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Challenges in applied oxidation catalysis

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ABSTRACT

Haldor Topsøe A/S works on several aspects related to oxidation catalysis. In three examples, the challenges related to the development of catalysts and processes in oxidation catalysis are discussed. While certain challenges like the lowest possible pressure drop over the catalyst and price considerations are common for almost all areas of oxidation catalysis, other challenges may be specific for a particular area. In the first example, it is shown that the catalytic combustion technologies for off-gas purification have to tolerate a large variety of trace species involving traditional catalyst poisons including halogens and sulphur. The second example deals with oxidation catalysis for automotive applications. The main challenges within this area are often related to catalyst efficiency at the cold-start of a motor and catalyst lifetime, which depends upon the lifetime of the vehicle. Finally, the third example presents challenges within catalytic partial oxidation (CPO) of natural gas for hydrogen and synthesis gas production. Here, a high catalyst activity and selectivity are of utter importance due to ultra-short residence times of the feed gas in the channels of a monolithic CPO reactor. The examples show that industrial catalyst and process developments are often tailor-made solutions for a specific application.

1. Introduction

Applied oxidation catalysis is an area the company Haldor Topsøe A/S has been involved in since the company was founded in 1940. Originally, the focus was on oxidation of sulphur dioxide to sulphur trioxide. This paper emphasises the oxidation of hydrocarbons and carbon. For this purpose, noble metal catalysts are applicable in almost every case. However, the challenges for a company producing commercial catalysts are to find the most optimal catalyst at the right price. Therefore, alternatives to noble metals are preferred in cases where these catalysts can do the job.

The work with oxidation of hydrocarbons and carbon has been ongoing for more than three decades and has resulted in more than 350 industrial installations. Besides the technologies for purification of off-gases by oxidation catalysis, new business opportunities within automotive applications have been pursued and the potential of using catalytic partial oxidation for various syngas applications has been evaluated during the last decade. Common for all these branches of hydrocarbon oxidation catalysis is the challenge to obtain a durable catalyst with low pressure drop at a reasonable cost.

2. Challenges in off-gas purification

Stationary catalytic combustion removes solvents and other volatile organic compounds (VOC's), according to Reaction 1, and inorganic combustibles such as CO, H_2S, NH_3 and HCN in off-gases from industrial processes [1–4]. A range of different catalytic systems and shapes is required to cover the diverse industrial conditions (Table 1):

$$\text{'HC'} + O_2 \rightarrow CO_2 + H_2O \tag{1}$$

Sufficient low-temperature activity is beneficial for applications where the feed gas has to be heated up. Unsupported metal oxide catalysts are superior to supported catalysts in these applications. For instance, an unsupported hopcalite catalyst (Cu-Mn mixed oxide) is superior to a supported hopcalite catalyst for use in air purification in nuclear submarines [5]. For hot feed gases or compounds that require elevated combustion temperatures for full conversion, supported metal oxides are chosen due to higher thermal stability.

A low pressure drop in the catalytic reactor is important for feed gases without excess pressure in order to avoid considerable energy costs for a gas blower. The shape of the catalyst is a crucial parameter in this respect. A range of pelletized supports with different shapes, but also foams and monoliths, can be applied to meet the pressure drop specifications. Fig. 1 shows the pressure drop characteristics of commercial pelletized or monolithic catalysts. The pressure drop in the catalytic reactor can be tuned in a wide range by choosing a proper catalyst shape. The optimum catalyst shape is a compromise between pressure drop and catalytic performance.

The decomposition products of VOC's can create a rather aggressive atmosphere in the catalyst bed. For instance, the

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Table 1
Commercial combustion catalysts and their application.

Catalytic system	Application
Mixed metal oxide (Cu, Mn, Fe, Ce)	Most applications, silicon resistant
Noble metals (Pd, Pt, Rh)	CO, alkanes, aromatics
Noble metals (Pt, Rh)	Sulphur tolerant
Metal oxide (Cr, Mn, V)	Halogenated hydrocarbons, halogen resistant
Metal oxide and noble metals	CO, halogenated hydrocarbons, halogen resistant
Mixed metal oxide and noble metals	H_2S, COS, CS_2, ammonia, sulphur resistant

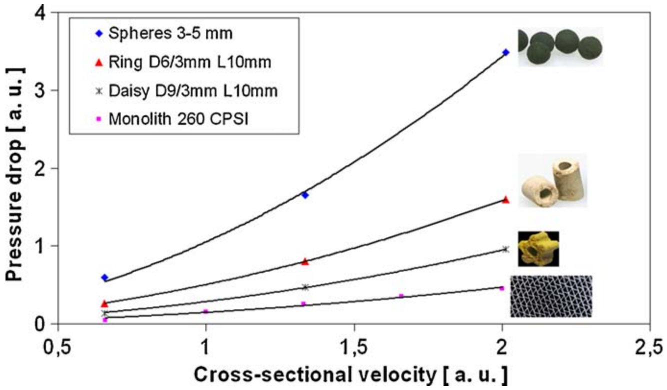

Fig. 1. Pressure drop characteristics of commercial pelletized and monolithic catalysts.

Table 2
Base metal oxide versus noble metal catalyst for VOC combustion.

	Relative price of catalysts for VOC combustion[a] [a.u.]		
	Base metal oxide	Pd-based	Pt-based
n-Hexane	1.00	2.08	3.64
Propylene	1.00	1.79	2.76
Formaldehyde	1.00	1.57	2.01
Methyl ethyl ketone	1.00	2.08	2.99
Toluene	1.00	1.27	2.22

[a] Relative price for equal catalytic performance within the guarantee period

combustion of Freon-12, CCl_2F_2, results in HCl and HF. Especially HF is very reactive and attacks the catalyst. Nonetheless, the catalyst has to maintain a high conversion level, 95% for 10,000 hours and longer. These requirements certainly demand a rather robust catalytic system. Pelletized metal oxide catalysts have shown a superior overall performance in industrial application in terms of price and catalytic performance compared to monolithic noble metal systems. Applications with high dust load require catalysts with high dust capacity to endure the covering of active phase with inactive matter and to avoid fast plugging and hence increase in pressure drop over the reactor. Optimised pellet shapes [6] as well as monolithic catalysts with proper channel size can be applied to obtain a compromise between void space and catalytic surface area. The resistance to chemical poisons such as sulphur is another aspect with respect to long-term performance [7]. Fig. 2 shows the result of a long-term test with monolithic catalysts on CO oxidation in exhaust gas from a biogas engine for power generation. The promoter clearly improves the performance of the catalyst. In addition, a prefilter is required to protect the catalyst from poisoning.

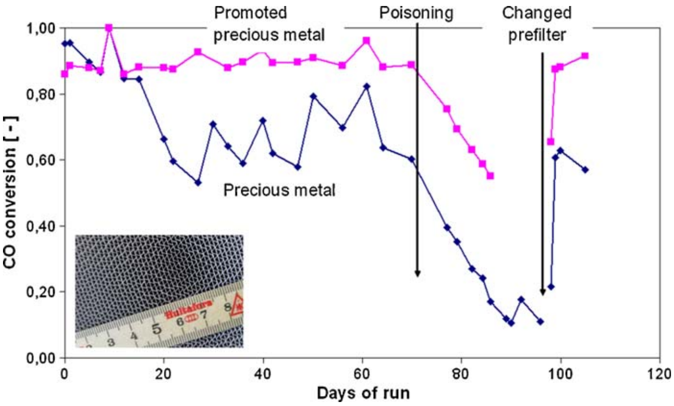

Fig. 2. Long-term test with monolithic catalysts on CO oxidation in exhaust gas from a biogas engine for power generation.

The price of the catalyst is also a major issue due to competition with non-catalytic cleaning techniques. Table 2 shows the comparison between metal oxide and precious metal catalysts for combustion of different VOC's based on relative catalyst cost. Cheap base metal catalysts are favoured over expensive noble metal catalysts.

3. Challenges in automotive oxidation catalysis

Exhaust after-treatment for diesel vehicles poses a different task than the well-established 3-way catalyst for petrol engines. Increasingly stricter limits for CO, HC, NOx and particulate matter (soot) emission has led to the development of a whole series of catalytic units: Diesel Oxidation Catalyst (DOC), catalysed Diesel Particulate Filter (cDPF), Selective Catalytic Reduction (SCR) followed by a NH_3 slip catalyst or Lean NOx Trap (LNT). One particular challenge is to integrate all these components into the very limited space in the engine compartment of a vehicle (Fig. 3).

Since regulated emission testing is performed with a cold engine start, DOC light-off temperatures for CO and HC have to be well below ∼200 °C because the exhaust gas is cold and the combustion process in the engine is not as efficient as with a warm engine (Figs. 4 and 5). Fast light-off can be obtained by placing the DOC close to the engine. Moreover, HC may be stored in zeolites inside the catalytic coating at low temperatures and subsequently be released at higher temperatures when the DOC is able to oxidise the hydrocarbons. One challenge to this solution is to formulate a durable catalytic coating that may be exposed to high exhaust temperatures at normal engine operation during the lifetime of the

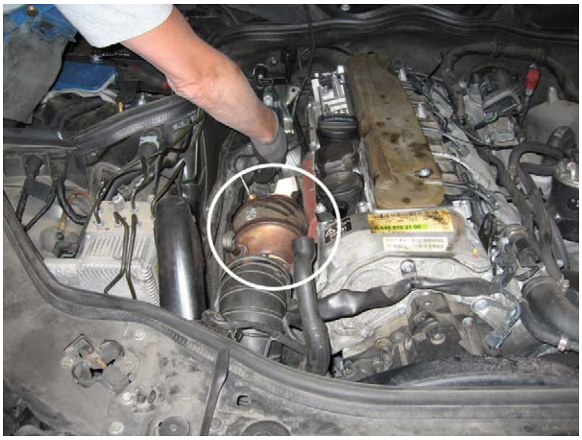

Fig. 3. Every litre of space is utilised in the engine compartment of a modern diesel passenger car. The volume of the exhaust gas treatment catalysts must be kept at a minimum. The white ring marks the top of the DOC.

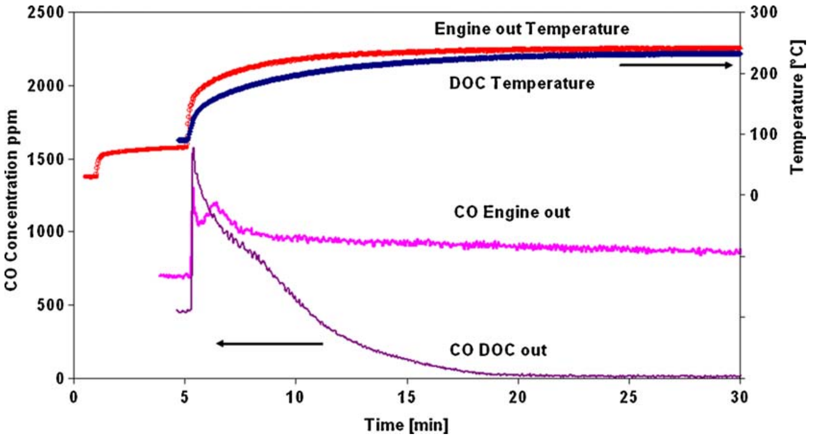

Fig. 4. Engine bench test of diesel oxidation catalyst with cold start. After 5 minutes of idling, the engine speed and load is increased to a constant level. The DOC is placed downstream the exhaust line. The engine CO emission is constant, whereas the DOC converts CO as the DOC is heated by the exhaust gas.

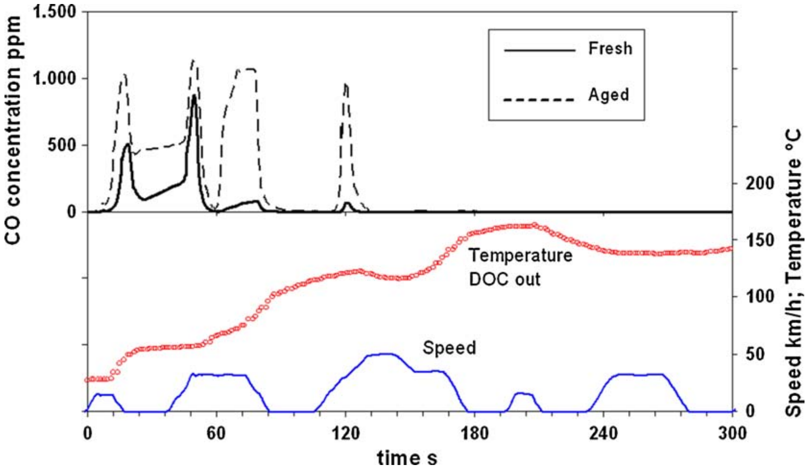

Fig. 5. Emission tests on passenger cars are performed on a chassis dynamometer following the New European Driving Cycle with cold start. CO emission is significant during the early part of the test until the DOC has reached the light-off temperature. Two commercial DOCs are tested: fresh, after 1400 km; and aged, after 21,000 km driving in city traffic. The delayed light-off of the aged DOC is evident.

car. Generally, a commercial DOC is based on noble metals. Cost has become a major challenge in the formulation of DOC.

Particulate matter is separated from the exhaust gas by ceramic wall flow filters, which need to be regenerated in order to keep the pressure drop low. Challenges in the design of Diesel Particulate Filters are pressure drop and the need for an efficient regeneration mechanism.

Combustion of the soot may take place by various mechanisms:

1) inclusion of a Fuel Borne Catalyst, typically Fe or Ce oxide-based, which lowers the regeneration temperature to 250–300 °C. The drawback is deposition of the remaining oxides inside the filter, which is gradually filled up with inert ashes;
2) oxidation of C by NO_2 formed from platinum-based catalysts, the so-called passive regeneration according to Reaction 2:

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \quad (2)$$

The NO_2-assisted reaction of C to CO, CO_2 and NO takes place at much lower temperatures than the O_2-assisted oxidation. NO oxidation over platinum oxidation catalysts led to increased NO_2 levels in city street air. Alternatively, the soot may be oxidised by O_2 if the exhaust gas temperature is increased to 600 °C by injection of extra fuel, which is oxidised over the DOC. This regeneration mechanism leads to higher fuel consumption;

3) contact with solid catalytic coating on the filter (Fig. 6), which e.g. is based on CeO_2. This mechanism will be effective at temperatures above 300–400 °C and needs a close contact between soot and filter coating. However, this method is not operative once the channels of the filter are filled with soot.

Several studies report that the degree of physical soot-catalyst contact influences the efficiency of catalytic soot oxidation [8–10]. In a recent study, CeO_2-catalysed soot oxidation was studied by using in situ TEM demonstrating that the catalytic soot oxidation reaction involved processes which were confined to the soot–CeO_2 interface region. The catalytic reaction resulted in motion of soot agglomerates toward the catalyst surface, which acted to re-establish the soot–CeO_2 interface in the course of the oxidation process [11,12]. These results both explain the need for a close contact between soot and filter coating and indicate why a loss of catalytic activity for soot oxidation is observed once the channels of the filter are filled with soot: a competition may prevail between re-establishing the soot–catalyst interface and bonding the soot agglomerate to the soot network. Thus, the soot–catalyst interface may break up, in which case soot transport to the catalyst surface will be rate-determining.

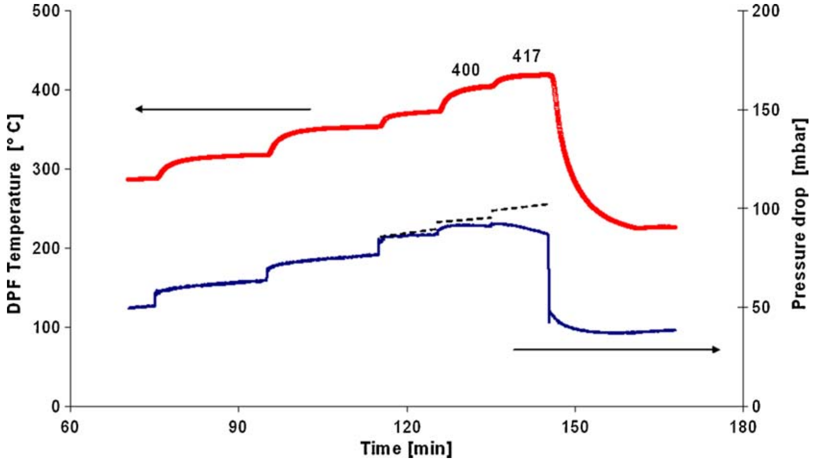

Fig. 6. Soot combustion on catalysed diesel particulate filter without DOC. The engine load is increased stepwise to increase exhaust gas temperature and cDPF temperature. Soot emission is constant thus leading to increased pressure drop across the DPF. When the catalytic soot oxidation starts, the pressure drop is decreasing. Dashed lines show extrapolated pressure drop without catalytic combustion.

4. Challenges in catalytic partial oxidation

The Partial Oxidation (POX) of methane, according to Reaction 3, has been applied for many years as one method for the large-scale generation of synthesis gas [13]. In recent years, the *catalytic* partial oxidation (CPO) of methane or natural gas has boosted the applicability of methane combustion, as this method can also be used in very small units for the generation of hydrogen, e.g. for fuel cells [13–15].

$$CH_4 + ½O_2 \rightarrow CO + 2H_2 \tag{3}$$

In a CPO reactor, the hydrocarbon feed and a sub-stoichiometric amount of O_2 (or air) are mixed and fed to a preheated catalyst, which auto-ignites the gas mixture (light-off). The combustion of methane is exothermic and leads to a strong temperature increase in the reactor (~1000 °C) and high-temperature gradient around the catalyst. Thus, thermally stable catalysts and carriers are essential for successful operation of a CPO process.

Before 1992, most studies were carried out at moderate or low space velocities with a residence time of 1 second or above. Current technologies apply space velocities well above 100,000 hr^{-1} and these short contact time (SCT) reactors require high activity catalysts in a form which minimises the pressure drop across the catalyst [16]. Thus, for large pellet-based reactors triangular catalyst loadings have been applied, while small reactors aimed at fuel cell applications are based on monoliths. Pioneering work on monolith-supported CPO catalysis has been done by Schmidt and co-workers [17–19]. The efforts to minimise the pressure drop over the catalytic system led to the development of corrugated monolithic reactors based on FeCrAlloy. This system (Fig. 7) carries the catalytically active system and has proven to have very good adhesion and thermal stability. Moreover, the monolith can be easily scaled according to its application in different fuel cell systems.

A large number of different catalysts have been suggested for CPO; the area has recently been reviewed [20]. Noble metals, nickel, and to a lesser extent cobalt are active catalysts in the CPO process, however, not all of these catalysts are stable on a long-term basis and the choice of a particular metal is often a balancing act between several critical parameters. These parameters comprise the catalytic activity and long-term stability, the selectivity towards synthesis gas production, a low propensity towards unwanted side-reactions (especially carbon formation), sensitivity towards sulphur poisoning and the price of the metal. Table 3 illustrates the relative price variation between a series of different catalyst formulations tested for a fuel cell CPO applications. Compromises between price and performance often need to be made for practical applications as illustrated below.

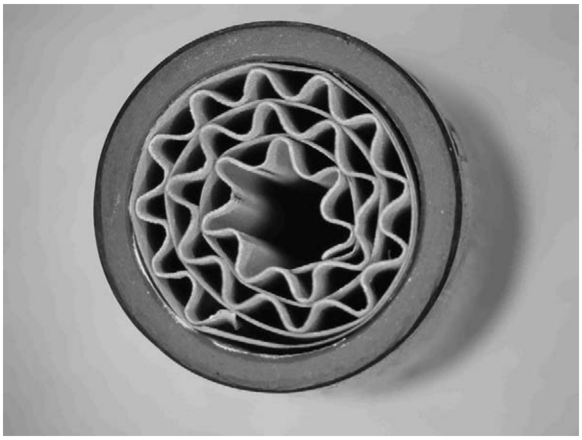

Fig. 7. CPO catalyst on a corrugated monolith.

Of the base metals, nickel catalysts show the highest activity, and they are attractive due to their low price; however, nickel catalysts are particularly sensitive to sulphur poisoning and to thermal sintering. Noble metal catalysts are generally recognised as superior in terms of activity and stability in CPO of methane as compared to base metal catalysts, but there are marked differences between the individual noble metals. Palladium is prone to rapid carbon formation at low O_2/HC stoichiometries leading to a build-up of pressure drop over the catalyst, but also catalysts based on platinum have revealed a propensity towards carbon formation [13]. This phenomenon is illustrated in Fig. 8, which includes a comparison of the relative catalyst pressure drop over a fixed

Table 3
Relative prices of noble metal-based catalysts for fuel cell CPO application.

	Relative price of CPO catalysts				
Catalyst formulation	A (Pd)	B (Ir)	C (Ir)	D (Ir)	E (Rh)
Relative price	1.00	0.60	0.36	0.18	0.68

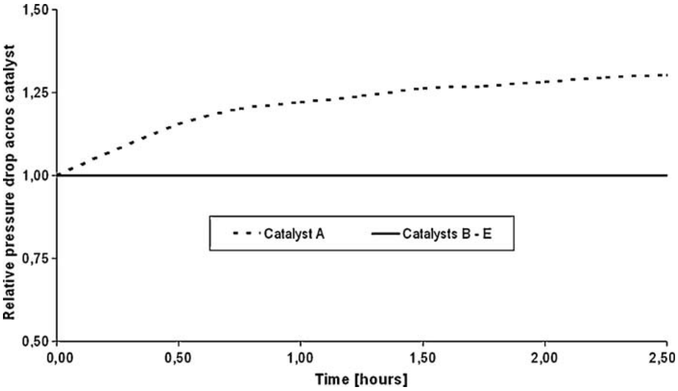

Fig. 8. Pressure drop across fuel cell CPO monolithic catalyst based on different noble metal formulations. The catalysts were all tested at similar conditions in a diluted premixed CH_4/O_2 gas prepared to $\varphi = 3.0$, a preheat temperature of 390 °C and a space velocity of 40,000 hr^{-1}.

Table 4
Light-off temperatures determined in diluted premixed CH_4/O_2 gases at space velocities around 40,000 hr^{-1}. φ is defined as the ratio between the actual fuel/oxidizer ratio relative to the fuel/oxidizer ratio required for complete combustion to carbon dioxide and water.

	Light-off temperature [°C]				
Catalyst formulation	A (Pd)	B (Ir)	C (Ir)	D (Ir)	E (Rh)
$\varphi = 2{,}5$	340	360	360	355	-
$\varphi = 3{,}0$	340	350	350	350	-
$\varphi = 3{,}5$	340	345	355	360	300

runtime for the different catalyst formulations in Table 3. As illustrated in Fig. 8, the pressure drop across the catalyst increases steadily for the palladium-based CPO catalyst, while all other formulations maintain a constant pressure drop.

A stable catalytic performance with low (< 400 °C) light-off temperatures in the CPO process can be obtained using rhodium, but often the rhodium price is prohibitive for large-scale facilities. Palladium, ruthenium and iridium catalysts are considerably less active than rhodium catalysts, but exhibit sufficient activity for many practical applications. Table 4 provides an overview of light-off temperatures at different stoichiometries for the fuel cell CPO catalyst formulations in Table 3. The light-off temperatures were determined at space velocities around 40,000 hr^{-1} in premixed CH_4/O_2 gases diluted in N_2. The data in Table 4 clearly illustrate the superior performance of rhodium in terms of lowest light-off temperature. An additional consideration that needs to be handled for certain noble metal catalysts is the fact that they may be exposed to oxidative atmospheres during industrial operations. Thus, the volatile oxides, which may be formed by ruthenium and iridium catalysts, require special precautions when utilising these particular noble metals in practical applications.

Many of the critical parameters for the choice of the active metal also depend on the choice of the support as specific metal-support interactions can e.g. influence the reducibility of a metal oxide or stabilise the particle dispersion of a metal. Widely investigated support phases are ZrO_2, TiO_2, CeO_2 and Al_2O_3. Another vast area, which by far has not been investigated in detail, is the CPO activity and stability of promoted metal systems and metal alloys. Spectroscopic investigations of novel catalytic systems under catalytic conditions can give valuable insight into the development of new CPO catalysts. As an example, in-situ XAFS investigations of supported Rh and Ni-Rh catalysts under CPO conditions showed different reducibilities of the samples at the ignition temperatures [21,22].

Other aspects of catalyst properties such as selectivity and operability may also come into play when choosing a catalyst for industrial applications. The selectivity towards higher hydrocarbons is important as they are prone to polymerise and form carbon in downstream equipment. The phenomenon is most pronounced when pure oxygen is applied as oxidiser, while negligible amounts are formed with air as the oxidant and using platinum or rhodium catalysts [23]. The typical dry-gas compositions obtained at the outlet of a monolithic reactor based on catalyst formulation D in Table 3 is illustrated in Fig. 9, which includes data from a test performed with a diluted premixed CH_4/O_2 system at $\varphi = 2.5$ and atmospheric pressure. The data are in agreement with expected trends, i.e. the concentration of products is at its highest at the highest temperature, while the methane slip increases as the temperature decreases. At all conditions, the outlet composition is completely depleted in oxygen, and there were no signs of higher hydrocarbons in the product gas composition. Finally, with respect to the operability of these catalysts, the ability to operate significantly below light-off conditions may be relevant in practical systems as the heat available for feed gas preheat is limited due to the overall heat integration and the ability to operate steadily between the light-off and quench temperature must be determined. Fig. 10 illustrates how the light-off temperature may be determined, and subsequently the self-sustainability of a fuel cell CPO may be evaluated when the preheating temperature is decreased below the light-off temperature. The system in Fig. 10 is

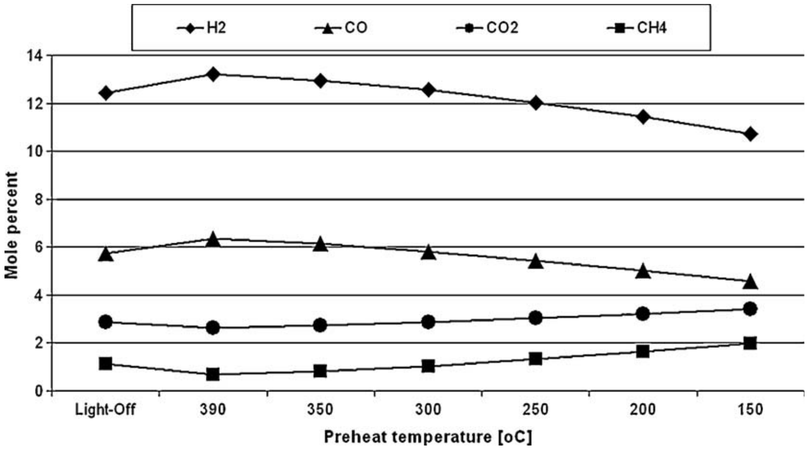

Fig. 9. Dry-gas composition determined as function of temperature between the light-off and quench temperature during a test of self-sustainability below light-off. The catalyst was in a diluted premixed CH_4/O_2 gas prepared to $\varphi = 2.5$ and a space velocity of 40,000 hr^{-1}.

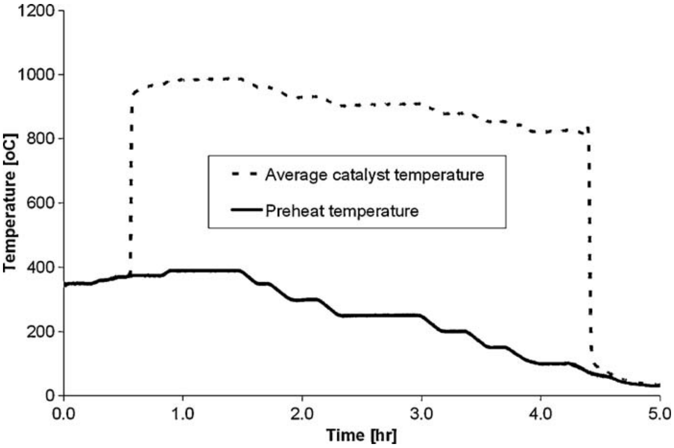

Fig. 10. Determination of required preheating to achieve light-off and subsequent test of self-sustainability below light-off until quench. The catalyst was in a diluted premixed CH_4/O_2 gas prepared to $\varphi = 2.5$ and a space velocity of 40,000 hr^{-1}.

the same as in Fig. 9, and the results included in Fig. 10 suggest that a well-insulated system based on catalyst formulation D in Table 3 is self-sustainable with an absolute minimum of preheating once the system has achieved light-off.

In summary, the optimal CPO catalyst for practical application may initially be a compromise between a sufficiently low-cost price and sufficiently high activity, but in addition several other aspects around by-products formation, durability and stability as well as shaping have to be considered.

5. Future challenges in catalytic oxidation

Present catalysts and technologies reflect the present availability of feedstock and present legislations. Many speculations are advanced regarding sort and availability of feedstock in the future: gas, oil, coal and biomass-derived feedstocks are mentioned, but often with high variations of their relative importance depending on the source. Regardless of their relative importance, certainly increased feedstock diversities can be expected in the future. Assumably, this will lead to additional gas cleaning and/or conditioning, which in part must be handled via applied oxidation catalysis.

Future legislation leading to tighter emissions may also be assumed in all parts of the world to minimise the impact of emissions on human health and our surrounding environment. To comply with these legislations, increasingly more effective catalysts will be required. However, the impacts on human health and our surrounding environment not only relate to emissions and the minimisation of these, catalyst productions must also be compatible to environmental standards and comply with the regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH). Finally, the prices of active substances used in catalyst production have been highly fluctuating during the last 5 years, which has motivated studies of cheaper bimetallic alloyed catalysts; this work has also revealed strong synergetic effects of alloying. Thus, to ensure supply stability and avoid price erosion in applied oxidation catalysis, continued work towards cheaper and more sustainable solutions can be expected.

In conclusion, industrial solutions must be tailor-made, and there is no universal solution to applied oxidation catalysis.

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