

## The Determination of Zeolitic Water and Thermal Stability of Nickel Exchanged X-Zeolites by TGA and DTA

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**Summary:** Five Samples of Ni<sup>2+</sup> exchange X-zeolites were prepared by ion exchange technique and were studied by chemical analysis, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) to determine their unit cell composition, zeolitic water and thermal stability. The percentage of cation exchange decreased with increasing the concentration of Ni<sup>2+</sup> cations in the exchange solution. The water contents of the zeolite X increased with increasing the Ni<sup>2+</sup> contents per u.c of the zeolite. The dehydration of Na X completed at 380 °C and those of Ni X-zeolite samples at 420-470 °C and the total weight loss occurred at 800 °C for Na X and Ni X zeolites at 900-980 °C depending on the Ni<sup>2+</sup> cation loading of the Zeolite. The thermograms were of lumpy nature indicated formation of a series of intermediate structures during dehydration. The endothermic peak of dehydration shifted towards high temperature for Ni X-zeolites indicated H<sub>2</sub>O molecules are more strongly bonded to Ni<sup>2+</sup> cations than Na<sup>+</sup> cations. The positions of exothermic peaks indicated that Calcined Ni X- zeolites samples are thermally less stable than Na X-zeolite. The DTA curves indicated that Na X-zeolite becomes amorphous at above 930 °C and Ni X-zeolites at 800-870 °C. The above results are discussed and possible interpretations are given.

### Introduction

Over the past fifty years, zeolite science has grown into a major branch of chemistry. A large number of new zeolite materials have been made by both direct hydrothermal synthesis and by post synthesis modification. This has led to a large number of new applications in such diverse fields as catalysis, adsorption, ion exchange, molecular sieve, pollution control, and zeolite membrane [1-6] in synthesis alone, over two hundred synthetic zeolites have been produced [7]. These are divided into two major classes: ones with low silicon to aluminium ratios (Si /Al < 10) and ones with high silicon to aluminium ratios (Si / Al > 10). The low silicon to aluminium ratio zeolites have hydrophilic surfaces, a large number of exchangeable cations and acid with moderate to high strength. On the other hand, the high silicon to aluminium ratio zeolites have an organophilic surfaces, a relatively small number of exchangeable cations and a relatively small number of acid sites with high strength [8-9].

The type X-zeolite in its sodium bearing form is called Na X has a general formula: Na<sub>86</sub>(AlO<sub>2</sub>)<sub>86</sub>(Si O<sub>2</sub>)<sub>106</sub>. m H<sub>2</sub>O, where m is the number of water

molecules and it has Si/Al ratio 1.23. The faujasite structure of this zeolite is well know [7, 10, 11]. It contains truncated octahedra arranged in a tetrahedral coordination forming a network of large cages (supercage) shaped like the hourglass [12]. The dimensions are about 2.37 nm in length, 0.13 nm in diameter. The bottlenecks are due to the interconnecting 12-rings and have 0.74 nm in diameter (Fig. 1). There are also smaller pores (β-cages) of 0.66nm in diameter, joined by 6 rings of 0.25 nm in diameter. These small cavities are accessible only for a few water molecules. The positions of Na<sup>+</sup> ions have also been proposed to be mostly in the single or double 6-rings as well as in the large cages [7]. Sites-I lie at the centers of hexagonal prisms. Sites II lie on the 6 ring faces of the sodalite cages, on the supercage side. Sites I' and II' lie on the other side of the corresponding 6 rings of the sites I and II respectively, within the sodalite cage, sites III are in the supecage and in the sodalite 4 ring. Cations located near the sites III are said to occupy the sites III'. The structural factors that are important for understanding ion exchange are that the exchange cations must diffuse through a series of

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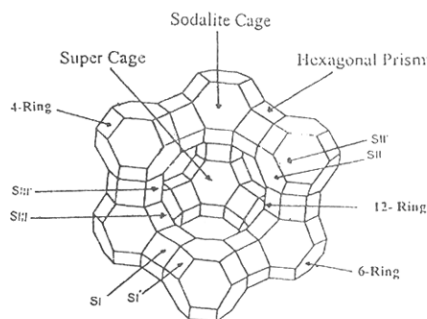


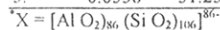
Fig. 1: Structure of Na X-zeolite, with the possible position of the Na<sup>+</sup> ions.

rings of 12 tetrahedra (12 rings) in order of ion exchange to occur in supercages. They must diffuse from these large cages through a 6-ring in order for the ingoing ions to replace Na<sup>+</sup> ions located in the network of small cages.

This paper aims to prepare Ni exchanged X-zeolites, loaded with different number of Ni<sup>2+</sup> ions per unit cell and to describe the affect of the concentration of the Ni<sup>2+</sup> ions solution on the % exchange. Moreover, the Na X and Ni<sup>2+</sup> X zeolite samples were subjected to thermal analysis for determination of zeolitic water from TGA and relative thermal stabilities were evaluated from differential thermal analysis (DTA) patterns of samples calcined for about 2 h in flowing nitrogen.

Table-1: Preparation and analysis of Ni<sup>2+</sup> exchanged X-zeolites

Sample No	Ni Cl <sub>2</sub> Solution Mol dm <sup>-3</sup>	Exchanged %	No. of Ni <sup>2+</sup> ions exchanged Per u.c	Unit cell formula of anhydrous Ni X-zeolite*
1.	0.0112	99.55	8.11	Ni <sub>8.11</sub> Na <sub>69.78</sub> X
2.	0.0225	91.32	14.92	Ni <sub>14.92</sub> Na <sub>56.16</sub> X
3.	0.0338	75.27	18.52	Ni <sub>18.52</sub> Na <sub>48.96</sub> X
4.	0.0446	58.79	19.07	Ni <sub>19.07</sub> Na <sub>47.86</sub> X
5.	0.0558	51.25	20.80	Ni <sub>20.80</sub> Na <sub>44.40</sub> X



## Results and Discussion

The samples of Ni X zeolite with different degrees of Ni<sup>2+</sup> exchange are presented in Table-1. All five samples of Ni<sup>2+</sup> exchanged X-zeolite were of green colours characteristic of hexaaqua Ni<sup>2+</sup> comp-lexes because Ni<sup>2+</sup> ions exist as fully hydrated octahedrally coordinated species in supercages of

hydrated Ni X-zeolites [13-15] similar to those Ni<sup>2+</sup> (H<sub>2</sub>O)<sub>6</sub> in solution. The Table-1 indicates that as the concentration of Ni<sup>2+</sup> ions in the solution increases the % exchange decreases. The reasons for this decrease are attributed to 'volume effect' [16] 'salt imbibent' [17, 18] and 'concentration valency effect' [19]. These reasons have been discussed in detail elsewhere.

The typical thermograms of TGA analysis curves and DTA curves of Na X and Ni<sub>8.11</sub> X are compared in figures 2 and 3 respectively. The thermograms of all zeolite samples investigated were continuous and smooth and showed that the dehydration started between 42 and 50 °C and maximum percentage weight losses (18.87 to 28.41) occurred at about 380-470 °C and dehydration completed at about 800-980 °C depending on the nature and number of Na<sup>+</sup> and Ni<sup>2+</sup> ions per unit cell of the zeolite samples. The relative data are given in table-2. The lumpy nature of thermogravimetric curves probably results from the formation of a series of intermediate structures.

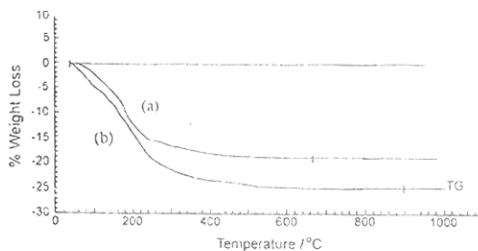


Fig. 2: Thermograms of (a) NaX and (b) Ni<sub>8.11</sub> X-zeolites.

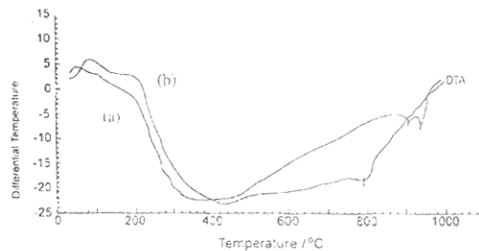


Fig. 3: DTA profiles for (a) NaX and (b) Ni<sub>8.11</sub> X-zeolites.

There are at least two types of water, mobile and immobile ones, in the narrow phase zeolite while there is only mobile water in the wide pore zeolite

Table 2 :- Thermal analysis (TGA, DTA) data of Na X and Ni X –zeolites.

Zeolite	% loss in wt.	Temperature, °C					
		Dehydration started	Mini. of Endothermic peak of dehydration	Mini. of endothermic peaks of recrystallization	Completion of dehydration	Maxi. of exothermic peaks of crystal collapse	No. of H <sub>2</sub> O molecules Per u.c
Na X	18.87	40	380	900,930	800	860,910	173
Ni <sub>811</sub> X	24.84	50	420	790,-	900	500,750	248.15
Ni <sub>1492</sub> X	26.41	40	430	760,-	940	510,700	272.10
Ni <sub>1852</sub> X	26.63	40	460	620,-	950	510,660	275.12
Ni <sub>1907</sub> X	26.81	40	460	580,-	980	530,720	275.80
Ni <sub>2080</sub> X	27.29	50	470	775,-	980	720,-	276.80

[20]. The thermograms showed that the maximum weight losses occurred at 280 °C for Na X and for Ni X zeolite samples at 280-340 °C depending on the number of Ni<sup>2+</sup> ions in the zeolite X (Table-2). This water is assumed to be sorbed and free mobile water inside the supercages and the water lost at above 280 °C was that forming hydration complexes such as Ni<sup>2+</sup>(H<sub>2</sub>O)<sub>6</sub> with the cations and near the periphery of suprecage tightly bonded to framework oxygens and in the small cages and pores of the zeolite samples [21]. The zeolites undergo endothermic changes between 40 and 380 °C for Na X and 40 to 470 °C for Ni X zeolites due to the desorption of zeolitic water. With increasing Ni<sup>2+</sup> ions content the peak temperature of the DTA endotherm increases from 380 to 470 °C. This suggests that water molecules are more strongly bonded to Ni<sup>2+</sup> cations than to Na<sup>+</sup> cation. A slight weight loss in Na X at 800 °C and in Ni X – zeolites at 900 to 980 °C may be due to dehydroxylation [22-23]. For strongly polarizing cations a water molecule yields a hydroxyl bonded to the cation plus proton, which attaches itself to the framework oxygen. Ultimately as the temperature rises the hydroxyls are destroyed with expulsion of water. In general, the dehydroxylation of zeolites is slow and occurs in the temperature range 500-800 °C [24]. It may not be accompanied by a distinct weight loss step in the TG curve but it shows a slow and continues weight loss up to 1- 1.5 % in this range.

The Table-2 indicates that Na X–zeolite contains 173 H<sub>2</sub>O molecules per u.c. and in the literature has been reported 257 [25] by weight loss at 600 °C and 243 weight loss at 800 °C [26]. The zeolitic water content depends on the number of Al ions in the structure of zeolite [21]. The number of Al per u.c. in Na X varies from 96 to 77. As the ratio Si/Al increases, the lattice constant of the zeolite decreases in accordance with the variation in Al – O (0.1728nm) and Si – O (0.1608nm) distance and the

hydrothermal stability as well as the hydrophobicity increases [11, 27, 28].

The Table-2 shows that the zeolitic water contents increase with increasing the number of Ni<sup>2+</sup> ions per u.c in X-zeolite. Gal and Radovanov [25], Bhomrah and Kulkarni [29] had also reported the increase in water contents of Ni X zeolites as compared to Na X-zeolite. Gal and Radovanov reported 324 H<sub>2</sub>O for Ni<sub>246</sub> X-zeolite, Coughlan and Carrol [30] determined 308 H<sub>2</sub>O molecules for Ni<sub>30</sub> X zeolite. The size, nature and number of cations obviously affects the quantity of water occupies the unit cell of the zeolite. The presence of different cations in the voids of the zeolite X affects the pore volume. The following reasons are given for the more zeolitic water of Ni X zeolites than Na X.

1. The cations and water molecules mainly locate in the cages of the zeolite X framework. When 2 Na<sup>+</sup> ions are replaced by one Ni<sup>2+</sup> ions, then the space left vacant in the cavities is filled by water molecules. Further, Ni<sup>2+</sup> ions have higher hydration capacity than Na<sup>+</sup> ions.

2. The Pauling radius of Ni<sup>2+</sup> ion is 0.069 nm and that of Na<sup>+</sup> is 0.095 nm, therefore Ni<sup>2+</sup> ion binds water molecules more strongly and form complexes with water molecules as described above. Moreover, in a structure as rigid as X type zeolite, the increase of zeolitic water occurs due to closer packing of water molecules around the Ni<sup>2+</sup> ions [25] and that is also the reason the amount of water increase.

3. The increase of zeolitic water of Ni X-zeolite samples can also be attributed to the high negative charge density of the framework of the zeolite X, which makes possible a more dense packing of both water molecules and nickel complexes. Water molecules interact with cations present in the zeolite and form hydrogen bonds with

negatively charged oxygen ions associated with the zeolite lattice.

The DTA patterns provided data to the thermal stabilities of the Na X and Ni X-Zeolite samples. The endothermic curves of DTA indicate (Fig. 3) a continuous water loss over a broad range commencing from 40 to about 380 °C for Na X and 40-50 °C to 420-470 °C (Table-2) for Ni X- zeolites depending on the Ni<sup>2+</sup> ions per u.c. The increase in peak temperature of the DTA endotherm of dehydration of Ni X – zeolite samples suggests that water molecules are more strongly bonded to Ni<sup>2+</sup> ions than Na<sup>+</sup> ions. The table-2 indicates the peaks of exothermic temperatures which correspond to the collapse of the crystalline structure. The two maxima of exothermic peaks of Na X at 860 and 910 °C indicate decomposition of the lattice followed by two maxima of endothermic peaks of recrystallization in an other form at 900 and 930 °C and at above 930 °C the zeolite becomes amorphous. About similar results of DTA studies of Na X have been reported by other authors. Breck and Flanigen reported [31] that exothermic peaks of Na X 772 and 933 °C indicate decomposition of the lattice followed by recrystallization to a new phase at 800 and 1000 °C. It was observed [11] that for Na X – zeolite most water is lost by about 400 °C, but strongly polarizations hold the last water tenaciously and thermal breakdown of Na X is near 760 °C. Bravo *et al.*, [26] reported by DTA pattern that Na X becomes amorphous at 964 °C. Gal and Radovanov reported [25] breakdown of the zeolitic framework of Na X by an exothermic peak at about 800 °C. The literature survey indicates that the different Si / Al ratios of the zeolite were found to be responsible for the different thermal behavior [22, 27, 32]. In general, there is a relation between silica to alumina ratio of a zeolite and its thermal stability. The thermal stability of Na X increases with silica content. It has been observed that for Si / Al=2.4 the thermal stability was up to 810 °C and for Si / Al = 6 up to 888 °C [33]. The breakage of Si-O (0.1608 nm) bond should require more activation energy than Al –O (0.1728 nm) bond.

The Table-2 and Fig. 3 show that the two maxima of exothermic peaks of Ni X- zeolites at 500-720 °C and 660-750 °C indicate decomposition of the lattice followed by one minimum of endothermic peak of recrystallization in other form at 580-790 °C and at above 800-870 °C the zeolites become

amorphous. The Table-2 indicates that the first exothermic peak of Ni X-zeolite increases with increasing the Ni ions in zeolite X for example first exothermic peak for Ni<sub>8.11</sub> X, is at 500 °C and that of Ni<sub>20.80</sub> X is at 720 °C. Schoonheydt *et al* [34] reported the same results from DTA curves for Ni X Zeolites. The exothermic nature of the crystal collapse has been attributed to the large amount of surface energy associated with the zeolite. At the temperature of framework collapse, the surface area decreases and the energy associated with the host surface appears in the form of liberated heat [21]. The data of thermal stability reported in Table-3 agree qualitatively with those reported by other authors [33]. However, quantitative agreement among authors is poor. Many factors affect the temperatures at which the exothermic peaks are observed, for example, heating rate, the particular temperature used, atmosphere, sample size.

The Table-2 indicates that the maxima of exothermic peaks of Ni X-zeolite samples are lower than Na X zeolite. The thermal stability of the zeolite framework depends [34, 35] considerably on the type of cation, their distribution among the non framework sites, and the degree of cation exchange. In general, cation exchange with multivalent cations and/or hydrogen enhances [35] the thermal stability. The results of less thermal stability of NiX are in consistent with the literature [19]. Bremer *et al.*, [33] reported the decrease of thermal stability of Ni X-zeolites with increasing of degree of exchange, then it increases, beginning with 20-40 % degree of exchange. Some general behavior of thermal stability with cations size and nature has been observed for other zeolites including zeolite type A [32]. It has been attributed the relation to the relative stability of the various cation to fill the voids in the crystal in the dehydrated zeolite [21, 36]. It has been confirmed [36] that in the case of dehydrated Ni X zeolite the Ni<sup>2+</sup> ions are distributed in the supercages and/or sodalite cavities and occupy preferentially the hexagonal prisms (site I) in octahedral symmetry. Ni<sup>2+</sup> ions in the site I position reduce the diameter of the six membered ring in the hexagonal prism because of strong polarization [33, 34, 36]. This lattice distortion should result in a decrease in thermal stability. According to Shiralkar and Kulkarni [35] the high temperature exotherm is attributed to a structure collapse or phase transformation and it is taken as a measure of the thermal stability of the zeolite. Thus, Na X structure collapses at above 930 °C and Ni X –

zeolite samples become amorphous at 800-870 °C depending on the degree of Ni exchanged.

### Experimental

All Ni exchanged X-zeolites were prepared from a single batch of sodium X-zeolite (lot # 216-2-083) powder form without binder was provided by UOP (USA). The reagents used were of analytical grade, glass wares were of pyrex and water used was deionized. The following procedure to prepare Ni<sub>20.80</sub>X is typical of the exchange methods used. 5 g of Na X zeolite was stirred in 75 cm<sup>3</sup> deionized water and the PH reduced to 7.0 by adding very dilute HCl (0.1 mol dm<sup>-3</sup>) with constant stirring. A solution of Ni Cl<sub>2</sub> (200 cm<sup>3</sup>, 0.0558 mol dm<sup>-3</sup>) was added slowly with constant stirring and the mixture stirred for 2h at 60°C. The slurry was filtered and the exchanged sample was washed several times with hot deionized water. The wet samples were dried overnight at 70 °C and then stored over Ca (NO<sub>3</sub>)<sub>2</sub> solution at room temperature in a desiccator for complete rehydration . The Ni<sup>2+</sup> ions content of the solution was analyzed before and after exchange by titration with 0.01 mol dm<sup>-3</sup> EDTA with mureoxide as indicator. The chemical analysis confirmed that according to valence rule 2 Na<sup>+</sup> ions were replaced by one Ni<sup>2+</sup> ion. In all five Ni X-zeolites were prepared with the general formula: Ni<sub>x</sub> Na<sub>86-2x</sub> (Al O<sub>2</sub>)<sub>86</sub> (Si O<sub>2</sub>)<sub>106</sub> nH<sub>2</sub>O with x = 8.11, 14.92, 18.52, 19.07, 20.80. All Ni exchanged X-zeolite samples were of green colour.

Thermal analysis (TGA, DTA) measurements were carried out with a Simultaneous STA-40 NETZSCH (Germany) thermal analyzer using high purity nitrogen as purge gas and heating rates of 10 °C /min . The zeolitic water was found by the % weight loss up to maximum temperature of 1000 °C and relative thermal stabilities of the crystals were investigated by observing cryrtallinity changes in zeolite samples heated in the temperature range from room temperature up to 1000 °C.

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### References

1. A. Galerneau, F. D. Renzo, F. Fajula and J. Vedrine, eds. Zeolites and Mesoporous Materials at the Dawn of the 21<sup>st</sup> century, stud. Surf. Sci, Catal. **135** (2001).
2. J. C. Jensen, M. Stocker, H. G Karge and J. Weitkamp, eds. Advaced Zeolite Scince and Applications, *Stud. Surf. Sci. Catal.*, **85**, (1994).
3. P. Misaelides, F. Macasek, T. J. Pinnavaia and C. Caletta, eds. Natural Microporous Materials in Environmental Technology; Dordrecht: Kluwer Academic (1999).
4. R. Szostak, Handbook of Molecular Sieves, New York: Van Nostrand Reinhold (1992).
5. H. V. Bekhum, E. M. Flanigen, P. A Jacobs and J. C Jansen eds; "Introduction to Zeolite Science and Practice", 2<sup>nd</sup> ed; Amsterdam: Elsevier, **137**, (2001).
6. H. G. Karge, J. Weitkamp, eds; Molecular Sieves: Science and Technology, Berlin: Springer, Verlag, **2** (2001).
7. W. M. Meier and D. H. Olson, Atlas of Zeolite Structure Types, Butterworth – Heinemann, London (1992).
8. M. L. Brent, F. P Gortsema , C. A. Messina, H. Rastelli and T. P. J. Izod, in : Intrazeolite Chemistry, A.C.S Symp. Ser. 218, eds. G. D Stucky and F. G. Dwyer, *Amer.Chem. Soc.*, Washington, D.C 41 (1983).
9. A. Auroux, *Topics in Catalysis*, **19**, 205 (2002).
10. J. V. Smith, *Adv. Chem. Ser.*, **101**, 171 (1971).
11. D. W. Breck, 'Zeolite Molecular Sieves', Structure Chemistry, and use, Wiley Inter-Science, New York, (1974).
12. L. Frunza, H. Kosslick, S. Frunza, R. Frick and A. Schonhals, *J. Non-Crystalline Solids*, **307-310**, 503 (2002).
13. T. A. Egerton, A. Hagon, F. S. Stone and J. C Vickeman, *J. C. S. Faraday I*, **68**, 723 (1972).
14. C. E. Garbowski and M. V. Mathiev, *C. R Acad. Sci. Paris*, **280**, 1125 (1975).
15. E. Gallei; D. Eisenbach and A. Ahmed, *J. Catal.*, **33**, 62 (1974).
16. R. W. Barrer, L. V. C Rees and J. Shamsuzzona, *J. Inorg Nucl. Chem.*, **28**, 629 (1966).
17. F. Hellferich, Ion Exchange, New York: Mc Graw Hill, 134 (1962).
18. R. M. Barrer and A. J. Walker, *Trans Faraday Soc.*, **69**, 191 (1964).
19. R. M. Barrer and J. Kliowski, *J. Chem. Soc.*

- Faraday Trans. I*, **70**, 2080 (1974).
20. F. Ucon, *Z. Naturforsch. Sect. A-J. Phys. Sci.*, **57** (5), 281 (2000).
  21. J. A. Rabo, *A.C.S. Monograph*, **171**, (1976).
  22. M.A.Heilbron and J.C.Vickermann, *J. Catal.*, **33**, 434 (1974).
  23. T. I. Barry and L. A Lary, *J.Chem. Phys.*, **50**, 4603 (1969).
  24. H. A. Banesi, *J.Catal.*, **8**, 368 (1967).
  25. I. J.Gal and P. Radovanov, *J. Chem. Soc. Faraday Trans. I*, **71**, 1671 (1975).
  26. R. V. Hercigonja, B. B. Radak and M. V. Radak, in 'The Properties and Application of Zeolites, Ed. R. P. Townsend, The Chemical Society Special Publication No **33**, London, (1980).
  27. J. G. Martinez, D. C Amaros and A. L. Solano, *Langmuir*, **18**, 9778 (2002).
  28. F. Scheffler, R. Herrmann, W. Schwieger and M. Scheffler, *Microporous and Mesoporous Materials*, **67**, 59 (2004).
  29. J. S. Bhomrah and S. B Kulkarni, *Indian Journal of Chemistry*, **16A**, 573 (1978).
  30. B. Coughlan and W. Carrol, *J.Chem. Soc. Faraday Trans. I*, **72**, 2016 (1976).
  31. D. W. Breck and E. M. Flanigm, Molecular Sieves, Society of Chemical Industry, London, 47 (1968).
  32. N. Y. Usachev, E. P.Belaruva, L. M. .Krukouki, S. A. Kanaev and O. K. A. Kazakov, *Russ. Chem. Bull.*, **52**, 1940 (2003).
  33. H. Bremer, W. Marke, R. Schoodel and F. Vogt, *Adv. Chem Ser.*, **121**, eds. W. M. Meier and J. B Uytterhoeven, *Amer. Chem. Soc.*, Washington, D.C. 249 (1973).
  34. R. A. Schoonheydt, L. J Vandamme, P. A. Jacobs and J. B. Uttyer Hoeven, *J.Catal.*, **43**, 292 (1976).
  35. V. P. Shiralkar and S. B. Kulkarni, *J. Thermal Anal.*, **25**, 399 (1982).
  36. L. Christine and C. Mickel, *J. Phys. Chem.* **100**, 3137 (1996).