# Acidity and Acid Strength of Zeolite Catalysts

Misako Ikemoto, Kazuo Tsutsumi, and Hiroshi Takahashi
*Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo*

(Received August 17, 1971)

The influence of pretreatment temperature, silica-to-alumina mole ratio, the kind of cation and degree of cation exchange on the number of acid sites, and the acid strength of zeolite catalysts were examined by means of amine titration. Strong acid sites whose $H_0$ function is lower than $-8.2$ were analyzed by ultraviolet spectroscopy. Though H-zeolites have fairly strong acid sites ($-10.8<H_0<-8.2$), the number of acid sites decreases with the decrease of the silica-to-alumina mole ratio, as a result of the collapse of the zeolite structure. Ca-zeolites have an acid site distribution similar to that of H-zeolites only when the silica-to-alumina mole ratio is larger than 4.6. Only La-form Y-zeolite has strong acid sites ($H_0<-10.8$). When the degree of La-exchange exceeds 85 mol%, zeolite shows an acid coloration even with dinitrotoluene with $\mathrm{p}K_a -12.8$.

In recent years, near-faujasite zeolite catalysts have been used in various reactions,[1] and their surface acidity has been investigated by means of infrared spectroscopy,[2-8] and titration with a base in nonaqueous solutions.[9,10] However, the nature of acid sites has not yet been clarified.

Hirshler measured the acidity of Linde Molecular Sieves 10X, 13X, and Li-X[11] by using Hammett indicators and $H_R$ indicators, which form stable carbonium ions on the catalytic surface.[9] He showed that the acidity of 13X is very weak and only develops a red color with butter yellow, while both Li-X and Ca-X possess strong acid sites.

Otouma *et al.* studied the acid character of X and Y zeolites replaced by hydrogen, calcium and lanthanum ions by means of Hammett indicators,[10] and found characteristic features of the acid sites of zeolite catalysts. The number of acid sites is generally larger on the zeolites (2—3 meq/g) than on an amorphous silica-alumina cracking catalyst (0.5 meq/g). The acid strength is more widely distributed in the zeolites ($H_0=+3.3\sim-8.2$) than in silica-alumina ($H_0<-8.2$). The acid sites increase not only in number but also in strength with the advance of ion exchange.

The present investigation deals with a study of the effects of pretreatment temperature, the silica-to-alumina mole ratio, and the ion exchange on the surface acidity of faujasite-type zeolites. The nonaqueous titration method using Hammett indicators was applied for measurement of the acid sites.[12,13] Though it has been reported that zeolite has a strong acid character, little work has been carried out on the strong acid sites ($H_0<-8.2$). Information was obtained also on the strong acid centers on zeolite by a spectrophotometric method.

## Experimental

Of the zeolite samples used in this study, $\mathrm{Na{-}X_{2.5}}$[14] and $\mathrm{Na{-}Y_{5.0}}$ were Linde Molecular Sieves 13X and SK-40, respectively, and $\mathrm{Na{-}Y_{3.25}}$, $\mathrm{Na{-}Y_{3.85}}$, and $\mathrm{Na{-}Y_{4.6}}$ were synthesized from silica-alumina gel and sodium hydroxide. The calcium-, lanthanum-, or ammonium-exchange was performed by immersing the sodium-form zeolite in an aqueous solution of respective metal chlorides or ammonium chloride. Treatment was repeated several times in order to obtain a high degree of exchange. The samples were then collected by filtration, washed until no chloride ion was detected with silver nitrate and finally dried. The degree of exchange was determined by chemical analysis and flame photometry.

All the indicators were Wako Pure Chemicals Co. products. They were purified by recrystallization from benzene.

Cyclohexane was Dotite Spectrosol and was dried with a Linde Molecular Sieve 4A. *n*-Butylamine (Wako S grade) was purified by distillation and dried with a Linde Molecular Sieve 4A.

The Hammett indicators are listed, together with their p$K_a$'s in Table I. Color changes of BY, DCA, BAP, and AQ are visible and the measurements were carried out with powdered samples. Since both acid and basic forms of absorbed PNT and DNT are colorless, the measurements were made by the aid of a spectrophotometer. Thin wafers were used as samples. Fifty mg of powdered zeolite was pressed into pellets between stainless steel blocks. The wafer "thickness" was 20 mg/cm$^2$.

The samples were placed in a vessel evacuated to $10^{-3}$

Table 1. Indicators used in acid strength distribution measurements

| Hammett indicators | p$K_a$ |
|---|---|
| Butter yellow (BY) | +3.3 |
| Diciannamalacetone (DCA) | −3.0 |
| Benzalacetophenone (BAP) | −5.6 |
| Anthraquinone (AQ) | −8.2 |
| *p*-Nitrotoluene (PNT) | −10.8 |
| 2,4-Dinitrotoluene (DNT) | −12.8 |

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1) P. B. Venuto and D. S. Landis, *Adv. Catal.*, **18**, 259 (1968).

2) J. L. Carter, P. J. Lucchesi, and D. J. C. Yates, *J. Phys. Chem.*, **68**, 1385 (1964).

3) J. B. Uytterhoeven, L. G. Christner, and W. K. Hall, *ibid.*, **69**, 2117 (1965).

4) J. R. Hughes and H. M. White, *ibid.*, **71**, 2192 (1967).

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7) H. Hattori and T. Shiba, *J. Catal.*, **12**, 111 (1968).

8) P. E. Eberly, Jr. and C. N. Kimberlin, Jr., Proc. 2nd Int. Conf. Molecular Sieve Zeolites, p. 283 (1970).

9) A. E. Hirschler, *J. Catal.*, **2**, 428 (1963).

10) H. Otouma, Y. Arai, and H. Ukihashi, This Bulletin, **42**, 2449 (1969).

11) This denotes the faujasite-type zeolite X with lithium ion.

12) H. A. Benesi, *J. Amer. Chem. Soc.*, **78**, 5490 (1956).

13) H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

14) Zeolite with silica-to-alumina mole ratio 2.5.

Torr, and the temperature was then slowly raised to the desired temperature and kept constant for 5 hr under $10^{-5}$ Torr.

Acidity measurements were carried out as follows. The sample was transferred from the evacuated vessel to a test tube in a dry-box. Two m*l* of dry cyclohexane and a proper amount of a 0.1 N solution of *n*-butylamine in cyclohexane were added. After the test tube was maintained at 60°C for 3 days, a few drops of 0.1% solution of the indicator in cyclohexane were added. After 2 days, it was determined whether the sample was basic or acidic to the indicator, either with the naked eye or by the use of a UV spectrophotometer.

## Results and Discussion

*Effect of Pretreatment Temperature.* Figures 1 and 2 illustrate the correlation between the pretreatment temperature and the number of acid sites of the Ca- and $NH_4$-form zeolites at $H_0=+3.3$. The number of acid sites of Ca-zeolites increases to a maximum and then gradually decreases when the pretreatment temperature is raised. The number of acid sites of Ca-zeolite with a lower ratio of silica-to-alumina changes greatly with the pretreatment temperature, while that of Ca-zeolite with a higher ratio remains nearly constant. Since the zeolites with lower silica-to-alumina ratios have a relatively large number of Al atoms, the bond distance between $Ca^{2+}$ and $AlO_2^-$ ions is small. Thus, it is difficult to break the bonds and only a small number of acid sites was measured with the sample evacuated at a lower temperature.

As clearly shown in Fig. 2, the acidity of H-form zeolites[15] is greatly influenced by silica-to-alumina ratio. The zeolite with a lower ratio showed a small number of acid sites at any pretreatment temperature, since it is thermally unstable and easily loses its crystallinity with heat treatment, when acid sites are lost. On the other hand, the zeolite with a higher ratio showed as many sites as Ca-zeolite because of its high thermal stability.

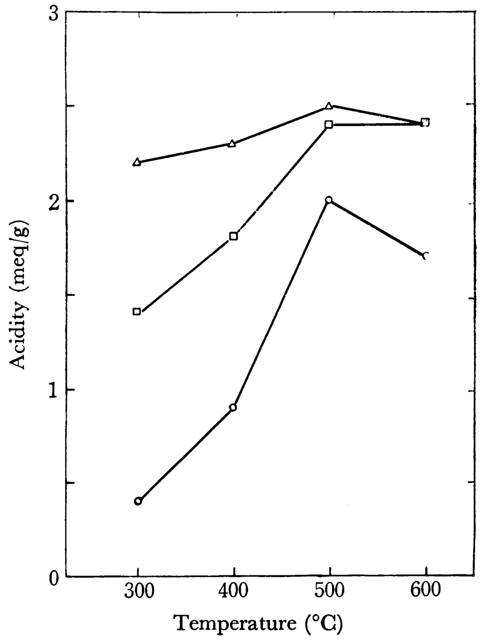

Fig. 1. Effect of pretreatment temperature on acidity of Ca-form zeolites ($H_0=+3.3$).
△: Ca-$Y_{5.0}$ ($Ca^{2+}$, 85 mol%)
□: Ca-$Y_{3.85}$ ($Ca^{2+}$, 90 mol%)
○: Ca-$X_{2.5}$ ($Ca^{2+}$, 99 mol%)

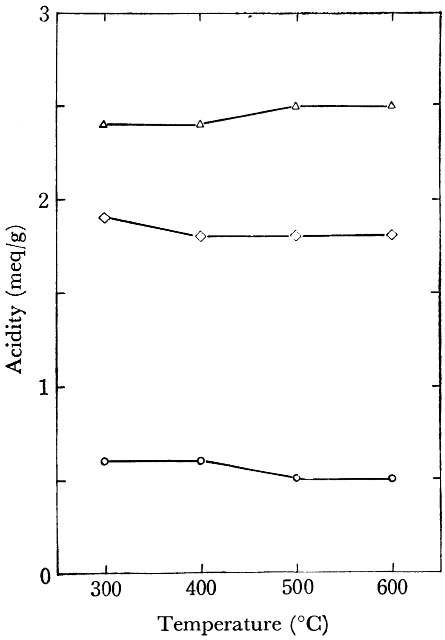

Fig. 2. Effect of pretreatment temperature on acidity of H-form zeolites ($H_0=+3.3$).
△: H-$Y_{5.0}$ ($H^+$, 92 mol%)
□: H-$Y_{4.6}$ ($H^+$, 89 mol%)
○: H-$X_{2.5}$ ($H^+$, 86 mol%)

*Effect of the Silica-to-Alumina Mole Ratio.* The effects of the silica-to-alumina mole ratio on the acidity

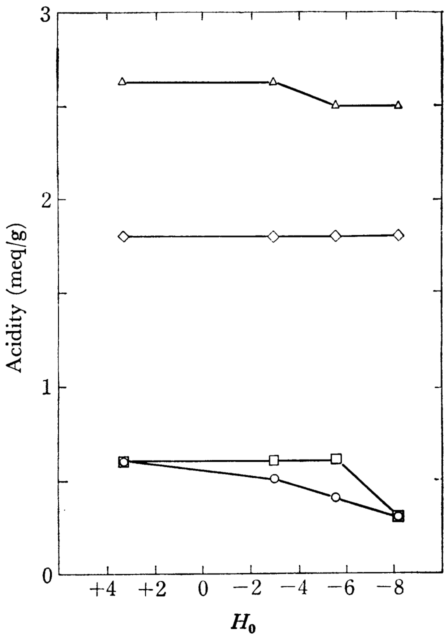

Fig. 3. Acid strength distributions of H-form zeolites.
△: H-$Y_{5.0}$ ($H^+$, 94 mol%), Pretreated at 500°C
◇: H-$Y_{4.6}$ ($H^+$, 89 mol%), Preatreated at 500°C
□: H-$Y_{3.86}$ ($H^+$, 86 mol%), Pretreated at 350°C
○: H-$X_{2.5}$ ($H^+$, 86 mol%), Pretreated at 350°C

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[15] $NH_4$-form zeolites change into H-form zeolites with liberation of $NH_3$ during pretreatment at above 300°C.

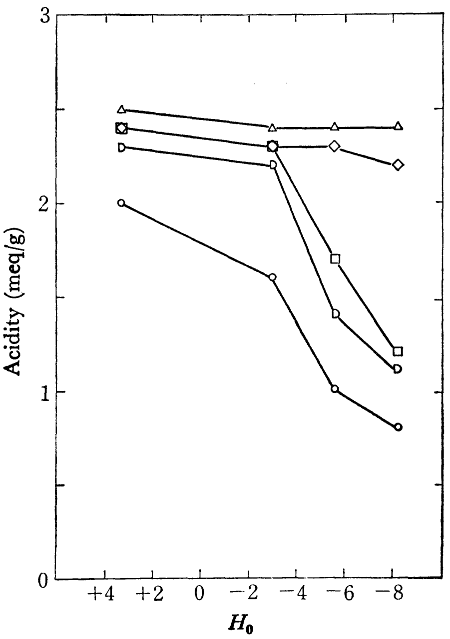

Fig. 4. Acid strength distributions of Ca-form zeolites pretreated at 500°C.

△: Ca-$Y_{5.0}$ ($Ca^{2+}$, 85 mol%)
◇: Ca-$Y_{4.6}$ ($Ca^{2+}$, 90 mol%)
□: Ca-$Y_{3.85}$ ($Ca^{2+}$, 90 mol%)
D: Ca-$Y_{3.25}$ ($Ca^{2+}$, 96 mol%)
○: Ca-$X_{2.5}$ ($Ca^{2+}$, 99 mol%)

of Ca- and H-zeolite were investigated. The distribution of acidity is shown in Figs. 3 and 4.

The maximum acidity in Ca-zeolite was 2.0 meq/g for Ca-$X_{2.5}$ and 2.5 meq/g for Ca-$Y_{5.0}$. The Ca-zeolites with silica-to-alumina mole ratios greater than 4.6 possess strong acid sites ($H_0 < -8.2$). However, the acid sites of Ca-zeolites with lower ratios of silica-to-alumina are distributed over a wide range of acid strength. The results agree with the fact that a strong electrostatic field is generated by heat treatment and easily produces $H^+$ ions in zeolites with a higher ratio of silica-to-alumina.[16] Though a decrease in the amount of alumina gives rise to a decrease in the number of cations, it makes the distance between cations and anions longer. As a result, separation between the positive and the negative charges becomes easier. Thus a strong electrostatic-field is generated and water is highly polarized.

On the other hand, H-zeolites with a higher ratio of silica-to-alumina possess acid sites as strong as those of Ca-zeolites. However, the number of acid sites of H-zeolites with a lower ratio is small due to the collapse of the structure resulting from the treatment. The higher the silica-to-alumina mole ratio, the less the number of anions in the zeolite structure. Protons with a low electric shield then become mobile and form strong acid sites.

*Effect of Ion Exchange.* Influence of the ion exchange of $Ca^{2+}$ and $La^{3+}$ ions on acidity was investigated. The acidity of Ca–Na–$Y_{3.25}$ and La–Na–$Y_{3.25}$ as a function of the degree of ion-exchange is shown in Fig. 5.

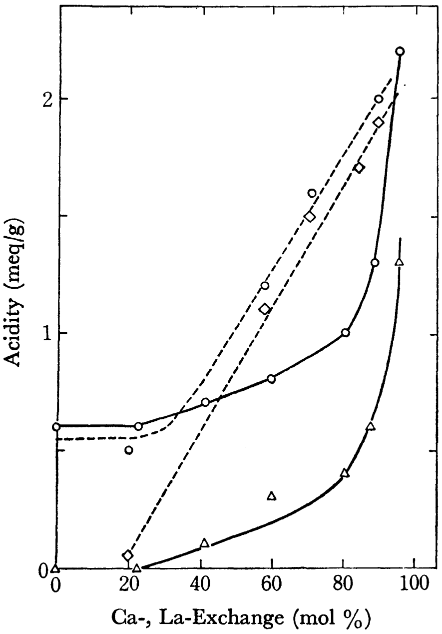

Fig. 5. Effect of Ca- and La-exchange on acidity of zeolites pretreated at 500°C.

——: Ca-$Y_{3.25}$, ----: La-$Y_{3.25}$
○: BY, △: BAP, ◇: AQ

The number of acid sites of Ca–Na–$Y_{3.25}$ is nearly equal to that of Na–$Y_{3.25}$ when the Ca exchange is lower than 40%, but increases rapidly above 80%. When sodium ions are replaced by calcium ions, calcium ions enter energetically stable sites in the beginning and the formation of acid sites by heat treatment is difficult.[17] Since the number of acid sites with $H_0$ values higher than −5.6 is almost constant, independent of ion exchange, the acid centers formed through calcium ion exchange have $H_0$ values lower than −5.6.

The acidity property of low-exchange sample is consistent with the fact that the electrostatic-field strength and the cumene-cracking activity of these samples were almost the same as those of the Na-form zeolites.[17,18] The divalent cations strongly prefer the $S_I$ cation sites connected to the large cavity through pores of about 2Å in diameter. As the pores are not large enough for the organic molecules to pass through, the cation-exchange does not influence the properties mentioned above.

In the case of the exchange with $La^{3+}$ ion, the acidity measured with BY begins to increase in proportional to the degree of exchange above 20%. Since $La^{3+}$ ion is highly charged, the bonds between $La^{3+}$ and $AlO_2^-$ ions are distorted remarkably, and many acid sites are formed even at lower exchange. Compared with the acidity measured with AQ, this acidity is distributed in a wider domain when the degree of exchange is 60% or less, and the acid sites with $H_0$ values lower than −8.2 are formed only above 60%.

*Measurement of Strong Acid Sites.* The UV spectra of PNT and DNT adsorbed on zeolites are shown in Figs. 6 and 7, respectively. The band at about 350 mμ in Fig. 6 is assigned to the acid form of PNT adsorbed

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[16] K. Tsutsumi and H. Takahashi, *J. Phys. Chem.*, **76**, 110 (1972).

[17] K. Tsutsumi and H. Takahashi, *ibid.*, **74**, 2710 (1970).

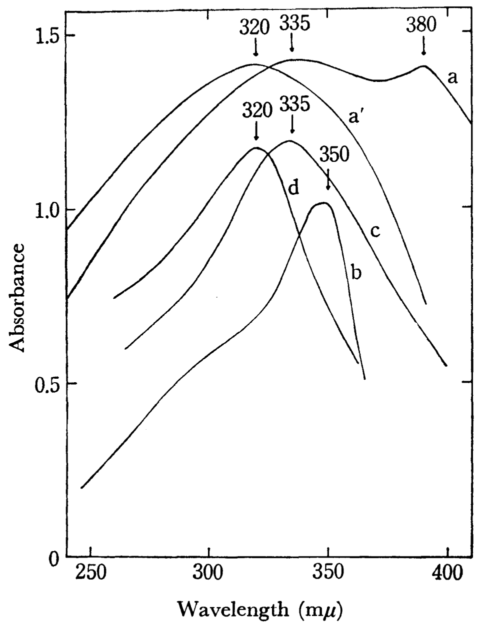

Fig. 6. UV spectra of PNT adsrobed on zeolites.
a: La-$Y_{3.25}$ ($La^{3+}$, 92 mol%)
a': Above+*n*-butylamine
b: La-$Y_{5.0}$ ($La^{3+}$, 85 mol%)
c: H-$Y_{4.6}$ ($H^+$, 85 mol%), H-$Y_{5.0}$ ($H^+$, 92 mol%)
d: Na-$Y_{3.25}$

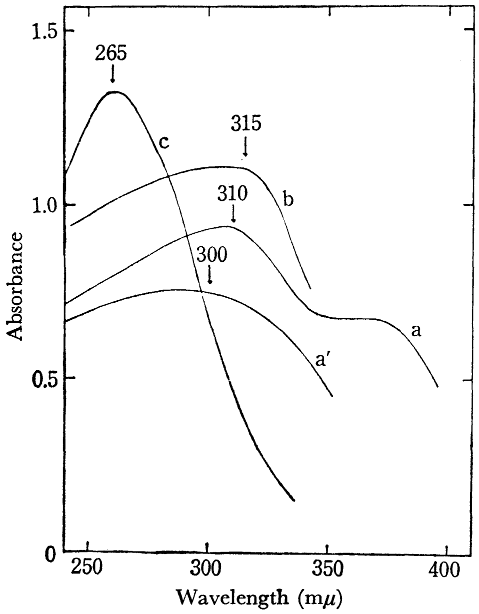

Fig. 7. UV spectra of DNT adsorbed on zeolites.
a: La-$Y_{3.25}$ ($La^{3+}$, 92 mol%)
a': Above+*n*-butylamine
b: La-$Y_{5.0}$ ($La^{3+}$, 85 mol%)
c: $\left\{\begin{array}{l}\text{H-Y}_{5.0}\ (H^+,\ 92\ \text{mol}\ \%)\\ \text{H-Y}_{4.6}\ (H^+,\ 85\ \text{mol}\ \%)\\ \text{Na-Y}_{3.25}\end{array}\right.$

on the zeolite surface, and that at 310 mμ in Fig. 7 to that of DNT.

The absorption maxima of the indicators adsorbed on various samples are listed in Table 2, together with those of cyclohexane solution and sulfuric acid solution. The absorption maxima of the indicators adsorbed on two kinds of silica-alumina (HA; $Al_2O_3$ 25% and LA; $Al_2O_3$ 13%) are also shown.

TABLE 2. ABSORPTION BANDS (mμ) OF UV SPECTRA OF VARIOUS INDICATORS SOLVED OR ADSORBED

| | BY | BAP | PNT | DNT |
|---|---|---|---|---|
| Cyclohexane | 400 | 300 | 260 | <230 |
| 10 wt% $H_2SO_4$ | 515 | | | |
| 50 wt% $H_2SO_4$ | | 435, 315 | 293 | 262 |
| 95 wt% $H_2SO_4$ | | 435, 315 | 310 | 262 |
| Fuming $H_2SO_4$ | | | 340, 288 | 327, 280, 255 |
| Silica-Alumina (LA) | | | 300 | 260 |
| Silica-Alumina (HA) | | | 300 | 260 |
| Na-$Y_{3.25}$ | 460 | 310 | 320 | 265 |
| H-$Y_{4.6}$($H^+$, 85 mol%) | 520 | 400, 310 | 335 | 265 |
| +*n*-BA[a] (0.5 meq/g) | 520 | 400, 310 | 335 | 265 |
| +*n*-BA (1.0 meq/g) | 480 | 310 | 330 | |
| +*n*-BA (2.0 meq/g) | 400 | 310 | | |
| +*n*-BA (3.0 meq/g) | 400 | | | |
| H-$Y_{5.0}$($H^+$, 92 mol%) | 520 | 400, 310 | 335 | 265 |
| +*n*-BA (0.5 meq/g) | 520 | | | |
| +*n*-BA (1.0 meq/g) | 520 | | 330 | |
| +*n*-BA (2.0 meq/g) | 400 | | | |
| La-$Y_{3.25}$($La^{3+}$, 92 mol%) | | | 380, 335 | 310 |
| +*n*-BA (1.0 meq/g) | | 260 | 320 | 300 |
| ($La^{3+}$, 85 mol %) | | 400 | 370 | 310 |
| ($La^{3+}$, 71 mol %) | | | 350 | 280 |
| ($La^{3+}$, 67 mol %) | | | 340 | 265 |
| ($La^{3+}$, 49 mol %) | | | 330 | 265 |
| La-$Y_{5.0}$($La^{3+}$, 85 mol %) | | | 350 | 315 |
| H-Mordenite ($H^+$, 92 mol %) | 520 | 390, 315 | 310 | 265 |

a) *n*-butylamine

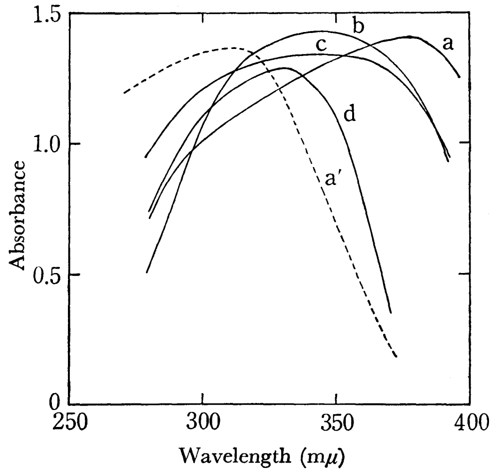

Fig. 8. UV spectra of PNT adsorbed on La-$Y_{3.25}$ having various degrees of La-exchange.
a: 85 mol%, a′: Above+*n*-butylamine b: 71 mol%, c: 67 mol%, d: 49 mol%.

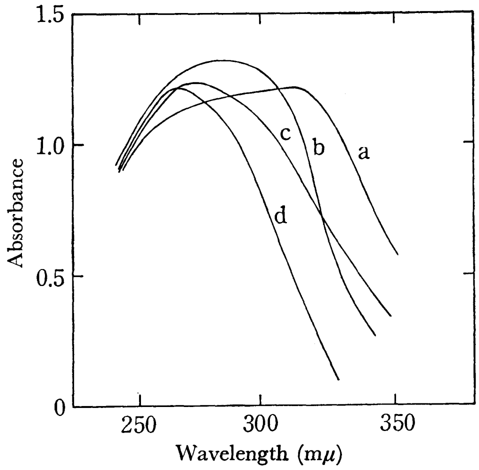

Fig. 9. UV spectra of DNT adsrobed on La-$Y_{3.25}$ having various degrees of La-exchange.
a: 85 mol%, b: 71 mol%, c: 67 mol%, d: 49 mol%

The results indicate that H–Y zeolite and H-mordenite which are considered to have a strong acid character, from the measurement with AQ, show basic colors of PNT and DNT. Their acid strength is therefore distributed in the $H_0$ range from −8.2 to −10.8. On the other hand, La–Y zeolites show acidic colors of both PNT and DNT as shown in Figs. 8 and 9. Thus, La–Y zeolites have very strong acid sites with $H_0$ values lower than −12.8. It is clear that the acid strength of La–Y is dependent on the degree of La-exchange. The La–Na–$Y_{3.25}$ showed an acid color of PNT when La-exchange exceeds 70% and even an acid color of DNT above 85%.

Such a strong acidity of La-form zeolite can be compared with that of fuming sulfuric acid. It turns out from this acidity that the cumene-cracking activity of La-form zeolite is much higher than that of H- and Ca-form zeolites.[18]

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[18] K. Tsutsumi and H. Takahashi, *J. Catal.*, **24**, 1 (1972).