Parallel Synthesis and Testing of Catalysts under Nearly Conventional Testing Conditions**

Christian Hoffmann, Anke Wolf, and Ferdi Schüth*

Dedicated to Professor Ewald Wicke
on the occasion of his 85th birthday

High-throughput techniques are well established in the pharmaceutical industry and have also received considerable interest in recent years in the fields of materials science and catalysis.[1] Several publications have appeared dealing with the preparation and testing of catalysts under high-throughput conditions. The first work in this field used IR thermography to analyze an array of 16 conventionally prepared catalyst pellets in the H_2/O_2 reaction.[2] This methodology was then substantially refined by the background correction technique introduced by Maier and co-workers[3] and later proved to be suitable for liquid-phase reactions, if it can be ensured that catalyst particles float on the liquid surface to prevent screening of the thermal effects by the liquid.[4, 5] Common to these approaches is the fact that no selectivity information can be obtained, which is crucial for most catalytic reactions of industrial interest.

The resonance enhanced multiphoton ionization (REMPI) technique introduced by Senkan et al.[6] is in principle suitable for analyzing selectivity as well; however, only benzene was detected and no information on selectivity was obtained. Quantification is not straightforward, and the analysis of complex product mixtures will be very difficult with REMPI spectroscopy.

Weinberg and his co-workers at Symyx used a scanning mass spectrometric technique to analyze libraries of catalysts.[7] This procedure is in principle able to detect activity of catalysts as well as selectivity; however, the technique is used under conditions which are very different from those for conventional catalyst testing.

The techniques mentioned are certainly very valuable in an early development stage (stage I screening), but promising candidates have to be analyzed in more detail in a next step that is closer to real operation conditions (stage II screening). Such a stepwise approach in the parallelized development is also used in the pharmaceutical industry. In addition to the concentration of previous studies on stage I testing, there is an additional problem with most of these investigations: Usually no validation of the data—for example a check of the reliability by repeated library synthesis and control of the catalytic data in conventional reactors—was given. Such information, however, is absolutely crucial for a high-throughput approach to be successful.

We therefore report studies on parallelized catalyst synthesis and testing a) which are close to conventional catalysis research, but parallelized, and b) for which reproducibility and precision of all steps have been checked carefully. The data presented show that catalyst synthesis and testing can be accelerated by between one and two orders of magnitude without much loss of information compared to conventional testing.

The identification and optimization of gold-based catalysts for the room-temperature oxidation of CO was chosen as a test case. These catalysts were discovered by Haruta,[8] but the synthesis is not completely documented and extremely ill reproducible. Therefore a large number of preparation and test experiments are necessary to establish proper synthesis conditions for highly active catalysts. The system described here is meanwhile used in routine operation in our laboratory for this purpose.

The synthesis system is based on a Gilson XL 232 automated dispenser. We prepared different Au/Co_3O_4 catalyts by coprecipitation and Au/TiO_2 catalysts by precipitation of gold onto the support with different concentrations, pH values during precipitation, temperatures of calcination, and support materials. The precipitation and coprecipitation reactions are carried out in 50-mL test tubes placed on a shaker tray to avoid settling of the precipitate. The suspensions of the precipitates are transferred by means of a stainless steel tube of 1 mm inner diameter, attached to the dispenser, to a filtration unit with 4 × 4 wells which has the same format as the catalytic test reactor. In this unit the suspensions are filtered and the collected solids rinsed with water. The whole filtration unit can then be placed in an oven with controlled atmosphere to prepare the final catalyst. After the thermal treatment, the catalysts are loosened with a spatula, transferred manually, and then weighed separately into the sinter plate. The weighing step is important to guarantee the identical space velocity over all 16 catalysts. Several sets of four identical catalyst batches were prepared, manually as well as in the automated system, in order to check the reproducibility of the synthesis. The synthesis of the gold-based catalysts is known to be difficult to reproduce. Seemingly identical preparations resulted in catalysts which differed in activity by 50% or more. Such high deviations were never observed for catalysts prepared automatically, although also in this case some scatter of up to 35% in activity occurred. This shows that automatic preparation, if carried out properly, is at least as reliable as manual catalyst synthesis. This advantage will become even more pronounced if, as in industrial laboratories, catalysts are frequently synthesized by different operators, which introduces an additional degree of uncertainty.

A schematic drawing of the test reactor is shown in Figure 1a, and a photograph in Figure 1b. It consists of a brass block with 16 wells of 1 cm diameter each, equipped with nine heating cartridges which ensure a homogeneous temperature over the whole reactor. Temperature differences between the wells, measured with thermocouples in the wells filled with catalyst under flowing air, are less than 1 K. The gas is admitted from the top to all 16 wells simultaneously. Catalysts are placed on a plate with 16 wells (inner diameter

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[*] Prof. Dr. F. Schüth, C. Hoffmann, A. Wolf
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr (Germany)
Fax: (+49) 208-306-2395
E-mail: schueth@mpi-muelheim.mpg.de

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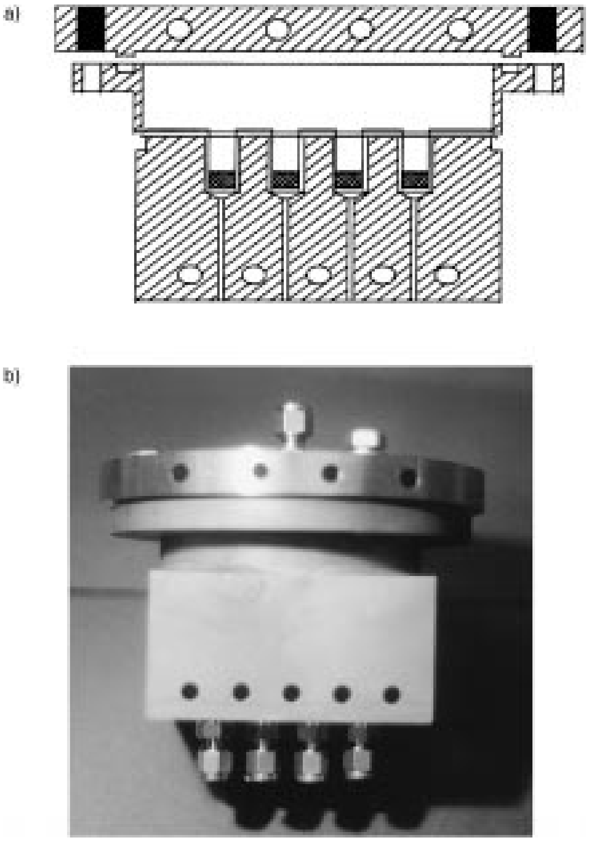

Figure 1. a) Schematic drawing of the 16-pass reactor and b) photograph of the reactor.

6 mm) which is sealed against the brass body. This plate can also be used to store the libraries. The gases are then passed through individual capillaries, each equipped with a three-way valve to switch the offstream of one catalyst to an analytical instrument. The remaining 15 streams of gas are passed to the reactor outlet. This means that during the entire test all catalysts are exposed to the reaction gas, so that the catalysts are equilibrated. If deactivation is a problem, the library can be scanned several times in order to monitor changes in catalyst activity.

Initial experiments with 16 identical catalysts in all wells proved that severe flow inhomogeneities can occur in the test module if no precautions are taken. An additional problem can be created by strong backmixing. The reactor was modified accordingly to solve these problems. Capillaries are placed in the offstream to present the major flow resistance, so that the highest pressure drop is not over the catalyst bed, but through the capillaries. Differences in the catalyst packing therefore do not substantially influence the flow through the individual wells. In addition, the line to the analytical instrument is equipped with a flow controller so that during analysis all catalysts are operated under identical flow conditions. The homogeneous distribution of the inlet gas and the prevention of backmixing is achieved through a diffusor plate which consists of 16 1-mm holes over the wells. The linear flow in these bores is so high that no backmixing is detectable. With all these precautions, conversion over the different wells with identical catalysts do not differ by more than ±5%. The result of such a run can be seen in Figure 2.

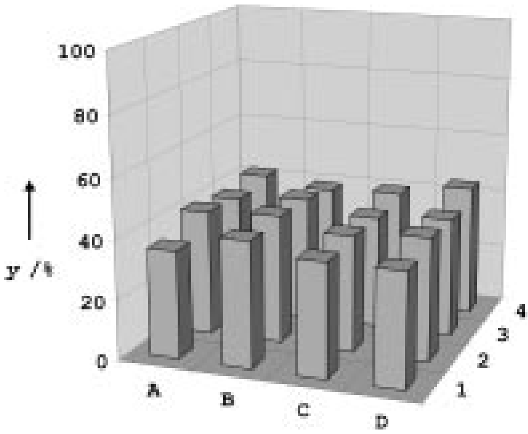

Figure 2. Parallel testing of 16 identical Pt/TiO_2 catalysts. y = yield of CO_2, space velocity over each catalyst = 20000 $\mathrm{mL\,h^{-1}\,g_{cat}^{-1}}$.

Reproducibility of the catalytic test was also better than 5% in different runs. These checks were all carried out under conditions where conversions were substantially lower than 100%, since at 100% conversion no activity differences could be detected.

There is in principle no limitation with respect to the analytical technique used to determine the activity of the catalysts. In this case nondispersive IR is used to determine CO and CO_2 concentrations, but GC or mass spectrometry are suitable as well. Catalytic testing of the gold catalysts was carried out at four different temperatures to identify not only the room-temperature active catalysts, but to also determine ignition temperatures of the less active materials.

Figure 3 shows the activity of one sample library of catalysts for the oxidation of CO. The library consists of Au/Co_3O_4 catalysts with different contents of Au (0.4–26.0 wt%). For half of the catalysts a second washing step was carried out after calcination, whereas the others were tested directly. The results show the eight catalysts that were washed after calcination already catalyze CO conversion at room temperature. The catalysts which were used without a second washing step only start to catalyze CO oxidation at or above 125 °C. The second washing step after calcination is therefore crucial for the removal of catalyst poisons deposited during preparation. X-ray fluorescence measurements show that the activity in CO oxidation increases with increasing Au content of the catalysts. According to high-resolution transmission electron microscopy (TEM), Au particles with a broad particle size distribution ranging from 2 to 200 nm are present. The catalyst with the highest activity had extremely large Au particles of 60–200 nm, although some particles that are smaller than the detection limit of TEM could be present.

To check another preparation technique the Au/TiO_2 catalyts, prepared by deposition–precipitation, were investigated. Various supports were used, including several commercial samples as well as anatase, mesoporous TiO_2, and microporous TiO_2, which were synthesized in our laboratory. The most suitable catalyst was based on anatase with a surface area of 180 $m^2\,g^{-1}$ and a Au particle size of 5 nm. This catalyst showed 100% conversion already at room temperature, which confirms Harutas results that highly dispersed Au particles are necessary for a high catalytic activity.

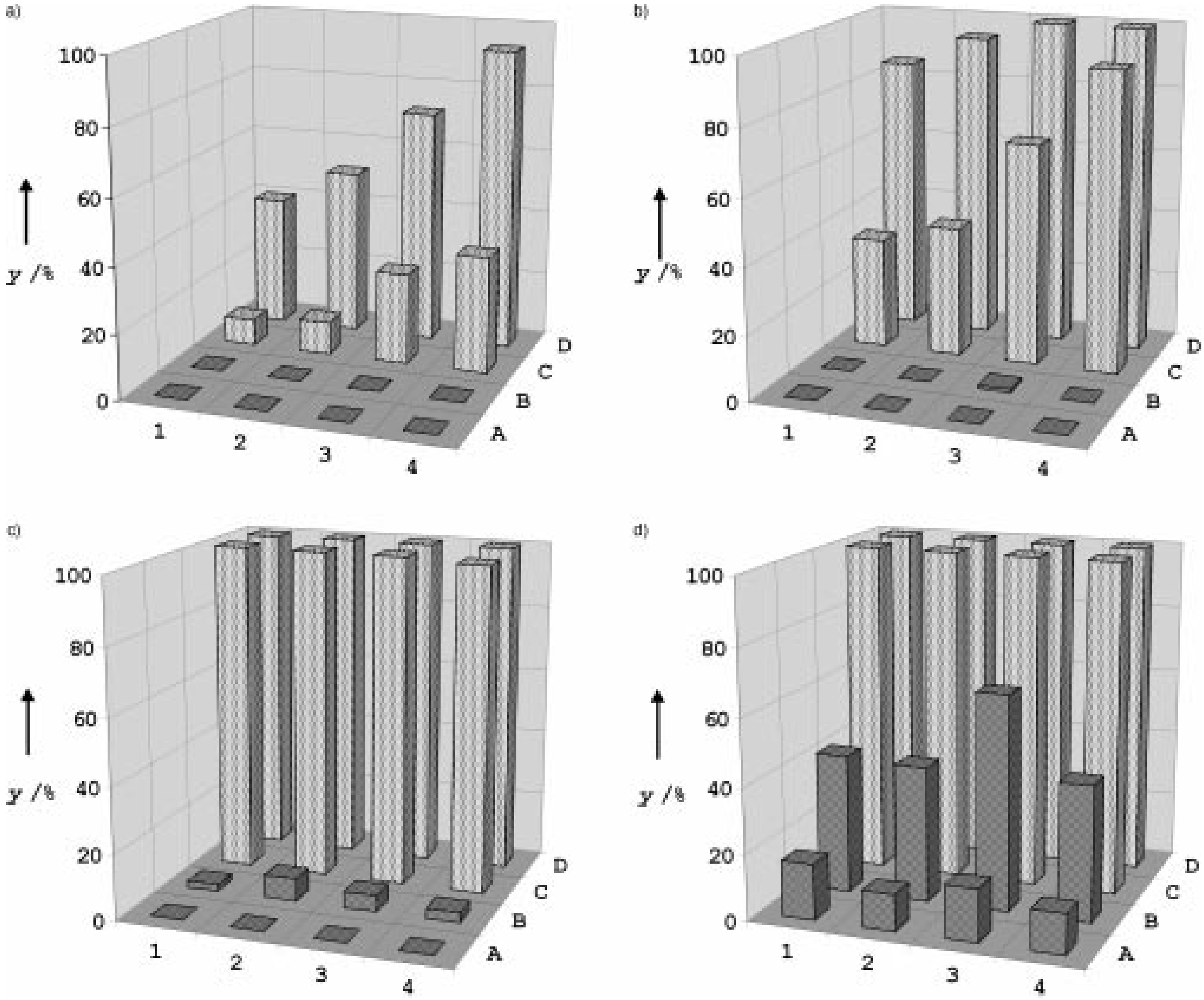

Figure 3. Parallel testing of Au/Co_3O_4 catalysts. y = yield of CO_2. Catalysts in the two front rows were not washed after calcination, those in the back rows were washed. Au content (wt %) from left to right and from front to back for the two sets of catalyst: 0.4, 1.0, 1.6, 3.4, 6.4, 9.8, 12.3, 26.0. $T_{\text{reactor}} = 25\,^\circ\text{C}$ (a), $70\,^\circ\text{C}$ (b), $125\,^\circ\text{C}$ (c), $180\,^\circ\text{C}$ (d).

Three of the catalysts for which the activity is low at room temperature, but increases at elevated temperatures, were also tested in the conventional flow system. Such materials with moderate activity allow the most meaningful comparison between the parallelized system and the conventional tests, since whole temperature/conversion curves can be compared. As can be seen in Figure 4, the activity curve measured in the parallel flow reactor and the conventional flow system differ by 10 K at most, which shows that reliable catalytic data can be obtained in the parallel flow system.

With this setup an acceleration of the development process by a factor of 15 was achieved. Higher integration is possible to a certain extent with similar reactor setups. However, one has to keep in mind that the probability of failures, for instance in valves, increases with the number of components present. Therefore, there is a limit to higher integration. Currently a 48-pass parallel flow reactor, which uses a multiport valve to simplify the setup, is in initial testing. This reactor is coupled to a GC instrument and will be used in the

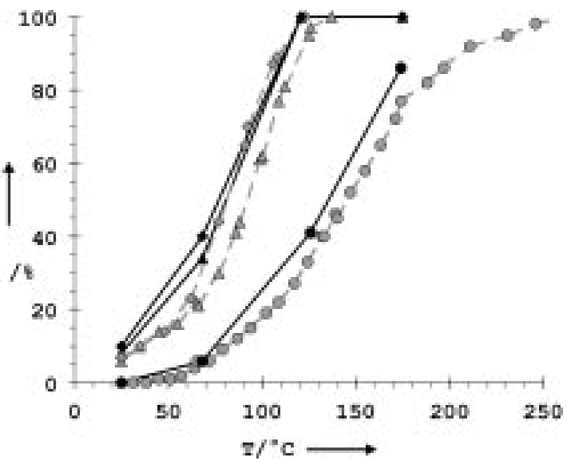

Figure 4. Comparison of parallel testing and testing in a conventional flow system for three different catalysts. Yield (y) of CO_2 as a function of catalyst temperature. Space velocity in all cases: $20000\ \text{mL}\,\text{h}^{-1}\,\text{g}_{\text{cat}}^{-1}$, (▲) 0.4 wt % Au/$Co_3O_4$, (◆) 1.0 wt % Au/$Co_3O_4$, (●) 15.6 wt % Au/$TiO_2$. Parallel test: solid line, conventional test: dashed line.

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near future for investigations of the partial oxidation of methane. The system will increase the throughput by another factor of 3, which will mean that 10000 catalysts per year can be tested using this technique.

Experimental Section

Synthesis: The synthesis system is based on a Gilson automated dispenser (model XL 232) which has been modified to suit our needs. The modifications are an integrated shaker (Heidolph, DSG-304), a bigger steel tube, and a filtration unit. Especially the precipitation step is somewhat difficult, since it normally involves relatively large amounts of liquids. Precipitation reactions are therefore carried out in relatively large vessels (50 mL) which are continuously shaken to prevent settling of the precipitate. The suspension is then pipetted onto a 16-well filtering unit which has the same dimensions as the catalytic reactor. The filtering unit is made of high-grade steel, with an outer diameter of 94 mm and a height of 40 mm. The bottom is formed from a sinter metal frit plate to allow filtration. The preparation steps described below were carried out in identical fashion in the automated module as well as manually.

Au/Co_3O_4 catalysts were prepared by coprecipitation. A solution of $H[AuCl_4]$ and $Co(NO_3)_2$ was added to a solution of 1 M Na_2CO_3. The mixture was agitated for 1 h. The resulting precipitate was isolated by filtration, washed several times, dried at 90 °C, and calcined in air at a temperature of 400 °C for 4 h. For several catalysts a second washing step was carried out after calcination.

Au/TiO_2 catalysts were prepared by deposition–precipitation. As support materials anatase, mesoporous TiO_2, and microporous TiO_2 were used. The support materials were prepared as described in the literature.[9, 10]

The support materials were suspended in H_2O. Aqueous solutions of $H[AuCl_4]$ and Na_2CO_3 were added in turn in three portions to the suspension. The mixture was then agitated for 10 h. The precipitates isolated by filtration were treated as above; the materials were calcined at 300 °C.

Catalysis: All catalysts were pretreated in air at 150 °C for 1 h in the catalytic test unit. Conventional catalytic measurements were carried out in a fixed bed flow reactor with 200 mg of catalyst sieved to 125–250 μm. For high-throughput experimentation 46 mg of powdered catalyst were inserted in each well without further preparation. A standard reaction gas of 1% CO in air was passed through the catalyst bed with 67 $mL\,min^{-1}$ for conventional tests and 250 $mL\,min^{-1}$ (15.6 $mL\,min^{-1}$ per well) for high-throughput experimentation to obtain the same space velocity of 20000 $mL\,h^{-1}\,1\,g_{cat}^{-1}$ for both systems. The concentrations of CO and CO_2 were determined by a nondispersive IR analyzer (URAS 3E, Hartmann and Braun).

Characterization: The gold contents were determined by X-ray fluorescence spectroscopy using a Philips PW-1400 apparatus. X-ray powder diffraction patterns were obtained on a STOE STADIP transmission diffractometer for Au/TiO_2 and on a STOE STADIP reflection diffractometer for Au/Co_3O_4. High-resolution electron micrographs were recorded using a Hitachi HF-200 microscope. The surface areas were determined with a Micrometrics ASAP-2010 analyzer.

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