

# Modification of the Acidic and Textural Properties of HY Zeolite by AHFS Treatment and Its Coke Formation Performance in the Catalytic Cracking Reaction of n-Butene

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**Abstract:** Coke formation on n-butene cracking catalyst is the main reason for the reducing of its lifetime. To study the effects of acidity and textural properties on the coke formation process, a series of HY zeolite-type catalysts were prepared by ammonium hexafluorosilicate treatment (AHFS). NH<sub>3</sub>-TPD and Py-IR-TPD were used to systematically study the change law of zeolite acidity. It was found that with the increase of AHFS concentration, the acid density decreased, whereas the ratio of Brønsted acid to Lewis acid first increased and then decreased. Meanwhile, the percentage of Brønsted acid inside the super cages increased. And the strength of Brønsted acid increased with the degree of dealumination. Combined with in-situ IR study on coke formation, the relationship between coking and acid site was revealed. It was found the rate of coke formation on zeolites was affected by acid density, which is the rate of coke formation decreased with the decline of acid density. When the acid density remains at the same level, it was the acid strength that determined the coke formation rate, which is the stronger the acid strength, the faster the coke formation rate.

**Keywords:** Butene cracking; Coke formation; In-situ IR; Y zeolite; acid density

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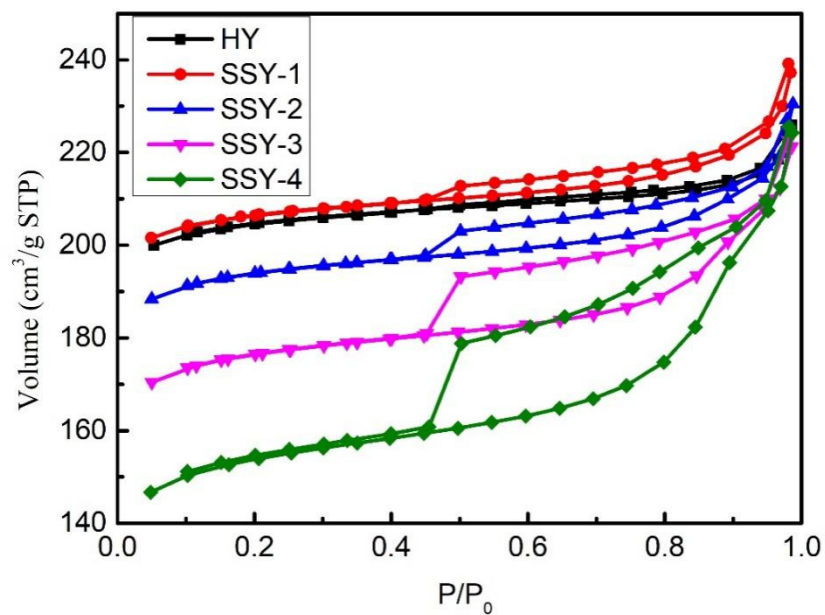


Figure S1. Nitrogen adsorption-desorption isotherms of the modified and parent zeolites.

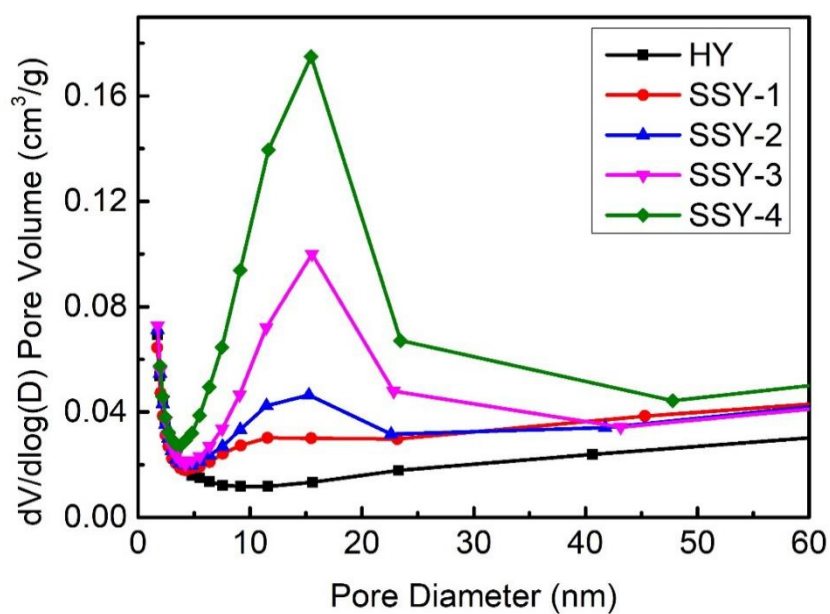
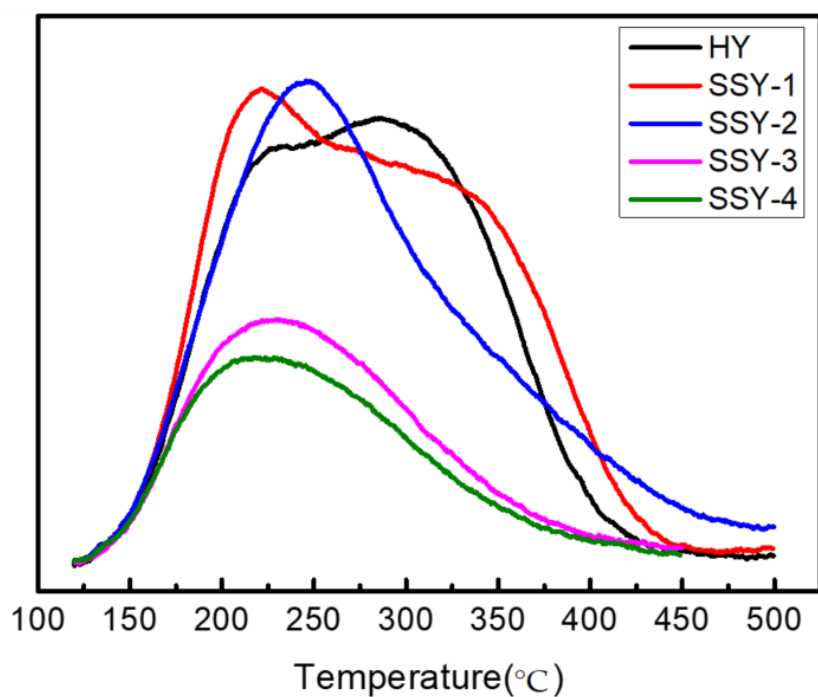
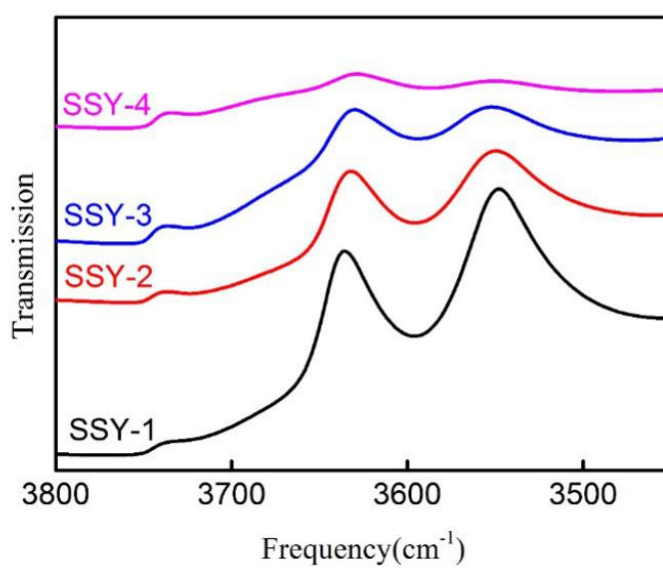


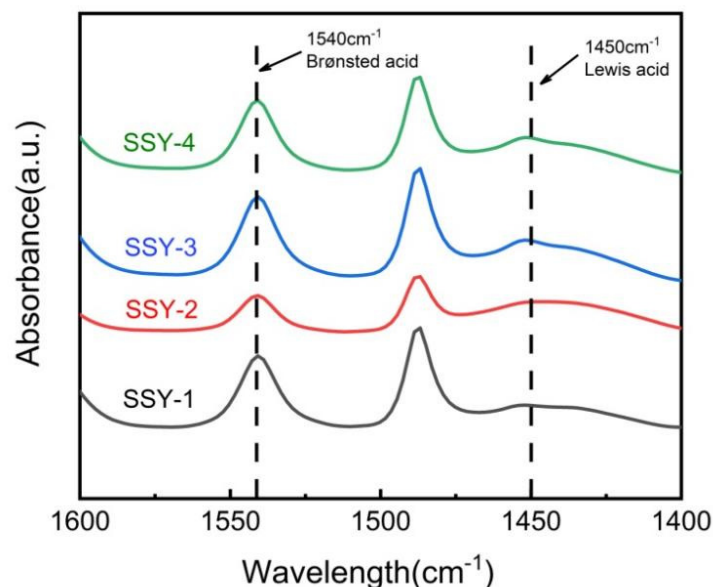
Figure S2. Pore size distributions of the modified and parent zeolites.



**Figure S3.** NH<sub>3</sub>-TPD spectra of parent HY and ammonium hexafluorosilicate modified zeolites.

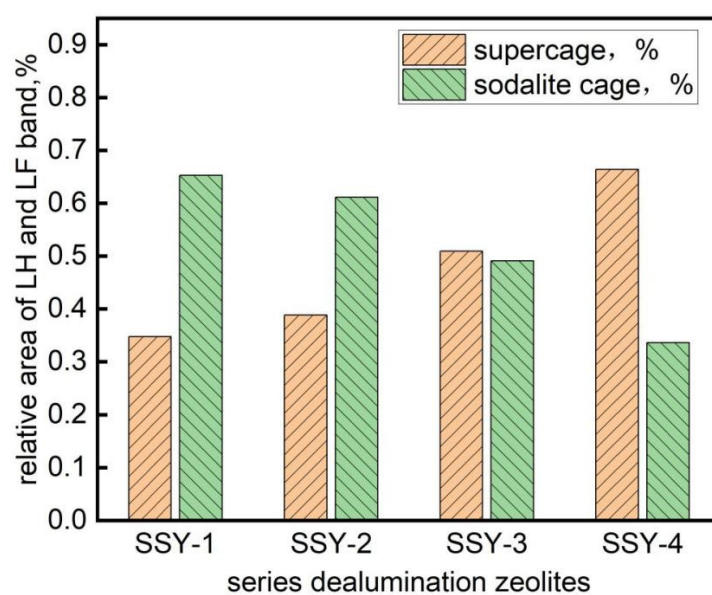


**Figure S4.** IR spectra of the ammonium hexafluorosilicate modified zeolites hydroxy groups.

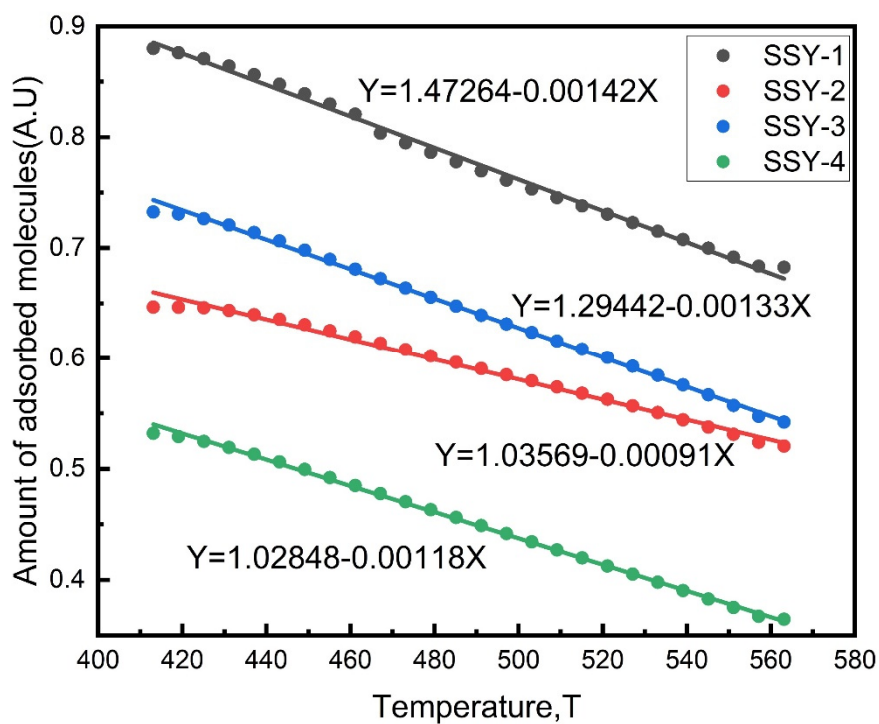


**Figure S5.** pyridine IR spectrum of ammonium hexafluorosilicate modified zeolites

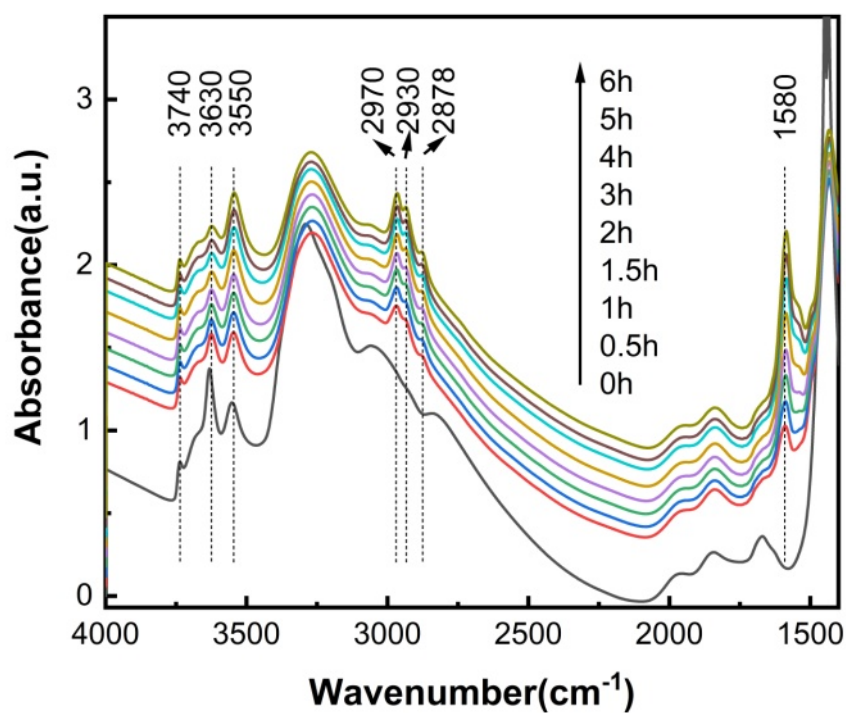
To characterize acid properties, FT-IR measurements after pyridine adsorption have been performed on all samples. Pyridine can interact with Brønsted acid sites to give a pyridinium ion (bands at  $1540\text{ cm}^{-1}$ ) and with Lewis acid sites via coordinative bond (bands at  $1450\text{ cm}^{-1}$ ). Fig.S5 shows the spectra of all the samples in the  $1400\text{--}1600\text{ cm}^{-1}$  region after pyridine adsorption and evacuation at  $200\text{ }^{\circ}\text{C}$  during 2 h. An intense band of pyridine bonded to Brønsted acid sites ( $1540\text{ cm}^{-1}$ ) is detected, while a very weak band corresponding to of pyridine coordinated to Lewis acid sites appears at  $1450\text{ cm}^{-1}$ . The result indicates that the EFAL are almost completely absent in these samples.



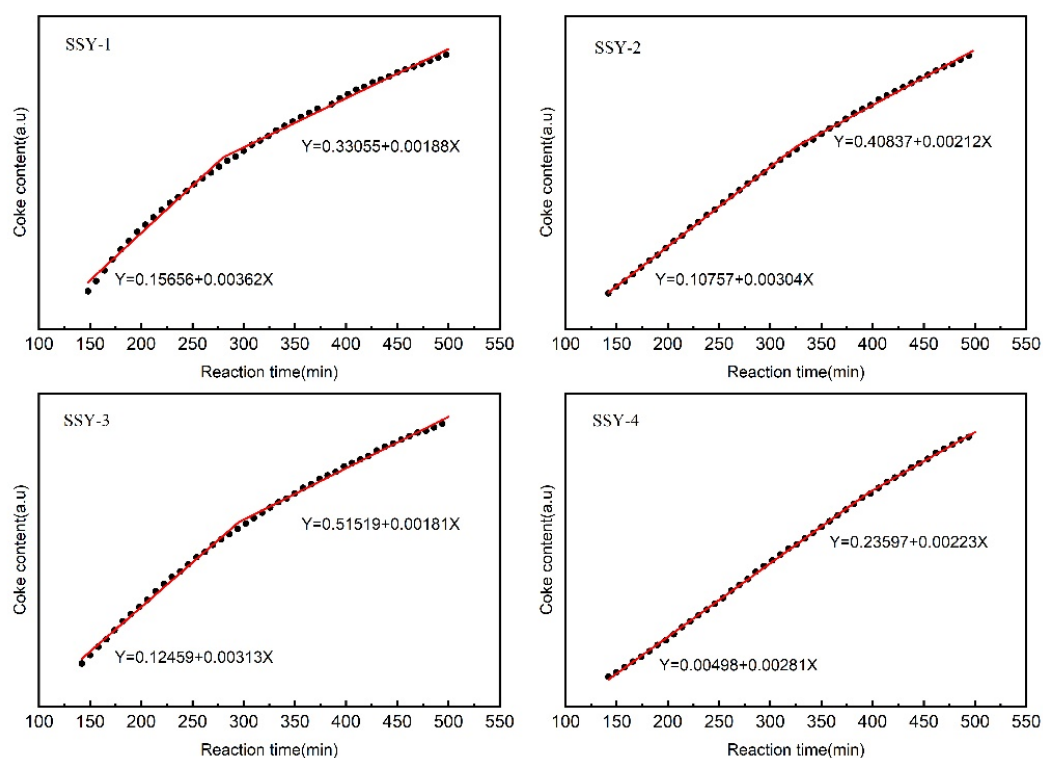
**Figure S6.** Intensity of the ammonium hexafluorosilicate modified zeolites HF and LF bands.



**Figure S7.** The ammonium hexafluorosilicate modified zeolites linearly fitting curve of pyridine coverage in Brønsted. The amount of adsorbed molecules can be obtained from the integration of the pyridine adsorption peak areas in Brønsted acid site ( $1540\text{ cm}^{-1}$ )

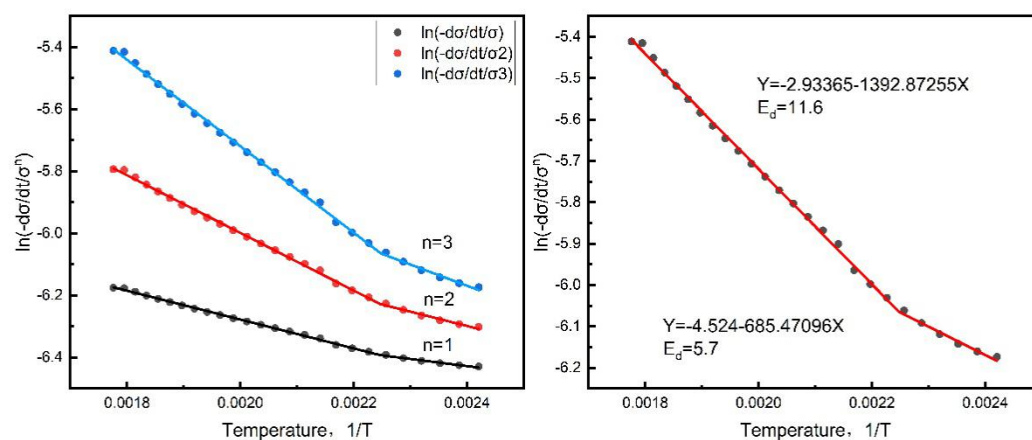


**Figure S8.** The ammonium hexafluorosilicate modified zeolites hydroxyl groups characterization during the coke formation reaction.

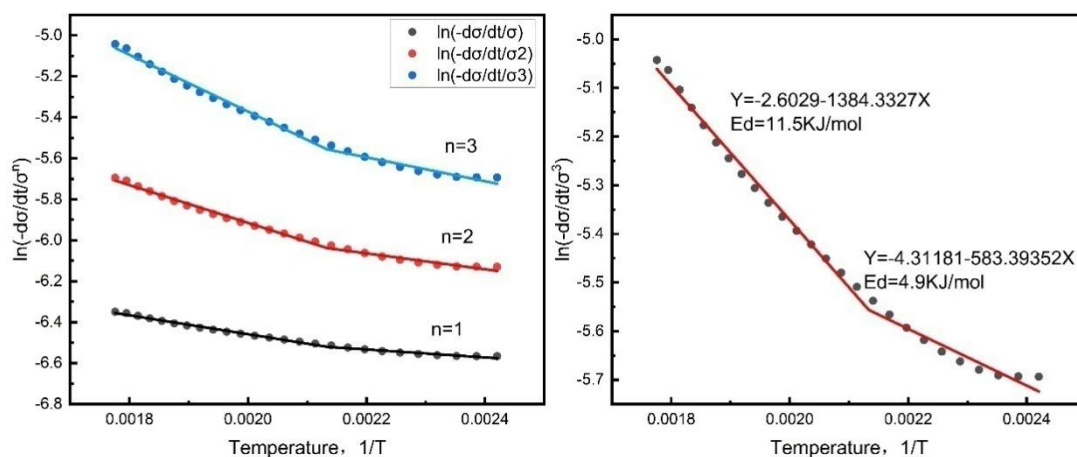


**Figure S9.** Coke formation rate of ammonium hexafluorosilicate modified zeolites. The amount of coke content can be calculated from the integration of the typical coke peak areas (at  $1580\text{ cm}^{-1}$ )

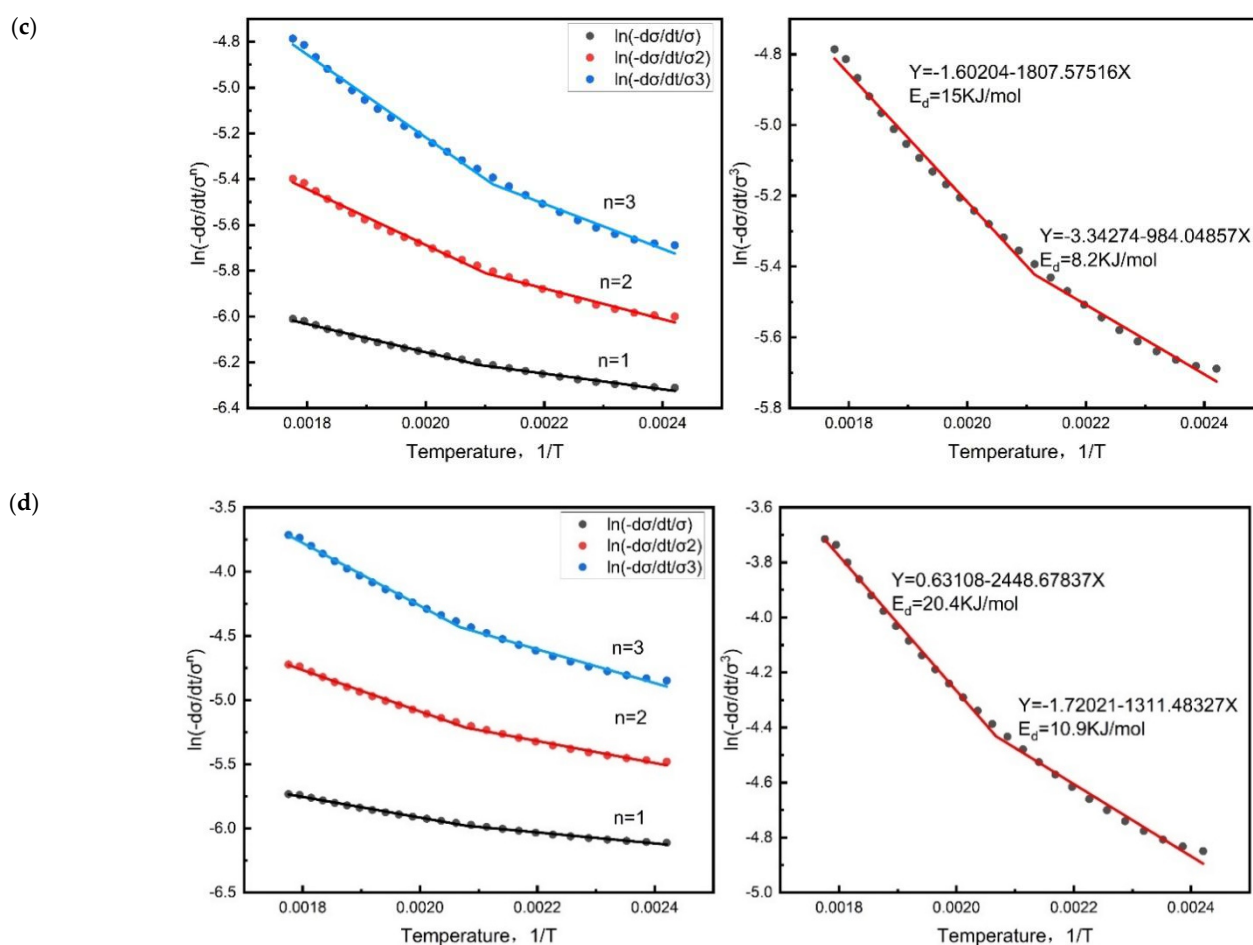
(a)



(b)







**Figure S10.** (a) The fitting curve and linear equation of SSY-1. (b) The fitting curve and linear equation of SSY-2. (c) The fitting curve and linear equation of SSY-3. (d) The fitting curve and linear equation of SSY-4.

The analysis of the best fitting-curves in each zeolite Figure 9a–d reveals that for samples SSY-1, SSY-2 and SSY-3, the desorption reaction order is 1, with further increasing delamination degree, the desorption reaction degree of SSY-4 became 3.

**Table S1.** textural properties of the modified and parent zeolites.

Sample	$S_{\text{micro}}^a$ $\text{m}^2/\text{g}$	$S_{\text{ext}}^b$ $\text{m}^2/\text{g}$	$V_{\text{micro}}^c$ $\text{cm}^3/\text{g}$	$V_{\text{meso}}^d$ $\text{cm}^3/\text{g}$
HY	604.58	46.11	0.30	0.04
SSY-1	608.26	48.61	0.30	0.06
SSY-2	565.91	52.39	0.28	0.07
SSY-3	504.17	60.23	0.25	0.10
SSY-4	419.60	73.94	0.21	0.14

<sup>a</sup> t-plot micropore area. <sup>b</sup> t-plot external surface. <sup>c</sup> t-plot micropore volume. <sup>d</sup> Mesopore volume ( $V_{\text{total}} - V_{\text{micro}}$ ),  $V_{\text{total}}$  is total pore volume test at  $p/p_0 = 0.99$ .

**Table S2.** The structural properties of the modified and parent zeolites.

Sample	$a_0(\text{\AA})$	Crystallinity, %	Framework Si/Al ratio	Global Si/Al ratio	Total Al	Framework Al	Extra-framework Al	B acid sites ( $\times 10^{-4} \text{mol/g}$ )
HY	24.641	100	3.021	2.550	54	48	6	43
SSY-1	24.582	151.8	3.660	3.720	41	41	0	37
SSY-2	24.536	162.5	4.325	3.905	39	36	3	32
SSY-3	24.492	147.3	5.145	4.535	35	31	3	28
SSY-4	24.467	126.2	5.755	5.495	30	28	1	25

**Table S3.** Acidic properties of ammonium hexafluorosilicate modified zeolites.

SAMPLE	Acid type	Total acid sites (10 <sup>-4</sup> mol/g)	B/L ratio	Strong acid sites (10 <sup>-4</sup> mol/g)	Weak acid sites (10 <sup>-4</sup> mol/g)
SSY-1	Brønsted acid	8.71	62.214	6.76	1.95
	Lewis acid	0.14		0.03	0.11
SSY-2	Brønsted acid	7.25	18.13	5.37	1.88
	Lewis acid	0.40		0.15	0.25
SSY-3	Brønsted acid	6.40	20.64	5.15	1.25
	Lewis acid	0.31		0.05	0.25
SSY-4	Brønsted acid	5.27	17	3.61	1.66
	Lewis acid	0.31		0.14	0.17

**Table S4.** The ammonium hexafluorosilicate modified zeolites E<sub>a</sub> value obtained from the slope of the best fitting-curve.

Zeolite	Ed strong(KJ/mol)	Ed weak(KJ/mol)
SSY-1	11.5	4.9
SSY-2	11.6	5.7
SSY-3	15	8.2
SSY-4	20.4	10.9

**Table S5.** The R-squared value calculation of ammonium hexafluorosilicate modified zeolites with pyridine desorption reaction order 1, 2 and 3 respectively

R-Square	SSY-1	SSY-2	SSY-3	SSY-4
ln(-dσ/dt/σ)	0.999118	0.99516	0.996022	0.997647
ln(-dσ/dt/σ <sup>2</sup> )	0.999117	0.995159	0.995974	0.997647
ln(-dσ/dt/σ <sup>3</sup> )	0.999113	0.995157	0.995904	0.99767

### A calculation method of the desorption rate of pyridine.

Under our experimental conditions, the desorption rate of pyridine was determined with the following Wigner-Polanyi equation<sup>1</sup>, assuming that the desorption is irreversible and the desorbed pyridine does not react or re-adsorb:

$$N(t) = -\frac{V_m d\theta}{dt} = v_n \theta^n \exp\left[\frac{-E_d}{RT(t)}\right] \quad (1)$$

Where N(t) is the desorption rate; V<sub>m</sub> is mono-layer saturated adsorption amount; θ is the surface coverage; V<sub>m</sub>dθ is amount of adsorption of pyridine; n is the reaction order; v<sub>n</sub> is a frequency factor; E is the desorption activation energy; R is ideal gas constant(8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T is the absolute temperature;

Considering a linear temperature program, one fixes the heating rate λ(°C/min) and the initial temperature T<sub>0</sub> to determine the change of temperature T with elapsed time t. To simplify the equations, take dσ = V<sub>m</sub>dθ and  $k_n = \frac{v_n}{\lambda V_m^n}$ .

$$T(t) = T_0 + \lambda t \quad (2)$$

Equation (1) can be rewritten in term of desorption temperature, as shown below:

$$-\frac{d\sigma}{dT} = k_n \sigma^n \exp\left[\frac{-E_d}{RT}\right] \quad (3)$$

Equation (4) can be obtained by taking natural logarithm for both sides of Equation (3).



$$\ln\left(-\frac{d\sigma}{\sigma^n dT}\right) = \frac{-E_d}{RT} + A_n \quad (4)$$

Where  $A_n$  is constant. The value of  $\sigma$  is amount of pyridine adsorption at temperature  $T$ , can be obtained by integration the corresponding peak areas,  $\frac{d\sigma}{dT}$  is evaluated from the slope of the curve of Fig.10a~d. A plot of  $\ln\left(-\frac{d\sigma}{\sigma^n dT}\right)$  against  $\frac{1}{T}$  can be constructed, after determining the reaction order. The  $E_d$  value can be obtained by determining the slope of the plot  $\ln\left(-\frac{d\sigma}{\sigma^n dT}\right)$  against  $\frac{1}{RT}$ .

Assuming that the reaction order for desorption are 1, 2 and 3, respectively, Equation (4) can be rewritten as shown below:

$$\ln\left(-\frac{d\sigma}{\sigma dT}\right) = \frac{-E_d}{RT} + A_1 \quad (5)$$

$$\ln\left(-\frac{d\sigma}{\sigma^2 dT}\right) = \frac{-E_d}{RT} + A_2 \quad (6)$$

$$\ln\left(-\frac{d\sigma}{\sigma^3 dT}\right) = \frac{-E_d}{RT} + A_3 \quad (7)$$

$\ln(-d\sigma/dT/\sigma^n)$ , with reaction order 1, 2 and 3 respectively, was designated as the ordinate and  $T^{-1}$  as the abscissa to establish curves. Each curve is fitted with a linear fit and the slope of the linear equation represents the desorption activation energy ( $E_d$ ). The fitting curves are shown in the Figure 9a~d, The scatter curve is the original data and the solid lines represent the fitting curves as shown in the left part. The linear equation and  $E_d$  can be obtained from the slope of the best fitting-curve (with highest  $R$ -squared value), as shown in the right part of Figure 9a~d.

#### A calculation method of extra-framework Al concentration of per unit cell

The number of EFAL per unit cell was then derived as the difference between the total number of aluminum atoms (measured by XRF) and the number of framework aluminum atoms (measured by XRD).<sup>2</sup>

$$\text{EFAL} = \frac{192}{a+1} - \frac{192}{b+1} \quad (8)$$

Where  $a$  is the global Si/Al, calculated by X-ray fluorescence (XRF) method, and  $b$  is the framework Si/Al, calculated by X-ray diffraction (XRD) method. Calculated values of extra-framework Al concentration of per unit cell are illustrated in Table 2.

#### A calculation method of B acid sites concentration

For zeolite, The composition is  $c(\text{SiO}_2) + 1(\text{AlO}_{1.5})$  and the isomorphous substitution of one Al atom generates one B acid site.<sup>3,4</sup> The B acid sites can be determined by the equation:

$$F = \frac{1}{C \times 60 + 51} \quad (9)$$

Where  $c$  is the framework Si/Al,  $F$  is the B acid sites concentration.

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