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High-throughput experimentation in catalyst testing and in kinetic studies for heterogeneous catalysis

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Abstract

Quantitative data in high-throughput experimentation are extremely important in the secondary development stage, comprising catalyst testing, kinetic studies, diagnostics, catalyst characterization (temperature programmed techniques), and stability tests. Even for systems that require long analysis times parallellization is worth application. The information from catalyst testing should be scalable. The reactor should be designed properly and the relevant criteria should be adhered to. The test reactor is not per se a scaled down version of the associated commercial reactor but in specific cases, e.g. riser technology the so-called Dinky Toy approach is appropriate. For structured reactors the scaled down version really simulates the commercial unit. Here, the Dinky Toy approach could well be the best. This is in particular attractive for the pharmaceutical industry.

Parallellization is the logical approach in catalyst testing, but single units will survive, however, where the reactor operation is too complex or when one of the aims is to produce semi-commercial amounts of products.

Analysis is crucial in design of parallel testing units. GC is the benchmark in quantitative studies, but other techniques should also be taken into consideration. This holds in particular for optical techniques, that offer the potential of fast and in situ analysis.

In catalyst testing in a packed bed it is usually advisable to dilute the catalyst bed. It is crucial to carry out the dilution such that a well-mixed bed is created. Even for a homogeneously mixed bed dilution should not be exaggerated and for gas systems the proposed criterion should be adhered to. This bed dilution case study shows the advantage of parallellization for situations where a highly quantitative comparison between different samples is required.

Keywords: High-throughput experimentation; Catalyst testing; Six-flow reactor; Bed dilution; Dinky Toy approach; Parallel testing

1. Introduction

Development and improvement of catalysts is essential in creating a sustainable society. A catalyst allows an efficient pathway to the desired products. In general, a complex network of elementary steps will be followed and it is not surprising that essentially a different optimal catalyst system is associated with any specific reaction. Fortunately, a vast amount of work has been performed and the library is *the* primary source of information. Nevertheless, for an optimal catalyst experimental (and computational) work is still essential; theory is still insufficient to predict the ideal catalyst for a specific reaction. The scheme in Fig. 1 summarizes the course of catalyst development [1]. The start will be of a rather qualitative nature. Several catalyst formulations will be

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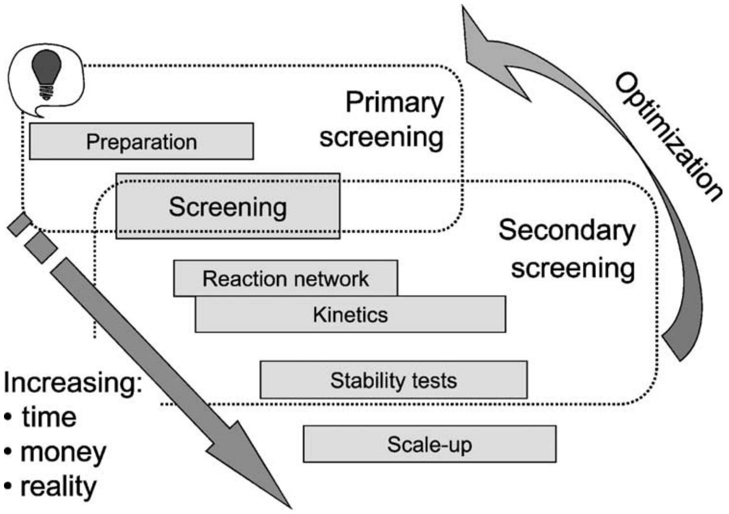

Fig. 1. Stages in the course of a catalyst development program.

tested. This should not be done in a completely random way but the open literature and patents will give the required inspiration. Discoveries of lead catalysts are aimed for. In general it is best to focus more on large numbers than on quantitative quality. Thorough catalyst characterization is not performed in this stage. After selection of the lead catalysts more quantitative information is needed. In this stage, that we called earlier secondary screening [1], the experimental procedures are quite different. In this stage catalysts will be more fully characterized and the ultimate description of the performance might be aimed at, viz. the kinetic model including terms for the catalyst decay.

In this paper catalyst testing will be treated from a chemical engineering point of view. First a general analysis will be presented of the reactors that are suitable for testing of solid catalysts. It will be shown that in the past scaling-down and automization have enabled considerable reduction in manpower needed and have led to a large increase in productivity. The recent trend of increased parallellization can be considered as a quantum jump in the quest for high productivity in research and development in heterogeneous catalysis. The benefit of parallellization will be illustrated with examples. One of the examples is the demonstration of the importance of good dilution procedures in catalyst testing. Parallellization enabled to establish a reliable novel criterion for gas phase systems. Also cases are indicated where parallellization is not applicable. Additionally, the potential of in situ monitoring is demonstrated.

2. Reactor selection

Reactor selection is ‘core business’ in chemical engineering. It is instructive to start from the selection of the reactor in chemicals production. In practice a large variety of types are used. More or less rational selection procedures have been developed [2]. A useful set of criteria is:

- high productivity and selectivity;
- high efficiency;
- high safety;
- high reliability; and
- low costs.

These criteria often lead to contradicting requirements. For instance, in a packed bed the particle size should be small from the point of view of high productivity and selectivity. However, the smaller the particle size the higher the pressure drop and, consequently, the lower the efficiency. Although fixed bed and slurry reactors are most commonly used, often they are not the best choice when starting from these criteria. Structured reactors often are to be preferred,

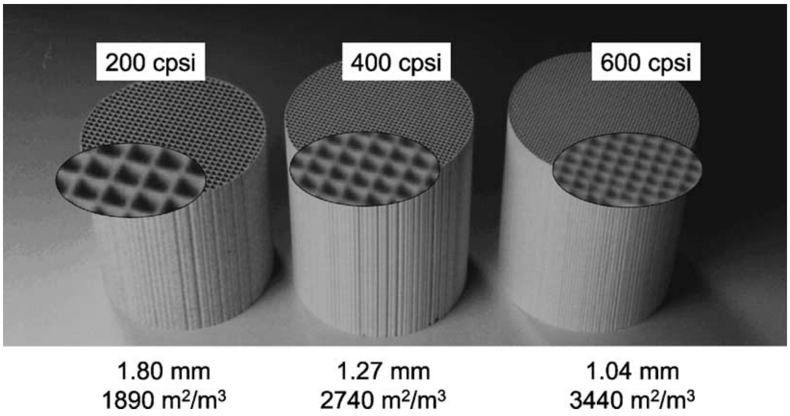

Fig. 2. . Examples of cordierite monolith structures of different cell density (cells per square inch, cpsi). Indicated are the channel size and geometric surface area.

both for single-phase and for multiphase reaction systems [3]. It is also fair to refer to reality: in practice, the criterion of *proven technology* plays a large role. It is understandable that companies hesitate being the first in a field and, consequently, a frustrating conservatism is present.

In catalyst testing the objective is the collection of information. Criteria in design are:

- delivering scalable information;
- high productivity;
- safety; and
- low costs.

These criteria lead to scaling-down rather than scaling-up as in reactors for production. Scaling-down results in lower costs of equipment, infrastructure, materials and utilities. Also safety is improved and toxicity is less of a problem. Automization results in higher productivity and higher reliability of the data produced. In particular for multi-phase systems well-defined fluid catalyst contact is essential.

In a sense the situation is analogous to reactors for production. Structured reactors often meet the criteria best, but because of their convenience fixed bed and slurry reactors are the workhorses. Nevertheless, it is to be expected that conservatism is not that important here, because of lower risks.

The information to be produced should be *intrinsic*, that means it should be independent of the reactor applied. As the information is used in scale-up this can be summarized by stating that it should be scalable. Also the analysis is very important; therefore the options for analysis should be kept in mind at or even integrated with the design of the reactor.

In catalyst testing often it is decided to take the same reactor type for testing as for the real production plant. So, for a fluid bed process a laboratory-scale fluid bed reactor is chosen. In general this is not a good reasoning. Laboratory-scale fluid bed reactors are usually not able to give scalable information. It is better to derive a kinetic model in a well-defined laboratory reactor of the design dedicated for kinetic studies. By applying an adequate model for scaling-up the information can then be used for design. This is well appreciated in the chemical engineering community. It has been summarized by stating that a ‘Dinky Toy’[2] approach is not clever [4]. However, in particular for structured reactors this axiom has lost its value. The most applied representative of structured reactors is the monolithic reactor [3]. Fig. 2 shows three monoliths with realistic cell sizes. A single channel of which the walls are covered with catalyst is the best laboratory reactor for giving information to be used in the design of a monolithic reactor. This can be coated in similar way as for full sized monoliths [5]. Such a channel is the perfect copy of the large-scale reactor and, consequently, it is a Dinky Toy approach.

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[2] Dinky Toy refers to the small, scaled-down replica’s of predominantly real vehicles, which were popular as a toy in the 1950s and 1960s of the previous century, the period in which more attention was being paid to good testing practice in catalysis.

Also in specific classical cases a Dinky Toy approach can be appropriate. An example will be given for FCC, where the catalyst is used in a riser configuration. Dependent on the type of information sought, a riser reactor may be the preferred testing reactor.

2.1. *The packed bed reactor*

The packed bed probably is most used in catalyst testing. It is very convenient. Nevertheless, care has to be taken to guarantee that the bed is designed well so that scalable information is acquired. The dimensions of the particles and bed should be such that on the scale of particle concentration and on the scale of particle and reactor temperature gradients are absent. Furthermore, the particles should be in good contact with the fluid and plug flow behavior should prevail [1,6,7]. For monolithic reactors dedicated designs are used in multiphase systems. The so-called screw impeller stirred reactor (SISR) and the turbine reactor give satisfactory results [8,9].

2.2. *The slurry reactor*

The slurry reactor is also commonly used. The major advantages are its flexibility and good temperature control. Disadvantages are the potential non-uniform distribution of the catalyst particles over the space of the reactor and the poor gas–liquid mass transfer. Moreover, large particles tend to exhibit attrition, while in the case of small particle the filtration for sampling may be awesome. Fig. 3 gives an example that might also be suited for parallelization [10]. Mixing is performed here by rotating a bent rod placed in a thin flexible tube that is positioned in the reactor like a thermocouple well. It can be used for small to medium reactor volumes (5–500 ml), while a feedthrough sealing is eliminated.

2.3. *Lab-scale riser reactor*

FCC catalyst performance testing is a well-known challenge. Usually, fixed bed technology is used (e.g. ‘MAT-test’). However, the time scale of a fixed bed reactor is not right. Extensive coke deposition takes place in the millisecond region, and, as a consequence, steep coke profiles are present in the bed. It is to be expected that the information gathered is not suitable for using for simulation of a riser reactor. A testing reactor was designed with the aim of generating scalable information. A riser reactor appeared to be a good choice [11,12]. Fig. 4 shows the scheme.

The reactor is a once-through laboratory-scale entrained flow reactor with variable length, isothermal and ideal plug flow for both catalyst and gases. The length can be varied from 0.2 to 20 m. The residence time can be varied from the millisecond region to several seconds. It was confirmed that coke deposition takes place in the millisecond scale without affecting the reactivity of the catalyst significantly.

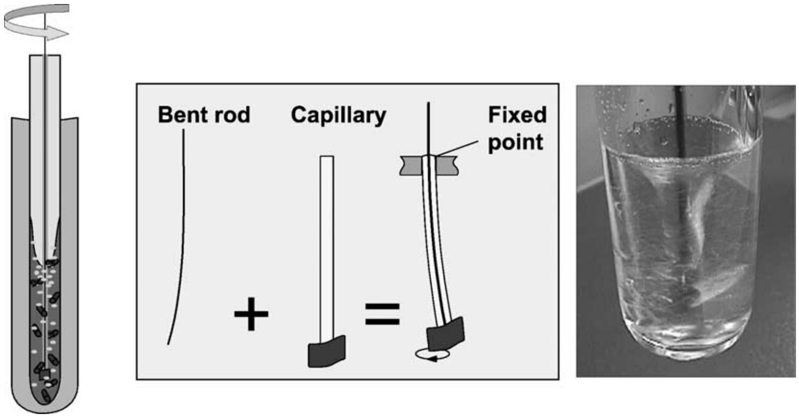


Fig. 3. The swinging capillary microautoclave [10].

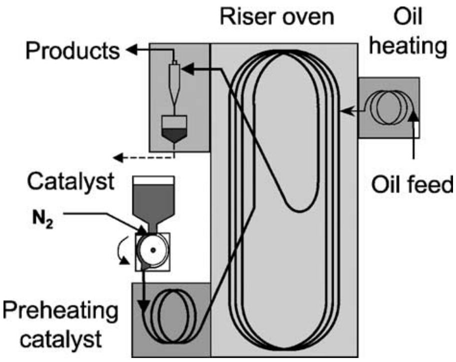


Fig. 4. Schematic of the lab-scale riser reactor [11,12].

Activity and coke formation are not related very much. Moreover, an important issue could be resolved. In practice, a maximum in gasoline production (as function of conversion) is observed. In principle this could be due to non-ideal behavior of the commercial plants but this could also have a kinetic origin. Fig. 5 summarizes some experimental results [12].

The gasoline yield does not go through a maximum up to 95% conversion levels. This result was further supported by separate experiments that showed gasoline to be a stable product under reaction conditions. The maximum in the gasoline yield observed in practice is therefore due to non-ideality of the commercial equipment. In fact, it was concluded that the inlet section is the reason. So, here, the Dinky Toy approach is appropriate.

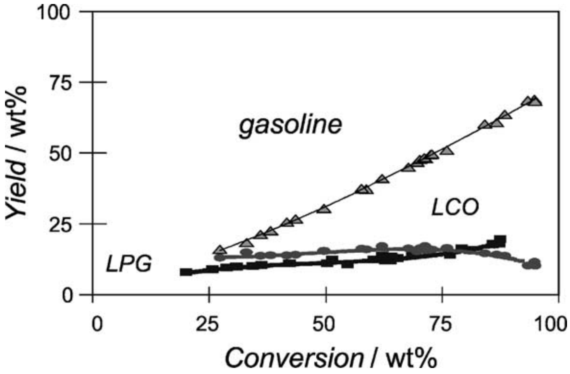


Fig. 5. Product yields in FCC of heavy cycle oil (HCO) in a laboratory riser reactor.

3. Parallellization

Sie published in 1996 an instructive figure (Fig. 6) showing the historical trend towards scaling-down and automation [4].

In the 1960s every reactor required full time human attention. In the 1970s and 1980s obvious benefit came from scaling-down and subsequently automation. For further progress a new paradigm was needed. Parallellization appeared to be the answer. However, ... is this really new? Since the early days of industrial catalyst developments test rigs have been used in parallel for screening series of new catalysts, the prime example given by the ammonia synthesis catalyst development efforts [13]. In fact, parallellization has been applied in many industrial and university laboratories for catalyst testing in the 1970s and 1980s in the currently well-known form of parallel reactors in on rig. As it was felt that it was that self-evident, it was not always explicitly published in the open literature. In the open literature already in 1980 we described a six-flow reactor set-up that contained six reactors operating at identical conditions by dividing the feed in six equal flows with passive restrictors [14]. Later followed by Australian work [15]. To avoid any risk in mal-distribution over the six reactors mass flow and back-pressure controllers were applied later. The work was not limited to catalyst testing, but also characterization by temperature programmed reduction (TPR) in CO was done in a six-flow reactor set-up [16]. So,

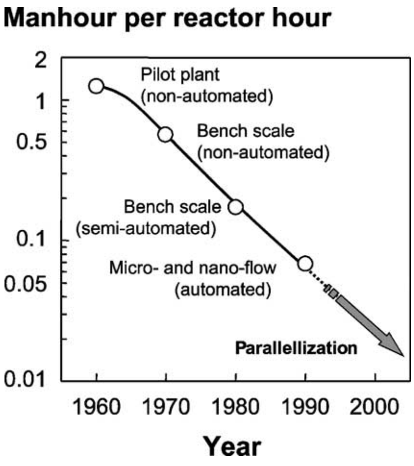


Fig. 6. Manpower needed in catalyst development, after Sie [4].

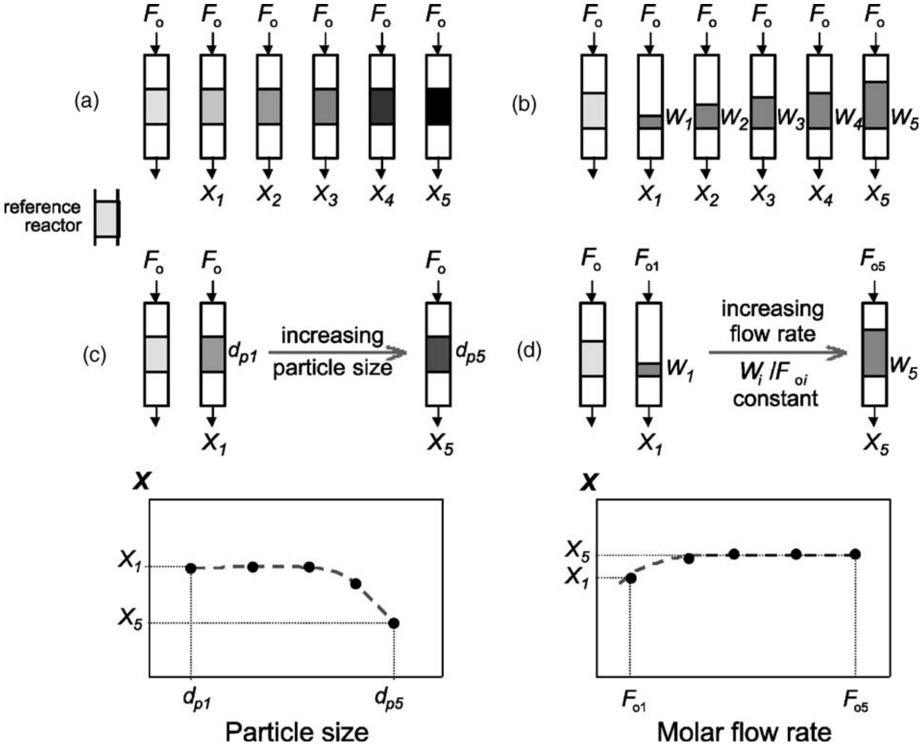


Fig. 7. Applications of parallel reactor systems: (a) comparing different catalysts; (b) kinetic studies; (c) and (d) diagnostic experiments for tests of intraparticle and extraparticle limitations, respectively.

in a sense the development of parallel testing is evolutionary rather than revolutionary. This evolution from parallel test rigs to a single set-up with parallel reactors and further miniaturization was enabled by the development of new and better experimental methods and techniques to control gas supply, fast analyses and computerization. Recent patent claims on this type of test rigs mainly describe the ideas behind old practice, and which have been described before in open literature.

Parallel reactor systems can be used for various purposes in catalyst development [1,17–23]. Fig. 7 gives two examples to check for mass transport interference in catalyst testing. Loading the different reactors with similar amounts of catalysts of different particle size will yield information about the absence or presence of intraparticle diffusion limitations. Loading different amounts and feeding with different flows such that the space time W_i/F_{0i} for each reactor i is the same, may reveal external mass transfer problems.

This figure is not exhaustive. Essentially all steps in catalyst development can benefit from parallel reactor set-ups. For instance, stability can be measured and from different loadings the deactivation as function of the bed length can be monitored. When the reactors are fed independently, many more possibilities exist. For instance, stability as function of feed composition can be measured directly. The flavor of the applications will be given from some examples. It will be shown that this technology is convenient and flexible, and that high-quality data are generated.

3.1. *Examples parallel reactor systems*

In our group a standard six-flow reactor set-up has been developed [1,6]. Fig. 8 gives a simplified flow scheme used for environmental catalysis research.

Except for the temperature and the composition, the pressure and space velocity can be separately controlled in each reactor. This gives a high flexibility in

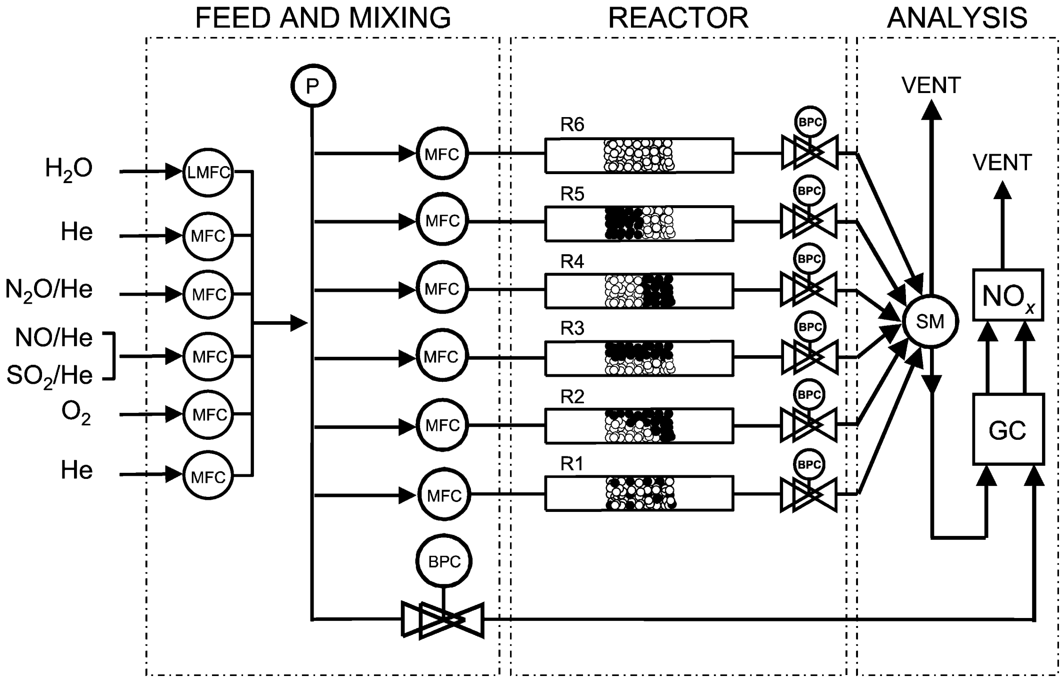


Fig. 8. Example of a six-flow reactor set-up scheme for environmental catalysis investigations.

the experiments. Of course, it is possible to construct a set-up in which the temperature and gas composition can be controlled individually, but that (i) would add to the costs and (ii) would not have much benefit in practice. However, in the future when controlling devices will be further scaled down at reduced costs by designing integrated multi-channel control units, probably it would make sense to go further with individually controlled reactor conditions. The present equipment gives quite reproducible data even with different operators and catalyst preparations, as is presented in Fig. 9. A typical example of catalyst screening in N_2O decomposition gives Fig. 10. In this set-up a chemiluminiscence detector was used for the effect of NO and NO_2 on the reaction [24].

The technology gives quickly reliable data. Similar equipment is in use by others, e.g. Synetix [8]. Commercial rigs are available at the market nowadays for various purposes. It is stressed here that using a reference reactor is crucial to derive good activity and especially kinetic data, accounting for homogeneous reaction contributions (e.g. homogeneous N_2O decomposition, gas phase equilibrium NO–NO_2) and the contribution due to reactor walls, catalyst support or ‘inert’ diluents.

In the design of every multi-reactor set-up a decision has to be made with respect to the number of reactors. Should it be 2, 4, 6, 12, ...? One of the crucial aspects is the time every analysis takes in relation with catalyst stability. In a study of Fischer–Tropsch synthesis we developed an analysis train that takes 45 min. Needless to say that this number poses a limit to the number of reactors to be used in parallel. Still in this case it is attractive to run in this mode in view of the time gain. The FT catalyst needs a relatively long time to stabilize, usually a couple of days, and an experimental set-up also needs a relatively long time to respond to changes in experimental settings due to the presence of long chain hydrocarbons that adsorb strongly at tubing walls, even when heat tracing is applied.

Additionally, this set-up allows a direct comparison of a fixed bed and a monolithic reactor by redirecting one of the six feed lines and placing them in parallel. It was demonstrated that the monolithic reactor outperforms the fixed bed reactor in terms of activity. It

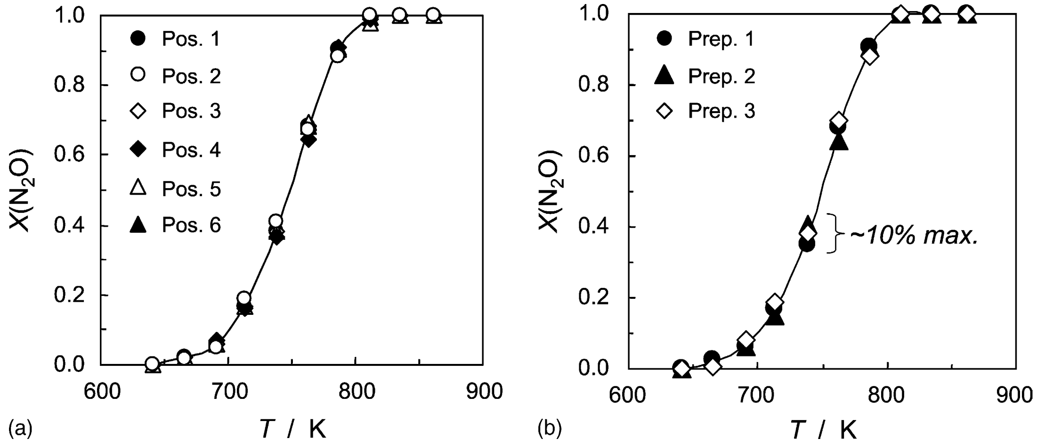


Fig. 9. Reproducibility studies in the six-flow reactor system. N_2O conversion vs. temperature over a Fe-ZSM-5 catalyst is presented: (a) the same catalyst sample with holder in the six positions (Pos.) of the six-reactor oven and (b) different catalyst sample bed preparations (Prep.) in the same position of the reactor oven. Conditions: 4.5 mbar N_2O in He; $P = 3$ bar; GHSV $= 60{,}000\,h^{-1}$. Conversions were calculated based on the analytical results using one of the reactors filled with SiC (reference material).

was also confirmed that the selectivity for alpha olefins was considerably different in the two types of reactors [25], thus parallel testing allows direct comparison of both reactor types.

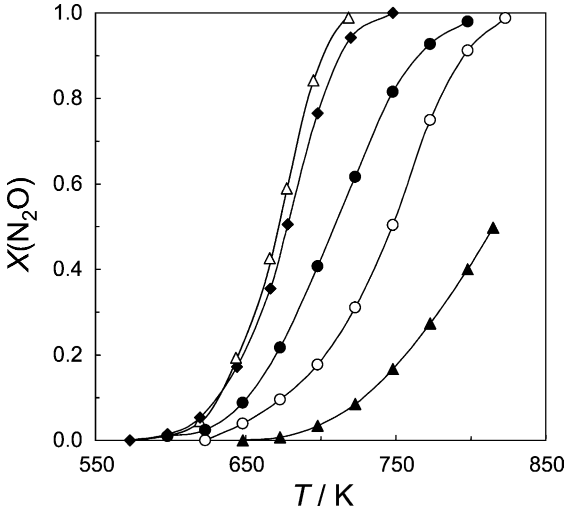
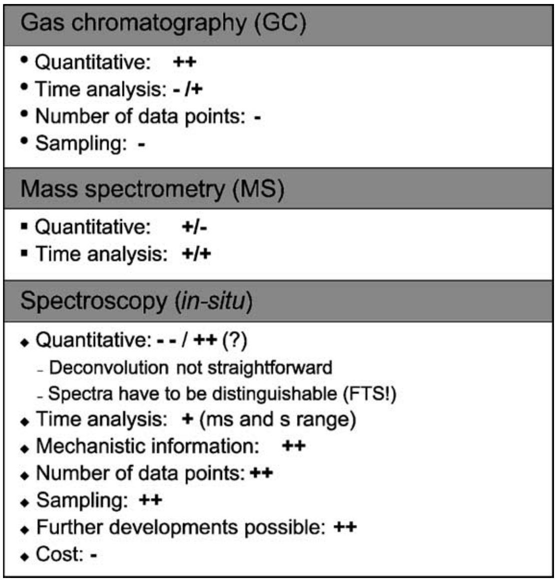


Fig. 10. Screening of Fe-ZSM-5 catalysts prepared by different recipes for direct N_2O decomposition: (◆) ex-framework method; (▲) calcined sample (before steaming); (○) solid ion-exchange; (●) liquid ion-exchange; and (△) sublimation. Conditions: 4.5 mbar N_2O in He; $P = 3$ bar; GHSV $= 36{,}000\,h^{-1}$. Details on catalyst preparation and testing can be found elsewhere [24,28,30].

3.2. *Analysis*

The analysis should be seen as an integrated part of the equipment. The big advantages of parallellization are high productivity and reliability. In the case of slow or unreliable analysis all advantages disappear. GC analysis is most commonly used in the quantification stage, although other techniques are applied as well. Fig. 11 summarizes the pros and cons of the three major analysis techniques: GC, mass spectrometry and vibrational spectroscopies (IR and UV-Vis).

GC is strong in being quantitative. In fact, it is generally used as benchmark for the other analysis techniques. Cons are that the analysis takes relatively much time and that the number of data generated is limited. This is especially a disadvantage in kinetic studies. Moreover, sampling is needed and in situ analysis is not possible. The disadvantage of the former is that the reaction mixture is disturbed and the sampling procedure leads to significant errors. Mass spectroscopy is very fast but limited as a quantitative tool, especially when larger molecules and isomers are involved. Vibrational spectroscopies are not yet fully developed. In particular, quantification is dependent on deconvolution of (often complex) spectra. Later it will be shown that they can be used in a highly quantitative manner. The time required for analysis is short and in situ analysis is well possible. Besides quantitative information



Gas chromatography (GC)

- Quantitative: ++
- Time analysis: - /+
- Number of data points: -
- Sampling: -

Mass spectrometry (MS)

- Quantitative: +/-
- Time analysis: +/+

Spectroscopy (*in-situ*)

- Quantitative: - - / ++ (?)
  - Deconvolution not straightforward
  - Spectra have to be distinguishable (FTS!)
- Time analysis: + (ms and s range)
- Mechanistic information: ++
- Number of data points: ++
- Sampling: ++
- Further developments possible: ++
- Cost: -

Fig. 11. Evaluation of the most common analysis techniques.

also mechanistic information (reaction intermediates) is generated. The number of data points is large. From this list it follows that spectroscopy is promising, to say the least. A limitation is that the spectra of reactants and products have to be distinguishable. For instance, for the Fischer–Tropsch synthesis example above it is of limited use.

3.3. Case studies

3.3.1. The in situ monitoring of the esterification of hexanoic acid and 1-octanol

In an atmospheric batch reactor provided with a reflux the esterification between hexanoic acid and 1-octanol was monitored by attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectroscopy. A typical sequence of spectra is given in Fig. 12, which shows the whole spectrum and the parts relevant for the reactants and products.

Apart from the water the three components of the reaction are well visible. Reactants disappear and the ester appears as function of the reaction time. The spectrum is dominated by the absorptions related to the solvent. Fortunately, deconvolution is that good that the contribution of the solvent can be fully corrected for.

To check if the data are quantitative, the results were compared with GC data. Fig. 13 shows the comparison. Clearly, the agreement is excellent. The technique is quantitative. It is believed that in situ IR will be of large importance for the success of parallel screening methods, both for primary and secondary screening. Especially when fiber optic ATR probes become less expensive and have less loss of signal due to absorbance of the fiber material, it can revolutionize the way catalysts are tested and in particular evaluation methods for deriving kinetic models will benefit from this technique.

Of course IR spectroscopy is not the only option, other optical methods include Raman, UV-Vis, fluorescence imaging, resonance-enhanced multiphoton imaging, photothermal deflection, etc. [26].

3.3.2. Evaluation of bed dilution for gas phase reactions by the HTE approach

Fixed bed reactors are commonly used in catalyst testing. Catalyst beds are often diluted in order to reduce temperature gradients on the scale of the reactor and to suppress potentially disturbing effects such as axial dispersion and bypassing. Often SiC is applied because it combines inertness and high heat conductivity. A priori, one might think that the higher the degree of dilution the better. However, this is not true. A high degree of bed dilution is not always favorable. It may reduce the conversion due to bypassing of the catalyst. The extent of the negative effect will depend on several factors, such as the amount of dilution, the conversion level, the reaction kinetics, the particle size and shape, the reactor geometry and the degree of segregation of catalyst and diluent. Dilution is associated with the disadvantage that bypassing can occur. In particular this should be expected for non-homogeneously packed beds. It was decided to check existing criteria and if needed to formulate better ones. In order to accurately measure the small differences in conversion due to the dilution high quality experimental data are needed. High-throughput experimentation showed the potential to generate such data.

The reaction selected was the catalytic decomposition of nitrous oxide:

$$2N_2O \rightarrow 2N_2 + O_2$$

The catalysts applied were based on Fe-ZSM-5 and a Co-La, Al mixed oxide. The kinetics is simple:

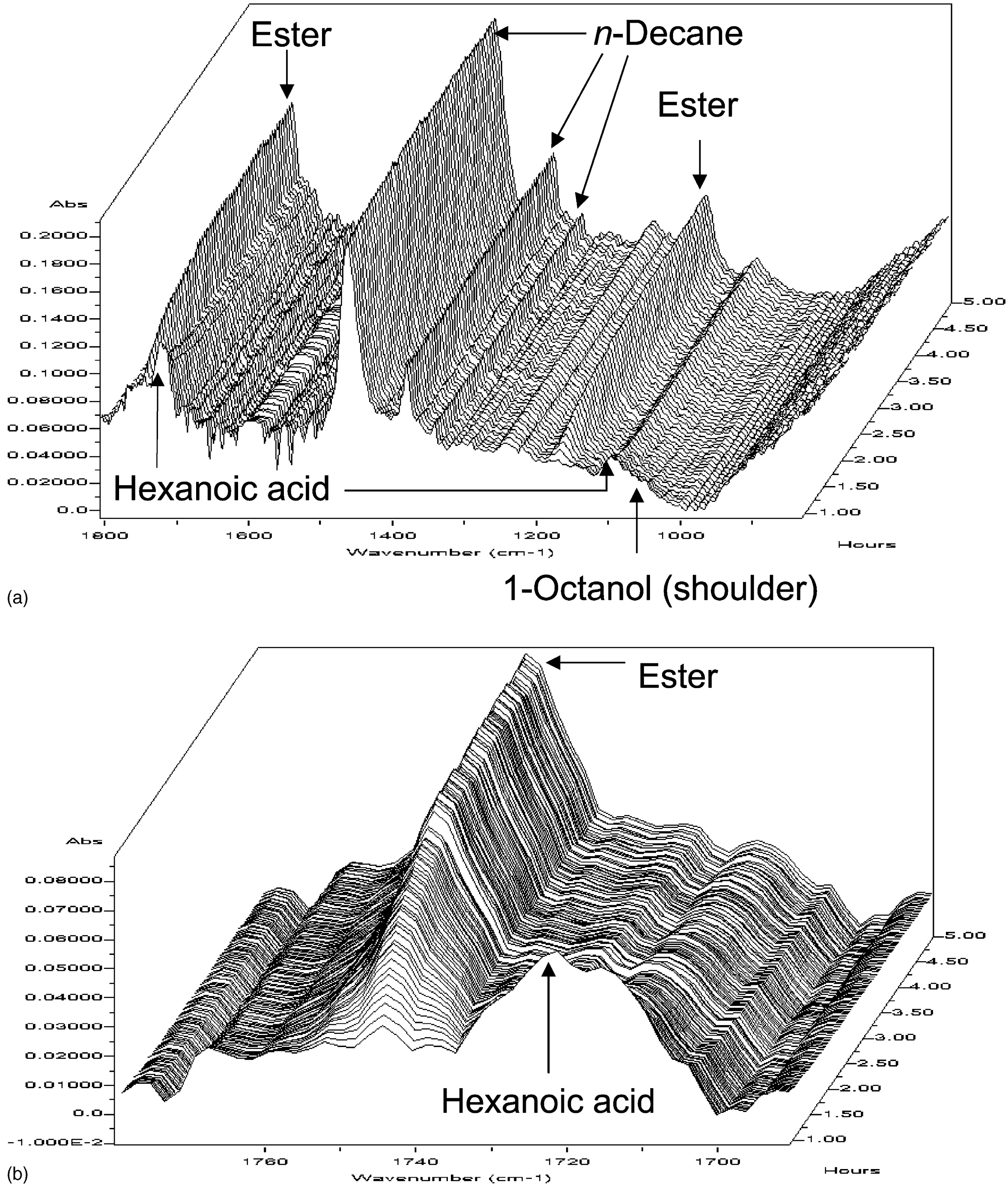


Fig. 12. Real time in situ monitoring of the reaction between hexanoic acid and 1-octanol: (a) complete spectrum; (b) 1780–1700 cm^{-1}; (c) after correction for the solvent contribution 1260–1000 cm^{-1}.

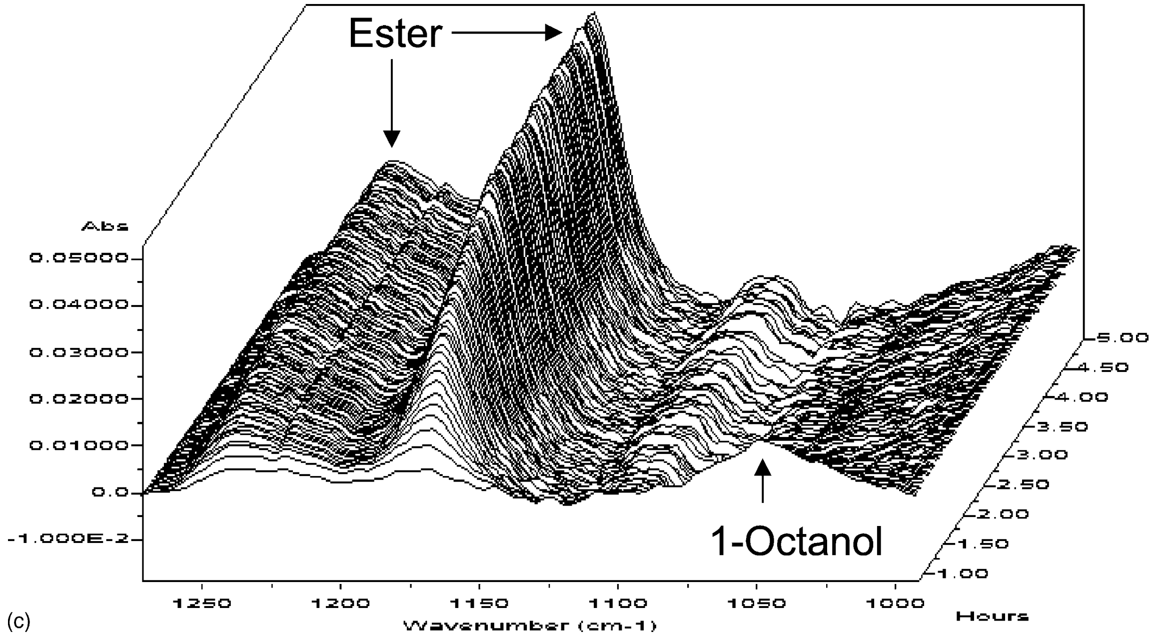


Fig. 12. (*Continued*).

first order, irreversible. Details are reported elsewhere [27–33].

The influence of the homogeneity of the bed and the degree of dilution in well-mixed beds were studied separately, experimentally as well as by simulation. The latter were carried out using a random particle distribution (RPD) model [34]. This model assumes plug flow throughout the reactor with superimposed axial and radial dispersion.

3.3.2.1. Non-homogeneous bed dilution. Non-homogeneous packing was studied by preparing different catalyst-diluent configurations [35]. Fig. 14 shows pictures of the eight diluted catalyst beds with

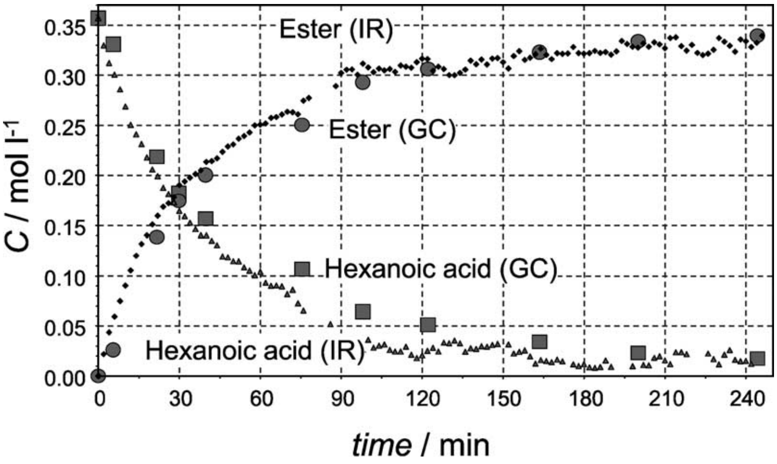


Fig. 13. Comparison of the in situ IR data with GC analysis for the esterification of Fig. 12.

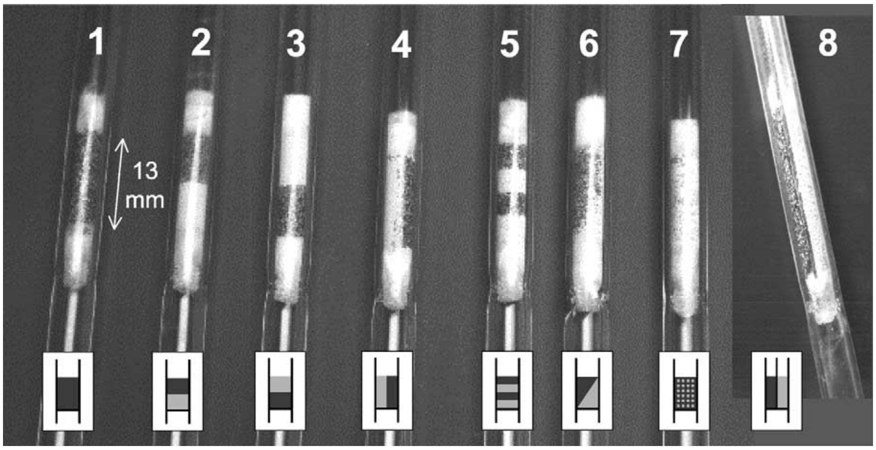


Fig. 14. Photographs of reactor loadings. The light grains are Fe-ZSM-5 catalyst particles, the dark grains SiC particles. The beds are kept between white quartz wool plugs and rest on a sintered quartz frit. The symbol used for each reactor loading is shown below its photograph.

different configuration of the mixing that were prepared. Fig. 15 gives the conversion results that were obtained as a function of temperature for the different configurations.

It is not surprising that the perfectly mixed bed (tube 7 in Fig. 14, open squares in Fig. 15) gives the highest conversion, while the poorest mixed bed, the bed with the thin divider (tube 8 in Fig. 14, solid squares in Fig. 15), gives the lowest conversion. The influence of the distribution of catalyst and inert in the catalyst bed on the temperature dependence is also clearly illustrated by the corresponding 'Arrhenius plots' (see Fig. 16). The apparent activation energies, calculated from the slopes of the curves, are shown in Fig. 17. It is clear that the apparent activation energy determined in the high temperature range is strongly dependent on the details of the packed bed. For non-homogeneous beds it can strongly diminish and even approach zero. This can lead to a wrong interpretation of the results and may explain the variance in reported values for

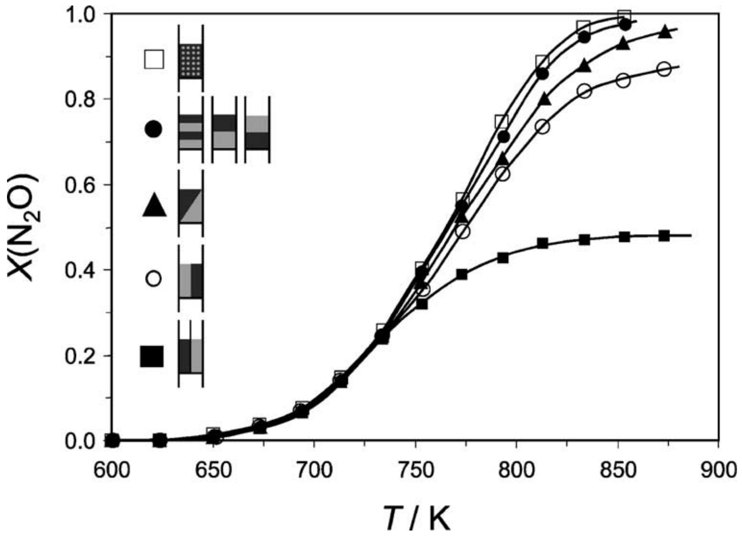


Fig. 15. N_2O conversion vs. temperature for different distributions of Fe-ZSM-5 (indicated in the schematic pictures with light gray) and SiC diluent (indicated dark gray). Conditions: $p(N_2O) = 1.55\,\text{mbar}$ in He; $P = 1.0\,\text{bar}$; $W_{cat} = 50\,\text{mg}$; $W_{cat}/F(N_2O)_0 = 8.65 \times 10^{-5}\,\text{g s mol}^{-1}$.

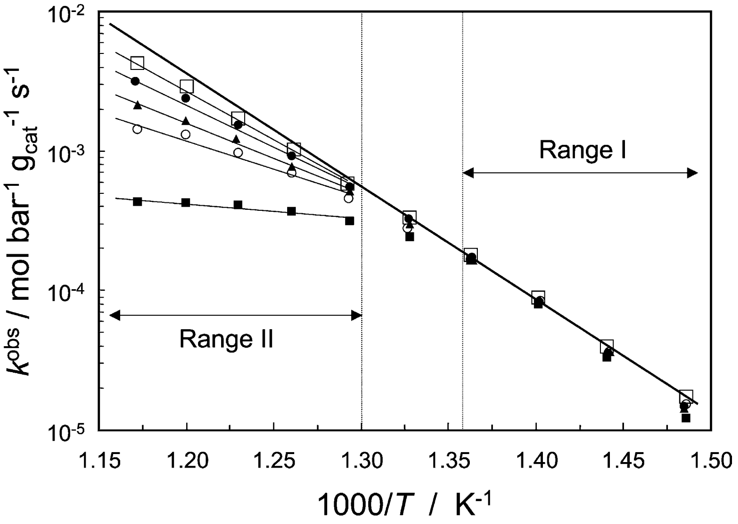


Fig. 16. Arrhenius plots obtained from the data shown in Fig. 15. The bold line represents the Arrhenius fit of the data obtained with the well-mixed bed (open squares); the slope corresponds with an apparent activation energy of 137 kJ mol^{-1} (key as in Fig. 15).

apparent activation energy values. Additionally, this effect may be confused with that caused by internal or external mass transfer limitations.

3.3.2.2. Homogeneous bed dilution. It may not be concluded, however, that achieving a homogeneous packing of the bed will eliminate all problems caused by dilution. Compared to an undiluted bed always some local bypassing on particle scale will always occur to some extent in a diluted bed, thus reducing the conversion for reaction orders higher than zero. The relative deviation in the observed conversion due to

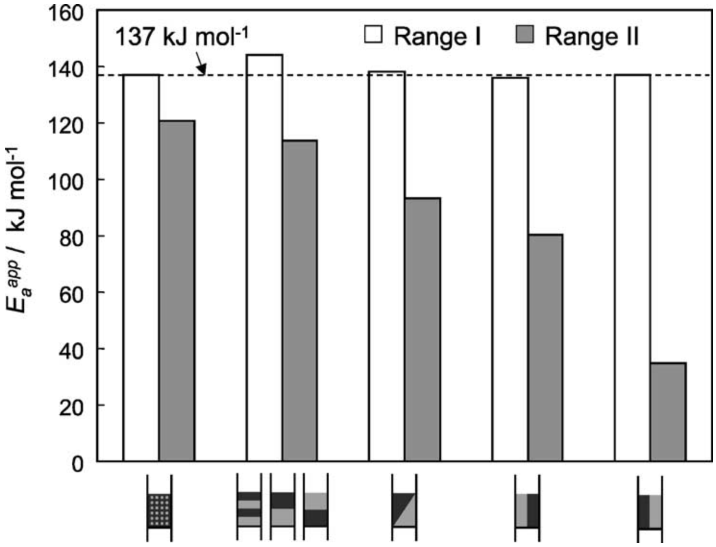


Fig. 17. Apparent activation energies (E_a^{app}) derived from Fig. 16. Ranges I and II are defined in Fig. 16. The dashed horizontal line corresponds with the apparent activation energy derived for the well-mixed bed in the low temperature region, i.e. 137 kJ mol^{-1}.

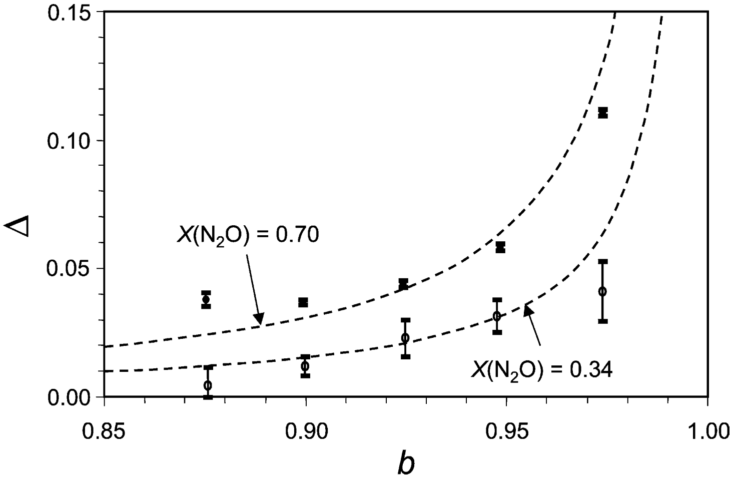


Fig. 18. Experimentally observed deviations in the N_2O conversion (Δ) due to the presence of inert bed diluent well-mixed with the catalyst at 700 K (conversion without dilution effect = 0.34) and 770 K (conversion without dilution effect = 0.70). Symbols represent experimental data and variance (lines Eq. (2)): Co-La; Al-ox catalyst; $p(N_2O) = 1.0$ mbar in He; $P = 2.5$ bar; $W_{cat} + W_{dil} = 400$ mg; $W_{cat}/F(N_2O)_0 = 5.58 \times 10^5\,g\,s\,mol^{-1}$.

dilution in homogeneously mixed beds, Δ, is defined as

$$\Delta \equiv \frac{x_{i,\mathrm{und}} - x_{i,\mathrm{dil}}}{x_{i,\mathrm{und}}} \tag{1}$$

where $x_{i,\mathrm{dil}}$ is the (fractional) conversion of a component i in the diluted bed, and $x_{i,\mathrm{und}}$ is the (fractional) conversion of component i in the undiluted bed.

The results of a large set of experiments using different amounts of dilution (with b varying from 0.875 to 0.975) and at two different total conversion levels are shown in Fig. 18. The dilution effect clearly increases with conversion and dilution.

The use of the six-flow reactor enabled us to perform the required experiments including several replicates in a reproducible way and in a reasonably short time. The resulting relatively small error bars allowed us to draw quantitative conclusions. The results were also modeled using the random particle model which finally resulted in the following expression for the dilution effect Δ [36]:

$$\Delta = \left(\frac{b}{1-b}\right)\left(\frac{d_\mathrm{p}}{h_\mathrm{bed}}\right)\frac{x_{i,\mathrm{dil}}}{2}n \tag{2}$$

where d_p is the particle diameter, b the dilution fraction (volume of inert material as fraction of total volume of solids), h_bed the height of the diluted bed, and n is the reaction order.

Fig. 18 shows that the results obtained with this expression describe the experimental results well and therefore it is generally recommended to use it to estimate the maximum amount of dilution to be used, i.e. by keeping $\Delta < 0.05$, the relative error as a consequence of applying dilution will be less than 5%.

It is thus very important to pack the diluted bed well and to avoid the combination of high dilution and high conversion levels.

4. Conclusions

In the development of new or improved catalysts the information from catalyst testing (secondary stage) should be scalable. The reactor should be designed properly and the relevant criteria should be adhered to. The test reactor is not per se a scaled down version of the associated commercial reactor but in specific cases, e.g. riser technology the so-called Dinky Toy approach is appropriate. For structured reactors the scaled down version really simulates the commercial unit. Here, the Dinky Toy approach could well be the best. This is in particular attractive for the pharmaceutical industry.

Parallellization is the logical approach in catalyst testing, to compare quantitatively various catalysts, characterize catalysts (temperature programmed techniques), perform kinetic studies or investigate catalyst stability. Single units will survive, however, where the reactor operation is too complex or when one of the aims is to produce semi-commercial amounts of products.

Analysis is crucial in design of parallel testing units. GC is the benchmark in quantitative studies, but other techniques should also be taken into consideration. This holds in particular for optical techniques.

In catalyst testing in a packed bed it is usually advisable to dilute the catalyst bed. It is crucial to carry out the dilution such that a well-mixed bed is created. Even for a homogeneously mixed bed dilution should not be exaggerated and for gas systems the criterion of Eq. (2) should be adhered to. This bed dilution study shows the advantage of parallellization for situations where a highly quantitative comparison between different samples is required.

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