Mesosilica Materials and Organic Pollutant Adsorption: Part A Removal From Air

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Mesosilica Materials and Organic Pollutant Adsorption: Part A Removal From Air.

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Abstract

This tutorial review focuses on the application of mesoporous silica materials, primarily MCM-41 and SBA-15, for the removal of organic pollutants in the vapour phase. After briefly providing an introduction into the types of mesosilica covered in this review article the information is presented on a topic by topic basis and covers mesosilica and its interaction with vapour phase organic pollutants under the general subject headings of (i) adorption isotherms and temperature programme desorption, (ii) dynamic adsorption experiments and (iii) gas separations.

1 Brief introduction to mesosilica adsorbents

A procedure for the preparation of low-density silica was reported in a patent filed by Chiola *et. al.* in 1971[1] which led to the synthesis of the first mesoporous silica material types. In 1990 Yanagisawa and colleagues[2] reported on the preparation of a microporous silica-based material through the interaction of alkyltrimethylammonium chloride and a layered polysilicate, Kanemite. The organic species was then removed by calcination, which resulted in three-dimensional SiO_2 networks. However, presumably because of the lack of characterisation data provided, the Yanagisawa results were largely ignored. Two years later

Beck *et. al.,*[3] at the Mobile Research and Development Corporation, reported the synthesis of a new family of ordered mesoporous silica materials through the use of a liquid crystal template. These materials had large pores (from 2 to 10 nm) and high surface areas (above 1000 m^2 g^{-1}) as a result of using a self-assembled molecular array of surfactants as the organic template rather than a single, solvated organic molecule or metal ion. The family of materials produced, collectively referred to as M41S, is classified according to the order of the pores. MCM-41, MCM-48 or MCM-50 possesses hexagonal, cubic or meso-lamellar phases, respectively, (where MCM stands for *Mobile Composition of Matter*: see Figure 1).

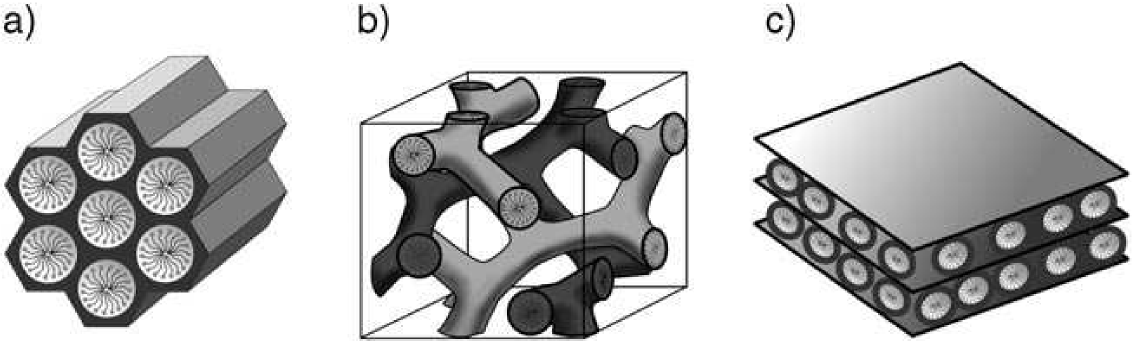

Figure 1: different structures of (a) MCM-41, (b) MCM-48 and (c) MCM-50[4]

In general mesosilica production involves the addition of a silicate source to an aqueous surfactant solution. Hydrolysis and condensation leads to a silica framework which builds around the surfactant micelles (see Figure 1a) and at this stage the materials are referred to as 'as-synthesised' mesosilica. Two mechanisms were originally presented[3] to describe mesosilica formation. The first mechanistic model described the addition of silicate to micelles formed using cetyltrimethylammonium bromide (CTAB); the silica polymerising around the previously formed micelles. The second model proposed that addition of silicate to an aqueous CTAB solution induced ordering of silicate-encased surfactant micelles simultaneously, that is micelle formation required silicate to be present. A schematic illustration of the formation mechanisms are given in Figure 2[4].

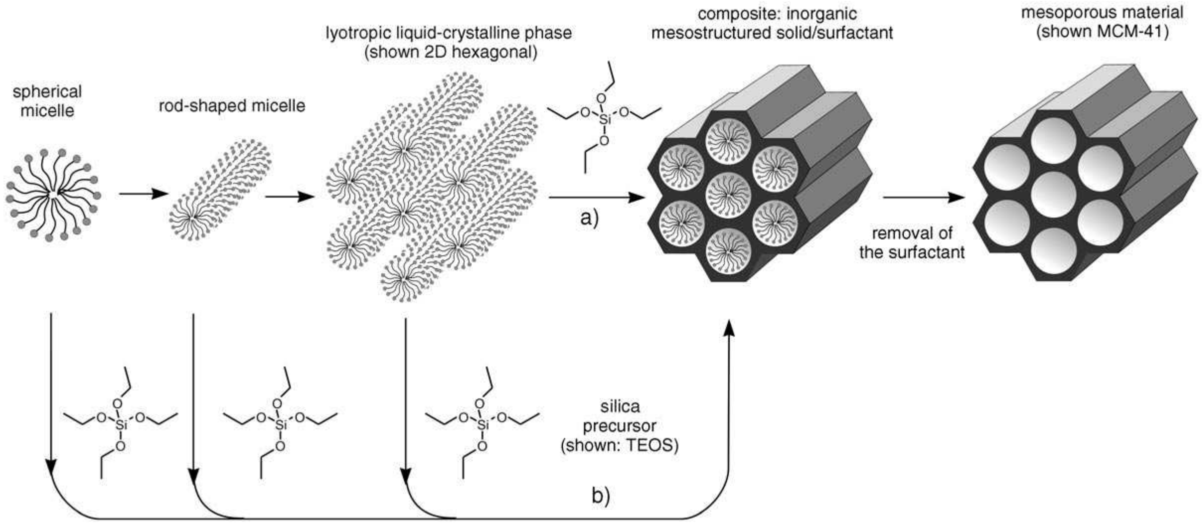

Figure 2: Schematic illustration of MCM-41 preparation by (a) the first proposed model and (b) the second proposed model[4]

After polymerisation the mesosilica becomes porous by removing the surfactant template by solvent extraction, calcination or microwave digestion. Although CTAB (which contains a C-16 hydrophobic tail) is arguably the most commonly used surfactant Beck[3], and other researchers, have used surfactants with smaller hydrophobic tails, (C-14, C-12, C-8) leading to the production of MCM-41 with smaller mesopores which correlate directly with the size of formed micelle; smaller micelles are created using surfactant cations, CTA^+ with smaller hydrophobic tails (see Figure 3).

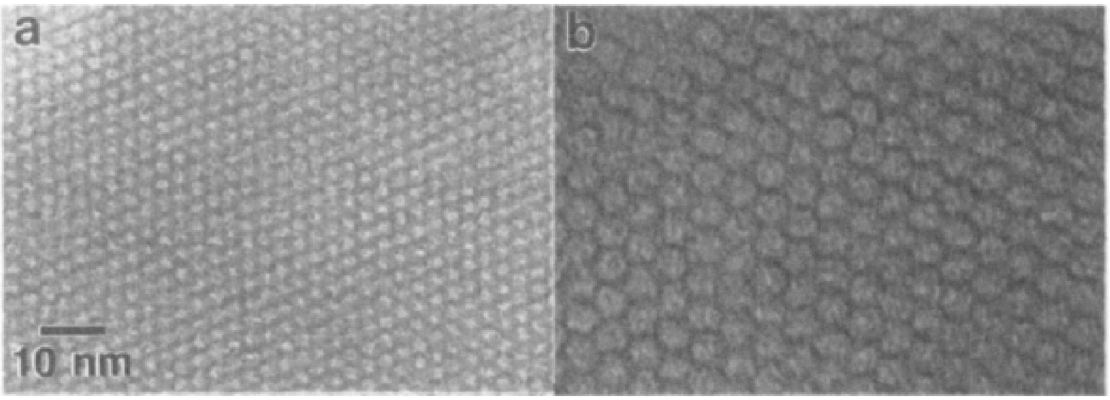

Figure 3: Transmission electron micrographs for MCM-41 indicating pore size for materials produced with (a) C-8 surfactant or (b) C-16 surfactant[3].

One year later[5] researchers described the original mechanistic models proposed[3] as insufficient when trying to establish a detailed understanding of mesosilica formation. It was recognised that mesosilica forms under conditions that would not normally support silica condensation (high pH, low silica and CTA^+ concentration) and that precipitation is observed immediately on addition of the silicate to the surfactant (C-8 to C-20) solution. Three factors were then presented as being crucial to the final mesosilica material formed: (i) multidentate binding of silicate oligomers, (ii) preferred polymerization of silicates at the surfactant-silicate interface and (iii) charge density matching across the interface.

In general MCM-41 is described as a mesoporous material which demonstrates long range ordering giving rise to mesoporous channels within the structure, MCM-48 has lower pore ordering but demonstrates periodicity in its macrostructure and MCM-50 is ordered in the solvent-surfactant phase but becomes unstable when the surfactant is removed. It should be emphasised that the silica framework is not crystalline but amorphous; in MCM-41 for example it is the mesopores which are arranged periodically within the structure. The pore regularity combine with high surface areas (1000 m^2 g^{-1}), large pore volumes and regular mesostructures to offer new opportunities as adsorption platforms with MCM-41 attracting most attention than the other family members as it is thermodynamically more stable and the easiest phase to synthesis[6].

The initial M41S studies led to demands for alternative mesoporous silica materials and in 1998[7] the research group led by Stucky at UC-Santa Barbara produced SBA-15; where SBA stands for *Santa Barbara Amorphous*. Like MCM-41, this material has earned much attention in the last decade due to its excellent thermal stability, variable pore size, and tailored particle morphology. The pore topology consists of a two dimensional mesoporous network formed by microporous walls and regularly spaced mesopores which form as a result of a liquid crystal micelle arrangement using amphiphilic triblock copolymers; poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (or PEO-PPO-PEO) as the organic structure directing agent template[5]. The micropore-mesopore network of SBA-15 (see Figure 4) material lowers diffusion limitations normally observed for adsorption applications of microporous zeolitic materials.

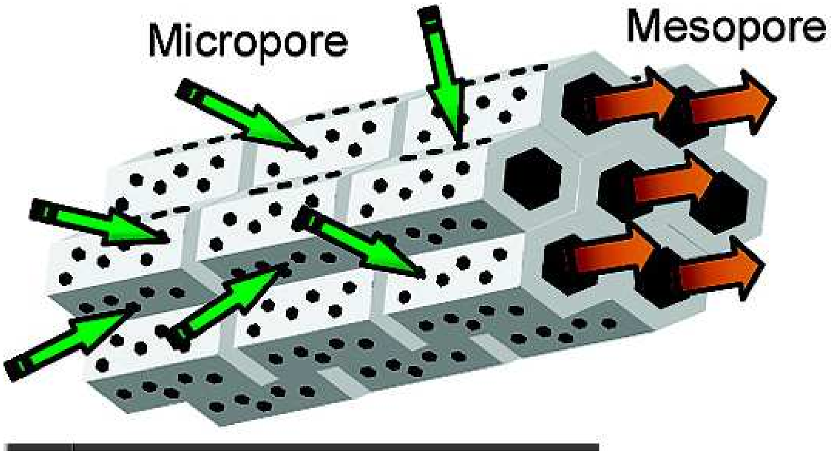

Figure 4: Schematic diagram of SBA-15 showing micropores in walls and mesoporous channels.[8]

2 General notes on the use of mesosilica to remove VOCs from air

To date, more than 9000 papers have been published on the synthesis and application of the M41S family of materials (see Figure 5). Most applications have focused on catalysis, but recently an expansion into other areas has led to material use in drug delivery, optical guides and low k dielectric layers in microelectronics. Environmental applications of mesosilica have permitted their use in a diverse range of applications from biosensors to optical devices. However, such applications will feature in other reviews and this article will focus solely on the application of mesosilica, primarily MCM-41 and SBA-15, for adsorption of organic pollutants from air. When used for this application, generally MCM-41 or SBA-15 are used as unmodified (> 75 % of published studies), calcined products (> 95% of published studies). Here, gaseous molecules will be physically adsorbed to the surface of the mesosilica materials by van der Waals forces (dipole-dipole interactions and London dispersion forces). The gas molecules can be introduced to the silica surface by passive or active sampling. In passive mode the mesosilica adsorbent is placed in the contaminated environment for an extended period of time (days) and the gaseous molecules diffuse to the surface of the adsorbent where they are physically adsorbed. In active mode, otherwise known as dynamic mode, a pump is used to force the contaminated air through an adsorbent bed, which is commonly held in a tube; sampling periods are for mins or hours depending on VOC concentration. Better performance is achieved by active (dynamic) sampling as there is more opportunity for the gaseous molecules to be ‘introduced’ to the silica surface.

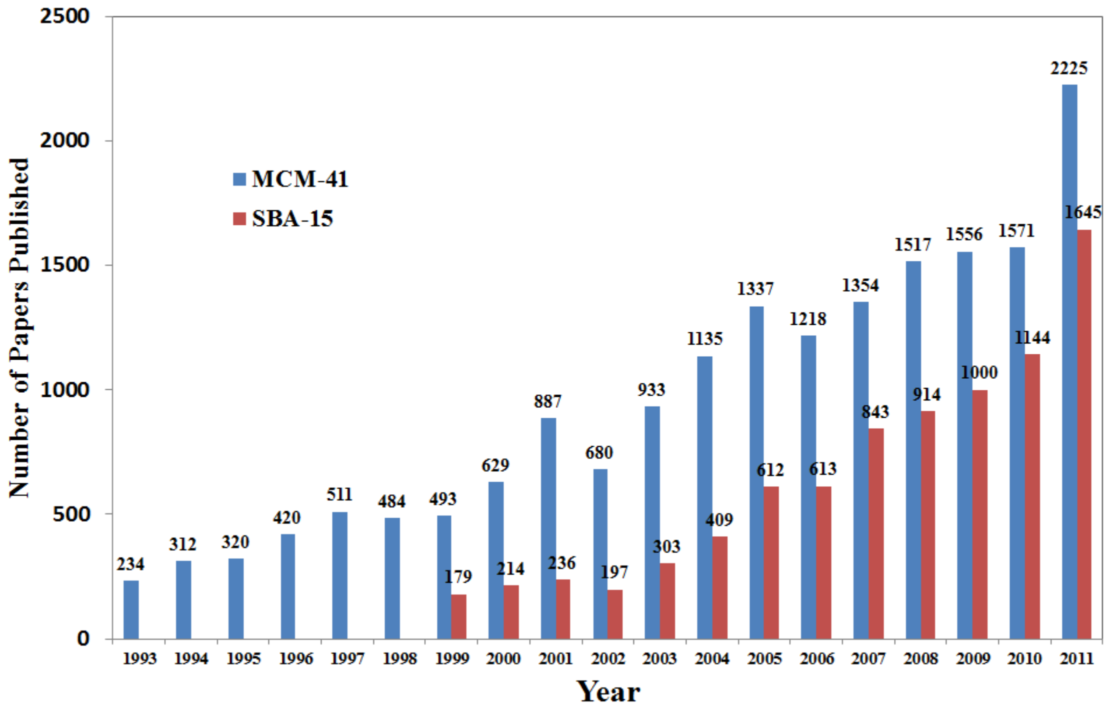

Figure 5: Number of published articles on the subject matter of MCM-41 or SBA-15 from 1993 – 2011.

In both passive and active sampling the adsorbent-adsorbate interactions are weak and so it is possible to remove the adsorbed VOCs from the surface by, for example, heating. This has prompted the use of derivatised mesosilica to provide active sites that can be used to permanently remove target VOCs from air. After derivatisation the adsorbent-adsorbate interaction is normally by chemisorption, where a strong chemical bond forms between the derivative and the gaseous molecule leading to the permanent removal of target pollutants from air. Surface modification is achieved by covalently bonding a functional group onto silanol sites by post-synthesis grafting (PSG)[9] or co-condensation[10] methods. The more commonly used PSG process (see schematic illustration in Figure 6) involves reacting an organosilane reagent with the silica surface, normally in an inert organic solvent (e.g. toluene) under reflux conditions and in the presence of silane coupling agents, such as alkoxysilanes or chlorosilanes[11,12]. This reaction must be performed under wet conditions as increasing the density of hydroxyl groups on the silica surface leads to self-condensation of the organosilane species away from the pore walls[13].

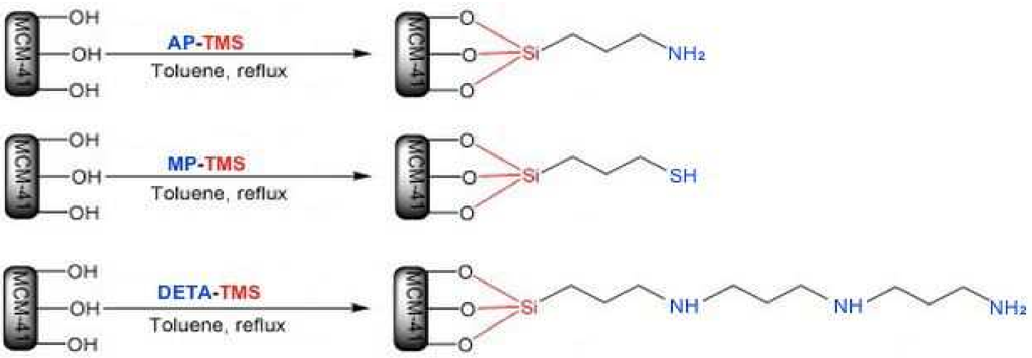

Figure 6: Structure directing agents used to functionalise silica surfaces

2.1 Adsorption capacities, surface properties and adsorption mechanisms by examination of VOC adsorption isotherms or temperature programme desorption.

Adsorption isotherms are used to measure the amount of gas adsorbed by a material at constant temperature as a function of pressure. Moreover, the materials can be characterised in terms of pore diameter, surface area and pore volume using the obtained gas adsorption data. Early adsorption isotherm studies of the M41S materials used unmodified calcined mesosilica adsorbents with individual adsorbates, of which the most commonly studied include hydrocarbons, monoaromatic hydrocarbons and alcohols (for example *n*-hexane, benzene, cyclohexane, toluene, *p*-xylene propan-1-ol, ethanol and methanol). In Beck's original paper[3] MCM-41 and MCM-48 adsorption capacity values of 49 % and 67 % by weight for *n*-hexane and benzene at 40-50 Torr were reported. This first encouraging result led to a number of future adsorption isotherm studies with these materials; although arguably most early studies recognised that the MCM-41 mesoporous system was an ideal framework to study fundamental adsorption phenomena such as hysteresis, pore size distribution and adsorption mechanism; rather than focusing conclusions on the capability of the material to extract VOCs from contaminated air. Other researchers examined adsorption isotherm data to probe the hydrophobicity of the silica surface by comparison of VOC adsorption data with that of water vapour. The surface was shown to be hydrophobic due to the presence of siloxane groups, however in the presence of water, surface silanol groups were created providing hydrophilic H-bonding sites[14-18]. Early adsorption isotherm data indicated that the pore volume of MCM-41 was accessible to a wide range of VOCs with adsorption capacity values generally in the range of approximately 0.5 – 5 mmol g^{-1}. The gas-adsorption mechanism of MCM-41 was described[19] as a 2-step process involving monolayer-multilayer adsorption onto the internal surface of the pore walls followed by spontaneous filling of the pores by capillary condensation. The condensation step may or may not involve hysteresis as this depends on the pore critical temperature, which in turn decreases with pore diameter. Capillary condensation without hysteresis is traditionally explained as being due to a combination of co-operative adsorbent-adsorbate interactions and the influence of the close proximity of the pore walls. The relationship between MCM-41 pore size and capillary condensation was first explored using alcohol adsorption isotherms[15] where capillary condensation was shown to occur over a narrow meso-pore size distribution with the area of the hysteresis loop correlating with the size of the adsorbate; in this case increasing from methanol to butan-1-ol.

Mechanism of adsorption of VOC gas molecules with the silica surface

Recognising that the pores of MCM-41 are longer than their diameters it was postulated that the radius may not be consistent along a pore length and that constrictions or imperfections would divide the pore into two so-called blind pores. The pore defects, which would be more likely to occur in pores with smaller radii, were proposed as potential nucleation sites for reversible adsorption[20]. To further probe potential reaction sites, the surface chemistry of MCM-41 was characterised using ^{29}Si NMR and FTIR before and after derivatisation with chlorotrimethylsilane[16]. Spectroscopic results confirmed that 3 types of silanol groups were present on the surface of the adsorbent (single, hydrogen bonded and germinal) and all of them provided adsorption sites for, in this study, pyridine molecules. It was also shown that, largely due to steric hinderance, only the free (single and germinal) silanols were accessible for derivatisation after which the newly introduced trimethyl groups made the adsorbent more hydrophobic. Indeed the number of silanol groups on the surface of the more ordered and condensed surface of MCM-41 was reported as 2.5-3.0 SiOH groups nm^{-2} which was, as expected, lower than amorphous silica at 5-8 SiOH groups nm^{-2}. This research group[21] followed with a study of benzene adsorption onto MCM-41 before and after derivatisation and noted that surface chemistry did not play a major role in adsorption whereas pore size and distribution were key factors. This result was in contrast to those obtained from TPD studies which noted that dispersion forces were thought to be the main mechanisms of interaction between the surface of MCM-41 and organic adsorbates (methanol, benzene, hexane and cyclohexane with methanol being most strongly held due to H-bonding)[22]. This affinity for MCM-41 towards polar molecules, despite its surface hydrophobicity, is a recognised feature of MCM-41 adsorption[22,23]. Polar molecules have demonstrated a well-defined monolayer coverage on the surface of silica materials. MCM-48 has also been shown[24] to favourably adsorb polar (methanol and acetone) over less-polar molecules (benzene, toluene and hexane). Similar results were demonstrated[25] for carbon tetrachloride where the isotherms were shown to be linear at low relative pressure region of the isotherm, this feature was again attributed to surface heterogeneity and the presence of favourable adsorption sites. In summary the published studies have demonstrated that mesosilica adsorbents provide hydrophobic adsorbent platforms with the ability to target polar molecules via H-bonding mechanisms or after derivatisation. Adsorption isotherm data suggest that the adsorbent-adsorbate mechanism of interaction involves adsorption of gaseous molecules onto the pore walls before capillary condensation occurs.

Removal of gaseous molecules from loaded mesosilica materials has also been used to probe adsorbent-adsorbate interactions. For example, TPD was used to study the interaction between MCM-41 and gaseous benzene molecules. At higher benzene loadings multiple TPD peaks were observed for the desorption of benzene from MCM-41[26], indicating the presence of heterogeneous adsorption sites when vapour phase concentrations were high; although it was demonstrated that peak multiplicity reduced at lower adsorbate loadings. Similar multiple desorption peaks have been observed for zeolitic materials and were attributed to the presence of flexible molecules bending though at 90° at intersections in the channels. However it was subsequently proposed[27] that multiple TPD peaks resulted from the ability of gaseous molecules to access different paths in zeolites. This importance of the size and shape of pore channels in adsorption interactions was also used to support the observation of different adsorption kinetics for trichloroethylene, which was faster with MCM-48 (branched interwoven pores) compared to MCM-41 (hexagonal channels)[28]. TPD studies have also been used to assess the efficacy of MCM-41, Al-MCM-41 or SBA-15 for the removal of toluene, isopentane and water (analytes commonly found in gasoline vapours)[29]. Being hydrophobic both materials adsorbed significant quantities of toluene and isopentane compared to water, with two adsorption site being suggested for isopentane but only one for toluene. The study also looked at the performance of Al-MCM-41, which has a hydrophilic surface, due to the presence of acidic sites, and its performance was shown to be significantly lower than MCM-41 due to the preferential adsorption of water molecules in humid environments. Although

SBA-15 demonstrated lower capacity values than MCM-41 the adsorbent-adsorbate interactions were stronger for both toluene and isopentane. Surface hydrophobicity of MCM-41 was again demonstrated when toluene and cumene were removed efficiently from air compared to water vapour[30]. This general recognition that unmodified calcined mesosilica materials have a hydrophobic surface aligning them towards a practical application for VOC adsorption in pollution control is a strand consistently running throughout the published literature. These hydrophobic surface-gas interactions can occur at one adsorption site, or more, depending on the gaseous molecule used as the adsorbate and the porous system in the material.

Influence of synthesis methods on the prepared material's adsorptive properties

Synthesis procedures were also shown to influence the absorptive properties of MCM-41; Serrano *et. al.*[29] concluded that MCM-41 had a weaker interaction with toluene when prepared via a hydrothermal method compared to MCM-41 prepared via a sol-gel method. The sol-gel synthesised material also had higher adsorption capacities for isopentane and water leading the authors to suggest that MCM-41 produced via a sol-gel method is an ideal adsorbent for removal of iso-paraffinic hydrocarbons from humid air due to a higher structural order and a lower condensation degree of the silica walls when MCM-41. More specifically, the increased performance was attributed to the presence of a disordered array of worm-like pores and a wider pore size distribution of this particular material and the study concluded with the hypothesis that the synthesis method (as well as chemical composition) can be tuned to provide mesosilica materials with different lipophilic properties which will in turn influence adsorption behaviour towards VOC extraction. As noted above most studies use calcined mesosilica for VOC extraction and one study[30] which compared the performance of calcined MCM-41 with as-synthesised MCM-41 (template not removed) for the extraction of toluene, cumene and water confirmed that all materials containing the template, or a portion of the template, did not perform as well as their calcined counterparts. Clearly the template prevents VOC molecules from entering the pores of the mesosilica preventing their interaction with the pore walls, significantly reducing adsorptive performance.

Microporosity v's mesoporosity

Moving from adsorption isotherm data to describe material characteristics to the suggested practical application of mesosilica as a potential VOC adsorbent came in 1998[21] when VOC removal by mesosilica was directly discussed and its efficacy compared to silicalite-1, zeolite Y and the commercially available activated carbon BPL. However, despite an appreciation of the potential practical application, the method of assessment still focused on data obtained by benzene, carbon tetrachloride and *n*-hexane adsorption isotherms. This paper however was first to report that mesosilica materials, which demonstrate type IV adsorption isotherms, would be less efficient VOC scavengers when the VOCs are present in air at low partial pressure. Indeed in this work, microporous materials outperformed mesosilica when VOCs were present at low vapour phase concentrations; and not until the adsorbates were present at higher vapour phase concentrations did MCM-41 outperform zeolites. This phenomenon can be explained by reference to Figure 7 which illustrates the type I and type IV adsorption isotherm for microporous and mesoporous materials, respectively. The volume of gas adsorbed ($cm^3\ g^{-1}$) at low relative pressure is significantly lower than that at higher relative pressure for mesoporous materials whereas, in contrast, a microporous material will adsorb its maximum gas capacity at lower partial pressure.

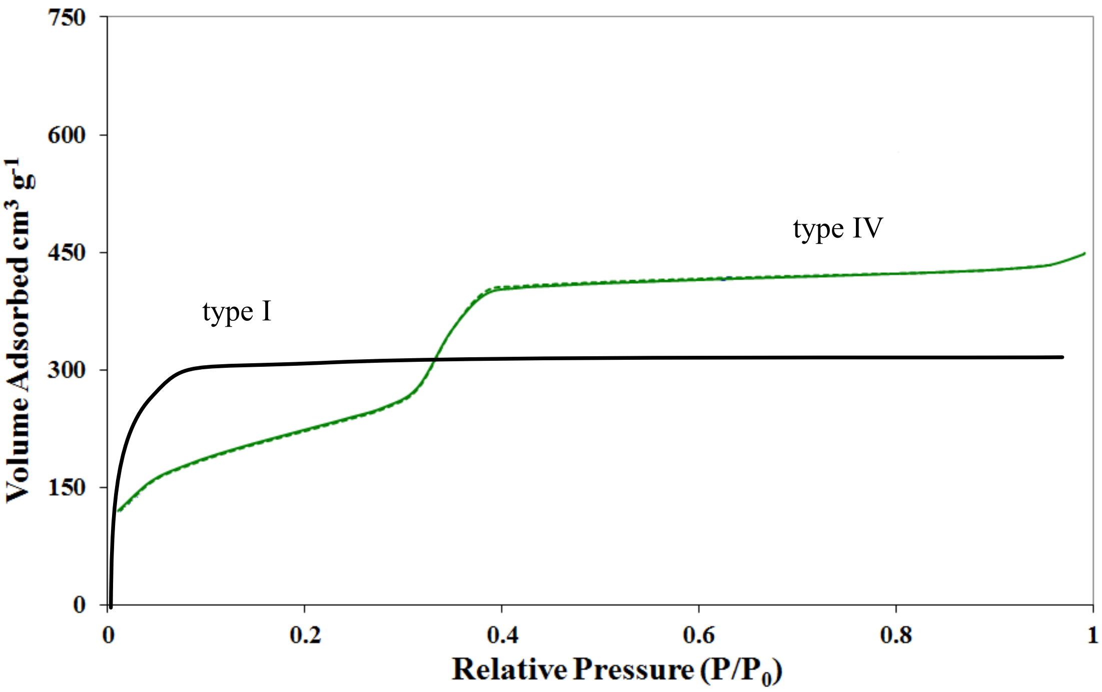

Figure 7: Illustration of type I and type IV adsorption isotherms for microporous or mesoporous materials, respectively.

This is a recognized feature of mesosilica and improvements in gaseous adsorbate extraction at low vapour phase concentration have been studied. Pore tailoring improved MCM-41 VOC extraction efficiencies for benzene adsorption at low concentration[31] when the pore opening was narrowed (from an average pore size of 3.0 to 1.4 nm). The mesosilica produced retained 80 % of its pore volume, exhibited a type I isotherm and the adsorption capacity value increased by 35 %. This correlation between microporosity and VOC adsorption at low concentration has been recognised in further studies which compared the VOC capacity performance of SBA-15 to MCM-41; in each case higher dynamic adsorption capacities were observed for SBA-15 (for example for toluene and benzene[8] and light hydrocarbons[32]) with increased performance being attributed to the presence and number of micropores in SBA-15. Thus control of microstructure, such as the availability and number of micropores present in a material, are now thought to be key factors to consider when optimising materials for gas adsorption and selectivity[33]. The success of microstructure adjustment was shown for SBA-15; when the pore size was adjusted to be approximately 0.6 nm (to match the size of a benzene molecule) benzene was selectively removed from toluene[34]. Contrasting reports[3,35] however indicating a decrease in benzene sorption capacity with decreasing pore diameter of MCM-41 or a decrease in adsorption capacity of *N*-nitrosodimethylamine[36] with decreasing pore diameter of MCM-48, suggest that in addition to tailoring pore size, the role of the micropore-mesopore system must also be considered when optimising the adsorbent for selective adsorbate extraction. Rather it might be that the micropores in SBA-15 act as adsorption sites but do not act efficiently on their own and require easy access routes which are facilitated by the micro-mesopore network[32]. Such interactions were shown for the diffusion of *n*-heptane and cumene onto SBA-15; the adsorption results indicated that intrawall micropores played a major role in molecular transport at low VOC concentration. Indeed it was shown that diffusion of *n*-heptane was controlled by a combination of micropore and mesopore diffusion resistances[37].

Removal of aldehydes by derivatised mesosilica surfaces

Adsorption isotherm data was also used to assess the ability of modified MCM-48 for the removal of acetaldehyde from air[18] as an environmental application to mitigate harmful pollutants from tobacco smoke. The silica surface was first modified with octyldimethylchlorosilane to increase the surface hydrophobicity and resistance to hydrolysis. Surface sites were also derivatised with aminopropyltrimethoxysilane (APTS) to introduce amino functionality providing the potential to chemisorb aldehydes and remove them permanently from air (evidence to substantiate derivatisation success was presented in the form of FTIR data). The amino derivatised MCM-48 outperformed C8-MCM-48 silica by a factor of 3. MCM-41 was also shown to remove formaldehyde from air (in passive mode) when exposed to 1 ppm vapour phase concentration for increased time periods[38]. Amine groups were incorporated into the framework using a range of siloxyamine derivatives and adsorption efficiency was shown to increase with increasing amount of amine functionality. Adsorption was best at 30 °C with lower efficiencies measured for increased temperatures.

Ease of desorption

TPD peaks have also been used[7,22] to indicate the ease at which organics can be removed from mesosilica adsorbents. The thermal desorption temperature required to release trapped VOCs (C_8-C_{12}) from MCM-41 was also shown to be moderate at 150 °C, whereas microporous carbon sorbents required higher desorption temperatures of 300 °C for sufficient analyte recovery[39]. This is a key advantage of mesosilica materials[8] compared to zeolites or activated carbon where the saturated sorbent can be reactivated with hot air at lower temperature[7] than is typically used for other microporous materials.

2.2 Extraction of VOCs using active (dynamic) mode experiments

Removal of VOCs from an air stream

General conclusions drawn from adsorption isotherm and TPD research were that VOC saturation adsorption capacities were high for mesosilica, however adsorption capacity dropped significantly when adsorbates were present at low vapour pressure; as the type IV adsorption isotherm predicts. Nonetheless many authors extrapolated their results to suggest the feasibility of mesosilica as potential VOC scavengers. The use of active mode, or dynamic flow, experiments which better simulate the use of adsorbents for VOC removal from contaminated air did not appear until the late 1990s. One year after Zhao[7] first discussed the potential of mesosilica for VOC extraction in air, breakthrough curves were examined for

MCM-48[40] using a fixed bed adsorption column. Similar breakthrough curves were obtained for benzene, cyclohexane and *n*-heptane and it was concluded that MCM-48 had potential industrial applications if the material was first reformed into pellets to reduce the backpressure created when pushing contaminated air through powdered mesosilica material. Crucially though, MCM-48 pressed into pellet formation had a 40 % reduction in pore volume and 20 % reduction in surface area leading to a reduction of approximately 30 % in adsorption capacity values. Similar effects had been reported previously for MCM-41 pellets[17] suggesting that optimisation of the pelletising method was crucial to ensure best performance of sorbents in industrial applications. This theory was further confirmed four years later[41] for pelletised SBA-15 which had significantly reduced performance for the adsorption of benzene and *n*-heptane when in pellet form. The lower adsorption capacities were reported to be, in part, due to irreversible destruction of a small fraction of the pores within SBA-15 during the pelletising. A different approach which allows sufficiently high (> 40 cm^3 min^{-1}) flow rates of air to pass over sorbents without pellitisation involves mixing the fine powdered adsorbent with glass beads. This approach was used with a tube containing 100 mg of MCM-48 for removal of $C_2 – C_{12}$ analytes[42] and for MCM-41 with 4 VOCs[43]. Su's work[42] indicated that MCM-48 was not efficient when used to trap lower molecular weight species unless it was cooled to –20 °C and attributed its poor performance to the lack of micropores in the material. However, at ambient temperature trapping was efficient for higher molecular weight compounds (> C_6) and quantitative adsorption was achieved for $C_4 – C_{12}$ at sub-ambient collection temperatures. This adsorption performance, together with the ease at which VOCs were desorbed (using desorption temperatures of 100 – 180 °C only 0.31-2.13 % of trapped VOCs remained in the pores) led the authors to discuss the potential applicability of the material for in-line VOC enrichment. The use of dynamic flow experiments, in combination with gas chromatographic determination of VOC breakthrough, was demonstrated for *n*-hexane and MCM-48[44] giving a dynamic adsorption capacity of 0.095 mmol g^{-1}, although the adsorptivity was shown to decrease in the presence of water. The efficiency of adsorption of a wide range of environmental VOCs (more than 50 target compounds varying size from $C_2 - C_{12}$) were examined for MCM-41 and commercial carbon-based molecular sieves[39]. The results indicated that carbon sorbents quantitatively trapped a wide range of VOCs from C_3 to C_{12} at room temperature whereas MCM-41 trapped considerably larger molecules from C_8 to C_{12} with the potential to go beyond C_{12}.

The influence of macrostructure on performance

The effect of pore structure on dynamic adsorption/desorption was also studied in dynamic mode for MCM-41 and SBA-15 synthesised to produce rod-like or fibrous materials[8]. MCM-41 had a surface area of 1154 m^3 g^{-1} whereas fibrous SBA-15 was 730 m^3 $g^{-1}$and rod-like SBA-15 materials were produced with surface areas of 757 (rod B) or 430 (rod C) m^3 g^{-1}. In spite of the different surface areas conclusions noted that the existence of micropores were essential for the production of a material with a high dynamic capacity; capacities increased with the overall number of micropores present. Breakthrough curves for toluene and benzene indicated that the fibrous SBA-15 material was a better adsorbent than rod-like SBA-15 or MCM-41. Moreover despite having similar pore sizes, the adsorption capacities of fibrous and rod-like SBA-15 were significantly different. Here it was shown that there was a combination effect between the micropores and the long 1-D channels which together provided superior VOC adsorption performance. Fibre-like SBA-15 materials were also used in another breakthrough study with 500 ppm toluene[45] which was passed over columns filled with 100 mg adsorbents at a flow rate of 10 cm^3 min^{-1} for 30 min. The toluene breakthrough was measured by gas chromatography. Like Kosgue[8], this study also confirmed that an optimised macrostructure between silica channels and micropores would produce a material with highest dynamic adsorption capacity. Best results were obtained for the material with the longest channels and largest number of micropores. It was hypothesised that the micropore volume related directly to the dynamic adsorption capacity whereas the length of the mesopore channel influenced breakthrough times. Therefore the material's macrostructure needs to be carefully considered for practical applications with deliberation given to whether capacity or breakthrough is prioritised. The pore size of MCM-41 was increased from 3.5 to 9.2 nm and the influence of the greater sized pores on VOC adsorption was studied in dynamic mode[46]. The pore expanded MCM-41 demonstrated stronger interactions with benzene and toluene compared to dichloromethane and chloroform but the adsorption capacity of the pore expanded MCM-41 was similar to conventional MCM-41 at 1.76 mmol g^{-1} or 1.88 mmol g^{-1}, respectively. Indeed higher adsorption capacities were also shown for MCM-41 with benzene (2.43 mmol g^{-1}) compared to its pore expanded counterpart (2.07 mmol g^{-1}). This trend in performance was reflected when the sorbents were used to remove the pollutants from a humid environment although in general the capacity values reduced. Using 100 mg of SBA-15 and a continuous stream of air containing 1000 ppm of benzene, higher adsorption capacities (0.83 mmol g^{-1}) were measured in a dry stream compared to one at 15 % relative humidity (RH) at 0.586 mmol g^{-1}. Similar results were shown for SBA-15 and MCM-41 where sorbents were shown to be strongly influenced by increasing the relative humidity from of a contaminated air stream containing toluene, ethylbenzene, cumene and dichlormethane from 25 to 80 %[43]. Reduced performance is due to the water vapour converting surface siloxane to silanol groups inducing hydrophilicity and reducing the capacity of the material towards hydrophobic adsorbates. The combined influence of humidity and functionalization using phenyl groups on benzene adsorption was also reported[47]. Dry air, or air conditioned to 13 % RH, containing 500 pm of benzene and cyclohexane was passed over 100 mg of crushed MCM-41 or SBA-15 before and after the introduction of surface phenyl groups. Interestingly, shorter breakthrough times were demonstrated for phenyl functionalised materials in dry and humid conditions and this decrease in performance was attributed solely to the reduction in surface area and pore volumes; perhaps due to partial blockage by the derivatising agent. However when comparing the performance of a material to its corresponding functionalised counterpart the previous observations were supported with lower adsorption capacity values for benzene of 0.53 and 0.50 mmol g^{-1} for MCM-41 and SBA-15 in humid air compared to 1.02 and 0.90 mmol g^{-1} in dry air.

Cigarette smoke/aldehydes

Dynamic mode experiments have been used to assess the performance of MCM-48 and SBA-15 to extract tobacco specific nitrosamines from a contaminated gas stream[36], although the extraction method used was not strictly adsorption but rather attempts were made to thermally decompose the molecules at elevated temperature (593 K). At this high temperature SBA-15 outperformed an acidic zeolite by a factor of 2 achieving a maximum VOC adsorption concentration of 0.03 mmol g^{-1}. Better results were achieved for SBA-15 which had been doped with 0.1 % CuO[48]. Extraction efficiencies of 63 % were reported for the removal of nitrosamines from cigarette smoke and 47 % from smoldering smoke. Wang *et. al.*[49] also assessed the extraction of nitrosamines determining their breakthrough by gas chromatography. In this study SBA-15 was shown to be more active towards the smaller nitrosamines removing approximately 50 % of the pollutants, however NaY or NaZSM zeolites were even better and removed 90 % of the smaller nitrosamines. A similar performance was observed for MCM-48 and cerium doped MCM-48 when used to extract polycyclic aromatic hydrocarbons (PAHs) from mainstream tobacco smoke[50]. Although smaller PAHs were not removed from the contaminated air stream the bulkier PAHs were selectively eliminated. Using MCM-48 or Ce-MCM-48 to extract PAHs from mainstream smoke extraction efficiencies/catalytic abilities were measured at 12.5 % or > 30 %. When the adsorbents were incorporated into a cigarette filter tip, these extraction efficiency values increased slightly to 15% for MCM-48 but the activity of Ce-MCM-48 decreased to 24 %. Despite most papers indicating that as-synthesised materials performed poorly when compared to calcined materials for VOC adsorption, recently a novel as-synthesised MCM-41 adsorbent was shown to be effective when removing phenol from tobacco smoke[51]. The reported unwarranted success of this material was, however, not attributed to the presence of the surfactant in the mesopores but to the presence of tetraethylenepentamine (TEPA) which was distributed in the template after synthesis. The surfactant micelles were reported to form a net-like amine fibre inside the mesoporous channel and the template incorporated MCM-41 material absorbed 4.54 mmol g^{-1} of phenol which was significantly higher than for MCM-41 at 0.14 mmol g^{-1}. Best performance was demonstrated for a sorbent loaded with 50 % w/w TEPA. The sorbents (60 mg) were then added to tobacco filters and assessed for selective phenol removal. These results were less promising for 7 phenolic compounds with similar mass reductions observed for as-MCM-41 and TEPA-as-MCM-41. Reduction of the TEPA concentration (w/w %) to 10 % did lead to an increase in extraction of phenolic compounds from 5 % to 18 %, however the result was reported to be disappointing as higher extraction efficiencies were expected. It was theorised that the reduced performance was a result of the micelles becoming rigid at the ambient smoking temperature subsequently reducing access to TEPA in the pores. Finally amine functionalization was used modify the surface of MCM-41 and SBA-15 for the extraction of formaldehyde vapour in dynamic mode[52]. Compared to non-functionalised materials breakthrough was significantly retarded when functionalised materials were used to extract formaldehyde from air. Indeed even when 24 cm^3 of air containing 1.4 mg m^{-3} of formaldehyde vapour was sampled no breakthrough was observed. The target was strongly bound and when back-flushed with air for 60 min at 100 cm^3 min^{-1}, no formaldehyde was removed from the aminated sorbents suggesting retention by chemisorption. Air contaminated with selected VOCs and formaldehyde were also sampled and no formaldehyde breakthrough was observed signifying that the material can play an active role in formaldehyde elimination in the environment. Although out-with the scope of this review, it is interesting to note that this article reports the first application of novel silica green nanoparticles (GNs) for VOC removal, prepared via an environmentally friendly, bioinspired synthesis route. Despite reduced surface areas, GNs were shown to have similar VOC dynamic extraction performance to MCM-41 or SBA-15 whilst being faster, more environmentally friendly and more economical to produce.

2.3 Silica adsorbents for gas separation

SBA-15[32] and hexagonal mesoporous silica[53] have been used to separate light hydrocarbons in an air stream. Both materials demonstrated higher affinities for alkenes over alkanes. As the silica surface is generally known to be hydrophobic the differentiation of alkenes and alkanes was thought to be ascribed to the higher quadrupole moments possessed by the alkene molecule compared to its corresponding alkane. The observed selectivity for unsaturated C_2 and C_4 compounds at low gas phase concentration led the authors to suggest that SBA-15 could be used for olefin enrichment in lean hydrocarbon streams. Further evidence of SBA-15's potential to separate C_2 alkenes from alkanes was published one year later[54]. In this study silica samples were also prepared with reduced microporosity, or no micropores, and the results confirmed that samples with higher microporosity had a higher affinity for ethylene. Furthermore the affinity of ethylene in the micropore-free SBA-15 was shown to be similar to that of MCM-41 with equilibrium capacity values for ethylene uptake of 0.89 and 0.48 mmol g^{-1}, respectively, which whilst being lower than obtained for a zeolite

(1.18 mmol g^{-1}), were used as evidence to confirm the importance of microporosity for sorbents designed to perform selective gas separation. Microfluidic devices were also used to explore the potential applications of SBA-15 for the separation of benzene, toluene and *o*-xylene when present in air at concentrations of 100 ppm[55]. The sampled gas mixture flowed through the sorbent bed for 30 min at a rate of 0.1 cm^3 s^{-1}. It was initially speculated that the adsorption of the monoaromatic species would be similar (via H-bonding between the pi-system and the silica surface) but this was not found to be the case and differences in adsorption capacity were linked to the molecules boiling point and to the multilayer interaction in the vapour and liquid phase inside the pores.

Functionalisation of mesosilica with organic groups has been used to modify adsorption properties by increasing surface area and hydrothermal stability, and to lead to greater adsorption selectivity of targeted compounds[11,56,57]. For example, to target the removal of benzene and cyclohexane the surface of SBA-15 was modified with methyl or phenyl groups[58]. Contaminated air (at 1000 or 500 ppm) flowed through 100 mg of sorbent at a flow rate of 50 cm^3 min^{-1} and breakthrough was determined by gas chromatography. The results indicated that adsorptive properties were enhanced only when the samples were prepared with a specific methyl/phenyl: silica ratio. For example benzene breakthrough was delayed only when the ratio of methyl:silica was 1:10, and no improvement in performance was shown for samples with ratios of 1:20 or 1:5. Phenyl groups, on the other hand, delayed toluene breakthrough for all ratios studied although best performance was noted for the sample prepared with a 1:10 phenyl: silica ratio. Differences were attributed to the increased hydrophobicity of the surface after functionalization but also noted the compromise due to decreased pore volume in increased functional group loading. This was demonstrated for SBA-15 which, although had the highest pore volume at 1.14 cm^3 g^{-1}, demonstrated a lower dynamic adsorption capacity value compared to the methyl- or phenyl-derivatised SBA-15 by

20 – 50 %. Moreover the phenyl-functionalised surface could selectively retain benzene over cyclohexane due to the pi-electron interactions allowing selectively retention of this specific gas molecule.

3. Conclusions and Discussions

Since the earliest assessment of mesosilica focused on VOC isotherms and TPD experiments, studies of adsorption performance have expanded to examine real application of gaseous molecule removal in dynamic and static mode. In most cases, the reported adsorption capacity values compare well, or exceed, competitive microporous materials supporting their potential to remove VOCs from contaminated air. However the importance of micropores in the adsorbent material for gaseous extraction should not be underestimated with best performance demonstrated for SBA-15 due to the microporous-mesoporous network. The ability to alter chemical functionality in the mesopores offers the ability to design/tailor materials for specific analytes of interest. Undoubtedly the interest in mesomaterials as adsorbents for organic pollutants will continue to grow and develop however before its successful implementation in environments remediation it is suggested that a shift in focus from simulated laboratory studies to real-monitoring is required; investigating material regeneration, the influence and connectivity of micro-mesopores, the effect of potential interferents and sorbent application in field studies (dynamic v’s passive mode). A current drawback is the cost of manufacture and the applicability of the powdered adsorbent in real applications. Perhaps more attention needs to be focused on cost-effective scale up in mesosilica production and on the implementation of adsorbents in-line before these materials will make a significant impact in the industrial/environmental sectors.

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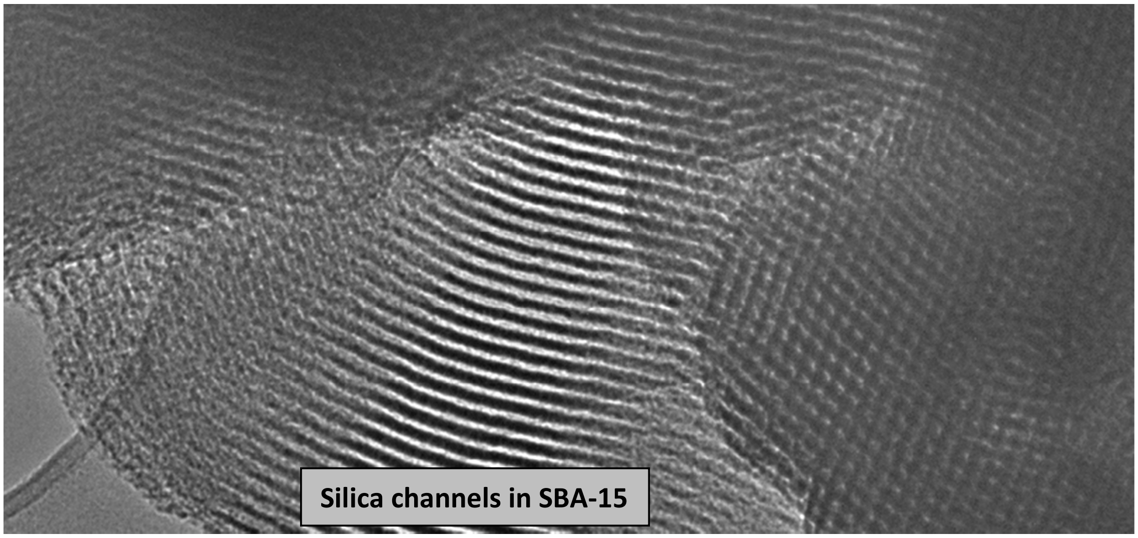
Silica channels in SBA-15

Mesosilica Materials and Organic Pollutant Adsorption: Part A Removal From Air

Learning Objectives:

1. Recognise the need for template removal prior to volatile organic compound extraction.
2. Understand how mesosilica textural properties and macrostructure influence the adsorbate-adsorbent interaction between silica and vapour phase organic pollutants.
3. Appreciate the limitations of extrapolating isotherm, or temperature programme desorption, data to practical applications of mesosilica for environmental remediation.
4. Be able select appropriate derivatising agents for improved extraction, or chemisorption, of target pollutants.
5. Understand the need for performance testing, in dynamic or static mode, to demonstrate the utility of the adsorbent in the field.

Lorraine T. Gibson is a senior lecturer in Analytical Chemistry at the University of Strathclyde, Glasgow. Her research interests include Heritage Science and Environmental Chemistry. In particular the design, development and synthesis of silica supports for environmental remediation applications in the vapour and aqueous phases.

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