Catalytic Performance of La$_{0.66}$Sr$_{0.34}$Co$_{0.2}$Fe$_{0.8}$O$_3$ Perovskite in Propane Combustion: Effect of Preparation and Specific Surface Area

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Abstract—Several compositions in a system of La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ perovskites are known as very good electronic and ionic conductors, as well as excellent catalysts for hydrocarbon oxidation. In this study La$_{0.66}$Sr$_{0.34}$Co$_{0.2}$Fe$_{0.8}$O$_3$ was selected as possibly the optimum composition. To assess the effect of preparation and calcination conditions on the activity in propane combustion, a series of different samples was prepared by a method based on slurry of reactive component precursors processed by freeze-drying. Three different materials were used as source of iron and the samples were aged at successively higher temperatures (1,153-1,343 K). The specific surface areas varied between 5.9 and 1 m^2/g, depending on iron precursor and/or aging. The activity was determined in an integral U-shape reactor, typically for 1 and 2 vol% propane in air, with 1 g catalyst and 200 or 100 ml/min flowrate. Kinetics determined on the basis of a wider range of concentrations (1-4.3 vol% propane; 10 vol%-pure oxygen) for a selected, the least aged sample indicated that the propane catalytic combustion is best represented by a Mars van Krevelen model with 0.5 order in oxygen and the two kinetic constants having E$_{app}$ of 83 and 81 kJ/mol, respectively. For the aged samples, the pseudo-first order E$_{app}$ varied from 85 to 98 kJ/mol.

Key words: La$_{0.66}$Sr$_{0.34}$Co$_{0.2}$Fe$_{0.8}$O$_3$ Perovskite Catalyst, Catalytic Combustion of Propane over Perovskites, Loss of Activity Due to High Temperature Calcination

INTRODUCTION

Catalytic combustion of gaseous fossil fuels is recognized as an economical and environmentally acceptable means of heat and energy generation [Hayes and Kolaczkowski, 1998; Pfefferle and Pfefferle, 1987; Zwinkels et al., 1993]. While natural gas, mainly composed of methane, is the most economical and produces the least amount of carbon dioxide per kJ of energy, propane remains very attractive for several applications, especially in regions and areas lacking a natural gas distribution network. Propane can also be used as a convenient auxiliary fuel for cleaning, by catalytic combustion, effluent streams containing low concentration of some volatile organic compounds to assure autothermal process. As is well known, success of catalytic combustion technologies relies on highly performing catalysts. These have to be not only sufficiently active to initiate the combustion without undue preheating, but above all they have to be thermally stable and durable to withstand operation at high temperatures and often high flowrates, both of which depend on the required energy output. For heat generators temperatures below 1,270 K are expected. Consequently, the requirements for the catalyst performance are less stringent than for higher temperature systems. Nevertheless, even if propane is relatively easy to ignite, it is desirable that the ignition temperature remains low. For propane combustion several transition metal based oxides show a very good activity [Moro-oka et al., 1967; Golodets, 1983; Finochio et al., 1995; Baldi et al., 1998a, b], often comparable to that of palladium oxide [van de Beld et al., 1995], but platinum is known as the

most active [Burch et al., 1998; Hubbart et al., 1993]. However, platinum is expensive and transition metal oxides are not sufficiently stable for higher temperature operations. Alternative, thermally stable catalysts may potentially be found from the family of perovskites [Nitadori and Misono, 1985; Nitadori et al., 1986]. In a previous study, La$_{0.66}$Sr$_{0.34}$Ni$_{0.3}$Co$_{0.7}$O$_{3-\delta}$ (LSNC) perovskite stabilized at 923 K, having high specific surface area (SSA), showed an excellent activity and kinetic study revealed that at temperatures below 650 K the reaction proceeds via a Mars van Krevelen mechanism [Song et al., 2001]. However, LSNC perovskite starts to decompose at temperatures higher than about 1,100 K. A different composition with a higher thermal stability was therefore searched. Based on the study of the La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ system, in which several compositions showed very good oxygen mobility and catalytic activity in methane and butane combustion [Teraoka et al., 1988; Zhang et al., 1990], and considering other available data on the effect of composition on activity [Kirchnerova et al., 1993; Seiyama, 1993], La$_{0.66}$Sr$_{0.34}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF) composition was selected as potentially very good candidate. Having slightly lower strontium content than the La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ perovskite that has been extensively studied for solid oxide fuel cells or oxygen permeating membranes [Tsai et al., 1997; Xu and Thompson, 1998] this new composition is considered as potentially more stable. To determine the effect of aging on the activity, especially on the light-off temperature of propane combustion, as well as approximate upper temperature of acceptable stability, samples of LSCF were prepared by using three different sources of iron, each requiring a slight modification of the preparation procedure, and all were aged for several hours up to 1,351 K. The catalytic activity was mostly evaluated for two different flowrates and propane concentrations. A sample aged at the low-

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est temperature was chosen for a brief kinetic study.

EXPERIMENTAL

1. Catalyst Preparation and Characterization

A series of samples of the same nominal composition (La$_{0.66}$Sr$_{0.34}$Co$_{0.2}$Fe$_{0.8}$O$_3$) was prepared by a method involving precursor aqueous slurry of reactive, in situ hydrated, metal oxides or hydroxides processed by freeze drying and subsequent calcination as described elsewhere [Kirchnerova and Klvana, 1999]. Either ferric nitrate nanohydrate or fine powders of red and black ferric oxide, having SSA of 10 and 3.2 m^2/g, respectively, were used as a source of iron. When ferric nitrate (as the iron precursor) was used, iron hydroxide was first precipitated by mixing the iron nitrate solution with a slurry of lanthanum hydroxide prepared in-situ by suspending pure lanthanum oxide (Molycorp) in distilled water. To complete the precipitation, diluted ammonia was added. After decantation of precipitate, about 75% of soluble salts were removed before incorporating the solution of strontium and cobalt nitrates by means of a high speed mixer. When iron oxide was used, typically corresponding to 80% of required iron, the powder was dispersed in a solution of cobalt, strontium and remaining quantity of iron nitrates in a high speed mixer and into this suspension a slurry of lanthanum hydroxide was incorporated. In either case the final fluid, but relatively stable precursor slurry (having a stoichiometric composition), was frozen by pouring in liquid nitrogen and dried under vacuum on a laboratory freeze-drier. To obtain perovskite phase, the freeze-dried material was typically calcined first 10 h at 860 K followed by 5 h at 923 K and finally 10 h at 1,128 K. The samples were then aged at temperatures between 1,028 and 1,350 K for up to 26 h. No intermittent grinding was needed. Formation of perovskite phase was monitored by X-ray diffractometry on Philips X'Pert diffractometer.

SSAs were determined by a single point BET method on Micromeritics Flowsorb 2300 apparatus by using 30 vol% nitrogen in helium.

2. Activity Determination

A steady-state activity of each sample was determined in an integral U-shape plug-flow reactor, using 1 or 0.5 g catalyst powder dispersed in 7 ml of precalcined pumice (particle size 300-500 μ, SSA 1 m^2/g), the feed mixture of 1 or 2% propane in air flowing across the catalytic bed at 200 or 100 ml/min [Klvana et al., 1994; Song et al., 2001]. The reactor consisted of a 30 cm long stainless steel tube, 0.7 cm inner diameter. The temperature, increased in steps of 25 degrees, was monitored by two K-type thermocouples touching the front and the end of the catalytic bed. The effluents, after being stripped of water by passing them over a drying agent, were analyzed by gas chromatography by using a Porapak Q separation column to determine concentrations of carbon dioxide and propane; molecular sieve 5 Å column was used to determine the presence of carbon monoxide, which, however, was never detected. Carbon dioxide and water were the only products. Typically, it took about thirty minutes to reach a steady temperature and conversion.

RESULTS AND DISCUSSION

1. Catalyst Preparation and Characteristics

Although the LSCF perovskite can be prepared directly from co-

balt and iron nitrates solution by admixing it with the lanthanum hydroxide/strontium nitrate aqueous slurry and processing the obtained gel-like mixture (by freeze-drying), the relatively high nitrate concentration makes the overall processing relatively difficult. For this reason we attempted to modify the preparation procedure in a way permitting to use effectively either the iron nitrate or to replace about 80% of total iron by reactive iron oxides. Each iron source required a somewhat modified procedure. When using iron nitrate, the modified procedure consisted of preliminary iron hydroxide precipitation, which allowed removal of more than about 75% of nitrates by decantation and washing. In this case, pure perovskite was formed at as low temperature as 973 K with SSA of 8 m^2/g. However, on further calcination (aging) samples prepared by this procedure lost the SSA rather quickly. Note that samples prepared from iron nitrate are identified as I-g, followed by a number corresponding to the highest temperature of aging. On the other hand, when iron oxides (red and black) were used, the temperature required to form perovskite was higher. With the less reactive black Fe$_2$O$_3$ (SSA 3.2 m^2/g) as the iron source, formation of perovskite phase was the most difficult (samples III-fo.b). For instance, XRD analysis of a sample calcined 8 h at 933 K and 12 h at 1,128 K (sample III-fo.b-855), indicated a presence of secondary phases, with only about 90% of perovskite. Nevertheless, on further calcination at higher temperature (1,253 K), pure perovskite was obtained. When more reactive red Fe$_2$O$_3$ (SSA=10 m^2/g) was used, pure perovskite was obtained on calcination at 1,223 K (16 h) (II-fo.r). Regardless of the iron source, all samples underwent sintering during high temperature calcination, losing their SSA. However, the rate of SSA decrease appears to be slower for samples based on iron oxides. Based on the observed loss of SSA, i.e., the degree of sintering as the temperature of aging was increased, 1,300 K seems to be approximately the upper temperature above which a fast and massive sintering occurs.
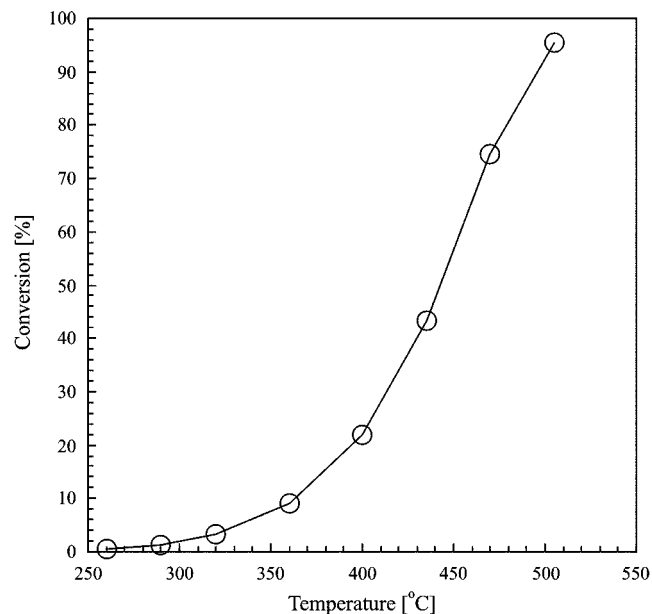

Fig. 1. Conversion of 1 vol% propane catalytic combustion in air as a function of temperature; 0.5 g LSCF-III-fo.b-855 catalyst, flowrate 100 ml/min.

2. Kinetics of Propane Combustion over LSCF Calcined at 1,128 K

In spite of the incomplete formation of perovskite phase, sample LSCF-III-fo.b-855 was selected for a kinetic study covering a relatively wide range of propane (1.1, 2.2, 3.3 and 4.3 vol%) as well as oxygen concentrations (10, 15, 20, 50 vol% as well as pure oxygen). In methane combustion, this sample was the most active, as discussed below. For each set of reactant concentrations, conversions were determined at five different temperatures. Fig. 1 illustrates the apparent activity for the case of 1 vol% flowing at 100 ml/min over 0.5 g catalyst allowing full conversion below 800 K. This is a fairly good activity, although lower than that of LSNC, having SSA 15 m^2/g, and for which comparative conversions were obtained at temperatures about 50 degrees lower [Song et al., 2001]. Nevertheless, for complete kinetic analysis, conversions up to about 30% or even lower, depending on propane concentration, were considered. Using the integrated forms, three different kinetic models were employed for fitting the collected experimental conversion data. The simple first order model tested as a starting point was clearly inadequate. As shown by representative plots in Fig. 2, for each set of data corresponding to given propane and oxygen concentrations a different Arrhenius plot was obtained, although the slopes of the lines were identical, resulting in an apparent activation energy E_{app} equal to 82 kJ/mol. Similar degree of poor fitting by the first order model was observed previously for LSNC, but in that case, the E_{app}, deduced for data at slightly lower temperatures (between 475 and 618 K), was lower (72 kJ/mol) [Song et al., 2001]. Based on our previous experience and some literature information, we have next tested two models: for simplicity and ease of application, a purely mathematical power law model ($r=k_{mn}P_p^m P_o^{0.3}$, m=0.5 and 0.4), and mechanistically based Mars van Krevelen model [$r=k_p P_p$ $k_o P_o^n/(5k_p P_p + k_o P_o^n)$, n=0.5 and 1)]. As evident from Fig. 3, the power low model with m=0.4 provided a fairly good fit, particularly for

Fig. 3. Arrhenius plot for the integrated kinetic constants k_{mn} (m= 0.4, n=0.3) of a power-law model for several different experimental conditions in propane combustion over LSCF-III-fo.b-855.

temperatures between 563 and 678 K, with E_{app}=81.4 kJ/mol. In contrast to LSNC [Song et al., 2001], this model gave a slightly better fit than that with m=0.5. This order in propane reaction is rather low in comparison with 0.94 and 0.68 reported by Moro-oka et al. [1967] for Co_3O_4 and Fe_2O_3 respectively, although that for oxygen falls well in to the range reported (0.16 to 0.4) for a variety of transition metal oxides.

The Mars van Krevelen model with n=0.5, which is compatible
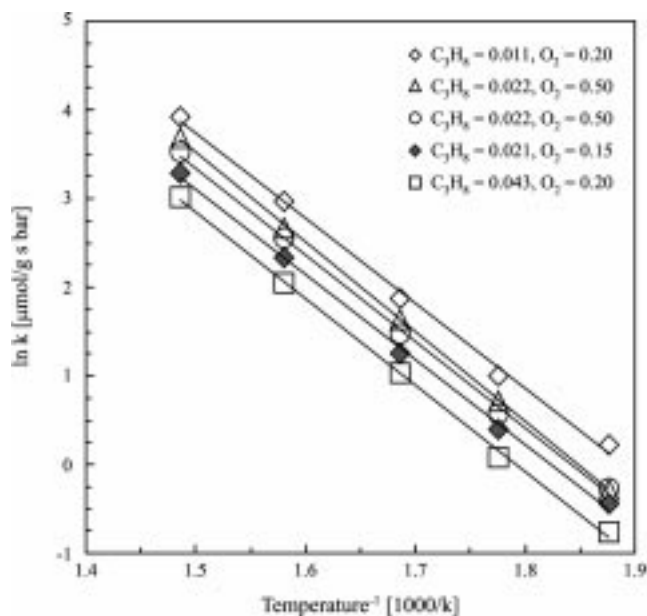

Fig. 2. Arrhenius plots for the integrated first-order kinetic constant for several experimental conditions for propane combustion over LSCF-III-fo.b-855.
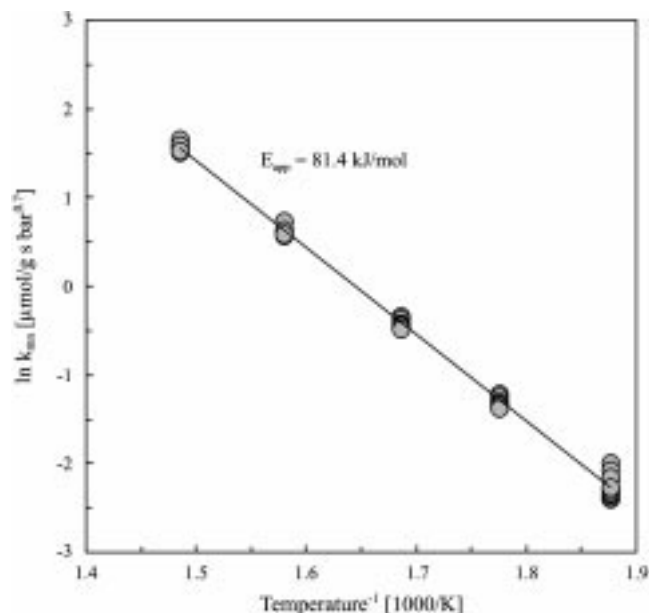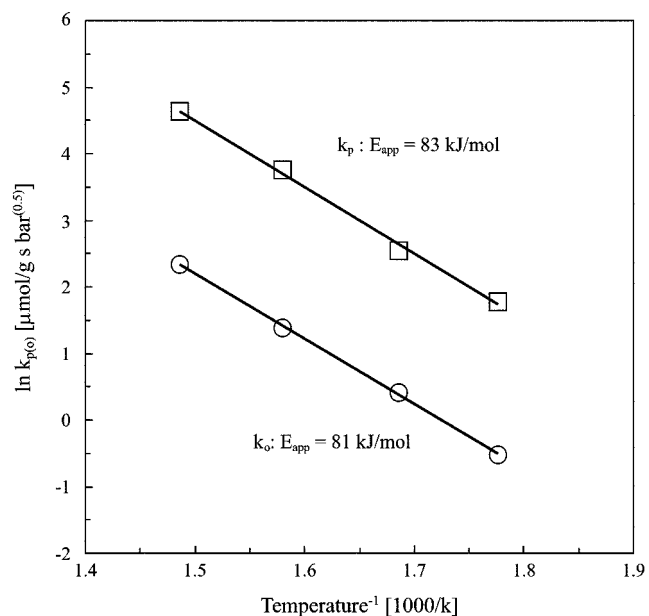

Fig. 4. Arrhenius plot for the two kinetic constants of the Mars van Krevelen model (Table 1) for propane combustion over LSCF-III-fo.b-855.
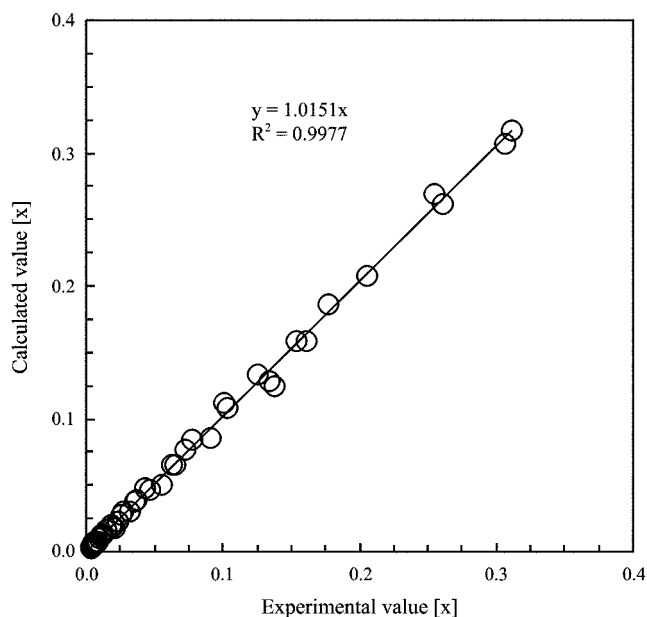
y = 1.0151x
R^2 = 0.9977

Fig. 5. Calculated versus experimental conversions of propane combustion in air over LSCF-III-fo.b-855 perovskite, Mars van Krevelen model (Table 1).

with the notion of a relatively slow equilibration between gas phase and catalyst bulk oxygen, clearly gave an excellent fit. Arrhenius plots for the two kinetic parameters (k$_p$ and k$_o$) are shown in Fig. 4, However, again, these plots cover the temperatures only above 563 K. The value of k$_p$ at 533 K was slightly above the indicated regression line. Fig. 5 illustrates the goodness of fit of this model. The observed increase in apparent activation energies with respect to those deduced for LSNC perovskite is most likely associated with the shift of the reaction to higher temperatures, where the bulk oxygen mobility, characterized by higher activation energy than that of surface oxygen exchange [Shaw et al., 2000], starts to contribute to the overall rate of propane combustion. At the higher temperatures, the rate of catalyst reoxidation increases in comparison with the rate of propane oxidation, or actually the catalyst "reduction" by propane. Thus, the ratio of k$_p$/k$_o$ for the catalyst of this work, LSCF-III-fo.b-855, is lower than it was for LSNC, i.e., ~15 and ~34, respectively. The values of derived kinetic parameters for the three models are given in Table 1.

3. Effect of LSCF Sample Aging on Activity in Propane Combustion

Activity of most of the aged samples was evaluated under 200 and 100 ml/min with 1 and 2 vol% propane, respectively, in air. All

Table 1. Kinetic parameters for three models fitted to conversion data for propane combustion in air over La$_{0.66}$Sr$_{0.34}$Co$_{0.2}$Fe$_{0.8}$O$_3$ (LSCF), sample III-fo.r-855

Model	Rate parameters[a]	E$_{app}$ kJ/mol	ln A[b] μmol/g s bar^{m+n}
r=k$_1$P$_p$	k$_1$=1.2×10^8 exp (−9850/T)	82	18.59
r=k$_{mn}$P$_p^{0.4}$P$_o^{0.3}$	k$_{mn}$=9.8×10^6 exp (−9790/T)	81	16.10
r=k$_p$P$_p$k$_o$P$_o^{0.5}$/(5k$_p$P$_p$+k$_o$P$_o^{0.5}$)	k$_p$=3×10^8 exp (−10024/T)	83	19.54
	k$_o$=2×10^7 exp (−9768/T)	81	16.84

[a]k$_1$, k$_p$: μmol/g s bar; k$_{mn}$=μmol/g s bar$^{0.7}$; k$_o$=μmol/g s bar$^{0.5}$
[b]Preexponential factors have the same units as corresponding rate constants k

LSCF-lg-880

1%) lnk = -10356/T + 20.63
2%) lnk = -10241/T + 19.67

E$_{app}$ = 86.1 kJ/mol

E$_{app}$ = 85.1 kJ/mol

○ C$_3$H$_8$ 1%
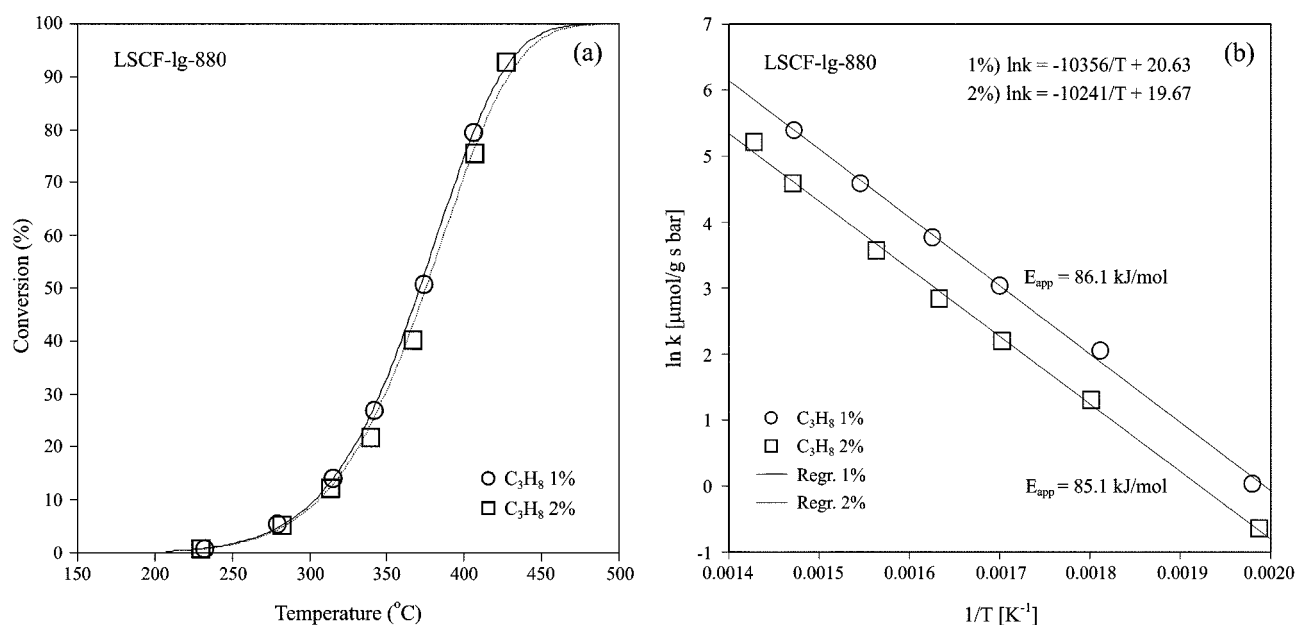□ C$_3$H$_8$ 2%
— Regr. 1%
---- Regr. 2%

Fig. 6. (a) Conversion of 1 and 2 vol% propane combustion in air as a function of temperature; 1 g LSCF-Ig-880, 200 and 100 ml/min, respectively. Points are experimental; the lines are calculated by using the pseudo-first order kinetic constants given in Table 2. (b) Arrhenius plots for the integrated first-order kinetic constant for the LSCF-Ig-880 perovskite, based on data in Fig. 6a.
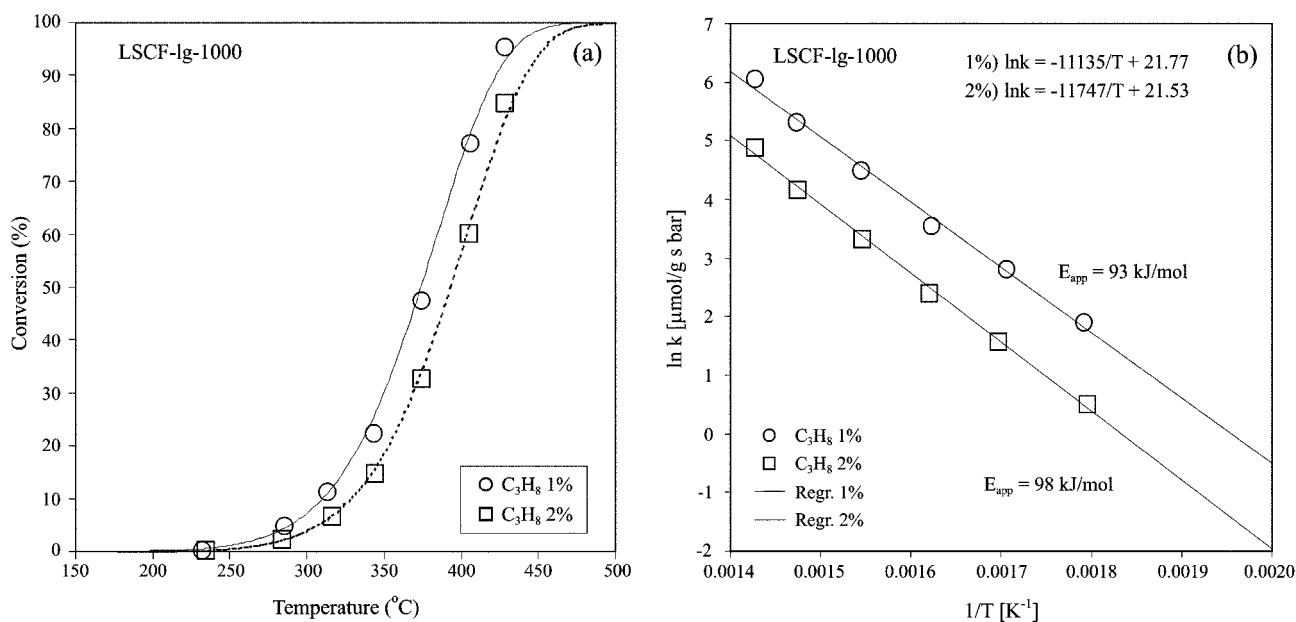
Fig. 7. (a) Conversion of 1 and 2 vol% propane in air as a function of temperature; 1 g LSCF-Ig-1000, 200 and 100 ml/min respectively. Points are experimental; the lines are calculated by using the pseudo-first order kinetic constants given in Table 2. (b) Arrhenius plots for the integrated first-order kinetic constant for the LSCF-Ig-1000 sample, based on data in Fig. 7a.

samples (1 g) showed reasonable apparent activity, giving full conversion below 750 K. However, evaluating the activity at two different flowrates provided some new, more or less unexpected results. In all cases, the light-off curves for the lower flowrate (100 ml/min) with higher propane concentration (2 vol%) were either identical to those for higher flowrate (200 ml/min, 1 vol% propane), or shifted to high temperatures, indicating considerably lower apparent first order rates for the lower flowrates, higher concentration. Representative examples are given in Fig. 6a and 7a for two samples prepared by the same procedure but aged at different temperatures. This seemingly unusual behavior, not observed in the case of methane combustion, can most likely be attributed to the fact that lower temperature propane combustion is to some degree controlled by a relatively slow step of catalyst reoxidation, i.e., it proceeds by Mars van-Krevelen mechanism. It is thus evident that comparison of apparent activities (rates) in propane combustion is not straightforward, unless the data are obtained at the same conditions. Although this is true for many other reactions, the effects of experimental conditions on the apparent activity of methane combustion, typically taking place at significantly higher temperatures, are much less pronounced, often being negligible or of different direction [Klvana et al., 1997]. To evaluate the effect of aging and preparation on the activity, for practical reasons we have opted for using, beside the temperatures of 10 and 50% conversion, the pseudo-first order kinetic parameters, in spite of their obvious limitations. Similarly as for the LSCF-III-fo.b-855 sample, this simple model provided, for given experimental conditions, an excellent fit to conversions over the whole range of temperatures, as shown by the calculated lines in Fig. 6a and 7a and by corresponding Arrhenius plots in Fig. 6b and 7b. For the other samples the degree of fitting for a given flowrate was the same. However, the difference between the two apparent activities varied from sample to sample, without suggesting some clear-cut correlation, as shown by data collected in

Table 2. While the difference between the two apparent first order constants is qualitatively understandable on the grounds of the following expressions,

$$k_1' = k_p/((5k_pP_p'/k_oP_o^{0.5})+1) \text{ and } k_1'' = k_p/((5k_pP_p''/k_oP_o^{0.5})+1)$$

where k_1' and k_1'' correspond to data based on 1 vol% propane (P_p'= 0.01) and 2 vol% (P_p''=0.02) respectively, quantitative interpretation of the k_1'/k_1'' ratio is not simple. Although in principle this ratio should not exceed the ratio of P_p''/P_p', i.e. 2, its value varied from 1.83 to 3.04, independently of aging or some other sample characteristics. Clearly, some unaccounted for factors must be involved in controlling the activity.

The effect of aging on the activity of two sets of samples (I-g and II-fo.r) in 1 vol% propane combustion is directly illustrated in Figs. 8 and 9, respectively. As is evident, the effect of aging was relatively small in the case of iron-hydroxide gel derived I-g samples. On the other hand, it was significant in the case of the two II-fo.r samples, which actually were the most active, regardless of the criteria of comparison. This situation contrasts the activity of the same samples in methane combustion, for which the effect of aging on activity was rather strong and in which the sample LSCF-III-fo.b was the most active. Although the activity data for methane combustion are not available for all the samples, those in Table 3 are very illustrative.

Let us now examine the relationship between the activity (in terms of k_1 at 700 K, i.e. k_{700}) and SSA represented graphically in Fig. 10. Although the overall correlation is rather poor, three different sets of data are easily distinguished. None of these passes through the origin, suggesting rather a common intercept. Interestingly, the lines of linear regression for all data and for I-g samples only are nearly identical. Although the activity of oxide type catalysts in oxidation reactions, in particular in complete hydrocarbon oxidation, is well known to depend on the specific surface area (SSA), the exact re-

Table 2. Effect of preparation procedure and aging on the apparent activity of LSCF perovskite in propane combustion

Sample[a]	Calcination+Aging K/h	SSA m^2/g	T$_{10}$ K	T$_{50}$ K	E$_{app}$ kJ/mol	ln A μmol/g s bar	k$_{700}$[b] μmol/g s bar
Data obtained for 1 vol% propane/air, 200 ml/min, 1 g catalyst							
Ig-880	878/12+1023/5+1153/16	2.4	577	645	86	20.63	340
Ig-1000	878/12+1023/5+1253/19+1273/3	3.9	583	650	93	21.77	350
Ig-980	878/12+1023/5+1253/26	1.5	591	658	86	20.23	225
Ig-1070	878/12+1023/5+1343 / 26	1.0	596	663	93	21.35	233
II-fo.r-950	933/8+1123/10+1223 / 16	5.9	563	623	89	21.72	600
II-fo.r-1078	933/8+1123/10+1351 / 26	1.3	582	650	84	19.97	273
III-fo.b-980	933/8+1128/12+1253/26	1.9	591	673	98	22.04	183
Data obtained for 2 vol% propane/air, 100 ml/min, 1 g catalyst							
Ig-880	878/12+1023/5+1153/16	2.4	579	648	85	19.67	154
Ig-1000	878/12+1023/5+1253/19+1273/3	3.9	600	673	98	21.53	115
Ig-980	878/12+1023/5+1253/26	1.5	-	-	-	-	123[c]
Ig-1070	878/12+1023/5+1343/26	1.0	596	663	92	20.51	115
II-fo.r-950	933/8+1123/10+1223/16	5.9	574	635	91	21.15	247
II-fo.r-1078	933/8+1123/10+1351/26	1.3	591	658	90	20.24	123
III-fo.b-980	933/8+1128/12+1253/26	1.9	-	-	-	-	82[c]
III-fo.b-855	933/8+1128/12	3.6	638[d]	713[d]	82[d]	18.59[d]	87[d]

[a]I-g samples prepared from gel, others from Fe$_2$O$_3$, the number indicates the aging highest temperature

[b]Pseudo-first order rate constant at 700 K

[c]Calculated from a single conversion data

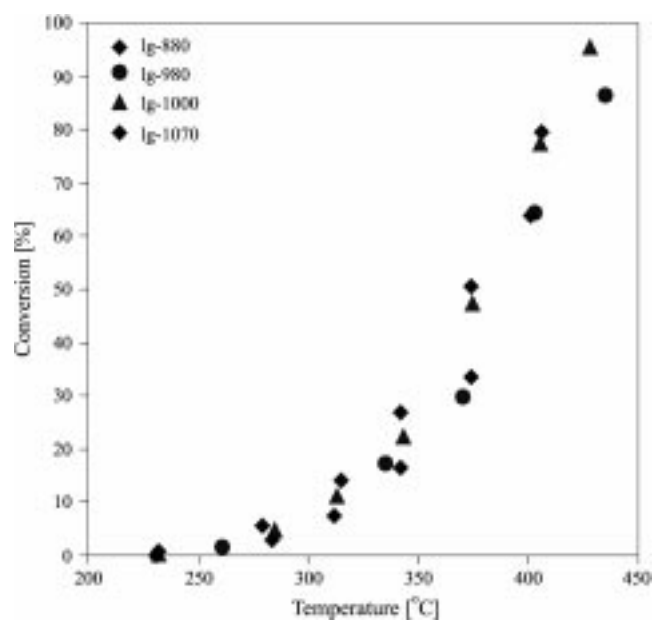[d]Data for 2 vol% propane/air, 100 ml/min, 0.5 g catalyst

Fig. 8. Conversion of 1 vol% propane combustion in air, as a function of temperature, over several differently aged LSCF perovskite prepared using iron hydroxide gel as source of iron (samples I-g).
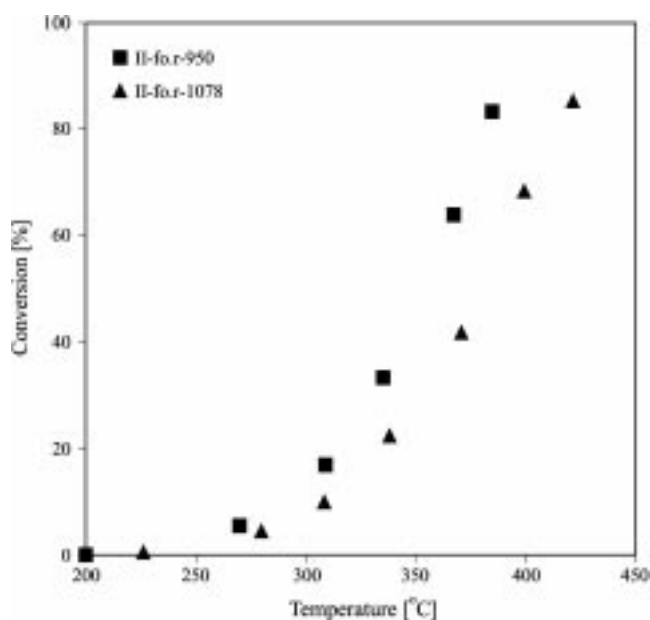

Fig. 9. Conversion of 1 vol% propane combustion in air, as a function of temperature, over two differently aged LSCF-II-fo.r samples (prepared using red iron oxide as a source of iron).

lationship between the two characteristics and the extent of its mutual dependence are not completely understood. Nevertheless, it is typically taken for granted that a direct linear relationship exists between the rate (of combustion) and SSA. Thus, activities, rate or rate constants, are often expressed per unit surface area (as areal), i.e., per

m^2. The results of this study shown in Fig. 10 indicate that a situation similar to that previously observed for combustion of methane over LSNC perovskite [Kirchnerova et al., 1993; Kirchnerova and Klvana, 1999] and over Sr$_{0.8}$La$_{0.2}$MnAl$_{11}$O$_{19}$ [Kirchnerova and Klvana, 2000] exists also in the case of propane combustion over LSCF perovskite. Other literature data also indicate the lack of direct linearity

Table 3. Effect of preparation procedure and aging on the apparent activity of LSCF perovskite in methane combustion[a]

Sample[a]	Calcination+Aging K/h	SSA m²/g	T_{10} K	T_{50} K	E_{app} kJ/mol	k_{1000} μmol/g s bar	k_{700} μmol/g s bar
Ig-1000	878/12+1023/5+1253/19+1273/3	3.9	750	852	102	1.67	8.7
Ig-1070	878/12+1023/5+1343/26	1.0	783	902	100	0.74	3.8
Ig-1078	878/12+1023/5+1351/26	0.9	826	948	102	0.37	1.9
III-fo.b-855	933/8+1128/12	3.6	740	837	107	2.35	8.9
III-fo.b-980	933/8+1128/12+1253/26	2.5	748	845	105	1.94	8.5
III-fo.b-1070	933/8+1128/12+1343/25	1.3	768	868	103	1.29	6.3

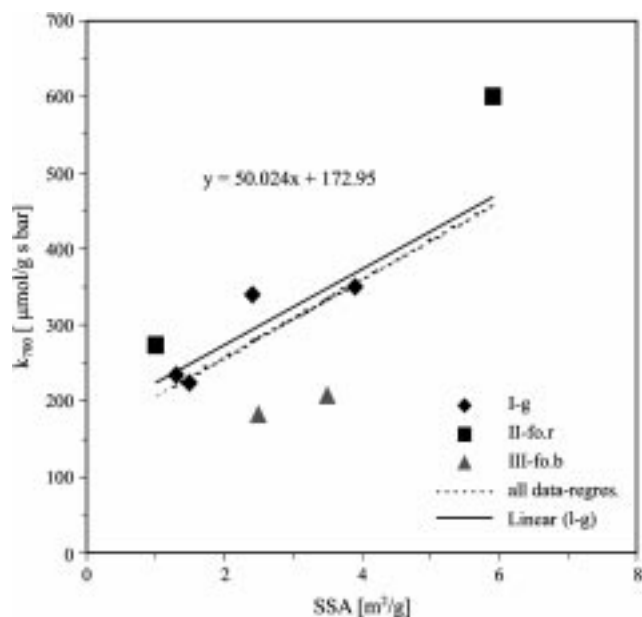[a]Activity determined for 1 g catalyst, 2 vol%methane/air, 400 ml/min; so far unpublished work

Fig. 10. Pseudo-first order kinetic constants as a function of SSA for 1 vol% propane combustion in air at 700 K over several LSCF perovskites prepared from three sources of iron and aged at different temperatures.

between activity and SSA [Arai et al., 1986; McCarty and Wise, 1990], reinforcing the argument against a widespread use of areal activities for the purpose of activity assessment.

The poor apparent activity of LSCF-III-fo.b-855 in propane combustion, in spite of being the most active in methane combustion (Table 3), could to a large part be attributed to different experimental conditions under which it was determined. Nevertheless, presence of secondary, less active phases in this sample could also be somehow responsible.

SUMMARY AND CONCLUSIONS

This study has shown that the $La_{0.66}Sr_{0.34}Co_{0.2}Fe_{0.8}O_3$ (LSCF) perovskite exhibits a very good activity in complete propane oxidation (combustion). Even samples subjected to extensive, high temperature, aging and consequently having rather low SSA retain a good activity. The propane combustion apparently proceeds via a Mars van Krevelen mechanism. In contrast to methane, the catalytic pro-

pane combustion is relatively easily initiated even over highly sintered LSCF samples. Furthermore, lower SSA seems to have much weaker effect on the activity. The apparent activity in propane combustion seems more dependent on the method of preparation rather than the calcination conditions, but it should not be forgotten, that the two factors are to some degree mutually dependent.

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