

Mesoporous M41S materials in capillary gas chromatography

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M-41S materials anchored to glass capillary columns via sol-gel techniques can be advantageously utilised for gas chromatographic separations.

Rapid advances in preparing mesoporous materials such as those of the M41S class (particularly MCM-41), pillared clays (PILCs) and analogues are due to their use as catalysts, especially in clean technology. However, MCMs have still to find practical application in this field, and it is possible they may instead be useful in others, such as separation technology. PILCs (pillared clays, which are micro/mesoporous) can separate inert gas mixtures and hydrocarbons,² which suggested using M41S solids in chromatographic separations, and in particular as stationary phases for gas-solid chromatography (GSC). Apart from benthone 34,³ and differently from packed columns (where zeolites have been in use for some time)⁴ other attempts to analyse liquid hydrocarbon mixtures by GSC on zeolites or expanded solids in general have failed, because strong sorption of individual components and/or their catalytic transformation due to intrinsic high acidity (at the relatively high temperatures required for elution) constitute limitations. Following successful use of mordenite in ion-exclusion chromatography,⁵ we have found that it is possible to coat GC

capillary columns with mesoporous silica-based MCM-41, which can separate organic molecules.

The MCM-41 used was prepared as in the original patent⁶ and gave the reported XRPD and BET N₂ (specific surface area = 995 m² g⁻¹). Fig. 1 shows both XRPD and an AFM image of the material. The latter shows that from toluene MCM-41 aggregates to form roughly platelet-shaped bundles of varying dimensions (typically 50–80 × 150–200 nm).

In a typical column preparation, a fused silica capillary (1 m long, 200 μm id; Composite Metal Services, UK) was modified with the silanizing agent, sulfanylpropyltrimethoxysilane [(MeO₃)Si(CH₂)₃SH, Aldrich] as follows. One end of the capillary was immersed in a vial containing 6 mol dm⁻³ HCl and the solution allowed to flow through under pressure for 3 h. The capillary was then washed with water and silanizing agent

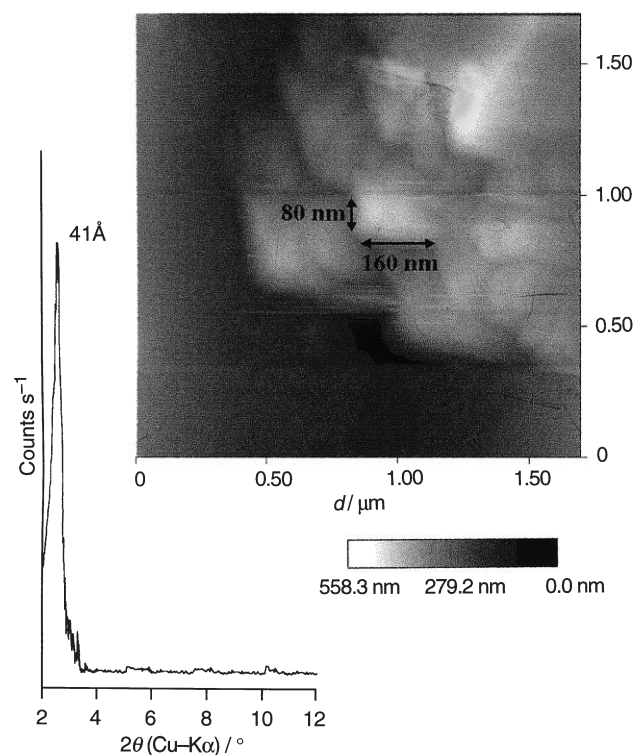


Fig. 1 XRPD of MCM-41 utilised and AFM image showing the MCM morphology [conditions: Digital Nanoscope III instrument, deposit from ambient toluene suspension onto muscovite mica (001), followed by heating at 200 °C for 3 h; tapping mode]

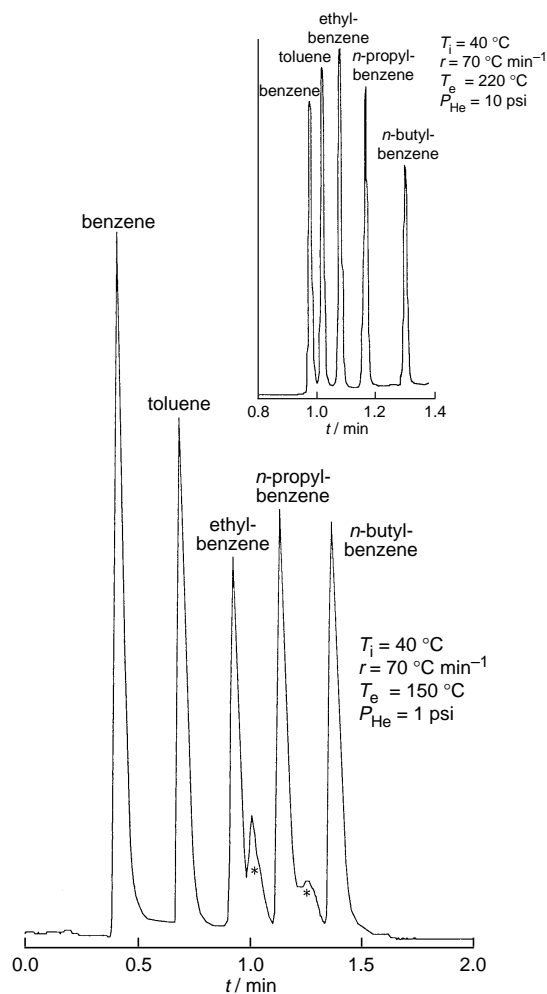


Fig. 2 GC separation of hydrocarbon mixture on the MCM-41 film capillary column. Inset shows separations performed on a HP-1 type (polydimethylsiloxane) column; conditions: $l = 25$ m, $id = 0.53$ mm. * = impurities.

by dipping one end of the tube, kept *ca.* 20 cm higher than the other end, into the reagent. The capillary was sealed using a sodium silicate solution and heated overnight (100 °C). After cooling, both ends of the capillary were cut, the solution decanted, and the capillary was dried, and then filled with a well shaken suspension of 0.5 g of the MCM-41 in dry toluene. The capillary was sealed and left to react at 60 °C overnight. After completion of the reaction, both ends of the capillary were cut and it was connected to a chromatographic delivery pump (Perkin Elmer, series 400 model) washed with hexane and PrⁱOH and dried under He.

Fig. 2 shows a typical separation of a light hydrocarbon mixture (1 : 1 : 1 : 1): separation is achieved at much lower temperatures, with much shorter retention times and on shorter

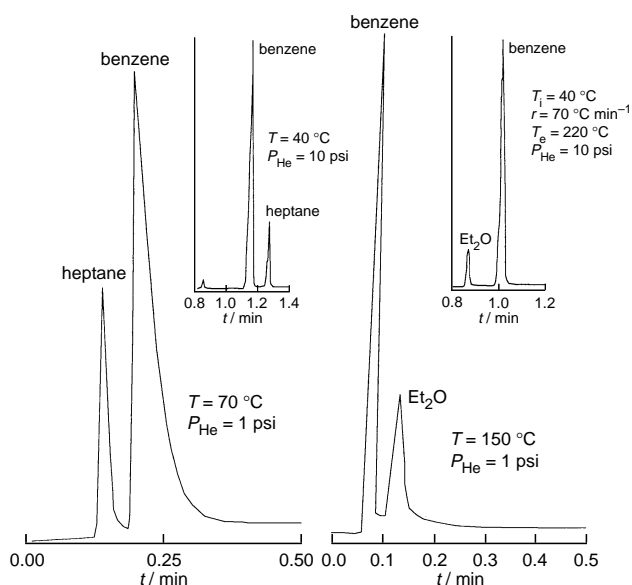


Fig. 3 GC separation of benzene–diethyl ether and benzene–heptane on the MCM-41 film capillary column. Insets, standard GC on polydimethylsiloxane (conditions as in Fig. 2).

columns (1 m) rather than the 25–30 m of conventional capillary columns (inset). In control experiments, no separation was possible on capillaries which were identical, except for the MCM-41 attachment step. That separation indeed occurs within the MCM-41 cavities and by a mechanism depending on the proton affinities of the compounds, is neatly demonstrated in Fig. 3. For both benzene–diethyl ether and benzene–heptane mixtures there is inversion in elution order compared with standard GC on polydimethylsiloxane (insets). It is well known that oxygen-containing molecules are retained strongly on zeolites due to onium ion formation,⁷ as is also benzene (*via* arenium ion formation⁸). It appears this is also the case for M41S materials. The generality of the behaviour (whether other porous silicas can be used) and other anchoring agents and separations are under investigation and the acidity of anchored MCM-41 is being modulated by cation exchange in order to maximise peak symmetry and separation factors.

Footnote

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