

# Stabilization of Zeolites Y For Separation by Gas Chromatography

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## GC분리에 의한 Zeolite Y 안정화

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A partially decationized Y zeolite was pretreated under specific conditions. It was found that this calcinated zeolite retains its separation properties for mixtures of the gases hydrogen, nitrogen, oxygen, carbon monoxide, and methane but has much lower affinity for water molecules than untreated, e.g., zeolites A type or X type. The observed effect is discussed on the basis of the results of adsorption measurements on the adsorption capacities, isotherms, and heats of adsorption.

부분적으로 양이온 교환된 Y 제올라이트를 특별한 반응조건하에서 예열 처리한 결과, 하소한 제올라이트는 수소, 질소, 산소, 일산화탄소 및 메탄기체 혼합물에 대한 분리특성을 보유하고 있으나 미처리한 시료, 예로서 A형 또는 X형 제올라이트보다 물 분자에 대한 친화성이 매우 낮음을 알 수가 있었다. 흡착성능, 흡착등온선 및 흡착열에 관한 측정결과를 근거로 하여 관찰효과를 검토하였다.

**Key words** : G C Separation, Zeolite Y, Decationization, Adsorption Isotherm, Adsorption Capacity

## I. Introduction

The various techniques of gas chromatography have resulted in very useful methods for the separation and quantitative analysis of gaseous mixtures.<sup>1,2)</sup> In particular, Patton et al.<sup>3)</sup> has shown good separations of some gases.

The different types of synthetic zeolites are at present the best available adsorbents for separation of some mixtures of gases by gas

chromatography. One of the first applications of zeolites was described by Kuryacos et al.<sup>4)</sup> The separation of the gases hydrogen, nitrogen, oxygen, carbon monoxide, and methane on zeolites at room temperature was published Martin et al.<sup>5)</sup> When carbon dioxide is present in the mixtures of gases the dual column system described by Murakami<sup>6)</sup> must be employed because of the very strong interaction of carbon dioxide with zeolites.

The strong interactions of zeolites with small polar molecules, e.g., carbon dioxide,

sulfur dioxide, hydrogen sulfide, and water, is due to the presence of cations in the zeolite lattice. The loss of the separation properties of zeolite in a chromatographic column is caused by blocking of the adsorption centers with water and carbon dioxide molecules, which can be desorbed only at temperatures above 325°C.

The number of cations present in a zeolite can be decreased by exchange of part of original sodium cations for ammonia ions and followed by thermal dissociation of ammonia.<sup>7)</sup> The partially decationized zeolite thus obtained is characterized by its decreased participation in specific interactions,<sup>8)</sup> but its thermal stability is not satisfactory.

The loss of crystalline structure occurs during dehydration at temperature 365°C and increases with increase in the number of hydration-dehydration cycles.

The sensitivity to thermal lattice collapse is also proportional to the number of cations in the original forms, i.e., NaY < NaX < NaA. Y-type zeolites are relatively more resistant and suitable thermal treatment can yield complete stability even for the decationized forms. Ultrastable Y-type zeolites, their synthesis and properties, were first described by McDaniel et al.<sup>9)</sup>

Other methods for the preparation of stabilized Y-type zeolites have since been published,<sup>10-12)</sup> and the crystal structures, sorption and catalytic properties of these substances have been described. All these zeolites are characterized by high thermal stability, but their sodium ion content is so low that their gas chromatographic separation properties are unsatisfactory.

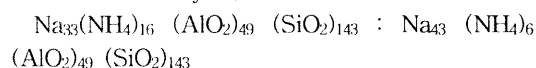
The purpose of this study was to prepare a stable form of the partially decationized Y zeolite, NaHY having suitable separation properties, i.e., with a higher content of sodium ion and with decreased sorption affinity for water molecules. Account has been taken of results obtained as the method described in the literature.<sup>11,13)</sup>

The literature concerning ultrastable zeolites and related materials was reviewed in Maher et al.<sup>14)</sup>

## II. Experimental

The cation exchange was effected by slurring the zeolite samples (about 1g) in 100ml of 0.1N NaOH solution for two hours followed by filtration, washing with 50ml of water, and drying. The samples were then analyzed. Anhydrous gaseous ammonia was used for ammoniation of the calcined products. Physically adsorbed ammonia was removed from the samples by slurring the zeolites in water for about two hours with a ten percent excess of Amberlite IRC-50, a carboxylic acid cation exchange resin in the hydrogen form. The resin in this form readily reacts with free bases, such as ammonia, but is too weakly acidic to effect salt splitting of the ammonium zeolite, and others were carried out on a method described by Kerr.<sup>11)</sup>

The initial material comprised the sodium-ammonium forms of NaNH<sub>4</sub>Y zeolites with the following unit cell compositions (based on chemical analysis) :



These contents correspond to sodium ion contents of 69 percent and 88 percent of the original NaY form. The stabilization was carried out in a quartz reactor under self-steaming conditions at 550°C.<sup>7,15)</sup>

The instrumental arrangement is simply showed in Figure 1.

The reactor has a capacity of 60ml volume, a height of about 90mm and 35mm in width, and manostat has a 800mm long.

The quartz reactor was about 60 percent filled with NaNH<sub>4</sub>Y zeolite and gradually heated in a tube oven to about 550°C at a rate of 2°/min. The pressure of the system was maintained at approximately 7.5 kilopascal by use of a manostat connected to the outlet from the reactor. The stabilized powder product was pressed into pellets without a binder, ground and sieved. The fraction of 0.2~0.5mm was employed in subsequent measurements.

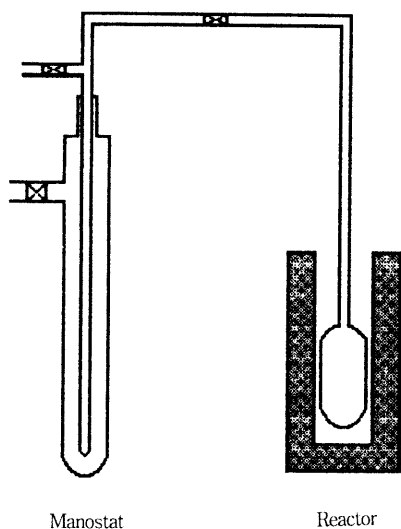


Figure 1. Schematic of apparatus for stabilization of zeolite.

The samples were designated NS-69 and NS-88 zeolites, where the numbers indicate the content of sodium ion percent relative to the original NaY form.

The adsorption capacities, kinetic curves and isotherms were measured on a quartz spring balance. The chromatographic measurements were carried out on a Gas Chromatograph (HP 5890A) equipped with a thermal conductivity detector. A glass column used was 60cm long and 4 mm in inner diameter. The hydrogen, nitrogen, oxygen, carbon monoxide, and methane gaseous mixture was separated at laboratory temperature. Heats of adsorption were calculated from the dependence of the retention volumes on temperature using the usual relationship.<sup>16,17)</sup>

### III. Results and Discussion

As has been reported,<sup>11)</sup> the lattice of unstable partially decationized zeolites collapses during dehydration. The degree of loss of crystalline structure is proportional to the number of hydration-dehydration cycles. As

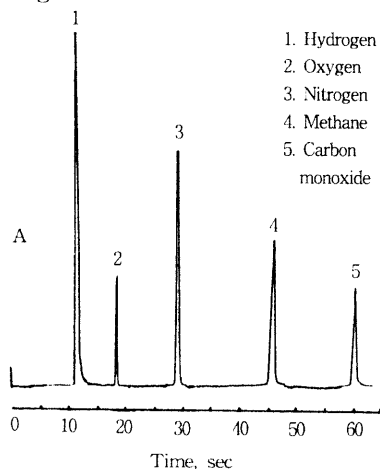
has been reported,<sup>8)</sup> this decrease in crystallinity is reflected most markedly in the sorption values, measured using argon. For comparison, Table 1 lists the capacity values for stabilized forms and nonstabilized forms having corresponding numbers of cations, before and after four cycles of hydration at 20°C with dehydration at 357°C in vacuo.

Table 1. Adsorption capacities of argon at -193°C with influence of repeated hydration-dehydration (RHD)

| Adsorbents | Adsorption capacity, mmole g <sup>-1</sup> |           |
|------------|--|-----------|
|            | Before RHD                                 | After RHD |
| NaHY-69    | 11.96                                      | 6.04      |
| NaHY-88    | 12.13                                      | 5.28      |
| NS-69      | 10.29                                      | 10.22     |
| NS-88      | 10.24                                      | 10.29     |

The decationization and stabilization processes have many chemical aspects in common. The results confirm the positive effect of stabilization. The influence is also important from the point of view of chromatographic separation, since loss of crystallinity of the adsorbent leads to a decrease in its separation effectiveness.

Chromatograms of gaseous mixtures of hydrogen, nitrogen, oxygen, carbon monoxide, and methane on NS-69 and NS-88 zeolites are shown Figure 2.



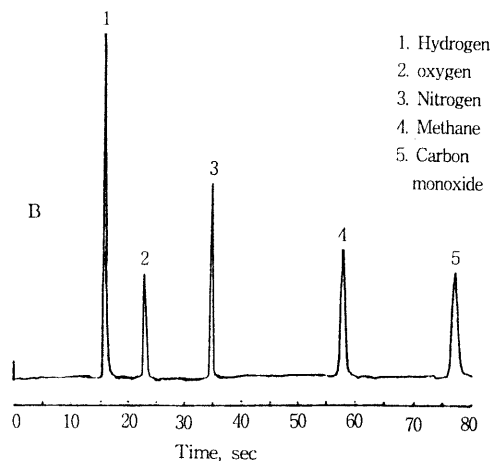


Figure 2. Separation of gas mixture on NS-69 zeolite(A) and NS-88 zeolite(B).  
Flow rate: 50cm/min, Heating temp: 20°C.

It is interesting that a decrease in the number of cations changes the retention times of all adsorbates by about 20 percent, regardless of their ability to interact with the cation. This suppression of specific interactions was also confirmed for ion stabilized zeolites by the values of the heats of adsorption, given in Table 2.

Table 2. Chromatographic heats of adsorption for some gases adsorbates on stabilized and nonstabilized NaHY zeolites.

| Adsorbents | Heats of adsorption, cal mole <sup>-1</sup> |                 |         |
|------------|---|-----------------|---------|
|            | Nitrogen                                    | Carbon monoxide | Methane |
| NaHY-69    | -   | 4,820           | 4,240   |
| NaHY-88    | -   | 5,470           | 4,200   |
| NS-69      | 3,800                                       | 4,770           | 4,100   |
| NS-88      | 3,780                                       | 4,840           | 4,250   |

It was found that the hydration process for stabilized zeolites exposed to the air at laboratory temperature proceeds more slowly than for the original sodium form.

The results of the study of the effect of kinetic factors on the rate of hydration of NS-form zeolites are shown in Figure 3.

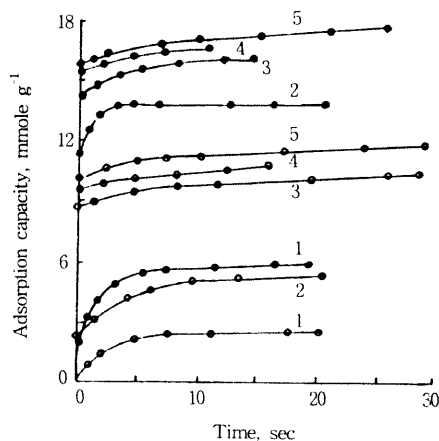


Figure 3. Kinetic curves for water adsorption on zeolites at 20°C.  
●- NaY zeolite, ○- NS-69 zeolite  
 $p_{H_2O}$  (Pa) : 1) 65, 2) 220, 3) 750, 4) 1,210, 5) 1,950.

The time required for attainment of equilibrium both for NaY and for NS-69 zeolites is not greater than 20 minute even for the greatest active site occupation.

For comparison, the values for the fully cationized form and for NS-69 zeolite are also listed. It follows that the equilibrium is established equally rapidly for both samples, indicating that kinetic factors have no effect on the observed differences in behaviour of the zeolites during hydration.

The different shapes of the adsorption isotherms of H<sub>2</sub>O for NaY and NS-69 zeolites are shown in Figure 4.

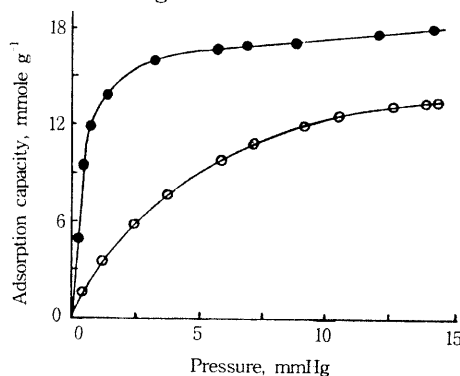


Figure 4. Adsorption isotherms of H<sub>2</sub>O on NaY and NS-69 zeolites at 20°C.  
●- NaY zeolite, ○- NS-69 zeolite

The practically rectangular isotherm on NaY, which is typical for zeolites, indicates that the marked adsorption occurs at very low partial pressures.

For example, at a relative humidity of 6 percent at 20°C, the NaY zeolite is saturated, corresponding to 76 percent of the adsorption capacity; at the same relative humidity, NS-69 zeolite exhibits only 27 percent of its overall adsorption capacity at this temperature. With NaY zeolite, 90 percent adsorption saturation is attained at a relative humidity of 26.4 percent, and for NS-69 zeolite at a relative humidity of 56.5 percent.

It follows that the stabilization process suppresses the cation sorption activity, i.e., decreases the participation of specific interactions. X-ray structural data and kinetic measurements, however, exclude the occlusion of cations by amorphous components and thus a decrease in their accessibility for adsorbate molecules.

It should be noted, however, that the stabilization process has a marked effect on the crystal lattice. It has been shown<sup>10</sup> that part of the lattice aluminium passes into the cation vacancies, that the values of the lattice constants decrease and that the cations are redistributed. It was found by X-ray photoelectron spectroscopy that the silica-to-alumina ratio and thus the number of cations in the surface layers is substantially different from the values found by elemental analysis of the crystal. This indicates the marked effect on the charge distribution in the crystal and thus on the character of the interaction of the zeolite with molecules that are preferentially adsorbed on cations. We feel that these facts are the reason for the marked difference in behavior of stabilized and nonstabilized forms of NaHY zeolites and could be important for the application of zeolites in gas chromatography.

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