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Microreactor Studies for Efficient Organic Oxidation Processes.

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Abstract: Industrially important partial oxidations of hydrocarbons are frequently characterized by low conversions and yields, which are mostly related to mass and heat transfer problems. Due to the reaction conditions, such processes include also important safety risks and are still not sufficiently understood. To study the influence of the process parameters on the product selectivity, a lab facility including a silicon-coated micro reactor of stainless steel has been developed and constructed. Due to its modular construction (e.g. replaceable capillary), it permits for the first time to perform catalysed and non-catalysed oxidations of hydrocarbons with oxygen as a two-phase process in a capillary reactor in wide ranges of residence times (some minutes to 24 h), temperatures and pressures.

As an example, the oxidation of isobutane to tertiary butyl hydroperoxide (TBHP) has been studied. The reaction has been investigated for the first time as a Taylor-Flow process in a micro reactor at different reaction conditions as a prerequisite to enhance the space-time yield of the process. The advantages of micro reactors are the high surface-to-volume ratio ensuring efficient heat transfer and the improved, nearly inherent, safety. These permit investigating yet unexplored process windows, for instance within the explosive region of a reaction mixture. The reaction has been studied for varying flow rates, temperature, pressure and the molar ratio of the starting products using two different initiators, namely TBHP and di-*t*-butyl peroxide (DTBP). For all experiments, the selectivity of the reaction products and the conversion of the reaction have been studied by sampling and analysing the reaction by GC/MS. The use of TBHP as initiator increased the selectivity of the reaction for the target product TBHP. TBHP as initiator yields a better selectivity since at high temperatures, which are common for DTBP, the formation of propanone already becomes important and favours the decomposition of TBHP. The replacement of the initiator diluent water by decane resulted in a faster reaction and the highest autocatalytic isobutane conversion (~18 %) obtained ever for this reaction in a micro reactor.

1. Introduction

20 % to 30 % of all production processes performed in the chemical industry contain partial oxidation reactions of hydrocarbons. The chemical substances produced by such processes amount to about 600 Mt/year and include alcohols, ketones, esters, hydrocarbon acids and diacids as well as hydroperoxides [1].

Industrial oxidation processes can be divided into catalysed and non-catalysed processes. Among the catalytic processes, some are performed with homogeneous catalysts in liquid phase, e.g. the oxidation of toluene to benzoic acid, of *o*-, *p*- and *meta* xylene to the corre-

sponding phthalic acids and of cyclohexane to adipic acid [2], Among the 10 to 15 % of all processes, which are performed by homogeneous catalysis, oxidation reactions have been estimated to constitute with about 56 % the most important part [3]. Heterogeneous catalysts are mostly used to perform gas phase reactions, e.g. n-butane to maleic acid. However, many oxidation processes are essentially auto-catalysed free radical reactions. The most important ones among them are the oxidations of e.g. cumene to cumene hydroperoxide, which is used for the production of phenol, cyclohexane to cyclohexanol and cyclohexanone, which are utilised for the production of adipic acid and isobutane to t-butyl hydroperoxide (TBHP), which is applied for the oxidation of propene to propylene oxide in the frame of the oxirane process [2]. Beside the use of TBHP is as oxidant for the epoxidation of alkenes at laboratory and industrial scale it is used as initiator for polymerisations (e.g. emulsion polymerisation of acrylic monomers [2]), as Diesel additive [4] and for waste water treatment [5]. Furthermore, the number of applications of TBHP developed in organic chemistry is still increasing [6] and such new processes with peroxides can be efficiently performed using micro reactors [7] which increases also the safety of such processes in view of the potentially explosive properties of peroxides.

The production chain of propylene oxide, where TBHP is an intermediate, has the highest specific energy consumption among the 18 top large-volume chemicals and is of considerable industrial importance (

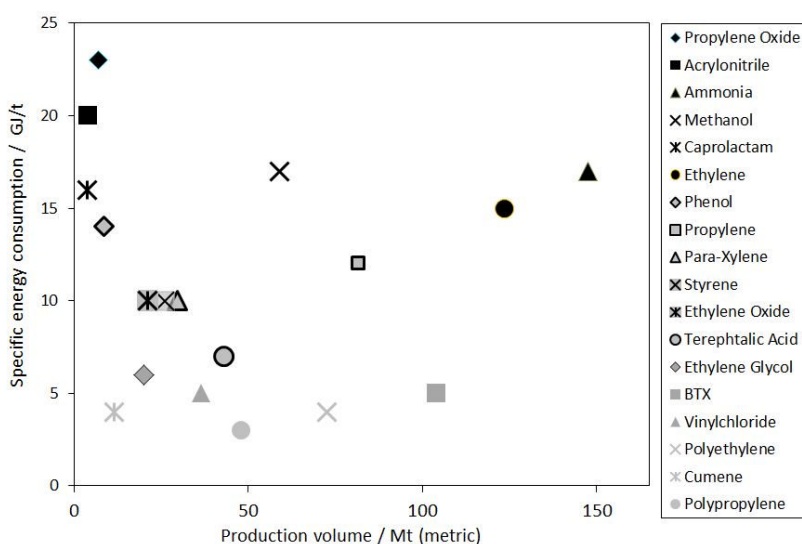


Figure 1) [8].

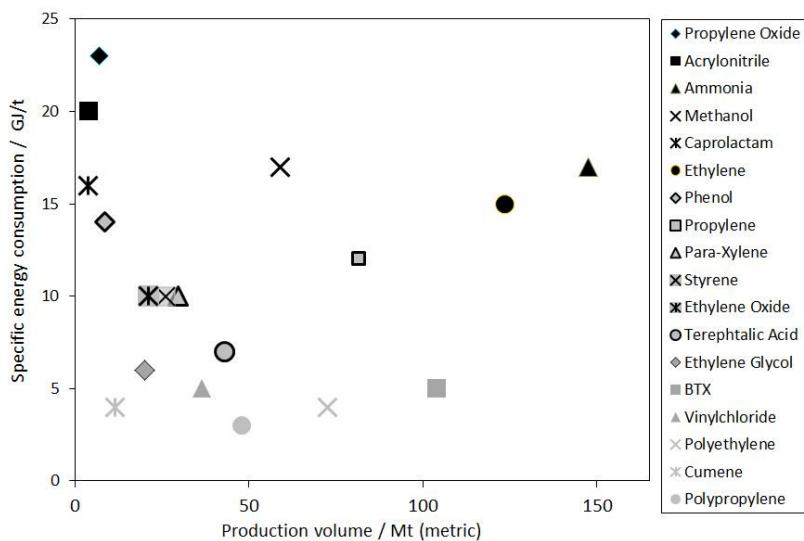


Figure 1: Energy consumption of 18 top large-volume chemicals [8].

The interest in epoxides such as propylene oxide is increasing since they are also used in the frame of sustainable chemistry reactions with carbon dioxide where epoxides can be used to realize ring opening co-polymerisations with carbon dioxide to poly carbonate [9]. TBHP might therefore become also even more important.

Although many production processes can be considered as established, most suffer from low product selectivities and rather low conversions. These are due to the higher reactivity of the products compared to the starting products, which are due to heat transfer and mass transfer limitations. The high hazard risk makes it difficult to study such reactions, especially using batch reactors where expensive safety measures are necessary to prevent explosion hazards due to runaway reactions and hydrocarbon-oxygen mixtures [10]. Therefore, many partial oxidation processes of hydrocarbons are little studied and, compared to other processes, still much research is necessary [11]. The advantage of micro and milli-structured reactors, compared to batch reactors, is their improved, nearly inherent, safety [12], due to the high ratio of surface to volume of such reactors (Volume 100 ml: micro reactor (inner diameter 1mm): 40 cm^{-1} ; batch reactor (depending on geometry): $\leq 1 \text{ cm}^{-1}$). The enhanced heat transfer prevents effectively runaway reactions [12]. Although also heterogeneous catalysis reactions can be performed [13], they are preferably used to realize homogeneous or gas-liquid reactions [14]. Using a Taylor flow for multiphase reactions (Figure 2) allows obtaining a defined liquid-gas interface and mass transfer due to the regular structure of the flow.



Figure 2: Taylor Flow in a micro reactor capillary (1: liquid slug, 2: gas bubble)

The mass transfer occurs by the thin film, which is present on the wall being in contact with the gas phase, and directly by the surface of the bubble. Colorimetric methods [15] have been used to study the mass transfer. The mass transfer is enhanced in both, in the liquid slug by currents due to friction with the wall of the tube and in the gas bubble due to vortex flows [16]. Although there are many studies concerning Taylor Flows, they are mostly considering water [17] whereas organic substances e.g. hydrocarbons are poorly studied and reactive systems, which are important for industrial processes [18,19], even less.

The partial oxidation of liquid isobutane by gaseous oxygen at industrial scale to TBHP, being an intermediate for the production of propylene oxide according to the oxirane process, is a typical multiphase process, conducted in industry at 120 to 140 °C and 25 to 35 bar in bubble tray reactors bubble columns or stirred tank reactors [20]. However, the conversion of the isobutane to TBHP is limited to 35 to 50 % in order to obtain a TBHP selectivity of 50 to 60 % minimizing the formation of by-products, which are caused by the decomposition of the TBHP due to the complex reaction mechanism. Beside safety aspects, the high reaction enthalpy of the oxidation as well as heat and mass transfer problems are further issues of this process. To study the influences of process parameters on conversion and product selectivity, overcoming the aforementioned limitations, the oxidation of isobutane to TBHP has exemplarily been studied for the first time as a Taylor-flow process in a micro reactor as a precondition to enhance the space-time yield of the process.

2. Experimental

2.1. Materials and methods

A SHIMADZU QP2010 Ultra has been used for GC/ MS analysis. To investigate the selectivities and conversions obtained in the oxidation experiments, a sampling procedure and a gas chromatographic (GC/ MS) method for the qualitative and quantitative analysis of the reaction products has been established [21]. After quenching the reaction in a micro heat exchanger directly at the outlet of the reactor capillary, the reaction products have been diluted in the sampling unit using a chilled heptane solution with an internal GC standard. This solution is directly analysed by GC/ MS or diluted with further heptane in case of high product concentrations. An extensive investigation and validation of the method has been performed in view of the thermal instability and high reactivity of peroxidic compounds towards metals and organic impurities containing alkenes, sulphur, ketones or other reactive functional groups. To take account of the thermo-labile compounds, a programmable temperature vaporizing (PTV) injector and an auto sampler with the possibility to cool the samples have been used. The temperature programs of the injector and the column started at 33 and 30 °C [21], respectively, to ensure the separation of highly volatile compounds in the beginning. TBHP has been vaporized at 70 °C, together with heptane, and traversed the

column at a temperature of 30 °C without decomposition. To prevent their reaction, only after the separation of TBHP, the second peroxidic and thus unstable compound, DTBP, traversed the column at 40 °C. The method used a complex GC/ MS configuration (Figure 3), which enabled the separation by two GC lines (and injectors) and MS analysis of higher hydrocarbons in liquid (line 1) and gaseous samples (line 2), as well as the analysis of permanent gases like methane, oxygen, nitrogen and carbon monoxide by a mole sieve column and a thermal conductivity detector (TCD) (line 2).

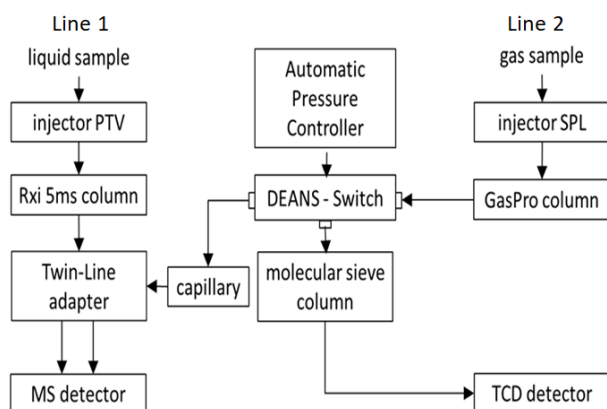


Figure 3: GC/ MS configuration [21].

2.2. The lab facility

To study the influence of the process parameters on the product selectivity, a lab facility including liquefied gas supply (isobutane), gas supply (oxygen and an inert gas), liquid supply (additive and a liquid initiator), a silicon-coated capillary of stainless steel as well as a heat exchanger and a sampling unit has been developed and constructed [22]. Because of the potential explosion hazard a sophisticated safety concept has been elaborated and implemented [22]. This permits to investigate yet unexplored process windows, for instance within the explosive region of a reaction mixture. Due to its modular construction (e.g. replaceable capillary), for the first time, catalysed and non-catalysed oxidations of liquid and gaseous hydrocarbons can be performed with pure oxygen as a two-phase process in a capillary reactor within wide ranges of residence times (r.t.: 1 to 24 h), temperatures (up to 160 °C) and pressures (up to 150 bar). To realize that range of residence times, the volume flow rates of the hydrocarbon has been set in the range of 200 $\mu\text{l/h}$ and 10 ml/h, those of the gases between about 1 and 10 ml/h. The initiator flow was adjustable between 0.2 $\mu\text{L/h}$ and 192 mL/h, in practice mostly a flow of 10 $\mu\text{l/h}$ to 100 $\mu\text{l/h}$ was necessary. The capillary length could be varied between 1 and 1000 m, where the upper limit depended also on the capillary diameter (0.25 to 2 mm). A process flow diagram and a picture of the lab facility are shown in Figure 4 and in Figure 5, respectively. Further details have been published elsewhere [22].

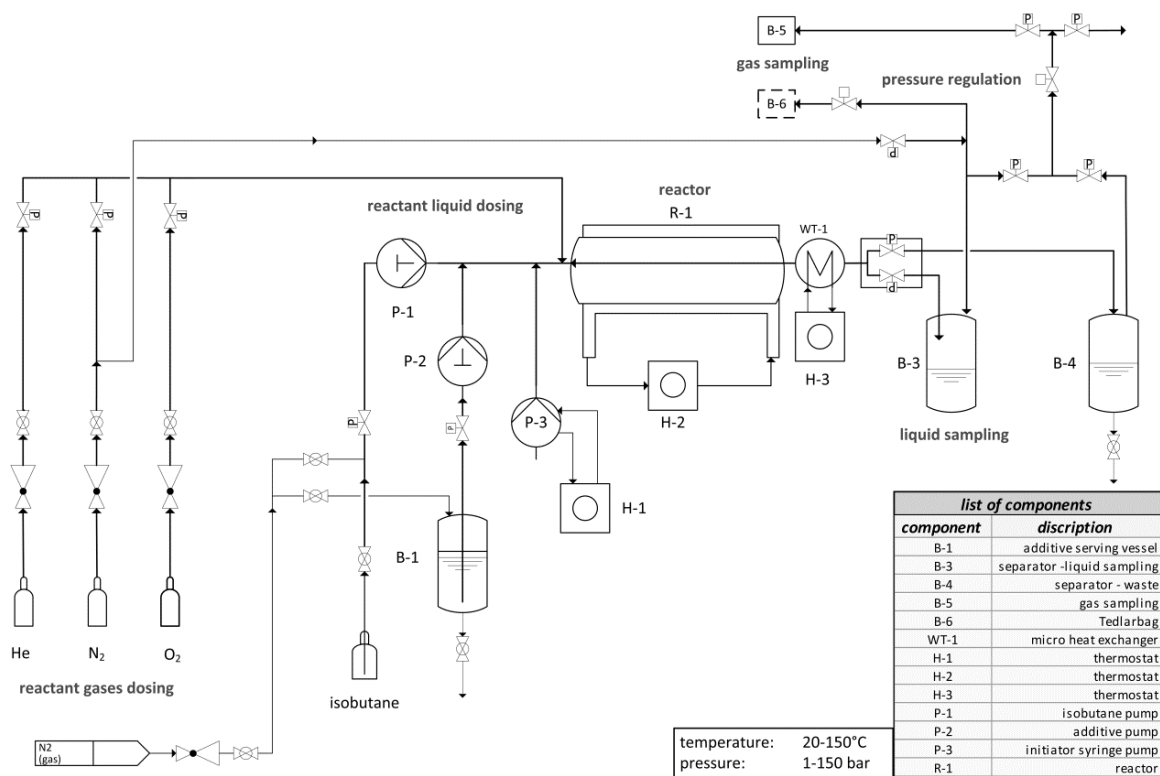


Figure 4: Process flow diagram of the lab facility.

On the basis of the kinetics given by Shah et al. [23] and simple thermodynamic relations the residence time range required to obtain a sufficient conversion has been calculated [22] depending on pressure, temperature and concentrations of reactants. Residence times in the range of 4 to 10 h have been realized using a 100 m micro capillary and a corresponding mass flow controller for oxygen and HPLC pump for isobutane [22]. Since micro calorimetric measurements have shown that TBHP is least sensitive to silicon [24], the capillary has been coated via chemical vapour deposition with a silicon layer having a thickness of about 500 nm (Silcolloy[®] coating made by SilcoTek[®]). Fischer et al. [19] used also a silicon coated micro reactor to obtain a higher selectivity for the target products of the cyclohexane oxidation.

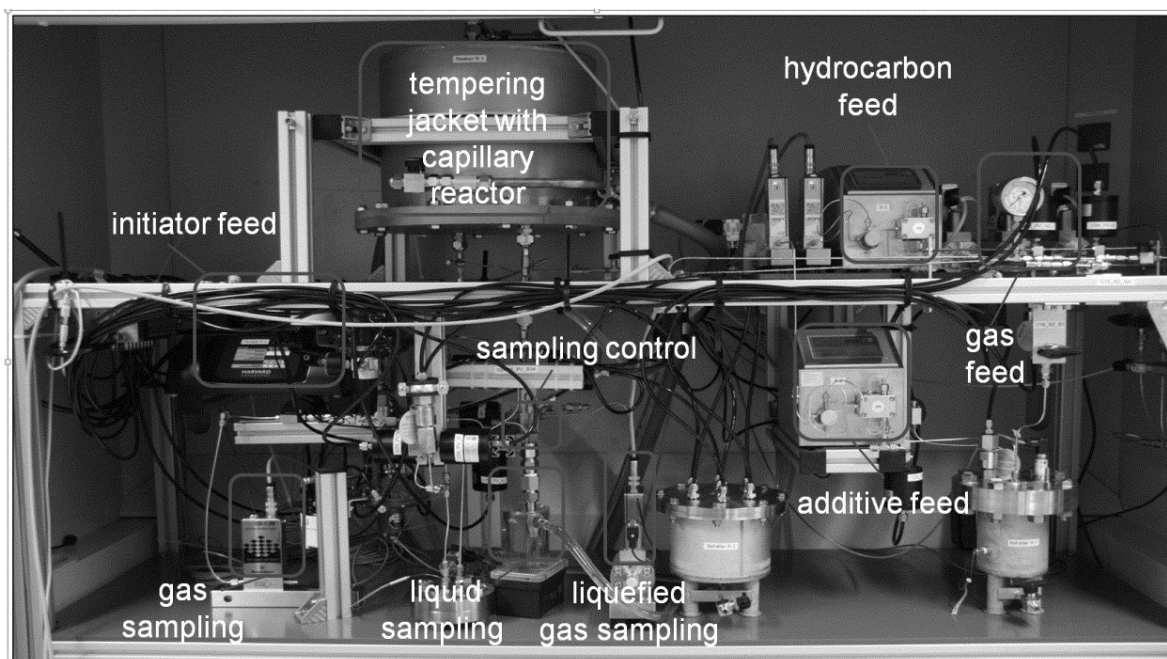


Figure 5: Lab facility with modular micro reactor for wide ranges of T (20 - 160 °C), p (1 - 150 bar) and residence time (r.t.) (1 - 24 h), including supply and sampling devices.

4. Results

4.1. Analytical results

Beside TBHP, by-products like t-butanol (TBA), acetone and DTBP were found by GC/MS. Additionally, traces of methanol, isobutene isopropanol and several formic acid esters could be identified. Methyl t-butyl ether (MTBE) has been used as internal standard. Further peaks belong to impurities, which are present in heptane. In Figure 6, an example of a chromatogram of a liquid sample is given.

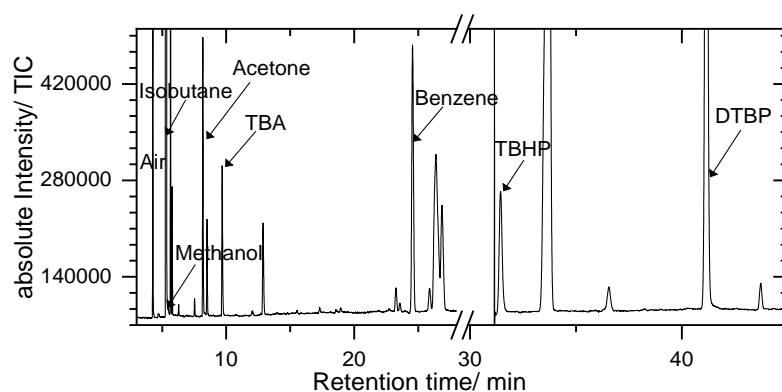
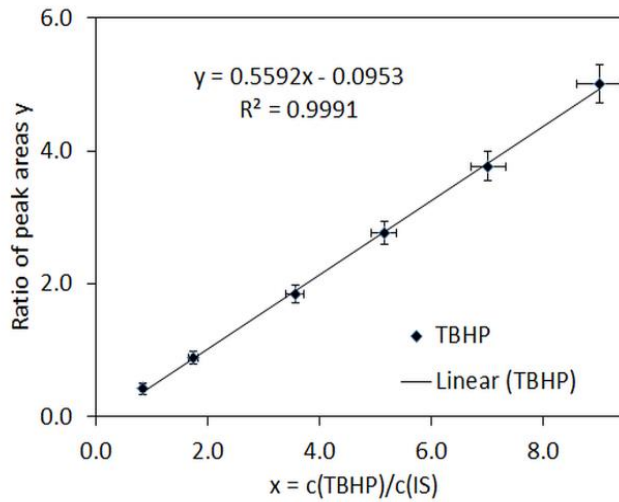


Figure 6: Chromatogram of the reaction mixture of the isobutane oxidation, dissolved in heptane. The solvent peak has been masked [21].

The quality of the calibrations obtained from such chromatograms for the considered reaction products of the isobutane oxidation (Figure 6), as shown by the correlation coefficients (R^2)



for TBHP (

Figure 7) and the most important by-products (e.g. DTBP) (Figure 8), had not been reached before ($R^2 > 0.99$). More details had been published elsewhere [21].

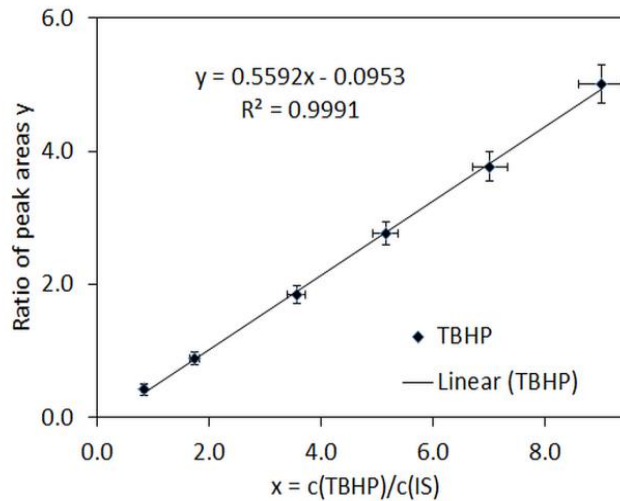


Figure 7: Calibration of TBHP in heptane (with error bars for x and y calculated on the basis of measurement errors) [21].

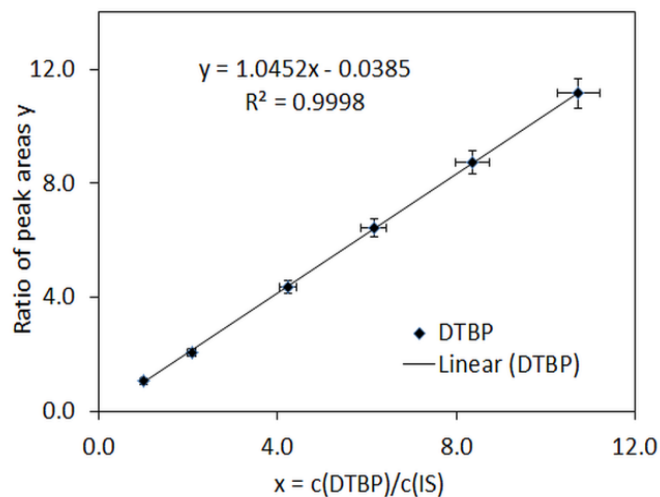


Figure 8: Calibration of DTBP in heptane (with error bars for x and y calculated on the basis of measurement errors) [21].

4.2. Results of oxidation experiments

Isobutane oxidation experiments have been performed under liquid phase (two-phase flow) conditions ($\leq 130^\circ\text{C}$, < 50 bar) as well as under supercritical conditions ($> 140^\circ\text{C}$, > 50 bar) using both, aqueous TBHP and TBHP in decane as initiators applying various residence times. Pure oxygen and oxygen nitrogen mixtures have been used as oxidants. An example for the start-up behaviour is given in Figure 9.

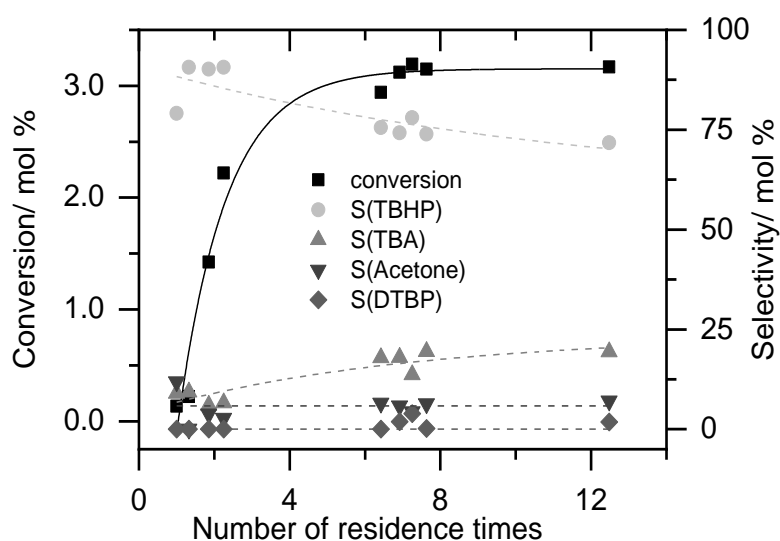


Figure 9: Example of start-up behaviour of the isobutane oxidation in liquid phase ($T = 130^\circ\text{C}$, $p = 42.5$ bar, r.t. = 4 h, 0.25 mol% DTBP, oxygen: isobutane = 1:1, no nitrogen).

The reaction time, given as number of residence times in Figure 9, which was required to attain the stationary state, was quite high considering the fact that for an ideal plug flow in a micro reactor theoretically one residence time would be enough to replace the reactor volume completely. Therefore, it could be assumed that back-mixing is occurring to a certain amount. The selectivity of TBHP under such conditions is more than 90 % in the beginning and still 73 % after 12 residence times. However, the conversion is only 3 %. The selectivities of DTBP and acetone are practically constant in the range of 12 residence times where the selectivity of acetone is significantly higher (~12 %) than that of DTBP. The selectivity of TBHP increases within about 8 residence times and then stays practically constant. This means that the selectivity loss of TBHP during in the further course of the experiment is mostly due to the decomposition of TBHP to TBA.

Only few (batch- or semi batch) experiments on the use of DTBP as initiator for the isobutane oxidation have been published in literature yet [25] [26]. Therefore, some experiments have

been performed with DTBP for comparison with TBHP (Figure 10, Figure 11). The selectivity of TBHP in case of the use of DTBP is always lower than in case of the use of TBHP as initiator. This result confirms the findings of Winkler and Herne [25].

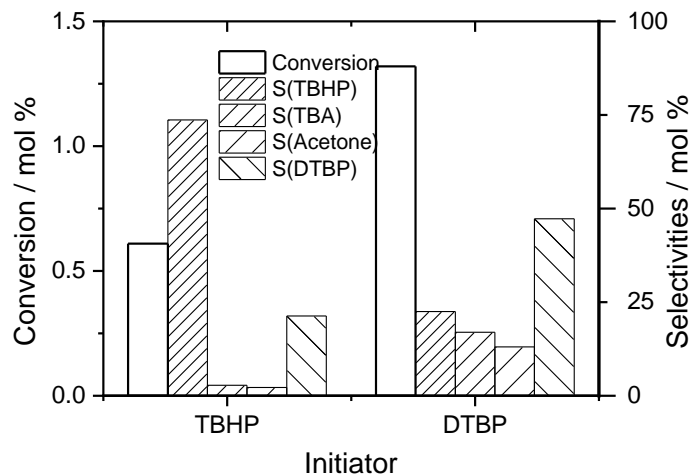


Figure 10: Conversions and selectivities with different initiators (2 phase flow: 130 °C, 42.5 bar, oxygen: isobutane = 1:1, 0.25 mol% initiator, r.t. 4 h) [27].

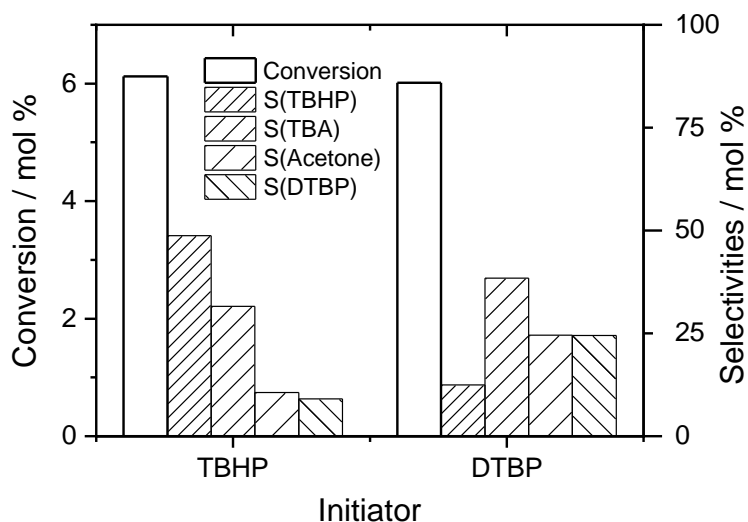


Figure 11: Conversions and selectivities with different initiators (supercritical: 145 °C, 55.0 bar, oxygen: isobutane = 1:1, 1.00 mol% initiator, r.t. 2 h) [27].

The lower selectivity of TBHP in case of using DTBP as initiator should be due to the fact that DTBP needs higher temperatures and residence times to decompose than TBHP and might therefore stay non-decomposed in part. Non-decomposed DTBP cleaves to t-butoxy radicals. Those can rather attack isobutane or the target product TBHP. In the latter case

DTBP can be reformed else TBHP forms from isobutane after reaction with oxygen.

If t-butoxy radicals form acetone preferably under non-polar conditions, this might explain why acetone has a significantly higher selectivity in the experiment with DTBP than in the case of aqueous TBHP. In case of aqueous TBHP, TBHP might be protected from the attack of t-butoxy radicals by water. In case of DTBP, this is not the case and hence t-butoxy radicals attack TBHP or decompose to acetone. This has not been found in previous findings [28] where in polar solvents (acetic acid, acetonitrile) with OH-bonding a stronger decomposition has been found than in aprotic solvents (chlorofluoroalkanes and -alkenes). However, the conditions are not fully comparable and other influences might be present since water is not comparable to the investigated acids.

In case of two-phase flow conditions, the conversion of isobutane stays generally lower than under supercritical conditions. This might indicate a mass transfer problem for two phase flow experiments as it has also been suspected by Jevtic et al. [18] for the cyclohexane oxidation in a capillary reactor. They compared the measured conversion with that calculated by the kinetics determined in a batch reactor and could exclude a surface problem by adding additional material pieces to increase the size of the surface area. However, Fischer et al. [19] who studied the same reaction, excluded a mass transfer problem by measuring the $k_L A$ value on the basis of a Taylor flow and suspect wall reactions and unselective side reactions as the reason for the lower conversion. It must be said though that, in the latter work, the influence of additional surface has not been verified and a Taylor flow has been proved only for room temperature but not for reaction conditions. As the following experiments show, in the present work, there might also be an influence of the initiator solvent in case of TBHP. For the first time, experiments have been performed with TBHP as initiator in decane. Under such conditions, the highest conversion of isobutane observed ever in a micro reactor for this reaction has been found (Figure) using 145 °C and 55 bar with 2.5 % TBHP as initiator.

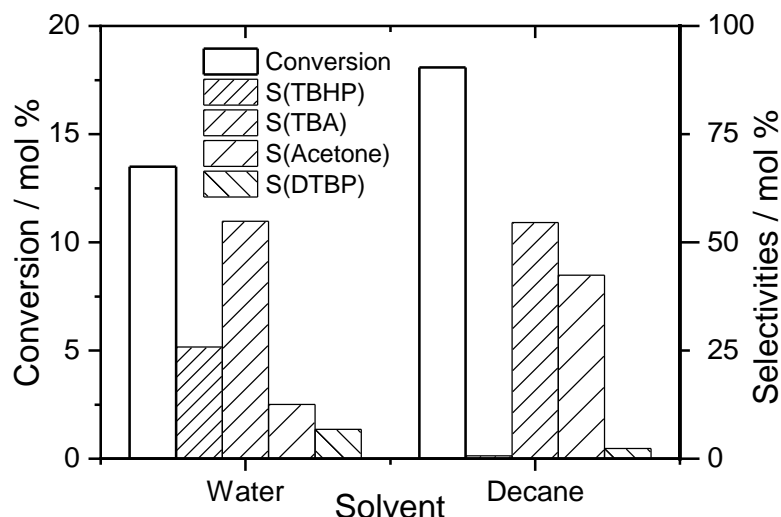


Figure 12: Isobutane oxidation using TBHP in water and decane (145 °C, 55 bar, 2.50 mol% TBHP, r.t. = 4 h, oxygen: isobutane = 1:1, no N₂) [27].

However, the selectivity of TBHP was reduced to zero. Since further experiments with TBHP and DTBP resulted also in a selectivity of zero, although the selectivity of the same experiments was much higher before (e.g. around 20 to 40 %). This can only be interpreted by destruction or modification of the silicon coating of the micro reactor as will be shown in the following.

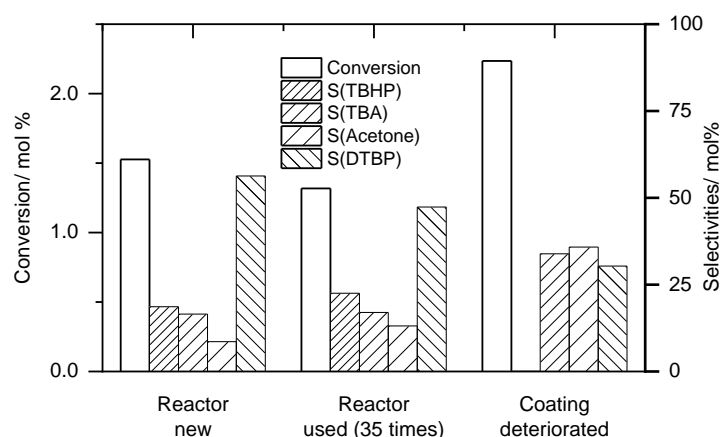


Figure 13: Comparison of conversions and yields of reference tests for the oxidation of isobutane using the initiator DTBP (reaction conditions: T = 130 °C, p = 42.5 bar, τ = 4 h, 0.25 mol% DTBP, oxygen: isobutane = 1: 1, no nitrogen).

As shown in Figure 13, the conversion in case of the intact reactors (new and used) is almost the same (new: ≈ 1.5 mol%, used: ≈ 1.3 mol%). The difference arises mainly from different yields of DTBP. In part, this might be due to inaccuracies of the sampling, in part to an

increased decomposition of DTBP and TBHP since, whereas the selectivity of TBA was constant, the selectivity of acetone in the experiment with the used reactor was significantly larger. This observation might be due to the formation of acid Si-OH groups on the surface of the reactor wall due to the longer operating life, which could catalyze the formation of acetone from TBHP. The experiment with the damaged reactor shows a much higher conversion (≈ 2.2 mol%), different from the two reference experiments with the intact reactors. Shah [29] observed also a wall effect for steel resulting in a lower selectivity and a higher reaction rate. In particular, it is striking that in the present work no TBHP has been found which also shows the high sensitivity of TBHP against steel [24]. In return, the yields of the decomposition products TBA and acetone increased significantly. Additionally, the higher conversion can be explained as a result of the immediate decomposition of formed TBHP since more radicals are in the system as long as TBHP is destroyed. This comparison shows clearly that the experiment using the damaged capillary coating did not happen at the same conditions as the ones with the intact reactors.

Thus, the real selectivity of the experiment with TBHP in decane must be considered as unknown since it is not known if the TBHP selectivity is a consequence of the reaction conditions or of the modified silicon coating. It must be said though that under such conditions also the by-products changed considerably. Beside the given compounds, also enhanced concentrations of formate esters, acetic esters and carbon dioxide have been found. The latter indicates a stronger decomposition of TBHP and other by-products. The selectivity of reaction products of formic acid, usually found in small concentrations in the sample oxidation, was increased. The high carbon dioxide selectivity could be explained by the reaction of TBHP with significant amounts of formic acid which might be responsible for the damaged silicon layer since a destruction of the silicon coating has been observed also after heating pure formic acid and TBHP in a silicon coated high pressure DSC steel crucible (Differential Scanning Calorimetry). Since the coating was damaged to a degree that the results of further experiments were unusable, the conclusion was drawn that another reactor wall material and/or another coating technology should be applied when using TBHP as initiator in non-aqueous solvents.

5. Conclusions

Performing the isobutane oxidation for the first time in a micro reactor at two-phase conditions using DTBP as initiator, beside the target product TBHP, mainly the by-products TBA, acetone and DTBP have been found. Furthermore, for the first time isopropanol and formic acid esters have been identified as side products [21]. Regarding the chemical analytics, important progress of the quality of the separation and calibration could be obtained compared to former works.

The number of residence times necessary to obtain the stationary state was higher than expected (> 6 residence times), which might be caused by back-mixing effects inside the reactor. Using aqueous TBHP as initiator, the selectivity of the product TBHP was generally higher than using DTBP, probably due to decomposition of TBHP induced by DTBP. At two-phase flow conditions, a conversion of 3 % has been obtained and a selectivity of 73 % after 12 residence times. Using supercritical conditions, generally higher conversions and a lower selectivity of TBHP have been obtained due to the higher temperature. At supercritical conditions, using 2.5 % initiator concentration, an unprecedented high conversion of 15% isobutane has been obtained in a micro reactor.

For the first time, decane has been used as solvent for the initiator. Using TBHP in decane, a higher isobutane conversion has been obtained than with aqueous TBHP. However, the by-products increased and changed considerably leading not only to formic esters, as usually the case, but also to acetic esters. Furthermore, probably due to a damage of the silicon coating of the capillary, after that experiment further test experiments gave very different results, e.g. significantly lower selectivities for TBHP than before. It seems that the coating of the steel capillary was not sufficiently stable at harsh conditions on the long term.

The use of a micro reactor reveals important challenges due to catalytic decomposition of TBHP and peroxy radicals by wall material, which reduces the conversion degree and the TBHP selectivity. However, there is still potential for improvement of the selectivity of TBHP since several measures could permit to improve it. Beside another wall material or coating of the wall, the addition of water and of neutralizing additives (phosphates, hydrogen carbonates) have not been tested yet.

6. Acknowledgements

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