Chemical Engineering Journal 145 (2009) 420–428

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Development of a microstructured reactor for heterogeneously catalyzed gas phase reactions: Part I. Reactor fabrication and catalytic coatings

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ARTICLE INFO

Article history:
Received 1 July 2008
Received in revised form
15 September 2008
Accepted 17 September 2008

Keywords:
Microstructured reactor
Heterogeneous catalysis
Catalytic coating
Binder material
Oxidative dehydrogenation
Propane
ODP
VO_x
Al_2O_3

ABSTRACT

Due to their superior heat transfer properties, microstructured reactors are well suited for performing strongly exothermic heterogeneously catalyzed gas phase reactions. In order to utilize the full potential of this reaction technology, a new low-cost manufacturing concept was developed, using a Ni–Ag–Sn solder system for bonding the individual structured steel platelets. Three different methods for depositing a VO_x/γ-Al_2O_3 material on the micro-channels were investigated with respect to morphology, mechanical stability and catalytic behavior of the obtained coatings. Especially the influence of different binder materials (Al-tri-sec-butylate, tetraethoxysilane, hydroxypropyl cellulose and polyvinyl pyrrolidone) was analyzed. For evaluating the performance of the coatings, the oxidative dehydrogenation of propane (ODP) served as a sensitive test reaction. The modules and the catalytic coatings withstood the applied reaction conditions (400–600 °C at ambient pressure), which makes them safe and flexible tools for research activities and small scale production processes.

1. Introduction

Microreaction technology (MRT) offers some outstanding advantages in comparison to conventional reactor systems such as extremely efficient heat and mass transfer properties, uniform residence time distributions, and enhanced process safety [1–4]. These advantages seem to be very useful for performing fast and strongly exothermic heterogeneously catalyzed gas phase reactions [5–11]. The oxidative dehydrogenation of propane (ODP) was found to be a well suited and sensitive test reaction, which shows many typical features of this class of reactions [12]. A simplified reaction model of the ODP is given through the following equations:

$$C_3H_8 + 0.5O_2 \rightarrow C_3H_6 + H_2O, \quad \Delta_R H_1 = -118\,\text{kJ}\,\text{mol}^{-1} \qquad (1)$$

$$C_3H_6 + 3O_2 \rightarrow 3CO + 3H_2O, \quad \Delta_R H_2 = -1077\,\text{kJ}\,\text{mol}^{-1} \qquad (2)$$

$$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O, \quad \Delta_R H_3 = -1926\,\text{kJ}\,\text{mol}^{-1} \qquad (3)$$

In addition, the ODP seems to be interesting because it offers an alternative route to produce propene opposed to conventional production processes [13]. Although propene is a very important base chemical, it is primarily obtained as a by-product from steam cracking and other refinery processes (e.g., fluid catalytic cracking and deep catalytic cracking). However, all of these processes are thermodynamically limited, extremely energy-intensive, and commonly suffer from catalyst deactivation by heavy coking. Therefore, a route that avoids most of these problems appears to be attractive. To this day, low selectivity towards propene has been the major drawback to an industrial application of the ODP, although it has been extensively investigated over the last decade [14–19]. Once catalyst development has reached a point where propene yield appears economically feasible, microstructured reactors might serve as an advantageous reaction technology to exploit the kinetic potential of these catalysts due to their superior heat and mass transfer properties.

However, among a number of challenges, high production costs for microstructured devices have prevented a break through of this innovative technology in the past. In order to utilize MRT for possible industrial applications, a new flexible and scalable manufacturing concept for microstructured reactors was developed and optimized. Special attention was paid to the preparation of the catalytic coatings and the soldering process of the reactor modules. The stability of both coatings and reactors is crucial for the maintenance of a high catalytic long-term performance, safe

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doi:10.1016/j.cej.2008.09.036

operation conditions, and economic feasibility. Many studies have been carried out investigating different means of catalyst preparation/deposition on micro-channels [20–30] and relevant results have been recently reviewed [31,32]. However, only few reports combine catalyst deposition with reactor fabrication in a single study, which is a major prerequisite for a coherent manufacturing concept. Especially, methods suitable for mass production of catalytic microstructured reactors such as soldering and spray coating technologies [33,34] are rarely described.

Our research activities were not exclusively focused on the ODP reaction. All methods and processes were developed with respect to the general applicability of microstructured reactors to heterogeneously catalyzed gas phase reactions. The results of this study will be published in two consecutive papers. The first paper deals with the development of a fabrication process for the reactor modules and the optimization of the catalytic coatings. In the second paper, the obtained reactors will be characterized and used for kinetic investigations of the oxidative dehydrogenation of propane.

2. Experimental

2.1. Reactor fabrication

The concept that was followed for fabricating the microstructured reactors is schematically shown in Fig. 1. In the first step, one micro-channel (31 mm length, 25 mm width, 0.23 mm depth, 0.169 cm^3 volume per channel, 7.35 cm^2 internal surface area per channel without considering roughness of the base material) was created by wet chemical etching on each stainless steel platelet (75 mm length, 75 mm width, 0.5 mm thickness, 1.4571). Similarly, platelets for inserting four thermocouples in between the catalyst-coated platelets were produced. Three thermocouples for temperature measurement were placed at equal distances along the catalyst bed, whereas the fourth thermocouple for temperature control was placed in some distance from the catalyst bed.

In the second step, a tailored solder system from individual layers of Ni (barrier layer between base material and solder material), Ag and Sn was deposited on the platelets by standard galvanic techniques (Atotech Deutschland GmbH) [35,36]. Coating thickness and thickness distribution were detected by XRF (Fischerscope XDVM-T5).

Afterwards, catalytic material was deposited on the micro-channels by spray coating. Areas subsequently used for bonding the individual structured steel platelets were protected with a peelable solder mask or a dry film photo-resist mask, respectively, leaving only the micro-channels exposed.

Before soldering the platelets to a complete microstructured reactor, the mask was removed to uncover the previously deposited solder materials. A total number of four catalyst-coated platelets was assembled with two thermocouple platelets, a bottom platelet (1 mm thick, 1.4571) and a top platelet (5 mm thick, 1.4571), pressed together and soldered at 400 °C in vacuum [36]. Tubes used as gas inlet and outlet were attached to the top platelets by welding before final assembly of the reactors.

Fig. 2a shows a schematic drawing of the single channel microstructured reactor, whereas Fig. 2b shows a photograph of a complete reactor equipped with four thermocouples for temperature measurement and control. For a variation of reactor volume or catalyst mass, additional channel platelets can be included in manufacturing the reactors.

Reactants enter the reactor through the inlet tube. The triangles directly under the inlet tube are etched through the platelet ("open manifold"), allowing the gas to pass the channels of the individual platelets in parallel. Since the bottom platelet seals the reactor from below, the flow has to be redirected in a 90° angle for passing the catalytic material deposited on the micro-channels. Afterwards, the gas flow has to be redirected again to leave the reactor through the outlet tube.

All microstructured reactors were tested for gas leaks before any further applications. The gas outlet was closed with a gas tight fitting and the gas inlet was connected to a pressure hose. The reactors were then submerged in water and set under pressure (2–3 bar) for 10 min. Leaks were detected by rising air bubbles. Some reactors were also tested for their thermal stability. They were heated up to 550 °C under a pressure of 1.5 bar for 3–9 days. After cooling they were tested for gas leaks again.

2.2. Catalytic coatings

2.2.1. Preparation of coatings

For a fast and efficient development and optimization of the catalytic coatings, unstructured test platelets made of the same stainless steel as the microstructured platelets were used for initial coating experiments. The coatings on these test platelets were taken for evaluating adhesion of the ceramic support on the metallic surface, analysis of the surface morphology, and determination of coating thickness. Furthermore, the coatings were scraped from the test platelets in order to obtain powders that can be used for physico-chemical analysis. In the second step, the most promising coating formulations were selected for manufacturing complete microstructured reactors.

Formulations for coating the micro-channels were prepared by dispersing either γ-alumina (Alfa Aesar, 99%, average particle size 3 μm) or pre-prepared VO_x/γ-Al_2O_3 particles in 2-propanol. The pre-prepared catalyst was obtained from a preparation technique developed prior to the present study [37]. Independent of the preparation method, chemical binder systems were used to stabilize the ceramic catalyst materials on the metallic reactor surface. The application of binder materials turned out to be essential for mechanically and thermally stable catalyst coatings. Several binder compositions were tested in order to produce coatings with a sufficient adhesion on solder-coated substrates. Said binders, i.e., tetraethoxysilane (Merck, 99%), Al-tri-sec-butylate (Aldrich, 97%), hydroxypropyl cellulose (Aldrich, 99%), and polyvinyl pyrrolidone (Merck, 99%) were obtained by dissolving the organic materials or pre-hydrolyzing the metal alkoxides in water or 2-propanol followed by addition of the alcoholic slurry of γ-Al_2O_3 or catalyst particles. Typical weight ratios of particle:binder were 5:1 and 10:1, respectively. The final mixtures ready for deposition were diluted to a solid content in the range of 10–25 wt.% and treated with ultrasound. The alcoholic slurries were spray coated onto the masked platelets followed by a thermal treatment at 100–120 °C for 1 h. The peelable solder mask/dry film photo-resist mask was removed and the platelets were weighed to calculate the catalyst loading. Most of the experiments were performed with formulations made from a binder and pre-prepared VO_x/γ-Al_2O_3 particles, which were deposited on the micro-channels prior to reactor assembly.

In an alternative series of experiments, platelets with pure γ-alumina coatings were assembled and soldered to a complete reactor. This reactor was then attached to a peristaltic pump to impregnate the γ-alumina coating with a pre-heated 0.04 $g\,l^{-1}$ solution of $VO(acac)_2$ (Fluka, 97%) in toluene. After soldering and before performance tests, the catalytic coating was calcined under a flow of synthetic air by keeping the entire reactor at 500 °C for 5 h.

In another series of experiments, a slurry of γ-alumina particles, dissolved $VO(acac)_2$, and binder material were coated on the micro-channels prior to reactor assembly. After soldering and before performance tests, the catalytic coating was calcined as described above.

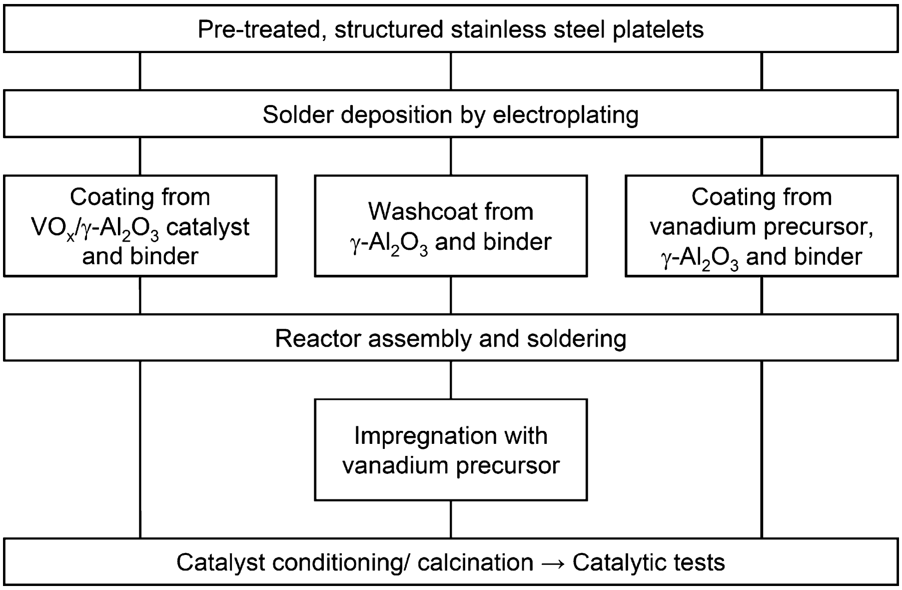

Fig. 1. Simplified manufacturing concept for microstructured reactors.

2.2.2. *Characterization of coatings*

Inductively coupled plasma-optical emission spectroscopy (ICP-OES, Varian 720-ES) was used to determine the vanadium, aluminum and silicon concentrations of the obtained powders. The powders were detached from the metallic substrates and dissolved in concentrated acids prior to ICP-OES measurements.

Specific BET surface areas of the catalytic materials were determined using nitrogen adsorption at 77 K using a Micromeritics Gemini III 2375 Surface Area Analyzer equipped with a Vacprep 061 degasser. Before measurements, the powders were heated for 90 min at 250 °C under vacuum (0.15 bar) to remove water and other adsorbed molecules from the sample surfaces.

The adhesion of all coatings was tested after applying a standard soldering temperature treatment to individual micro-channel platelets by tape test (ASTM D 3359-02). A strip of defined size and adhesive strength was pressed on the catalytic coating and rapidly removed. Coatings with sufficient adhesion (i.e., 4 or higher on the tape test scale corresponding to only minor amounts of particles on the adhesive strip) were used for manufacturing entire reactors and successive performance tests as described below.

The morphology of coatings prepared from different binder compositions was investigated using scanning electron microscopy (SEM, Cambridge S360). Prior to analysis, the samples were gold coated (Bal-Tec SCD050). Typical resolutions of the images were 20–200 μm.

Coating thickness and coating uniformity were monitored with an optical microscope (Olympus BX51M) on cross-sections of coated micro-channels.

2.2.3. *Catalytic performance tests*

The microstructured reactors containing the catalytic coatings were heated between two brass plates (on top and below the reactor) equipped with four heating cartridges. Both the reactor and the heating plates were placed in a hotbox for thermal insulation. In case of reactor leakage, the interior of the hotbox was constantly flushed with nitrogen to create an inert atmosphere. In addition to

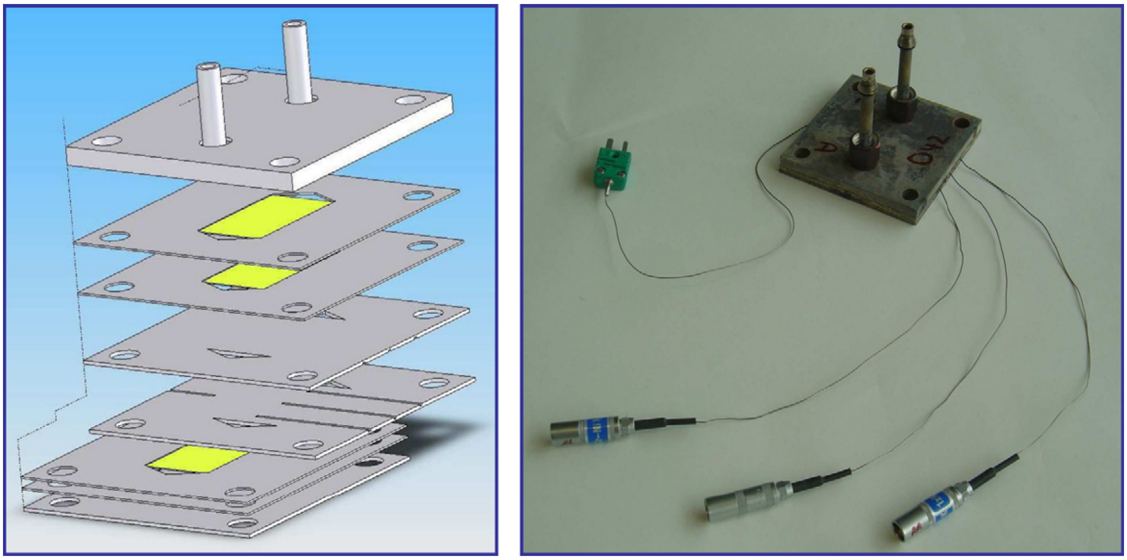

Fig. 2. (a) Schematic drawing of a microstructured reactor (single channel design) and (b) photograph of a microstructured reactor equipped with four thermocouples.

experiments with reactors containing catalytic coatings, reactors without coatings were also tested for evaluating catalytic activity of the reactor material. For comparing the performance of the differently prepared coatings, standard reaction conditions were chosen as follows: the reactor temperature was kept at 450 °C and the ratio of the $C_3H_8/O_2/N_2$ inlet flow was 2/1/4, using synthetic air as oxygen source. In order to achieve different degrees of propane conversion, total volume flows were varied from 30 to 240 $ml_n\,min^{-1}$. The mass of the catalytic coatings varied between 48 and 228 mg. Reaction products were analyzed by a specially modified gas chromatograph (Shimadzu GC-2014) equipped with two packed columns (HayeSep Q and molecular sieve 13X) for the separation of O_2, N_2, CO, CO_2, and C_{1+} hydrocarbons. Oxygen and nitrogen were detected by a thermal conductivity detector, whereas hydrocarbons and methanized carbon oxides were detected by a flame ionization detector. The duration of one GC analysis was about 28 min, which is long enough to achieve steady state conditions after reaction parameters were changed. Propane conversion and propene selectivity were calculated from inlet and outlet concentrations corresponding to the following equations:

$$X = \frac{c_{C_3H_8,0} - c_{C_3H_8}}{c_{C_3H_8,0}} \quad (4)$$

$$S = \frac{c_{C_3H_6}}{c_{C_3H_8,0} - c_{C_3H_8}} \quad (5)$$

3. Results and discussion

3.1. Reactor fabrication

The applied manufacturing method for the reactor modules with a catalytic coating deposited on the micro-channels prior to soldering (catalyst "pre-coat") led to low-cost microstructured components. The soldering technique enables a full area metallic contact between individual reactor platelets leading to an enhanced heat conductivity compared to competitive assembly technologies like laser-welding or the use of fasteners and sealings without a full metallic contact in the structured part of the reactor.

Undesired gas bypasses are also suppressed through this manufacturing concept. However, due to the fabrication process, the modules cannot be opened after a performance test without destroying them. Compared to the potential of a low-cost mass production process and the enhanced heat transfer properties, this aspect seems to be only a minor drawback.

Various tests resulted in sufficient temperature and pressure stability of the modules up to 600 °C at ambient internal pressure, making them safe tools for performing strongly exothermic reactions at high temperatures in a large range of feed compositions. Typical burst pressures of such stacks range between 20 and 30 bar at room temperature. Higher pressure stability can be reached with either a thicker bottom platelet (e.g., 5 mm thickness) or a housing for the reactors.

3.2. Catalytic performance tests

3.2.1. Activity of reactor material

Prior to experiments with microstructured reactors containing catalytic coatings, the internal reactor surface was tested for activity in the oxidative dehydrogenation of propane. Fig. 3a shows conversion of propane and propene as a function of temperature, whereas Fig. 3b shows corresponding oxygen conversion degrees. The reactor was assembled from four structured single channel platelets and two thermocouple platelets. Feed composition of $C_3H_x/O_2/N_2$ was 2/1/4 at a constant flow rate of 60 $ml_n\,min^{-1}$.

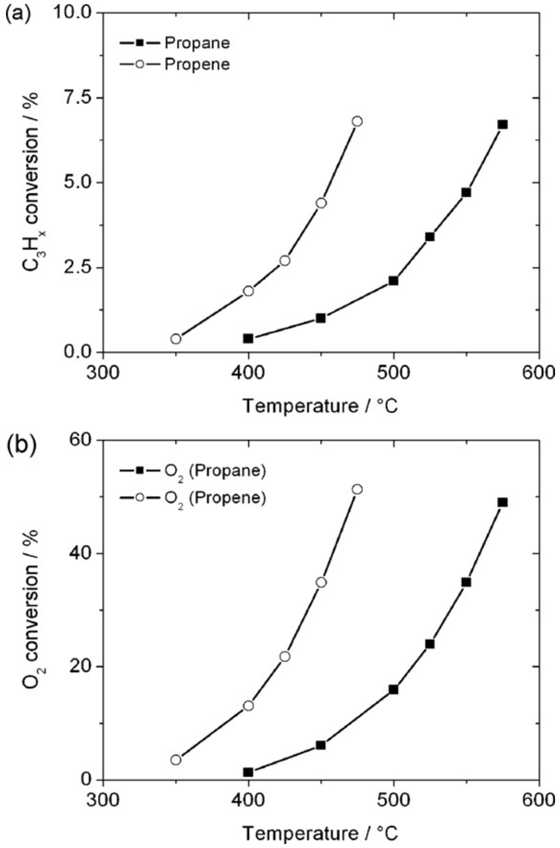

Fig. 3. Activity of reactor material for (a) C_3H_x conversion and (b) O_2 conversion ($C_3H_x/O_2/N_2$ = 2/1/4, flow rate 60 $ml_n\,min^{-1}$).

Conversion of C_3H_x and O_2 exponentially increases with increasing temperature. The main reaction product was analyzed to be CO_2. Importantly, propene is converted at substantially lower temperatures than propane, which makes the desired product more prone to unselective consecutive reactions. This might be attributed to a small proportion of catalytic activity that originates from the exposed metal surfaces and to a significant proportion of cracking that cannot be neglected in this temperature range [38]. However, compared to catalyst loaded reactors, C_3H_x/O_2 conversion is very small.

3.2.2. Coatings from VO_x/γ-Al_2O_3 particles

For all coatings in this series, the same catalytic material was used in order to ensure comparable results. Prior to experiments, the material was analyzed by ICP-OES resulting in a vanadium content of 4.6 wt.% and an aluminum content of 44.3 wt.%. BET surface areas were determined for the plain γ-alumina support (78.7 $m^2\,g^{-1}$), the catalyst used for the coatings (51.5 $m^2\,g^{-1}$) and the inorganic binder materials after hydrolysis (alumina ex Al-tri-sec-butylate – 345 $m^2\,g^{-1}$ and silica ex tetraethoxysilane – 281 $m^2\,g^{-1}$).

Upon numerous coating formulations, the most promising for each binder system was chosen for further experiments. The decision was mainly based on preliminary adhesion tests. Table 1 summarizes the characteristics of these formulations.

All coatings were prepared with a particle:binder weight ratio of 5:1 and showed sufficient adhesion on the metallic substrate rated with 4 on the tape test scale (i.e., only minor amounts of particles on the adhesive strip). It is likely that these coatings will also endure more severe ODP process conditions. Specific surface areas of the formulations were influenced by the type of binder material

Table 1
Formulations for preparing coatings from $VO_x/\gamma\text{-}Al_2O_3$ particles.

Coating formulation	Cat:binder	Adhesion	S_{BET} ($m^2\,g^{-1}$)	Loading (mg)
$VO_x/\gamma\text{-}Al_2O_3$ + Al-tri-sec-butylate	5:1	4	104.8	71.0
$VO_x/\gamma\text{-}Al_2O_3$ + tetraethoxysilane	5:1	4	85.9	48.0
$VO_x/\gamma\text{-}Al_2O_3$ + hydroxypropyl cellulose	5:1	4	51.6	65.0
$VO_x/\gamma\text{-}Al_2O_3$ + polyvinyl pyrrolidone	5:1	4	50.5	82.0

that was used. In case of the inorganic binders, S_{BET} was substantially increased, which can be attributed to the high surface area of the hydrolyzed binder materials. Similar findings were frequently reported in the literature when applying alkoxides or silicates as support or binder materials [20,23,24]. In contrast, S_{BET} of the formulations containing organic binders were only slightly influenced compared to the original $VO_x/\gamma\text{-}Al_2O_3$ particles. Catalyst loading of the fabricated microstructured reactors varied between 48 and 82 mg.

In order to examine adhesion and morphology of the coatings on a microscopic level, SEM was applied. Fig. 4 shows a coating made from $VO_x/\gamma\text{-}Al_2O_3$ particles and Al-tri-sec-butylate in two different magnifications (scale bar 200 and 20 μm, respectively). It can be seen that the coating is relatively uniform and homogenous, but slightly rough and porous.

In comparison, Fig. 5 shows a coating containing polyvinyl pyrrolidone as binder material in two different magnifications (scale bar 200 and 20 μm, respectively). This coating also looks uniform and homogenous. However, it appears less rough and shows individual pores and cracks on the surface.

SEM images were also taken from other coatings, but are not shown for sake of brevity. Their optical impression changes with the application of different binder materials. However, all coatings were sufficiently uniform and homogeneous.

The thickness of the coatings made from $VO_x/\gamma\text{-}Al_2O_3$ particles and binder materials was determined by analyzing cross-sections from different parts of the steel platelets. It was measured to be in the range of 5–25 μm after soldering treatment. Similar values were found for all other preparation methods. The cross-sections also confirmed uniformity and homogeneity of the coatings.

The microstructured reactors containing differently prepared coatings were then tested in the oxidative dehydrogenation of propane. Their catalytic performance was compared to a powder reference catalyst (i.e., the original catalytic material that was used for preparing the coating formulations tested in a tubular quartz glass reactor). In order to ensure comparability of coatings made from organic and inorganic binders, the extra mass of binder materials was taken into account (i.e., additional mass contributions from the binder materials were subtracted for calculating the reactor loading). By normalizing via the modified residence time

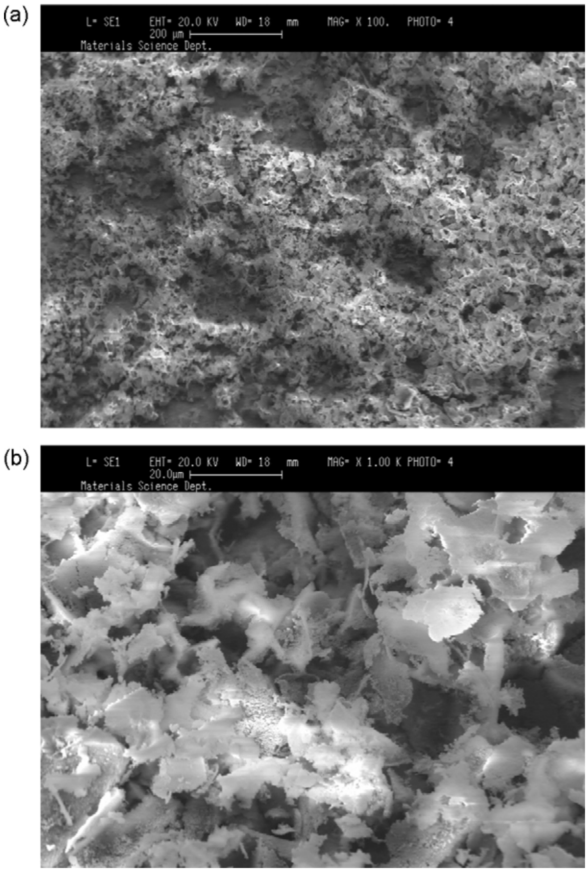

Fig. 4. SEM images of a coating made from $\gamma\text{-}Al_2O_3$ particles containing Al-tri-sec-butylate as binder material, scale bar (a) 200 μm and (b) 20 μm.

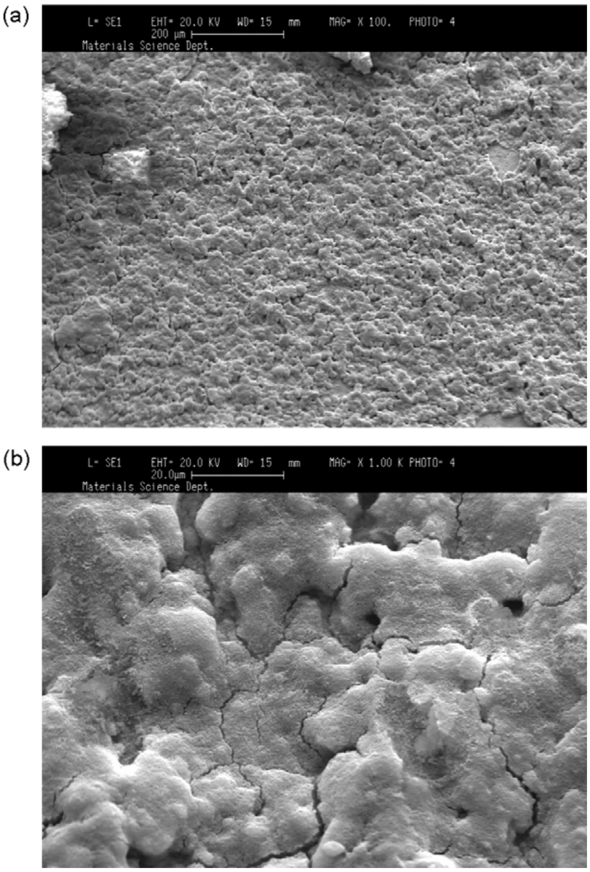

Fig. 5. SEM images of a coating made from $\gamma\text{-}Al_2O_3$ particles containing polyvinyl pyrrolidone as binder material, scale bar (a) 200 μm and (b) 20 μm.

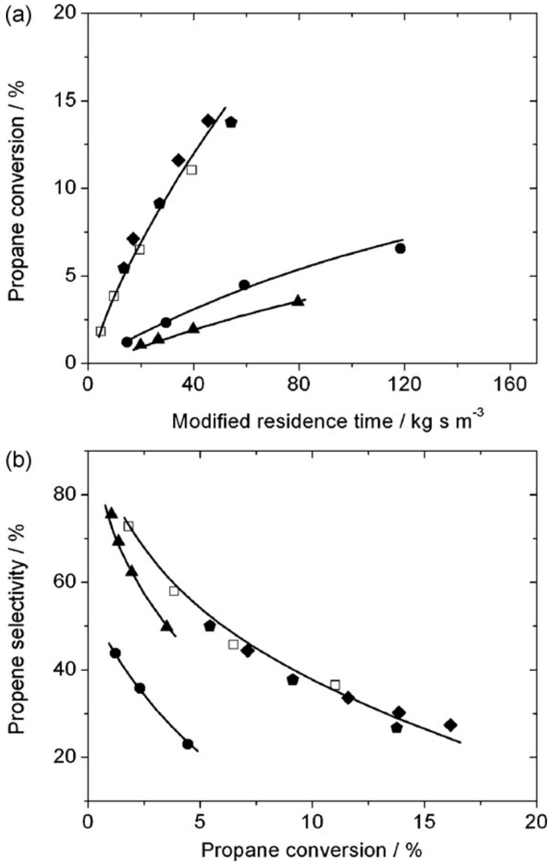

Fig. 6. Activity (a) and selectivity (b) of catalytic coatings (□) reference catalyst 4.6 wt.% V, (●) Al-tri-sec-butylate, (▲) tetraethoxysilane, (⬟) hydroxypropyl cellulose, and (♦) polyvinyl pyrrolidone (450 °C, $C_3H_8/O_2/N_2 = 2/1/4$, flow rate 30–240 ml$_n$ min^{-1}, catalyst mass 48–82 mg).

(catalyst mass divided by volume flow of reactants), comparability of results can be achieved.

Activity behavior of coatings made from organic binders (hydroxypropyl cellulose and polyvinyl pyrrolidone) seems to be almost identical compared to the reference catalyst. Inorganic binders such as Al-tri-sec-butylate and tetraethoxysilane clearly decrease catalytic activity of the coatings compared to the reference catalyst. A similar behavior was observed for propene selectivity. Organic binders do not influence selectivity, whereas inorganic binders show a negative influence on the selective formation of propene. Results of the performance tests of the microstructured reactors are shown in Fig. 6.

Since all organic binders are assumed to be removed during preparation of the coatings by temperature treatment, the properties of the catalytic material appear to be unchanged. No carbon residues were found in the catalytic coatings after the soldering procedure. The complete removal of organic binder materials from the coating was also observed by Pfeifer et al. [29]. This is not the case when inorganic binders are applied since they stay within the coatings. They substantially decrease activity for propane conversion and selectivity towards propene. Since activity and selectivity are decreased, propene yields for these coatings were among the worst. This might be due to a change of the morphology of the catalysts, in particular the relationship between support material (γ-Al_2O_3) and the active VO_x surface species. It is known that the performance of the ODP reaction is sensitively influenced by the vanadium loading and different support materials [37,39–43]. If the composition of the catalytic material is changed through the insertion of an inorganic binder material, it might be possible that also the catalytic behavior will be changed. Another explanation for the decreased activity might be the encapsulation of catalyst particles by binder material particles. If catalytically active surface species are buried under a thin layer of alumina or silica, these surface species might not be accessible for gas phase reactants anymore. The same reason for decreased catalytic activity of their coatings was proposed by Nijhuis et al. [44] and Groppi et al. [45], who used sodium silicate (waterglass) and silica sols as binder materials. However, the origin of the influence of inorganic binder materials on catalytic performance has not been finally resolved yet and might be investigated in further detail.

3.2.3. Coatings from γ-Al_2O_3 particles plus impregnation

The impregnation of porous support materials with precious metals or transition metal precursors is a common pathway for the preparation of catalysts for a wide range of heterogeneously catalyzed gas phase reactions [26,29,46]. Therefore, this preparation route is potentially interesting for many reactions that can benefit from microreaction technology. Our technique of impregnating γ-alumina with a solution of vanadyl acetylacetonate in toluene was first developed by Frank et al. [12] and further investigated prior to the present study [47].

Similar to the experiments described above, all tested binder systems were used to deposit stable γ-alumina coatings on the micro-channels. These formulations were also characterized in terms of adhesion, specific surface area, and coating morphology. Results were comparable to the results from the first preparation method and are not shown here for sake of brevity.

For impregnating these γ-alumina coatings with a solution of $VO(acac)_2$ in toluene, only tetraethoxysilane was chosen as a binder system for further experiments since it yields the most stable coatings. After one impregnation cycle, vanadium contents of the coatings were determined to be about 1–2 wt.%. This is in good accordance with results from previous experiments, where γ-alumina particles were similarly impregnated with a vanadium precursor solution [12,47]. The relative low receptivity of the support material for $VO(acac)_2$ molecules is probably due to the large acetylacetonate complex that occupies substantial proportions of the support material's surface. Therefore, multiple impregnation cycles with interim calcination procedures have to be applied to achieve higher VO_x concentrations.

The reactor obtained from this manufacturing route was also compared to a powder catalyst that was tested in a tubular quartz glass reactor. Fig. 7 shows activity and selectivity behavior of the catalytic coating (1.1 wt.% vanadium) and the powder catalyst (1.4 wt.% vanadium). The powder catalyst was also prepared by an impregnation technique as described in [12,47].

It can be seen that activity and selectivity of the catalytic coating measured in the microstructured reactor are somewhat lower than for the powder catalyst. The slight deviations might be due to several reasons: the catalytic materials are not identical in terms of vanadium content, chemical composition (in case of the coating, silica is also present due to the inorganic binder that was used to prepare the coating in the first place), and impregnation conditions. Especially the influence of the inorganic binder might be responsible for both decreased activity and selectivity in case of the coating. Similar results were reported by Zapf et al. [26], who compared catalytic coatings made from γ-Al_2O_3/polyvinyl alcohol, γ-Al_2O_3/boehmite, and γ-Al_2O_3/α-Al_2O_3 in the methanol steam reforming reaction. However, it could be shown that this particular manufacturing route for our microstructured reactors is a possible way to insert catalytically active material into the microstructure after assembly and soldering.

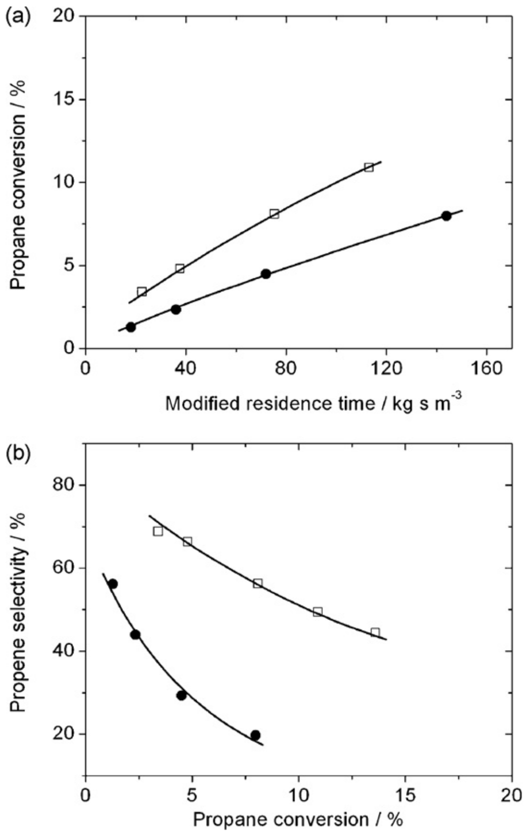

Fig. 7. Comparison of activity (a) and selectivity (b) of impregnated coating (●) and reference catalyst (□) (450 °C, $C_3H_8/O_2/N_2$ = 2/1/4, flow rate 30–240 ml$_n$ min^{-1}).

3.2.4. *Coatings from vanadium precursor and γ-Al_2O_3 particles*

In order to simplify preliminary catalyst and subsequent coating preparation, this method combines both steps in one. Since very similar conditions are applied during the two preparation processes, the catalytically active material can be created "in situ", while the coating formulation is produced. Therefore, the vanadium precursor, γ-alumina particles, and the binder material are mixed into one solution that is afterwards deposited on the microstructured channels similar to procedures presented by Steinfeldt et al. [9] and Schimpf et al. [23]. Table 2 summarizes the properties of the most promising formulations that were tested in the present study.

In summary, adhesion on the metallic substrate was found to be sufficient for further experiments. However, in case of the Al-tri-sec-butylate and the hydroxypropyl cellulose binder material, the tape test showed only a value of 3 on the tape test scale (i.e., small amounts of particles on the adhesive strip). In terms of specific surface area, the same dependencies as for the first preparation route were found. Inorganic binders increase S_{BET} values substantially, whereas organic binders show only minor influence on the surface area compared to the VO_x/γ-Al_2O_3 reference material. Vanadium contents of the coatings varied between 3.6 and 5.0 wt.%, which is similar to the vanadium content of the pre-prepared VO_x/γ-Al_2O_3 particles (4.6 wt.% vanadium).

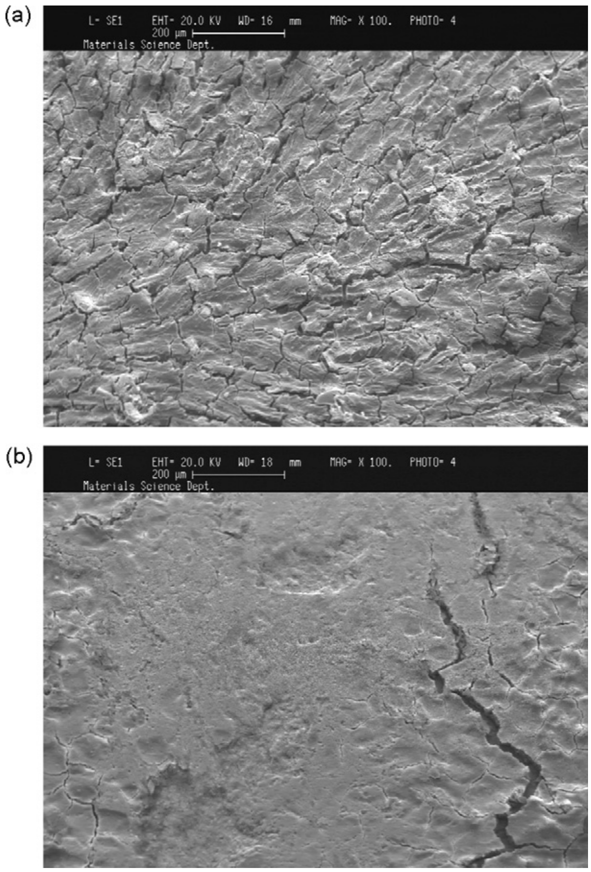

Fig. 8. SEM images of coatings made from γ-Al_2O_3 particles containing (a) Al-tri-sec-butylate and (b) polyvinyl pyrrolidone as binder materials (scale bar 200 μm).

Since most of the coating properties appear to be comparable to the coating properties that were found for the first preparation route, SEM was applied to analyze any deviations that might prevail in terms of coating morphology. Fig. 8a shows an image of a coating made from Al-tri-sec-butylate, whereas Fig. 8b shows an image of a coating made from polyvinyl pyrrolidone (scale bar 200 μm).

These coatings appear more compact than the coatings made from pre-prepared VO_x/γ-Al_2O_3 particles. However, especially the coating made from Al-tri-sec-butylate looks relatively fractured, which might explain its weaker adhesion. In general, it can be observed that the coatings from the first preparation route are more porous, whereas the coatings from this preparation route show a higher density. Even though these optical deviations can be found, uniformity and homogeneity is satisfactory for coatings made from vanadium precursor, γ-alumina particles, and binders.

As described above, the preparation method for the catalytic coatings following this route is very similar to the route that was applied for the first type of reactors. Therefore, reactors from this manufacturing route were catalytically compared to reactors from the first route. Activity and selectivity behavior for coatings

Table 2
Formulations for preparing coatings from $VO(acac)_2$ and γ-Al_2O_3 particles.

Coating formulation	Cat:binder	Adhesion	S_{BET} (m^2 g^{-1})	Loading (mg)	V (wt.%)	Al (wt.%)
$VO(acac)_2$ + γ-Al_2O_3 + Al-tri-sec-butylate	5:1	3	138.9	79.2	4.4	53.4
$VO(acac)_2$ + γ-Al_2O_3 + tetraethoxysilane	5:1	4	227.6	30.0	3.6	34.2
$VO(acac)_2$ + γ-Al_2O_3 + hydroxypropyl cellulose	5:1	3	50.9	151.7	4.6	45.0
$VO(acac)_2$ + γ-Al_2O_3 + polyvinyl pyrrolidone	5:1	4	54.8	87.5	5.0	43.3

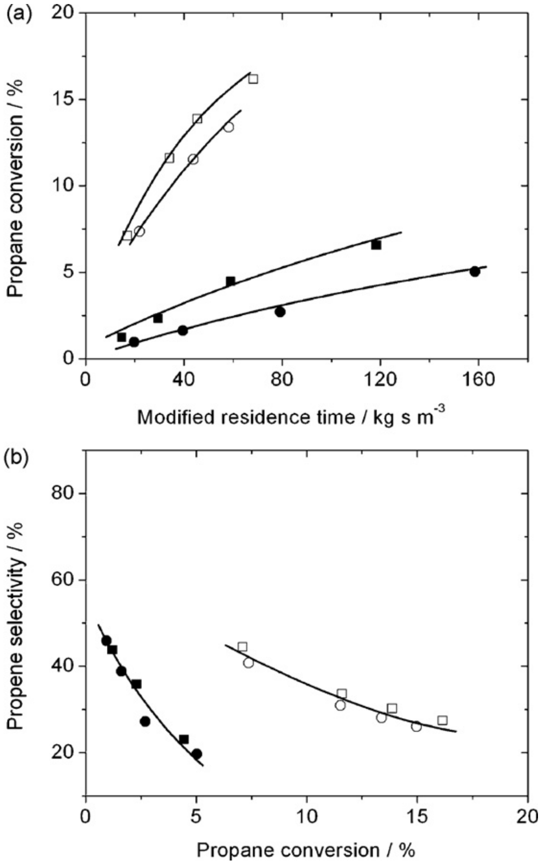

Fig. 9. Comparison of activity (a) and selectivity (b) of coatings made from VO_x/γ-Al_2O_3 particles (■, □) and $VO(acac)_2/\gamma$-alumina particles (●, ○), (closed symbols) Al-tri-sec-butylate and (open symbols) polyvinyl pyrrolidone as binder material (450 °C, $C_3H_8/O_2/N_2 = 2/1/4$, flow rate 30–240 ml$_n$ min^{-1}).

made from polyvinyl pyrrolidone and Al-tri-sec-butylate binders is shown in Fig. 9.

Reactors containing coatings stabilized with organic binders show very similar catalytic behavior. The same is true for coatings stabilized with inorganic binders. Therefore, it can be concluded that both preparation methods lead to essentially the same coating characteristics.

3.2.5. *Catalytic long-term performance*

Since long-term stability is a major objective in a later phase of the development process, one of our microstructured reactors (hydroxypropyl cellulose as binder material for pre-prepared VO_x/γ-Al_2O_3 particles, catalyst mass approximately 68 mg) was tested over 150 h under reaction conditions. The temperature was kept at 500 °C during the whole testing period, whereas the feed gas composition was changed from 100 ml$_n$ min^{-1} $C_3H_8/O_2/N_2 = 2/1/4$ during working hours and 60 ml$_n$ min^{-1} N_2 at night time. Propane conversion, propene selectivity and propene yield are shown in Fig. 10 as a function of time.

It can be seen that all parameters slightly decrease over time. However, an average propene selectivity of 34.8% at a propane conversion of 18% can be sustained over 150 h. The decrease in catalytic activity and selectivity might be due to the deposition of small amounts of coke on the surface of the catalyst. Reaction conditions were chosen to work under full oxygen conversion in order to maximize propene yield. Therefore, the oxygen concentration towards the end of the catalytic bed steadily decreases to almost zero, which favors coke formation. However, the catalyst can easily be regenerated if pure oxygen or air is fed to the reactor for the combustion of any carbon depositions. If oxygen conversion is adjusted to an intermediate degree, coke formation can be kept to a minimum.

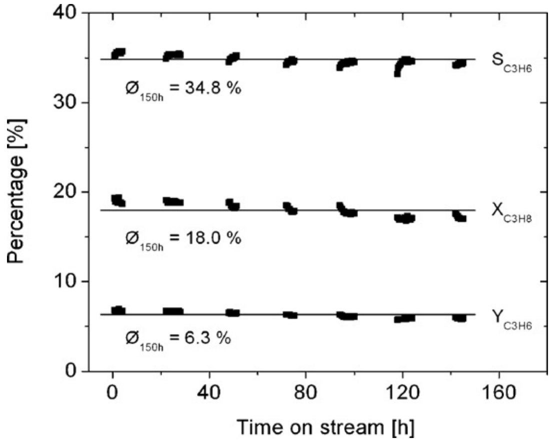

Fig. 10. Long-term performance over 150 h (hydroxypropyl cellulose as binder material, 500 °C, $C_3H_8/O_2/N_2 = 2/1/4$, flow rate 100 ml$_n$ min^{-1}, catalyst mass 68 mg).

4. Summary

Microstructured reactors are well suited for performing strongly exothermic heterogeneously catalyzed gas phase reactions. So far, these devices have been relatively expensive due to the lack of an adequate low-cost manufacturing concept. Therefore, a new and flexible production method has been developed in order to make the application of microstructured reactors more feasible for small and medium scale industrial processes.

In the present study, a Ni–Ag–Sn soldering procedure was applied for manufacturing the reactor modules. In addition, three different techniques for coating the micro-channels with catalytic materials were investigated. The obtained reactors containing the active coatings turned out to be sufficiently stable under reaction conditions of the oxidative dehydrogenation of propane. In order to stabilize the ceramic catalyst coatings on the metallic reactor material, different binder formulations were applied. It was shown that inorganic binder materials substantially decrease catalytic activity and selectivity, whereas organic binders do not influence catalytic behavior.

Due to the various coating preparation methods and chemical binder systems that were investigated, a highly flexible toolbox for manufacturing low-cost microstructured reactors is available. Catalyst support and active components can be adapted to alternative reactions with minor effort. In addition, all manufacturing methods were chosen to be easily scaled-up for the production of larger reactor modules.

In a second step, the obtained microstructured reactors have to be characterized in more detail, especially with respect to residence time distributions, thermal and catalytic behavior, which will be done in Part II of this paper.

Acknowledgements

Financial support by the “Deutsche Forschungsgemeinschaft (DFG)” as part of the collaborative research centre “Structure, dynamics and reactivity of transition metal oxide aggregates” (Sonderforschungsbereich 546) and by the “Fonds der Chemischen Industrie (FCI)” is acknowledged. In addition, O. Schwarz would like to thank the State of Berlin for providing a NaFöG scholarship.

Furthermore, the authors are grateful to M. Hardenberg, H. Hübner, and S. Khennache for experimental support.

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