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Impact of zeolitic water content on exchange of calcium ions

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Abstract

4A and P zeolites were thermally treated to dehydrate them to different extents. The residual water content and calcium exchange capacity (CEC) values of the treated zeolites were evaluated. The study revealed that the CEC of the zeolites depended upon the zeolitic water level. Anhydrous zeolites are devoid of exchange capacity. Mixed zeolites demonstrated mineralisation effect and an additional peak in the thermal studies. © 1997 Elsevier Science B.V.

Keywords: Zeolites; Calcium; Thermal

1. Introduction

Zeolites are three-dimensional networks of (Si, Al) and O_4 tetrahedra-linked by sharing of oxygen atoms into rings and cages. The overall negative charge of the anion is balanced by cations that are located in the cavities in the network. Zeolites have pore structures with interconnecting channels which are large enough for ions and small molecules such as water to pass freely without disrupting the network [1,2]. Two types of zeolites, namely, 4A [with structure $Na_{12}(AlO_2)_{12}$ $(SiO_2)_{12}$. $27H_2O$] and P [with structure $Na_6(AlO_2)_6.(SiO_2)_6.15H_2O$] have been shown preference in the detergent industries for use as builders. The extent of structural water present in the zeolite changes with the nature of the zeolite and the thermal pre-history of the product. The structural zeolitic water is generally conceived of as a 'pool' or 'well' inside the cage. Hardness ions of water are present as hydrated sheaths. Hence, it was felt that the zeolitic pool of water will have a definitive role in the exchange capacities. The current investigation examines the same with Ca^{2+} ions as a typical probe.

2. Materials and methods

2.1. Materials

Three different commercial samples of 4A and P zeolites were obtained for this study. Two of them were found to be pure samples (by XRD) and coded as I and II whereas the third was a mixed zeolite coded as III.

2.2. Methods

Commercial zeolite samples of 4A and P were dried and calcined at different temperatures in the range of 100–900°C while monitoring the weight loss. TGA

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and DTGA of the samples were carried out to obtain the water content and thermal behaviour.

The samples prepared at different temperatures were subjected to XRD studies with a Siemens crystalloflex diffractometer using nickel-filtered CuK_α radiation.

Calcium exchange measurements were made by the EDTA titration using Eriochrome Black-T as the indictor [3]. The CEC values were expressed on an anhydrous basis.

To quantify the presence of the mixed zeolitic phase, synthetic mixtures of 4A/P were prepared and subjected to XRD studies. The XRD technique was employed to substantiate the role of the mineralisation effect with mixed zeolites.

3. Result and discussion

3.1. Nature of commercial zeolites

The XRD patterns of samples of 4A and P are presented in Fig. 1. It is clear from Fig. 1(a) that P zeolite has characteristic prominent fingerprints at 12.4 and 21.8°(2θ) and 4A has prominent fingerprints at 7.2, 10.1, 12.4, 21.6, 24.0, 27.0 and 29.9°(2θ).

It is easy to identify the nature of the zeolitic builder by making a cursory examination of the peaks at 2θ: 12.4 and 7.2 and their relative intensities.

Some commercial samples contained mixed phases of zeolites (4A and P). This is demonstrated in Fig. 1(c). (Fig. 1(d) is for 1:1 mixed blend of the zeolites).

3.2. Zeolitic water

The amount of zeolitic water present is dictated by the type (nature) of zeolite and the manufacturing conditions. Thus, for 4A zeolite, the theoretical water content should be 22%. TGA of sample II gave ~21% and the loss on ignition (LOI) studies showed 22%. Hence the match was good.

For P zeolite the LOI ranges between 16.2 to 21.4% normally. This is indeed dictated by the levels of Al and Si. Two different P zeolite samples were examined. One of them showed 19% by TGA as well as LOI studies (Fig. 2).The TGA of pure and mixed zeolite P are presented in Fig. 2. Similar patterns were noted with pure and mixed zeolite 4A. An examination of Fig. 2 revealed the possibility of identifying mixed zeolite phases by this thermal technique.

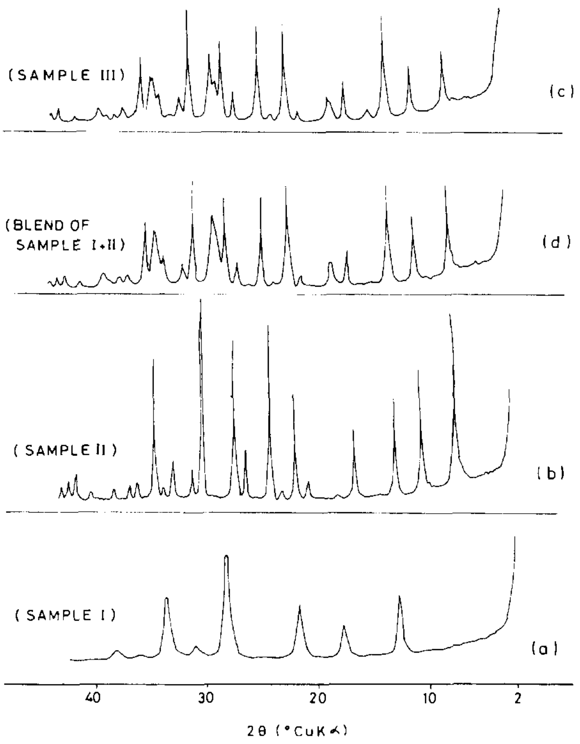

Fig. 1. XRD patterns of commercial zeolites:(a) Sample I–zeolite P(b) Sample II–zeolite 4A(c) Sample III–(mixed zeolite)(d) Blend of Samples I and II (50:50 w/w)

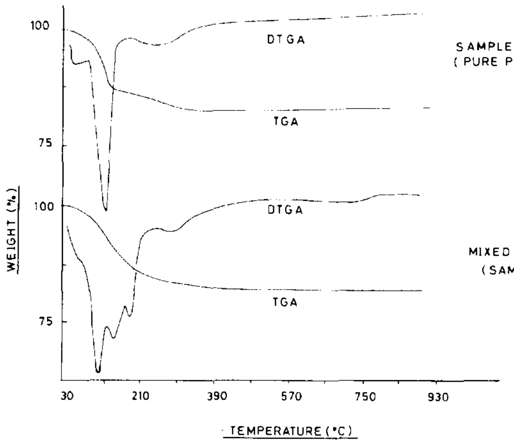

Fig. 2. TGA and DTGA of pure and mixed zeolite P

3.3. Dehydration

Upon dehydration, water is lost from the pool of the network to different extents. The loss of weight on heating increased with temperature. As the loss of weight at any particular temperature is known, the water still present in the sample at that temperature is obtained by the difference.

3.4. Exchange capacity

The water present in the original sample, and the water still present after the drying step are known. The CEC is first arrived at experimentally as the number of mg of $CaCO_3$ per g of zeolite. By dividing this CEC value by (100-% water content)/100, the CEC values on an anhydrous basis were obtained. These are presented in Figs. 3 and 4 A closer examination of these figures reveals:

1. Pure 4A and pure P zeolites show a similar trend (in the CEC dependence on temperature), P zeolite being marginally superior throughout the temperature range studied.
2. Zeolite P with 4A impurity has shown marginally superior CEC values in the low temperature domain (to even pure 4A and pure P).
3. CEC is dictated by the zeolitic water content.
4. Anhydrous zeolites have no building potential.
5. Powders dried at lower temperature have higher CEC values.

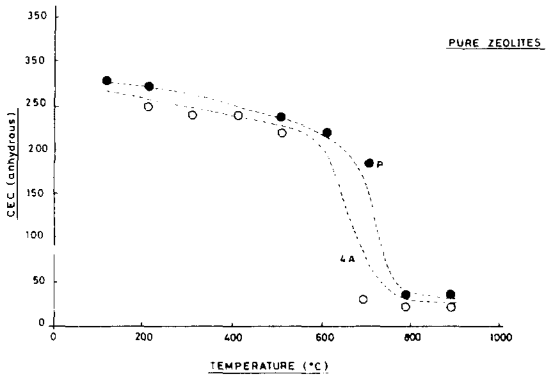

Fig. 3. Dependence of CEC on the drying temperature of pure zeolites

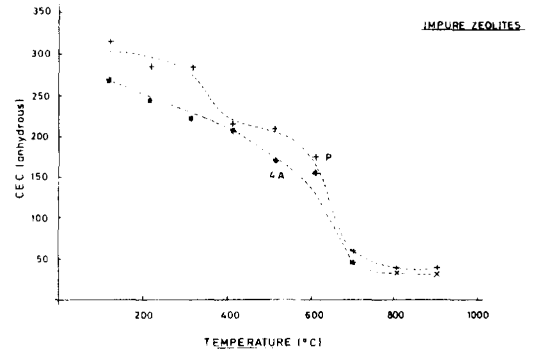

Fig. 4. Dependence of CEC on the drying temperature of impure zeolites

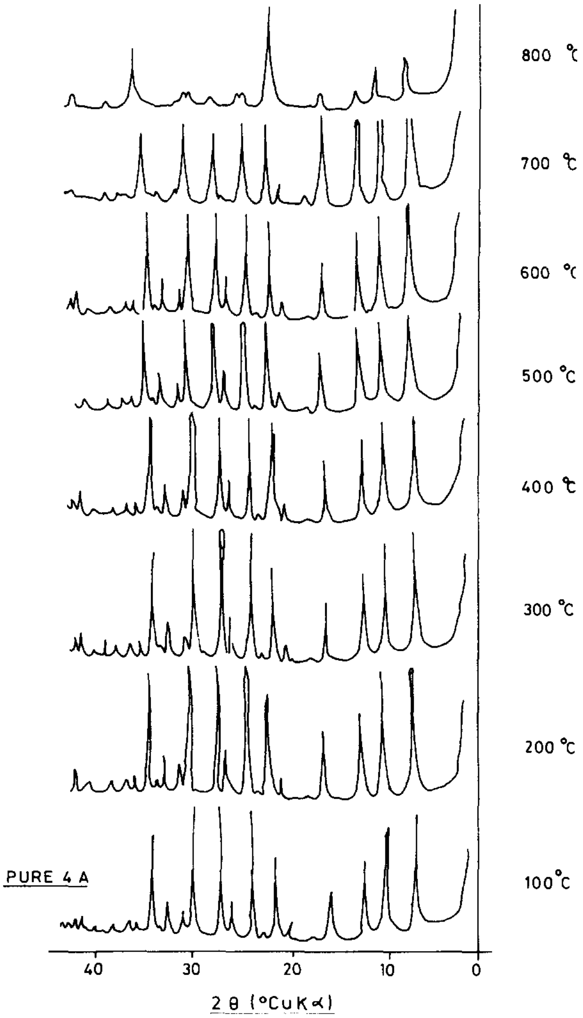

Fig. 5. XRD patterns of pure 4A heated to different temperatures.

3.5. Mineralisation effect

The presence of the impurity phase influences the thermal behaviour of the pure component. This is well known in high temperature clay chemistry and this phenomenon is generally referred to as 'mineralisation effect.' The XRD patterns of pure and mixed 4A and P samples were examined for establishing this effect. Results obtained with 4A are presented in Figs. 5 and 6. Similar observations were made with zeolite P.

It is evident from these figures that:

1. Mixed zeolites collapse at a lower temperature than the pure sample.
2. P has a tapotactic transition at around 350°C and gets converted into a different stable crystalline form of zeolite.

3.6. Structure collapse and CEC

1. In the case of pure zeolites, the crystallinity is retained even at higher temperatures. For instance, the crystallinity is $>$ 90% even at 800°C, whereas in the case of impure 4A, the crystallinity dropped to about 90% at ~500°C. Around 650°C, the peak corresponding to 4A fingerprints in the lower 2θ range (2–20°), disappeared.
2. The crystallinity values of pure 4A samples treated at 800 and 850°C were 90 and ~10% respectively. The CES's of the above-treated samples were ~25 mg/g of 4A. This finding indicates that the CEC reaches a minimum value prior to the collapse of the structure.
3. In the case of zeolite P, though a tapotactic phase transition had occurred at ~350°C, the CEC values did not show any abrupt variation. This seems to suggest that the cubic or tetragonal types of zeolite P should not have any influence on the CEC.

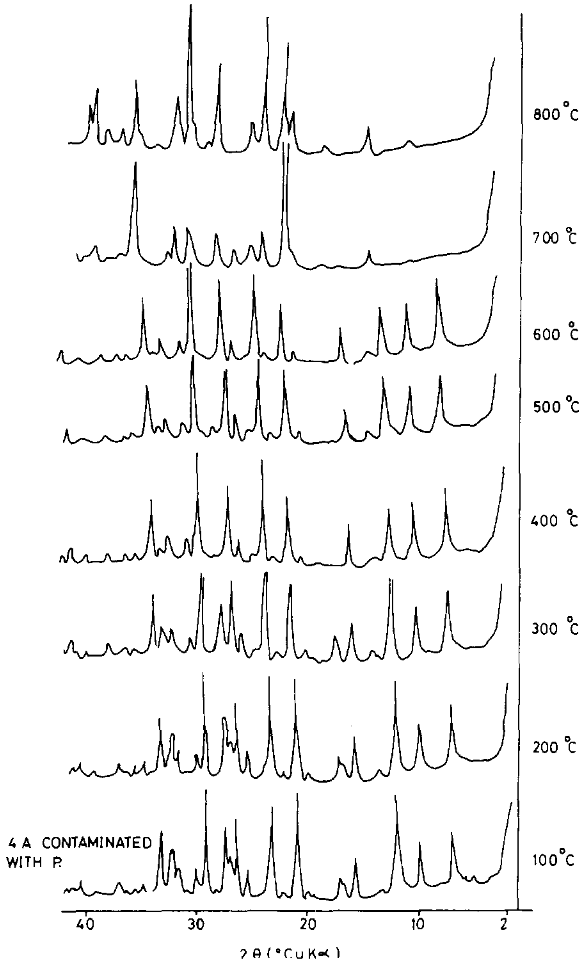

Fig. 6. XRD patterns of impure 4A (contaminated with P) heated to different temperatures.

References

[1] N.H. Ray, Inorganic Polymers, Academic Press (1978),128.
[2] D.W. Breck, Zeolite Molecular Sieves: Structure, Chemistry and Use, John Wiley & Sons (1974).
[3] A.I. Vogel, A Text Book of Quantitative Analysis, including Elementary Instrumental Methods of Analysis, ELBS and Longman (1969), 436.