

Studies on the NaX Zeolite & Its Scandium Substituted Forms

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Nature and physical properties of NaX zeolite and its scandium substituted form have been studied by different physical techniques using nitrogen gas as the adsorbate. Substitution of sodium ions of NaX zeolite by scandium ions does not lead to destruction of the crystal structure of the former. The differential thermal analysis of the samples studied, shows that all the samples lose their water of hydration and then water adsorbed on the surface in the range 100-200°C, with the maximum loss of the adsorbed water occurring at 160°C. The specific surface area of NaX degassed at different temperatures has been determined by BET, DP and the sharp knee point methods. The specific surface area increases with the degassing temperature, reaches the maximum value at 400°C and then decreases at 450°C. The specific surface areas of scandium substituted NaX zeolites have been also investigated.

The structure and physical nature of zeolites have been studied by many investigators¹⁻⁶. Natural zeolites are aluminosilicates with a framework structure enclosing cavities occupied by large ions and water molecules, both of which have a considerable freedom of movement, permitting ion exchange and reversible dehydration¹. The zeolite crystal does not disintegrate on heating and evacuation as do most of the other water bearing crystals, but becomes active towards adsorption of a wide variety of molecules in a highly selective manner². Zeolites have an open channel structure which allows the cation exchange in aqueous solution affecting the adsorptive and the catalytic properties of these zeolites³. Synthetic zeolites are designated into types X and Y with different Al₂O₃/SiO₂ ratios. NaX zeolite has the same crystalline structure as the naturally occurring faujasites, with a slightly larger cubic unit cell and somewhat different Al₂O₃/SiO₂ ratio⁴. Zeolites lose most of their water between 25 and 300°C, with a slight expansion in the case of NaX zeolite⁵.

The aim of the present work is to study the physical nature of NaX zeolite and its scandium substituted forms by applying different physical methods, viz. X-ray analysis, differential thermal analysis and volumetric adsorption measurements and using nitrogen gas as an adsorbate.

Materials and Methods

NaX zeolite (Russian made) was used as a starting material for preparation of the applied adsorbent. Scandium replaced forms of NaX zeolite were prepared as follows: 5 g of NaX zeolite powder was shaken with 60 ml of 0.1 N scandium chloride solution at room temperature for 20 min. After the ion exchange process was completed the material was filtered; the scandium replaced form was designated

NaXSc₁ zeolite. The other forms of scandium replaced zeolite e.g. NaXSc₂, NaXSc₃ and NaXSc₄ were prepared by repeating the above process, two, three and four times, respectively using fresh scandium chloride solution and lower scandium replaced form each time. To obtain NaXSc₅ zeolite sample, NaXSc₄ was left overnight immersed in scandium chloride solution.

The scandium content in the samples was determined colorimetrically using alizarin red S as an indicator. A known weight of zeolite sample was first shaken with the indicator and then left overnight in 0.1 N HCl solution; the solution was filtered and the filtrate was made up to a definite volume and subjected to colorimetric analysis. The filtrate of the starting NaX sample was used as the blank solution. The scandium content in the obtained scandium replaced forms was as follows:

Sample	NaXSc ₁	NaXSc ₂	NaXSc ₃	NaXSc ₄	NaXSc ₅
Wt % of Sc	3.7	4.23	6.46	6.87	10.70

Nitrogen gas, used as an adsorbate, was purified by passing it through a well packed column of reduced copper turnings heated at 400°C, then through a series of drying and purifying gas adsorbents. The pure dried gas (99.5% pure) was then stored for use. Helium gas was purified and dried by the same procedure. X-Ray analysis, differential thermal analysis and adsorption measurements of nitrogen were carried out by methods described earlier^{8,9}.

Results and Discussion

X-Ray analysis of the original NaX zeolite and its scandium substituted forms, NaXSc₁, NaXSc₂, NaXSc₃, NaXSc₄ and NaXSc₅, showed that all the samples were crystalline and gave well defined sharp peaks. The ion exchange of three sodium ions of NaX

zeolite by one scandium ion as well as the degree of exchange does not affect the crystalline structure of NaX zeolite and even at a high degree of displacement the crystallinity changes very slightly. The differential thermal analysis of NaX zeolite and its scandium replaced forms was carried out in the temperature interval 25-1200 C using α -Al₂O₃ as the reference. It was found that all the samples studied lose their water of hydration and then the adsorbed water, in the range 100-200 C (Fig. 1). The original NaX zeolite readily loses its water of hydration up to 160 C, whereas the scandium substituted forms with high degree of hydration show a more or less diffused peak below 160 C. The hydration peaks increase in intensity with increasing scandium content, the water molecules are more tightly attached to the surface of scandium replaced forms than to the surface of the original NaX zeolite. Increasing the degree of replacement of sodium ions by scandium ions in NaX zeolite increased the stability of the crystalline structure towards the thermal treatment up to 100 C, as shown by the decrease of the exothermic effects between 700 and 1000 C (Fig. 1). The effect of the degassing temperature on the rate of adsorption of nitrogen on the NaX zeolite and its scandium replaced forms at -195 C, is shown in Fig. (2).

NaX zeolite was degassed in the temperature interval 30-450 C, at 10⁻⁵ Torr for 4 hr, with a rate of increase of temperature of 3 C per min. Adsorption of the gas takes place in the early stages in two steps: a

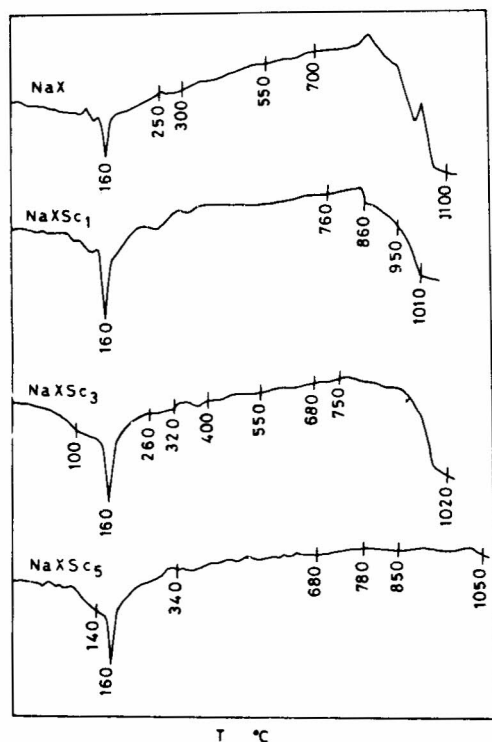


Fig. 1—DTA of NaX, NaXSc₁, NaXSc₃ and NaXSc₅ zeolites.

slow but large initial adsorption step, followed by a small but relatively rapid adsorption step. In the pressure range of 0.01 to 0.1, the equilibrium is usually reached in less than 2 hr; then, equilibrium time up to 10 hr has practically no effect on the adsorption capacity. Once the initial slow adsorption stage is completed, further adsorption of nitrogen is quite rapid and the equilibrium is usually reached in less than 30 min. All the isotherms are initially very steep and exhibit plateaus in the relative pressure range 0.05 to near saturation. In all the cases the adsorption is reversible with no hysteresis. From the adsorption isotherms of nitrogen at -195 C, on degassed NaX zeolite and its scandium replaced forms of the zeolite, the specific surface areas of the six studied samples degassed at different temperatures and the per cent mass loss of the adsorbents were calculated (Table 1) using different adsorption equations like BET⁸, DP^{9,10}, and the sharp knee point of the isotherm. These different adsorption equations were used to find the specific monolayer capacity (V_m) which is necessary for the calculation of the surface area of the adsorbent.

The different values of surface areas obtained by these equations may be due to the restricted applicability of the different equations, i.e. only within

Table 1—Surface Areas of NaX Zeolite, Degassed at Different Temperatures, Determined by Different Equations at -195 C

Degassing temp. (C)	Mass loss (%)	S(m ² g)		
		BET	DP	Knee point
30	8.0	101	138	108
100	16.2	203	346	257
200	20.5	388	445	409
300	24.2	435	535	500
400	25.0	557	642	610
450	25.2	507	582	552

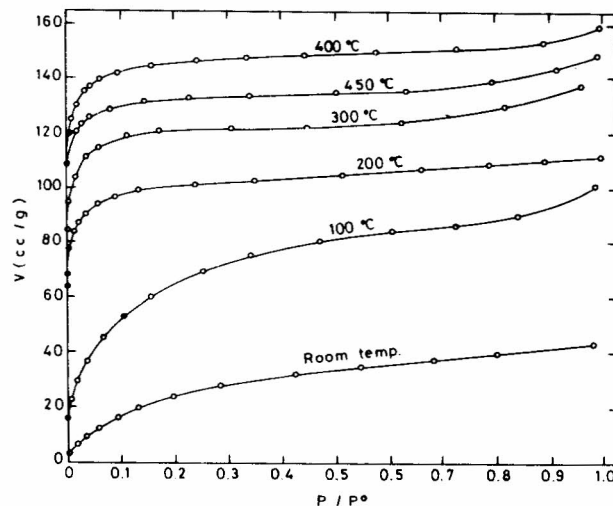


Fig. 2 Adsorption of N₂ at -195 C on NaX zeolite degassed for 4 hr at different temperatures

limited ranges of relative vapour pressures. BET equation is found to be obeyed in a narrow range of the relative vapour pressures. This may be due to the assumption that the surface of an adsorbent is energetically uniform which is implicit in the BET theory. However, the surface of most solids is heterogeneous in the energetic sense. As a result of this shortcoming of BET method, the two other methods were applied to interpret nitrogen isotherms. The DP method, which is based on the equation derived by Dubinin from Polanyi potential theory, is only valid at high relative vapour pressures. The results given in Table 1 show that the lowest values of surface areas are obtained by BET equation and the highest are obtained by DP equation. The surface areas calculated by sharp knee point method are in between and slightly lower than those determined by DP equation. Generally, the surface areas determined by the different methods of calculations were found to increase on increasing the degassing temperature, reaching a maximum value at 400°C. At higher temperature (450°C), the specific surface area decreased. This suggests that at 400°C degassing is highly effective, and accordingly all the surface is considered accessible to adsorption.

The percentage of the mass loss of NaX zeolite on degassing at different temperatures (Table 1) increased with rise of temperature from 30 to 450°C. The progressive increase in the percentage of mass loss is attributed to the removal of both physically and chemically adsorbed water. It runs parallel to the increase in the adsorption capacity up to 400°C. The small adsorption capacity at lower degassing temperatures may be a result of the presence of a lattice space in which water molecules can enter (remaining as ice in the lattice space) particularly at temperature as low as -195°C.

The effect of the degree of the gradual replacement of sodium ions by scandium ions on the sorption capacity of nitrogen, on the six samples having 0.0, 3.70, 4.23, 6.24, 6.87 and 10.70% scandium, degassed at 400°C under reduced pressure of 10^{-5} Torr, is less in the initial part of adsorption isotherm (Fig. 3). The equilibrium is attained within 2-3 hr. At high relative pressures, the equilibrium is attained in less than 30 min. In all the cases, the adsorption of nitrogen at -195°C was reversible and the adsorbed vapour could be completely removed by degassing. The nitrogen adsorption on the six zeolite samples at -195°C indicates that the adsorption isotherms are parabolic in shape but occasionally isotherms with very steep initial parts occur.

The specific surface areas of these six samples of the zeolite, calculated by different methods, are given in Table (2).

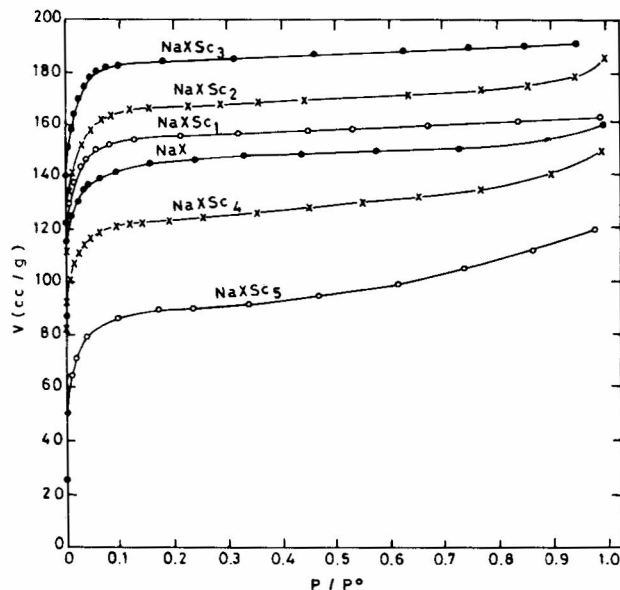


Fig. 3—Adsorption of N_2 at $-195^\circ C$ on NaX, NaXSc₁, NaXSc₂, NaXSc₃, NaXSc₄ and NaXSc₅ zeolites degassed at $400^\circ C$ for 4 hr

Table 2—Calculated Surface Areas of the Six Samples of the Zeolite Degassed at $400^\circ C$ for 4 hr at Reduced Pressure (10^{-5} Torr)

Sample	Mass % Sc	$S m^2/g$		
		BET	DP	Knee point
NaX	0	557	642	610
NaXSc ₁	3.70	574	690	652
NaXSc ₂	4.23	595	730	717
NaXSc ₃	6.46	670	805	783
NaXSc ₄	6.87	450	545	509
NaXSc ₅	10.70	333	406	370

The adsorption capacity attained the maximum value on increasing the scandium content to 6.45%. At higher scandium contents (6.87 and 10.70% Sc) the adsorption capacity was greatly reduced, even to values less than that of NaX zeolite. The increase in adsorption capacity may be attributed to an increase in the effective pore diameter. The higher degree of replacement may practically result in a collapse of the pore structure leading to a reduced adsorption capacity. This was confirmed by the slight decrease in the degree of crystallinity of NaXSc₄ and NaXSc₅, as indicated by the X-ray pattern. Therefore, the adsorption capacity of zeolites may be affected by many factors. One of these important factors is the accessibility of sites which depends on the geometry of the internal pores of the system, molecular shape, selectivity and the rate of diffusion.

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