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The Basicity and Acidity of Beta Zeolites after Ion-Exchange with Alkali Metal Cations: a Physicochemical Characterization

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Abstract : The structure, basicity and acidity properties of the alkali metals (*Na*, *K* and *Cs*) exchanged zeolite beta were investigated in this work. Infrared (IR) and X-ray diffraction (XRD) were used for structural characterizations, while Temperature programmed desorption (TPD) of CO_2 and NH_3 were use for the determination of basicity and acidity, respectively. Results reveal that the framework structure of zeolite beta is retained after the exchange but with a successive decrease in the relative crystallinity after the modification. The acidity of zeolite beta was strongly affected by the crystallinity of the ion-exchanged zeolite beta, in which the acidity has decreased significantly with the decrease in the crystallinity. However, the basicity after the exchange was not very significant in comparison to the acidity. The effect of the crystallinity and the type of alkali metal cations on basicity is also shown.

Keywords : acidity, basicity, zeolite beta, ion-exchange, alkali metal cation

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1 INTRODUCTION

The acidity and basicity of zeolites plays an important role in their catalytic and adsorption properties. For instance, heterogeneous acid catalysis by zeolites has been intensively investigated especially in petroleum refinery and cracking process [1]. In addition, the basicity is important in processes that require catalytic acid-base pairs, e.g. alcohol dehydrogenation or selective sorption and separation [2]. Thus, fundamental studies on heterogeneous basic catalysts become necessary in order to achieve the success like those heterogeneous acid catalysts.

Zeolite is reported having base property. The fascinating of basicity in zeolitic materials was reviewed recently by Hattori [2] and Barthoumeuf [3-5]. According to Barthomeuf, acids and bases are conjugated, where the existence of protons in zeolites has to be associated with that of basic sites. The origin of basicity in zeolite is due to the oxygen atom derived from alumina tetrahedral. Basicity of zeolite can be enhanced by changing the electronegative charge of the framework and or by introduction of basic guest in their structure [2-7].

Studies on base zeolite have usually focused on the faujasites structure due to their high aluminum content. Quite a number of reports reviewed the effectiveness of the base zeolite X and Y in the base catalyzed reaction [8-10]. However, some other zeolitic materials, which have not yet been investigated with regards to their basicity, might have interesting base structure and character.

Zeolite beta is a high-silica and large pore crystalline aluminosilicate material. The framework structure of zeolite beta possesses three-dimensional 12-membered ring pores with an interconnected channel system [11]. Zeolite beta has high thermal stability and large pore property that desirable for catalyst modification and catalytic activity. It was reported that zeolite beta possess base properties that are greater than expected from its low aluminum chemical composition alone [3, 12]. Nevertheless, only several attempt have been reported in preparing base zeolite beta [12-14]. Here, we study the acidity and basicity of zeolite beta after ion-exchange with alkali metal cations by using Temperature programmed desorption (TPD) of CO_2 and NH_3, X-ray diffraction (XRD) and Fourier transform infrared (FTIR) in order to corre-

late the acidity and basicity with the structural properties.

2 EXPERIMENTAL

2.1 Preparation

Protonic zeolite beta ($HBeta$) with $SiO_2/Al_2O_3 = 25$ supplied by Zeolyst was used as a starting material in this study. Alkali metal (Na, K, Cs) exchanged zeolite beta were prepared by adding $HBeta$ into 1.0 M aqueous solution of the corresponding metal nitrate or acetate at $80 \sim 90^oC$ and stirred overnight. The ratio of zeolite to volume of metal solution that used was $1:10$ g/ml. It was then filtered and washed with distilled water. This procedure was repeated for six times. Finally, it was dried at 100^oC overnight and calcined in air at 500^oC for 6 hours with the heating rate of 1^oC/min. The exchanged zeolite was labeled as $MBeta$, where M referred to the alkali metals (Na, K and Cs).

2.2 Characterizations

The exchanged zeolites samples were characterized by XRD and IR. The diffractogram was recorded on D500 Siemens Kristalloflex X-ray diffractometer with CuK_α as the radiation source with $\lambda = 1.5418$ Amstrong at 40 kV and 30 mA. Samples were measured in the range of 2θ of 2° to 60° at room temperature with step time of 0.02^o/s. The FTIR spectra were recorded at room temperature with 4 cm^{-1} resolutions between $4000 \sim 400$ cm^{-1} by using FTIR Perkin Elmer 1600 series. While, the IR spectra of hydroxyl groups for the exchanged zeolite beta were recorded on the FTIR Shimadzu 8000 series. Self-supported wafers (~ 10 mg) were heated at 400^oC under vacuum for 2 h. The spectra were then recorded at room temperature in absorbance mode with 2 cm^{-1} resolutions.

The basicity property of the prepared base zeolite beta was characterized by TPD-CO_2, acquired using TPD/R/O 1100 ThermoFinnigan. Sample weighing $0.15 \sim 0.25$ g was pretreated in a flow of nitrogen at 400^oC for 2 h. Sample was then exposed to CO_2 at a rate of 20 ml/min for 30 min at 40^oC. The temperature was raised from $40 \sim 600^oC$. The desorbed gases were analyzed by TCD. TPD-NH_3 has also been carried out with the same condition. The samples were pretreated at 450?C and the NH3 is adsorbed at 80^oC.

3 RESULTS AND DISCUSSION

3.1 Physical properties

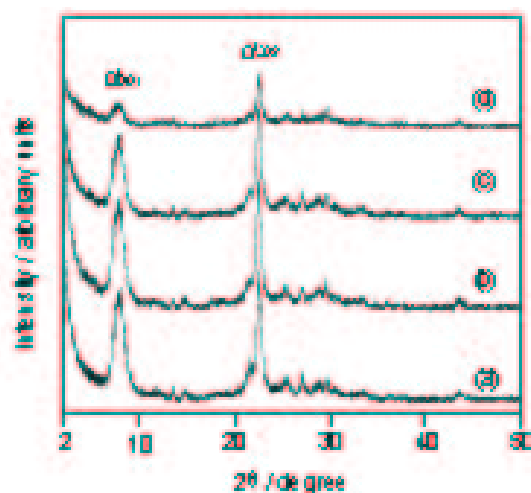The XRD diffraction pattern of the exchanged zeolite beta is shown in Fig. 1. Peaks at 7.8^o, 16.5^o,

FIGURE 1: X-ray diffraction patterns of the exchanged zeolite beta: (a) $HBeta$, (b) $NaBeta$, (c) $KBeta$ and (d) Cs-$Beta$.

21.4^o, 22.5^o, 25.3^o, 26.9^o, 28.8^o, 29.5^o and 43.5^o were observed. Both intense peaks at 7.8^o and 22.5^o are assigned to the d_{001} and d_{302} respectively, as reported by Perez-Periente et al. [15]. The broad peaks at 7.8^o is the characteristic peak for the faulted structure, while the sharp peak at 22.5^o is due to the tetragonal and monoclinic symmetry structure of zeolite beta. The presence of all the typical diffractions peaks of zeolite beta (Fig. 1) in each sample indicates the retaining of the framework structure of zeolite beta after ion exchanging with 1.0 M aqueous solution of alkali metal cations, i.e. Na^+, K^+ and $Cs+$. However, the intensity of the diffraction peaks of the exchanged samples decreases consecutively after the exchanged indicating the deterioration of the crystal structure of zeolite beta has occurred.
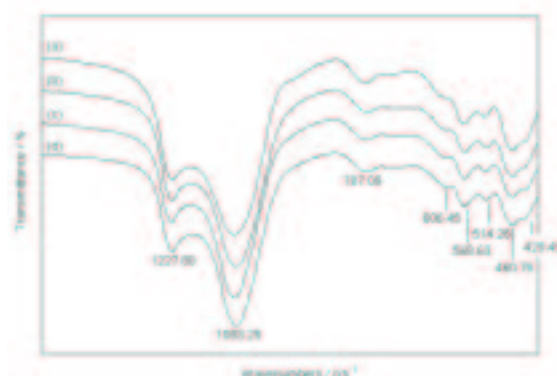

FIGURE 2: IR spectra of the exchanged zeolite beta: (a) $HBeta$, (b) $NaBeta$, (c) $KBeta$ and (d) $CsBeta$.
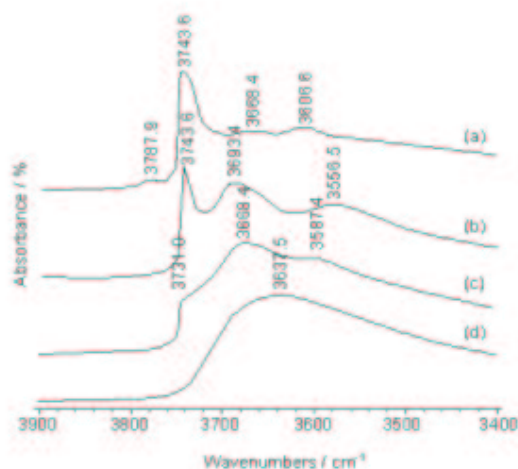
FIGURE 3: IR spectra of the exchanged samples after heated at 400^oC for 2 h under vacuum: (a) *HBeta*, (b) *NaBeta*, (c) *KBeta* and (d) *CsBeta*.

FIGURE 4: *TPD-CO_2* thermograms of the exchanged zeolite beta: (a) *HBeta*, (b) *NaBeta*, (c) *KBeta* and (d) *Cs-Beta*.

The relative crystallinity of the exchanged zeolite beta was tabulated in Table 1. It was calculated based on the intensity of the peak at 22° in comparison with the parent *HBeta*. It is shown that the relative crystallinity of zeolite beta decreases with the increase in size and the electropositive character of alkali metal cations, in the order of $Na^+ < K^+ < Cs^+$. It was suggested that the decreased in the crystallinity might be due to the strong interaction of the cation with the oxygen atom of the alumina tetrahedral in the zeolite framework. As the electropositive characteristic of the cations increased from Na^+ to Cs^+, the stronger interaction of the cations with the oxygen atoms of the alumina tetrahedra is expected, thus weaken the bond of the oxygen with the rest of zeolite framework. It then explained the decrease of about 60% of the crystallinity of *Cs*Beta compared to the parent *HBeta*.

The IR spectra of the exchanged zeolite beta samples are shown in Fig. 2. There are several typical bands that can be observed in the spectrums for all samples. The bands in the region of $1250 \sim 1200$ cm^{-1}, $1100 \sim 1050$ cm^{-1} and $800 \sim 750$ cm^{-1} are assigned to the external asymmetric stretching, internal asymmetric stretching and symmetric stretching of TO_4 ($T = Si, Al$) respectively. The double 6-membered ring and double 4-membered ring vibrations that can be observed respectively at $570 \sim 560$ cm^{-1} and $520 \sim 510$ cm^{-1} indicate the framework structure of zeolite. Meanwhile, band at around 462 cm^{-1} is assigned to the $T - O$ bending. This result is in an agreement to the XRD findings, where it shows the retaining of the structure after the exchanged.

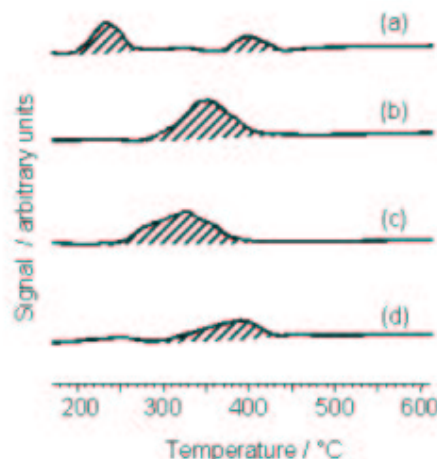Fig. 3 shows the IR spectra of the dehydrated ex-changed zeolite samples at the OH stretching region. Bands that appeared in the samples are *Si-(OH)-Al* groups in the framework (3606.6 cm^{-1}), and the hydroxyl group that bonded with the extraframework aluminium (3668.4 cm^{-1}). A small band near ?3780 cm^{-1} is only observed in parent *HBeta*. This band is assigned to the isolated extra-framework $AlOOH^+$ species. The vibration band at 3743 cm^{-1} is assigned to the $O - H$ stretching of silanol group [16-18]. The intensity of this band however decreases with the increase of the size of the cations exchanged. This suggests that besides the ion-exchange process which occurred at the oxygen vicinity of the alumina tetrahedral framework, some of the alkaline metals might have exchanged with the silanol defect sites and occluded at this sites, causing the decrease in the intensity of the silanol group.

Cs^+ has the largest size compare to Na^+ and K^+ and most of the cations shows predominantly to occupy the defect sites rather than the normal ion-exchanged process of the narrow channels from the zeolite framework. This explained the missing band of the OH silanol group in *Cs-Beta* sample.

3.2 Basicity and acidity

Basicity and acidity properties were characterized by Temperature programmed desorption (TPD) to measure the number and strength of base and acid sites that available on the surface of a catalyst. A mild acidic CO2 was used as probe for basicity and NH_3 for acidity. The strength and amount of base sites are reflected in the desorption temperature and the peak area, respectively, in a TPD plot.
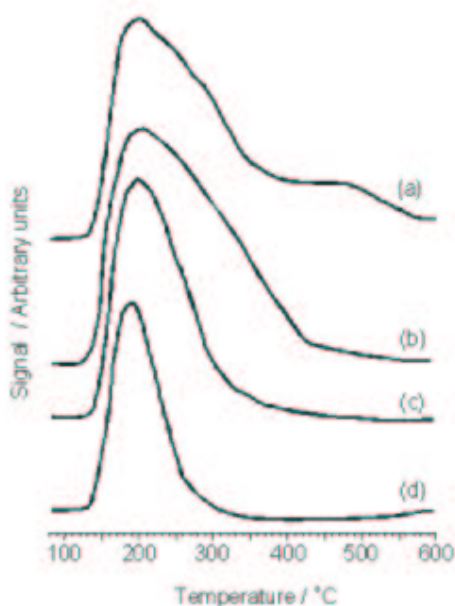
that the base strength and the amount of the base sites affect the basicity, the Sanderson electronegativity equivalence method (SEEM) [19] is adapted. The SEEM can determine the negative charge carried by the oxygen in zeolite frameworks. The intermediate electronegativity S_{int} of a given material reflects the mean electronegativity reached by all the atoms as a result of electron transfer during formation of the compound. For a compound $P_p Q_q R_r$, the intermediate electronegativity S_{int} is given by,

$$S_{int} = \left(S_P^p \, S_Q^q \, S_R^r \right)^{1/p+q+r} \; , \qquad (1)$$

where the composition of the catalyst is $P_p Q_q R_r \cdots$, S is the elemental electronegativity, and S_{int} is the intermediate electronegativity. The electronegativity gives access to the negative partial charge on the oxygen atom in the framework by,

$$\delta_0 = \frac{S_{int} - S_0}{2.08 \sqrt{S_0}} \; . \qquad (2)$$

The oxygen charge of the ion-exchanged zeolite beta that calculated based on SEEM are tabulated in Tab. 1. As shown in Tab. 1, it is found that the basicity of the *HBeta*, *NaBeta* and *KBeta* is correlated with their oxygen charge. Thus, the basicity of zeolite beta is depending on the amount of sodium and potassium that has been exchanged in the zeolite beta framework. On contrary, cesium exchanged zeolite beta has lower basicity even though the calculated oxygen charge is the highest among all the samples. This might due to the cesium cations are located at the silanol defect sites which is corresponded to the peak around 3740 cm^{-1} in Fig. 3 [16]. This argument is supported by the fact that the silanol defect sites band in the IR hydroxyl group study is disappear (Fig. 3). Since the base strength is also dependent on the structure, it should be noted that the basicity is also affected by the crystallinity of the *CsBeta*. One considers that the lower the crystalinity, the higher is the amount of the silanol defect sites. It confirms that if the crystallinity is taking into account, as shown in Tab. 1, the value of the oxygen charge ($-\delta_o times$ relative crystallinity) which is related to the basicity is become low. Therefore, the low basicity that due to the occupancy of cesium at defect site in *CsBeta* is correlated with the oxygen charge.

The acidity was also measured with TPD by using NH_3 as probe. The *TPD-NH$_3$* thermograms that obtained are as shown in Fig. 5. The acidity of zeolite beta decrease significantly after exchanging with alkali metal cations in the order of $H^+ > Na^+ > K^+ > Cs^+$. By exchanging the proton in zeolite beta framework with alkali metal cations, the crystallinity of the

FIGURE 5: *TPD-NH$_3$* thermograms of the exchanged zeolite beta: (a) *HBeta*, (b) *NaBeta*, (c) *KBeta* and (d) *Cs-Beta*.

The *TPD-CO$_2$* thermograms of the exchanged zeolite beta is as shown in Fig. 4. One expects that by exchanging the protons with alkali metal with a lower electronegativity, the oxygen charge will increase and thus increase the basicity of the zeolite. However, the results show no increament of the basic strength in zeolite beta after exchange with sodium, potassium and cesium compared to the parent H-Beta. As shown in Fig. 4, the broad peaks at 240°C and 390°C for *HBeta*, 350oC for *NaBeta*, 330°C for *KBeta* and 390°C for *CsBeta* were observed. It reveals that the trend of the basic strength of *HBeta*, *NaBeta*, *KBeta* and *CsBeta* does not follow the trend of the size and the electropositive character of alkali metal cations ($Na^+ < K^+ < Cs^+$). The basic strength also does not follow the trend of the relative crystallinity (see Tab. 1). *CsBeta* is supposed to create the highest the basic strength. However, it shows that its basic strength is similar to those the parent *H-Beta*.

Tab. 1 gives the number of base sites counted from *TPD-CO$_2$*. From TPD results it was observed that the amount of base sites among the samples was different. Compared to *HBeta*, the concentration of base sites in *NaBeta* and *KBeta* is significantly higher. It also reveals that the concentration of base sites in *CsBeta* and *HBeta* are about the same. Theoretically, the basicity must be affected by the strength and the amount of the base sites. In order to show

TABLE 1: Properties of alkali metal exchanged zeolite beta, where unit cell composition was determined by elemental analysis using atomic absorption analysis (AAS), while negative charge on oxygen atom calculated from the hypothetical framework composition by SEEM.

Sample	Unit cell composition	Relative crystallinity (%)	Acidity (μmol g^{-1})	Basicity (μmol g^{-1})	$-\delta_0$	$-\delta_o \times$ Relative crystallinity
$HBeta$	$H_{4.74}Al_{4.74}Si_{59.26}O_{128}$	100	1751	6	0.210	0.210
$NaBeta$	$Na_{4.74}Al_{4.74}Si_{59.26}O_{128}$	80	1272	12	0.244	0.195
$KBeta$	$K_{2.55}H_{2.19}Al_{4.74}Si_{59.26}O_{128}$	79	666	10	0.234	0.182
$CsBeta$	$Cs_{3.77}H_{0.97}Al_{4.74}Si_{59.26}O_{128}$	41	388	5	0.252	0.103

samples decrease and the amorphization become obvious in the order of $H^+ < Na^+ < K^+ < Cs^+$. In crystalline structure, the framework is in the maximize resonance. The Si-O bond is strengthen, thus weaken the O-H bond. As a result, the interaction between proton and the framework structure become weaker such that the acid property increases. On the other hand, the resonance is weaker in the amorphous structure causing the decrease in acid properties compared to the crystalline structure [20]. It then explains the significant decrease in the acidity, i.e. about 4- and 5-fold in $KBeta$ and $CsBeta$, respectively than the parent $HBeta$.

Since the basicity of exchanged samples is insignificant, the decrease in the acidity is not due to the cation exchanged but rather to the crystallinity of the samples. A good correlation ($R^2 = 0.7631$) is found when the acidity is correlated against the relative crystallinity (Tab. 1). This suggests that the crystallinity affects the acidity in zeolite. In addition, as shown in Tab. 1, no correlation was observed between acidity and basicity. This suggests that the acidity and basicity properties of the ion-exchanged zeolite beta are independent.

4   CONCLUSION

The acidity and basicity properties of zeolite beta can be modified through ion exchange with alkali metal cations (K^+, Na^+ and Cs^+). The acidity property in zeolite beta reduces significantly after exchanged with a larger size of alkali cations with retaining the framework structure. The acidity of the ion-exchanged zeolite beta was decrease after ion exchange with K^+, Na^+ and Cs^+ cations as indicated by the amount of the NH_3 desorption in the TPD experiments. However, the acidity does not seem to depend on the type of alkali metal cations, but strongly depend on the crystallinity of the ion-exchanged beta zeolite. Furthermore, the basicity of the ion-exchanged zeolite

beta is not significant, since the amount of the basic sites was always lower compared the acidity. It was found that the basicity was affected by both the crystallinity and the type of alkali metal cations.

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