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Evaluation of some cobalt and nickel based perovskites prepared by freeze-drying as combustion catalysts

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A series of cobalt and nickel based perovskite type catalysts with high specific surface area (8–20 m^2/g) was prepared by spray-freezing/freeze-drying method. The catalytic activity of all samples in methane combustion was evaluated by measuring the light-off temperature, the conversion at 823 K and the temperature of the end of the reaction. The experimental data suggest higher activity than reported in literature for similar or other perovskites, and confirm its strong dependence on the specific surface area. Among eleven tested catalysts, including seven new compositions four of which showed excellent activity, $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ was the best performing.

Keywords: Perovskite catalysts; methane combustion; $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$; freeze-drying

1. Introduction

The advantages of a catalytic (flameless) combustion of light hydrocarbons, in particular of methane (natural gas), are numerous [1–3]. In the presence of active catalysts a *complete* combustion may be achieved at temperatures several hundred degrees lower than in the flame (thermal noncatalytic) combustion [3]. This low combustion temperature is at the origin of all the advantages. For example, the formation of noxious nitrogen oxides is almost eliminated [3].

Evidently, the catalyst plays the most important role in the process and its choice is critical for the success of the combustion process design.

For their excellent activity supported platinum or palladium catalysts have so far been used almost exclusively [2–5]. However, their high price, tendency to poisoning, and volatility in some applications of the active component (nobel metal) have pushed ahead a search for suitable substitutes.

Initially, several simple transition metal oxides have been investigated as a replacement for nobel metal combustion catalysts (ref. [6] and references therein). Today, however, for their generally well established higher catalytic activity, transition metal based mixed oxides with perovskite-type structures are preferred and well on the way of becoming industrially acceptable.

A wide interest in catalytic properties of perovskites has started when Meadowcroft published a report on a high catalytic activity as oxygen electrode of $La_{0.8}Sr_{0.2}CoO_3$ [7], and when Libby proposed $LaCoO_3$ as a potential auto exhaust catalyst [8]. Since then, these and a variety of other transition metal (Mn, Ni, Fe, Cu, Cr) perovskite-type oxides of the general formula $AA'BB'O_3$ attract attention as catalysts in a wide range of reactions [9–11]. With respect to the specific application as catalysts in flameless combustion, perovskite oxides have been investigated and studied only since 1980 [12–25], mainly in Japan. The first report of this kind seems to be that by Nakamura et al. [12] who studied catalytic oxidation of propane, methane and of CO on several $LaBO_3$ with B = Co, Mn, Ni, Fe, and lanthanum substituted (Ca, Sr, Ba Ce) perovskites prepared by coprecipitation. The general tendency of the catalytic activity was found to be in the order $Co > Mn > Ni > Fe > Cr$, and strontium was the most effective to enhance the activity of a given composition. The same authors also found that among the cobaltates, $La_{0.8}Sr_{0.2}CoO_3$ was the most active and its activity was comparable or higher than those of Pt, Pd and Ni catalysts. Similar order of activities which correlates with a well known order of catalytic activities in other oxydo-reduction reactions over transition metal oxides and perovskites [26] was confirmed by other workers [14,21]. The effect of the degree of strontium substitution in different perovskites studied by several groups [14,15,17] has been found to depend on the transition metal (B). Overall, it seems clear that the intrinsic catalytic activity of perovskites depends largely on the potential oxygen vacancies in the structure and on the rate of oxygen ion diffusion. These have been shown to be promoted by partial substitution by other transition metals at the B site [27,28]. However, so far the effect of a partial substitution at the B site on the catalytic activity in combustion reactions has been studied very little [22].

Apart from their intrinsic activity, the performance of perovskite catalysts is well known to depend on their morphology, in particular on their specific surface area (SSA) [9–11]. One of the important factors influencing the SSA is the calcination temperature. The classical ceramic solid–solid synthesis requiring long calcination times at high temperatures, and still in wide use, yields powders of low SSA ($< 2\ m^2/g$). Only a method which can use the least thermally stable highly reactive precursors and starting from very homogeneous mixtures (solutions) can potentially yield the best results. It was shown a while ago that among a variety of solution based preparatory methods producing powders of $SSA > 10\ m^2/g$, which include freeze-drying, spray-drying and coprecipitation, spray-freezing/freeze-drying offers the best results [29,10,11]. Introduced in catalyst preparation in 1970 by Tseung and Bevan [30], freeze-drying has in spite of its numerous advantages been rather neglected, especially in the area of perovskite preparation. This is possibly due to a need of a relatively specialized equipment and so far an insufficient understanding of the process. To yield good results, this method, depending on several critical parameters [32], has to be properly performed.

Realizing its high potential, we have recently reevaluated the overall process of spray-freezing/freeze-drying for the preparation of perovskite electrocatalysts and have developed a technique by which high surface area perovskites can routinely be prepared [31,32]. Currently we are extending our experience to the area of combustion with the goal to develop a low cost highly active catalyst suitable for use in either fluidized, or fixed bed reactors. In this paper results of the evaluation study to select the best performing compositions are presented.

2. Experimental

2.1. CATALYST PREPARATION

All catalyst samples were prepared from filtered 1 M (total metal concentration) solutions, made up by dissolving required stoichiometric amounts of individual metal nitrates, and having the pH adjusted by ammonia to 4.5 ± 0.5 or in the case of iron containing solutions to 1.9. The solutions were spray-frozen in a liquid nitrogen bath by means of a glass pneumatic sprayer (droplets <0.02 cm). The frozen droplets were removed from liquid nitrogen by means of a fine nylon screen, placed with the screen into an insulated glass vessel and then vacuum dried at pressures <0.5 Pa on a Labconco Lyph.Lock 4.5 freeze-drier with a condenser refrigerated to 208 K and equipped with a Leybold D8 dual stage vacuum pump. In the initial stage of drying, the temperature of the frozen droplets was typically between 243 and 248 K due to a fast sublimation of solvent (water). In this vacuum drying stage part of the hydration water was also removed.

The freeze-dried material was completely dehydrated and partially decomposed by slow heating to ~ 623 K under vacuum to give a black highly porous agglomerated powder. From this powder the perovskite structure was formed on calcination at 858 K for 15 h. To determine the effect of calcination temperature on specific surface area, selected samples were calcined for longer times or at higher temperatures. No grinding was used in the overall preparation process.

2.2. CATALYST CHARACTERIZATION

In all samples the formation of the perovskite phase was confirmed by X-ray diffractometry performed on a Philips PW1130 diffractometer with Cu radiation. Specific surface areas (SSA) were determined by a single point BET method with nitrogen (30% in helium) as the adsorbate on a Micromeritics Flow Sorb II 2300 apparatus. Apparent resistivity of powders was determined on unsintered pellets obtained by compressing the powder at 1.44×10^3 kg/cm^2. The density of the pellets was typically 2.80 ± 0.5 g/cm^3, i.e. the pellets were more than 60% porous.

Catalytic performance in the combustion of methane was evaluated by measuring the temperature of the reaction beginning (LOT, light-off temperature), the end of reaction temperature (ERT), and by determining the methane conversion at 823 K. The reaction was carried out in a U shape stainless steel tubular reactor 1 cm diameter, 13.5 cm^3 volume, filled with 1 g of catalyst powder diluted by 11 cm^3 of inert particles (pumice) 250–500 μm large. Before use, the catalyst was crushed by hand in a mortar to a mean particle size of 10 μm. The catalyst diluent was used to provide a quasi-isothermicity of the reactor and to ensure good permeability. A gaseous mixture of methane (4 vol%) and air was fed into the reactor at a flow rate 4.2–5 cm^3/s. The temperature was measured by a K-type thermocouple at the exit of the catalyst bed. The reaction products first stripped of water by passing over $CaSO_4$ were analysed by gas chromatography, using a Porapak Q filled column. Products other than CO_2 were not detected. The LOT was the temperature at which the presence of CO_2 (~ 2% conversion) was detected in the product mixture, while ERT was the temperature at which all methane was converted to CO_2 (no methane detected).

3. Results and discussion

The catalyst compositions studied in this work and tested previously for their electrocatalytic activity in oxygen evolution reaction [31,33] are listed in table 1 along with some of their physical characteristics data and with the results of the evaluation of their catalytic activity in methane combustion. For convenience they are listed in the order of their increasing activity expressed as an apparent rate of methane conversion at 823 K, obtained simply from conversion divided by residence time W/F_{CH_4}, where W is the weight of the catalyst and F_{CH_4} is the molar flowrate of methane. For residence times between 0.10 and 0.125 g s/μmol conversions between 45 and 93% were obtained, and the LOT and ERT varied between 553 and 638 K, and between 883 and 973 K respectively. In the case of three compositions data for two different samples prepared at similar conditions are included. As can be seen, the reproducibility of the results is within 20 K for LOT and ERT and within 10% for the apparent activity.

The compositions were selected on the basis of the following criteria: high reported activity for methane combustion, high reported oxygen ion diffusion, and a low cost of precursor salts. Based on theoretical considerations and on experimental data for published catalytic activities in all oxygen involving reactions, the following order of activities for $LaBO_3$ is expected at low temperatures: Ni > Co > Fe > Mn > Fe > Cr. This order was in fact shown to hold even in methane combustion [21], although nonconclusively. More often cobalt or manganese based perovskites performed better [12,14]. Although the above order does not necessarily apply at high temperatures, the seemingly contradictory results may in part be related to two factors: (i) the low stability of $LaNiO_3$ at high temperatures

Table 1
Physical characteristics and catalytic performance in methane combustion of several perovskite catalysts prepared by spray-freezing/freeze drying

Composition	δ[a]	rsst[b] (Ωcm)	SSA (m^2/g)	LOT[c] (K)	ERT[d] (K)	Activity at 823 K[e]	
						(μmol/(s g))	(μmol/(s m^2))
$La_{0.4}Sr_{0.6}Mo_{0.1}Ni_{0.9}O_3$	0.3	870	10.3	613	973	4.54	0.44
$La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$ 1	0.3	5.4	8.1	638	963	4.62	0.57
$La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$ 2	0.3	7.9	10.4	623	945	4.26	0.41
$La_{0.4}Sr_{0.6}Mn_{0.4}Ni_{0.6}O_3$	0.3	480	15.9	633	933	5.92	0.37
$La_{0.53}Sr_{0.47}Fe_{0.2}Co_{0.8}O_3$	0.235	4	13.4	593	923	6.52	0.49
$La_{0.55}Sr_{0.45}Mn_{0.1}Ni_{0.3}Co_{0.6}O_3$	0.225	5	15.0	613	923	6.74	0.45
$La_{0.55}Sr_{0.45}Fe_{0.05}Ni_{0.3}Co_{0.65}O_3$	>0.225	1.3	15.2	623	923	7.28	0.48
$La_{0.8}Sr_{0.2}CoO_3$	0.1	12	16.5	583	913	7.55	0.46
$La_{0.66}Sr_{0.34}CoO_3$	0.17	0.2	17.4	598	948	8.11	0.47
$La_{0.7}Sr_{0.3}Ni_{0.3}Co_{0.7}O_3$ 1	>0.15	0.4	20.2	583	873	8.13	0.40
$La_{0.7}Sr_{0.3}Ni_{0.3}Co_{0.7}O_3$ 2	>0.15	0.7	22.7	573	888	8.30	0.37
$La_{0.5}Sr_{0.5}Fe_{0.04}Ni_{0.1}Co_{0.86}O_3$	>0.25	5	19.6	623	893	8.25	0.42
$La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ 1	>0.17	0.8	18.8	553	873	8.25	0.44
$La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ 2	>0.17	0.1	16.6	553	883	9.11	0.55

[a] δ: maximum oxygen vacancy based on Sr substitution, potentially higher due to Ni substitution.

[b] rsst: apparent resistivity of powders compressed at 1.44×10^3 kg/cm^2 to pellets having a density of 2.85 ± 0.05 g/cm^3.

[c] LOT: light-off temperature, CO_2 detected in the reaction gas mixture (~ 2% conversion).

[d] ERT: end off reaction temperature, no methane detected in the reaction gas mixture.

[e] Apparent activity is based on the conversion (45–93%, i.e 0.45–0.93 mol fraction) for residence times between 0.10 and 0.125 g s/μmol.

[34] and an obvious difficulty in its preparation, (ii) inherently higher specific surface areas of manganese based perovskites. The latter factor is in our opinion not negligible, but it seems to have escaped the attention of other workers. Analysing the available data, it has further come to our attention that at intermediate temperatures (800–1100 K) the catalytic activity could possibly be correlated to the stability in oxidizing atmosphere of transition metal spinels. In this respect, cobalt and or mixed nickel/cobalt in 1 : 2 ratio perovskites would be expected as the best, since only Co_3O_4 and $NiCo_2O_4$ spinels form readily without being oxidized to higher oxides.

Thus, we have concentrated our effort primarily on cobalt and nickel based perovskites. Two compositions previously reported as highly active ($La_{0.8}Sr_{0.2}CoO_3$ [6,14,15] and $La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$ [22]) were included in the series for comparison. Other perovskites were formulated in a way to maximize their overall performance. For example, the tendency to reduce the lanthanum content below 0.66 was driven by its highest cost among all components.

Two main factors determine the properties of the perovskites: the character of the transition metal(s) on the B site and the substitution by strontium on the A site. In principle, the effect of these factors can be related to the maximum potential oxygen vacancy δ given mainly by strontium substitution, with possible contribution by the B metal, in particular by nickel. The available data would suggest that the optimum δ may approximately be 0.2 [14,26].

Most of the transition metal strontium substituted perovskites are good ionic (O^{2-}) and electronic conductors and this property may be related to their catalytic activity. Indeed, the measurement of apparent resistivity of compressed conductive powders (rsst) which depends not only on the inherent resistivity of a given perovskite, but also on the homogeneity and the morphology of the powder, can serve as a simple characterization tool [30,31,35]. This technique [30,35] when combined with other characteristics may provide important information about the state of the catalyst. As shown in table 1 the values of resistivity (rsst) range from 0.1 to 870 Ω cm, obviously depending on composition. The two nickel based catalysts have much higher resistivity than the others, apparently in relation with their high values of δ.

The importance of specific surface area in the catalytic activity of perovskites has been recognized since these compounds have attracted attention as catalysts [8,29,30] and a variety of preparatory methods permitting to maximize this characteristics was investigated [29,9,10], although not necessarily for combustion catalysts. The available data on SSA permit to conclude that highest values of about 40 m^2/g can be obtained for $LaMnO_3$ when calcining at <923 K for short times [19]. In the case of $LaCoO_3$ the highest reported value is 32 m^2/g for a sample calcined only 1 h at 873 K [36]. The SSAs of strontium substituted manganates or cobaltates which usually require slightly higher calcination temperatures, are generally lower, mostly below 30 and 15 m^2/g for manganates and cobaltates respectively. These high SSAs have mostly been obtained by coprecipitation methods [19,36], although Johnson et al. [29] have shown that freeze-drying can yield even better results. Our own recent study has confirmed that indeed, spray-freezing/freeze-drying gives excellent results [31,32].

Extensive investigation of various effects of the operational parameters controlling this process applied for the preparation of $La_{0.8}Sr_{0.2}CoO_3$ and of $La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$ [31,32] has permitted to determine general optimum conditions leading to the formation of well crystallized high specific surface area perovskites. These conditions including the calcination at 858 K for 15 h have been applied for the preparation of all other compositions.

As seen in table 1, the samples evaluated in this study had the SSA between 8 and 22 m^2/g. Although SSA depends on the overall conditions of preparation, the values listed in table 1 may be considered as representative of a given composition, while not necessarily the best. Clearly, the lowest values were obtained for compositions with the highest strontium substitution and with high content of iron. This trend parallels well the literature data, but our SSA values appear significantly higher.

Although the evaluation experiments were run on samples calcined at the lowest temperature required to form perovskites (each sample contained less than about

5% of foreign phases) a parallel study has shown [32], that well prepared samples are resistant to loss of SSA nearly up to 1000 K, depending obviously on time, as illustrated by data in table 2. Thus, if the catalysts could be used below this temperature, as suggested by the ERT in table 1, their activity may remain stable during the operation. In fact, other examples of similarly good resistance of SSA to moderate temperatures, as well as of a faster loss of SSA at temperatures above ~ 1050 K can be found in literature [29,36,37].

Table 2
The effect of calcination on specific surface area of several perovskites prepared by spray-freezing/freeze-drying technique

Composition	Calcination (K)	Calcination (h)	SSA (m^2/g)
$La_{0.53}Sr_{0.47}Fe_{0.2}Co_{0.8}O_3$	858	12	13.5
	858	22	11.5
	858	32	11.1
	923	2[a]	10.8
	973	2[a]	9.9
	1073	2[a]	8.2
	1123	2[a]	4.8
$La_{0.66}Sr_{0.44}CoO_3$	858	12	18.1
	858	22	17.0
	923	2[a]	15.3
	979	2[a]	14.7
	1073	2[a]	8.1
	1128	2[a]	5.6
$La_{0.7}Sr_{0.3}Ni_{0.3}Co_{0.7}O_3$	858	10	22.7
	858	15	21.5
	923	2[a]	20.2
	1073	2[a]	11.7
$La_{0.5}Sr_{0.5}Fe_{0.04}Ni_{0.1}Co_{0.86}O_3$	858	10	19.6
	858	20	17.0
	973	2[a]	16.0
	1073	2[a]	10.8
	1128	2[a]	8.0
$La_{0.55}Sr_{0.45}Mn_{0.1}Ni_{0.3}Co_{0.6}O_3$	858	10	15.0
	858	20	13.1
	973	2[a]	11.5
	1073	2[a]	10.1
	1128	2[a]	9.2

[a] Additional heating after the initial calcination step (858 K, 10 or 12 h).

Judging from the values of LOT, ERT and of the apparent activities at 823 K, all reflecting the catalytic performance, the perovskite compositions studied in this work may be separated in three groups: (1) good performers with activity of ~ 5 μmol/(s g); (2) better performers, activity 6 to 7 μmol/(s g); and (3) excellent performers, activity > 8 μmol/(s g). It can be noted that this classification parallels very closely the groups according to δ and SSA, i.e. the good performers have $\delta \geqslant 0.3$ and SSA 10 m^2/g, while the excellent performers have $\delta \leqslant 0.2$ and SSA~ 20 m^2/g. Two exceptions to this classification are found. In the first group $La_{0.4}Sr_{0.6}Mn_{0.4}Ni_{0.6}O_3$ has SSA = 15.9 m^2/g and correspondingly its activity is significantly higher than that of the other two compositions. Similarly, $La_{0.5}Sr_{0.5}Fe_{0.04}Ni_{0.1}Co_{0.86}O_3$, a composition with $\delta > 0.25$ but SSA = 19.6 m^2/g, falls by its activity in the third group rather than in the second.

It would seem that SSA has by far the highest effect on the activity. This importance of SSA is well known, and some authors prefer to express activity in terms of surface area instead of weight of the sample, such as the values in the last column of table 1. Indeed, the range of these activities is so narrow that the samples would appear to have nearly identical performance, although when taking into account the LOT and ERT values, $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ remains the best.

Even though the activity is strongly dependent on SSA and in some cases this dependence may appear to be directly proportional [36], it can be shown by other data that direct proportionality is not general and therefore simple normalization of activities to SSA may yield fairly misleading data. In fig. 1 we have plotted activities for several samples of $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ and of $La_{0.7}Sr_{0.3}Ni_{0.3}Co_{0.7}O_3$,

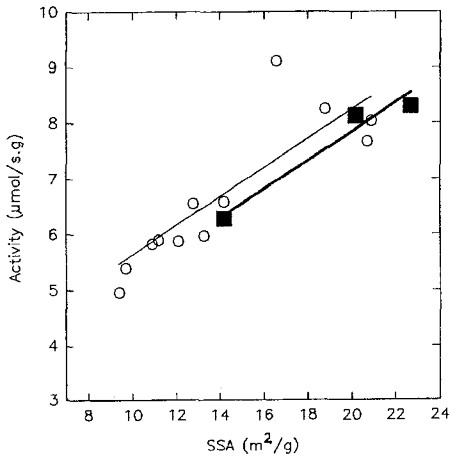

Fig. 1. Apparent activity in methane combustion (4% CH_4, air, 4.2–5 cm^3/s) as a function of SSA for samples of (○) $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ and of (■) $La_{0.7}Sr_{0.3}Ni_{0.3}Co_{0.7}O_3$ prepared by spray-freezing/freeze-drying. Variation of SSA is a result of different preparation conditions and/or calcination temperatures.

obtained by varying the conditions of preparation, against their SSA values. The two sets of data can evidently be fitted by two pseudo-linear functions differing only by the values of the intercept (3.06 and 2.65 µmol/(s g) respectively). In view of the similarity of the two compositions their very similar dependence on SSA is not surprising, but this may change for different compositions and is likely to be a function of temperature as well. The data by Arai et al. [14] can serve as another example. In the case of manganates these authors have observed reduction of activities of only about 50% for samples whose SSA was reduced by calcination by approximately 90% (about ten times). Similar behavior is evident from the data by Tanaka et al. [16], shown in table 3. Due to a lack of reliable and consistent data further speculation on this subject is not warranted at this point.

Finally, we have attempted to make a comparison of our results with those available in literature, although it is understood that unless determined under the same conditions, particularly for very similar contact times, a direct comparison of experimental activities may not be entirely objective. In table 3, the available catalytic activities expressed as µmol Co_2/(s g) or as µmol CO_2/(s m^2) when presented

Table 3
Literature values for activity of some perovskite catalysts in methane combustion at 823 K

Catalyst	SSA (m^2/g)	Activity (µmol/(s g))	Ref.	Experimental conditions
$LaCoO_3$	~ 6	8[c]	[21]	3.8% CH_4, air, 3.3 cm^3/s, 0.04 g catalyst, temperature programmed reactor
$LaFeO_3$	~ 5	6.6[c]	[21]	idem
$La_{0.8}Sr_{0.2}YO_3$	a	3.2 (55%)[d]	[24]	2% CH_4, air, 1.7 ml/s, 0.25 g catalyst
$La_{0.8}Sr_{0.2}FeO_3$	a	1.6 (30%)[d]	[24]	idem
$La_{0.8}Sr_{0.2}CoO_3$	a	0.9 (15%)[d]	[24]	idem
$La_{0.8}Sr_{0.2}MnO_3$	a	0.8 (15%)[d]	[24]	idem
$La_{0.6}Sr_{0.4}MnO_3$	3.1	3.8 (48%)[d]	[17]	6% CH_4, air, 5000 h^{-1}, 0.4 g catalyst
$La_{0.6}Sr_{0.4}MnO_3$	3.3	4.6 (78%)[d]	[14]	2% CH_4, air, 50000 h^{-1}, temperature at the center of the catalyst bed
$LaMnO_3$	4	2.8 (40%)[d]	[14]	idem
$LaMnO_3$	2.9	2.3 (27%)[d]	[17]	6% CH_4, air, 5000 h^{-1}, 0.4 g catalyst
$SmCoO_3$	3.1	0.45 (75%)[d]	[16]	2% CH_4, 10% O_2, 6000 h^{-1}
$SmCoO_3$	30[b]	0.67 (90%)[d]	[16]	2% CH_4, 10% O_2, 6000 h^{-1}
$LaCrO_3$	1.2	0.006[c]	[23]	1% CH_4, 4% O_2
		µmol/(s m^2)		
$LaMnO_3$	~ 15	0.38[c]	[21]	1.5% CH_4, 4.2% O_2, 3.3 cm^3/s, 0.04 g catalyst, temperature programmed reactor
$La_{0.2}Sr_{0.8}Fe_{0.4}Co_{0.6}O_3$	–	0.2[c]	[22]	1.5% CH_4, 20% O_2, 1 g catalyst

[a] Unspecified SSA, range of 0.5–15 m^2/g given.

[b] SSA increased by submicron grinding.

[c] Initial rate of combustion.

[d] Activity calculated from conversion values given for convenience in brackets.

as such in literature, or calculated from other available data are presented. The activities should further be normalized to the same methane concentration, more precisely to the same contact time. However, since the complete data permitting the calculation of the latter were mostly not available, we prefer to only indicate the conditions at which the activities were obtained.

Inspection of table 3 indicates that only in few cases the reported activities would be comparable to our data, even if normalized directly to 4% of methane in air. However, in these cases, the conversions were determined over an undiluted catalyst bed. Furthermore, most of our activity values are conservative since they were obtained from conversions over 80%. Thus, we may suggest with confidence that the activities of the majority of our samples, in particular of the new compositions, not only compare very well with those available in literature, but can be considered as superior.

4. Conclusion

This study has demonstrated that spray-freezing/freeze-drying should be the method of choice for preparation of new combustion catalysts. Although all eleven tested compositions showed comparable or better activity than similar perovskite-type catalysts reported in literature, the new mixed transition metal compositions $La_{1-x}Sr_xB_{y'}Ni_yCo_{1-y-y'}O_{3-\delta}$, where x and $y = 0.34 \pm 0.05$, and $y' \leqslant 0.05$ and consequently $\delta \leqslant 0.17 \pm 0.03$, were significantly better. The high activity of such compositions is likely to be general. By several criteria $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ was the best performing, although highest value of activity per m^2 was observed for $La_{0.4}Sr_{0.6}Fe_{0.4}Co_{0.6}O_3$. These compositions were selected for a complete kinetic study to be reported separately.

Specific surface area which to some extent depends on the catalyst composition appears to be a critical parameter determining the catalyst activity. This parameter should always be used as part of the catalyst characterization. However, as demonstrated by the data in this study and by some from the literature, the catalytic activity is not always directly proportional to SSA. Therefore, the practice of normalizing the activity directly to SSA can be misleading.

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