Thermochimica Acta, 132 (1988) 127–131
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

STANDARDIZATION OF TMA (DILATOMETRY) FOR APPLICATION OF THE STUDY OF SYNTHETIC ZEOLITES

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(Received 17 December 1987)

ABSTRACT

Standardization of experimental parameters for the TMA (dilatometry) of powdered synthetic zeolites has been accomplished. Effects of variable heating rate, probe tray loading and sample type are shown to be of only minor consequence. The use of pelletized samples shows that direct examination of aggregated forms of zeolites, used for their catalytic and molecular sieving properties, is facile by this technique.

INTRODUCTION

Changes in volume with temperature for metals, glasses and ceramics have long been studied using dilatometers. The traditional dilatometer has been supplemented by the thermomechanical analyser which can measure changes in sample length under negligible load (thermodilatometry) or at constant load (TMA) as the temperature is altered [1]. The technique of thermomechanical analysis measures dimensional properties under load or no load by observing the extent of penetration with changes in temperature, and useful information on mechanical features of materials, e.g. coefficients of expansion, can be obtained [2].

Zeolites often undergo changes in unit cell dimensions during dehydration which usually results in shrinkage of the unit cell. The deformations have been attributed to the redistribution of the cations, and remaining water molecules, from their original positions in the hydrated form to new positions in the dehydrated form [3]. These processes can be studied by TMA in its penetration mode [4,5].

These earlier studies made no attempt to determine the optimal operating conditions. This work examines the effect of changes in parameters, heating rate, probe weight loading and sample form for several synthetic zeolites.

0040-6031/88/$03.50

EXPERIMENTAL

The synthetic zeolites studied were A, X and Y supplied as powders in the particle size range 1–5 μ by Laporte Inorganics (Widnes, U.K.). In some experiments the zeolites were used as a packed bed inside a specially constructed glass holder in which the probe from a Dupont 941 thermomechanical analyser could be allowed to rest on top of the bed. The analyser was connected to a Dupont 900 thermal analyser module in the normal way. In other experiments the sample was in the form of a cylindrical pellet of zeolite. This pellet was produced using a stainless steel pellet press with a pressure shaft of internal diameter 3.5 mm. By using the same amount of zeolite powder a pellet of 5 mm length was produced. The pellet was formed without heating, by tightening the press in a hand vice. Blank runs showed that features observed in the TMA were not due to changes in the glass holder.

RESULTS

Effect of heating rate

Packed beds of A, X and Y were examined measuring their expansion and contractions (probe displacement) at constant sample size and probe weight loading whilst varying the heating rates. The results obtained are shown in Figs. 1–3.

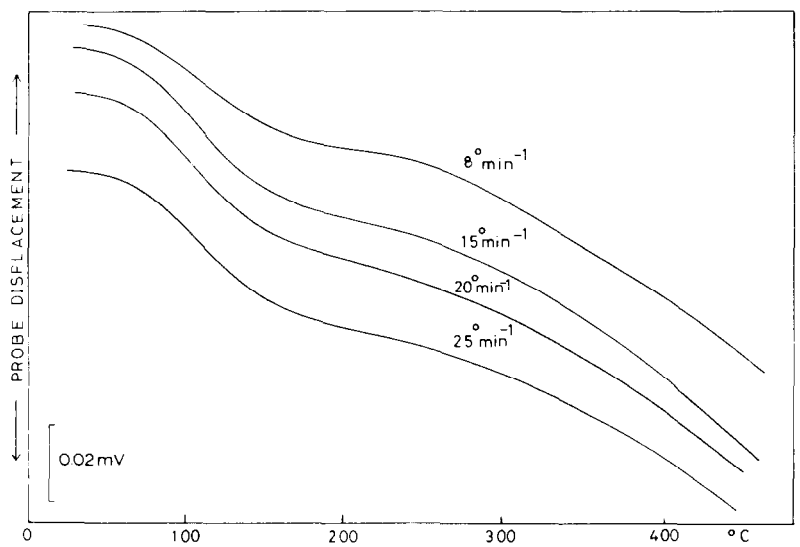

Fig. 1. Effect of heating rate on TMA curve for NaA zeolite (sample height, 5.0 mm; tray loading, 50 mg).

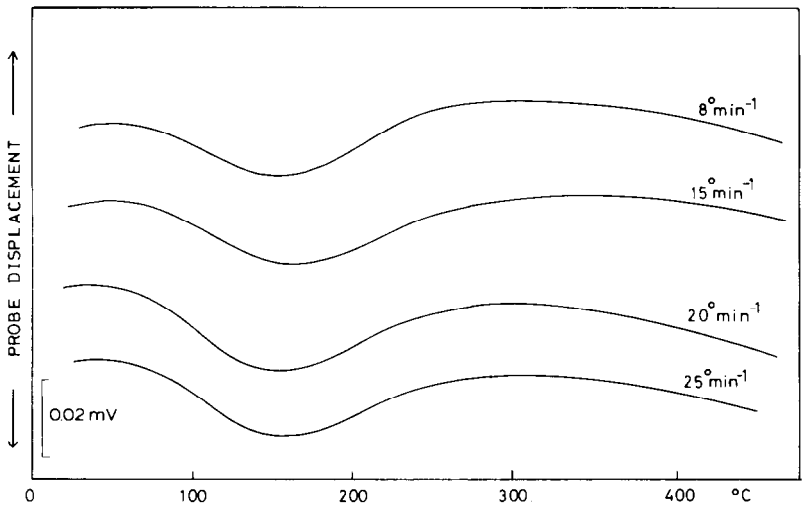

Fig. 2. Effect of heating rate on TMA curve for NaY zeolite (sample height, 50 mm; tray loading, 100 mg).

Effect of loading on the probe tray

Similar experiments to those described above were performed holding sample size and heating rates constant whilst varying the load on the probe by introducing weights to the tray on top of the probe. The TMA traces recorded are shown in Fig. 4 (only those for A are shown).

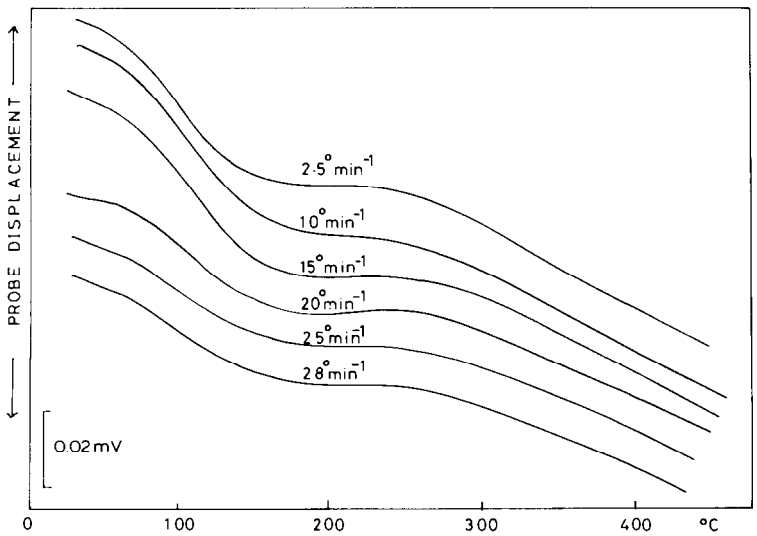

Fig. 3. Effect of heating rate on TMA curve for NaX zeolite (sample height, 5.0 mm; tray loading, 50 mg).

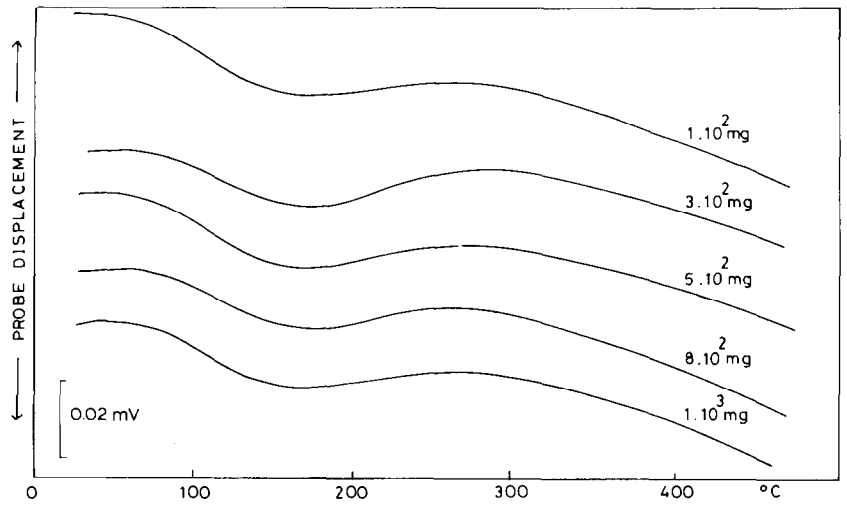

Fig. 4. Effect of tray loading on TMA curve for NaA zeolite (sample height, 5.0 mm; heating rate, 10 °C min^{-1}).

Use of zeolite pellets

Pelletized zeolite Y was examined under conditions appropriate for comparison with bad samples. Typical results are shown in Fig. 5.

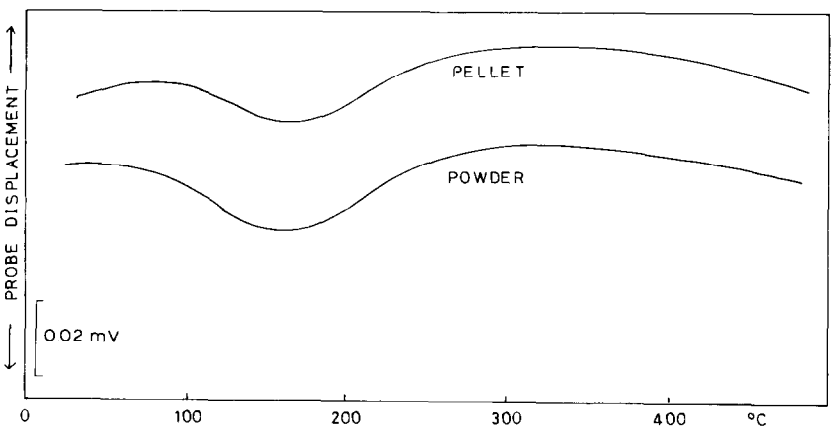

Fig. 5. Effect of sample preparation on TMA curve for NaY zeolite (sample height, 5.0 mm; tray loading, 50 mg; heating rate, 10 °C min^{-1}).

DISCUSSION

It can be seen from Figs. 1–3 that changes in heating rate had only a minimal effect on the form of the TMA curves, certainly in the range 2.5–20 °C min^{-1}, for the synthetic zeolites A, X and Y. Perhaps it could be argued that the lower heating rates clarify features, but this was not as clear as it is with DTA, TGA and DSC techniques, where it is well known that peak shapes and maxima vary with heating rate.

Similarly the effect of a tenfold increase in tray loading (100–1000 mg) had no discernible consequences (Fig. 4).

Finally, the traces observed for NaY pellets were identical to a powder bed of the same zeolite (Fig. 5). This last observation is encouraging because it suggests that pelletized zeolites can be directly examined by TMA. As this is the form in which these materials are used (catalysts, drying agents and molecular sieves) this adds to the utility of the TMA technique.

ACKNOWLEDGEMENT

Laporte Inorganics are thanked for the gift of zeolite samples.

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