

ning 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 600 000 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 multiphase catalysts can be rationally designed to optimize their performance. For example, the new high-strength (ca. 400 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 Zamaraev 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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Their main example of shape-selective, monophasic, zeolite-based catalysts is admittedly a development in which rational ideas about the spatial requirements for diffusion of reactants or transition states in reactions allow the control of reactivity in favorable cases in which the reactant molecules have large structural differences. For any given general case with more subtle structural differences in the desired reactants, the concept of shape selectivity finds its current limits in details such as undisputed "kinetic openings", the influence of the crystallite size on mass transport, and the zeolite lattice dynamics under reaction conditions. A number of empirically derived chemical modifications such as that of the external surface and pore openings were applied, which indicates how chemical intuition can be used to solve problems without a rigorous analysis of the physical background of the application problem.

The second example of "designed multiphasic catalysts" is a further illustration for the general problem. It is simply not feasible to inductively design a catalyst for a reaction, the mechanism of which is not known in detail, and use components with unknown synergetic functions for the catalyst. The important field of selective oxidation catalysis is characterized by the existence of qualitative concepts^[3] such as "remote control" which summarize the practical experience of researchers over about 25 years. These concepts are, however, not based on fundamental chemical principles nor can they be used in a quantitative way like a theory.

In view of the formidable complexity of mechanisms for any selective oxidation reactions, such working concepts are of great practical value in guiding the chemical intuition required in developing catalytic processes such as those mentioned by Thomas and Zamaraev. The successful search for such qualitative guiding rules which are commonly used also in other fields of chemistry was inspired by the rational approach of surface physics to the problem of interface reactivity. It is the invaluable contribution of surface science^[4] to catalysis that provides guiding ideas and concepts such as that of the active site, geometric reaction control, surface thermodynamics, surface restructuring, and the dynamic nature of reactive systems. The large pool of detailed knowledge about surface reactions under surface-science conditions serves as a source of background information for the development of practical catalyst systems. In this way catalysis has gained a scientific basis in the form of a set of intuitively founded, qualitative working rules. This is, however, not to be mistaken as a quantitative, physically exact, and scientifically proven theory with the predictive power required for the "design approach" in catalysis. The efforts in conducting increasingly complex in situ experiments on existing catalyst systems may find one justification in providing arguments

to rationalize the working rules with practical, operating examples.

The "possibilities and limitations of a deductive approach to the development of industrial catalysts" was also analyzed from the viewpoint of a technical chemist.^[5] Rieckert concludes that it should be in principle impossible to design a catalyst owing to the inherently metastable and kinetically heterogeneous nature of an active catalyst material. This statement may be too restrictive, as we may not require starting catalyst design from first principles and we are also allowed to use some empirical testing in a rational design approach. In his analysis Rieckert advocates an evolutionary approach mimicking the controlled "trial-and-error" strategy of nature.

In a recent analysis of the impact of surface science on catalysis^[6] it was stated that the direct (rational) impact of surface science in the timeframe of a decade is limited. The indirect impact along the lines of providing working rules and modifying the thinking in catalyst development was, however, estimated as highly important. Catalysis is defined in this analysis as an "interesting mixture of science, engineering, and art". This conclusion is rather similar to that as reached in the initial highlight article.

It is obvious, and I fully agree with Thomas and Zamaraev, that significant progress has been made in selected cases in elucidating a number of aspects of the structure-reactivity relation. We do need, however, a great deal more hard facts about this relation to supplement our set of qualitative rules. There is no need to be pessimistic about an ever-increasing efficiency of catalyst development by the influx of scientific elements, and the semantic polarization of catalyst development strategies into either "scientific" or "intuitive" should also be avoided. Creating unjustified expectations about the potential of rational catalyst design by overestimating the state of our undisputed knowledge about operation principles in catalysis is unproductive and potentially detrimental to the field of catalysis science. Closing the experimental gaps between surface science and catalysis as described in the highlight article is one way to efficiently contribute towards the ideal of a rational approach in catalysis.

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