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Thermal analysis of *n*-butylamine sorbed on FeHNaY zeolites

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Abstract

The thermal analysis of *n*-butylamine (NBA) sorbed on FeHNaY zeolites has been studied. TG and DTG showed three distinct stages of weight loss. The first peak in the DTG, at 120-160°C, was due to the physisorbed and weakly chemisorbed *n*-butylamine molecules. The second DTG peak was at 330-400°C corresponding to the NBA molecules sorbed on sodium ions, or medium strength acidic centres. The third DTG peak was at 570-640°C and can be attributed to the NBA molecules sorbed on ferric ions or strong Brönsted acidic centres. The DTG of NBA sorbed on NaY showed only two peaks. Owing to the thermal treatment at 500°C, ferric ions in the supercages migrate to the sodalite cages or hexagonal prisms. As a result, the number of NBA molecules corresponding to the second and third peak was decreased. The nature of the interacting centres with the percentage of ion exchange and the migration of ferric ions is discussed.

Keywords: Butylamine; DTA; DTG; FeHNaY; TG; Zeolite

1. Introduction

We have reported [1-8] the physicochemical properties and sorption of *n*-butylamine [3] and water [5] in ferric-exchanged Y zeolites. The presence of hexa-aquo-complexes of iron, $[Fe(OH)(H_2O)_5]^{2+}$, was established by thermal analysis and visible spectral studies [1]. The DTA of dehydration showed three peaks at 120, 290

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and 400°C. The first peak corresponds to the desorption of physisorbed or weakly chemisorbed water. The second peak at 290°C is attributed to the desorption of water co-ordinated to the ferric ions. The third peak is due to the dehydroxylation of $[Fe(OH)]^{2+}$ species at 400°C. The irreversible migration of ferric ions from supercages to the sodalite cages or hexagonal prisms takes place on thermal activation of FeHNaY at 500°C. The localization of aquo-complexes of iron in the supercages of fresh FeNaY was supported by the electrical conductivity measurements [2].

In this paper, we report the thermal analysis of *n*-butalyamine sorbed on FeHNaY zeolites in order to understand the nature of the interacting centres with the increase in the number of ferric ions and the migration of ferric ions.

2. Experimental

The ferric-exchanged Y zeolites were prepared by treating Linde NaY (SK-40, Union Carbide) with aqueous solutions of ferric acetate–acetic acid at about pH 4 at 27–30°C. Details of the preparation and the chemical compostition as shown in Table 1 have been reported elsewhere [1]. The catalysts were activated at 350°C for 2 h and at 500°C for 2 h. The sorption of *n*-butylamine (NBA) was carried out in a vacuum desiccator for a minumum of 2 h in NBA atmosphere. The vacuum desiccator was pre-evacuated and saturated with NBA vapour, keeping the NBA at the bottom. Thermal analysis was carried out in flowing nitrogen at constant flow rate. All sample transfers were carried out quickly and mostly in nitrogen atmosphere. The total amount of NBA sorbed is comparable, although slightly less, than that observed with the sorption carried out using a vacuum unit. All thermograms were recorded under identical conditions on an automatic derivatograph (Model MOM-102, Hungary). The heating rate was 10 K min^{-1}. The DTA sensitivity was maximum (1/1). Pre-heated, finely powdered α-alumina was used as a reference material.

3. Results and discussion

Fig. 1 shows typical measured curves of *n*-butylamine sorbed on FeNaY (46, 350, 2). The DTG shows three minima corresponding to the three stages of desorption of NBA from the catalyst. The first DTG peak is observed at 125°C corresponding to the desorption of physisorbed or weakly chemisorbed NBA molecules. The second NBA peak at 330°C in DTG is attributed to the desorption of NBA sorbed particularly on cations like Na^+, Fe^{3+} and Lewis acidic centres. At 330°C, NBA molecules are desorbed as butene and ammonia

$$\underset{\text{(NBA)}}{H_2N{-}(CH_2)_3{-}CH_3} \xrightarrow{330^\circ C} \underset{\text{(butene)}}{CH_2{=}CH_2{-}CH_2{-}CH_3} + NH_3 \qquad (1)$$

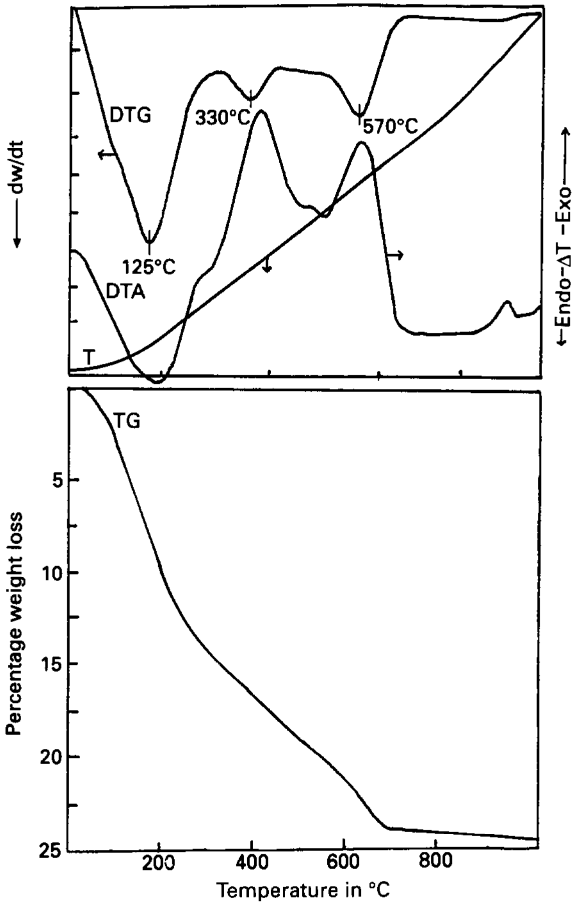

Fig. 1. Typical measured curves of NBA (*n*-butylamine) absorbed on FeNaY (46, 350, 2).

The desorbed products, butene and ammonia, were detected by mass spectrometry for the desorption of NBA on mordenite [9]. The third DTG peak was observed at 570°C which is attributed to the cracking of NBA into ammonia, CO_2 and lower olefins.

The reaction of *n*-butylamine was carried out at 320°C, 0.5 h^{-1} WHSV (weight hourly space velocity) over 4 g FeHNaY zeolite. The products were analysed by Orset analysis and gas chromatography. The presence of butene and ammonia in the product was detected, confirming Eq. (1).

The DTA of the desorption of NBA sorbed on FeNaY (46, 350, 2) shows one endotherm at about 130°C and two exotherms at about 360 and 570°C. The curves were obtained in the presence of flowing nitrogen. The reactions of NBA over this catalyst above 300°C, corresponding to the second and third peaks, are exothermic in nature.

Table 1
Chemical composition of FeNaY zeolites

Zeolite	Unit cell composition	Unit cell constant in Å
NaY	$Na_{57}(AlO_2)_{57}(SiO_2)_{135}(268H_2O)$	24.601
FeNaY (37)	$Fe_5Na_{39}H_3(AlO_2)_{57}(SiO_2)_{135}(269H_2O)$	24.586
FeNaY (46)	$Fe_{8.4}Na_{29.6}H_2(AlO_2)_{57}(SiO_2)_{135}(272H_2O)$	24.617
FeNaY (82)	$Fe_{15.6}Na_{10.2}(AlO_2)_{57}(SiO_2)_{135}(252H_2O)$	24.515
NaY (–, 500, 2 NBA),	(NaY was heated at 500°C for 2 h and NBA was sorbed)	24.495
FeNaY (37, 500, 2 NBA)	FeNaY (37) was heated at 500°C, for 2 h and NBA was sorbed)	24.759
FeNaY (46, 500, 2, NBA)	(FeNaY (46) was heated at 500°C, for 2 h and NBA sorbed)	24.539
FeNaY (82, 500, 2, NBA)	(FeNaY (82) was heated at 500°C for 2 h and NBA was sorbed)	24.547

Table 2
Thermal analysis of *n*-butylamine sorbed on FeNaY zeolites

Zeolite	Peak temperature in °C corresponding to			Exotherm (DTA) for structure breakdown in °C
	First DTG peak (peak minimum)	Second DTG peak (peak minimum)	Third DTG peak (peak minimum)	
NaY (–, 350, 6)	40–320 (160)	320–480 (395)	480–800 (No peak)	900
FeNaY (37, 350, 6)	40–280 (130)	280–440 (350)	440–800 (broad peak)	960
FeNaY (46, 350, 6)	40–260 (125)	260–360 (330)	360–800 (570)	900, 930
FeNaY (82, 350, 6)	40–260 (120)	260–460 (360)	460–800 (625)	910, 1000
NaY (–, 500, 6)	40–320 (170)	320–500 (410)	500–800 (–)	905
FeNaY (37, 500, 6)	40–300 (150)	300–460 (395)	460–800 (broad peak)	910
FeNaY (46, 500, 6)	40–320 (160)	320–480 (410)	480–800 (broad peak)	960
FeNaY (82, 500, 6)	40–280 (110)	280–440 (360)	440–800 (640)	900, 1000

Fig. 2 shows the DTG of NBA sorbed on NaY, FeNaY (37), FeNaY (46) and FeNaY (82) pre-activated at 350°C for 2 h. The DTG of NBA–NaY shows two peaks at 160 and 395°C. The peak at 395°C is due to the desorption of NBA co-ordinated, in particular with sodium ions. The first DTG peak of NBA sorbed on NaY (–, 350, 2), FeNaY (37, 350, 2), FeNaY (46, 350, 2), FeNaY (82, 350, 2), FeNaY (46, 350, 2) and FeNaY (82, 350, 2) was at 160, 130, 125 or 120°C respectively, as given in Table 2. This indicates that with the increase of ferric exchange, the temperature corresponding to the desorption of physisorbed NBA molecules decreases. The weight loss corresponding to the temperature range of

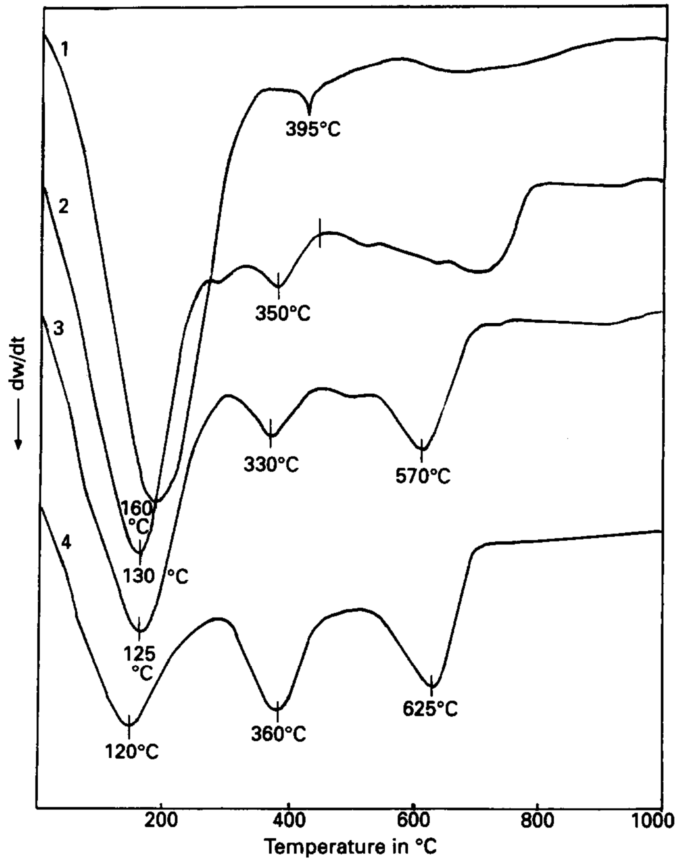

Fig. 2. DTG of NBA (*n*-butylamine) absorbed on (1), NaY(–, 350, 2); (2), FeNaY (37, 350, 2); (3), FeNaY (46, 350, 2); (4), FeNaY (82, 350, 2).

40–320°C, was 20.63, 15.60, 14.20 and 8.90 wt% respectively, while the total weight loss for NaY, FeNaY (37) and FeNaY (46) was practically the same (Fig. 3). The physisorbed or weakly chemisorbed NBA molecules were increased in NaY. In the supercages of NaY zeolites, 32 sodium ions are present [1]. However, sodium ions from the supercages were exchanged by ferric ions resulting in strong but fewer interacting centres. The sorption of NBA on ferric ion is strong and directional; therefore, the physisorbed molecules in the supercages of Y were fewer in number. The NBA–Fe^{+3}/H^{+} interaction is much stronger in FeHNaY resulting in distinct DTG peaks. The FeNaY (46) showed Brönsted acidic centres of higher strength.

In the case of NaY, FeNaY (37), FeNaY (46) and FeNaY (82) activated at 350°C, the wt% loss corresponding to the second DTG peak was 1.6, 2.85, 3.10 and 6.4 respectively. The total weight loss during the desorption of NBA was 24% for NaY, FeNaY (37) and FeNaY (46) catalysts. For FeNaY (82), 21 wt% of total

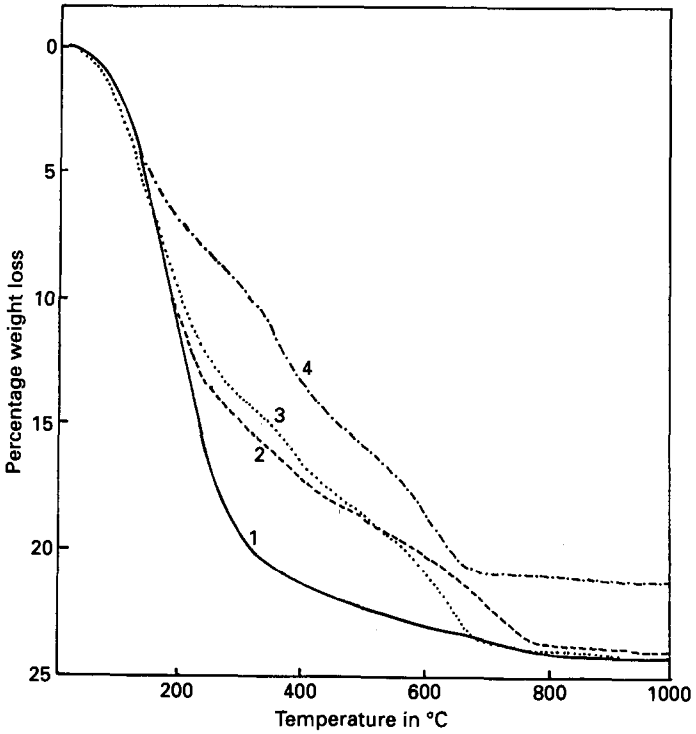

Fig. 3. TG of NBA (*n*-butylamine) on: (1), NaY (–, 350, 2); (2), FeNaY (37, 350, 2); (3), FeNaY (46, 350, 2); (4), FeNaY (82, 350, 2).

weight loss was observed. Fig. 3 shows typical TG curves of NBA sorbed on NaY and FeNaY activated at 350°C for 2 h.

Fig 4 shows DTG of NBA sorbed on NaY and ferric-exchanged Y zeolites pre-activated at 500°C for 2 h. The first peak in DTG of NBA sorbed on NaY (–, 500, 2), FeNaY (37, 500, 2), FeNaY (46, 500, 2) and FeNaY (82, 500, 2) is at 170, 155, 160 and 100°C, respectively. The second DTG peak is observed in the temperature range of 360–440°C. The third DTG peak is at about 620–640°C. The NBA–NaY system shows only two peaks, and NBA–FeNaY shows three peaks, and the corresponding desorption processes are as discussed above (as in Figs. 1 and 2).

In the case of NaY, FeNaY (37), FeNaY (46) and FeNaY (82) pre-activated at 500°C for 2 h, the weight loss corresponding to the temperature range of 40–320°C, i.e. first DTG peak is 15.95, 14.88, 14.20 and 8.50 wt% respectively. The weight loss corresponding to the second DTG peak in temperature range of 280°C (320°C) to 440°C (500°C) is 4.22, 2.63, 3.00 and 3.25 wt%, respectively, as given in Table 3. The sorption corresponding to the second DTG peak decreased due to the thermal treatment at 500°C. This is attributed to the migration of ferric ions from the supercages to the sodalite cages or hexagonal prisms. The same observation was made in the analysis of the dehydration of FeNaY zeolites [1].

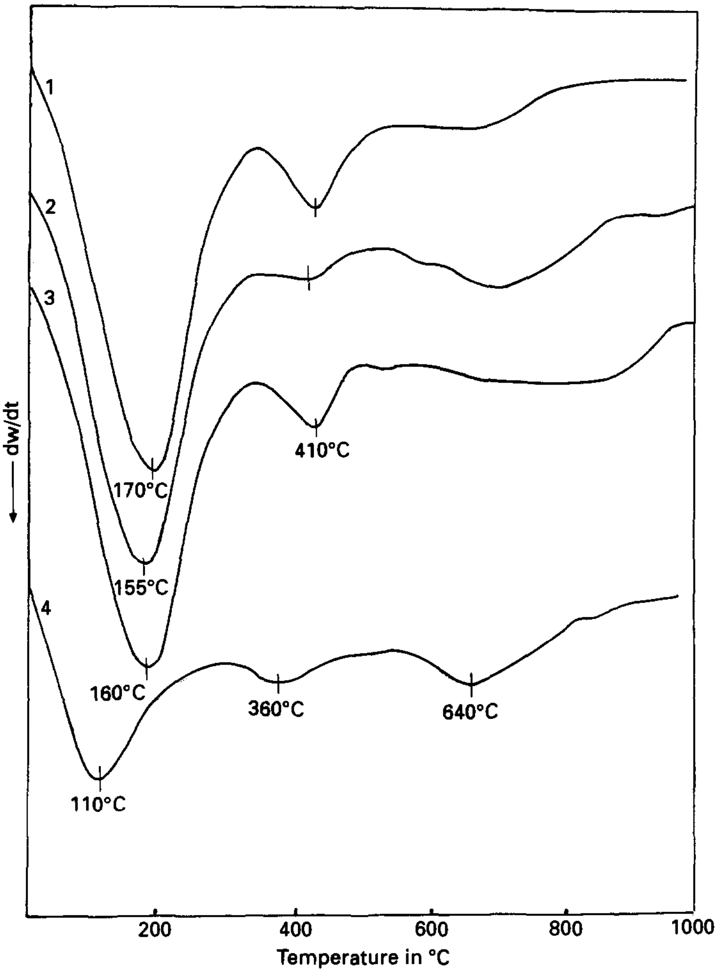

Fig. 4. DTG of NBA (*n*-butylamine) on: (1), NaY (–, 500, 2); (2), FeNaY (37, 500, 2); (3), FeNaY (46, 500, 2); (4), FeNaY (85, 500, 2).

The apparent activation energies for the desorption of *n*-butylamine sorbed on the activated FeNaY zeolites were determined using the Coats–Redfern equation [10]

$$\log\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \log\left[\frac{AR}{aE}\left(1-\frac{2RT}{E}\right)\right] - \left(\frac{E}{2.303RT}\right) \qquad (2)$$

where α is the fraction of NBA desorbed, a the heating rate, T the absolute temperature, R the gas constant, and E the apparent activation energy. The values of the apparent activation energies for the desorption of NBA given in Table 4. A typical Coats–Redfern plot of $\log[\ln(1-\alpha)/T^2]$ against $1/T$ is shown in Fig. 5, for FeNaY (37, 350, 2, NBA) zeolite.

Table 3
Percent weight loss and number of *n*-butylamine molecules desorbed per unit cell

Zeolite	Percent weight loss (NBA molecules desorbed per unit cell)[a]			
	First peak	Second peak	Third peak	Total wt. loss in %
NaY (–, 350, 2)	20.63 (36.14)	1.60 (2.80)	0.27 (0.47)	22.50 (39.41)
FeNaY (37, 350, 2)	15.38 (26.63)	2.35 (4.07)	4.27 (7.40)	22.00 (38.14)
FeNaY (46, 350, 2)	14.40 (24.91)	2.10 (3.63)	4.96 (8.58)	21.46 (37.12)
FeNaY (82, 350, 2)	8.90 (15.34)	5.06 (8.72)	3.70 (6.38)	17.66 (30.44)
NaY (–, 500, 2)	15.95 (27.94)	4.22 (7.39)	1.30 (2.44)	21.47 (37.61)
FeNaY (37, 500, 2)	14.88 (25.80)	2.63 (4.56)	3.10 (5.38)	20.61 (35.73)
FeNaY (46, 500, 2)	14.20 (24.57)	3.00 (5.19)	3.46 (5.99)	20.66 (35.74)
FeNaY (82, 500, 2)	8.50 (14.65)	3.25 (5.60)	3.00 (5.17)	14.75 (25.42)

[a] The corrections are made for the water contents of the zeolites, from Ref. [1].

Table 4
Activation energy for the desorption of *n*-butylamine sorbed on the activiated FeNaY zeolites

Catalyst	Activation energy for the desorption of NBA in kJ mol^{-1}	
	First peak in DTG	Second paek in DTG
NaY (–, 350, 2)	27.006	38.310
FeNaY (37, 350, 2)	21.453	71.832
FeNaY (46, 350, 2)	19.540	68.002
FeNaY (82, 350, 2)	15.325	51.718
NaY (–, 500, 2)	25.830	91.946
FeNaY (37, 500, 2)	16.091	61.296
FeNaY (46, 500, 2)	19.281	90.619
FeNaY (82, 500, 2)	13.496	69.412

The activation energies for the desorption of NBA over NaY (–, 350°C, 2 h) FeNaY (37, 350, 2), FeNaY (46, 350, 2) and FeNaY (82, 350, 2), corresponding to the first DTG peak at about 120–160°C, are 27.006, 21.453, 19.540 and 15.325 kJ mol^{-1}, and for the second peak 38.310, 71.832, 68.002 and 51.718 kJ mol^{-1}, as given in Table 4, respectively. The activation energies for the desorption of NBA decreases with the increase in ferric exchange corresponding to the first DTG peak. The activation energies for the second peak increases for the ferric-exchanged zeolites. This is because of the strong interactions of NBA with sodium and ferric ions. For these zeolites, iron is in the $[Fe(OH)]^{2+}$ form and sodium may be in a hydrated form [1].

The activation energies for the desorption of NBA over NaY (–, 500, 2), FeNaY (37, 500, 2), FeNaY (46, 500, 2) and FeNaY (82, 500, 2), corresponding to the first DTG peak at about 100–160°C, are 25.836, 16.091, 19.281 and 13.496 kJ mol^{-1},

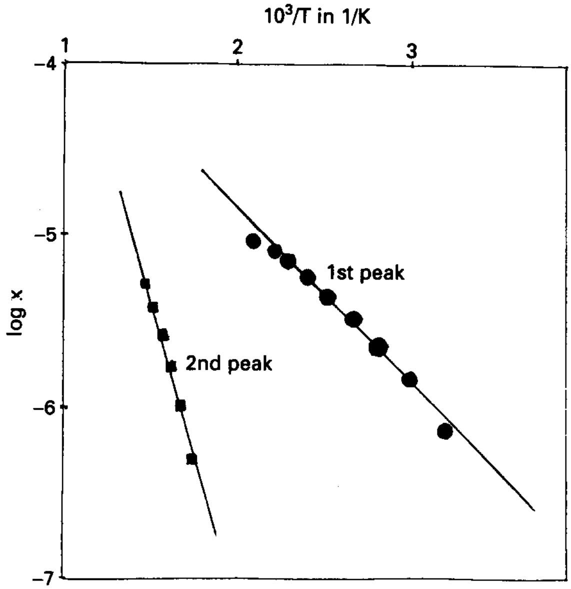

Fig. 5. Coats–Redfern plot for TG of FeNaY (37, 350, 2, NBA).

and for the second peak 91.946, 91.296, 90.619 and 69.412 kJ mol^{-1} respectively, as depicted in Table 4. The activation energies corresponding to the first peak are typical of physically or weakly chemisorbed NBA molecules. However, the activation energies corresponding to the second peak are higher. The factors affecting the activation energies are the dehydration and dehydroxylation of the cations and framework at 500°C, and the migration of the ferric ions. The NBA molecules desorbing in the range 320–480°C interact with the sodium and ferric ions and the dehydroxylated framework.

4. Conclusions

The DTG of NBA sorbed on NaY showed two peaks corresponding to the physisorbed or weakly chemisorbed molecules and NBA coordinated to sodium ions.

DTG, TG and DTA of NBA sorbed on FeHNaY showed three peaks. The first peak (approx. 120°C) corresponds to the physisorbed or weakly chemisorbed molecules. The second DTG peak (approx 350°C) is due to NBA molecules coordinated to sodium or medium-strength acidic centres. The third DTG peak (at 650°C) is attributed to the NBA molecules sorbed on Fe^{3+} and H^+ ions.

Due to the thermal treatment at 500°C for 2 h, ferric ions migrate from supercages to sodalite or hexagonal prisms, resulting in the decrease in the number of NBA corresponding to the second and third DTG peaks.

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