H_2O) / kPa$	T/K	k_{IP}	$k_{ m SR}$	$k_{\text{PBR}(3)}$ R ^{2,a}		,a
		$/ 10^{-4} \mathrm{s}^{-1}$	/ 10 ⁻⁴ s ⁻¹	$/ 10^{-4} \mathrm{s}^{-1}$	differential	integral
0.81	363.4	4.87	0.86	0.87	0.9945	0.9991
	367.0	7.12	1.47	2.10	0.9991	0.9992
	369.5	10.64	1.95	3.60	0.9970	0.9960
	373.1	32.26	2.94	5.09	0.9990	0.9980
	375.8	45.05	4.49	9.45	0.9989	0.9986
	378.6	68.97	5.49	10.43	0.9960	0.9958
3.65	373.5	2.68	0.62	0.48	0.9920	0.9992
	376.7	6.34	1.01	1.34	0.9940	0.9992
	379.4	10.20	1.56	1.55	0.9967	0.9994
	382.0	13.07	2.21	2.39	0.9959	0.9993
	384.4	25.25	3.10	4.48	0.9990	0.9991
	387.7	34.36	4.50	20.22	0.9300	0.9923
	389.3	79.37	6.50	22.87	0.9138	0.9934
8.63	382.1	2.32	0.89	0.31	0.9731	0.9974
	384.6	4.25	0.64	1.29	0.9672	0.9856
	387.7	11.24	1.64	2.27	0.9674	0.9744
	390.5	16.53	1.93	3.65	0.9915	0.9967
	394.4	31.75	3.68	4.85	0.9861	0.9929

^a Determination coefficient of the nonlinear squares analysis.



Figure S25. Conventional Arrhenius plots for the respective reaction steps at each $p(H_2O)$ value, applied to the rate constants optimized on the basis of the IP–SR–PBR(2) model: (a) IP, (b) SR, and (c) PBR(2).



Figure S26. Conventional Arrhenius plots for the respective reaction steps at each $p(H_2O)$ value, applied to the rate constants optimized on the basis of the IP–SR–PBR(3) model: (a) IP, (b) SR, and (c) PBR(3).

Table S9. Apparent Arrhenius parameters obtained through the conventional Arrhenius plots applied to the respective reaction steps at each $p(H_2O)$ value

Model	Reaction step	<i>p</i> (H ₂ O) / kPa	$E_{\rm a}$ / kJ mol ⁻¹	$\ln(A / s^{-1})$	$-\gamma^{a}$
IP-SR-PBR(2)	IP	0.81 ± 0.01	215.0 ± 17.4	63.4 ± 5.7	0.9872
		3.64 ± 0.04	234.1 ± 17.6	67.2 ± 5.6	0.9862
		8.63 ± 0.06	269.2 ± 23.3	76.5 ± 7.3	0.9889
	SR	0.81 ± 0.01	141.7 ± 4.9	37.6 ± 1.6	0.9976
		3.64 ± 0.04	179.2 ± 4.5	48.0 ± 1.5	0.9984
		8.63 ± 0.06	177.4 ± 32.5	46.1 ± 10.1	0.9533
	PBR(2)	0.81 ± 0.01	187.2 ± 17.2	53.1 ± 5.6	0.9835
		3.64 ± 0.04	235.9 ± 24.9	66.4 ± 7.9	0.9732
		8.63 ± 0.06	247.7 ± 50.6	68.5 ± 15.7	0.9427
IP–SR–PBR(3)	IP	0.81 ± 0.01	215.0 ± 17.4	63.4 ± 5.7	0.9872
		3.64 ± 0.04	234.1 ± 17.6	67.2 ± 5.6	0.9862
		8.63 ± 0.06	269.2 ± 23.3	76.5 ± 7.3	0.9889
	SR	0.81 ± 0.01	140.8 ± 4.8	37.3 ± 1.6	0.9977
		3.64 ± 0.04	174.4 ± 4.3	46.5 ± 1.4	0.9985
		8.63 ± 0.06	164.9 ± 37.9	42.3 ± 11.8	0.9292
	PBR(3)	0.81 ± 0.01	187.6 ± 17.2	52.9 ± 5.6	0.9837
		3.64 ± 0.04	294.1 ± 30.1	84.7 ± 9.5	0.9748
		8.63 ± 0.06	262.2 ± 59.9	72.7 ± 18.6	0.9299

^a Correlation coefficient of the linear regression analysis.



Figure S27. Modified Arrhenius plots using the AF in Eq. (7) with (a, b) = (0,1) applied to the rate constants for the respective reaction steps at each $p(H_2O)$ value, optimized on the basis of the IP–SR–PBR(2) model: (a) IP, (b) SR, and (c) PBR(2).



Figure S28. Modified Arrhenius plots using the AF in Eq. (7) with (a, b) = (0,1) applied to the rate constants for the respective reaction steps at each $p(H_2O)$ value, optimized on the basis of the IP–SR–PBR(3) model: (a) IP, (b) SR, and (c) PBR(3).

Table S10. Apparent Arrhenius parameters obtained through the modified Arrhenius plots using the AF in Eq. (7) with (a, b) = (0, 1) applied to the respective reaction steps at each $p(H_2O)$ value

Model	Reaction step	<i>p</i> (H ₂ O) / kPa	$E_{\rm a}$ / kJ mol ⁻¹	$\ln(A / s^{-1})$	$-\gamma^{a}$
IP–SR–PBR(2)	IP	0.81 ± 0.01	212.4 ± 17.5	62.6 ± 5.7	0.9868
		3.64 ± 0.04	226.5 ± 17.6	65.0 ± 5.6	0.9853
		8.63 ± 0.06	255.5 ± 22.6	72.4 ± 7.0	0.9885
	SR	0.81 ± 0.01	139.2 ± 4.9	36.8 ± 1.6	0.9976
		3.64 ± 0.04	171.7 ± 4.5	45.7 ± 1.5	0.9983
		8.63 ± 0.06	163.7 ± 32.7	42.1 ± 10.2	0.9450
	PBR(2)	0.81 ± 0.01	184.7 ± 17.1	52.3 ± 5.6	0.9833
		3.64 ± 0.04	228.4 ± 25.1	64.2 ± 7.9	0.9713
		8.63 ± 0.06	233.9 ± 49.9	64.4 ± 15.5	0.9381
IP-SR-PBR(3)	IP	0.81 ± 0.01	212.4 ± 17.5	62.6 ± 5.7	0.9868
		3.64 ± 0.04	234.1 ± 17.6	67.2 ± 5.6	0.9862
		8.63 ± 0.06	269.2 ± 23.3	76.5 ± 7.3	0.9889
	SR	0.81 ± 0.01	138.3 ± 4.8	36.5 ± 1.6	0.9976
		3.64 ± 0.04	166.9 ± 4.3	44.2 ± 1.4	0.9983
		8.63 ± 0.06	151.2 ± 38.2	38.3 ± 11.9	0.9161
	PBR(3)	0.81 ± 0.01	185.1 ± 17.0	52.2 ± 5.6	0.9835
		3.64 ± 0.04	286.5 ± 30.4	82.4 ± 9.6	0.9730
		8.63 ± 0.06	248.5 ± 59.2	68.6 ± 18.4	0.9246

^a Correlation coefficient of the linear regression analysis.





Figure S29. Modified Arrhenius plots using the AF in Eq. (7) with the restriction of a = b applied to the rate constants for the respective reaction steps over different $p(H_2O)$ values, optimized on the basis of the IP–SR–PBR(2) model: (a) IP, (b) SR, and (c) PBR(2).





Figure S30. Modified Arrhenius plots using the AF in Eq. (7) with the restriction of a = b applied to the rate constants for the respective reaction steps over different $p(H_2O)$ values, optimized on the basis of the IP–SR–PBR(3) model: (a) IP, (b) SR, and (c) PBR(3).

Figure S31. Modified Arrhenius plots using the AF in Eq. (7) without any restrictions for *a* and *b* applied to the rate constants for the respective reaction steps over different $p(H_2O)$ values, optimized on the basis of the IP–SR–PBR(3) model: (a) IP, (b) SR, and (c) PBR(3).

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