

A new method for preparing nanometer-size perovskitic catalysts for CH₄ flameless combustion

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A novel method based on flame hydrolysis of aqueous solutions of precursors has been set up for preparing perovskite-type mixed oxide catalysts in nanometer size particles of high surface area and high thermal stability. After optimising the shape and size of the various parts of the equipment and all the operational parameters, the method has been applied to the preparation of a series of samples of general formula $\text{La}_{1-x}\text{M}_x\text{CoO}_{3+\delta}$, with $x = 0, 0.1$ and $\text{M} = \text{Ce}, \text{Eu}$. Perfectly crystalline powders, made of 200-600 Å microspherical particles, generally clustered into 100-500 nm conglomerates, with S_{BET} typically of 20-30 m²/g, were obtained. The catalysts proved highly thermally resistant and up to one order of magnitude more active than samples of identical composition, but prepared through traditional methods, allowing to attain 100% methane conversion at temperature as low as 560°C.

1. INTRODUCTION

Perovskite-like mixed oxides are currently widely studied and proved to possess a comparable activity as substitutes of noble metal catalysts for the abatement of CO, HC and NO_x from fossil fuel combustion exhausts and for the catalytic flameless combustion (CFC) of hydrocarbons [1]. Particularly, being carried out at considerably low temperature, CFC allows a substantial reduction or even elimination of harmful combustion products, especially NO_x. The usual calcination-milling (CM) route [2] for preparing such materials in a thermally stable form, involving several high-temperature CM cycles of the precursor powder mixture, ends in a low-surface-area, coarse-size particles of relatively low catalytic activity. Then several techniques have been proposed for preparing higher surface area perovskites [3,4], the most commonly used being the so-called sol-gel-citrate (SGC) method [5]. However, the final calcination in SGC being made usually at $T < 800^\circ\text{C}$, the material so obtained rapidly sinterises under the CFC conditions.

Silica can be prepared in very fine particles by flame hydrolysis (FH) of SiCl₄. However, to our knowledge, so far the FH process has been applied to monocomponent oxides only [4,6,7], possessing at least one volatile precursor. The aim of the present work was then to prepare perovskitic catalysts in nanometer-size particles of high surface area, by extending the FH method to a multicomponent aqueous solution of precursors, hydrolysed in a high-temperature flame. After characterisation by several techniques, the catalytic activity of each sample was tested for the CFC of CH₄.

2. EXPERIMENTAL

The nitrates, acetates or citrates of precursors in the desired ratios were dissolved in water. When necessary, the dissolution was aided by employing 10 % aqueous HNO_3 as solvent, instead of pure water. In some cases (*vide infra*) an aqueous solution of citric acid (1/1 or 0.5/1 molar ratio with respect to the sum of metal salts) was added to the metal precursors. The resulting solution was nebulised by means of a pyrex glass nozzle (fed with 0.150 to 0.225 m³/h of air) into a H_2+O_2 flame. The nanometric particles of perovskites so forming were collected by means of an electrostatic precipitator.

BET surface area (S_{BET}), elemental composition, particle size and nature of phase(s) have been determined by means of a Micromeritics ASAP 2010 apparatus, a Jordan Valley EX-310 X-ray fluorescence (XRF) spectrometer, a Cambridge Stereoscan 150 scanning electron microscope (SEM) and a Philips PW 1820 powder diffractometer, respectively. The XRF quantitative elemental analysis was done after calibration by means of standard samples of known composition. The XRD analysis was made by using the Cu $K\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$).

Catalytic activity tests have been carried out by means of a bench-scale apparatus, centred around a quartz-tube continuous microreactor (I.D. = 0.6 cm, length = 45 cm). The catalyst (ca. 200 mg) was activated *in situ* overnight at 650°C in 40 cm³/min flowing air. After cooling down to 250°C, the air flow was switched to a gas mixture composed of 20 cm³/min of 1 vol% CH_4 in N_2 and 20 cm³/min of air. A 4°C/min temperature ramp was then begun, up to 650°C, while analysing the outcoming gas every 12 min by gas chromatography. An extended time-on-stream run (80 h) was also performed at 560°C on the most active catalyst.

3. RESULTS AND DISCUSSION

Besides flow rate of H_2 and O_2 to the burner, the size and shape of the latter and of the nebuliser and the value of at least four parameters can be varied to control the FH process, so to get the desired sample composition, structure and particle size. The four parameters are: *i*) nature of the precursor salts, *ii*) concentration of the latter in the aqueous solution, *iii*) flow rate and *iv*) humidity degree of the air fed to the nebuliser.

3.1. Equipment

Our goal was the preparation of crystalline $\text{La}_{1-x}\text{A}_x\text{CoO}_{3\pm\delta}$ samples, with $\text{A} = \text{Ce}, \text{Eu}$, $x = 0, 0.1$ and S_{BET} at least one order of magnitude higher than that (0.5 to 3 m²/g) usually obtained by preparation through the usual CM process. The optimisation of both the nebuliser and electrostatic precipitator was then performed by preparing a series of Ce-doped ($x = 0.1$) samples (Table 1, samples 1 to 4). Characterisation of these catalysts allowed defining the best geometrical and working parameters of our equipment, in order to maximise surface area, phase purity and crystallinity and to minimise particle size.

3.1.1. Nebuliser

The shape and dimensions of the nebuliser govern productivity and influence the physical-chemical properties of the samples obtained. Indeed, the smaller the orifice of the nozzle, the smaller are the droplets formed and consequently the smaller is the size of the particles produced. However, the smaller the orifice, the higher is the pressure drop through the nozzle. Furthermore, the higher the flow rate of air through the nozzle, the lower becomes the hydrolysis temperature. Moreover, the higher is reflux rate within the nebuliser, the lower is productivity. In addition, properly moistened air is needed to feed the nebuliser, to avoid the progressive change in

concentration of the solution during nebulisation. In fact, the higher the concentration of the solution, the higher is productivity, but the higher is the particle size and consequently the lower is the BET surface area of the powder obtained.

Table 1. Main characteristics of the catalysts prepared

Sample no.	Catalyst	Precursors ^a	Solution conc. (wt.%)	Additives	S _{BET} (m ² /g)
1	La _{0.9} Ce _{0.1} CoO _{3+δ}	La(NO ₃) ₃ Ce(NO ₃) ₃ Co(NO ₃) ₃	11.58	none	39.7
2	La _{0.9} Ce _{0.1} CoO _{3+δ}	La(NO ₃) ₃ Ce(NO ₃) ₃ Co(NO ₃) ₃	6.96	Citric acid 1:1(mol)	18.7
3	La _{0.9} Ce _{0.1} CoO _{3+δ}	La(Ac) ₂ Ce(Ac) ₂ Co(Ac) ₂	5.80	HNO ₃	27.0
4	La _{0.9} Ce _{0.1} CoO _{3+δ}	La(Ac) ₂ Ce(Ac) ₂ Co(Ac) ₂	5.75	HNO ₃ Citric acid 1:1(mol)	17.5
7	La _{0.9} Ce _{0.1} CoO _{3+δ}	La(Ac) ₂ Ce(NO ₃) ₃ Co(Ac) ₂	6.78	HNO ₃ Citric acid 0.5:1(mol)	24.0
8	LaCoO _{3+δ}	La(Ac) ₂ Co(Ac) ₂	5.83	HNO ₃ Citric acid 0.5:1(mol)	18
9	La _{0.9} Eu _{0.1} CoO _{3+δ}	La(Ac) ₂ Eu(Ac) ₂ Co(Ac) ₂	5.85	HNO ₃ Citric acid 0.5:1(mol)	18.3

a) Ac = acetate

3.1.2. Electrostatic precipitator

A first type of multipin effluviator, made of chromium-plated brass, proved unsatisfactory, since the pins were slowly corroded, due to the relatively high temperature of the discharging tips and to partial condensation of chemicals on them. As a consequence, undesired Cr, Cu and Zn oxide impurities were found in the samples produced. An AISI 316 stainless steel effluviator was then designed and mounted, which allowed overcoming the problem. The optimisation of both nebuliser and electrostatic precipitator led to a substantial improving of the overall process yield, from the very low initial value (5%) to over 80%.

3.2. Influence of flame temperature and of process parameters

Two different fuel/oxygen (F/O) combinations were tried, both in stoichiometric F/O ratio. When natural gas was employed, the flame temperature hardly attained 1600°C during the FH process. As a consequence, the degree of XRD crystallinity of the resulting powder was very low. By substituting hydrogen for natural gas the flame temperature was much higher (>2000°C) and the XRD pattern matched perfectly the typical reflections ($2\theta = 23, 40, 46, 54, 59^\circ$) of the perovskite-type structure [8].

The nature of the precursor salts on one hand may hinder the formation of a clear solution of the desired composition. On the other hand it may help in keeping the FH process to a sufficiently high temperature. Several salts with different anions were then tried, both inorganic

and organic, for preparing the solution to be nebulised. Organic anions, acting as additional fuels, allowed a higher hydrolysis temperature. The further addition of an equimolar amount of citric acid led to a better crystallinity (Fig.1*a-c*) and to a more uniform distribution of particle size, however accompanied by a lower surface area (Table 1, samples 1-4). Moreover, the complexing action of the citrate anion helped in obtaining a perfectly clear and stable feeding solution. As for the overall concentration of the latter, too high values (>10 wt%) led to a higher surface area, but also to XRD amorphous powders, while too low values (<3 wt%) depressed unacceptably productivity. The best compromise was then found for concentration around 6 wt%.

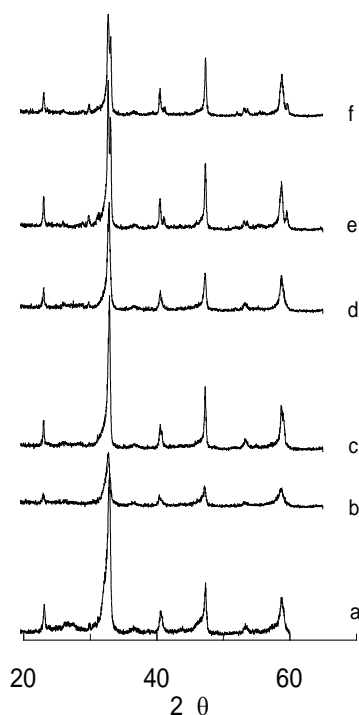


Fig.1. XRD patterns of the powders obtained. *a-c*) Samples 2-4, respectively; *d-f*) samples 7-9, Tab.1

Fig.2. (*a-d*) Typical SEM micrographs of samples 3, 7, 8, 9, Table 1.

All the samples so prepared showed a high phase purity and good crystallinity. This confirms that there is not a preferential decomposition of anyone of the precursors with respect to the other ones, the FH process taking place almost instantaneously, as expected. This is due to the effect of both high flame temperature and very tiny size of the nebulised solution droplets.

Table 1 data show also that higher values of S_{BET} (up to ca. 40 m²/g) were obtained in the absence of organic salts (sample 1) and with more concentrated precursor solution. However, this was accompanied by a low degree of crystallinity. Conversely, when employing organic salts (acetates) as precursors, S_{BET} dropped to less than 30 m²/g (sample 3), but the size of the powder particles was more uniform (Fig.2*a*). The addition of an equimolar amount of citric acid (sample 4) further lowered S_{BET} , down to less than 20 m²/g, accompanied by a considerable increase of the degree of crystallinity (Fig.1*c*). However, when the molar ratio of citric acid to the metal precursors was halved (sample 7) the degree of crystallinity practically did not change (Fig.1*d*), but the S_{BET} value (Table 1) increased to 24 m²/g and the particle size of the powder became much more uniform. Indeed, SEM micrographs (Fig.2*b-d*) showed that the powder is composed

of microspherical particles 200 to 600 Å in diameter, generally clustered into 10 to 500 nm conglomerates.

Finally, a proper degree of humidity of the air sent to the nebuliser allows to keep constant the concentration of precursors' solution, so keeping constant the particle size of the powder and the production rate of the process.

3.3. Preparation of the optimised samples of catalyst

The equipment so optimised was then employed for the preparation of a series of samples with general formula $\text{La}_{1-x}\text{M}_x\text{CoO}_{3+\delta}$, with $x = 0, 0.1$ and $\text{M} = \text{Ce}, \text{Eu}$, whose characteristics are shown in Table 1 (samples 7, 8 and 9) and in Figs 1 and 2. The composition of all three catalysts, checked by XRF analysis, coincided within the experimental error ($\pm 2\%$) with the nominal one, calculated from the weighed amount of precursor salts.

3.4. Activity and durability tests

Activity comparison tests have been carried out on the series of three catalysts (samples 7-9, Table 1) prepared as described. A first aim of these tests was to compare the performance of the catalyst (sample 8, Table 1) prepared by the present FH method with catalyst samples of identical composition, but prepared by the SGC method [5] or by the CM method [2], respectively. The results are shown in Fig. 3. It can be noticed that the sample prepared by the FH method is about four times as active than that prepared by the SGC method and one order of magnitude more active than that prepared by the CM method.

Another aim of the activity comparison tests was to investigate the effect of the partial substitution of Ce or Eu for La in our perovskite-type La-cobaltite. The results are given in Fig. 4. The Ce-promoted catalyst confirmed [9] to be the most active with respect to both the unpromoted and to the Eu-promoted samples, which showed a comparable activity.

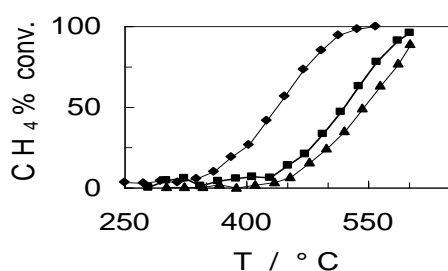


Fig.3. Activity comparison tests for CFC of methane over the $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3+\delta}$ catalyst, prepared by: (♦) the present FH method, (■) the SGC method and (▲) the CM method. Catalyst loading: 0.2 g, reactants feeding rate: 40 cm³/min of a 0.5 vol% CH_4 , 10 % O_2 , balance N_2 , gas mixture.

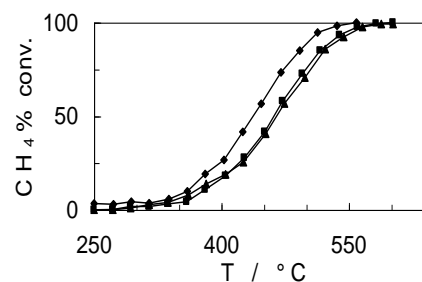


Fig.4. Effect of 10 mol % substitution of Ce or Eu for La on the activity of $\text{LaCoO}_{3+\delta}$ catalyst for CFC of CH_4 : (♦) sample 7, (▲) sample 8, (■) sample 9, Table 1. Reaction conditions as for Fig.3.

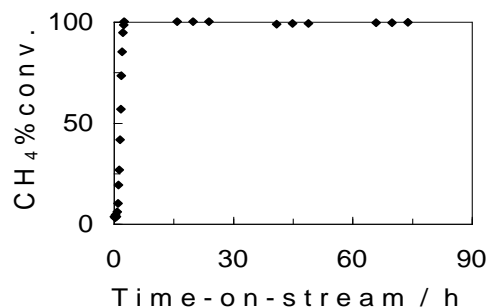


Fig.5. Extended time-on-stream activity test. Catalyst 7, Table 1. Reaction temperature increased by 4°C/min and then maintained to 560°C. Other reaction conditions as for Fig.3.

At last, the durability test was carried out on the most active catalyst (sample 7) only, under the usual reaction conditions. Reaction temperature was increased by 4°C/min up to 560°C, the lowest value at which this catalyst attained 100% conversion and then kept to such a value for ca. 80 hours on-stream. The results are given in Fig. 5 and confirm the very good thermal resistance of the present catalysts.

4. CONCLUSIONS

- i)* A FH preparation method, starting from aqueous solutions of precursors and leading to nanometer-size perovskite-type transition metal oxide catalysts has been set up successfully.
- ii)* Crystalline perovskites, with high surface area and very good thermal resistance can be easily prepared by this method.
- iii)* These catalysts proved up to one order of magnitude more active than traditionally prepared catalysts of the same composition, for the flameless combustion of CH₄, down to reaction temperature as low as 560°C.

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REFERENCES

1. Y. Teraoka, H. Fukuda, S. Kagawa, Chem. Lett., (1990) 1.
2. M.F.M.Zwinkels, S.G.Järås, P.G.Menon, T.A.Griffin, Catal. Rev. Sci. Eng., 35 (1993) 319.
3. L.G.Tejuca, J.L.G.Fierro, Properties and Applications of Perovskite-type Oxides, Dekker, New York, 1993.
4. W.R.Moser, J.D.Lennhoff, J.E.Cnossen, K.Fraska, J.W.Schoonover and J.R.Rozak, in Advanced Catalysts and Nanostructured Materials, W.R.Moser, ed., Academic Press, New York, 1996, p.535.
5. M.S.G.Baythoun and F.R.Sale, J. Mater. Sci., 17 (1982) 2757.
6. J. Long et S. J. Teichner, Rev. Hautes Temper. et Refract., 2 (1965) 47.
7. W.R.Moser, ed., Advanced Catalysts and Nanostructured Materials, Academic Press, New York, 1996.
8. Selected Powder Diffraction Data, J.C.P.D.S. Swarthmore,PA, Files no. 40-1100, (1992).
9. D.Ferri and L.Forni, Applied Catal., B: Environmental, 16 (1998) 119.