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Wash-coat Catalysts Applied for Partial and Total Oxidation Reactions of Propane in Micro-channels

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Abstract

Commercial platinum, palladium and rhodium and proprietary home-made catalysts were wash-coated into microstructured testing reactors and applied for the total and partial oxidation of propane. At 400°C reaction temperature and a at a space velocity of 10 Ndm³/min/g_{cat}, full conversion could be achieved with none of the commercial catalysts for total oxidation. Platinum showed highest activity but conversion deteriorated in excess air due to inhibition effects of the oxygen surplus. Additionally, undesired selectivity towards carbon monoxide was found at stoichiometric feed ratio. Palladium and rhodium were much lower in activity and showed deactivation on the short term, but were exclusively selective towards carbon dioxide. Home-made catalyst samples were therefore developed which outperformed the platinum catalyst concerning activity, selectivity and did not show inhibition effects in oxygen surplus. The catalyst proved stability for more than 600 hours already. Over the commercial rhodium catalyst, full propane conversion was achieved at a low reaction temperature of 700°C and 15 Ndm³/min/g_{cat} space velocity.

Keywords: Fuel Processing, microstructures, propane, total oxidation, partial oxidation

1 Introduction

For mobile and portable applications of fuel cell technology there is a need for compact hydrogen supply systems [1]. Generally, size is a critical issue of integrated fuel processor systems. Here micro-structured reactors offer benefits concerning process intensification and integration. Firstly the suppression of mass transfer limitations due to the small channel dimensions and thin coatings applied. Secondly heat-exchanging capabilities may be introduced, which is not feasible when conventional technologies such as ceramic or metallic monoliths are applied. This is crucial especially in the case of endothermic reactions such as steam reforming.

Basically, a fuel processor is composed of a reformer reactor and in most cases catalytic gas purification reactors to remove the carbon monoxide out of the reformate being harmful at least for PEM fuel cells, which are the most common fuel cells for small scale applications.

By applying integrated microstructured heat-exchanger reactors the endothermic steam reforming reaction may be closely coupled to an exothermic reaction, preferably total oxidation of the fuel (see Fig.1). However, this approach, though often claimed, has hardly been applied so far. Merely a recent application on methanol steam reforming was published by Reuse et al.[2]. The power for the endothermic steam reforming was generated in this case by the exothermic combustion of hydrogen stemming from the off-gas of the fuel cell anode, which still contains some 10 % hydrogen or more. The energy supply from the hydrogen is sufficient in the case of methanol steam reforming.

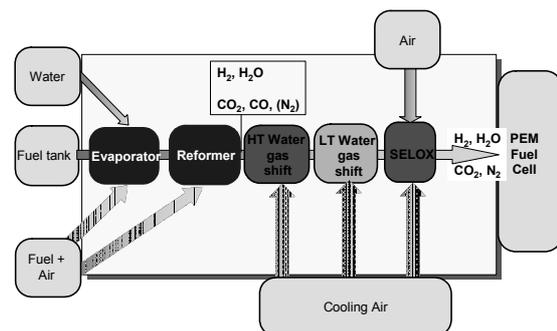Additionally, total oxidation may be applied for feeding integrated evaporators with energy.

Fig.1: Principle flow scheme of a fuel processor based upon catalytic CO-clean-up

Another option to generate hydrogen from fuels is partial oxidation, where major challenges are both coke formation and hot spots generated by the highly exothermic reaction, which may be overcome due to the short residence times and the introduction of heat exchanging capabilities as mentioned above. The exothermic partial oxidation reaction may be operated in an integrated heat-exchanger to remove the heat of reaction, which avoids hot spot formation and has potential for improving catalyst performance.

At IMM, both partial oxidation and steam reforming [3] of hydrocarbons are currently under investigation. However, the low residence times feasible in micro-channels make it frequently necessary to either adapt commercial catalyst systems to the specific needs of this new reactor type or even to develop new catalyst systems. The oxidation process needs to be complete (ideally 100.0 % conversion), robust

against air surplus, which is necessary to adjust the appropriate operation temperature, and long-term stable.

2 Reactors and Catalyst Preparation

The testing reactors applied for catalyst testing have a sandwich design with two micro-structured platelets being attached face to face. The platelets carry 14 channels each, which are 25 mm long, 500 μm wide and 250 μm deep. The channels together with the inlet and outlet region were prepared by wet chemical etching. Each couple of platelets was coated with the individual carrier/catalyst system and subsequently sealed by laser welding, which allowed for leak-tightness of the reactors at operation temperatures exceeding 900°C. Inlet and outlet tubes were attached to the reactors by laser welding, too. Fig.2 shows the components of the reactor before and after welding. The heating of the reactors was performed by a heating cartridge of 100 W power introduced into a drilling of a metal block.

The wash-coating procedure was applied for preparation of the catalysts, as a high flexibility of surface thickness and surface area is achievable by this method [4]. Table 1 gives an overview of some of the catalyst samples tested.
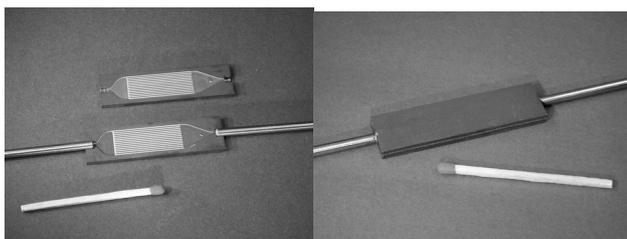

Fig.2: Reactor applied for propane partial and total oxidation; left: coated platelets with tubing; right: welded platelets

Table 1: Catalysts tested for total and partial oxidation of propane

Catalyst	Carrier	Active Component [wt%]	SA m²/g
Comm. Rh Catalyst (G-213 KR/D from DEGUSSA)	Al_2O_3	5.0	127
Comm. Pd Catalyst (E 213 R/D from DEGUSSA)	Al_2O_3	5.0	143
Comm. Pt Catalyst (F-214 VH/D from DEGUSSA)	Al_2O_3	5.0	265

3 Total Oxidation of Propane

The catalytic performance of commercial, alumina-based platinum, rhodium and palladium catalysts containing 5 wt.% of the active species each was determined at a space

velocity of 10 dm³/gcat/min and reaction temperatures of 350°C, 400°C and 450°C subsequently. The application standing behind this catalyst development work is an evaporator, which needs to be supplied by an integrated catalytic burner with heat. The results generated at a stoichiometric molar oxygen/propane feed ratio of 5:1 are summarised in Tab.2.

Tab.2 Conversion achieved for total oxidation at various temperatures; oxygen/propane ratio 5 (stoichiometric)

Catalyst	Conversion (350°C)	Conversion (400°C)	Conversion (450°C)
Comm. Rh	16.5	42.6	74.3
Comm. Pd	17.7	57.1	84.5
Comm. Pt	94.8	95.6	99.2
Home-made	98.9	100.0	100.0

The rhodium catalyst showed the lowest activity at all reaction temperatures. It was selective exclusively towards carbon dioxide at 450°C. However, it showed significant deactivation at all reaction temperatures within 1.5 hours of test duration (see Fig.3). The palladium catalyst was slightly more active (see Tab.2) and showed no deactivation except for the highest reaction temperature (450°C). This sample showed exclusively selectivity towards carbon dioxide as well. The highest activity of the commercial samples was achieved for the platinum containing one. No deactivation was visible within short term. However, the only drawback of this sample at reaction temperatures of 400°C and higher was a minor selectivity towards carbon monoxide. It reached 0.75 % at 450°C reaction temperature.
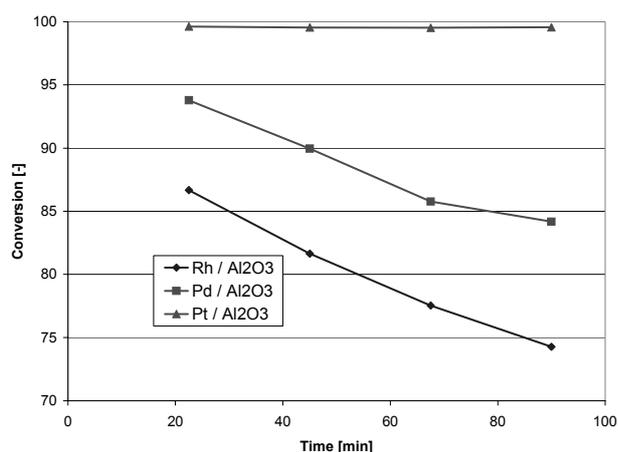

Fig. 3 Short-term stability of commercial catalysts in propane total oxidation; 450°C reaction temperature; oxygen/propane ratio 5

When increasing the oxygen/propane ratio from 5:1 to 7:1 over the platinum catalyst, the excess oxygen caused a

decrease of conversion due to inhibition effects, which was also found in literature [5],[6]. However, this was not the case for palladium. Thus different mechanisms are obviously valid for total oxidation of propane over platinum and palladium catalysts.

A home-made catalyst sample based upon γ-alumina and proprietary active species outperformed all the commercial samples (see Tab.3). 98.9 % conversion could be achieved at 350°C reaction temperature already. The selectivity of the sample was superior compared to the commercial Pt catalyst. Additionally, the sample showed no deterioration of the conversion when exposed to an excess of air in the feed.

Tab.3 Conversion and selectivity of commercial Pt and proprietary home-made catalyst samples at 450°C reaction temperature

Catalyst	Oxygen / Propane	Reaction Temperature [°C]	Conv.	$S(CO_2)$	$S(CO)$	$S(CH_4)$
Pt	5	450	99.6	99.2	0.8	0
Pt	7	450	99.0	100	0	0
Home-made	5	450	100	98.7	0.4	0.9
Home-made	7	450	100	100	0	0

The sample has undergone long-term stability testing. As indicated in Fig. 4, no apparent deactivation was observed up to a time on stream of more than 500 hours to date. 1,000 hours test duration is foreseen. The next step will the stability testing at higher reaction temperature (700°C) heading for future heat supply of a steam reformer reactor.
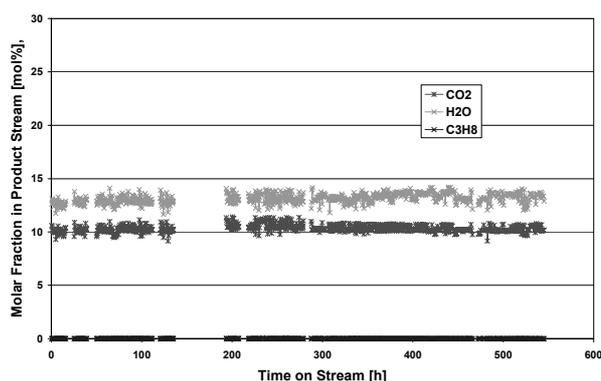

Fig. 4 Long-term stability test for total oxidation of propane

4 Partial Oxidation of Propane

The rhodium catalyst, which had shown poor performance for propane total oxidation at moderate reaction temperature, converted the propane completely, when applied for the partial oxidation reaction. The reaction was performed at temperatures between 700°C and 850°C. The selectivity towards the undesired product methane decreases with increasing reaction temperature (see Fig.5), which appears to be guided mostly by thermodynamics.
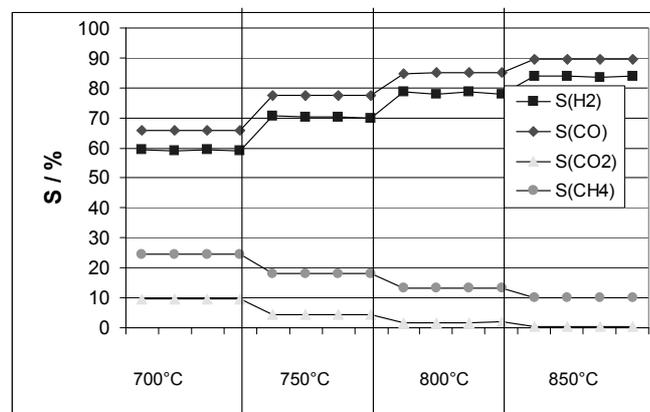

Fig.5 Product selectivities S(x) found for a commercial rhodium catalyst for propane partial oxidation at various reaction temperatures

5 Integrated Reactor Concepts

The design concepts of micro-structured reactors need to be adopted to their field of application. Testing devices frequently have the option to exchange the catalyst carrier plates and they are mostly electrically heated. Thus, gaskets may be applied and heating may be done by heating cartridges. This makes the reactors relatively bulky compared to the size of the micro-structured plates incorporated. As another step towards system integration, IMM has developed a testing reactor for the preferential oxidation, which is a hybrid between testing and processing devices [7]. The reactor itself is an integrated counter-flow heat-exchanger and designed for a 100 W methanol reformer. It is coupled with two counter-flow heat-exchangers (see Fig. 6).

This highly integrated device still carries graphite gaskets to allow for changing the micro-structured plates. Later on, a laser-welded device was built as a prototype, which is considerably smaller due to the lack of sealing and screws. Generally, the amount of wall material of fuel processing devices needs to be minimised to reduce their energy demand during start-up.

At IMM another integrated reactor with similar dedication compared to the device presented by Reuse et al.[2] (see also above) has been realised. It is a 100 W methanol reformer combined with a catalytic afterburner, which combusts the anode of-gas of the fuel cell (see Fig. 7). Currently a laser-welded reforming reactor, water-gas shift reactors and PrOX reactors for a 5 kW application are tested at IMM in the scope of a project which is heading for a complete fuel processor operating with iso-octane reforming.
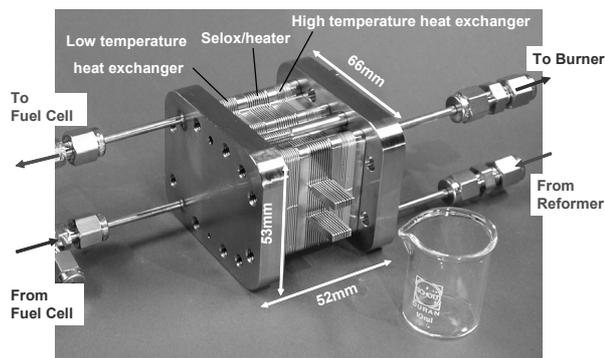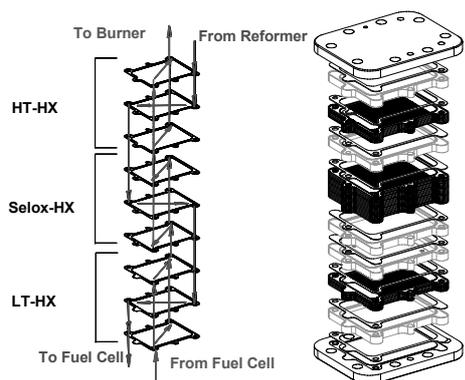
Fig.7 Combined steam reformer/catalytic burner for methanol resp. fuel cell anode off-gas

Fig. 6 Testing Reactor designed for the selective oxidation of CO; top left: flow paths; top right: explosion view; bottom: mounted device
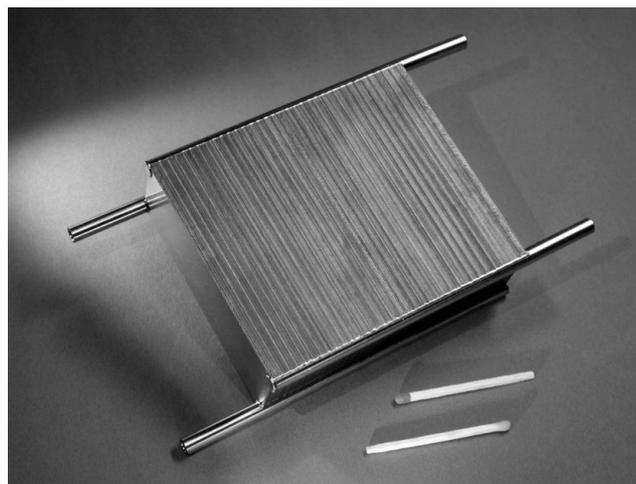
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