

# Acceleration in catalyst development by fast transient kinetic investigation

A.C. van Veen, D. Farrusseng, M. Rebeilleau, T. Decamp, A. Holzwarth,<sup>1</sup>  
Y. Schuurman, and C. Mirodatos\*

*Institut de Recherches sur la Catalyse, 2 Avenue Albert Einstein, F-69626 Villeurbanne cedex, France*

Received 29 July 2002; revised 16 October 2002; accepted 6 November 2002

## Abstract

This study intends to illustrate the application of transient kinetics in combinatorial research. Thus, it is shown through various case studies how high-throughput transient kinetics may both accelerate the search for new catalytic materials and bring fundamental insights in reaction mechanisms. As a first case study, the cracking reactions of the C<sub>6</sub> isomers (*n*-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,3-dimethylbutane) over a fluidised catalytic cracking (FCC) catalyst at temperatures between 300 and 650 °C have been studied in a temporal-analysis-of-product (TAP) reactor. A mathematical model taking into account the extra- and intracrystalline transport phenomena was used to determine the diffusion, sorption, and kinetic parameters for the hydrocarbons studied. Sorption and diffusion decrease with increasing branching in agreement with literature data. Except product distribution, the activation energies for the overall cracking of the C<sub>6</sub> isomers are similar for all isomers. As a second case study, a “paralleled” TAP reactor with a multisample holder is shown to be an efficient tool for acquiring adsorption/desorption parameters for a series of zeolites, tested to evaluate their potential as catalyst supports in the oxidative dehydrogenation of ethane. Finally, the applied combinatorial study was found also suitable for discovering new materials precursors of dense oxygen-conducting membranes. From high-throughput transient TAP and TPD experiments, it was possible to derive a strategy directing the rapid combinatorial evolution within the available parameter space. It was shown that high-quality information is accessible from these data, providing all parameters necessary for a well fitting description with a kinetic model.

© 2003 Elsevier Science (USA). All rights reserved.

**Keywords:** Combinatorial catalysis; High-throughput transient kinetics; FCC catalysts; BiMeVO<sub>x</sub>; Bismuth vanadate; Membrane reactor; Solid oxide fuel cell; Oxygen surface exchange; Temporal-analysis-of-products (TAP)

## 1. Introduction

Due to an increased pressure for short time-to-market development, lowered costs in chemical processing as well as a need to fulfill environmental regulations such as using cheaper and greener feedstocks, a significantly higher speed and efficiency in process optimisation, and new materials discovery is required today. The combinatorial strategy based on high-throughput experimentation (HTE) fulfills these needs (i) by increasing the probability for new materials discovery, (ii) by increasing speed and efficiency for process development and optimisation (higher and faster access to optimised operating conditions through the development of micropilot technologies), and (iii) by improving

safety and environmental aspects (reduced reactor volumes and integrated mass and heat transfer for a beneficial overall energy balance) [1,2].

Progress in HTE methods in catalysis research and development has reached an impressive rate. Companies implementing these techniques have recognised their power and importance in increasing productivity and adding value to processes and products [3]. Companies providing technologies, instrumentation, and expertise are also expanding their effort, looking for a wider array of clients' needs [4–8]. In parallel, among the academia groups having initiated an effective approach of combinatorial research under a more fundamental basis during the last 5 years, some of them including our laboratory are now increasing their effort not only for tools and software development but also for finding new concepts trying to combine understanding and stochastic approaches [9–16].

With testing and comparing of different catalytic compositions belonging to a given library (prepared or not by

\* Corresponding author.

E-mail address: [mirodato@catalyse.univ-lyon1.fr](mailto:mirodato@catalyse.univ-lyon1.fr) (C. Mirodatos).

<sup>1</sup> Present address: European Patent Office, Bayerstrasse 34, 80335 Munich, Germany.

HT automated synthesis techniques), the combinatorial strategy is generally restricted to the evaluating as rapidly as possible simplified catalytic performances such as activity expressed by the degree of conversion of a key reactant, selectivity of the reaction to desired products, and therefore yield at simplified standard conditions. This is generally carried out by means of parallel reactors [2,12,13,17] and permits only a primary ranking among various materials, which requires neither high accuracy in the process control nor sophisticated analytical techniques determining effluent compositions. However, this fast simplified testing procedure may eliminate good candidates which could have been revealed under other appropriate operating conditions. Accordingly, testing conditions should ideally be varied for each catalyst, looking out for maximum performance by probing several contact times/space velocities, temperatures, and partial pressures and eventually integrating time-on-stream deactivation. As such, basic kinetics derived from inter- and extrapolating in the multiparameter space could hint at optimum conditions, allowing a fair comparison of catalytic materials. However, such a mode of data acquisition is in general far too time consuming to accommodate the overall high throughput of the combinatorial loop.

An elegant and efficient way to solve the problem is to perform fast kinetic measurements under transient conditions. As a matter of fact, in a study confined to steady state kinetics, only lumped kinetic parameters can be estimated rapidly whereas determining all relevant intrinsic parameters is possible but requires a large number of time-consuming experiments [18]. By generating transient input signals, one observes signals out of the steady state and their relaxation may be related to the time scale on which the corresponding global reaction occurs at steady state. In turn, mathematical analysis of the relaxation curves may rapidly provide all the relevant intrinsic parameters of the reaction kinetics. In the steady-state-isotopic-transient-kinetic analysis (SSITKA), a reactant is stepwise substituted by its isotope-labelled equivalent and the isotopic concentration relaxation can be analysed under overall steady-state conditions [19]. In the temporal-analysis-of-product (TAP) reactor, concentration transients are generated by pulsing small and known amounts of reactants through a catalyst bed maintained under vacuum, and the pulse expansion and relaxation are analysed at the reactor exit with a time resolution below milliseconds [20]. Numerous studies and reviews have demonstrated the unique power of these transient techniques for investigating key catalytic phenomena such as a nonuniform surface and combination of kinetic, thermal, and hydrodynamic parameters [21–27].

In this paper, it is shown through various case studies how transient kinetic methods applied under HTE conditions may both accelerate the search for new materials and bring advanced fundamental insights into reaction mechanisms by providing kinetic parameters as descriptors of a given catalytic system.

The first case study deals with the use of HT fast kinetics for testing either various industrial FCC catalysts or a large number of different probe reactions which may be part of the FCC reaction mechanism. This approach aims at discovering relationships between the different explored parameters. The cracking reactions of the C<sub>6</sub> isomers (*n*-hexane, 2-methylpentane, 3-methylpentane, 2,3-dimethylbutane, and 2,3-dimethylbutane) over a fluidised catalytic cracking (FCC) catalyst at temperatures between 300 and 650 °C have been studied with the TAP reactor. A mathematical model taking the extra- and intracrystalline transport phenomena into account was used to describe the experimental data and allowed determination of the diffusion, sorption, and kinetic parameters for the hydrocarbons studied. The parameters obtained are compared with published values obtained by independent methods, to find out some correlation between molecule structure and kinetic behaviour (sorption and diffusion) for the cracking reaction. Such an approach, like in an expert system, aims at developing a predicting tool for optimising operating conditions in the complex field of FCC reactions.

As a second case study, a TAP reactor “paralleled” with a multisample holder is described for acquiring adsorption/desorption parameters over a series of zeolite materials, to investigate their potential as catalyst supports in the oxidative dehydrogenation of ethane.

The third chosen case study deals with the preparation and testing of mixed oxides materials for developing dense ion-conducting catalytic membranes. A high-throughput TAP investigation using differently composed BiMeVO<sub>x</sub> and perovskite samples is reported, searching for relationships between key parameters such as activation energy of oxygen uptake and material formulation such as the nature and concentration of additives and structural properties. Here, the kinetic parameters are considered as indicators to find the right balance between high ionic conductivity and the ability to take up oxygen, maximising the performance of the membrane reactors prepared from the optimised precursors materials.

## 2. Results

### 2.1. Case study 1: Use of fast kinetics for a combinatorial approach of FCC model reactions mechanism

In a recent study we investigated as a model reaction the cracking of isooctane over different FCC catalysts in the TAP reactor [28] (Table 1). It has been shown that by modelling of the transient responses the transport, sorption, and kinetic parameters can be obtained. Table 2 shows the parameter estimates for the different samples and the different pretreatments.

This table shows that the method is very sensitive to changes of the solid properties of the samples. The sorption parameters correlate well with the BET surface areas and

Table 1  
Composition of the FCC catalysts tested for isooctane cracking

Catalysts	Characteristics					
	Y zeolite (wt%)	Y zeolite (Si/Al)	Overall (Si/Al)	REO (wt%)	Ni (ppm)	V (ppm)
A	30	2.5	1.1	0.9	3200	3700
B	33	2.5	1.1	1.7	660	1330
C	32	2.5	1.1	1.5	700	1500

are independent of the sample pretreatment. However, the activation energy depends both on the specific sample and the pretreatment procedure. The determination of the product selectivities is much more difficult by this method because the analysis is done by mass spectroscopy and due to the overlapping mass fragments only a limited number of species can be analysed quantitatively. Further qualitative information can often be obtained from the transient responses. Here, it is demonstrated that the TAP reactor is a fast and efficient tool for investigating transport, sorption, and reaction properties of microporous materials, in agreement with the work from Keipert and Baerns showing how intracrystalline diffusion coefficients can be determined in ZSM-5 zeolites [29].

A slightly different approach is to take several different model components to obtain insight into the different reaction routes that are molecule structure dependent. In a recent study [30] C<sub>6</sub> paraffins (*n*-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane) were used as model components to investigate the different cracking routes over FCC catalysts to hydrogen, methane, and propane. Table 3 gives the model parameters for the different hexanes. The sorption parameters correlate with molecule branching and the adsorption increases with increasing degree of branching. The micropore diffusivity is similar for all hexane isomers studied. The activation energies for the overall disappearance of the C<sub>6</sub> paraffins, lumping contributions of dehydrogenation and C–C bond cleavage, vary only slightly with the degree of branching. The yields for hydrogen and methane are very different as shown in Fig. 1.

The reactivity and product distribution of the various isomers can be explained from stability considerations of the carbenium ion formed as a result of the collapse of the carbonium ion transition state. The protolytic attack on a C-

methyl bond, producing methane, is strongly favoured by the degree of substitution of the carbon atom, while the formation of hydrogen is clearly related to the possibility of forming tertiary carbenium ions [31–35]. This example shows that very detailed mechanistic information can be obtained from model components provided that the various products can be properly analysed by mass spectrometry [26,30].

## 2.2. Case study 2: HT investigation of ethane adsorption in a “paralleled” TAP reactor

The slowest steps in the experimental procedure for TAP measurements are generally related to the desorption of polar molecules such as water before the measurements (on the order of hours), the pretreatment procedure, and the temperature programs. The actual pulse experiment takes only a few minutes. All the slow steps mentioned above can be realized simultaneously on a multitude of samples by using parallel reactor technology. In this case a significant gain in time can be realized. For this purpose a parallel reactor that can contain 12 samples has been constructed and tested. Fig. 2 shows a photograph of the “paralleled” TAP reactor.

This reactor is connected to the pulse valve manifold by means of a commercial multiport valve (Valco). This multiport valve allows a continuous flow to be directed to 11 of the 12 samples simultaneously or all 12 reactors to be addressed sequentially for pulse experiments.

For the TAP experiment, a library of 10 different zeolite samples was loaded into the 12-vessels sample holder. One sample was loaded twice to check for the reproducibility of the measurement and the last vessel was filled with quartz particles only to correct the data for the transport through the reactor without adsorption. A mixture of 50/50 neon/ethane was pulsed over all 12 samples. Neon does not adsorb onto the zeolite and was used as an internal reference. The experiment was carried out at 50, 75, and 100 °C.

Fig. 3 shows the 12 transient responses at 100 °C. It also follows from this figure that a good reproducibility is obtained, as the samples that are close in composition give similar transient responses. From the experiments as a function of temperature the adsorption enthalpy can be extracted by a moment analysis.

Table 2  
Conversion and parameter estimates for the cracking of isooctane over the different industrial FCC catalysts tested for isooctane cracking

Catalyst	Conversion at 500 °C	$D_{\text{eff}}$ (m <sup>2</sup> s <sup>-1</sup> )	$\Delta S_{\text{ads}}$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta H_{\text{ads}}$ (kJ mol <sup>-1</sup> )	$k_a^0$ <sup>a</sup> (m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	$E_a^0$ (kJ mol <sup>-1</sup> )
A/H <sub>2</sub>	0.38	$1.0 \pm 0.5 \times 10^{-10}$	$-54 \pm 2$	$-37 \pm 3$	$2 \pm 1.2 \times 10^5$	$126 \pm 5$
B/H <sub>2</sub>	0.75	$2.2 \pm 1.0 \times 10^{-10}$	$-71 \pm 3$	$-47 \pm 5$	$4 \pm 2.1 \times 10^7$	$149 \pm 6$
B/O <sub>2</sub>	0.61	$2.2 \pm 0.9 \times 10^{-10}$	$-71 \pm 3$	$-47 \pm 5$	$2 \pm 1.0 \times 10^7$	$151 \pm 6$
B/used	0.50	$2.2 \pm 0.9 \times 10^{-10}$	$-71 \pm 3$	$-47 \pm 5$	$5 \pm 2.9 \times 10^8$	$175 \pm 7$
C/used	0.48	$2.3 \pm 1.2 \times 10^{-10}$	$-75 \pm 3$	$-49 \pm 5$	$1 \pm 0.6 \times 10^7$	$130 \pm 5$

<sup>a</sup>  $k_a^0$  is calculated by assuming a constant value of  $N_s$ , the concentration of active sites, equal to  $20 \text{ kmol m}_{\text{cat}}^{-3}$ .

Table 3  
Adsorption, diffusion, and kinetic parameters for linear and branched C<sub>6</sub> isomers

C <sub>6</sub> paraffin	Conversion at 600 °C	D <sub>eff</sub> (m <sup>2</sup> s <sup>-1</sup> )	ΔS <sub>ads</sub> <sup>a</sup> (J mol <sup>-1</sup> K <sup>-1</sup> )	ΔH <sub>ads</sub> (kJ mol <sup>-1</sup> )	k <sub>a</sub> <sup>0b</sup> (m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )	E <sub>a</sub> <sup>0</sup> (kJ mol <sup>-1</sup> )
<i>n</i> -Hexane	0.13	1.6 ± 0.5 × 10 <sup>-10</sup>	-78 ± 2	-42.6 ± 0.5	1 × 10 <sup>7</sup>	186.0 ± 1
2-Methylpentane	0.11	2.2 ± 0.7 × 10 <sup>-10</sup>	-75 ± 2	-43.9 ± 0.5	1 × 10 <sup>7</sup>	188.9 ± 1
3-Methylpentane	0.19	2.4 ± 0.8 × 10 <sup>-10</sup>	-75 ± 2	-44.2 ± 0.5	1 × 10 <sup>7</sup>	183.8 ± 1
2,2-Dimethylbutane	0.18	2.5 ± 0.8 × 10 <sup>-10</sup>	-63 ± 2	-37.5 ± 0.5	1 × 10 <sup>7</sup>	180.0 ± 1
2,3-Dimethylbutane	0.25	6.1 ± 0.7 × 10 <sup>-11</sup>	-65 ± 2	-40.2 ± 0.5	1 × 10 <sup>7</sup>	179.3 ± 1

<sup>a</sup> Calculated assuming the C<sub>6</sub> saturation concentration to be 200 mol m<sup>-3</sup>.

<sup>b</sup> Fixed.

Fig. 4 shows the van't Hoff plot for the 11 zeolite samples. The adsorption enthalpy varies between -4 and -16 kJ/mol. For the Na- and H-ZSM-5 samples the adsorption enthalpy decreases with increasing Si/Al ratio. A similar trend has been reported for the adsorption ethane on faujasite zeolites [36]. These values are rather low compared to those from studies using a single TAP reactor (ca. -30 kJ mol<sup>-1</sup> for ethane on ZSM-5 or on silicalite [37,38]), or other adsorption methods (ca. -30 kJ mol<sup>-1</sup> for ethane on silicalite [39], or -20 to -26 kJ mol<sup>-1</sup> for FAU [36]). This might be due to the fact, that at variance with the latter cases, a fast modelling procedure has been used for the present study, lumping adsorption and diffusion. The so-called adsorption enthalpy could therefore reflect essentially diffusion through zeolite pores, which would both explain the general trend for low values and also could fit with the ranking of zeolites according to their pore opening and dimensionality (from large pores mordenite to small pores Na-ZSM-5). Complementary measurements for an advanced modelling of the signals obtained in the TAP reactor equipped with the HT multisample holder are in progress.

Thus, the TAP reactor is an efficient tool for high-throughput screening of sorbent materials. Although not shown in this example, this approach can also be applied for kinetic investigations of solid catalyst samples and the

restrictions that apply are the same as those for a single TAP reactor.

### 2.3. Case study 3: HT preparation and testing of mixed oxides materials for developing dense ion-conducting catalytic membranes

Catalytic membrane reactors and related devices are attractive configurations for carrying out major chemical processes as their multifunctional action is supposed to allow for comparably small plant dimensions and reduced operation costs [40]. Systems using microporous permselective membranes for a well-controlled oxygen supply in hydrocarbon partial oxidation processing are expected both to avoid restrictions to feedstock composition originating from explosion limits and to improve heat management [41]. However, until now, yields in target products are too low for any industrial application. Using oxygen-conducting dense membranes might offer a much enhanced yield toward value-added products as the direct use of permeated lattice oxygen in the absence of gas-phase oxygen will limit combustion reactions. In addition, air can be used on the feed side, which avoids the costly preparation of pure oxygen, while NO<sub>x</sub> formation is unlikely along the catalytic cycle. However, the main obstacle for dense membranes is that the best performing materials are oxide based, which means

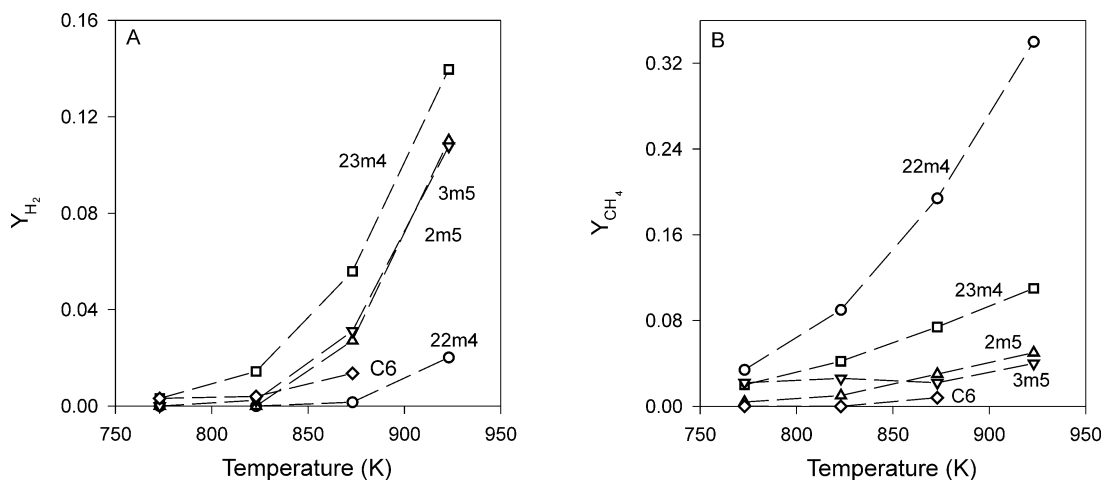


Fig. 1. Yields of hydrogen (A) and methane (B) as a function of temperature from pulses of *n*-hexane, C<sub>6</sub>; 2-methylpentane, 2m5; 3-methylpentane, 3m5; 2,2-methylbutane, 22m4; and 2,3-methylbutane, 23m4.



Fig. 2. The TAP sample holder with the chamber that contains the multiport valve.

they require high process temperatures and might become reduced under reaction conditions, leading to a dramatically decreased lifetime. To reach the attractive goal of using economically favourable membrane processes in oxidation, the working conditions of the oxygen-supplying inorganic membrane and the catalytic systems have to match. Novel mixed ionic electronic-conducting materials have to be searched with an increased transfer rate throughout the bulk or at feed- and permeate-side interfaces or with a decreased membrane thickness. The material candidates should allow for high oxygen fluxes at moderate temperatures (i.e., well below 700 °C) and exhibit a high intrinsic stability preserving a highly oxidized state of the bulk structure. On a microscopic scale this requires a sufficient rate for the activation of gas-phase oxygen at the feed side surface, which may be revealed by a rapid oxygen uptake. However, the oxygen release on the permeate side must not be limited by a too high re-adsorption rate. On the other hand the transfer of oxygen

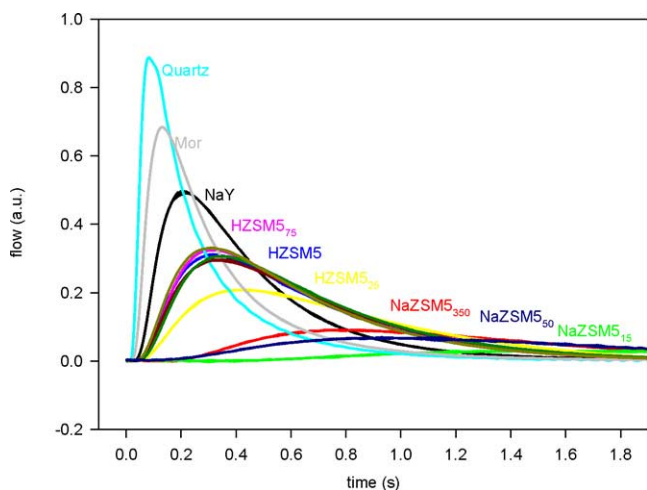


Fig. 3. Transient responses of ethane over different zeolite samples at 100 °C.

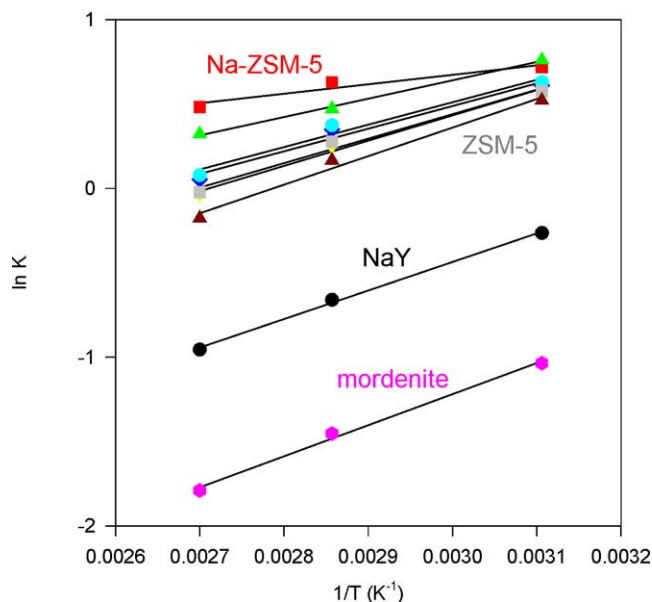


Fig. 4. Van't Hoff plot for the adsorption of ethane on different zeolite samples.

throughout the dense membrane requires a rapid oxygen ion bulk diffusion. Accordingly, a highly ambi-polar, i.e., a well-balanced electronic and ionic conductivity, is required for a mixed conducting membrane.

Perovskite structured materials have already demonstrated a promising oxygen permeability [42–48] but improvements aiming at increasing ionic conductivity to balance the overwhelming electronic conductivity are needed. Another class of oxygen-conducting materials based on bismuth oxide, so-called BiMeVO<sub>x</sub>, exhibiting a high ionic conductivity could also be regarded as promising candidates [49–52]. However, even upon extensive modification of the parent component Bi<sub>2</sub>VO<sub>x</sub> by transition metal cation doping, the electronic conductivity remains too low to balance the high ionic conductivity and as described below the oxygen uptake is also hindered.

The most promising strategy for discovering novel enhanced performing materials is therefore a skilled combination of the two former material classes, e.g., by introducing bismuth into a fluorite [48] or even better into a perovskite [46] structured material. However, the formation of a perovskite structure is only possible in a limited number of cases and depends strongly on the ratio between ion radii of A-site cations, B-site cations, and oxygen anions as described by the tolerance factor [53]. Unfortunately, ion radii depend strongly on the respective oxidation states, which can hardly be predicted.

Because of the lack of fundamental knowledge, a combinatorial approach was conducted to discover stable Bi-containing perovskites. To enlarge the serendipity for obtaining “hits” and decreasing the number of materials to be tested, a pool of elements and composition ranges has been selected according to tolerance factors based on coarse literature-derived assumptions. In view of facilitating future

application, a special preference was given to formulations with a limited number of cations. This strategy leads us to the successful discovery of a mixed electronic ionic conduction perovskite phase as detailed thereafter and a HT screening by means of transient techniques was carried out to evaluate the material properties toward oxygen activation.

### 2.3.1. Experimental

Synthesis of mixed oxides was carried out following an adapted procedure [54,55] by using an automated workstation (Sophas robot from Zinsser Analytic allowing a parallel synthesis of 48 samples within a few hours). Only stabilized noncorrosive liquid precursors were used to avoid equipment corrosion (i.e., no direct dissolution in nitric acid) or to synthesize too large particles (e.g., by following a ceramic synthesis procedure). The nitrate precursors were dissolved in water using appropriate amounts of complexing agents (EDTA, citric acid) under precise pH control. The stabilized precursor solutions were dispensed in proper amounts to 8-ml glass vials supported on carriers upon shaking and heating. After water evaporation, gels were formed and then dried in an oven at 250 °C to yield foams. The samples were then transferred to ceramic crucibles and calcined at 900 °C for 8 h. X-ray diffraction patterns were recorded using a Bruker D5005 system in the  $2\theta$  range of 3 to 80°, a step width of 0.02°, a counting time of 1 s, and Cu-K $_{\alpha 1+\alpha 2}$  radiation (1.54184 Å).

The capability to take up oxygen and to release it upon temperature-programmed desorption (TPD) was evaluated using the TAP system. Each reactor was loaded with 20 or 200 mg of a powder sample, evacuated, and heated to 600 °C. Hydrocarbon residuals were removed by introducing several oxygen pulses until no further carbon oxide responses (amu 28 and 44) were detectable. Then, the reactor was flushed with oxygen at atmospheric pressure and cooled down to room temperature. Subsequently, TPD experiments were performed under vacuum with a heating ramp of 30 °C min<sup>-1</sup> up to 600 °C, followed by pulse experiments injecting a 1:1 mixture of O<sub>2</sub> and Ne (Air Liquide, commercial grade) with an intensity of approximately 10<sup>15</sup> molecules per pulse in the range of 100 to 600 °C. The pulse responses were recorded as a function of time by a quadrupole mass spectrometer using the masses characteristic of O<sub>2</sub> (amu 32) and Ne (amu 20). For quantitative analysis, the mass spectrometer was calibrated by reference experiments using the same experimental procedure over an inert quartz bed. The TAP experiments were simulated with a one-dimensional pseudo-homogeneous model accounting for three zones (inert/active/inert) and temperature gradients in the inert sections. Calculations were performed by simultaneously solving the partial differential equations, denoting for the time ( $t$ ) and space ( $z$ ) dependency of partial pressure ( $p$ ) and coverage ( $\theta$ ), with a FORTRAN program [56] based on a home-modified version of the PDASAC algorithm [57]. Assuming a nonreversible molecular Langmuir adsorption, the processes in the ac-

tive zone are described by the partial differential equations for gas-phase oxygen (Eq. (1)) and an adsorbed (Eq. (2)) species, respectively:

$$\frac{\partial p}{\partial t} = D_{\text{eff}} \cdot \frac{\partial^2 p}{\partial z^2} - \rho_s \cdot k_0 \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot p \cdot (1 - \theta), \quad (1)$$

$$\frac{\partial \theta}{\partial t} = k_0 \cdot \exp\left(-\frac{E_a}{R \cdot T}\right) \cdot p \cdot (1 - \theta). \quad (2)$$

The mass transfer in the inert sections is completely described by Knudsen diffusion (first term in Eq. (1)) as no change in coverage occurs here (Eq. (2) is zero). The effective diffusion coefficient ( $D_{\text{eff}}$ ) of oxygen traversing the catalytic bed was derived from the pulse responses of the inert standard neon, taking the square root mass dependency under Knudsen conditions into account. The kinetic parameters, site density  $\rho_s$ , frequency factor  $k_0$ , and activation energy  $E_a$ , were determined by their variation until the best possible fit between model prediction and experimental result had been achieved.

### 2.3.2. Results

Fig. 5a shows diffraction patterns of various samples with the composition Ba<sub>0.5</sub>A<sub>0.5</sub>Fe<sub>y</sub>Bi<sub>1-y</sub>O<sub>x</sub> indicating a non-structured parallel presence of different oxides. In contrast, Fig. 5b displays diffraction patterns of the BBFO sample (composition BaBi<sub>0.4</sub>Fe<sub>0.6</sub>O<sub>x</sub>) along with those of two reference materials, La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.6</sub>Fe<sub>0.4</sub>O<sub>x</sub> (LSCFO) [42–44] and Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>x</sub> (BSCFO) [45,47], showing the formation of a well-crystallized perovskite with cubic structure. Furthermore, the band position shifts indicate an increase of the elementary cell dimension ranking LSCFO < BSCFO < BBFO (see Table 4). In turn, it is reasonable to assume an enhanced ionic conductivity for the novel BBFO material.

The release of oxygen from the samples was studied by temperature-programmed desorption (TPD) experiments. The respective desorption spectra are depicted in Fig. 6.

The BiMeVO<sub>x</sub> materials showed almost no desorption signal, indicating a very slow release of oxygen. In the case of the perovskite samples a release of O<sub>2</sub> from LSCFO is observed above 180 °C followed by BSCFO at 230 °C and BBFO at 250 °C.

The uptake of oxygen with different materials was studied by HT transient experiments in the TAP reactor. Fig. 7 shows the oxygen uptake as a function of temperature, calculated from the remaining oxygen observed in the outlet pulses.

Three distinct behaviours can be outlined: (i) Perovskite reference materials (LSCFO and BSCFO, using a sample weight of 20 mg) lead to a practically complete oxygen uptake over the investigated temperature range. (ii) In contrast, almost no oxygen uptake is observed for materials of the BiMeVO<sub>x</sub> family, even with a much higher reactor loading than 200 mg. (iii) Finally, the BBFO material takes an intermediate position as a reactor loading of 200 mg

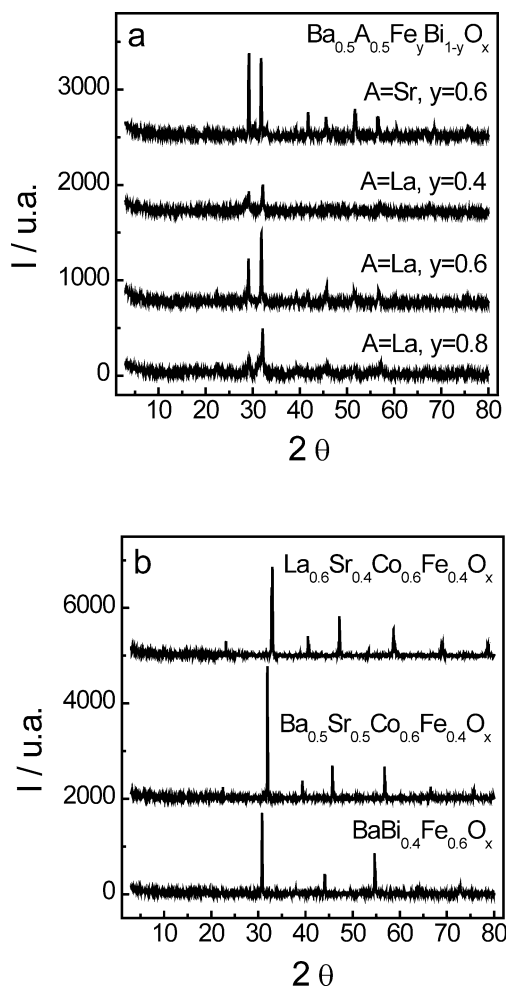


Fig. 5. XRD patterns of different material compositions ((a) shows patterns of samples synthesized by an automated protocol using the combinatorial approach; (b) depicts the pattern of the BBFO sample and other materials with cubic perovskite structure for comparison).

causes an increasing oxygen uptake ranging from 40% at 150 °C to 85% at 250 °C.

Due to such a temperature dependence, it was possible to perform a modelling study in the case of the novel BBFO material to derive rapidly in-depth kinetic information.

Modelling the experimental results obtained with a smaller amount of 21 mg of the BBFO material was performed in the wide 100 to 600 °C temperature range.

Fig. 8 reports both the experimental pulse responses (expressed as molecular flux ( $\varphi$ ) of oxygen leaving the reactor) and those calculated assuming a nonreversible molecular adsorption of oxygen. The modelling had to be performed by

Table 4  
Lattice parameter  $a$  of the various materials exposing a cubic perovskite structure

Material	$a$ (pm)
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_x$	384.8
$\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.6}\text{Fe}_{0.4}\text{O}_x$	397.1
$\text{BaBi}_{0.4}\text{Fe}_{0.6}\text{O}_x$	406.8

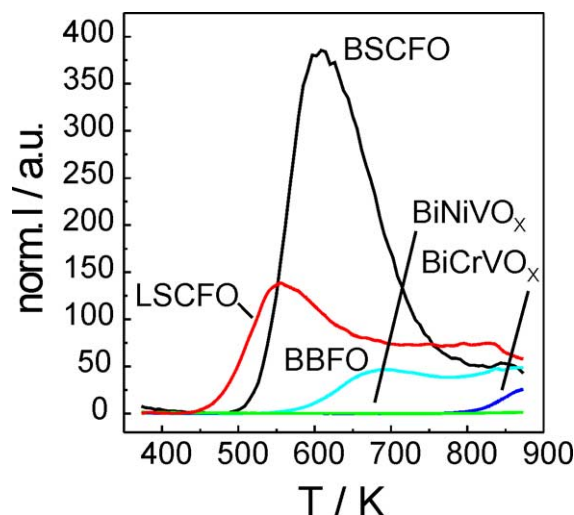


Fig. 6. Sample weight normalized temperature-programmed desorption spectra of various material candidates of membrane materials.

solving numerically the differential equations as a simplified approach using linear equations (i.e., assuming a negligible coverage) did not yield suitable description. The parameters allowing the best fit between model and experiment were an active site density  $\rho_s$  of  $6.5 \times 10^3 \text{ mol m}^{-3}$ , a frequency factor  $k_0$  of  $1.8 \times 10^2 \text{ Pa}^{-1} \text{ s}^{-1}$ , and an activation energy  $E_a$  of  $40 \text{ kJ mol}^{-1}$ .

### 2.3.3. Discussion

A primary screening of different material classes (i.e., perovskites and  $\text{BiMeVO}_x$  materials) by means of fast transient kinetics for oxygen interaction allowed us to derive a strategy for a secondary screening with a good probability to discover a material with an improved intrinsic property (i.e., formation of a perovskite structure with a large elementary cell). This knowledge-guided approach led to the discovery of the BBFO composition  $\text{BaBi}_{0.4}\text{Fe}_{0.6}$ .

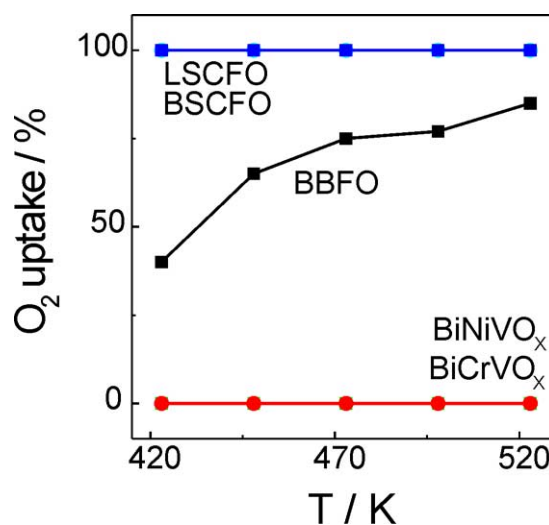


Fig. 7. Oxygen uptake in the TAP experiment of various material candidates of membrane materials as a function of the sample temperature.

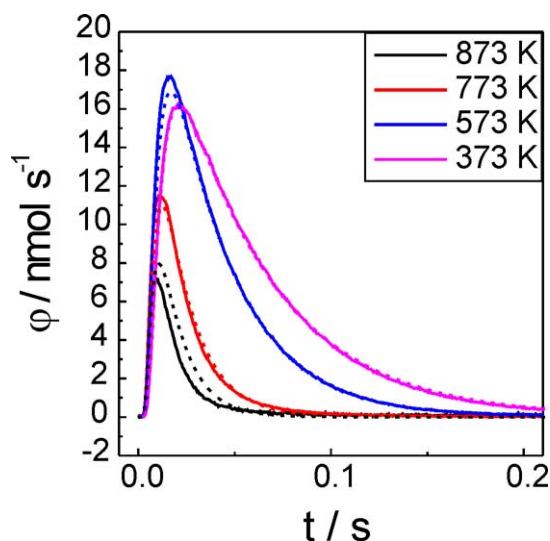


Fig. 8. Comparison of the experimental pulse responses (solid traces) and the results of modelling calculations (dashed traces) expressed as molecular flux ( $\phi$ ) leaving the reactor at various temperatures.

With use of an easily observable objective function (e.g., the formation of the perovskite structure probed by XRD), the overall development/optimisation cycle was accelerated. Note however that this objective function has to be selected very carefully and might require a combination of detailed information from different sources.

Thus, if one considers only the results of  $\text{O}_2$ -TPD experiments, the LSCFO material showing the lowest onset temperature should display an enhanced performance as an oxygen-conducting membrane. However, the oxygen permeation data reported in the literature [42–45,47] do not reflect this tendency. It can therefore be concluded that using information from this technique as a unique objective function is not suitable for discovering new improved material formulations.

In good agreement with our recent studies [54],  $\text{BiMeVO}_x$  materials showed a comparable poor oxygen uptake, implying (i) either a low concentration of oxygen vacancies necessary for dioxygen dissociation and further diffusion on the surface or in the bulk of the solid (ii) and/or too poor activity of these sites for performing these different elementary steps. As former studies have been carried out with sintered materials, we could greatly speed up the screening by using powders. However, on the larger scale enforced by the use of higher pulse intensities, it is not possible to distinguish the fine differences between differently doped samples. On the other hand, the virtually complete oxygen uptake of the perovskite reference materials LSCFO and BSCFO indicates a strong interaction with gas-phase oxygen. Unfortunately, a brand strong sticking of oxygen can also limit the overall oxygen permeation as oxygen release at permeate side might become hindered due to strong re-adsorption. With use of high-throughput TAP investigations, the oxygen uptake of the BBFO material was found to greatly surpass the one of the  $\text{BiMeVO}_x$ , but to stay below that of other per-

ovskites. Due to this and to the supposed high ambi-polar conductivity, it is likely that this material will display a superior stability in the reducing hydrocarbon atmosphere of a membrane reactor (under testing).

The successful modelling of BBFO TAP responses stresses once more the potential of the sketched approach, integrating in-depth kinetic/mechanistic information within the combinatorial loop. Thus, by evaluation of the relative importance between two key factors such as vacancies concentration and intrinsic reactivity, a more efficient strategy can be chosen for designing further libraries of materials.

The oxygen release properties of the different material candidates were studied by means of temperature-programmed desorption as this technique is generally known to be a powerful tool in deriving the respective information. However, a detailed kinetic study on solid systems characterized with a pronounced capacity for dissolving adsorbed species into the bulk—as this is the case for membrane materials—is complicated by a coupling of desorption phenomena and a successive replenishing of surface sites by the bulk lattice [58]. Furthermore, a complete quantitative analysis of the desorption spectra obtained with the TAP reactor system is time consuming due to the extensive calibration needed. On the other hand, a direct qualitative (i.e., straightforward) interpretation of the obtained spectra is facilitated by the major advantage of short contact time and reduced pressure conditions, leading to a dramatically reduced re-adsorption probability. In turn, we have not attempted to deduce kinetic parameters from the respective spectra.

### 3. Conclusion

Facing the scepticism formulated sometimes against the combinatorial approach considered in a first approximation as essentially statistical, this paper illustrates by various case studies how high-throughput transient kinetics carried out in addition to high-throughput catalyst synthesis and testing both accelerate the search for new catalytic materials and bring fundamental insights into reaction mechanisms. Supporting the view of Boudard [59] that “without kinetic guidance, to go through a combinatorial campaign is to play dice with high technology,” we strongly believe that a fair evaluation of the successive generations of catalysts prepared by automated synthesis requires an advanced knowledge of kinetics applying to each tested material (at least the most performing ones). From the kinetic models derived from HT transient kinetics, the best operating conditions can be derived which will accelerate the scaling up for the “hits” selected during the “primary screening.” In addition, all this knowledge on kinetics and mechanisms may easily be stored in databases and ease future catalyst discoveries in view of advanced data mining and expert system development. In summary, these developments help the combinatorial research in heterogeneous catalysis to become more and more mature, specifically as the initial simple approach to pick-up



hits by doing as many experiments as possible is currently replaced with a much more rational one which exploits a knowledge of fundamental principles using computer sciences and high-tech tools for a large information basis.

## Acknowledgments

The XRD service at IRC is fully acknowledged for high-throughput measurements. Part of this work was supported by the EC programmes “COMBICAT” (GRRD-CT 1999-00022) and “CERMOX” (G55RD-CT-2000-0035).

## References

- [1] J.R. Engstrom, H. Weinberg, *AIChE* 46 (2000) 2–5.
- [2] S. Senkan, K. Krantz, S. Ozturk, V. Zengin, I. Onal, *Angew. Chem. Int. Ed.* 38 (1999) 2794–2799.
- [3] P. Cohan, *Abstr. Pap. Am. Chem. Soc.* 221 (2001) BTEC-056.
- [4] I.E. Maxwell, *Nature* 394 (1998) 325–326.
- [5] W. Ehrfeld, H.J. Hartmann, V. Hessel, S. Kiesewalter, H. Lowe, in: *Micro Total Anal. Syst.* 2000, 4th Proc. mu.TAS Symp., 2000, pp. 33–40.
- [6] P. Cong, R.D. Doolen, Q. Fan, D.M. Giaquinta, S. Guan, E.W. McFarland, D.M. Poojary, K. Self, H.W. Turner, W.H. Weinberg, *Angew. Chem. Int. Ed.* 38 (1999) 484–488.
- [7] P. Cong, Y. Liu, R. Doolen, Q. Fan, D. Giaquinta, H. Weinberg, in: *Book of Abstracts, 218th ACS National Meeting, New Orleans (22–26 August 1999)*, 1999, CATL-001.
- [8] I.M. Dahl, A. Karlsson, D.E. Akporiaye, B.K.M. Vanden, G.P. Towler, R. Wendelbo, *Eur. Pat. Appl.*, Uop Llc, USA, Ep, 2001, p. 12.
- [9] W.F. Maier, *Angew. Chem. Int. Ed.* 38 (1999) 1216–1218.
- [10] F. Schuth, C. Hoffmann, A. Wolf, S. Schunk, W. Stichert, A. Brenner, *Comb. Chem.* (1999) 463–477.
- [11] O. Lavastre, *Actual. Chim.* (2000) 42–45.
- [12] U. Rodemerck, P. Ignaszewski, M. Lucas, P. Claus, *Chem. Eng. Technol.* 23 (2000) 413–416.
- [13] U. Rodemerck, D. Wolf, O.V. Buyevskaya, P. Claus, S. Senkan, M. Baerns, *Chem. Eng. J. Special Issue SI 82 (1–3)* (2001) 3–11.
- [14] A. Holzwarth, P. Denton, H. Zanthoff, C. Mirodatos, *Catal. Today* 67 (2001) 309–318.
- [15] D. Wolf, O.V. Buyevskaya, M. Baerns, *Appl. Catal. A* 200 (2000) 63–77.
- [16] D. Farrusseng, L. Baumes, C. Hayaud, I. Vauthey, P. Denton, C. Mirodatos, in: E. Derouane, et al. (Eds.), *Principles and Methods for Accelerated Catalyst Design*, in: NATO Science Series, Kluwer Academic, Amsterdam, 2002, pp. 469–479.
- [17] J. Perez-Ramirez, R.J. Berger, G. Mul, F. Kapteijn, J.A. Moulijn, *Catal. Today* 60 (2000) 93–109.
- [18] D. Wolf, *Catal. Lett.* 27 (1994) 207.
- [19] C. Mirodatos, *Catal. Today* 9 (1991) 83.
- [20] J.T. Gleaves, J.R. Ebner, T.C. Kuechler, *Catal. Rev.–Sci. Eng.* 30 (1988) 49.
- [21] G.F. Froment, et al. (Eds.), *Studies in Surface Science and Catalysis*, Vol. 109, Elsevier, Amsterdam, 1997.
- [22] G.B. Marin, R.A. van Santen (Eds.), *Appl. Catal.* (1997) 160.
- [23] M. Rothaemel, M. Baerns, *Ind. Eng. Chem. Res.* 35 (1996) 1556–1565.
- [24] Y. Schuurman, C. Mirodatos, *Appl. Catal.* 151 (1997) 305–331.
- [25] C. Mirodatos, in: A. Parmaliana, et al. (Eds.), *Natural Gas Conversion V*, in: *Studies in Surface Science and Catalysis*, Vol. 119, Elsevier, Amsterdam, 1998, pp. 99–106.
- [26] Y. Schuurman, A. Pantazidis, C. Mirodatos, *Chem. Eng. Sci.* 54 (1999) 3619–3625.
- [27] O. Hinrichsen, A.C. van Veen, H.W. Zanthoff, M. Muhler, in: J.F. Haw (Ed.), *In-Situ Spectroscopy in Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2002, pp. 237–269.
- [28] Y. Schuurman, A. Pantazidis, C. Mirodatos, *Chem. Eng. Sci.* 54 (1999) 3619–3625.
- [29] O.P. Keipert, M. Baerns, *Chem. Eng. Sci.* 53 (1998) 3623–3634.
- [30] V. Fierro, Y. Schuurman, C. Mirodatos, J.L. Duplan, J. Verstraete, *Chem. Eng. J.* (2002), in press.
- [31] W.O. Haag, R.M. Dessau, in: *Proceedings, 8th International Congress on Catalysis*, Vol. 2, Berlin (1984), Chemie, Weinheim, 1984, p. 305.
- [32] A. Corma, J. Planelles, J. Sanchez-Marin, F. Tomas, *J. Catal.* 93 (1985) 30.
- [33] E.A. Lombardo, W.K. Hall, *J. Catal.* 112 (1988) 494.
- [34] Y. Zhao, G.R. Bamwenda, B.W. Wojciechowski, *J. Catal.* 142 (1993) 465.
- [35] G. Yaluris, J.E. Rekoske, R.J. Aparicio, R.J. Madon, J.A. Dumesic, *J. Catal.* 153 (1995) 54.
- [36] H. Stach, U. Lohse, H. Thamm, W. Schirmer, *Zeolites* 6 (1986) 74–90.
- [37] T.A. Nijhuis, L.P.J.v.d. Broeke, J.M.v.d. Graaf, F. Kapteijn, M. Makkee, J.A. Moulijn, *Chem. Eng. Sci.* 54 (1999) 4423.
- [38] P. Ciavarella, PhD thesis, University C. Bernard, 1999.
- [39] W. Zhu, J.M.v.d. Graaf, L.J.P.v.d. Broeke, F. Kapteijn, J.A. Moulijn, *Ind. Eng. Chem. Res.* 37 (1998) 1934–1942.
- [40] J.A. Dalmon, in: *Handbook of Heterogeneous Catalysis*, Vol. 3, 1997, pp. 1387–1398.
- [41] A. Julbe, D. Farrusseng, J.C. Jalibert, C. Mirodatos, C. Guizard, *Catal. Today* 56 (2000) 199–209.
- [42] H.M. Zhang, Y. Shimizu, Y. Teraoka, N. Miura, N. Yamazoe, *J. Catal.* 121 (1990) 432–440.
- [43] Y. Teraoka, H.M. Zhang, S. Furukawa, N. Yamazoe, *Chem. Lett.* (1985) 1743–1746.
- [44] J.E. ten Elshof, H.J.M. Bouwmeester, *Solid State Ionics* 99 (1997) 15–22.
- [45] Z. Shao, H. Dong, G. Xiong, Y. Cong, W. Yang, *J. Membr. Sci.* 183 (2001) 181–192.
- [46] Z. Shao, G. Xiong, Y. Cong, W. Yang, *J. Membr. Sci.* 164 (2000) 167–176.
- [47] Z. Shao, W. Yang, Y. Cong, H. Dong, J. Tong, G. Xiong, *J. Membr. Sci.* 172 (2000) 177–188.
- [48] J. Han, Y. Zeng, Y.S. Lin, *J. Membr. Sci.* 132 (1997) 235–243.
- [49] F. Krok, W. Bogusz, P. Kurek, M. Wasiucionek, W. Jakubowski, J.R. Dygas, *Mater. Sci. Eng.* (1993) 70–76.
- [50] S. Lazure, C. Vernochet, R.N. Vannier, G. Nowogrocki, G. Mairesse, *Solid State Ionics* 90 (1996) 117–123.
- [51] L. Qui, Y.L. Yang, A.J. Jacobson, *J. Mater. Chem.* 7 (1997) 249–253.
- [52] C. Vernochet, R.N. Vannier, M. Huvé, C. Pirovano, G. Nowogrocki, G. Mairesse, G.V. Tendeloo, *J. Mater. Sci.* 10 (2000) 2811–2817.
- [53] N. Ramadass, *Mater. Sci. Eng.* 36 (1978) 231–239.
- [54] A.C. van Veen, Z.P. Shao, D. Farrusseng, C. Mirodatos, *Separation and Purification Technology*, 2002, submitted.
- [55] A.C. van Veen, D. Farrusseng, C. Mirodatos, *Desalination* 146 (2002) 41–47.
- [56] A.C. van Veen, Verlag dissertation.de, Berlin, 2001, ISBN 3-89825-213-2 [in German].
- [57] M. Caracotsios, W.E. Stewart, *Comput. Chem. Eng.* 19 (1995) 1019–1030.
- [58] M. Mavrikakis, J.W. Schwank, J.L. Gland, *J. Phys. Chem.* 100 (1996) 11389–11395.
- [59] M. Boudart, *Catal. Lett.* 65 (2000) 1–3.