

## HIGHLIGHT

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## The discovery of mesoporous molecular sieves from the twenty year perspective†

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Charles T. Kresge\*<sup>a</sup> and Wieslaw J. Roth\*<sup>bc</sup>

By the combination of prior knowledge, observation skills, and novel synthetic approaches, we discovered a family of mesoporous molecular sieves including discrete structures – MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (lamellar). These materials were formed unlike that of our classical microporous structures involving reagent induced-macromolecular templating mechanism. Based on synthetic data and working with others, we were able to establish a predictive mechanism of formation and identify a broad class of templating reagents. These initial findings generated great interest and effort worldwide. It resulted in tremendous expansion of knowledge and skills with many new additional discoveries that established a new area of ordered mesoporous materials. They are integrated with zeolites (microporous materials) and based on surfactant inorganic chemistry.

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<sup>a</sup> The Dow Chemical Company, Midland, Michigan 48674, USA

<sup>b</sup> Faculty of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland

<sup>c</sup> J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Dolejškova 3, CZ-182 23 Prague 8, Czech Republic

† Part of the mesoporous materials themed issue.

## Introduction

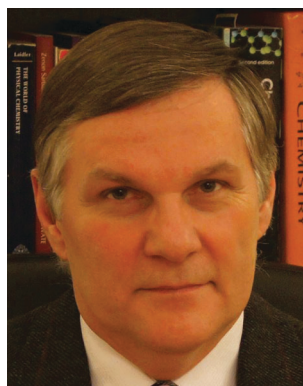
Almost twenty years ago, patents and journal publications from Mobil disclosed the synthesis and characterization of a new class of porous materials, a family of uniform pore, silicate based, mesoporous molecular sieves, named the M41S family.<sup>1–4</sup>



Charles T. Kresge

Charles T. Kresge is R&D vice president at the Dow Chemical Company. Kresge joined Dow in 1999 from the Mobil Oil Corporation. He was the co-recipient of the Donald W. Breck award in Molecular Sieve Science; recipient of an R&D 100 award for Innovation; the Thomas Alva Edison Patent award; and the Robert A. Welch foundation invited lectureship in Nanochemistry; Chair, Gordon Research Conferences on Zeolitic

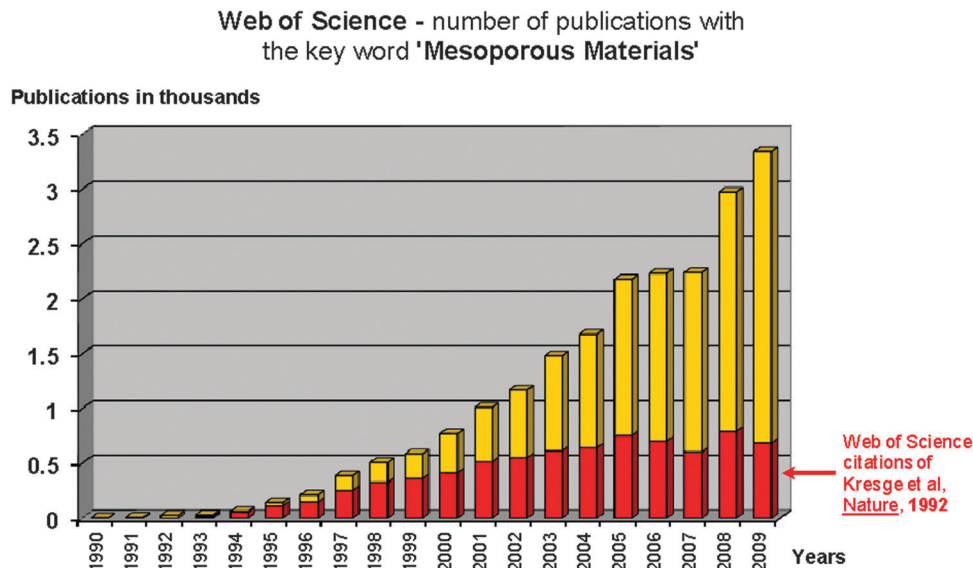
and Layered Materials; Guest editor, *Current Chemistry: Current Opinion in Colloid and Interface Science*; past member Editorial Board, *Journal of Solid State Chemistry* and Editorial Advisory Board, *Advanced Functional Materials*; past member of the Boards for the International Zeolite Association, Mesoporous Materials Association, the International Congress on Catalysis and the Board of Chemical Sciences and Technology of the National Academies. Dr Kresge is a member of the National Academy of Engineering.



Wieslaw J. Roth

Wieslaw J. Roth is currently an associate professor at the Faculty of Chemistry, Jagiellonian University of Krakow, Poland, and has close collaboration as visiting scientist with J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, in Prague. He retired in 2009 after working on zeolite synthesis for 21 years with Mobil and ExxonMobil in Paulsboro and Clinton, NJ. Wieslaw graduated from

Technical University of Wroclaw in Poland and received PhD from Southern Illinois University in Carbondale. Before joining Mobil R&D in 1988, he was post-doc with Prof. F. A. Cotton at Texas A&M University in College Station. He was the co-recipient of the Donald W. Breck award in Molecular Sieve Science for 'the discovery of mesoporous molecular sieves'.



**Fig. 1** The growth in the number of publications on mesoporous materials and citations of the initial Kresge *et al.* Nature paper till 2009.

They were obtained by surfactant assisted synthesis, called liquid crystal templating, under conditions employed to crystallize microporous solids like zeolites. This announcement created an extraordinary amount of interest in the scientific community that still continues today. Many groups and laboratories developed programs dedicated to the study and advancement of these new materials and the application of surfactants in synthesis in general.<sup>5–7</sup> Thanks to these efforts, there has been enormous expansion of publications and knowledge, resulting in a plethora of other new materials, phenomena and concepts. Ordered mesoporous materials (OMM) became an independent area closely integrated with zeolites and microporous solids.<sup>8,9</sup> The very popular area of metal–organic frameworks (MOFs), while compositionally different and not as dependent on using structure directing agents, can be considered as developing complementary to OMMs in some areas. In numerous citations, the Mobil disclosure is referenced as ‘the true start of the studies on the template effect of micelles’,<sup>7,10</sup> albeit sometimes with caveats to be addressed below. These initial results were published in two pioneering publications, which, judging from their citation numbers, launched a broad worldwide research effort and resulted in a new, independent area of ordered mesoporous materials. This is illustrated here by the number of publications with the key word ‘Mesoporous’ in the ‘Web of Science’ database shown in Fig. 1. Between 1987 and 1991, there were less than 10 publications per year, while the year 1992 marked a quick ascent in the number of publications. Simultaneously, the citation numbers of the Kresge *et al.* Nature publication<sup>1</sup> increased steadily with each year. However, the foundation of this discovery was developed many years earlier.

## Path to discovery

The details of how the discovery in Mobil came about and the initial effort can be found in two earlier publications.<sup>11,12</sup>

Like most discoveries of novel materials, the discovery of Mobil’s M41S mesoporous molecular sieves was an unanticipated outcome of the application of observational skills, knowledge, and techniques developed over many years. Like many major petroleum companies, Mobil had an exploratory material synthesis effort attempting to identify new zeolites that could selectively convert high molecular weight petroleum based molecules. In the mid-1980’s, Mobil Technology Company had a significant effort in developing pillared layered materials, in part, to escape the “1 nm prison” beyond which there was little zeolites could offer at that time. This class of materials, theoretically, offered the ability to tune the pore size, the active site density, and composition; variables that the traditional aluminosilicate zeolites did not possess. By varying the pillar size and pillar density, the goal was to produce materials having a pore system that could be tuned for a desired application. The pillar composition could also be adjustable so various chemistries could be effected.

Pillared layered materials have been explored since about the mid 1970’s.<sup>13</sup> Many scientists have previously examined the concept of swelling and pillaring layered materials. One in particular, Richard M. Barrer investigated the swelling of clays using alkyltrimethylammonium compounds.<sup>14</sup> Unfortunately, although significant progress was made in designing these pillared layered materials, realistically they did not have sufficient thermal and hydrothermal stability or catalytic activity to be used in most petroleum processes.<sup>15</sup> Furthermore, the pillar composition could not be as varied as initially conceived. These shortcomings of the layered solids could be summarized as lacking zeolite character.

Towards the end of the 1980’s, a small group of four researchers at Mobil’s Paulsboro Laboratory approached this quest for large pore frameworks by attempting to combine both the concepts of the pillared layered materials and the formation of zeolites. The approach was to consider that some zeolites

were formed *via* layered intermediates. Indeed, newly discovered zeolite MCM-22 showed an unprecedented feature of producing a lamellar precursor MCM-22P with one unit cell thick monolayers.<sup>16</sup> Upon calcination, these lamellar precursors condensed into 3D zeolite. However, if this intermediate was isolated, it could be used as a layered composition to form pillared porous materials and the resultant product should exhibit zeolite character.

Using the as-synthesized zeolite material, with the template intact and prior to any thermal exposure, we attempted to delaminate or separate these crystalline layers of the MCM-22 precursor. The pillared layered material resulting from this delamination and subsequent pillaring was obtained and identified as MCM-36.<sup>17,18</sup> The process involved the initial intercalation of the layers using an alkyltrimethylammonium compound followed by the insertion of stable inorganic pillars using a reactive silica source such as tetraethylorthosilicate. This area has since been evolving independently and expanding to other zeolites. It is now also of great interest and has begun to be referred to as 2-D zeolites.<sup>18</sup>

Complete delamination of the intermediate layered zeolite "precursor" initially presented a significant challenge. One synthesis approach was to interrupt the typical zeolite syntheses, isolate the layered zeolite precursors, and then use these potential crystalline layered materials as reagents to form large pore active catalysts. The interruption could be initiated at any point within ~25 to 75% of the total expected synthesis time. High concentrations of the intercalate, a long chain alkyltrimethylammonium salt, at high pH were added to this interrupted zeolite precursor media. In other syntheses, a reactive silica source, tetramethylammonium silicate, was also added as a potential pillaring agent. These new synthesis mixtures were then subjected to additional hydrothermal treatment in an attempt to form the zeolite-layered hybrid. In many instances, the resulting product exhibited some very unusual properties.

The X-ray diffraction pattern was essentially featureless except for one broad low angle peak at about  $2^\circ$   $2\theta$  (Cu K $\alpha$  radiation). This X-ray diffraction pattern was intriguing since the original zeolite templating agent still existed in the synthesis composition. Since the reaction conditions, time and temperature sequence were changed during the addition of the quaternary salt, apparently this inhibited the formation of the originally intended zeolite. Normally even this low angle line might not have been observed, except that we were using a chromium X-ray source instead of the typical copper tube. The chromium source, which is very useful for low angle peak detection, was a remnant from our pillared layered material research effort. The other unusual properties of this unknown material were the extremely high BET surface areas and hydrocarbon sorption capacities. These BET surface area values, up to 1000 m<sup>2</sup> g<sup>-1</sup> and more, exceeded those normally observed for zeolite samples. The hydrocarbon (*n*-hexane and cyclohexane) sorption capacities were in excess of 50 weight percent, also abnormally high compared to our typical microporous samples. In fact, our analytical laboratories initially, incorrectly, believed that their

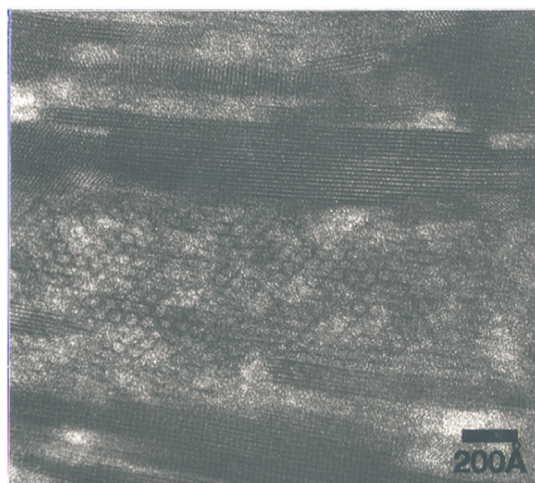
test equipment was broken or out of standard due to the results obtained from these initial mesoporous materials.

In a separate and concurrent synthesis approach, the hexadecyltrimethylammonium hydroxide was used directly as a structure-directing agent in zeolite-like hydrothermal syntheses. The products' properties were similar to those generated in the layered zeolite precursor systems, *i.e.* characterized by a low angle line in an X-ray diffraction pattern corresponding to large *d*-spacing, unusually high BET surface area and adsorption capacities. Thus, both interrupted zeolite precursor systems described above and the direct introduction of alkyltrimethylammonium hydroxide as a template resulted in the mesoporous molecular sieve products. As described below, subsequent detailed characterization studies allowed elucidation of the remarkable nature of these unusual materials.

Obviously, these above-mentioned unprecedented physical properties are characteristics of the mesoporous molecular sieves. However, with only one broad low angle X-ray diffraction peak and the uniquely high values for both surface area and hydrocarbon sorption as data, this was insufficient to fully identify the nature and structure of these materials. We initially concluded from this one broad X-ray diffraction peak material that we had completely disrupted the interlayer connectivity of layered zeolite hybrids and the resulting X-ray diffraction was simply a repeat of the thickness of the layered precursor of about 4.0 nm. A key in the identification of this new class of porous materials was the observation, by TEM analyses, of a trace amount of MCM-41 in one of our samples. At this time, our small research group had the luxury of having as one of the members, a microscopist, Mike Leonowicz, who typically would conduct analyses on some of our more unusual samples. The observation of trace quantities of MCM-41, the uniform hexagonal pore structure, in one of the interrupted synthesis preparations provided us with hard evidence of this new class of materials (Fig. 2).

In a relatively short time, we were able to produce sufficient excellent quality samples of MCM-41 to characterize these materials by X-ray diffraction, pore size distribution, sorption capacities, and NMR and to evaluate them for catalytic applications. Many researchers at both Mobil's Paulsboro and Princeton Laboratories were involved in this effort. In all cases, we were analyzing a new class of materials that presented unique data. For example, the pore size distribution was remarkable; the narrow pore size appeared to be like that of microporous materials but within the mesopore range. As mentioned previously, the hydrocarbon sorption capacity was unique. Benzene sorption isotherms clearly indicated pore condensation inflections at benzene partial pressures indicative of mesopore size channels. These inflections were typically not observed with microporous materials due to the low partial pressures needed. We were also able to synthesize various pore size materials using both different alkyl chain lengths of the cationic surfactant as well as taking advantage of micellar swelling.<sup>19</sup> These techniques improved as our knowledge of micelles and liquid crystal chemistry grew more detailed. Both this knowledge base and the resultant samples helped to





## United States Patent [15]

Kresge et al.

Patent Number: 5,098,684

Date of Patent: Mar. 24, 1992

## [54] SYNTHETIC MESOPOROUS CRYSTALLINE MATERIAL

[75] Inventors: Charles T. Kresge, West Chester, Pa.; Michael E. Leonowicz, Medford Lakes, Wis.; James C. Vartuli, West Chester, Pa.

[73] Assignee: Mobil Oil Corp., Fairfax, Va.

[21] Appl. No.: 625,245

[22] Filed: Dec. 10, 1990

## Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 470,008, Jan. 25, 1990.

[51] Int. Cl. C01B 32/34

[52] U.S. Cl. 423/306; 423/326; 423/328; 502/62; 502/64; 502/66; 502/68; 502/71

[58] Field of Search 423/328, 320, 277, 305, 423/306, 326; 502/62, 64, 65, 66, 71

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Primary Examiner—R. Bruce Brennan

Attorney, Agent, or Firm—Alexander J. McKillop,

Charles J. Speciale, Dennis P. Santini

## [57] ABSTRACT

This invention relates to a new synthetic composition of ultra-large pore crystalline material and use thereof as sorbent and in catalytic conversion of organic and inorganic compounds. The new crystalline material exhibits unusually large sorption capacity demonstrated by its benzene adsorption capacity of greater than about 15 grams benzene/100 grams at 50 torr and 25° C., a hexagonal electron diffraction pattern that can be indexed with a d<sub>100</sub> value greater than about 18 Angstrom Units and a hexagonal arrangement of uniformly sized pores with a maximum perpendicular cross section of at least about 13 Angstrom units.

59 Claims, 21 Drawing Sheets

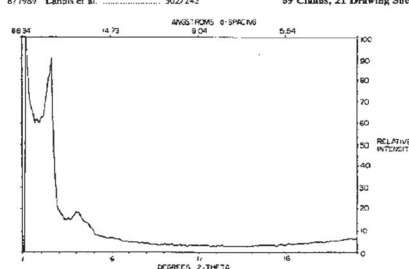


Fig. 2 The identification of a novel porous material.

establish the basis for the mechanism of formation of these materials.

In retrospect, the synthesis conditions that we were using to try and obtain our layered zeolite hybrids, high pH, high surfactant concentration, and a reactive silica source, were synthesis conditions conducive to the formation of the mesoporous

molecular sieves. The discovery and identification of other members of this new class of porous materials, MCM-48 and MCM-50, came several months later as a result of a detailed study relating the effect of surfactant concentration on the silica reagent (Fig. 3).<sup>20</sup> The discovery of these additional two members of the mesoporous molecular sieve family was

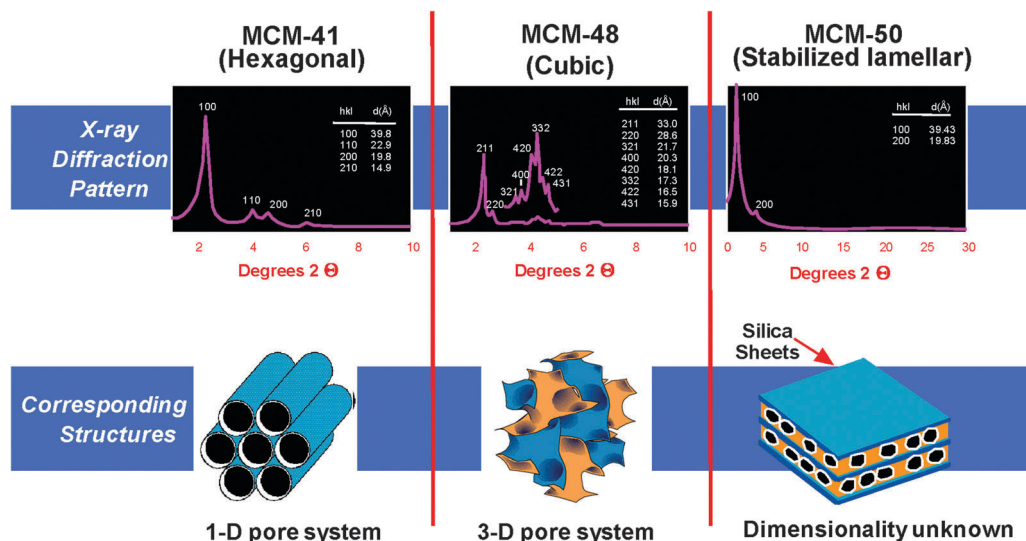


Fig. 3 The M41S family of mesoporous molecular sieves including MCM-41, MCM-48, and MCM-50.

another key factor in developing the proposed mechanism of formation.

The discovery of this new class of materials, mesoporous molecular sieves, posed several challenges for our understanding of the formation of porous materials. Numerous observations suggested a close relationship to the surfactant behavior, which was amply exploited in the following exploration and extension of initial work, but the details had to be worked out. Various possibilities were discussed including the crystalline phases predicted by Smith and Dytrych,<sup>21</sup> known as the 81(*n*) family of frameworks. The theoretical XRD pattern of this family almost matched that of some of our best samples of MCM-41. In the end, the evidence, such as Si NMR, indicating predominantly amorphous walls and continuous variation of hexagonal lattice constant suggested that XRD patterns could be generated by the order of the pores and not the crystalline structure, which was another key (unique) feature of this new class of porous materials.

The mechanism of formation was called liquid crystal templating (LCT) by analogy to the surfactant-water liquid crystal phases of the alkyltrimethylammonium salts in water (hexadecyl, dodecyl)<sup>22</sup> that the materials MCM-41, MCM-48 and MCM-50 were mimicking. In many cases, XRD patterns were not sharp and resolved enough to allow structure assignment and these were referred to as M41S-type. The LCT mechanism in its literal sense turned out to be inoperative in a vast majority of cases and was reformulated into a more general scheme. One of the key pieces of evidence that surfactant originating concepts such as cmc (critical micelle concentration) and straight liquid crystal analogy cannot be applied was provided by the experiments that studied the effect of various levels of surfactant (SUR). By changing the SUR/Si molar ratio, we were able to synthesize MCM-41, -48 and -50 while keeping all of the other synthesis conditions the same.<sup>20,23</sup> These conditions would then exclude the possibility of any preformed liquid crystalline phase prior to the formation of the silicon phase. These data

supported the concept that the anion, in this case, the silicate species, significantly affected the formation of the resultant template of the mesoporous molecular sieves (Fig. 4). These data were some of the evidence that led us to propose the possible mechanisms of formation that we published in our initial articles<sup>1,4</sup> and later in a still more elaborate form.<sup>24</sup>

In retrospect, both initial proposed pathways (1 and 2) proved to be valid. The predominant pathway appears to be the anionic species initiated one (using cationic surfactants). This concept was explained and expanded upon by many researchers, specifically by the group at the University of Santa Barbara headed by Prof. Galen Stucky<sup>25,26</sup> and termed cooperative self-assembly. A Michigan State University group, headed by Prof. Thomas Pinnavaia, expanded this mechanistic pathway further to include neutrally charged directing agents such as polymers.<sup>27,28</sup> Later, researchers at the University of South Hampton demonstrated the other proposed pathway, originally labeled the liquid crystal phase initiated pathway.<sup>29,30</sup> Prof. George Attard and his co-workers used a preformed liquid crystal phase to synthesize both a silica and a metal (platinum alloy) mesoporous molecular sieve.

The ideas of cooperative self assembly and supramolecular templating adequately explain, conceptually, the formation of OMMs but do not address the mechanism at a molecular level. In contrast, one can readily imagine assembly of zeolite frameworks with mono-molecular templating by addition of small fragments and building of nuclei and crystals. As far as we know, analogous assembly of larger surfactant mediated structures has not been elucidated. Here it may be of interest to mention the amazement of Prof. Luzzatti, one of the pioneers in the study of liquid crystal phases, at the formation of OMMs. It was due to the fact that one can rationalize the former because they are found as equilibrium systems. In contrast, the OMMs are not believed to be formed at equilibrium, however, no thorough analysis from this perspective has been carried out. In comparing the liquid crystal initiated templating with the silica initiated one,

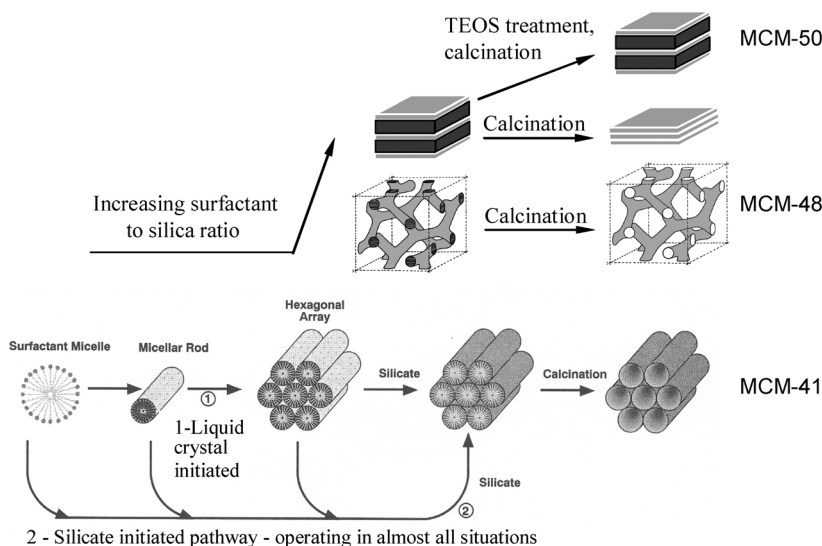


Fig. 4 The initially proposed LCT mechanism of formation pathways (lower half) and its further additions.

we can say that “more molecular details” (specificity) have been lost and may warrant closer attention and study.

The years following the initial publication of the M41S materials and LCT mechanism experienced an explosion of effort, innovation and further discoveries. It must be credited to the skills, dedication and ingenuity of many investigators, who expanded the area beyond our expectations. We are hardly in a position to present a comprehensive summary having moved to other areas and responsibility with only occasional work in this new field. Therefore we shall not discuss this in detail. Instead we would like to offer some personal reflections.

## Beyond M41S

The years following M41S discovery were replete with many unexpected findings both fundamental and practical. The number of reviews are too numerous to mention. In general, one can find an overview in some recent general publications/books on zeolites and porous materials. For example, ref. 7–10 may be a good start for further inquiry. It took a relatively short time for recognition of the new mesoporous materials, often identified with MCM-41, to be considered as remarkable and special. Editor and science writer Philip Ball expressed it in the following way, “One of the most important new materials of the 1990s is the mesoporous form of silica known as MCM-41 – this makes MCM-41 a scaled-up version of the aluminosilicate zeolites that are widely used in the chemical industry as highly selective catalysts and “molecular sieves” – their smaller pores are the width of small molecules”.<sup>30</sup> Prof. Geoffrey Ozin refers to this new chemistry as, “the escape from 1 nm prison (of pores)”.

Among the myriad new findings upon expansion of the mesoporous area most are positive and exciting, but there are also some disappointments. In the latter category one counts the catalytic activity, which was initially found in most cases to be much weaker than zeolites (as it had to be since the walls are amorphous  $\text{SiO}_2$  or  $\text{SiO}_2\text{-Al}_2\text{O}_3$ ). Even the most promising performances were not of sufficient improvement to justify (cost and labor) expedited commercial implementation. In some cases, the catalytic results from the mesoporous catalysts led to improvement in the more conventional catalysts which then offset the initial promising advantage shown by some new mesoporous material. A true commercial application in the refinery was implemented around the year 2000 by ExxonMobil. The exact application remains proprietary, but a hydrotreating or mild hydrocracking process<sup>31</sup> seemed to be the most likely candidates. The largely amorphous nature of the walls of OMM was considered responsible for its much lower activity compared to zeolites. This has generated a lot of activity aiming at synthesizing OMM with ‘zeolitic walls’ or as micro- meso-porous hybrids.<sup>32</sup> Again too many outstanding and diverse results have been produced to mention them all. In the end it seems that a full circle has been made. By using appropriately designed surfactants, Prof. R. Ryoo and his collaborators have shown a possible pathway to synthesis of zeolites with mesopores.<sup>32</sup>

In hindsight, we can also view conceptually the discovery of M41S materials as the onset of the area – inorganic chemistry of

the surfactants or ‘chemistry at the surfactant–inorganic interface’. The surfactant–inorganic interactions before the 1990’s were being primary of the textbook type of ‘physical change’. Mesoporous materials represented the ‘chemical change’ with the ability to ‘organize things’ while their supramolecular templating contrasted the mono-molecular templating of zeolites.

As mentioned above, Mobil’s disclosure of mesoporous materials is almost unanimously acknowledged as ‘the true start of the studies on the template effect of micelles’,<sup>7,10</sup> which we take as tantamount to referring to the entire area of OMMs. We now know that formation of some kind of ‘M41S’ type product is almost inevitable in the presence of surfactant and some reactive medium. This ubiquity has led to speculations that certainly someone must have made such material previously. It is true that once you are aware of the recipe parameters, MCM-41 is a facile synthesis. In addition, in the past, many scientists have used alkyltrimethylammonium compounds with silicate reagents. However, as in all discoveries, one must not only synthesize the material, but equally important, one must recognize and identify the novel material and its significance. There are no literature records that suggest an earlier discovery of this class of materials.

Two cases are often cited as the putative predecessor syntheses and described as producing ‘ordered hexagonal silica’ and ‘ordered mesoporous material’. They were by no means identified as such prior to M41S, but their identity and/or importance was characterized post-M41S as “not being realized at that time” (*i.e.* when made and/or announced). The first case, a 1971 patent, concerns a material obtained by the reaction of tetraethylorthosilicate with cetyltrimethylammonium cationic surfactant and reported with limited characterization. The nature of the resultant product is obscure. However, the example was repeated in 1997, with the benefit of M41S knowledge, and deemed to have been a mesoporous material.

The second case is the 1989 study of layered silicate kenemite expansion with alkyltrimethylammonium surfactant at high pH,<sup>33</sup> which appears to be contemporaneous with the discovery of M41S. It can be interpreted as involving the dissolution of the layered silicate and formation of the hexagonal phase by liquid crystal templating like MCM-41 as we suggested.<sup>34</sup> However, an alternative explanation, the Folding Sheet Mechanism was proposed for this case,<sup>33</sup> but it explains only the formation of hexagonal material and not the entire family of mesoporous molecular sieves.

When considering the discovery timeline and the 1992 publication by Mobil, one must take into account that the first date of patent filing was January 25, 1990 (*i.e.* over two years before the disclosure)<sup>3</sup> and the actual studies had to be carried out much earlier. As shown in Fig. 2, we believed, from the onset, that we had formed an ordered mesoporous molecular sieve and our conclusions cited in our initial publications remain valid even after 20 years.

Looking historically we can clearly see, in hindsight, the initial work leading to and producing M41S family as progressing in two directions: one, the fast track explosive development of the ordered mesoporous materials that attracted enormous effort throughout the world creating a separate area, and the second, a slow evolution of what we now refer to as 2-D zeolites.



In fact, the two areas seemed to come together again in the form of a layered form of zeolite ZSM-5 being obtained by design of a special type of surfactant molecule.<sup>35</sup> Even more important is the fact, mentioned above, that the last program may have succeeded with reaching the original, till now unfulfilled original target: preparation of mesoporous materials with zeolite walls.

One more area that advanced tremendously, in both theory and practice, with the discovery of M41S materials, was adsorption and characterization of pore structures. The OMMs were found immediately very exciting to study as 'model adsorbents' exhibiting unprecedented adsorption characteristics with capillary condensation.<sup>36</sup> To address specific challenges like accurate pore size determination, pore connectivity and new isotherm and hysteresis loop profiles great progress has been made.<sup>37</sup> M41S were mainly aluminosilicates and AlPO materials templated with cationic surfactants although many-element encompassing compositions were claimed. This was extended to all types of common surfactants *i.e.* anionic, neutral, and zwitterionic. Pore sizes expanded from initial max of 10 nm to 30 nm. This expansion culminated with meso-cellular foams (MCF's) having around 90% void volume, similar to Xerosils, but with a well defined structure and narrow pores judged from nitrogen isotherm profiles.<sup>38</sup> New well defined structures, based on crystallographic symmetry, were synthesized and increased the mesoporous structures from the initial three. At the same time, diversity increased as exemplified by SBA-15 with micro- and meso-pores. Numerous compositions have been documented including alumina based OMM's, which may be particularly valuable for catalysis.<sup>39</sup>

On the synthesis side we believe two additional events merit mentioning. One is the commercial, *i.e.* large scale synthesis of MCM-41, described in more detail elsewhere.<sup>12</sup> It is notable as proving practical and economic viability of the mesoporous materials. The second is simple synthesis of the intriguing cubic material MCM-48, which initially used rather exotic reagents. In the end, it turned out to be possibly commercially viable using common reagents under conditions similar to synthesis of MCM-41.<sup>40</sup>

## Acknowledgements

We are grateful to the management and technical staff of Mobil Research and Development Corp. for their support, encouragement and contributions to this work. Among numerous contributions we would like to highlight the expert work of technicians K. Simmons and D. T. Geston. W. J. Roth wants to acknowledge the present support from the Grant Agency of the Czech Republic (Centre of Excellence – P106/12/G015).

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