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DC CONDUCTIVITY OF H^+ , Cd^{++} AND Zn^{++} MODIFIED ZSM-5 AND ZEOLITE Y USING FROM COAL FLY ASH

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ABSTRACT :

Zeolites synthesized from coal fly ash were attracting huge attention in current era of research because of their uncomplicated, unhazardous synthesis way. The eco-friendly properties have opened a wide field of applications of using these materials in different technologically important fields such as catalysis, adsorption and gas separation. Hence, the commercial zeolite ZSM-5 and zeolite Y with their modified forms which were synthesized from coal fly ash is used to test their applications as adsorbents and ion conducting materials

Zeolites are ion conducting and dielectric materials. The complex electrical properties such as of zeolite have been the subject of intense studies for more than three decades. These properties of the zeolites are mainly related to the chemical composition, Si/Al ratio, the type of exchangeable cations, degree of exchangeable cations, the state of hydration and temperature.

Compared with other ionic crystalline solids, zeolites have a high electric conductivity. This conductivity results from the great mobility of exchangeable cations. Thus zeolites can be regarded as weak electrolytes. Their conductivity is of the cations between close sites. Dc conductivity of modified form of ZSM-5 and Y were studied.

KEYWORDS: CFA, Si/Al ratio, DC Conductivity, modified form of ZSM-5 and Y.

INTRODUCTION:

The study of variation of DC conductivity with $1000/T$ over fly ash prepared HZSM-5, HY and their modified form with Cd^{++} and Zn^{++} . The circuit diagram is as shown in Figure -1 It contains ionic conductivity cell, muffle furnace, DC source, DC voltmeter, DC micrometer. Its melting point is 1500 OC and low coefficient of thermal expansion. The pellet of sample under study can be sandwiched between two brass electrodes, B1 and B2, which internally make good contacts with the central rod F and one supporting rod G of the frame through the base plate respectively. The maximum height of the sample which could be sandwiched between two electrodes is about 1mm. The marble tiles are used to support the entire frame, also serve as electrical and thermal insulators. The muffle type furnace is used to give temperature up to 1000 OC. For measurement of ionic conductivity in micro porous materials, water must be removed from the pores, as the presence of any water has been observed to significantly affect the conductivity.

All the samples of the modified forms of zeolite were pelletized under an appropriate amount of pressure of 5 tons. The diameter ($d = 13mm$) and thickness ($t = 1mm$) of sample pellet is measured. The pellet is placed between two brass electrodes of the conducting cell. The central rod is tightened to make good contact between brass electrodes and pellet surface. The conducting cell is placed inside the muffle furnace, such that marble foil M1, has got the same size as that of the muffle furnace, covers the mouth of the furnace. The connections are made as shown in Figure -1. The temperature of the furnace increased gradually from ambient to 900 OC. To make good electrical contacts, tighten the rod F further. The temperature of the furnace is measured by a thermocouple calibrated directly to give the temperature in

centigrade. The current is noted at a constant known voltage at different temperature when substance is allowed to cool

The type of zeolite used is called Mobil Synthetic Zeolite ZSM-5, which was developed by Argauer and Landolt in 1972. Since its inception, ZSM-5 has been widely used for hydrocarbon inter conversion in the petroleum industry. ZSM-5 zeolites in protonic type (HZSM-5) have been extensively used in this research¹. The topology of the zeolite framework is given by a unique three-letter code, which is not related to the composition of the material. Generally, based on the pore openings zeolite ZSM-5 is a medium pore zeolite material with Mobil Five (MFI) topology.

The MFI structure is built up by ²⁻⁵ secondary building units (SBU); the smallest number of TO4 units, where T is Si or Al, from which zeolite topology is built which are linked together to form a chain and the interconnection of these chains leads to the formation of the channel system in the structure Faujasite Y is according to the International Zeolite Association, the structure is a FAU type⁶⁻⁹ which crystallizes in the cubic space group Fd_3m with a lattice constant ranging from about 24.2-25.1Å, depending on the framework aluminum concentration, cations, and state of hydration. This zeolite is most conveniently visualized as being formed from 24- tetrahedra cubic octahedral units (sodalite cages), joined through hexagonal prisms (also known as double 6-rings), The structure can be viewed as the diamond structure, with the sodalite cages playing the role of carbon atoms, and the double 6-rings the role of C-C bonds

Zeolite Y is the most important catalytic zeolite, and is generally synthesized in the Na form. Most of the catalysis of interest is acid catalysis, which requires replacing the Na cations by protons, converting the sieve into the H-form. This cannot be done by direct ion exchange, since most H-faujasite are not acid stable. An indirect strategy is therefore used. An ammonium exchange is carried out, followed by a calcination to decompose the NH_4^+ cations into ammonia and protons. Solid ion conducting materials have grown interest due to their potential applications in various electrochemical devices such as fuel cells, batteries, sensors and electro chromic display devices¹⁰. Although, a vast number of various solid electrolytes have already been identified but the development of chemically and thermally stable super ionic conductors still remains one of the prime goals of research in solid state electrochemistry and material science. Currently considerable efforts are being devoted to the synthesis and characterization of inorganic materials, which form a new class of solids with properties, combining the high chemical and thermal stability.

The electrical properties of zeolites solid ion conducting materials and related pore or channel structures have been the object of intense studies for more than three decades. Most of the experiments on these micro porous solids have been done by Freeman and Stamires and by Schoonheydt and Uytterhoeven¹¹⁻¹⁴ focusing on the mobility of the exchangeable cations in zeolites by means of dielectric spectroscopy. Zeolite contains mobile cations which are located in sites, in cavities, on the channel walls and free within the channels co-ordinate with water molecule¹⁵. These cations compensate the negative charge of the zeolite framework. Since cations are free, they can move to new positions under the influence of an external electric field, which causes the electric charge transport. It's conductivity and dielectric relaxation. Compared with other ionic crystalline solids, zeolites have a high electric conductivity¹⁶⁻¹⁸. This conductivity results from the great mobility of exchangeable cations. Thus zeolites can be regarded as weak electrolytes. Their conductivity is of the cations between close sites. The mobility of exchangeable cations in zeolites has been investigated by electrical conductivity measurement¹⁹⁻²². Beattie and Dyer have shown that electrical conduction of zeolites occurs by the migration of cations⁴¹. At room temperature the conductivity increases sharply on adsorption of water in the zeolites. Freeman and Stamires served a strong dependence of activation energy on the type of cation in ZSM-5 and Y type zeolite and proposed the existence of at least two types of cation sites²³⁻²⁵.

EXPERIMENTAL:

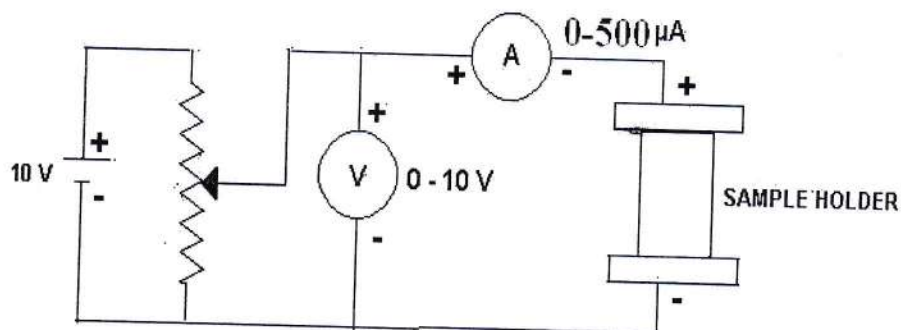


Figure -1: Circuit diagram to measure DC conductivity

RESULTS AND DISCUSSION:

D. C. Conductivity of HZSM-5 and modified forms of HZSM-5 with Cd⁺⁺ and Zn⁺⁺:

Figure -2 represent the plot of variation of dc conductivity with $1000/T$ of HZSM-5. From the conductivity plot of HZSM-5 sample it is observed that as temperature increases the conductivity increases linearly. With pure ZSM-5, in which less number of mobile free carrier are available hence the density of mobile ions for conduction leads to the less conductivity. It could be expected that exchange with high mobility protons H⁺ would create an increase of the conductivity. In case of modified HZSM-5 samples with divalent Cd⁺⁺ and Zn⁺⁺ the conductivity is also high for high temperature. But the conductivity for H⁺ forms was sharper than divalent metal forms of ZSM-5 which is illustrating in the Figure 3.8 and Figure 3.9. This may be due to increased ionic radii of zinc and cadmium with respect to protons, which has been suggested as a potential reason for the increased activation energy and decreased conductivity of the metal modified zeolite.

Another reason may affect that, in zeolites, the anionic framework sites are created by framework aluminum and are univalent ⁴⁹. During the ion exchange two of these univalent sites must be in an appropriate arrangement to electro statically charge balance a divalent ion, from the geometry of the framework and distribution of aluminum among the T site, could lead to a reduced number of mobile cations and a reduced number of accessible hopping sites (increasing the distance between available sites, decreasing the conductivity), thereby decreasing the conductivity and increasing the hopping activation energy in zeolite. The specific conductivity in H.T. region is depends on the number of ions per unit cell, on the nature of the exchangeable ion. As the ZSM-5 samples modified with increasing in Zn⁺⁺ and Cd⁺⁺ metal ion percent in exchange solutions during ion exchange, the dc conductivity of the modified samples were gradually decreases as the ion percent increases in the exchange solution, this may be due to reducing the number of accessible hopping sites. Fig. 3 and 4 comparative illustration of the variation of conductivity with respect to the $1000/T$ for H⁺ and post modified forms of zeolites (Cd⁺⁺ and Zn⁺⁺) with increasing of metal ions percent. From the conductivity plots it was observed that conductivity not only a function of exchangeable metal ions but also the percent of the metal ions present in the zeolite. In case of all the pre and post modified forms the linearity predicted by

Arrhenius law is almost perfect in the region of the higher temperature (H.T.). At low temperature (L.T.) important deviations of linear behavior were observed. This may be indicating that other mechanism occur at that temperature. The deviation from straight line behavior in the low temperature region is further dependent on the relative importance of two phenomenons: Ionic conductivity and dipole absorption

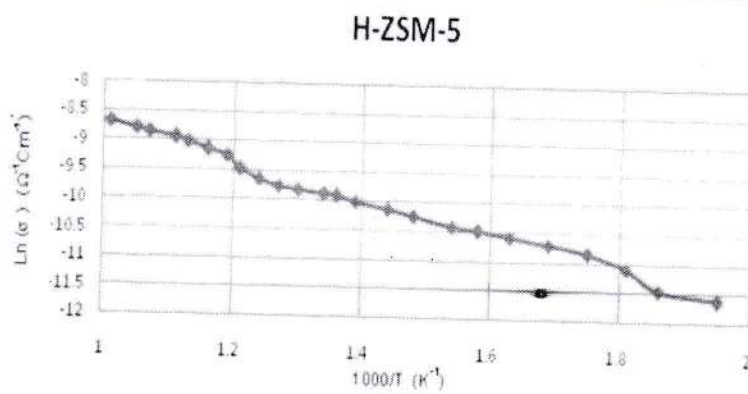


Fig. 2 : D.C. conductivity of fly ash synthesized HZSM-5 Zeolite

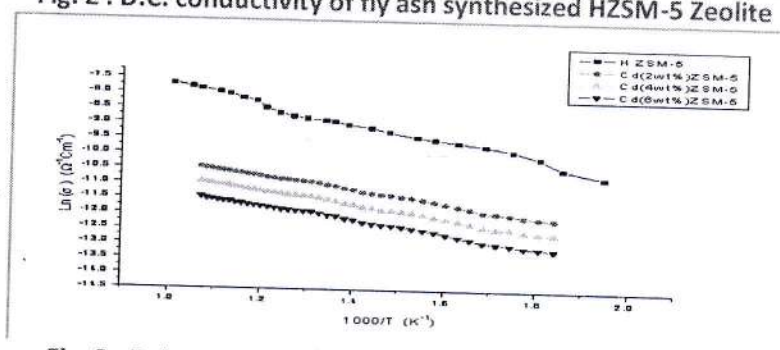


Fig. 3 : D.C. conductivity of fly ash synthesized HZSM-5 and Cd ZSM-5 (2wt %), Cd ZSM-5 (4wt %) and Cd ZSM-5 (6 wt %) Zeolites

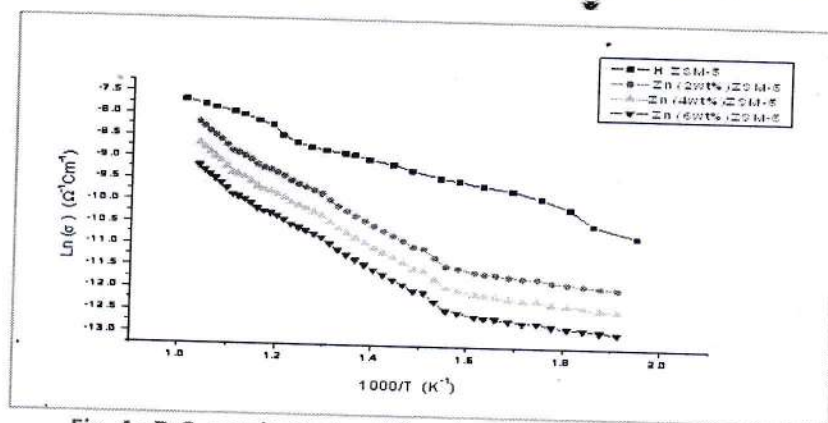


Fig. 4 : D.C. conductivity of fly ash synthesized HZSM-5 and Zn ZSM-5 (2wt %), Zn ZSM-5 (4wt %) and Zn ZSM-5 (6 wt %) Zeolites

From the above observations the conductivity is greater in H-ZSM-5 sample than Zn (2wt%, 4wt% and 6wt %) ZSM-5 and Cd (2wt%, 4wt% and 6wt %) ZSM-5. The variation of the conductivity as a function of nature of exchangeable cations follows the order $H^+ > Zn^{++} > Cd^{++}$ for ZSM-5 zeolite. From the plot it is learnt that at higher temperature the conductivity is high and it linearly reduces with temperature. It is observed that as the metal percent of divalent cations increases the activation energy increases which leads to decrease in conductivity.

D.C. Conductivity of HY and modified forms of HY with Cd⁺⁺ and Zn⁺⁺:

Zeolite Y have received the greatest attention in literature on the conducting properties of zeolites, perhaps due to early reports revealing a high frequency relaxation in these materials, or because of the wealth of crystallographic knowledge pertaining to the FAU structure, i.e., aluminum framework sites, cation positions, etc. Fig. 4 represent the plot of dc conductivity verses temperature ($1000/T$) of HY. It is seen that in all the modified forms of Y samples with Zn⁺⁺ and Cd⁺⁺, the conductivity is high for high temperature. It observed that conductivity increases with increasing temperature. For each sample the linearity predicted by Arrhenius law is almost perfect in the region of the higher temperature (H.T.). At low temperature (L.T.) important deviations of linear behavior are observed. The specific conductivity is greater in HY sample than Zinc and Cadmium modified forms with the different metal ion percents.

This is because protonic forms mobility values are much greater when compare to the Zinc and Cadmium ions due to its structural features. In zeolite Y, activation energy for cation transport was observed to monotonically increase with increasing cation percent; this was attributed to decreased electrostatic interaction between the charge balancing cation and the anionic framework site. As the metal ion percent of zinc and cadmium increases (in the exchange solution) the same trend was observed as that was observed for zeolite ZSM-5 samples. Cd (6wt %) Y sample given lowest conductivity when compared with the other 2wt% and 4wt% of CdY forms. The variation of the conductivity as a function of nature of exchangeable cations follows the order $H^+ > Zn^{++} > Cd^{++}$ for Y zeolite.

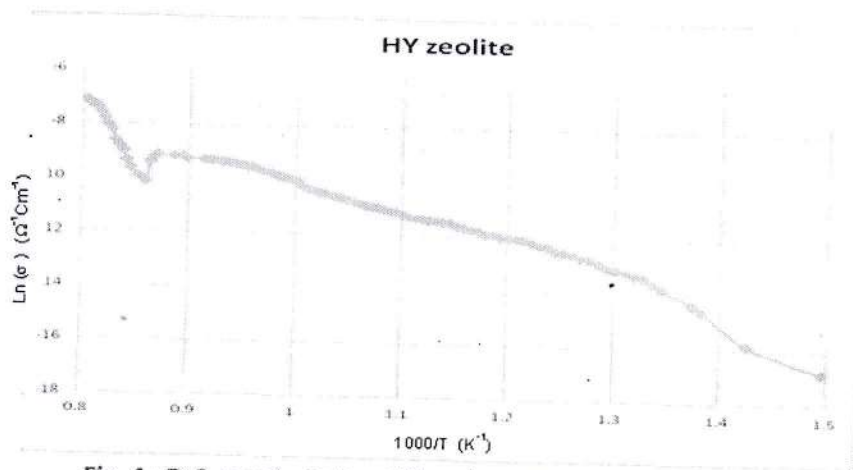


Fig. 4 : D.C. conductivity of fly ash synthesized HY Zeolites

Dielectric study of H⁺, Zn⁺⁺ and Cd⁺⁺ modified Zeolite ZSM-5 and Zeolite Y synthesized from fly ash:

The dielectrical studies have been performed on pre and post modified forms of zeolites ZSM-5 and Y. These studies deal with the influence of absorbed molecules or cation exchanges on electrical properties of the sample. Electrical conductivity and dielectric properties have been experimentally studied for many synthetic and natural zeolites, with various cationic compositions (di-valent cations with increasing cation concentration) in the presence of different adsorbents or in dehydrated form. At low frequencies (up to 10 MHz) dielectric properties are dominated by cation jumps between sites located at the same or different zeolites cavities. Thus they are very important to understand ion exchange, molecular sieve effects or high temperature catalysis and also to evaluate zeolites as a solid electrolyte. Local (intra sites) motions are expected to contribute at higher frequencies.

SUMMARY AND CONCLUSION:

The dc conductivity, dielectric properties of HY, HZSM-5 zeolites prepared from coal fly ash and their modified forms were measured. In our observations Conductivity as a function of nature of exchangeable cations follows the order $HY > ZnY > CdY$ zeolite and $H\ ZSM-5 > Zn\ ZSM-5 > Cd\ ZSM-5$ zeolite. In both the type

of the samples as the metal percent increases the Al frame work content decreases and the conductivity decreases. In ZSM-5 samples, the conductivity is high for high temperature. In the case of zeolite Y samples as the temperature increases sudden drop in the conductivity was observed in the case of H⁺, it may appear due sudden decrease in framework aluminum content. Further for each sample the linearity predicted by Arrhenius law is almost perfect in the region of the higher temperature (H.T.). At low temperature (L.T.) important deviations of linear behavior are observed in both type of sample. The deviation from straight line behavior at high temperature region is dependent on the relative importance of ionic conductivity and dipole absorption.

From the observations it is learnt that at higher temperature the conductivity is high and it linearly reduces with temperature. In the study of dielectric constant as a function of frequency the dielectric constant continually increases as frequency decreases, all metal loaded zeolite samples shows the same pattern. The dielectric relaxation in zeolites is assumed to be due to a change of dipole moment vector, formed between the cations in the cavities and framework anions, when the cations migrate. The adsorbed polar water affects the relaxation phenomenon. In our observations metal loaded zeolites capacitance, dielectric constant (ϵ') decreases as the frequency increases this was verified by the literature that due to the decrease in the dipole distance the freedom of the lattice decreases which in turn changes the electrical properties of the zeolites.

REFERENCES:

1. Barauh A.K. et. al. Impact of sugar mill and distillery effluent on water quality of River Gelabil, Assam, *Indian.J.Env.Health*, 35(4), (1993), P.288-293.
2. Over view and comparison of conventional treatment technologies of water presented in *International work shop of Nanotechnology and water and development* 10-12 October, (1996), p. 13-16.
3. Gupta P.K., Soil, plant, water and fertilizer analysis, *Agrobios (India) publication*, Jodhpur (2000).
4. Vasanth Kumar K., Treatment of dye bearing waster water by Adsorption technique using sugar industrywastes, *Res. J. Chem. Environ.* 7(3), (2003), p. 72-75.
5. APHA. 1993. Standard methods for examination of water and waste water (American Public Health Association, Washington DC).
6. G. Zhifeng, M. Ruixin, and L. Guojun, *Chem. Eng. J.*, 119, (2006), p. 55.
7. O. Dusart, S. Souabi, and M. Mazet, *Environ. Technol.*, 11, (1990), p. 721.
8. Berkgaut, V., Singer, A, High capacity cation exchanger by hydrothermal zeolitization of coal fly ash. *Appl. Clay Sci.* 10, (1996), p. 369– 378.
9. Breck, D.W., Ion Exchange Reactions in Zeolites. Chapter 7 of *Zeolite Molecular Sieves, Structure, Chemistry, and Use* Robert (1984).
10. Chang, H.L., Shih, W.H., Conversion of fly ash to zeolites for waste treatment. *Ceram. Trans.* 61, (1995), p. 81–88.
11. V. Badillo-Almaraz, P. Trocellier, I. Davila-Rangel, *Nucl. Instrum. Methods Phys. Res. B* 210 (2003), p. 424.
12. R.M. Barer, Zeolites and Clay Minerals as Sorbent and Molecular Sieves, *Academic Press, New York*, (1987).
13. M.B. Hafez, A.F. Nazmy, F. Salem, M. Eldesoki, *J. Radioanal. Chem.* 47 (1978), p. 115.
14. E. Galli, G. Gottardi, H. Mayer, A. Preisinger, E. Passaglia, *Acta Crystallogr. Sect. B* 39 (1983) p. 189.
15. K.D. Mondale, R.M. Carland, F.F. Aplan, *Miner. Eng.* 8 (1995), p. 535.
16. D.W. Breck, *J. Chem. Edu.* 41 (1964) p. 678.
17. J.W. McBain, "The Sorption of gases and vapors by Solids" chap.5, *Rutledge and sons, London* (1932).
18. Peterson, Stephen, A novel ion-exchange media for removing lead from wastewater streams: *Zeotech Corp.*, (1996), p. 3.
19. R.M. Carland, F.F. Aplan, *Miner. Metall. Process.* 11 (1995), p. 210.
20. M.S. Joshi, R.P. Mohan, *J. Colloid Interface Sci.* 95 (1983), p. 131.
21. G. Blanchard, M. Maunaye, G. Martin, *Water Res.* 18 (1984), p. 1501.

22. M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren, D.E. Shanks, *Sep. Sci. Technol.*
23. U.D. Joshi, P.N. Joshi, S.S. Tamhankar, V.V. Joshi and V.P. Shiralkar, "Adsorption Behavior of N₂, Water, C₆ Hydrocarbons, and Bulkier Benzene Derivative (TMB) on Na- X Zeolite and Its K⁺, Rb⁺, and Cs⁺ - Exchanged Analogues" published in *Journal of Colloid and Interface Science* 235,
24. Holler, H. and Wirsching, U.: Zeolite formation from fly ash. *Fortschritte Mineralogie*, 63,
25. F. R. Ribeiro, A. E. Rodrigues, L.D. Rollmann, C. Naccache Zeolites : Science and Technology. *Martinus Nijhoff Publishers*, the Hague, (1984).

