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# Effect of sulphur poisoning on perovskite catalysts prepared by flame-pyrolysis

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ABSTRACT

$ABO_3$ perovskite-like catalysts are known to be sensitive to sulphur-containing compounds. Possible solutions to increase resistance to sulphur are represented by either catalyst bed protection with basic guards or catalyst doping with different transition or noble metals. In the present work $La_{(1-x)}A'_xCoO_3$, $La_{(1-x)}A'_xMnO_3$ and $La_{(1-x)}A'_xFeO_3$, with A′ = Ce, Sr and $x$ = 0, 0.1, 0.2, either pure or doped with noble metals (0.5 wt% Pt or Pd), were prepared in nano-powder form by flame-pyrolysis. All the catalysts were tested for the catalytic flameless combustion of methane, monitoring the activity by on-line mass spectrometry. The catalysts were then progressively deactivated *in operando* with a new procedure, consisting of repeated injection of some doses of tetrahydrothiophene (THT), usually employed as odorant in the natural gas grid, with continuous analysis of the transient response of the catalyst. The activity tests were then repeated on the poisoned catalyst. Different regenerative treatments were also tried, either in oxidising or reducing atmosphere.

Among the unsubstituted samples, higher activity and better resistance to poisoning have been observed in general with manganites with respect to the corresponding formulations containing Co or Fe at the B-site. The worst catalyst showed $LaFeO_3$, from both the points of view of activity and of resistance to sulphur poisoning. $La_{0.9}Sr_{0.1}MnO_3$ showed, the best results, exhibiting very high activity and good resistance even after the addition of up to 8.4 mg of THT/g of catalyst. Interesting results were attained also by adding Sr to Co-based perovskites. Sr showed a first action by forcing Mn or Co in their highest oxidation state, but, in addition, it could also act as a sulphur guard, likely forming stable sulphates due to its basicity. Among noble metals, Pt doping proved beneficial in improving the activity of both the fresh and the poisoned catalyst.



## 1. Introduction

The catalytic flameless combustion (CFC) of methane outperforms conventional flame combustion because of lower emission of pollutants (HC, CO and $NO_x$) and high thermal efficiency. The catalysts traditionally used for CFC are mainly based on supported noble metals, such as Pd and Pt, which ensure high activity, however accompanied by some drawbacks, due to high cost and poor thermal and chemical stability. La-based catalysts with $ABO_3$ perovskite-like structure [1–4] have been proposed as a valid alternative for the present application. Indeed, perovskite catalysts combine low cost, thermo-chemical stability at high operating temperature and satisfactory catalytic activity [5–8]. In spite of this, there are still some open questions, especially regarding their resistance to sulphur poisoning when used for the CFC of methane. Indeed, the poisoning mechanism of perovskite-like catalysts has not been completely understood and only a few papers deal with this very important topic.

The deactivation mechanism due to exposure to $SO_2$ has been investigated by means of complementary techniques. After $SO_2$ adsorption, unstable surface species form, which promptly react with activated oxygen to form sulphates, sulphites and/or sulphides, depending on temperature and catalyst formulation [5,9–12]. The migration of these species from the surface to the bulk has been also observed [1]. Due to its basicity, lanthanum oxide is prone to interact with $SO_2$ forming the corresponding sulphate, whereas no evidence of cobalt sulphate formation was found when treating $LaCoO_3$ with $SO_2$ [1]. Depending on the extent of poisoning, the complete destruction of the active phase has been sometimes reached, with formation of segregated B-ion oxide and lanthanum sulphate. The conversion of methane and the resistance of the catalyst to sulphur poisoning have been studied with various combinations of A- and B-site metals and by adding MgO as promoter [5,10,11,13]. However, though the latter option seems to guarantee a sufficient resistance to poisoning, the promoter essentially acts as a shield, forming stable sulphates and hence competing with the active phase for $SO_2$ adsorption. Its protective action is of course time-limited by its consumption.

Based on the above summarised topics, S-poisoning begins with $SO_2$ adsorption on oxygen vacancies and it is essentially

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a surface-based mechanism. Therefore, catalyst nanostructuring can deeply affect the resistance towards S-containing impurities. In the recent past, attention has been devoted to catalyst nanostructuring, aiming at obtaining high surface area and defectivity, which should enhance oxygen mobility through the lattice and ensure good catalytic activity. To this purpose, we set up and optimised a flame-pyrolysis (FP) apparatus for the one-step synthesis of perovskitic mixed oxides. It is based on a specially designed burner fed with oxygen and an organic solution of the precursors, the solvent acting as fuel for the flame. FP-synthesized perovskites, showed good phase purity, along with nanometer-size particles and hence very high surface area (sometimes in excess of 100 $m^2/g$) [2–4]. In addition, the high temperature of the flame in principle should also ensure thermal stability.

In the present work we prepared a set of samples by FP, namely $La_{(1-x)}A'_xBO_3$, with A′ = Ce, Sr, B = Mn, Co, Fe and $x$ = 0, 0.1, 0.2, either pure or doped with noble metals (Pt or Pd). The catalysts were tested for the CFC of methane, monitoring the activity by on-line mass spectrometry. The effect of sulphur poisoning was then investigated "*in operando*", by monitoring the catalyst transient response during pulsed injection of tetrahydrothiophene (THT). This represents a new testing procedure with respect to those reported in the literature, which mainly repeat standard activity tests after exposure to $SO_2$. The effect of catalyst composition, as well as of nanostructuring, on activity and stability has been investigated.

## 2. Experimental

### 2.1. Samples preparation

All the precursor solutions were prepared by dissolving in propionic acid (Aldrich, pur. 97%) salts the selected metals: $La(CH_3COO)_3{\cdot}2H_2O$ (Aldrich, pur. 99.9%), $Mn(CH_3COO)_2{\cdot}4H_2O$ (Aldrich, pur. 99.9%), $Fe(AcAc)_3$ (Aldrich, pur. 97%, AcAc = acetylacetonate), $Co(CH_3COO)_2{\cdot}4H_2O$ (Fluka, pur. 99%), $Sr(CH_3COO)_2$ (Aldrich, pur. 99%), $Ce(CH_3COO)_3$ (Aldrich, pur. 99.9%), $Pd(CH_3COO)_2$ (Fluka, Pd 47 wt%), $Pt(AcAc)_2$ (Aldrich, pur. 97%) in the desired ratio and metal concentration.

The FP apparatus has been described in detail elsewhere [2]. Briefly, it consists of a capillary tube (inner diameter 0.6 mm) ending in the centre of a vertical nozzle and connected with a syringe pump (Harvard, mod. 975), feeding the solution of the mixed oxide precursors. The nozzle was co-fed with oxygen (SIAD, pur. > 99.95%, flow rate 5 L/min), acting both as oxidant and as dispersing agent, able to form micro-droplets of solution. The main flame is ignited and supported by a ring of 12 premixed $O_2 + CH_4$ (flow rates 1 L/min and 0.5 L/min, respectively) flamelets. Gas flow rate was regulated by MKS (mod. 1259C) mass flow meters, controlled by a MKS (mod. 247C) control unit. The synthesized nano-particles were collected by means of a 10-kV electrostatic precipitator [14].

### 2.2. Catalyst characterisation

The structure of the prepared lanthanum perovskites was determined by X-ray powder diffractometry on a Philips PW3020 diffractometer. The patterns obtained were compared with literature data for phase recognition [15]. The surface area of the synthesized powders was measured by $N_2$ adsorption/desorption at 77 K on a Micromeritics ASAP2010 apparatus, after outgassing at 300 °C overnight. Scanning electron microscopy (SEM) analysis was carried out on a LEICA LEO 1420 instrument. The main properties of the prepared catalysts are summarised in Table 1.

**Table 1**
Main catalyst properties. SSA = specific surface area (BET). Particle size determined from SEM analysis.

| Catalyst | SSA ($m^2/g$) | Particle size (nm) |
|---|---|---|
| $LaMnO_3$ | 56 | 35–40 |
| $LaCoO_3$ | 43 | – |
| $LaFeO_3$ | – | – |
| $La_{0.9}Sr_{0.1}MnO_3$ | 51 | 25–35 |
| $La_{0.8}Sr_{0.2}MnO_3$ | 70 | 25–60 |
| $La_{0.9}Ce_{0.1}MnO_3$ | 61 | 30–45 |
| $La_{0.9}Sr_{0.1}CoO_3$ | 52 | 20–60 |
| $La_{0.9}Ce_{0.1}CoO_3$ | 62 | – |
| 0.5% $Pt/LaMnO_3$ | 63 | *ca.* 40 |
| 0.5% $Pt/LaCoO_3$ | 58 | *ca.* 50 |
| 0.5% $Pd/LaMnO_3$ | 53 | 30–35 |
| 0.5% $Pd/LaCoO_3$ | 54 | – |

### 2.3. Catalytic activity testing

Catalytic activity tests were carried out by means of a continuous quartz tubular reactor on *ca.* 0.15 g of catalyst, pelletized, ground and sieved to 0.15–0.25 mm particles. Prior to each run, the catalyst was activated in flowing air (20 $cm^3$/min), while increasing temperature by 10 °C/min up to 600 °C, then kept for 1 h. The activity tests were carried out by feeding a mixture composed of 0.34 vol.% $CH_4$, 33.3 vol.% air, He balance, while increasing temperature by 10 °C/min from 200 °C up to 600 °C. Gas flow rate was regulated by means of mass flowmeters (Brooks Instruments, mod. 5850) governed by a control unit (Brooks, mod. 0154). The total gas flow rate was 30 ml/min. The outcoming gas was analysed in line by means of a quadrupolar mass spectrometer (MKS, PPT Residual Gas Analyzer), selecting proper mass fragments.

Catalyst poisoning was done in the same apparatus at 450 °C by injecting 4 doses of 0.15 mg of THT (Fluka, pur. > 97%) per 1 g of catalyst, each group of four injections being defined as cycle (corresponding to 0.6 mg THT/g of catalyst). The catalytic activity was monitored "*in operando*" during poisoning, by continuously analysing the relevant mass fragments ($CH_4$, $O_2$, THT, $SO_2$, $SO_3$, CO, $CO_2$, $H_2O$) and plotting them as partial pressure *vs.* time. The data have been elaborated by calculating the slope of some descriptive lines, indicating the transient response of the catalyst during poisoning, as better detailed in Section 3.4. The standard activity test was then repeated after each poisoning cycle. In some cases the amount of poison was increased, after the standard four cycles, until a decrease in conversion was observed. In such cases, "forced" poisoning cycles were used to observe any effect for some very resistant catalysts. Anyway, the total amount of THT injected has been specified in the text (*vide infra*).

Catalyst regeneration was attempted first by heating in air at 600 °C for 1 h. A second procedure was based on hydrogen treatment at 500 °C followed by reoxidation in air at 600 °C. After each treatment activity was checked following the standard procedure.

## 3. Results and discussion

All the present catalysts were characterised by high phase purity, since no reflection of extraneous phases has been ever observed for the fresh samples, even in the case of samples doping. This indicates dopant incorporation into the framework or at least very high dispersion as small aggregates, whose size was lower than the detection limit of the XRD technique. Peak broadening has been observed for every sample due to the small particles size. Sometimes a bi-modal crystal-size distribution has been observed. BET surface area ranged between 43 $m^2/g$ for $LaCoO_3$ to 70 $m^2/g$ for $La_{0.8}Sr_{0.2}MnO_3$, due to the flash calcination characterising the FP technique, which limits any deep sintering of the powder. No