

Investigation of Heterogeneous Catalytic Reactions by the *in situ* ^1H NMR Microimaging

I. V. KOPTYUG¹, A. V. KULIKOV², A. A. LYSOVA^{1,2,3}, V. A. KIRILLOV², V. N. PARMON² and R. Z. SAGDEEV¹

¹International Tomography Center, Siberian Branch of the Russian Academy of Sciences, Ul. Institutskaya 3A, Novosibirsk 630090 (Russia)

E-mail: koptyug@tomo.nsc.ru

²G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)

³Novosibirsk State University, Ul. Pirogova 2, Novosibirsk 630090 (Russia)

Abstract

The NMR microimaging is used for the first time as an *in situ* method to study two model three-phase heterogeneous catalytic reactions with strong exothermicity. It is shown for the α -methylstyrene hydrogenation that in the course of the reaction, two domains coexist inside the catalyst grain which differ in the liquid phase content. The 2D maps of the liquid distribution in the course of this reaction are obtained. The reaction of the hydrogen peroxide decomposition at moderate activity of the catalyst and the H_2O_2 concentrations in the range of (0.03–3) M is shown to occur only in a thin layer near the catalyst surface. The influence of the medium inhomogeneity on the behavior of the Belousov – Zhabotinsky chemical oscillator reaction is investigated as well.

INTRODUCTION

Heterogeneous catalytic processes occur inside the porous catalyst grains and are affected strongly by the spatial distributions of reagent, intermediate and product concentrations, temperatures, etc., which are specific for each catalyst and each reaction. The experimental investigation of the spatial organisation and progress of catalytic processes inside catalyst grains seem to be accessible only by the application of an *in situ* imaging methods.

Recently, a number of tomographic methods has been suggested for a direct visualisation of chemical processes inside catalyst grains. The ^1H NMR imaging has been shown in the last years as a powerful nondestructive method for the *in situ* studies of various physicochemical processes in porous medium, e. g. liquid sorption and desorption [1, 2]. A much more challenging task is to apply the ^1H NMR imaging for studying *in situ* some chemical re-

actions, especially those inside porous catalyst pellets.

In our study we have applied for the first time the NMR microimaging for the *in situ* investigation of three heterogeneous catalytic reactions in order to visualise the progress of these reactions inside the catalyst grains, including the catalytic processes at elevated temperatures. Besides, NMR flow imaging which can yield liquid and gas flow velocities [3, 4] was employed to demonstrate the possibility to observe the convection of liquid outside the catalyst grain induced by a catalytic reaction.

As the first objects of the investigation we have selected several model heterogeneous catalytic processes such as hydrogen peroxide decomposition and α -methylstyrene hydrogenation. These catalytic processes proceed inside the catalyst grain in the three-phase regime. The NMR imaging allows to visualise the content of the liquid phase and its distribution within the grain and thus to get information

on the catalyst state during the progress of the catalytic reaction.

The investigation of the reactions mentioned above is of both theoretical as well as practical interest. Indeed, many heterogeneous catalytic reactions in industry, especially in petrochemical synthesis, occur in the reactors with the fixed bed of catalyst and the co- or counter-current gas-liquid flow. Usually such reactors work in the stationary regime, but under certain conditions the occurrence of dangerous critical phenomena such as hot spot formation, temperature and phase composition oscillations, exothermic reaction by-passing are possible. All this can result in a rapid heating of the catalyst grain because of the possibility of porous structure drying and a subsequent reaction acceleration due to transition of reaction from a liquid phase to a gaseous phase. Such processes are known to lead to the reactor runaway [5].

Thus, it is highly desirable to investigate experimentally the critical phenomena on a porous catalyst grain under conditions of an exothermic reaction which is accompanied by evaporation in order to determine the safety conditions of the reactor operation. In particular, it is important to investigate the distribution of the liquid phase inside the porous catalyst grain, the dynamics of the grain drying for an exothermic reaction and particle runaway.

The state of the catalyst grain in the reactors with the fixed catalyst bed and the co-current gas-liquid downward flow is studied using the exothermic α -methylstyrene hydrogenation mentioned above as a representative example. As a different example, we have investigated also the three-phase exothermic reaction of hydrogen peroxide decomposition. Also, we studied some peculiarities of the occurrence of the Belousov – Zhabotinsky (BZ) reaction in an inhomogeneous medium.

EXPERIMENTAL

All ^1H NMR microimaging experiments were performed at 299 MHz on a Bruker DRX spectrometer equipped with a vertical bore superconducting magnet and an imaging add-on de-

vice capable of providing pulsed magnetic field gradients of up to 100 Gs/cm.

Acquisition of the spatially resolved images by the ^1H NMR microimaging method is based on the use of the pulsed magnetic field gradients [6–8]. Since the resonance frequency of the NMR signal depends linearly on the strength of the magnetic field applied to the sample, the resonance frequency becomes the function of the nuclear spin coordinate along the direction of the gradient when the field gradient is turned on. This allows to determine the distribution of the spin density (the quantity of a substance) in the sample under study with the spatial resolution of some hundreds or even some tens of microns. The use of the selective radio-frequency pulses with the magnetic field gradients allows one to detect only the NMR signal of those nuclear spins which are located within a slice of a certain thickness and orientation. This gives a possibility to obtain a two-dimensional projection of the selected slice which characterises the distribution of the substance in the slice plane. Sufficiently short nuclear spin relaxation times of solid materials and low density of gas and vapour in the experiments ensure that only the NMR signal of the liquid phase is detected.

Catalytic decomposition of hydrogen peroxide

The NMR imaging experiments were carried out on an individual $\text{Ag}/\gamma\text{-Al}_2\text{O}_3$ catalyst grain. The impregnation with silver was performed from a salt solution, after that the grain was calcined at high temperature. The initial $\gamma\text{-Al}_2\text{O}_3$ had 134 m^2/g surface area and 0.31 cm^3/g pore volume. The experiments were carried out at an atmospheric pressure and an ambient temperature. The H_2O_2 solution of 3 M concentration was prepared from the 30 % H_2O_2 by its dilution with distilled water.

A catalytic cell which was placed in an NMR probe is shown in Fig. 1. A cylindrical grain of the catalyst (diameter 3.6 mm) was located in the centre of a glass ampoule (inner diameter 9 mm). The grain was placed into the aqueous solution of H_2O_2 . The sample holders contained several holes so that the dioxygen gas produced in the reaction could escape from the reactive

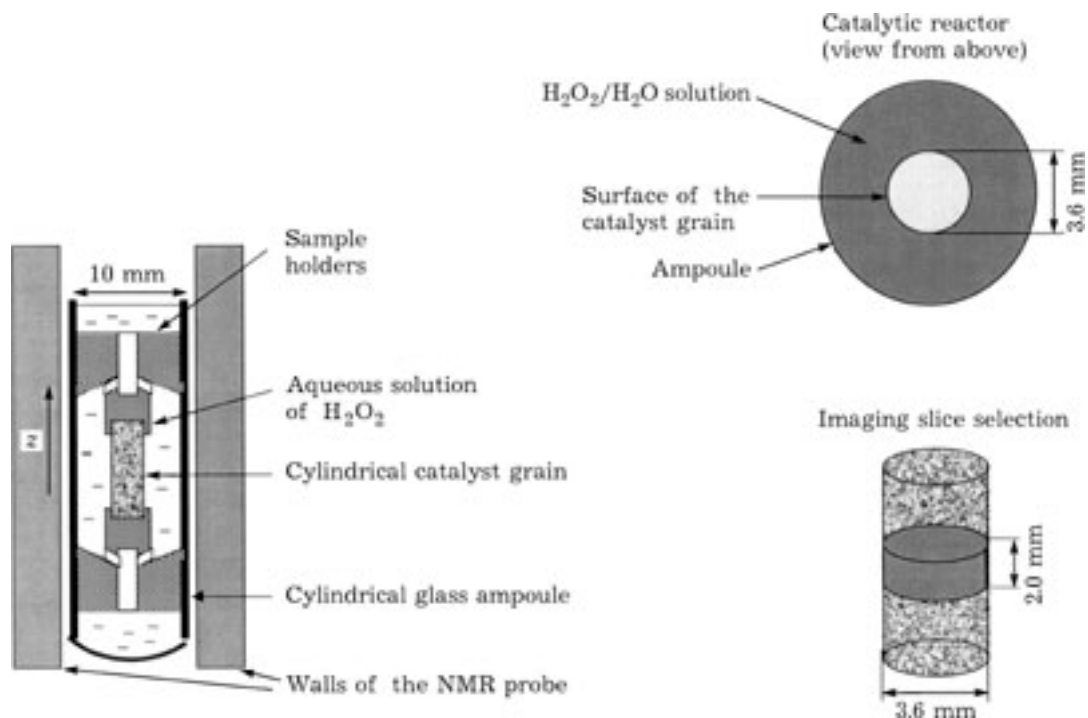


Fig. 1. A scheme of the imaging experiments on the hydrogen peroxide decomposition.

volume. We obtained two-dimensional projections of the NMR signal intensity in the plane perpendicular to the axis of the grain (Fig. 2). This figure demonstrates the dynamics of the dioxygen bubble formation on the grain sur-

face and the evolution of the O_2 bubbles in the course of the hydrogen peroxide decomposition. The NMR signal of water outside the grain was initially partially suppressed by the fast repetition of the pulse sequence of the

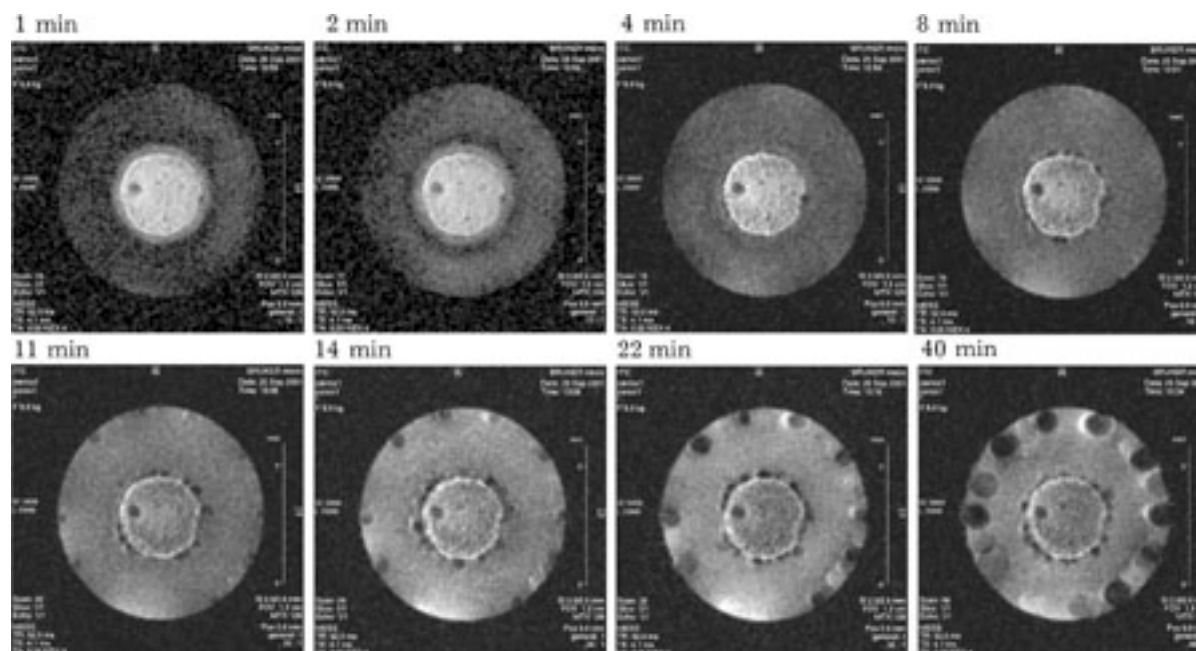


Fig. 2. Formation and evolution of the dioxygen bubbles in the course of the hydrogen peroxide decomposition over $Ag/\gamma-Al_2O_3$: two-dimensional projections. The detection time of each projection is 27 s. The time corresponding to each two-dimensional projection is specified in the figure. 128×128 pixels correspond to (1.2×1.2) cm^2 . The spatial resolution is $SR = (90 \times 90)$ μm^2 .

experiment, and thus the area outside the grain appears dark. The colour outside the grain is seen to become lighter (*i. e.*, the signal of water protons outside the grain becomes stronger) during the first minutes of the experiments due to shortening of the T_1 time of water protons which results from the release of the paramagnetic dioxygen molecules into water.

Note, that the dioxygen concentration appears to increase uniformly in the entire volume of the liquid. It means that during the time between the detection of the first and the second 2D images (1 min) the dioxygen molecules have enough time to travel from the grain surface to the ampoule wall (the distance is equal to 3.2 mm). The coefficient of the dioxygen diffusion calculated from these data appears to be significantly greater than the corresponding reference data [9].

Thus, we think that the evolved dioxygen molecules are transferred by a convection flow rather than due to diffusion. To verify this we have carried out the experiment which confirms the existence of a convection flow of the liquid along the catalyst grain because of the vigorous bubble formation on the grain surface (Fig. 3). In this Figure, the spatial map of the flow velocities of water flowing along the catalyst grain is depicted. One can see that near the grain surface where the bubble formation occurs, the liquid flow is upwards while near the ampoule walls it moves in the opposite direction. The velocity of the convective liquid transfer is *ca.* 0.2–0.3 mm/s. Since the

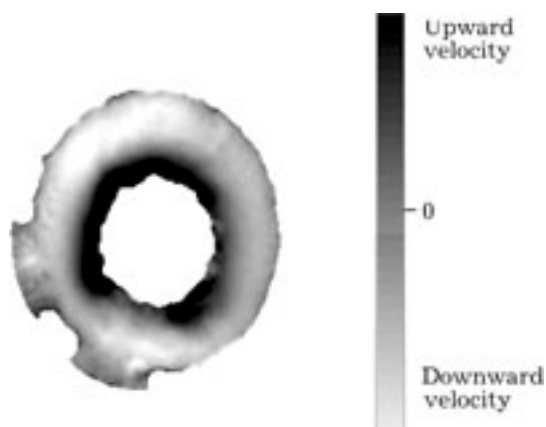


Fig. 3. A typical spatial map of the flow velocities of water flowing along the cylindrical catalyst grain in the course of the hydrogen peroxide decomposition.

height of the grain is 15 mm, during the time between the detection of the first and the second 2D projections a uniform concentration of dioxygen can be established in the entire volume of the liquid.

We have carried out experiments intended to establish the state of the grain in the course of the hydrogen peroxide decomposition. For these experiments, a composite catalyst grain consisted of an activated part and a non-activated part was prepared. Such composite grain is necessary to perform a meaningful comparison of the one-dimensional projections of the liquid content in the activated and the non-activated parts of the grain in the course of hydrogen peroxide decomposition (Fig. 4). In the NMR imaging experiments, by changing the resonance frequency we could reposition the selected slice so that the interleaved detection of the separate projections of the slices in the activated and non-activated parts of the grain could be performed (see Fig. 4).

The composite catalyst grain was initially filled with water and then placed into the 3 M H_2O_2 solution. Since the T_2 relaxation time of the H_2O_2 aqueous solution is much shorter than the T_2 relaxation time of pure water, the signal intensity in the non-activated part of the grain decreases after immersing the grain into the H_2O_2 solution due to the hydrogen peroxide diffusion into the grain (see Fig. 4, curve 1). An estimation of the H_2O_2 diffusion coefficient from this curve gives $1.5 \cdot 10^{-5} \text{ cm}^2/\text{s}$ that is about two times lower than the self-diffusion coefficient of the water molecules. It is known that the diffusion coefficient in the porous medium is lower than in the bulk liquid by a factor which is equal to the ratio of the porosity and tortuosity of the medium (a factor of 2–3 for $\gamma\text{-Al}_2\text{O}_3$).

One can see that the intensity of the NMR signal inside the activated part of the grain practically does not change during the experiment in contrast to the non-activated part of the grain (see Fig. 4, curve 2). It means that under the experimental conditions, hydrogen peroxide does not diffuse into the catalyst grain in the course of the reaction and that the decomposition occurs only in a thin surface layer of the grain.

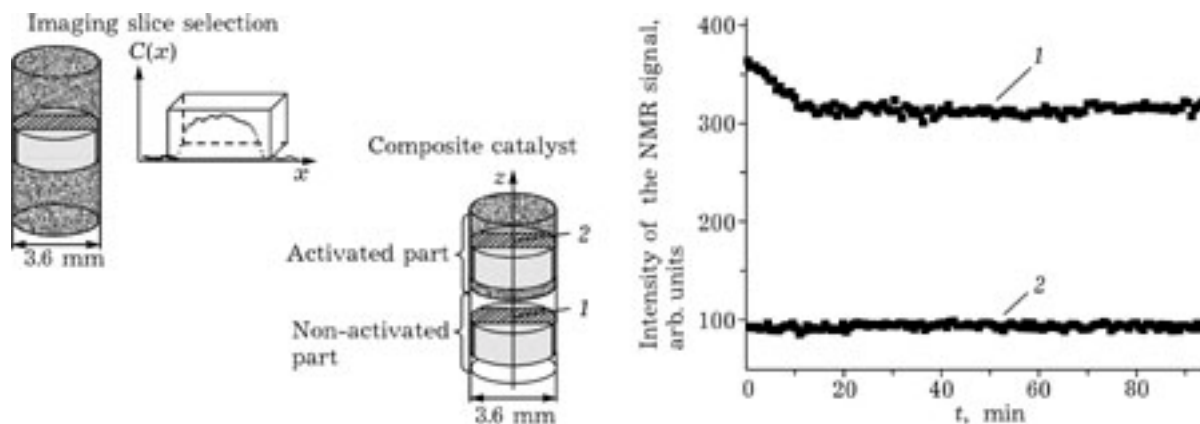


Fig. 4. The change of the NMR signal intensity in the center of the composite $\text{Ag}/\gamma\text{-Al}_2\text{O}_3$ catalyst grain in the course of the 3 M H_2O_2 decomposition: 1 – the non-activated part of the grain; 2 – the activated part of the grain.

Catalytic hydrogenation of α -methylstyrene

The most interesting results concern the three-phase exothermic catalytic reaction of the α -methylstyrene (AMS) hydrogenation. For the first time we have carried out the experiments under conditions when the operating reactor was placed directly inside the NMR imaging probe. Note that the experiments were carried out for the first time at elevated temperatures (the gas flow temperature was 68 °C and the pellet temperature was 185 °C).

It is known [5] that α -methylstyrene hydrogenation (boiling point 165 °C) to cumene (boiling point 152 °C) inside a porous catalyst grain can proceed in several stationary heat regimes: (i) when the catalyst grain is situated in the stream of dry hydrogen and the liquid reagent is supplied simultaneously, the process is characterized by a hysteresis of the grain temperature. In this case, the grain temperature on the upper branch of the hysteresis curve is higher than the temperature of the flowing gas, while on the lower branch it is lower than the temperature of the flowing gas; (ii) when the catalyst grain is positioned in the stream of hydrogen gas saturated with α -methylstyrene vapour, and simultaneously the liquid reagent is supplied, the grain in the stationary regime is either practically dry and strongly overheated or flooded with the liquid phase. In the latter case, the grain temperature is equal to the temperature of the flowing gas.

The earlier studies of these regimes were carried out by monitoring the grain tempera-

ture with thermocouples [5]. For a chemical reaction accompanied by the liquid phase evaporation, such monitoring gives only the indirect possibility to observe the distribution of the liquid phase inside the porous structure. In our work, the different regimes of the catalyst grain operation mentioned above were investigated to characterise experimentally the liquid phase distribution inside the porous particle directly in the course of the catalytic reaction.

The experiments were carried out on an individual cylindrical catalyst grain of 15 % mass $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ (diameter 4.7 mm and height 4.7 mm). The catalyst has the specific surface area of 206 m^2/g and the pore volume of 0.65 cm^3/g . AMS and gaseous hydrogen were used without a preliminary purification.

A scheme of the catalytic reactor which was placed directly into the NMR probe is shown in Fig. 5. The 2D projections of a 2 mm thick axial slice of the grain saturated with the liquid phase are obtained with the in-plane spatial resolution of $230 \times 140 \mu\text{m}^2$. The acquisition time of each image was 4 min 22 s. The time corresponding to the middle of the detection period of each image is indicated in Fig. 6. A stream of hydrogen heated to 67–69 °C and saturated with AMS was supplied to the pellet at the flow rate of 18.5 cm^3/s . A thermocouple was implanted into the pellet through its left side and appears in the images as an area void of signal (see Fig. 6). One can see that the pellet temperature raised 40 °C above that of the gas due to the exothermic nature of the reaction. The grain tempera-

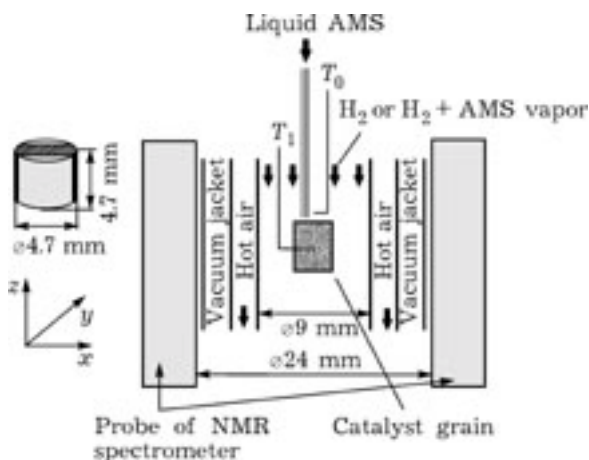


Fig. 5. A scheme of NMR imaging of the AMS hydrogenation. The location of the central slice within the grain in which the distribution of the liquid phase in the course of the experiment was detected is shown.

ture is also shown in Fig. 6. The first image in Fig. 6 shows the existence of the liquid phase within the pellet even though no liquid is supplied to the pellet at this stage, possibly due to the adsorption/condensation of AMS and cumene within the pores. Then, before the detection of the second image was stated, a supply of liquid AMS to the top of the pellet via

a capillary was turned on (the flow of liquid AMS was $0.43 \cdot 10^{-3}$ g/s). This led to the increase of the liquid content in the pellet (see Fig. 6, image 2). The brighter shade of the image corresponds to the stronger NMR signal intensity and therefore to a higher liquid concentration, while the darker shade of the image corresponds to the weaker signal intensity and to the smaller liquid content. In the upper part of the grain to which liquid AMS is permanently supplied, the NMR signal intensity is much stronger than in the lower part of the grain. This corresponds to the higher liquid phase content in the upper part of the grain. The NMR signal intensity is lower in the periphery of the grain as a result of the evaporation process that occurs in this part of the grain. The evaporation front of the liquid is located inside the catalyst grain and the vapor produced reacts on the non-wetted part of the porous structure. This leads to a temperature increase (from 141 °C at 11 min of the experiment to 167 °C at 20 min of the experiment). The increase of the liquid AMS supply up to $0.57 \cdot 10^{-3}$ g/s was made during the detection of the 4th image. As a result, the evaporation

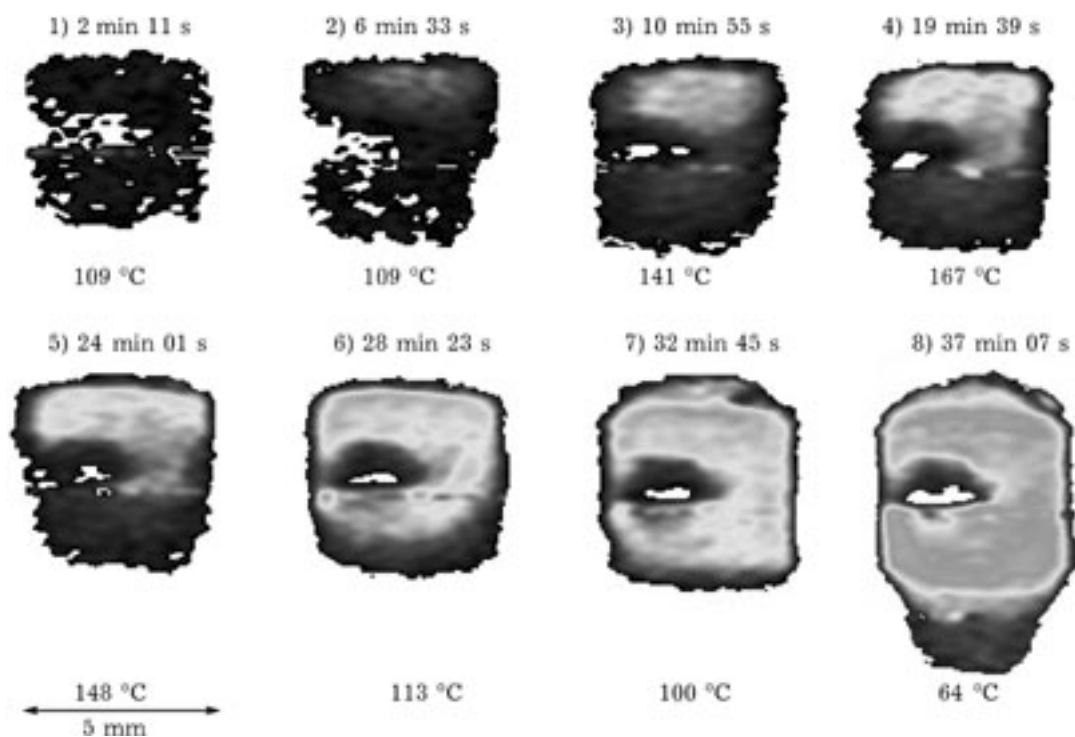


Fig. 6. The spatial distribution of the liquid phase inside the $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$ catalyst pellet in the course of the AMS hydrogenation under conditions of the simultaneous supply on the dry heated grain of the liquid AMS and hydrogen saturated with AMS vapour. See text for the details.

front moves deeper into the grain and the grain temperature decreases to 113 °C (image 6). In this regime the catalyst grain is almost completely filled with the liquid phase. A narrow front of evaporation and the vapor-phase reaction is located near the lower end of the grain. The front of the liquid phase propagation inside the grain is uneven. It is bound with the intensive evaporation process and hydrogenation process. The front of the liquid phase propagation deep into the grain in the experiment without the reaction (without hydrogen supply) is even.

When the liquid AMS supply was increased to $0.71 \cdot 10^{-3}$ g/s the grain became completely filled with the liquid (image 7). The grain temperature decreased rapidly to 64 °C which is lower than the gas flow temperature (image 8). It is related with the absence of the reaction in the gas-vapor phase and endothermic evaporation of the liquid phase from the catalyst grain surface. On the lower end of the pellet a drop of the liquid is formed.

The other regimes of the reaction proceeding on the individual catalyst grain were also investigated: (i) We have obtained several images illustrating the dynamics of the liquid phase distribution inside the catalyst grain when dry hydrogen flow is used with the simultaneous supply of liquid AMS; (ii) The distribution of the liquid phase inside the catalyst grain in the course of the AMS hydrogenation under conditions of the decreasing of the liquid AMS supply to the grain initially fully saturated with liquid AMS was studied.

Thus, the *in situ* NMR imaging demonstrates that impregnation of the porous catalyst with a liquid reagent under conditions of the simultaneous endothermic reagent evaporation and its exothermic hydrogenation can lead to the formation, inside the catalyst grain, of the two domains with the strongly differing liquid phase content: the upper part of the grain completely filled with the liquid phase and the lower part of the grain which is almost dry and filled with the gas-vapor phase where the vapor-phase hydrogenation occurs. The evaporation process occurs at the boundary between these two domains inside the grain. The location of the boundary depends on the liquid flow rate, thermal conductivity of the grain,

and the ratio of the evaporation and hydrogenation rates.

The Belousov–Zhabotinsky reaction in homogeneous and heterogeneous media

There are only a few publications concerning the use of the NMR imaging to study chemical reactions, mostly the polymerisation processes and the oscillating BZ reaction [10, 11]. The latter reaction is the oxidation of some organic compounds by bromate-anions catalysed by transition metals ions. This reaction is characterised by the oscillations of the reactant concentrations and the generation of propagating waves due to an inherent coupling of the molecular diffusion and the chemical reaction.

All reported NMR imaging investigations of the BZ reaction were performed in homogeneous medium in the presence of agar-agar in order to prevent the distortion of chemical waves by convective flow of the liquid solvent. We have studied the BZ reaction in a homogeneous medium modified with starch. The oscillations of the homogeneous catalyst (Mn^{2+}) concentration were recorded as changes in the water protons relaxation times because the oxidised and reduced states of the manganese cations have different influence on these times.

Figure 7 shows the propagation of the concentration waves in the homogeneous reaction medium stabilised by starch. The figure shows the one-dimensional projections of the signal intensity on the vertical axis of a 4.7 mm glass ampoule filled with the reaction medium. The space resolution of the image patterns in these projections was 320 μm . The acquisition time of each projection was 3.2 s. The signal intensity in each pixel of the image depends on the concentrations of Mn^{2+} and Mn^{3+} ions. It is known that the Mn^{2+} ions affect the T_1 relaxation time of water protons much stronger than the Mn^{3+} ions. Since we carried out the experiment in such a way that the contrast of the images was governed by the T_1 time, the brighter shade in the image corresponds to a higher Mn^{2+} concentration while the darker shade corresponds to the higher Mn^{3+} concentration. It is obvious that the waves are emitted periodically by at least several pacemakers. Each pacemaker emits a spherical wave, and we see in

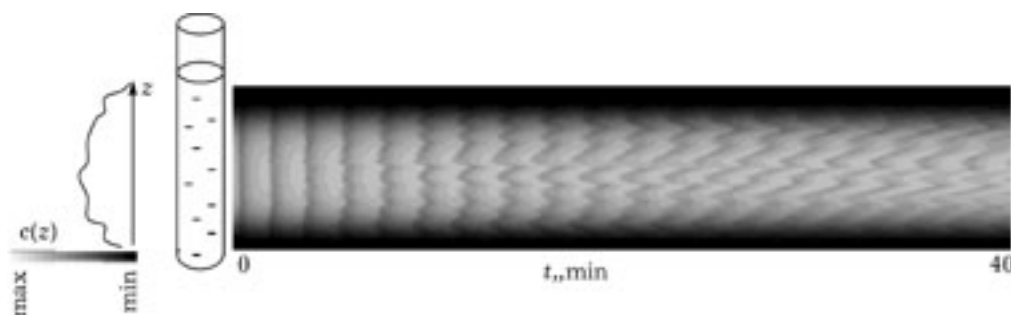


Fig. 7. Displacement-time graphs in the starch solution of the following starting composition: $[\text{KBrO}_3] = 0.05 \text{ M}$, $[\text{KBr}] = 0.06 \text{ M}$, $[\text{MA}] = 0.15 \text{ M}$, $[\text{MnSO}_4] = 0.0006 \text{ M}$, $[\text{H}_2\text{SO}_4] = 0.2 \text{ M}$, $[\text{H}_3\text{PO}_4] = 3.0 \text{ M}$, 0.7 % mass starch.

Fig. 7 two branches of the wave, that are the projections of the upper and lower boundaries of a spherical wave. The downward moving front of the wave that was emitted by one of the pacemakers collides and annihilates with another upwards travelling wave emitted by another pacemaker. The plane in which the pacemaker is located as well as the plane in which the wave trains collide and annihilate moves down with time.

We studied also the behaviour of the propagating waves inside model porous medium consisted of small glass beads of 0.5 and 3 mm in diameter and filled with an aqueous solution. In such system, we also observed formation of spherical propagating waves. The velocity of the waves practically does not depend on the size of the beads and remains practically constant in comparison with the homogeneous reaction medium stabilised by starch. Indeed the velocity v of the wave front in a reaction diffusion system is proportional to $(kD)^{1/2}$ [11], where k is the rate constant of the rate-determining step in an autocatalytic sequence and D is the diffusion coefficient of the autocatalytic species. It is known that in heterogeneous system D depends on the ratio of porosity and tortuosity of the grains, this ratio being only weakly dependent on the size of the beads. Also, one can assume that D in heterogeneous systems consisting of the beads is close to that in the homogeneous medium stabilized by starch. Thus, the replacement of the starch stabilized homogeneous medium by the heterogeneous system consisting of small beads influence the behavior of the system only slightly.

CONCLUSION

The above results demonstrate the first application of the ^1H NMR imaging to the *in situ* investigation of model heterogeneous catalytic reactions. The NMR imaging investigation was carried out for different systems and demonstrates its productivity.

Acknowledgements

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REFERENCES

- 1 I. V. Koptug, V. B. Fenelonov, L. Yu. Khitrina *et al.*, *J. Phys. Chem. B*, 102 (1998) 3090.
- 2 I. V. Koptug, S. I. Kabanikhin, K. T. Isakov *et al.*, *Chem. Eng. Sci.*, 55 (2000) 1559.
- 3 I. V. Koptug, L. Yu. Ilyina, A. V. Matveev *et al.*, *Catal. Today*, 69 (2001) 385.
- 4 E. Fukushima, *Ann. Rev. Fluid Mech.*, 31 (1999) 95.
- 5 A. V. Kulikov, N. A. Kuzin, A. V. Shigarov *et al.*, *Catal. Today*, 66 (2001) 255.
- 6 P. T. Callaghan, *Principles of Nuclear Magnetic Resonance Microscopy*, Clarendon Press, Oxford, 1991.
- 7 W. Kuhn, *Angew. Chem. Int. Ed. Engl.*, 29 (1990) 1.
- 8 S. L. Talagala and I. J. Lowe, *Concepts Magn. Reson.*, 3 (1991) 145.
- 9 A. Tzalmona, R. L. Armstrong, M. Menzinger *et al.*, *Chem. Phys. Lett.*, 174 (1990) 199.
- 10 Y. Gao, A. R. Cross and R. L. Armstrong, *J. Phys. Chem.*, 100 (1996) 10159.
- 11 L. Kuhnert, H. J. Krug and L. Pohlmann, *Ibid.*, 89 (1985) 2022.

