

## Pore Opening of a Small-port Mordenite by Air-calcination

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Depending on the calcination procedure, the HM (M = mordenite) forms derived from small-port  $\text{NH}_4\text{M}$  can be of the large-port or small-port type, thus ruling out the hypothesis of pore blocking by cations.

According to X-ray diffraction studies,<sup>1</sup> mordenite should possess an open structure with a pore diameter of about 0.7 nm. However except for the so-called large-port mordenite (L.P.M.) first synthesised by Sand<sup>2,3</sup> most other samples present sorptive properties consistent with a pore diameter of 0.42 nm only<sup>4,5</sup> (small-port mordenite: S.P.M.). It is well established that S.P.M. can acquire some L.P.M. properties by acid leaching under severe conditions;<sup>3,6,7</sup> two different mechanisms have been proposed for this transformation: (i) during acid attack amorphous material is extracted out of the channels,<sup>3,8</sup> or (ii) the cations localised in the pores are removed by acid exchange.<sup>3,8</sup>

The latter mechanism has also been proposed by other workers<sup>9,10</sup> on the basis of studies on  $\text{NH}_4\text{NaM}$  forms. A third hypothesis has been suggested by Meier:<sup>6</sup> the effective pore diameter of S.P.M. is reduced to 0.42 nm by stacking faults. Streaks in the electron diffraction patterns of S.P.M. have already been reported by several authors:<sup>11-13</sup> they can be

interpreted in terms of glide vector defects (0, 0, 1/2), *i.e.*, parallel to the main channels (0, 0, 1). Therefore such defects cannot reduce the effective aperture of these channels.

We report here that S.P.M. can be converted into L.P.M. by controlled calcination of the  $\text{NH}_4$  form. We used as starting materials small-port synthetic NaM from 'La Grande Paroisse' (Alite 150) and large-port synthetic NaM from 'Norton Co' (Zeolon 100 Na). The  $\text{NH}_4\text{M}$  forms were prepared in the conventional manner by exchanging ( $\times 3$ ) the NaM forms in 2 M aqueous  $\text{NH}_4\text{NO}_3$  at 100 °C during 4 h, to provide exchange levels of >99.4%.

For all the experiments the L.P. or S.P.  $\text{NH}_4\text{M}$  powder (2 g) was placed in a quartz reaction vessel 30 mm in diameter between two plugs of quartz wool, with a gas stream passing through the zeolite bed. Two different procedures were used: (i) dry air; a low heating rate of 125  $\text{K h}^{-1}$  with a 1 h step at 523 K, and a high flow rate of dry air of 30  $\text{l h}^{-1}$  ( $\text{g solid}^{-1}$ ); (ii) deep bed-like; a high heating rate of 250  $\text{K h}^{-1}$ , and a low flow rate of dry air of 1  $\text{l h}^{-1}$  ( $\text{g solid}^{-1}$ ).

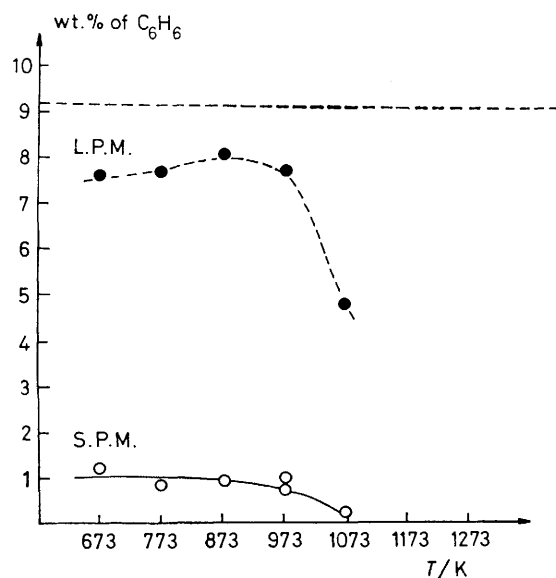


Figure 1. Adsorption of benzene by L.P.M. and S.P.M. Procedure (i), dry air. The horizontal dashed line represents the theoretical adsorption capacity of the HM form.

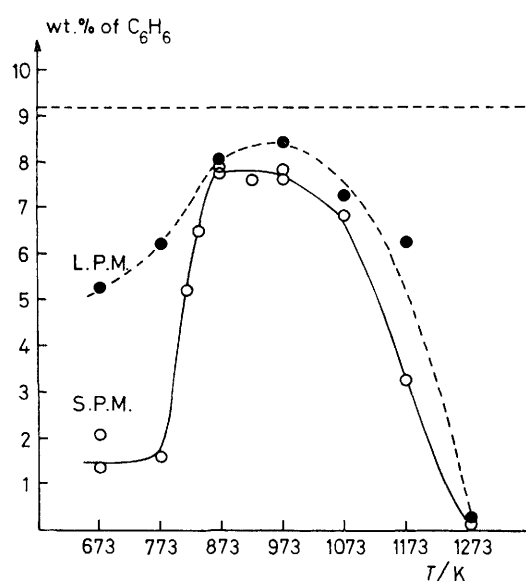


Figure 2. Adsorption of benzene by L.P.M. and S.P.M. Procedure (ii), deep bed-like. The horizontal dashed line represents the theoretical adsorption capacity of the HM form.

The samples were characterised by *X*-ray diffraction, electron diffraction, i.r. spectroscopy, measurement of the Al *X*-ray fluorescence  $K_{\beta}$  line shift, B.E.T. surface area determinations, and chemisorption properties with several hydrocarbons.

In this paper we present only the benzene adsorption results, at 303 K, and with  $p/p^s = 0.25$  (where  $p$  and  $p^s$  are the adsorption and saturated vapour pressures, respectively).

The dry air results (Figure 1) show that S.P.M. samples adsorb about 1 wt % of benzene irrespective of the calcination temperature, and the adsorption capacities do not change even when all the ammonia has evolved, *i.e.*, above 773 K. In contrast the values obtained for L.P.M. are always high even when the crystal lattice begins to collapse above 973 K.

The deep bed-like results (Figure 2) show that in the temperature range 773–873 K a sudden deblocking of the porosity of S.P.M. occurs and at higher temperatures the adsorption capacities of both L.P.M. and S.P.M. samples are very similar. The decrease observed above 1073 K is related to a loss of crystallinity.

The results for calcination in dry air clearly demonstrate that small-pore HM forms do exist, and thus the cations are unlikely to be the cause of the blocking of the channels. On the other hand S.P.M., when treated under deep bed-like conditions, can adsorb molecules as large as benzene; such an adsorption is typical of L.P.M. This is another way in which the porosity of S.P.M. may be opened, without any acid leaching. We cannot choose definitively between the two other hypotheses but we suggest that the deblocking of the channels during calcination under deep bed-like conditions is caused by the extraction of a large proportion of the aluminium atoms from the framework by the action of water. As a result of this, holes are likely to occur in the structure creating a

second micropore system. The extraction of aluminium in this way is supported by precise measurements of the Al *X*-ray fluorescence  $K_{\beta}$  line shift, details of which will be published elsewhere.<sup>14</sup>

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