

## Silicate 上에서의 아민의 吸着. Protonic 酸 자리와 Aprotionic 酸 자리의 區別

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## The Adsorption of Amines on Silicates. Distinction between Protonic and Aprotionic Acid Sites

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**요 약.** 여러가지 陽이온이 交換된 silicate 上에 pyridine, tertiary butylamine, ethylenediamine 을 吸着시켜 IR spectra 를  $4000\sim 1200\text{ cm}^{-1}$  의 範圍에서 그리고 여러 다른 脫氣溫度에서 얻었다. 이 結果 protonic 酸 자리와 aprotionic 酸 자리를 區別할 수 있었으며 陽이온이 交換된 모든 silicate 는 Brönsted 酸과 Lewis 酸을 모두 나타내었다. 그리고  $\text{Na}^+$  이온이 交換된 silicate 가 adsorbate 와의 反應성이 가장 적게 나타났다. Tertiary butylamine 의 band intensity 의 상대적인 比는 交換된 陽이온의 polarizing power 와 비례하고 두개의 amino group 을 가지고 있는 ethylenediamine 은 tertiary butylamine 에 比해서 silicate 表面으로부터 쉽게 脫着되지 않았으며 또한 Lewis 酸 자리와 coordination bond 를 이루는 경우와 Brönsted 酸 자리와  $\text{NH}_3^+$  종을 만드는 경우외에 migrating proton 을 떼어 냄으로써 달미암아 表面酸素와의 水素結合을 이루는 경우가 確認되었다.

**ABSTRACT.** The infrared spectra obtained in the region of  $4000\sim 1200\text{ cm}^{-1}$  has been measured for pyridine, tertiary butylamine, and ethylenediamine adsorbed on various cation-exchanged silicates at various degassing temperature. It was possible to distinguish between protonic and aprotionic acid sites of all cation-exchanged silicates which exhibited both Brönsted and Lewis acidity. The sodium form appeared to be the least reactive towards adsorbates. The relative ratio of the band intensities of tertiary butylamine was directly related to the polarizing power of exchanged cations. Ethylenediamine was less easily desorbed from silicate surface than tertiary butylamine due to the additional amino group to react with surface active site, and probably to form either hydrogen bond with surface oxygen by liberating migrating proton besides the coordination bond with Lewis acid site and the formation of  $\text{NH}_3^+$  species with Brönsted acid site.

## 1. INTRODUCTION

The acid properties of various catalysts and catalyst supporters have been the subjects of a number of investigations. A wide variety of techniques to measure acidities of the substrates such as titration of acid sites with base solutions using indicators<sup>1,2</sup>, ammonia chemisorption at various temperatures<sup>3,4</sup> as well as infrared spectroscopy of the surface molecules<sup>5-9</sup> have been utilized. The infrared spectroscopy of adsorbed molecules of these techniques is known as an effective way to distinguish between protonic and aprotic acid sites which is equivalent to Brønsted and Lewis acid sites. For this purpose, ammonia ( $pK_b=4.75$ ) or pyridine ( $pK_b=8.75$ ) has been often used as an adsorbate. Parry<sup>6</sup>, Basila *et al.*<sup>10</sup>, and Eberly<sup>9</sup> have employed this technique for characterizing the surfaces of silica, alumina, silica-alumina cracking catalysts, and faujasites. Nevertheless, the interaction between pyridine and silica weakly takes place mainly due to the hydrogen bonding. Alumina possesses strong Lewis acidity. Silica-alumina catalysts, on the other hand, exhibit both Brønsted and Lewis acidity. Faujasites exhibit different acidity according to cation-exchanged forms.

However, the ammonia band that was used to determine the coordinately bonded ammonia was found to be subject to some interference, while pyridine was found to be too weak as base to accept a proton from the weak acid surfaces<sup>8</sup>. Therefore, these authors have used as adsorbate tertiary butylamine (TBA,  $pK_b=3.17$ ) and ethylenediamine (EDA,  $pK_b=3.29$ ), stronger bases than the others to determine the weak acid sites of surface. Since each EDA molecules have two identical functional group, we also intended to measure IR spectra of EDA adsorbed on silicate to see whether two adsorbates behave differently each other with silicate surfaces or not.

## 2. EXPERIMENTAL

The silicate mineral obtained from Yungil, Korea, was carefully prepared. From the X-ray diffraction pattern of the powder sample, it was confirmed that this silicate contained zeolite of philipsite group. The various cation-exchanged silicates were prepared by treating the fractions of less than  $1\mu$  size with solution of chloride salts of  $NH_4^+$ ,  $Na^+$ ,  $Cu^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Al^{3+}$ , in excess of the cation-exchange capacity at  $90^\circ C$  for 2 hours. After centrifuging, the supernatant liquid was poured out and the solution of chloride salts was added again. After this process was repeated three times, silicate suspensions were placed in dialysis bags and dialyzed against distilled water until no further chloride ions were detected with silver nitrate solution. The self-supported thin films of those cation-exchanged silicate were prepared by air drying those suspensions in the aluminum foil dishes.  $H^+$ -silicate was prepared by exchanging the sodium ions with ammonium ions and calcinated at  $500^\circ$  to liberate  $NH_3$  from  $NH_4^+$ -silicate.

Three amines, TBA, EDA, pyridine were obtained from Katayama chemical Co., Japan. All three amines were purified by redistillation followed by treating with a molecular sieve to exclude trace amount of water and kept in a refrigerator at  $-10^\circ$ .

In order to remove adsorbed water existing in the film, the film was pretreated in the electric furnace  $400^\circ$  and followed by degassing up to  $10^{-4}$  torr at  $300^\circ$  for 4 hours within the heatable gas cell. Details of the heatable gas cell have been previously<sup>11</sup> described. The infrared spectra of the films fixed in the heatable gas cell were taken by a Hitachi model EPI-G<sub>2</sub> infrared spectrometer at  $25^\circ$ ,  $70^\circ$ ,  $120^\circ$ , and  $200^\circ$  adjusted by a Hitachi model IRC-2 temperature controller.

Each back ground spectrum after degassing was recorded before adsorbates vapor was admitted to contact the film within the gas cell at about 40 torr for 30 minutes. Then gas cell was evacuated at various elevated temperature in order to obtain the final spectrum in the region of  $4000\sim 1200\text{ cm}^{-1}$ , expanding 5 times on the abscissa frequency scale. X-ray diffractogram of the silicate powder was taken by a Shimadzu VD-I X-ray diffractometer using Cu-K $\alpha$  radiation and Ni-filter, at 500 cps.

### 3. RESULTS AND DISCUSSION

#### Adsorption of Pyridine on Surface Sites.

From previous works on the spectra of pyridine adsorbed on the solid surfaces, it has been possible to distinguish between various types of adsorbed molecules<sup>6,10</sup>. The protonated form of pyridine is best characterized by a band near  $1540\text{ cm}^{-1}$ . Coordinately bound pyridine formed by interaction with Lewis type sites has a band near  $1450\text{ cm}^{-1}$ .

In the IR spectra of pyridine on Na<sup>+</sup>-silicate and Cu<sup>2+</sup>-silicate at 25° shown in Fig. 1, a sharp band appeared at  $1441\text{ cm}^{-1}$  for Na<sup>+</sup>-silicate and  $1447\text{ cm}^{-1}$  for Cu<sup>2+</sup>-silicate was responsible for the interaction of pyridine with Lewis acid site of surface. And a few weak bands appeared in the region of  $1560\sim 1520\text{ cm}^{-1}$  to indicate that there were more than two kinds of Brønsted sites and the silicate mineral had two types of acidity.

With the monovalent ions, Eberly<sup>9</sup> reported that no Brønsted acidity was observed. A number of workers have demonstrated that addition of alkali ions to cracking catalysts destroys or reduces its activity. We observed, however, very weak bands characterizing Brønsted acidity of Na<sup>+</sup>-silicate as shown in Fig. 1. Nevertheless, the intensities of the species adsorbed on Na<sup>+</sup>-silicate are relatively weaker than that of

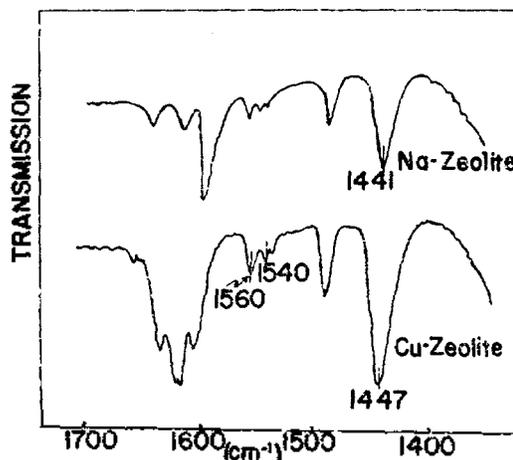


Fig. 1. IR spectra of pyridine species adsorbed on Na<sup>+</sup>-silicate and Cu<sup>2+</sup>-silicate at 25°.

species adsorbed on Cu<sup>2+</sup>-silicate. This is in good agreement with the fact found by Benesi<sup>1</sup> that the treatment of a cracking catalyst with excess sodium ion, then calcining, gave a catalyst which still showed acidity.

**Adsorption of TBA on Surface Sites.** In order to find weak Brønsted acid sites to transfer a proton to pyridine, we studied the spectra of TBA adsorbed on seven different cation-exchanged silicates. Colthup and Daly<sup>12</sup> referred that the NH<sub>3</sub><sup>+</sup> groups exhibited the symmetrical and asymmetrical bending vibration bands in the regions of  $1550\sim 1505$  and  $1600\sim 1575\text{ cm}^{-1}$  respectively. The asymmetrical NH<sub>3</sub><sup>+</sup> bending vibration, however, absorbs same region of IR as that of the NH<sub>2</sub> bending vibration, and consequently we were unable to ascertain the presence of NH<sub>3</sub><sup>+</sup> species by this band. On the contrary, the band at  $1550\sim 1505\text{ cm}^{-1}$  due to symmetrical NH<sub>3</sub><sup>+</sup> bending vibration seems to be of great advantage for the purpose, because it is in the region independent from the NH<sub>2</sub> bending vibration.

The IR spectra of TBA adsorbed on Na<sup>+</sup>-silicate and Cu<sup>2+</sup>-silicate pretreated at 300° in vacuo after calcination in electric furnace at

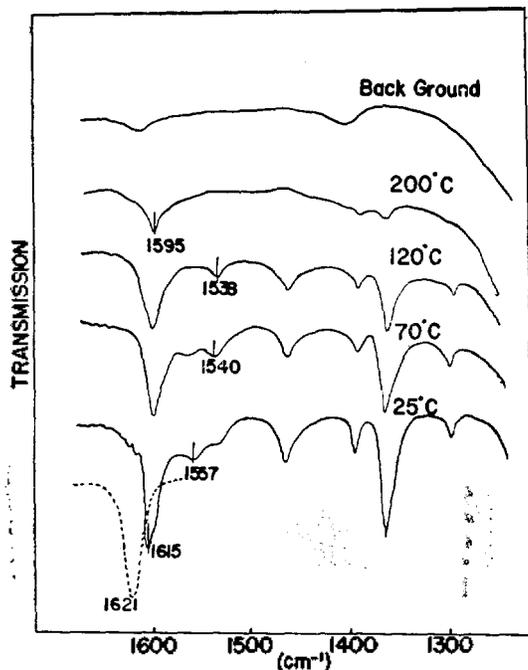


Fig. 2. IR spectra of TBA adsorbed on Na<sup>+</sup>-silicate at various degassing temperature.

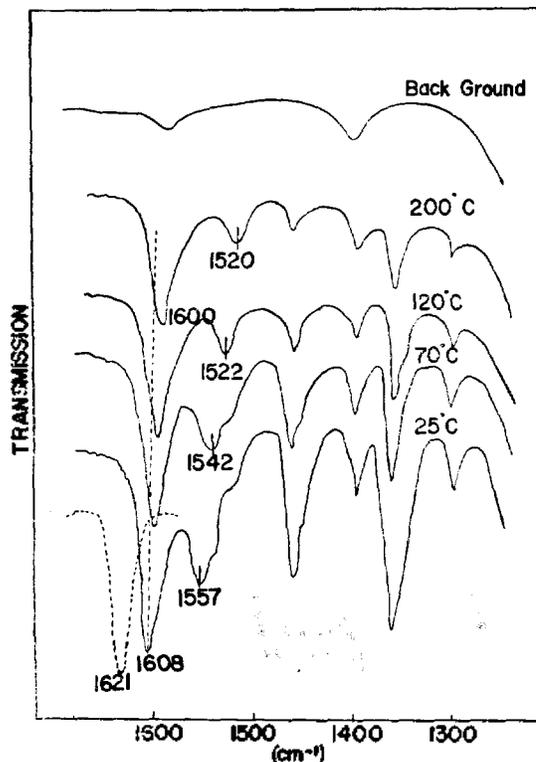


Fig. 3. IR spectra of TBA adsorbed on Cu<sup>2+</sup>-silicate at various degassing temperature.

500°, obtained at various degassing temperature, are shown in Fig. 2 and Fig. 3 respectively. Similar spectra were observed with other cation-exchanged silicates. The spectra of TBA adsorbed on Na<sup>+</sup>- and Cu<sup>2+</sup>-silicate have the bands at 1557~1520 cm<sup>-1</sup>, which is considered to come from the symmetrical NH<sub>3</sub><sup>+</sup> bending vibration as stated above. By pumping off adsorbate vapour from the gas cell at elevated temperature, the intensities of the bands decreased and at the same time the frequencies of the band shifted to lower wavenumber in the sense that constituents of higher frequencies in the band diminish more rapidly than those of lower frequencies (Fig. 2, Fig. 3). Similar tendencies were observed on each samples of silicates. These results indicate that NH<sub>3</sub><sup>+</sup> species are adsorbed on the surfaces of acid sites of different strength and that TBA adsorbed on the stronger site persist up to higher tempera-

Table 1. Frequency shifts of symmetrical NH<sub>3</sub><sup>+</sup> bending vibrations (cm<sup>-1</sup>).

Absorbent	Degassing temperature			
	25°	70°	120°	200°
Na <sup>+</sup> -silicate	1557	1540	1538	—
H <sup>+</sup> -silicate	1558	1540	1523	—
Ca <sup>2+</sup> -silicate	1558	1540	1520	—
Cu <sup>2+</sup> -silicate	1557	1542	1522	1520
Co <sup>2+</sup> -silicate	1558	1538	1524	1519
Ni <sup>2+</sup> -silicate	1552	1530	1522	1522
Al <sup>3+</sup> -silicate	1558	1542	1522	1519

ture. The absorption frequencies of the TBA most intensively adsorbed in the range of the symmetrical NH<sub>3</sub><sup>+</sup> bending vibration are listed in Table 1 as a function of evacuation temperature.

The intensive bands of the NH<sub>2</sub> bending vi-

bration appeared at about  $1610\text{ cm}^{-1}$  and shifted gradually from  $1610$  to  $1595\text{ cm}^{-1}$  for  $\text{Na}^+$ -silicate  $1608$  to  $1600\text{ cm}^{-1}$  for  $\text{Cu}^{2+}$ -silicate, when the sample films were heated at elevated temperature as illustrated in Fig. 2 and Fig. 3. Furthermore, it is to be noted that this band remains even after heating the film at  $200^\circ$  in vacuo to illustrate the strong interaction of TBA with Lewis acid site. If TBA molecules are adsorbed on Lewis acid sites, the  $\text{NH}_2$  bending vibration should still remain. In reacting with a Lewis acid site, the nitrogen in TBA shares its free electron pair to fill the vacancy of the Lewis acid site, thus maintaining the TBA structure. By comparing the spectra of TBA and pyridine adsorbed on silicate, it seems reasonable to consider that the bands at  $1610\sim 1595\text{ cm}^{-1}$  are attributed to TBA strongly adsorbed on Lewis acid sites of silicate.

In the spectra of TBA in pure vapor state two bands were observed at  $3325$  and  $3230\text{ cm}^{-1}$ , which supposed to be related with asymmetrical and symmetrical  $\text{NH}_2$  stretching vibration bands. These two bands also shifted to lower wavenumber to the extent of  $85\sim 92\text{ cm}^{-1}$  for asymmetrical band and  $50\sim 57\text{ cm}^{-1}$  for symmetrical band (Table 3). It is considered that these band shifts are the results of interaction of TBA with Lewis sites of surface.

The band intensities of TBA adsorbed on  $\text{Na}^+$ -silicate were shown as the weakest among those adsorbed on cation-exchanged silicates and similar results were obtained with pyridine. TBA was desorbed considerably more from  $\text{Na}^+$ -silicate surface as compared with other cation forms (Fig. 2). It is considered to be due to the effect of sodium poisoning on both types of acid sites<sup>6,13</sup>.

The variation in the type and amount of acidity with nature of the cation saturated on the mineral surface seems particularly interesting. The ratio of the band intensities near  $1610\text{ cm}^{-1}$  (A band) and  $1560\text{ cm}^{-1}$  (B band) was different according to cation-exchanged forms

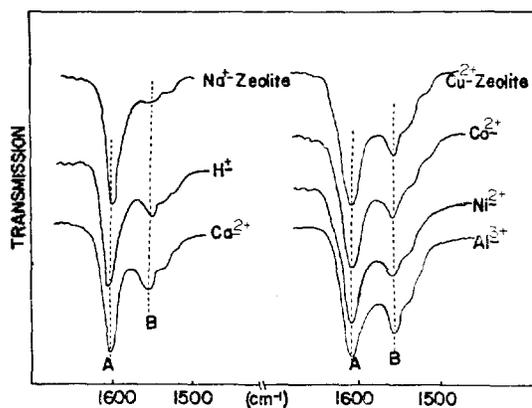


Fig. 4. IR spectra of TBA species adsorbed on the cation-exchanged silicates at 40 torr and followed by degassing to  $10^{-3}$  torr at  $25^\circ\text{C}$ .

Table 2. The relative ratios of band intensities of TBA characterizing two types of acid sites.

Adsorbent	Ionic radius (Å)	Polarizing power (e/r)	Intensity of A band ( $I_A$ )	Intensity of B band ( $I_B$ )	Ratio of band intensity ( $I_B/I_A$ )
$\text{H}^+$ -silicate			2.0	0.9	0.45
$\text{Na}^+$ -silicate	0.95	1.05	1.8	0.4	0.22
$\text{Ca}^{2+}$ -silicate	0.99	2.02	3.1	1.6	0.52
$\text{Cu}^{2+}$ -silicate	0.92	2.17	4.6	2.8	0.60
$\text{Co}^{2+}$ -silicate	0.72	2.78	2.3	1.4	0.61
$\text{Ni}^{2+}$ -silicate	0.69	2.90	1.9	1.2	0.63
$\text{Al}^{3+}$ -silicate	0.50	6.00	2.8	2.2	0.80

as shown in Fig. 4. The ratio of these bands were in increasing order of  $\text{Na}^+ < \text{H}^+ < \text{Ca}^{2+} < \text{Cu}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Al}^{3+}$ . We related these ratio to polarizing power of the cations as defined by the ratio of ionic charge to ionic radius ( $e/r$ ). Since no information was available on the size of these ions in silicates, Pauling's crystal radii were used<sup>14</sup>. The Brønsted acidity apparently increase with the polarizing power of the cation (Table 2). These results suggest that cations of high polarizing power are able to perturb nearby hydroxyl groups causing the hydrogens to become acid enough to protonate TBA.

**Adsorption of EDA on Surface Sites.** The adsorptions of EDA were carried out on the cation supported silicates pretreated at  $300^\circ$  in vacuo. EDA was chosen simply because it has two amino groups, equally reactive with surface site. Therefore, we can see that EDA can be desorbed less easily from silicate surface at elevated degassing temperature unlike TBA. The spectra of EDA adsorbed on  $\text{Al}^{3+}$ -silicate at various temperature is shown in Fig. 5 and Fig.

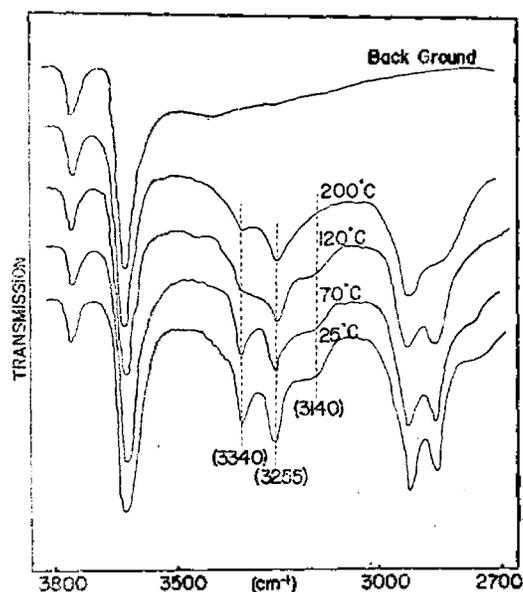


Fig. 5. IR of EDA adsorbed on  $\text{Al}^{3+}$ -silicate at various degassing temperature.

6. Similar spectra were also observed with other cation-exchanged silicate. The interaction of EDA with the substrates eventually causes shifts in their absorption bands from the position observed for the free amine in  $\text{CCl}_4$  solution. The  $\text{NH}_2$  stretching vibration bands, at  $3408\text{ cm}^{-1}$  and  $3315\text{ cm}^{-1}$  in solution<sup>15</sup>, shifted to lower wavenumber as much as  $58\sim 63\text{ cm}^{-1}$  for

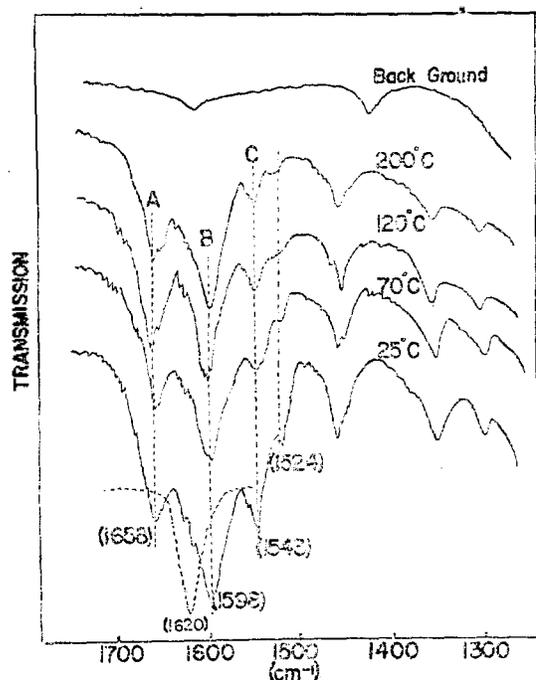


Fig. 6. IR spectra of EDA adsorbed on  $\text{Al}^{3+}$ -silicate at various degassing temperature.

Table 3.  $\text{NH}_2$  stretching band shifts of amines.

Adsorbent	EDA ( $\text{cm}^{-1}$ )		TBA ( $\text{cm}^{-1}$ )	
	$\Delta\nu_3$ 3408	$\Delta\nu_1$ 3315	$\Delta\nu_3$ 3325	$\Delta\nu_1$ 3230
$\text{H}^+$ -silicate	58	45	85	50
$\text{Na}^+$ -silicate	58	45	—	—
$\text{Ca}^{2+}$ -silicate	58	48	85	50
$\text{Cu}^{2+}$ -silicate	63	52	87	51
$\text{Co}^{2+}$ -silicate	63	51	92	57
$\text{Ni}^{2+}$ -silicate	60	52	92	57
$\text{Al}^{3+}$ -silicate	61	51	92	57

asymmetrical band and  $42\sim 52\text{cm}^{-1}$  for symmetrical band (Table 2). The band near  $3140\text{cm}^{-1}$  is assigned as the overtone of  $\text{NH}_2$  deformation band.

Although Colthup and Daly<sup>12</sup> referred that  $\text{NH}_3^+$  stretching vibration bands appeared between  $3200\text{cm}^{-1}$  and  $2800\text{cm}^{-1}$ , we failed to find  $\text{NH}_3^+$  stretching band due to the overlap with the overtone bands of  $\text{NH}_2$  deformation and the  $\text{CH}_2$  stretching frequencies.

The strong bands (B and) near  $1600\text{cm}^{-1}$  due to the interaction EDA with Lewis acid sites, and the absorption bands (C band) in the region of  $1545\sim 1520\text{cm}^{-1}$ , bending vibration of  $\text{NH}_3^+$  species, due to the adsorption on Brönsted acid sites were observed. These phenomena were similar to the case of TBA adsorbed on silicates except a new band (A band) appeared at about  $1660\text{cm}^{-1}$  as the result of  $\text{NH}_2$  deformation band shifted to higher wavenumber than that of free amine. Primary amines also show a  $\text{NH}_2$  deformation absorption at about  $1650\text{cm}^{-1}$ , and, along with the resulting shift of stretching vibration, this is subject to frequency shifts on hydrogen bonding<sup>16</sup>. Consequently, the bands near  $1660\text{cm}^{-1}$  are assigned to  $\text{NH}_2$  deformation band, which is responsible for the interaction of EDA with surface oxygen through hydrogen bonding. As illustrated in Fig. 6 at elevated degassing temperature, the intensity of B band is strong and rather consistent in comparison with those of A and C bands. Moreover, it seems that A and C bands interchange each other at elevated temperature. From this fact, we suggest that one of two amino groups of EDA probably interact with Lewis acid sites and the other interacts with

surface hydroxyl group to form  $\text{NH}_3^+$  species which possibly lead to liberate migrating proton as the following mechanism.

The ratio of band intensities of B bands due to Lewis site and C bands due to Brönsted site were not correlated with polarizing power of cations. This fact probably supports the adsorption mechanism as suggested above.

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