contrast to the silica-based AMM-Cr_2Si, the titania-based AMM-Cr_2Ti shows no significant selectivity for formation of acrolein or another product at this temperature, indicating a strong matrix effect on the catalyst activity and selectivity of the active site element Cr. In contrast to the other catalysts, the Rh-containing AMM-Rh_2Si shows a high selectivity for benzene formation from propene, indicative of an oxidative dehydrocyclization.

It has been shown here for the first time that significantly different selectivities of the components on catalyst libraries can be automatically detected by spatially resolved mass spectrometry. Advantages of the setup shown are the relatively low cost owing to the use of a commercial quadrupole-based gas analyzer, a commercial pipetting robot to control spatial resolution and analysis time, and the direct analysis of catalytic performance on the library without the need for a special reactor. This combination also allows reuse of the spatial information of the synthesis program as an integral part the screening procedure. Prerequisite for the use of such high-throughput screening procedures are the absence of induction periods of the catalysis studied. New catalysts requiring time-consuming activations cannot be discovered by such fast methods. However, this may not necessarily be a disadvantage since catalysts without an induction period are also of interest.

A disadvantage of the protocol presented here is its limitation to normal pressure. The fact that the complete library can be heated to the reaction temperature may be an advantage in oxidation reactions (regeneration of all components not under investigation), but a disadvantage for reduction reactions, where catalysts may have to be reduced to be active for hydrogenation reactions. Simple hydrogenation reactions, however, have already been conducted in our setup without problem. Presumably the small total amount of catalyst is reduced rapidly with the hydrogen-containing feed gas.

This investigation also opens the door for further developments of combinatorial methods in catalyst development. Especially the direct combination of IR thermography with spatially resolved mass spectrometry seems attractive, since on large libraries with several hundred or thousand components only active components can be selected for mass spectrometric identification of selectivity. Furthermore, the setup used can be readily modified, and by variation of the capillaries attached to the capillary bundle in the robot a large number of analytical techniques such as GC, GC-MS, IR, UV/VIS, and Raman spectroscopy, and capillary electrophoresis can be applied to libraries in a spatially resolved manner.

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[1] Special issue "Combinatorial Chemistry": *Acc. Chem. Res.* **1996**, *29*.
[2] G. Lowe, *Chem. Soc. Rev.* **1995**, *24*, 309.
[3] S. R. Wilson, A. W. Czarnik, *Combinatorial Chemistry –Synthesis and Application*, Wiley, **1997**.
[4] D. R. Liu, P. G. Schultz, *Angew. Chem.* **1999**, *111*, 36; *Angew. Chem. Int. Ed.* **1999**, *38*, 37.
[5] J. Klein, C. W. Lehmann, H.-W. Schmidt, W. F. Maier, *Angew. Chem.* **1998**, *110*, 3557; *Angew. Chem. Int. Ed.* **1998**, *37*, 3369.
[6] P. G. Schultz, X.-D. Xiang, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 153.
[7] T. Bein, *Angew. Chem.* **1999**, *111*, 335; *Angew. Chem. Int. Ed.* **1999**, *38*, 323.
[8] W. H. Weinberg, B. Jandeleit, K. Self, H. Turner, *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 104.
[9] A. Holzwarth, H.-W. Schmidt, W. F. Maier, *Angew. Chem.* **1998**, *110*, 2788; *Angew. Chem. Int. Ed.* **1998**, *37*, 2647.
[10] M. T. Reetz, M. H. Becker, K. M. Kühling, A. Holzwarth, *Angew. Chem.* **1998**, *110*, 2792; *Angew. Chem. Int. Ed.* **1998**, *37*, 2647.
[11] P. Cong, R. D. Doolen, Q. Fan, D. M. Giaquinta, S. Guan, E. W. McFarland, D. M. Poojary, K. Self, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111*, 508; *Angew. Chem. Int. Ed.* **1999**, *38*, 484.
[12] W. H. Weinberg, E. W. McFarland, P. Cong, S. Guan (Symyx Technologies), WO-A 98/15969 A2, **1998** [*Chem. Abstr.* **1998**, *128*, 289491].
[13] T. Zech, D. Hoenicke, *Erdoel Erdgas Kohle* **1998**, *114*, 578.
[14] H. Orzesek, R. P. Schulz, U. Dingerdissen, W. F. Maier, *Chem. Eng. Technol.* **1999**, *22*, 691.
[15] S. Bukeikhanova, H. Orzesek, U. Kolb, K. Kühlein, W. F. Maier, *Catal. Lett.* **1998**, *50*, 93.
[16] Current review: B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111*, 2648; *Angew. Chem. Int. Ed.* **1999**, *38*, 2494.

High-Throughput Testing of Heterogeneous Catalyst Libraries Using Array Microreactors and Mass Spectrometry**

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Combinatorial chemistry holds the promise to significantly accelerate the pace of research for the discovery and optimization of heterogeneous catalysts and to contribute to our understanding of catalytic function. However, to realize this potential advances must be made in two complementary areas: 1) the rapid generation and processing of a large diversity of structurally and compositionally different solid-state materials, and 2) high-throughput testing of these libraries for desired catalytic properties.[1]

Solid-state libraries can be prepared using techniques that can basically be categorized into two major groups: 1) thin film deposition based methods of synthesis,[2–4] and 2) solution-based methods for preparation of combinatorial libraries.[5–7] These techniques recently were used for the discovery

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and optimization of superconducting,[2a] magnetoresistive,[2b] and luminescent materials[3–5, 8] as well as electrochemical[6] and heterogeneous catalysts.[7, 9]

Once solid-state catalyst libraries are prepared, they have to be tested for activity, selectivity, resistance to poisoning, and operational lifetimes to identify leads that are of practical significance. To date several methods have been proposed to screen heterogeneous catalyst libraries: 1) in situ optical methods based on IR thermography,[10, 11] the use of fluorescent indicators,[6] and resonance enhanced multiphoton ionization (REMPI) spectroscopy;[7, 12] and 2) probe sampling followed by mass spectrometry.[9]

Optical methods allow the high-speed acquisition of data on the activities of catalysts in libraries without the need to take samples. However, their applications present some challenges. For example, in the case of IR thermography, no information on selectivity or specific reaction products is generated. Fluorescence screening requires that either the products are fluorescent or that product-specific fluorescent indicators are available or can be developed for each product. Among the optical methods, REMPI spectroscopy represents the most broadly applicable catalyst screening technique. However, in this case the development and availability of suitable REMPI strategies for the desired reaction products are necessary.[7]

On the other hand, mass spectrometry is a mature and universal detection technology and can readily be used to analyze complex gaseous mixtures. However, its application to combinatorial catalysis requires the development and implementation of new strategies. Recently, Cong et al.[9] reported a mass spectrometer based system to screen heterogeneous catalyst libraries in a sequential fashion. The total time to heat and screen one catalyst site was reported to be about one minute. It is important to recognize that the sequential screening system developed by Cong et al.[9] is slow and is only useful to determine the initial activities and selectivities of catalysts. Consequently, it will be of limited utility to identify leads for practical applications. The limitation arises from the fact that the activities and selectivities of heterogeneous catalysts significantly change (decrease and sometimes increase) with time on stream, which renders short-time data practically useless to assess the long-time performance of catalysts.

Array microreactors developed earlier in our laboratories are well suited to monitor the activities and selectivities of heterogeneous catalyst libraries over extended periods of time in a parallel fashion.[7] Recently we also coupled our array microreactors with capillary microprobe sampling and on-line mass spectrometry for the high-throughput testing of heterogeneous catalyst libraries. Here we report the results of time-on-stream testing of a Pt/Pd/In library with 66 combinations for the catalytic dehydrogenation of cyclohexane to benzene, a system that was previously studied using REMPI screening as well.[7]

The catalyst library consisted of 66 ternary combinations of Pt, Pd, and In prepared in 0.1 wt% increments of each metal with a total metal loading of 1 wt% on alumina using the conventional coimpregnation method. Pellets were prepared by compacting high surface area γ-Al_2O_3 powder (30 mg, 150 $m^2 g^{-1}$) into a cylindrical shape (0.4 cm diameter, 0.1 cm height) using a die. These pellet dimensions were chosen to allow for easy characterization and scale-up of newly discovered and/or optimized catalysts for commercial applications. Stock solutions of the metal precursors were prepared from high-purity $H_2[PtCl_6]$, $PdCl_2$, $InCl_2$, and aqueous HCl. The solution library was prepared automatically by mixing predetermined volumes of different catalyst precursor solutions into individually addressable test tubes in an array using a computer-controlled x,y,z translation table and a high-accuracy liquid-delivery system. Alumina pellets were then added into each test tube and allowed to impregnate under competition with HCl. Subsequently, the solutions were slowly evaporated, and the pellets dried and then calcined at 500 °C for 2 h.

Catalyst reduction and testing were accomplished in a modified version of the array microreactors described previously.[7] In the present design, each reactor array consisted of 20 rectangular channels that were micromachined on a flat nonporous silica ceramic slab (7.5 cm × 3.75 cm × 0.63 cm). Channels were 0.1 cm wide, 0.1 cm deep, and 2 cm long, and possessed a cylindrical well (0.4 cm diameter, 0.2 cm deep) to hold the cylindrical catalyst pellets (0.4 cm diameter, 0.1 cm high). In this configuration, the flat top surface of the catalyst pellet, when placed into the well would be flush with the bottom of the reactor channel. A similar flat ceramic slab was used to cover the microreactor array slab and to form isolated channels. The flat and rigid nature of the ceramic slabs also result in the formation of a good gas seal, thereby isolating each channel from one another under a broad range of temperatures. This design results in unobstructed gas flow through the channels, with only "wall skin friction" providing flow resistance. Consequently, nearly identical flow rates in each channel, and therefore identical contact times between the reactant gases and the catalyst pellets in each microreactor, were feasible. Gas flow rates in the channels were determined to be within 5% of one another using hot-wire anemometry measurements.

In the current arrangement four microreactor arrays, each having 20 channels, were stacked and placed inside an aluminum heating block (Figure 1). Thus it was possible to test 80 different catalysts in parallel. Clearly, a larger number of catalysts can easily be tested by stacking more arrays or by increasing the number of channels in each array. In Figure 1, one of the arrays has been pulled out to show internal details. The heating block was precision machined from a single piece of aluminum.

As can be seen in Figure 1, each array was surrounded with 1.25 cm thick aluminum walls to ensure temperature uniformity and compact design. Individual microreactor arrays were also fitted with dedicated quartz feed lines to separately adjust their flow rates. However, in the present set of experiments feed gas flow was maintained at the same rate for each array. Feed lines pass through a preheater system that was also machined from a solid aluminum block. The reactor and preheat blocks were thermally insulated using a porous ceramic board (Figure 1). During the actual catalyst testing process, a ceramic panel is also attached to the front of the reactor to further minimize heat loss and to maintain temper-

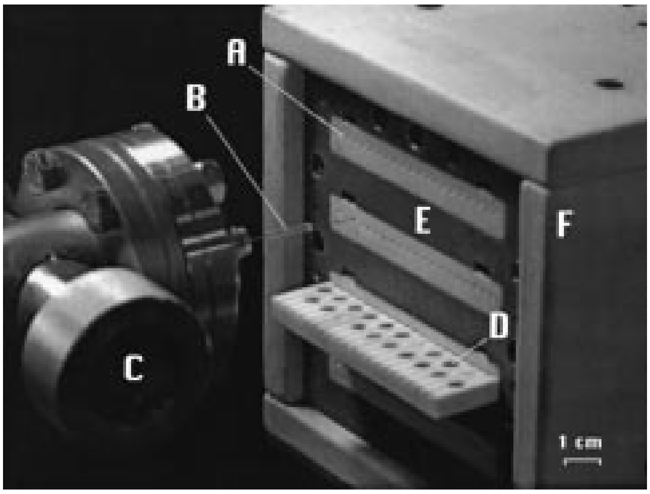

Figure 1. Microreactor system for catalyst screening. A: Array microreactor; B: capillary sampling probe; C: mass spectrometer; D: catalyst pellets; E: aluminum heating block; F: insulation.

ature uniformity within the array. This panel has been removed in Figure 1 to better illustrate the details of the reactor system. The temperatures of the array microreactors were regulated with electrical heating cartridges and thermocouples inserted into the aluminum blocks and by using PID controllers. Gas temperatures in the vicinity of the catalyst sites were separately monitored by small thermocouples inserted from the reactor exit to assess uniformity across the array, and to determine the time periods for heat-up and cool-down. These studies revealed the presence of a nearly uniform temperature, within 1 °C, across each array and between the arrays.

The entire reactor system was mounted on a stand that was part of a high-precision, computer-controlled *x,y,z* movement mechanism. Catalyst testing proceeded in the following manner: First, all 66 calcined pellets, together with selected duplicates and blanks (pure aluminum oxide), were placed into the wells of the microreactors, and the library was heated to 350 °C under argon as carrier gas. Upon reaching the set point temperature, the gas flow was switched to pure hydrogen and the pellets were reduced for 2 h. After reduction, the gas flow was changed back to argon and the temperature was lowered to the desired test temperature. Once the test temperature was reached, the gas stream was switched to the feed stream (about 10 % cyclohexane in argon). Under the experimental conditions, the nominal contact time between the feed gas and the pellets was about 0.004 s.

The levels of the reactants, products, and the inert carrier gas were determined by withdrawing a small stream (about 1 cm^3 min^{-1}) from each microreactor channel using a capillary sampling probe (50 μm diameter). The probe was inserted 2 mm into the channels to ensure the acquisition of representative samples. The gas was analyzed by quadrupole mass spectrometry (QMS). The sampling probe and the analysis system are also indicated in Figure 1. Each microreactor effluent was sequentially analyzed by moving the heated reactor block relative to the stationary sampling probe with the aid of the *x,y,z* positioning system. Gas samples entering the QM spectrometer were immediately subjected to 70 eV energy electrons and analyzed. To accelerate the data acquisition and to minimize the volume of data acquired, only selected mass ions, determined earlier in the scoping experiments, were monitored during the testing process. These were: cyclohexane (C_6H_{12}, 84 Da), cyclohexene (C_6H_{10}, 82 Da), C_6H_8 (80 Da), benzene (C_6H_6, 78 Da), and argon (40 Da). It is particularly interesting that although different levels of benzene production were observed from different catalysts, partially dehydrogenated cyclohexane products were not detected in any of the reactor effluents under the conditions investigated.

The data were acquired by rapidly inserting the capillary probe into each microreactor channel and sampling for about five seconds. This time period was adequate to acquire 2–5 sets of data, which was deemed sufficient for the present work. The probe subsequently was withdrawn from the channel and positioned into the next channel. By repeating this approach for each microreactor, we were able to screen the entire 80-channel library in about 10 min. Further acceleration of the data acquisition process is clearly possible. However, this was not necessary for the library size considered here. Even the conservative screening rate of 80 microreactors per 10 min achieved with the present system represents an improvement by a factor of 8 over the scanning mass spectrometer system of Cong et al.[9]

In Figure 2 the benzene ion current signals determined by QMS during the screening process are presented as a function of nominal channel number (reaction at 300 °C). The peaks correspond to benzene levels measured in each microreactor effluent, while the sharp drops correspond to the movement of the capillary probe from one site to the next. As evident from Figure 2, the measurement technique developed allows for easy discrimination of the individual sites. The relative activities of the different catalyst sites are readily discernible, illustrating the potential utility of the system as a high-throughput screening tool. Particularly significant are the stark differences that exist between catalytic and blank sites.

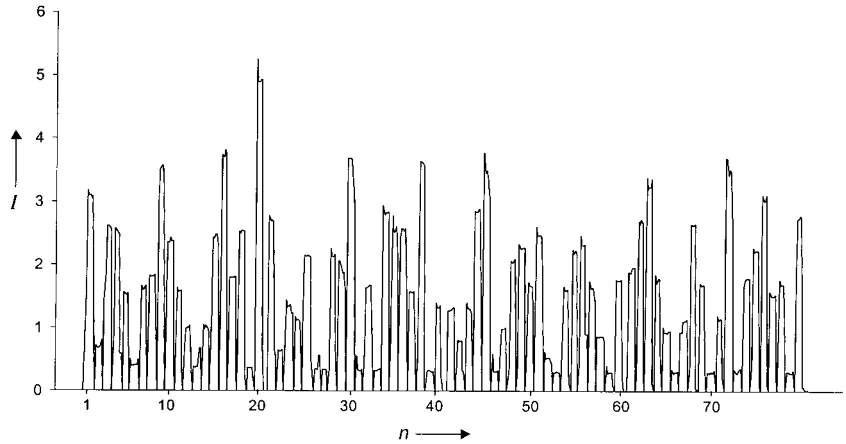

Figure 2. Intensities *I* of the benzene signals as a function of microreactor channel number *n*. The total time to acquire this information was less than 10 min.

The data presented in Figure 2 were also transformed into a triangular bar chart indicating the catalyst composition (Figure 3). It is seen that both Pt and Pd individually exhibited catalytic activities, with Pt being more active than Pd. On the other hand In was not catalytic towards benzene production from cyclohexane, and the ternary mixture of 0.8 % of Pt, 0.1 % of Pd, and 0.1 % of In exhibited superior benzene productivity when compared to all other metal combinations investigated. These results are in complete agreement with those obtained using REMPI screening and the same catalyst and operating conditions.[7]

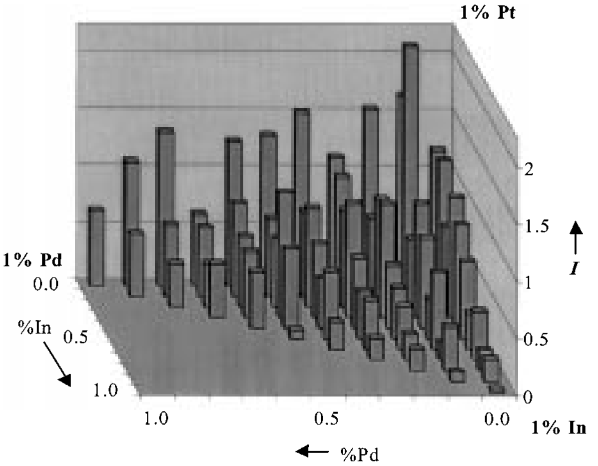

Figure 3. Initial activity *I* for benzene formation of the 66-combination Pt/Pd/In catalyst library.

As noted earlier, an important concern in the development of practical catalysts is time-on-stream performance. For example, although catalysts can exhibit high initial activities, this may degrade with time as a consequence of a number of events that can include coking, sintering, or poisoning. Alternately, selectivities to desired products can also change with time. The array microreactors coupled with QMS can readily address these concerns. To demonstrate this capability, we evaluated the performance of our ternary Pt/Pd/In catalyst library over 24 h. In Figure 4, the levels of benzene in the reactor effluents are presented as a function of time for the higher activity catalysts. Data for other catalysts were omitted to avoid congestion. The legend on the right side of Figure 4 indicates the catalyst compositions. It should be noted that the time-on-stream data points shown in Figure 4 represent only a subset of the data acquired by QMS to avoid clutter and to clearly illustrate a number of issues. First, as evident from Figure 4, all the catalysts, without any exception, experienced deactivation over the 24 h period investigated; deactivation was most significant early on in the experiments. Surface analysis of the used catalysts indicated that the mechanism of deactivation was coke formation. This was supported by the fact that most of the initial activity was regained after calcination in air. Second, it is significant that different catalysts deactivated at different rates, with the activity profiles of some catalysts crossing each other over time. These issues clearly demonstrate the inadequacy of the initial activity/selectivity data as a screening criterion for catalyst development.[9]

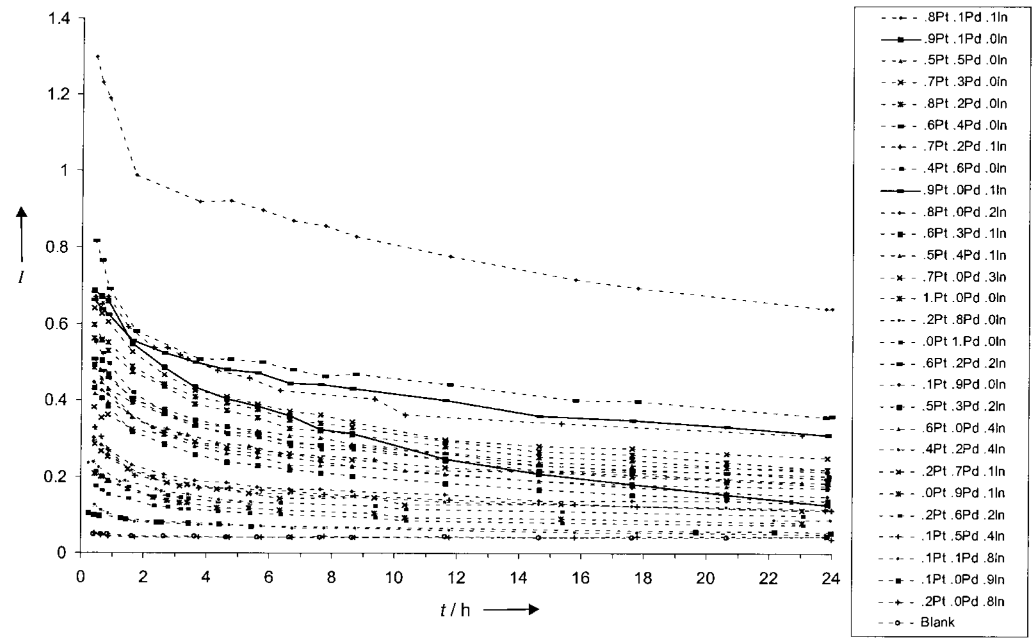

Figure 4. Activity *I* of selected catalysts as a function of time on stream.

The trends presented in Figure 4 also provide useful practical and fundamental insights on catalyst formulation. For example, consider the comparative deactivation behavior of catalysts with 0.9 % of Pt/0.1 % of Pd and 0.9 % of Pt/0.1 % of In (solid lines). As evident from Figure 4, both catalysts exhibited virtually the same initial activity. However, the catalyst with 0.9 % of Pt/0.1 % of Pd deactivated significantly faster than the catalyst with 0.9 % of Pt/0.1 % of In, suggesting the positive impact of In in slowing the rate of coke formation.

In Figure 5 the bar diagrams for benzene levels in the exhausts of all the microreactor channels are presented at the beginning of the reaction and after 2, 4, and 24 h of operation. The ternary mixture of 0.8 % of Pt, 0.1 % of Pd, and 0.1 % of In, which exhibited the highest initial activity, maintained its relative superiority over the entire testing period. However, the activities of all the catalysts decreased significantly during the testing period.

The array microreactor and QMS system developed also was used for the acquisition of information on reaction kinetics, from which reactor design parameters can be determined. To illustrate this we studied the effects of reaction temperature on benzene formation. This was accom-

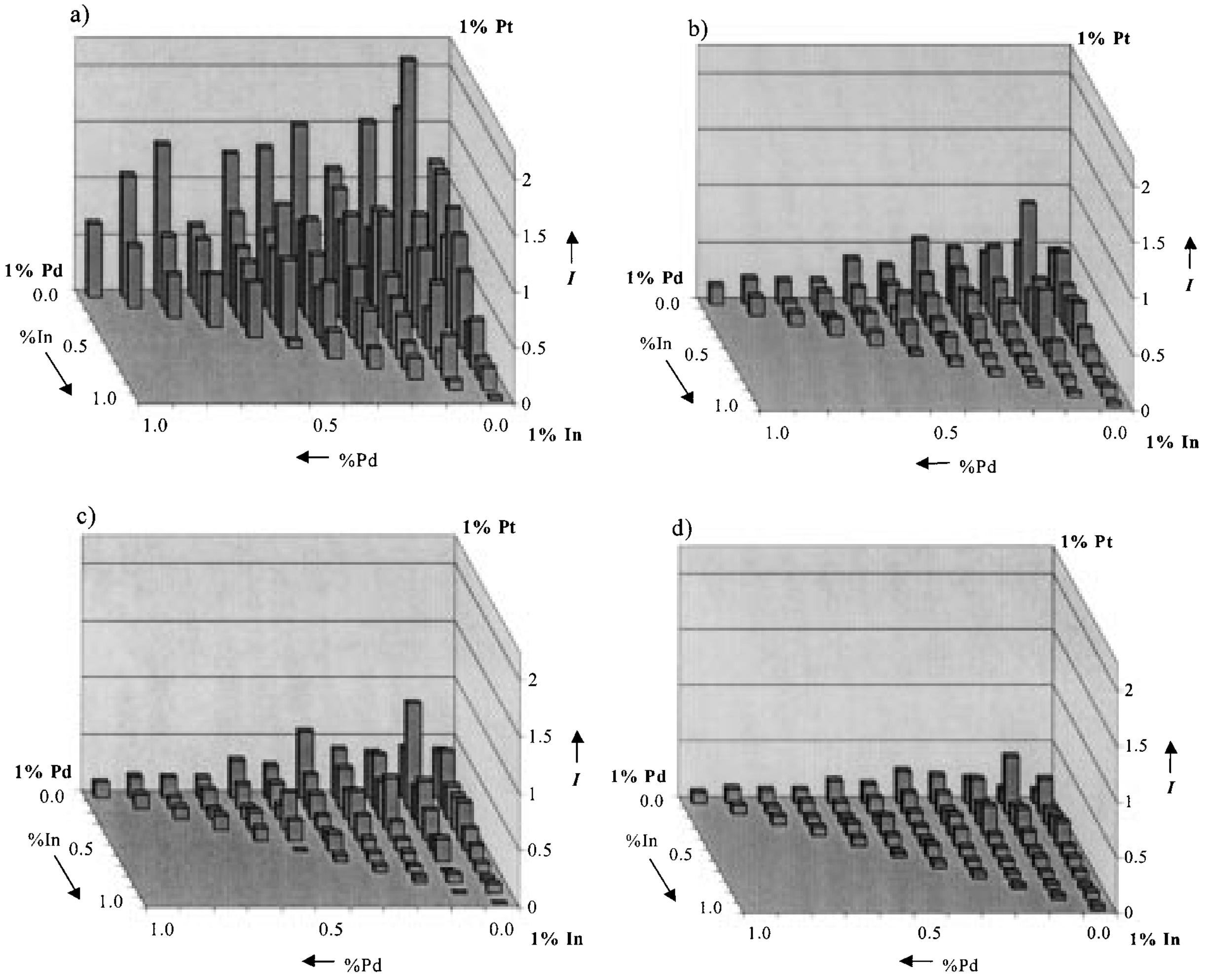

Figure 5. Benzene formation activity for the 66-combination Pt/Pd/In catalyst library: a) initial activity; b) after 2 h; c) after 4 h; d) after 24 h.

plished by starting with a freshly calcined—that is, coke-free—catalyst library. The array microreactor system was first heated to 150 °C and then screened for activity and selectivity. At 150 °C both benzene formation and catalyst deactivation rates were low. After data acquisition, the temperature of the reactor was increased to 200 °C, again under an inert gas flow. Following the establishment of the steady reaction temperature, the catalyst library was again screened for activity and selectivity. This procedure was repeated at 250 °C and then 300 °C. The total time to screen 80 microreactor channels at four different temperatures was about 3 h.

Heterogeneous reactions in porous catalyst particles proceed through a number of sequential events. These events include the transport of reactants to the external surface of the particle followed by internal (pore) diffusion, adsorption, and surface reactions.[13] Products then desorb from the surface and are transported back through the pores into the bulk gas stream. The temperature influences each of these steps differently. Generally surface reaction kinetics and desorption rates dominate product formation rates at lower temperatures due to their higher activation energies. However, increasing temperatures increase intrinsic reaction and desorption rates significantly more than diffusion rates, and thus the latter begin to influence the overall rate of conversion. These changes typically manifest themselves by decreases in observed (apparent) activation energies with increasing temperature.[13] In other words, Arrhenius diagrams (plots of ln(rate) versus $1/T$) exhibit nonlinear behavior.

To explore the above issues with the current catalyst system, the benzene signals measured at different temperatures have been analyzed using Equation (1). Here $I_{C_6H_6}$ is

$$d[I_{C_6H_6}]/dt = k_0 e(-E/RT) f(C) \tag{1}$$

the intensity of the benzene signal, which is proportional to the concentration, t the time, k_0 the preexponential factor, E the apparent (overall) activation energy, and $f(C)$ the concentration-dependent part of the rate expression, which can be in any functional form. Assuming differential conversion of cyclohexane, the Equation (1) can be integrated along the pellet and, under isothermal conditions, arranged to yield Equation (2). Here τ is the total contact time for the pellet, which is a constant for each microchannel reactor.

$$\ln(I_{C_6H_6}) = \ln(k_0) - E/RT + \ln(f(C)) + \ln(\tau) \tag{2}$$

In Figure 6 the benzene data are presented in accordance with the above relationship, again for the higher activity

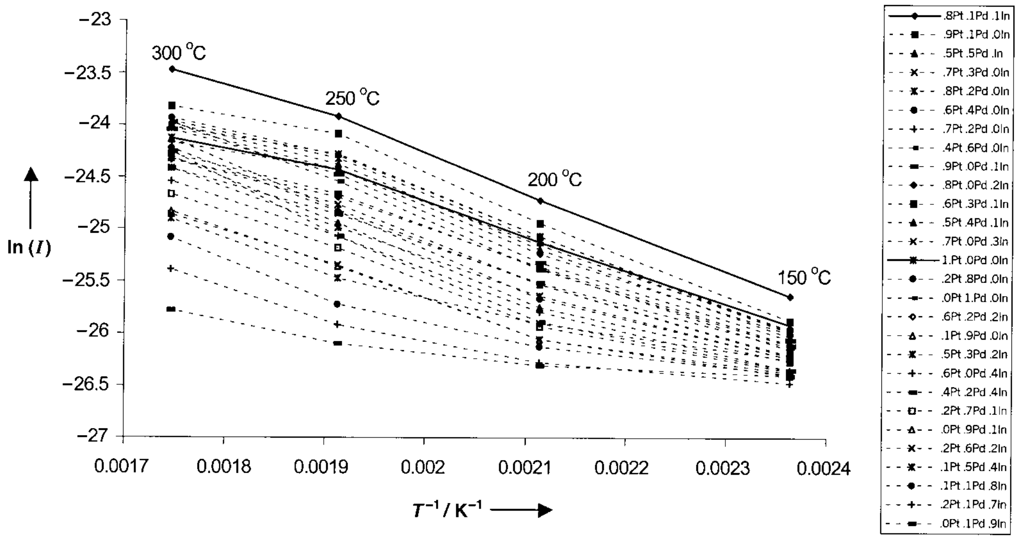

Figure 6. Arrhenius diagrams for selected catalysts.

catalysts. All the catalysts exhibited nonlinear Arrhenius behavior, suggesting changes in rate-controlling mechanisms with increasing temperature. In particular, the rate of formation of benzene exhibited higher apparent activation energies at lower temperatures than at higher temperatures for the higher activity catalysts, suggestive of the increasing importance of diffusion limitations with increasing temperature. Clearly, it is also possible that catalyst deactivation could have contributed to this behavior. However, due to the shortness of the test period (15 min at each temperature) and the fact that experiments at lower temperatures were conducted first, coke formation should not be a significant factor even at 300 °C. For the highest activity catalyst (0.8 % of Pt/0.1 % of Pd/0.1 % of In), the apparent activation energy was about 7 kcal mol^{-1} in the temperature interval 150–250 °C, but decreased to 5 kcal mol^{-1} in the temperature range 250–300 °C (see the upper solid line in Figure 6).

For the pure Pt catalyst (1.0 % of Pt), the apparent activation energy was about 6 kcal mol^{-1} over the 150–200 °C range (lower solid line in Figure 6). This value is smaller than that reported earlier from packed bed experiments (9.6 kcal mol^{-1}) where 40–65 mesh pellets of Pt catalysts were used.[14] However, these results are consistent with the fact that, owing to the larger pellets used in our experiments, the reactions would be more prone to diffusion limitations and thus exhibit smaller activation energies.[13]

It is also interesting that the activation energies of lower activity catalysts increased with increasing temperature over the temperature ranged considered (Figure 6). In addition, all of these catalysts were rich in indium, a fundamentally significant result that could be useful for the development practical catalysts.

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[1] Current review on combinatorial materials science and catalysis: B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111*, 2648; *Angew. Chem. Int. Ed.* **1999**, *38*, 2476.
[2] a) X.-D. Xiang, X. Sun, G. Briceno, Y. Lou, K.-A. Wang, H. Chang, W. G. Wallace-Freedman, S.-W. Chen, P. G. Schultz, *Science* **1995**, *268*, 1738; b) G. Briceno, H. Chang, X.-D. Sun, P. G. Schultz, X.-D. Xiang, *Science* **1995**, *270*, 273.
[3] X.-D. Sun, C. Gao, J. Wang, X.-D. Xiang, *Appl. Phys. Lett.* **1997**, *70*, 3353.
[4] E. Danielson, J. H. Golden, E. W. McFarland, C. M. Reaves, W. H. Weinberg, X. D. Wu, *Nature* **1997**, *389*, 944.
[5] X.-D. Sun, K.-A. Wang, Y. Yoo, W. G. Wallace-Freedman, C. Gao, X.-D. Xiang, P. G. Schultz, *Adv. Mater.* **1997**, *9*, 1046.
[6] E. Reddington, A. Sapienza, E. Guraou, R. Viswanathan, S. Sarangapani, E. S. Smotkin, T. E. Mallouk, *Science* **1998**, *280*, 1735.
[7] S. Senkan, S. Ozturk, *Angew. Chem.* **1999**, *111*, 867; *Angew. Chem. Int. Ed.* **1999**, *38*, 791.
[8] J. Wang, Y. Yoo, C. Gao, I. Takeuchi, X.-D. Sun, H. Chang, X.-D. Xiang, P. G. Schultz, *Science* **1998**, *279*, 1712.
[9] P. Cong, R. Doolen, Q. Fan, D. M. Giaquinta, S. Guan, E. McFarland, D. M. Poojary, H. W. Turner, W. H. Weinberg, *Angew. Chem.* **1999**, *111*, 508; *Angew. Chem. Int. Ed.* **1999**, *38*, 483.
[10] F. C. Moates, M. Somani, J. Annamalai, J. T. Richardson, D. Luss, R. C. Willson, *Ind. Eng. Chem. Res.* **1996**, *35*, 4801.
[11] S. J. Taylor, J. P. Morken, *Science* **1998**, *280*, 267.
[12] S. M. Senkan, *Nature* **1998**, *394*, 350.
[13] C. N. Satterfield, *Mass Transfer in Heterogeneous Catalysis*, MIT Press, Boston, **1970**.
[14] K. Ahmed, H. M. Chowdhury, *Chem. Eng. J.* **1992**, *50*, 165.