

The Dehydration Sequence of Nickel-Exchanged A Zeolites

SHER AKBAR

Department of Chemistry, University of Baluchistan, Quetta, Pakistan.

(Received 16th July, 1981)

Summary: Five nickel (II) A - Zeolites (16.6 -76.6% exchanged) were investigated using volumetric, gravimetric, spectroscopic and magnetic susceptibility techniques. Upto 65% exchanged the following vacuum dehydration sequence was determined:

$\text{Ni}^{2+}(\text{H}_2\text{O})_6$ (Octahedral) 340K $\text{Ni}^{2+}(\text{H}_2\text{O})_3(\text{O}_x)_3$
(quasi octahedral) 400K $\text{Ni}^{2+}(\text{H}_2\text{O})_2(\text{O}_x)_3$ (Trigonal bipyramid)
 620K $\text{Ni}^{2+}(\text{O}_x)_3$ (Trigonal)

(Where (O_x) represents the oxygen atom of the lattice of the zeolite).

All the zeolites except 77% exchanged, showed the retention of the aluminosilicate framework structures both after preparation and upto 620K evacuation.

Introduction

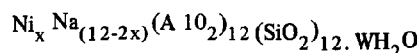
Rigidly anionic crystalline aluminosilicate framework of synthetic sodium A - zeolite consists of alpha and beta cavities which have direct access through 8- and 6-oxygen rings respectively and the 12 Na^+ ions per unit Cell (pseudo) are located at three non-equivalent sites in dehydrated zeolite (1, 2). The intracrystalline surface area of the A- type zeolite depends on the factors such as the chemical nature of the cation, the degree of ion exchange, cation location and the thermal stability of the lattice structure.

There is continuing interest in the ability of zeolite molecular sieves to sustain charge balancing metal ions in unusual coordination environments (3). The aim of the present investigation was to examine the effect of nickel (II) metal ion exchange in A- type zeolite on their adsorption properties, the crystalline structures of the fully hydrated, dehydrated and partially dehydrated forms of zeolite and show that by simple adsorption methods the retention or collapse of structure can be investigated. Special attention is given to trace formation and disappearance of different types of complexes of Ni^{2+} ion with zeolite water molecules and lattice oxygen ions on dehydration, which was studied originally by Klier and Ralek (4,5).

Experimental

Five samples of Ni^{2+} exchanged Ni Na A-zeolites were prepared by ion exchange from nickel chloride solution. Synthetic Na A-zeolite used for cation-exchange with nickel (II) was supplied by the Union Carbide International company USA, and had a lot

number 4941040757. The standard procedure for exchange techniques were similar to those described previously (6). Volumetric analysis confirmed that each nickel (II) ion replaced exactly two sodium ions. Five zeolites were prepared with the general formula:



where $X = 1.0, 2.4, 3.2, 3.9, \text{ and } 4.6$ and $30 < w < 48$.

Procedure for measuring monolayer equivalent area, using krypton adsorption at 77K, was carried out as previously described (6). The amount of samples taken were between 40 - 80 mg of hydrated weight. Water contents of the zeolites during dehydration at different temperatures was determined gravimetrically on a McBain spring, sensitivity 25 cm g^{-1} , with a liquid nitrogen cooled trap situated near to the balance was attached to a standard high vacuum system of pyrex glass. The high vacuum system could be evacuated to $1 \times 10^{-6} \text{ torr}$. * The quantity of the samples taken in the bucket of the spring were between 150-300 mg of the fully hydrated weight. The sample was outgassed at every particular temperature for several hours till a stationary reading was reached.

Diffuse reflectance spectra were measured at 298 K on a pye unicam SP800 spectrophotometer using a SP890 diffuse reflectance accessory. The spectra were recorded in the range $11,500 \text{ to } 32,500 \text{ cm}^{-1}$. For taking the spectrum of the sample after different degree of dehydration in vacuum between 298 - 620K, a vacuum cell of pyrex was constructed which had an optical window.

Magnetic susceptibilities were obtained on a Gouy magnetic balance. Each sample was outgassed in vacuum

* 1 Torr = 133.3 Pa.

at 340K in a specially constructed pyrex flat-bottomed tube for 30 hours until its colour changed to pale pink. Then it was sealed off in vacuum. It has been shown (7,8) that nickel A-zeolite obey the curie-weiss law with $\theta \simeq 0$, so magnetic moments were calculated from measurements at 298K.

Results

Surface areas of Na A, Ni_{1.0}A, Ni_{3.2}A, Ni_{3.9}A, and Ni_{4.6}A, zeolites were calculated by point 'B' method by using the adsorption of krypton at 77K after outgassing each in vacuum at 400, 520 and 620K respectively (table 1.). The table 1 shows that the surface area increases rapidly after introducing more than one Ni²⁺ ion per unit cell. In case of highly exchanged zeolite i.e. Ni_{4.6}A (77% exchanged), the surface area has decreased. Gravimetric results are given in table 2. The table shows that the water content per unit cell increases with increasing the nickel (II) ions. For each zeolite except Ni_{1.0}A, the ratio of H₂O molecules to Ni²⁺ ions after evacuating at 340 and 400K are 3.5+0.5 and 2.0 respectively. For Ni_{1.0}A the values of 6.3 and 3.7 reflect several water molecules not coordinated to the nickel(II) ion.

The hydrated zeolites, as is well known (4,5,7, -10) show the spectrum of aqua octahedral nickel(II), with slight shifts of the band maxima towards higher frequency with increasing metal content of the zeolite unit cell (11), but not so systematically as was observed in CoA-Zeolites towards low frequency (11). For Ni_{1.0}A, Ni_{2.4}A and Ni_{3.2}A reflectance spectra suggest that dehydration proceeds through four distinct stages only,

TABLE 1.
Surface areas (m² g⁻¹) after evacuating
the zeolites at different temperatures.

Zeolites.	Hydrated.			Dehydrated.
	400 K	520 K	620 K	620 K
NaA	5.0	4.0	—	—
Ni _{1.0} A	9	—	20	27
Ni _{2.4} A	190	213	250	338
Ni _{3.2} A	—	207	217	306
Ni _{3.9} A	191	214	189	278
Ni _{4.6} A	57	50	26	39

Table . 2

Zeolite	No of water molecules per unit cell before dehydration	No of water molecules lost per unit cell during dehydration			Rate of water molecules to Ni ²⁺	
		At 340 K	At 400 K	At 620 K	At 340 K	At 400K
Na A	30	—	26.6	3.2	—	—
Ni _{1.0} A	32	25.6	2.6	3.7	6.3	3.7
Ni _{2.4} A	34	26	3.4	4.6	3.4	2.0
Ni _{3.2} A	39.3	26.4	5.6	7.0	4	2.0
Ni _{3.9} A	45.3	31.4	5.0	8.5	3.5	2.0
Ni _{4.6} A	47.8	32.4	5.0	10.0	3.3	2.0

in colour pale green, pink, yellowish, and dirty yellow. The spectra of Ni_{2.4} after evacuating at 340, 400 and 620K are shown respectively by curves 1,2 and 3 in Fig 1. The pink colour is most strongly developed on dehydration at 340K, and the yellowish and dirty yellow by 400 and 620K respectively. Ni_{3.9}A becomes pale cream in colour at 340K and is pale yellow and light brownish respectively at 400 and 620K. Ni_{4.6}A, remains green at 340K, becoming very pale green and dark brown respectively at 400 and 620K due to structural collapse. The spectra of Ni_{2.4}A, Ni_{3.9}A and Ni_{4.6}A at 340K, are compared in Fig 1, respectively by curves 1,2, and 3. The magnetic moment at this stage of dehydration (340K) was the same for each of the zeolites at 3.8 B.M. The diffuse reflectance spectra, corrected according to the Kubelka - Munk function (12, 13).

The spectra of the partially rehydrated samples after exposing the dehydrated samples to air (water vapours) for different periods were also recorded (11). The completely rehydrated samples of all Ni A-zeolites except Ni_{4.6}A, were greenish in colour. The Ni_{4.6}A could not be fully rehydrated even after 14 weeks in a desiccator over calcium nitrate solution, which was yellow in colour.

Discussion

The surface area were evaluated using both point 'B' and B.E.T. methods. The surface areas found by B.E.T. plots were 10-40% smaller than obtained by point 'B'. The B.E.T. plots were not linear. The adsorption isotherms by point 'B' method were considered more reliable than the B.E.T. plots(2). As compared to Na A

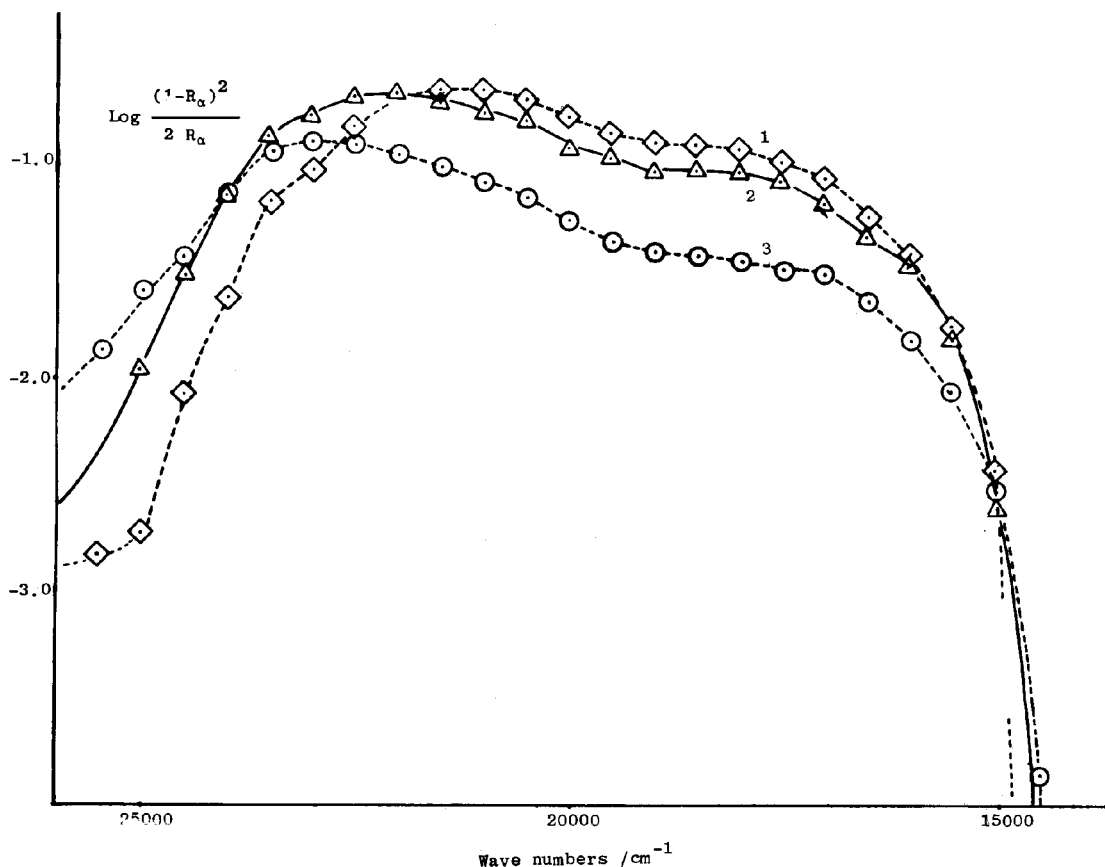


Fig. 1 : Diffuse reflectance spectra of $\text{Ni}_{2.4}\text{A}$: (1) Dehydrated in vacuum at 340K; (2) dehydrated in vacuum at 400K; (3) dehydrated in vacuum at 620K (inner scale).

and $\text{Ni}_{1.0}\text{A}$, the surface areas of $\text{Ni}_{2.4}\text{A}$, $\text{Ni}_{3.2}\text{A}$ and $\text{Ni}_{3.9}\text{A}$ are very high, because these areas are due to their internal crystalline surface as well as the external surface. It is suggested that when more than 25% of Na A- zeolite is exchanged by Ni^{2+} ions, the 8-rings start to become free of Na^+ ions, similarly as previously reported (2) for Ca A- zeolites, then the adsorption of krypton increases with increasing the Ni^{2+} content per unit cell. This is reflected in the increased surface area of zeolites.

The structure instability of Ni A- zeolites has been under discussion in literature for a long time (14, 15, 16). Coughlan et al (10) suggested that when A type zeolite contains 4.5 Ni^{2+} ions, then the Ni^{2+} ions replace Na^+ ions at the 8-oxygen ring sites, causing structural instability of the zeolite. This suggestion can be ruled out on the basis of high surface areas of $\text{Ni}_{2.4}\text{A}$, $\text{Ni}_{3.2}\text{A}$ and $\text{Ni}_{3.9}\text{A}$, which have showed the displacement of Na^{2+}

ions from the 8-rings (table 1). The low surface area of $\text{Ni}_{4.6}\text{A}$, indicates the instability of the structure on outgassing in vacuum between 298 and 400K.

There is general agreement (4, 5, 7, -10) that in the green complex the nickel ion is octahedrally coordinated to six water molecules, of most interest is the stage of dehydration where, although the $\text{H}_2\text{O}/\text{Ni}$ ratio remains constant the colour of the complex changes from pink to green as the nickel content increases from 1 to 4.6, atoms per unit cell. The magnetic moment of the complex, at 3.8. B.M. did not vary with nickel ion concentration. Klier and Ralek (4) Observed the pink spectrum for a $\text{Ni}_{1.8}\text{A}$ zeolite and proposed a distorted tetrahedral structure $\text{Ni}(\text{H}_2\text{O})(\text{O}_x)_3^{2+}$. This structure can be rejected since the $\text{H}_2\text{O}/\text{Ni}$ is 3.5:1. Also, the spectrum 1 (Fig 1) is not consistent with a tetrahedral complex with four oxygen ligands, where a strong band in the red region of the spectrum would be expected rather than

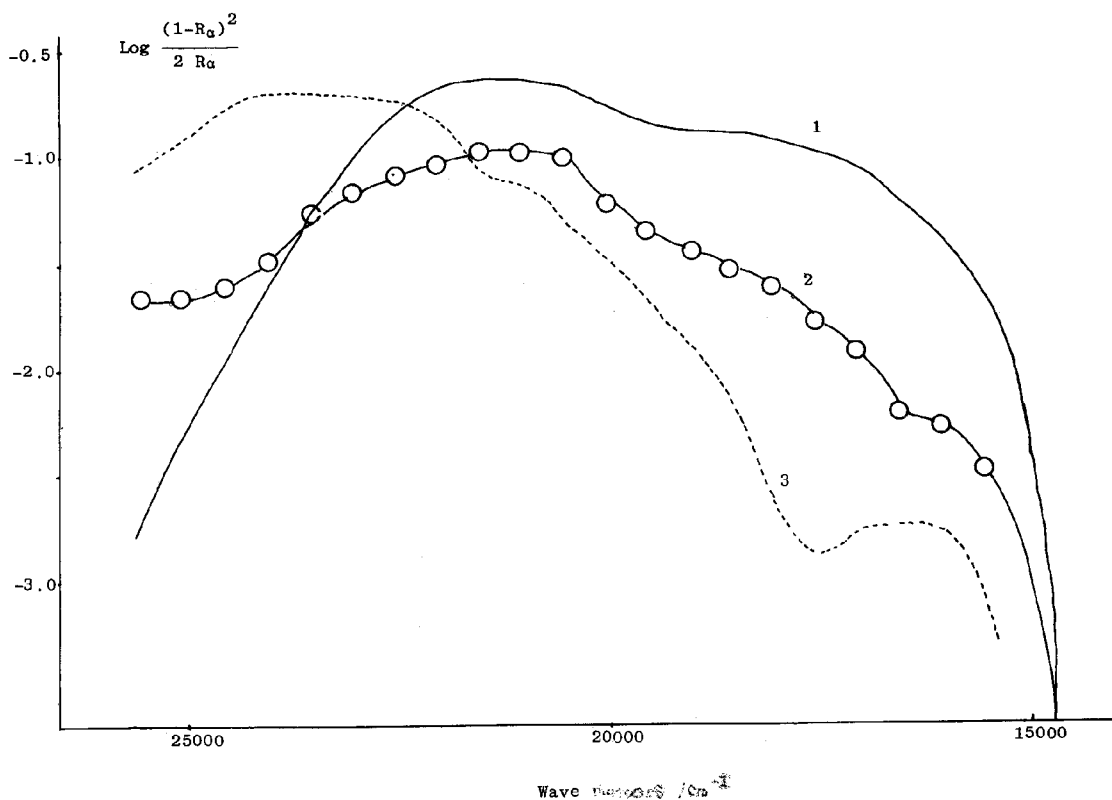
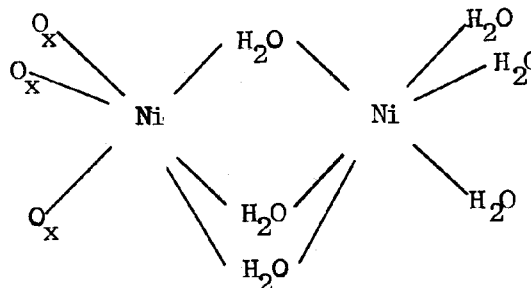


Fig 2 : Diffuse reflectance spectra of nickel exchanged A-zeolites dehydrated at 340K; (1) $\text{Ni}_{2.4}\text{A}$; (2) $\text{Ni}_{3.9}\text{A}$; (3) $\text{Ni}_{4.6}\text{A}$.

a weak band in the green.

For $\text{Ni}_{1.0}\text{A}$, $\text{Ni}_{2.4}$ and $\text{Ni}_{3.2}$ the quasi-octahedral structure $\text{Ni}(\text{O}_x)_3(\text{H}_2\text{O})_3$ (C_{3v} symmetry) is proposed. The spectrum I (Fig 1), is almost identical to that observed for dehydrated nickel in the zeolite NH_4Y , where distorted octahedral coordination in the double six-ring occurs (10). There is also possibility, the preference of nickel for near octahedral coordination wherever possible (17). Thus many compounds which exhibit the square planar structure in non-coordinating solvents become octahedral in the condensed phase, or in a coordinating solvent. The quasi-octahedral structure is also sterically favourable, since the water ligands are directed to the center of the large cavity in the zeolite-A structure; The magnetic moment, at 3.8 B.M. is rather high for an octahedral complex. It is interesting to note that Egerton and Vickerman(7) observed no increase in magnetic moment above the normal value for octahedral nickel, (3.3. B.M.), on dehydrating of a $\text{Ni}_{3.6}\text{A}$ -zeolite. The proposal of octahedral complexes for the three lower nickel content zeolites also suggests an explanation for the spectral changes occurring at

higher nickel contents. For $\text{Ni}_{4.6}\text{A}$ the band maximum shifts to $23,500\text{ cm}^{-1}$ a position very similar to that of normal octahedral nickel complexes. At high nickel contents it seems likely that crowding in the large cavity leads to the formation of dimeric (and possibly trimeric) complexes such as:-



Analogous sharing of oxygen atoms (18) occurs in the octahedral trimer complex $\text{Ni}_3(\text{acac})_6$, (acac = pentane-2,4-dione). Formation of dimeric complexes is expected to reduce steric hindrance in the large cavity and would also explain the observance of a more typically octahedral spectrum.

For Ni^{2+} ions contents <4 per unit cell, the reflectance spectra of dehydrated samples curve 3 of Fig 1 is identical to that reported by Klier and Ralek (4-5) for dehydrated $\text{Ni}_{1.7}\text{A}$ -zeolite. Klier and Ralek assigned this spectrum to nickel (II) trigonally coordinated to oxygen atoms in the 6 ring, $\text{Ni}^{2+}(\text{O}_x)_3$. For $\text{Ni}_{4.6}\text{A}$ the surface area study showed the collapse of the structure at 400K. Gravimetric investigation indicated the black metallic lustre of $\text{Ni}_{4.6}\text{A}$ at 620K. The spectroscopic study showed that dehydrated sample could not be completely rehydrated. Thus the lattice breakdown is suggested on evacuating between 340 and 400K as previously reported by Gal-et al (14) and Dyer and Wilson, (15). The spectrum 2 (Fig 1) is due to the intermediate stage of dehydration (yellowish colour) of the sample. The gravimetric results showed that at this stage of dehydration the ratio of water molecules to Ni^{2+} are 2:1. As the Ni^{2+} ion ultimately resides in the 6 rings, therefore it is suggested that the structure of the Ni^{2+} ion is $\text{Ni}(\text{II})(\text{O}_x)_3(\text{H}_2\text{O})_2$, with trigonal bipyramidal structure, one water molecule pointing in to the large cavity and one in to the sodalite unit. This structure is further supported for the following reasons.

1. Five coordinate complexes of nickel(II) are well known with trigonal bipyramid structure (17, 19, 20.). Sacconi (20) has shown the spectrum of trigonal bipyramidal complex of Ni^{2+} I.e; $(\text{Ni Br}(\text{Me}_6\text{tren})\text{Br})$, which has similar features to spectrum 2 of Fig

2. Akbar and Joyner (3) showed by gravimetric and reflectance spectroscopy the existence of identical trigonal bipyramid structure of $\text{Co}^{2+}(\text{O}_x)_3(\text{H}_2\text{O})_2$ in partially dehydrated (at 400K) CoA zeolite. Yanagida et al (21) have established by X-ray diffraction the presence of an identical 5-coordinate complex of manganese (II), in $\text{Mn}^{2+}_{4.5}\text{A}$ -zeolite.

3. This structure is assumed comparatively stable because according to Yanagida et al (21), both axial water molecules can form hydrogen bonds to framework oxygen atoms.

Acknowledgement

The author carried out this work as a part of his postgraduate research programme under the supervision of Dr. R.W. Joyner at the Department of Physical Chem-

istry, University of Bradford, Bradford, BD7 1DP (England). The author is grateful to Government of Pakistan for a postgraduate Grant.

References

1. K. Seff, *Accounts Chemical Research* 9, 121 (1976).
2. D.W. Breck, "Zeolite Molecular Sieves" structure, Chemistry and use, Wiley-Interscience, New York, 1974.
3. S. Akbar and R.W. Joyner, *J.C.S. Chem; Comm.* 548 (1978).
4. K. Klier, and M. Ralek, *J. Phys. Chem. Solids*, 29, 945 (1968).
5. K. Klier, and M. Ralek, *J. Phys. Chem. Solids*, 29, 951 (1968).
6. S. Akbar, and R.W. Joyner, *J. Chem. Soc; Faraday Trans. I*, 77, 803 (1981)
7. T.A. Egerton, and J.C. Vickerman, *J. Chem. Soc; Faraday I*, 69, 39 (1973).
8. J.M. Jablonski, J. Molak and W. Romanski, *J. Chem. Soc; Faraday I*, 47, 147 (1977)
9. E. Garbowski, Y. Kadratoff, M.-V. Mathiev and B. Imelik, *J. Chim. Phys.* 69, 1386 (1972).
10. E. Garbowski, M.V. Mathiev, *Compte Rendus C.* 280, 1125 (1975).
11. S. Akbar, and R.W. Joyner, unpublished results.
12. K. Klier, *Catalysis Rev*, 1(2), 207 (1967).
13. R. Kellerman and K. Klier, *Surface and Defect properties of solids*, 4, 1 (1975).
14. J.I. Gal, O. Jankovic, S. Maleic, P. Radovanov, and M. Todorovic, *Trans, Faraday Soc*; 69, 999 (1971).
15. A. Dyer, and M.J. Wilson, *Thermochemica Acta*, 11, 55 (1975).
16. B. Coughlan, W. M. Carol, W. A. Mc Cann, *Proc. Roy. Ir. Acad.* 76B, 349 (1976).
17. F.A. Cotton, and G. Wilkinson, *Advanced Inorganic Chemistry*. Pub Wiley - Interscience, New York, (1972).
18. J.C. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.* 4, 456 (1965).
19. M. Ciampolini, and N. Nardi, *Inorg. Chem.* 5, 1150 (1966).
20. L. Sacconi, *Pure Appl. Chem*; 17, 95. (1968).
21. R.Y. Yanagida, T.B. Vance, and K. Seff, *Inorg. Chem.* 13, 723 (1974).