ELSEVIER

Chemical Engineering Journal 134 (2007) 35–44

Chemical Engineering Journal

www.elsevier.com/locate/cej

Chaos in catalyst pores
Can we use it for process development?

Bernhard Blümich[a], Leonid B. Datsevich[b,*], Andreas Jess[b],
Thomas Oehmichen[b], Xiaohong Ren[a,1], Siegfried Stapf[a]

[a] *Institute of Technical and Macromolecular Chemistry, Technical University of Aachen (RWTH-Aachen),
Worringer Weg 1, D-52056 Aachen, Germany*

[b] *Department of Chemical Engineering, University of Bayreuth, Universitaetsstr. 30, D-95447 Bayreuth, Germany*

Abstract

Since 1939 when Thiele and Zeldovich developed a theory devoted to the reaction mechanism in a catalyst particle, nothing has disturbed the scientific paradigm in catalysis. In multiphase reactions, as is widely accepted, liquid occupies catalyst pores, remaining an immovable medium through which the reacting compounds “slowly” diffuse to active centres where the reaction takes place. Some years ago, it was predicted that in gas–liquid/liquid reactions with gas or heat evolution, liquid could chaotically move in catalyst pores with velocities up to 300 m/s causing a great impact on the reaction performance in a catalyst particle and a reactor. The present paper deals with some experimental confirmation of the oscillatory mechanism and illustrates some phenomena that can purposefully be used for process and catalyst development.

Keywords: Multiphase (gas–liquid–solid/liquid–solid) reactions; Oscillation theory; Internal mass transfer; NMR imaging; Catalyst engineering

1. Introduction

Over the past decades, heterogeneous catalysis has become a frontier area in science, combining different disciplines in chemistry and physics. Despite the fact that sophisticated techniques have provided catalysis science with new insights into the reaction mechanism, we are still far away from the comprehensive understanding of the processes in catalyst pores.

Two main phenomena take place in the reactor with porous catalysts: the transportation (i.e. diffusion) of the reacting compounds and the reaction itself. In liquid and gas–liquid reactions, the diffusion processes play an exclusively great role. They control the whole behavior of a chemical reactor: the delivery of reactants from the reactor bulk to a catalyst particle and, then, to active centres in the catalyst pores where the reaction takes place, afterwards, the reverse withdrawal of products to the reactor bulk. In obedience to the conventional science, the pores of a catalyst particle during a multiphase reaction should be wetted with liquid because of a very strong capillary pressure excluding whatever forced motion.

A theory developed by Thiele [1] and Zeldovich [2] in 1939 revealed the relationship between the reactivity and diffusivity in catalyst pores. Many generations of chemists and chemical engineers appreciate this theory very much because it always serves a helpful tool for comprehending and modeling chemical processes in both laboratory and industry. According to the Thiele/Zeldovich theory, mass transfer of reacting compounds in catalyst pores has the conventional molecular nature. That means that reacting species diffuse very slowly to the active centres in pores through the immovable liquid. The main outcome of the theory is the correlation between the reactivity, diffusivity and the particle size as well as the statement of a very simple fact: the deeper the location inside the catalyst, the less the concentrations of reactants and, therefore, the slower the reaction rate should be. This model shows that in many industrial processes (especially in fixed-bed reactors where big catalyst particles are used), as a rule, only an insignificant part of pores located near the catalyst shell takes part in the reactions because of the comparatively low-speed diffusion, leaving almost the whole catalyst body without working [3].

However, the conventional Thiele/Zeldovich model cannot always be appropriate for many industrial applications. A new,

---

* Corresponding author.
E-mail addresses: datsevich@gmail.com, datsevich@uni-bayreuth.de (L.B. Datsevich).

[1] Present address: Schlumberger-Doll Research Center, 36 Old Quarry Road, Ridgefield, CT 06877, USA.

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.03.058

Nomenclature

$C_{\mathrm{H_2O_2}}$	concentration of hydrogen peroxide (mol/m^3)
d_{pore}	diameter of the catalyst pore (m)
D_{Dl}	diffusion coefficient of the gas compound in the liquid phase (m^2/s)
D_{eff}	effective diffusion coefficient (m^2/s)
$D_{\mathrm{eff,oscil}}$	effective diffusion coefficient at oscillations (m^2/s)
D_{mol}	molecular diffusion coefficient (m^2/s)
Da_{pore}	criterion number Da related to the reaction with gas or heat production and based on y_{pore}
$Da_{\mathrm{pore,gas}}$	criterion number Da related to the reaction with gas production and based on y_{pore}
$Da_{\mathrm{pore,heat}}$	criterion number Da related to the reaction with heat production and based on y_{pore}
g	strength of pulses gradient (T/m)
H	Henry coefficient
$-\Delta H$	heat of the reaction (J/mol)
M	molar mass of the evaporated compound (kg/mol)
n	stoichiometric coefficient in the reaction with gas production A (liquid) $\rightarrow$ B (liquid) + nD (gas) (e.g. H_2O_2 decomposition)
q	wave vector, Fourier conjugate variable to displacement (m^{-1})
r_{s}	reaction rate related to pore surface (mol/(m^2 s))
r_{vapor}	heat of vaporization per mol (J/mol)
R	gas constant (8.314 J/(mol K))
T	current temperature in the pore (K)
T_{s}	temperature on outer surface of the particle (K)
U_{displace}	velocity of displacement motion (m/s)
U_{fill}	velocity of filling motion (m/s)
y_{cr}	length of pore at which oscillation appears (m)
y_{displace}	distance of displacement (m)
y_{pore}	length of the pore (m)
Greek letters	
δ	duration of gradient pulse (s)
γ	gyromagnetic ratio (1.761×10^{11} T^{-1} s^{-1})
$\lambda_{\mathrm{liquid}}$	thermal conductivity of liquid (W/(m K))
μ	viscosity of liquid (N s/m^2)
ρ_{liquid}	density of liquid (kg/m^3)
ρ_{vapor}	density of vapor (kg/m^3)
σ	liquid surface tension (N/m)
$\Delta\tau_{\mathrm{displace}}$	time of the displacement (s)
$\Delta\tau_{\mathrm{fill}}$	time of pore filling (s)
$\Delta\tau_{\Sigma}$	time of one oscillation (s)

the so-called Oscillation theory [4–6] predicts the existence of a chaotic motion of liquid in pores in some reactions with gas or heat production. According to this theory, the liquid in catalyst pores can periodically move with velocities of about 100 m/s at frequencies of 1 Hz or significantly more. Such a phenomenon is called the oscillatory behavior, i.e. alternating motion of liquid in a catalyst pore.

Specifically, the oscillatory motion of liquid in pores during multiphase reactions takes place due to failure of the conventional molecular mechanism (thermo conductivity and diffusion) to remove the produced heat and/or gas from the pore. It is well known that the maximum possible pressure inside the pore is equal to the sum of the pressure in the reactor and the capillary pressure. During the reaction with heat or gas production, the partial pressure of saturated vapor or gas increases. If the total pressure of vapor and gas exceeds the maximum possible pressure inside the pore, the bubble consisting of vapor and/or gas appears in the pore and starts pushing the liquid out of the pore. In the part of the pore occupied by the bubble, the reaction ceases, and because of the dissipation processes, the pressure inside the pore returns to the initial value (the pressure in the reactor) so that a new portion of reacting compounds comes into the pore again, driven by capillary effect, and the process of the bubble formation repeats.

The occurrence of such behavior can be estimated with the help of the criterion number Da_{pore} that is equal to the ratio of the rate of heat or gas production inside the pore to the maximum possible rate of the heat or gas removal according to the conventional heat conductivity or molecular diffusion models [4–6].

For exothermic reactions this criterion number can be found as

$$Da_{\mathrm{pore,heat}} = y_{\mathrm{pore}}^2 r_{\mathrm{s}} \frac{r_{\mathrm{vapor}} \rho_{\mathrm{vapor}} (-\Delta H)}{\lambda_{\mathrm{liquid}} \sigma T M} \tag{1}$$

for reactions with gas production such as A (liquid) → B (liquid) + nD (gas) (e.g. H_2O_2 decomposition)

$$Da_{\mathrm{pore,gas}} = y_{\mathrm{pore}}^2 r_{\mathrm{s}} \frac{nRT}{D_{\mathrm{Dl}} \sigma H} \tag{2}$$

One of the most important characteristics of the oscillatory process is the point inside the pore at which the bubble embryo appears. The distance from the pore mouth to this point is called the distance of oscillation penetration y_{cr}.

For exothermic reactions

$$y_{\mathrm{cr}} = \sqrt{\frac{\lambda_{\mathrm{liquid}} \sigma T M}{r_{\mathrm{s}} (-\Delta H) r_{\mathrm{vapor}} \rho_{\mathrm{vapor}}}} \tag{3}$$

and for reactions with gas production

$$y_{\mathrm{cr}} = \sqrt{\frac{D_{\mathrm{Dl}} H \sigma}{r_{\mathrm{s}} n R T}} \tag{4}$$

Depending on the reaction rate, pore diameter and physical properties of the reacting system, this distance can vary in a very large range, from several to hundred micrometers. The velocity of liquid motion inside the pore (especially on the pore part y_{cr}) also depends on the nature of the reaction and catalyst pores and can reach values of 10–100 m/s or more.

According to the oscillation model, many approaches to catalyst and process development, to scaling-up and modeling industrial reactors should be revised (see Table 1).

The oscillation model covers many classes of chemical reactions with heat or gas evolution that are of great significance

Table 1
Oscillation theory: consequences and practical importance

NN	Features	Short description	References and comments
Consequences important for practical applications			
1.	Alternating motion of liquid	Liquid velocity up to 300 m/s with frequency up to 2000 Hz	[4–6]
2.	Different macrokinetics	Change in the reaction order(s). There are parameters (e.g. surface tension) that influence the reaction rate	[4,6]
3.	Existence of distinct temperature difference between the surface of the catalyst particle and its centre	Up to ten times more than predicted by the Thiele/Zeldovich model	[4,7]
4.	Initial loss of catalyst activity	Deposition of non-evaporating species on y_{cr} excludes this part of the pore out of function	[5]
5.	Enhancement of internal mass transfer	In the part of the pore y_{cr}, $D_{eff}/D_{mol} \gg 1$	[4,5] and present paper
6.	Acceleration of external mass transfer[a]	Up to a 500-fold increase. Dependence of mass transfer coefficients on the reaction rate	[4–6,10,11,32] and the present paper
7.	Existence of stagnation zones (two zones simplification)	The part of particle where oscillations do not penetrate and which can be isolated by gas phase	[4]
8.	Pressure pulsations inside the particle; Cavitations in pores with catalyst destruction	Minimum pressure alternation is $\pm\Delta p_{capillary}$ (the real values are still higher because of hydraulic impacts of liquid with $U = 300$ m/s)	[10]
Directions for process and catalyst development			
1.	Process intensification by choice of a solvent	The nearer properties of a solvent to the critical point, the more vigorous oscillations are provoked	[4,5]
2.	Process intensification by modification of the catalyst pore structure	Use of interplay between macro- and micropores: productivity of a catalyst can be increased by 20–200%	[9,10]
3.	Creation of special pumping pores	Liquid motion through the catalyst bulk can be set in the demanded direction	[10] and the present paper
4.	Process intensification by an additional reaction	The oscillations can be induced by an additional reaction with gas or heat evolution	[4,5]
5.	Process intensification by heat or pressure modulation[b]	Oscillations can be induced by numerous methods even if the reaction runs without oscillations (e.g. Eddy current, electrical conductivity and other special effects)	[4,5,10]

[a] First ideas by Turek and Lange [26].

[b] For example, the concept of a breathing catalyst by Van Den Heuvel et al. [27–29] and Agar and co-workers [30,31].

in production of a large variety of substances: from food and perfume additives to medicines, fuels, dyes, monomers, etc. It is important that this model offers new opportunities for substantial process intensification by the induction of oscillations by different physical methods or by production of special catalysts.

Some predictions made on the basis of the oscillation model, e.g. a strong temperature gradient inside the catalyst, influence of the chemical reaction on external mass transfer, enhancement of the efficiency of the catalyst by creation of macropores and the destruction of a catalyst due to cavitations have already been proved experimentally [7–10].

In this paper, we continue to present new issues devoted to the oscillatory phenomenon. The reaction of hydrogen peroxide decomposition is used for the validation of the theoretical predictions published earlier.

It is necessary to point out that a qualitative description of the oscillatory behavior is possible only for a single pore and cannot be extended directly to the whole ensemble of pores: if the oscillations take place in some individual pore that is a part of a porous structure, it exerts an influence on the neighboring pores, causing accompanying disturbances in them. Conversely, the oscillations in the surrounding pores also affect the oscillatory performance in this individual pore. As a result, the interaction of liquid flow in different pores should produce an incoherent pattern in the velocity and in the distribution of the reacting compounds inside a catalyst [10]. Such an interaction and superposition of liquid motion in connected pores should produce an extremely chaotic pattern. Different zones should exist in a real catalyst particle: regions of intensive oscillations in the part of a pore from the pore mouth to y_{cr}; areas of weak oscillations or even stagnant zones in the depth of the catalyst bulk. These zones can migrate, coalesce, expend and shrink in the course of the reaction.

It is necessary to point out that in reactions with both gas and heat production, the character of oscillations is the same. For underlining some specific features inherent in the oscillation mechanism, the reaction with gas production—hydrogen peroxide decomposition (Table 2) is chosen in this paper as a model system because of its comparative simplicity in carrying out the experiments described below.

2. Some oscillation parameters in the reaction of hydrogen peroxide decomposition

If the catalyst particle can be thought of as a structure consisting of the parallel pores of equal diameters, the oscillatory parameters can easily be calculated on the basis of assumptions given in [4–6].

An elementary oscillation can be regarded as the repeating processes of (i) pore filling, (ii) the birth of a bubble (at y_{cr}) and (iii) the displacement motion of liquid out of the pore. The processes of pore filling and liquid displacement in a single pore can be characterized by velocities U_{fill} and $U_{displace}$ as well as

Table 2
Characteristics of hydrogen peroxide decomposition: $H_2O_2 \xrightarrow{\text{cat}} H_2O + 0.5O_2$

NISAT catalyst [9]	
Active component	Ni (52%)
Form	Cylinder (6 mm × 6 mm)
BET porosimetry	
Specific area (m^2/g)	120.8
Mean pore diameter (μm)	4.53×10^{-3}
Mercury porosimetry	
Specific area (m^2/g)	62
Mean pore diameter (μm)	1.73×10^{-2}
Porosity	0.482
Density (kg/m^3)	1.38×10^3
Kinetic data [11]	
Range of operating conditions	
Temperature (°C)	15–30
Pressure	Atmospheric
H_2O_2 concentration (mol/m^3 or mass%)	$0–9.7 \times 10^3$ or 0–30%
Rate of intrinsic reaction based on the particle volume	$r_V = k_V C_{H_2O_2}$; $K_V = k_0 \exp(-E/RT)$
Frequency factor k_0 (s^{-1})	3.12×10^{12}
Activation energy E (J/mol)	77.0×10^3
Physical data used for calculations (at 25 °C) [12,13]	
Henry's coefficient O_2/water H $C_{O_2,l} = HC_{O_2,g}$	2.92×10^{-2}
Diffusion coefficient of O_2 in water $D_{O_2,l}$ (m^2/s)	2.41×10^{-9}
Diffusion coefficient of H_2O_2 in water $D_{H_2O_2}$ (m^2/s)	1.2×10^{-9}
Liquid surface tension σ (N/m)	74×10^{-3}
Viscosity of liquid μ (Pa s)	0.96×10^{-3}

the corresponding time $\Delta\tau_{\text{fill}}$ and $\Delta\tau_{\text{displace}}$. For the process of the liquid displacement, the important parameter is y_{displace} that presents the part of the pore in which the liquid is displaced by the growing bubble. If $y_{\text{displace}} > y_{\text{cr}}$, the bubble that appears in the pore can be observed on the outer surface of the catalyst particle in the pore mouth. For more details, it can be recommended to consult previous publications [4–6,10].

In order to have a better understanding about how powerful the oscillations can be, some oscillatory characteristics at $C_{H_2O_2} = 30\%$ calculated according to the above-mentioned references are presented in Table 3. As can be seen, the intensity of oscillations in a macropore grows with an increase in the diameter since a larger macropore contains a higher number of smaller pores branching off it so that these smaller pores contribute a much greater quantity of the generated gas, causing the more intensive bubble formation.

The velocity of liquid in the process of pore filling can reach values of about 100 m/s or even more. The characteristic time of pore filling (for macropores) is in the range of 10^{-8} to 10^{-6} s while the time of displacement is in the diapason of 6×10^{-4} to 3×10^{-2} s (see footnotes (a) and (b) in Table 3).

According to Table 3, the bubbles should be observed in the mouths of pores which diameter is greater than 0.13 μm because the distance of displacement for these pores is more than the distance of oscillation penetration. The appearance of the bubbles in these pores can be viewed in movie [14], in which the process of 30% hydrogen peroxide decomposition on a NISAT catalyst has been shot.

It is necessary to point out once more that the character of the oscillatory motion of liquid is extremely chaotic as a result of the interaction between oscillating pores connected with each other. The oscillation theory developed on the basis of the deterministic approaches permits only to have a principal insight into the reaction performance and fails to comprehend the exceedingly complex mechanism.

Nevertheless, the suggested model allows us to predict some phenomena in order to use them for practical purposes.

3. Verification of oscillations by the NMR technique

If it were possible to have a look into a catalyst particle under oscillations, what would be seen inside?

By contrast to the Thiele/Zeldovich model, the catalyst pores should not be occupied with liquid entirely. In the parts of pores alongside the particle shell (in the distance of oscillation penetration), an alternating motion of liquid should be observed with comparatively high frequencies. In the catalyst bulk, the areas with a different content of gas/gas–vapor and liquid should exist, and these areas should shrink, expand, and migrate, coalescing with each other.

Despite the fact that all macrokinetic dependences predicted by the oscillation theory exactly correspond to those observed in

Table 3
Some oscillatory parameters in macropores in the reaction of hydrogen peroxide decomposition ($C_{H_2O_2} = 30$ mass%)

d_{pore} (μm)	Da_{pore}	y_{cr} (μm)	U_{displace} (m/s)[a]	y_{displace} (μm)	$\Delta\tau_{\text{displace}}$ (s)[b]	U_{fill} (m/s)	$\Delta\tau_{\text{fill}}$ (s)
0.13[c]	1.98×10^6	6.4	2.4×10^{-7}	6.4	26.7	0.48	1.3×10^{-5}
1	1.42×10^7	2.4	1.2×10^{-5}	330	0.19	9.2	2.6×10^{-7}
2	2.85×10^7	1.7	5.0×10^{-5}	1,300	0.03	26.1	6.5×10^{-8}
3	4.27×10^7	1.4	1.1×10^{-4}	3,000	0.01	47.9	2.9×10^{-8}
4	5.7×10^7	1.2	2.0×10^{-4}	5,300	0.006	73.8	1.6×10^{-8}
5	7.12×10^7	1.1	3.1×10^{-4}	8,300	0.003	100	1.0×10^{-8}
10	1.42×10^8	0.8	1.2×10^{-3}	33,000	0.0006	290	2.6×10^{-9}

Calculated according to [5,6].

[a] In reality, the velocity of displacement U_{displace} is far more than presented in table.

[b] In reality, the displacement time $\Delta\tau_{\text{displace}}$ is much less than given in table.

[c] The appearance of bubbles in the pore mouths should be observed for pores with $d_{\text{pore}} > 0.13$ μm since in these pores $y_{\text{displace}} > y_{\text{cr}}$.

the course of reactions (see Table 1), one but essential question is often posed: do the oscillations in pores really exist?

Unfortunately, so far, there are no engineering methods permitting the measurement of the liquid flow in catalyst pores. The complexity of the direct detection of the liquid motion comes from the dimension of pores, the diameters of which vary from several angstroms to several micrometers, and, as a result, from the absence of techniques and sensors that can be used inside such restricted space. Moreover, any invasive method for measuring the liquid motion in a pore under oscillations will vigorously distort the situation in the pore because of altering the pore geometry.

The NMR imaging can be considered an effective technique to observe the processes that cannot be surveyed by any other methods. During the last decade, the NMR technique has been used for direct and, more important, non-invasive determination of some dynamic characteristics in blood vessels, chemical reactors, etc. [15–22].

In this work, the NMR methods have been used for visualization of the internal motion of liquid in the pores and the determination of the effective diffusion coefficients outside the catalyst particle near its shell.

Since the concentration of ferromagnetic Ni in the NISAT catalyst is comparatively high, the NMR technique cannot permit to obtain the appropriate images inside the catalyst bulk.

The catalyst particles with a considerably less content of an active metal have been prepared especially for illustrative pur-

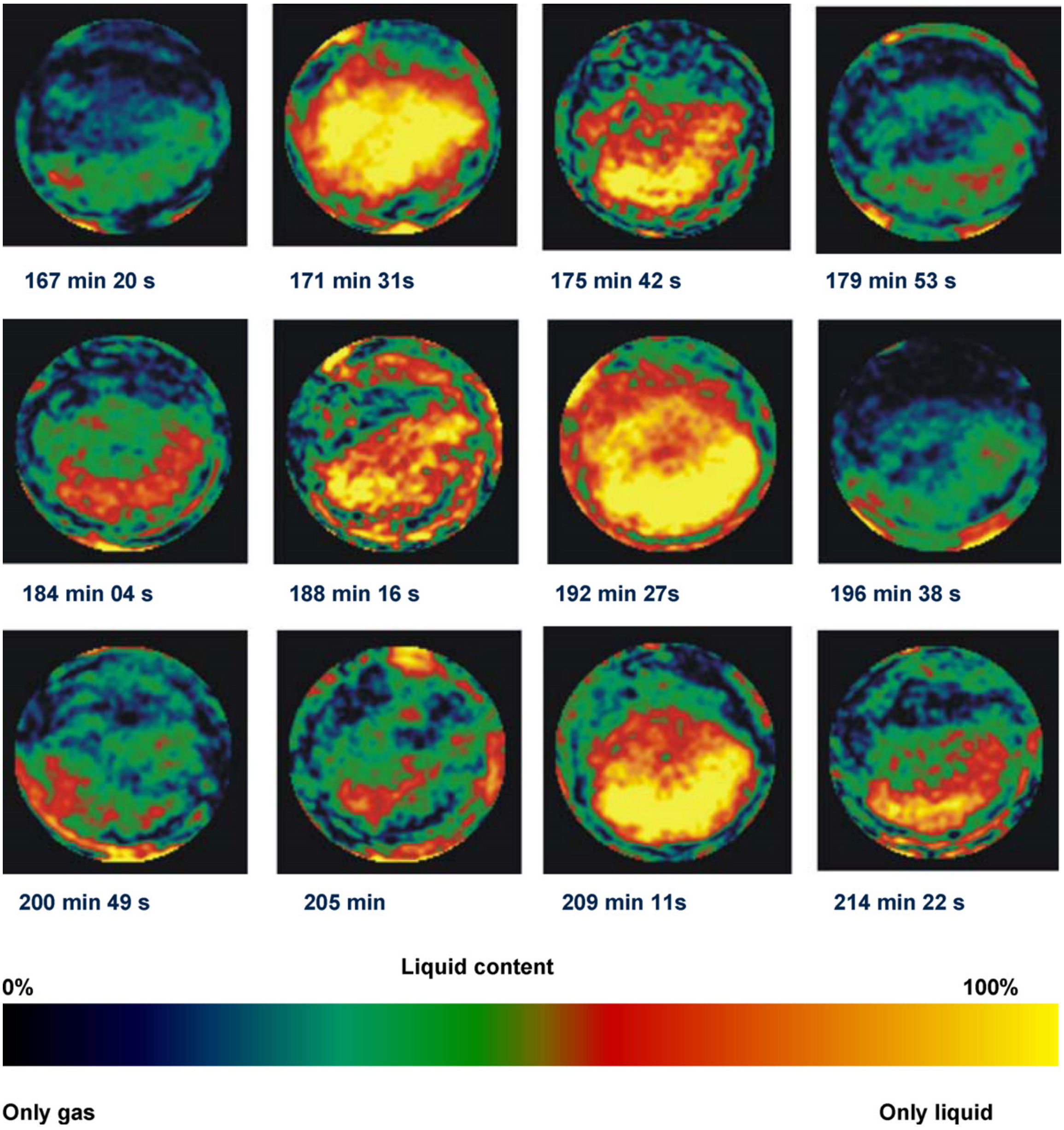

Fig. 1. Spatial distribution of liquid in the catalyst pellet in the course of hydrogen peroxide decomposition on Fe/Al_2O_3 catalyst (4.5 mm × 4.5 mm). The initial concentration of H_2O_2 is 22.5 mass%.

poses so that the NMR signal from the internal space can be detected. It is necessary to point out that such a catalyst has been used only for the demonstration of the oscillatory behaviour and has not been destined for kinetic experiments.

In Fig. 1 and movie [23] received by the NMR experiments (see Appendix A.1), the distribution of the liquid phase averaged during the acquisition time in a specially prepared Fe/Al_2O_3 catalyst (4.5 mm × 4.5 mm) is exposed. As is seen, the liquid in the catalyst particle performs irregular and chaotic motion, which contradicts the conventional understandings postulating the absence of any motion inside the catalyst pores.

Unfortunately, the existing NMR technique does not allow monitoring the individual oscillation in a single catalyst pore with high velocities and frequencies since both the acquisition time and the spatial resolution are not enough to localize an extremely small pore and to detect a signal from the liquid moving with velocities of 10–300 m/s and frequencies of 1–10 Hz. Only a change in the liquid content averaged during the acquisition time in a rather large slice of the catalyst comprising many pores can be observed. Nevertheless, the obtained NMR images exactly demonstrate the existence of the liquid motion predicted by the theory.

As can be realized, the character of the liquid movement has a distinctive feature of the chaotic behavior caused by the network of the pores and the impact of one pore on others: the zones with different frequencies of the liquid motion and even stagnation zones can be observed. It is interesting that the zone of the catalyst particle adjusted to its shell – where according to the theory, the elementary oscillations take place on the distance of oscillation penetration – can also be determined.

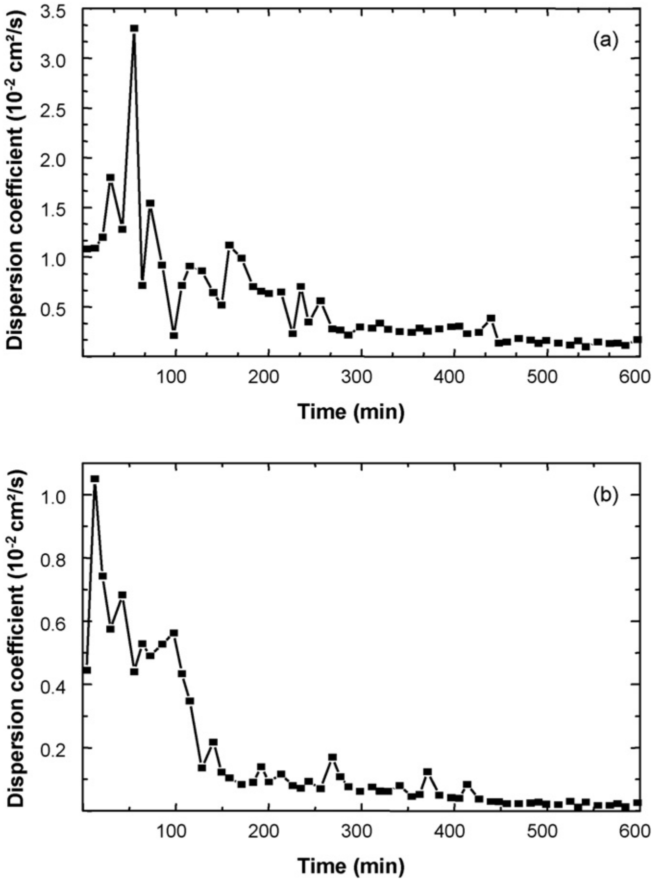

Fig. 2. Dispersion (effective diffusion) coefficient outside the catalyst pellet (Fe/Al_2O_3, 4.5 mm × 4.5 mm) alongside its shell. (a) Initial concentration of H_2O_2 is 22.5 mass%; (b) initial concentration of H_2O_2 is mass 7.5%. For comparison: the diffusion coefficient of H_2O_2 is 1.92×10^{-5} cm^2/s.

According to the oscillation theory, the motion of liquid in pores with velocities of 100 m/s should induce extremely vigorous vortices around the catalyst particle that should in turn result in an acceleration of external mass transfer.

This theoretical conclusion has also been verified by the NMR experiments. In Fig. 2, the effective diffusion coefficients of hydrogen peroxide under oscillations are given. As is shown, the oscillations can lead to a 500-fold increase in mass transfer compared to the conventional molecular diffusion. It is clear that during the reaction, the reaction rate and, as a result, the intensity of oscillations decrease because of hydrogen peroxide conversion so that the effective diffusion also becomes less.

4. Internal mass transfer

The alternating motion of liquid in pores cannot only cause a substantial increase in external mass transfer as illustrated above, but also accelerate internal mass transfer.

In exothermic reactions, in the part of the pore where there are oscillations, the effective diffusion coefficient can be evaluated as

$$D_{\mathrm{eff,oscil}} = \frac{y_{\mathrm{cr}}^2}{\Delta\tau_{\Sigma}} \tag{5}$$

where $\Delta\tau_{\Sigma}$ is the time of a single oscillation. For pores in which $y_{\mathrm{displace}} > y_{\mathrm{cr}}$, Eq. (5) yields [4]

$$D_{\mathrm{eff,oscil}} = \frac{\lambda_{\mathrm{liquid}}}{\rho_{\mathrm{liquid}} C_p} \tag{6}$$

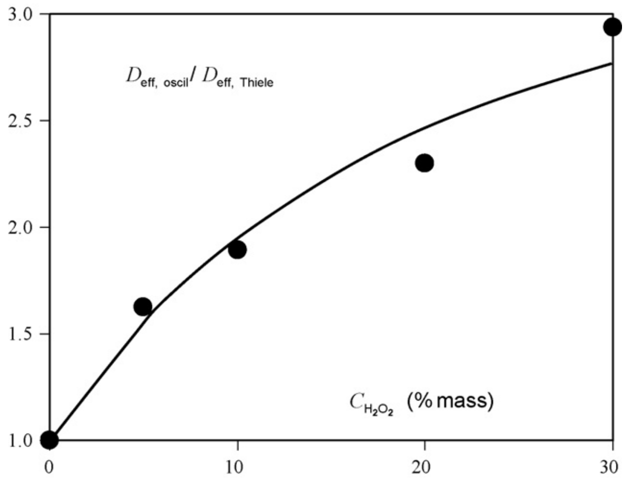

Fig. 3. Dependence of the effective diffusion coefficient on the concentration of hydrogen peroxide in the reaction of hydrogen peroxide decomposition on the NISAT catalyst 6 mm × 6 mm (Süd-Chemie).

According to Eq. (6) the effective diffusion coefficient can be about 10 times more than the molecular diffusion coefficient of individual reacting species.

In reactions with gas production, acceleration of effective diffusion can also be expected since the oscillations should induce an intensive exchange of liquid between the catalyst bulk and the surrounding flow. (Unfortunately, Eq. (5) does not permit to evaluate the effective diffusivity for reactions with gas evolution because in reality, $\Delta\tau_{\text{displace}}$ is significantly less than given in Table 3.)

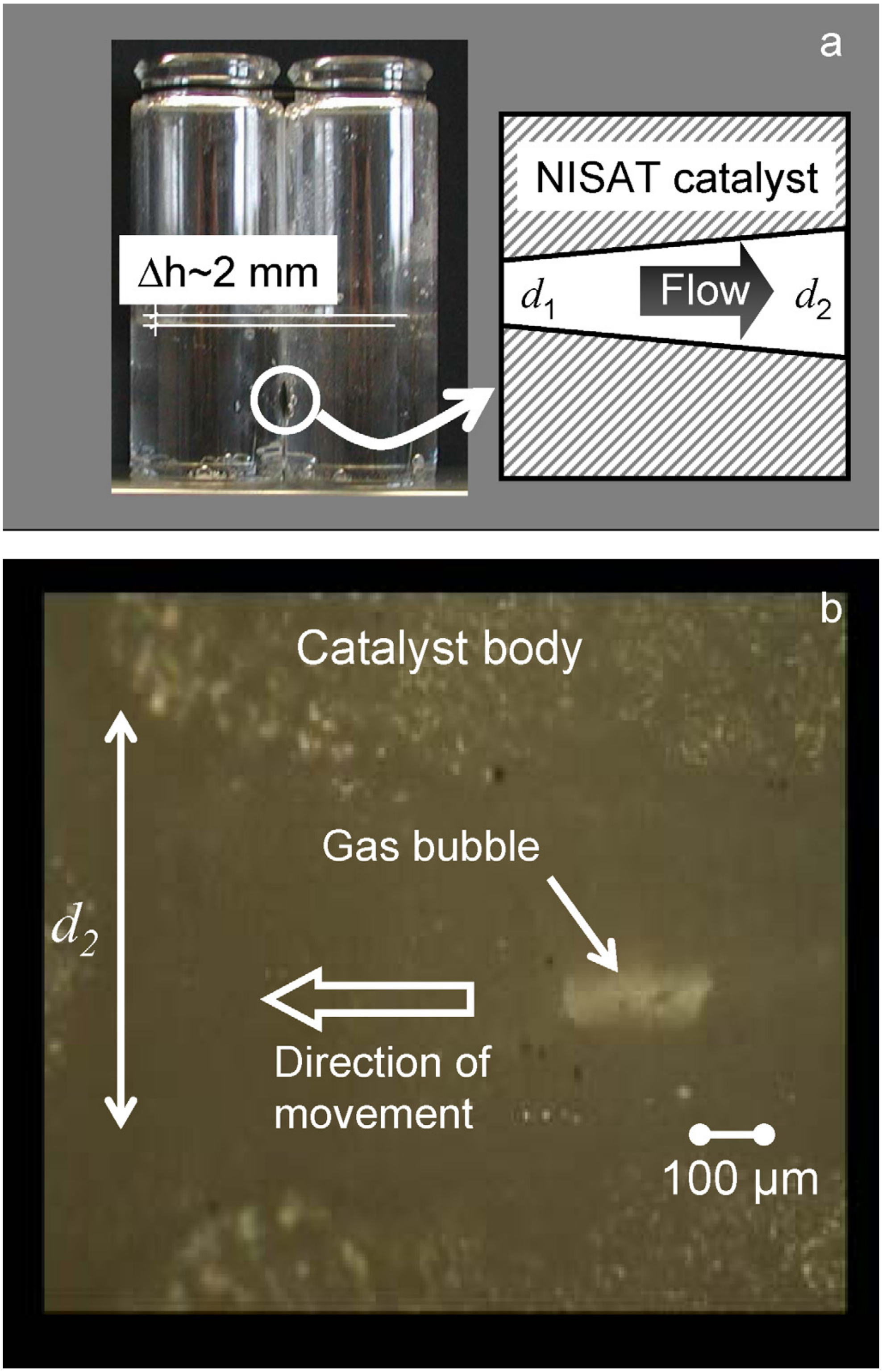

Fig. 4. Pumping through the conical pore in the reaction of hydrogen peroxide decomposition on the NISAT catalyst (6 mm × 6 mm, Süd-Chemie). (a) Growth in the liquid level in the flask of larger pore diameter ($d_1 = 0.6$ mm, $d_2 = 1.1$ mm); (b) frame from Movie 5 [33]. The bundle of gas and liquid formations is driven by the capillary effect in the direction of larger diameter ($d_2 = 0.6$ mm).

The impact of oscillations on internal mass transfer has been investigated in the reaction of hydrogen peroxide decomposition with the help of deuterium oxide D_2O used as a tracer (see Appendix A.2). The advantage of this substance in comparison to the others is that from a chemical point of view, it does not differ from water and, therefore, does not influence the reaction.

Fig. 3 shows the ratio of the effective diffusion coefficient of deuterium fragments $D_{\mathrm{eff,oscil}}$ under the reaction to the effective diffusion coefficient $D_{\mathrm{eff,Thiele}}$ measured in the absence of the reaction. It is necessary to point out that the latter represents the conventional diffusivity in a porous structure used in the Thiele/Zeldovich model.

As is seen, the internal mass transfer depends on the chemical reaction: the higher the concentration of hydrogen peroxide and, therefore, the higher the reaction rate, the more intensive the internal convections in catalyst pores.

5. Pumping through a catalyst particle: catalyst engineering

Our previous work [10] discusses some methods that permit to organize the motion of liquid through the catalyst bulk in the demanded direction, for example, with the help of conical pore as if a liquid pump were inserted inside the catalyst particle.

The experimental confirmations of such a theoretical conclusion are presented in Fig. 4. A conical pore forces the liquid to move in the direction from its smaller diameter to the greater one so that the level of liquid in the right flask becomes higher (Fig. 4a). Fig. 4b represents a frame extracted out of Movie 5. In this real-time movie, a particle of the NISAT catalyst (6 mm × 6 mm) with a conical pore bored in the axial direction was used (see Appendix A.3).

6. Conclusion

Although the oscillation theory can qualitatively describe some oscillation stages in a single pore, it fails to comprehend the whole assembly of the pores. The oscillatory mechanism in a real catalyst particle is much more complex than can be imagined. The porous structure, consisting of pores differing in diameters and branching off one another, imposes extremely chaotic behavior that cannot be modeled by any deterministic models because there is a very strong mutual interaction between pores.

Nevertheless, the oscillation model can be regarded as a useful tool for investigations. It is noteworthy that all phenomena including those described in this paper have first been predicted by the oscillation theory and afterwards verified by experiments.

In our opinion, the application of the knowledge about the oscillatory mechanism can allow us to completely utilize the catalyst potential for practical purposes.

Acknowledgment

Financial support from Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.

Appendix A. Experimental

A.1. NMR experiments

For the NMR experiments, a Fe/Al_2O_3 catalyst was prepared by impregnation of cylindrical particles of γ-Al_2O_3 (SN 380H/02 by Süd-Chemie: 4.5 mm × 4.5 mm, BET surface area 194 m^2/g) with a 5% aqueous solution of iron (III) nitrate ($Fe(NO_3)_3 \times 9H_2O$).

The NMR measurements were performed on DSX 200 MHz Bruker Spectrometer equipped with a vertical super wide bore 4.7 T magnet, and a microimaging gradient system providing a maximum gradient of 0.93 T/m is applied.

The NMR signals were detected in a single catalyst pellet fixed in the middle of a 10 mm NMR tube in which H_2O_2 was charged (Fig. 5). In order for the NMR images to be received, a spin-echo sequence with echo time of 630 μs was employed to map the distribution of the liquid within a 2 mm thick axial slice of the pellet with a spatial resolution of 78 μm × 78 μm. Four accumulations with a recycle delay of 500 ms were acquired so that the whole acquisition time of each image made up 4 min 11 s. During the reaction, a sequence of about 100 images is obtained some of which are presented in Fig. 1. The motion of liquid inside the particle can be observed the movie [23] produced by splicing all images.

Additionally to the motion patterns, the diffusion coefficients outside the catalyst particle nearby its shell were defined by the application of the 13-interval alternating pulsed gradient stimu-

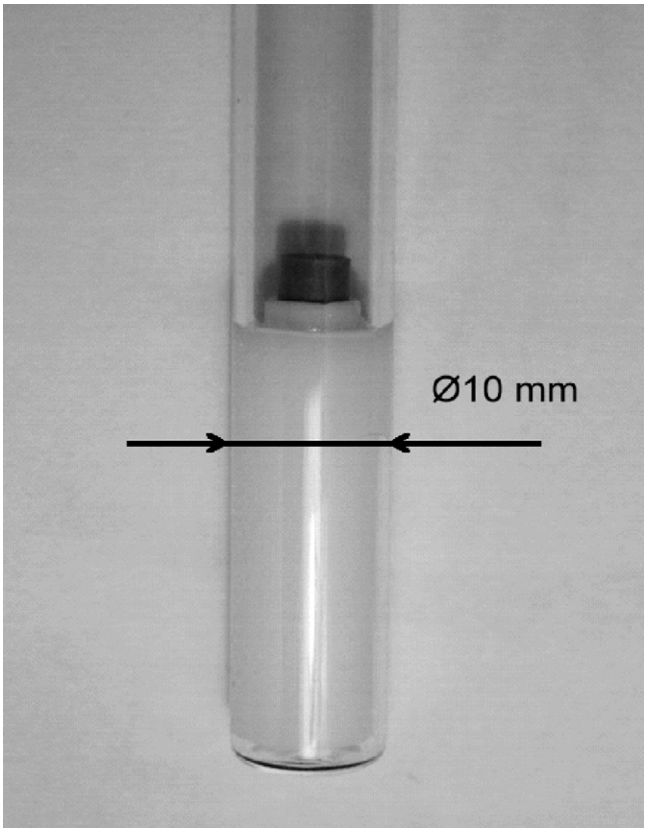

Fig. 5. A catalyst particle inside the NMR tube.

lated echo sequence with bipolar gradients. The strength of the gradient pulses g with the duration δ of 800 μs was varied in 16 steps to a maximum value of 0.11 T/m. The diffusion encoding time was fixed at 118 ms, and 8 signals were accumulated for each step. The values of the diffusion coefficients were obtained from the low-q defined as $q = \gamma\delta g/(2\pi)$ limit of a plot of the modified spin-echo modulus as a function of the pulsed gradient parameters (the Stejskal–Tanner equation [24]). The calculation of diffusion coefficient also took 4 min 11 s.

A.2. Experiments with deuterium oxide exchange

The effective diffusion coefficients were defined in the experiments in which deuterium oxide diffuses out of the porous structure of catalyst particles in the surrounding medium.

Prior to the experiments, the particles of the NISAT catalyst had been placed in deuterium oxide for more than 12 h. Just before the experiment, the particles were taken out and the liquid covering the outside particle shell was soaked up by the blotting paper wetted partially. Five catalyst pellets were charged into a basket which was then fixed inside a stir vessel with 20 g of hydrogen peroxide solution (0–30 mass%) in water. In all experiments, the conversion of hydrogen peroxide was less than 10% so that its concentration was assumed to be constant.

For definition of the internal mass transfer coefficients, the concentration of deuterium fragments in the reaction mixture was analyzed by FT-IR spectrometer (Thermonicolet) and plotted versus the reaction time.

The accumulation rate of the deuterium fragments in the reacting mixture depends on the effective diffusion and can be evaluated analytically by methods of mathematical physics (see, e.g. Section 6.3 in [25]). Proceeding from the best fit between the analytical solution and the experimental plot, the effective diffusion coefficient was defined for the given hydrogen peroxide concentrations.

A.3. Preparation of a catalyst particle with a conical pore for the observation under a microscope

In a particle of the NISAT catalyst (6 mm × 6 mm), a conical pore was axially bored. The pellet was then thinned down up to the axis. The rest part of the catalyst was glued to the microscope preparation glass (Fig. 6). For observation and movie shooting, the particle was submerged in the hydrogen peroxide solution so that the conical pore under the glass was placed towards the microscope lens.

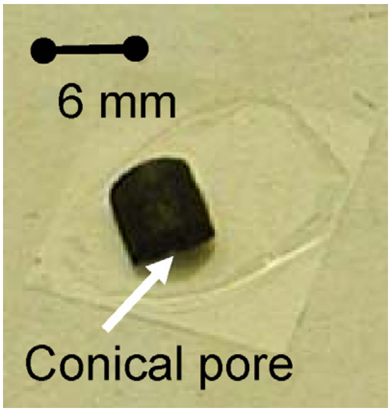

Fig. 6. Catalyst particle with a conical pore prepared for shooting under a microscope.

References

[1] E.W. Thiele, Relation between catalytic activity and size of particle, Ind. Eng. Chem. 31 (1939) 916–920.

[2] Y.B. Zeldovich, To the theory of the reaction on a porous or powder catalyst, J. Acta Physicochim. U. R. S. S. X 4 (1939) 584–592.

[3] C.N. Satterfield, Mass Transfer in Heterogeneous Catalysis, MIT Press, Cambridge, 1970.

[4] L.B. Datsevich, Oscillations in pores of a catalyst particle in exothermic liquid (liquid–gas) reactions. Analysis of heat processes and their influence on chemical conversion, mass and heat transfer, Appl. Catal. A 250 (2003) 125–141.

[5] L.B. Datsevich, Alternating motion of liquid in catalyst pores in a liquid/liquid–gas reaction with heat or gas production, Catal. Today 79–80 (2003) 341–348.

[6] L.B. Datsevich, Some theoretical aspects of catalyst behaviour in a catalyst particle at liquid (liquid–gas) reactions with gas production: oscillation motion in the catalyst pores, Appl. Catal. A 247/1 (2003) 101–111.

[7] L.B. Datsevich, Oscillation theory. Part 1. Temperature difference between the center of a catalyst particle and its surface: contradiction to Thiele/Zeldovich model, Appl. Catal. A 262 (2004) 149–153.

[8] L.B. Datsevich, Oscillation Theory: Part 2. Heat flux from the catalyst surface. Contradiction to the Thiele/Zeldovich model, Appl. Catal. A 273 (2004) 151–156.

[9] L.B. Datsevich, Oscillation theory: Part 3. Enhancement of a commercial catalyst by a pore modification, Appl. Catal. A 279 (2005) 181–185.

[10] L.B. Datsevich, Oscillation theory. Part 4. Some dynamic peculiarities of motion in catalyst pores, Appl. Catal. A 294 (2005) 22–33.

[11] T. Oehmichen, Zur effektiven Kinetik und zur Bildung oszilltorischer Fluidbewegungen bei Flüssig-Fest-Reaktionen unter Bildung einer Gasphase- Modelluntersuchungen zur H_2O_2-Zersetzung und zur Darstellung von Raney-Nickel, Diplom Thesis, CVT, Bayreuth University, 2005 (http://www.cvt.uni-bayreuth.de/Lehrstuhl/veroeffentlichungen/DiplomarbeitOehmichen.pdf).

[12] H. Stephen, T. Stephen, Solubilities of Inorganic and Organic Compounds, vol. 1, Pergamon Press, Oxford, 1963.

[13] http://www.h2o2.com/intro/properties.html.

[14] Movie 1, Oscillatory behaviour in the reaction of hydrogen peroxide decomposition, http://mpcp.de/movies.

[15] L.F. Gladden, Applications of in situ magnetic resonance techniques in chemical reaction engineering, Top. Catal. 8 (1999) 87–95.

[16] L.F. Gladden, M.D. Mantle, A.J. Sederman, E.H.L. Yuen, Appl. Magn. Reson. 22 (2002) 201.

[17] L.F. Gladden, Magnetic resonance: ongoing and future role in chemical engineering research, AIChE J. 49 (2003) 2–9.

[18] L.F. Gladden, M.H.M. Lim, M.D. Mantle, A.J. Sederman, E.H. Stitt, MRI visualisation of two-phase flow in structured supports and trickle-bed reactors, Catal. Today 79 (2003) 203–210.

[19] J. Götz, K. Zick, C. Heinen, T. König, Visualisation of flow processes and local dispersion coefficients, Chem. Eng. Process. 41 (2002) 611–629.

[20] M.D. Mantle, A.J. Sederman, L.F. Gladden, Single- and two-phase flow in fixed-bed reactors: MRI flow visualisation and lattice-Boltzmann simulations, Chem. Eng. Sci. 56 (2001) 523–529.

[21] X.-H. Ren, S. Stapf, B. Blümich, NMR velocimetry of flow in model fixed-bed reactors of low aspect ratio, AIChE J. 51 (2005) 392–405.

[22] X.-H. Ren, S. Stapf, B. Blümich, Magnetic resonance visualization of flow and pore structure in packed beds with low aspect ratio, Chem. Eng. Technol. 28 (2005) 219–225.

[23] Movie 4. NMR images of the oscillatory motion of liquid inside a catalyst particle in the reaction of hydrogen peroxide decomposition, http://mpcp.de/movies.

[24] L.L. Latour, L. Li, C.H. Sotak, Improved PFG stimulated-echo method for the measurement of diffusion in inhomogeneous fields, Magn. Reson. Ser. B 101 (1993) 72–77.

[25] J. Crank, The Mathematics of Diffusion, Clarendon Press, Oxford, 1975.

[26] F. Turek, R. Lange, Mass transfer in trickle-bed reactors at low Reynolds number, Chem. Eng. Sci. 36 (1981) 569–579.

[27] J.W. Huisman, J.C. van den Heuvel, S.P.P. Ottengraf, Enhancement of external mass transfer by gaseous end products, Biotechnol. Prog. 6 (1990) 425–429.

[28] J.C. van den Heuvel, L.H.J. Vredenbregt, I. Portegies-Zwart, S.P.P. Ottengraf, Acceleration of mass transfer in methane-producing loop reactors, Antonie van Leeuwenhoek 67 (1995) 125–130.

[29] J.C. van den Heuvel, I.P. Zwart, L.H.J. Vredenbregt, Convective acceleration of mass transfer in three-phase systems by pressure oscillations, Chem. Eng. Sci. 51 (1996) 2391–2398.

[30] I. Zirkwa, R. Werneke, M. Grünewald, D.W. Agar, Intensivirung des Stofftransportes bei heterogen katalysierten Reaktionen durch Druckoszillation, Chem. Ing. Technol. 76 (2004) 955–961.

[31] P.L. Silveston, R.R. Hudgins, Periodic pressure forcing of catalytic reactions, Chem. Eng. Sci. 59 (2004) 4055–4064.

[32] B. Blümich, L.B. Datsevich, A. Jess, T. Oehmichen, X. Ren, S. Stapf, Oscillation theory: Part 5. External and internal mass transfer in multiphase reactions over a porous catalyst, in preparation.

[33] Movie 5. Catalyst engineering: induced pumping through a catalyst particle in the reaction of hydrogen peroxide decomposition, http://mpcp.de/movies.