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Nanoengineered catalysts for high-temperature methane partial oxidation

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Abstract

Novel nanoengineered catalysts for the high-temperature direct oxidation of methane to synthesis gas have been synthesized via a microemulsion-mediated sol–gel route. Through the addition of Pt-salts, catalysts with large surface areas, a well-controlled morphology and very homogeneous distributions of highly active Pt-nanoparticles in a hexaaluminate (BHA) matrix are obtained. The catalysts show syngas yields significantly exceeding the yields over conventional catalysts. Furthermore, excellent high-temperature stability of the materials is observed with no measurable deactivation or metal particle sintering over prolonged reactor operation at high-temperature reaction conditions. Overall, the materials seem highly promising candidates for syngas formation and hydrogen production from hydrocarbons.

Keywords: Nanocatalysts; Methane oxidation; Synthesis gas; High-temperature catalysis

1. Introduction

The high-temperature direct partial oxidation of methane over noble metal-based catalysts has been shown to be a highly efficient process for the production of synthesis gas. In contrast to conventional steam reforming processes, the direct oxidation route is mildly exothermal and thus allows for autothermal processes. The main interest in this reaction route, however, is based on the fact that due to the very high-temperature conditions ($T = 800$–$1200\,^{\circ}\mathrm{C}$) extremely high catalytic reaction rates and thus very short catalyst contact times (1–50 ms) can be realized.

In previous studies, extruded alumina monoliths, foam monoliths and alumina spheres were typically used as catalyst supports, and noble metals such as Pt and Rh were coated onto these supports by precipitation from corresponding salt solutions [1–3]. While for these catalysts Pt showed highest methane conversions, Rh gave best results with respect to syngas selectivities and yields [4]. However, particularly the Pt catalysts lack long term stability at high-temperature conditions, as indicated by noble metal deposition on the reactor walls and inert packings downstreams of the catalyst bed. Also, the results reported in the literature so far are still well below equilibrium conversions and selectivities, which are essentially 100% for stoichiometric methane/air as well as methane/oxygen mixtures (at a molar ratio of $CH_4/O_2 = 2.0$) at ambient pressure conditions and reaction temperatures around $1000\,^{\circ}\mathrm{C}$, leaving significant room for improvements.

While we had previously shown that by using heat-integrated reactor concepts methane conversions and syngas yields could be substantially increased [5,6], in the present study we focus on the development of novel catalysts to improve the

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high-temperature stability of the catalyst as well as reaction yields.

2. Motivation: reaction simulations

First, the influence of several catalyst characteristics as well as reactor parameters were studied in a detailed reaction simulation to identify potential ways to influence the reaction progress and thus improve overall syngas yields. Results from earlier experimental and numerical investigations into methane partial oxidation over platinum catalysts had already indicated that preferential oxygen adsorption is responsible for significant selectivity losses, since this preferred adsorption leads to oxygen-enriched conditions on the Pt catalyst surface near the reactor entrance and hence to total oxidation of some of the methane feed [6–8]. One of the aims of the new study was therefore to identify potential ways to influence the local oxygen coverage on the catalyst surface.

The simulations were based on the reaction and reactor model developed in our previous studies [7], and a more detailed report on the results of the numerical investigations will be the subject of a future publication [9]. The most significant result for the present study into the development of improved catalysts for this reaction system was that particularly the specific surface area of the catalyst has a strong influence on synthesis gas yields over Pt catalysts. As shown in Fig. 1, the simulations predict a significant increase in both CO and H_2 yields with increasing catalyst surface area.

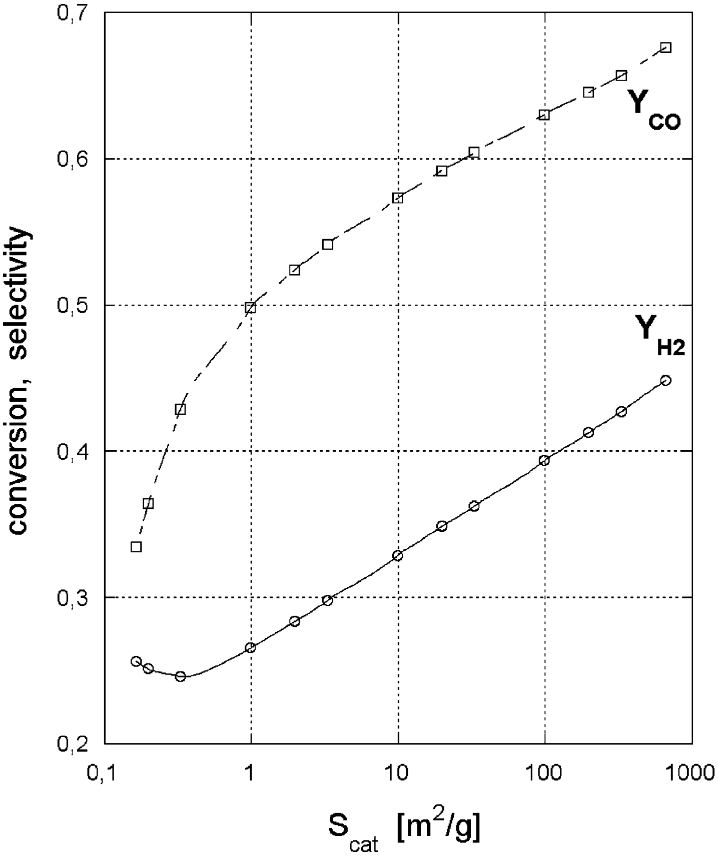


Fig. 1. Results from detailed reactor simulations of catalytic methane oxidation with air over platinum ($CH_4/O_2 = 1.6$). Shown are syngas yields vs. specific catalyst surface area. A strong increase in both in CO and H_2 yields with increasing catalyst surface area is observed.

This effect can be traced back to a reduction in the oxygen coverage near the catalyst entrance, since for high surface area materials ($\geq$100 m^2/g) the amount of species that can be adsorbed onto the catalyst surface becomes comparable to the number of atoms or molecules in the gas phase. Hence, large surface area catalysts can suppress the accumulation of strongly adsorbing species simply by offering a sufficient number of adsorption sites. While typical alumina monoliths and spheres have surface areas between 1 and 10 m^2/g at 1000 °C, the simulation results indicate that surface areas in excess of 100 m^2/g would be desirable for this reaction. Based on this result, we therefore turned our attention towards the development of high surface area catalysts for high-temperature reactions.

3. Catalyst synthesis

High-temperature stable catalytic materials have been the focus of intense research in the past 15 years in the context of catalytically stabilized combustion of natural gas (i.e. total oxidation). Particularly the group of hexa-aluminates, i.e. thermally stabilized aluminas initially developed by Arai and coworkers, were found to show excellent high-temperature stability in combination with decent combustion activity [10]. More recently, Ying and Zarur demonstrated that by synthesizing these hexa-aluminates in a reverse microemulsion and doting the materials with Ce, ignition temperatures for methane combustion can be significantly reduced [11].

In a first step, we therefore synthesized barium–hexaaluminate (BHA) powders through hydrolysis of the respective metal alkoxides. An inverse (water-in-oil) microemulsion was prepared with the help of different non-ionic surfactants. A metal-alkoxide precursor solution (Al- and Ba-i-propylate in i-octane) was added to the microemulsion and the solution was aged for 48 h under constant stirring. After vacuum drying and calcination at 600 °C, the materials were characterized by means of N_2-sorption to determine the BET surface area (Micromeritics ASAP 2010) and transmission electron microscopy (TEM) to determine the homogeneity of the materials as well as particle sizes and distributions.

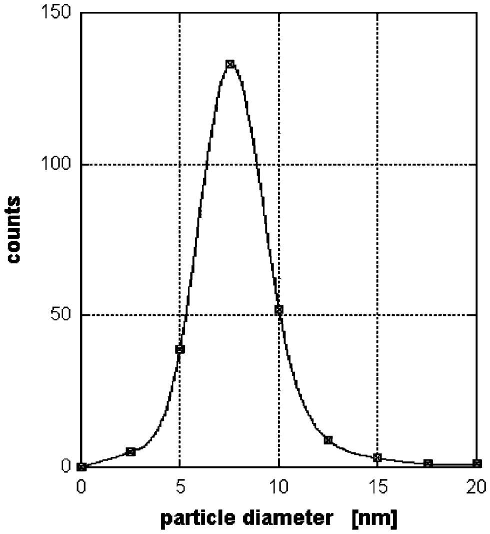
Dry powders with rather large surface areas of 200–300 m^2/g (dependent on the surfactant) were obtained. The materials have rather narrow size distributions (determined by measuring the particle sizes of at least 250 individual nanoparticles in different TEM pictures) and show good thermal stability with surface areas of about 50–150 m^2/g at 1100 °C and 10–20 m^2/g at 1300 °C (Fig. 2). With the help of an alcohol as a co-surfactant and through thermally induced phase-separation (TIPS) by cooling of the microemulsion after aging, these surface areas increased to about 350 m^2/g at 600 °C, about 100–150 m^2/g at 1100 °C and 15–25 m^2/g at 1300 °C.

In contrast to their relatively high combustion activity, however, the catalysts showed only poor methane conversions and very low selectivities towards partial oxidation products for fuel rich methane/air mixtures (molar ratios of $1.0 < CH_4/O_2 < 3.0$).

Therefore, the catalysts were further modified through the addition of highly active noble metals. These metals are known to show good activities and selectivities for catalytic partial oxidation of hydrocarbons at high-temperature conditions. However, reactor tests show that the usual catalyst preparation by the incipient wetness method yields catalysts with insufficient high-temperature stability leading to measurable noble metal losses after prolonged reactor operation at higher reaction temperatures.

The above described synthesis of the BHA materials was hence modified by adding the respective noble metal salts into the water phase of the inverse microemulsion before addition of the alkoxide precursor solution. In the following, we restrict the present report to the results with platinum-modified BHA through the addition of H_2PtCl_6. In a forthcoming paper, we will report results using a number of other catalytic metals, further demonstrating the versatility of this approach.

Through the described synthesis, we obtained catalytic materials with a very fine distribution of Pt metal nanoparticles in the ceramic matrix while maintaining the large surface area of the host material. Since the microemulsion serves simultaneously as template both for the aluminate phase as well as the noble metal, well-mixed nanoparticles of similar size (typically between 6 and 9 nm, see also Fig. 2) are produced for either material. During aging, these particles form loose agglomerates with typical diameters between 0.3 and 1 mm. Typical Pt loadings for our standard catalyst as determined by ICP-AES were about 8 wt.% Pt. In comparison to a conventional synthesis via the incip-



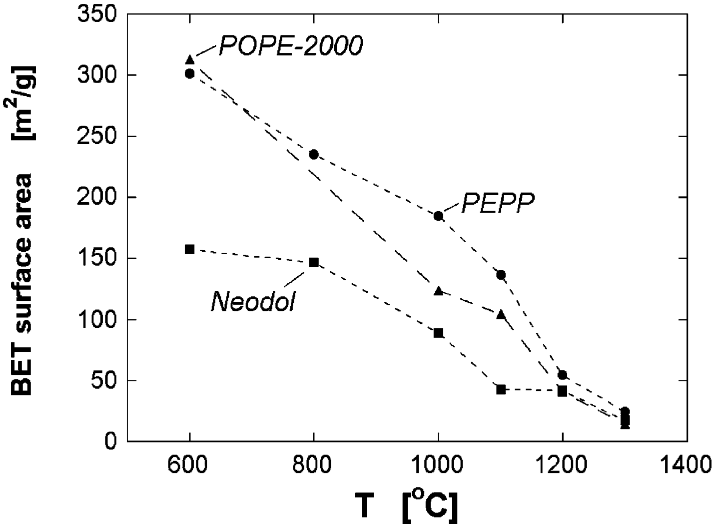


Fig. 2. Particle size distribution for a typical BHA catalyst after calcination at 600 °C (top graph) and BET surface area vs. calcinations temperature for BHA powders as prepared with three different non-ionic surfactants (bottom graph).

ient wetness method, the catalysts not only show a much more narrow size distribution of the noble metal particles, but also overall a far superior homogeneity of the material (Fig. 3).

4. Catalyst tests

The novel catalysts were tested in a simple quartz-glass tubular reactor at typical reaction conditions for direct partial oxidation of methane, i.e. with fuel-rich methane/air as well as methane/oxygen mixtures (both for molar ratios $CH_4/O_2 = 1.0–2.5$) under autothermal conditions. The reactants (methane and air, or methane and oxygen) were fed though mass-flow controllers and premixed in an inert zone filled with glass beads before flowing through the catalyst bed. Typical gas flow rates in the experiments were between 1 and 3 slpm (standard liters per minute), corresponding to catalyst contact times in the order of 1–10 ms.

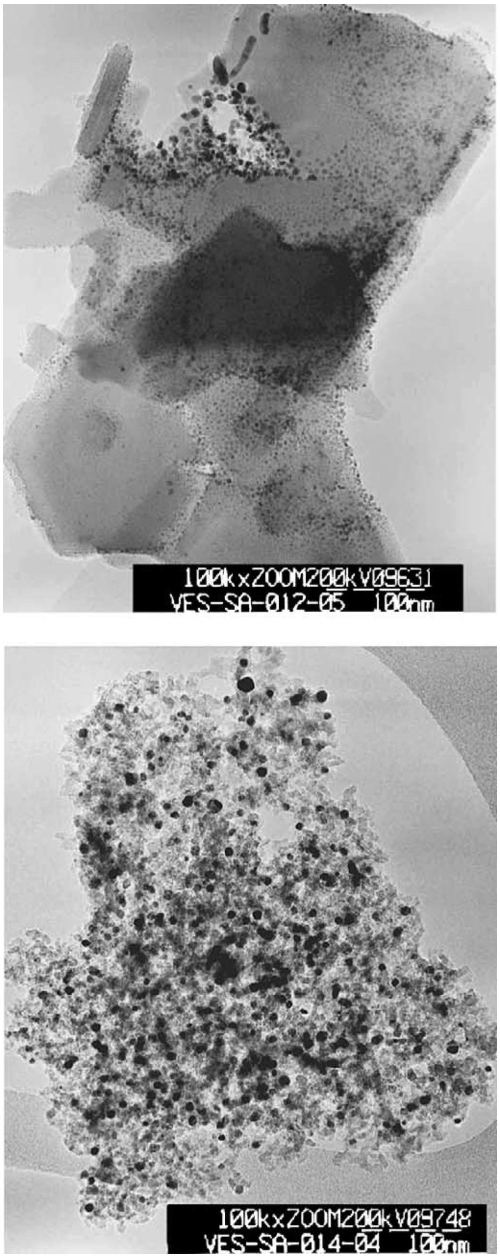


Fig. 3. TEM images of the platinum distribution on BHA supports: typical distribution of Pt particles on BHA prepared by the incipient wetness method (top) vs. Pt incorporated into the BHA matrix as obtained in the parallel synthesis method reported here (bottom).

The catalyst bed consisted of 200 mg of the catalyst powder, resulting in a bed height of about 4–5 mm. The powders were placed as prepared between inert ceramic fiber mat materials and placed onto a quartz-glass frit in the tubular reactor. All reactant gases (CH_4, O_2, H_2, H_2O, CO and CO_2) were detected by a double-oven gas chromatography system (Shimadsu GC-14A), and all atom balances closed to better than 5% in a typical run. No indications for other reaction products such as methane coupling products were found in the experiments.

Fig. 4 shows results for autothermal reactor operation with air for the novel Pt-BHA catalysts in comparison with a conventional Pt-coated alumina monolith prepared by incipient wetness. While the trends in methane conversions and syngas selectivities with methane-to-oxygen ratio are essentially unchanged, methane conversions and hydrogen selectivities are drastically improved, CO selectivities are slightly reduced and autothermal catalyst temperatures drop drastically in comparison to the monolithic catalyst. Furthermore, the maxima in the syngas selectivities are shifted from a CH_4/air ratio of about 1.2 for the monolith to about 1.7 for the Pt-BHA catalyst.

This shift in the maxima in syngas selectivities is a strong indicator for the drastic improvement of the Pt-BHA versus the Pt-coated monolith: stoichiometrically, one should expect the maximum in syngas selectivities at a methane-to-oxygen ratio of 2.0. However, the observed maxima for all syngas catalysts reported so far in the literature are significantly shifted towards lower values, since at these values the increasing amount of oxygen allows for some methane combustion which leads to increased reaction temperatures and thus thermodynamically favors the (less exothermic) partial oxidation pathway. The superposition of the composition effect and this temperature effect thus lead to maxima which are shifted towards a methane-to-oxygen ratio of 1.0. A ‘perfect’ catalyst which catalyses only partial oxidation should therefore show the maximum in syngas selectivities exactly at 2.0, and any incremental improvement in the catalytic properties of a less-than-perfect catalyst will show up in the experimental results as a shift towards this stoichiometric point. Thus, the location of the maximum in syngas selectivities is a simple but sensitive indicator for the quality of a syngas catalyst.

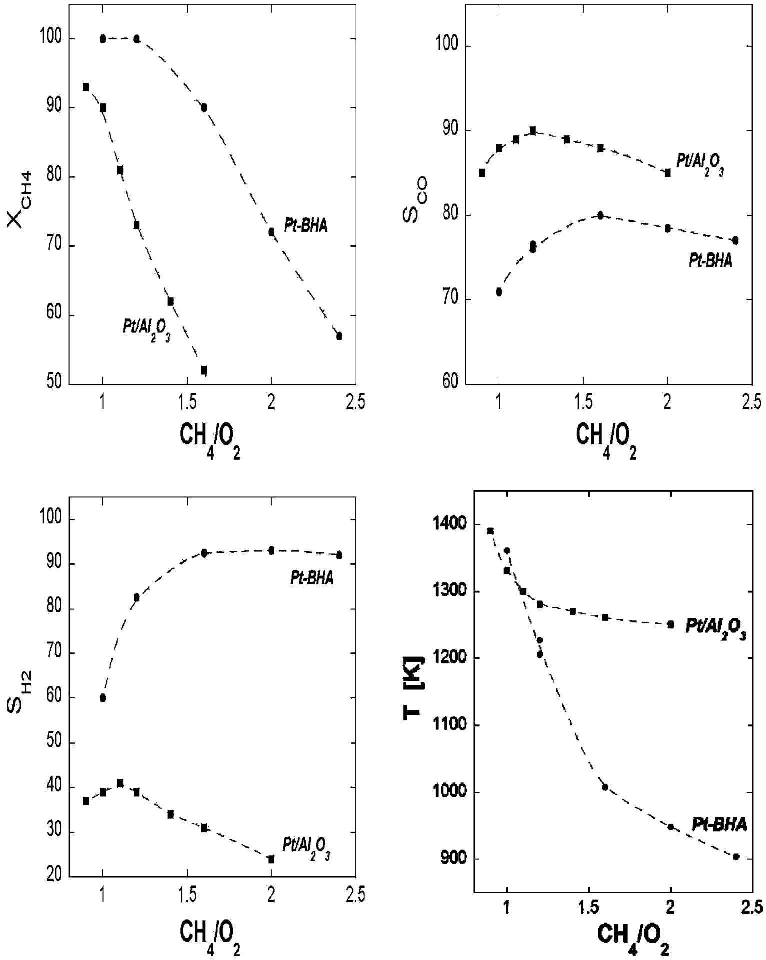


Fig. 4. Experimental results for autothermal methane oxidation with air over a Pt-coated alumina foam monolith (squares) and a novel Pt-BHA (circles). Shown are methane conversion (top left), CO selectivity (top right), H_2 selectivity (bottom left) and catalyst temperature (bottom right) vs. methane-to-oxygen ratio.

One can further see in the results in Fig. 4 (bottom right graph) that, due to the strongly increased hydrogen selectivity, the reaction runs at substantially lower autothermal reaction temperature over the BHA catalysts compared to the alumina monolith (about 700 °C versus 1000 °C, respectively). Since thermodynamic calculations show that reaction temperatures of at least 900 °C are necessary for optimal syngas yields [5], further experiments were conducted with increased reaction temperatures by (a) putting the quartz-glass reactor into an oven held at 750 °C, and (b) by running the reaction with oxygen instead of air, thus removing nitrogen as unreactive diluent from the feed.

Fig. 5 shows the experimental results for the autothermal operation with air (squares) in comparison to the operation with external oven-heating (circles) and the autothermal operation with oxygen (triangles). As expected, the increase in reaction temperature leads in both cases to a further improvement in syngas yields, with both syngas selectivities and methane conversions increasing by 5–15%. It seems noteworthy that H_2 selectivities now approach almost 100%. A further improvement can be expected by combining the two effects of heating the reactor and replacing air with pure oxygen, but the expected results seem obvious and those

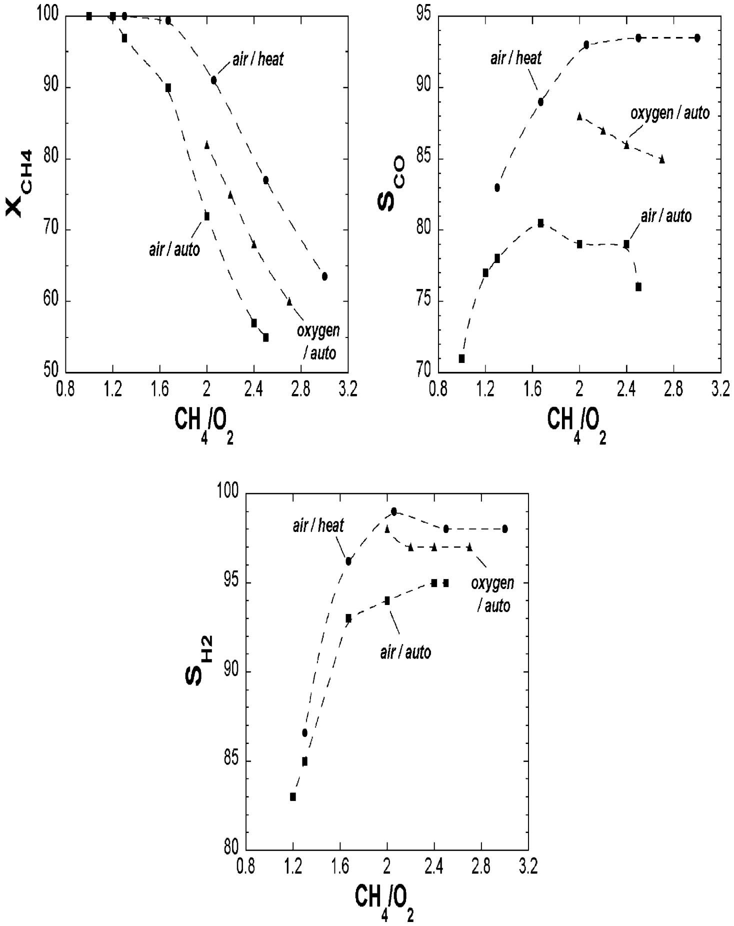


Fig. 5. Experimental results for the Pt-BHA catalysts. Autothermal reactor operation with air (squares) is shown in comparison to operation with additional external heating (circles) and autothermal operation with pure oxygen (triangles). Shown are methane conversion (top left), CO selectivity (top right) and H_2 selectivity (bottom) vs. methane-to-oxygen ratio.

experiments were therefore not conducted in this study.

Given the importance of the thermal characteristics of the catalyst and catalyst bed [6,7], one should expect that at least some of the improvement of the reaction yields over the Pt-BHA catalyst versus the Pt-coated monolith is due to the fine powderous form of the BHA materials. To distinguish between effects that are due to this formulation of the catalyst against effects that are due to the well-controlled size and distribution of Pt-nanoparticles in the Pt-BHA catalyst, another catalyst was prepared in which Pt was precipitated by the incipient wetness method onto a BHA powder which was prepared by the reverse microemulsion method as described above (see TEM pictures in Fig. 3). The two catalysts therefore show the same granularity as well as the same support material, and should only differ in the distribution of the Pt on the support material.

Experimental results are shown in Fig. 6. One can see that the Pt-BHA catalyst is clearly superior to the catalyst prepared by the incipient wetness method (‘Pt on BHA’). Methane conversions as well as CO and H_2 selectivities are improved by 5–15% throughout the whole range of CH_4/O_2 ratios. Comparing the results in Fig. 6 with those in Fig. 4, however, it is also apparent that a significant part of the improvement of the Pt-BHA catalyst over the Pt-coated alumina monolith—in particular in H_2 selectivities—must be

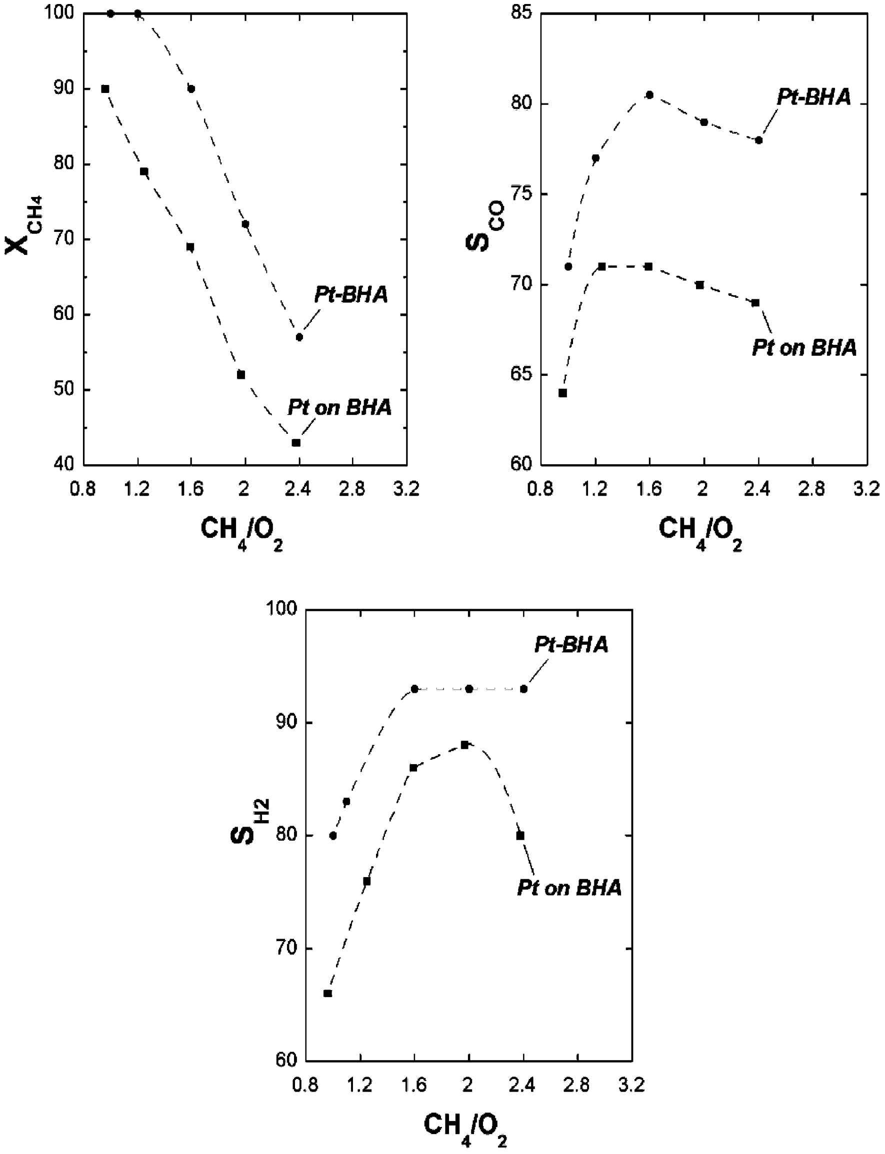


Fig. 6. Autothermal methane oxidation with air over the novel Pt-BHA catalyst (circles) in comparison with Pt precipitated onto BHA powder by the incipient wetness method (squares). Shown are methane conversion (top left), CO selectivity (top right) and H_2 selectivity (bottom) vs. methane-to-oxygen ratio.

due to the finely powderous form of the BHA catalyst. As indicated above, we attribute this to the different thermal properties of the relatively dense particle bed in comparison to the open monolith structure. Nevertheless, this experiment suggests strongly that the well-controlled morphology of the Pt-BHA catalyst is a crucial characteristic of this catalyst. The significance of the particle size distribution in these catalyst systems is currently the subject of more detailed investigations.

The extremely high activity of this catalyst is illustrated by another set of experiments in which the contact time of the gases with the catalyst bed was systematically varied. Variations were achieved both through

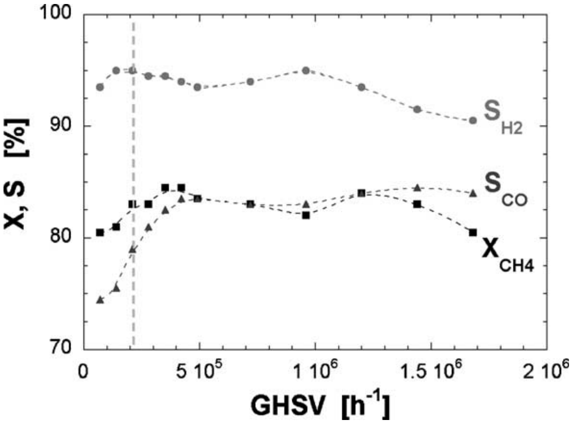


Fig. 7. Autothermal methane oxidation with air over Pt-BHA: H_2 selectivity (circles), CO selectivity (triangles) and methane conversion (squares) upon variation of the contact time (given as GHSV) by an order of magnitude. The operating conditions in the other experiments reported here correspond to the GHSV indicated by a dashed line. Extremely high reactor throughputs can be achieved without loss in syngas yields.

variations in the total gas flow rate and through variations of the catalyst bed height. Results are shown in Fig. 7, where syngas selectivities and methane conversions are shown against the gas hourly space velocity (GHSV) of the gases in the reactor, calculated based on the empty tube volume of the catalyst bed. The standard conditions for the other experiments reported in this publication are indicated by the vertical dashed line.

The Pt-BHA catalyst shows a rather flat profile in syngas selectivities and methane conversions over a rather wide range of space velocities. In particular, the reactor throughput can be increased by almost an order of magnitude beyond the standard conditions of this study without a significant loss in selectivities or conversions. It seems noteworthy that the data at the highest GHSV were measured over a catalyst ‘bed’ of only 50 mg (corresponding to a ‘bed height’ of about 1 mm), i.e. we are converting a gas flow of 5 slpm methane/air over as little as 4 mg of active Pt. Clearly, the Pt-BHA catalyst shows an unusually high catalytic activity for methane partial oxidation.

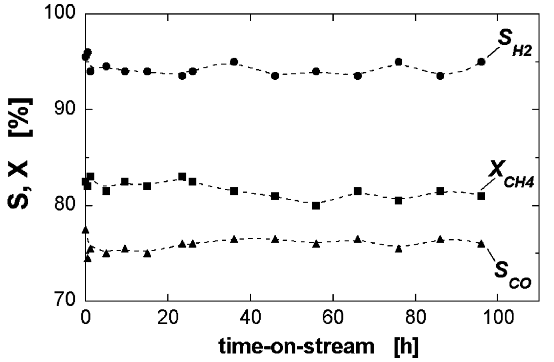


Fig. 8. Test for high-temperature stability of the Pt-BHA catalyst during catalytic methane oxidation with air ($CH_4/O_2 = 1.7$). H_2 selectivity (circles), CO selectivity (triangles) and methane conversion (squares) are given vs. time-on-stream. No deactivation is measurable even after 100 h of continuous operation.

Finally, the long-term stability of the catalysts was tested in a 100-h uninterrupted test run in the quartz-glass flow reactor at autothermal operation with a CH_4/air ratio of 1.7. GC samples were automatically withdrawn and analyzed every 30 min during that test, and only some representative data points of this experiment are shown in Fig. 8. It can be seen that the catalyst shows no signs of deactivation over the course of this test, with stable methane conversions of about 82% and CO selectivities and H_2 selectivities of about 76% and 95%, respectively. Only during the first 20 min after ignition, a slight drop of about 2–3% can be observed in syngas selectivities. This is typically observed immediately after ignition with every one of these catalysts (including previously used catalysts) and is most likely due to a thermal overshoot in the catalyst bed during ignition. During the first minute after ignition the catalyst bed is still relatively cool, and these low-temperatures lead momentarily to significant amounts of total oxidation. Due to the strong exothermicity of methane combustion, this results in an overshooting of the local catalyst temperature and to a corresponding temporary increase in syngas selectivities until the catalyst bed has reached a thermal steady-state.

Similar test at the higher reaction temperatures of the operation with external heating also showed no signs of catalyst deactivation, and an ex situ inspection of the catalyst after operation at these high reaction temperatures revealed no significant sintering of the metal nanoparticles. This sintering resistance of the Pt-BHA materials seems rather remarkable, since one has to expect severe sintering for metallic nanoparticles at the very high-temperatures reached during methane partial oxidation. It appears that a strong interaction between the Pt nanoparticles and the ceramic matrix should be the reason for this high-temperature stability, but at this point we have no consistent explanation for the nature of this interaction.

5. Summary

We presented results from a study towards the development of highly active and selective catalysts for methane partial oxidation to synthesis gas at high-temperature conditions. The study was motivated by simulation results which indicated that high surface area catalysts should give significantly better syngas yields than conventional monolith-based catalysts.

The novel catalyst systems were synthesized through a microemulsion-mediated sol–gel synthesis of thermally stabilized aluminas (here: barium–hexaaluminates) which were made active for partial oxidations through the addition of Pt-salts during the synthesis. This parallel synthesis of Pt-nanoparticles with the BHA matrix is not only a rather simple process, but also leads to a catalyst with a very well-controlled morphology and extremely high catalytic activity. The catalyst show rather large, high-temperature stable surface areas of about 100–200 m^2/g at the intended reaction temperatures of about 1000 °C.

The catalytic tests showed syngas selectivities and methane conversions over Pt-BHA well in excess of those over conventional catalysts, even exceeding the predictions of our initial reaction simulations. Raising the reaction temperature by using pure oxygen instead of air or by preheating the feed gases further improved selectivities and conversions to about 89% yield in CO and 96% yield in H_2, with H_2 selectivities approaching almost 100% at the stoichiometric feed of $CH_4/O_2 = 2.0$. While we can not rule out that the discrepancy with the simulation results might be due to shortcomings of our elementary-step kinetic model or the rather simplified description of the catalyst bed, we assume that it might in fact be due to the fact that the nanoscale noble metal particle behave significantly different from the bulk material as has been shown previously for Au nanoparticles in catalytic low-temperature CO oxidation [12]. We are currently further investigating this aspect through a systematic variation of the Pt content as well as Pt particle size in these materials.

Beyond their very high activity for methane partial oxidation, the catalysts also showed excellent high-temperature stability with no measurable deactivation or sintering of the metal nanoparticles even at reaction temperatures as high as 1000 °C. This is rather surprising, considering the typically very fast sintering of metallic nanoparticles at temperatures in excess of 700–800 °C. However, at this point, we have no consistent explanation for the nature of this observed stability of the materials.

In summary, we see these novel catalysts as highly promising candidates for the high-temperature direct oxidation of methane to synthesis gas as well as for similar processes for hydrogen production by catalytic partial oxidation of hydrocarbon fuels. An extension of the described catalyst synthesis onto other metal components gave similarly good results for several other metals and will be published in a forthcoming report.

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