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Fiber-supported perovskites for catalytic combustion of natural gas

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Abstract

Based on previous work, highly performing combustion catalyst consisting of an iron doped nickel–cobalt-based perovskite supported on commercial fiber blankets has been developed. The catalyst is particularly suitable for use in combustion of lean natural gas mixtures. With 12–15 wt% perovskite loadings the catalyst exhibits activities comparable to those of commercial fiber-supported platinum. At temperatures below 1000 K the catalyst activity seems stable, and resistant to low levels of mercaptan used as an odorant. Unlike platinum (or palladium) the catalyst promotes deep methane oxidation, i.e. no carbon monoxide formation, even in methane-rich mixtures. The combustion is inhibited by carbon dioxide, but water has no measurable influence. A simple kinetic model which takes the inhibition effect of carbon dioxide into account and permits more realistic conversion estimates is proposed: $r_{CO_2} = k_{CH_4}P_{CH_4}/(1 + k_{CO_2}P_{CO_2})$. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic combustion of lean natural gas mixtures represents the most efficient means to significantly reduce, or even eliminate NO_x, which are otherwise emitted during conventional combustion for heat generation [1–5]. To make catalytic combustion widely acceptable, new reliable technologies need to be developed [6,7]. Highly performing low-cost catalysts are an integral and necessary part of these developments. Current technologies still mostly rely on precious metals, especially on platinum and palladium [8], and a lot of effort is made to improve their overall performance. This applies particularly to less expensive palladium which as an oxide at low temperatures well below its decomposition (1023 K) is the most active reported methane combustion catalyst [9]. However, for intermediate temperatures of operation, palladium (oxide) has to be supplemented by highly expensive platinum. There is therefore a need for the development of low-cost highly performing catalysts which would compete with platinum. Such catalysts can be found among lanthanum–strontium transition metal-based perovskites.

Over the last 15 years a number of transition metal-based perovskites has been shown as highly active in methane combustion [10–16]. In view of their low cost and potentially good resistance to low levels of sulfur bearing odorizers (mercaptans) [17,18,20], selected perovskites hold some promise for industrial applications in catalytic combustion technologies operating at lower temperatures.

One of the challenges to meet requirements for industrial applications of perovskite catalysts is the development of suitable forms maximizing the cata-

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lyst dispersion without exerting high pressure drops in fixed-bed type reactors. Ceramic fibers and/or monoliths represent two suitable supports for lower heat output generators. Although over the years of active research on these catalysts a number of articles concerning development of supported perovskites has been published [19], none of these concern fibers, which for specific applications, such as radiant pads, seem to be the best choice.

Previous work from this laboratory has shown that high surface area nickel–cobalt-based perovskites prepared by freeze-drying nitrate solutions show excellent activity [13,15], and several exploratory supported forms, including fibers, of a composition $La_{0.66}Sr_{0.34}Ni_{0.3}Co_{0.7}O_3$ (LSNC), have been developed [20].

This paper presents results of further development in which attempt was made to improve the catalyst performance both by doping the composition with iron or manganese, and by efficient perovskite dispersion on the fiber support.

2. Experimental

2.1. Catalytic pad preparation

Four different fiber blankets, all purchased from Zircar, were initially evaluated in this work. Before use, pieces of blanket, about 5×10 cm, were calcined 10 h at 1030 K.

One molar stock metal nitrates solution of desired perovskite precursor composition was prepared by dissolving required amounts of each component. Exact metal content in individual metal nitrates was determined by volumetric analysis.

Preparation of the catalytic pads consisted of following steps:

- incipient wetting of the fiber blanket with the precursor solution, typically 0.2 M,
- fast freezing of the solution wet blanket by immersion in liquid nitrogen,
- vacuum drying of the frozen material,
- vacuum dehydration and decomposition of nitrates at higher temperatures, and
- calcination of the precursor impregnated fibers in air to form perovskite phase.

Labconco Lyph.Lock 4.5 freeze-drier equipped with Leybold D8 dual stage vacuum pump was used for freeze-drying.

2.2. Physical characterization

Samples were characterized by measuring specific surface areas (SSA) using a single point BET method with krypton (0.1% in helium) as the adsorbate on a Micromeritics Flow Sorb II 2300 apparatus. Porosity of fiber substrates was determined both gravimetrically as a wetting capacity, and by mercury intrusion porosimetry using Micromeritics Poresizer 9320.

Formation of perovskite phase on the fiber substrate was confirmed by XRD analysis on a Philips X'Pert Diffractometer. Morphology of perovskite deposits was examined on Jeol J-840 scanning electron microscope.

2.3. Catalytic activity evaluation

Catalytic activity was evaluated in an integral U-type stainless steel reactor [15]. The reactor, 0.7 cm inner diameter, 10 ml reaction zone, 30 cm overall length, was loaded with a mixture of 0.5 g catalyst cut in small pieces and of blank fibers also in small pieces to approximate isothermicity. The reactor was heated in intervals of about 15–30°. Care was taken to attain a stable temperature. At each stable temperature methane conversions in effluents of reaction mixtures of 3% methane (pure, or commercial odorized natural gas) in air flowing over the catalyst at 100 ml/min (or 200 ml/min) were determined by gas chromatography, after removing water. Carbon dioxide was the only product detected.

3. Results and discussion

3.1. Support material

The characteristics data of the four fiber support materials consisting of alumina (APA paper, and AM mat), alumino-silicate (ASPA paper), and yttria stabilized zirconia (zirconia felt, ZYF-100) are given in Table 1. These materials differed not only in fiber composition and their length, but also in the pore structure. However, the SSA of all fibers was compar-

Table 1
Characteristics of tested fiber supports

Parameter	Material			
	ASPA	AM	APA	ZYF-100
Composition	47%Al_2O_3–52%SiO_2	95%Al_2O_3–5%SiO_2	95%Al_2O_3–5%SiO_2	92%ZrO_2, 8%Y_2O_3
Thickness (mm)	6.3	25–33	1.3	2.6
Porosity (%)	95	97–98	96	96
Fiber diameter (μm)	2–4	2–4	2–4	4–6
Pore diameter[a] (μm)	36–40	50–200	29–35	41–45
Wetting capacity (ml/g)	8.6	9.5	8.6	3.1
Fiber density[a] (g/ml)	2.6	2.9	2.7	4.6
SSA (m^2/g)	1.2	2.2	2.4	1.2

[a] Determined by mercury porosimetry.

able and in view of the average relatively high fiber diameter, thus facilitating good wetting with precursor solution and adhesion of perovskite phase. Of the four initially tested materials only ASPA, 6.3 mm thick blanket of short fibers, and AM, about 25 mm thick blanket of long fibers, were retained for final development. APA and particularly ZYF-100 lacked the mechanical integrity of ASPA and of AM. APA was found too thin for convenient handling, especially when wet, whereas ZYF-100 tended to lose fibers. Nevertheless, even these materials were relatively easily loaded with 5–25 wt% perovskite, the activity of final catalysts corresponding to that of pure powder, or to that of previously described LSNC/Kaowool catalysts [20].

3.2. *Catalyst preparation and physical characteristics*

Of the two retained support materials, ASPA had the advantage of uniform porosity and a thickness allowing fast freezing and drying of the precursor solution. Thus highly reproducible loadings, controlled by the solution concentration, were achieved. In contrast, highly open structure and large thickness of AM dictated more elaborate handling, and resulted in lower reproducibility of the quality.

To maximize the catalyst performance, low perovskite loadings were targeted. However, best performance was obtained for 12–15 wt% achieved by using 0.17 M (all metal) solution.

Following the procedure described above and calcining 10 h at 860 K and 4 h at 900 K perovskite phase was well developed (Fig. 1), the average size of the crystallites being about 0.3 μm, with SSA typically about 25 m^2/g_{per}. On further calcination at 1110 K for 6 h no change in the perovskite phase occurred, but larger crystallites formed, causing lowering SSA to 12 m^2/g_{per}. This is demonstrated by narrowing the width of the principal perovskite peaks.

3.3. *Catalytic performance*

Initial experiments with LSNC composition on APA fibers at loadings 25.7, 9.5, and 4.4 wt% confirmed previous exploratory results [20], but not much improvement in specific activity (per g_{per}) was obtained by higher dispersion. On the other hand, composition containing 2% iron ($La_{0.66}Sr_{0.34}Ni_{0.29}$-$Co_{0.69}Fe_{0.02}O_3$, i.e. LSNCF) showed significantly better activity, which appeared to be only little dependent on the support. Well prepared samples with loadings higher than 10 wt%, the apparent optimum at 12–15%, had specific activities two to three times higher than corresponding unsupported powder, while bare fibers showed no measurable activity. Typical conversion curve for LSNCF/ASPA is shown in Fig. 2. Replacing iron with manganese ($La_{0.66}Sr_{0.34}Ni_{0.29}Co_{0.69}$ $Mn_{0.02}O_3$, i.e. LSNCM) resulted in slightly lower apparent activity, as illustrated by conversion data and apparent first order rate constants for several samples given in Table 2. The role of iron in improving the apparent activity of LSNCF over LSNC and LSNCM may possibly be related to its acidity. For LSNCF it was found that whether supported on alumina mat (AM), or on alumino-silicate paper (ASPA),

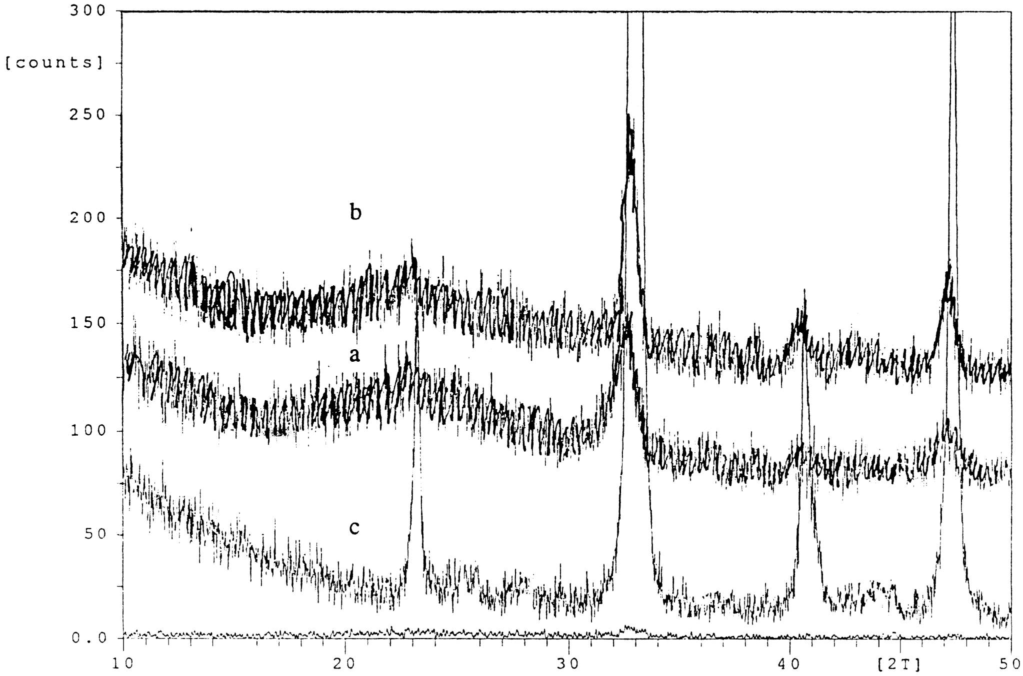

Fig. 1. X-ray diffractograms showing the formation of perovskite phase on ASPA fiber support (LSNCF (11%)/ASPA): (a) calcined 10 h at 860 K and 4 h at 900 K; (b) after additional calcination at 1110 K 6 h; (c) LSNCF powder at the same sensitivity.

the activity was comparable to that of commercial fiber-supported platinum evaluated under the same conditions. In fact, at temperatures below 825 K the new catalyst showed higher activity as illustrated in Fig. 3 in terms of Arrhenius plots for the integrated first order model used only for comparison of different catalysts. While this most frequently used first order model provides for given restricted conditions a good fit, different rates are obtained for different flow rates, as shown in Fig. 4. This is in part caused by inhibition

Table 2
Catalytic activity data for fiber-supported perovskites

Catalyst	SSA (m^2/g_{per})	$T_{30\%}$[a] (K)	$T_{50\%}$[a] (K)	$T_{95\%}$[a] (K)	E_{app}[b] (kJ/mol)	$k(823)_{app}$[c] (μmol/g s bar)
Pd/fiber[d]	–	673	710	785	100[e]	2600
Pt/fiber[d]	–	805	853	910	160[f]	150
LSNCF (27%)/AM	27	713	750	853	92	350
LSNCF (14%)/AM	22	733	784	878	79	175
LSNCF (15%)/ASPA	24	770	820	905	89	170
LSNCF (12%)/ASPA	27	773	823	915	88	138
LSNCM (20%)/ASPA	18	703	825	923	93	85
LSNCM (15%)/ASPA	23	790	832	928	94	103

[a] Temperature of 30%, 50% and 95% conversions of 3% methane in air; 0.5 g catalyst, 100 ml/min.
[b] Apparent activation energy for the first order rate constant.
[c] Apparent first order rate constant at 823 K.
[d] Commercial fiber-supported catalysts, loading presumably 2 wt% in the case of Pt.
[e] For temperatures above 690 K.
[f] For temperatures above 800 K.

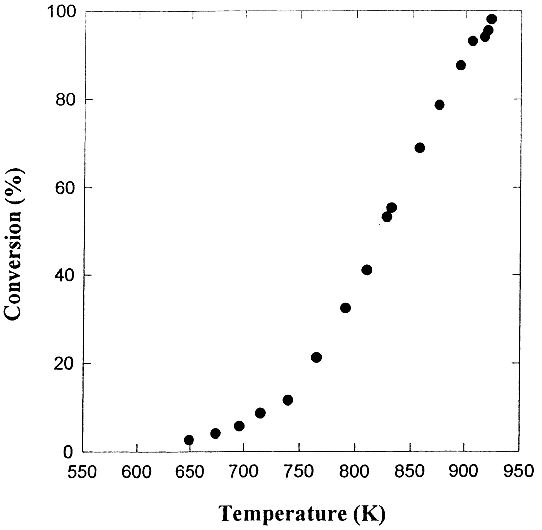

Fig. 2. Typical conversion curve for LSNCF (12%)/ASPA catalyst (0.5 g, 3% methane/air, 100 ml/min, reaction volume 10 ml).

effect of CO_2 discussed previously [20] and reported before for some spinels [21], and also for palladium oxide [22]. It has to be mentioned that activity of perovskites is not, unlike that of palladium, affected by water.

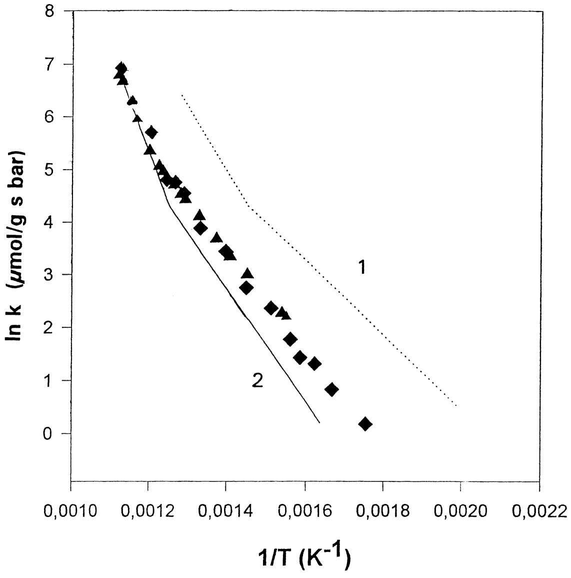

Fig. 3. Arrhenius plots of the integrated first order model for several fiber-supported catalysts. Lines 1 and 2 correspond, respectively, to commercial palladium and platinum-based catalysts. (◆) LSNCF (15%)/ASPA calcined 10 h at 860 K and 4 h at 900 K; (▲) after additional calcination 2 h at 970 K.

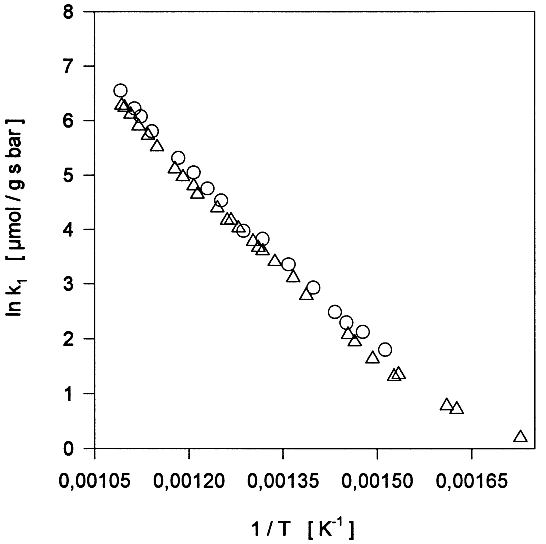

Fig. 4. Arrhenius plots of the integrated first order model for LSNCF (11%)/ASPA; data obtained at 100 ml/min (△), and 200 ml/min (○).

The inhibition effect of CO_2, which seems to be an activated process, is documented by the data in Table 3. This effect can be accounted for by a simple rate model proposed previously [20]: $r_{CO_2} = k_{CH_4}P_{CH_4}/(1 + k_{CO_2}P_{CO_2})$. Using the data in Table 3 the parameter k_{CO_2} was found to be equal to $1.4\times10^4 \exp(-5400/T)\ \mathrm{bar}^{-1}$. Arrhenius plots for the integrated inhibition model shown in Fig. 5 indicate an improvement in the data fit over that in Fig. 4.

Table 3
Effect of added CO_2 on the apparent activity of LSNCF (11%)/ASPA

Flow rate (ml/min)	Temperature (K)	Conversion[a] (%)	
		3% CH_4/air	(3% CH_4+3% CO_2)/air
100	793	58.9	47.0
	831	30.0	23.7
	885	14.2	13.6
200	823	18.0	12.2
	888	45.4	30.6

[a] 0.35 g catalyst, i.e. 0.039 g perovskite used in the experiment.

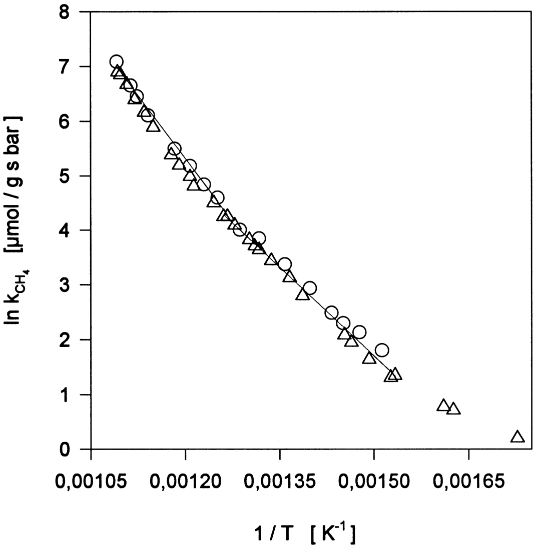

Fig. 5. Arrhenius plots of the integrated $r_{CO_2} = k_{CH_4}P_{CH_4}/(1+k_{CO_2}P_{CO_2})$ model, $k_{CO_2}=1.4\times10^4 \exp(-5400/T)\,\mathrm{bar}^{-1}$ for the same data as in Fig. 4.

3.4. Long-term performance in odorized natural gas

Previous experiments have shown that at 773 K and $W/F_{\mathrm{ong}}=0.32$ g_{per} s/μmol of odorized natural gas the activity of LSNC/Kaowool catalyst has not changed for four days, although it was slowly poisoned by 150 ppm mercaptan in the feed [20]. The new catalyst is also sensitive to poisoning by high levels of mercaptan [18], but again the rates of poisoning are lower than those reported for other perovskite compositions [17]. Furthermore, when smaller amount of LSNCF (12%)/ASPA, such that $W/F_{\mathrm{ong}}=0.03$ g_{per} s/μmol, was tested at 825 K in mixture of 3% odorized natural gas/air, i.e. 0.3 ppm CH_3SH in the feed, the activity has not changed significantly over more than 10 days. The activity was similarly stable at 900 K. This supports predictions made on the basis of poisoning model [18].

4. Conclusions

Fiber-supported perovskite (nickel–cobalt-based) catalysts represent one of the several industrially applicable forms of highly performing low-cost combustion catalysts. At operating temperatures between 800 and 1000 K perovskite loadings of 12–15 wt% may compete in activity with 2 wt% platinum. These catalysts show a good stability and resistance to low levels of mercaptan in the feed. In addition, these catalysts promote complete methane oxidation, even in fuel-rich mixtures.

To achieve maximum activity, uniform dispersion of high surface area perovskite has to be assured. This can be achieved by an in situ perovskite formation via freeze-drying of fiber blanket wetted with precursor solution and subsequent controlled calcination.

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