# Solvent nature effect in preparation of perovskites by flame pyrolysis

## 2. Alcohols and alcohols + propionic acid mixtures

G.L. Chiarello, I. Rossetti, L. Forni*

Dip. Chimica Fisica ed Elettrochimica, Università degli Studi di Milano,

v. C. Golgi, 19, I-20133 Milano, Italy

P.Lopinto, G.Migliavacca

Stazione Sperimentale per i Combustibili, S. Donato Milanese (Milano), Italy

**ABSTRACT**

The effect of either pure alcohols or alcohols + propionic acid mixtures as solvents for the preparation by flame pyrolysis of a standard $LaCoO_3$ catalyst, to be employed for the catalytic flameless combustion of methane, has been investigated. All the catalysts proved very active for the mentioned reaction. Low-MW pure alcohols showed however less suitable than alcohols-propionic acid mixtures, leading to lower perovskite phase purity, less particle size homogeneity and lower specific surface area. The high volatility of the solvent seems to be the major cause, together with the improper behaviour of nitrates (forced by solubility reasons) as perovskite metals precursors. However, the addition of propionic acid to the alcohols allowed to use the acetates as precursors and hence to obtain high perovskitic phase purity, high SSA and uniform particle size. Moreover, the increase of combustion enthalpy of the solvent, through the addition of higher-MW alcohols, leading to progresively higher flame temperature, strongly improved the thermal resistance of the catalyst, without lowering catalytic performance.

 * Corresponding author: Fax: +39-02-50314300, e-mail: lucio.forni@unimi.it

1

# 1 - INTRODUCTION

Recently we reported on a flame pyrolysis (FP) route for the synthesis of perovskitic oxides [1,2]. The method consists of feeding an organic solution of the oxide precursors into a nozzle, co-fed with oxygen. A systematic study on a $LaCoO_3$ model catalyst allowed to conclude that every parameter decreasing the residence time of the precursors into the flame, and/or decreasing flame temperature and/or decreasing the concentration of the primary particles into the flame, leads to an increase of catalyst SSA. This can positively affect catalytic activity, but it can also lead to insufficient thermal resistance for any high temperature application.

After analysing the effect of fluid dynamics of the flame on the properties of the catalysts prepared by FP [1,2], an extensive and systematic investigation was undertaken by our group on the effect of different solvents on SSA, particle size, crystallinity, activity for the catalytic flameless combustion (CFC) of methane and thermal resistance of the selected model $LaCoO_3$ perovskite catalyst. The effect of carboxylic acids as solvents has been reported in a previous paper [3]. In the present part of the work pure alcohols or alcohols + propionic acid have been investigated.

# 2 - EXPERIMENTAL

## 2.1 – Catalyst preparation

$La(CH_3COO)_3 \cdot 2H_2O$ (Aldrich, purity >99.9%) or $La(NO_3)_3 \cdot 2H_2O$ (Aldrich, purity >99.9%) and $Co(CH_3COO)_2 \cdot 4H_2O$ (Merck, purum) or $Co(NO_3)_2 \cdot 4H_2O$ (Merck, purum) were dissolved in the selected solvent in 1:1 metal ions ratio and 0.1 M overall concentration. Methanol, ethanol and 1-propanol, either pure or mixed with propionic acid in 1:1 (vol/vol)

ratio were tested. In addition, mixtures of propionic acid with 1-pentanol or 1-octanol were also investigated.

The organic solution was fed (2 mL/min) to the flame reactor extensively described in previous papers [1-3], together with 5 L/min of oxygen (SIAD, purity >99.95%). Some additional tests were also carried out with lower $O_2$ feeding rate. The cross section area of the main nozzle was adjusted so to have a pressure drop through the nozzle of 1.5 bar. Feeding rates to the ring of main-flame-supporting flamelets were $CH_4$ = 0.5 L/min and $O_2$ = 1.0 L/min).

High-resolution IR imaging and temperature local values, independently measured by means of a thermocouple, helped in mapping the flame temperature in detail [2,3].

## 2.2 – Catalyst characterisation

SSA was measured by $N_2$ adsorption/desorption at 77K on a Micromeritics ASAP 2010 apparatus. Morphological analysis was carried out by a LEICA LEO 1430 scanning electron microscope (SEM). XRD analysis was made by a Philips PW1820 powder diffractometer, by using the Ni-filtered Cu K$\alpha$ radiation ($\lambda$=1.5148 Å). The diffractograms obtained were compared with literature data for phase recognition [4]. Thermogravimetric analysis (TGA) of the as-prepared powder was carried out in flowing air by means of a Perkin-Elmer TGA7 apparatus, while heating the sample by 10°C/min from 30 up to 800°C.

## 2.3 – Catalytic activity tests

Catalytic activity tests for the CFC of methane were carried out by means of the continuous, quartz tubular reactor previously described in detail [1-3]. The catalyst (*ca.* 0.2 g, 0.15-0.25 mm particle size) was diluted 1:10 by volume with 1.3 g of quartz particles of the same size. Before 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 0.5 vol% $CH_4$, 49.5 vol% He and 50 vol% air, while increasing temperature by 2°C/min from 250 up to 600°C. The total flow rate of the reactants mixture was calculated by referring to the mass of active phase, so to have for every test an identical value of time factor $\tau$ = 10 (mg of perovskite·min/cm$^3$ of overall gas flow rate). The outcoming gas was analysed in line by gas chromatography.

### 2.4 - Accelerated thermal deactivation tests

Accelerated thermal deactivation was measured after keeping the sample at the temperature ($T_f$) of maximum conversion for 48 h, by determining the residual conversion every 24 h. Then repeated cycles of reaction/deactivation were made by increasing temperature (10°C/min) up to 800°C, kept for 1 h. The temperature was then brought back to $T_f$, kept for 3 h, during which the residual conversion was measured.

## 3 - RESULTS AND DISCUSSION

### 3.1 – Pure alcohols as solvents

In the first part of the present investigation [3] the effect of pure carboxylic acids as solvents was analysed, acetates being in that case the precursor metal salts. As alternative solvents, pure alcohols have been reported for the FP synthesis of some materials, such as $Y_3Al_5O_{12}$ [5], $Bi_2O_3$ [6,7], $SiO_2$ [8], $Al_2O_3/TiO_2$ [9]. Unfortunately, La acetate is not sufficiently soluble in pure alcohols. Hence the nitrates were tried as precursors. At first, three samples were prepared from methanol, ethanol and 1-propanol solutions, by keeping constant all the FP operating conditions. The XRD patterns of these samples are reported in Fig.1. A lower phase purity was observed with respect to the samples prepared from carboxylic acids [3]. Indeed, the presence of $La_2O_3$ and $Co_3O_4$ was

evident in some cases, together with a different quasi-perovskitic $La_2CoO_4$ phase, very likely indicating a different mechanism for particle formation.

As expected, the reflections became narrower and more intense when going from methanol to propanol. Furthermore, when lowering $O_2$ flow rate from 5 NL/min (standard value for comparison with the other catalysts of the present series) to 2 NL/min, at constant pressure drop ($\Delta P = 1.5$ bar) through the nozzle, a progressive and considerable increase of phase purity and crystal size of the powder was observed. In spite of this, some traces of $La_2CoO_4$ were still present even at $O_2$ flow rate of 2 NL/min, the lowest value permitted by our equipment for the selected value of pressure drop. Moreover, the lower the quenching effect due to oxygen excess, the higher was particle size and hence the lower became SSA [1].

Similarly to what observed with pure carboxylic acids [3], TGA analysis, coupled with temperature-programmed oxidation (TPO), revealed the presence of carbonaceous residua. No dramatic difference was observed when substituting pure alcohols for acids, nor any significant dependence of the amount of residual carbonaceous matter on chain length of the alcohol. In every case, except for methanol, a more or less pronounced peak appeared at 300-350°C in the TGA-TPO patterns, connected with residual carbon combustion. The weight loss varied from 4 to 10 wt% for each sample.

SSA (Table 1) decreased as expected on going from methanol to 1-propanol as solvent, the increasing of combustion enthalpy ($\Delta H_{cv}$, referred to unit volume of liquid solvent) leading to a progressive increase of flame temperature [1-3] and hence to a more extensive particle sintering ($D_{BET}$, Table 1). However, the whole set of samples showed a rather low SSA with respect to the samples prepared from pure carboxylic acids. A comparative catalyst prepared from pure propionic acid is reported in the same Table 1 (sample 10), showing a SSA in excess of 50 $m^2$/g. This is partly due to the higher $\Delta H_{cv}$ of the alcohol with respect to the corresponding acid, however counterbalanced by the effect

of the nitrates as precursors, which do not contribute to flame temperature as acetates do, the nitrates decomposition being endothermic. Another important factor is the high volatility of alcohols, compared with carboxylic acids, which imparts an additional endothermic effect. Similar results were reported for the preparation of $ZrO_2$ from the propionate dissolved in 2-propanol, pure or mixed with 2,2,4-trimethylpentane, which led to much lower SSA (*ca.* 20 m$^2$/g) with respect to the sample from propionic acid (*ca.* 60 m$^2$/g) [10]. This was ascribed to a different decomposition mechanism, which enhanced the gas-phase reactivity when using the acid rather than the alcohol as fuel. Indeed, in the case of carboxylic acids, the fast heating causes the formation of a metal complex in the gas phase, which subsequently decomposes to the oxide. Small primary particles then form, successively growing through collision and sintering. Decarboxylation can also occur, especially with long chain carboxylic acids. The hydrocarbon so formed boils at a much lower temperature with respect to that at which decarboxylation occurs, leading to bursting of the droplet/particle. By contrast, if the solvent has a too low boiling point, lumps of precursors suddenly form and subsequently decompose, with possible phase segregation in the case of mixed oxides synthesis [11]. This is what very likely happens in the present case, when using light alcohols as solvents. However, this effect can sum up to that of the improper selection of the precursor, imposed by the solubility restrictions.

## 3.2 Effect of metal precursors

The use of pure alcohols as solvents did not show any improvement with respect to carboxylic acids and therefore the series was not continued. However, some doubts still remained about the effect of the nitrate precursors, due to the rather different decomposition mechanism observed during the preparation of different materials. Indeed, every component of the original droplet (precursors or solvent) evaporates and/or decomposes at different rates. When the diffusion time in liquid phase is much lower than

the mean droplet lifetime, the most volatile component evaporates, followed by the evaporation of the other components. This can affect particle formation in gas or liquid phase, possibly leading to phase segregation. By contrast, when the droplet lifetime is very low, a much more uniform concentration in the droplet is expected [12,13]. A cooperative effect should therefore be expected between the solvent and the precursor in determining the mechanism of particle formation during the FP synthesis, as shown for $SiO_2$ and $Bi_2O_3$.[7].

To evaluate the contribution of precursors nature on catalyst properties, we compared acetates and nitrates, dissolved in mixed solvents, due to the poor solubility of La acetate in alcohols and of nitrates in carboxylic acids. Hence, 1:1 (vol/vol) mixtures of 1-propanol and propionic acid were prepared. The nitrates were first dissolved in propanol and then diluted with propionic acid and *viceversa* for the sample from acetates. Propanol was selected as a compromise between boiling point (too high volatility being undesirable) and $\Delta H_{cv}$, significantly higher for alcohols than for the corresponding acids (Table 1, samples 3 and 10). Similar carbon chain length should lead to similar decomposition rate. The addition of propionic acid to the propanol solution of nitrates lowers the $\Delta H_{cv}$ of the solution with respect to the pure alcohol (Table 1, samples 3 and 4), so a decrease of flame temperature and hence a higher SSA are expected. By contrast, the addition of propanol to a propionic acid solution of acetates increases the $\Delta H_{cv}$ with respect to the pure carboxylic acid (Table1, samples 7 and 10).

Lower phase purity can be observed in XRD patterns (Fig.1) for sample 4 (from nitrates), characterised by higher $La_2O_3$ segregation. After calcination at 600°C for 1 h, *i.e.* by simulating the activation procedure preceding the activity test, an increase of intensity of the perovskitic phase reflections was noticed. However, no complete disappearance of the segregated impurities was observed. Much better results were obtained by using acetates as precursors (sample 7), which led to a pure $LaCoO_3$ perovskitic phase (see

samples 3 and 10 in the Figure for comparison). The addition of propionic acid (sample 4) and the consequent decrease of $\Delta H_{cv}$ with respect to pure propanol (sample 3) led to a slight decrease of reflections intensity, showing a decrease of crystal size (Table 1). By contrast, the increase of flame temperature due to the addition of the alcohol to propionic acid improved crystal size (samples 7 and 10, Table 1).

The decrease of $\Delta H_{cv}$ due to propionic acid addition to propanol led to a small increase of SSA with respect to the pure alcohol (from 14 to 20 $m^2$/g, Table 1). Again, a direct comparison between the two precursors in mixed solvent showed much better results when using acetates instead of nitrates as precursors (*ca.* 60 $m^2$/g and 20 $m^2$/g, respectively). Hence, one may conclude that the use of acetates as precursors permits the preparation of high SSA materials, accompanied by good phase purity.

A confirmation of the acetates *vs.* nitrates different decomposition mechanism comes from SEM analysis (Fig.2). Sample 7, from acetates, was composed of very uniform-size nanoparticles, whereas sample 4, from nitrates, was characterised by bigger particles (in line with the much lower SSA) and mainly by non uniform size distribution (from *ca.* 80 to *ca.* 350 nm). A similar behaviour was observed when preparing other materials from nitrates as precursors, such as $CeO_2$ [14], $Bi_2O_3$ [6,7], $Y_2O_3$ [15], $Al_2O_3$ [16].

The main problem arising from the use of nitrates is their tendency to melt at relatively low temperature. If the precursor partially melts before decomposition, as *e.g.* for lanthanum nitrate [17], this can lead to coalescence into both dense and hollow bigger particles [16]. The drawback can be partly overcome by using different precursors, such as metallorganic complexes or chlorides (when possible, due to availability and/or solubility in the selected solvent) [16,18]. However, the selection of a different precursor can entrain further problems: metal-carbon bonds participate in combustion; metal-chloride bonds would hydrolyse, often generating corrosive by-products; metal-nitrates show usually highly ionic bonds and decompose without combustion [6,16,19]. Of course, particles

morphology and properties are tightly connected with the decomposition of the precursor, which can take place by following two main paths: precipitation/conversion in the droplet and evaporation and nucleation in the gas phase. However, the decomposition path depends on solvent nature and properties, particularly on its volatility and viscosity, as reported *e.g.* for $Bi_2O_3$ from acetic acid solution [6] and for $CeO_2$ [14].

We can conclude that acetates are better precursors than nitrates for the preparation of high SSA perovskites. Furthermore, pure alcohols are less desirable than carboxylic acids as solvents, mainly because they require nitrates as metal precursors and because their high volatility leads to unfavourable decomposition mechanism.

Catalytic activity of the samples prepared from propionic acid + propanol and from nitrates or acetates (samples 4 and 7, respectively) is reported in Table 1 as $T_{1/2}$ and $T_f$, *i.e.* the temperature needed to attain 50 and 100% conversion of $CH_4$, respectively. Both these samples showed very active in spite of the low phase purity and the low SSA of one of them (sample 4), showing similar light-off temperature (*ca.* 250°C) and allowing to completely burn out methane at T≤500°C. Sample 7 was slightly more active than sample 4, partly because of the higher SSA, but mainly due to the higher phase purity, which likely favours the high temperature bulk oxygen mobility. The comparison between sample 7 and sample 10 allows to conclude that the increase of $\Delta H_{cv}$, and hence of flame temperature, consequent to propanol addition to propionic acid, does not affect appreciably catalytic activity. Indeed, sample 10 showed slightly less active than sample 7, in spite of the lower $\Delta H_{cv}$ of the solvent, in line with the data relative to pure carboxylic acids as solvents [3], showing that the increase of $\Delta H_{cv}$ of the solvent scarcely affects catalytic activity.

The results of deactivation tests of samples 4 and 7 are reported in Fig. 3 in comparison with sample 10. The initial behaviour of sample 4, from nitrates, could be ascribed to the lower SSA, *i.e.* larger particle size, leading to less extensive sintering during overheating. However, the third deactivation cycle brought about a further decrease

of activity. Sample 7, from acetates, showed a deeper dropping of initial activity, but a better behaviour after the following deactivation cycles, the residual $CH_4$ conversion remaining a rather stable value of *ca.* 65%. Hence it can be concluded that acetates can ensure a better long-term stability. However, when both these samples are compared with sample 10, prepared from a pure propionic acid solution, the advantage of increasing the $\Delta H_{cv}$ of the solvent becomes evident.

### 3.3 Mixed solvents: alcohols + propionic acid

The use of pure alcohols as solvents showed unsatisfactory with respect to pure propionic acid, due to the use of nitrates as precursor salts. However, this main drawback can be overcome by using a mixture of propionic acid + propanol, so allowing to use acetates (with much better results as for phase purity and SSA) and to increase the $\Delta H_{cv}$ of the solvent mixture, with consequent improvement of catalyst thermal resistance for high temperature application. This prompted our systematic experimentation on various solvents mixtures. At first we tried to modulate the $\Delta H_{cv}$ of the solution by adding linear alcohols (C1 to C8, 1:1 by volume) to propionic acid and using acetates as metals precursor salts. The addition of the selected alcohols, except methanol, entrained the expected increase of flame temperature (see *e.g.* Table 2). A considerable increase (*ca.* 800°C) of flame temperature can be inferred from such data when increasing the alcohol chain length from 3 to 8 carbon atoms and hence the $\Delta H_{cv}$ of the solvents mixture (from -23.7 to –27.0 kJ/cm$^3$, Table 1). As a consequence, lower SSA, higher crystallinity and bigger particle size are expected when moving from methanol to octanol as additional fuel to propionic acid.

Good phase purity was obtained for every sample of this series, with crystallinity increasing with the $\Delta H_{cv}$ of the solvent mixture (Fig.1). The average crystal size increased with increasing flame temperature (Table 1), confirming however the obtainment of

nanostructured materials in every case. Hence, high values of SSA were always obtained (Table 1). The addition of methanol slightly lowered the $\Delta H_{cv}$ of the solvent, but no sensible change of SSA was noticed. Moreover, the dependence of SSA on $\Delta H_{cv}$ is less linear than for pure solvents. Indeed, alcohols are more volatile than the corresponding carboxylic acids. Hence, their behaviour during flame combustion is partly bound to the thermodynamics of the decomposition (represented by the combustion enthalpy) and partly to the dynamics and kinetics of combustion: volatilisation, decomposition, combustion, etc. Ethanol and propanol are still much more volatile than propionic acid. So it can be hypothesised that they evaporate (with an endothermic effect) before the starting of the precursor decomposition. This can explain the high values of SSA of samples 6 and 7 (Table 1), similar or even higher than for sample 10, in spite of the higher combustion enthalpy of the solution. Similar SSA was observed when comparing samples 8 and 10, the boiling temperature of the two components of the solvent mixture being very similar. Finally, when the additional fuel was much less volatile than propionic acid, the expected decrease of SSA was observed (sample 9, Table 1).

A comparison between the present samples from mixed solvents and the series relative to pure carboxylic acids [3], confirms that both the $\Delta H_{cv}$ and the mechanism of decomposition/volatilisation/combustion have to be taken into account during solvent selection, at least when relatively low-boiling co-solvents are used. Indeed, the $\Delta H_{cv}$ of the pentanol + propionic acid mixture lies between those of pure butyric and hexanoic acids. However, likely due to the slightly higher volatility or to easier decomposition of the co-solvent, the SSA of the present sample 8 was higher than that of the samples from butyric or hexanoic acid [3]. Furthermore, hexanoic acid, possessing $\Delta H_{cv}$ and volatility values similar to those of the octanol + propionic acid mixture, led to a sample with SSA = 48 m$^2$/g, very similar to that of the present sample (sample 9, Table 1). This confirms that

some drawbacks can arise from volatile solvents, whereas the high-boiling ones meet the general expectation.

Though the above reported measures of flame temperature are hardly comparable with those recorded for the pure carboxylic acids series [3], the expected decrease of SSA with increasing flame temperature was confirmed. Indeed, higher SSA was obtained with the present sample 7 ($T_{flame} \approx 1100°C$, SSA = 59 $m^2$/g), followed by sample 10 (1400°C, 56 $m^2$/g), then by sample 9 (1800°C, 49.2 $m^2$/g) and finally by the sample prepared from octanoic acid (2000°C, 43 $m^2$/g).

$T_{1/2}$ and $T_f$ values (Table 1) show that a slightly higher activity was obtained with sample 10 and a bit lower by sample 5, all the other samples behaving exactly in the same manner. This confirms that a too high volatility of the FP fuel can negatively affect the performance of the catalyst. The difference is however minimal, confirming that solvent nature does not strongly affect catalytic activity, provided that a good phase purity of the sample has been obtained. The opposite is true as for thermal stability (Fig. 4): the increase of $\Delta H_{cv}$, due to the addition of the alcohol as co-fuel, improves catalyst resistance at high temperature. Indeed, the residual activity after repeated deactivation cycles showed progressively higher for the samples prepared with solvent mixtures of higher $\Delta H_{cv}$. Furthermore, once the catalyst underwent the first sintering due to overheating, no sensible decrease of catalytic activity was observed.

## 4 – CONCLUSIONS

Low-MW pure alcohols as solvents proved less satisfactory than carboxylic acids for the preparation by FP of a good $LaCoO_3$-based catalyst for the CFC of $CH_4$, leading to lower phase purity, less particle size homogeneity and lower SSA. Possible causes are the high volatility of the solvent and the improper behaviour of nitrates (forced by solubility

reasons) as metals precursors, especially in leading to a pure perovskitic phase. However, the addition of propionic acid to the alcohols allowed to use metal acetates as precursors and hence to obtain high phase purity, high SSA and uniform nanoparticle size. Moreover, the increase of solvent combustion enthalpy, through the addition of longer-carbon-chain alcohols, strongly improved the thermal resistance of the catalyst, without affecting appreciably catalytic performance.

**REFERENCES**

1. G.L. Chiarello, I. Rossetti, L. Forni, J. Catal., 236 (2005) 251.
2. G.L. Chiarello, I. Rossetti, P.Lopinto, G.Migliavacca, L. Forni, Catal. Today, 117 (2006) 549.
3. G.L. Chiarello, I. Rossetti, L. Forni, P. Lopinto, G. Migliavacca, Appl. Catal., B: Environmental, submitted.
4. Advanced Selected Powder Diffraction Data, Miner. DBM (1–40), J.C.P.D.S., Swarthmore, PA.
5. R.M. Laine, J. Marchal, H. Sun, X.Q. Pan, Adv. Mater., 17(7) (2005) 830.
6. L. Mädler, S.E. Pratsinis, J. Am. Ceram. Soc., 85 (7) (2002) 1713.
7. R. Jossen, W.J. Stark, L. Mädler, S.E. Pratsinis, Chem. Ing. Tech., 75 (2003) 1129.
8. L. Mädler, H.K. Kammler, R. Mueller, S.E. Pratsinis, J. Aerosol Sci., 33 (2002) 369.
9. S. Kim, J.J. Gislason, R.W. Morton, X.Q. Pan, H.P. Sun, R.M. Laine, Chem. Mater., 16 (2004) 2336.
10. H. Morisaka, T. Tani, H. Kaga, K. Takatori, J. Ceram. Soc. Japan, 112(9) (2004) 514.
11. W.J. Stark, L. Mädler, M. Maciejewski, S.E. Pratsinis, A. Baiker, Chem. Commun., (2003) 588.
12. M.C. Heine, S.E. Pratsinis, Ind. & Eng. Chem. Res., 44 (2005) 6222.
13. W.A. Sirignano, *Fluid dynamics and transport of droplets and sprays*; Cambridge University Press, Cambridge, U.K., 1999.
14. L. Mädler, W.J. Stark, S.E. Pratsinis, J. Mater. Res., 17(6) (2002) 1356.
15. A. Camenzind, R. Strobel, S.E. Pratsinis, Chem. Phys. Lett., 415 (2005) 193.
16. T. Hinklin, B. Toury, C. Gervais, F. Babonneau, J.J. Gislason, R.W. Morton, R.M. Laine, Chem. Mater., 16 (2004) 21.

17. L. Fabbrini, I. Rossetti, L. Forni, Appl. Catal. B: Environm., 56(3) (2005) 221.

18. J. Marchal, T. John, R. Baranwal, T. Hinklin, R.M. Laine, Chem. Mater., 16 (2004) 822.

19. D. Perednis, O. Wilhelm, S.E. Pratsinis, L.J. Gaukler, Thin Solid Films, 474 (2005) 84.

**Table 1:** Selected data on the solvents employed and the samples prepared. PA= propionic acid; MeOH=methanol; EtOH=ethanol; PrOH=1-propanol; PeOH=1-pentanol; OcOH=1-octanol. (*) = nitrates as precursors. Unmarked samples prepared from acetates. $\Delta H_{cv}$ = combustion enthalpy referred to unit volume of the alcohol (fuel);. $\Delta H_{cv}$ mix = combustion enthalpy referred to unit volume of the alcohol + propionic acid mixture. Average crystal size determined both from BET data ($D_{BET}$) and by applying the Scherrer equation to two selected XRD reflections: $2\theta = 23.3°$ ($D_{XRD1}$) and $47.6°$ ($D_{XRD2}$)

| Sample no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| solvent | MeOH * | EtOH* | PrOH * | PA + PrOH * | PA + MeOH | PA + EtOH | PA + PrOH | PA + PeOH | PA + OcOH | PA |
| density [g/ml] | 0.79 | 0.79 | 0.80 | 0.80 | 0.79 | 0.79 | 0.80 | 0.81 | 0.83 | 0.99 |
| $\Delta H_{cv}$ [kJ/ml] | -17,7 | -23,5 | -26,8 | -26,8 | -17,7 | -23,5 | -26,8 | -30,6 | -33,5 | -20.6 |
| $\Delta H_{cv}$ mix [kJ/ml] | - | - | - | -23,7 | -19,1 | -22,0 | -23,7 | -25,6 | -27,0 | - |
| PA/alcohol (mol/mol) | - | - | - | 1,00 | 0,54 | 0,78 | 1,00 | 1,45 | 2,10 | - |
| SSA ($m^2$/g) | 26 | 21 | 14 | 20 | 56 | 64 | 59 | 59.4 | 49.2 | 56 |
| $D_{BET}$ (nm) | 31.7 | 39.2 | 58.8 | 41.2 | 15.8 | 12.9 | 13.9 | 13.9 | 16.7 | 14.6 |
| $D_{XRD1}$ (nm) | n.d.[a] | n.d.[a] | 32.2 | 26.5 | 17.2 | 18.3 | 14.7 | 21.5 | 25.1 | 17.8 |
| $D_{XRD2}$ (nm) | n.d.[a] | n.d.[a] | 31.0 | 35.9 | 15.1 | 12.7 | 11.5 | 16.4 | 17.6 | 12.6 |
| $T_{1/2}$ (°C) | - | - | - | 400 | 390 | 383 | 382 | 416 | 383 | 380 |
| $T_f$ (°C) | - | - | - | 506 | 485 | 480 | 482 | 520 | 480 | 460 |

[a] unreliable fitting of XRD reflections due to peak overlapping.

**Table 2:** Average value (measured on 5 points by the IR camera) of the maximum flame temperature (°C).

| PA/1-propanol | | PA/1-octanol | |
|---|---|---|---|
| $T_{max}$ (°C) | s.d. | $T_{max}$ (°C) | s.d. |
| 1086 | 107 | 1825 | 118 |

**FIGURE CAPTIONS**

**Fig.1:** XRD patterns of the $LaCoO_3$ samples prepared. Figures refer to samples number (Table 1). Main reflections of impurities: (○) $La_2O_3$; (x) $Co_3O_4$; (+) $La_2CoO_4$.

**Fig.2:** Typical SEM micrographs of $LaCoO_3$ prepared from nitrates (sample 4) or acetates (sample 7).

**Fig.3:** Thermal stability tests for selected samples (Table 1). The last three points refer to the residual $CH_4$ conversion after every overheating cycle at 800°C for 1 h.

**Fig.4:** Thermal stability tests of samples 6 and 9, prepared from PA + ethanol or PA + octanol, respectively, in comparison with sample 10, prepared from pure PA. The last three points of each curve refer to the residual $CH_4$ conversion after every overheating cycle at 800°C for 1 h.
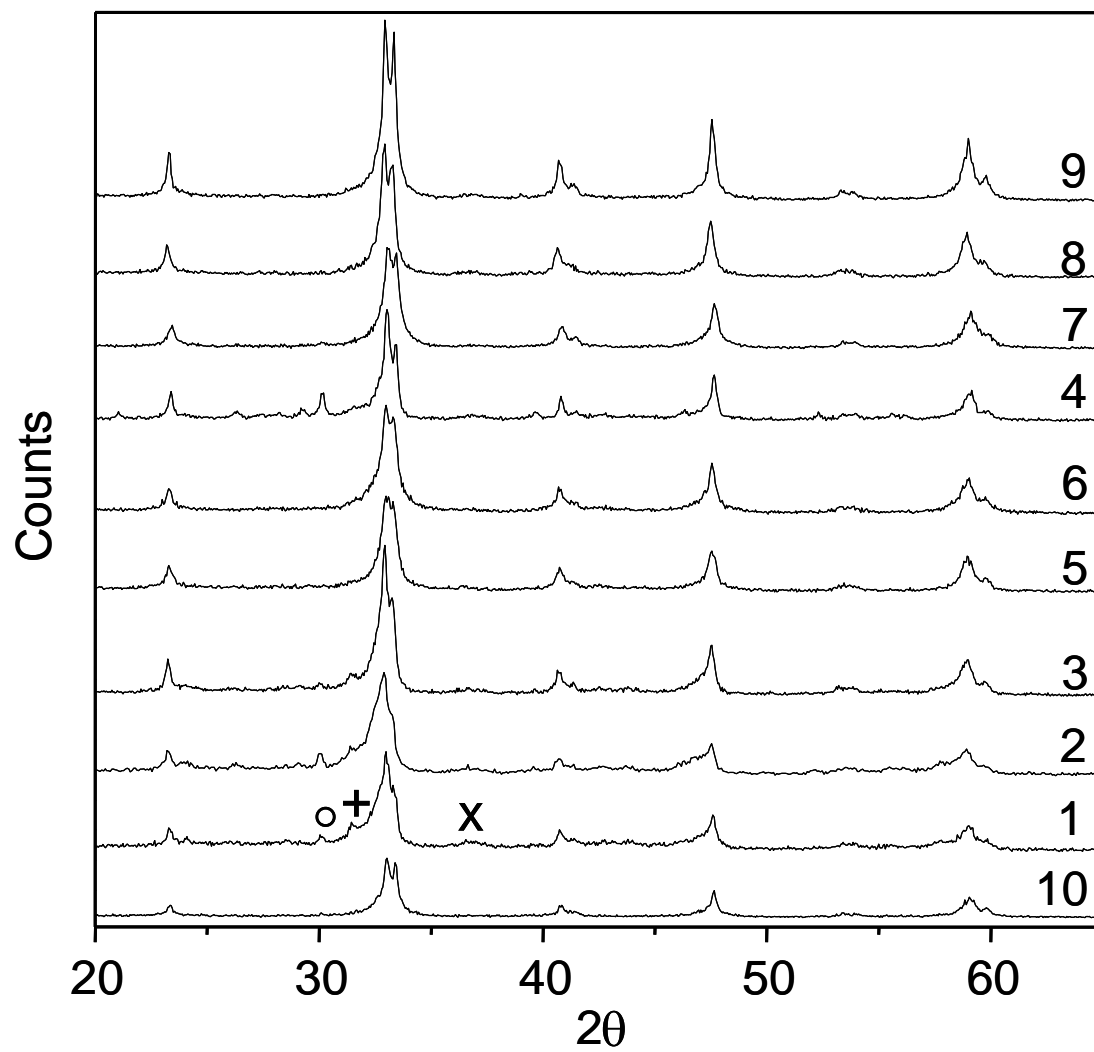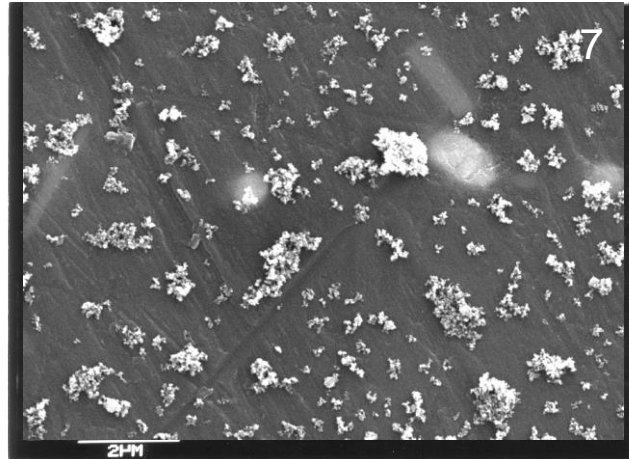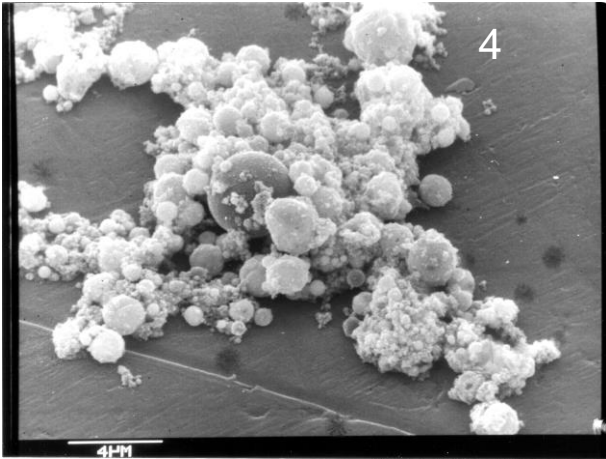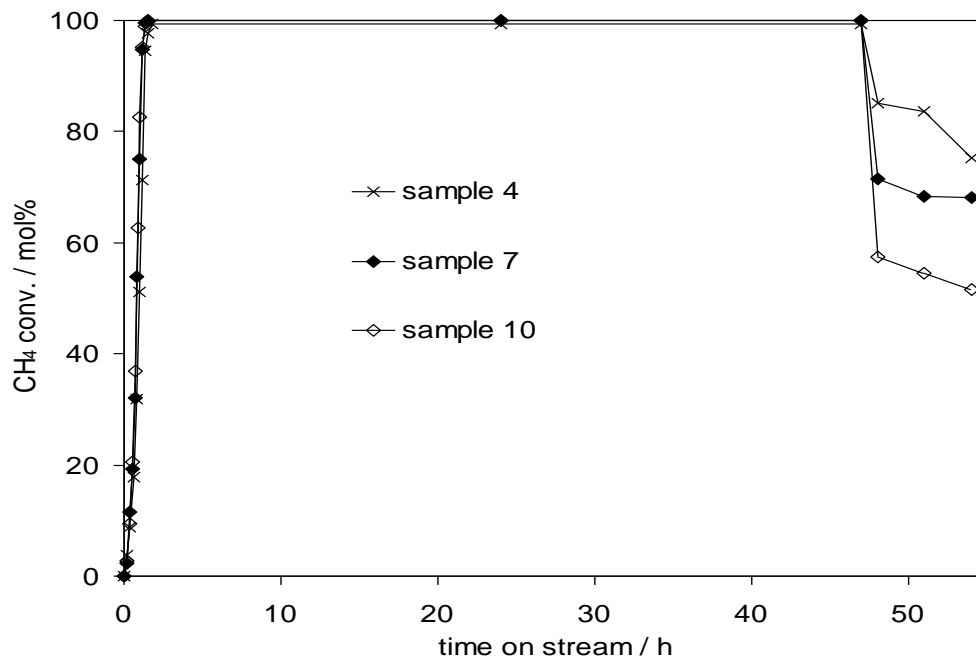
Fig. 1

Fig. 2

Fig. 3



Fig. 4