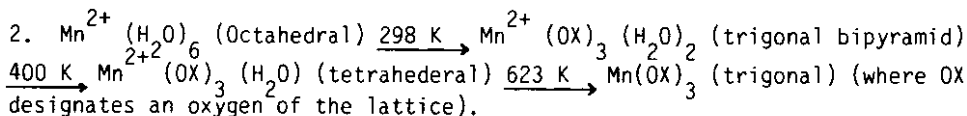
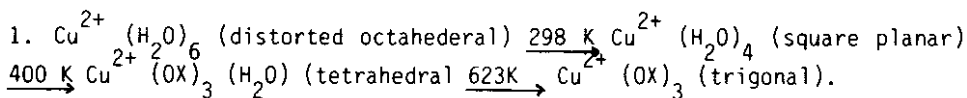


## Reflectance Spectroscopic and Thermogravimetric Identification of Complexes in the Dehydration of Cu<sup>2+</sup> and Mn<sup>2+</sup> A-zeolites

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**Summary:** A series of five samples of Cu<sup>2+</sup> A and only one sample of Mn<sup>2+</sup> A-zeolites were prepared and investigated. Diffuse reflectance spectroscopic and thermogravimetric techniques were employed for identification of the species arising from the dynamic vacuum dehydration of the samples at different temperatures.



Jahn-Teller effect is responsible for the formation of the elongated octahedral (tetragonal) complex of Cu<sup>2+</sup> in hydrated Cu<sup>2+</sup> A-zeolites. Reflectance spectra of Mn<sub>3,5</sub><sup>2+</sup> A were featureless, because the transitions are spin-forbidden, therefore the species are identified mainly by thermogravimetry. No structural collapse was detected, only Cu<sub>4,9</sub> A gave partial lattice destruction.

### Introduction

Zeolites are very important inorganic compounds, have a very open framework which exhibit a very high surface activity inside a pore system of molecular dimensions. By applying suitable combinations of ion exchange, chemical modifications and thermal activation procedures, zeolites acquire industrial importance based on their high surface activity. Zeolites after drying, are powerful adsorbent which can be made selective for particular compounds. Zeolites are made into very active catalysts for cracking of hydrocarbons and for other important industrial operations.

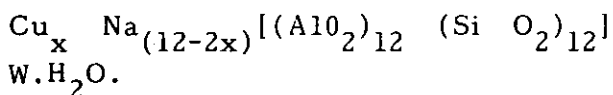
It is now well established that transition metal ions in zeolites act as specific adsorption centres for various molecules, which are bound as ligands [1]. Intrazeolitic complexes, formed in this way, the transition metal ions are often bonded partly to the zeolite lattice and partly to the adsorbing molecules and can vary their coordination and their position, depending upon the nature of the ligands and the temperature and the concentration of the adsorbing molecules. Zeolites play a peculiar role "cation-solvent" and cation stabilizer" for unusual valence states. The zeolites, with its regular and

unique structure can be a useful matrix for studying new spectroscopic properties of transition metal ions.

This paper deals with the combined application of the results of the thermogravimetric and reflectance spectroscopic techniques for identification of copper (II) and manganese (II) complexes formed in type A-Zeolite at different degrees of hydration. Previously no systematic study has been reported in literature about Cu A and Mn A-zeolites. Here a series of five Cu A-zeolites (16.6 to 81.6% exchanged) and only one sample of Mn A-zeolite have been examined.

### Experimental

Five synthetic type A-zeolite samples having exchange levels of 16.6%, 50%, 58.3%, 66.7%, and 81.6%  $\text{Cu}^{2+}$  and represented respectively by the formulas,  $\text{Cu}_1\text{A}$ ,  $\text{Cu}_3\text{A}$ ,  $\text{Cu}_{3.5}\text{A}$ ,  $\text{Cu}_4\text{A}$ , and  $\text{Cu}_{4.9}\text{A}$ , were prepared by ion exchange from copper nitrate solutions. Synthetic Na A-zeolite (lot No. 4941040757) employed for ion-exchange with copper (II) and manganese (II) was kindly supplied by the Union carbide international company USA. The five samples of Cu A-zeolites prepared, having the following general composition per unit cell.



where  $x=1.0, 3.0, 3.5, 4.0$  and  $4.9$  and  $30 < W < 34.7$ : only one sample of  $\text{Mn}_{3.5}\text{A}$  (58.3% exchanged) was prepared by ion exchange from manganese (II) chloride solution. The standard method for exchange techniques were similar to those previously described (2). Volumetric analysis confirmed that each  $\text{M}^{2+}$  ion ( $\text{Cu}^{2+}, \text{Mn}^{2+}$ ) replaced exactly  $2\text{Na}^+$  ions.

Procedure for reflectance spectra and gravimetric measurements have already been explained [3]. Diffuse reflectance spectra were recorded at room temperature on a Pye Unicam SP 800 UV/visible spectrophotometer with a diffuse reflectance attachment, zeolite contained in a specially constructed vacuum cell. Gravimetric study was carried out in a standard, high vacuum system using a Mc Bain spring with a trap cooled to 77K situated close to the balance case.

### Results

Table I shows a summary of the "monolayer equivalent areas" of hydrated and dehydrated [2]  $\text{Cu}_1\text{A}$ ,  $\text{Cu}_3\text{A}$ ,  $\text{Cu}_{3.5}\text{A}$ ,  $\text{Cu}_4\text{A}$ ,  $\text{Cu}_{4.9}\text{A}$  and  $\text{Mn}_{3.5}\text{A}$  zeolites determined by the point "B" method using adsorption of krypton at 77K, after outgassing the sample in vacuum at 620K for at least 2 hours. The table indicates, the surface area

Table-1: Monolayer Equivalent Areas of Hydrated and Dehydrated  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  A-Zeolites

Sample	Surface are/ $\text{m}^2 \text{g}^{-1}$	
	Hydrated	Dehydrated
$\text{Cu}_1\text{A}$ .	29	39
$\text{Cu}_3\text{A}$ .	398	537
$\text{Cu}_{3.5}\text{A}$ .	347	462
$\text{Cu}_4\text{A}$ .	367	491
$\text{Cu}_{4.9}\text{A}$	279	376
$\text{Mn}_{3.5}\text{A}$ .	448	585

\*In calculation the weight of the hydrated sample was taken.

Table-2: Thermogravimetric Data of Copper (II) and Manganese (II) Exchanged A-Zeolites.

Zeolite	H <sub>2</sub> O Molecules per unit cell	Numbers of Water molecules lost per unit cell at different temperatures.			H <sub>2</sub> /Cu <sup>2+</sup> and H <sub>2</sub> O/Mn <sup>2+</sup> ratios at:	
		298K	400K	620K	298K	400K
Cu <sub>1</sub> A	30.3	22.8	5.8	1.6	7.4	1.6
Cu <sub>3</sub> A	31.5	18.4	10.8	2.3	4.3	0.8
Cu <sub>3.5</sub> A	32.7	18	10	4.7	4.2	1.3
Cu <sub>4</sub> A	33.2	16.7	12	4.6	4	1
Cu <sub>4.9</sub> A	34.7	16.3	14.4	4	3.7	0.8
Mn <sub>3.5</sub> A	29.4	19.6	7.4	2.4	2.8	0.7

has increased very sharply after exchanging more than one Cu<sup>2+</sup> ion per unit cell of zeolite A. The gravimetric results are given in table 2. The table shows that the number of water molecules per unit cell increases with the Cu<sup>2+</sup> ions concentration and the ratios of water molecules to Cu<sup>2+</sup> ion after outgassing in vacuum at 298K and 400K are 4.0 and 1.0 respectively. Similarly the ratios of water molecules to Mn<sup>2+</sup> ion after out-gassing Mn<sub>3.5</sub>A in vacuum at 298 and 400K are 3.0 and 1.0 respectively.

Diffuse reflectance spectra of hydrated Cu A-zeolites (turquoise blue colour) and transmission spectrum of aqueous Cu (NO<sub>3</sub>)<sub>2</sub> were recorded in the range 11,500 to 32,500 cm<sup>-1</sup> are shown by curves in Fig.1 All the hydrated Cu A-zeolites showed one broad band and it is slightly asymmetric towards the low frequency side, the

reflectance spectra showed their peak at 12000 cm<sup>-1</sup>. The intensity of the peak increases with increasing Cu<sup>2+</sup> loadings in the zeolite. The spectrum of Cu (NO<sub>3</sub>)<sub>2</sub> solution (curve 6) shows its peak at ~12200 cm<sup>-1</sup>.

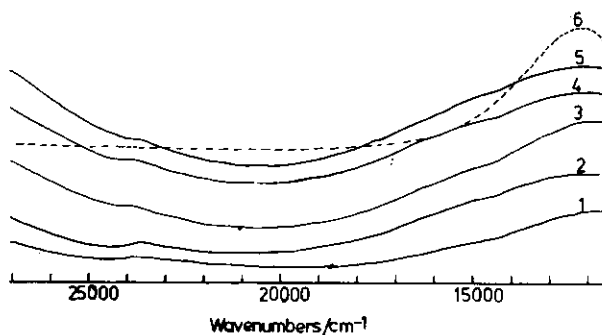


Fig. 1: Diffuse reflectance spectra of the hydrated Cu<sup>2+</sup> A-zeolites and transmission spectrum of the aqueous Cu(NO<sub>3</sub>)<sub>2</sub> : (1) Cu<sub>1</sub> A; (2) Cu<sub>3</sub> A; (3) Cu<sub>3.5</sub> A; (4) Cu<sub>4</sub> A; (5) Cu<sub>4.9</sub> A; (6) Cu(NO<sub>3</sub>)<sub>2</sub> solution.

All five Cu A-zeolites were dehydrated in vacuum at room temperature (298K) for at least 20 hours and then spectra were taken. No new band emerged in the spectrum, only the band maxima at  $12000\text{ cm}^{-1}$  shifted  $300\text{ cm}^{-1}$  towards lower frequency. The colours of the partially dehydrated samples were remained turquoise blue. All partially dehydrated samples were then subjected to vacuum dehydration at 400K for at least  $2\frac{1}{2}$  hours, the colour of the samples turned green. The band at  $\sim 12000\text{ cm}^{-1}$  shifted about  $700\text{ cm}^{-1}$  towards lower frequency. On further vacuum dehydration of the samples at 620K, the colour of the samples turned pale blue. Two new bands emerged at  $13800 (\pm 100)\text{ cm}^{-1}$  and  $14600 (\pm 100)\text{ cm}^{-1}$  except for  $\text{Cu}_4\text{A}$  and  $\text{Cu}_{4.9}\text{A}$  where no band emerged at  $13800\text{ cm}^{-1}$ , moreover,  $\text{Cu}_1\text{A}$  produced the band at  $15000 (\pm 500)\text{ cm}^{-1}$  instead of  $14600 (\pm 100)\text{ cm}^{-1}$ . The spectra of  $\text{Cu}_{3.5}\text{A}$  after evacuating at 298, 400 and 620K respectively for 20,  $2\frac{1}{2}$  and 3 hours are shown by curves 1, 2, and 3 in Fig. 2.

The reflectance spectra of hydrated, partially dehydrated and dehydrated of  $\text{Mn}_{3.5}\text{A}$  showed negligible absorption in the wavelength range investigated.

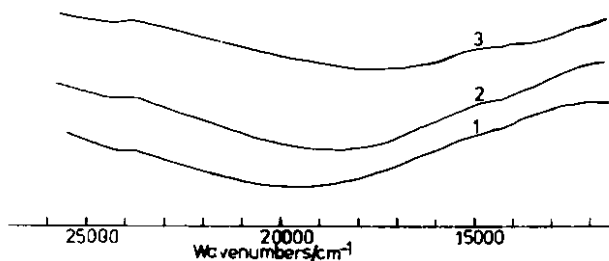


Fig. 2: Reflectance spectra of dehydrated  $\text{Cu}_{3.5}\text{A}$ ; (1) Dehydrated in vacuo at 298 K for 22 hrs; (2) Dehydrated at  $\sim 400\text{ K}$  for  $2\frac{1}{2}$  hrs; (3) Dehydrated at 623 K for 3 hrs.

## Discussion

The surface areas obtained by B.E.T. plots were smaller than point 'B' method. The B.E.T. plots were not linear, because, the initial  $P/P_0$  (Where  $p$  was the equilibrium pressure and  $P_0$  is the saturation pressure of krypton at 77 K) values were smaller than 0.05 (4). The surface areas measured by point 'B' method were considered more reliable than the B.E.T. plots (5). The table 1 shows the surface area of  $\text{Cu}_{1.0}\text{A}$  is very small as compared with other Cu A-zeolites. The reasons for the low surface area of  $\text{Cu}_{1.0}\text{A}$  is related to the structure of type A-zeolite (5,6). In dehydrated  $\text{Cu}_1\text{A}$ , the eight 6-rings are occupied on average by 8-cations ( $7\text{ Na}^+ + 1\text{ Cu}^{2+}$ ) and the six 8-rings are partially blocked by  $3\text{ Na}$  ions. The pore opening of the partially blocked 8-ring is  $3.6\text{ \AA}$  at 77K and the kinetic diameter of krypton is  $3.9\text{ \AA}$  (5). Thus the kinetic diameter of krypton is  $0.3\text{ \AA}$  larger than the partially blocked 8-ring. This difference in sizes is sufficient to exclude the adsorbate (here krypton) from diffusion in the  $\alpha$ -cavities from the 8-rings (5). Hence it is suggested that the surface area of  $\text{Cu}_1\text{A}$  (table 1) is only its external area. The surface areas of  $\text{Cu}_3\text{A}$ ,  $\text{Cu}_{3.5}\text{A}$ ,  $\text{Cu}_4\text{A}$ ,  $\text{Cu}_{4.9}\text{A}$  and  $\text{Mn}_{3.5}\text{A}$  are very high, because these areas are due to their internal crystalline surface as well as the external surface. The table 1 shows that the surface area of  $\text{Cu}_{4.9}\text{A}$  is less than  $\text{Cu}_3\text{A}$ ,  $\text{Cu}_{3.5}\text{A}$  and  $\text{Cu}_4\text{A}$ . The most likely reason is the partial collapse of the structure at the temperature of evacuation, similarly as reported (2,3) for  $\text{Co}_{4.9}\text{A}$  and  $\text{Ni}_{4.6}\text{A}$  zeolites.

The results of surface areas of Cu A and Mn A-zeolites in general confirmed their structural integrity after high temperature dehydration in vacuum. The low temperature adsorption

of krypton also proved that cations ( $\text{Na}^+$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ) prefer to be located in the 6-rings of the dehydrated type A-zeolite. If there are more than 8-cations per unit cell, then those excess of 8-would lodge in the 8-rings and partly block them.

As far as different number of water molecules per unit cell of Cu A-zeolites (table 2) are concerned, it has been shown (5) that the presence of different cations in the zeolite voids affects the pore volume. A small divalent cation increases the voids volume by reducing the total number of cations and increasing the space unoccupied. In this case, in addition to, the  $2\text{Na}^{2+}$  ions are exchanged by  $1\text{Cu}^{2+}$  ion the ionic radius of  $\text{Cu}^{2+}$  ( $0.73 \text{ \AA}$ ) is smaller than ionic radius of  $\text{Na}^+$  ( $0.95 \text{ \AA}$ ) (7) therefore, the space occupied by water molecules increases by exchanging  $\text{Na}^+$  ions by  $\text{Cu}^{2+}$  ions. Moreover, the  $\text{Cu}^{2+}$  ions have the capability of forming complexes with water molecules which are tightly packed and thus cause the increase in the water contents of the zeolite.

The number of water molecules per unit cell i.e. 29.4 determined for  $\text{Mn}_{3.5}\text{A}$  is less than 32.7 found for  $\text{Cu}_{3.5}\text{A}$  (table 2), probably due to the large size of  $\text{Mn}^{2+}$  ( $0.80 \text{ \AA}$ ) as compared to  $\text{Cu}^{2+}$  ( $0.72 \text{ \AA}$ ). Moreover, manganese (II) has zero crystal field stabilization energy for octahedral complexes, therefore water molecules cannot be tightly packed. The water contents obtained here for  $\text{Mn}_{3.5}\text{A}$  also agrees nearly to 29.5 reported (8) for  $\text{Mn}_{4.5}\text{A}$  by X-ray diffraction techniques.

No systematic gravimetric and spectroscopic studies of copper (II) A-zeolites have been reported before in literature, therefore the nature of

spectra is interpreted mainly by comparison with spectra of Cu X and Cu Y-zeolites. The diffuse reflectance spectra of hydrated Cu A-zeolites resemble the transmittance spectrum of aqueous  $\text{Cu}(\text{NO}_3)_2$  (fig.1). Copper (II) ions in hydrated Cu A-zeolites are considered to form hexa-aquo complexes  $\text{Cu}^{2+} (\text{H}_2\text{O})_6$  with an elongated octahedral (tetragonal) configuration due to Jahn-Teller effect. The following reasons are proposed for this structure.

1. As the  $\text{H}_2\text{O}/\text{Cu}^{2+}$  ratio in hydrated type A-zeolites is more than 6, so tetragonally distorted octahedral structures can easily form.
2. It has been reported (9) that aquo  $\text{Cu}^{2+}$  ion has the absorption maximum at  $\sim 12500 \text{ cm}^{-1}$  which nearly agrees to  $12200 \text{ cm}^{-1}$  recorded here for aqueous  $\text{Cu}(\text{NO}_3)_2$  and resembles with spectra of hydrated Cu A-zeolites (Fig.1).
3. It has been previously shown (10-13) by optical spectroscopy that in fully hydrated Cu X and Cu Y-zeolites,  $\text{Cu}^{2+}$  ions exist mainly as hexa-aquo complexes with an elongated octahedral structures. Turkevich et al [14] showed by electron spin resonance  $\text{Cu}^{2+}$  ions in hydrated Cu Y-zeolites form distorted octahedral complexes.

It has been previously reported by Breck [5] that both alpha and beta-cages are easily accessible to water molecules. The zeolitic water can be outgassed continuously over a wide temperature range by heating in vacuum (table 2). The table 2 indicates that the  $\text{H}_2\text{O}/\text{Cu}^{2+}$  ratio after evacuation the Cu A-zeolites at 298K is  $\sim 4.0$ . The reflectance spectrum recorded for each

Cu A-zeolite after this first stage of dehydration is shown by curve 1 in Fig.2. There was no significant change in colour and the spectrum is similar to that of hydrated Cu A-zeolites, only the band maxima shifted  $\sim 300 \text{ cm}^{-1}$  towards lower frequency. At this stage of dehydration the formation of square planar copper (III) complex  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  is suggested due to the following reasons:

1. The loss of the two weakly bonded axial water molecules of the tetragonally distorted octahedral complex and the free water molecules leaves the square planar complex.

2. Similar square planar complexes have already been reported [11] in partially dehydrated Cu Y-zeolites by using optical spectroscopy technique. Wilde et.al. [11] recorded the optical spectrum for  $\text{Cu}^{2+} (\text{H}_2\text{O})_4$  complex which is identical to the spectrum 1 shown in figure 2.

3. Copper forms many square planar complexes (9).

Spectrum 2 (fig.2) is expected to be due to tetrahedral complex of copper  $\text{Cu}^{2+} (\text{Ox})_3 (\text{H}_2\text{O})$ , because at this stage of dehydration (400 K) the  $\text{H}_2\text{O}/\text{Cu}^{2+}$  ratio is 1.0. The tetrahedral complex is formed because the  $\text{Cu}^{2+}$  ultimately locates itself in the 6-ring (with effective charge of 3-Ve) where it is bonded to three oxygens of the ring and one water molecule pointing in the alpha-cavity (fig.3). A similar spectrum was recorded by De Wilde et al. [11] in partially dehydrated Cu Y-zeolite which they proposed due to a  $\text{Cu}^{2+}$  ion linked to 3 lattice oxygen atoms and one water molecule. Schoonheydt et.al. [16] also reported

that when dehydrated Cu A-zeolite (10% exchanged) was exposed to  $\text{NH}_3$  molecules then the possibility of the formation of  $[(\text{Ox})_3 \text{---} \text{Cu-NH}_3]^{2+}$  tetrahedrally coordinated  $\text{Cu}^{2+}$  ion expected, spectrum 3 which shows about three weak bands between the region  $11,500\text{-}15,000 \text{ cm}^{-1}$  is suggested to be due to trigonal planar complex  $\text{Cu}^{2+} (\text{Ox})_3$  which is located in the 6-ring. This complex is proposed because the gravimetric results confirmed the complete loss of water molecules in vacuum dehydration at 623K, therefore  $\text{Cu}^{2+}$  is expected to locate itself in the 6-ring by analogy with other transition metal exchanged zeolites (3,8,15). It has been reported (16) by using e.p.r. signal that in dehydrated Cu A the  $\text{Cu}^{2+}$  ions are surrounded by oxygen containing ligands of 6-rings. The reflectance spectrum of dehydrated Cu A-zeolites reported (12,16,17) is identical to spectrum 3 (Fig.2) and suggested the presence of  $\text{Cu}^{2+}$  in a trigonal site of the distorted 6-ring.

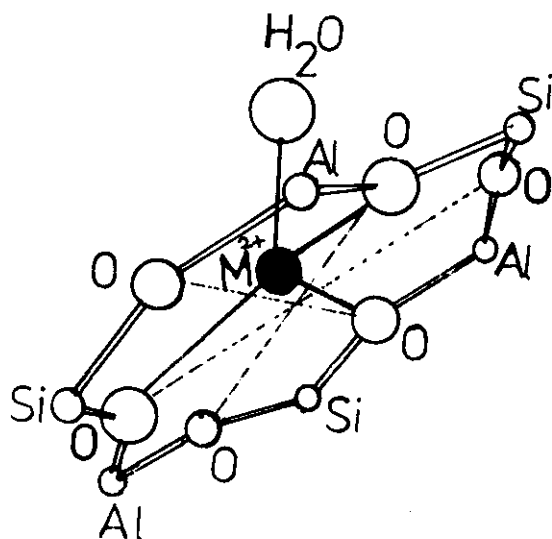


Fig.3: Tetrahedral structure where  $\text{M}^{2+}$  represents  $\text{Cu}^{2+}$  or  $\text{Mn}^{2+}$ .

The diffuse reflectance spectra of hydrated, partially dehydrated and dehydrated  $Mn_{3.5}A$ -zeolite were all the same in shape and were featureless, resembling the spectrum of unexchanged hydrated Na A-zeolite. The optical spectrum of bivalent manganese have low intensity [18] because the transitions are spin forbidden, this may be the reason for the lack of optical investigations in literature of manganese (II) exchanged zeolites. Kellerman and Klier [12] indicated that the high spin manganese ions have no spin-allowed electronic transitions in  $D_{3h}$  or  $C_{3v}$  symmetry complexes and no ligand field stabilization energy. Here the gravimetric results (table 2) indicates the  $H_2O/Mn^{2+}$  ratio greater than 6 in hydrated  $Mn_{3.5}A$ -zeolite, therefore, the presence of hexa-aque complex of  $Mn^{2+}$  i.e.,  $Mn^{2+}(H_2O)_6$  is suggested. The octahedral complex is proposed, because of the very light mauve colour of the hydrated  $Mn_{3.5}A(9)$ . The ratio of  $H_2O$  to  $Mn^{2+}$  determined after first stage of dehydration (at 298K) was 2.8 which gives the possibility of the formation of trigonal bipyramidal structure  $Mn^{2+}(OX_3)(H_2O)_2$  provided by three equatorial oxygen atoms derived from 6-ring and two axial water molecules. It has been reported [8] for hydrated  $Mn_{3.5}A$ , by using X-ray diffraction technique the existance of trigonal bipyramidal structure similar as suggested above. After outgassing the sample at 400K, the tetrahedral complex  $Mn^{2+}(OX)_3(H_2O)$  is proposed (fig.3) because at this stage of dehydration the  $H_2O/Mn^{2+}$  ratio is 1.0. In agreement with Yanagida et.al. [8] the  $Mn^{2+}$  ions in  $Mn_{3.5}A$  after vacuum dehydration at 623K, are suggested to

be trigonally coordinated with three oxygen atoms of the distorted 6-rings.

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### References

1. K.Klier, *Adv.Chem.Ser.*, **101**,480 (1971)
2. S.Akbar and R.W.Joyner, *J.Chem.Soc., Faraday,Trans. I* **77**, 803 (1981)
3. S.Akbar, *J.Chem.Soc.of Pak.*, **4**,(2) 71 (1982)
4. S.Brunauer, D.H.Emmett, and E.Teller, *J.Amer.Chem.Soc.*, **60**,309 (1938)
5. D.W.Breck, "Zeolite Molecular Sieves", *Chemistry and Use, Wiley-Interscience, New York* (1974)
6. K.Seff, *Accounts Chem.Res.*, **9**,121 (1976)
7. T.A.Egerton and F.S.Stone, *J.Chem.Soc.Faraday Trans, I*, **69**,22 (1973)
8. R.Y.Yanagida, T.B. Vance, and K.Seff, *Inorg.Chem.*, **13**,723 (1974)
9. F.A.Cotton, and G.Wilkinson, *Advanced Inorganic Chemistry, pub.Wiley-Interscience, New York* (1972)
10. N.H.Kuzmenko and V.T.Lygin, *Proceedings, Third International Conference on Molecular Seives, ed. J.B.Uytterhoeven, Leven University press* 347 (1973)
11. W.D.Wilde, R.A. Schoonheydt and J.B. Uytterhoeven, *Molecular Sieves-II. A.C.S. Symp. Ser.*, **40**, 132 (1977)

12. R.Kellerman and K.Klier,  
*Surface and Defect properties of solids* 4, 1 (1975)
13. A.V.Kiseleu, N.M.Kuzmenko and  
V.I. Lygin,  
*Russ.J.Phys.Chem.*, **49**, 1804 (1975)
14. J.Turkevich, Y.ono and J.Sorio,  
*J.Catal*; **25**, 44 (1972)
15. S.Akbar and R.W.Joyner,  
*J.Chem.Soc.Chem.Comm.* **548** (1978)
16. R.A.Schoonheydt, P.Peigneur and  
J.B.Uytterhoeven,  
*J.Chem.Soc.Faraday I trans No.77*,  
2250 (1978)
17. J.Jenter, D.H.Strome, R.G.  
Hermann and K.Klier,  
*J.Phys.Chem.* **81**, 333 (1977)
18. I.D.Mikheiken, G.M.Zhidoniro,  
V.B.Kazanskii,  
*Russ.Chem.Rev.*, **41**, 468 (1972).