Synthesis of enamel-protected catalysts for microchannel reactors: Application to methane oxidative coupling

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HIGHLIGHTS

► Strontium/lanthanum are selective catalysts for the oxidative coupling of methane.
► However, they are poisoned by Cr when directly used in microstructured reactors.
► A protective layer of enamel blocks Cr and enhances the catalyst adherence.
► Two chromium transport mechanisms have been identified.

GRAPHICAL ABSTRACT

Sr/La perovskites catalysts applied in steel microstructured reactors are contaminated by chromium, thus changing the selectivity of the oxidative coupling of methane (OCM) towards complete oxidation. Pre-coating of a dense enamel layer can effectively protect the catalyst. The dominant chromium transport mechanism occurs via gaseous CrO₃ species. Exposure of the catalyst to bare steel will result in chromium contamination and thus catalyst deactivation.

ABSTRACT

Lanthanum based oxides are good catalysts for the oxidative coupling of methane (OCM). However, when applied in stainless steel microstructured reactors, these catalysts quickly lose selectivity to ethane and ethylene. This is due to the incorporation of chromium, originating from the steel, into the catalyst surface. This study explores the possibility of protecting the catalyst layer from chromium poisoning by applying a dense inert protective layer inside the microchannels on which the catalyst is then deposited. Comparison of three different protective layers has revealed the incompatibility of alumina primer coatings with lanthanum catalysts and the insufficient blocking efficiency of spinel layers at 900 °C. The coating of enamel layers on micro-reactor platelets has shown good efficiency against the migration of chromium into OCM catalysts even at 900 °C. The enamel protective ability appears to be correlated to its density. The firing procedure responsible of the enamel densification requires heat treatments above 1000 °C. Above these temperatures the chromium oxide solid-state diffusion through the enamel becomes an important pathway during the enamel densification step. Densification of the enamel is optimal at 1050 °C with short dwell times. Influence of the enamel composition has also been studied, revealing that zirconium and barium oxides are undesirable.

La/Sr catalysts deposited on enamel layers show good ethylene and ethane selectivity that only slightly decreases with time on stream. Exposure of the enamel/catalyst to unprotected steel at 800 °C, however, leads to rapid deactivation by chromium contamination. This is in line with the diffusion of gaseous CrO₃ as the main pathway for chromium contamination.

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1. Introduction

Natural gas is widely used as feedstock for the production of chemicals and energy with proven abundant reserves of over 150 trillion m$^3$ and 200 trillion m$^3$ as potential reserves [1]. It is estimated that approximately 30% of the natural gas reserves are stranded. Building liquefaction plants or pipelines is not economically viable in these cases. Conversion of natural gas to liquid hydrocarbons (GTL) has shown to strongly improve the economic relevancy of these stranded sources via the transport of valuable liquids [2]. Thus the Fischer–Tropsch process has proven its benefits as an efficient GTL process. However, the process requires syngas as a feedstock which can only be produced via an energy intensive reforming step [3].

The oxidative coupling of methane (OCM) to ethane and ethylene has been studied for many years as a potential alternative route for the production of valuable hydrocarbons from natural gas without going through reforming. Many catalysts have been screened for this reaction, but the C$_2$ yields are always well below 25% [4–6]. This limits industrial application of OCM [7]. Recently, oxide based catalysts were reported with C$_2$ yields around 20% exhibiting good stability [8]. The use of micro-reactor technology might present a solution for these limitations through the possibility to control the temperature in OCM reactors [9–11]. This compact and integrated technology also fits well with the constraints of stranded natural gas locations [12]. Moreover, micro-channels induce low pressure drops and Ekstrom et al. have reported the strong inhibitory effect of the pressure on the OCM C$_2$ selectivity in fixed bed reactors [13]. However several technical issues lower the extensive use of micro-reactors. The development of coated catalysts has often been reported as problematic [14]. In previous studies carried out in our laboratory, we developed a coating method via suspended catalyst powder in water [15,16]. This simple method led to well-adherent and stable coatings but has only been studied for alumina or oxide supported catalysts.

A second technical issue is related to the use of reactors based on steel at high temperatures. Corrosion and related phenomena are often reported [17,18]. Studies concerning solid oxide fuel cells (SOFCs) have revealed that lanthanum-based perovskites catalysts were poisoned by elements from the metal substrates. The depletion of lanthanum and strontium from the perovskite electrode and their reaction with chromium leads to the formation of a mixture of lanthanum/strontium/chromium spinels and perovskites [19]. The same phenomenon should be expected with regular OCM catalysts since lanthanum sesquioxide and strontium monoxide often enter in the composition of the most active catalysts [8]. Calle–Vallejo et al. have indeed reported that the formation of lanthanum–chromium or strontium–chromium perovskites from the base oxides is strongly favoured [20]. The contamination of the perovskites by chromium appears to be caused by two different mechanisms. At temperatures higher than 700 °C under oxidative atmospheres, chromium migrates via solid-state diffusion inside the perovskites layers as Cr$_2$O$_3$ and as chromium–manganese spinels [21]. Sublimation of chromium oxide, mainly as CrO$_3$, also occurs [22]. Gaseous chromium oxide can then react with the perovskite surface. Extensive work has been performed on the protection of perovskites by manganese based – electroplated spinels on the steel substrate [23–25]. However the spinels cannot be electroplated on steel micro-reactors because the metals will be deposited on the entire surface and the edges of the platelets have to remain clean for welding.

Zhang et al. [26] have shown that spinel precursors – typically chlorides – dissolved in ethylene glycol with citric acid as a chelating agent lead to similarly efficient protection layers as electro-plated spinels after thermal treatments. Moreover, the coating method enables to selectively coat the platelets channels and to keep their edges clean for welding.

In parallel, intensive work has been done on the coating of catalysts on steel substrates [14]. Well-known alumina coatings are stable and strongly adherent to steel micro-reactors. Valentini et al. [27] reported that the use of a pre-coating of alumina before the OCM catalyst could increase the oxide catalyst adherence onto the micro-channels.

Finally, vitreous enamelling is a common method to protect steel reactors against corrosion. It acts mainly as a physical barrier between the steel substrates and the environment. The adherence of enamel on steel substrates is not trivial because of its low thermal expansion coefficient. Indeed the enamel often needs to be doped with metals – typically cobalt or nickel [28] – to increase the compatibility of steel and enamel. For OCM applications, doping cannot be considered because metal-doped enamels present a firing temperature below the OCM reaction temperatures. Smectetto et al. [29] have recently presented glass seals that were efficient to block the solid state diffusion of chromium at 800 °C even after long time experiments. However, no evidence has been shown yet that a lanthanum or strontium based catalyst is protected by this type of glass layers.

In this work, we compare the ability of alumina, spinels and enamel coatings to prevent chromium diffusion and to enhance the adherence and the long-time stability of OCM catalyst coatings onto steel microstructured platelets. Stability experiments under OCM conditions were performed in a reactor containing 2 microstructured platelets.

2. Experimental

2.1. Stainless steel platelets

The platelets used for the coating experiments were fabricated from ASTM 310 steel (ThyssenKrupp, 24.1 wt.% Cr, 19.1 wt.% Ni, 1.4 wt.% Mn, Fe balance). Each of them carried 10 micro-channels with a length of 40 mm, a channel height of 400 µm and a width of 800 µm.

Prior to coating, the steel platelets were immersed in a 10 M sodium hydroxide solution and were sonicated for 60 min at 60 °C. The platelets were then washed successively with distilled water and acetone.

2.2. Catalysts preparation

Two OCM catalysts were used: 1 wt.% Sr/La$_2$O$_3$ (white, Johnson–Matthey) and 10/20/70 wt.% La/Sr/CaO prepared via the nitrate and citric acid sol–gel method [8]. Coating studies were focused on the Sr/La$_2$O$_3$ catalyst due to its better air stability. Strontium and calcium oxide are hygroscopic and coatings of La/Sr/CaO are unstable under moist air. The La/Sr/CaO catalyst has been reported as one of the most active and selective and has therefore been used in the activity experiments [8]. Lanthanum and strontium containing catalysts are known to be stable under OCM conditions [30]. Our experiments have confirmed this, as the methane conversion and C$_2$ selectivity were found stable during 60 h run in a fixed bed reactor.

Catalysts were crushed and ball-milled to obtain a particle size around 1–5 µm. The preparation of the coating slurry has been described in detail [15]. Catalyst suspensions were prepared by mixing 40 g of distilled water with 20 wt.% of catalyst and 0.8 wt.% of binder for the Sr/La$_2$O$_3$ sample and 40 g of distilled water with 8 wt.% of catalyst and 0.4% binder for La/Sr/CaO sample. Tylose H300 (SE Tylose GmbH, Germany), a cellulose derivative,
was used as a binder and a few drops of an anti-foaming agent were added (Polypolypropylene glycol)-block-poly(ethylene glycol)-block-poly(polypropylene glycol) – average Mn ~ 3,300, Aldrich). The suspension was stirred for at least 48 h before the coating procedure.

2.3. Protective layers preparation

γ-Alumina coatings have already been detailed by Peela et al. [31]. The primer solution of 2 wt.% Disperal S (boehmite, Condea) diluted in water was peptized with 0.4 wt.% HNO₃ for 48 h. 4 wt.% of polyvinylalcohol (PVA, Alfa Aesar) was added and the solution was stirred for 2 h prior to coating. The slurry solution was prepared by mixing 20 wt.% of γ-alumina and 0.4 wt.% of Tylose H300 in water. A slurry for coating of 14 wt.% γ-alumina, 6 wt.% of unpeptized Disperal S and 2 wt.% of PVA in water was also prepared.

Spinel solutions were prepared following Zhang’s method [26], 2 wt.% nickel, copper or cobalt chlorides (NiCl₂, 6H₂O/CuCl₂, 2H₂O/CoCl₂, 6H₂O, Sigma–Aldrich), 2 wt.% manganese chloride (Sigma) and 4 wt.% of citric acid (monohydrate, Aldrich) were dissolved in ethylene glycol (EG).

Enamel solutions were prepared by mixing the enamel frits (Ferro group, composition given in Table 1) and a solvent with a spatula. Three different solvents were tested:

- MX 54 (Ceradel, France), a pine oil based organic solvent.
- S 63 M (Ceradel, France), an aqueous solvent.
- Distilled water.

A fixed concentration of 33 wt.% of the glass frits was studied. By default MX 54 was used as a solvent.

2.4. Coating of the metallic platelets

The platelets were coated following an in-house wash-coating method [16]. The suspension was spread with a syringe into the channels and the coated platelets were dried in air at ambient temperature for 24 h. The layers were annealed in air in an oven between 600 °C and 1100 °C or reduced under a 10% H₂-90% N₂ flow at 800 °C. Typically the platelets were loaded with 5–30 mg of solids.

The enamel solutions were spread with a spatula into the channels and dried in an oven by different methods. The enamel deposited on the edges of the platelets was removed with a razor blade. The platelets were finally annealed in air at temperatures between 1000 and 1300 °C.

Coated samples were tested under mechanical stress applying a 1/4" tubing. Coated samples were tested under mechanical stress applying a 1/4" tubing. Platelets were coated following an in-house wash-coating method [16]. The suspension was spread with a syringe into the channels and the coated platelets were dried in air at ambient temperature for 24 h. The layers were annealed in air in an oven between 600 °C and 1100 °C or reduced under a 10% H₂-90% N₂ flow at 800 °C. Typically the platelets were loaded with 5–30 mg of solids.

Comparison of the activity of poisoned and clean catalysts in a powder form was carried out in a u-shape fixed-bed quartz reactor (internal diameter = 6 mm) placed in an electric tubular oven. The catalyst (100–120 mg) was placed between quartz wool plugs in the bottom of the reactor. The reactor pressure was kept at 1.1 bars. The catalyst bed temperature was monitored with a thermocouple (Ø 0.3 mm) placed inside the catalyst bed. Olivier et al. have reported that lanthanum-based oxide catalysts presented the highest C₂ productivity at 800 °C [8]. Catalysts have therefore been tested at 800 °C with a mixture of 9.9 mL/min CH₄, 3.3 mL/min O₂ and 86.6 mL/min Ar. The effluent gas was analyzed on-line, by a mass spectrometer (Inficon). The different m/e signals were measured and corrected for the different contributions of other products. Response factors were calculated relative to the aragon response. The spectrometer was regularly calibrated using different mixtures of reactants and products. To check the results a carbon mass balance was established for each experiment.

Activity experiments of coatings were carried out in a 2-platelets μ-reactor (see Fig. 1). Three blocks constitute the reactor:

- The gas inlet part consists of 20 enamelled channels and 2 separated gas entries. 10 channels are devoted to the CH₄/N₂ mixture and the rest to O₂. Channels have a diameter of 0.8 mm. Injection of O₂ into the CH₄/N₂ flow is carried out by 300 μm diameter holes placed 500 μm from the end of the O₂ channels.
- Micro-structured platelets are tightened between two stainless steel (AISI 310) blocks by 6 screws.
- The outlet part consists of 10 enamelled channels connected to a 1/2" tubing.

Sealing of the three blocks is performed by two perforated mica/silicone sheets. The three blocks and the seals are tightened by four threaded rods. The inlet gas composition was 80/20/5 CH₄/O₂/N₂ ml/min. Nitrogen was used as an internal standard. Experiments were carried out at 800 °C.

The effluent gases from the microstructured reactor were analyzed by micro gas chromatography (μGC 3000, SRA Instruments, France). CO₂ and the C₂ were separated on a PLOT U column with a PLOT Q pre-column at 70 °C with helium as carrier gas. H₂, O₂, N₂, CH₄ and CO were separated on a Moleisieve column with a PLOT U pre-column at 100 °C with argon as carrier gas. Gas concentrations were measured by a thermal conductivity detector.

The unprotected platelets are referred to as “OCM platelets” and the enamelled platelets as “ENM + OCM platelets”. Both were coated with the La/Sr/Cao catalyst.

Methane conversion, C₂ selectivity and C₂ yield were determined according to equation 1, 2 and 3 (see Appendix 1), respectively.

### Table 1

<table>
<thead>
<tr>
<th>Reference</th>
<th>Thermal expansion COE + 10E-7°C</th>
<th>Firing temperature (°C)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>B₂O₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>ZrO₂</th>
<th>ZnO</th>
<th>BaO</th>
</tr>
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<tbody>
<tr>
<td>VTR 213</td>
<td>122</td>
<td>1020–1050</td>
<td>a</td>
<td>a</td>
<td>a</td>
<td>b</td>
<td>b</td>
<td>b</td>
<td>c</td>
<td>b</td>
<td>b</td>
<td>b</td>
</tr>
<tr>
<td>VTR 258</td>
<td>303</td>
<td>Not specified</td>
<td>a</td>
<td>b</td>
<td>a</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>a</td>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>VTR 100</td>
<td>205</td>
<td>980–1020</td>
<td>a</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>a</td>
<td>a</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>b</td>
</tr>
<tr>
<td>VTR 102</td>
<td>192</td>
<td>980–1020</td>
<td>a</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>a</td>
<td>a</td>
<td>c</td>
<td>c</td>
<td>c</td>
<td>c</td>
</tr>
<tr>
<td>VTR 105</td>
<td>168</td>
<td>1020–1050</td>
<td>a</td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>b</td>
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</table>

- Concentration above 8 wt.%.
- Concentration between 2 and 2 wt.%.
- Less than 2 wt.%.
2.6. Coating samples characterization

Morphology and thickness of the coated layers were studied using a JEOL 5800 Scanning Electron Microscope operated at 15 kV. 10 mm slices were cut from the platelets and immersed into an epoxy resin. The resulting pellets were polished using silicon carbide disks and covered with a sputtered gold film. The layers thickness was determined by averaging of 50 length measurements along three different channels per samples using the ImageJ software package. Enamel loading and thickness were used to calculate the enamel density. Only small variations (~5%) of the catalyst and enamel layers thickness were found suggesting that the layers are uniform along the channels. EDX line scans were performed at catalyst–enamel–steel interfaces. As the main constituent of the enamel, Si was chosen as representative of the enamel layer. Lanthanum was selected to represent the catalyst, Fe for the steel and Cr to follow its diffusion inside the enamel and catalyst layers.

Energy-dispersive X-ray analyses (EDX) of these contaminated films are hindered by the overlap of the major peak of chromium (Kα1 = 5.989 keV) and one of the peaks of lanthanum (Lα2 = 5.891 keV). The quantification of chromium traces into concentrated lanthanum oxide via EDX is strongly limited by this overlapping. Yokokawa et al. [22] have reported that chromium contamination of lanthanum oxide presents a yellow–brownish color although La2O3 should be white. Correlation of the chromium content with the intensity of the yellow color could then be possible.

Colorimetric measurements were performed with an optic fiber (FCR-7xx400-2-ME, Avantes) connected to a white light-emitting source. Reflection of the white light was directly collected by the optic fiber and analyzed by a spectrometer (Avalight-XE, Avantes) and treated by the Avasoft software. Kubelka–Munk transform (KMT, Eq. (4)) of the white light transmittance spectrums of poisoned catalyst presents a peak around 450 nm. And the slope of this peak is correlated to the intensity of yellow in the catalyst. Elementary analysis showed that the catalyst contained 1.55 wt.% of chromium. Activity experiments in a fixed bed reactor are shown in Fig. 2. It appears that the chromium contamination has no impact on the conversion of oxygen but it significantly lowers the CH4 conversion and the selectivity toward C2. The contamination leads to methane combustion with lower methane conversion at complete oxygen conversion due to the change of the reaction stoechiometry.

3. Results and discussion

3.1. Alumina protective coatings

Alumina layers are commonly used to improve the adherence of the coating of alumina based catalysts on steel substrates [27]. Coatings of 20 wt.% alumina or 14 wt.% alumina + 6 wt.% boehmite led to fully adherent layers after firing at temperatures between 800 and 1100 °C for 2 h. The Sr/La2O3 catalyst was deposited by slurry coating on top of the alumina layer. The Sr/La2O3 catalyst did not adhere onto the alumina. A complete weight loss of the catalyst was recorded in the drop test.

The primer deposition of boehmite fired at 600 °C for 5 h or at 1100 °C for 2 h followed by the coating of the γ-alumina slurry solution also led to an adherent coating after calcination at 600 °C for 5 h. Again the Sr/La2O3 catalyst was deposited by slurry coating on top of the alumina layer, but no adherence was obtained. Thus no conclusions could be drawn on the efficiency of alumina layers to prevent chromium diffusion into the oxide sample.

3.2. Spinel coatings

The work of Zhang et al. [26] suggests that nickel and manganese chlorides dissolved in ethylene glycol mixed with citric acid should be an efficient preparation for the coating of spinels on steel substrates. Cobalt and copper manganese spinels have been shown to be good protective barriers in SOFC applications. (Mn,Ni)3O4, (Mn,Cu)3O4 and (Mn,Co)3O4 precursors diluted in ethylene glycol with 4 wt.% of citric acid led to a strong corrosion of the platelets after firing in air at 800 °C for 10 h. Weight losses of more than 100% were recorded and the platelets could no longer serve as micro-reactor stacks. Reduction of similar coatings under hydrogen at 800 °C for 10 h followed by oxidation under air avoided steel corrosion but led to weakly adherent layers. Low
weight losses of the spinels coatings were obtained with citric acid-free solutions of the (Mn,Ni)₃O₄ and (Mn,Co)₃O₄ precursors and reduction under hydrogen. (Mn,Cu)₃O₄ coatings remained moderately adherent to the platelets after reduction or oxidation at 800 °C. Subsequent Sr/La₂O₃ catalyst coating led to a complete adherence to the citric acid-free and reduced (Mn,Ni)₃O₄ coating after calcination at 800 °C for 2 h. Low adherence was found after catalyst coating on citric acid-free (Mn,Co)₃O₄ and (Mn,Cu)₃O₄ coatings.

Colorimetric measurements on the catalyst layers showed no poisoning of the catalyst by chromium after thermal treatment at 800 °C for 2 h for the three citric acid-free and reduced spinels coatings. However, chromium contents between 2 wt.% and 3 wt.% were measured in the catalyst layers after calcination of the catalyst at 900 °C for 10 h.

During the OCM reaction hot spots might occur, thus the protective layers should guarantee a full protection even at 900 °C. Thus manganese-based spinels coated via the chlorides method cannot be considered as a completely satisfying protection of the lanthanum catalyst.

3.3. Enamel coatings

Initial experiments with different glass frits annealed at 1000 °C led to completely adherent and homogeneous coatings. Even if these enamels are not doped with metals, the micro-structured shape of the platelets seems to render the enamel layers more stable and seems to avoid the formation of cracks. These layers were perfectly stable during drop tests and exposure to ultrasounds. Moreover, the subsequently coated Sr/La₂O₃ catalyst was completely adhesive to the previously enamelled platelets (less than 10% of weight loss after drop tests and cleaning with compressed air) and remained free of chromium after 2 h at 800 °C. Consequently, the temperature during the catalyst calcination step was increased to 900 °C for 10 h to better compare the enamel preparations.

3.3.1. Optimization of the enamel coating procedure

The solvent used to prepare the enamel has an influence on the chromium blocking effect of the final layer. Fig. 3 shows a chromium content of 0.35 wt.% on the coated Sr/La₂O₃ catalyst with MX 54 as a solvent and contents above 0.80 wt.% with the aqueous solvents, i.e. the use of the MX 54 solvent led to a more efficient protection against chromium diffusion. Enamel densities have been estimated from SEM micrographs. The density of the enamel coated with MX 54 is nearly 1 g/cm³ higher than that the coating prepared with the aqueous solvents.

Different drying conditions have been investigated and the results are summarized in Fig. 4. The density of the enamel layer and the chromium blocking efficiency are clearly influenced by...
Fig. 6. SEM pictures and EDX line scans of the four studied enamel coatings. Enamels were annealed at 1000 °C (1 °C/min) and 1125 °C (5 °C/min) for 2 h and the catalytic films were annealed at 900 °C for 10 h. (a) frit VTR 105, (b) frit VTR 102, (c) frit VTR 213 and (d) frit VTR 100.
the drying step. Drying at room temperature for extended periods of time led to dense and fully protective glass layers. While fast drying at 90 °C and 150 °C directly followed by calcination led to less dense films and stronger chromium contamination.

Fig. 5 shows the results of a comparative study of the different frits for the protection of the Sr/La2O3 catalyst. The composition of the frits is presented in Table 1. The frit VTR 100 appears to form the most efficient protective layer after a firing of the enamel at 1000 °C or 1125 °C for 2 h. Calcination of the catalyst protected by the frit VTR 100 at 900 °C for 10 h resulted indeed in a white and chromium-free layer. After firing at 1000 °C, the coating of frit VTR 298 did not lead to a glass layer and the subsequent coating of the catalyst led to a black layer where lanthanum oxide was mixed with the protective layer.

3.3.2. Optimization of the enamel firing step

SEM pictures of slices of the platelets after enamel and catalyst deposition and the corresponding EDX line analyses are regrouped in Fig. 6. After the coating of four different enamels and a firing step at 1125 °C, the glass layers were perfectly dense. Only Si, La, Fe and Cr contents are shown in Fig. 6 because the firsts three are representative of the enamel, the catalyst and the steel, respectively. In the EDX plots, zero (on the left hand side) on the x-axis indicates the position of the catalyst, while on the right hand side is the steel. Diffusion of chromium oxide was observed into all enamel layers after firing the enamel at 1125 °C for 2 h at a temperature ramp of 5 °C/min. Diffusion of manganese has also been observed to some extent, but due to its much lower concentration (15 times less than chromium) it is neglected in this study. No other elements from the two layers or from the steel have shown such a pronounced migration. The formation of a chromium–enamel mixture at the enamel–steel interface seems to justify the good adherence of enamel onto the platelets despite their different thermal conductivities. Fig. 6a shows that the diffusion of chromium occurred into half the thickness of the frit VTR 105 in the form of fibers. The same irregular shape of diffusion can be observed on Fig. 6b but only into 35% of the enamel layer thickness. In the case of the frit VTR 213 (Fig. 6c), chromium oxide completely covered the enamel layer. Finally, 25% of the frit VTR 100 enamel was filled with a regular chromium oxide layer.

A deep penetration of chromium occurs into the enamel layers of the frits VTR 105 & 213 (Fig. 6a and c). Both frits contain barium oxide. Yang et al. [32] have shown a chemical reaction of barium oxide with chromium that leads to the formation of pores in the glass. This phenomenon enables chromium oxides to diffuse through the enamel layers.

The frits VTR 105 and 102 present the formation of chromium oxide fibers that deeply penetrate the glass layer (Fig. 6a and b). The frits VTR 102 and 105 indeed contain zirconium oxide, which promotes the diffusivity of oxygen ions into ceramic layers. Zirconia doped with yttrium oxide is indeed commonly used in SOFC as an interconnecting material because of its high ionic conductivity [33]. Consequently, the formation and the migration of chromium oxide are promoted in these enamel layers. The diffusion of chromium into the enamel layer is even more profound in the case of the VTR 105 (Fig. 6a) because of the association of zirconia and barium oxide. According to SEM images in Fig. 6a and b, some of these chromium oxide fibers seem to have reached the catalyst–enamel interface, leading to catalyst contamination.

The migration of chromium oxide is severely limited in case of the frit VTR 100 with the formation of a chromium oxide layer stabilized near the metallic substrate (Fig. 6d). The constituting elements of each glass frit have a strong influence on the protection efficiency of the enamel layers. The absence of barium or zirconium oxides in the frit VTR 100 leads to a complete protection of the catalyst layer after the firing at 1125 °C.

Results presented in Fig. 5 have shown a great improvement of the chromium blocking ability of the VTR 100 enamel layer with the increase of the firing temperature from 1000 °C to 1125 °C. Consequently, the influence of the firing temperature on density and catalyst protection has been measured between 1000 °C and 1300 °C. Higher firing temperatures have not been considered be-
cause of their proximity with the melting temperature of the steel (around 1400 °C). Using SEM analysis the chromium oxide layer thickness has been measured after exposure at the different firing temperatures, reported in Fig. 7b. Fig. 7a shows that an increase of the firing temperature from 1000 °C to 1080 °C leads to a significant improvement in the blocking capacity of the enamel layer. Between 1000 °C and 1080 °C, only a thin layer of chromium oxide covers about 10% of the enamel layer. At the same time the chromium content of the catalyst is reduced from 0.35 wt.% at 1000 °C to 0.01 wt.% at 1080 °C. This is accompanied by an increase of the enamel layer density from 8 g/cm³ to 10 g/cm³ (Fig. 7b). Apparently, the enamel layer density at 1000 °C is not sufficient to block the migration of gaseous CrO₃, leading to catalyst contamination. Indeed, a correlation between the enamel layer density and the Cr content of the catalyst can be established for all the data below 1125°C, as shown in Fig. 8.

Above 1125 °C the Cr content of the catalyst increases with the temperature. So does the chromium oxide layer on the enamel layer. However, the density of the enamel layer does not change any longer. An almost linear increase of the chromium oxide layer thickness with temperature is observed, indicating a strongly acti-

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**Fig. 9.** SEM images (a) and EDX analysis (b) of the optimized enamel coating fired at 1050 °C during 150 min with a temperature ramp of 5 °C/min.

**Fig. 10.** C₂ selectivity for the OCM, ENM + OCM and ENM + OCM/Bare platelets in the 2 platelets µ-reactor. Operating conditions: the inlet gas composition was 80/20/5 CH₄/O₂/N₂ ml/min, 800 °C, 0.066 s contact time, X_{CH₄} = 10%, 98% carbon balance.
through gaseous intermediates, likely CrO₃ species. This diffusion is known to result in a strong chromium contamination, despite the good density of the enamel layer. At these temperatures the Cr₂O₃ and chromium-manganese spinels solid-state diffusion into the enamel is strongly activated and it becomes the dominant mechanism of chromium transport \[22\].

Thus temperatures around 1080°C lead to dense enamel layers and are low enough to limit solid-state Cr diffusion. An optimal temperature of 1050°C has been found by further varying the time of exposure at the firing temperature. Fig. 9 presents the SEM picture and the corresponding EDX line scan of this optimized coating. As expected, the enamel layer has blocked chromium diffusion and the catalyst is completely adherent to the protective layer.

3.4. Activity experiments

Fig. 10 compares the performance of the La/Sr/CaO catalysts on steel microchannel platelets with and without enamel protection. Three different microstructured reactor/catalysts configurations were tested, schematically represented in Fig. 11. The methane conversion is similar for the three systems \(X_{\text{CH}_4}=\sim 10\%\). In the case of the unprotected catalyst sample a low C₂ selectivity is observed initially, rapidly dropping to zero. The main product is carbon dioxide, suggesting that the poisoned catalyst constituted of chromium perovskites and chromium oxide, which catalyzes methane combustion instead of coupling \[34\]. Colorimetric analysis of the unprotected sample showed indeed 3 wt.% of chromium on the catalyst layer after the activity experiments. The enamel-protected sample shows a much higher C₂ selectivity up to 35% that only slightly declines with time on stream. This is cannot be attributed to Cr contamination as colorimetric analysis showed no chromium on the catalyst layer after the experiment. SEM images and EDX analysis of the enamelled platelets after 30 h of reaction showed no difference with fresh enamel layers.

In the last case where the enamel protected catalyst is tested in a microchannel that contained one side of exposed steel \(X_{\text{CH}_4}=\sim 10\%\). A very low C₂ selectivity is observed initially, rapidly dropping to zero similarly as in the case of the unprotected catalyst. Colorimetric analysis of the catalyst sample showed again Cr contamination. This result confirms the importance of the diffusion of chromium through gaseous intermediates, likely CrO₃ species. This diffusion mechanism might also limit the use of La based catalyst for OCM in industrial fixed bed reactors, as these will be constructed most likely out of chromium containing steel.

4. Conclusions

Strontium/lanthanum based catalysts show good performance in the oxidative coupling of methane to ethane and ethylene in fixed bed reactors. Their use in stainless steel microstructured reactors revealed very poor performance. This is due to a contamination by Cr (and to a lesser extend Mn) diffusing from the steel to the catalyst. In order to block Cr diffusion to the catalyst layer, three different protective layers have been compared. Alumina primers are not compatible with these oxide catalysts resulting in a complete lack of adherence. Spinels layers \[24\] performed well at 800°C, but at 900°C Cr diffusion across the layer occurred. The use of enamel layers showed good catalyst adherence and good blocking efficiency even at 900°C. The enamel has been optimized in terms of composition and deposition procedure. It has been found that enamels containing either barium or zirconium oxides should be avoided. Complete Cr blocking and excellent catalyst adherence were obtained with the frit VTR 100 after drying at room temperature for 21 h followed by 3 h at 90°C and then firing at 1050°C for 150 min using a 5°C/min ramp. This protected catalyst shows good C₂ selectivity with only a slow decline in performance with time on stream that cannot be attributed to chromium contamination.

The optimized procedure leads to very dense coatings that stabilize the chromium oxide layer near the metallic substrate. In fact below a firing temperature of 1125°C the layer density can be directly correlated to the Cr blocking efficiency. The dominant route of Cr contamination occurs through the diffusion of gaseous chromium oxide species and subsequent deposition on the catalyst surface. The denser the enamel layer the less chromium oxide sublimation occurs. Above a temperature of 1125°C the solid-state diffusion of Cr becomes more and more significant, allowing eventual the Cr to reach the catalyst layer, independent of the density of the enamel layer. The latter process occurs during the densification of the enamel. Thus the optimal firing temperature is a compromise between a temperature high enough to obtain very dense layers and not too high to avoid solid state chromium diffusion.

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**Appendix A**

**Methane conversion:**

\[
X_{CH_4} = \frac{F_{in} - F_{out}}{F_{in}}
\]

with \(F\) the molar methane flow.

\[
C_2 = \frac{2(F_{C_2H_6} + F_{C_2H_4})}{2F_{C_2H_6} + F_{C_2H_4} + F_{CO} + F_{CO_2}}
\]

\[
C_2 = \frac{X_{CH_4} \times S_c}{Y_{CH_4} - \frac{1}{2} - \frac{1}{2}}
\]

Kubelka-Munk Transform (KMT):

\[
\text{KMT} = \left[1 \frac{1}{2\% T} \right] \times 100\%
\]

where \(\%\) stands for the transmittance.

**References**


