S. Moehmel, N. Steinfeldt, S. Engelschalt, M. Holena, S. Kolf, M. Baerns,
U. Dingerdissen, D. Wolf, R. Weber, M. Bewersdorf

New catalytic materials for the high-temperature synthesis of hydrocyanic acid from methane and ammonia by high-throughput approach

S. Moehmel [a], N. Steinfeldt [a,*], S. Engelschalt [a], M. Holena [a], S. Kolf [a],
M. Baerns [a,c], U. Dingerdissen [a], D. Wolf [b], R. Weber [b], M. Bewersdorf [b]

[a] *Leibniz-Institute for Catalysis at the University of Rostock, Branch Berlin, Richard-Willstaetter-Street 12, D-12489 Berlin, Germany*
[b] *DEGUSSA, Rodenbacher Chaussee 4, D-63457 Hanau-Wolfgang, Germany*
[c] *Fritz-Haber-Institute of MPG, Dept. Inorg. Chem., Faradayweg 4-6, D-14195 Berlin, Germany*

Abstract

For converting methane and ammonia to hydrocyanic acid, catalysts were prepared and tested in a 48-parallel channel fixed-bed reactor unit operating at temperatures up to 1373 K. The catalysts were synthesized with a robot applying a genetic algorithm as the design tool. New and improved catalyst compositions were discovered by using a total of seven generations each consisting of 92 potential catalysts. Thereby, the catalyst support turned out as an important input variable. Furthermore, platinum, which is well known as a catalytic material was confirmed. Moreover, improvements in HCN yield were achieved by addition of promoters like Ir, Au, Ni, Mo, Zn and Re. Multi-way analysis of variance and regression trees were applied to establish correlations between HCN yield and catalyst composition (support and metal additives). The obtained results are considered as the base for future even more efficient screening experiments.
© 2007 Elsevier B.V. All rights reserved.

Keywords: High-throughput experimentation; Evolutionary catalyst development; Genetic algorithm; Hydrocyanic acid; High-temperature equipment; Multi-way analysis of variance; Regression trees

1. Introduction

Combinatorial methods are increasingly used for the development of heterogeneous catalysts [1–4]. Besides an efficient design of the experiments, e.g., by a genetic algorithm [5], a high-throughput mode of synthesis and catalytic testing of the desired materials is necessary for an economic and successful search for new and improved catalysts. Several different reactor systems were described in literature for high-throughput experimentation [6–8] so far; none of them was, however, dedicated to high-temperature catalytic reactions carried out up to 1373 K. This has to be ascribed to the difficulties associated with achieving a homogeneous temperature distribution over the parallel reactors at such high temperatures. Further challenges, which have to be overcome at these temperatures, are choosing the appropriate material for

the reactor, which has to be inert under the applied conditions, and its specific design. Moreover, the connections of the single channels with the feed-gas manifold and with the analytical equipment needed specific solutions.

A high-temperature process applied in industry is the formation of hydrocyanic acid (HCN) from methane and ammonia. It is realized in two variants, i.e., the oxygen-assisted auto thermal Andrussow process [9] and the BMA process [10]. The oxygen free conversion of ammonia and methane to hydrocyanic acid (BMA process) is an extremely endothermic process typically runs at temperatures between 1273 and 1573 K in ceramic tubes with a platinum-containing catalytic layer on the inner walls [10]. Besides other materials like Al_3N_4, BN_3, TiN_3 and Si_3N_4 predominantly Al_2O_3 is chosen as catalyst support [11]. The following two main reactions dominate the conversion of the reactants:

$$CH_4 + NH_3 \rightarrow HCN + 3H_2 \tag{1}$$

$$2NH_3 \rightarrow N_2 + 3H_2 \tag{2}$$

As a by-product N_2 (reaction (2)) is formed by decomposition of ammonia, which limits the yield of the desired HCN formation (reaction (1)). The mechanistic picture of the catalytic process is still incomplete. So far, it is assumed that the main reaction pathway of the HCN formation occurs via reaction of adsorbed CH_x and NH_x species [12,13]. Identified intermediates are CH_3N_2 or CH_2NH [12,14], which rapidly dehydrogenate to HCN at the applied reaction temperature. Additionally, the possibility of a C–N coupling reaction between atomic C_{ads} and N_{ads} species on Pt (1 1 1) surfaces was discussed [15]. Results of temporal analysis of products (TAP) studies propose that the decomposition of ammonia is the rate-determining step for the formation of HCN on Pt-catalysts [16].

The aim of the presented work was to demonstrate that the application of high-throughput experimentation in materials synthesis and catalyst testing in combination with an effective design tool lead to new or improved catalytic materials even for high-temperature reactions ($T = 1373$ K), such as the BMA process. Furthermore, the influence of the catalyst composition (i.e., support and active element) on the obtained HCN yield was investigated applying data analysis methods. For a qualitative assessment of the most significant influence of catalyst composition on the HCN yield, the analysis of variance was used. For a quantitative approximation of the dependence of HCN yield on the support and on the fractions of the individual active elements, regression trees were applied.

2. Experimental

2.1. Design of the test unit

The flow sheet of the testing unit consisting of parallel reactor tubes is shown in Fig. 1. The volumetric flow rates of ammonia, methane and argon, the latter is being used as an inert diluent, are controlled by digital mass-flow meters. For ensuring an equal distribution of the flow rates through the reactor tubes, the gas mixture passes through a gas distributor with individual pressure-drop devices for each channel.

The oven with the 48 fixed-bed reactors (ID = 5 mm, $L = 200$ mm) is designed in a symmetric and circular manner to enable reaction temperatures up to 1373 K with only small temperature deviations ($\pm 2\%$). A circular heating chamber (Fig. 2), 20 mm wide and 30 mm high, contains two separately controlled heating resistors, which were placed at the inner and outer side of the ceramic rings, respectively. Alumina was used as reactor material, ensuring sufficient inertness, gas tightness and thermal stability as well as relatively good heat conductivity. For each reactor a small alumina tube was fitted into a bigger one. The catalytic material was then placed on a sieve lying on the resulting step in the tubes (see Fig. 3). The connection between the single reactor outlets and the on-line analysis of the reactor effluent was realized by means of four multi-port-valves.
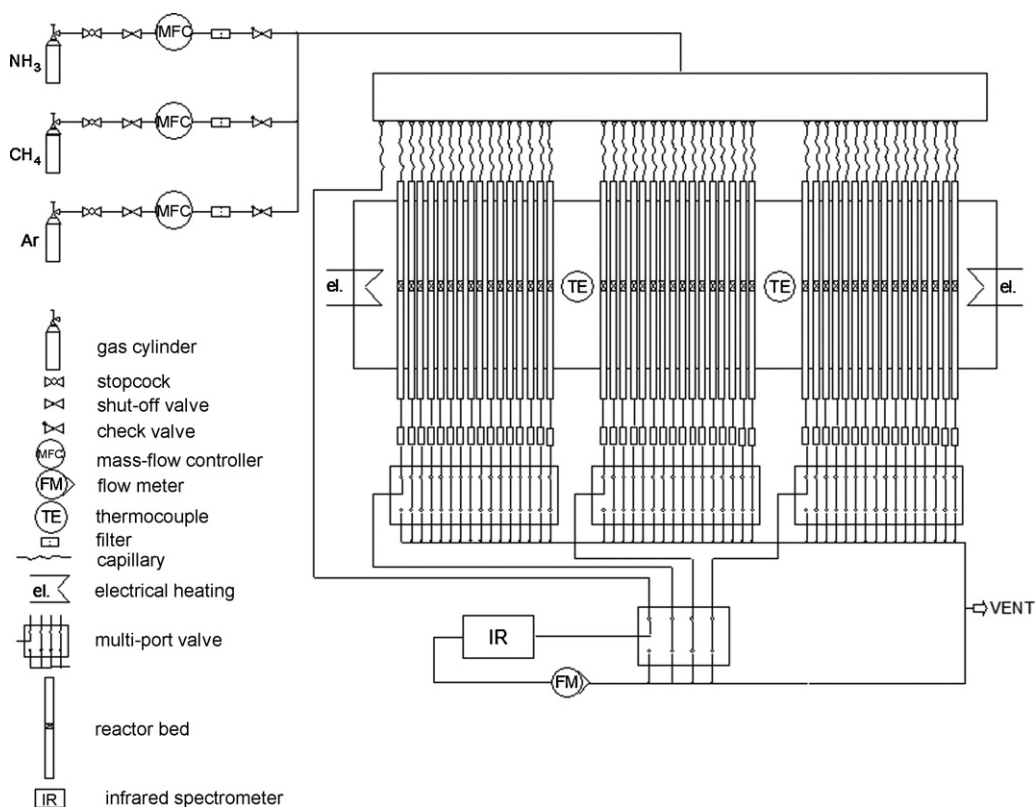

Fig. 1. Scheme of the equipment comprising the 48-channel reactor and auxiliary equipment.
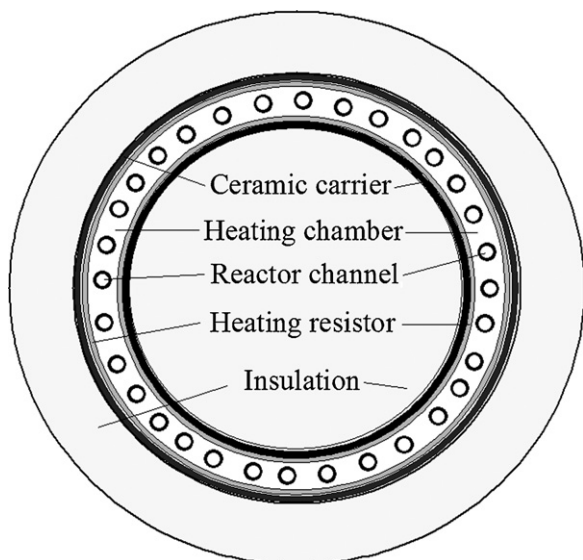
Fig. 2. Illustration of the heating system for the 48-channel reactor.

2.2. Analytics

The quantitative analysis of the effluent gas from the reactor was accomplished by on-line IR spectroscopy using a multi-component process photometer MCS 100 UV/(N)IR (Fa. Sick/Maihak). IR absorption of the single compound was measured at a certain wavelength where its IR absorption is not influenced by the IR absorption of the other compounds (NH_3, 6150 nm; CH_4, 7700 nm and HCN, 6970 nm) and at a wavelength where no IR absorption takes place (reference wavelength for all

compounds: 5250 nm). The evaluation of the IR absorption with the internal hard and software gives a signal linear to its concentration. After a final calibration the concentrations of the corresponding compounds are calculated directly from the software of the IR photometer. With this method the NH_3 and CH_4 concentrations were obtained directly. Due to the lack of an exact calibration standard for HCN, it was not possible to determine the absolute concentration of HCN by means of the IR analyzer. Therefore, HCN concentration in the effluent gas was calculated from the carbon balance by taking the difference of the CH_4 concentration at the inlet and outlet of the reactor and assuming that all converted CH_4 is consumed for HCN formation. The amount of coke deposited on the reactor wall was generally low. Conversion of NH_3 and CH_4 (1) as well as the yield of HCN ((2), always related to NH_3) were calculated using the following equations (indices: $i = CH_4$, NH_3; I, inlet; E, exit):

$$X_i = 1 - \frac{\dot{n}_i^E}{\dot{n}_i^I} \tag{1}$$

$$Y_{HCN/N} = \frac{\dot{n}_{CH_4}^I - \dot{n}_{CH_4}^E}{\dot{n}_{iNH_3}^I} \tag{2}$$

In order to evaluate whether CH_4 is converted to other products (e.g., acetylene) the correlation between the calculated HCN yield and the IR intensity for HCN was checked for all experiments. A typical plot is shown in Fig. 4. It can be seen that the calculated HCN/N yield correlates linearly with the IR intensity for HCN determined with the IR analyzer. This result is also supported by additional experiments using IR and GC analytics in parallel, where at the time on stream used for the high-throughput experimentation (about 10 h), other hydrocarbons beside HCN were detected only in minor amounts.
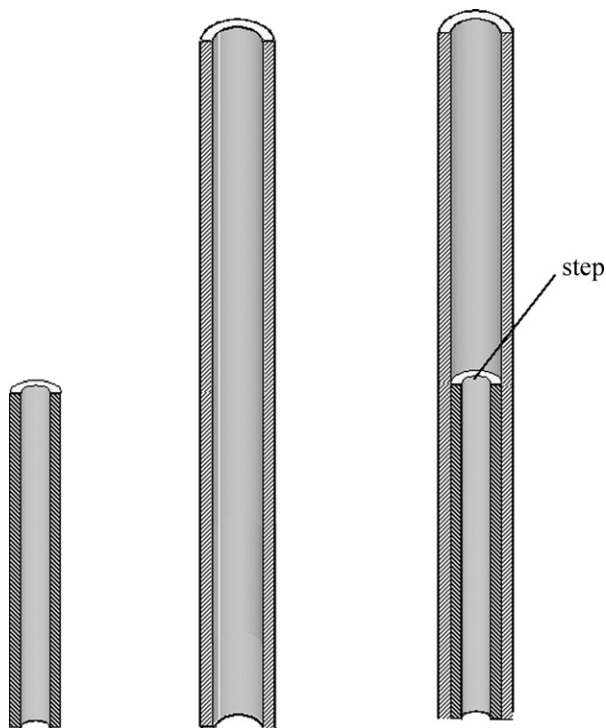

Fig. 3. Illustration of the assembly of reactor tubes used in the 48-channel reactor.
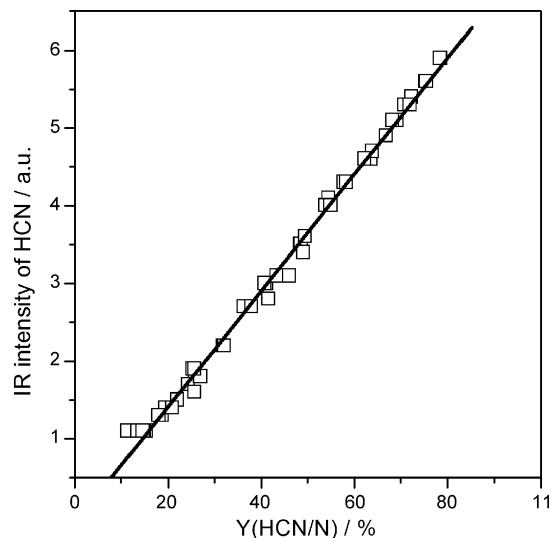

Fig. 4. Correlation between the HCN/N yield (calculated) and the IR intensity for HCN in the effluent gas measured for a single experiment with 46 catalysts, $T = 1373$ K, $NH_3 = 10.7$ vol.%, $CH_4 = 9.3$ vol.%, rest Ar, $\dot{Q}$ (reactor) = 10 ml/min, $m_{cat} = 50$ mg).

Table 1
BET surface areas (S_{BET}), Pt loadings (wt.%) and apparent surface densities of Pt (D_{Pt}) for the different materials

No.	Support	S_{BET} (m^2/g)	Pt (wt.%)	D_{Pt} (Pt/nm^2)	Pt (wt.%)	D_{Pt} (Pt/nm^2)	Pt (wt.%)	D_{Pt} (Pt/nm^2)
1	AlN	n.d.						
2	Alsint	0.7	0.02	1	0.22	10	2.2	100
3	BN	0.2	0.006	1	0.06	10	0.6	100
4	CaO	0.3	0.01	1	0.10	10	1.0	100
5	MgO	2.7	0.08	1	0.80	10	8.1	100
6	Mo$_2$C	n.d.						
7	Nb$_2$O$_3$	0.16	0.005	1	0.05	10	0.5	100
8	Si$_3$N$_4$	0.7	0.02	1	0.22	10	2.2	100
9	SiC	1	0.03	1	0.32	10	3.1	100
10	Sm$_2$O$_3$	0.2	0.006	1	0.06	10	0.6	100
11	SrO	0.1	0.003	1	0.03	10	0.3	100
12	TiB$_2$	0.7	0.02	1	0.22	10	2.2	100
13	TiN	n.d						
14	TiO$_2$	0.15	0.005	1	0.05	10	0.5	100
15	ZrO$_2$	0.3	0.01	1	0.10	10	1.0	100

n.d., not determined.

2.3. Catalyst preparation

Due to the small reactor diameter (ID = 5 mm) radial temperature gradients are lower than radial temperature gradients in the ceramics tubes used in industry. In contrast to the commercially applied coated wall catalyst supported catalyst pellets with an average diameter of 100–250 μm, which could be considered isothermal, were used.

Besides pure alpha-Al$_2$O$_3$ (alsint) 11 different materials, i.e., thermally stable compounds of predominantly basic character (CaO, MgO, Nb$_2$O$_3$, SrO, ZrO$_2$, TiO$_2$, Sm$_2$O$_3$, SiC, Si$_3$N$_4$, TiB$_2$, BN) bound in an alumina matrix were tested as supports. These supports were synthesized by mixing the oxide powders (particle size ≪ 100 μm) with alsint and polyvinyl alcohol as a binder and subsequent calcination at 1100 °C. The BET surface areas of these supports – determined with Krypton – are listed in Table 1. The BET surface of the different supports was generally lower than 1 m^2/g (exception: MgO and SiC).

Before applying the genetic algorithm, experiments were carried out with different supports and amounts of Pt in order to find out the metal loading that reflects the catalytic performance of the reference catalyst prepared from alumina and Pt according to Ref. [17]. For the alsint support, three Pt containing samples were prepared with a Pt loading of 0.02, 0.22 and 2.2 wt.%. In order to achieve a comparable apparent surface density of platinum (Pt atoms/nm^2) for the different supports, the weight of the metal loading of the alsint samples (0.02, 0.22 and 2.2 wt.%) was multiplied with the ratio of the BET surface of the corresponding support and the BET surface of alsint. Table 1 summarizes the Pt loading and the apparent surface density of Pt for the catalytic material studied. From the comparison of the catalytic performance of these Pt catalysts with those of the reference catalyst a total amount of 2.2 wt.% metal additives was selected for the genetic algorithm.

For high-throughput preparation of the catalysts a synthesis robot (ZINSSER SOPHAS) was used: 1 ml of an aqueous solution of one compound (ReCl$_3$, IrCl$_4$, NiCl$_2$, H$_2$PtCl$_6$, HAuCl$_4$, AgNO$_3$, Y(NO$_3$)$_3$, La(NO$_3$)$_3$, Zn(NO$_3$)$_2$, ZrO(NO$_3$)$_2$ and H$_2$MoO$_4$; c_{max} = 1 mol/l) was given to 300 mg of the

supports while shaking at 600 rpm. The liquid was then evaporated at 373 K within 30 min during the reaction mixtures were shaken. After drying, the next compound was added. Finally, the catalyst precursor was reduced with 1 ml of 0.1 M hydrazinium hydroxide solution; after 30 min the excess solution was removed before drying at 120 °C for 2 h. Then, 0.05 g of each sample was filled in a reactor tube.

2.4. Reaction conditions

The inlet composition of the feed gas amounted to 10.7 vol.% ammonia, 9.3 vol.% methane and 80 vol.% argon. The total volumetric flow rate for the 48 reactor tubes was 480 ml/min. In comparison to methane an excess of ammonia was used in order to minimize the formation of carbon species on the catalyst surface and the alumina tube, similarly to production level. The catalyst was initially heated in an ammonia/argon mixture up to 1373 K with a heating rate of 6° min^{-1}. After having attained the temperature of 1373 K methane was added stepwise to the feed until its concentration amounted to 9.3 vol.%. The catalytic performance was then measured between 1173 and 1373 K. In general testing, one reactor tube was charged with the reference catalyst and one reactor tube contained a thermocouple in order to control the temperature of the oven.

3. Methodology

3.1. Genetic algorithm (GA)

In the evolutionary approach 12 supports (see Section 2.3) and 11 different metal additives (Y, La, Zr, Mo, Re, Ir, Ni, Pt, Zn, Ag and Au) were used as variables for the genetic algorithm. Details of the genetic algorithm can be found in Ref. [5]. For this number of variables, seven generations with a population size of 92 samples per generation were generated. For the first generation one support and three metal additives from the pool of supports and the active elements were randomly chosen by the genetic algorithm for preparation of the

different catalysts. After testing the 92 catalytic compositions of this first generation, the catalysts were ranked using the HCN yield as the objective function. For the following generations, the single catalyst was loaded with up to six different metal additives corresponding to the composition given by the genetic algorithm. Those combinations of metal additives with the highest HCN yield after optimization were additionally combined with three additional supports (Mo_2C, TiN and AlN) and tested to elucidate the influence of these supports on catalyst performance.

3.2. Data analysis

The aim of data analysis was to identify key factors of the catalysts which are important for a high HCN yield. With these factors, the catalytic performance of new catalyst can be predicted. Furthermore, the results of the data analysis have to be considered as a base for an efficient design of future experiments. With the results obtained, the number of variables can be considerably diminished and limits for the different metal additives can be defined, which allow, e.g., a systematic study of the impact of a single metal additive near the maximum with a lower number of experiments. The proposed concept for catalyst development is summarized in Scheme 1.

The *analysis of variance* is a traditional statistical approach to study the influence of variation of the values of categorical input variables (e.g., the qualitative composition of the catalyst) on the values of the output variables (such as conversion, selectivity or yield). In the present case, there are 12 categorical input variables: the kind of support and the presence of the metal additives of the elements Y, La, Zr, Mo, Re, Ir, Ni, Pt, Zn, Ag, Au, whereas the yield of HCN serves as an output variable. The approach assumes that each output variable follows some statistical model, in which the expectation of the output variable is viewed as the sum of effects of individual input variables (called main effects), possibly superimposed by their interactions of various complexity [18,19]. Thus, in the present case,

Scheme 1. Proposed concept for catalyst development.

the expectation of HCN yield, EY_{HCN} equals the sum of main effects, $\alpha_{support} + \alpha_Y + \ldots + \alpha_{Au}$, to which interactions of two variables (e.g., $\alpha_{support,Y} + \alpha_{support,La} + \alpha_{Y,La} \ldots + \alpha_{Ag,Au}$) or even of more variables (e.g., $\alpha_{support,Y,La} + \ldots$) can be added. The amount of the available data for each combination of values of the input variables determines how complex the basic model will be. In the present case, there are 15 different supports, whereas each of the metal additives can be either present or absent in the catalytic material. Then, in case of the basic model considering only main effects, data are needed about at least one material with each support, and for each metal additive, data about at least one material in which that additive is present and at least one in which it is absent. Similarly for each combination of support and metal additive in case of the basic model with two-variables interactions, data are needed for at least one material, in which that combination is present and at least one, in which that support is present but the additive is absent. The principle of the method is to test the hypothesis that a particular effect or interaction can be left out from that model without significantly changing the value of the output variable. For example, in case of the basic model $EY_{HCN} = \alpha_{support} + \alpha_Y + \ldots + \alpha_{Au}$, the hypothesis that the effect of support can be left out from the model means that this model can actually be simplified to $EY_{HCN} = \alpha_Y + \ldots + \alpha_{Au}$. If the tested hypothesis is valid, then both models give the same error. Therefore, the ratio of both errors is computed in the analysis of variance method, and if that ratio significantly differs from the value 1, the tested hypothesis is rejected. Provided that the individual errors are normally distributed, also the distribution of the error ratio is known (it is the Fisher–Snedecor distribution). Using this distribution, the probability can be computed that the error ratio is as high as or higher than the value corresponding to the measured data. That probability is called *achieved significance* of the test. The smaller it is, the more unlikely could the measured data occur if the simplified model is valid.

Application of *regression trees* is a nonlinear regression method that approximates the unknown dependency of an output variable on the input variables with a piecewise-constant regression function [20,21]. Differently to the analysis of variance, the input variables do not have to be categorical, also numerical variables are allowed. In the present case, the output variable was again the HCN yield, but the input variables were the support and the relative amounts of the individual metal additives, instead of only their presence. Whereas the support is a categorical variable, the relative amounts of metal additives are numerical. The principle of the method consists in splitting the value set of each input variable in such a way that the sum of the empirical variances of the output variable computed for data in both partitions is minimized. In this way, the method forms a hierarchy of partitions of the value set for the input variables. Such a hierarchy can be visualized as a tree graph. After the splitting procedure is stopped, the regression function is defined in each part of the final partition (corresponding to a leaf of the tree) as the average value of the output function on the data in that part. Depending on the number of repetitions of the splitting procedure needed until it is stopped, trees of different sizes are obtained. The choice of the most appropriate tree size
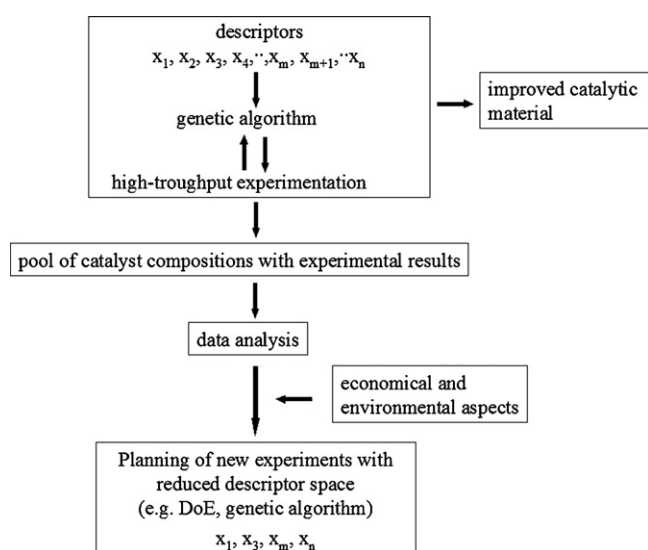
is usually based on the generalization error of the tree (error on data not used to construct that tree), estimated by means of a method called cross validation: the data are divided into k folds, i.e., approximately equally-sized parts, and each of them is then used as test data for a tree of the considered size that was constructed using data of the remaining $k-1$ folds. As a final estimate of the generalization error, the test data error averaged over all k folds is used.

4. Results and discussion

It is first shown that the catalyst test unit, which was developed for the provision of reliable and reproducible catalytic results for high-temperature processes works sufficiently. Then, it is demonstrated that the applied optimization strategy led to new and improved catalyst formulations for the BMA process. Finally, the results of data analysis are interpreted and proposals for further catalyst optimization are derived.

4.1. Validation of the high-throughput approach

4.1.1. Validation of the high-throughput testing unit
The reliability and reproducibility of the catalytic results obtained with the high-throughput-testing unit were ensured on the basis of several experiments. Equal gas flow through all the parallel channels was checked before and after every test run by measuring the flow of argon through each channel using a mass-flow meter. The flow rates between the single reactor tubes differed only slightly. For example, for a volumetric flow rate of 8.25 ml/min, a standard deviation of 0.085 ml/min was calculated for the 48 different channels with a minimum flow of 8.1 ml/min and a maximum flow of 8.4 ml/min.

The temperature distribution within the different reactor tubes was also measured. For a mean temperature of 1373 K, differences between the single reactor tubes were lower than ±23 K. The standard deviation for this temperature over all channels was lower than 10 K.

This appears to be acceptable considering the high-temperature level of the set-up. The temperature deviations between the different reactors are attributed to small differences in the position of the insulation material and the heating resistors and to the presence of bushings for additional thermocouples, which are used to control the temperature inside the heating zone. The axial temperature gradients within the individual reactor tubes were also measured and an isothermal zone was found over a length of 5 mm, in which the catalytic material was located.

The time period necessary to achieve a constant concentration inside of the IR cell when switching from one reactor tube to the other depends generally on the flow rates. The time period for the temporal change of the ammonia concentration inside the IR cell after switching from one tube to the other lasted 2 min for the applied inlet flow rate of 10 ml/min. During this time the tubes behind the reactor and the cell of the IR spectrometer are completely flushed and replaced by the new gas mixture. Shorter times can be realized by higher flow rates.

Furthermore, it was checked whether HCN formation does already occur in the absence of the catalyst and whether the position of the reactor tube in the furnace would have any influence on the catalytic performance. Therefore, empty reactor tubes as well as 10 reactor tubes filled with catalytic material (50 mg Pt/Al_2O_3) were fed with an $NH_3/CH_4/Ar$ mixture at different temperatures. In the empty tubes, mainly decomposition of ammonia to N_2 and H_2 occurred and almost no HCN formation was observed (Y(HCN) < 5%). In the presence of catalytic material ammonia and methane were converted to HCN. Fig. 5 shows the results at different temperatures for the reactors charged with catalytic material distributed over the furnace. At a constant inlet gas flow rate both, CH_4 and NH_3 conversion as well as the yield of HCN increase with rising temperatures. The highest HCN yield (about 62%) was obtained at 1373 K. For all applied temperatures the conversion of the feedstock (NH_3 and CH_4) and the HCN yield is approximately independent on the position of the reactor tube in the furnace (standard deviation below 5%). These results clearly indicate that the presence of catalytic material is required for HCN formation; the impact of the position of the tube in the furnace on the catalytic performance can be neglected.

The testing unit can be applied within the following boundaries:

- catalyst weight between 200 and 10 mg;
- isothermal catalytic zone of 5 mm within each tube;
- temperatures up to 1373 K.

4.1.2. Validation of the high-throughput preparation
So far, it was confirmed that reproducible results were obtained with the high-throughput testing unit. The automated parallel catalyst preparation was also tested concerning reproducibility using up to three different catalytic active components deposited on the support. For this purpose, the compositions of 92 samples (first generation of the genetic algorithm) were randomly generated, synthesized twice, subsequently tested in four experiments. The results of these reproducibility experiments are shown in Fig. 6 for 46 of the 92 samples. The differences in HCN yield (shadowed) between two samples of the same composition, but prepared and tested in different beakers and tubes are usually less than 8%. Higher deviations were only observed for catalysts samples exhibiting visible inhomogeneities (no. 12, 18, 27, 40 and 45, respectively). With an improved protocol for the catalyst preparation these kinds of inhomogeneities were later avoided.

4.2. Catalytic results on bare and Pt-loaded supports

Catalytic results at 1373 K based on these materials partly loaded with different amounts of Pt are presented in Table 2. For the pure supports only low CH_4 conversion and HCN yield (<20%) were obtained. Decomposition of NH_3 to N_2 and H_2 was higher than 80% for most of the pure supports studied. Differences in HCN yield and conversion of NH_3 and CH_4 by
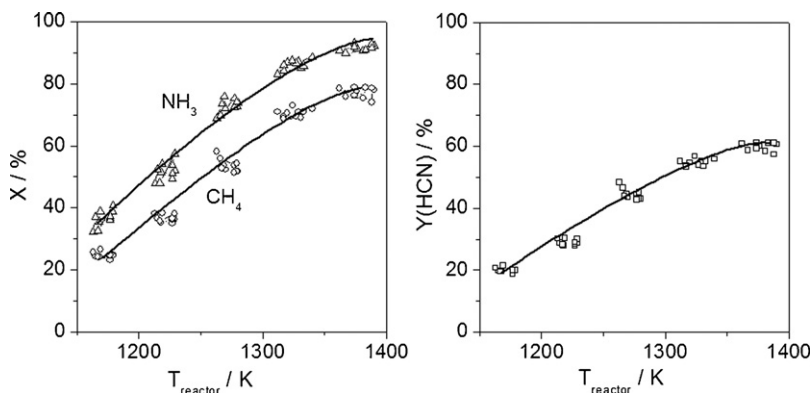
Fig. 5. Conversion of NH$_3$ and CH$_4$ (left) as well as yield of HCN (right) for the same catalyst in different reactor channels (NH$_3$, 10.7 vol.%; CH$_4$, 9.3 vol.%; rest Ar; $\dot{Q}$ (reactor) = 10 ml/min; m_{cat} = 50 mg).

using different supports are comparatively small. For some supports (Si$_3$N$_4$, SiC and MgO) CH$_4$ conversion and yield of HCN increase clearly with increasing Pt loadings. The interaction of Pt with these supports leads to catalytically active species or phases. The other supports loaded with different amount of Pt show high ammonia decomposition as already observed using the pure supports but low CH$_4$ conversion, and consequently low HCN yield. Loading of these supports with Pt does not lead to active and selective catalyst for HCN formation. Only on BN as support no activation of ammonia occurred even at the highest Pt loading. The highest HCN yield of about 66% was obtained with the Pt/Si$_3$N$_4$ catalyst loaded with 2.2 wt.% of Pt. This yield is close to the value for the reference catalyst (Y(HCN) = 64%), which was prepared from alumina and Pt according to Ref. [17] and shows that with this Pt amount active and selective catalysts can be obtained.

4.3. Results of catalyst development by the use of an evolutionary procedure (GA)

Most catalysts prepared in the seven generations according to a GA show an ammonia conversion higher than 80% under
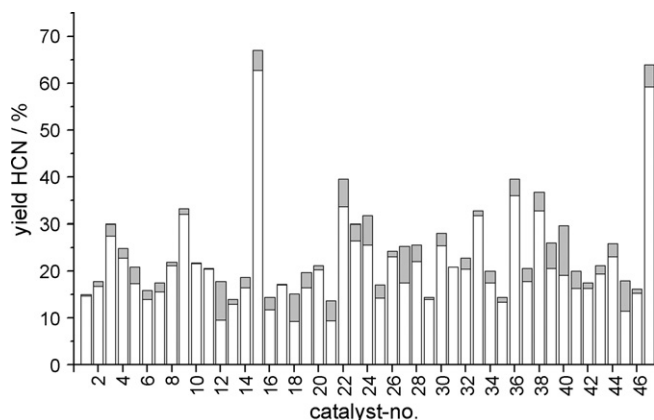

Fig. 6. Influence of repeated preparation on HCN yield. The shadowed bars show the difference between the first and second preparations of the same catalyst compositions of the first generation, prepared and tested separately (position 47 corresponds to the reference catalyst, T = 1373 K; NH$_3$, 10.7 vol.%; CH$_4$, 9.3 vol.%; rest Ar; $\dot{Q}$ (reactor) = 10 ml/min; m_{cat} = 50 mg).

the applied conditions at 1373 K. This is independent of the utilized catalyst composition (support and active components). Solely with the BN support, NH$_3$ conversions lower than 40% were obtained even with loading of Pt and different mixtures of metal additives. Methane conversion was clearly lower than the corresponding NH$_3$ conversion due to the decomposition of ammonia indicated by the high yield of nitrogen for most catalysts tested. In order to obtain a high HCN yield the catalytic material needs to activate ammonia and methane simultaneously. With the experience gained in the evolutionary process of catalyst optimization, catalytic materials could be divided into three groups:

- inactive material, which shows low NH$_3$ and CH$_4$ conversion ((X(NH$_3$) < 40%, X(CH$_4$) < 25%, Y(HCN) < 25%);
- materials catalyzing NH$_3$ decomposition but no CH$_4$ activation, leading to a high yield of N$_2$ but only to a low amount of HCN;
- active as well as selective catalysts which are able to activate NH$_3$ and CH$_4$ simultaneously (X(NH$_3$) > 94%, X(CH$_4$) > 70%), resulting in high yields of HCN (Y(HCN) > 65%) and hence a lower yield of N$_2$.

The same catalytic behavior was already observed when using different supports and Pt as the only active metal additive (see Table 2). This clearly indicates that the interaction of the support and platinum particles at the support surface has an important influence on HCN formation. If there is only little activation of methane by the Pt/support catalyst, addition of further metallic additives leads only to a comparatively small increase in methane activation (see also paragraph 4.4. Data analysis).

The support and the composition of the catalysts with the highest HCN yield obtained after seven generations are shown in Table 3. Again, as observed with Pt as the single active element, Si$_3$N$_4$ turned out to be the most suitable support. Furthermore, all of the most active and selective catalysts systems given in Table 3 contain Pt. The relative Pt fraction related to the total mass of the active elements (2.2 wt.%) varied between 0.55 and 0.7. Interestingly, the addition of further metallic components leads to obvious higher HCN yield as compared to the basis catalytic system Si$_3$N$_4$/Pt

Table 2
Catalytic performance (HCN yield, conversion of CH_4 and NH_3) of the bare supports and the supports loaded with Pt in the BMA process (D_{Pt}, apparent surface density of Pt; $T = 1373$ K; 10.7 vol.% NH_3; 9.3 vol.% CH_4; $\dot{Q} = 10$ ml/min; $m_{cat} = 0.05$ g)

Support	$X(CH_4)$				$X(NH_3)$				$Y(HCN/N)$			
	D_{Pt} (Pt/nm^2)				D_{Pt} (Pt/nm^2)				D_{Pt} (Pt/nm^2)			
	0	1	10	100	0	1	10	100	0	1	10	100
Alsint	16	24	34	36	81	89	89	80	13	19	27	28
BN	20	22	21	21	14	12	15	10	16	18	16	16
Si_3N_4	19	30	65	84	84	90	89	91	15	24	51	66
SiC	24	25	47	70	86	87	85	87	19	20	37	55
TiO_2	18	20	20	22	92	93	93	93	14	16	16	17
MgO	30	26	40	70	92	92	92	92	24	20	31	55
TiB_2	17	18	19	16	80	92	90	88	13	15	15	12
ZrO_2	21	28	23	23	89	92	89	88	17	22	18	18
Nb_2O_3	16	15	19	17	87	90	90	89	13	12	15	13
SrO	26	29	22	26	93	92	93	93	20	23	18	20
Sm_2O_3	24	20	20	19	93	92	92	92	19	16	15	15
CaO	21	26	19	35	74	92	99	99	17	20	16	30

(Y(HCN) = 64.8). In order to explain the observed increase in HCN yield by addition of promoters like Au, Zn, Ni, Mo, Ir, Ag or Re to the base system Si_3N_4/Pt, further studies are necessary particularly with respect to the interaction of the different elements with platinum.

As expected, increasing yields of HCN were obtained throughout the evolutionary development of the catalytic material, going from generation 1 to 7 (Fig. 7). Both, the HCN yield of the best catalysts and the mean value of HCN yield of the best 10 catalysts of each the single generation increased, e.g., the maximal HCN yield amounts to 65% in the first generation and to about 77% in the seventh generation.

The formation of HCN from NH_3 and CH_4 is, as already mentioned, a strong endothermic reaction. In order to achieve high HCN formation, temperatures higher than 1000 K have to be applied [12]. At 1373 K, it is thermodynamically possible to convert the introduced CH_4 completely to HCN ($K_x \approx 10^3$ [12]). CH_4 is used in a stoichiometrically deficient proportion in comparison to NH_3 in the inlet gas (NH_3, 10.7 vol.%; CH_4, 9.3 vol.%). If both NH_3 and CH_4 are converted completely, some of the NH_3 has to decompose to nitrogen because NH_3 was in excess. The maximum fraction of NH_3 which can be converted to HCN under the condition applied is 87% (9.3 vol.% CH_4/10.7 vol.% NH_3). Assuming a HCN selectivity of 100% for its formation from CH_4, the maximum yield of

HCN related to ammonia (HCN/N) can achieve only 87%. This stoichiometric limit for HCN formation and the catalytic performance of the best catalysts is shown in Fig. 8. It can be seen that the best catalysts are not far away from this value.

The high number of catalysts tested does not necessarily guarantee that the catalyst formulations leading to the highest HCN yield had been already found. In order to limit the number of further experiments for searching of the maximum HCN yield methods of data analysis can be applied to identify the most important factors and areas of catalyst composition, which lead to high yield of HCN. The latter was already previously demonstrated in screening for optimized catalyst composition in oxidative dehydrogenation of propane [22].

4.4. Data analysis

The influence of catalyst composition (support and active elements) on the HCN yield for 700 tested catalysts was further investigated by means of the multi-way analysis of variance and regression trees. For both methods, the implementation in the Statistics Toolbox of Matlab$^{®}$ was employed [23]. Besides the results of the seven generations of the genetic algorithm, also

Table 3
HCN yield and catalyst composition of the best catalysts obtained after seven generations of the genetic algorithm ($T = 1337$ K, 10.7 vol.% NH_3, 9.3 vol.% CH_4, $\dot{Q} = 10$ ml/min, $m_{cat} = 0.05$ g)

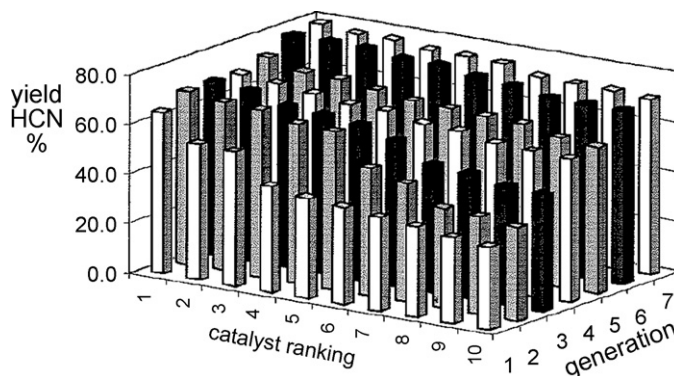| Composition[a]	HCN-yield (%)
Si_3N_4-Re(0.17)Ir(0.16)Pt(0.66)	78.5
Si_3N_4-Y(0.11)Zn(0.11)Ag(0.0041)Au(0.089)Pt(0.68)	77.9
Si_3N_4-Re(0.36)Ni(0.086)Pt(0.55)	77.6
Si_3N_4-Y(0.063)La(0.059)Ir(0.15)Ag(0.0023)Au(0.049)Pt(0.68)	77.6
Si_3N_4-Y(0.13)Zn(0.13)Ag(0.0048)Au(0.052)Pt(0.68)	77.2

[a] Sum of metal components is 2.2 wt.%.

Fig. 7. HCN yield obtained with the best catalysts in each generation for the different steps of the genetic algorithm.
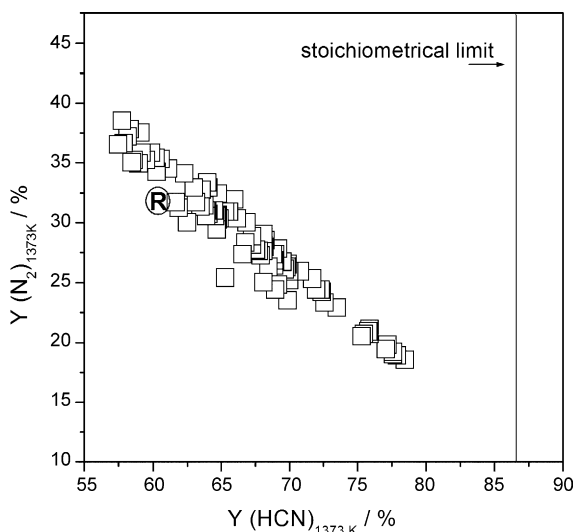
Fig. 8. Yield of N_2 versus yield of HCN for the best catalysts obtained after seven generations (®, reference catalyst, the solid line shows the stoichiometric limit according the inlet gas mixture).

Table 4
Variables used for the multi-way analysis of variance and obtained significance values

Variable	Achieved significance (%)
support	$<10^{-14}$
Pt	$<10^{-14}$
Ag	32.6
Au	0.1
Ir	2×10^{-6}
La	4.6
Mo	2×10^{-4}
Ni	0.4
Re	16.0
Y	3.0
Zn	0.2
Zr	98.9

the results of the additionally prepared and tested AlN, TiN and Mo_2C support-based catalysts are included.

The results of the analysis of variance are presented in Table 4. The basic model applied included only main effects because the available data are not sufficient for a model with interactions – some combinations of support and metal additives are not available in them. Consequently, only the influence of a single variable (support, the presence of a particular metal additive) on HCN yield has been tested. Most significant was the influence of the support and Pt as active

metal component. For both parameters, the achieved significance was nearly zero. That means that the support and the presence or absence of Pt will strongly influence the HCN formation. Significant influence on HCN formation (significance < 0.4%) was also observed for the presence or absence of the metal additives Ir, Mo, Zn, Au and Ni. On the other hand, from a significance level of 98.9% it can be concluded that the presence or absence of Zr has no influence on HCN yield. A relatively low influence on HCN formation is obtained for the metal additives Ag and Re. The presence or absence of these elements alone has only a small influence on HCN formation.

Besides this qualitative data analysis, a quantitative data analysis was also carried out using regression trees (Fig. 9). To this end, the tree with the lowest estimate of the generalization
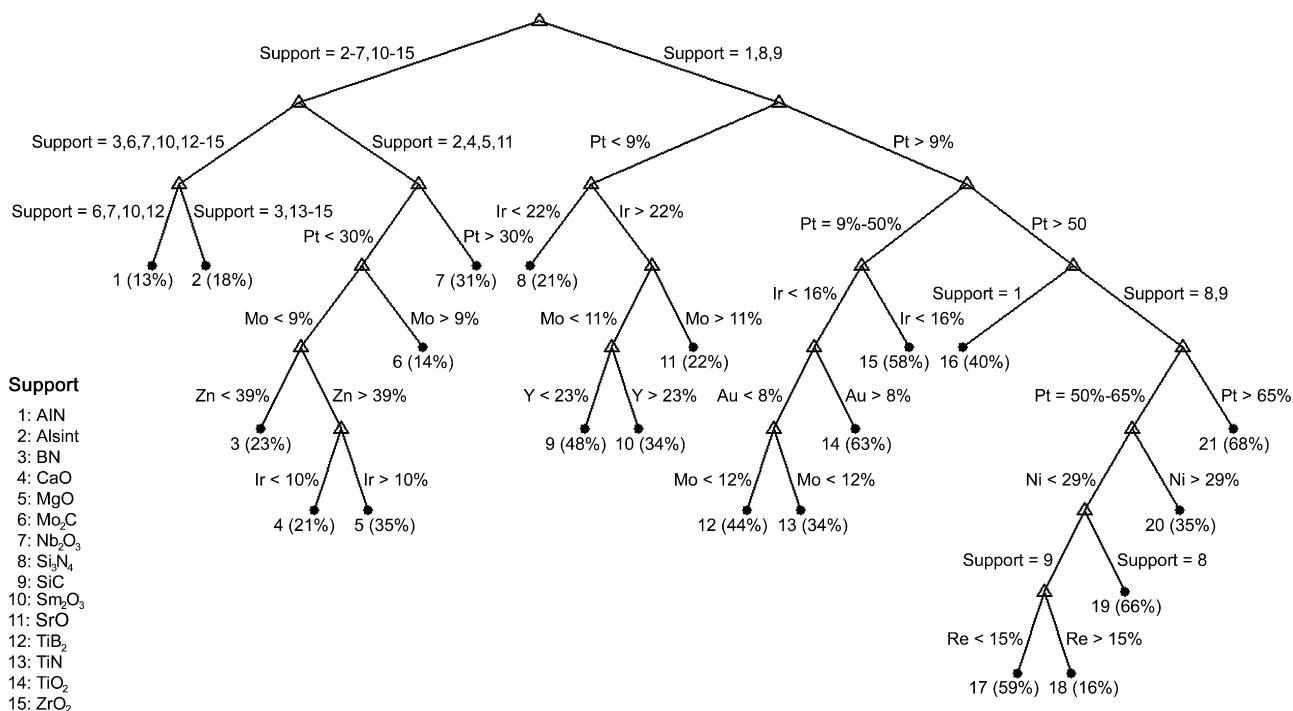

Fig. 9. Regression tree obtained for the regression of HCN yield on the support and on the relative amounts of 11 metal additives (in parentheses behind the leaf number, the mean value of HCN yield for the catalysts belonging to that leaf, % value give the relative metal loading related to the total metal loading of 2.2 wt.%).

error was used, obtained by means of a 10-fold cross-validation. This tree was chosen because its information allows the most precise prediction in HCN yield for new catalyst compositions. The number for the metal loading in Fig. 9 is always related to the total amount of the metal loading (2.2 wt.%), e.g., a value of >65% means that the catalyst is loaded with more than 1.44 wt.% of the corresponding element. The leaves of this tree are numbered, and for each of them, the mean value of the HCN yield is given (in parentheses). For example, the 1., 2., 4. and 5. catalysts in Table 3 belong to the leaf 21 (mean value of the HCN yield: 68%) and the 3. catalyst in Table 3 belongs to the leaf 19 (mean value of the HCN yield: 66%). A further split up of both leaves is possible, however, it leads to an increase of the generalization error. The most important input variable in order to achieve high yields of HCN is the catalyst support, which was also indicated by the analysis of variance. Using the supports with the numbers 2–7, 10–15 (see also Table 1), the mean value of HCN yield is at most 35% (leaves 1–7). With the supports 3 (BN), 6 (Mo_2C), 7 (Nb_2O_3), 10 (Sm_2O_3), 12 (TiB_2), 13 (TiN), 14 (TiO_2) and 15 (ZrO_2), only catalysts with low mean value of HCN yield will be obtained (leaves 1, 2). The mean values of HCN yield for the supports 2 (alsint), 4 (CaO), 5 (MgO), 11 (SrO) increases slightly with the relative amount of Pt (leaf 7, 31%), and the metal additive Ir (leaf 5, 35%). However, the mean value of HCN formation for these supports is comparatively low. The supports AlN (1), Si_3N_4 (8) and SiC (9) can deliver catalysts of high HCN yield (leaves 8–21). With these supports, active species or phases for HCN formation are formed at their surface after heating the catalytic material to 1373 K and stepwise addition of methane. The mean value of the yield of HCN for these supports depends mainly on the relative Pt amount. If the Pt amount was lower than 9%, a mean value of HCN yield below 48% was achieved (leaves 8–11). For a relative Pt amount between 9 and 50%, combinations of Pt with Au (>8%) or Ir < 16% lead to active and selective catalysts with mean HCN yields of 63% (leaf 14) and 58% (leaf 15), respectively. The highest mean values of HCN yield (68%) are obtained on Si_3N_4 and SiC supports with a relative Pt loading > 65% (leaf 21).

Based on the results of the data analysis, it is possible, to design future experiments using a lower number of variables (support and metal additives) and taking into account economical or environmental aspects (e.g., costs for the metal additive, toxicity) too. For the development of an active and selective catalyst with a Pt loading < 50%, the screening should be carried out with the support materials Si_3N_4, SiC and AlN containing the metal additives Pt, Ir and Au. For a further optimization of the HCN yield without any limitations of variables, the supports Si_3N_4, SiC and AlN with a Pt loading > 50 should be investigated in more detail. As metal additives, Ni (<30%) and Re (<15%) as well as Ir (<16%) and Au (>8%) have to be considered.

5. Conclusions

A high-throughput test unit for high-temperature reactions was successfully developed and tested for the formation of hydrocyanic acid from methane and ammonia at 1373 K. The test unit exhibits uniform reaction conditions within the 48 different reactor tubes and a good reproducibility of the obtained catalytic results. A new and suitable way has been opened for the inclusion of high-temperature reactions in the high-throughput experimentation in catalyst development.

New catalyst compositions resulting in HCN yields close to the stoichiometric limitation were detected by screening 700 differently composed catalytic materials obtained applying a genetic algorithm for experimental design. In addition to supported Pt, which is well known as active element for this reaction, promising catalyst compositions containing both Pt and further metals (e.g., Ir, Au, Ni and Re) supported on Si_3N_4 and SiC were found.

Data analysis methods like analysis of variance and regression trees were applied to identify key factors, which are important for achieving high yields of HCN. It was found that the support material and the absence or presence of Pt has the largest impact on HCN yield. Using Si_3N_4 and SiC as support and a Pt amount between 1.43 and 2.2 wt.%, catalysts with HCN yields higher then 60% can be expected under the applied conditions.

References

[1] H. Weinberg, H.W. Turner, in: A. Hagemeyer, P. Strasser, A.F. Volpe (Eds.), High-Throughput Screening in Chemical Catalysis, Wiley-VCH, Weinheim, 2004, pp. 1–15.
[2] U. Rodemerck, M. Baerns, in: M. Baerns (Ed.), Basic Principles in Applied Catalysis, Springer Series in Chemical Physics, 2004, 259–280.
[3] S. Senkan, Angew. Chem. Int. Ed. 40 (2001) 312–329.
[4] A. Holzwarth, H.-W. Schmidt, W.F. Maier, Angew. Chem. Int. Ed. 37 (1998) 2644–2647.
[5] D. Wolf, O.V. Buyevskaya, M. Baerns, Appl. Catal. A 200 (2000) 63–77.
[6] I. Hahndorf, O. Buyevskaya, M. Langpape, G. Grubert, S. Kolf, E. Guillon, M. Baerns, Chem. Eng. J. 89 (2002) 119–125.
[7] U. Rodemerck, P. Ignaszewski, M. Lucas, P. Claus, Chem. Eng. Technol. 23 (2000) 413–416.
[8] U. Rodemerck, P. Ignaszewski, M. Lucas, P. Claus, M. Baerns, Topics Catal. 13 (2000) 249–252.
[9] L. Andrussow, Chem.-Ing. Tech. 27 (1955) 469–472.
[10] E. Koberstein, Ind. Eng. Chem. Process Des. Dev. 12 (1973) 444.
[11] L. Hippel, C. Bussek, J. Sauer, M. Sauer, D. Arntz, DE 196 17 040 C1.
[12] L.D. Schmidt, D.A. Hickmann, in: J.R. Kosak, T.A. Johnson (Eds.), Catalysis of Organic Reactions, Marcel Dekker, New York, 1994, pp. 195–212.
[13] M. Diefenbach, M. Brönstrup, M. Aschi, D. Schröder, H. Schwarz, J. Am. Chem. Soc. 121 (1999) 10614–10625.
[14] R. Horn, G. Mestl, M. Thiede, F.C. Jentoft, P.M. Schmidt, M. Bewersdorf, R. Weber, R. Schlögl, PCCP 6 (2004) 4514–4521.
[15] E. Herceg, M. Trenary, J. Am. Chem. Soc. 125 (2003) 15758–15759.

[16] S. Delagrange, Y. Schuurman, Catal. Today 121 (2007) 204–209.
[17] M. Witzel, P. Kleinschmidt, W.-D. Pfeifer, C. Voigt, P. Albers, DE 37 23 535 A1.
[18] H. Scheffé, The Analysis of Variance, Wiley, New York, 1999.
[19] H. Sahai, M.I. Ageel, Analysis of Variance: Fixed, Random and Mixed Models, Birkhäuser, Boston, 2000.
[20] L. Breiman, J. Friedman, R.A. Ohlsen, C.J. Stone, Classification and Regression Trees, Wadsworth, Belmont, 1984.
[21] T. Hasti, R. Tibshirani, J. Friedman, The Elements of Statistical Learning, Springer, New York, 2001.
[22] M. Holena, M. Baerns, Catal. Today 81 (2003) 485–494.
[23] Statistics Toolbox for Use with Matlab, The MathWorks, Inc., Natick, 2004.