

Catalyst performance testing: the influence of catalyst bed dilution on the conversion observed

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Abstract

A study was performed to investigate the influence of inert dilution on the conversion in a gas–solid laboratory micro-reactor for an irreversible reaction, viz. the catalyzed N_2O decomposition over two different catalysts: FeZSM-5 and Co-La, Al mixed oxide (denoted as Co-La Al-ox). Vertically and horizontally segregated beds, as well as mixed beds with different degrees of dilution were considered. The results showed that catalyst dilution should be applied with caution since it may significantly influence the conversion and lead to an erroneous interpretation of data from catalyst activity measurements and kinetic studies. If the catalyst and the diluting particles are not well-mixed, the conversion reduces significantly due to bypassing and axial dispersion. Also apparent activation energies are reduced. The effects are stronger at high conversion levels (>0.4).

Also over beds in which the catalyst and the diluent are perfectly mixed the conversion may be negatively affected by the dilution. It was found that the relative deviation in conversion caused by the dilution can be well estimated from observable parameters, i.e. the observed conversion, the volume fraction of bed dilution, the bed height, and the particle diameter. The relative deviation is approximately proportional to the reaction order. The combination of a high degree of dilution and high conversion should be avoided in catalyst activity measurements. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Catalyst testing; Bed dilution; Radial dispersion; Axial dispersion; Laboratory reactor; Kinetics; Modeling; Simulation; N_2O decomposition; Apparent activation energy

1. Introduction

Many activity measurements of heterogeneous catalysts are carried out in a fixed-bed reactor. Usually, the reactor is operated in the integral mode and the reactor model to describe the performance is based on plug-flow behavior. Gas-flown catalyst beds are often diluted with inert particles in order to improve the isothermicity of the bed and to suppress other potentially disturbing effects such as axial dispersion and bypassing. Low-surface-area materials such as glass, quartz, α -alumina, and especially silicon carbide (SiC) are preferred as dilution because of their relative inertness and good heat transfer properties. It should be noted that bed dilution does not primarily reduce the temperature gradients around the catalyst particles, but only the temperature gradients on reactor scale; i.e. the radial and axial temperature gradients in the packed bed, which are generally the largest. If the aim is to determine intrinsic kinetics, it is in any case recommended to perform a complete check

concerning mass and heat transport limitations. There is extensive literature related to this subject, see e.g. [1,2].

Inert bed dilution is now increasingly applied by many researchers [3–5], and the increasing use of parallel catalyst testing units [5] may even further enhance this. Dilution of a bed consisting of complete catalyst bodies with fine inert particles is also applied in laboratory gas–liquid–solid trickle-bed reactors but for different reasons: to increase catalyst wetting and liquid hold-up and to suppress axial dispersion and wall-effects [6–8].

However, bed dilution may also negatively influence the reactant conversion due to local bypassing of the catalyst. The extent of the negative effect depends on the amount of dilution, the reaction kinetics, the particle and reactor geometry, and the degree of segregation of catalyst and diluent. A simple example, taken from van den Bleek et al. [9] demonstrates the negative effect of bed dilution on the conversion. A first-order irreversible reaction is carried out in three fixed beds with identical total amounts of catalyst and dilution but with a different distribution, as shown in Fig. 1. If plug-flow behavior is assumed, the conversions x_1 , x_2 , and x_3 can be calculated as follows (the notation and symbols are explained in Nomenclature) and the results are shown

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Nomenclature

| | |
|------------------|--|
| A | area of peaks in GC analysis |
| b | dilution factor (volume of inert material as fraction of total volume of solids) ($m_{\text{dil}}^3 m_{\text{dil+cat}}^{-3}$) |
| B_o | Bodenstein number |
| C | concentration (mol m^{-3}) |
| d | size or diameter (m) |
| D | dispersion coefficient ($\text{m}^2 \text{s}^{-1}$) |
| D_m | bulk molecular diffusivity ($\text{m}^2 \text{s}^{-1}$) |
| E_a | activation energy ($\text{J mol}^{-1} \text{K}^{-1}$) |
| F_i | molar flow of component i (mol s^{-1}) |
| h_{bed} | height of the diluted bed (m) |
| k | rate coefficient ($\text{mol bar}^{-1} \text{g}^{-1} \text{s}^{-1}$) (in Eq. (1): $\text{m}^3 \text{g}^{-1} \text{s}^{-1}$) |
| m | turbulence factor (Eq. (9b)) |
| n | reaction order |
| p_i | partial pressure of reactant i (bar) |
| P | total pressure (bar) |
| Re_p | particle Reynolds number |
| T | temperature (K) |
| u | superficial gas velocity at reaction conditions (m s^{-1}) |
| W_{cat} | catalyst weight (g_{cat}) |
| x_i | (fractional) conversion of component i |

Greek

| | |
|---------------------|--|
| Δ | deviation of the conversion due to the dilution (see Eq. (2)) |
| ε | porosity |
| ρ | density (kg m^{-3}) |
| τ | space time ($W_{\text{cat}}/F_{\text{N}_2\text{O},0}$) (g s mol^{-1}) |
| τ_{bed} | tortuosity of the bed |
| ϕ_r | volumetric flow at reactor inlet at 1 bar and 273 K (ml min^{-1}) |

Superscripts

| | |
|-----|------------------------------|
| app | apparent |
| obs | observed |
| rad | radial (in radial direction) |

Subscripts

| | |
|-----|------------------------------|
| a | activation |
| ax | axial (in axial direction) |
| bed | bed |
| cat | catalyst particle |
| dil | diluted bed |
| p | particle |
| r | reactor |
| und | undiluted bed |
| 0 | reactor feed (reactor inlet) |

graphically in Fig. 1.

$$\begin{aligned}
 x_1 &= 1 - \exp(-kC_0\tau); & x_2 &= 1 - 0.5[\exp(-2kC_0\tau) + 1]; \\
 x_3 &= 1 - 0.25 \left[\exp\left(-\frac{1}{2}kC_0\tau\right) + \exp(-kC_0\tau) \right. \\
 &\quad \left. + \exp(-2kC_0\tau) + \exp\left(-\frac{1}{2}kC_0\tau\right) \right]
 \end{aligned} \quad (1)$$

Conversion x_2 , which corresponds with the case that all dilution is located at one side of the reactor, is significantly less than if the dilution is more homogeneously distributed. A large amount of diluent tends to increase the inhomogeneity of the distribution and consequently the deviation. If the fractional conversion in the bed is low (i.e. less than approximately 0.15), however, the effect of dilution on the conversion is in absolute and also in relative sense much smaller.

If the catalyst and the diluent are well-mixed, the distribution of the diluent will be much less inhomogeneous than in the example and the effect on the conversion will be smaller. In fact x_1 and x_2 are the two extremes. If the reaction order is positive, the presence of diluent always decreases the conversion. This example shows that inert bed dilution does not lower the activity homogeneously throughout the bed. Catalyst particles keep their intrinsic activity, but they are dispersed in an inert surrounding, giving rise to a discrete particle problem, i.e. locally in the bed reaction takes place or not. Hence, catalyst-diluent particle distribution and radial bed transport seem to be important parameters.

If one intends to investigate well-mixed catalyst-diluent samples, the distribution of catalyst particles and inert particles that is obtained may be worse than expected. Besides insufficient attention to the mixing procedure, this may be due to a non-ideal behavior of the particles (e.g. particles which tend to agglomerate [10]) or non-equal size distributions or different shapes of the particles. Additionally, in particular when using a high inert bed dilution, the assumption of plug-flow behavior is often not allowed. Radial dispersion will decrease the concentration differences in radial direction and consequently increase the conversions x_2 and x_3 in the example given earlier. Axial dispersion may also influence the results. In a previous paper [11], we have investigated the influence of mixing of catalyst and diluent on macroscale on the conversion and the influence of radial and axial dispersion. The results were also used to estimate the radial and axial dispersion coefficient and the bed tortuosity at experimental conditions typically used in laboratory micro-fixed-bed-reactors.

Van den Bleek et al. [9] showed already in 1969 that the influence on the conversion as a consequence of applying dilution cannot be completely eliminated by perfect mixing of the catalyst and the diluent particles. They introduced the ‘dilution effect’ Δ as a relative measure of the deviation in the conversion:

$$\Delta \equiv \frac{x_{i,\text{und}} - x_{i,\text{dil}}}{x_{i,\text{und}}} \quad (2)$$

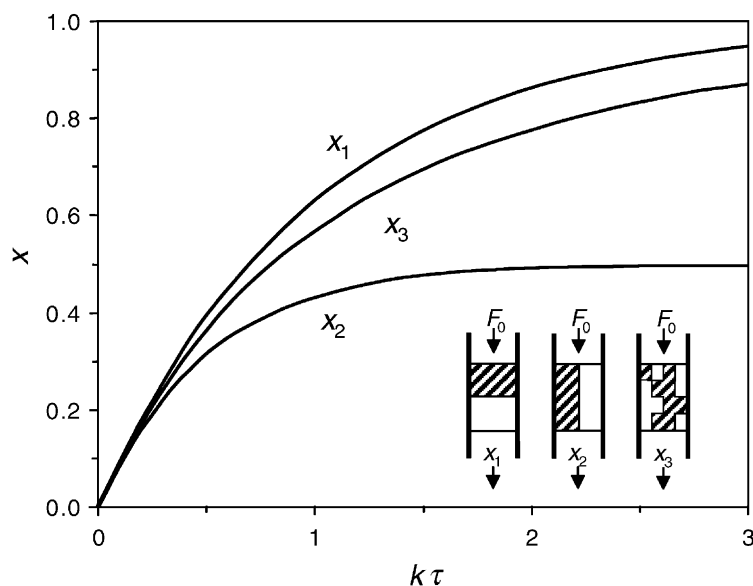


Fig. 1. Effect of different distributions of inert diluent in catalyst beds on the conversion for an irreversible first-order reaction.

The conversion in the undiluted bed ($x_{i,\text{und}}$) is in fact the conversion that would be obtained if the catalyst activity would be homogeneously distributed over the entire catalyst bed volume and if plug-flow behavior can be assumed.

In a second paper [12], we modeled the reactor performance using different randomly generated well-mixed catalyst/diluent distributions. The fractional deviation (Δ) of the conversion from ideal plug-flow behavior in gas–solid systems for an irreversible first-order reaction can be estimated from only observable parameters using:

$$\Delta = \left(\frac{b}{1-b} \right) \left(\frac{d_p}{h_{\text{bed}}} \right) \frac{x_{i,\text{dil}}}{2} \quad (3)$$

This paper gives a comprehensive overview of the influence of applying dilution on the conversion for single phase (apart from the solid catalyst) systems, which comprises the effect of distribution and the degree of dilution on the conversion. Additionally, the effect of the reaction order is considered.

2. Experimental

2.1. Catalysts

The effect of the catalyst distribution on the conversion was investigated experimentally by means of a first-order irreversible reaction, i.e. the catalytic decomposition of N_2O into N_2 and O_2 . Two catalytic systems were used: FeZSM-5 and Co-La Al-ox. FeZSM-5 was prepared by an ex-framework method and Co-La Al-ox was obtained from the thermal decomposition at 723 K of a hydrotalcite containing these metals. Details on the preparation and

characterization of the catalysts have been reported elsewhere [13,14]. Both catalysts show a high activity and a stable performance in N_2O decomposition in a wide range of temperatures [14–16]. All the characteristics of these catalytic systems are summarized in Table 1. The porosity (ε_p) of the particles was measured using mercury porosimetry and nitrogen physisorption. The bed porosity (ε_{bed}) of the

Table 1
Data on the catalysts, catalyst bed, and experimental conditions during the activity tests

| | Catalyst | |
|---|----------------------|--------------------------|
| | FeZSM-5 | Co-La Al-ox ^a |
| Catalyst bed | | |
| d_r (mm) (i.d.) | 4 | 4 |
| d_p (μm) | 125–200 ^b | 106–212 ^b |
| $\rho_{\text{cat,solid}}$ (kg m^{-3}) | 1780 | 5150 |
| ρ_{SiC} (kg m^{-3}) | 3200 | 3200 |
| ε_p | 0.3 | 0.68 |
| ρ_{cat} (kg m^{-3}) | 1246 | 1627 |
| ε_{bed} | 0.45 | 0.45 |
| W_{cat} (g _{cat}) | 50 | 5–25 |
| W_{SiC} (mg) | 150 | 375–395 |
| b (well-mixed case) | 0.54 | 0.875–0.975 |
| h_{bed} (mm) | 13 | 18 |
| Activity evaluation | | |
| T (K) | 600–875 | 700–770 |
| P (bar) | 1 | 2.5 |
| $p(\text{N}_2\text{O})$ (mbar) | 1.55 | 1 |
| ϕ_r (ml(STP) min^{-1}) | 50 | 30–150 |
| u (m s^{-1}) | 0.195 | 0.082–0.41 |
| Re_p | 0.051 | 0.07–0.35 |
| $W_{\text{cat}}/F_{\text{N}_2\text{O},0}$ (g s mol^{-1}) | 8.65×10^5 | 5.58×10^5 |

^a More details concerning this catalyst can be found elsewhere [14,15].

^b SiC of the same particle size range was introduced as diluent.

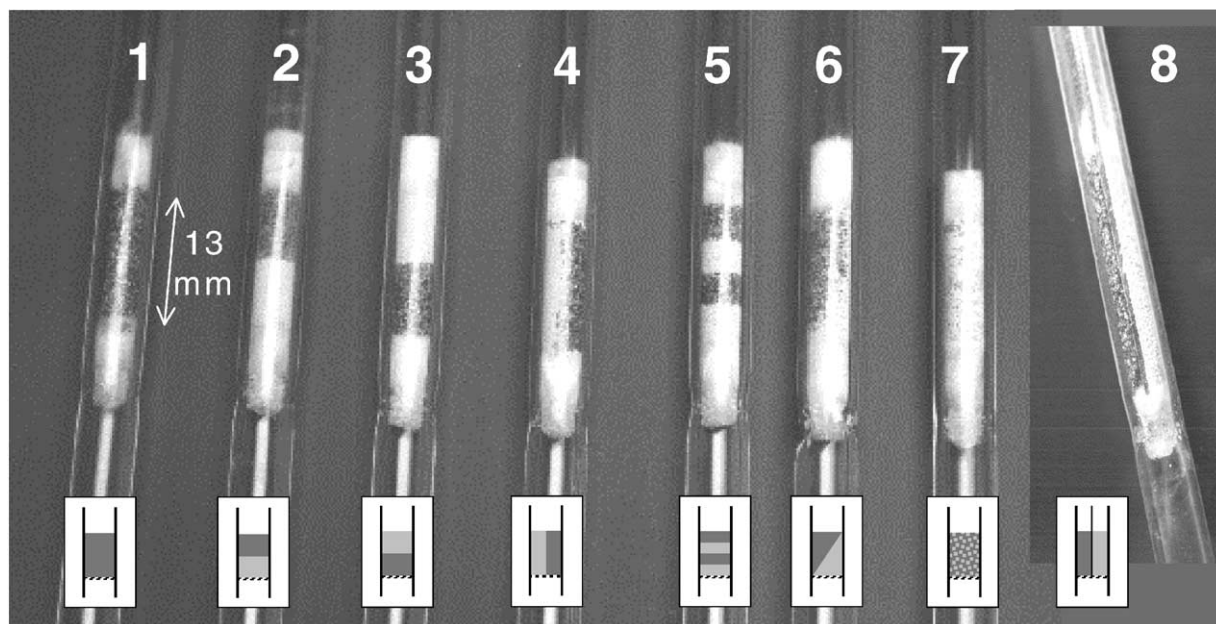


Fig. 2. Photographs of reactor loadings. The light grains are FeZSM-5 catalyst particles, the dark grains SiC particles. Above and below the beds are white quartz wool plugs; the beds are positioned on a sintered quartz frit. The scheme used for each reactor loading is shown below its photograph.

catalysts (the interparticle void space) was calculated from the bed heights obtained in the reactor tubes.

2.2. Bed configurations

Different bed configurations were prepared with the catalyst and the diluent (SiC). Fig. 2 shows the different bed configurations for the FeZSM-5 system, including a well-mixed bed (number 7), a poorly-mixed bed (number 6) vertically segregated beds (numbers 2, 3, and 5), and horizontally segregated beds (numbers 4 and 8). The difference between the configurations 4 and 8 is the presence of a thin divider of non-porous quartz (thickness 0.3 mm) between the catalyst and the SiC compartments in number 8, eliminating the transverse diffusion of gas between them. A thin (0.3 mm) stainless steel foil was used during loading of the samples. In order to avoid movement of any catalyst particles to the dilution side while carefully removing the steel foil, additional thin horizontal beds of diluent were added below and above the beds on both sides (these additional beds were omitted in reactor number 4 in the photograph). All the samples were captured between two quartz-wool plugs and positioned on a quartz frit located in the middle of the quartz reactor tubes having an internal diameter of 4.0 mm. The schematic representation of bed distributions used along the manuscript is indicated below the corresponding photograph.

The experiments to investigate the influence of varying amounts of dilution in well-mixed beds were carried out with the Co-La Al-ox catalyst. The catalysts were tested using different degrees of dilution ($b = V_{\text{dil}}/V_{\text{cat}} + V_{\text{dil}}$), keeping the total mass of the bed constant at 400 mg. The space velocity (the ratio $W_{\text{cat}}/F_{\text{N}_2\text{O},0}$) was kept constant at

$5.58 \times 10^5 \text{ g s mol}^{-1}$ by adjusting the volumetric flow rate. The dilution was varied between 0.87 and 0.98. The catalyst and the diluent were mixed with special care as described in an earlier paper [12]. The bed height in all reactors was about 1.8 cm. More experimental details regarding the reactor configuration can be found in Table 1.

Two criteria for allowing the assumption of plug-flow behavior, defined by Mears [17] are also discussed here. The criterion to assume a flat radial velocity profile, Eq. (4), is fulfilled (Table 1).

$$\frac{d_r}{d_p} > 8 \quad (4)$$

The criterion to neglect the effect of axial dispersion, Eq. (5), depends on the conversion.

$$\frac{h_{\text{bed}}}{d_p} > \frac{20}{Bo} n \ln \frac{1}{1-x_i} \quad (5)$$

where Bo is the Bodenstein number for axial mass transport

$$Bo = \frac{u_0 d_p}{D_{\text{ax}}} \quad (6)$$

Gierman [18] refined this criterion and concluded, based on their practical experience, that this could be relaxed by using a factor of 8 instead of the factor 20.

2.3. Experimental set-up

The activity tests were carried out in a fully automated six-flow reactor system. This set-up has been described previously [2,11,12,16]. Five reactors were filled with the samples to be tested whereas the sixth reactor was filled with

SiC dilution material only to serve as a reference. The flow direction was downwards. The thermocouples were directly inserted in the catalyst beds. The temperature differences between the six reactors were always <1.5 K. The experimental conditions used in the activity measurements are shown in Table 1.

The product gases were analyzed by gas-chromatographic analysis (Chrompack 9001) equipped with a thermal conductivity detector, using a Poraplot Q column (for separation of N₂O) and a Molsieve 5 Å column (for separation of N₂ and O₂). The reactors were allowed to stabilize for 1 h before the analysis of the product gases was started. In none of the beds, the catalyst showed a measurable deactivation. The mass balance for N and O closed within <1 and <2%, respectively; only in the experiments with the Co-La, Al-ox catalyst at 700 K both closed within <2 and <5%, respectively. The ratios N₂ (formed)/N₂O (converted) and O₂ (formed)/N₂O (converted) were at all times very close to 1 and 0.5, respectively, thus indicating steady-state operation. The selectivity of the reaction to N₂ and O₂ was 1.0 in all experiments. The N₂O conversions were calculated according to:

$$x_{\text{N}_2\text{O}} = 1 - \frac{A_{\text{N}_2\text{O}}}{A_{\text{N}_2} + A_{\text{N}_2\text{O}}} \quad (7)$$

where A is the peak area corrected for the response of the different gases in the GC analysis.

3. Results and discussion

3.1. Influence of bed distribution

3.1.1. Activity tests

The conversion-temperature plots over FeZSM-5 obtained with the different catalyst-diluent distributions are shown in Fig. 3. According to what might be expected, the highest conversions are obtained if the catalyst and the diluent are well-mixed (open squares). If the catalyst and the dilution are not mixed but inserted in separate horizontal layers, the conversion is slightly lower (dots). Applying the catalyst layer on top of the diluent layer, the other way around, and applying two catalyst layers and two diluent layers instead of one (reactor numbers 3, 2 and 5 in Fig. 2, respectively) yielded similar results. The difference in conversion with respect to that obtained in a well-mixed bed is due to back-mixing of the reactants and products as a consequence of axial dispersion. The sample referred to as ‘poorly mixed’ yields a significantly lower conversion (solid triangles) due to bypassing; the number of catalyst particles that are ‘met’ by the gas packages flowing in axial direction through the reactor is not independent of the entrance position. An even lower conversion is obtained if the catalyst and the diluent are placed completely in parallel to each other (‘half-half’ distribution; indicated by the open circles). In that case, 50% of the reactant bypasses the catalyst (see Fig. 1, x_2). Nevertheless, the conversion becomes higher than 50% due radial

dispersion, which counteracts the bed non-uniformity. If the effect of radial dispersion is suppressed by applying a solid non-porous quartz wall between both halves, the conversion decreases and the maximum attainable conversion amounts to 50%.

Although the different catalyst-diluent distributions strongly affect the conversion at conversions >0.5, there are hardly any visible effects at conversions <0.3. This is explained by the fact that the concentration profile in the reactor reduces to a by approximation linear function of the axial coordinate at low conversion.

3.1.2. Apparent activation energies

For an irreversible first-order reaction, such as the reaction in this study, and in the absence of transport limitations, the observed reaction rate coefficient (k^{obs}) can be calculated from the conversion using Eq. (8):

$$k^{\text{obs}} = \frac{1}{(W_{\text{cat}}/F_{\text{N}_2\text{O},0})p_{\text{N}_2\text{O},0}} \ln \left(\frac{1}{1 - x_{\text{N}_2\text{O}}} \right) \quad (8)$$

The k^{obs} -values calculated from the data in Fig. 3 were used to construct the Arrhenius plot shown in Fig. 4. In the absence of transport limitations and if the kinetics follow an Arrhenius’ behavior, such plots should result in straight lines of which the slope corresponds with the apparent activation energy (E_a^{app}) divided by the universal gas constant. This applies for the well-mixed case, except for some values at the highest temperatures which slightly deviate from the straight line that was fitted through all the available data within the conversion range 0.01–0.8. This slight deviation is caused by internal diffusion limitation. The fitting resulted in an apparent activation energy of 137 (±3) kJ mol⁻¹ and a k value at 580 K equal to 5.4 (±0.5) 10⁻⁷ mol bar⁻¹ g⁻¹ s⁻¹. For the other samples, in which the catalyst and the diluent are segregated or improperly mixed, the slope tends to decrease significantly at higher temperatures. The apparent activation energies derived from the slopes within range II of Fig. 4 are significantly lower than 137 kJ mol⁻¹, which is elaborated in Fig. 5. The results are spectacular. As long as one uses only the data at conversions <0.25 (corresponding with range I in Fig. 4), all the samples do yield the same apparent activation energy. However, the data at high temperature are very much dependent on the configuration of the bed.

This decrease of the slope at high temperatures should not be confused with that due to diffusion limitations in and around a single catalyst particle. This latter case is extensively discussed in the catalysis engineering literature (e.g. [1]); if there is pore-diffusion limitation only, the slope is reduced by a factor of two; if diffusion limitation through the film surrounding the catalyst particles is dominant, the slope decreases to almost 0). The phenomenon here is due to a combined effect of particle segregation in the bed, resulting in a kind of diffusion limitation on the bed level, and the incorrect plug-flow assumption for data contaminated with axial dispersion. The small internal diffusion limitation which was observed for the well-mixed case at the highest

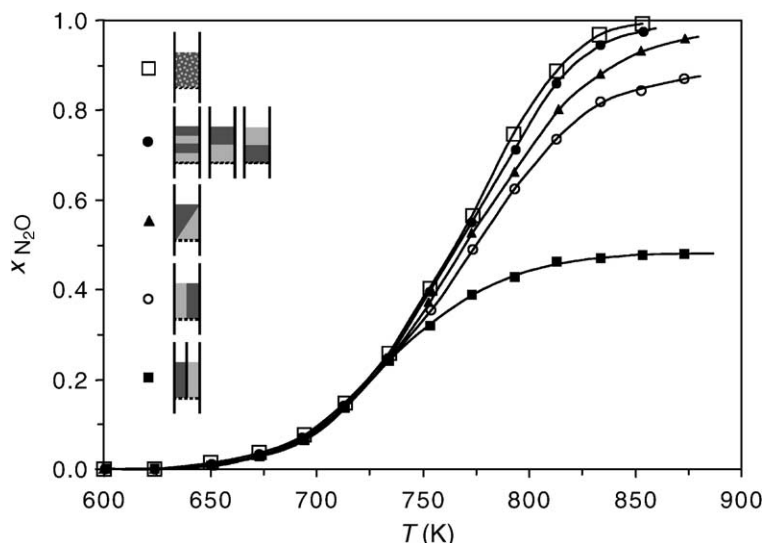


Fig. 3. N_2O conversion vs. temperature for different distributions of FeZSM-5 (indicated in the schematic pictures with light gray) and SiC diluent (indicated dark gray) at $P = 1.0$ bar, $p_{\text{N}_2\text{O}} = 1.553$ mbar, balance He, $W_{\text{cat}} = 50$ mg, $W_{\text{cat}}/F_{\text{N}_2\text{O}} = 8.65 \times 10^5$ g s mol $^{-1}$.

temperature also occurred in the other samples, but since the absolute size of that effect is equal in all cases (for an irreversible first-order reaction), it is largely negligible in comparison to the effect caused by the diluent.

3.1.3. Axial and radial dispersion coefficients

The activity results obtained with the different bed distributions give information on the axial and radial dispersion. The difference between the conversion versus temperature curves obtained with the vertically segregated beds (reactor numbers 2, 3 and 5) and that obtained with the well-mixed bed can be used to estimate the axial dispersion coefficient. The difference between the curves obtained

with the two horizontally segregated beds (reactor numbers 4 and 8) can be used to estimate the radial dispersion coefficient.

The axial dispersion in a fixed-bed reactor represents the transport that occurs in axial direction superimposed on that due to the convection. At low gas velocities, i.e. in the laminar flow regime, the dispersion is mainly caused by diffusion. At higher gas velocities, i.e. in the turbulent flow regime, the dispersion is enhanced due to eddies. The radial dispersion also contains a contribution from diffusion and a contribution due to turbulence, although the latter is generally smaller compared with that in axial dispersion.

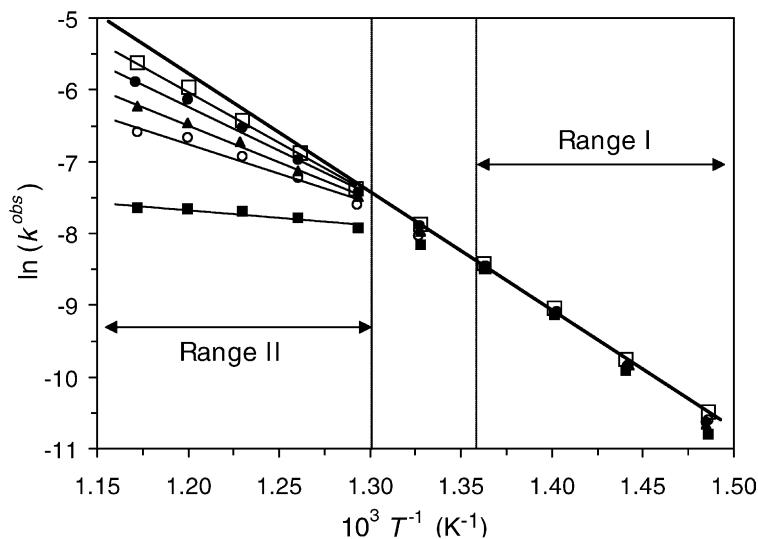


Fig. 4. Arrhenius plots obtained from the data shown in Fig. 3. The bold line represents the Arrhenius fit of the data obtained with the well-mixed bed (open squares); the slope corresponds with an apparent activation energy of 137 kJ mol $^{-1}$. Symbols as used in Fig. 3.

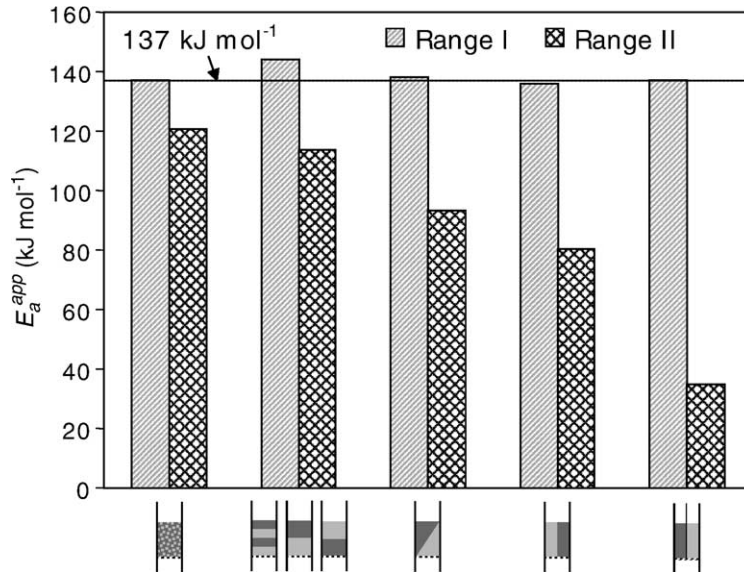


Fig. 5. Apparent activation energies (E_a^{app}) derived from the Arrhenius plot in Fig. 4. Ranges I and II are defined in Fig. 4. The dashed horizontal line corresponds with the apparent activation energy derived for the well-mixed bed in the low temperature region, i.e. 137 kJ mol^{-1} .

The axial and the radial dispersion coefficients in fixed beds (D) can be described using the following relations, proposed by Wakao et al. [19] and Wakao and Kaguei [20].

$$\frac{D}{\varepsilon_{\text{bed}}} = \frac{D_m}{\tau_{\text{bed}}} \quad \text{for } Re_p < 1 \quad (9a)$$

$$\frac{D}{\varepsilon_{\text{bed}}} = \frac{D_m}{\tau_{\text{bed}}} + md_p u \quad \text{for } Re_p > 5 \quad (9b)$$

According to these authors, $m = 0.1$ for radial dispersion, and $m = 0.5$ for axial dispersion. In most laboratory micro-scale gas–solid fixed-bed experiments, Re_p is < 1 . In all experiments discussed in this paper, Re_p amounts to approximately 0.1 and therefore the dynamic term present in Eq. (9b) does not have to be taken into account. This implies that at low Re numbers the axial and the radial dispersion become equal.

The static term consists of the bulk molecular diffusivity (D_m) and tortuosity of the bed (τ_{bed}). The bed tortuosity is thus the only unknown in Eq. (9a) and may be estimated from the results shown in Fig. 3. This estimation was done previously [11] and it appeared that the bed tortuosity of the Fe-ZSM5 catalyst bed lies within the range of 1.8–2.0. Similar experiments done with the Co-La Al-ox catalyst yielded a bed tortuosity of 1.2–1.8. The experimental results also confirmed that the radial and axial dispersion were equal within the experimental error and at the low Re_p numbers that were used. Both values agree well with those reported by others. Wakao et al. [19] report that the values typically range from 1.25 to 1.67. Edwards and Richardson [21] reported a similar value: 1.37, while Suzuki and Smith [22] reported a slightly higher value (2.3).

3.2. Influence of well-mixed diluent on the conversion

3.2.1. Activity tests

The conversions measured for the Co-La Al-ox catalyst at 700 and 770 K with five different degrees of dilutions (b) varying from 0.875 to 0.975 were used to calculate the deviations of the conversions according to Eq. (2). The deviations are shown in Fig. 6 as small circles with addition of the error bars. The results show that Δ depends on the conversion: at 70% N_2O conversion Δ is about two times higher than at 34% conversion. It also appears that Δ increases with the dilution fraction b and that this increase enhances strongly when b approaches 1.

3.2.2. Models to describe the deviation Δ

Fig. 6 also shows the deviation calculated using the equation van den Bleek et al. derived in their paper [9], which is valid for an irreversible first-order reaction:

$$\Delta = \frac{0.6\sqrt{3}d_p b}{4h_{\text{bed}}(1-b)} \quad (10)$$

This equation does not incorporate the conversion level, which is of major importance. At high dilutions it under- or overestimates the deviation, depending on the conversion level [12].

Sofekun et al. [23] extended the calculations of van den Bleek et al. [9] and reported the following equation to estimate the deviation of the conversion:

$$\Delta = 0.4315 b \left(\frac{d_p}{h_{\text{bed}}(1-b)} \right)^{1.01} \times \left(\frac{(k\tau^2) e^{-k\tau}}{1 - e^{-k\tau}} \right)^{1.02} \times n^{0.37} \quad (11)$$

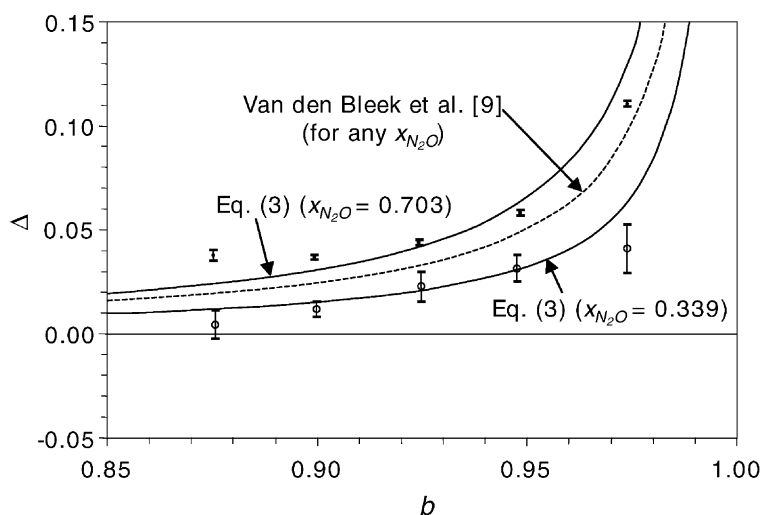


Fig. 6. Experimentally observed deviations in the conversion (Δ) due to the presence of inert bed diluent well-mixed with the catalyst at 700 K (conversion without dilution effect: 0.339), the lower curve and symbols, and 770 K (conversion without dilution effect: 0.703), the upper curve and symbols. The dashed curve is obtained using the equation from van den Bleek et al. [9] for both conversions ($P = 2.5$ bar, $p_{N_2O} = 1.0$ mbar, balance He, Co-La Al-ox catalyst, $W_{cat} + W_{dil} = 400$ mg, $W_{cat}/F_{N_2O} = 5.58 \times 10^5$ g s mol $^{-1}$).

Although this equation gives reasonable fits of the experimental data [12], it suffers from ‘the chicken and the egg’ problem since it requires the rate coefficient and reaction order, which are on beforehand unknown in kinetic investigations.

Additionally, Fig. 6 contains the curves calculated using Eq. (3). This convenient equation adequately incorporates the effect of the conversion, does not need any input of a priori unknown reaction kinetic parameters, and describes the experimental trend well. The equation was derived by analytically modeling the conversion obtained if all the catalytic activity would be homogeneously distributed over the catalyst bed and that obtained in the presence of dilution [12]. In this derivation, the fixed bed is described by a stack of layers composed of square cells having a size equal to that of the particles. The effect of radial dispersion, which could not be incorporated in the analytical derivation to estimate Δ , was implemented by means of a fit parameter in the denominator equal to 2, which represents the number of particles in a single cell used to describe the fixed bed.

As mentioned earlier, the reactor performance obtained in the well-mixed diluted bed was also simulated numerically using a model (the ‘random particle distribution model’) which takes into account the effect of radial dispersion and applies different, randomly generated, catalyst-diluent distributions [12]. The reactor model used describes the fixed bed as a stack of layers comprising cubic cells of the size of a single catalyst or diluent particle. The catalyst cells and the diluent cells are randomly distributed over the reactor. The individual cells are assumed to act as ideally stirred reactors. The model accounts for convection, radial and axial dispersion, and reaction. Although the model described the tendencies well, the values of Δ obtained using a bed tortuosity of 1.8 are approximately two times lower than the

ones experimentally found. This factor 2 is in fact already incorporated in Eq. (3) as a fit factor. Additional simulations showed that this difference can be overcome by using a cell size of 0.3 mm which is a factor of 5/3 larger than the average particle size (0.18 mm).

Several reasons can be suggested to explain this discrepancy. In practice, particles are not spheres of identical diameter, but they exhibit a size distribution and the shape will be non-uniform. Additionally, the average particle size that was estimated by volume-averaging the particle size range used (106–212 μ m) may be a too low estimate. Crushing of pellets and subsequent sieving usually yields a significant fraction of oblong-shaped particles having a size in the longest direction that is larger than the mesh size. The size of oblong particles obtained by sieving is determined by the size in the direction in which it is the smallest. Another possible cause of the discrepancy may be that the bed is highly non-ideal, for instance due to particle agglomeration. Moulijn and Van Swaaij [10] showed that agglomeration is a typical phenomenon in fixed beds with particles smaller than 2 mm. It is due to a non-uniform distribution of the fine particles, as a consequence of large interaction forces between the particles compared to the gravity forces. It results in channeling, the gas mainly flows through specific routes and hardly flows through the higher-density areas (‘agglomerates’). Agglomeration is known to enhance the axial dispersion and may also have influenced the results.

Although several phenomena influencing the deviation of the conversion in well-mixed diluted beds are not yet well understood, the simple Eq. (3) that requires only observable parameters can be recommended for use since it has a fundamental basis and it properly describes the experimental data obtained at different conversions (x_i) and dilution degrees (b). Additional confidence in Eq. (3) is obtained from

the sensitivity analysis performed using the complete model, which showed that Δ increases proportionally with particle size (d_p) and decreases proportionally with increasing bed height (h_{bed}).

3.2.3. Influence of the reaction order on Δ

The random particle distribution model [12] was used to investigate the influence of the order of the reaction on the deviation in the well-mixed case. It was found that the deviation is approximately proportional with the value of the reaction order. Therefore Eq. (3) can be generalized to:

$$\Delta = \left(\frac{b}{1-b} \right) \left(\frac{d_p}{h_{bed}} \right) \frac{x_{i,dil}}{2} n \quad (12)$$

For zero-order reactions the deviation Δ appears to be equal to 0, as long as there do not exist areas (cells) where total conversion is attained. This can be easily understood since for zero-order reactions the reaction rate does not depend on conversion; and only at complete conversion the reaction rate drops suddenly to 0. In agreement with the discussion on the first-order reaction in the previous part of this paper, the conversion decreases for positive reaction order. For negative order by-passing is favorable and the conversion observed exceeds the intrinsic conversion.

It is emphasized that the dilution effect discussed here is a systematic type of error that, for a positive reaction order, always decreases the conversion. It should not be interpreted as a random type of error that may both increase or decrease the conversion. The maximum allowed error as a consequence of the dilution should therefore not be directly related to the measurement error, as it is often done in the literature [9,23]. Instead, it should be treated in a way similar as e.g. the maximum allowed negative effect of external

transport limitation through the gas film surrounding the particles (i.e. the Carberry number), which is usually set at 0.05 (i.e. 5% deviation).

3.2.4. Effect on rate coefficient

In kinetic investigations, the measured conversions are used to calculate the rate coefficient, e.g. to determine the apparent activation energy of the catalytic reaction. For an irreversible first-order reaction, the reaction coefficient can be calculated directly from the conversion using Eq. (13)

$$k = \frac{1}{(W_{cat}/F_{i,0}) p_{i,0}} \ln \left(\frac{1}{1-x_i} \right) \quad (13)$$

Therefore it is in most cases more useful to calculate the deviation of this k instead of the deviation of x_i . If this is done using Eq. (3), the following expression for the deviation of the rate coefficient (Δ_k) is obtained (with Δ according to Eq. (3)):

$$\Delta_k = \frac{k_{und} - k_{dil}}{k_{und}} = \frac{\ln[(1-x_i(1-\Delta))/(1-x_i)]}{\ln(1/(1-x_i))} \quad (14)$$

Fig. 7 shows the results of this calculation for several values of Δ_k as a function of the dilution and the conversion for a constant $h_{bed}/d_p = 100$. The figure should be read as follows: an experiment at $x_{N_2O} = 0.5$ and $b = 0.95$ (and $h_{bed}/d_p = 100$) will result in a deviation of the calculated rate coefficient due to the dilution (Δ_k) between 5 and 10% (approximately 7%). The shaded area in Fig. 7 corresponds with conditions where the deviation exceeds the criterion of 5% deviation and it should be avoided in particular if the aim is to measure intrinsic reaction kinetics. The figure clearly illustrates that most of the experimental data obtained at the

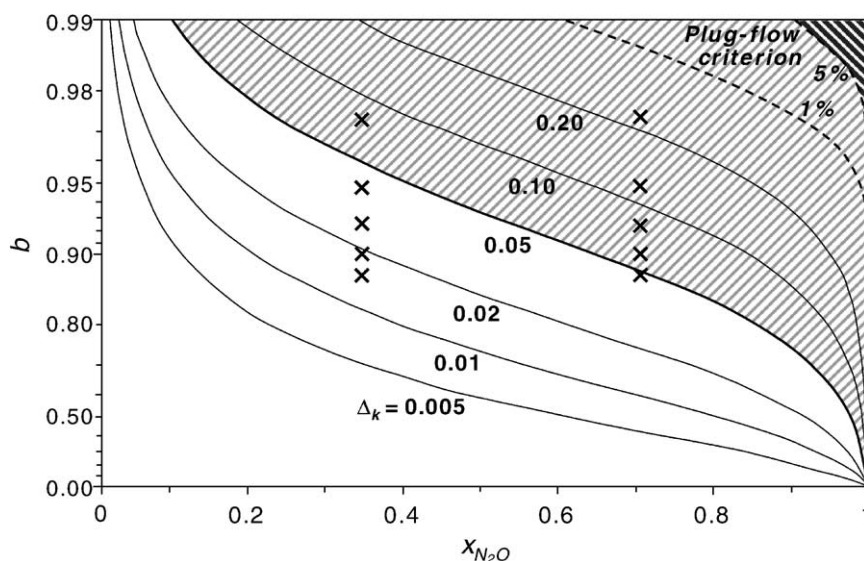


Fig. 7. Calculated effect of conversion and dilution on Δ_k , the relative deviation in the first-order rate coefficient calculated from the conversion, using Eq. (14) for an h_{bed}/d_p ratio of 100. Dashed lines represent the criterion for neglecting the effect of axial dispersion at $W_{cat}/F_{N_2O} = 5.58 \times 10^5 \text{ g s mol}^{-1}$ and $W_{cat} + W_{dil} = 400 \text{ mg}$. Symbols represent the conditions used in the dilution experiments.

high conversion of 0.703 exceed the 5% criterion for Δ_k . Therefore, one should always try to avoid the combination of high degree of bed dilution and high conversion levels. It is noted that Eq. (3) and thus also Eq. (13) have not been validated at conversion levels >0.75 and dilutions <0.8 , but they can be used as a safe rule of thumb.

The plug-flow criterion for 1 and 5% deviation of the conversion due to axial dispersion is also included in Fig. 7. The small dark shaded area corresponds with conditions where this deviation exceeds the criterion of 5%. The curves tend to lower conversions at high dilutions due to the simultaneous decrease of the flow rate in order to keep $W_{\text{cat}} + W_{\text{dil}}$ and $W_{\text{cat}}/F_{i,0}$ constant. The criterion is easily satisfied due to the high h_{bed}/d_p ratio used as a consequence of the application of a high degree of dilution. This is not generally valid; dilution is used amongst other to satisfy this criterion, but on the other hand it creates a deviation in the observed conversion. So there should be a dilution degree at which both criteria will yield similar constraints. This dilution degree depends strongly on the system in question.

4. Conclusions

The frequently applied dilution of catalyst beds by inerts in laboratory micro- or nano-flow reactors should be applied with caution. Care should be taken to achieve a homogeneous mixture between catalyst and diluent in the bed. Improper mixing inevitably results in bypassing of the catalyst-rich zones, thus decreasing the overall conversion. The decrease of conversion is larger if the segregation between catalyst and diluent increases. Vertical layering has a stronger influence than horizontal layering. These effects are far from negligible: the decrease can be as large as that due to internal and external transport limitations for catalyst particles. Since a completely homogeneous distribution of catalyst and diluent is difficult to achieve, the use of data obtained at high conversions with highly diluted fixed beds should preferentially be avoided. It can affect the observed catalyst activities and lead to a wrong interpretation of the kinetic data derived from these, e.g. the apparent activation energy may vary from the intrinsic value even down to 0.

It was found that the degree of bed dilution in perfectly mixed beds also influences the conversion significantly. This is due to same phenomenon, bypass of catalyst particles, but then on particle scale instead of reactor scale. Eq. (12) can be used to estimate the deviation of the conversion caused by the dilution. The change of the conversion is approximately proportional with the reaction order; it is negative for positive reaction orders and positive for negative reaction orders. Eq. (14) and Fig. 7 can be used to get insight in the effect of dilution on the calculated rate coefficient for a first-order reaction.

If one aims to measure intrinsic kinetics significant deviations of the conversion due to the dilution should be avoided. It is therefore recommended to avoid combining

high conversion levels and high dilutions, and to pay particular attention to a proper mixing of catalyst and diluent.

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