SUMMARY

This thesis deals with the study of synthetic molecular sieve, obtained from Union Carbide Corporation, USA, in powder form. This molecular sieve has a pore size of 4Å with sodium as the cation and has unit cell contents corresponding to \( \text{Na}_{12} \text{Al}_{12} \text{Si}_{12} \text{O}_{48} \cdot 27\text{H}_2\text{O} \). The cation exchange and interaction/adsorption behaviours of this molecular sieve have been investigated with five metal ions, having valency states +1, +2 and +4, and two organic reagents; Chrome Azurol S and Eriochrome Black T. Of the two reagents one contains sulphur and chlorine and other sulphur and nitrogen. The experimental methods used in the investigations are:

1. Flame photometric determination of sodium(II) in synthetic zeolite 4Å and its cation exchanged derivatives for exchange studies. Carbon, hydrogen and nitrogen were estimated in interacted derivatives with the help of Elemental analyser. The determination of the percentage compositions of the cation exchanged derivatives helps to show the extent of cation exchange and also the changes brought about in the silicon aluminium ratio of synthetic zeolite 4Å as a result of cation
exchange. Percentages of carbon, hydrogen and nitrogen give an indication of the adsorption of organic reagents on 4A and other exchanged derivatives after interaction.

2. X-ray analysis of these samples helps to determine the change, if any, in the crystalline structure of 4A zeolite on cation exchange as well as adsorption with organic reagents.

3. The IR spectrophotometric data help in a qualitative evaluation of the structures of these zeolite derivatives.

4. The thermo chemical studies have been utilised in the determination of thermal stabilities of the zeolite derivatives. This thesis is divided into three chapters.

CHAPTER I

This chapter includes the basic informations on the class of materials known as inorganic cation exchangers and zeolites molecular sieves. This chapter deals with the introductory discussion
on molecular sieves, their structures, properties and classification as well as mechanisms of ion exchange. Applications of zeolites in the various fields are also mentioned. All relevant references on the subject, from the earliest available, are also included at the end of this chapter.

CHAPTER II

This chapter deals with the instrumental methods used in the present investigation from the point of view of their principles, techniques and special uses in zeolite studies. Procedures adopted for the preparation of cation exchanged and adsorbed derivatives have also been described.

All the prepared derivatives and the original synthetic zeolite 4A have been characterised by XRD, IR spectrophotometric and TG studies as well as by analysing them for their major constituents by quantitative methods.

All the cation exchanged and adsorbed/interacted forms were subjected to structural studies by X-ray diffraction method using copper radiation between 2θ values 5° and 50°, IR spectrophotometric studies between 4000 cm⁻¹
and 400 cm⁻¹, and Thermogravimetric studies upto 1000°C at 15°C/min. rate of heating to determine the thermal changes like dehydration, desorption and dehydroxylation as well as the thermal stability of these derivatives. The cation exchanged forms were also analysed for silicon and sodium (I) so as to determine the extent of cation exchange and changes in alumina silica ratio. Relevant references justifying the use of these techniques in zeolite studies have been included at the end of the chapter.

CHAPTER III

Chapter III is devoted to the discussion of results by the various established methods described in Chapter II. Data have been tabulated and plots reproduced for XRD, IR and TG studies. The results of these studies lead to the following conclusions.

1. The exchange of the major cation sodium (I), present in synthetic zeolite 4A, varies with the different cations and the degree of exchange follows the sequence in decreasing order, Fe(II), Ce(IV), Cu(II), V0(II) and Hg(I).
From this, it is seen that Hg(I) ion is exchanged to a minimum about 84% and Fe(II) to a maximum extent 99.7%. Zeolite 4A is, therefore a fairly good ion exchanger for most cations. This exchanger can be useful in removing a potentially toxic heavy ion like mercury (I). Some important transition metal ions like Copper (II), Iron (II), Cerium (IV) and Vanadyl (II), can be introduced in the zeolite 4A medium for using in catalytic processes. Coloured forms of zeolite 4A and its cation exchanged derivatives can be also prepared by interaction with Chrome Azurol S and Eriochrome Black T organic reagents which may be used as colouring agents in paint industry.

2. The XRD and IR studies have helped to characterise the prepared samples and indicate the variation in their properties. Thus Vanadyl (II), Cerium(IV) and Iron (II) exchange diminishes the crystallinity of zeolite 4A while most others do not affect this property of the exchanger. The X-ray data evaluated from the X-ray diffractograms have been tabulated and the plots reproduced.
The IR spectra of the various zeolite derivatives show, basically, the characteristics of hydrated alumino silicate structures. The absorption bands appearing in the IR spectra have been assigned to Si-O and Al-O bond vibrations in the region 400 cm\(^{-1}\) - 1200 cm\(^{-1}\) and free OH, hydrogen bonded OH and usual bending vibration of water at 3700 cm\(^{-1}\) - 3400 cm\(^{-1}\) and 1600 cm\(^{-1}\) respectively. IR spectra of these cation exchanged derivatives and interacted derivatives after heating to 800°C show negligible structural changes except loss of water and adsorbed species. All the IR spectral data and IR spectra have been tabulated and illustrated.

3. The thermal studies show expected steps for dehydration, dehydroxylation, desorption and decomposition. Dehydration, both in synthetic zeolite 4A and its cation exchanged derivatives, occur in many steps and can be classified as loss of physically adsorbed and chemically adsorbed water molecules and also low temperature and high temperature dehydration processes. In the case of adsorbed/interacted derivatives multi-step weight loss processes
occur due to dehydration, dehydroxylation, desorption and decomposition of the adsorbates, and the various interacted species. The thermal processes and other derivatives which were initially coloured lead to change of colours in the case of those cation-exchanged.

4. The analytical data for mainly Sodium (I) and Silicon (IV), reported as percentages of Sodium (I) and Silicon (IV) help to establish the composition of zeolite 4A and the other derivatives prepared. The cation exchange is due to cation hydrolysis.

The discussions have been based on earlier work on similar types of materials which are quoted at the end of the chapter.

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