

Supplementary Information

Insight into the Nature and the Transformation of the Hydroxyl Species in the CeY zeolite

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Table S1. Element components in the zeolite samples used (without H₂O) deduced from the data detected by the XRF.

Sample	XRF (wt %)	
	Ce	Na
NaY	-	8.775
0.0025CeNaY-1	1.029	8.111
0.005CeNaY-1	1.837	7.728
0.01CeNaY-1	3.847	6.638
0.015CeNaY-1	6.640	5.270
0.025CeNaY-1	9.274	3.869
0.05CeNaY-1	12.298	2.534
0.075CeNaY-1	12.310	2.529
0.1CeNaY-1	12.306	2.516
0.05CeNaY-2 ^a	17.342	1.031

a: Ce ion exchange concentration is 0.05 mol L⁻¹ and exchange-calcination process repeated twice.

Table S2 Summary of Plausible OH groups on CeY zeolite.

	OH group	$\nu_{\text{O-H}}$, cm ⁻¹
	terminal silanol groups (Si-OH)	3744
	Extra-framework Al hydroxyl species (Al-OH)	3690
	Isolated Si-OH-Al in the supercage (Si-OH-Al)	3640
	Si-OH-Al in the supercage (O(1)H)	3635
HF band	perturbed Si-OH-Al in the supercage (O(1)H...O(H)Ce ³⁺)	3622
	perturbed Si-OH-Al in the supercage (O(1)H...O(H)Al ³⁺)	3613
	Si-OH-Al in the sodalite cage (O(2)H or O(3)H)	3556
LF band	perturbed Si-OH-Al in the sodalite cage (O(2)H...O(H)Ce ³⁺)	3523
	Ce hydroxyl species (Ce-OH)	3574

Table S3 Distribution of Brønsted and Lewis acidity in the 0.05CeNaY samples with various calcination temperature.

Samples	150 °C (mmol/g)	
	BAS	LAS
0.05CeNaY-200 ^a	0.1481	0.0726
0.05CeNaY-350 ^b	0.1595	0.0759
0.05CeNaY-550 ^c	0.1023	0.0599

^a Calculations based on the method reported by Emeis (*J. Catal.*, 1993, 141, 347–354), BAS and LAS represent the amount of Brønsted and Lewis acid, respectively.

Table S4 Distribution of Brønsted and Lewis acidity in the xCeNaY-c samples.

Samples	150 °C (mmol/g)		400 °C (mmol/g)	
	BAS ^a	LAS ^a	BAS ^a	LAS ^a
NaY	0	0.1245	0	0.0100
0.0025CeNaY-c	0.0097	0.1631	0.0026	0.0047
0.005CeNaY-c	0.0141	0.1691	0.0044	0.0027
0.01CeNaY-c	0.0308	0.1665	0.0106	0.0047
0.015CeNaY-c	0.0511	0.1258	0.0176	0.0087
0.025CeNaY-c	0.0749	0.1038	0.0344	0.0173
0.05CeNaY-c	0.1066	0.0546	0.0502	0.0233

^a Calculations based on the method reported by Emeis (*J. Catal.*, 1993, 141, 347–354), BAS and LAS represent the amount of Brønsted and Lewis acid, respectively.

Table S5 Summary of Plausible OH and respective OD groups on CeY zeolite.

OH group	$\nu_{\text{O-H}}$, cm^{-1}	$\nu_{\text{O-D}}$, cm^{-1}
terminal silanol groups (Si-OH)	3744	2754
Si-OH-Al in the supercage O(1)H	3635	2670
perturbed Si-OH-Al in the supercage O(1)H...O(H)Ce	3622	2635
Si-OH-Al in the sodalite cage O(2)H	3556	2620
perturbed Si-OH-Al in the sodalite cage O(2)H...O(H)Ce	3523	2596

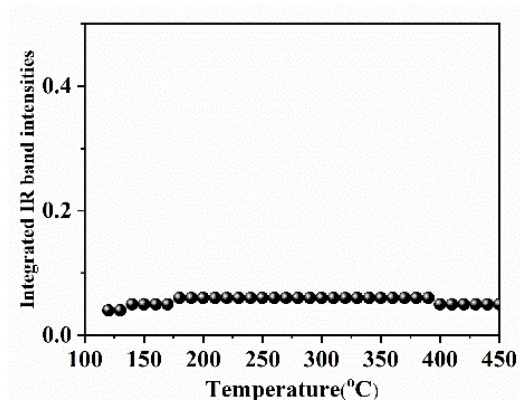


Figure S1. Temperature dependence of integrated IR band area for the silanol groups for the 0.05CeNaY-1-h sample.

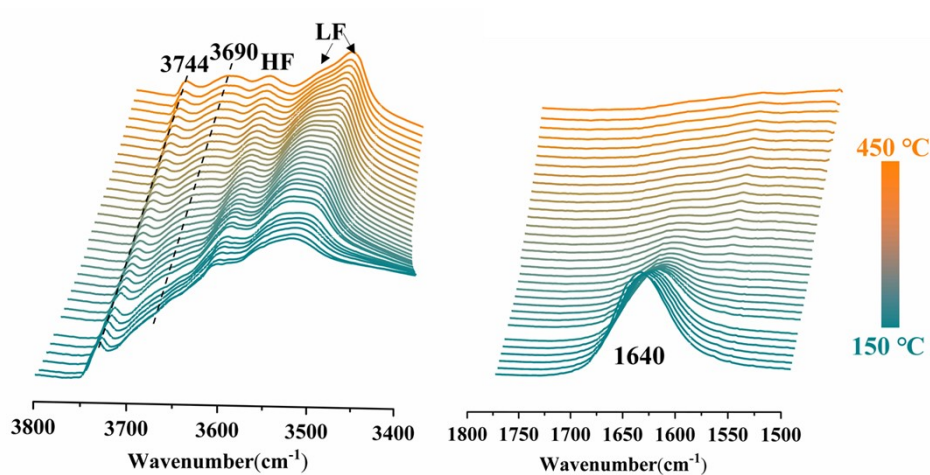


Figure S2. FTIR spectra acquired during dehydration of the 0.05CeNaY-2-h sample at various temperature. The words “HF” and “LF” reference as the high-frequency (HF) bands occurred at 3650-3610 cm^{-1} and the low-frequency (LF) bands occurred at 3600-3515 cm^{-1} , respectively.

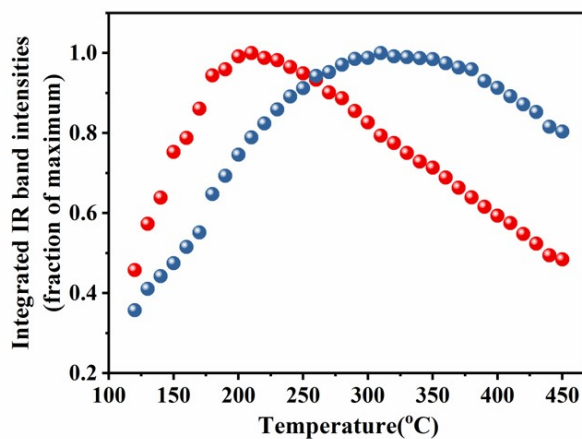


Figure S3. Temperature dependence of normalized integrated IR band intensities (fraction of maximum) for the HF bands (red) and LF bands (blue) presented in Figure S1 for the 0.05CeNaY-2-h sample.

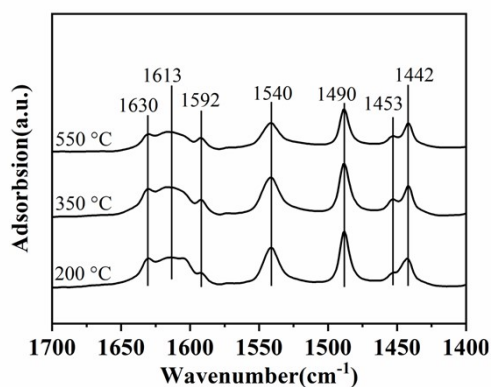


Figure S4. Py-FTIR spectra of the 0.05CeNaY samples with various calcination temperature.

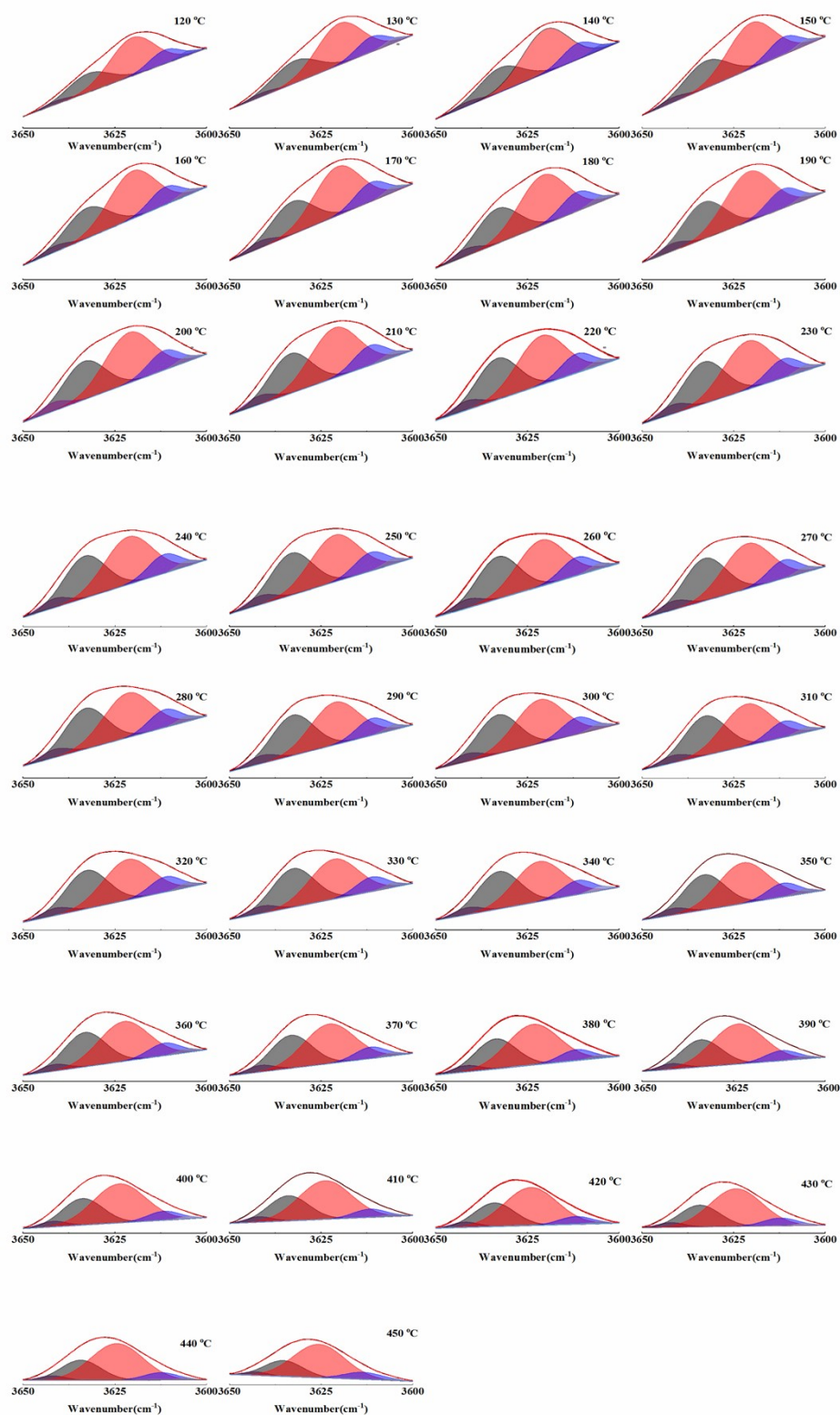


Figure S5. Deconvolution of the IR HF band of the 0.05CeNaY-1-h sample (*cf.* Figure 2) using four valid single bands. The color of purple, black, red and blue represent the bands of 3640 cm^{-1} , 3633 cm^{-1} , 3622 cm^{-1} and 3613 cm^{-1} , respectively.

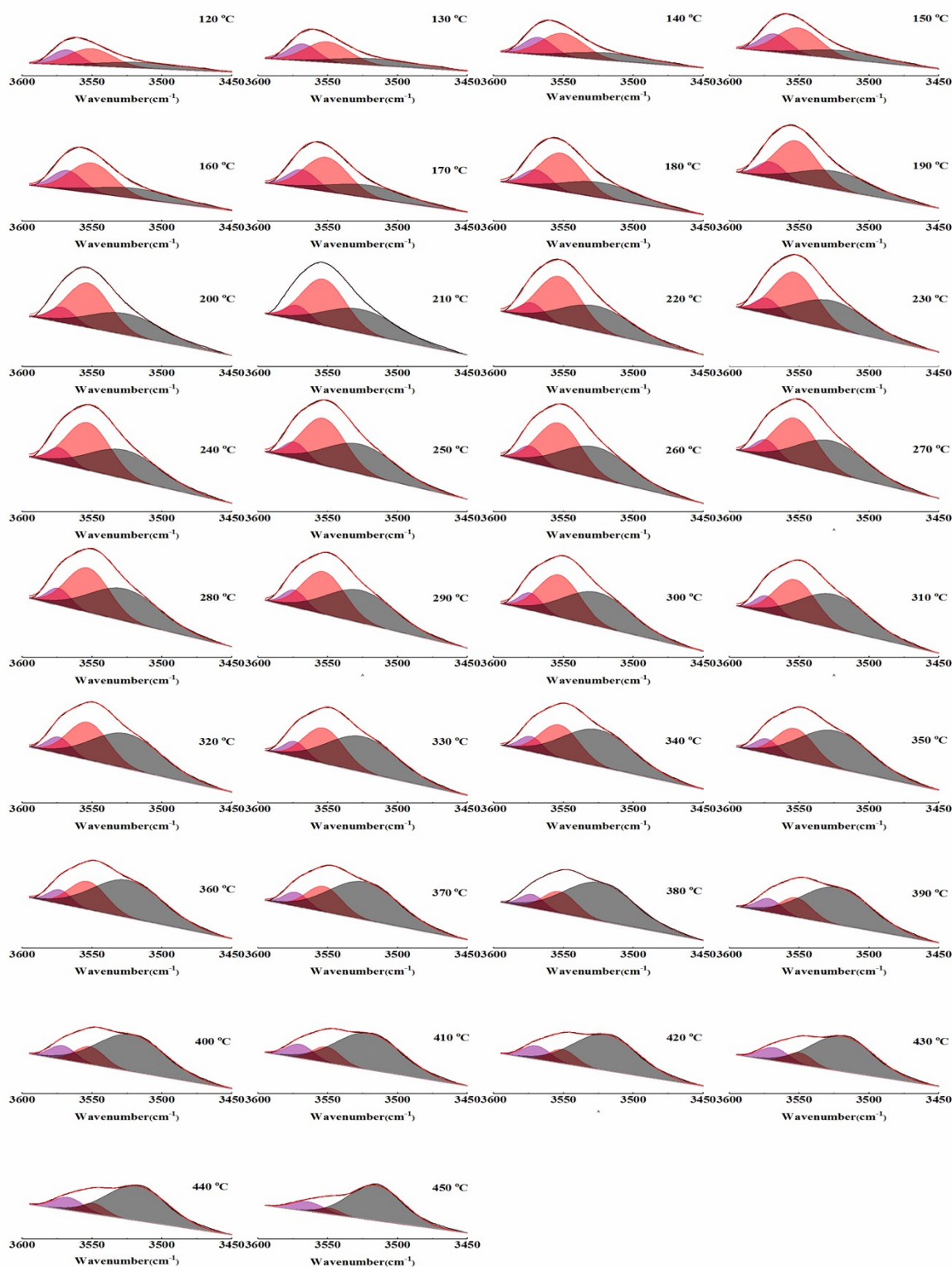


Figure S6. Deconvolution of the IR LF band of the 0.05CeNaY-1-h sample (*cf.* Figure 2) using three valid single bands. The color of purple, red and black represent the bands of 3574 cm^{-1} , 3556 cm^{-1} , and 3523 cm^{-1} , respectively.

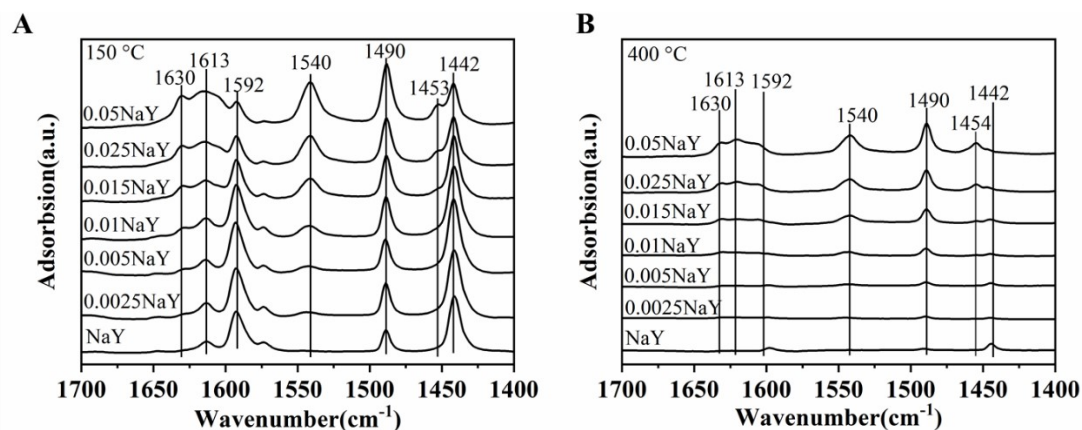


Figure S7. Py-FTIR spectra of the different samples adsorbed at (A) 150 °C and (B) 400 °C.

Note: The band at ca. 1540 cm^{-1} assigned to the Brønsted acid sites can be observed. Besides, two bands at ca. 1442 cm^{-1} , and ca. 1453 cm^{-1} can be found which can be attributed to pyridine molecules coordinated to the Na^+ ions and the extra-framework aluminum species, respectively. The amount of Brønsted acid sites on the $x\text{CeNaY-c}$ samples correspondingly increases with the Ce concentrations (*cf.* Fig. S7 and Table S4). This is because that the H^+ ions polarized by Ce hydroxylated species at the higher Ce concentrations are enough to replace the Na^+ ions of NaY zeolite. Besides, the amount of Brønsted acid have a significant increase when the initial Ce concentration is between 0.0025 $\text{mol}\cdot\text{L}^{-1}$ and 0.025 $\text{mol}\cdot\text{L}^{-1}$. Afterward, they show a trend of slow intensification (*cf.* Fig. S8). The result shows that Ce hydroxylated species remain in the supercage to occupy the proton sites and affect the hydroxyl groups in the supercage with the increase of Ce concentrations. Besides, it can be seen that the intensity of the band at 1453 cm^{-1} strengthens with the initial Ce concentration rising, indicating that the number of extra-framework aluminum species correspondingly increase and further suggesting that the framework structure of Y has a slightly

destruction at the higher initial Ce concentration.

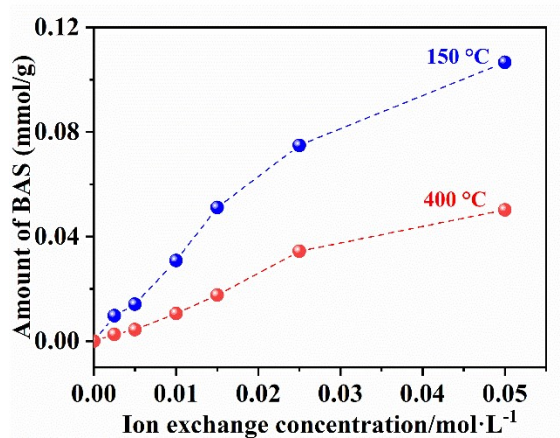


Figure S8. The amount of Brønsted acid in the $x\text{CeNaY-c}$ samples with various Ce concentration.

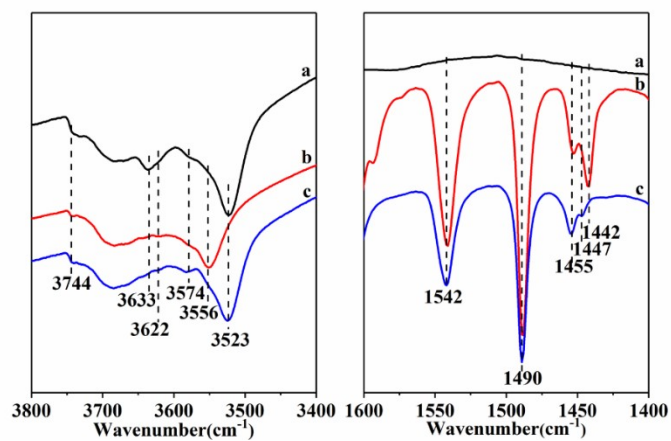


Figure S9. The FTIR spectra recorded after Pyridine adsorption for the 0.05CeNaY-1-c sample. (a: background b: 150 °C desorption c: 400 °C desorption)

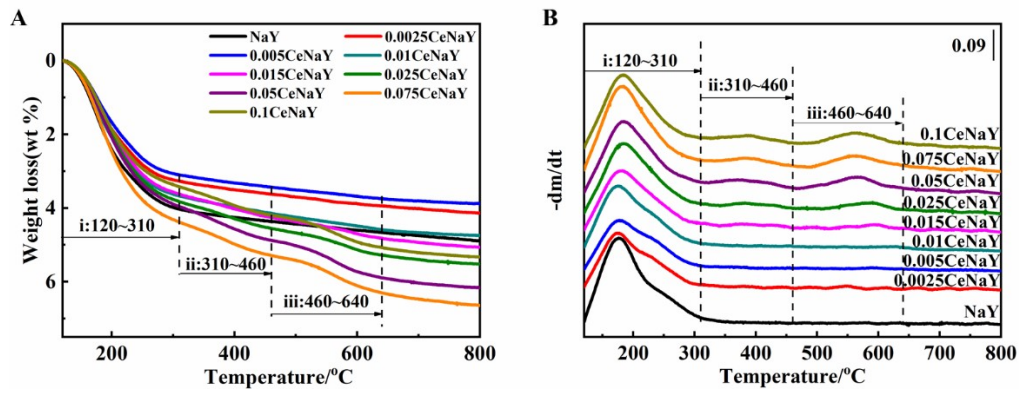


Figure S10. The TG curves (A) and the DTG curves(B) of xCeNaY-h zeolite samples with various Ce ion exchange concentration.