Rationally Designed Inorganic Catalysts for Environmentally Compatible Technologies**

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In a recent analysis[1] of the future prospects pertaining to the design of new catalysts and to the improvement of the performance of existing ones, Schlögl viewed the world through the prism of ammonia synthesis. He traced the heroic work that started with Haber, continued with Mittasch, and which has since been the subject of intense study by generations of subsequent investigators, all of whom, in their respective ways, have struggled to understand the behavior of the iron-based catalyst for the large-scale manufacture of ammonia. But Schlögl's assertions must be challenged, especially the following: "All of the catalytic processes vital to industry were developed by purely empirical methods and countless screening experiments". "This heuristic approach has led to the opinion that catalysis research is not a science but rather 'black magic' ". Schlögl further asserts that "...industrial chemists tend to be rather sceptical toward inductive-scientific strategies in heterogeneous catalysis, since it is evident that our understanding of *the relationship between structure and reactivity is inadequate*" (our italics). These are strong, strident words with which we disagree for the reasons given below.

Whilst it is true, as Schlögl describes, that the laboratory world of iron single-crystals, cleaned in ultrahigh vacuum and studied under modest pressure, is vastly different from that of the catalyst in the ammonia synthesis reactor, and whilst it is undeniable that, as yet, no new industrially viable ammonia synthesis catalyst (with the possible exception of the recently commissioned, supported ruthenium catalyst) has emerged as a direct consequence of the de novo investigations of single-crystal metal catalysts, his statements cited above are untrue when applied to other important classes of catalysts. There are numerous examples in which causal relationships between crystalline structure and catalytic performance have been incontrovertibly established.

Some examples of the veracity of our claims are contained in a number of recent publications.[2-11] One of these,[2] published in *Angewandte Chemie* five years ago, is entitled "Uniform Heterogeneous Catalysts: The Role of Solid-State Chemistry in their Development and Design". In another[3] numerous chapters support the view that designed catalysts have already been commercialized and are likely to play a pivotal role in the chemistry of the 21st century. Yet other publications[4, 5] address the timely question of designer catalysts in the quest for cost-effective, environmentally compatible technologies. If Schlögl's claims were true, future employers and boardroom protagonists could well underestimate or misjudge the contributions that the research chemist could make to the future of their industry, and employment prospects for numerous highly trained physical scientists would be bleak.

Examples of intentional design in the genesis and evolution of new catalysts are quite numerous. So relevant and progressive is this sector of solid-state chemical research in devising environmentally acceptable catalysts and processes that we summarize four distinct categories of catalysts:

1) An ever-expanding family of monophasic, microporous, microcrystalline solids, some members of which already function on the industrial scale as essentially shape-selective catalysts.
2) Multiphasic systems embracing supported metals, supported oxides, mixed oxides, and mixed sulfides of "designed" solids nowadays function as robust industrial catalysts.
3) Proven examples where new concepts in the design of molecular and extended (solid-state) catalysts have been demonstrated.
4) Improvements on preexisting industrial catalysts which stemmed from a fundamental reexamination of chemical engineering practice; worthwhile commercial and environmental improvements have already been achieved.

Whilst some amplification of all four theses is given in a recent book,[3] we present here the salient points that constitute our rebuttal of the assertions made by Schlögl.[1]

Shape-selective inorganic catalysts[9] are in extensive commercial use worldwide for the conversion of methanol to gasoline, the isomerization of xylene (maximizing yield of the *para* isomer), the conversion of ethene and benzene to ethyl benzene, the disproportionation of toluene to benzene and paraxylene, and the conversion of phenol to hydroquinone and catechol.[12] Many other processes currently being tested at either the pilot plant or laboratory stage entail the use of shape-selective solid

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catalysts. These include the production of ε-caprolactam by the isomerization of cyclohexanone oxime, the conversion of cyclohexanone into its oxime, the transformation of methanol into light olefins, the selective production of dimethylamine from ammonia and methanol, the isomerization of 1-butene to 2-methylpropene, and the production of diisopropylnaphthalene (DIPN) isomers. The particular monophasic catalysts used for these processes all have well-defined crystal structures possessing channels and cavities lined with active sites of known identity. Typical examples are H-ZSM-5, H-ferrierite, Theta-1, zeolite rho, HZSM-23, acidic clays, mordenite, and the silicoaluminophosphates H-SAPO-34, H-SAPO-11, etc., which, like ZSM-5, are Brönsted solid acids.[5, 8-12] They are all examples of so-called uniform heterogeneous catalysts in which the active sites are distributed in a spatially uniform way throughout their bulk. Another uniform shape-selective catalyst designed for the function it now has industrially (in the selective oxidation of phenol to hydroquinone) is Ti-silicalite, which is nonacidic.

The germ and genesis of the rational concept of shape-selective molecular sieves was the work of Weisz et al.,[9] who demonstrated that by a *controlled* variation of cavity size—exercised by simple application of the principles of crystal engineering—the selectivity of the catalytic dehydration of alkanols could be profoundly changed. In the thirty years that have elapsed since Weisz and his colleagues first reported their results, numerous successful attempts have been made to adapt the structures of naturally occurring molecular sieves (e.g. the well-known zeolite mordenite) and to synthesize a host of new ones. SAPOs and MeAlPOs—in which some of the phosphorus or aluminum atoms of the aluminium phosphate microporous framework are replaced by silicon (in SAPO) or divalent ions (in MeALPO), respectively—are now being designed and synthesized for specific catalytic reactions.[4, 10-16] One strong thrust is in the area of large-pore solid acid catalysts, many of which have recently been prepared[14] with the reactions of bulky molecules in mind.

We agree that the statement "No correlation exists between the bulk X-ray diffraction data and catalytic performance" was convincingly demonstrated by Schlögl[1] in the case of ammonia synthesis (iron-based) catalysts. But for the uniform shape-selective catalysts discussed here there is an indisputable link between the powder diffraction pattern, on the one hand, and the catalytic activity, on the other. See, for example, the published correlation between diffraction pattern, crystal structure, and catalytic performance for the Ni^{2+} ion-exchanged zeolite Y catalysts in the cyclotrimerization of acetylene.[17]

Indeed, so well understood is the correlation between crystal structure and selectivity among acidic shape-selective catalysts that computational chemistry has already contributed significantly to the evolution of superior catalysts for a given task. We cite two examples: the acid-catalyzed isomerization of 1-butene into 2-methylpropene, which is calculated[5, 18] to be facilitated better by Theta-1 than by ZSM-5, and the alkylation of naphthalene by propene to yield 2,6-diisopropylnaphthalene as the desired product.[4] Using computational procedures[18-20] that are by now quite routine for evaluating the energetics of docking of reactants and products inside zeolites, and for diffusion of species out of such shape-selective catalysts, Cusumano reports[4] that acidic mordenite is the favored catalyst to replace the environmentally harmful $AlCl_3$ now used for this reaction. (The $AlCl_3$ catalyst yields both the 2,6- and 2,7-disubstituted isomers as well as undesirable tri- and tetrasubstituted products.) DIPN can be selectively oxidized (Fig. 1) to give a number of monomers which may then be copolymerized into speciality high-performance polymers such as polyethylene naphthanate[4] which are of great potential in the liquid crystal and synthetic polymer markets.

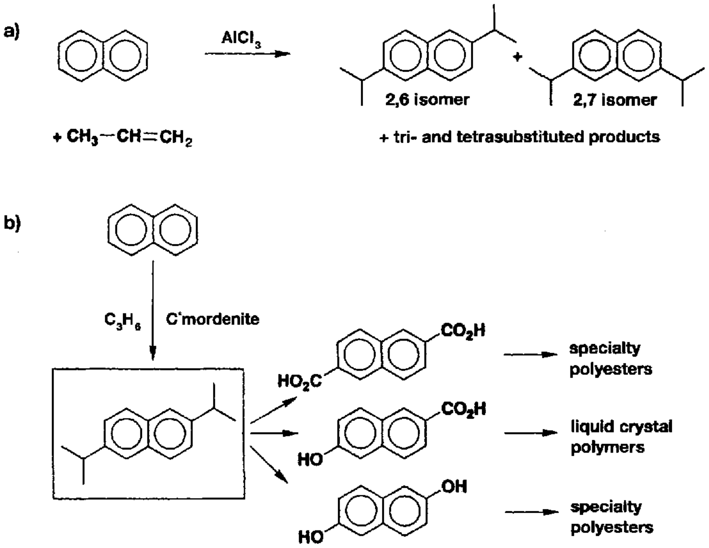

Fig. 1. Alkylation of naphthalene by propene catalyzed by a) $AlCl_3$ to give a mixture of products, b) by mordenite to give 2,6-diisopropylnaphthalene cleanly which can be converted to a number of monomers for specific polymers.

The second category consists of designed multiphasic catalysts. As a typical example, consider a new family of carbon-supported palladium catalysts[21] developed at the Boreskov Institute of Catalysis, Novosibirsk, by Likholobov, Yermakov, et al. These catalysts are prepared by the successive accretion of Pd atoms attached to certain functional groups of the support. A typical procedure is shown schematically in Figure 2. Supported particles of Pd (crystalline or amorphous) of remarkably uniform size can be obtained in this way. Based on laboratory tests to ascertain the activity of such supported catalysts (for reactions such as the hydrogenation of trifluoromethylnitrobenzene to provide the corresponding aniline), industrial catalysts for large-scale reductions are now in operation with particle sizes in

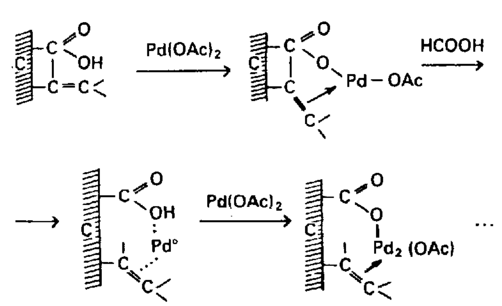

Fig. 2. Accretion of Pd atoms for the production of carbon-supported palladium catalysts.

the range 10 to 30 Å. It is also noteworthy that a new high-strength (ca. 400 kg cm^{-2}) carbon support containing essentially no micropores was especially designed[21] for this catalyst preparation and is already in use industrially.

Designer multiphasic catalysts have also been commercialized to alleviate environmental problems caused by H_2S. This pollutant is found as an impurity in many sources of natural gas, and also in many natural bodies of water, the Black Sea, in particular. One popular method of eliminating H_2S has been to use a stoichiometric then a catalytic reaction sequentially [Eq. (a)].

$$H_2S \xrightarrow{+O_2} SO_2 \xrightarrow[\text{cat.}]{+H_2S} S\downarrow + H_2O \qquad \text{(a)}$$

A superior method now on the verge of commercialization for the purification of natural gas[22] is based on a mixed-metal oxide that catalyzes the conversion of H_2S directly into S_2 at such a low temperature that methane remains unoxidized. Natural gas "poisoned" by H_2S may soon by purified efficiently with this designer oxide catalyst.

For removing H_2S from natural bodies of water inorganic photocatalysts that mimic natural bacterial photosynthesis have been designed, prepared, and proven effective.[24] Reaction (b) was demonstrated to proceed quite smoothly in pilot plants upon illumination of semiconductors with visible light.[23]

$$H_2S \xrightarrow{h\nu} H_2 + \tfrac{1}{2}S_2\downarrow \qquad \text{(b)}$$

With the heterojunction arrangement of Figure 3 the whole solar light spectrum is captured, and the efficiency achieved is comparable with that of living organisms.

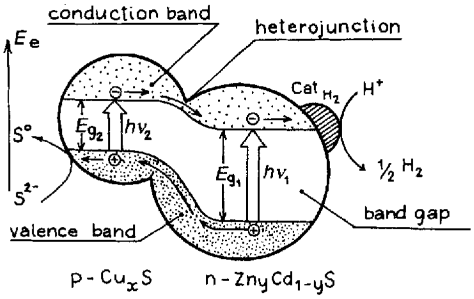

Fig. 3. Energy diagram for the photoseparation of charges and scheme for the catalytic process in a suspended semiconductor particle with the microheterojunction $CuS_x/Zn_yCd_{1-y}S$. E_e is the electrochemical potential of an electron; E_{g1} and E_{g2} are the widths of the band gaps of the semiconductor phases; $h\nu_1$ and $h\nu_2$ are the corresponding quanta of light required to promote an electron into the conduction band.

Another example is the heterogeneous Ziegler–Natta $TiCl_3/MgCl_2$ catalyst for stereoselective polymerization of propene and its copolymerization with other alkenes. Once the mechanism of its mode of action was rationally established, it became possible to tune the catalyst structure and morphology, and the reaction conditions for predominant production of stereoregular polymers with desired physical and mechanical properties.[3] With these carefully designed catalysts one can maximize the yield of the commercially required product and minimize the formation of wastes and consumption of raw material and energy.

A well-known family of inorganic molecular catalysts consists of metal complexes dissolved in liquids (homogeneous) or anchored to solid supports (heterogeneous). Among them, catalysts with chiral ligands for stereocontrolled organic synthesis are particularly noteworthy. The most renowned is the Monsanto rhodium-based catalyst for synthesis of L-dopa, a drug for treating Parkinson's disease (see ref. [4] for further details). Numerous other examples of rationally designed metal complex catalysts are known.[3, 4] The active site of one, a bimetallic (Pd + Co)/SiO_2 catalyst for hydroformylation of olefins, has been designed by Likholobov and co-workers.[3]

The third category of catalysts includes proven examples in which molecular systems and extended solids have been tailored for a specific catalytic purpose. We cite several noteworthy examples, the first of which relates to the rational development of a system for the photocleavage of water.[23] Here vesicles, microspheres several hundred Å in diameter with walls composed of a bi- or monolayer membrane of amphiphilic molecules, are employed. Aqueous solutions of the appropriate composition are found on either side of this membrane, and the photocatalyst may be "placed" inside the vesicle. The membrane serves to prevent recombination of the photogenerated, energy-rich electron–hole pair. In this way, with the agency of the encapsulated inorganic catalyst—which could be CdS particles of nanoscopic dimension that could serve as a quantum solid with energy levels different from those in the continuous solid—oxidation of water to oxygen and reduction to hydrogen may be smoothly effected.

But inorganic membrane catalysts are already occupying a central role in the development of new catalysts. Palladium-based membranes have been designed by Gryaznov and co-workers[24] at Moscow for numerous selective hydrogenations. In the current industrial production of vitamin K_4[24] a membrane made of a palladium alloy is used that permits facile passage of hydrogen from one compartment to other reactants at the membrane interface. The fundamental principle that governs the mode of operation of a membrane catalyst, be it metal alloy or inorganic (such as a zeolite[25] or a mixed-oxide electrolyte), is that it enables one (or more) crucial reactant(s) to be delivered to an interface in such a manner as to circumvent thermodynamic or other restrictions. Many potentially viable commercial applications, including fuel cells for the direct conversion of chemical into electrical energy in the presence of the appropriate electrocatalyst, are currently being tested.

With the goal of combating the greenhouse effect stemming from the buildup of carbon dioxide in the atmosphere and also exploring new ways of producing alternative feedstocks for C_2-C_3 production, Russian scientists[26] have developed catalytic membranes not based on precious metals for the conversion $CH_4 + CO_2 \longrightarrow 2CO + H_2$; here syn gas is produced with an advantageous $CO:H_2$ ratio.

The fourth category of catalyst research encompasses advances in the application of rationalized new ideas relating to the design and mode of operation of catalytic reactors. The most environmentally useful example to cite here emerged from a recent analysis conducted by Boreskov and Matros of the optimal conditions for the catalytic oxidation of SO_2 to SO_3,[27, 28] the basis of sulfuric acid production. Instead of pursuing the traditional practice of operating the catalytic reactor under steady-state conditions, Matros[28] explored the merits of running a so-called unsteady-state operation. This entails oxidation of the SO_2 under "forced" conditions for the passage of the reaction mixture through the catalyst bed. The principal advantage of this approach is that, compared with the conventional methods for the production of sulfuric acid, more dilute feedstocks (of SO_2) may be handled, and the size of the plant itself is significantly reduced, thereby limiting the required capital expenditure. Thanks to this work, copper and nickel refining in Russia, which hitherto released its sulfur by-products into the atmosphere as SO_2 leading to acid rain, now produces some 600000 tons of sulfuric acid and processes over 3 billion cubic meters of waste gases per annum.

Numerous other reactor design features have already been implemented commercially. One important example, reactive distillation (otherwise known as catalytic distillation), is the basis of a viable method of etherifying alkenes to produce gasoline additives such as methyl *tert*-butyl ether[29] by the addition of methanol to 2-methylpropene (now readily produced by the isomerization 1-butene[7, 30]).

It is also relevant to note that the pore structure in multiphasic catalysts can be rationally designed to optimize their performance. For example, the new high-strength (ca. 400 $\mathrm{kg\,cm^{-2}}$) carbon support, containing predominantly mesopores and almost no micropores and macropores, was especially designed for the Pd catalysts described in Figure 2. Likewise the honeycomb-shaped monolithic catalyst supports for pollution control in power plants and vehicles are the product of rational design.

It is simply not true that the quest for new catalysts is tantamount to black magic. Still less valid is the assertion that all the catalytic processes vital to industry were developed by empirical methods. We concede, however, that although it is already possible, de novo, to compute the rates of diffusion[19] of reactants and products into and out of the pores of shape-selective catalysts, a great deal more must be done before the prospect of computing and accurately predicting catalytic rate coefficients for bond rupture and formation is realized.

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Reply

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In our original highlight article[1] we described the possibilities and limitations of in situ experiments as a modern tool for unraveling the relationships between the structure of a working catalyst and its reactivity. Our conclusion was that although tremendous insight into the complexities of this problem has been gained, our knowledge about the crucial structure–reactivity relationship is, in general, still inadequate for the rational design of a catalyst for a given reaction.

In the immediately preceding correspondence[2] our conclusions are criticized as being only applicable to simple reactions such as the ammonia synthesis (which was not the main subject of the highlight article). Thomas and Zawaraev give an expert description of recent ingenious developments in heterogeneous catalysis; however, proof that these developments are based upon an understanding of the structure–reactivity relationship is lacking.

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