Chemical Engineering Journal 89 (2002) 119–125

Chemical Engineering Journal
www.elsevier.com/locate/cej

Experimental equipment for high-throughput synthesis and testing of catalytic materials

Ina Hahndorf, Olga Buyevskaya, Martin Langpape, Gerd Grubert,
Stephan Kolf, Emmanuelle Guillon[1], Manfred Baerns*

ACA Institute for Applied Chemistry Berlin-Adlershof e.V., Richard-Willstätter-Straße 12, D-12489 Berlin, Germany

Received 28 August 2001; accepted 2 January 2002

Dedicated to Professor Wolf-Dieter Deckwer on the occasion of his 60th birthday

Abstract

A set-up for fast parallel preparation and testing of catalytic materials is presented. A commercial synthesis robot is used for automated parallel preparation of catalyst libraries. An adapted method for the synthesis of supported multicomponent catalytic material by sequential impregnation of an alumina support with different precursor solutions is described. It is shown that the catalytic performance of the materials prepared with the synthesis robot is comparable to manually prepared materials. In testing materials for the oxidative dehydrogenation of light alkanes to olefins a 64 multi-channel ceramic reactor module was used being connected to a fast GC/MS analysis. The reactor module is suitable for parallel testing of heterogeneous catalysts for various gas-phase reactions close to conventional laboratory conditions. Reliability and efficiency of the reactor are illustrated for the oxidative dehydrogenation of propane and ethane.

Keywords: High-throughput synthesis and screening; Catalytic materials; Parallel testing; Automated preparation; Oxidative dehydrogenation of ethane

1. Introduction

The application of high-throughput experimentation including combinatorial methods for the discovery of new heterogeneous catalysts is a fast developing area, which has attracted world-wide attention. Different high-throughput techniques for the preparation and the assessment of the catalytic performance of a large number of materials have been developed; this process is still continuing for meeting the different needs in catalyst research. Combinatorial methods originally developed in the pharmaceutical industry are now also applied in other areas such as advanced materials and catalysts. Schultz and coworkers [1] have reported in 1995 the first application of high-throughput experimentation and combinatorial methods in the search of solid materials with specific properties. They examined solid material libraries for superconductivity and magnetoresistance [2]. Those investigations initiated the application of high-throughput experimentation in material science [3] and hence later also in heterogeneous catalysis. For the parallel screening of catalytic materials a multitude of apparatuses of different concepts have been designed. One has to differentiate between so-called first- and second-stage screening concepts. First-stage screening instruments allow the testing of a large quantity of materials (up to 1000 and more) in the microgram range under simplified (standard) reaction conditions. The catalytic materials are prepared in the form of thin films on small wafers [4,5]. The feed gas is passed over the potential catalytic film. By mass spectrometry (MS) [6] or IR thermography [7] as analytical tools mostly only the activity of the material is examined without any quantitative assessment of selectivity for complex reactions. In second-stage screening, usually quantities in the 100 mg range are tested mostly in fixed-bed reactors under conditions close to those conventionally applied in laboratory experiments. In this way certainly more meaningful results than in first-stage screening are obtained. The number of tested materials is smaller (up to 100), the reaction conditions are well defined and the conversion and selectivity of the reaction is determined by usual analytical methods. Second-stage screening is also used to study “hits” of the first-stage screening in more detail.

Such high-throughput experimental set-ups consisting of multi-tubular reactor modules made of stainless steel, quartz or ceramics have been developed recently by various groups, e.g. Delft University of Technology [8]; MPI, Mühlheim

---

* Corresponding author.
E-mail address: baerns@aca-berlin.de (M. Baerns).

[1] On temporary leave from Institut Français du Pétrole.

1385-8947/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1385-8947(02)00005-0

[9]; SYMYX [10] and ACA, Berlin [11,12]. An overview of the actual development can be found in [13]. Generally, gas chromatography or mass spectroscopy are used as analytical method. An alternative has been described by Senkan [14], where activity and selectivity are determined by spatially resolved resonance enhanced multi-photon ionisation (REMPI). This method was successfully applied, e.g. to the dehydrogenation of cyclohexane to benzene.

In the present work, our experimental set-ups are described which have been used for synthesis and parallel testing of heterogeneous catalysts for the oxidative dehydrogenation of propane (ODP) and ethane. Using a robot, various libraries of α-Al_2O_3-supported multi-metal-oxide catalytic materials were prepared by impregnation. Catalytic testing was carried out under different reaction conditions in a 64-channel fixed-bed reactor module coupled with an efficient fast online analysis; a data acquisition system was used to collect and evaluate the experimental data.

2. Equipment

2.1. Robotic preparation of catalytic material

Preparation of catalytic material was performed on a PC-controlled robot (Zinsser Sophas Kat, Zinsser Analytic GmbH, Frankfurt, Germany). This machine comprises an automated workbench including three shakable platforms (vortexers) for racks containing preparation vials (12, 24, 48 or 96) and a robotic arm movable in *x*, *y*, *z*-direction. Attached to the arm are four needles for adding liquid solutions of metal salts, a pipetting device for dispensing granulated materials, and a robotic handler for moving the racks.

On the vortexers which are independently controlled the racks can be shaken up to 1800 rpm and simultaneously heated up to 150 °C. The addition of liquids to the vials can be performed during shaking. Additionally, for filtering of precipitates and their washing a vacuum block can be used.

The synthesis robot is controlled by a proprietary software (SOPHAS from Zinsser Analytical GmbH). An in-house written software is used to transform catalyst data, i.e. as compositions and preparation modes into the corresponding synthesis data, e.g. required volumes of solutions and order of dosing. These data are then easily imported into the SOPHAS software to control the robot.

For illustration, the synthesis of α-Al_2O_3-supported multi-metal-oxide catalysts (20% active component), which were applied in the oxidative dehydrogenation of light alkanes, is described. Sixty-membered libraries for ODP and oxidative dehydrogenation of ethane (ODE) were prepared by sequential wet-impregnation of the support with aqueous precursor solutions. Ag, Ca, Co, Cr, Cu, Fe, Ga, La, Mg, Mn, Ni and Zr can be added as solutions of the nitrates, which generally have a high solubility in water and decompose under the conditions of calcination, whereas B, Mo, P and W may be added as H_3BO_3, H_2MoO_4, $(NH_4)_2HPO_4$, $(NH_4)_6W_{12}O_{41}\cdot 6\ H_2O$. V_2O_5 and Sb_2O_3 after being dissolved in oxalic acid or tartaric acid, respectively.

The following steps were applied during the sequential wet-impregnation process:

1. Approximately 1 g of α-Al_2O_3 (CONDEA, $d = 1$ mm, $S_{BET} = 23\ m^2/g$) applied as support material was filled automatically into each of the 24 PTFE tubes (6 ml of volume) contained in one synthesis rack. Three racks can be used in parallel for one synthesis run.
2. Individual precursor solutions of up to 1 ml were added subsequently to the support. If the total required volume of one individual precursor solution was, e.g. 8.5 ml then eight injections of 1 ml and one injection of the last 0.5 ml diluted with 0.5 ml distilled water were applied.
3. After each addition of 1 ml of precursor solution, the samples were dried on the robotic machine at 100 °C while shaking.
4. Steps 2 and 3 were repeated until all precursor solutions had been added.
5. After drying, the catalytic materials were transferred manually into crucibles and then calcined in an oven at 500 °C.

Using this synthesis method no precipitates, which were not attached to the support, were formed during the preparation process. Large volumes of precursor solutions can be added in several steps so that the volume of the reaction tubes (6 ml) is not exceeded (see also above). Using small volumes allows faster shaking required for keeping the support in motion so that homogeneity of the catalytic material is achieved. For illustration, the catalytic performance of materials in the ODP reaction either prepared by manual or robotic synthesis could be reproduced in the frame of the usual experimental accuracy as shown in Table 1. The impregnation method has also been applied for the preparation of catalytic materials for the ODE. In this case α-Al_2O_3 with a particle size of 250–355 μm and a BET surface of $5\ m^2/g$ has been used as support material. The active mass of the catalytic materials amounted to 20 wt.%. After drying, the samples were calcined at 350 °C for 12 h in air.

Table 1
Comparison of the catalytic performance in the ODP reaction of materials prepared by manual and robotic synthesis (testing conditions: $T = 500\,^{\circ}C$, $m_{cat} = 100$ mg, $\tau = 0.12\ g\,s\,ml^{-1}$)[a]

Catalyst	Preparation	$X_{propane}$ (%)	$S_{propene}$ (%)	$Y_{propene}$ (%)
$W_{0.27}Mn_{0.13}Mo_{0.32}Fe_{0.27}$	Manual	5.6	49.1	2.8
	Robotic	6.1	46.2	2.8
$W_{0.24}Mn_{0.54}Ag_{0.13}Fe_{0.1}$	Manual	9.4	39.1	3.7
	Robotic	8.6	42.9	3.7

[a] Experimental error is estimated to be about 10%.

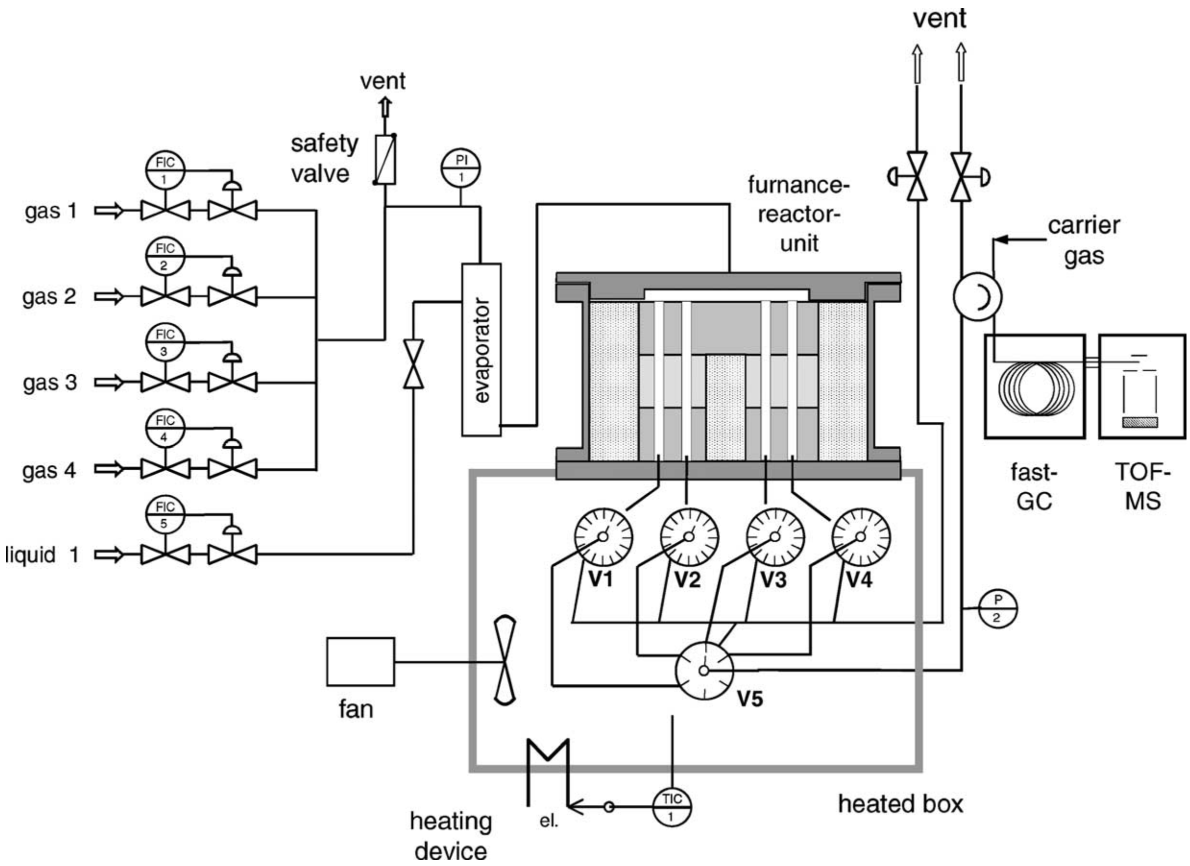

Fig. 1. Flow sheet of the overall experimental set-up.

2.2. Catalytic testing in a 64 multi-channel reactor module

2.2.1. Reactor description

The in-house built ceramic multi-channel reactor module for testing catalytic material enables to ascertain catalytic testing conditions similar to those in micro fixed-bed reactors. However, the testing in the multi-channel reactor was significantly accelerated, i.e. by a factor of approximately 30–50 as compared to conventional procedures (i.e. one catalyst at a time). The reactor module has been used for various reactions such as the oxidative dehydrogenation of light alkanes, the oxygenation of hydrocarbons and the $DeNO_x$ reaction.

The total 64-channel reactor system is shown in Figs. 1–3. The set-up consists of three cylindrical ceramic modules ($\varnothing = 140$, $h = 40$ mm) with 64 channels ($\varnothing_{ID} = 5$ mm) used as fixed-bed reactors, which are concentrically arranged with respect to the axis of the module. The catalyst bed is situated in the central module. The upper ceramic module contains a bed of fine quartz powder in each channel serving as pressure drop device (see below). Either narrow-meshed stainless steel grids or ceramic frits are used as support for the quartz layer and the catalytic bed. Polished planes accomplish the sealing between the different modules.

All three ceramic modules are enclosed in a stainless steel cylinder sealed with O-rings to avoid any gas leakage. A silicon or graphite sealing that is bakable up to 250 or 600 °C seals the lower ceramic module towards the reactor outlets.

The central module containing the catalytic bed is made of Al_2O_3 to insure relatively good heat conduction as compared to the two low heat-conducting cordierite modules serving as heat insulators towards the sealings. To ensure isothermicity of the reaction zones in the ring-shaped central ceramic module, heating is provided by an inner and an outer electrical heating element of rotational symmetry. Axial and radial temperature profiles are controlled by thermocouples placed in each concentric ring of the reactor channels and it has been shown that the radial differences do not exceed 5 K.

Following a common practice, equal flow rates in each channel are obtained by equally sized layers of fine quartz powder ($\varnothing = 10$ μm) located in the upper cordierite module establishing an equal pressure drop in each channel (flow restrictor). The gas flow through all channels is controlled before and after parallel catalytic testing by measuring the flow of an inert gas through each channel using a mass-flow meter. The flow rates shown in Fig. 4 differ only slightly.

For sampling the reactor-channel effluent the outlets are connected individually to a set of multi-port valves (4 × 16 port and 1 × 6 port valves, bakable, Valco Instruments, see Fig. 1) which allow fast switching between the different

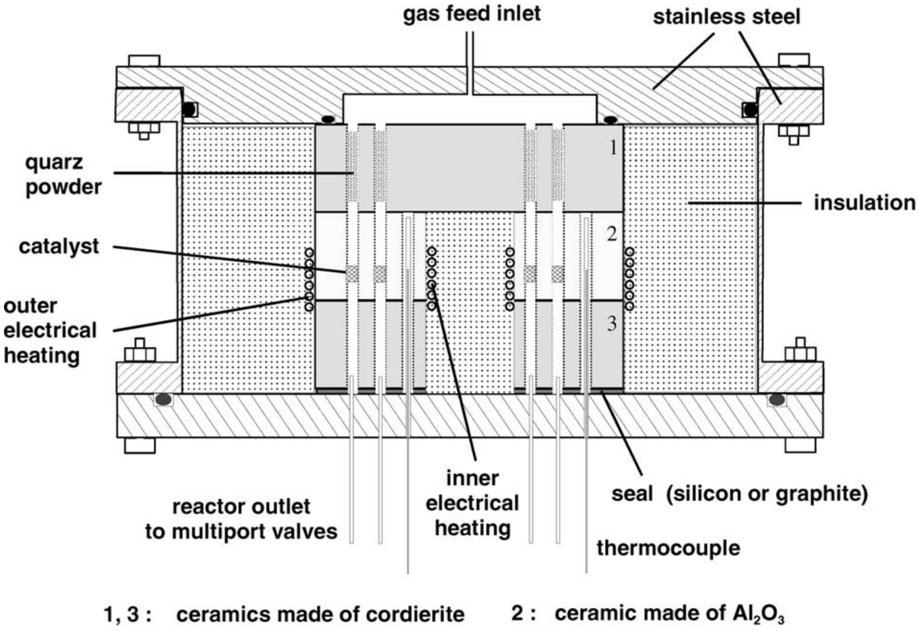

Fig. 2. Scheme of the 64-channel reactor module.

reactor channels for sequential analysis of the reaction products without interruption of the gas flow. To avoid condensation, polymerisation or thermal decomposition of products a strict temperature control of the output piping and the multi-port valves is required; therefore they are installed in a heated box underneath the stainless steel cylinder. The output piping is made of SiO_2-passivated tubing (inner $\varnothing = 1$ mm, Silco Steel) to exclude any consecutive reactions.

The different feed gases and one liquid are supplied by mass-flow controllers (Bronkhorst). The mixing of liquid and gases occurs in an evaporator. To avoid steam condensation in the feeding lines the tubing between evaporator and reactor module is heated.

By ascertaining close isothermicity and nearly equal flow rates in each channel of the reactor module the device is suited for comparing the performance of different catalytic materials charged to the individual channels. The reactor set-up can be operated at pressures up to 3 bar and temperatures up to 550 °C. Each reactor channel was filled with 50–200 mg of catalytic material. All reactor channels are permanently on-stream; in this way also activation or deactivation of the catalytic materials may be observed by multiple screening of the reactor channels.

2.2.2. Product analysis

Often in high-throughput screening of catalyst libraries only the activity for a specific reaction by means of the

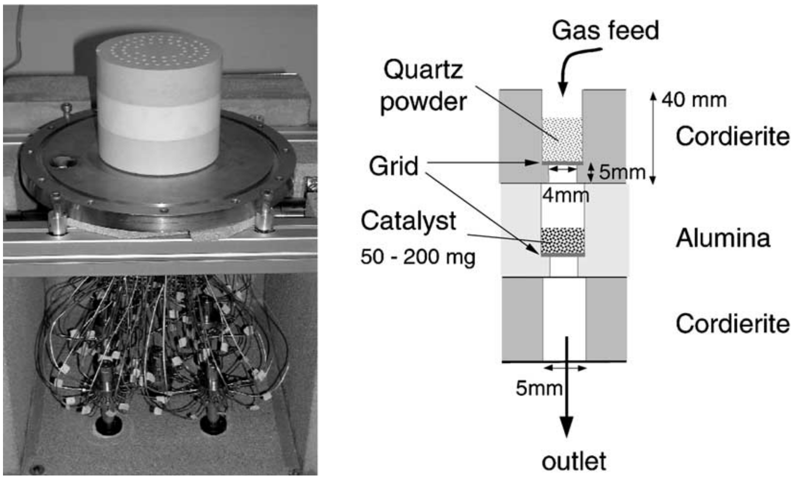

Fig. 3. Details of the high-throughput testing equipment: (a) view on the 64-channel reactor module consisting of three ceramic blocks and five multi-port valves; (b) sketch of one reactor channel comprising the catalytic bed and the layer of quartz powder to generate a defined pressure drop.

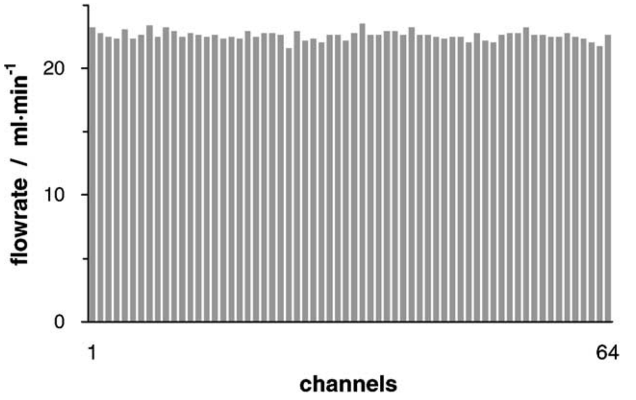

Fig. 4. Flow rates in the 64 reaction channels (argon, $F = 22.3 \pm 1.7\,\mathrm{ml\,min^{-1}}$).

degree of conversion or the reaction heat released is determined [7]. For selectivity frequently only the main products of interest are quantified [4,14]. Usual analysis techniques, such as gas chromatography or MS, which are often applied for product detection in the oxidative dehydrogenation of light alkanes, show some drawbacks if applied in high-throughput experimentation. Gas chromatography allows a selective and sensible detection of all products; however, the time for separation of all compounds ranging from 4 to 15 min for one analysis is generally considered to be too long. Complete analysis by MS is often restricted due to superposition of fragment signals.

For the oxidative dehydrogenation of light alkanes a fast and complete qualitative and quantitative analysis of the effluent gas of each reactor channel was accomplished by a combination of a fast GC (HP6890, Agilent Technologies) and a time-of-flight (TOF) mass spectrometer as detector (Pegasus II, LECO). Results are shown in Fig. 5 for the oxidative dehydrogenation reaction of propane.

Due to a high linear carrier gas velocity in the GC-column ($l = 25\,\mathrm{m}$, $\varnothing = 0.2\,\mathrm{mm}$, $v = 68\,\mathrm{cm/s}$) a fast primary separation of the products is obtained by lumping several components in one peak. Subsequently, the peaks (approximate width <0.5 s) are deconvoluted by MS detection. The required high scanning rates (up to 200 scans/s) are only achieved by a TOF-MS. A GC-base-line separation is not required because of the mass-selective detection of the products. Mass superposition in MS is avoided by suitable primary GC separation of the compounds (see Fig. 5). A complete separation of all compounds, i.e. feed reactants and products from ODP, is achieved in less than 50 s.

The above-described fast analysis set-up for high-throughput screening is also suitable for other types of reactions such as DeNO_x.

2.2.3. Reproducibility

The reproducibility and reliability of testing catalytic materials in the 64-channel reactor set-up are illustrated for ODP. Different catalytic materials and the pure α-$\mathrm{Al_2O_3}$ support were tested in parallel. Additionally, some of the channels were left empty and the same catalyst material was charged to nine different channels. The testing results were compared to the corresponding results from a conventional single tubular reactor under the same experimental conditions (500 °C, $\tau = 0.12\,\mathrm{g\,s\,ml^{-1}}$); the results are shown in Fig. 6.

2.3. Automation and data handling

The above-described experimental equipment is PC-controlled for automatic testing of catalytic materials.

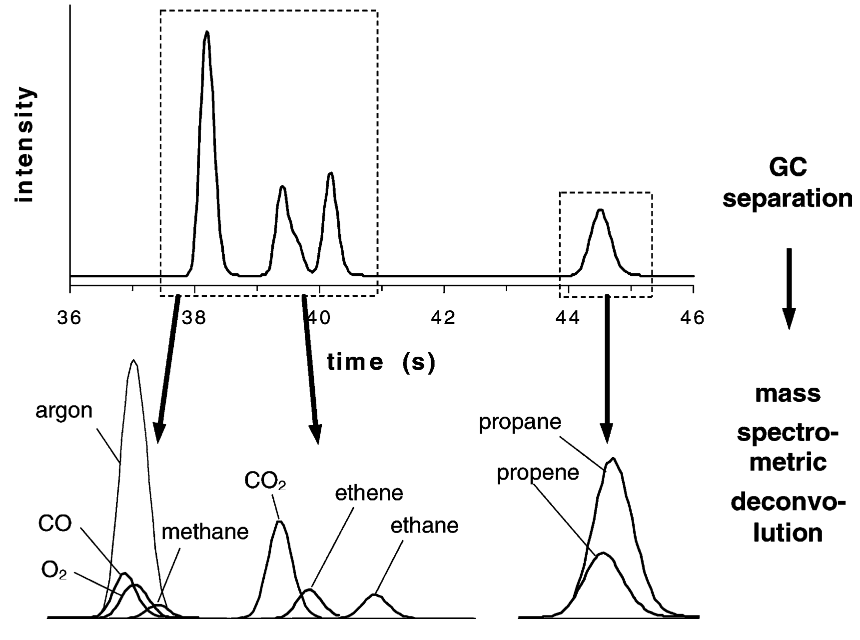

Fig. 5. Example for the separation of the reactor effluent of the ODP by a fast GC using a TOF-MS detector.

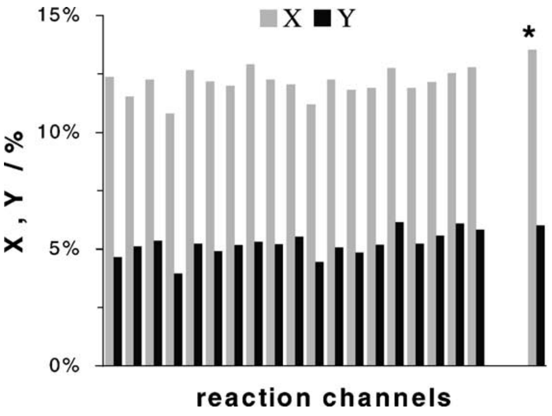

Fig. 6. Catalytic results for the ODP for the same catalytic material in different channels of the 64-channel reactor module and from a conventional single tubular reactor (∗) (500 °C, $m_{cat} = 100\,mg$, $\tau = 0.12\,g\,s\,ml^{-1}$).

By a customer-designed software (AMTEC, Chemnitz, Germany) reaction parameters (temperatures, gas feed, etc.) are controlled, the multi-port valves are coordinated to select the reactor channel for analysis and finally the injection of product gas into the GC/TOF-MS system and data acquisition and data processing are controlled. From the feed- and effluent-gas composition the degree of conversion and the yield as well as the selectivity for each of the reaction products are derived for each material.

The data of composition and preparation of materials and their characterisation as well as the catalytic testing results and the respective conditions are stored in an in-house designed database. This database is used partly as a basis for the optimisation of materials for enhanced catalytic properties by applying a genetic algorithm [11] and for deriving relationships between catalytic performance and material properties by applying neural networks. Moreover, it is planned to extract knowledge from the database leading to structure–activity relationships that will then be used for further catalyst optimisation.

3. Catalytic results

Results for the ODP reaction have been already presented elsewhere [15]. In this paper, results obtained for

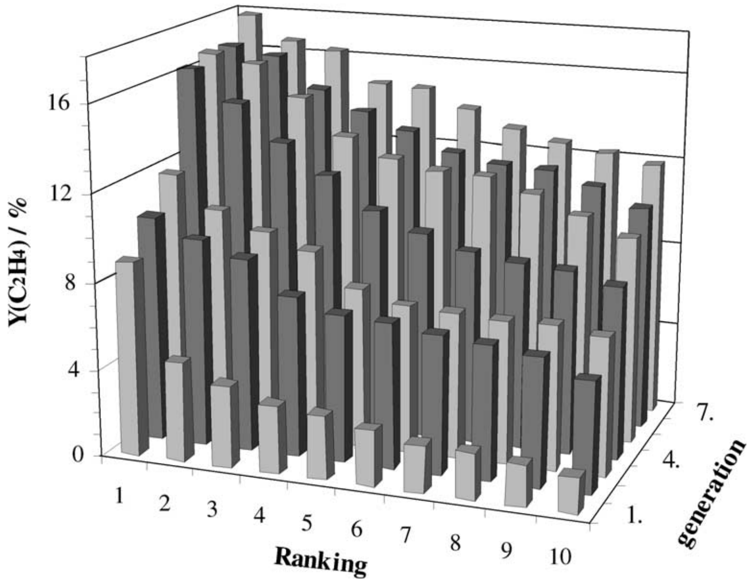

Fig. 7. Development of the ethylene yield with proceeding generations for the best 10 materials after each generation, obtained under standard conditions ($T = 773\,K$, $C_2H_6/O_2/Ar = 20/10/70$, $\tau = 0.4\,g\,s\,ml^{-1}$).

Table 2
Catalytic results for the ODE reaction: composition and performance of the seven best materials of the seventh generation, obtained under standard conditions ($T = 773\,K$, $C_2H_6/O_2/Ar = 20/10/70$, $\tau = 0.4\,g\,s\,ml^{-1}$)

Rank	Composition	X (C_2H_6) (%)	X (O_2) (%)	S (C_2H_4) (%)	S (CO_2) (%)	S (CO) (%)	Y (C_2H_4) (%)
1	$Co_{0.280}Cr_{0.398}Sn_{0.158}W_{0.164}O_y$	28	82	63	27	11	18
2	$Cr_{0.710}Mo_{0.290}O_y$	24	48	69	4	27	17
3	$Co_{0.350}Cr_{0.249}Sn_{0.197}W_{0.205}O_y$	26	39	63	27	10	16
4	$Mn_{0.467}P_{0.533}O_y$	37	73	40	39	21	15
5	$Au_{0.023}Cr_{0.693}Mo_{0.284}O_y$	25	55	59	9	26	15
6	$Cr_{0.448}Mn_{0.130}Mo_{0.422}O_y$	27	75	52	24	22	14
7	$Au_{0.074}Cr_{0.657}Mo_{0.269}O_y$	19	24	69	11	20	13

the ODE reaction are shown for illustration. The aim of the ODE study was the discovery of new materials showing high ethylene yields at low temperatures (<823 K) using an evolutionary strategy described previously [11]. Since V-containing metal-oxides are already well known as good performing redox-catalysts in the given temperature range [16–18], we excluded vanadium in the starting pool of primary elements. The following elements were selected: Cr, P, Sn, Ga, Co, Ca, W, Mn, Cu, Mo, Zr, La and Au (in trace amounts). Seven generations each of 60 catalytic materials were prepared and tested.

The principal method of preparation and some generic conditions for the 420 materials were already described above. The testing conditions for the ODE reaction are the following ones: ambient pressure, for avoiding ignition of the reaction mixture on the catalyst surface the feed was diluted with argon ($C_2H_6/O_2/Ar = 20/10/70$), reaction temperature was varied between 673 and 773 K and contact time between 0.1 and $1\,g\,s\,ml^{-1}$; standard conditions were defined as $T = 773$ K and $\tau = 0.4\,g\,s\,ml^{-1}$.

The ethylene yields of the best 10 materials of each generation, obtained under standard reaction conditions, are presented in Fig. 7. As a result of the evolutionary procedure a continuous improvement of the catalytic performance from the first to the seventh generation was found. The best ethylene yield in each generation measured under standard conditions increased from 9% in the first to 18% in the seventh generation. The composition and the catalytic performance of the best seven materials of the seventh generation are given in Table 2. The best performing materials can be divided into two types: one containing mainly Co, Cr, W and Sn and the other containing mainly Cr and Mo. These compositions result, under the applied conditions, in ethylene yields comparable to a vanadium-containing material (V–Nb–Mo) used in this work as a standard. Although optimisation has not yet converged it is obvious that the high-throughput experimentation techniques outlined above, combined with an evolutionary strategy, resulted in new catalytic compositions for the ODE reaction. Up to the authors' knowledge these compositions have not been reported before as active materials for the ODE reaction at low temperatures (<823 K).

4. Conclusions

By parallelisation of the preparation of catalytic materials the required synthesis time was approximately reduced to about 10% of the time requirement in consecutive manual preparation. The 64-channel reactor set-up including the fast analysis of the reactor effluent for parallel testing of catalytic materials has become an essential part in high-throughput screening. For oxidative alkane dehydrogenation testing time could be reduced to 20% of the time needed in consecutive single testing experiments. The success in applying the described high-throughput equipment was demonstrated by discovering a new class of catalytic materials for the ODE at temperatures <773 K.

Acknowledgements

This work has been supported by different funding agencies: German Federal Ministry for Education and Research, Federal State of Berlin, European Commission and Fonds der Chemischen Industrie.

References

[1] D. Xiang, X. Sun, G. Briceno, Y. Lou, K.-A. Wang, H. Chang, W.G. Wallace-Freedman, S.-W. Chen, P.G. Schultz, Science 268 (1995) 1738.
[2] G. Briceno, H. Chang, X. Sun, P.G. Schultz, X.-D. Xiang, Science 270 (1995) 273.
[3] E. Danielson, J.H. Golden, E. McFarland, C.M. Reaves, W.H. Weinberg, X.D. Wu, Nature 389 (1997) 944.
[4] W.H. Weinberg, B. Jandeleit, K. Self, H. Turner, Curr. Opin. Sol. State Mater. Sci. 3 (1998) 104.
[5] P. Cong, R.D. Doole, Q. Fan, D.M. Gianquinta, S. Guan, E.W. McFarland, D.M. Poojary, K. Self, H.W. Turner, W.H. Weinberg, Angew. Chem. 111 (1999) 507.
[6] M. Orschel, J. Klein, H.-W. Schmidt, W.F. Maier, Angew. Chem. Int. Ed. 38 (1999) 2791.
[7] A. Holzwarth, H.-W. Schmidt, W.F. Maier, Angew. Chem. Int. Ed. 37 (1998) 2644.
[8] J. Perez-Ramirez, R. Berger, G. Mul, F. Kapteijn, J. Moulijn, Catal. Today 60 (2000) 93.
[9] C. Hoffman, A. Wolf, F. Schüth, Angew. Chem. Int. Ed. 38 (1999) 2800.
[10] P. Cong, A. Dehestani, R. Doolen, D. Giaquinta, S. Guan, V. Markov, D. Poojary, K. Self, H. Turner, W. Weinberg, Proc. Natl. Acad. Sci. USA 96 (1999) 11077.
[11] D. Wolf, O.V. Buyevskaya, M. Baerns, Appl. Catal. 200 (2000) 63.
[12] U. Rodemerck, P. Ignaszewski, M. Lucas, P. Claus, M. Baerns, Top. Catal. 13 (2000) 249.
[13] S. Senkan, Angew. Chem. 113 (2001) 322.
[14] S.M. Senkan, Nature 394 (1998) 350.
[15] O.V. Buyevskaya, A. Brückner, E.V. Kondratenko, D. Wolf, M. Baerns, Catal. Today 67 (2001) 369.
[16] E.M. Thorsteinson, T.P. Wilson, F.G. Young, P.H. Kasai, J. Catal. 52 (1978) 11.
[17] F. Cavani, M. Kotyrev, F. Trifiro, Catal. Today 28 (1996) 319.
[18] L. Ji, J. Liu, Chem. Commun. (1996) 1203.