

## Unusual Type of Adsorption Isotherm describing Capillary Condensation without Hysteresis

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Adsorption isotherms of cyclopentane and nitrogen on a new porous crystalline aluminosilicate from the family MCM-41 are characterized by the volume filling of channels by capillary condensation without hysteresis, which commences in the region prior to the lower closure point at the hysteresis loop.

Recently, new porous inorganic crystals have been synthesized with uniform open pores of larger than 1 nm.<sup>1,2</sup> Because of their unique texture, they have great potential as model adsorbents for fundamental adsorption studies.<sup>3</sup> The present study describes unusual adsorption properties of a new porous

crystalline aluminosilicate first reported in 1992.<sup>4</sup> It belongs to the family of materials, designated as MCM-41, characterized by a regular hexagonal array of uniform parallel channels, the dimensions of which can be tailored in the range of 1.4 to 10 nm or more.

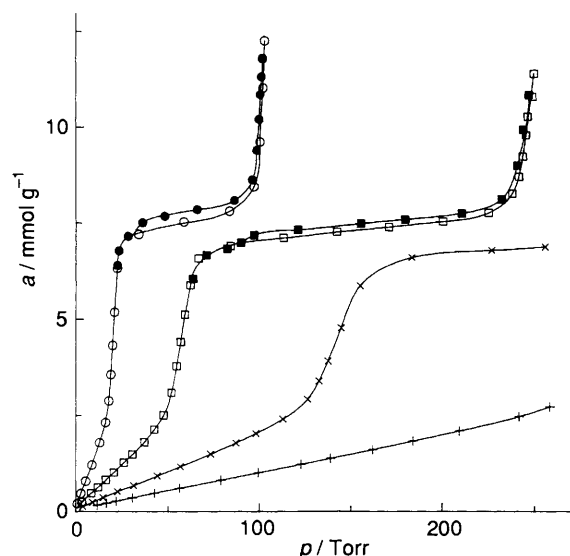


Fig. 1 Adsorption isotherms of cyclopentane vapour on MCM-41 at 273 K (O), 293 K (□), 313 K (×) and 333 K (+) (1 Torr = 133.3 Pa)

The material studied here was synthesized according to the modified example 10 of the Mobil Oil patent.<sup>5</sup> A solution of sodium aluminate, prepared from 1.56 g  $\text{Al}(\text{OH})_3$  (98%, Baker) and 0.95 g NaOH (99%, Merck) in 1.1 g of demineralized water was mixed with 46.3 g of 20% aqueous tetraethylammonium (TEA) hydroxide solution (Merck), and then added to 46.3 g of colloidal silica (40%  $\text{SiO}_2$ , Ludox HS-40, DuPont). After having stirred the mixture vigorously for 20 min, the gel was mixed with 71.15 g of hexadecyltrimethylammonium (HDTMA) hydroxide solution (18%) prepared from a hexadecyltrimethylammonium bromide solution by a hydroxide-for-bromide exchange using AgOH. The mixture was heated at 375 K for 7 days. The resulting solid product was washed with demineralized water and then calcined in air at 813 K for 20 h. The final reaction mixture had the following composition in terms of mol per mol  $\text{Al}_2\text{O}_3$ : 1.1 mol  $\text{Na}_2\text{O}$ , 3.25 mol  $(\text{TEA})_2\text{O}$ , 2.125 mol  $(\text{HDTMA})_2\text{O}$ , 25.66 mol  $\text{SiO}_2$ , 1207 mol  $\text{H}_2\text{O}$ .

The adsorption isotherms of nitrogen and cyclopentane were measured with an Accusorb 2100 E instrument by the procedure described in ref. 6.

Texture parameters of the material studied were determined from the adsorption isotherm of nitrogen at 77.2 K, the shape of which was similar to that published in ref. 4. The surface area  $S_{\text{BET}}$ , the cumulative surface area and the volume of mesopores, calculated from the desorption branch of the hysteresis loop,<sup>7</sup> were 1072  $\text{m}^2 \text{g}^{-1}$ , 78  $\text{m}^2 \text{g}^{-1}$ , and 0.658  $\text{cm}^3 \text{g}^{-1}$ , respectively. The volume of micropores of 0.724  $\text{cm}^3 \text{g}^{-1}$  was determined from the corrected adsorbed amount in the lower closure point of the hysteresis loop according to eqn. (2) from ref. 6.

Fig. 1 shows adsorption isotherms of cyclopentane vapour at four temperatures. These isotherms are highly unusual as they exhibit two regions in their reversible parts. While the adsorption increases only gradually with pressure in the first region, its rise in the second one is much steeper. The hysteresis loop is characterized by a steep part in the pressure range close to the saturation pressure. Obviously, it can be assigned to the capillary condensation in mesopores of the aggregates of crystals.

The unusual shape of adsorption isotherms in the reversible part can be analysed by means of an  $\alpha_s$ -plot,<sup>8</sup>  $\alpha_s$  being the normalized adsorption on a standard nonporous adsorbent (placing  $\alpha_s = 1$  at  $p/p_s = 0.4$ ). It is an advantage of this method that the isotherm on the standard adsorbent is normalized by a

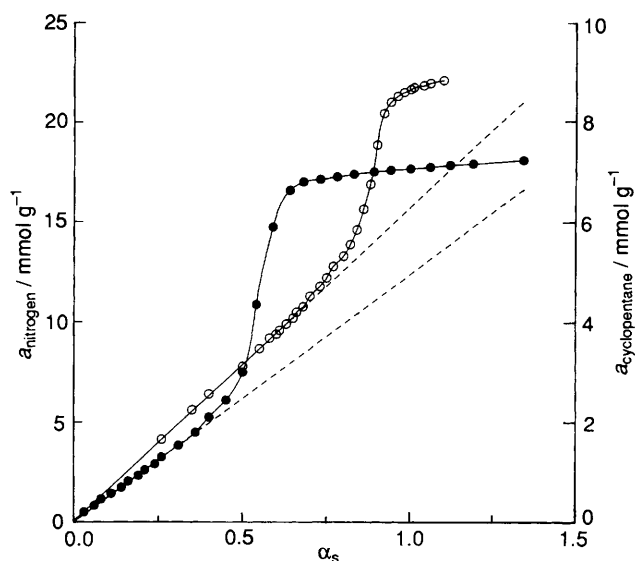


Fig. 2  $\alpha_s$ -Plots of cyclopentane (●) at 293 K and of nitrogen at 77 K (○)

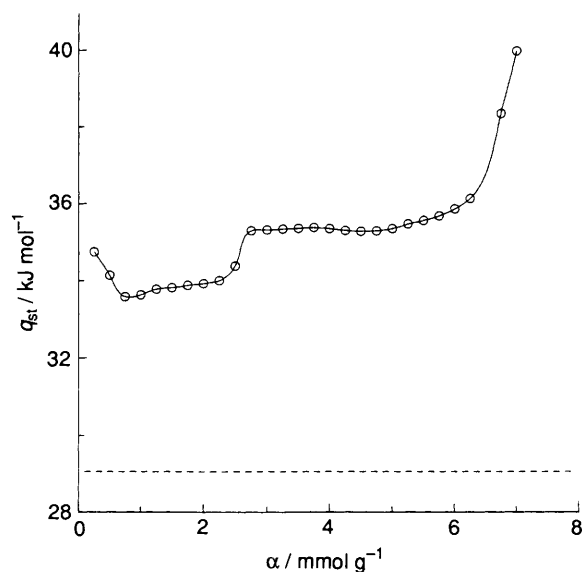


Fig. 3 Dependence of the isosteric heat of adsorption ( $q_{\text{st}}$ ) of cyclopentane on the amount adsorbed. The dashed line corresponds to the heat of condensation of cyclopentane.

factor corresponding approximately to the adsorption at the lower closure point of the hysteresis loop. The  $\alpha_s$ -plot of cyclopentane at 293 K (Fig. 2) shows an upward swing commencing at  $\alpha_s = 0.36$  ( $p/p_s = 0.14$ ). This phenomenon may be explained as capillary condensation without hysteresis.<sup>9</sup> It was described for amorphous solids, in which it occurred only in a small fraction of the pore system. In contrast to ref. 9, owing to the unique texture of our material (regular array of uniform channels with hexagonal cross-section, small surface area of mesopores), practically *only* the capillary condensation without hysteresis is responsible for the steep increase of the adsorption commencing at  $\alpha_s = 0.36$ .

The  $\alpha_s$ -plot of nitrogen gives a picture similar to that of cyclopentane (Fig. 2), *i.e.* it is also characterized by capillary condensation without hysteresis. For this material the Brunauer-Emmett-Teller (BET) surface area is physically meaningful, it may be used for an assessment of the size of

pores which are filled by this mechanism. Their radius, which can be calculated for the tubular model as  $2V/S$ , equals 1.46 nm. ( $V$  stands for the volume of micropores,  $S$  for the BET surface area minus the cumulative surface area of mesopores.)

Fig. 3 shows the dependence of the isosteric heat of adsorption of cyclopentane on the amount adsorbed. This dependence, which was calculated from adsorption isotherms (Fig. 1), provides further support for the occurrence of capillary condensation without hysteresis. The step change of isosteric heats at the adsorption of *ca.* 2.8 mmol g<sup>-1</sup> corresponds to the enhanced adsorbate-adsorbate interaction during the volume filling of micropores.

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