Chemical Engineering Journal 213 (2012) 31–40

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

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

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

Thomas Serres, Lamia Dreibine, Yves Schuurman *

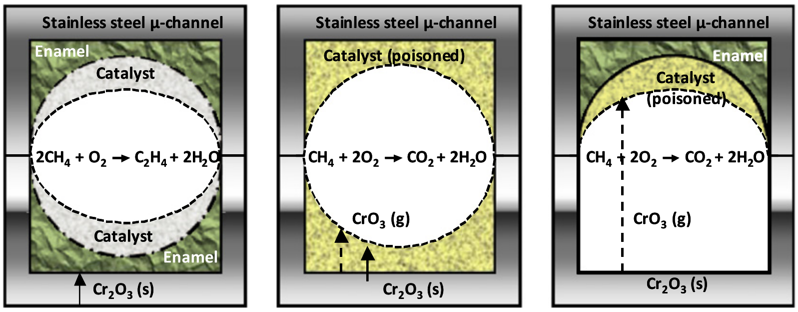
IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256 CNRS, Université de Lyon1, 2 Avenue Albert Einstein, 69626 Villeurbanne, France

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 perovkites 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 at OCM conditions occurs via gaseous CrO_3 species. Exposure of the catalyst to bare steel will result in chromium contamination and thus catalyst deactivation.



ARTICLE INFO

Article history:
Received 20 June 2012
Received in revised form 5 September 2012
Accepted 13 September 2012
Available online 13 October 2012

Keywords:
Microreactors
Stainless steel
Chromium
Poisoning
Ethylene
La/Sr oxides

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 spinels 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 CrO_3 as the main pathway for chromium contamination.

---

* Corresponding author. Tel.: +33 472445482; fax: +33 472445399.
E-mail address: yves.schuurman@ircelyon.univ-lyon1.fr (Y. Schuurman).

1385-8947/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2012.09.061

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 presents 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_2O_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. Smeacetto 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_2O_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_2O_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_2O_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,