

Zeolites: physical aspects and environmental applications

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Research into zeolites continues apace, both in a search to elucidate their fundamental properties with the view to synthesising specifically-tailored materials for particular applications, and in finding new applications from the considerable existing knowledge about these important and remarkable materials, especially in relation to providing cleaner (“green”) processes with less impact on the environment, and in environmental remediation strategies. Advances in theoretical methods are likely to play an increased role in predicting the features and synthetic viability of modified and novel zeolite structures. As pressure mounts on the World’s finite and dwindling supplies of hydrocarbons—obtained mainly from crude oil (and increasingly from coal and natural gas)—developments in the use of zeolites as catalysts to render known hydrocarbon cracking and oxidation chemistry more efficient, and the discovery of new catalytic processes, involving zeolites, both for the procurement and modification of hydrocarbons are to be expected.

1. Introduction

“La Roca magica”, so printed a Cuban newspaper,¹ in applaud of one of its country’s greatest mineral resources—*Zeolites*. The first zeolite was identified in 1756 (marking last year as its 250th anniversary) by the Swedish mineralogist (Baron) Friedrich Axel Cronstedt, who observed that on heating the stones he had gathered, in a blow-pipe flame, they danced about in a froth of hot liquid and steam, appearing as if the stones themselves were boiling. He thus coined the name “zeolite” which from Greek derivation (*zein*, “to boil”; *lithos*, “a stone”) means “stones that boil”.² The phenomenon he observed provides a vital clue to an essential property of zeolites, which is their ability to absorb a substantial proportion—perhaps half their own volume, depending on the type of zeolite—of water, and indeed of other liquids. Zeolites are aluminosilicates whose essential structure consists of a negatively charged “honeycomb-like” framework, containing (micro)-pores of molecular dimensions, normally less than 13 Angstroms (1.3 nanometres) in diameter. The pores contain sufficient (positively charged) cations to neutralise the framework electric charge, but these are loosely bound and may be exchanged with other cations from solutions placed in contact with the zeolite.³ This combination of features confers particular properties upon zeolites and from which unfold a wealth of applications for them. Four million tonnes of natural zeolites are mined annually, of which 2.5 million tonnes are shipped to China, mainly to make concrete to supply a burgeoning construction industry as the country undergoes an unprecedented

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phase of industrialisation.⁴ There are 48 different types of zeolite known to occur naturally, while another 150 or so have been artificially synthesised.⁵ Synthetic zeolites can be engineered with a selectivity to perform specific tasks, and they are in any case of a more homogeneous composition than their naturally occurring counterparts. A good example of a tailored zeolite is H-ZSM-5. It is designated “H” because it is the hydrogen (proton) exchanged form that is referred to, “ZSM” because these are the initial letters of the surnames of the three scientists who created the framework material, and “5” because it was the fifth attempt that worked, attesting to the often serendipitous nature of zeolite synthesis. H-ZSM-5 was introduced⁶ by Mobil in the 1970’s to catalyse the “methanol to gasoline” (MTG) process, in which it cracked methanol (an organic compound with just one carbon atom) into hydrocarbon mixtures (generally of compounds containing 6 to 9 carbon atoms) which are suitable for combustion in internal combustion engines. H-ZSM-5 is also used on a large scale for the selective production of *para*-xylene, which is oxidised to terephthalic acid and then esterified with glycols to make “polyesters” for the clothing industry.⁴

For environmental applications, it is preferable to use a natural zeolite which can be mined (ideally locally to minimise transportation requirements) and used with the minimum of processing: just crushing the raw material into a powder may be all that is needed. Natural zeolites are produced by the forces of volcanism, and are often associated with mountainous regions, *e.g.* the Caucasus and the Balkans, while there are also deposits found in the Himalayas and in Switzerland, and in the US around the Gulf of Mexico (including Cuba), which has a volcanic history. Essentially, the force of molten magma, which pushes up mountains can escape through a volcanic vent and the volcanic rocks (solidified lava) and ash layers that are produced may transform (crystallize) into a zeolite by contact and reaction with alkaline/saline lake or ground-waters. Beds of zeolite may be hundreds of meters thick. Zeolites have also crystallized in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins, and are found in some ocean sediments.³ Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential. Some of the more common mineral zeolites are: analcime, chabazite, heulandite, clinoptilolite, natrolite, philipsite and stilbite. Stilbite is the modern classification of the mineral originally discovered by Cronstedt.² An example mineral formula is: $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$, which is that for natrolite.

As noted the applications of zeolites are manifold, of which the following list is merely illustrative:^{1,3-9}

- Cation exchange: radioactive decontamination, *e.g.* removal of Sr^{2+} and Cs^{+} from “dump waters” of nuclear power stations; industrial “water softeners”, to prevent lime-scale blocking up cooling pipes in manufacturing facilities; removal of heavy metals from the environment, *e.g.* lead, zinc, copper, mercury, cadmium.
- Use of zeolites as a “builder” in detergents, to remove and encapsulate Ca^{2+} and Mg^{2+} cations which make water “hard”, rather than polyphosphates. Around 1.4 million tonnes of zeolite A is synthesised annually for this purpose. This avoids the “algal-bloom” effects of pollution by phosphates which were formerly used on a similarly large scale in detergent formulations.^{4,5}
- Anion absorption. Environmental contamination by toxic anions may also be removed, by reaction with heavy metal cations previously exchanged into the zeolite,

e.g.: Ag^+ -zeolite + Na^+ + $\text{I}^- \rightarrow \text{Na}^+$ -zeolite + AgI (precipitated). In this example, a silver exchanged zeolite can be used for removing radioactive iodine (iodide ions) in the form of insoluble AgI , which is both formed and contained within the zeolite pores. When it is saturated, the material may be removed for disposal. The principle may be adapted for the management of other toxic anions: *e.g.* cyanide, arsenic (both arsenite and arsenate), chromate, molybdate and others.

- Molecular sieves: small pore zeolites selectively absorb small polar molecules, *e.g.* water, and so zeolite “molecular sieves” are highly efficient drying agents for removing traces of water from other solvents.

- Hydrocarbon sieving: linear *n*-alkanes (needed for detergent manufacture) can be separated from branched alkanes, since the former pass more slowly through a column packed with zeolite 5A in consequence of their preferential absorption within the zeolite pores, which results in a more tortuous passage through the material. Millions of tonnes of *n*-alkanes are produced annually by this method.

- H^+ exchanged zeolites (*e.g.* H-ZSM-5) are used as solid acid catalysts, *e.g.* for “cracking” in the petrochemical industry.

- Medical applications: Hemosorb and QuikClot are commercial products based on zeolites which when applied to wounds (in accidents or surgery) are said to cause an “instant” cessation of bleeding. Zeolites are also used in kidney dialysis machines, to absorb ammonia from blood and prevent it from building up in the body (a job that healthy kidneys normally do).

- Agriculture: for supplying K^+ and NH_4^+ to plants from soils that have been enriched with zeolites exchanged specifically with these cations. It is suggested that such “zeoponics”, as the strategy is called, might be used to grow food on long space missions.

- Separation of gases: there are commercial units that can provide oxygen of 95% purity for use in hospitals or for patients *e.g.* suffering from emphysema and other forms of Obstructive Pulmonary Disease (OPD), by separating it from air. Nitrogen (80% of air) is preferentially absorbed over oxygen because of its much larger molecular electric quadrupole moment, and so enables oxygen to separate from air almost in a state of purity.

- Use in more efficient heating systems. Essentially, the adsorbed water can be driven out of a zeolite by heat, but when the water is readsorbed, heat is given out. The principle can be incorporated into a heat-pump system which uses more of the available energy for actual heating, most of which would otherwise be wasted.

- Desulphurisation of diesel: *e.g.* Ni^{2+} exchanged zeolites have been demonstrated to absorb sulphur compounds from diesel in accord with an aim to reduce “acid-rain” emissions from transportation.

- Reduction in NO_x emissions from vehicles, using zeolite-loaded “catalytic converters”.

- Use of natural “tuff” as a light-weight building material, since the rock is soft enough to be cut with a hand saw and durable in fairly dry climates, or it can be fabricated into light-weight cements, *e.g.* in China which consumes 2.5 million tonnes of zeolite per annum for this purpose.

Zeolites are also effective in remediation strategies, *e.g.* around 500 000 tonnes of zeolites were used in the clean-up after the nuclear power plant disaster at Chernobyl, which involved monopolising virtually every zeolite production facility in the entire former USSR. Zeolites were fed to cattle in an effort to keep the radioactive ions out of the milk, and were baked into bread and into biscuits (cookies) for children similarly in an effort to minimise radioactive contamination in

humans.^{4,7} Zeolites were also used (albeit on a smaller scale since the problem was far more contained) at “Three Mile Island” a decade or so before Chernobyl. Contaminated, *e.g.* Brown Field land may be rendered fit for building and even for agriculture by treating the soil with sufficient quantities of zeolites.^{1,4} In accord with such an importance for zeolites, the published literature on them is huge. In the period 1945–2006, “Web of Science” has identified 40 236 papers under the heading “zeolite*”, and a closer examination demonstrates the very rapid growth in the field, with just 14 papers published during (1945–1954), 19 (1955–1959), 90 (1960–1964), 1667 (1977–1981), 2370 (1982–1986), 3532 (1987–1991), 7902 (1992–1996), 10 537 (1997–2001), 12 205 (2002–2006), with 2518 published in the year 2006, alone. In view of the relevance of zeolites to environmental applications and in fuel and energy production (surely the greatest challenge to the world currently), it seems likely that research into zeolites will continue to rise in effort, although perhaps less in the fundamental “blue skies” fields of their properties, and more into working their practical usefulness. A recent broadcast of the programme “Material World” considered some aspects of zeolites and their applications.⁸ A recent review was published on the subject of free radicals adsorbed on reactive surfaces, and their role in reactions catalysed by solid materials including zeolites.¹⁰ The coverage of the zeolite literature herein is therefore selective, in view of its extensiveness and diversity, however, it is intended to touch on many of the more important aspects and applications of these materials, especially in relation to the environment, emphasising particularly papers published during the period 2005–2006.

2. Studies of gases adsorbed in zeolites

Here we are concerned mainly with the adsorption of homonuclear diatomic gases such as H₂, O₂, N₂. It is unexpected that these molecules would show infra-red absorption spectra since they possess no permanent electric dipole moment. Put another way, the electronic centre of gravity and the molecular centre of mass are coincident. However, it has been known since 1953¹¹ that the application of an external electric field to dihydrogen could induce IR absorptions from it. It was Forster and co-workers who first reported crystal-field-induced transmittance spectra of hydrogen adsorbed in Na-A and NaCa-A zeolites at low temperatures.^{12,13} The influence of the applied field is to polarise the molecule thus displacing electron density from the centre of mass and inducing a dipole moment which classically can couple with the electromagnetic radiation field, resulting in the absorption of IR frequencies that correspond to the stretching mode of the polarised molecule. In general, there is a shift to frequencies lower than those measured for the unperturbed molecules from their Raman spectra. In some cases,¹⁴ satellite bands are observed symmetrically displaced from the main absorption, believed to arise from the translational motion of hydrogen molecules parallel to the walls of the cavities. Rotational structure has been seen too, both on the fundamental and overtone bands from H₂ adsorbed in various zeolites using an IR diffuse reflectance method, which permits a relatively high spectral resolution to be obtained. In zeolite Na-Y, a splitting of frequencies of 5.8 cm^{−1} from *ortho* and *para* hydrogen isotopes was detected on both fundamental and overtone bands.¹⁴ Molecular hydrogen was also employed as a simple molecular probe for the localisation sites of cations in zeolites A, X, Y, ZSM-5 and mordenite, as adsorbed at 77 K. It was found that the degree of the H–H bond polarisation, estimated from the size of the low-frequency shift of the fundamental H–H stretching vibration in perturbed H₂ molecules, was

strongly dependent on the basicity of the neighbouring framework oxygen atoms, and hence not only is the nature of the cation and the site of its location important but also the structure of the zeolite framework in determining the coordination of the molecular probe.¹⁵ In a related study of zeolites A, X and Y, different frequencies were measured from a distribution of complexes in the various exchanged zeolites, and it was found that the H–H stretching frequencies depended strongly on the charge of the cations. For alkaline-earth metal cation (Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) exchanged forms of high-silica zeolites the frequency shifts were found to correlate well with the polarising power of the cations. The importance of any “hydrolysis” of the cations, *i.e.* the reaction $\text{M}^{n+} + \text{H}_2\text{O} \rightarrow \text{M}(\text{OH})^{(n-1)+} + \text{H}^+$, in determining the extent of hydrogen polarisation is emphasised.¹⁶ Various weakly interacting molecular probes have been used to characterise the acid and base sites in zeolites, as observed by FTIR spectroscopy. Bronsted acidity can be determined by the effect of hydrogen-bonding (to the probe molecule) on surface O–H frequency shifts when N_2 and CO are employed as the probes. Additionally, shifts in the C–O stretching frequency are found which generally parallel those of the O–H groups. In the case of N_2 , the interaction induces an absorption by the molecule which provides information as to its nature. Theoretical calculations were done to clarify the type of adsorption interaction and the effect of it on the vibrational properties of the particular probe molecule. In zeolites exchanged with small cations like Li^+ and Na^+ , Lewis acidity was found to dominate the process, and as the cation increased in size, more basic properties were found to develop. In all cases of CO, CO_2 , N_2 and CH_4 interacting with cations in zeolites, the interaction energy was found to decrease as the cation radius increased, in accord with the fall in polarising power (e/r) of the cation. At very low equilibrium pressures of CO, the siting of Na^+ cations and the Al (Lewis site) distribution in the six-rings (S_{II} -sites) could be investigated; CH_4 was found to interact with cations in a C_{3v} -symmetric configuration of the kind $\text{M}^+ \cdots \text{H}_3\text{CH}$. It is also shown that there is a potential use for C–H acids such as Cl_3CH (Cl_3CD), acetylene and methylacetylene as a probe for base sites at zeolite surfaces, on the basis of observed C–H frequency shifts when adsorption has taken place.¹⁷

There is an adaptation of the general method, and that is variable-temperature I.R. spectroscopy, which can be turned usefully to the determination of the thermodynamics of weak gas–solid interactions, as has been well described in a recent tutorial review of the topic.¹⁸ By equating the van't Hoff equation with the Beer Lambert law and the Langmuir isotherm, by measuring the temperature dependence of the intensity of an IR band characteristic of the adsorbed state (the band becomes more intense as the temperature is decreased), the enthalpy, ΔH and entropy, ΔS for the equilibrium between the gas-phase and adsorbed state of a probe molecule can ideally be determined. A good example is the adsorption of N_2 on H-ZSM-5. As a general rule, zeolites in their proton exchanged form show absorption bands from O–H groups associated with Bronsted sites $\text{Si}(\text{OH})\text{Al}$. These bands appear in two frequency ranges, 3650–3600 and 3580–3530 cm^{-1} : the higher wavenumber range corresponds to Bronsted acid O–H groups located inside large cavities while the lower range is from O–H groups vibrating in smaller voids. More often than not, adsorbed molecules are not permitted access to the smaller cavities (formed by rings of lower than eight members). When N_2 is adsorbed into H-ZSM-5, the band at 3616 cm^{-1} from Bronsted acid sites begins to decrease in intensity while the band from silanols at 3747 cm^{-1} is barely affected; however, a new broad band is detected from hydrogen-bonded $\text{OH} \cdots \text{N}_2$ complexes at around 3500 cm^{-1} ,

simultaneously with the activation of the N–N stretching vibration at 2331 cm^{-1} . From the temperature dependence of these changes, values¹⁸ of $\Delta H = -19.7(\pm 0.5)\text{ kJ/mol}$ and $\Delta S = -125(\pm 0.5)\text{ J/mol/K}$ were obtained for the enthalpy and entropy of adsorption for N_2 on H-ZSM-5 in good accord with the heat of adsorption of -19 kJ/mol that may be deduced from microcalorimetry measurements¹⁹ for this system. It is interesting that density functional theory (DFT) calculations²⁰ for the interaction between N_2 and $\text{H}_3\text{Al}(\text{OH})\text{AlH}_3$ cluster model Bronsted acid site predict an interaction energy of -10.6 kJ/mol , appreciably less than the -19.7 kJ/mol estimated experimentally; however it is important to note that the acidity of the OH group in the cluster model is substantially reduced from that of actual Bronsted acid sites in zeolites.²¹ When molecular hydrogen is adsorbed in alkali-metal cation exchanged zeolites at 77 K , a main adsorption band is observed in the region $4070\text{--}4100\text{ cm}^{-1}$, and corresponds to the fundamental H–H stretching mode of the adsorbed H_2 molecule. The presence of cations and their neighbouring framework oxygen atoms provide centres for adsorption of H_2 with the additional effect that the vibrational frequency is reduced from the 4136 cm^{-1} Raman-active band measured for the free molecule in the gas phase. Values of $\Delta H = -10.3(\pm 0.5)\text{ kJ/mol}$ and $\Delta S = -121(\pm 10)\text{ J/mol/K}$ were obtained for H_2 adsorbed in Na-HSM-5.²² The enthalpy of adsorption here may be compared with the enthalpy for the liquefaction of hydrogen, which at a temperature of 20.45 K is -0.9 kJ/mol . Thus, the much larger energy involved in confining H_2 in the zeolite than in liquid hydrogen offers promise that zeolites might be used as storage media for hydrogen, as we discuss in the section immediately following. The value of $\Delta H = -10.3(\pm 0.5)\text{ kJ/mol}$ for H_2 in Na-ZSM-5 can be compared with its equivalent of $\Delta H = -6.5(\pm 0.5)\text{ kJ/mol}$ for H_2 in Li-ZSM-5²² and $\Delta H = -9.1(\pm 0.5)\text{ kJ/mol}$ for H_2 in K-ZSM-5.²³ A useful comparison may be made between the entropy change on adsorption on Na-ZSM-5, $\Delta S = -121(\pm 10)\text{ J/mol/K}$, and the absolute entropy for dihydrogen of 163 J/mol/K at a temperature of 100 K and a pressure of 1 mm Hg (conditions comparable to those under which the variable temperature IR measurements were made in zeolites). Thus the standard entropy of the adsorbed phase is about 40 J/mol/K , and this is consistent with a considerable freedom for the adsorbed molecules, probably arising from the conversion of translational modes (gas) to low-lying vibrational modes (of surface “bonds”) and the preservation of a considerable degree of rotational freedom.¹⁸

2.1 Hydrogen storage in zeolites

In an effort to address the twin-problems of dependence of nations upon imported hydrocarbon fuel and forcing climate change through global warming induced by emissions of CO_2 from burning fossil fuels, hydrogen is being investigated as a clean, carbon-free fuel that could be made on a national (or regional) basis.⁴ However, hydrogen is not actually a “fuel” but an energy carrier. That is to say that hydrogen is not available in an aboriginal form as are oil, coal or gas, (which are known as “primary fuels”), but rather it must be “made” by some artificial means. Most of the hydrogen currently used in the world (mainly for chemical purposes, such as the wholesale manufacture of ammonia for fertilisers and oil refining) is produced from natural gas by a process known as “steam reforming” sometimes with the use of a zeolite as a catalyst or to separate²⁴ the carbon monoxide formed when the carbon is “extracted” from methane by its reaction with steam: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$, or to separate carbon dioxide when that CO is used to squeeze-out another molecule of H_2 by adaptations of the “water-gas shift reaction”: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$.

Zeolites are also used more generally to remove CO₂ from natural gas.²⁴ Ideally, hydrogen should be “green”, *i.e.* made by electrolysis of water using electricity produced from renewable sources, *e.g.* wind power, but it is arguable that those electrons would be more effectively used in forms of battery technology for driving vehicles and other electrical appliances. Nonetheless, efforts toward the putative hydrogen economy continue, and of greatest concern is the development of materials in which hydrogen might be effectively stored, including zeolites.⁴ A major advance has been made, which it is proposed may help address the vexed problem of storing hydrogen on the enormous scale which will be required if it is to be used to power vehicles to any significant extent. Researchers in Spain²⁵ have found that a zeolite-Y partially exchanged with magnesium cations (Mg²⁺) has an unprecedented high adsorption enthalpy of -17.5 kJ/mol, which is close to the value of -15 kJ/mol recently proposed as optimum²⁶ for a material that will efficiently both bind and release H₂ according to the demand of its supply: *i.e.* the gas should neither be too strongly adsorbed otherwise it will not be released in a “fuelling station” situation, nor too weakly adsorbed otherwise the material is ineffective for storing it in the first place. The effect is attributed to the high polarising power (e/r) of Mg²⁺ cations. The effect of polarisation both induces an IR active vibration from adsorbed H₂ and reduces the fundamental H–H stretching frequency from 4163 cm^{-1} measured by Raman spectroscopy in the gas phase for unperturbed molecules, in this case to 4056 cm^{-1} . The value of -17.5 kJ/mol is significantly greater than those previously reported for the adsorption of H₂ in alkali-metal cation exchanged zeolites,^{22,23,27} and is around 20 times higher than the liquefaction enthalpy of H₂ of -0.9 kJ/mol (at 20.45 K). Nonetheless, there does remain the issue of exactly how much hydrogen can be imbibed by a zeolite for practical purposes. For commercial applications, an acceptable energy density for a hydrogen storage tank is deemed to be that it can efficiently hold an amount of hydrogen equal to 6.5 wt% of the weight of the tank and 62 kg H₂/m³ in terms of volume.^{27,28} However, although investigations of hydrogen storage methods have been carried out for over 30 years, there has been no single method devolved which fulfils these demanding criteria. Some approaches meet the weight target, but occupy unsatisfactorily large volumes (*e.g.* tanks of compressed hydrogen gas) yet others achieve the volume target but not the weight ratio (*e.g.* metal hydride absorbents). To approach the matter from a theoretical perspective, a molecular mechanics study has been made of the thermodynamic limits on hydrogen storage in sodalite framework materials, built up from TO₄ (where T = Al, Si, Ge, P) tetrahedra.³⁰ It is concluded that cation-free sodalite structures could accommodate eight hydrogen molecules per cage as an optimum loading, at which point the density of the hydrogen is almost equal to that in liquid hydrogen, and the calculated limiting useful density of 65 kg H₂/m³ can be achieved, at least theoretically, for most structures based on sodalite. For pure liquid hydrogen the figure is 70.8 kg H₂/m³ which is the normal density of the liquid at a temperature of 20.28 K. However, to liquefy hydrogen costs around 30% of the energy that might be recovered from the material as a fuel.³¹ There is however a considerable discrepancy between the loading of H₂ into a sodalite found experimentally,³² 0.26 and 0.4 wt% for all-Si (Si₉₆O₁₉₂) and AlP (Al₄₈P₄₈O₁₉₂), and the calculated³⁰ capacities of 4.8 and 5.2 wt%, respectively. However, the theoretical maximum capacities are based solely on energetic considerations, and do not address effects such as ions, water or other impurities that might act to block access to part of the internal volume of the sodalite crystals. There is also no influence of entropy included in the calculations which are in effect performed at zero Kelvin. In an

extension of the theoretical work, adsorption isotherms of H_2 in various sodalite materials were calculated using a grand canonical Monte Carlo method.³³ It is concluded that at loading capacities of technical interest, 573 K and 100 bar, a storage capacity of around 0.1 wt% might be achieved for each type of sodalite structure. However, the really technologically desirable capacities of above 4% are likely to only be met under conditions of extremely low temperature and/or extremely high pressure.³³ The results make an interesting comparison with theoretically estimated maximal storage capacities for hydrogen in zeolitic materials. In effect, the adsorption can be thought of as a facilitated liquefaction, where the solid–gas interaction causes condensation at conditions of temperature and pressure that are more convenient than those required to form the bulk liquid. One such study³⁴ was made which used the force-field method and performed its calculations within the *Discover* module of the Materials Studio 2.2 package of Accelrys Inc.³⁵ The progressive filling with H_2 of twelve purely siliceous models of common zeolite frameworks was simulated in order to determine the effect of framework properties including flexibility on the maximum adsorption capacity for hydrogen. It was deduced that the flexible non-pentasil zeolites (RHO, FAU, KFI, LTA and CHA)⁵ show the highest maximal capacities, in the range 2.65–2.86 wt% of H_2 . The predicted adsorption capacities were found to correlate well with experimental results obtained at low temperatures (77 K), but these materials are well below the 6.5 wt% target value set for hydrogen storage in a practical device. The zeolite chabazite (CHA) has received particular attention in its context as a potential material for storing H_2 since it was rated as having the largest capacity of any zeolite in this regard.^{31,36} For a H-exchanged (protonic) chabazite, H-SSZ-13 (Si/Al = 11.8), an absorption capacity of 1.28 wt% was determined at 77 K, slightly above that for zeolite-A at 1.24 wt% and for H-CHA itself (Si/Al ratio = 2.1) at 1.10 wt%.³¹ The hydrogen is described as “liquid hydrogen” in the zeolite, and it is shown that the available volume of a chabazite (H-SSZ-13) cage can contain seven hydrogen molecules at the density of liquid hydrogen. Actually in the zeolite, the results indicate that at 77 K, 57 K above the boiling point of liquid hydrogen, about five hydrogen molecules are confined to each cage. This implies that conditions close to liquefaction are achieved when hydrogen is adsorbed into H-SSZ-13 zeolite at 77 K, a result of sufficient importance that the paper was published in JACS.³¹ The point was investigated further by similarly measuring the volumetric uptake of H_2 at 77 K and a transmission IR measurement of H_2 absorption at 15 K, in H-SSZ-13, (the isostructural silico-aluminophosphate material with the same Bronsted site density) H-SAPO-34, and H-CHA itself. It was found there is an improvement in H_2 uptake when the acid strength of the Bronsted sites is increased (moving from H-SAPO-34 to H-SSZ-13), while conversely, increasing the density of Bronsted sites (moving from H-SSZ-13 to H-CHA) impacts negatively on the adsorption process. The latter result is quite counter-intuitive but an explanation is offered that the additional Bronsted sites are in mutual interaction *via* H-bonds inside the small cages of the chabazite framework and for most of them the energetic cost of displacing the adjacent OH ligand is higher than the adsorption enthalpy gained in forming the $OH \cdots H_2$ complex.³⁶ The record set by H-SSZ-13 for a hydrogen storage capacity in a zeolite of 1.28 wt%³⁶ at 77 K and one atmosphere pressure of H_2 gas has been broken using low silica type-X zeolites (LSX, Si/Al = 1) fully exchanged with alkali-metal cations (Li^+ , Na^+ , K^+).³⁷ Hydrogen adsorption isotherms were determined separately at 77 K and a pressure of <1 atm, and at 298 K and <10 MPa (about 100 atm). It was found that the adsorption capacity of

the zeolite depended strongly on the radius of the exchange-cation and on the density of cations located on the exposed sites. As expected, the interaction energies between H_2 and the cations follow the order $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, in order of the increasing cation radii: 0.068, 0.097, 0.133 nm, respectively. Li-LSX had an adsorption capacity of 1.5 wt% at 77 K and 1 atmosphere pressure, and a capacity of 0.6 wt% at 298 K and 10 MPa pressure, which places it among the best of known sorbents for H_2 . The possibility of enhancing the uptake of H_2 by bridged hydrogen spillover was also investigated, for which a simple and effective method was found to construct carbon bridges between the dissociation catalyst and the zeolite to facilitate spillover of hydrogen atoms. By this means, the hydrogen storage capacity was enlarged to 1.6 wt% (*i.e.* by a factor of 2.6) at 298 K and 10 MPa pressure of hydrogen gas. This is by far the greatest hydrogen storage capacity achieved using a zeolite material at ambient temperature.³⁷ A theoretical study was made of the hydrogen adsorption isotherms for a range of clathrasil frameworks. A clathrasil is a framework with Si_6O_6 as its largest ring aperture. The properties were calculated for twelve known clathrasils and seven hypothetical energetically stable versions. Under all conditions of temperature and pressure, high adsorption energies were predicted for small volume cages ($< 400 \text{ \AA}^3$) in consequence of the larger contact area between the cage wall and H_2 . Nonetheless, the H_2 loading into the material is quite low because of the large internal surface-to-volume ratio which leaves little void space for the H_2 molecules to occupy. It is concluded that clathrasils are unlikely to become of any use in practical hydrogen storage applications.³⁸ An experimental study has been reported of the physisorption of H_2 into zeolite types A, X and ZSM-5 under moderately high pressures of 2–5 MPa. The highest storage capacity found was 2.55 wt% for Na-Y zeolite at 77 K and 4 MPa pressure. In CaA, NaX and ZSM-5 zeolites, the hydrogen uptake was found to be proportional to the specific surface area of the adsorbent, and which were associated with the available void volumes of the zeolites.³⁹

In conclusion, the prospect of using zeolites for practical hydrogen storage appears limited. More promising appear to be certain zeolite-templated porous carbons, and for one example a hydrogen uptake of 4.5 wt% and 45 g/L weight and volumetric densities, respectively, were reported at 77 K and 20 atmospheres (2 MPa) pressure.⁴⁰ Still greater capacities for H_2 are reported for porous coordination-framework materials giving uptakes of up to 6 wt%, at 78 K and pressures less than 20 atm., which are therefore likely to receive further attention as potential candidates for practical hydrogen storage systems.⁴¹ I conclude this section by noting one paper⁴² entitled “Hydrogen Storage: The major technological barrier to the development of hydrogen fuel cell cars”, which provides a useful survey of the whole contentious business. I would also recommend the *wikipedia* entry on hydrogen storage.⁴³ However hydrogen might be used, either as a pure substance or as adsorbed into zeolites or other porous materials, the energy costs of cryogenic cooling and compression must be born and factored into the energy balance equation for the hydrogen economy.

3. Studies of diffusion in zeolites

A combination of pulsed field gradient (PFG) NMR and quasi-elastic neutron scattering (QENS) has been exploited to improve the measurement of the diffusion of *n*-alkane homologue molecules, up to *n*-tetradecane, in MFI-type zeolites. It is found that the diffusivities are of an intermediate magnitude between those measured for NaCaA and NaX zeolites, and in order of their respective pore

diameters. As is the case for the zeolite NaA, the diffusion rates decrease in a monotonic fashion as the carbon chain length increases, which contrasts with the behaviour of *n*-alkanes adsorbed into NaCaA where there is a striking departure from this trend for chain lengths of six carbon atoms and above. While there is a general agreement found between the two techniques, the diffusivities measured by PFG NMR are up to one order of magnitude smaller than those determined using QENS. This apparent disparity is explained by the difference in motional “distance” that is accessed by these methods: PFG NMR monitors molecular scale displacements of an order typically of microns (10^{-6} m), and so can reflect additional transport resistances and diffusion barriers imposed throughout the entirety of the zeolite grain, which are of no consequence for QENS since it measures excursions of molecules over far shorter distances.⁴⁴ Two recent developments of the PFG NMR technique have been presented with the view to measuring the diffusion of molecules in multi-component liquids adsorbed into zeolites. Such an approach is of particular importance since in essentially all technical applications involving zeolites, the zeolite comes into contact with a system that is a mixture of components rather than with a single substance. The methods include options for enhancing the sensitivity with respect to displacements over smaller dimensions by a novel principle of field gradient pulse matching and with respect to selectivity between different components by combining PFG NMR with magic angle spinning MAS NMR with a micro-imaging gradient system. The diffusion coefficients were determined for ethane, ethene, water and benzene adsorbed in zeolite NaX, and the results are compared with those measured previously for these materials present in simpler adsorbed systems.⁴⁵ The energetic and entropic contributions controlling the adsorption of benzene on acidic (H/ZSM-5) and non-acidic (Silicalite-1) MFI type materials have been studied using gravimetric and calorimetric methods and *in situ* IR spectroscopy with the aim to follow both qualitatively and quantitatively the interactions of benzene with the pores and the functional Si(OH) and Si(OH)Al groups within the structure. The model derived to describe the adsorption isotherms indicates that there are sterically constrained adsorption sites for benzene in MFI type materials. The interaction between benzene molecules and the pore walls mainly controls the adsorption energetics, while the localized interaction with the bridging hydroxyl groups is of only minor importance. If benzene is located close to Si(OH)Al groups a perturbation in their stretching frequency is observed which reflects the local adsorption geometry of benzene molecules in addition to the acid strength of the OH group and the base strength of benzene. Two kinds of OH perturbation were observed and are assigned to two orientations of the benzene molecules inside the pores: *i.e.*, one with the ring parallel to the pore wall and another with the ring being oriented towards the bridging OH groups. At higher coverage, benzene adsorbs at Si(OH)Al groups additionally in an unconstrained environment, most probably at the openings of the pores.⁴⁶ Measurements of transport diffusivities for perdeuterated benzene in NaX zeolite have been reported from neutron spin-echo results. Corrected diffusivities were obtained in order to facilitate comparison with recently reported molecular dynamics simulations. The experimental diffusivities were measured with benzene loadings of 1, 2, 3 and 4.5 molecules per NaX cage, and at temperatures of 300, 350 and 400 K. It was found that both corrected and transport diffusivities increase as the loading increases from 1 to 3 benzene molecules per cage, then decrease sharply when an average of 4.5 molecules are present in each cage. There is an excellent accord met between the experimental and simulated results in terms both of the loading dependence and in the overall magnitudes of the corrected

diffusivities, which are mostly in the range 10^{-12} – 10^{-11} m² s⁻¹.⁴⁷ The heat capacity behaviour of benzene and hexafluorobenzene confined in the pores of NaY zeolite has been determined, both for the individual components and as a 1:1 binary mixture of them.⁴⁸ Both these molecules are planar and non-polar, with molecular electric quadrupole moments of comparable magnitude⁴⁹ but opposite sign (-29 C m² for benzene and $+31.7$ C m² for hexafluorobenzene). They melt at the same temperature to within half a degree C, and have exactly the same boiling point of 80.2 °C. The heat of vapourisation is the same for both too, while the heat of fusion for C₆H₆ is 86% that for C₆F₆. Strong loading dependencies were found, and extremely large heat capacities were determined at intermediate loadings which indicates a situation in which more energy levels become rapidly accessible after a first energy gap has been overcome. This might be expected if excitation of shallow (“soft”) highly anharmonic modes of the adsorbate species occurs. In the adsorbed 1:1 mixture of C₆H₆ and C₆F₆ the heat capacity is dominated largely by intramolecular interactions between C₆H₆ and C₆F₆ molecules, rather than by their interactions with the zeolite. There is a notable absence of phase transitions observed over a large range of temperature and loading, which significantly is reminiscent of the behaviour of supercritical fluids.⁴⁸ Another paper attempts to clarify the ostensibly different diffusion behaviour of alkanes adsorbed in zeolites that may be deduced depending on the particular technique employed to measure it. It is shown that when various data-sets reported in the literature are corrected for the loading of the alkane employed in their determination, a much closer correspondence is obtained between them.⁵⁰ The zero length column (ZLC) method has been applied in the investigation of the diffusion of linear alkanes (*n*-hexane to *n*-tetradecane) in zeolite NaCaA. The diffusivity values are found to decrease monotonically with increasing chain length from *n*-hexane to *n*-undecane, to increase slightly on going from *n*-undecane and *n*-tridecane, and finally level-off at *n*-tetradecane. The values measured are in fair accord with results obtained from PFG-NMR measurements, but do not show the marked pronounced maximum found in a recent neutron spin echo study. An explanation for a difference between the infinite dilution ZLC data and the microscopic techniques cannot be found in terms of the intrusion of surface resistances since partial loading experiments provide clear evidence that the measurements are controlled by internal diffusion. It is concluded that the activation energies for the diffusion of linear alkanes in NaCaA all lie in the range 20–26 kJ mol⁻¹.⁵¹ New QENS data are available for the self-diffusion of normal alkanes up to hexadecane in silicalite. Measured diffusivities at 300 K are higher than are those in Na-ZSM-5 and agree with the predictions of molecular dynamics and a hierarchical transition-state theory/ Brownian dynamics calculations made for the same systems. Activation energies for diffusion are around 5 kJ/mol for a carbon chain of one to six units, but rise with carbon number for C₈–C₁₆ to approximately 15 kJ/mol for C₁₆. An explanation is suggested from the hierarchical simulation, which indicates that C₁–C₆ tend to be located entirely within the voids of single channel segments and diffuse by jumps across energetically less favourable channel intersections; in contrast, longer molecules straddle channel intersections and must undergo conformational readjustments in order to diffuse. The agreement found between the QENS measurements and the simulations is met because the two methods probe motion over the same small (nm) length scales. Self-diffusivities measured by PFG-NMR in the same systems are appreciably lower. This is because PFG-NMR probes motion over significantly longer (micron; 10^{-6} m) length scales (as noted earlier) and is therefore more sensitive to defects in the silicalite crystals.⁵² An extension has been

made of the force-field used to describe the interactions between linear alkanes and Na^+ cations in FAU type zeolites, so as to include Ca^{2+} cations. The force field was fitted to reproduce the Na^+ and Ca^{2+} cation positions in zeolite LTA and the adsorption properties of *n*-alkanes over all available temperatures and pressures from the vast literature available on the subject.⁵³ A critical re-examination of experimental data, originally reported in 1973,⁵⁴ which showed an unusual oscillatory variation of the apparent microcrystalline diffusivity of *n*-alkanes in zeolite-T with carbon number, has been reported.⁵⁵ This phenomenon was termed the “window effect”. However, it is now shown that the source of the variation was in fact an artefact of the original analysis,⁵⁴ and that the observed pattern of uptake rates can actually be accounted for by the intrusion of finite heat transfer resistance and isotherm non-linearity, taking only the expected monotonic dependence of the intrinsic diffusivity with chain length.⁵⁵ A series of Grand Canonical Monte Carlo simulations of water adsorption in the faujasites NaY and NaX and in silicalite-1 have been reported.⁵⁶ The existence of cyclic water hexamers located in the 12-ring windows in NaX, recently disclosed by neutron diffraction experiments⁵⁷ was reproduced in the simulations. Interestingly, similar cyclic hexamer clusters were also observed in the case of NaY, in which no stabilizing cation is present in the 12-ring window. It is proposed that the method and forcefield used in this work should be useful for technically important applications such as the prediction of multi-component mixture adsorptive separations in various stable zeolites, since it provides a means to predict the effect of the small quantities of water that are almost invariably present in zeolite-based separation processes.⁵⁶ A similar approach was used to investigate the adsorption of water from the vapour phase into the zeolite silicalite. For fully hydrophobic micropores, the simulations predict there should be essentially no adsorption of water at low pressures, but followed by rapid pore filling as pressure is increased. The effect of silanol defects in real silicalite samples was explored through simulations using “seeded” water molecules to represent hydrophilic defects. These defects were predicted to promote adsorption of some water at low pressures, as molecules form hydrogen-bonded clusters around the defects, and they also cause the pores to fill at a lower pressure than for the completely hydrophobic material.⁵⁸ Molecular dynamics simulations have been carried out to address the question of cation migration upon adsorption of methanol in NaY and NaX faujasites as a function of the loading. For NaY, it has been shown that, at low and intermediate loadings, SII cations can migrate toward the centre of the supercage due to strong interactions with the adsorbates, followed by a hopping of SI' from the sodalite cage into the supercage to fill the vacant SII site. A SI' cation can also migrate across the double six ring and takes a SI' vacant position. SI cations mainly remain trapped in their initial sites irrespective of the loading. Under conditions of high loading, only limited motions are observed for SII cations in consequence of steric effects induced by the presence of adsorbates within the supercage. For NaX, the SIII' cations which occupy the most accessible adsorption sites shift position significantly upon coordination to the methanol molecules, exhibiting a maximum displacement at a loading of 48 methanol molecules per unit cell before decreasing at higher loadings due to steric hindrance. In addition, the SI' and SII cations remain almost trapped in their initial sites whatever the loading. It is thought that the most probable migration mechanism involves SIII' cation displacements into nearby SIII' sites.⁵⁹ The same group have used molecular dynamics simulations to further investigate the concentration dependence of the self-diffusion of methanol in the faujasites. The evolution of the self-diffusivity was investigated as

a function of coverage for DAY and NaY systems with the aim to study the effect of both the pore confinement and the presence of the extra-framework cations within the supercage. It was found that the self-diffusivity decreases with loading for DAY, whereas for NaY it passes through a maximum at intermediate coverage, in agreement with PFG NMR and QENS data reported in similar systems. For the fully loaded materials, it was seen that the methanol molecules form a one-dimensional hydrogen-bonded chain along the channels in DAY whereas only dimers are present in NaY.⁶⁰ A combination of Monte Carlo and molecular dynamics simulations and neutron scattering experiments were employed collectively to investigate the adsorption and diffusion of H₂ and D₂ in zeolite Rho in the temperature range 30–150 K. In the molecular simulations, quantum effects are incorporated *via* the Feynman-Hibbs variational approach. A new set of potential parameters for hydrogen are proposed, which can be used with the Feynman-Hibbs variational approach when it is used for quantum corrections. The dynamic properties obtained from molecular dynamics simulations are in excellent agreement with the experimental results and show significant quantum effects on the transport at very low temperature. The molecular dynamics simulations show that the quantum effect is very sensitive to pore dimensions and indeed can lead to a reverse kinetic molecular sieving effect where deuterium diffuses faster than hydrogen.⁶¹ The pressure and local density dependence of the ¹²⁹Xe chemical shift was analysed using the virial expansion of the chemical shift according to the density of xenon atoms adsorbed in zeolites measured using an *in situ* high pressure probe at pressures of up to 10 MPa. It appears that the second virial coefficient is sensitive to the pore size and shape, and that the void space influences Xe–Xe interactions in both microporous and mesoporous materials. To interpret the magnitude of the virial coefficient in terms of the local structure of the adsorbed xenon atoms, an analysis was made of the local structure of adsorbed xenon in zeolite 5A in terms of Xe_n clusters, thus permitting a description to be obtained of the density dependence of the chemical shift. The validity of the cluster model was demonstrated by applying it to 13X and ZSM-5 zeolites. It was shown that xenon adsorbed in the ZSM-5 micropores exists as an atomic monomer up to a loading of about 0.6, but as the density of xenon increases, clusters of up to *n* = 4 may be produced.⁶² A precursor (diphenylcyclopropenone) was used to generate CO molecules in the channels of the mesoporous MCM-41 silica by photodissociation with a nanosecond laser pulse. The CO was monitored by time-resolved Fourier transform infrared (FTIR) spectroscopy using both step-scan and rapid-scan modes. A very broad absorption of CO was observed in the region 2200–2080 cm^{−1} at room temperature that underwent a biphasic decay. Two-thirds of the band intensity was observed to decay on a microsecond timescale (lifetime = 344 ± 70 μs) which reflects the escape of the molecules through the mesopores into the surrounding gas phase, for which a diffusion constant of 1.5 × 10^{−9} m² s^{−1} was derived. The broadness of the absorption profile is attributed to contact of the randomly hopping CO molecules with siloxane and silanol groups on the surface of the pore. These are the first observations made on the diffusion behaviour of carbon monoxide in a mesoporous material at room temperature.⁶³

4. Photocatalysed oxidation in zeolite cages

Many of the more important processes in the chemical industry involve oxidation of organic molecules, generally of small alkanes, alkenes and aromatic compounds. The

most widely available oxidant is naturally molecular oxygen, but using it as such with the degree of specificity and control generally required is less readily achieved. Direct oxidations by O_2 almost invariably result in the production of large quantities of unwanted byproducts which require separation using processes that are demanding in terms of their energy costs. The main reason for this lack of selectivity is that such oxidation reactions occurring in gas or liquid phases proceed *via* free radical intermediates, which are notorious for resulting in over-oxidation and other products of radical coupling and disproportionation. Reactions with O_2 tend also to be relatively exothermic, and unrestricted mobility of free radicals in gas or liquid states encourages indiscriminate attack on initial hydrocarbon and primary oxidation products. It is unfortunate in this respect that the oxidised product molecules tend to be more reactive toward free radicals than their parent hydrocarbons, and hence the kinetic competition favours the formation of poly-substitution or over-oxidation products. The lack of control gets worse as the products accumulate, and limits conversion to the desired products to a mere few percent in most practical situations.⁶⁴ There have been various approaches explored recently, in the optimisation of oxidation reactions to more viable ends. One method involves the activation of O_2 and a hydrocarbon so to induce an electron transfer from the latter to the former, resulting in the formation of the hydrocarbon radical cation and the superoxide radical anion ($O_2^{\cdot-}$). Since alkane and alkene radical cations are highly acidic, there is the considerable tendency for them to transfer a proton to the superoxide moiety, giving rise to a mixture of an alkyl or allyl radical and the hydroperoxyl radical (HOO^{\cdot}), and while these are the same radicals that are produced in normal gas- or liquid-phase oxidation reactions, if they are generated at ambient temperature and in a restricted environment, a control might be imposed on their reactivity and hence on the oxidation products finally obtained. In principle, a charge-transfer of this kind can be induced by the absorption of a photon by a collisional complex of a hydrocarbon molecule and an O_2 molecule. Indeed, light-induced production of hydrocarbon- O_2 charge-transfer (C.-T.) states was first observed in the 1950's by workers in the eminent groups of Evans⁶⁵ and Mulliken.⁶⁶ Optical absorptions were recorded in the UV region corresponding to collisional C.-T. pairs in oxygen-saturated liquid hydrocarbons and gas- O_2 mixtures under high pressures, which present themselves in the form of long, structureless absorption-tails. Although products were observed from such systems under UV irradiation, and their formation interpreted in terms of the above cited C.-T. mechanism, a multitude of different compounds was produced in each case studied.^{67–70} Considerable success has been achieved by the group of Frei in oxidising hydrocarbons with O_2 as adsorbed in zeolites, under conditions of light-excitation, as is the subject of two informative reviews, although there is considerable overlap between the material covered in them but which illustrates some development of perspective in the two years that elapsed between their respective publication dates.^{71,72} A solvent-free cation-exchanged zeolite provides an environment of micropores into which reactant molecules may be adsorbed thus imposing constraints on diffusion and hence preventing radical coupling reactions that dominate the chemistry in a fluid system. In a sense, the zeolite-contained molecules are like a “matrix-isolated” system, able to react with other very local species, but protected from undesired further reactions by diffusion, as is used extensively in methods of spectroscopy.¹⁰ Furthermore, the alkali metal or alkaline earth metal cations present in zeolites so exchanged with them are poorly “solvated” by the zeolite framework, and create in their vicinity large electrostatic fields that can stabilise the highly polar C.-T. states of

hydrocarbon–O₂ collisional complexes if their electric dipoles are aligned parallel with the surface electrostatic field. If the stabilisation were large enough, it might be feasible to excite oxidation reactions *via* C.-T. using visible light only, not requiring UV energies. Use of longer-wavelength visible radiation rather than UV, would ensure the formation of primary photo-products with a minimum amount of excess energy, thus minimising bond homolysis (especially of weak bonds *e.g.* O–O in peroxides or hydroperoxides) and random coupling reactions of resulting free radicals. Hence the decomposition of sensitive compounds such as peroxides, and over-oxidation would be avoided. From a further cost perspective, visible light is much cheaper to produce than is light at UV wavelengths. The practical demonstration of these principles in the successful production of mostly single products in high yields, by photochemically driven oxidation of alkenes, alkanes and alkylbenzenes with molecular oxygen in zeolites is now considered.

The first report from this series of reactions was the oxidation of 2,3-dimethylbut-2-ene adsorbed in zeolite-NaY (Si/Al = 2.4). Further experiments were conducted using BaY and also both Na⁺ and Ba²⁺—exchanged forms of zeolite-L. These particular zeolites have been employed in most of the subsequent work too. Essentially, zeolite-Y contains a 3-D network (honeycomb) of spherical supercages 13 Å in diameter, connected by “windows” of 8 Å aperture. In contrast, zeolite-L is a one-dimensional structure containing channels 7 Å in diameter. These zeolites are very useful for the present purpose, because they can be prepared free of either Bronsted or Lewis acid sites when dehydrated under vacuum, the presence of which could otherwise complicate the resulting chemistry therein. At the loadings used, on average there were 1–2 molecules of hydrocarbon for each supercage of zeolite-Y, and one O₂ molecule per 3–4 supercages. It was found that irradiation of 2,3-dimethylbut-2-ene at light wavelengths even as long as 750 nm resulted in oxidation of the alkene to yield the product 2,3-dimethyl-3-hydroperoxyl-1-butene, along with a small quantity (2%) of acetone arising from thermal decomposition of the primary alkene hydroperoxide.^{73,74} The optical spectrum of this system shows a long absorption tail which extends into the red region of the spectrum (to 750 nm) arising from the C.-T. absorption.⁷⁵ When 2,3-dimethylbut-2-ene and O₂ are present together in the liquid or the gas phase, the C.-T. tail begins only at 400 nm, which implies there is a stabilisation of the excited C.-T. complex by the zeolite surface electrostatic field to the tune of up to 350 nm or of the order of 3.5 eV. The formal negative charge per supercage wall in zeolite-Y is –7, which is located on the framework oxygen atoms, and counterbalanced by poorly shielded cations resulting in an electrostatic field strength of 0.3 V/Å and 0.9 V/Å for NaY and BaY, respectively.⁷² Thus the large dipole of the C.-T. ion pair of around 15 Debye units will interact strongly with the internal surface field thereby greatly assisting its formation in the zeolite matrix.

The oxidation of propylene⁷⁶ was found to require somewhat shorter wavelengths (<520 nm), in accord with the greater ionisation potential of propylene (9.7 eV) compared with 8.3 eV for 2,3-dimethylbut-2-ene, but the system was more difficult to achieve product selectivity from. The initial product allyl hydroperoxide was found to be stable when the zeolite was maintained at a temperature of –100 °C and was the main product along with 13% of propylene oxide. If the zeolite containing allyl hydroperoxide was allowed to warm with excess propylene still present, propylene oxide was produced, but only acrolein if the excess propylene was pumped-off before warming. These results may be explained if allyl hydroperoxide is the primary product of photo-oxidation of propylene, and which is converted to acrolein by

dehydration. In contrast, propylene oxide is produced by a “dark” reaction involving transfer of an “O” atom from the hydroperoxide to excess propylene, yielding additionally allyl alcohol. A high quantum efficiency of 20% was deduced for the formation of the primary hydroperoxide in 98% selectivity, both of which are remarkable for the oxidation of propylene or any simple alkene for that matter.⁷⁶

Another challenge for commercial synthetic oxidation chemistry is the conversion of toluene to benzaldehyde, an important industrial chemical used in the manufacture of various flavours, fragrances and agrochemicals.⁷⁷ However, there is no process known that can oxidise toluene selectively to benzaldehyde. Indeed, in the autoxidation of toluene, catalysed by Co^{3+} ions, a major problem is over-oxidation of the benzaldehyde to benzoic acid.⁷⁷ In contrast, when toluene is incorporated with molecular oxygen in either zeolite BaY or CaY and irradiated with light of wavelengths < 600 nm, benzaldehyde is the sole organic product.⁷⁷ When the process was conducted in a zeolite cooled to -60 °C, benzyl hydroperoxide was trapped but which underwent a spontaneous dehydration on warming the matrix to room temperature, which indicates that the hydroperoxide is the primary photo-product and the critical intermediate in the formation of benzaldehyde. This selectivity was complete even at a toluene conversion of 50%. In the presence of visible light, over-oxidation of benzaldehyde to benzoic acid is obviated because the latter has a substantially greater ionisation potential (9.5 eV) than toluene does (8.8 eV). Consequently, the benzaldehyde– O_2 C.-T. absorption does not reach into the visible region thus rendering the material inaccessible to photolysis at these wavelengths.⁷⁸ A similar conversion of ethylbenzene to acetophenone was made in BaY zeolite with again complete selectivity.⁷²

It is also possible to perform selective photo-oxidations on alkanes in zeolites using molecular oxygen.^{79–81} Cyclohexane has almost the same ionisation potential as propylene and Irradiation of a cyclohexane and O_2 -loaded zeolite NaY with green or blue light (< 520 nm) resulted in oxidation of the alkane to cyclohexylhydroperoxide and cyclohexanone (plus water) as the sole products. The hydroperoxide was found to rearrange thermally and cleanly to cyclohexanone. A complete selectivity in attaining the final oxidation product cyclohexanone remains even at high ($> 40\%$) conversion of cyclohexane. The chemistry was monitored by *in situ* FT-infrared spectroscopy and the visible reactant absorption by diffuse reflectance spectroscopy with an onset at about 500 nm. The absorption is attributed to the cyclohexane– O_2 C.-T. transition, which is shifted from the UV into the visible range by the very high electrostatic field of the zeolite cage.⁷⁹ Similarly, *iso*-butane and oxygen gas loaded into zeolite BaY could be made to react upon irradiation with green or blue light to yield *tert*-butylhydroperoxide in a single-photon process. The selectivity was 98%, even at 50% conversion of the reactants loaded into the zeolite.⁸⁰ As a representative instance of oxidation of a low alkane the case of propane is worth mentioning.⁸¹ Acetone and water were detected by reflectance IR as the final products when 150–300 mm Hg of propane and 1 atm pressure of O_2 were adsorbed into zeolite BaY and exposed to blue or green light from either a tungsten lamp or a laser. There were additional bands too that could be ascribed to isopropylhydroperoxide, a species that was noted to disappear under dark conditions with the concomitant increase in features from acetone and water. It is concluded that isopropylhydroperoxide is the primary photo-product, as is confirmed by repeat experiments made using perdeuteropropane.⁸¹ The possibility that thermal oxidations of alkanes might take place in zeolites in the absence of light was also explored. Indeed, even at room temperature for propane in CaY, some oxidation was found to occur.⁸¹ The effect of

zeolite Y ion-exchanged with a series of alkaline-earth cations on selective propane oxidation at room temperature was studied with *in situ* infrared spectroscopy. Isopropylhydroperoxide was observed as a reaction intermediate and can be decomposed into acetone and water. Contrary to previous studies, BaY was found to be active at room temperature. The reaction rate increased in the order BaY < MgY < SrY < CaY based on the rate of formation of adsorbed acetone. Surprisingly, the acetone/water ratio was found to increase with cation size, while no other products could be detected. Moreover, the acetone/isopropyl hydroperoxide ratio decreased as the number of Brønsted acid sites decreased. Both observations prove the involvement of Brønsted acid sites in this reaction, in addition to the alkaline earth metal cations. A two-step mechanism is proposed in which the conversion of propane into isopropyl hydroperoxide takes place on the cations, while the decomposition into acetone occurs at Brønsted acid sites.⁸² An investigation of the number of supercages that participate in the visible light-induced reaction between 2,3-dimethylbut-2-ene and O₂ in NaY zeolite was made. The growth of the sole product, 2,3-dimethyl-3-hydroperoxy-but-1-ene was studied using rapid-scan FT-IR spectroscopy using a 150 ms photolysis pulse. Since the pulse duration is short in comparison with the estimated timescale over which cage-to-cage diffusion occurs, it is possible to determine the number of cages involved, and the estimate was made that a minimum of 1% of all NaY supercages in fact take part in the photo-reaction. As the researchers themselves stress, it is important to recognise that this is between 1 and 3 orders of magnitude greater than the concentration of any defect sites (Lewis acid or free radical sites) that might be present in the zeolite, and confirms that the sole relevant physical property of the zeolite cage in the photo-reaction is the high electrostatic field in the vicinity of the Na⁺ cations, which is responsible for inducing the reaction, as has been assumed.⁸³ Frei has published a note which stresses that the rate of diffusion of the products out of the zeolite poses a major limitation to scaling-up the technology for commercial production.⁸⁴ The importance of the relative orientation of the photo-reactants in the zeolite cage to accessing the C.-T. complex is also discussed. Interestingly, another paper reports Density Functional Theory (DFT) calculations on the initial C.-T. step for alkene photo-oxidation in zeolite Y. The model system used represents a part of the Y-zeolite supercage containing two II sites with alkaline-earth cations and 2,3-dimethylbutene-2 (DMB) and O₂ co-adsorbed on them. It is predicted that the electrostatic field of the zeolite cavity plays only a minor role for the stabilization of a charge-transfer state, while the relative orientation and the distance between the DMB and O₂ molecules are the critical factors. On the basis of these results, the photo-oxidation is considered to be due to a confinement effect in which the reagents are oriented in a suitable “pre-transition state” configuration. This is indeed an interesting development.⁸⁵ The same group have reported a further DFT study of the conformations of alkanes adsorbed on zeolite cations.⁸⁶

5. “Ship-in-a-bottle” complexes in zeolites

A “ship-in-a-bottle” is a wonder to children, and a mystery that is rendered commonplace as they become older and learn that the essential framework components of the ship—mast and all—are first brought together inside the bottle, then assembled, and finally the mast is “pulled- up” from outside as a *pièce de résistance*. In a reasonable analogy, relatively large molecules may be assembled inside the supercages of zeolites from condensation and coordination reactions of smaller

species adsorbed therein. In some instances, a photochemical “string” may be included with which to draw-up the final extent of the structure by the external means of light. Some recent reports of interesting and potentially useful materials that were created using ship-in-a-bottle methods are now considered. For example, prefluorescent probe dansyl-TEMPO (DT) was synthesized within NaY supercages by means of a base-catalyzed ship-in-a-bottle synthesis to yield the supramolecular assembly DT@NaY, providing the first example of base-catalyzed synthesis in the normally acidic zeolite cavities. This material was successfully employed in the solid state as a sensor to monitor intercavity diffusion of carbon-centered radicals produced by AIBN thermolysis and in a slurry to study the inter-pore diffusion of carbon-centered radicals produced in solution from a suitable precursor (3,3'-diphenyl-3H,3'H-[3,3']bibenzofuranyl-2,2'-dione). The dynamics of hydrogen atom transfer from a good donor, such as the synthetic lactone antioxidant 3-phenyl-2-coumaranone, to DT@NaY were also investigated in benzene slurry.⁸⁷ 3-Hydroxyflavone (3-HOF) was incorporated in zeolite micropores by ship-in-a-bottle synthesis, in a strategy that consists of constructing the molecule by reaction of small precursors within the cavity. 3-HOF molecules were found to exhibit excited-state intramolecular proton transfer and a tautomeric equilibrium between the 3-HOF-excited structures N* and T*. This equilibrium is strongly affected by the protonic nature and polarity of the surrounding medium. The physical and spectroscopic characterization of the dye-loaded zeolite colloids enabled the study of the correlation between the optical properties of the dye and the zeolite microporous environment.⁸⁸ The 2,4,6-triphenylthiapyrylium ion has been produced encapsulated within the supercages of the 3-D large pore zeolites Y and beta *via* ship-in-a-bottle synthesis from chalcone and acetophenone in the presence of hydrogen sulfide. The resulting solids are efficient and robust photo-catalysts that can degrade phenol and aniline in water with a higher efficiency than the P-25 TiO₂ standard catalyst. Preliminary tests have shown that these encapsulated dye materials are also efficient photo-catalysts for the oxidative degradation of malodorous sulphur-containing molecules.⁸⁹ Fluorescein (2-(6-hydroxy-3-oxo-(3H)-xanthen-9-yl)benzoic acid) has been prepared inside the pores of zeolite-Y *via* ship-in-a-bottle synthesis. Fluorescein, whose dimensions prevent it from entering through the 7 Å windows of the faujasite zeolite used, was prepared by the acid-catalyzed reaction of resorcinol and phthalic anhydride. Initial spectroscopic data are presented as well as one example of these fluorescence-labelled nano-particles which might serve for imaging applications such as confocal fluorescence microscopy. A remarkable increase in photo-stability of the encapsulated fluorescein is noted.⁹⁰ The first molecular switch encapsulated within the cavities of a zeolite was reported, which showed a dramatic increase in the lifetime of the charge-separated (C.-T.) state. A [2]-catenane consisting of a bipyridinium cyclophane and a dioxybenzene macrocyclic polyether has been encapsulated within the supercages of zeolite Y using ship-in-a-bottle synthesis; laser flash photolysis reveals that the charge-separated species decays over a period of hundreds of microseconds in contrast to the few picoseconds previously reported for the same transient in acetonitrile solution. Hence photochemical quenching is largely prevented in the zeolite matrix.⁹¹ Catalytic centres of many and various kinds can be encapsulated into zeolite micropores, often using ship-in-a-bottle methods, to create materials suitable especially for use in oxidation reactions. Sometimes the resulting materials are termed *zeozymes*, “*zeolite mimics of enzymes*” in analogy with enzymes given their broadly comparable nature, though none of these synthetic counterparts based on zeolites quite match the specificity and rate acceleration of the

latter category. Two recent reviews of materials of this kind are available.^{92,93} The first review focusses on aspects of “green chemistry”, stressing the current need for cleaner fuels (free of aromatics and with minimal sulphur content) or fuels that convert chemical energy directly to electricity, silently and without production of noxious oxides and particulates; chemical, petrochemical and pharmaceutical processes that may be conducted in a one-step, solvent-free manner and that use air as the preferred oxidant; and industrial processes that minimize consumption of energy, production of waste, or the use of corrosive, explosive, volatile, and non-biodegradable materials. Nanoporous catalysts based on zeolites are highlighted for specific examples which include the production of adipic acid avoiding the use of concentrated nitric acid nor the production of greenhouse gases such as nitrous oxide; the production of caprolactam (the precursor of nylon) without the use of oleum and hydroxylamine sulfate; and the terminal oxy-functionalization of linear alkanes in air, which is important on a practical scale for detergent manufacture. It reads thus as a manifesto for “Green Chemistry”.⁹² The second review refers more generally to supramolecular Host–Guest complexes in zeolites prepared by ship-in-a-bottle synthesis, and provides an excellent overview and coverage of history, characterisation, synthesis and current applications of zeolites paying particular attention to ship-in-a-bottle methods.⁹³ There is a nice reminder made too of the essential thinking behind synthesising zeolites carried out seminally by Barrer in the 1950’s, which was based on an attempt to mimic the conditions that were thought to exist in the Earth to form zeolite minerals by natural processes, and which led to the synthesis of zeolite Y.⁹⁴ There are also available two highly informative reviews on zeolite-encapsulated catalysts for use in selective liquid phase oxidation reactions.^{95,96}

6. Zeolite acidic strength and its role in catalysis

As recently as 1994, H-exchanged zeolites were almost ubiquitously referred to as “superacids”, meaning that they were in possession of an acidic strength in excess of that for concentrated sulphuric acid. Consequently, the mechanisms of the reactions for almost all processes of practical importance, such as hydrocarbon cracking, were ascribed in terms involving simple carbenium ions and were rationalised on the basis of the accepted chemistry of these and other exotic high energy intermediates, as gleaned from studies made of truly superacidic systems. Subsequent information has refuted this picture, and it is probably more reasonable to refer to H-zeolites as examples of “solid acids” or “solid acid catalysts”, rather than to specify a particular degree of that acidity. The subject has been reviewed by Haw.⁹⁷ It is true that solid acidity is difficult to define since a given material may contain various Bronsted (proton) acid sites and Lewis acid sites, and some zeolites contain polyvalent cations and surface defect sites too that can function in an acidic fashion, so the property is furthermore rather difficult to measure. In terms of Hammett acidity (from Bronsted acid sites) here have been a number of spectroscopic methods employed for example in conjunction with the adsorption of a probe base molecule, to measure the strength of the resulting base-acid “neutralisation”. Indeed it is surmised that the use of Hammett indicators adsorbed on the surfaces of zeolites and other solid acids may have been the cause of much of the confusion about the acid strength of these materials.⁹⁷ The Hammett acidity (H_{BH^+}) of 100% sulphuric acid is -12 , and is taken as the threshold value above which a system is defined as a superacid. Zeolite acid strengths were often cited as being in the range -12 to -24 and so clearly they would be considered as solid superacids! In a nutshell, methods that rest upon

measuring colour changes are at best difficult in solid media. Haw *et al.* used NMR to measure directly the degree of protonation in four common Hammett indicators. The results show that while the strong base *p*-fluoroaniline ($H_{BH+} = +2.4$) is protonated in both HY and H-ZSM-5 zeolites, the weak base *p*-fluoronitrobenzene ($H_{BH+} = -12.4$) is not. Hence zeolites are not superacids in the Hammett sense of the term.⁹⁸ This conclusion is supported by ¹⁵N MAS NMR studies which show that other Hammett indicators close to -12 are not protonated in typically encountered aluminosilicate zeolites.⁹⁷ Much experimental work by Haw's group on NMR studies of products formed in zeolite catalysed reactions was limited to temperatures of 523 K or less by the limitations of the materials used in the construction of the NMR probe, which is somewhat less than that used in most applications where zeolites are present as catalysts. Generally, while Haw⁹⁷ found no significant difference between measurements made at room temperature and 523 K, but the possibility remained that the zeolites might develop a much higher acidic strength at the higher temperatures at which they were typically employed for real catalytic applications. Indeed, this hypothesis was sometimes upheld to defend the superacid description of zeolites, and their function as such in chemical reactions. However, important light was cast upon the matter by Roduner and Dilger⁹⁹ in their study of the entropy change associated with deprotonation of a zeolite. They showed that H-zeolites are in fact less strongly acidic at elevated temperatures, as indeed are aqueous solutions of mineral acids. Accordingly, if a zeolite is not a superacid at ambient temperature it certainly will not become so at higher temperatures. However, if zeolites are not superacids, other more complex mechanisms must be invoked to explain their chemistry. Many important products from reactions catalysed by H-zeolites contain aromatic hydrocarbons. Solid state ¹³C NMR spectra of benzene in zeolite HY taken in comparison with those for benzene measured in solid and in frozen "magic acid" (a genuine superacid) confirm that there is little or no proton transfer to benzene from the zeolite.¹⁰⁰ Hydrogen-deuterium isotope exchange has been observed to occur for a variety of hydrocarbons when they are adsorbed in H/D-zeolites, and most commonly this is attributed to protonation of the hydrocarbon with the formation of carbocation (carbenium or carbonium ion) intermediates caused by the superacidic nature of the zeolite. In a study of H-D exchange for methane adsorbed in zeolites, it was concluded that a concerted mechanism was responsible and not a five-coordinate free carbonium ion intermediate.¹⁰¹ A study was made of perdeuteriobenzene (C₆D₆) adsorbed on H-zeolites using ¹H MAS NMR, in which the benzene proton signal was monitored, formed by D-H exchange with the zeolite. Activation energies of 60.2 kJ/mol, 84.9 kJ/mol, 107 kJ/mol were measured, respectively for the zeolites H-ZSM-5, USY and Na,HY.¹⁰⁰ These values are close to those determined from a theoretical model similar to that used to describe the H-D exchange for methane. In terms of the wider issue of the cracking of alkanes, it has been shown that the gas-phase proton affinity of *n*-hexane is 665 kJ/mol which is too weak for complete proton transfer to occur in a zeolite.¹⁰² Theoretical studies have provided convincing model mechanisms in which alkane cracking occurs through transition states in which basic framework oxygen atoms near to the Bronsted site act to stabilise both the proton and an activated fragment of the hydrocarbon. The significant difference from the accepted mechanism is that only partial charge transfer is required rather than the existence of free carbocations.^{103,104} They are indeed related to those transition states alluded to earlier which pertain for methane and benzene H-D exchange in H-zeolites.

The Methanol to Gasoline (MTG) process⁶ provides a method for manufacturing synthetic gasoline from methanol and is catalysed using the zeolite H-SZM-5, as mentioned in the Introduction section of this article. However, despite the elapse of thirty years since its development, during which there has been a considerable extent of research on the topic, the mechanism by which it takes place is still the subject of controversy.^{105–107} Interest in the general process of converting methanol to hydrocarbons has shifted somewhat from the original goal of making synthetic fuel to its conversion into light olefins using the less strongly acidic silico-aluminophosphate catalyst (HSAPO-34). This so named methanol-to-olefins (MTO) process is of particular interest since it is thought that thereby a means may be found to the conversion of methane to polyolefins.¹⁰⁶ The complete strategy would involve steam-reforming methane from natural gas to form a mixture of H₂ and CO (Section 2.1) which is usually known as “synthesis gas” because it can be used to synthesise methanol using a Cu/ZnO/Al₂O₃ catalyst. If an economically viable method is found to convert the methanol to light olefins, the world plastics industry has only to depend on natural gas rather than imported oil. From a mechanistic perspective, either MTG or MTO process poses the same enigma: namely, how it the first C–C bond formed from a feedstock of molecules containing just a single carbon atom, *i.e.* methanol? There have been many mechanisms offered to account for this event, at least 20 different ones in fact, including those based on CH₃⁺ carbenium ions, oxonium ylides, *e.g.* Si₂O⁺–CH₂[–], and free radical species.^{105–107} The latter are particularly attractive in their simplicity, since formation of a C–C bond from CH₃OCH₂[•] radicals if they are formed in the conversion of methanol by H-ZSM-5 would be almost inevitable.¹⁰⁸ The existence of radicals in the gas-stream when dimethyl ether (the primary product formed by dehydration when methanol interacts with H-ZSM-5) has been evidenced in spin-trapping experiments,¹⁰⁸ although it is not clear that they are key intermediates in the MTG process.¹⁰⁹ Indeed, radical species may be spin-trapped from the gas-phase of a variety of different model catalytic systems, but how important they are in real catalytic reactions is a matter for conjecture.¹¹⁰ Cogent to the whole matter of the MTG process is the demonstration of a co-catalytic affect when a mixture of methanol and toluene was injected into the reactor containing H-SZM-5.^{111,112} The proposal made to account for this observation involved the formation of resonance stabilised carbenium ion intermediates in the zeolite by a side-chain alkylation mechanism.^{111,112} This essential line of thinking made no progress until the mid-1990’s when Dahl and Kolboe advanced the “hydrocarbon pool” mechanism in which the function of methanol is to methylate hydrocarbon molecules of unknown structure adsorbed on the catalyst’s surface, and leading ultimately to olefins through parallel reaction pathways.^{113,114} The group of Haw began in earnest a search for key intermediates of the hydrocarbon pool using experimental pulse-quench *in situ* NMR methods and supported by theoretical calculations. Methanol conversions catalysed by both H-ZSM-5^{115,116} and H-SAPO-34^{117,118} were investigated. Among the species identified in H-ZSM-5 were the 1,3-dimethylcyclopentenyl carbenium ion in equilibrium with a related neutral cyclic diene, and methyl substituted benzenium carbenium ions in equilibrium with neutral methylated benzene derivatives. On H-SAPO-34, the critical reaction centres are methylated benzene derivatives. Haw has concluded that the initiation step in MTO/MTG catalysis is really a phantom, and that the first hydrocarbon pool species are formed by organic impurities either as present in the methanol, or in the catalyst itself in consequence of incomplete calcination when it is thermally activated. Haw contends that only an “indirect” hydrocarbon pool

mechanism accounts for the observed outcome of MTO/MTG methanol conversion catalysis, and if any “direct” reaction happens at all it does so at rates much slower than typical rates involving the hydrocarbon pool. Hence initiation of the MTO/MTG reaction is generally caused by organic impurities that form the first few reaction centres.¹¹⁹ The impurities in the mixture undergo repeated methylation and subsequent olefin elimination with re-initialisation of the catalytic cycle. The impurities are larger organic molecules termed “organic reaction centres” and they function as a scaffold onto which the reactants are tacked together and from which the products are removed. This circumstance avoids the need to invoke the high-energy intermediates that are required by all of the “direct” mechanisms. The rate of formation of the initial reaction centres and hence the duration of the induction period can be determined by the nature of the impurity species. Secondary reactions of primary olefin products are strongly reflective of the topology and acid strength of the porous catalysts. Reaction centres are proposed to form *via* some secondary routes that “age” into polycyclic aromatic hydrocarbons which eventually deactivate (“poison”) the catalyst. It is helpful to think of each cage or channel with its occluded organic and inorganic species in its entirety as a supramolecule that acts as a reactant to form various product species. This manner of depiction permits an identification of structure-activity and structure-selectivity relationships and to modify the nature of the catalyst with degrees of freedom that appear closer to homogeneous catalysts than heterogeneous catalysts.¹²⁰ However, the matter has not met with universal closure, and the issue of forming the very first C–C bond remains the subject of investigation and speculation, although this may amount to essentially dotting “i’s” and crossing “t’s”, if the more salient features really are now understood. Because of an observed kinetic induction period preceding hydrocarbon formation, the hydrocarbon pool model implies that reactions occurring during this induction phase need not necessarily be similar to those on a working catalyst. It remains unresolved however, which induction reactions—if any—might contribute to the hydrocarbon pool. The results of a theoretical study¹²¹ have been published which aims to integrate a large range and variety of possible direct reactions and so to deduce whether ethylene can be produced solely from methanol, and which stable intermediates might thereby be formed directly, to provide an understanding of how that vexed first C–C bond is indeed formed. Over 80 stationary points in the MTO process were calculated which provided both rate coefficients at 720 K and reaction barriers at 0 K. This enabled a quantitative evaluation of the steps most likely to occur. However, no sequential pathway was identified from methanol to ethylene (or for that matter to any intermediate containing a C–C bond), and which is entirely in accord with methanol/dimethylether being fairly unreactive on H-ZSM-5 in the absence of organic impurities to provide a hydrocarbon pool. Two bottlenecks were identified clearly from the calculations: one being the instability of ylide intermediates, and also that the frequently invoked concerted C–C bond formation reactions actually have very high energy barriers, in consequence of the weakly basic character of the zeolite oxygen bridge. The calculations do allow a clear definition of those intermediate species which are likely to interact with the hydrocarbon pool, and which are not only the mixture of methanol and its condensation products dimethyl ether and water but also the trimethyloxonium cation, which might act as a source of methyl groups, and also of methane and formaldehyde. The authors have summarised their results, saying that neither a single mechanism nor a combination of steps among the calculated scheme of reactions can link methanol to ethylene. They conclude that the theoretical work provides hence strong support for the

hydrocarbon pool view of the MTO process which obviates any highly activated concerted steps.¹²¹

Some details of the H–D exchange reactions of propene over D-ZSM-5, its boron analogue D-(B)ZSM-5 and D-SAPO-34 have been reported which are delicately significant to the mechanisms involved. Given the huge excess of exchangeable deuterium atoms on the catalyst, for the number of hydrogen atoms in the propene loading, complete exchange would be expected, yielding C₃D₆ as the exclusive equilibrium product of the reaction. The outcome is more subtle, however, and a distribution of exchanged propene isotopomers was found by mass spectrometry: 6% D₄, 72% D₅ and 22% D₆ propene. When the size of the propene pulse was increased, the deuterium distribution was reproducibly and substantively different: 28% D₄, 44% D₅ and 29% D₆ propene; additionally, the product distribution was found to include not only propene but additional products from cracking and oligomerisation, butenes, pentenes and hexenes. These observations are rationalised mechanistically.¹²² In a separate study, the H–D exchange reaction of 2,2-dimethylpropane (neopentane) over D₂O-exchanged zeolites (MOR, FAU, BEA, MFI) using a batch recirculation reactor was studied by means of gas chromatography coupled with a mass spectrometer. It was found that H–D exchange proceeds without any side reactions at short contact times, in the temperature range 473–573 K. The activation energies of the H/D exchange between neopentane and zeolites are the same for all zeolites which, it is concluded, indicates a common carbonium ion type transition state, in analogy with the exchange between methane and liquid superacids; hence the deuterium exchange rates in neopentane were tentatively related to the acidity of the solids. However the order of activity MOR > MFI > BEA > FAU seems to be related to the size of the pores, which may suggest the involvement of a confinement effect in the zeolites cavities.¹²³ However, in view of the previous discussion in this section, the involvement of a genuine carbocation mechanism here appears dubious. Ivanova *et al.* have contributed a short review on the impact of *in situ* ¹³C and ¹H MAS NMR on the elucidation of the mechanisms whereby alkylaromatic compounds are transformed over zeolite catalysts. Transformations of deuterated benzene and cumene derivatives on protonic forms of zeolites are used to account for H–D exchange in the aromatic ring and in the alkyl chain. The nature of ¹³C label transfers during the course of the rearrangements of specifically labeled benzene, cumene, *n*-propylbenzene and ethylbenzene are interpreted to provide deeper insight in the mechanisms of transalkylation, disproportionation, skeletal and nonskeletal rearrangements of alkyl chain, fragmentation and dealkylation/alkylation processes over zeolites. The main factors controlling selectivity of zeolite catalysts in alkylbenzenes transformations are thus elucidated. From an analysis of the influence of zeolite type on the mechanism of transformation of alkylbenzenes by various zeolites, the results suggest that the dominant factor controlling the particular reaction pathway is the zeolite geometry, *i.e.* “shape-selectivity” is at work. The paper provides a clear illustration that *in situ* MAS NMR, in combination with specific isotopic labelling of organic reactants, can provide great insight into the detailed mechanisms of catalytic reactions.¹²⁴ This section ends with some controversy, beginning with a paper published by Jiang *et al.* which is concerned with the formation of primary hydrocarbon products during MTO catalysis, in which they propose that “the decomposition of surface methoxy groups results in the formation of primary hydrocarbons on acidic zeolite catalysts”.¹²⁵ Haw *et al.* have published a rebuttal¹²⁶ of this notion, citing a theoretical study¹²¹ which found no evidence for it and an experimental study by themselves¹²⁷ which provided no

evidence that H–D exchange reactions occur for methoxyl groups on the surface of an acidic MTO catalyst. Hence it is concluded that both carbene or ylide mechanisms can be eliminated.¹²⁶ Jiang *et al.*¹²⁸ have published a response to the criticisms by Haw *et al.*¹²⁶ of their original paper.¹²⁵

7. Preparation and properties of novel zeolites

Post-synthetic modification^{129,130} has proved an effective means to reduce the effective channel dimensions of a zeolite, reduce the number of framework acid sites or to introduce some new desired reactive functionality. Haw and his coworkers recently reported the functionalisation of the large-pore zeolite H-beta by its reaction with trimethylphenylsilane at 648 K, which was found to convert some of the acid sites to their trimethylsilyl derivatives.¹³¹ They have extended this work in developing a two-step post-synthetic sequence in which zeolite HZSM-5 is functionalised with a high selectivity and at room temperature. In the first step the framework acid sites of the zeolite are reacted with phenylsilane to replace the acidic proton with a hydrosilyl ($-\text{SiH}_3$) group covalently linked to the framework. This group readily couples to acetone in a second step to form a framework-bound hydrosilyl isopropyl ether that is thermally stable at 473 K, but which decomposes when moisture is present. These reactions were characterized using ^{29}Si , ^1H and ^{13}C MAS NMR methods. Theoretical modelling studies using DFT and cluster models of the zeolite acid site confirmed that both reaction steps were exothermic and provided estimates of values for chemical shifts that were in excellent agreement with those determined experimentally.¹³² It has been shown that desilication of a zeolite by its treatment with alkaline solutions provides a relatively convenient means to obtain mesoporous ZSM-5 zeolites while preserving the integrity of the essential structure. The process of framework silicon extraction is controlled by framework aluminium and makes desilication selective towards the creation of intracrystalline mesopores. A Si/Al ratio range of 25–50 has been identified as optimal for the process while at higher Si/Al ratios the extraction of framework silicon becomes excessive and unselective, while at lower ratios comparatively little extraction of silicon occurs. The presence of non-framework aluminium species, for example obtained by steam treatment (as in USY), inhibits mesopore formation by alkaline treatment since these species become reinserted into the zeolite framework. It is proposed that the development of mesoporous zeolites *via* desilication should induce a more efficient usage of the zeolite crystal due to an improved accessibility and a facilitated transport to and from the active sites.¹³³ Dry-gel conversion is a relatively new approach for molecular sieve synthesis. The technique involves treating the pre-dried gel powder with water vapour at elevated temperature and pressure. However, the role of water vapour in this apparent solid-state transformation is not clear. In an effort to explore some mechanistic details of the process, ^{17}O -labelled water vapour was employed in the crystallization of AlPO₄-11 and monitored using ^{17}O MAS NMR spectroscopy. Several dipolar-coupling based double-resonance methods including ^{17}O {Al-27}, ^{17}O {P-31} rotational-echo double-resonance, $^{17}\text{O} \rightarrow ^{31}\text{P}$ and $^1\text{H} \rightarrow ^{17}\text{O}$ cross polarization techniques were used to resolve different ^{17}O species. The results show that water from the vapour phase initially undergoes a slow exchange with water molecules that are strongly bound to the AlPO intermediates; subsequently, ^{17}O atoms are gradually incorporated in both P–O–H and P–O–Al units in the layered intermediate.¹³⁴ The effect of particle size in the range of 0.16–2.01 microns on the hydrothermal stability of H-Y zeolite under hydrothermal

treatment conditions similar to those used in Fluidised Catalytic Cracking (FCC) processes has been investigated. The optimum particle size for zeolite H-Y to retain a high percentage of crystallinity upon hydrothermal treatment was found to be 0.45 microns. An alternative correlation equation was derived by plotting the relative crystallinity (C/C_0) against the reciprocal of the square root of the particle size (d_0) of the zeolite, and which provides an accurate prediction of the hydrothermal stability of Y zeolite in the small to medium particle size ranges at a given temperature. However, the correlation breaks down for the larger particles of Y zeolite (>0.45 microns), and this is thought due to the presence of a greater number of structural defects in the zeolite, according to the higher Bronsted/Lewis acid ratios which are exhibited.¹³⁵ To resolve the problem of whether the H-form of natrolite exists, the thermal decomposition of NH_4 -exchanged natrolite (as a precursor of the H-form) was studied by gas chromatography, IR spectroscopy and X-ray diffraction. It was found that throughout the decomposition, the de-ammoniation is immediately followed by dehydroxylation, thus providing evidence for the instability of H-natrolite formed after the removal of NH_3 . In the final step of decomposition, the adsorption of NH_3 onto Lewis acid centres which have accumulated in the now amorphous framework hinders the loss of ammonia. Accordingly, the activation energy observed for NH_3 desorption increases from 117 (± 13) kJ/mol in the initial step to a final value of 270 (± 20) kJ/mol. If the NH_4 -exchanged natrolite is degassed smoothly under vacuum at 550 K, a partial de-ammoniation is observed rather than formation of H-natrolite.¹³⁶ There has been a communication published of the synthesis of ionothermal materials using unstable deep-eutectic solvents as template-delivery agents. A deep-eutectic solvent (DES) is a mixture of two compounds which together result in a depression in the freezing point of the mixture compared with those for the separate components. In this study, the controlled use is described of DES which are unstable at high temperatures and so the organic template is not added in the normal manner to the reaction mixture but is delivered to the reaction by the breakdown of one of the components in the DES itself. This is an interesting adaptation of the DES methodology.¹³⁷ Using a novel combination of analytical techniques, Weckhuysen *et al.* have shed light on the mechanism of zeolite formation and provided experimental evidence which supports the notion that molecular organisation takes place before crystallisation occurs. It is molecular recognition that creates the seeds of order around which complex lattices grow.^{138–140} The effect of the introduction of phosphorus on H-ZSM-5 zeolite before and after hydrothermal treatment was studied. The samples were characterized by XRF, nitrogen adsorption, ^{27}Al -27 and ^{31}P MAS NMR, *n*-propylamine temperature-programmed decomposition, *n*-hexane cracking and vacuum gas-oil cracking. It is shown that the presence of phosphorus stabilizes the ZSM-5 zeolite structure by preventing the separation of the framework Al atoms during the steaming treatment. In addition to the classical framework tetracoordinated aluminium, which is mostly responsible for the acidity of the samples, a second tetrahedral aluminium (probably in a distorted environment) also seems to be active in *n*-hexane cracking, in addition to favouring the formation of light olefins during gasoil cracking.¹⁴¹ One paper has been published which demonstrates the solution of a complex zeolite structure by means of a combination of powder diffraction and electron microscopy employing the FOCUS algorithm.¹⁴²

7.2 Zeolite membranes

Zeolite NaA membranes have been prepared reproducibly by seeded hydrothermal synthesis on the inner-side of porous alpha-alumina tubular supports using a

semi-continuous system in which the gel was periodically renewed inside the tubes. A cross-flow filtration technique was used to allow a controlled seeding of zeolite NaA crystals from a suspension. The influence of the renewal rate during the synthesis, as well as the seeding weight gain (SWG), on the pervaporation performance of the membranes prepared was investigated. An optimal SWG value was found to be around 0.15 mg cm^{-2} of membrane area. The use of a semi-continuous system allowed to obtain zeolite membranes with selectivities up to 16 000 at fluxes of $0.50 \text{ kg m}^{-2} \text{ h}^{-1}$ at 323 K for the pervaporation of 90:10 wt% ethanol/water mixtures.¹⁴³ The dehydration performance of zeolite NaA membranes was investigated for the pervaporation (PV) of ethanol/water mixtures. The PV performance of the as-synthesized membranes was explored at 303–363 K for water contents of 1–60 wt% and for feed and permeate pressures in the range 0–7 bar (relative) and 2–70 mbar, respectively. The selectivity was found to show a maximum at a water feed composition in the range 5–10 wt% and to rise with temperature. Water and ethanol fluxes were successfully fitted to an adsorption-solution model derived from the Maxwell-Stefan theory, where ethanol flux is coupled with water flux. It appears that the PV performance of zeolite NaA membranes is determined mainly by the adsorption of water and ethanol.¹⁴⁴ The synthesis of zeolite A membranes and an analysis of the essential factors for achieving this successfully are reported.¹⁴⁵ ZSM-5 zeolite membranes were synthesized, by means of the secondary growth procedure, over porous alpha-alumina supports from clear template-free precursor solution and their permeation properties were compared with membranes prepared using templates. The templated membrane (M1) contained smaller crystals with a greater number of faces than their template-free counterpart (M2). The introduction of micro-defects during the calcination procedure meant that the expected size selectivity could not be achieved for M1 as this membrane possessed some micro-defects. The required size selectivity was achieved for M2 at ambient temperatures and shape selectivity found at 200 degrees C. A selectivity ratio of 44 was achieved for butane isomers through M2 with *n*-butane molecules experiencing maximum a maximum activation energy of 43 kJ/mol, through a mechanism of activated diffusion. As a general rule, the permeation values measured for M2 membranes were an order lower than those for M1 membranes.¹⁴⁶ In another study, two synthesis methods were used to prepare zeolite beta membranes of thickness around 1000 nm on beta seeded, commercial Trumem disk supports. The first synthesis method produced an alkali-free zeolite beta layer with a Si/Al ratio of 40. A Na-containing zeolite beta layer with a Si/Al ratio of 13 was obtained using the second synthesis method. Nitrogen permeation experiments indicated that the mechanism for permeation was controlled by surface diffusion. Only those membranes prepared by the former method were found effective in separating di- from mono-branched alkanes as evaluated from pervaporation experiments at 303 K with a 50:50 wt% 2-methylpentane (2MP) and 2,2-dimethylbutane (22DMB) mixture, giving a selectivity of 1.5 in favour of 2MP and higher than the expected Knudsen selectivity. Simulated adsorption energies for 2MP and 22DMB in zeolite beta were -48 kJ/mol and -42 kJ/mol , respectively.¹⁴⁷ Asymmetrically structured zeolite membranes of a hydrophobic MFI (ZSM-5) type and hydrophilic type, NaA were prepared as thin layers of 10–30 microns thickness on ceramic substrates and tested by pervaporation with binary water-ethanol mixtures and with pure water and pure ethanol. It was determined that good separations could be attained using the hydrophobic membranes for ethanol-water mixtures even at low temperatures. On the basis of a comparison of single and mixture permeance, it was deduced that different

separation mechanisms operate for MFI and NaA membranes, and which were influenced strongly by the structure of the membrane support.¹⁴⁸ An H-ZSM-5 membrane has been employed for xylene isomerization and for the separation of *p*-xylene from its other isomers. MFI membranes (silicalite-1 and H-ZSM-5) were prepared by seeded growth on porous stainless steel supports. The membranes were tested for separation of the xylene isomers in the temperature range 100–400 °C. The H-ZSM-5 membrane showed higher *p*-xylene permaselectivity [$(para/ortho) = 4.3$ at 300 °C] and lower permeance to *p*-xylene ($3.55 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 300 °C) compared to the silicalite-1 membrane ($(para/ortho) = 2.1$ (permeance to *p*-xylene $7.4 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 300 °C). However, neither were completely defect-free.¹⁴⁹ A method for preparing Nafion/acid functionalized zeolite Beta (NAFB) nanocomposite membranes by *in situ* hydrothermal crystallization has been reported for use in a direct methanol fuel cell (DMFC). The nanocomposite membranes were found to have a slightly lower proton conductivity but a markedly lower methanol permeability (*ca.* 40% reduction). When tested with a 1 M methanol feed, the DMFCs with the NAFB composite membranes demonstrated a slightly higher open circuit voltage (OCV; 3%) and much higher maximum power density (21%) than those with the pure Nafion 115 membranes. When a higher methanol concentration (5 M) was used, the DMFCs with the NAFB composite membranes showed a 14% higher OCV and a 93% higher maximum power density than those with the pure Nafion 115 membranes.¹⁵⁰ An experimental study is reported on the pervaporative dehydration of ethylene glycol (EG)/water mixtures using commercial nanoporous NaA zeolite membranes. The concentration range investigated (C-EG > 70 wt%) was selected according to existing industrial requirements. It was found that at 70 °C and with an initial EG concentration of 70 wt%, larger fluxes and separation factors could be obtained, *i.e.*, $0.94 \text{ kg m}^{-2} \text{ h}^{-1}$ and 1177, respectively. The Pervaporation Separation Index (PSI) of the membrane was found to be high compared to that of polymeric membranes.¹⁵¹ Other applications of pervaporation through zeolite membranes include the separation of water from ethanol-water mixtures using NaA and NaY membranes,¹⁵² the separation of xylene isomers using polyurethane membranes containing ZSM-5¹⁵³ and the separation of various dichlorinated compounds (dichloromethane, 1,2-dichloroethane and *trans*-1,2-dichloroethylene) from water in their aqueous solutions using a silicalite-1 membrane.¹⁵⁴ In the latter example, fluxes of dichlorinated compounds in the range $0.2\text{--}71 \text{ g m}^{-2} \text{ h}^{-1}$ were measured with separation factors of 12–332 being observed, depending on the mole fraction of the organic material. It is concluded that the silicalite-1 membrane is suitable for the selective removal of dichlorinated organic compounds from their dilute solutions in water and at a comparatively low temperature.¹⁵⁴

7.3 Porous carbons and zeolites

Carbon nanotubes (CNTs) with an internal diameter range of 20–30 nm have been employed as templates for the growth of nano-crystalline ZSM-5 and NaY zeolites. By means of a combination of X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), it was confirmed that the nanocrystals possess typical structural features for nanodimensional zeolites which are quite distinct from those of microdimensional zeolites.¹⁵⁵ The decomposition of tripropylamine (TPA) molecules adsorbed in the channels of AlPO₄-5 (AFI) and Cobalt-incorporated AlPO₄-5 (CoAPO-5) zeolite crystals was investigated using Fourier transform Infrared

(FTIR) spectroscopy and thermogravimetry (TG) methods. The carbonization temperature of TPA molecules inside the channels of Co-AFI crystals is notably decreased from that required in the pure material, demonstrating the catalytic role of the Co atoms, and their presence assists the formation of 0.4 nm SWNTs in the channels, which is conferred by a significant decrease in the formation energy for these nanotubes.¹⁵⁶ HY was used as the template material for the preparation of an ordered microporous carbon containing an amorphous carbon core and a graphitic carbon shell. The electrochemical properties of Pt supported on the carbon samples were examined and compared with a commercial catalyst. It was observed that a Pt catalyst supported on a carbon with a core/shell structure has a higher specific activity for room-temperature methanol oxidation than does the commercial catalyst.¹⁵⁷ In another report is a description of microporous carbons being prepared using the ammonium form of zeolite Y as a template and furfuryl alcohol as the carbon precursor, which reduces the procedure to a simple impregnation method followed by pyrolytic carbonisation. Very high surface area materials arise from this approach, in one case giving a N₂ BET surface of 3683 m²/g.¹⁵⁸

8. Hydrocarbon conversion reactions over zeolites

In view of its importance in hydrogenation reactions, *e.g.* of alkenes, the adsorption of hydrogen on HY and Pd(0)-HY zeolites was investigated in the temperature interval of 20–300 K, using IR and EXAFS measurements, and the energy barriers for diffusion of hydrogen in the internal voids of the faujasite structure were calculated from *ab initio* methods. It was found that H₂ is adsorbed at 20 K inside the supercages of zeolite HY giving rise to 1:1 –OH...H₂ H-bonded complexes with the Brønsted acid sites, and additionally less specific interactions with the cage walls. H₂ is prevented from entering the sodalite-cages by the high energy barrier to penetrating the framework hexagonal apertures. On Pd(0) containing zeolites, hydrogen is adsorbed in atomic form resulting in a metal-hydride phase; subsequent spill-over effects allow confinement of hydrogen in the small sodalite-cages, which is demonstrated by H/D isotopic substitution experiments.¹⁵⁹ There is a report of a theoretical study of methane activation over PdO/H-ZSM-5 using DFT methods. The crucial initiation step is the activation of the first C–H bond, after which the reaction of the remaining C–H moieties occurs fairly easily. This work supports the notion that the oxygen atom in PdO is directly involved in methane activation meaning that PdO is the active Pd species. The Brønsted acid sites in the zeolite are able to assist the process thus reducing its activation energy.¹⁶⁰ The heterolytic dissociation of CH₄ over silver cationic clusters (Ag_{*n*}⁺) in Ag⁺-exchanged zeolites leads to the formation of silver hydride (Ag_{*n*}-H) and methyl cations, which then react with ethylene (C₂H₄) to form propene (C₃H₆). This process causes a methane conversion of 13.2% at 673 K to afford higher hydrocarbons, such as toluene. Under these reaction conditions, H-ZSM-5 only catalyzes ethylene conversion to higher hydrocarbons, such as butenes, and no methane conversion occurs. The reaction of CH₄ with benzene also proceeds to form toluene and xylenes over Ag-ZSM-5 at 673 K. Zeolites prepared by exchange with other metal cations, including In and Ga, also activate CH₄ in the presence of C₂H₄. Using ¹³CH₄ as a tracer, propene is shown to be a primary product of the ethene reaction, based on the observation of a significant proportion of singly ¹³C-labelled propene. In-ZSM-5 catalyzes the formation of benzene and toluene, in addition to propene. ¹³C label atoms are not found in the benzene thus produced, indicating that benzene

originates entirely from C_2H_4 . However, the occurrence of singly ^{13}C -labelled toluene implies that toluene is formed by the reaction of benzene with $^{13}CH_4$.¹⁶¹ This is a complex scheme, and is in many ways reminiscent of the “hydrocarbon pool” mechanism discussed earlier in Section 6. Another theoretical investigation was reported this time using *ab initio* methods of the reactivity of isobutane on zeolites. Calculated activation energies for cracking (52.3 kcal/mol), for primary hydrogen exchange (29.4 kcal/mol), for tertiary hydrogen exchange (29.9 kcal/mol) and for dehydrogenation (59.4 kcal/mol) were obtained.¹⁶² Yet another theoretical study deals with the alteration of fundamental zeolite properties by functionalisation of an essential MFI framework with bridging methylene groups, which is predicted to enhance the acidity of the zeolite.¹⁶³ Some final potentially useful reactions of hydrocarbons (or primary oxidation products of hydrocarbons) on zeolites include the oxidation of benzene to phenol over a FeAlPO catalyst using N_2O as the oxidant,¹⁶⁴ the synthesis of nopol by condensing β -pinene with paraformaldehyde over Zn–Al–MCM-41 catalysts,¹⁶⁵ the synthesis of dimethyl carbonate and dimethoxymethane by the oxidative carbonylation of methanol over Cu–ZSM-5¹⁶⁶ and the use of an “organic zeolite” (Bisurea macrocycles) to perform a highly stereoselective photodimerisation of 2-cyclohexenone.¹⁶⁷

9. Zeolites in energy-related applications

Among the energy-related problems that humankind needs to solve is how to dispose of the billions of abandoned used motor-tyres (tires), and ideally to convert them into useful products in a viable recycling programme. In one study, whole tire pyrolysis oil was distilled and the resulting distillates were redistilled to separate the limonene. Vacuum distillation yielded on average 25.5 wt% naphtha containing 16.3 wt% limonene, and redistillation increased the limonene concentration to approximately 32–37 wt%. It was found that the reaction of R-(+)-limonene with methanol in the presence of activated beta-zeolite yielded its methyl ether in 87.5% yield and with a selectivity of 89.7%.¹⁶⁸ In a similar vein, means must be found to dispose of vast quantities of plastics (poly-hydrocarbons), ideally by turning these too into useful feedstocks for new processes. One study deals with the catalytically assisted copyrolysis of a Turkish lignite with low-density polyethylene (LDPE). The catalysts used were red mud (which is a waste product of an aluminium factory in Turkey), zeolite A and K_2CO_3 . An increase in temperature leads to increased gas yields. The use of catalysts during the co-pyrolysis procedure also leads to improved gas generation. A remarkable synergetic effect between lignite and LDPE on improving the yields of tars is also reported.¹⁶⁹ An effective adsorbent for the separation of ethylene from ethane has been prepared by the dispersion of CuCl in large NaX crystals, which is ascribed to the strong interaction due to the formation of π -complexes between ethylene and CuCl.¹⁷⁰ The similarity in volatility between C_2H_4 and CO_2 make separation of the latter from a CO_2 stream *via* conventional cryogenic distillation difficult. The alternative catalytic combustion method is an energy-inefficient process, especially when it is combined with the cryogenic distillation. However, it is shown that while both NaY and HY have poor adsorption selectivities for C_2H_4 from the C_2H_4/CO_2 stream because of a stronger competition from CO_2 for the physical adsorption sites, Ag^+ -exchanged NaY and HY zeolites, favoured by the strong chemical adsorption of C_2H_4 by Ag^+ ions, are able to remove C_2H_4 from the CO_2 stream effectively.¹⁷¹ The removal of CO_2 from natural gas using zeolite 13X as the adsorbent coupled with a vacuum pressure swing method has been

reported.¹⁷² One possible source of non-imported hydrocarbons might stem from methanol, and in this regard, the catalytic activity of H-ZSM-5 impregnated with copper oxide has been investigated. An enhancement in hydrocarbon yield was found, which reached maximum at a 7% loading of CuO.¹⁷³ Fischer-Tropsch Synthesis (FTS) waxes are high molecular weight materials that need to be introduced as a feedstock for fluid catalytic cracking (FCC), in order to provide useful smaller hydrocarbons in a range suitable for use in internal combustion engines, and hence improve the overall fuel yield obtainable by FTS of hydrocarbons from syngas ($\text{H}_2 + \text{CO}$). A high gasoline fraction (70 wt%) with a very low concentration of aromatics can be obtained. As a result of the formation of *iso*-paraffins, *n*-olefins and *iso*-olefins the gasoline is expected to show an acceptable octane number. Since sulphur and nitrogen compounds are absent from the feed, extremely clean transportation fuels are obtained. The addition of H-ZSM-5 to an equilibrium catalyst allows the production of significant amounts of light olefins, in particular propene (16 wt%) and butene isomers (15 wt%).¹⁷⁴

The latter paper leads on neatly to the situation when the hydrocarbon is significantly laden with sulphur compounds, and methods by which these can be removed before the material might be processed into a useful fuel. This is a matter of particular importance as the restrictions imposed by governments worldwide on lowering the sulphur content in transportation fuels become ever more stringent, and should be done especially by alternative means than conventional hydrodesulphurisation, to avoid adding to the atmospheric burden of SO_2 . A very high sulphur removal capacity has been observed for NiY (42 mg/g) and CuY (31 mg/g) zeolites. These and other ion-exchanged zeolites such as FeY and ZnY have been found to effectively remove sulphur from commercial diesel, although the capacity in the latter case was lower than that observed with model diesel.¹⁷⁵ A potential inhibition influence of aromatic nitrogen compounds and polyaromatic hydrocarbons (PAH) on the desulphurisation capacity of Cu(I)Y zeolite was investigated since amounts up to a few hundred parts per million of nitrogen compounds and 1.4–11% of PAH may occur in transportation fuels depending on where they come from, and the season in which they are extracted. Their effect on the high sulphur selectivity of the catalyst was in fact only moderate because a low sulphur fuel was used.¹⁷⁶ A direct performance comparison between the two copper-containing materials Cu(I)Y and Cu(II)Y in the removal of sulphur compounds from hydrocarbon streams has been made. It is concluded that Cu(I)Y zeolite is rather more effective than Cu(II)Y in removing thiophene from various fuel blends. The capacity of both materials for thiophene is reduced markedly by the presence of aromatics and/or olefins, and Cu(I)Y immediately turns dark on exposure to such feeds. Both materials exhibit some capability to transform thiols to disulfides at ambient temperature.¹⁷⁷ The desulphurisation of Tier 2 gasoline (<30 ppmw S) by Cu(II)Y zeolite was examined. In part, sulphur compounds are formed with greater molecular weights and sizes than those present in the initial feed. Some of these heavier sulphur species are eluted but many do not elute, resulting in a desulphurisation mechanism that occurs by the physical entrapment of sulphur-containing molecules in addition to a pathway involving direct interaction between the copper and sulphur atoms.¹⁷⁸ Other papers on this general theme include studies of the desulphurisation of high-sulphur jet fuel by π -complexation with palladium and copper containing adsorbents, including CuY,¹⁷⁹ the influence of the alkali metal cation in zeolite-Y on its competitive selectivity for toluene/thiophene¹⁸⁰ and the mechanism of the removal by adsorption and catalytic decomposition of *tert*-butanethiol by AgY zeolite, under ambient conditions.¹⁸¹

The heating-cooling aspect of zeolites in contact with a working evaporative fluid such as water have found application in the development of heating-refrigeration systems containing them, which can potentially save energy and so I mention some of them now under this heading. For example, a “solar-powered cooling tube” is described which uses the working pair: zeolite13X/water. The operating principle of this device, which consists of four major components, a solar collector, an adsorbent bed, a condenser, and an evaporator all in one glass tube, is also presented. The experimental results show that a solar adsorption cooling tube is capable of heating 4 kg of water to about 50 °C in daytime and 4 kg of water to about 39 °C at night, as well as producing a refrigeration capacity of about 276 kJ. Its coefficient of performance (COP) can reach 0.22.¹⁸² Another device has been designed that supplies water chilled to 8–12 °C for the fan coil in the operator cabin of a train. This system is driven by the heated (350–450 °C) exhaust gas generated by the internal combustion engine of the locomotive. The designed refrigerating power and COP are 5 kW and 0.25, respectively, according to the requirements for the refrigeration output in the locomotive operator cabin and the waste heat provided by the engine. The maximum theoretical refrigerating power of the machine is 10 kW with a gas inlet temperature of 450 °C and an evaporating temperature of 6.5 °C. The adsorber can be heated from 97 °C to 423 °C or cooled from 423 °C to 97 °C in 1320 s.¹⁸³

10. Environmental pollution management using zeolites

In this section we are mostly concerned with the use of zeolites and zeolite-based materials as sorbents for pollutants either in protecting the environment from them *ab initio* or in remediation strategies. In the related literature the words “sorbent(s)”, “sorb” and “sorption” are used, presumably because not all uptake occurs onto a surface *per se*. We will follow this convention in the following. Bowman has published a review of the preparation, properties, characterisation and effectiveness of surfactant-modified zeolites (SMZ) in environmental remediation. These are interesting materials with multiple sorbent properties that can take-up mixtures of toxic inorganic anions and organic species, *e.g.* chromate and perchloroethylene. They tend not to be high capacity materials, and are best suited for the removal of toxic agents present, *e.g.* in water, in relatively low concentrations.¹⁸⁴ A specific example of the adsorption of ionisable organic solutes (phenol and aniline) by clinoptilolite, modified by hexadecyltrimethylammonium (HDTMA) cations has been reported.¹⁸⁵ Details of the adsorption of chromate anions on SMZ were determined, and interestingly it was found that planar nitrate anions adsorb more effectively on the SMZ surfaces than chromate anions which are tetrahedral. Indeed in cases when sulphate or nitrate were simultaneously present, inhibition of chromate adsorption was observed.¹⁸⁶ The processes involved in the sorption of chromate, selenate and sulphate anions by SMZ have been studied in some detail. The sorption data for each anion were found to be well described by the Langmuir isotherm adsorption equation.¹⁸⁷ The sorption of arsenic from soil-washing leachate by SMZ has been demonstrated with a maximum adsorption value of 72.0 mmol/kg of arsenic/kg (5.4 g/kg) of SMZ at 25 °C.¹⁸⁸ Surfactant-modified sorbents have been proposed for the removal of organic compounds from aqueous solution. In one study, one cationic (HDTMA) and three anionic (DOWFAX-8390, STEOL-CS330, and Aerosol-OT) surfactants were tested for their sorptive behavior onto different sorbents (alumina, zeolite, and Canadian River Alluvium). These surfactant-modified materials were then used to sorb a range of hydrophobic organic chemicals of

varying properties (benzene, toluene, ethylbenzene, 1,2-dichlorobenzene, naphthalene, and phenanthrene), and their sorption capacity and affinity were quantified. The HDTMA-zeolite system proved to be the most stable surfactant-modified sorbent studied because of the limited surfactant desorption. Both anionic and cationic surfactants resulted in modified sorbents with higher sorption capacity and affinity than the unmodified Canadian River Alluvium containing only natural organic matter.¹⁸⁹ It has been shown that it is possible to regenerate SMZ after saturation with chromate and perchloroethylene.¹⁹⁰ The removal of BTEX (benzene, toluene, and xylenes) from water using SMZ has also been demonstrated.¹⁹¹ By the simple act of cation-exchange, it is possible to remove toxic cations from an aqueous medium using zeolites, including radioactive cations from the cooling *etc.* waters of a nuclear power plant (NPP). In particular, radioactive $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ are always present among the products arising from the fission of uranium-235 (^{235}U). ^{134}Cs is also produced but it is less of a problem for long-term disposal since it has a half-life of about 2 years, compared with closer to 30 years each for ^{137}Cs and ^{90}Sr , and hence loses most of its radioactivity in 20 years rather than 1000 years (10 half-lives each). Natural zeolites are most often used for this purpose, generally clinoptilolite, for example in cleaning the waters from the NPP at Metsamor in Armenia, using zeolite-rich tuffs (geologically modified volcanic rocks) mined in the north of the country.^{4,8} Similarly, tuffs mined in Mongolia have been evaluated for their ability to take-up radioactive cations (^{137}Cs , ^{90}Sr , ^{90}Y) in competition with other cations present in an aqueous medium. As a general rule, the order of elemental cation uptake follows the series: $\text{Cs}^+ > \text{K}^+ > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+}$, although depending on the precise Si/Al ratio and the concentration and nature of the cations present altogether, the ability of a zeolite to take-up Cs^+ and Sr^{2+} varies, as is discussed. The typical selectivity and high affinity of clinoptilolite for the latter cations among the suite produced by ^{235}U fission is demonstrated, however.¹⁹² Another paper reports that clinoptilolite mined in Iran (in its Na^+ -exchanged form) is particularly effective for removing radioactive Cs^+ and Sr^{2+} from nuclear wastewaters and Ni^{2+} and Ba^{2+} from municipal wastewater since the affinity of the mineral for these cations is relatively high.¹⁹³ A study and comparison is made between different sorbent/ion-exchange materials for this same purpose, namely removing radioactive strontium from liquid radioactive waste and high hardness groundwaters. In the latter case, the presence of fairly high concentrations of *e.g.* Ca^{2+} and Mg^{2+} cations competes for and reduces the uptake of Sr^{2+} . This is a very informative paper, which covers the background to this topic well.¹⁹⁴ The post-event use of natural zeolites for the purpose of radioactive decontamination on the large scale (using 500 000 tonnes of zeolite) after the Chernobyl disaster was referred to earlier.^{4,7,8} Nano-sized large-pore titanium silicate materials ETS-10 and ETAS-10 with different Ti/Al ratios were used in the successful removal of heavy-metal cations (Cu^{2+} , Co^{2+} , Mn^{2+} and Zn^{2+}) from their aqueous solutions, as described by various adsorption equations of which the Langmuir-Freundlich isotherm fitted best. Significantly, thermodynamic measurements suggest that while the adsorption is endothermic (positive ΔH , negative ΔG), the positive entropy of adsorption indicates that the cations are not stably adsorbed on the surfaces of these materials, probably because of the increase in translational energy that is gained when they are displaced from their primary adsorption sites.¹⁹⁵ A potentially large problem is contamination of soils and groundwaters by Zn^{2+} and Pb^{2+} (from tin-solder) resulting from run-off of rain from galvanised roofs. In order to intercept such contamination at source, both clinoptilolite and geotextile filters have been employed. While the geotextile filter was

ineffective is retaining these heavy metal cations, the clinoptilolite filter could hold-back 97% of the initially determined contamination.¹⁹⁶ Similarly, lead and zinc cations were removed from their aqueous solutions using natural Turkish zeolite minerals which contained 45% clinoptilolite and 35% mordenite.¹⁹⁷ The potential application of natural Turkish clinoptilolite to removing Co^{2+} , Cu^{2+} , Zn^{2+} and Mn^{2+} from the wastewaters of metal finishing processes has been described.¹⁹⁸ A significant improvement of the ability of natural clinoptilolite to take-up Zn^{2+} was reported when the zeolite was first exchanged with Na^+ cations by chemical conditioning with 1 M NaCl solution.¹⁹⁹ A somewhat unusual paper describes an investigation of the “Radiation removal” of lead from aqueous solutions. In essence, an aqueous solution of Pb^{2+} cations is treated with various sorbent materials (activated carbon, bentonite and zeolite) and exposed to radiation from an electron beam. While the results were somewhat variable as to the efficacy of the irradiation in its effect on lead removal, a substantial increase in the effectiveness of the process is indicated when the solution is saturated with nitrous oxide.²⁰⁰ However, this will never become a practical decontamination method on the large scale—it is too demanding in terms of electricity and only fairly small volumes of liquid could be so treated.

As a result of their negative charge, unmodified zeolite surfaces show no affinity for anions, and in fact repel them. However, a neat trick may be employed which is to first exchange the zeolite with particular cations which form complexes of low solubility with anions that it is desired to remove from a particular aqueous medium, and which will therefore precipitate within the zeolite matrix. For example, in the adsorption of chromate anions by clinoptilolite, the degree of uptake was found to be proportional to the solubility product (K_{sp}) of the chromate precipitate, and the amount of the exchangeable cation present in the zeolite. In the series of cations studied, Pb^{2+} was found most effective in removing chromate.²⁰¹ In connection with radioactive decontamination, the removal of iodide anions, particularly ^{131}I with a half-life of just 8 days (hence highly radioactive) formed in 2.77% yield among the products from the fission of ^{235}U , from nuclear wastewaters using zeolites has been investigated. It was found that clinoptilolite is a more promising material for this purpose than natrolite, and that the adsorption was highest in its Ag^+ , Pb^{2+} and Ti^+ -exchanged forms.²⁰² A particularly active research group in the field of cation and anion decontamination using zeolites is that of Faghihian *et al.* based in Tehran, who have reported the following studies, which may be taken as representative of the field as a whole: adsorption of arsenate anion by Fe, Pb and Ag-exchanged clinoptilolites,²⁰³ uptake of cerium by zeolite A prepared from natural tuffs,²⁰⁴ thorium cation uptake again using zeolite A prepared from natural clinoptilolite tuffs,²⁰⁵ removal of cyanide anions from industrial liquid wastes using cation-exchanged clinoptilolite (the cobalt form of the zeolite showed the highest uptake of 1.95 meq of cyanide per gram of zeolite, whereas the uptake of natural forms is 0.070 meq/g),²⁰⁶ synthesis of Na-P-c zeolite from perlite and its use in cyanide adsorption,²⁰⁷ removal of radioactive iodide anions using a surfactant-modified zeolite (SMZ),²⁰⁸ adsorption of molybdate anions by natrolite and clinoptilolite-rich tuffs.²⁰⁹ Catalytic converters are well known as devices installed into the exhaust-systems of vehicles to reduce their toxic gas emissions, especially mixtures of nitrogen oxides, collectively termed NO_x . Among the Cu-ZSM-5 catalysts used for direct NO decomposition it is found that Cu-SZM-11 and Cu-SZM-12 have about twice the efficiency of Cu-ZSM-5 for this purpose.²¹⁰ This topic is developed in more detail in a following full-paper, where it is concluded that a higher activity is

conferred by the presence of only straight microporous channels where either more catalytic centres are formed or there is improved accessibility to them, in the higher zeolite, whereas ZSM-5 has both straight and sinusoidal channels.²¹¹ In another paper it is reported that for commercial zeolites (MFI, FER, BEA, MOR, FAU) with very low levels of iron impurity ($\text{Fe/Al} < 0.01$) there is a significant influence of the framework type on the decomposition of N_2O .²¹² Selective hydrogenation has been demonstrated as a means for removing nitrate anions as contaminants from water, using a Cu–Pd/mordenite catalyst.²¹³ Another catalytic application in the elimination of a pollutant is the oxidation of 1,2-dichlorobenzene over various protonic zeolites (H-FAU, H-BEA, H-MFI, H-MCM-22 and ITQ2) and their corresponding Pt loaded equivalents. The process is found to be effective at 350–400 °C, and while the presence of platinum enhances the activity of the catalyst, it tends to increase the yield of by-products such as 1,2,4-trichlorobenzene.²¹⁴ In another paper it is reported that ammonium cations can be removed as a contaminant from their aqueous solutions using a Romanian natural volcanic tuff even in the presence of Zn^{2+} and Cd^{2+} which appear not to decrease the ammonium adsorption capacity of the material.²¹⁵ It has been shown that the bactericidal activity of a silver-exchanged zeolite is similar to that of silver nitrate solution. It is proposed that the contact of the bacterial cell with the zeolite causes the transfer of Ag^+ cations into the cell, with the consequent generation of reactive oxygen species which are involved in the mode of bactericidal action of the Ag-zeolite.²¹⁶ A critical overview has been published of hemostatic dressings for wounds in battle situations, some of which are based on zeolites (e.g. QuikClot). However, the effectiveness of these new dressings on wounds actually sustained in combat is still questionable. It is concluded that more research is needed to draw definite conclusions about the effectiveness of these materials in a combat setting.²¹⁷

Clearly, the uses of zeolites are manifest, and unique environmental benefits are offered by them. Indeed, the Cuban designation¹ “La Roca Magica” appears to entitle these zeolites superlatively. I recall that synonyms in Spanish for “Magica” (the adjective form of “Magico”) include “Estupenda” and “Maravillosa”, and who could disagree with either one?

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References

- 1 F. A. Mumpton, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**, 3463.
- 2 A. F. Cronstedt, *Kongl. Vetenskaps Akad. Handl. Stockholm*, 1756, **17**, 120.
- 3 R. M. Barrer, *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*, Academic Press, London, 1978.
- 4 C. J. Rhodes, <http://ergobalance.blogspot.com>.
- 5 <http://en.wikipedia.org/wiki/Zeolite> and links therein.
- 6 S. L. Meisel, J. P. McCulloch, C. H. Lechthaler and P. B. Weisz, *Chem. Tech.*, 1976, **6**, 86.
- 7 T. Armbruster, in *Studies in Surface Science and Catalysis 135 Zeolites and Mesoporous Solids at the Dawn of the 21st Century*, eds. A. Galarnau, F. Di Renzo, F. Faujula and J. Vedrine, Elsevier, Amsterdam, 2001, p. 13.
- 8 http://www.bbc.co.uk/radio4/science/thematerialworld_20060119.shtml.

- 9 J. D. Sherman, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**, 3471.
- 10 C. J. Rhodes, *Progress in Reaction Kinetics and Mechanism*, 2005, **30**, 145, (actually published, 2006).
- 11 M. F. Crawford and I. R. Dagg, *Phys. Rev.*, 1953, **91**, 1569.
- 12 H. Forster and M. Schmidt, *J. Mol. Struct.*, 1978, **47**, 339.
- 13 H. Bose, H. Forster and W. Frede, *Chem. Phys. Lett.*, 1987, **138**, 401.
- 14 K. Beck, H. Pfeifer and B. Staudte, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 3995.
- 15 L. M. Kustov and V. B. Kazansky, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2675.
- 16 A. Yu. Khodakov, L. M. Kustov, V. B. Kazansky and C. Williams, *J. Chem. Soc., Faraday Trans.*, 1991, **88**, 3251.
- 17 H. Knozinger and S. Huber, *J. Chem. Soc., Faraday Trans.*, 1998, **94**, 2047.
- 18 E. Garrone and C. Otero Arean, *Chem. Soc. Rev.*, 2005, **34**, 846.
- 19 S. Savitz, A. L. Myers and R. J. Gorte, *J. Phys. Chem. B*, 1999, **103**, 3687.
- 20 K. M. Neyman, P. Strodel, S. Ph. Ruzankin, N. Schlensog, H. Knozinger and N. Rosch, *Catal. Lett.*, 1995, **31**, 273.
- 21 I. N. Senchenya, E. Garrone and P. Ugliengo, *J. Mol. Struct. (THEOCHEM)*, 1996, **368**, 93.
- 22 C. Otero Arean, M. Rodriguez Delgado, G. Turnes Palomino, M. Tomas Rubio, N. M. Tsyganenko, A. A. Tsyganenko and E. Garrone, *Microporous Mesoporous Mater.*, 2005, **80**, 247.
- 23 C. Otero Arean, O. V. Manoilova, B. Bonelli, M. Rodriguez Delgado, G. Turnes Palomino and E. Garrone, *Chem. Phys. Lett.*, 2003, **370**, 631.
- 24 en.wikipedia.org/wiki/Adsorption.
- 25 C. Turnes Palomino, M. R. Llop Carayol and C. Otero Arean, *J. Mater. Chem.*, 2006, **16**, 2884.
- 26 S. K. Bhatia and A. L. Myers, *Langmuir*, 2006, **22**, 1688.
- 27 P. Nachtigall, E. Garrone, G. Turnes Palomino, M. Rodriguez Delgado, D. Nachtigall-ova and C. Otero Arean, *Phys. Chem. Chem. Phys.*, 2006, **10**, 2286.
- 28 B. D. James, G. N. Baum, F. D. Lomax Jr, C. E. Thomas and I. F. Kuhn, Jr, *Comparison of onboard hydrogen storage for fuel cell vehicles, Task 4. 2 Final Report under subcontract 47-2-R31148, prepared for Ford Motor Company and U.S. Department of Energy*, Arlington, Virginia, May, 1996, p. 2–2.
- 29 Available from (<http://www.eere.energy.gov/hydrogenandfuel-cells/pdfs/bk28424.pdf>).
- 30 A. W. C. van den Berg, S. T. Bromley and J. C. Jansen, *Microporous Mesoporous Mater.*, 2005, **78**, 63.
- 31 A. Zecchina, S. Bordiga, J. G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjorgen and K. Petter Lillerud, *J. Am. Chem. Soc.*, 2005, **127**, 6361.
- 32 J. Weitkamp, D. Schmid, M. Fritz, F. Cubero and S. Ernst, *Wasserst. Energietraeger, Kolloq. 1994 Sondersforschungsbereichs 270 Univ. Stuttgart*, 1994, p. 287–300.
- 33 A. W. C. van den Berg, S. T. Bromley, J. C. Wojdel and J. C. Jansen, *Microporous Mesoporous Mater.*, 2006, **87**, 235.
- 34 J. G. Vitello, G. Ricchiardi, G. Spoto and A. Zecchina, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3954.
- 35 *Materials Studio 2.2, Discover module*, Accelrys Incorporated, San Diego, CA, 2002.
- 36 L. Regli, A. Zecchina, J. G. Vitillo, D. Cocina, G. Spoto, C. Lamberti, K. P. Lillerud, U. Olsbye and S. Bordiga, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3197.
- 37 Y. Li and R. T. Yang, *J. Phys. Chem. B*, 2006, **110**, 17175.
- 38 A. W. C. van den Berg, M. A. Zwijnenburg, S. T. Bromley, E. Flikkema, R. G. Bell, J. C. Jansen and J. Schoonman, *J. Mater. Chem.*, 2006, **16**, 3285.
- 39 X.-M. Du and E.-D. Wu, *Chinese Journal of Chemical Physics*, 2006, **19**, 457.
- 40 Z.-X. Yang, Y.-D. Xia, X.-Z. Sun and R. Mokaya, *J. Phys. Chem. B*, 2006, **110**, 18424.
- 41 X. Lin, J. Jia, X. Zhao, K. M. Thomas, A. J. Blake, G. S. Walker, N. R. Champness, P. Hubberstey and M. Schroder, *Angew. Chem. Int. Ed.*, 2006, **45**, 7358.
- 42 D. K. Ross, *Vacuum*, 2006, **80**, 1084.
- 43 http://en.wikipedia.org/wiki/Hydrogen_storage.
- 44 H. Jobic, W. Schmidt, C. B. Krause and J. Karger, *Microporous, Mesoporous Mater.*, 2006, **90**, 299.
- 45 A. Pampel, F. Engelke, P. Galvosas, C. Krause, F. Stallmach, D. Michel and J. Karger, *Microporous, Mesoporous Mater.*, 2006, **90**, 271.
- 46 A. Jentys, R. R. Mukti, H. Tanaka and J. A. Lercher, *Microporous, Mesoporous Mater.*, 2006, **90**, 284.
- 47 H. Jobic, H. Ramanan, S. M. Auerbach, M. Tsapatsis and P. Fouquet, *Microporous, Mesoporous Mater.*, 2006, **90**, 307.

- 48 G. Zhao, B. Gross, H. Dilger and E. Roduner, *Phys. Chem. Chem. Phys.*, 2002, **4**, 974.
- 49 J. H. Williams, *Acc. Chem. Res.*, 1993, **26**, 593.
- 50 E. Beerdsen and B. Smit, *J. Phys. Chem. B*, 2006, **110**, 14529.
- 51 A. Gunadi and S. Brandani, *Microporous, Mesoporous Mater.*, 2006, **90**, 278.
- 52 H. Jobic and D. N. Theodorou, *J. Phys. Chem. B*, 2006, **110**, 1964.
- 53 E. Garcia-Perez, D. Dubbeldam, T. L. M. Maesen and S. Calero, *J. Phys. Chem. B*, 2006, **110**, 23968.
- 54 R. L. Goring, *J. Catal.*, 1973, **31**, 13.
- 55 D. M. Ruthven, *Microporous, Mesoporous Mater.*, 2006, **96**, 262.
- 56 A. Di Lella, N. Desbiens, A. Boutin, I. Demachy, P. Ungerer, J.-P. Bellat and A. Fuchs, *Phys. Chem. Chem. Phys.*, 2006, **8**, 5396.
- 57 G. Hunger, *et al.*, *J. Phys. Chem. B*, 2006, **110**, 342.
- 58 C. E. Ramachandran, S. Chempath, L. J. Broadbelt and R. Q. Snurr, *Microporous, Mesoporous Mater.*, 2006, **90**, 293.
- 59 G. Maurin, D. F. Plant, F. Henn and R. G. Bell, *J. Phys. Chem. B*, 2006, **110**, 18447.
- 60 D. F. Plant, G. Maurin and R. G. Bell, *J. Phys. Chem.*, 2006, **110**, 15926.
- 61 A. V. A. Kumar, H. Jobic and S. K. Bhatia, *J. Phys. Chem. B*, 2006, **110**, 16666.
- 62 H. Omi, T. Ueda, N. Kato, K. Miyakubo and T. Eguchi, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3857.
- 63 L. K. Andersen and H. Frei, *J. Phys. Chem. B*, 2006, **110**, 22601.
- 64 J. Fossey, D. Lefort and J. Sorba, *Free Radicals in Organic Chemistry*, Wiley, Chichester, 1995.
- 65 D. F. Evans, *J. Chem. Soc.*, 1953, 345.
- 66 H. Taubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, 1960, **82**, 5966.
- 67 K. S. Wei and A. H. Adelman, *Tetrahedron Lett.*, 1969, 3297.
- 68 J. C. W. Chien, *J. Phys. Chem.*, 1965, 4317.
- 69 K. Onodera, G. Furusawa, M. Kojima, M. Tsuchiya, S. Aihara, R. Akaba, H. Sakuragi and K. Tokumaru, *Tetrahedron*, 1985, **41**, 2215.
- 70 N. Kulevsky, P. V. Sneeringer, L. D. Grina and V. I. Stenberg, *Photochem. Photobiol.*, 1970, **12**, 395.
- 71 H. Frei, F. Blatter and H. Sun, *CHEMTECH*, 1996, **26**, 24.
- 72 F. Blatter, H. Sun, S. Vasenkov and H. Frei, *Catalysis Today*, 1998, **41**, 297.
- 73 F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1993, **115**, 7501.
- 74 F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1994, **116**, 1812.
- 75 F. Blatter, F. Moreau and H. Frei, *J. Phys. Chem.*, 1994, **98**, 13403.
- 76 F. Blatter, H. Sun and H. Frei, *Catal. Lett.*, 1995, **35**, 1.
- 77 R. A. Sheldon and J. K. Kochi, *Metal-catalysed Oxidation of Organic Compounds*, ch. 11, Academic Press, New York, 1981.
- 78 H. Sun, F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1994, **116**, 7951.
- 79 H. Sun, F. Blatter and H. Frei, *J. Am. Chem. Soc.*, 1996, **118**, 6873.
- 80 F. Blatter, H. Sun and H. Frei, *Chem. Eur. J.*, 1996, **2**, 385.
- 81 H. Sun, F. Blatter and H. Frei, *Catal. Lett.*, 1997, **44**, 247.
- 82 J. Xu, B. L. Mojet, J. G. van Ommen and L. Lefferts, *Phys. Chem. Chem. Phys.*, 2003, **5**, 4407.
- 83 S. Vasenkov and H. Frei, *J. Phys. Chem. B*, 1998, **102**, 8177.
- 84 H. Frei, *Science*, 2006, **313**, 309.
- 85 E. A. Pidko and R. A. van Santen, *J. Phys. Chem. B*, 2006, **110**, 2963.
- 86 E. A. Pidko and R. A. van Santen, *ChemPhysChem*, 2006, **7**, 1657.
- 87 A. Ricci, M. N. Chretien and J. C. Sciano, *Chem. Mater.*, 2004, **16**, 2669.
- 88 T. Doussineau, M. Smaïhi, S. Balme and J.-M. Janot, *ChemPhysChem*, 2006, **7**, 583.
- 89 M. Alvaro, E. Carbonell, H. Garcia, C. Lamaza and M. N. Pillai, *Photochem. Photobiol. Sci.*, 2004, **3**, 189.
- 90 M. N. Chretien, B. Shen, H. Garcia, A. M. English and J. C. Sciano, *Photochem. Photobiol.*, 2004, **80**, 434.
- 91 M. Alvaro, M. N. Chretien, B. Ferrer, V. Fornes, H. Garcia and J. C. Sciano, *Chem. Commun.*, 2001, 2106.
- 92 J. M. Thomas and R. Raja, *Ann. Rev. Mater. Res.*, 2005, **35**, 315.
- 93 A. Corma and H. Garcia, *Eur. J. Chem.*, 2004, 1143.
- 94 R. M. Barrer, *Mol. Sieves Pap. Conf.*, 1968, 39.
- 95 R. A. Sheldon, I. W. C. E. Arends and H. E. B. Lempers, *Catalysis Today*, 1998, **41**, 387.
- 96 I. W. C. E. Arends and R. A. Sheldon, *Appl. Catal. A*, 2001, **212**, 175.
- 97 J. F. Haw, *Phys. Chem. Chem. Phys.*, 2002, **4**, 5431.

- 98 J. B. Nicholas, J. F. Haw, L. W. Beck, T. R. Krawietz and D. B. Ferguson, *J. Am. Chem. Soc.*, 1995, **117**, 12350.
- 99 E. Roduner and H. Dilger, *J. Am. Chem. Soc.*, 2001, **123**, 7717.
- 100 L. W. Beck, T. Xu, J. B. Nicholas and J. F. Haw, *J. Am. Chem. Soc.*, 1995, **117**, 11594.
- 101 G. J. Kramer and R. A. van Santen, *J. Am. Chem. Soc.*, 1995, **117**, 1766.
- 102 K. C. Hunter and A. L. L. East, *J. Phys. Chem. A*, 2002, **106**, 1346.
- 103 S. A. Zygmunt, L. A. Curtiss, P. Zapol and L. E. Iton, *J. Phys. Chem. B*, 2000, **104**, 1944.
- 104 S. R. Blazzkowski, M. A. C. Nascimento and R. A. van Santen, *J. Phys. Chem.*, 1996, **100**, 3463.
- 105 C. D. Chang, *Catal. Rev.*, 1983, **25**, 1.
- 106 M. Stocker, *Microporous Mesoporous Mater.*, 1999, **29**, 3.
- 107 F. J. Keil, *Microporous Mesoporous Mater.*, 1999, **29**, 49.
- 108 J. K. A. Clarke, R. Darcy, B. F. Hegarty, E. O'Donoghue, V. Amir-Ebrahimi and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1986, 425.
- 109 C. J. Rhodes and C. S. Hinds, in *Radicals on Surfaces*, eds. A. Lund and C. J. Rhodes, Kluwer, Dordrecht, 1995, p. 119.
- 110 R. J. Rooney, personal communication.
- 111 T. Mole, J. A. Whiteside and D. Seddon, *J. Catal.*, 1983, **82**, 261.
- 112 T. Mole, G. Bott and D. Seddon, *J. Catal.*, 1983, **82**, 435.
- 113 I. M. Dahl and S. Kolboe, *J. Catal.*, 1994, **149**, 458.
- 114 I. M. Dahl and S. Kolboe, *J. Catal.*, 1996, **161**, 304.
- 115 J. F. Haw, J. B. Nicholas, W. G. Song, F. Deng, Z. K. Wang, T. Xu and C. S. Heneghan, *J. Am. Chem. Soc.*, 2000, **122**, 4763.
- 116 P. W. Goguen, T. Xu, D. H. Barich, T. W. Skloss, W. G. Song, Z. K. Wang, J. B. Nicholas and J. F. Haw, *J. Am. Chem. Soc.*, 1998, **120**, 2650.
- 117 W. G. Song, J. F. Haw, J. B. Nicholas and C. S. Heneghan, *J. Am. Chem. Soc.*, 2000, **122**, 10726.
- 118 W. Song, H. Fu and J. F. Haw, *J. Am. Chem. Soc.*, 2001, **123**, 4749.
- 119 W. Song, D. M. Marcus, H. Fu, J. O. Ehresmann and J. F. Haw, *J. Am. Chem. Soc.*, 2002, **124**, 3844.
- 120 J. F. Haw, W. Song, D. M. Marcus and J. B. Nicholas, *Acc. Chem. Res.*, 2003, **36**, 317.
- 121 D. Lesthaeghe, V. Van Speybroeck, G. B. Martin and M. Waroquier, *Angew. Chem. Int. Ed.*, 2006, **45**, 1714.
- 122 D. M. Marcus, M. J. Hayman, Y. M. Blau, D. R. Guenther, J. O. Ehresmann, P. W. Kletnieks and J. F. Haw, *Angew. Chem. Int. Ed.*, 2006, **45**, 1933.
- 123 S. Walspurger, Y. Y. Sun, A. S. S. Sido and J. Sommer, *J. Phys. Chem. B*, 2006, **110**, 18368.
- 124 I. I. Ivanova, N. S. Nesterenko and C. Fernandez, *Catalysis Today*, 2006, **113**, 115.
- 125 Y. Jiang, W. Wang, V. R. Reddy Marthala, J. Huang, B. Sulikowski and M. Hunger, *J. Catal.*, 2006, **238**, 21.
- 126 J. F. Haw, D. M. Marcus and P. W. Kletnieks, *J. Catal.*, 2006, **244**, 130.
- 127 D. M. Marcus, K. A. McLachlan, M. A. Wildman, I. O. Ehresmann, P. W. Kletnieks and J. F. Haw, *Angew. Chem. Int. Ed.*, 2006, **45**, 3133.
- 128 Y. Jiang, W. Wang, V. R. Reddy Marthala, J. Huang, B. Sulikowski and M. Hunger, *J. Catal.*, 2006, **244**, 134.
- 129 M. Niwa, S. Kato, T. Hattori and Y. Murakami, *J. Chem. Soc., Faraday Trans. 2*, 1984, **80**, 3135.
- 130 N. R. E. N. Impens, P. van der Voort and E. F. Vansant, *Microporous Mesoporous Mater.*, 1999, **28**, 217.
- 131 W. Song, D. M. Marcus, S. M. Abubakar, E. Jani and J. F. Haw, *J. Am. Chem. Soc.*, 2003, **125**, 13964.
- 132 S. M. Abubakar, J. C. Lee, D. M. Marcus, J. O. Ehresmann and J. F. Haw, *J. Phys. Chem. B*, 2006, **110**, 14598.
- 133 J. C. Groen, J. A. Moulijn and J. Perez-Ramirez, *J. Mater. Chem.*, 2006, **16**, 2121.
- 134 B. H. Chen and Y. N. Huang, *J. Am. Chem. Soc.*, 2006, **128**, 6437.
- 135 S. Sombatchaisak, P. Praserttham, C. Chaisuk and J. Panpranot, *Ind. Eng. Chem. Res.*, 2004, **43**, 4066.
- 136 A. Y. Likhacheva, S. A. Veniaminov, E. A. Paushtis and J. A. Belitsky, *Eur. J. Mineral.*, 2006, **18**, 345.
- 137 E. R. Parnham, E. A. Drylie, P. S. Wheatley, A. M. Z. Slawin and R. E. Morris, *Angew. Chem. Int. Ed.*, 2006, **45**, 4962.

- 138 A. M. Beale, A. M. J. van der Eerden, S. D. M. Jacques, D. M. Simon, O. Leynaud, M. G. O'Brien, F. Meneau, S. Nikitenko, W. Bras and B. M. Weckhuysen, *J. Am. Chem. Soc.*, 2006, **128**, 12386.
- 139 M. G. O'Brien, A. M. Beale, C. R. A. Catlow and B. M. Weckhuysen, *J. Am. Chem. Soc.*, 2006, **128**, 11744.
- 140 R. A. van Santen, *Nature*, 2006, **444**, 46.
- 141 G. Caeiro, P. Magnoux, J. M. Lopes, E. R. Ribero, S. Menezes, A. F. Costa and H. S. Cerqueira, *Appl. Catal. A*, 2006, **314**, 160.
- 142 F. Gramm, C. Baerlocher, L. B. McCusker, S. J. Warrender, P. A. Wright, B. Han, S. B. Hong, Z. Liu, T. Ohsuna and O. Terasaki, *Nature*, 2006, **444**, 79.
- 143 M. Pera-Titus, R. Mallada, J. Llorens, F. Cunill and J. Santamaria, *J. Membrane Sci.*, 2006, **278**, 401.
- 144 M. Pera-Titus, J. Llorens, J. Tejero and F. Cunill, *Catalysis Today*, 2006, **118**, 73.
- 145 A. Pak and T. Mohammadi, *Desalination*, 2006, **200**, 68.
- 146 S. Gopalakrishnan, T. Yamagichi and S. I. Nakao, *J. Membrane Sci.*, 2006, **274**, 102.
- 147 M. L. Maloney, A. W. C. van den Berg and J. C. Jansen, *Microporous Mesoporous Mater.*, 2005, **85**, 96.
- 148 M. Weyd, H. Richter, I. Voigt, C. Hamel and A. Seidel-Morgenstern, *Desalination*, 2006, **199**, 308.
- 149 S. Haag, M. Hanebuth, G. T. P. Mabande, A. Avhale, W. Schwieger and R. Dittmeyer, *Microporous Mesoporous Mater.*, 2006, **96**, 168.
- 150 Z.-W. Chen, B. Holmberg, W.-Z. Li, X. Wang, W.-Q. Deng, R. Munoz and Y.-S. Yan, *Chem. Mater.*, 2006, **18**, 5669.
- 151 O. G. Nik, A. Moheb and T. Mahannnnadi, *Chem. Eng. Tech.*, 2006, **29**, 1340.
- 152 H. Ahn, H. Lee, S. B. Lee and Y. Lee, *Desalination*, 2006, **193**, 244.
- 153 S. J. Lue and T. H. Liaw, *Desalination*, 2006, **193**, 137.
- 154 H. Ahn and Y. Lee, *J. Membrane Sci.*, 2006, **279**, 459.
- 155 K. Tang, Y. G. Wang, L. J. Song, L. H. Duan, X. T. Zhang and Z. L. Sun, *Mater. Lett.*, 2006, **60**, 2158.
- 156 J. P. Zhai, Z. K. Tang, X. J. Hu, X. X. Zhang and P. Sheng, *phys. stat. sol.*, 2006, **243**, 3082.
- 157 F. N. Su, H. J. Zeng, Y. J. Yu, L. Lv, J. Y. Lee and X. S. Zhao, *Carbon*, 2005, **43**, 2368.
- 158 F. Su, X. S. Zhao, L. Lv and Z. Zhou, *Carbon*, 2004, **42**, 2821.
- 159 D. Scarano, S. Bordiga, C. Lamberti, G. Ricchiardi, S. Bertarione and G. Spoto, *App. Catal.*, 2006, **307**, 3.
- 160 J. G. Wang and C. J. Liu, *J. Mol. Catal.*, 2006, **247**, 199.
- 161 T. Baba and K. Inazu, *Chem. Lett.*, 2006, **35**, 142.
- 162 X. B. Zheng and P. Blowers, *J. Phys. Chem. A*, 2006, **110**, 2455.
- 163 D. Lesthaeghe, G. Delcour, V. van Speybroeck, G. B. Marin and M. Waroquier, *Microporous Mesoporous Mater.*, 2006, **96**, 350.
- 164 N. Raveendran Shiju, S. Fiddy, O. Sonntag, M. Stockenhuber and G. Sankar, *Chem. Commun.*, 2006, 4955.
- 165 M. Selvaraj and S. Kawi, *J. Mol. Catal.*, 2006, **246**, 218.
- 166 Y. H. Zhang, I. J. Drake, D. N. Briggs and A. T. Bell, *J. Catal.*, 2006, **244**, 219.
- 167 J. Yang, M. B. Derwal and L. S. Shimzu, *J. Am. Chem. Soc.*, 2006, **128**, 8122.
- 168 M. Stanculescu and M. Ikura, *J. Anal. App. Pyrol.*, 2006, **75**, 217.
- 169 A. Sinag, M. Sungur and M. Canel, *Energy and Fuels*, 2006, **20**, 1609.
- 170 A. van Miltenberg, W. Zhu, F. Kapteijn and J. A. Moulijn, *Chem. Eng. Res. Des.*, 2006, **84**, 350.
- 171 J.-X. Zhou, Y.-C. Zhang, X.-W. Guo, A.-F. Zhang and X.-M. Fei, *Ind. Eng. Chem. Res.*, 2006, **45**, 6236.
- 172 S. Cavenati, C. A. Grande and A. E. Rodrigues, *Energy and Fuels*, 2006, **20**, 2648.
- 173 H. A. Zaidi and K. K. Pant, *Can. J. Chem. Eng.*, 2005, **83**, 970.
- 174 X. Dupain, R. A. Krul, C. J. Schaverien, M. Makkee and J. A. Moulijn, *App. Catal. B*, 2006, **63**, 277.
- 175 V. M. Bhandari, C. H. Ko, J. G. Park, S. S. Han, S. H. Cho and J. N. Kim, *Chem. Eng. Sci.*, 2006, **61**, 2599.
- 176 A. Jayaraman, F. H. Yang and R. T. Yang, *Energy and Fuels*, 2006, **20**, 909.
- 177 D. L. King and L. Y. Li, *Catalysis Today*, 2006, **116**, 526.
- 178 D. L. King and C. Faz, *App. Catal. A*, 2006, **311**, 58.
- 179 Y. H. Wang, F. H. Yang, R. T. Yang, J. M. Heinzel and A. D. Nickens, *Ind. Eng. Chem. Res.*, 2006, **45**, 7649.

- 180 C. Laborde-Boutet, G. Joly, A. Nicolaos, M. Thomas and P. Magnoux, *Ind. Chem. Eng. Res.*, 2006, **45**, 8111.
- 181 K. Shimizu, N. Kobayashi, A. Satsuma, T. Kojima and S. Satokawa, *J. Phys. Chem. B*, 2006, **110**, 22570.
- 182 X. D. Ma, Z. Y. Liu and H. Z. Zhao, *Energy and Fuels*, 2006, **20**, 1738.
- 183 D. C. Wang, Z. Z. Xia and J. Y. Wu, *Energy Conversion and Management*, 2006, **47**, 590.
- 184 R. S. Bowman, *Microporous Mesoporous Mater.*, 2003, **61**, 43.
- 185 Z. Li, T. Burt and R. S. Bowman, *Environ. Sci. Technol.*, 2000, **34**, 3756.
- 186 Z. H. Li, I. Anghel and R. S. Bowman, *J. Disp. Sci. Technol.*, 1998, **19**, 843.
- 187 G. M. Haggarty and R. S. Bowman, *Environ. Sci. Technol.*, 1994, **28**, 3756.
- 188 E. J. Sullivan, R. S. Bowman and I. A. Legiac, *J. Env. Qual.*, 2003, **32**, 2387.
- 189 H. K. Karapangioti, D. A. Sabatini and R. S. Bowman, *Water Res.*, 2005, **39**, 699.
- 190 Z. H. Li and R. S. Bowman, *Water Res.*, 2001, **35**, 322.
- 191 J. M. Ranck, R. S. Bowman, J. L. Weeber, L. E. Katz and E. J. Sullivan, *J. Env. Eng.*, 2005, **131**, 432.
- 192 A. Dyer, A. Chimedtsogzol, L. Campbell and C. Williams, *Microporous Mesoporous Mater.*, 2006, **95**, 172.
- 193 H. Faghihian, M. G. Maragheh and H. Kazemian, *App. Rad. Isot.*, 1999, **50**, 655.
- 194 D. V. Marinin and G. N. Brown, *Waste Management*, 2000, **20**, 545.
- 195 J. H. Choi, S. D. Kim, Y. J. Kwon and W. J. Wha, *Microporous Mesoporous Mater.*, 2006, **96**, 157.
- 196 K. Athanasiadis, B. Helmreich and P. A. Wilderer, *Acta hydrochemica et hydrobiologica*, 2004, **32**, 419.
- 197 N. Beyazit, P. Ibrahim and O. Nuri, *Int. J. Env. Poll.*, 2003, **19**, 160.
- 198 Erdem, N. Karapinar and R. Donat, *J. Colloid Interface Sci.*, 2004, **280**, 309.
- 199 K. Athanasiadis and B. Helmreich, *Water Res.*, 2005, **39**, 1527.
- 200 M. Pospisil, V. Cuba, V. Mucka and B. Drtinova, *Radiat. Phys. Chem.*, 2006, **75**, 403.
- 201 H. Faghihian and R. S. Bowman, *Water Res.*, 2005, **39**, 1099.
- 202 H. Faghihian, M. G. Maragheh and A. Malekpour, *J. Radioanal. Nucl. Chem.*, 2002, **254**, 545.
- 203 H. Faghihian, *Iran. J. Sci. Tech. A*, 2005, **29**, 189.
- 204 H. Faghihian, M. K. Amini and A. R. Nezamzadeh, *J. Radioanal. Nucl. Chem.*, 2005, **264**, 577.
- 205 H. Faghihian, M. G. Maragheh, M. K. Amini and A. R. Nezamzadeh, *Adsorption Sci. Tech.*, 2004, **22**, 707.
- 206 H. Faghihian, *Int. J. Env. Pollution*, 2004, **22**, 732.
- 207 H. Faghihian and M. Kamali, *Int. J. Env. Pollution*, 2003, **19**, 732.
- 208 H. Faghihian, A. Malekpour and M. G. Maragheh, *Adsorption Sci. Tech.*, 2003, **21**, 373.
- 209 H. Faghihian, A. Malekpour and M. G. Maragheh, *Int. J. Env. Pollution*, 2002, **18**, 181.
- 210 M. Y. Kustova, A. Kustov, S. E. Christiansen, K. T. Leth, S. B. Rasmussen and C. H. Christensen, *Catal. Comm.*, 2006, **7**, 705.
- 211 M. Y. Kustova, S. B. Rasmussen, A. L. Kustov and C. H. Christensen, *App. Catal. B*, 2006, **67**, 60.
- 212 A. H. Oygarden and J. Perez-Ramirez, *App. Catal. B*, 2006, **65**, 163.
- 213 K. Nakamura, Y. Yoshida, I. Mikami and T. Okuhara, *App. Catal. B*, 2006, **65**, 31.
- 214 M. Taralunga, J. Mijoin and P. Magnoux, *Catal. Comm.*, 2006, **7**, 115.
- 215 E. Maranon, M. Ulmanu, Y. Fernandez, I. Anger and L. Castrillon, *J. Hazardous Mater.*, 2006, **137**, 1402.
- 216 Y. Matsumura, K. Yoshikata, S.-I. Kunisaki and T. Tsuchido, *App. Env. Microbiol.*, 2003, **69**, 4278.
- 217 M. C. Neuffer, J. McDivitt, D. Rose, K. King, C. C. Cloonan and J. S. Vayer, *Military Medicine*, 2004, **169**, 716.