Corrections

COLLOQUIUM PAPER. For the article "Synthetic zeolites and other microporous oxide molecular sieves" by John D. Sherman, which appeared in number 7, March 30, 1999, of *Proc. Natl. Acad. Sci. USA* (**96,** 3471–3478), the author notes the following corrections: (*i*) in *Linear Paraffins for Biodegradable Detergents*, OP ADS-34

should read UOP ADS-34; and (*ii*) in *Impacts of Molecular Sieves on Human Welfare*, the phrase, "From these numbers," should be deleted.

CELL BIOLOGY. For the article "Tyrosine phosphorylation of p62[dok] by p210[bcr-abl] inhibits RasGAP activity" by Nobuhiro Kashige, Nick Carpino, and Ryuji Kobayashi, which appeared in number 5, February 29, 2000, of *Proc. Natl. Acad. Sci. USA* (**97,** 2093–2098), the authors note that the image in lane 12 of Fig. 6*a* was mistakenly deleted in the printing process. The complete figure and its legend are shown below.

GENETICS. In the article "Toward *Anopheles* transformation: *Minos* element activity in anopheline cells and embryos" by Flaminia Catteruccia, Tony Nolan, Claudia Blass, Hans-Michael Müller, Andrea Crisanti, Fotis C. Kafatos, and Thanasis G. Loukeris, which appeared in number 5, February 29, 2000, of *Proc. Natl. Acad. Sci. USA* (**97,** 2157–2162), the authors note that three mistakes were introduced inadvertently in assembling Fig. 4. The revised Fig. 4 printed below includes the correct photograph of E7 insertion at 21E, as well as the correct chromosomal locations of E4 at 25D (2L) and E5 at 36B (3R).
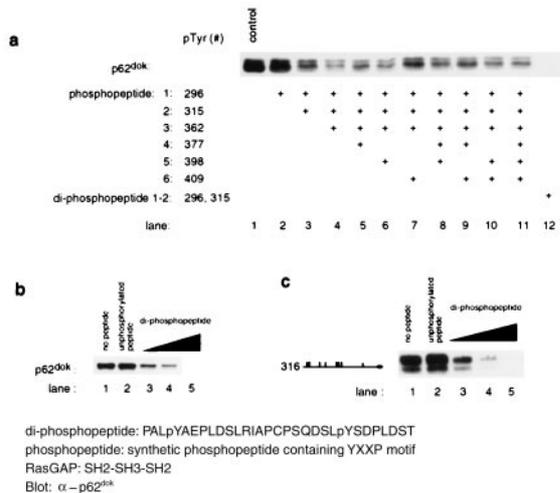

Fig. 6. Peptide competition analysis indicates that Tyr-296 and Tyr-315 play a critical role in the binding of p62[dok] to RasGAP. The ability of the diphosphopeptide to inhibit binding of Dok-1 to GAP suggests that the proper positioning of pTyr-296 and pTyr-315 in tandem is critical for the interaction of the two molecules. (*a*) Combinations of phosphopeptides corresponding to the regions surrounding individual tyrosines in p62[dok] fail to inhibit the binding of p62[dok] to RasGAP. However, a diphosphopeptide corresponding to residues 293–322 is able to inhibit binding of Dok-1 to the GAP SH2-SH3-SH2 region. Binding analysis was conducted as described. Synthetic phosphopeptides used for this experiment were: 1, SPPALpYAEPLDS (pTyr-296); 2, SQDSLpYSDPLDS (pTyr-315); 3, PKEDPIpYDEPEGL (pTyr-362); 4, VPPQG LpYDLPREPK (pTyr-377); 5, RVKEEGpYELPYNPATDD (pTyr-398); 6, NPATDD pYAVPPPR (pTyr-409); and diphosphopeptide, PALpYAEPLDSLRIAPCPSQDS LpYSDPLDST (pTyr-296 and pTyr-315). For control, unphosphorylated peptides were used. Each phosphopeptide was added in concentration of 50 μM. (*b*) Dose-dependent inhibition of p62[dok] binding to RasGAP by diphosphopeptide (Dok-1 aa 293–322). The diphosphopeptide was added in concentration of 0.5, 5, or 50 μM. The unphosphorylated peptide was added in concentration of 50 μM. (*c*) Dose-dependent inhibition of a truncated Dok-1 (the truncation construct 316: residues 316–481) binding to RasGAP by diphosphopeptide. The diphosphopeptide was added in concentration of 0.5, 5, or 50 μM. The unphosphorylated peptide was added in concentration of 50 μM.

Fig. 4. (*A*) Sequences of the *Minos* insertion sites in the genome of Sua 5.1* and Sua 4.0 cells. Chromosomal flanking sequences are represented with capital letters in italics. Small lettering represents the sequences of the *Minos* end. The expected TA dinucleotide of the insertion site is shown in bold. The chromosomal divisions and subdivisions from which the flanking sequences were derived are indicated with the chromosomal arm listed in parenthesis. (*B*) Typical results of determining the location of origin of the rescued genomic fragments by *in situ* localization to polytene chromosomes of the Suakoko mosquito strain.

PLANT BIOLOGY. For the article "*Oryza sativa PSK* gene encodes a precursor of phytosulfokine-α, a sulfated peptide growth factor found in plants" by Heping Yang, Yoshikatsu Matsubayashi, Kenzo Nakamura, and Youji Sakagami, which appeared in number 23, November 9, 1999, of *Proc. Natl. Acad. Sci. USA* (**96,** 13560–13565), the authors note the following correction. In line 18 of the first column on page 13565, "+5 positions" should read "+3 positions."

CORRECTIONS

*This paper was presented at the National Academy of Sciences colloquium "Geology, Mineralogy, and Human Welfare,"
held November 8–9, 1998 at the Arnold and Mabel Beckman Center in Irvine, CA.*

Synthetic zeolites and other microporous oxide molecular sieves

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ABSTRACT Use of synthetic zeolites and other microporous oxides since 1950 has improved insulated windows, automobile air-conditioning, refrigerators, air brakes on trucks, laundry detergents, etc. Their large internal pore volumes, molecular-size pores, regularity of crystal structures, and the diverse framework chemical compositions allow "tailoring" of structure and properties. Thus, highly active and selective catalysts as well as adsorbents and ion exchangers with high capacities and selectivities were developed. In the petroleum refining and petrochemical industries, zeolites have made possible cheaper and lead-free gasoline, higher performance and lower-cost synthetic fibers and plastics, and many improvements in process efficiency and quality and in performance. Zeolites also help protect the environment by improving energy efficiency, reducing automobile exhaust and other emissions, cleaning up hazardous wastes (including the Three Mile Island nuclear power plant and other radioactive wastes), and, as specially tailored desiccants, facilitating the substitution of new refrigerants for the ozone-depleting chlorofluorocarbons banned by the Montreal Protocol.

Relationships of Synthetic Zeolites to Natural Zeolites and Other Minerals. Only 6 of the >63 natural zeolites commonly occur in large beds: analcime (ANA),* chabazite (CHA), clinoptilolite (HEU), erionite (ERI), mordenite (MOR), and phillipsite (PHI) (1); ferrierite (FER) occurs in a few large beds. Each of the seven also has been synthesized, but only mordenite and ferrierite are manufactured in large quantity. Significantly, synthetic mordenite has large pores whereas natural mordenite has small pores (2).

Besides mordenite and ferrierite, the principal synthetic (aluminosilicate) zeolites in commercial use are Linde Type A (LTA), Linde Types X and Y (Al-rich and Si-rich FAU), Silicalite-1 and ZSM-5 (MFI), and Linde Type B (zeolite P) (GIS). Other commercially available synthetic zeolites include Beta (BEA), Linde Type F (EDI), Linde Type L (LTL), Linde Type W (MER), and SSZ-32 (MTT). All are aluminosilicates or pure silica analogs.

Recently, new nonaluminosilicate, synthetic molecular sieves became available commercially. They include aluminophosphates (family of AlPO4 structures); silicoaluminophosphates (SAPO family); various metal-substituted aluminophosphates [MeAPO family, such as CoAPO-50 (AFY)]; and other microporous framework structures, such as crystalline silicotitanates.†

Most current commercial applications use aluminosilicate zeolites or their modified forms. Undoubtedly, commercial uses both for zeolites and other molecular sieves will continue to grow.

Development of Synthetic Zeolites and Other Microporous Oxides. The first zeolite mineral (stilbite) was described in Sweden by Baron Cronstedt in 1756 (3–5). Highlights of the history of adsorption studies of zeolites were reviewed by Breck (6).

By 1926, the adsorption characteristics of chabazite were attributed to tiny pores (<5 Å in diameter) that allowed small molecules to enter but excluded larger ones: hence, the term "molecular sieve" (7).

By 1945, Barrer classified zeolite minerals into three classes depending on the size of the molecules adsorbable rapidly, slowly, or not appreciably at room temperature or above (8, 9). However, zeolites did not find any significant commercial use until synthetic zeolites were discovered and developed (large, mineable deposits of natural zeolites were not discovered until the late 1950s). Barrer's 1948 synthesis of small-port mordenite at high temperatures and pressures heralded the era of synthetic zeolites (10).

From 1949 through the early 1950s, the commercially significant zeolites A, X, and Y were discovered by Milton and Breck at the Tonawanda, New York, laboratories of the Linde Air Products Division of Union Carbide Corporation. These zeolites were synthesized from readily available raw materials at much lower temperature and pressure than used earlier. Many of the new synthetic zeolites had larger pore size than most of the known natural zeolites, allowing applications involving larger molecules. In addition, many had larger pore volume, giving higher capacity.

In 1953, Linde Type A zeolite became the first synthetic zeolite to be commercialized as an adsorbent to remove oxygen impurity from argon at a Union Carbide plant (11). Synthetic zeolites were introduced by Union Carbide as a new class of industrial adsorbents in 1954 and as hydrocarbon-conversion catalysts in 1959. New zeolites and new uses appeared steadily through the 1960s. An explosion of new molecular sieve structures and compositions occurred in the 1980s and 1990s from the aluminosilicate zeolites to the microporous silica polymorphs to the microporous aluminophosphate-based polymorphs and metallo-silicate compositions (12). Molecular sieves now serve the petroleum refining, petrochemical, and chemical process industries as selective catalysts, adsorbents, and ion exchangers.

Many zeolites can be synthesized with SiO_2 higher or lower than in nature for the same framework type. Higher SiO_2 generally gives greater hydrothermal stability, stronger-acid catalytic activity, and greater hydrophobicity as adsorbents. Conversely, lower SiO_2 gives greater cation exchange capacity and higher adsorbance for polar molecules. Controlling the synthesis process optimizes a zeolite for different applications.

Abbreviations: SAPO, silicoaluminophosphate; 8R, eight-ring; EB, ethylbenzene; PSA, pressure swing adsorption; VSA, vacuum swing adsorption; tpd, U.S. tons of O_2 per day; 3D, three-dimensional.
*The three-letter International Zeolite Association Structure Commission code for the framework topology of each zeolite is given in parentheses at the first mention of that zeolite in this paper (the full list is at http://www-iza-sc.csb.yale.edu/IZA-SC/).
†The molecular sieves of AlPO4s, SAPOs, MeAPOs, etc., were discovered in the 1980s by scientists in the Tarrytown, NY laboratories of Union Carbide Corporation's Catalysts, Adsorbents and Process Systems (CAPS) group. In 1988, Union Carbide Corporation's Catalysts, Adsorbents and Process Systems and the Process Division of UOP of AlliedSignal merged to form a partnership company, called UOP, which is jointly owned by AlliedSignal and Union Carbide. UOP LLC has continued to develop both the materials and their applications.

Many synthetic zeolites have framework topologies not found to date among the natural zeolites. The natural zeolite faujasite has the same framework (FAU) and similar framework composition to the Type Y synthetic zeolite but is rare in nature.

Where both natural and synthetic forms of the same zeolite are available in commercial quantity, the variable phase purity of the natural zeolite and the chemical impurities, which are costly to remove, can make the synthetic zeolite more attractive for specific applications. Conversely, where uniformity and purity are not important, the cheapness of a natural zeolite may favor its use. Hence, natural and synthetic zeolites seldom compete for the same applications.

Structure and Properties of Synthetic Molecular Sieves. Zeolites have the chemical formula $M_{2/n}OAl_2O_3xSiO_2yH_2O$, where the charge-balancing nonframework cation M has valence n, x is 2.0 or more, and y is the moles of water in the voids. The Al and Si tetrahedral atoms, or T-atoms, form a three-dimensional (3D) framework of AlO_4 and SiO_4 tetrahedra linked together by shared oxygen ions. Although an SiO_4 tetrahedra is charge-balanced, an AlO_4 tetrahedra has a negative charge balanced by a positive charge on M. Related pure SiO_2 frameworks, such as silicalite-1 (MFI), are charge-balanced and do not need nonframework cations.

Variants involve Ge substitution for Si in the framework or involve substitution of Fe, Co, Mn, Zn, Ti, or Mg for Al. In the related aluminophosphates ($AlPO_4$), each negatively charged AlO_4 tetrahedron is balanced by a positively charged PO_4 tetrahedron, and nonframework cations are not needed. Still other variants include the silicoaluminophosphate (SAPO) structures in which Si substitutes some P in the $AlPO_4$ framework; each added Si needs a nonframework cation to balance the charge on the framework.

The pore geometry and volume in a specific microporous oxide are determined by the specific topology of the particular 3D framework. The lower the T-atom density per volume of the zeolite crystal, the higher the void fraction inside the crystal. The void fraction is 50% for NaX and 47% for NaA. The size of the largest pore in a zeolite is determined by the number of oxygen ions rimming the pore and its shape; e.g. a planar, circular eight-ring (8R) pore rimmed by eight oxygen ions has a diameter of 4.1 Å, as in Linde Type A zeolite, whereas the elliptical 8R pore of NaP zeolite (GIS) is 4.5×3.1 Å.

Applications in separation and purification processes often used the ability of zeolites and other molecular sieves to exclude molecules too large to enter the pores and admit smaller ones. Similarly, shape-selective catalysis takes advantage of the ability of the pores to favor the admission of smaller reactant molecules, the release of smaller reaction product molecules, or the restriction of the size of transition-state complexes inside the micropores of the zeolite (13).

Petroleum Refining Processes for the Production of Fuels

Catalytic Cracking. The prime goal in petroleum refining is efficient conversion of crude oil into high-quality fuel components. Desired fuel fractions in order of increasing molecular weight are gasoline, aviation jet fuel, and diesel fuel. Gasoil and asphalt, with even higher molecular weight, are most often further processed by thermal cracking, catalytic cracking (to make gasoline) (14), and catalytic hydrocracking (to make jet fuel). A lower-boiling fraction, light straight-run naphtha, rich in pentanes and hexanes and some butane, is further processed by catalytic hydroisomerization.

Strong acid catalytic activity of X and Y zeolites was discovered in 1957 by Rabo and was related to their crystallinity (15). This discovery laid the basis for zeolites in cracking, hydrocracking, and isomerization of hydrocarbons. From the early 1960s on, use of synthetic zeolites in catalysis and in related adsorption separation processes has dramatically transformed petroleum refining by vastly increasing the yield of high-quality fuels and reducing capital and operating costs, energy requirements, and adverse

environmental impact. Zeolites also played a major role in allowing the efficient reformulation of gasoline to the present lead-free gasoline.

In modern petroleum refineries in the world, gasoil and other heavier fractions from the crude oil fractionation unit are fed to fluid catalytic cracking units, which use small, fluidizable catalyst particles containing Type Y zeolite or other zeolites, or to hydrocracking units, which use fixed beds of larger catalyst particles also containing zeolites. The fluid catalytic cracking and hydrocracking units convert higher-molecular-weight hydrocarbons to lighter ones suitable for gasoline, light fuel oils, olefins, and other uses.

In both fluid catalytic cracking and hydrocracking, zeolite catalysts provide vastly superior combinations of strong acid catalytic sites, uniformity of pore structure, and stability, all of which provide improved selectivity, yield, durability, and cost over nonzeolite alternatives. In addition, these zeolites have provided much higher yield of gasoline and other high-quality fuels per barrel of crude oil, significantly reducing crude oil imports to the U.S. (>400 million barrels a year) and to other countries.

Hydrocracking. The early 1960s saw increasing demand for high-octane gasoline for the high-compression-ratio engines in new high-performance cars. Demand also grew for diesel fuel for diesel-electric locomotives and low-freeze-point jet fuel. These needs were met by rapid growth in hydrocracking of the more-refractory crude fractions that were not converted to gasoline and lighter products in the catalytic cracking units. This growth was accompanied by the pioneering development by Roland Hanford at Union Oil, now Unocal, of new, zeolite-based hydrocracking catalysts with dramatically improved activity and selectivity. Hydrocracking grew rapidly in the 1960s and 1970s inside and then later outside the U.S. Worldwide hydrocracking capacity should grow from ≈2.5 million barrels per day in 1990 to ≈3.5 million in 2000 (16).

In hydrocracking, hydrocarbon molecules and hydrogen gas pass over the zeolite catalyst, which converts higher-molecular-weight petroleum fractions to lower-molecular-weight fuels (17). For example, UOP's Unicracking process (developed jointly by the Molecular Sieve Department of Union Carbide, now part of UOP, and Unocal) uses base- or noble-metal hydrogenation-activity promoters impregnated on combinations of zeolite- and amorphous-aluminosilicates for cracking activity (18). The specific metals chosen and the proportions of the metals, zeolite, and nonzeolite aluminosilicates are optimized for the feedstock and desired product balance. The Isocracking process of Chevron also uses hydrocracking catalysts, some containing zeolites to increase the cracking function of these dual-function catalysts (19).

The zeolites most frequently used in commercial hydrocracking catalysts are partially dealuminated and low-sodium, or high-silica, Type Y zeolites in hydrogen or rare-earth forms. Other zeolites and mixtures of zeolites also are used. The zeolites often are imbedded in a high-surface-area amorphous matrix, which serves as a binder. The metals can reside inside the zeolite and on the amorphous matrix.

Catalytic Dewaxing. Catalytic dewaxing yields various grades of lube oils and fuel components suitable for extreme winter conditions. Paraffinic (waxy) components, which precipitate out at low temperatures, are removed. In the UOP Catalytic Dewaxing process, the first stage saturates olefins and desulfurizes and denitrifies the feed via hydrotreating (20). In the second stage, a dual-function, non-noble-metal zeolite catalyst selectively adsorbs and then selectively hydrocracks the normal and near-normal long-chain paraffins to form shorter-chain (nonwaxy) molecules. Alternatively, as in the recently commercialized Chevron Isodewaxing process, the dewaxing results from isomerizing the linear paraffins to branched paraffins by using a SAPO-11 molecular sieve catalyst containing platinum (21, 22).

Light Paraffin Hydroisomerization. Lead was added to gasoline to increase its octane number, especially for vehicles, introduced in the early 1960s, that had modern high-compression-

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ratio, high-performance engines. The subsequent U.S.-legislated reduction of lead in gasoline required increased use of the catalytic hydroisomerization of the light straight-run naphtha fraction mentioned earlier.

Some versions of UOP's hydroisomerization processes use highly active zeolite-based, Pt-containing hydroisomerization catalysts, such as UOP I-7, which contains modified synthetic (large-port) mordenite. In the presence of hydrogen at moderate conditions, such catalysts optimize isomerization and minimize hydrocracking (23). Linear paraffins in the feed convert to branched paraffins with higher octane number. The Sud-Chemie HYSOPAR catalyst used in CEPSA's CKS ISOM process also uses a zeolite for the hydroisomerization of light naphtha.[‡]

To further increase octane level, products from a hydroisomerization unit can be sent to the Molex process, where the remaining lower-octane, linear paraffins are separated from the other compounds by using a zeolite adsorbent and a liquid desorbent; the Molex process is an example of UOP's Sorbex simulated-moving-bed technology (24). The extracted linear paraffins are recycled to the hydroisomerization unit, and the remaining higher-octane fraction is recovered for gasoline blending. The combination of the hydroisomerization and Molex processes boosts the research octane number of a typical feed from 68–70 to 89–92.

Alternatively, if a refinery can use the linear paraffins, it need not recycle them to a hydroisomerization unit. For example, the paraffins may be added to the feed of an ethylene steam cracker, thus increasing the efficiency of the cracker and leading to lower energy consumption and a purer product. Linear paraffins also are used as intermediaries in some food processing.

UOP's once-through zeolitic isomerization process (formerly known as the Shell Hysomer process) also uses a strongly acidic zeolite with a noble metal to hydroisomerize the light naphtha (25). Refiners with idle catalytic reformers or hydrotreaters can convert this equipment to use this process. To achieve higher octane levels, UOP's TIP total isomerization process uses the once-through isomerization process combined with UOP's IsoSiv process, which uses size-selective zeolite adsorption of the unreacted linear paraffins so that they can be recycled and converted to extinction (32). Both the TIP and IsoSiv processes originally were developed at Union Carbide's Molecular Sieve Department, now part of UOP.

Petrochemicals Processing for Aromatics Production and Derivatives

Ethylbenzene Synthesis. Styrene monomer, made by dehydrogenating ethylbenzene (EB), is the basic chemical for all polystyrene products. Ethylbenzene is made by using various catalysts to alkylate benzene with ethylene. Until 1980, nearly all EB was produced by liquid-phase alkylation reactions using aluminum chloride catalyst. In 1980, vapor-phase alkylation using a heterogeneous catalyst was introduced to eliminate many problems of waste disposal and special metallurgy involving aluminum chloride. In 1990, liquid-phase zeolitic technology began to replace the Mobil/Badger vapor-phase process, based on ZSM-5 zeolite.

The 1990 Lummus/UOP ethylbenzene liquid-phase process, using highly stable, poison-resistant zeolite catalysts manufactured by UOP, operates at low benzene-to-olefin ratio and high selectivity to EB.[§] The UOC-4120 catalyst from UOP, used initially for both alkylation of benzene with ethylene and transalkylation of polyethylbenzenes and benzene to produce more EB, operated successfully for 7 years, with >5 million metric tons of capacity installed or ordered. The extremely low xylene content

of the EB product permits the production of the highest-purity styrene monomer and lowers the costs in the styrene production unit. Current designs use the EBZ-100 catalyst for transalkylation and the EBZ-500 catalyst for alkylation. The new Mobil/Badger-Raytheon EBMax process commercialized in 1995 uses an MCM-22 (MWW) zeolite catalyst for liquid-phase alkylation; Mobil's TRANS-1 modified MFI catalyst for vapor-phase transalkylation of polyethylbenzene and cracking of C_6 and C_7 naphthenes; and TRANS-4 catalyst for liquid-phase transalkylation of polyethylbenzenes (26).

Cumene Synthesis. More than 95% of the 7 million metric tons per year of cumene is used worldwide as the principal chemical for production of phenol and its acetone byproduct. The phenol yields phenolic resins, bisphenol-A, caprolactam, and other products. Phenolic resins are used extensively to bond plywood and composition board. Both phenol and acetone are used increasingly in the production of polymers such as epoxy, polycarbonate resins, and nylon-6.

Most cumene is made by alkylating benzene with propylene over an acid catalyst, mostly solid phosphoric acid and minor $AlCl_3$. Recent awareness of the negative environmental impact of spent-catalyst disposal has spurred a search for more benign alternatives. The world's leading technology (90% open market) for producing cumene is the UOP Catalytic Condensation process, which uses inexpensive solid phosphoric acid catalyst. Its high-purity cumene product has set the standard. However, side reactions over the solid phosphoric acid catalyst result in a 4–5% loss in cumene yield.

The UOP Q-Max process, commercialized in 1996, uses the new, environmentally benign QZ-2000 zeolite catalyst for direct alkylation of benzene with propylene and incorporates a second step (transalkylation) to react the diisopropylbenzene, a byproduct of the first step, with benzene to form additional cumene.[¶] It produces a higher-quality cumene product (>99.97% purity) at overall cumene yield of 99.7% and lower investment cost.

The Mobil-Badger process using aluminum chloride catalyst also yields cumene. Recently, Mobil/Raytheon also developed a zeolite catalyst based on the relatively new zeolite MCM-22. Similarly, Dow and Kellogg developed "3D-DM" catalysts based on dealuminated forms of mordenite (27): Enichem, a catalyst based on zeolite Beta, and CD-Tech/Lummus, a catalytic distillation zeolite catalyst.

para-Xylene Production from Mixed C_8 Aromatics. Polyester fibers have revolutionized clothing. Many people in the U.S. take for granted wash-and-wear and permanent press clothing, and ironing of shirts is out of fashion. Demand has grown in developing countries because of the great comfort of fabrics made from cotton–polyester fibers blended in any proportion for any climate, as well as low cost, excellent durability, and ease of washing with little water and detergent (M. M. Sharma, personal communication).

The worldwide annual production of 12–15 million tons *p*-xylene is expected to rise to ≈17–18 million tons in 10 years. Most *p*-xylene is used to make purified terephthalic acid, which is reacted with ethylene glycol to make the poly-(ethylene terephthalate), the basis of polyester fibers. The *p*-xylene is separated from mixed C_8 aromatics (containing *o*-, *m*-, and *p*-xylenes and EB) by using either crystallization or adsorption processes. Since 1971, the new UOP's Parex adsorption separation process captured 60% of the worldwide *p*-xylene production. Another large and growing use for *p*-xylene is in the manufacture of poly-(ethylene terephthalate) for bottles recyclable and environmentally benign.

The Parex process uses the Sorbex technology mentioned earlier (28). Its critical ingredient is a special, *p*-xylene-selective adsorbent. Ion-exchanged forms of synthetic FAU zeolite are

‡Floyd, F. M., Gilbert, M. F., Pascual, M. P. & Kohler, E., Middle East Petrotech 98: Second Middle East Refining and Petrochemicals Conference and Exhibition, September 14–16, 1998, Bahrain.

§Woode, G. B., Zarchy, A. S., Morita, M. & Shinohara, K., Sud-Chemie Group 1998 International Styrene Symposium, June 14–18, 1998, Sapporo, Hokkaido, Japan.

¶Jeanneret, J., Greer, D., Ho, P., McGehee, J. & Shakir, H., 22nd Annual DeWitt Petrochemical Review, March 18–20, 1997, Houston, TX.

used with desorbent liquids to recover >97% *p*-xylene at >99.9% purity from a raffinate containing EB and *o*- and *m*-xylenes.

Xylene Isomerization. The raffinate from the Parex unit can go to an Isomar unit (29), licensed by UOP, for isomerization to a near-equilibrium mixture of xylenes, which are recycled to the Parex unit. The Isomar unit itself also uses UOP zeolite acid catalysts, such as the Pt-bearing I-9 catalyst, which converts EB to xylenes, and the I-100 catalyst, which dealkylates EB to benzene. Both provide efficient EB conversion with excellent xylene retention.

Disproportionation of Toluene and Transalkylation of Toluene and Trimethylbenzenes. Recent strong demand for *p*-xylene has begun to exceed the supply of mixed xylenes. Incorporating the Tatoray process (originated with Toray Industries in Japan and further developed and licensed by UOP) into the aromatics complex in a refinery can more than double the yield of *p*-xylene from a naphtha feedstock (30). The zeolite-based TA-4 catalyst has two principal functions, disproportionation of toluene into the more-valuable benzene and mixed xylenes, and transalkylation of toluene and trimethylbenzenes to mixed xylenes. The mixed xylenes then are added to the Parex unit to produce more *p*-xylene.

p-Xylene Synthesis from Toluene. Xylenes can be produced by the zeolite-catalyzed disproportionation of toluene alone. Mobil developed the MTPX (Mobil toluene to *para*-xylene) process for internal use, and the licensed MSTDP (Mobil selective toluene disproportionation) process, based on ZSM-5 (MFI) "product shape-selective" zeolite catalysts (31). The toluene disproportionation generates mixed xylenes inside the catalyst, but the overall relative yield of *p*-xylene is greater than the thermodynamic equilibrium allows because the *p*-xylene diffuses more rapidly out of the zeolite than do the *o*- and *m*-xylenes. UOP's recent PX-Plus process also uses a zeolite catalyst for *p*-xylene synthesis by shape-selective disproportionation of toluene.

Aromatics from Light Hydrocarbons. UOP's Cyclar process converts low-value LPG (propane, butanes) or light feedstocks containing olefins and paraffins to high-value, easily transportable, petrochemical-grade liquid aromatic products, particularly BTX (benzene, toluene, and xylenes). It uses a single gallium-modified zeolite catalyst developed by BP and UOP in conjunction with UOP's CCR continuous catalytic regeneration system (32, 33). Acidic sites on the zeolite catalyze dehydrogenation, oligomerization, and cyclization. The shape-selectivity of the zeolite cavities helps promote the cyclization reactions and limits the size of the rings (34).

M-Forming. Catalytic reforming produces a high-octane liquid reformate product rich in aromatics and hydrogen gas; light hydrocarbon gases, such as LPG; and C_6 to C_9 paraffins. Mobil's M-Forming process selectively hydrocracks linear and singly branched paraffins in gasoline reformate fractions to LPG by size-selective catalysis by using medium-pore ZSM-5 zeolite (35). Olefins produced from paraffin cracking alkylate the aromatics and also form some aromatics by oligomerization.

Other Aromatics Produced by Sorbex Separations. Some other applications of the Sorbex zeolite-based simulated-moving-bed technology (36) are MX the Sorbex process, *m*-xylene from EB and *o*- and *p*-xylenes; the Cymex process, *m*- and/or *p*-xylene from a mixture of cymene isomers; and the Cresex process, *m*- and/or *p*-cresol from mixtures of cresol and xylenol.

Petrochemicals Processing for Olefins Production

Light Olefin Production by Methanol-*to*-Olefins (MTO) Process. Only ≈110 of the ≈2,500 billion cubic meters of natural gas produced annually is wasted (burned in flares). About 103 billion cubic meters per year of natural gas are processed to make liquefied natural gas, but at high cost. Alternatively, natural gas can be converted first to syngas (CO and H2) and then to the more-valuable, easily shipped methanol. However, the methanol market is too small for the available natural gas.

The new UOP/HYDRO MTO process provides the means to efficiently convert methanol to even more valuable light olefins (ethylene, propylene, and butenes), which have large, commodity-type petrochemical markets: Ethylene and propylene represent the largest, together accounting for 120 million MTA, and growing (37). This process uses the product-shape-selective UOP MTO-100 catalyst based on a unique molecular sieve. During the late 1980s, Norsk Hydro, assisted by Sintef, started independent work, and UOP and Hydro agreed on joint development of the process, now available from UOP for commercial licensing. Norsk Hydro is running a large (0.75 metric tons/day) UOP/HYDRO MTO demonstration plant in Porsgrunn, Norway.

Olefin Isomerization. The 1990 Clean Air Act increased the demand for blendable ethers in motor fuels and created a demand for isobutene to make methyl tertiary butyl ether and for isopentene to make tertiary amyl methyl ether. In anticipation, the UOP I-500 catalyst, based on a SAPO structure, and two new processes were developed: Butesom for isobutene isomerization and Pentesom for pentene isomerization (38–41). In both processes, coke progressively accumulates on the catalyst and is periodically removed by a simple carbon burn-off in the reactor. The Lyondell IsoPlus process (42, 43) uses a ferrierite (FER) zeolite for the isomerization of olefins to isoolefins, and a Mobil patent (44) describes using a medium-pore zeolite catalyst (for example, ZSM-5) for similar applications.

Oxygenates Removal Unit. Zeolite adsorbents are used in a UOP oxygenate removal unit down to >1 ppm total of trace oxygenates (e.g., DME, methanol, and methyl tertiary butyl ether) from C_4 streams. Depending on the flow scheme, the C_4 stream generally goes to a motor fuel alkylation (sulfuric acid or hydrofluoric acid) process or is recycled to a dehydrogenation-etherification complex, which has a UOP Oleflex unit and a methyl tertiary butyl ether unit. The advantages of the oxygenate removal unit is that it minimizes the acid consumption otherwise associated with these oxygenates, thus minimizing the acid neutralization wastes, a significant environmental benefit (B. V. Vora, personal communication). In dehydrogenation, the oxygenate removal unit improves catalyst stability and lowers costs of methyl tertiary butyl ether production.

Petrochemicals Processing for Detergents Production

Linear Paraffins for Biodegradable Detergents. Petroleum derivatives account for most of the total surfactant production and household detergents. During the 1940s and 1950s, sodium dodecylbenzene sulfonate was the most widely used synthetic detergent. However, the dodecyl paraffin side group on the benzene ring is highly branched and not easily biodegraded. In the early 1960s, environmental concerns led to development of linear alkylbenzene sulfonate (LAS) detergents, which are both biodegradable and cost-effective.

The key to the manufacture of the linear paraffins required to make linear alkylbenzene (LAB) and, hence, LAS is the use of size-selective synthetic zeolites that adsorb linear paraffins but exclude branched paraffins, naphthenes, and aromatics from mixtures spanning a range of boiling points, as in kerosene (C_{12} to C_{18}). Although anticipated by the work of McBain (7) and Barrer (8–10), such a class separation of molecules spanning a range of boiling points was virtually impossible before development of the synthetic molecular sieves by Union Carbide in the 1950s. Two different processes, one vapor phase and the other liquid phase, are used.

The vapor-phase IsoSiv process was developed at Union Carbide originally for octane improvement. To produce linear paraffins for detergents, kerosene feed, pretreated to acceptable quality and the desired carbon number range, passes at elevated temperature and just over atmospheric pressure through a bed of zeolite adsorbent that adsorbs just the linear paraffins. Just enough hexane vapor follows the kerosene feed to displace the nonadsorbed feed and isomeric hydrocarbons from the void spaces in the adsorber vessel. The effluent from this step is

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combined with the adsorption effluent stream. The linear paraffins adsorbed in the zeolite are desorbed by purging the bed in the opposite direction with hexane. The hexane in the effluent is separated by distillation and is recycled. The remaining linear paraffins comprise the desired product.

The liquid-phase Molex process, mentioned earlier, is most often used to produce plasticizers (C_6-C_{10}), LABs (C_{10}-C_{15}), and detergent alcohols (C_{13}-C_{22}+, but usually heavier than C_{16}). To make linear paraffins for LAB, increased linearity and low aromatics content are desired. The new high-purity Molex process has improved product purity to 99.7% and reduced aromatics content to 0.05 wt %. In addition, the new OP ADS-34 zeolite adsorbent provides improved long-term separation performance in the Molex process.

The linear paraffins made in the Molex process can be sent to UOP's Pacol and DeFine processes (45) for catalytic conversion to monoolefins. These pass to a UOP Detergent Alkylate process (46), which uses a hydrofluoric acid catalyst, or to a Detal process (offered for license in 1995∥), which uses a more environmentally friendly solid, heterogeneous catalyst to produce LAB from the monoolefins plus benzene. Unreacted linear paraffins are recycled to the Pacol and DeFine units and are converted to extinction. These catalytic processes use nonzeolite catalysts.

Linear Olefins for Detergent Alcohols. As discussed previously, LAB accounts for half of the detergent intermediate market. Detergent alcohols made from linear olefins are another quarter. Detergent alcohols are made from C_{10}-C_{15} alpha olefins derived from ethylene or from C_{10}-C_{15} internal olefins derived from lower-cost kerosene feed.

Linear olefins of improved purity are increasingly sought. Linear paraffins from the new high-purity Molex zeolite adsorption process are sent to the Pacol and DeFine processes to convert them to a mixture of monoolefins plus unreacted linear paraffins. The mixture is fed to UOP's Olex process, which uses a zeolite adsorbent in a Sorbex simulated-moving-bed process to separate the linear olefins and the unreacted paraffins, which are recycled back to the Pacol and DeFine units to extinction. The Olex process now uses the new UOP ADS-32 zeolite adsorbent, which provides improved capacity and rates. The linear olefins product has improved product purity (reduced aromatics and diolefins) as a result of improvements in the zeolite adsorbents and in the nonzeolite catalysts and operating conditions in the Molex-Pacol-DeFine-Olex sequence of processes.

Separation and Purification Process Applications

Molecular sieve adsorbents are used in many other separation and purification applications: (*i*) petroleum refining processes, used to remove CO_2, chlorides and mercury from a variety of streams; to dry and purify liquids and gases in diverse applications; to treat alkylation unit feed to reduce acid consumption, regenerator use, and corrosion, and to treat refinery hydrogen to prevent corrosion in downstream equipment; to dry and desulfurize refined products; and to dry and purify feed and recycle hydrogen in isomerization units; (*ii*) petrochemicals, used to dry hydrocarbon liquids, cracked gas, and hydrogen; to dry and purify natural gas liquids, ethane and propane feedstocks in ethylene and polymer plants; and in ethylene, propylene, butadiene, butylenes, amylenes, and various other comonomers and solvents; (*iii*) natural gas treating, used to dry and desulfurize natural gas to protect transmission pipelines and to remove undesirable impurities from home cooking and heating gas and to desulfurize ethane, propane, and butane and for H_2O and CO_2 removal before cryogenic processing; (*iv*) industrial gas production and purification, used to remove H_2O and CO_2 from air before

liquefaction and separation by cryogenic distillation, for pressure swing adsorption (PSA) separation of air, and in PSA purification of hydrogen by using zeolites and other adsorbents, such as activated carbon; (*v*) specialty and fine chemicals and pharmaceuticals, used for drying; for removal of impurities, including odors; and for other applications in the manufacture of specialty and fine chemicals and pharmaceuticals. Common features of these uses are now summarized.

Preprocessing of Gases before Cryogenic Separations. Deep drying and CO_2 removal are required before cryogenic liquefaction and subsequent separation processing to prevent formation of ice and dry ice, which would plug up the cryogenic processing equipment. Several synthetic zeolites exhibit great affinity for polar compounds such as H_2O and CO_2 and have high adsorption capacity at ambient temperature. They are used extensively in processing natural gas to make liquefied natural gas or to recover hydrocarbon liquids or helium; in processing air to make O_2, N_2, and Ar in cryogenic air-separation plants; and in treating ethylene and other olefins formed in ethylene steam-cracking plants before separation in cryogenic distillation separation units. These pretreatments work to perfection: Passing ambient air over such zeolite adsorbents at room temperature makes the air drier (−60°C dew point or lower) than in the coldest part of Alaska in the depth of winter.

Because the adsorbed impurities are strongly held on the zeolite adsorbents, they are regenerated for subsequent reuse in thermal-swing processes that pass a hot regeneration gas over the spent zeolite to heat it and to carry away the adsorbed compounds. The zeolite then is cooled to ambient temperature and is used to treat more gas.

Removal of Impurities from Gases and Liquids Down to Low Levels. Because zeolites bind strongly to polar compounds, including hydrogen sulfide, mercaptans, organic chlorides, CO, and to mercury, they can purify many streams in petroleum refineries, petrochemical plants, natural gas production plants, and chemical plants. In refineries, zeolite adsorbents remove impurities detrimental to downstream processing, including catalyst poisons (e.g., oxygenates and sulfur), corrosive agents, and chloride compound byproducts from processes using chloride catalyst promoters (e.g., catalytic reformers).

In natural gas production, zeolite adsorbents are used to dry the gas to prevent freezing and corrosion in pipelines, to remove sulfur compounds from the gas or LPG fractions to prevent corrosion in burners, and to remove compounds that are obnoxious or toxic (such as the odoriferous hydrogen sulfide and mercaptans in natural gas that form sulfur dioxide pollutants when burned for home cooking and heating). Worldwide, >1,000 units process tens of billions of cubic feet of natural gas daily.

Zeolites are used in the preparation of very high-purity fluids for special uses: e.g., gases used in the manufacture of electronics or gases and liquids used in modern analytical laboratory instruments.

Air Separation by Pressure Swing Adsorption (PSA) Processes. The following draws primarily from reviews (47–52) plus the author's personal reflections from direct involvement in zeolite adsorbent development over the last 30 years. Many zeolites adsorb N_2 more strongly than O_2 [the possible use of zeolites in air separation was indeed the principal impetus for the pioneering work of Milton (11)]. Also, because zeolites adsorb more of both N_2 and O_2 from air with increasing pressure, air can be separated by using a PSA process. The air is passed at an elevated pressure through a bed of zeolite particles that adsorb the N_2 more strongly and hold it on the bed but allow O_2 to pass through the bed. Then, the adsorbed N_2 is discharged from the feed end of the bed as the pressure in the bed is lowered. Many variations on the process cycle were developed to improve efficiency and capital and operating costs.

The PSA and vacuum-swing adsorption (VSA) processes use zeolite adsorbents to produce O_2 of 90–94% purity (the balance is primarily argon). The O_2 is used, for example, in the manu-

facture of steel, glass, pulp, paper (in delignification and bleaching), and chemicals and in nonferrous metal recovery, waste incineration, and bioremediation. Zeolites provide benefits in energy efficiency, process efficiency, improved processing rates and product quality, and environmental impact.

Over the last 25 years, improvements in the PSA and VSA O_2 processes were driven by the development of zeolite adsorbents with improved N_2 capacity and selectivity. Zeolites such as NaX and CaA made possible the development of the first economical PSA O_2 process at a relatively small scale [up to ≈ 15 U.S. tons of O_2 per day (tpd)] in the early- to mid-1970s. Second-generation adsorbents, such as CaX (53), and third-generation adsorbents, such as LiX (54), LiCaX or LiSrX (55, 56), and MgA (57), together with improved (vacuum PSA or VSA) processes have dramatically reduced both capital and operating costs. Of the third-generation Type X zeolites, only LiX has been used commercially as of 1997.**

From the mid-1980s to the mid-1990s, these improvements provided a 5-fold reduction in adsorbent inventory and a nearly 2-fold reduction in power requirements. The commercial viability of a simple two-bed VSA system expanded to well over 100 tpd, and that of an even simpler one-bed system expanded to well over 40 tpd, allowing use of these noncryogenic systems in many applications formerly served by the cryogenic distillation of air. For the delivery of O_2 of 90–94% purity, single-bed units are more economical because of lower capital costs (although with higher energy costs) than liquid O_2 delivery in the 4–57 tpd range. Two-bed units have lower energy costs (but higher capital costs) and are more economical than either liquid O_2 delivery or on-site cryogenic plants in the 57–235 tpd range.†† In 1994, VSA plus PSA O_2 production was estimated to be 4–4.5% of the world demand for O_2, the fourth largest chemical at 39 billion pounds in 1995 (51). In 1996, PSA/VSA O_2 production was estimated to be >3,500 tpd in the USA and >10,000 tpd (>265,000 $Nm^3 O_2$ per hour) worldwide (47). Assuming a value of $20 per ton of O_2, this production corresponds to a total market value of more than $75 million per year, and growing.

Manufacturing Industries and Consumer Products Applications

Small Oxygen Concentrators for Medical Use (Medox). In the U.S., a dozen companies manufacture small-scale PSA oxygen concentrators for patients with emphysema and chronic obstructive pulmonary disease. As with the large-scale PSA O_2 units, these small PSA concentrators use zeolites to produce 90 and 95% pure oxygen, the balance mainly argon and nitrogen. They can dramatically improve the quality of life.

The PSA units are engineered to be small (about the size of a small end table), readily transportable, (weighing ≈ 40 pounds), quiet, and reliable. They use 3–7 pounds of zeolite adsorbent to produce between 3 and 6 liters per minute of oxygen. Users are freed from needing high-pressure cylinders of oxygen delivered or stored in their homes. Use of these concentrators has grown substantially over the last 20 years (S. R. Dunne, personal communication). In 1996, home medical equipment reimbursements (from U.S. Medicare) associated with oxygen concentrators totaled $1.1 billion (58). Most are PSA units, the rest being primarily membrane units, which produce much lower oxygen concentration.

Automotive Air-Conditioning and Stationary Refrigerant Drying. Zeolite desiccants remove water and acids formed by breakdown of the refrigerant mixed fluid thus protecting the system from freeze-up and corrosion. UOP supplied zeolite 4AXH-5 desiccant for automotive use and 4A-XH-6 for stationary refrigerant drying. These desiccants dominated the refrigerant industry

for use with refrigerants R-12 and R-22 and the associated mineral oil lubricants. However, the 1987 Montreal Protocol heralded their demise because the very long life of fugitive R-12 emissions in the atmosphere became linked to ozone depletion and global warming.

The leading contender to replace R-12 was R-134a refrigerant, but R-134a was found to be unstable in the presence of the 4AXH-5 desiccant, leading to acids, sludge, deterioration of the desiccant, and possible failure of the refrigerant system. A UOP team developed the new XH7 zeolite desiccant, which is compatible with the new R134a lubricant systems, to meet the critical legislated deadlines. The deadlines for original automotive equipment manufacture and fleet testing were set at 3 years before system production, an extremely short development time for such a complex application.

Another new zeolite desiccant, XH9, was developed a couple of years later; in addition to automobiles, it is widely used in refrigerators (home refrigerators, supermarket freezers, and display cases) and stationary air conditioners. Because XH7 and XH9 desiccants are also compatible with systems using R12 refrigerant and mineral oil lubricants, dryers using the new desiccants can be prefit into R12 systems before total conversion to R134a systems. The XH7 desiccant today holds almost all of the automotive air-conditioning market formerly held by the 4AXH-5 desiccant before the advent of the new refrigerants. Consumers benefited because the availability of current systems was not disrupted and any danger to the environment was alleviated: hence, the American Chemical Society Heroes of Chemistry Award in March 1998 to the UOP team (A. P. Cohen, S. L. Correll, P. K. Coughlin, and J. E. Hurst).

Worldwide, millions of pounds of zeolite desiccants are installed in air conditioning units in passenger cars and light trucks. For stationary systems, most refrigerators in the U.S. and many elsewhere use zeolite desiccants to dry and remove acids from the refrigerants. The new desiccants, together with hermetically sealed systems with internal pumps, have extended the service life of refrigeration units by at least two to three times.

Air Brake Dryers for Heavy Trucks and Locomotives. Most goods produced worldwide are moved to market by heavy trucks and locomotives whose brake systems are actuated mostly by clean dry air at high pressure. Air brake systems are engineered to be fail-safe: When the air supply system fails, the brakes engage and prevent the trucks or locomotives from moving.

A key element of the air supply systems of a truck is a PSA dryer, typically using a single packed bed of ≈ 3 pounds of molecular sieve to dry the compressed gas; locomotives require more absorbent. The air compressor on a truck runs for 1–3 min at a time. The compressed gas is dried and passed to a reservoir that in turn supplies air pressure to the brakes to prevent the unintended actuation of the brakes while the truck is moving. When the reservoir is full, a signal shuts off the compressor; the dryer is depressurized, and a little dry air is bled back through the dryer to partially regenerate the bed of molecular sieve (S. R. Dunne, personal communication). These dryers have significantly improved the reliability and safety of braking systems for large trucks and locomotives.

Insulated Glass Windows. Most insulated glass produced worldwide is manufactured with desiccant contained in channels (or in matrices) that separate the panes of double-, triple-, or quadruple-paned windows. The desiccant scavenges moisture and other trace compounds, such as solvents or plasticizers, that may evolve during manufacturing. Although the sealants used for the manufacture of insulated glass windows are excellent, a finite amount of moisture still leaks into the windows over time. Desiccants, primarily zeolites, prevent fogging, mists, or formation of dew between the windowpanes because they lower the dew point of the gases inside the windows to levels far below the lowest expected surface temperature of the glass. Insulated glass provides aesthetic features, improved human comfort, and energy savings that make them a truly economical and beneficial addi-

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**Notaro, F., Schaub, H. R. & Kingsley, J. P., Second Joint China/U.S. Chemical Engineering Conference, May 22, 1997.

††Notaro, F., Schaub, H. R. & Kingsley, J. P., Second Joint China/U.S. Chemical Engineering Conference, May 22, 1997.

tion to both commercial buildings and homes (S. R. Dunne, personal communication). Residential and nonresidential dual-pane (insulating) windows and patio doors containing zeolite adsorbents have a total window area of $\approx$46 billion square feet worldwide. The estimated present energy savings in heating during winter and cooling during summer from the use of these insulating windows is equivalent to 450 million barrels of oil per year.

Environmental Protection Applications

In addition to the benefits already listed, many other applications provide environmental benefits.

Builders for Phosphate-Free Laundry Detergents. In the 1960s, growing public awareness of eutrophication of natural waters led to efforts to reduce the inflow of plant nutrients, especially phosphate and ammonia or nitrate. Dead algae sinks to the bottom of a pond or lake, where it depletes the oxygen in the water. Too much growth of algae depletes oxygen so much that fish die. As a result, many states, particularly those bordering the Great Lakes, banned phosphate in laundry detergents.

The prime function of phosphate "builders" in laundry detergent powders is removal of the hardness ions Ca^{2+} and Mg^{2+} in the wash water by complexing. Zeolite ion exchangers in powder form also can provide this service by removing Ca^{2+} and Mg^{2+} ions from the solution and replacing them with soft ions such as Na^+. Zeolite NaA was known to have high selectivity and capacity for calcium, and its application as a builder in heavy-duty powder detergents was developed in the 1970s, primarily by scientists at Henkel (59, 60, ‡‡) in Germany and Procter and Gamble (61, 62) in the U.S. Round NaA zeolite particles, a few micrometers across, are small enough to pass through the openings in the weave of the fibers in clothing and are not filtered out to form encrustations on the cloth. Recently, zeolite P (GIS), as maximum aluminum P or MAP, was developed by scientists at Unilever (and Crossfield) (63) as an alternative builder for the same applications, and debate on the relative merits of NaA and NaP zeolites continues (64). Today, the conversion of the USA detergent market to zero-phosphate formulas is virtually complete. In Europe, one-third of the powder detergents are zeolite based, and Canada is $\approx$50% converted. Latin America and many of the Pacific region countries continue to use phosphates (65).

In 1987, the Kao Corporation in Japan introduced Attack, a compact powder detergent that has higher bulk density and higher surfactant level and needs lower dosage. Use of compact powders in the Japanese laundry market grew to >90%. In the U.S., from 1990 to 1994, the use of compact powders grew from 2% to >90%. All compact powders in the U.S., Europe, and Japan have no phosphates. Zeolites used as builders in compact powders serve as particle-formation aids. This use of zeolites has facilitated changes in the process of detergent manufacture from spray drying and to alternative processes such as agglomeration. This shift, in turn, has led to increased use of zeolites in laundry detergent powders.

Automotive Emissions Control. New stable zeolites have been used successfully in diverse automotive emissions control problems. A very serious challenge in automotive emissions control today is control of nitrogen oxides (NO_x) emitted from lean-burn diesel engines. Many catalyst developers and academic researchers are using zeolites with a wide array of added base and precious metals as catalysts to enable hydrocarbon storage, NO_x reduction, and oxidation of both hydrocarbons and CO. Today, zeolites are used commercially for enhanced hydrocarbon oxidation in conventional diesel engines and NO_x reduction. Four-way catalysts, which provide NO_x reduction, HC oxidation, CO oxidation, and particulate control, are being developed.

For gasoline-fueled vehicles, the most-serious problem is the cold-start period. Over 90% of the hydrocarbon emission by a car during a cold start occurs within the first 3 min of engine operation. A hydrocarbon trap must contain an adsorbent that captures most of the hydrocarbons during this period. Once captured, most of the hydrocarbons must be held by the adsorber until the catalytic converter has heated up enough to be capable of oxidizing them. Then the adsorber must release the hydrocarbons to be oxidized, rendering them harmless to the atmosphere.

The adsorber also must be mechanically, thermally, and hydrothermally durable enough to withstand the harsh environment of the exhaust gas stream. Especially since 1995, major advances have been achieved in the development of hydrocarbon traps. Improved hydrothermal stability of the molecular sieve adsorbent, improved chemistry of the wash coating, and the addition of a noble metal catalyst directly onto the adsorber brick are technical milestones that enable successful implementation of hydrocarbon traps in emissions control (S. R. Dunne, personal communication).§§

Several major automakers have demonstrated excellent emissions reduction and system durability. General Motors achieved 50,000-mile-aged converter performance that surpasses Environmental Protection Agency requirements for use on a car designated as a low-emissions vehicle: i.e., a vehicle must emit nonmethane hydrocarbons at a weighted rate <0.075 grams per mile in the U.S. federally mandated test protocol. Mercedes Benz has achieved emissions that beat the ultralow-emissions vehicle standards of <0.04 grams per mile in the same testing (S. R. Dunne, personal communication).

The total U.S. car and light truck production rate is $\approx$12 million vehicles per year. Over the next 10 years, emissions control technologies of all kinds will be implemented to keep the auto manufacturers in compliance with the law. Europe has a larger vehicle production rate and more eligible vehicles.

Radioactive Waste Management. A special use category that is small in both the quantity of both molecular sieves and the gases and liquids processed is radioactive waste management, in which zeolites and other new molecular sieve ion exchangers (66, 67), adsorbents, and catalysts have been used for >25 years. Although only small quantities are used, the past and future environmental benefits are large indeed.

UOP's IONSIV zeolite ion exchangers were used for the radioactive waste cleanup at Three Mile Island; the West Valley commercial nuclear fuel reprocessing site; and the Hanford, Savannah River, Oak Ridge, and other U.S. Department of Energy nuclear waste storage sites (67). Most recently, and of special interest, is the current use of the new IONSIV IE-911 crystalline silicotitanate (CST) ion exchangers for the cleanup of the radioactive wastes in the Melton Valley tanks at Oak Ridge (68) and the planned use elsewhere in similar and other applications. The effectiveness of CST was discovered (69) by researchers at Sandia National Laboratories and Texas A & M University, and its further product and manufacturing process development and commercial manufacture was carried out in 1994–1995 by UOP under a Cooperative Research and Development Agreement with Sandia (70, 71). In 1996, this work earned an R&D 100 Award for the Sandia, Texas A & M, and UOP researchers (72).

Other Smaller Environmental Applications. Many smaller applications of zeolites in catalysis and adsorption, although important and beneficial to mankind, are not discussed here because of space limitations. Noteworthy are the growing uses of zeolites and other molecular sieves as adsorbents in separations of volatile organic compounds and other pollutants, in desiccant cooling and dehumidification, and as ion exchangers for pollution abatement and toxic waste management.

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‡‡Schwuger, M. J. & Smolka, H. G., 49th National Colloid Symposium, June 1975, Clarkson College, Potsdam, NY.

§§Dunne, S. R. & Taqvi, S. M., AIChE Annual Meeting, Session on Environmental Catalysis, November 1997, Los Angeles, CA.

Conclusions

Likely Future Applications. Use of zeolites as catalysts in the manufacture of some fine chemicals should expand. New zeolite and other microporous oxide catalysts should be developed with improved selectivity and new functionalities, perhaps for strong base and oxidation catalysis, chiral synthesis, and possibly, membrane reactors. Desiccant cooling and dehumidification, and sorption heat pumps, may achieve serious success. New ion exchange applications of new microporous oxides also may be expected. Experience has taught that the availability of new materials normally precedes by many years the discovery of all of their useful properties and the conception and development of new uses.

Impacts of Molecular Sieves on Human Welfare. From these numbers, Roth estimated the value of fuels and chemicals produced using catalysts in 1989 to be $891 billion per year, or 17% of the U.S. gross national product, and judged the corresponding worldwide product values for fuels and chemicals to be $2.4 trillion per year (73). Of course, not all catalysts are based on zeolites, but for petroleum-based fuels and petrochemicals, most catalysts are now zeolitic. Thus, the impact of zeolites in these areas is clearly great. Likewise, the use of zeolites in catalytic converters to reduce undesirable emissions from vehicles also represents a significant present market (with large growth potential) and substantial benefits to mankind in pollution abatement.

As described earlier, synthetic zeolites play critical roles in the production of fuels, petrochemicals, and other products essential to modern societies; in pollution avoidance or abatement; in energy efficiency; and in the efficient use of natural raw materials. They also contribute to the quality and performance of the ultimate products because of the greater purity and uniformity of the intermediates made by using zeolites.

The many benefits achieved from the applications of zeolites and other molecular sieves are the fruits of the basic investments made decades ago, and into the present, in the research areas of mineralogy, geology, geochemistry, structure and properties of natural zeolites, exploratory materials synthesis, materials characterization methods and their application, and exploratory research on structure, property, and functionalities. The basic concepts and understanding from these efforts, coupled with creative consideration of how the properties and functionalities so discovered might be of service to solve the needs of mankind, continue to create new benefits.

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