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A Multipurpose Parallelized 49-Channel Reactor for the Screening of Catalysts: Methane Oxidation as the Example Reaction

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A 49-channel parallel reactor for the high throughput screening of catalysts has been developed. The reactor consists of a stainless steel body connected to a multiport valve via capillaries. For product analysis almost any technique can be used. In case of methane oxidation a two-GC setup with a hot and a cold column provided the necessary speed of analysis. The reactor was shown to give data of a quality close to the data quality obtained from measurements in a conventional single-tube flow reactor. Using this reactor setup it is possible to achieve a test capacity of 49 samples per day. If tests are to be performed at several different temperatures and different residence times, the cycle times are becoming correspondingly longer. © 2001 Academic Press

Key Words: **parallel reactor; combinatorial; heterogeneous catalysis; methane oxidation.**

INTRODUCTION

Combinatorial chemistry and the correspondingly developed techniques for high throughput synthesis and screening of organic molecules for their activity against target molecules and ultimately for their potential as drugs has revolutionized part of pharmaceutical research. Similar approaches are increasingly used for the evaluation of homogeneous and heterogeneous catalysts (1–3). Such strategies are often called "combinatorial catalysis," in analogy to the term "combinatorial chemistry" used in the drug industry. However, most of the concepts are not directly transferable to the development of homogeneous catalysts, even less so to the development of heterogeneous catalysts. We therefore prefer to speak of "parallelized approaches" or—more generally—"high throughput experimentation," since the final goal is in all cases the decrease of development times for novel catalysts, no matter how this reduction is achieved, be it via truly combinatorial methods or by a high degree of parallelization, or any other suitable technique.

As in the drug industry, a staged approach will probably be the most productive one, with a massive degree of parallization in the stage I, or the discovery stage, which in turn corresponds to very low amounts of catalysts (typically on the order of less than a milligram) and a low information depth. In stage II, or the optimization stage, techniques that are closer to conventional catalyst development must be used, so that the data obtained by the parallel test can be directly used for further scale-up. This entails typically higher amounts of catalyst, on the scale between milligram and gram, and a full product analysis, which usually means analysis times longer than those in stage I and a correspondingly lower throughput.

Most of the attention in catalysis research so far has been focused on stage I screening techniques. Thermographic imaging, which had already been used by Razon and Schmitz (4) in the 1980s to monitor differently active areas on catalytic surfaces during the reaction, has been used by Moates *et al.* (5) to simultaneously analyze an array of 16 different catalysts for the hydrogen/oxygen reaction. A more refined version of this technique was subsequently used by Holzwarth *et al.* (6) in different oxidation reactions and by Reetz *et al.* (7) and Taylor and Morken (8) to evaluate homogeneous catalysts. However, thermography gives only limited information, i.e., thermal effects. For instance, in technically important partial oxidation reactions, the hottest spot often probably corresponds to the worst possible catalyst, which only catalyzes total combustion of the hydrocarbons.

Therefore, techniques have been developed to also assess the selectivity of the catalysts, mostly using different kinds of scanning mass spectrometry (9–11). In these cases selectivity information could be obtained. However, the conditions of the experiments with respect to residence time and flow conditions through the catalysts are typically rather ill defined. With the exception of the work of Senkan *et al.* (11), the catalysts were not operated under flow-through conditions, but the reaction gas was rather flowed over the catalyst and then analyzed. In addition, two more specific techniques have been developed. Senkan has used resonance-enhanced multiphoton ionization to detect benzene as the dehydrogenation product of cyclohexane (12), and Reddington *et al.* (13) have used the signature of a pH-dependent luminescence dye to evaluate the potential of different ternary catalysts for the anode reaction in the

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methanol fuel cell. When looking at the data reported so far, it is also obvious, that a validation of the results using conventional equipment was lacking with the exception of the work on the methanol fuel cell catalysts.

Since scalability is one of the crucial issues in high-throughput catalysis research, we have focused on stage II techniques, which are not as highly parallelized, but provide more detailed information that can be directly used for further development. In a first generation we have described a 16-channel parallel brass reactor with 16 solenoid valves for switching the product stream either to the vent or to the NDIR analysis (14). This reactor is in routine use in our laboratory for testing low-temperature CO oxidation and propene epoxidation catalysts. However, this reactor was limited in various respects: the degree of parallelization with 16 channels was not satisfactory for more ambitious projects, the use of brass limited the upper operation temperature, and the analytical technique used, NDIR, was not suitable for reactions with a more complex product spectrum. In the following we describe a versatile reactor that solves all the problems mentioned. This reactor is used for the search of new methane oxidation catalysts, and first results on this reaction will be reported as well in the following.

EXPERIMENTAL

A schematic drawing of the reactor is given in Fig. 1a, a photograph of the semi-assembled reactor in Fig. 1b. The central part of the system is a cylindrical stainless steel body

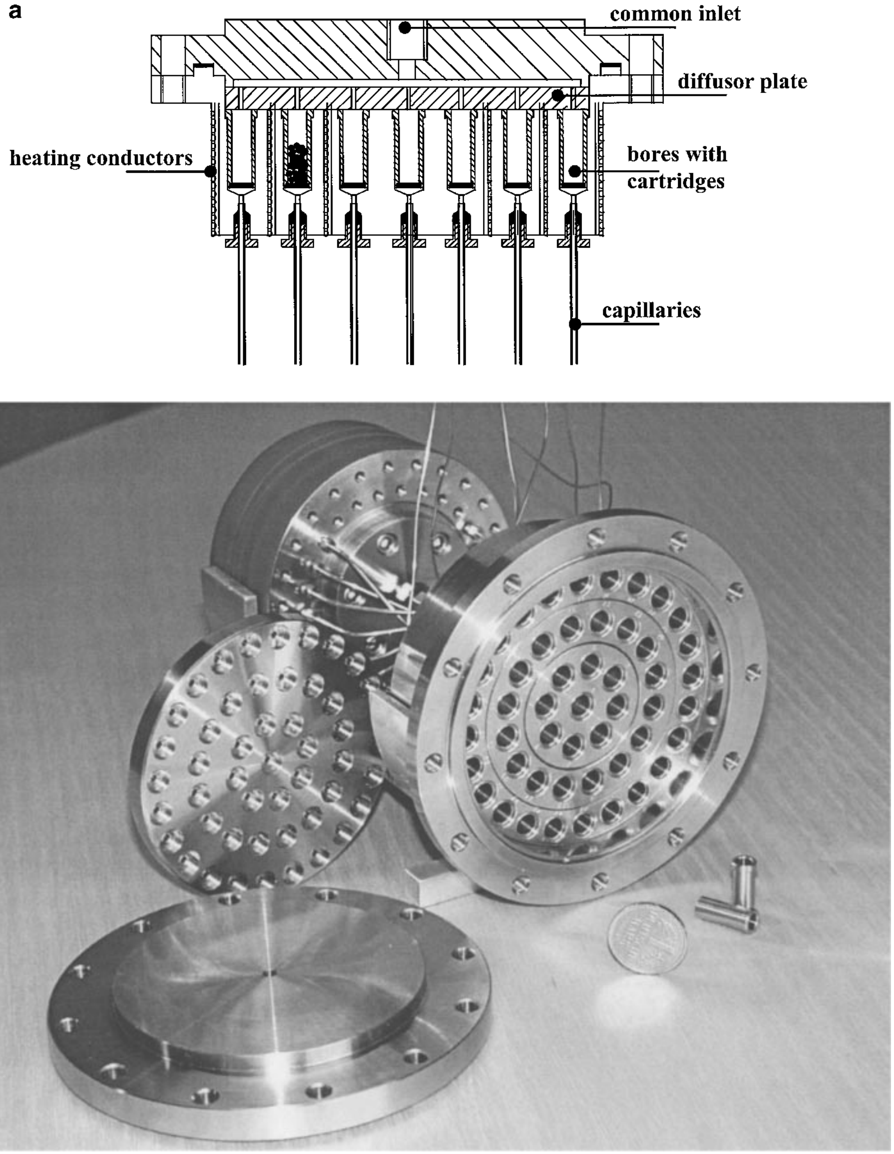

FIG. 1. Schematic drawing of a 49-pass reactor (a). Photograph of reactor (b).

with a diameter of 98 mm, a height of 54 mm, and 49 bores of 7 mm. For heating, the body is fitted with 3 concentric metal-mantled heating conductors (90 W/m). Temperature is controlled via thermocouples placed between wells on each circle; each heating conductor is controlled by an independent PID controller.

To avoid contamination of the reactor and to make loading of the reactor easier, catalysts are placed in 18-mm-long stainless steel cartridges (5 mm inner diameter), which are inserted into the bores and sealed against them via a polished metal rim. A sinter metal frit in the bottom of each cartridge supports the catalyst, which can be used as powder or split, which was the case in our studies (fraction between 1000 and 500 μm). Gas is admitted to the reactor through one common inlet in the removable top of the reactor. Homogenous distribution of the inlet gas and the prevention of backmixing is assured by a diffusor plate with a 2-mm bore opening into a conical hole on top of every reaction channel. The linear flow in these bores is so high that no backmixing with the gas from other channels was detectable within the range of flow rates investigated here.

At the exit of each reaction channel a capillary with a diameter of 1.6 mm, with an inner diameter of 0.8 mm and a length of approximately 140 mm is attached via fittings built in-house. The capillaries serve two purposes: First, they thermally decouple the reactor from the valve that cannot be heated to the maximum reactor temperature of 550°C, and second, they provide an additional flow resistance of the system, thus dampening the effect of different pressure drops over the catalyst beds. The capillaries are attached to a homebuilt multiport valve that directs the exhaust of one channel to the GC; the exhaust from the other channels is vented. In the line to the GC a mass flow controller that fine-tunes the flow through the channel analyzed so that all catalysts are measured at identical residence times, even if there are slight deviations between wells for the rest of the time (hot wire anemometry being the physical principle for the flow meter), is integrated. The change in thermal conductivity due to changing gas compositions, depending on conversion, is neglected here. The effect, however, is estimated to not be substantial, since conductivity changes only by about 10% for a gas composition of 20% CH_4, 10% O_2, and argon between 0% and 100% conversion. For other reactions, however, this could have a substantial effect, and in such cases other solutions will have to be found.

The whole reactor is integrated in a flow system. Feed composition is controlled via mass flow controllers (Bronkhorst) and gases are premixed thoroughly before entering the reactor. All tubes downstream of the reactor are heated to 120°C to prevent condensation of products. Products are analyzed via a combination of two GCs, one operating with a cold column (SUPELCO, Carboxen 1006 Plot) at 90°C for separation of the permanent gases, one with a hot column (SUPELCO, Carboxen 1006 Plot) at 150°C for the separation of methane partial oxidation and coupling products. Both GCs were equipped with a methanizer, so that FID detection was possible for all reaction products except hydrogen which could not be analyzed. Carbon balances closed always better than 5%, but typically were within 2%. With an optimized cycle an analysis time of 3.8 min. could be achieved, in which all possible C_2 products had left the column. If coupling products higher than C_2 are formed, this will not be detected immediately, but as stray GC peaks in subsequent runs. If that is the case, the cycle time for analysis must be extended. However, in all experiments conducted so far only C_1 and C_2 products were observed.

For comparison, experiments were also performed in a single-tube reactor. It consists of a quartz tube of 12 mm inner diameter and 380 mm length. This is placed in a PID controlled tube furnace and connected to a separate gas handling system. Analysis, however, is done via the same GC setup as in the parallel reactor via a three-way valve. The catalyst is placed on a quartz frit in this reactor, and flow rates are adjusted to obtain identical space velocities in the parallel and in the single-tube reactor.

Catalysts were prepared in an automated mode via incipient wetness impregnation of the sieved support material in a system described previously (14). Stock solutions of $Cu(NO_3)_2$, $[Pt(NH_3)_4](NO_3)_2$, $(NH_4)_6H_2W_{12}O_{41} \cdot aq$, and $(NH_4)_2MoO_4$ were used. The reliability and reproducibility of the preparation procedure had been checked in separate experiments for different ways of preparation (14), and was found to be at least as high as for manual sample preparation. Additional checks were performed in this study with the same results. Weighed amounts of the catalyst split were loaded into the reactor manually, which is one of the most time-consuming steps of the whole synthesis and testing procedure. However, automating this step has proved to be impossible so far due to the problems related to precisely handling small solid samples with widely differing properties. For testing the properties of the reactor, a commercial 5 wt.% Pt/alumina (MERCK) catalyst was used in order to have sufficient amount of material to fill all wells with the same catalyst.

Prior to each experiment the catalysts were heated in flowing argon at 450°C and then exposed to the reaction gas with a composition of 20% methane, 10% oxygen, and 70% argon. The total flow rate entering the reactor was 735 ml/min, which corresponds to a space velocity of 9,000 ml/h g for each catalyst. Reactions were carried out at different temperature levels, mostly 350, 450, and 550°C. Since catalysts might deactivate over the time needed for a full analytical cycle over all catalysts, typically two or three cycles were performed to detect changes of catalyst activity with time. In the case study presented here, no deactivation was observed. Should the catalysts deactivate rapidly, one either must evaluate the deactivating catalysts more carefully in single-tube reactors or find means to monitor these changes in a comparable fashion in the multitube system.

Stainless steel has some blank activity in hydrocarbon oxidation. Under the conditions used here, however, the blank activity of the reactor was below 3% conversion at 550°C and below 1.5% conversion at 450°C. If higher temperatures or easier-to-oxidize hydrocarbons are used, one would have to passivate the reactor surface by the methods that are common practice in conventional reactor engineering.

RESULTS AND DISCUSSION

In order to obtain reliable and comparable data from all wells, good temperature homogeneity over the reactor is mandatory. Since gas flow might change the temperature profile of the reactor, tests were carried out under gas flow with a special reactor cover and a movable thermocouple that could be placed in every well. For this experiment the wells were filled with support material to detect the intrinsic temperature deviations due to the reactor construction. At a temperature of 450°C, the temperature of the wells did not deviate by more than ±5 K. Most deviations were much smaller, but the wells near the point where the heating conductors entered the reactor were about 5 K hotter than the other wells, since in this reactor design, heating conductors with hot ends had been used. This problem can thus easily be solved in an improved version of the reactor by the use of heating conductors with cold ends and bigger dimensions. However, since the reactor operates between isothermal and adiabatic, the situation can change if highly exothermic reactions are being carried out, so that under reaction conditions higher thermal deviations between wells can occur (see below).

As stated earlier, rough equilibration of the flow through all wells is achieved by the use of capillaries downstream from the catalyst-loaded cartridges. Deviations in flow rate usually did not amount to more than ±10% even if the catalyst was loaded into the wells. For fine adjustment of the flow rates a mass flow controller was operated in the tube to the GC. This guarantees identical flow through all catalysts at least during the measurement. This fine adjustment changes the pressure drops over the different catalyst beds, according to the different flow resistance they present. If the rate expression is highly sensitive to total pressure, this introduces an additional source of error in the determination of kinetic parameters. However, for most reactions the sensitivity toward total pressure (other than toward partial pressures) is rather low. In addition, for a catalyst that reacts slowly to changes in the gas phase composition and does not reach the steady state within about four minutes (time between switching the multiport valve and sampling for GC analysis), this would lead to small deviations from the real activity. In our case no indication for such effects has been observed. This can, however, never be fully excluded, unless each catalyst is analyzed several times after adjusting the flow in order to determine the time needed to reach a stationary state again. In such cases one must compromise between speed and reliability of the analysis.

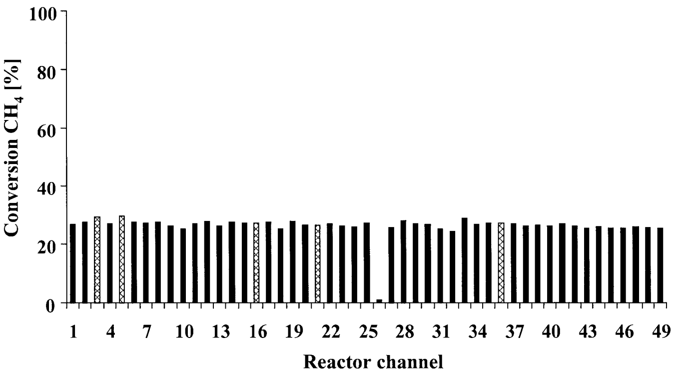

FIG. 2. Results from parallel test of 48 identical Cu/Al_2O_3 catalysts, showing the conversion of CH_4 vs each reactor position. Position 26 included a cartridge containing 0.1 g of the Al_2O_3 support. Gas mixture used was 1.5% CH_4, 6% O_2 in argon, 450°C, and space velocity over each catalyst = 11,500 ml/h $g_{(cat)}$. After the extensive series of experiments in which the reliability of the reactor had been tested, it was observed that five channels were fully or partly plugged. These channels are indicated as hatched columns. The results from these channels were not taken into account in the determination of the standard deviation.

After checking the temperature and flow homogeneity through the reactor, the reproducibility of the synthesis and the multireactor was tested. For this purpose the reactor was charged with 48 cartridges loaded with 2% Cu/Al_2O_3 from one automated synthesis with 48 identical batches. One position was charged with a cartridge with the support as a blank. Figure 2 shows the result of this experiment. Only total oxidation was observed and hence conversion corresponds to CO_2 production. As can be seen from the figure, deviations between different wells are relatively small. The conversion under these conditions is 26.7 ± 1.0% (standard deviation) corresponding to a relative error of ±3.5%. The catalyst activity increases with increasing temperatures; at 500°C the conversion is 62.2 ± 4.1% (standard deviation) with a corresponding relative error of ±6.5%. This shows that the reproducibility of the reactor is acceptable. The measured deviations are the sum of different effects: There are contributions from differences of the catalyst, since they were all prepared in individual batches by the automated system. In addition, there can be slight differences in the amounts of catalyst in each well. The contribution from these factors could be detected by changing the position of cartridges between different channels. Also contributing are the temperature differences, which influence the result obtained for a well independent of the catridge inserted.

Since the methane oxidation under these conditions releases an appreciable amount of heat due to the high gas flow and the high conversion, and since the reactor operates

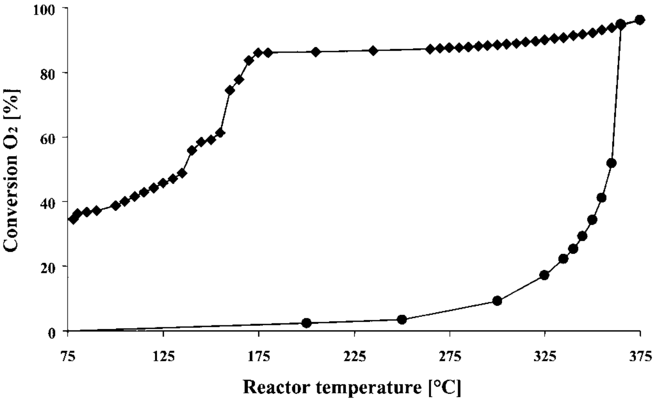

FIG. 3. Ignition/extinction curve of a catalyst in the parallel reactor showing conversion of O_2 vs reactor temperature: (●) ignition curve and (◆) extinction curve. 2.5 wt.% Pt/TiO_2, 20% CH_4, 10% O_2 in argon, WHSV = 9,000 ml/h $g_{(cat)}$.

between isothermal and adiabatic conditions, pronounced ignition/extinction phenomena can be observed (Fig. 3). Up to a reactor temperature of about 340°C the conversion increases steadily with increasing temperature. Then the conversion suddenly jumps to close to 100%, indicating that the lower steady state has become unstable. Decreasing the reactor temperature again does not lead to extinction of the reaction. Instead, a very pronounced hysteresis is observed, which, depending on the conditions, can extend over more than 100 K. In the example shown in Fig. 3 the lower steady state is not reached down to reactor temperatures of 75°C; the reaction is almost autothermal under these severe conditions. In addition, one can see that there seem to be steps in the curve recorded with decreasing reactor temperature. These are due to the thermal crosstalk with the neighboring wells, which have their own ignition and extinction points. The ignition point is not identical in all wells, since it is very sensitive to the energy balance of each well. Ignition of one well can trigger ignition of the reaction in neighboring wells, so that small differences in the activity between wells can lead to large differences in ignition temperature. This problem must be kept in mind when analyzing highly exothermic reactions. Conditions, where multistability can occur, are not suitable for comparison of different catalysts. In this case, either the catalyst must be diluted—possibly using longer catalyst beds, reaction conditions must be changed—or other types of parallel reactors in which heat transfer is improved must be used, for instance, reactors that resemble technical multitubular reactors with heat transfer fluids. These, however, are more difficult to construct, so that one must compromise again between precision of the results and difficulties in constructing and operating reactors. In any case, the ignition/extinction bistability problem described here is not unique to a parallel reactor setup, but can also occur in conventional single-tube reactors, as often described in the literature. The data shown and the discussion above should just demonstrate that care must be taken when comparing ignition temperatures in parallel reactors or conversions near an ignition instability, since there might be very strong effects, depending on whether the system is in the ignited or the extinct state. Therefore, for the evaluation of different catalysts in methane oxidation presented here—see below—more dilute gases have been used, so that the energy released by the reaction cannot lead to multistability.

One crucial factor in using parallel reactors is the question of how the data obtained in a parallel reactor compare to those from a conventional single-tube reactor. It has been shown that the results obtained for a 16-channel parallel reactor are quite similar to those obtained from conventional single-tube reactors (14). Such experiments were thus also conducted for the 49-channel reactor. Many of these comparison runs have been performed and two typical examples for quite different catalysts are shown in Fig. 4. As can be seen, the data from the two reactor systems agree quite well. The deviations especially at high conversions for the low-activity Cu/Al_2O_3 catalyst are due to different heat removal conditions for the multipass and the single-tube reactor. The characteristics of the single-tube reactor are actually closer to an adiabatic system, so that high conversions are observed at identical oven temperature. This is probably due to the higher inner diameter, which makes heat removal from the center of the catalyst bed more difficult, and the air gap between the reactor wall and the tube furnace.

Having ascertained the reliability of the catalytic data with the 49-pass reactor, the system was used for catalyst screening of potential methane oxidation catalysts. The goal of these ongoing experiments is to develop catalysts with high selectivity for partial oxidation products. Although this goal has not been reached, yet, these experiments do

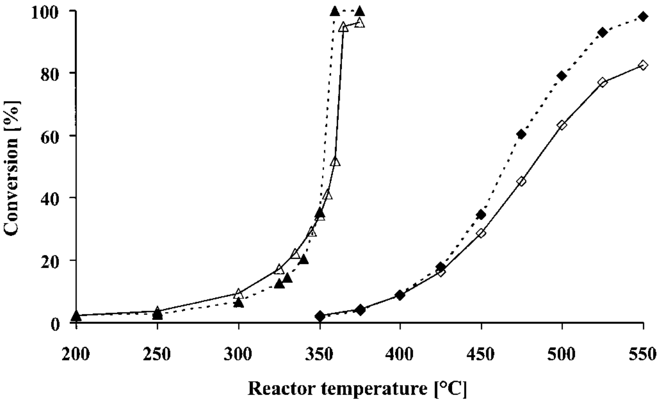

FIG. 4. Comparison of parallel test and test in conventional flow system for two different catalysts: (▲) 2.5 wt.% Pt/TiO_2, (◆) 2.0 wt.% Cu/Al_2O_3 showing conversion as a function of reactor temperature. Pt system: 20% CH_4, 10% O_2 in argon, WHSV = 9,000 ml/h $g_{(cat)}$. Cu system: 1.5% CH_4, 6.0% O_2 in argon, WHSV = 11,500 ml/h $g_{(cat)}$. In the parallel test reactor nitrogen was used instead of argon as the balance gas. The parallel test is the solid line, the conventional test the dashed line.

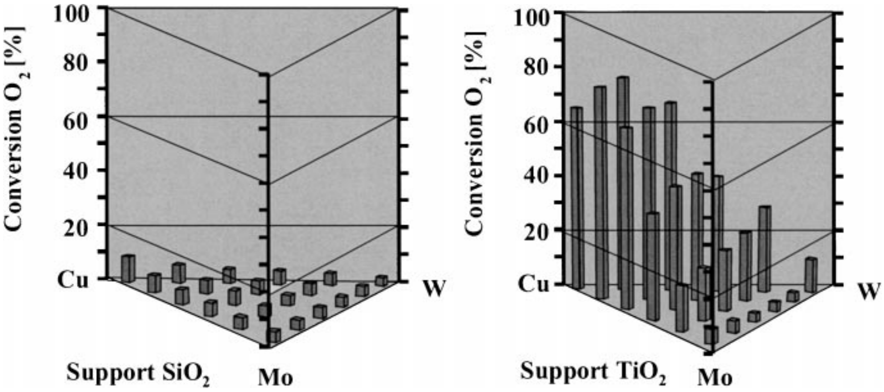

FIG. 5. Parallel test of a three-component-system with Σ 5 wt.% Cu/Mo/W on two different supports (SiO_2, TiO_2), 20% CH_4, 10% O_2 in argon, space velocity over each catalyst = 9,000 ml/h $g_{(cat)}$.

demonstrate the speed with which data can be generated. We have analyzed catalysts containing various amounts of Cu, Ni, Ba, Zr, Mn, Fe, La, Cr, Ag, Pt, Co, Cs, Sr, Ce, W and Mo. Figure 5 shows as an example the result of the evaluation of 42 catalysts. This evaluation was conducted from synthesis of the catalysts to analysis of the performance for two different temperatures within three days. The catalysts are based on copper, molybdenum, and tungsten, the amount of active component totaling 5 wt.%, supported on SiO_2 and TiO_2. Under the conditions used predominantly deep oxidation has been observed. Only minor amounts (less than 0.1% selectivity) of formaldehyde and carbon monoxide were detected; the major reaction product was carbon dioxide. However, the data clearly indicate that TiO_2 is a much better support, if total oxidation is the desired reaction. In fact, TiO_2 shows some blank activity at 450°C, for which the data are shown in Fig. 5. At a lower temperature of 350°C, the activity of all catalysts was very low and did not exceed 5% conversion of oxygen. In addition, the fact that CO and formaldehyde levels below 0.1% could be reliably detected demonstrates that detailed selectivity information can be obtained.

The efforts to find suitable catalysts for low-temperature conversion of methane to valuable products are continuing in our laboratory. The productivity that can be achieved with the reactor introduced here reaches about 150 catalysts per week, if experiments are being conducted at two to three different temperatures.

CONCLUSION AND OUTLOOK

We have demonstrated that it is possible to analyze catalysts under close-to-conventional conditions with a throughput of 150 catalysts per week, resulting in the production of data that are comparable to data obtained from conventional single-pass reactors. However, during these experiments several issues that should be considered when designing such reactors have been identified:

For highly exothermic reactions cross talk and thermal gradients must be taken into account. To avoid those effects, more diluted gas streams must be used, the catalysts must be diluted, or different types of reactors, such as systems resembling technical multitubular reactors with fluid heat transfer media, are necessary.

Homogeneous flow through the different wells is crucial to generate reliable and reproducible data. Flow constrictions in regions other than the catalyst bed itself and control of the flow to the analytical system are suitable means for solving this problem.

Pelletizing and loading weighed amounts of catalyst into the reactor is becoming the bottleneck that limits throughput. Automated methods to carry out these tasks need to be developed.

In order to have even more versatile systems for the parallel evaluation of solid catalysts, novel systems are in development. These include reactors suitable for higher pressures up to 50 bar and systems in which non-volume-constant reactions can be reliably investigated. For such reactions controlling the flow to the analytical system does not guarantee constant space velocity over each catalyst any longer. New solutions for handling the flow distribution thus must be developed. Steps in this direction are being taken in our laboratory, and we are confident that such techniques using parallel reactor technology can be developed to a standard tool in catalysis research over the next years.

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