Explosion Initiation, Propagation, and Suppression Inside a Micro Structured Reactor

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The present contribution reports on specific aspects of safety engineering in heterogeneously catalysed oxidation reactions. Results for ethene-oxygen-mixtures in a continuous-flow micro reactor are reported related to the safety issues of the ethylene oxide process. Initial pressure is ranging from below 1 bar up to 10 bar at initial temperatures ranging from room temperature up to 673 K. Micro structured reactors offer an extended range of operating conditions. The key issue to be discussed in the present contribution is how to safely operate a micro reactor at conditions in conventional devices to be characterised as inside the explosion region. Within certain limits suppression of explosion inside a micro reactor can be achieved. This holds true for chain reactions as well as runaway reactions. Nevertheless it is not possible to safely operate micro structured reactors at any condition. Therefore, explosion propagation through a micro structured reactor and initiation of gas phase explosions by hot spots inside the reactor were investigated. The investigation methods applied are subject to actual standardization.

1. Introduction

Micro reaction technology has become increasingly attractive for industrial applications since it provides several advantages over conventional reaction technology, such as enhanced heat and mass transfer as well as large specific surfaces. Although micro structured reactors are not inherently safe, they may enhance operating of difficult to control reactions in a wider range of operation conditions. Heterogeneously catalysed gas phase partial oxidations are an important class of reactions, usually characterized by high rates of heat production. Conventional laboratory and production reactors are typically operated outside the explosion region. It is known that explosions of flammable gases in micro structured reactors can be suppressed (Pfeifer et al., 2005). On the one hand, application of the definition of the explosion region according to existing standards may lead to an inappropriately high restriction in the operating conditions. On the other hand, postulation of completely inherent safety of micro structured reactors might lead to hazardous operating conditions when sensitive substances are processed.

Operating inside the explosion region according to established macroscopic investigation standards explosion inside the micro structure could occur due to different ignition sources. One of those is a detonative explosion entering the reactor from outside and travelling into (and/or through) the micro reactor. An external detonation entering the reactor is the strongest ignition source to initiate explosion inside the micro structure, an incident in general necessary to be prevented from occurring. Nevertheless after the mixing unit the gas mixture is detonable and thus detonation cannot be disregarded.

In case of heterogeneously catalysed reactions another source of initiation of explosion could be a hot-spot at the catalyst surface inside the micro reactor. Hot-spots are weaker ignition sources; they are not believed to be likely to occur in micro reactors due to their extended heat transfer (Hugo and Lopez, 2009; Klais et al., 2009). If a hot-spot is emerging inside a micro reactor a flame detachment can occur, i.e. an initiation of explosion. Thus, in the following both of the two ignition scenarios are investigated.

2. Experimental

A micro structured reactor with slit-like channel geometry similar to the DEMIS-design (Klemm et al., 2008) was used. The reactor consists of two steel plates enclosing an inner space when screwed together. This micro structure is essentially of rectangular shaped space of 20 mm width, 150 mm length and heights of 0.25 mm, 0.50 mm and 1.00 mm. The height of the reactor depends on the bottom plate installed. The catalyst was coated in a groove of 0.25 mm depth inside the bottom plate avoiding the gas flow to be disturbed. The coated area was 50 mm by 20 mm and placed in the middle of the flow channel. Instead of an Ag/Al2O3 EO-synthesis-catalyst, a V2O5/TiO2 catalyst was used due to its higher activity and selectivity towards total oxidation reaction. Using a catalyst with high activity is from the safety point of view on the conservative side when investigating hot-spot development. Preparation and characterisation of the catalyst is described in (Lange et al., 2012), coating technique is described in (Schwarz et al., 2010). Figure 1 depicts the inner space of the reactor, its adjacent macroscopic volumes and parts of the apparatus, respectively.

A window installed in the top plate of the micro reactor allowed for in-situ observation of the entire surface of the catalyst layer. For this purpose a near infrared camera and a high speed video camera were applied. Up to four pressure sensors could be mounted to the reactor's top plate in order to trace explosion propagation inside the micro reactor. Dynamic pressure measurements were performed using piezoelectric pressure sensors, providing a resonant frequency of 500 kHz. The signals were recorded at a sampling rate of 1 MS/s using a data acquisition unit.

Two macroscopic volumes were connected to the micro reactor. The primary chamber in the reactor feed is used as ignition chamber in several experiments. The secondary chamber was placed in the outlet of the reactor representing the product storage tank and exhaust pipe, respectively. The macroscopic volumes consist of tubes with a length of 700 mm and an inner diameter of 11 mm. Both of the macroscopic volumes were equipped with pressure sensors tracing the explosion entering and leaving the micro reactor.

During experiments the apparatus was fed with a constant gas flow of homogenized reaction mixture. Mixture composition was controlled using thermal mass flow controllers. Behind the secondary chamber, the explosive gas mixture was diluted with large amounts of air in order to exhaust a mixture outside the explosion region.
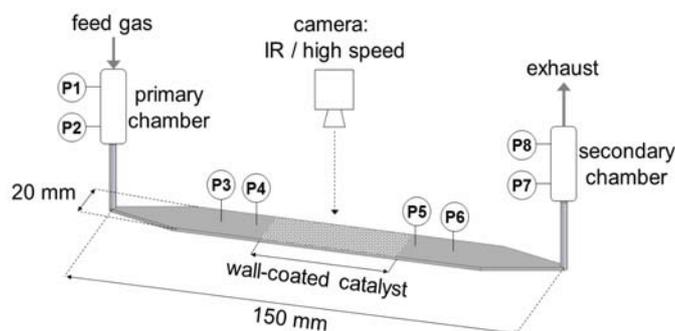

Figure 1: Scheme depicting the inner volume inside the micro reactor, primary and secondary chamber, pressure sensors (P1–P8) and IR-camera and high-speed-camera, respectively. The distances between the pressure sensors were the following: P1–P2: 100 mm, P3–P4: 24 mm, P4-P5: 74 mm, P5–P6: 24 mm and P7-P8: 100 mm

3. Results and Discussion

Two types of experiments were carried out. In the first type the ignition source used was a detonation. In the second type the potential of provoked hot-spots on the catalyst's surface acting as ignition source was investigated.

3.1 Propagation experiments

One issue concerning explosion safety of micro reactors is the possibility of an explosion traveling through the micro structure. In this test-scenario an incoming explosion serves as ignition source. The most effective ignition source is the explosion entering the micro structure. In such cases, the first question that

arises is whether the explosion will propagate inside the reactor. If propagation inside the micro reactor is obtained then the second question concerning the possibility for explosion to leave the micro structure and to act as an ignition source in adjacent macroscopic volumes becomes relevant.

In these experiments an explosion was initiated in the primary chamber, i.e. a pipe feeding the educts to the micro structured reactor. Propagation of the explosion was traced by 8 pressure sensors and a high-speed camera. The composition of the gas mixture and the initial pressure were varied stepwise. The results of these ignition tests are depicted in Figure 2. Lower explosion limit (LEL) and upper explosion limit (UEL) are marked by crosses. LEL and UEL were determined with the classical EN 1839 (macroscopic) method.

The upper explosion limit found in the micro reactor was significantly shifted towards lower fuel content compared to the UEL. Note that the explosion region does not disappear completely. Due to the high surface to volume ratio in micro structures quenching of deflagration can be achieved. Flames are hindered from expanding and propagating because of recombination of radicals and heat transfer at the wall.
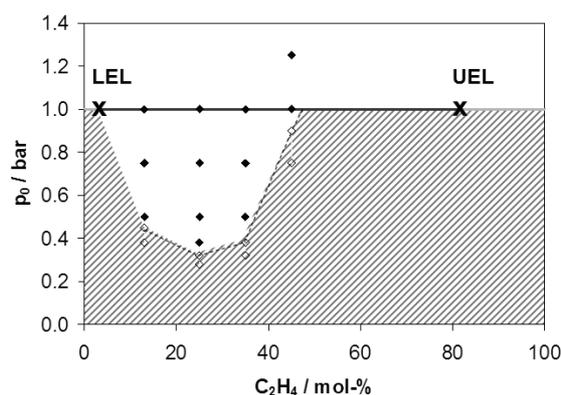

Figure 2: Scheme depicting the shift of upper explosion limit due to micro effects for ethene-oxygen-mixtures. Full dots correspond to ignition attempts resulting in an explosion, open dots depict unsuccessful ignition attempts. The shaded area below 1 bar is the safe conditions outside explosion region. Above 1 bar further investigation are to be performed.

Propagation of explosion through micro structures into adjacent macroscopic volumes in principle is already known which strictly necessitates safety considerations in this field (Gödde et al., 2009; Kockmann and Roberge, 2011). When gas phase oxidations were performed inside the explosion region safety problems like runaways or even explosions in many cases did not occur.

To clarify whether the explosion propagated from the micro reactor into the adjacent secondary chamber the pressure signals were used. The propagation speed is calculated between a corresponding pair of pressure sensors. P1 and P2 are mounted at the primary macroscopic chamber whereas P7 and P8 belong to the secondary macroscopic chamber. Figure 3 depicts the detonation propagation velocities at various initial pressures for the ethene-oxygen mixture at an equivalence ratio of $\Phi=1.0$. Three different behaviours of the propagation velocity could be distinguished. In case of sufficiently high initial pressure (the white cylinders at 1013 hPa) only slight deviation of propagation velocities inside the reactor from Chapman-Jouguet values were observed.

For an intermediate range of initial pressure (around 500 hPa), explosion propagation through the reactor is still possible and it is obviously still in detonative mode but shows some velocity deficits. Starting at a low velocity behind the reactor entrance it accelerates to a constant, somewhat higher detonation velocity that is still below the velocity of the stable detonation mode. In principle, velocity deficits are already known from investigations dealing with ideal geometries, i.e. tubes (e.g. Fischer et al., 2009). It indicates that this is no longer the stable detonation mode investigated in cell size measurements. This gives reason for a safety factor when cell size data is applied in safety considerations for micro structures.

In the third case when the initial pressure is even lower (320 hPa in Figure 3), propagation velocity at P3-P4 is almost identical to the medium initial pressure experiment but between the following measurements positions fading out instead of running up again. In the adjacent secondary chamber no explosion was observed. In Figure 3 this is at P7-P8 where the grey cylinder is reporting the detonation propagation velocity to be zero and also no deflagrative pressure rise was observed.
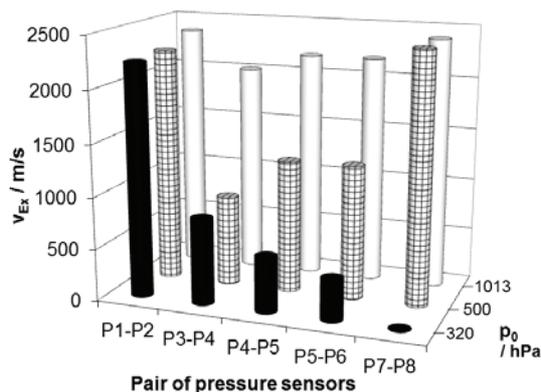
Figure 3: Detonation propagation velocities at various initial pressures between neighboring sensors. Ti=RT, y(C₂H₄)=0.25, y(O₂)=0.75. Position of pressure sensors: see Figure 1

These effects strongly depend on mixture composition. For the safety assessment of production reactors where different equivalence ratios can be ensured it is sufficient to investigate the range of fluctuations of mixture compositions possible. Apart from mixture composition several parameters, such as geometry of the micro device as well as design of its connectors, are influencing explosion propagation.

3.2 Hot-Spot Experiments

Another issue of interest is to study safety effects under reaction conditions, i.e. at higher initial temperatures and initial pressures with an active catalyst placed inside the reactor. A constant gas flow was established over the active catalyst placed inside the micro reactor. Infrared temperature measurement for two different reaction conditions is given in Figure 4. The x-axis and the y-axis correspond to the physical dimensions of the catalyst surface while the temperature is depicted on the T-axis. The thickness of the catalyst layer was 0.25 mm. It was found that a significant stable hot-spot can occur in the micro reactor, see Figure 4a. This hot-spot was located at the beginning of the catalyst layer. The location of the hot-spot did not depend on flow conditions. Increasing the feed gas flow (at constant mixture composition) was just increasing the maximum of the hot-spot temperature observed. Above a certain flow rate an ignition of a chain reaction in the gas phase was observed. Figure 4b depicts the situation about 17 ms before the hot-spot ignited the gas phase. According to the knowledge of the authors it was shown for the first time that the catalyst's hot spot can act as ignition source inside a micro structured reactor with subsequent propagation of the explosion in detonative mode into the adjacent macroscopic volumes.

In conventional (laboratory) fixed bed reactor it would be expected the location of a hot-spot to depend on the flow conditions. Increasing the flow rate usually should shift the hot-spot towards the end of the reactor. In the present investigation such a shift was never observed in the micro reactor, regardless of what flow rate was applied. A fluid dynamic calculation of the flow conditions inside the reactor showed a homogenous flow distribution throughout the catalyst layer. Additional experimental investigations showed that the heat transfer strongly depends on the thickness of the catalyst layer and thus, when the thickness of the catalyst layer was reduced to 50 %, much lower hot-spot temperatures were found not leading to explosion any longer. The location of the hot-spot maximum temperature remained at its original place. An important conclusion must be drawn from these observations. When dealing with micro structured reactors, a safety concept a priori shall not include attempts to drive a hot-spot out of the reactor by increasing the flow rate since this kind of reactor safety management could be hazardous.

To initiate a gas phase explosion inside a micro structure by a hot-spot acting as an ignition source the ignition temperature (IT) as defined in (Safekinex report #5, 2005) has to be reached. The over-temperature distribution on the catalyst is essentially influenced by the interplay of initial temperature, the heat transfer in the reactor (volume to surface area ratio) and the reaction rate. IT is based on the ability to generate radical species concentration high enough to initiate a chain reaction. Those radical species are generated by a slow pre-combustion-reaction. The radical concentration depends on the reaction rates generating and consuming reactive species, respectively. Reaction rates depend on local temperature distribution, mixture composition and initial pressure. The ability to store unused educts and radical species in micro reactors is limited because of the limited volume inside the reactor. The volume to surface ratio supports a high rate of radical recombination, the mechanism that also serves for quenching of

deflagration. This makes deflagration fail to start. Investigations concerning ignition temperatures e.g. (Safekinex report #5, 2005) provide the IT dependence of initial pressure, mixture composition and vessel volume for ethene-air mixtures. IT-values were ranging from 425 °C to 280 °C. It is to be expected that ethene-oxygen mixtures will provide significant lower ignition temperatures compared to those for ethene-air-mixtures at identical initial pressure and identical equivalence ratio. In the micro reactor investigated it was possible to obtain stable hot-spot-temperatures, not acting as an ignition source, of more than 100 K above the IT-values of corresponding fuel-air-mixtures. Thus, the ignition temperature inside a micro reactor (μ-IT) is much higher than the IT derived by application of standard investigation methods.
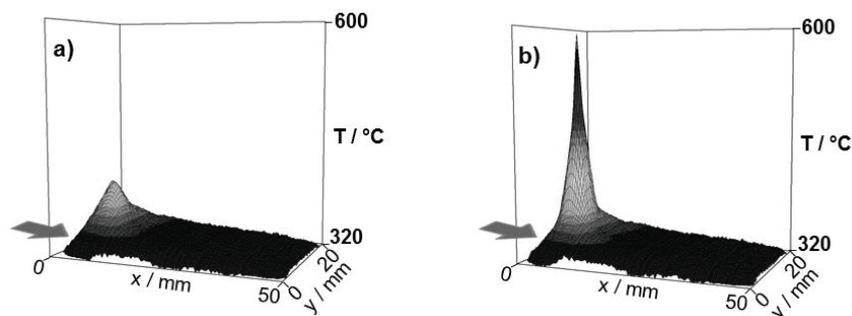

Figure 4: Temperature distribution on the catalyst surface at P_o = 10 bar, Ti = 320 °C, y(C$_2$H$_4$)=0.25, y(O$_2$)=0.75. a) stationary hot-spot at V = 240 NmL/min; b) V = 600 NmL/min, 17 ms before gas phase explosion. The arrows depict the direction of feed gas flow

Furthermore the question of the limiting conditions for deflagration propagation in confinements is related to the quenching distance. According to Gödde et al. (2009) the quenching distance for this mixture is reported to be 0.19 mm at T=298 K and p=100 kPa. The problem with the parameter values for quenching distance, a parameter of a deflagrative explosion, lies with the determination method applied. The standard apparatus for the determination of quenching distances is designed in a way, that two half spheres separated by a slit with defined width and adjustable height are brought together. Inside the inner macroscopic volume of the sphere an ignition is initiated. In the standard apparatus described in IEC 60079-1-1 it cannot be excluded a priori that a strong overpressure of the explosion drives a significant flow through the test slit enhancing an ignition of the surrounding space. Thus parameter values of quenching distances for detonable gas mixtures taken from literature or database should be carefully evaluated when applied in safety assessment.

If a deflagrative explosion could be initiated in the gas phase and if the reactor offers a sufficiently large channel length then it is possible to obtain a deflagration-to-detonation transition (DDT) even inside a micro structure (Wu et al., 2007). If inner dimensions additionally offer enough space in all three dimensions in a way that detonative cellular structure can develop then a stable detonation could be achieved. In tubes this is known to be the case if tube diameter is a least one third of the detonation cell width. The explosion observed following the hot-spot shown in Figure 4b has undergone the transition to a detonation. This was verified by the pressure-time-records.

4. Conclusions

Two types of safety tests for micro reactors operating in the explosive region were reported using the example of ethene-oxygen-mixtures related to the ethylene-oxide process. It was shown that this sensitive gas mixture could be handled safely in micro reactors in a much wider process window than in macroscopic reactors. Nevertheless also for micro reactors, limits of safe operation conditions were found. Furthermore it was shown that explosions inside the reactor could be induced by hot-spots on the catalyst surface and a transition to detonation and propagation into adjacent macroscopic devices could be obtained.

Explosion limits from macroscopic determination methods are not applicable for micro reactors. Standard ignition temperatures are not useful when dealing with micro reactors. Detonation cell size data is difficult to apply, it does not lead to design criteria of the micro structure. The current investigation is an illustrative example but cannot be used to set up design criteria without model based investigations. There is a lot of follow on work to be done. Detailed investigations of the ignition temperature in micro reactors are necessary, modelling work should be done in order to better understand the effects observed and to set up

design principles suitable to enhance those micro effects in order to enlarge safe operation conditions of micro structured devices. The development of appropriate test methods is subject of current standardisation work (DIN SPEC 12981, 2012).

Parallel to the reported investigations, aspects of reaction technology, such as selectivity and space-time yield, are being investigated at the University of Stuttgart. Combination of these two key issues, safety engineering and reaction technology aims at an assessment of the potential of micro structured reactors operated within the explosion region. Safety issues in macroscopic plants are well known and safety measures are well established. Micro reactors still are not applied so widely, yet, and thus appropriate safety measures are to be developed. Further investigations are in progress in order to find general design criteria for micro reactors improving their safety.

Acknowledgement

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