Korean J. of Chem. Eng., **6**(4) (1989) *313-320*

CATALYTIC PROPERTIES OF DEALUMINATED AND CATION-EXCHANGED Y-TYPE ZEOLITES

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(Received 16 March 1989 • accepted 1 June 1989)

Abstract—Cumene dealkylation activity was determined for a series of dealuminated zeolites which were prepared by treatments with EDTA, $SiCl_4$, and steam at elevated temperatures. Upon dealumination the catalytic activity increased progressively up to 50% of framework aluminum removal. This is related to the increase of acid strength after aluminum removal and the extraction of weak acid site. However, beyond Si/Ai ratio close to 6, the acid strength of zeolite do not vary and the TOF based on framework aluminum is constant. Nonframework aluminum played a positive role in the enhanced catalytic activity. The variation of catalytic activity with cation was also examined. Catalytic activity is greatest for the small polyvalent cations. Comparison of the hydroxyl group with catalytic activity shows that the active sites are the acidic hydroxyl groups.

INTRODUCTION

Synthetic zeolites have recently gained prominence as catalysts and adsorbents. The X and Y type zeolites dealuminated or exchanged by cations have been investigated as catalysts for many reactions including cracking, isomerization, alkylations, and alcohol dehydration[1-4].

Dealumination is one of several methods of modifying zeolitic frameworks. Various methods have been used to dealuminate the framework of zeolite while still maintaining much of the crystallinity of the sample. Dealumination of a zeolite was first reported by Barrer and Makki who progressively removed aluminum from natural clinoptilolite by washing it with hydrochloric acid [5]. In 1968, Kerr reported the preparation of dealuminated Y type zeolites by extraction of aluminum from the framework with ethylenediaminetetraacetic acid (EDTA) [6]. Using this method, up to about 50 percent of the aluminum atoms was removed from the zeolite in the form of a water soluble chelate, without any appreciable loss in zeolite crystallinity.

Calcination of the ammonium-exchanged Y zeolites at high temperature in the presence of steam causes part of the framework aluminum to migrate into nonframework positions [7,8]. The resulting product, referred to as ultrastable Y zeolite, possesses improved thermal and hydrothermal stability, smaller unit cell size and lower ion exchange capacity as compared with the original Y zeolite. Beyer and Blenykaia were able to prepare highly dealuminated Y zeolites by reacting them with silicon tetrachloride vapors at high temperatures [9]. Framework substitution of silicon from $SiCl_4$ for aluminum takes place, while the resulting $AlCl_3$ is volatilized. More recently, dealumination was achieved by fluorination of zeolites at ambient temperature with a dilute fluorine in air stream, followed by high temperature calcination [10]. The suggested reaction mechanism involves the formation of different aluminum-fluorine compounds along with zeolites containing hydroxyl and fluorine nests.

On the other hand, the catalytic properties of cation-exchanged zeolites have recently received considerable attention. Exchange of sodium ions by alkaline earth or rare earth cations in faujasite type zeolites results in profound changes in catalytic activity. The ion-exchanged zeolite catalyst has the ability to crack various hydrocarbons, the product distribution of which is similar to that obtained with a silica-alumina cracking catalyst [11,12]. It has been proposed that the catalytic activity may be explained in terms of the hydrolysis of cation, yielding protons [13-15]. From investigations of various cation-exchanged forms it has been concluded that electrostatic fields associated with the cation are the seat of activity [16]. It has also been suggested that acidic hydroxyl groups are the centers

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of activity [17,18].

In a previous paper from this laboratory, we reported the characterization of Y type zeolites dealuminated by treating them with $SiCl_4$, steam, and EDTA [19]. The purpose of this work was to examine the catalytic activity of dealuminated and cation-exchanged Y type zeolites. Cumene dealkylation was selected as a test reaction because of its simplicity, extensive earlier use, and requirement of medium acid site which yield useful information. Of particular importance here is the effect of aluminum concentration on catalysis since total acid site concentration in proportional to framework aluminum concentration.

EXPERIMENTAL

1. Zeolite samples

The starting material used in the preparation of dealuminated and cation-exchanged Y type zeolites was a Linde sodium Y zeolite (SK40). The sodium Y zeolite had the following composition: Na_2O, 12.7%; Al_2O_3, 22.2%; SiO_2, 64.5%. The zeolite was dealuminated by reaction with EDTA, accordant to the procedure described by Kerr [6]. The zeolites were then washed with distilled water and ion exchanged 3 times, 12 hr each, in 1 M NH_4Cl at 70°C to remove any remaining Na^+ ion. These samples are denoted by a symbol of EDY (Si/Al), where the silicon to aluminum ratio is given in parentheses.

A steam-dealuminated zeolite Y (SDY) was prepared according to the method of Ward [20]. A sample of Linde NH_4NaY was heated under N_2/H_2O flow at 5°C/min, to 600°C, held at 600°C for 1 hr and cooled under the flow of steam. Sodium was then removed through a NH_4^+ ion exchange, and the resulting zeolite was heated to 500°C.

A $SiCl_4$-dealuminated zeolites Y (DY) were prepared according to the procedure described by Beyer et al. [9]. A sample of Linde NH_4NaY was dealuminated by reaction with flowing $SiCl_4$ vapor. Samples having a range of Si/Al ratios were prepared by reacting 2g of the zeolite with $SiCl_4/N_2$ at temperatures from 200 to 570°C. After reaction at the lower temperatures (200-350°C) the temperature of the zeolite was increased to 570°C under flowing N_2. The zeolites were then washed with distilled water and ion exchanged three times, 12 hr each, in 1 M NH_4NO_3 at 70°C to remove any remaining Na^+ ions.

A NH_4Y zeolite was prepared by treating the NaY zeolite with 1 M NH_4NO_3 3 times at 70°C for 12 hr each. The alkaline earth and rare earth zeolites were prepared by ion exchange with a solution of the corresponding cation chloride at 30-90°C.

2. Instruments

The infrared spectra of the hydroxyl groups were obtained with a Bruker FTIR spectrophotometer. The self-supporting zeolite wafers contained 6-9 mg/cm^2. Prior to obtaining the spectra the samples were heated under vacuum at 400°C for 2 hr. The samples for skeletal vibration bands were in the form of wafers prepared from a mixture of 1 mg of zeolite in 300 mg of KBr. The wavenumbers were calibrated using a band at 907 cm^{-1} in a polystyrene film.

The zeolites were checked by X-ray diffraction for crystallinity, and the unit cell parameter was determined relative to $Pb(NO_3)_2$ ($a_o = 7.8568$ Å). The X-ray diffraction patterns were obtained with a Jeol model JDX-88 diffractometer using copper target and nickel filter at 30 kV and 800 cps. The concentration of framework aluminum atoms was determined according to the equation (21),

$$N_{Al} = 107.1\,(a_o - 24.238) \qquad (1)$$

where N_{Al} is the number of Al atoms/UC.

3. Catalytic reaction

The zeolites listed in Table 1 were tested as catalysts for cumene dealkylation. Catalyst samples were prepared by mixing the zeolite with silica (Davison 952 grade SiO_2) in order to keep conversions low. Most of the catalyst samples were pressed into wafers (500 kg/cm^2), broken, and sieved: the 20-45 mesh portion was used in the reactions.

Catalytic activities were measured in a pulse microreactor constructed of 1/4 in. stainless-steel. For each experiment, 0.01g of catalyst was loaded into a reactor. The reactor was packed with quartz chips that both positioned the catalyst sample near an external thermocouple and served as a preheating stage for the reactant gases. The catalyst samples were activated in situ by heating them under flowing N_2 gas for 1 hr at 100°C, 1 hr at 200°C, 1 hr 300°C, and 2 hr at 400°C. Pulses of 1 μl cumene were injected into a N_2 gas stream which passed over catalyst at 15 ml/min. The reactions were carried out at 300-450°C. Samples of the products were analyzed with a Shimadzu 3 BT gas chromatograph using a 3 m Bentone 34 on chromosorb W column at 130°C.

RESULTS AND DISCUSSION

1. X-ray diffraction and infrared studies

Typical X-ray diffraction patterns of the parent material and of progressively EDTA-dealuminated samples of Na-Y zeolite are given in Fig. 1, together with that of $SiCl_4$-dealuminated zeolite. The EDY samples are evidently highly crystalline, until about 50%

Table 1. Analyses and catalytic activity of zeolites

Zeolite	Unit cell constant(Å)	Al per unit cell			Activity μmol/g		
		Framework[a]	Nonframework	Total[b]	300°C	350°C	400°C
NH_4Y(2.4)	24.746	55.6	0	56.0	23.6	66.0	118.0
EDY(2.6)	24.735	53.1	0	53.1	31.2	75.6	144.5
EDY(2.9)	24.696	48.9	0	49.0	48.4	108.1	213.2
EDY(3.4)	24.652	44.2	0	44.6	75.1	164.2	261.1
EDY(4.9)	24.542	32.4	0	32.4	85.6	197.1	361.2
EDY(5.9)	24.498	27.7	0	27.8	110.9	226.1	473.3
EDY(8.3)	24.431	20.6	0	20.8	69.9	195.3	33.9
SDY(4.6)	24.556	34.1	20.0	54.1	146.0	316.2	521.0
SDY(5.0)	24.536	31.9	22.7	54.6	217.1	397.2	623.1
DY(10.2)	24.386	17.2	28.2	45.4	105.3	218.1	417.1
DY(17.6)	24.325	10.3	31.8	42.1	72.1	135.5	221.2
DY(27.2)	24.293	6.8	19.9	26.7	25.2	73.7	11.4
DY(45.4)	24.270	4.1	18.7	22.8	17.8	41.0	55.0
DY(255.0)	24.245	0.75	11.75	12.5	2.1	4.4	7.0

a. Determined according to the equation, $N_{Al} = 107.1\,(a_o\text{-}24.238)$, where a_o is unit cell constant.
b. Based on atomic absorption data.

of aluminum atoms was removed from the zeolite framework. Upon dealumination of above 50% of aluminum atoms, the samples began to lose their crystallinity gradually. These results are in good agreement with those of other investigators [6,22]. However zeolite samples remained crystalline after $SiCl_4$ treatment only if the bed height was small (about 2 cm). The high degree of crystallinity is indicated by the X-ray diffraction pattern of Fig. 1 for the DY (225).

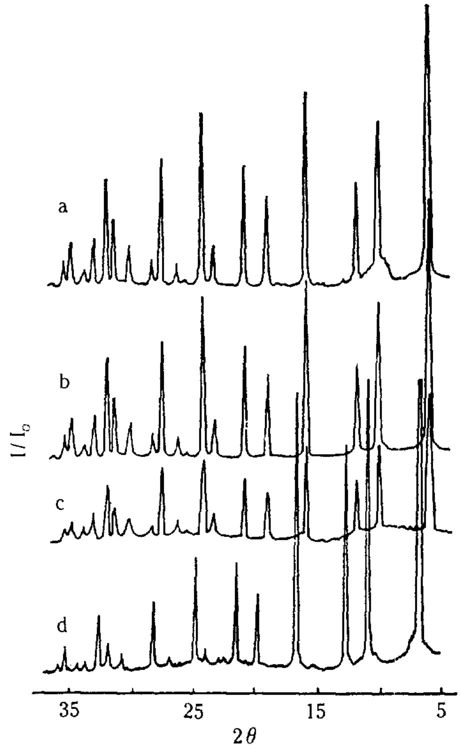

Fig. 1. X-ray diffraction patterns of:
(a) NH_4Y(2.4), (b) EDY(3.4), (c) EDY(8.3), and (d) DY (225).

The unit cell contracts upon dealumination as a consquence of the replacement of Al-O linkages (bond length 1.69 Å) by Si-O linkage (1.61 Å). Mid-infrared spectroscopy is a very sensitive tool for investigating structural changes and Si/Al ratios of zeolite framework [21]. In the infrared spectra of dealuminated zeolites, bands associated with the framework tetrahedra show a shift to higher wavenumbers due to the decrease in aluminum content. This is a direct result of the shortening of the average of T-O (T = Si, Al) bond length, the resolution of infrared spectra being insufficient to distinguish between Si-O and Al-O stretches. A set of spectra for samples of progressively decreasing aluminum content is shown in Fig. 2. The bands in the spectra of dealuminated zeolite are considerably sharper than those of starting zeolite, indicating a higher degree of order within the framework.

2. Effect of dealumination on catalytic activity

One of the standard tests for the characterization of

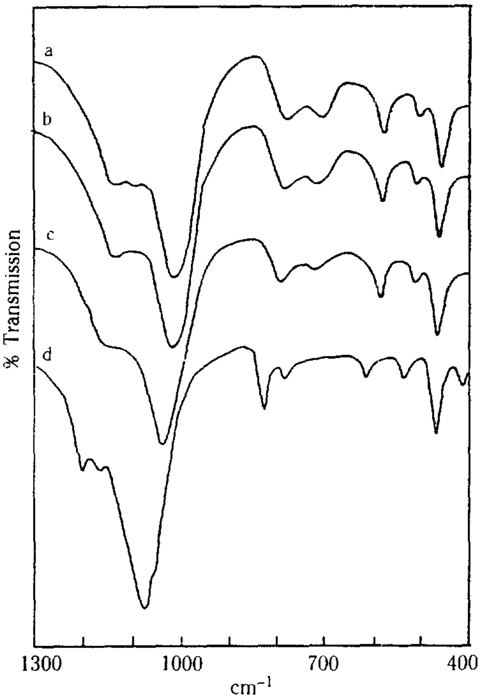

Fig. 2. Infrared spectra of NH_4Y and dealuminated Y zeolites:
(a) NH_4Y(2.4), (b) EDY(2.7), (c) EDY(5.9), and DY (225).

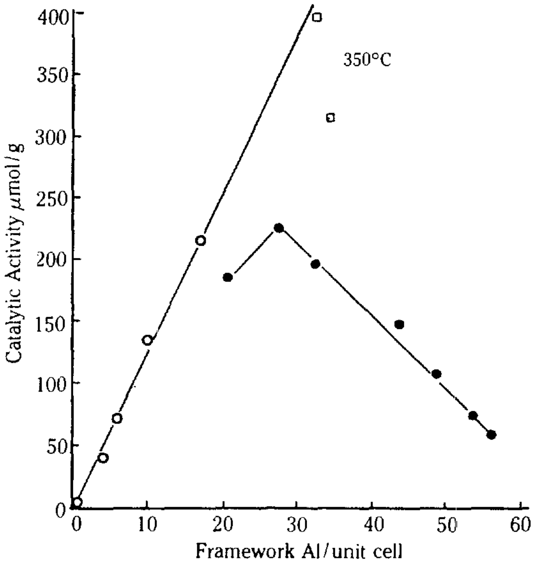

Fig. 3. Dependence of cumene dealkylation activity on framework aluminum content:
(●) EDY series, (○) DY series, and (□) SDY series.

cracking catalysts is the dealkylation reaction of cumene. The reaction is of the Friedel-Crafts type and is generally rationalized in terms of proton attack at an aromatic carbon atom with displacement of the side chain as a carbonium ion. At 300, 350, and 400°C cumene was dealkylated to form benzene and propylene. The catalysts typically were diluted with inert SiO_2.

The initial activity of the dealuminated zeolites was determined by the pulse method and was given in terms of μmole cumene converted per g zeolite during the first pulse reaction (Table 1). As shown in Fig. 3, there is a correlationship between cumene dealkylation activity and the number of framework aluminum ions per unit cell. However, the dealuminated zeolites fall into two regions of activity. The activity increases with the dealumination to a maximum and then decreases. When the number of framework aluminum ions per unit cell changes from 56 to 28, activity increases progressively. This is probably related to the increase of acid strength after aluminum removal and the extraction of weak acid site. In Y zeolites the location of all the framework aluminum atoms is crystallographically identical. However it has been observed that 35% of these atoms are chemically different since they may be easily removed without eliminating the strong acidity [23,24].

The above result is in good agreement with that of infrared spectra reported in a previous paper [19]. The frequency of acidic hydroxyl band changed from 3640 cm^{-1} to 3630 cm^{-1} progressively according to the dealumination. This has been related to an increase in acid strength or alternatively to a decrease in the framework interaction [25,26]. However, when a wide Si/Al range is considered, beyond a ratio close to 6, the frequency of the hydroxyl groups remained virtually unchanged. Similar correlations between acidity and wavenumber have been proposed on the basis of data obtained for a variety of different zeolites, and Jacobs has pointed out that the frequency of the hydroxyl groups remained virtually unchanged for Si/Al ratios>6 [26]. It has been suggested that at these low Al contents the AlO_4^- tetrahedra are diluted within the SiO_4 tetrahedra, so that no interaction occur and the corresponding protons reach maximum freedom [27].

In fact, there is a linear relationship between cumene dealkylation activity and the number of framework aluminum ions per unit cell, over the range 0.75-32 Al/UC. The correlation includes zeolites dealuminated with $SiCl_4$ and by steaming. This linear relationship implies that the TOF based on framework aluminum is constant. It is further implied that the acid strength of the zeolite does not vary over this same range, at least to the extent that cumene dealkylation can probe the acid strength. This finding supports the prediction of Beaumont and Barthomeuf that acid site strength in dealuminated faujasite should be constant for $Si/Al \geq 6$[24,28]. Similar results, with hexane cracking over a series of H-ZSM-5 materials, $20 \leq Si/Al \leq 20{,}000$, were reported by Haag et al. [29].

3. Effect of cation on catalytic activity

Properties of zeolites depend strongly on the nature and content of the cation. A number of investigators have shown that location of cations is important to consider. It depends on several factors, such as the valency of the ion and the pretreatment temperature. It is generally accepted that acidic hydroxyl groups formed through the hydrolysis of cations are responsible for the catalytic activity [30].

Under the conditions of our experiments NaY zeolite was essentially completely inactive. The inactivity of NaY is expected from the low tendency of Na^+ to hydrolyze. This agrees with the observation that no infrared absorption band of acidic hydroxyl groups was not detected on NaY zeolite after evacuation at 400°C (Fig. 6). Eberly also reported no hydroxyl groups on NaY zeolites after dehydration at 427°C [31]. Since NaY zeolite, which has only a few weak acid sites ($Ho \geq +3.3$) [32], does not show any activity, the stronger acid sites than those of NaY would be effective for the cumene dealkylation.

Fig. 4 shows the correlation between the catalytic activity and the degree of Ca^{2+} ion exchange on NaY zeolite preheated at 400°C. The sample begins to show catalytic activity when the degree of Ca^{2+} ion exchange exceeds 25%, and upon further exchange exhibits a progressive increase for the activity. The increase in catalytic activity becomes notable after the cation-exchange exceeds about 50%. This result is similar to the report that there is no strong acid activity with alkaline earth-Y zeolite up to about 45% cation exchange [33]. It is to be noted here that, when the degree of ion exchange is adequately low, the activity does not appear. This can be rationalized as follows. The faujasite zeolite has several kinds of cation sites [34], of which the most stable site, S_I is remote from the large cavity by a pore composed of a six-oxygen ring. The divalent cations strongly prefer this site, and they occupy selectively the S_I site when the degree of ion exchange remains low. There is no interaction between the reactants and the divalent cations at S_I site because the reactants can not pass the pore. These behaviors resemble the results observed for the hexane cracking and isomerization on Ca Y catalysts reported by Tung et al. [35].

The alkaline earth and rare earth forms of Y zeolite have been shown to be active catalysts for many reactions by a number of workers [14-18,30]. Several different concepts have been used to explain the activity of these zeolites. The catalytic activities for cumene dealkylation are listed in Table 2 and are illustrated in Fig. 5. Examination of Table 2 and Fig. 5 shows that as the ionic radius of the exchanged cations is decreased the catalytic activity increases in a regular manner. It was found that the tendency to cation hydrolysis increases with the polarizing power (charge^2/ionic radius) [30]. The pKh (negative log of the first hydrolysis constant) of cations is listed in Table 2 [36], together with polarizing power.

Upon cation hydrolysis in Y zeolite, two distinct hydroxyl groups are formed: One of them is attached to the zeolite cation while the other is linked to the framework Si-O-Al sites. The catalytically effective acid

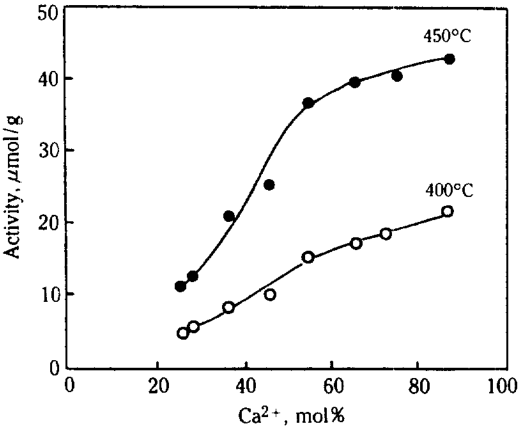

Fig. 4. Change of catalytic activity with degree of calcium ion exchange.

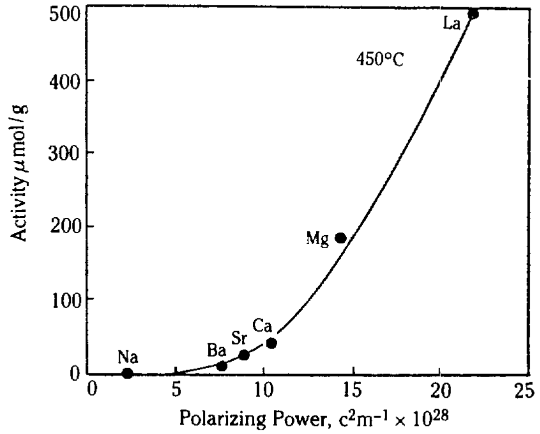

Fig. 5. Catalytic activity at 450°C against the polarizing power of cations.

Table 2. Catalytic activities and physical parameters for exchanged cations

Zeolite	Ionic radius (Å)	Polarizing power Z^2/r, ($e^2m^{-1} \times 10^{28}$)	pKh	Catalytic activity (μmol/g)		
				350°C	400°C	450°C
NaY	0.95	2.2	14.48	0	0	0
*87 MgY	0.65	14.3	11.42	78.5	147.2	187.5
87 CaY	0.99	10.3	12.70	15.6	22.1	41.2
86 SrY	1.13	8.8	13.18	3.0	7.5	26.6
85 BaY	1.35	7.6	13.82	1.2	2.8	9.1
87 LaY	1.15	21.8	10.70	188.4	334.9	500.2
50 LaY				121.2	227.1	341.4
87 LaY(O_2)				2.5	7.8	15.0
NH_4LaY				212.7	365.3	542.7

*This figure means mole% of exchanged cations.

sites in these bi or multivalent cation Y zeolites are the acidic hydroxyls linked to framework Si-O-Al sites [33]. The spectra in the hydroxyl-stretching region of several of the cation forms of the Y zeolite after evacuation at 400°C for 2 hr are shown Fig. 6. The presence of hydroxyl groups with frequencies near 3640 cm^{-1} have been related to the catalytic activity of bi or multivalent zeolites. It was shown that the presence of the 3640 cm^{-1} coincided with the presence of Brönsted acidity and cracking activity [30]. The comparison of Fig. 6 with Table 2 shows that catalytic activity increases with the intensity of hydroxyl groups near 3640 cm^{-1}. The acidic hydroxyl groups of cation-exchanged zeolites are similar to those of hydrogen Y zeolite. Na Y zeolite without acidic hydroxyl group does not exhibit activity at all while 86-LaY sample with an intensive acidic hydroxyl band is the most effective for catalytic activity. 50-LaY sample exhibited lower catalytic activity compared with 86-LaY as seen from small intensity of acidic hydroxyl band in Fig. 6. 86-LaY (O_2), which were prepared by treating 86-LaY in the flow of O_2 at 500°C for 5 hr, dropped in both catalytic activity and intensity of acidic hydroxyl band as shown in Fig. 6. However, with NH_4LaY (O_2) which were prepared 86-LaY (O_2) by treating with 1M NH_4Cl solution 3 times at 70°C for 12 hr each, both the catalytic activity and intensity of acidic hydroxyl band were recovered completely. From the above results, it is clear that the hydroxyl groups near 3640 cm^{-1} are related to the catalytic activity of zeolites. The band near 3520 cm^{-1} has been assigned to the hydroxyl group attached to the alkaline earth or rare earth cation [37,38]. In agreement with other investigatores [37,39], the 3740 cm^{-1} band is believed to represent silica type hydroxyl groups.

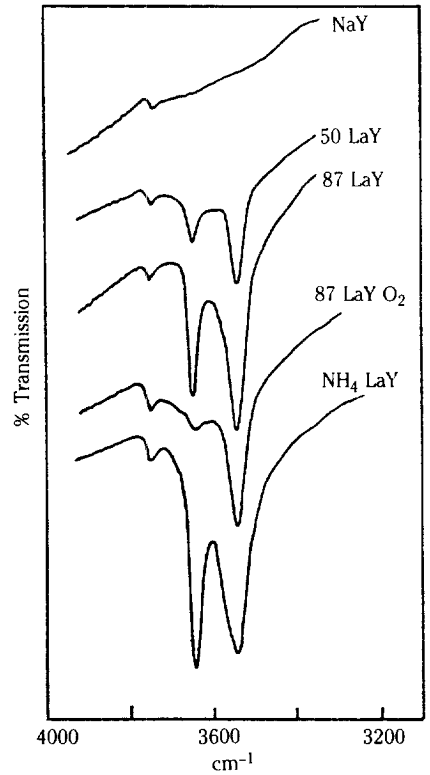

Fig. 6. Infrared spectra of NaY and LaY zeolites evacuated at 400°C in the OH stretching region.

4. Effect of nonframework aluminum on catalytic activity

It is necessary to investigate the effect of nonframework aluminum on the catalytic activity for cumene dealkylation. As shown in Table 1, a lot of nonframework aluminum remains in dealuminated zeolites except EDY series zeolites. In addition to the earlier X-ray diffraction data there is support from recent NMR, IR and ion exchange studies that under the conditions of these experiments at least part of the nonframework Al resides inside the small cavities, presumably in a cationic form. As nonframework species Al^{3+}, AlO^{+}, $Al(OH)^{2-}$, $Al(OH)_2{}^{+}$, $AlO(OH)$, and $Al(OH)_3$ etc. were suggested [8,19]. For comparison, cumene dealkylations were carried out both on EDY without nonframework aluminum and SDY with nonframework aluminum. The results for these materials with similar framework composition are summarized in Table 1. SDY samples exhibited higher catalytic activities than EDY samples. The highered activity exhibited by SDY samples means that nonframework aluminum species entrained in the lattice during hydrothermal treatment are playing a positive role in the enhanced performance. This is in agreement with the investigations of Ward and Carlson [40], who found that high hydrocracking activity was observed when ammonium hexafluorosilicate-treated zeolites were subjected to a hydrothermal treatment, thereby producing nonframework aluminum entrained in the zeolite. The strength of Brönsted acid is probably increased through the electron attraction of acidic hydroxyl group by nonframework aluminum species. Lunsford proposed that the strength of Brönsted acid may be increased by electron attraction by Lewis sites [41]. The positive effect of nonframework aluminum on cracking activity has been noted previously [42].

A clue to the enhanced activity of the dealuminated zeolites can be found in the effect of lanthanum ions on the activity of NH_4LaY (Table 2). In dehydrated La-exchanged faujasite type zeolites X-ray diffraction studies have shown the presence of La^{3+} ions at SI′ sites with oxygen bridges to adjacent lanthanum ions [43]. The oxygen is believed to be present as H_2O ligands, and a recent neutron diffraction study has confirmed the partial hydrolysis of the water according to the equation [44]

$$La(H_2O)_x^{3+} \rightarrow La(H_2O)_{x-1}(OH)^{2+} + H^+ \quad (2)$$

Thus the $La(OH)^{2+}$ species occupies a site which might have been filled by a monovalent ion. The presence of the small trivalent cation may, in turn, enhance the acidity of protons attached to structural oxygens through inductive effects. Maher et al. found that Al also occupied SI′ sites in ultrastable zeolite [8]. These aluminum ions inside the sodalite unit likewise may activate the protons which are associated with the framework aluminum.

CONCLUSIONS

Dealumination from framework zeolite up to 50% gives rise to the activity enhancement for cumene dealkylation. Over the range of 0.75-32 Al/unit cell, the activity changed in a linear manner with respect to the number of framework aluminum atoms, indicating a constant turnover frequency for each acid site. SDY samples exhibited higher activity than EDY sample although both samples had similar framework aluminum atoms per unit cell, suggesting that nonframework aluminum species play a positive role in the enhanced catalytic activity. It seems likely that the acid strength of Brönsted acid is increased through the inductive effect of nonframework aluminum species.

ACKNOWLEDGEMENT

This work was supported by the Korean Science and Engineering Foundation (1986-1987).

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