Preparation and characterization of $CaTiO_3$-based perovskitic oxides as catalysts for partial oxidation of light hydrocarbons

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Received 29 July 1992; accepted 18 December 1992

A series of perovskites of the formula $Ca_{1-x}Sr_xTi_{1-y}M_yO_{3-\delta}$, M=Fe, Co, Cr or Ni, $x = 0$–1, $y = 0$–0.6, has been synthesized by a modified sol–gel method using citrate. Several of these materials were proved to be stable under operating conditions in reducing atmospheres of air and hydrocarbons. An outline of the synthesis procedure is given, together with the results of XRD, SEM, BET, TG, DTA and IR characterization before and after catalytic testing. The solubility of Ni and Cr in this perovskite was very limited, and the solubility of Co decreased abruptly above 1173 K. The solubility range of Ca and Sr on alkaline earth sites is 100%.

Keywords: Perovskites; oxidative coupling of methane; XRD; SEM; TGA; BET; $CaTiO_3$-based catalyst; sol–gel method

1. Introduction

It is well known that some oxides conduct owing to oxide ion mobility [1], and the oxygen transport can influence the oxidation reaction through oxygen supply from the oxide catalyst. We studied the oxidation of olefins by using an electrochemical reactor aided by yttria-stabilized zirconia (YSZ), i.e. Mo–Bi oxide catalyst, Au/YSZ/Ag where YSZ serves as an oxygen pump coupled with Au and Ag electrodes [2]. The most likely use of mixed conductors, such as perovskite-type oxides, which conduct both electrons and oxide ions is promising in the oxidation of hydrocarbons, because of their ability directly to supply oxygen from the oxides to surface-adsorbed species. However, only a few papers [3] have dealt with successful use of perovskites such as $BaCeO_{3-\delta}$, $BaPb_{1-x}Bi_xO_{3-\delta}$ and $CaTiO_3$ in the oxida-

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tive coupling of methane, even though many perovskites based on $LaCoO_3$ and $LaMnO_3$ are well known to be active for deep oxidation of hydrocarbons [4].

The present work has been performed in the search for a catalyst for partial oxidation of light hydrocarbons in an electrochemical reactor with a zirconia electrolyte. We will report on screening tests in fixed bed reactors as well as experiments in electrochemical cells later. A search for a material with the following characteristics was required: (1) The catalyst should be mechanically and chemically stable during operation under reaction conditions. (2) The catalyst should be able to activate hydrocarbons, and show significant selectivity. (3) To be able to use the catalyst in an electrochemical reactor, the catalyst should have considerable conductivity for both electrons and oxide ions. (4) If possible, the material should have thermal properties that match fairly well to the substrate zirconia.

Several perovskites are believed to have interesting properties in this respect, and chemical stability is found among the titanates. Results from tests on oxidative coupling of methane (OCM) over titanates show interesting properties, although they are not completely consistent [2]. The recent work by Xu et al. [3] shows optimal conversion for a substitution of 10% Sr on A-sites in $CaTiO_3$. To increase the electrical and ionic conductivity, lower valent ions should be substituted into the Ti lattice. Several works pointed out that p-type conductivity is preferable for the oxidative coupling of methane [5]; this property may also be obtained by introducing a lower valent metal ion on B-sites in titanates in the present study. Here, we report on the synthesis of a series of perovskites of the formula $Ca_{1-x}Sr_xTi_{1-y}M_yO_{3-\delta}$, M=Fe, Co, Cr or Ni, $x = 0$–1, $y = 0$–0.6, and their characterization by XRD, SEM, BET, TG, DTA and IR.

2. Experimental

2.1. PREPARATION OF THE CATALYST

A series of perovskites with the general formula $Ca_{1-x}Sr_xTiO_3$ was prepared according to the Pechini patent [6] with some modifications of the procedure. Starting solutions containing Ca/Ti and Sr/Ti, respectively, were prepared as follows. Ethylene glycol (>99.5% Chameleon Guaranteed Reagent) was placed in an ice/water bath. Tetraisopropyl orthotitanate (Tokyo Chemicals EP) was slowly added under continuous vigorous stirring. The container for this reagent was kept closed when not in use. When these precautions were added to the Pechini patent no irreversible precipitation of titanium occurred, and Ti was quantitatively used. Citric acid (>98%, Wako Pure Chemicals) was added and the mixture was manually stirred before heating was started. Carbonate of Ca or Sr (both >99.9%, Soekawa Chemicals) was added according to Pechini. One litre of the final aqueous solution contained 100 ml ethylene glycol, 80 g citric acid and 0.16 mol of Ti and Ca or Sr.

Similar solutions containing 0.160 mol/ℓ of respectively Fe and Ca, Fe and Sr, Co and Sr, Ni and Sr, and Cr and Sr were prepared in order to obtain catalysts with lower valent ions in the Ti lattice. The solutions containing iron were prepared from iron(III) citrate hydrate (Chameleon Analytical Reagent): the dissolution of this citrate in water needed about 343 K and 1 h of stirring. The starting material for cobalt ions was cobalt(II) acetate hydrate (Soekawa Chemicals, >99%). The acetate was dissolved in water, and the amount of ethylene glycol and citric acid required for the Pechini procedure was added, as well as an amount of citric acid required to replace acetate ions. Acetic acid was removed in an evaporator at 343 K, leaving a citrate solution; acetate ions in the gel which is the precursor for the catalyst will lead to precipitation of salts and the loss of the metal dispersion. A similar procedure was used to transform solutions of nickel(II) nitrate hydrate (Kokusan Chemicals, >99.9%) and chromium(III) nitrate hydrate (Soekawa Chemicals, >99.9%) into citrate by dissolving in citric acid solutions followed by the evaporation of nitric acid in an evaporator at 373 K. The alkaline earth metals were always added according to the Pechini procedure [6].

All the resulting solutions were homogeneous and transparent with the colour of the respective metal ions, and starting from these various compositions, catalysts were easily prepared by pipetting out corresponding volumes of the unimolar solutions. Normally one batch of catalyst was produced from 100 ml of a mixture of the above mentioned solutions, yielding approximately 3 g of the final catalyst. The volumes of the solutions were reduced to about the half in an evaporator, before the sol was transferred to an open beaker. Heating was continued with continuous stirring on an electrical heating plate until the sample became dry and black. The samples to be used in catalytic tests were calcined at 1123 K for 5 h as the tests were performed up to 1073 K. One set of catalysts formed by calcination at 873 K for 5 h showed the same XRD patterns as samples calcined at 1123 K, but the surface areas were considerably higher.

2.2. CHARACTERIZATION OF THE CATALYST

The powder X-ray diffraction (XRD) patterns of the catalyst were recorded by using MXP-18 (MAC Science Co.) with Cu Kα radiation. Scanning electron microscope (SEM) images were obtained by using a Hitachi S 800 machine. Surface area of the catalyst was measured with a Micrometrics model 2200. Thermal analyses (TGA/DTA) were carried out by using Shimadzu TGA 50 and DTA 50 containing an electrobalance.

2.3. CATALYTIC TESTING OF THE CATALYST

The results of catalytic testing will be reported separately in this journal. All the catalyst samples in the present paper referred to as "before catalytic testing" are, unless otherwise mentioned, calcined at 1123 K for 5 h. Samples referred to as

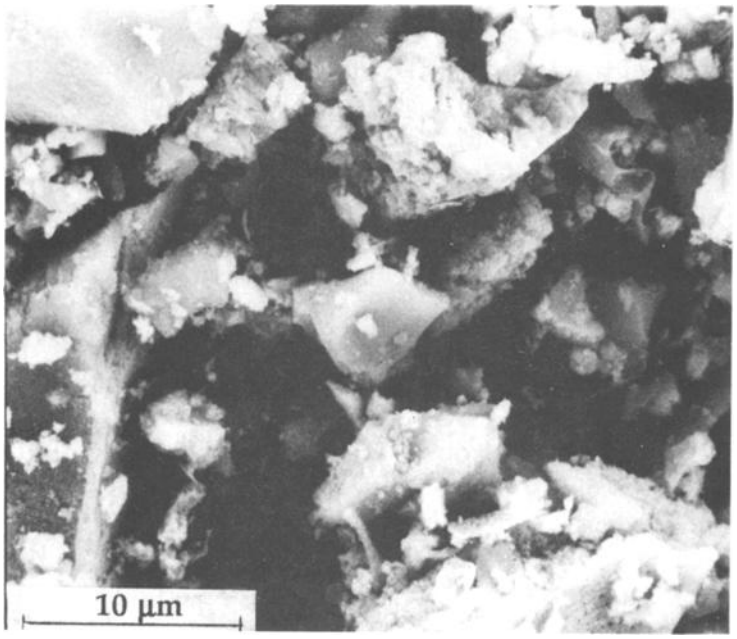

Fig. 1. Scanning electron micrograph (SEM) of $Ca_{0.9}Sr_{0.1}TiO_3$ after calcination at 1123 K.

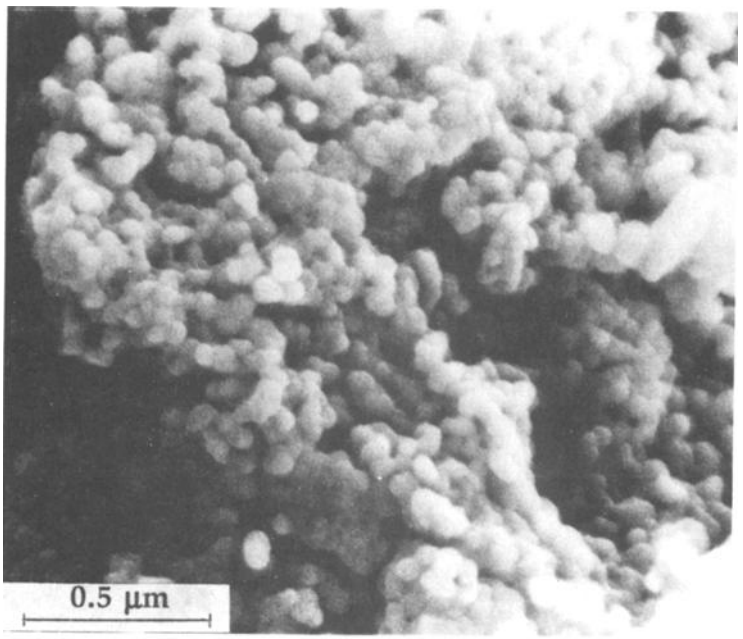

Fig. 2. Close up of one particle in fig. 1, showing the size of the crystallites in the catalyst.

"after catalytic testing" have been exposed to mixtures of ethane and air (1/2 in vol. ratio) at 773–1023 K, as well as mixtures of methane and air (5.4/1 in vol. ratio) at 973–1073 K. Experiments in ethane were finished at the highest temperature. Steady state was in all experiments obtained within 15 min after any change of parameters.

3. Results and discussion

X-ray diffraction measurements showed that Ni or Cr could not be dissolved on the Ti sites of the perovskites by the present method (vide infra), and therefore no further data concerning these metals will be reported. In the present study, the materials examined are as follows: $Ca_{1-x}Sr_xTiO_3$, $x = 0$, 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0; $CaTi_{1-x}Fe_xO_{3-\delta}$, $x = 0$, 0.2, 0.3, 0.4 and 0.6; $SrTi_{1-x}Fe_xO_{3-\delta}$, $x = 0$, 0.2, 0.4, 0.6, 0.8, 0.9 and 1.0; $Ca_{1-x}Sr_xTi_{1-x}Fe_xO_{3-\delta}$, $x = 0$, 0.2, 0.4, 0.6 and 1.0; and $Ca_{1-x}Sr_xTi_{1-x}Co_xO_{3-\delta}$, $x = 0, 0.2, 0.4, 0.6$ and 1.0.

3.1. SCANNING ELECTRON MICROSCOPY

Several samples of the catalyst material were subject to scanning electron microscope (SEM) study, one example is given in fig. 1, showing $Ca_{0.9}Sr_{0.1}TiO_3$ after calcination at 1123 K. The catalyst is composed of particles about 10 μm in diameter. Some surfaces seem to be smooth, while others reveal a porous structure within these particles. A close-up of the lower left part of this figure is shown in fig. 2, revealing an aggregate of small crystallites (average diameter approximately 0.03 μm). When Fe was introduced in the perovskites the agglomerate size remained the same, as seen for $Ca_{0.8}Sr_{0.2}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ in fig. 3. However, the size of single crystals is about 0.2 μm in average, partly sintered together, as can be seen in fig. 4. The porosity between the single crystals is, however, preserved.

3.2. SURFACE AREA OF THE CATALYST

With the particle size observed by SEM one may calculate the specific surface area of this catalyst, assuming spherical particles, using an estimated density of 5.1 g/cm^3 (taken from unit cell parameters). Due to the intergrowth of particles such a calculation will give only an upper limit to the surface area. For the material ($Ca_{0.9}Sr_{0.1}TiO_3$) shown in figs. 1 and 2, the area is expected to be less than 20 m^2/g, while the material containing Fe ($Ca_{0.8}Sr_{0.2}Ti_{0.8}Fe_{0.2}O_{3-\delta}$) has an area of less than 3 m^2/g (figs. 3 and 4).

The surface area of catalysts in the series $Ca_{1-x}Sr_xTiO_3$ measured by BET method is shown in fig. 5. The results obtained with the catalyst after heating at 1123 K (about 15 m^2/g) is in good agreement with the calculated value as above. The surface areas of the same catalysts after heating at a lower temperature (873

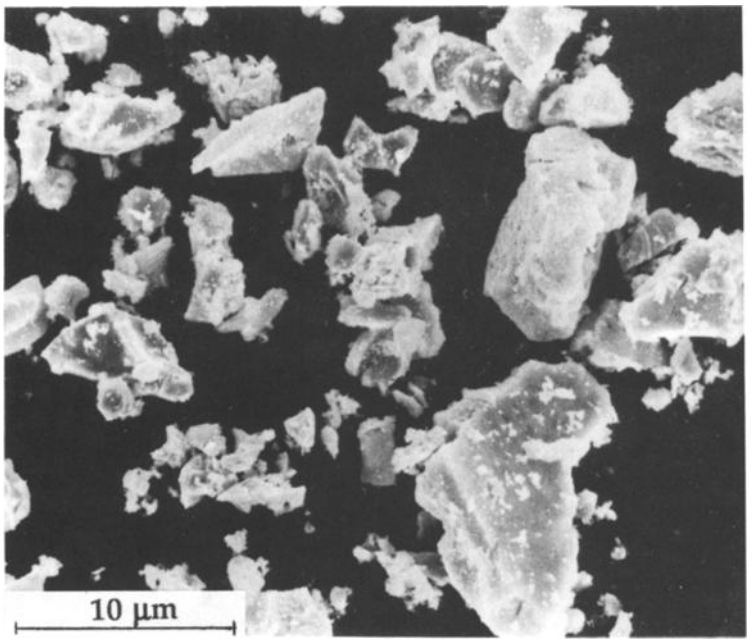

Fig. 3. Scanning electron micrograph (SEM) of $Ca_{0.8}Sr_{0.2}Ti_{0.8}Fe_{0.2}O_{3-\delta}$ after calcination at 1123 K.

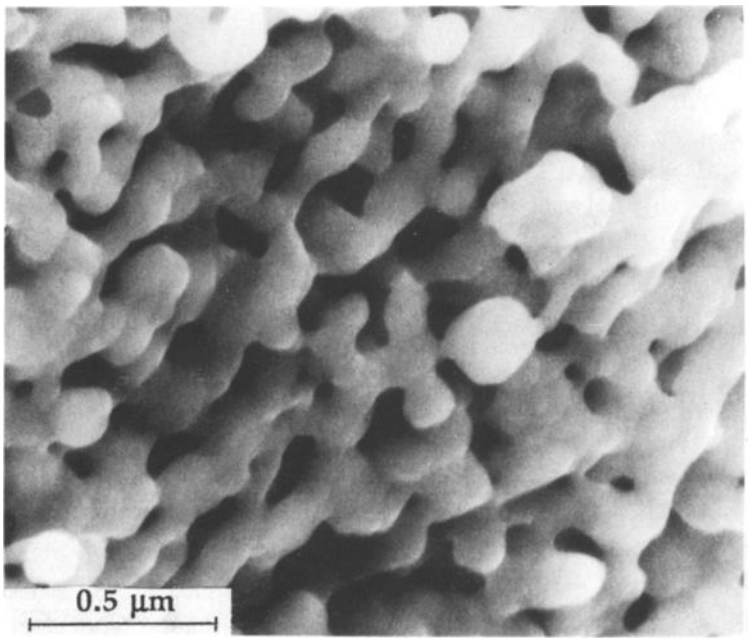

Fig. 4. Close up of one particle in fig. 3 showing the size of crystallites in the catalyst.

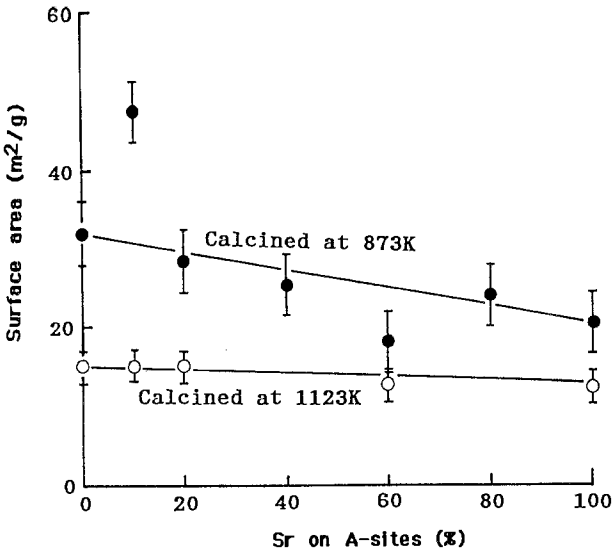

Fig. 5. Specific surface area for catalysts with the composition $Ca_{1-x}Sr_xTiO_3$ as a function of x. Results included are taken after calcination at 873 and 1123 K.

K) are also shown in fig. 5, revealing that these perovskites may be produced with a relatively high surface area when they are prepared at lower temperatures. The specific surface area of samples containing Fe was too small to be reproducibly measured on the available BET apparatus, but the data showed an area around 1 m^2/g, in agreement with the calculated value. The reason for the lower surface area of Fe-containing samples is that the mobility of ions and electrons increases rapidly when lower valent ions are introduced in the Ti lattice, thus diffusion and sintering is enhanced.

3.3. X-RAY DIFFRACTION ANALYSES OF THE CATALYST

X-ray diffraction studies were performed on catalyst samples freshly prepared and after testing in reaction mixtures of hydrocarbons and air. Just after the catalytic reaction, the reactor was removed from the furnace and quickly immersed in cold water with the reaction mixture still present in order to quench any phases present under catalytic operation. However, unless where specifically mentioned, none of the catalysts reported in this study showed reduction, phase separation or carbonate formation in the XRD studies.

In the series of materials $Ca_{1-x}Sr_xTiO_3$ calcined at 1123 K, a gradual change from the orthorhombic cell of $CaTiO_3$ to the cubic cell of $SrTiO_3$ was observed when Ca was replaced by Sr. All cell parameters followed monotonous, smooth curves as a function of composition x, showing that there is complete miscibility between the two perovskites at 1123 K. No lines were observed in addition to the

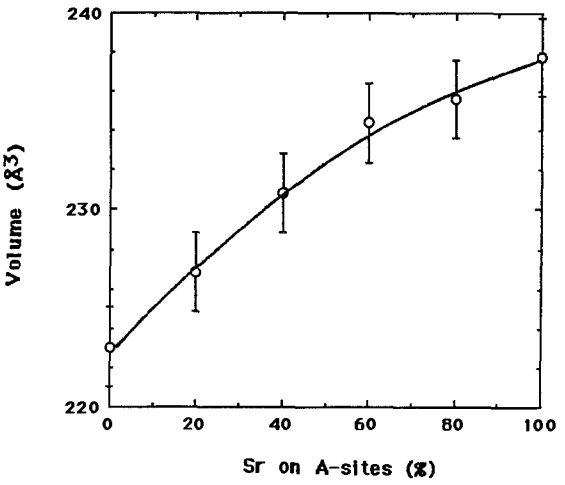

Fig. 6. Volume of four formula units of $Ca_{1-x}Sr_xTiO_3$ as a function of x after calcination at 1123 K.

perovskite reflexions. A similar study by Ceh et al. [7] at temperatures above 1573 K showed a small deviation from Vegards law. Our results confirm complete solubility at temperatures down to 1123 K, but we observed a larger deviation from Vegards law at this temperature (fig. 6).

In the series of $CaTi_{1-x}Fe_xO_{3-\delta}$, single phase diagrams were obtained for the samples with $x<0.6$. The sample with $x = 0.6$ contained a second phase even after repeated grinding and calcination. Thus, the limit of the solubility of Fe in the Ti lattice is likely to be around $x = 0.5$ at 1123 K. The same phenomenon has been observed at 1373–1673 K by Iwahara et al. [8], where a gradual transformation from the orthorhombic to the cubic cell was observed as Fe was dissolved in the Ti sites. This transformation did not occur under the present conditions. There were no significant changes in d values, and thus not in cell parameters either, in this series of materials as a function of composition. Iwahara et al. [8] measured the conductivity of oxide ions and electrons in $CaTi_{1-x}Fe_xO_{3-\delta}$. They found a maximum in the conductivity of oxygen ions around $x = 0.3$, and an increasing p-type conductivity with the amount of Fe in the structure, indicating that the presence of Fe^{4+} in the lattice introduce p-type conductivity in this material. The same authors also carried out experiments with Co and Ni, but the solubilities were low. In the present study, the sol–gel method gave a better precursor than the solid state method used by Iwahara et al., and a better solubility of Co was obtained. Ni, however, is hardly soluble in this perovskite.

In the series $SrTi_{1-x}Fe_xO_{3-\delta}$ a continuous solubility range was observed for $0 \leqslant x \leqslant 1$. The XRD patterns showed a cubic cell for all compositions, but the cell constant decreases with increasing x, as shown in fig. 7. The cell constant deviates from Vegards law; an observation also made by Clevenger [9] and Brixner [10]. The present study is in good agreement with the values given by the former

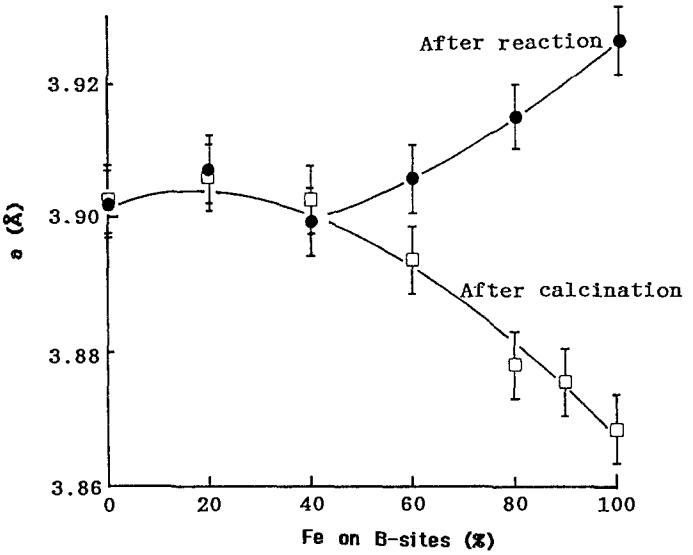

Fig. 7. Cubic cell parameter for $SrTi_{1-x}Fe_xO_{3-\delta}$ as a function of x after calcination in air and after catalytic testing in reducing atmospheres, respectively.

author. A maximum in the cell constant seems to be present at $x = 0.2$. Clevenger [9] has shown that for $0 < x < 0.2$ there is no Fe^{4+} in the lattice. Thus, the dissolution of Fe is probably charge compensated by vacancies in the oxygen lattice,

$$Fe_2O_3 = 2Fe'_{Ti} + 3O_O + V_{\ddot{O}} .$$

Oxygen vacancies introduce electrostatic repulsive forces between cations in the lattice, thus, the overall cell constant will increase. For $0.2 < x \leqslant 1.0$ the iron introduced in the lattice is partly Fe^{4+} (ionic radius 0.59 Å). This ion is smaller than Ti^{4+} (0.69 Å), and leads to the contraction of the cell parameter which dominates in fig. 7. A sharp increase in conductivity has been reported above $x = 0.2$, and these oxides are p-type conductors at high temperatures. The $SrFeO_{3-\delta}$ has been reported to have nearly metallic character for small values of δ [11]. After catalytic testing in reducing mixtures of hydrocarbons and air all catalysts still showed the cubic symmetry, but the cell constants had increased considerably as shown in fig. 7. This increase in cell parameter is related to the reduction of Fe^{4+} to Fe^{3+} and the introduction of oxygen vacancies in the lattice. Samples of $Ca_{1-x}Sr_xTi_{1-x}Fe_xO_{3-\delta}$ were studied in the range $0 \leqslant x \leqslant 1$, and all were single phase perovskites. The structure changed gradually from orthorhombic to cubic, as for $Ca_{1-x}Sr_xTiO_{3-\delta}$, and the impact of Fe on the cubic lattice parameter was observed as for $SrTi_{1-x}Fe_xO_{3-\delta}$.

Perovskites containing Co in the series $Ca_{1-x}Sr_xTi_{1-x}Co_xO_{3-\delta}$ were synthesized with $x = 0$, 0.2, 0.4, 0.6 and 1.0; the last sample did not yield any perovskite or single phase. $SrCoO_{3-\delta}$ may be produced along a different procedure [12], but accord-

ing to the same literature this material is not expected to be stable under catalytic reaction conditions. The sample with $x = 0.4$ needed repeated grinding and calcination to produce a single phase of perovskite. After catalytic testing, however, small amounts of CoO were observed in addition to the perovskite for $x = 0.6$, indicating a phase separation.

3.4. TGA AND DTA OF THE CATALYST

No particular weight loss or DTA signals were observed when heating $Ca_{1-x}Sr_xTiO_3$ in air or N_2. For $CaTi_{1-x}Fe_xO_{3-\delta}$ a weight loss (<0.1%) was observed for large x, and a minor DTA peak at 793 K for $x = 0.3$ was probably due to impurities. For $SrTi_{1-x}Fe_xO_{3-\delta}$ the weight loss was considerable at high iron contents. Fig. 8 shows the weight loss of $SrFeO_{3-\delta}$ upon heating in air and N_2. These observations are in fair agreement with the oxygen content at various temperatures reported by Takeda et al. [13]. The same authors have reported four phases of $SrFeO_{3-\delta}$, $0 < \delta < 0.5$, depending on the oxygen content. However, at temperatures above 673 K, the cubic structure exists in a continuous homogeneity range. In the present study, the cubic structure was observed both in fresh and tested samples, and no DTA peaks were detected upon heating. Indications of the phases reported by Takeda et al. could be reproduced, however, after cooling the sample slowly in N_2 (1 K/min). This procedure led to weak DTA signals at 553 and 663 K, in agreement with the reported phase transitions.

One sample of $SrFeO_{3-\delta}$ used for catalytic testing was studied by TGA in air at a constant temperature of 673 K. A weight increase of 1.6% was observed due to the filling of oxygen vacancies created during testing. According to Takeda et al., the composition in air at 673 K is $SrFeO_{2.77}$, thus, the sample after catalytic testing should be $SrFeO_{2.59}$. At 1073 K, where catalytic testing was terminated, this is

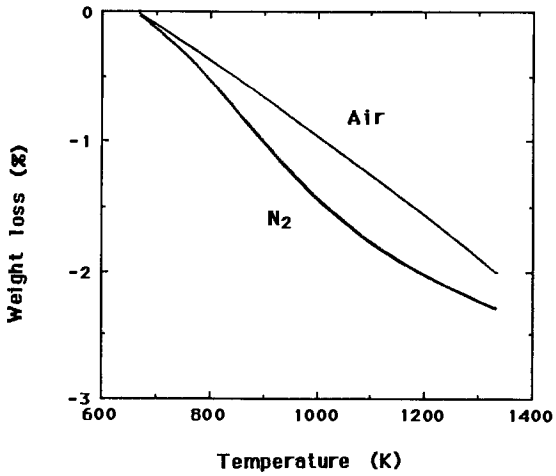

Fig. 8. Thermogravimetry of $SrFeO_{3-\delta}$ during heating (10 K/min) in N_2 and air.

inside the homogeneity range for the cubic phase. The composition in one atmosphere of air at 1073 K is $SrFeO_{2.63}$ [13]. Under such conditions the exchange of oxygen between the gas phase and the bulk of the catalyst should be favourable. No experiments of $Ca_{1-x}Sr_xFeO_{3-\delta}$ are included in this study, but Shin [14] has proved that the perovskite is stable with $0.8 \leqslant x \leqslant 1$ in reducing atmospheres and with $0.4 \leqslant x \leqslant 1$ in oxidizing atmospheres.

Iwahara et al. [8] were not able to dissolve large amounts of Co in $CaTiO_3$. In the present study, however, Sr seems to stabilize up to 60% Co in the lattice of $Ca_{1-x}Sr_xTi_{1-x}Co_xO_{3-\delta}$. However, a phase separation was observed after catalytic testing in reducing atmospheres. By TGA and DTA, a severe weight loss was observed above 1098 K in N_2 and above 1238 K in air. XRD of these samples after TG/DTA experiments confirmed the phase separation as observed after catalytic testing. Thus, the use of $Ca_{1-x}Sr_xTi_{1-x}Co_xO_{3-\delta}$ in reducing catalytic reaction conditions is limited to lower temperatures. Furthermore, the lack of solubility observed by Iwahara et al. [8] may be due to the high calcination temperature used in that study (1373–1673 K).

4. Conclusions

Several perovskites of formula $Ca_{1-x}Sr_xTi_{1-y}M_yO_{3-\delta}$ have been successfully synthesized at relatively low temperature by a modified Pechini method. The homogeneity ranges for $Ca_{1-x}Sr_xTiO_3$, $SrTi_{1-x}Fe_xO_{3-\delta}$ and $Ca_{1-x}Sr_xTi_{1-x}Fe_xO_{3-\delta}$ is 100%, while $CaTi_{1-x}Fe_xO_{3-\delta}$ exists with $x < 0.5$. Nickel and chromium cannot be dissolved on Ti sites in the perovskite, and Co may be dissolved to at least $x = 0.6$ with the present synthesis procedure, but undergo phase separation in reducing atmospheres at high temperatures. Compositions near $SrFeO_{3-\delta}$ are expected to show interesting features of conductivity for electron holes as well as oxygen ions, and easy exchange of oxygen between bulk and gas is expected.

Acknowledgement

The grant from Agency of Industrial Science and Technology, MITI, is highly acknowledged by AGA to do this work in NCLI.

References

[1] C.B. Choudhary, H.S. Maiti and E.C. Subbarao, in: *Solid Electrolytes and Their Applications*, ed. E.C. Subbarao (Plenum Press, New York, 1980) pp. 1–80.

[2] T. Hayakawa, T. Tsunoda, H. Orita, T. Kameyama, H. Takahashi, K. Takehira and K. Fukuda, J. Chem. Soc. Chem. Commun. (1986) 961;
T. Hayakawa, T. Tsunoda, H. Orita, T. Kameyama, M. Ueda, K. Fukuda and K. Takehira,

J. Chem. Soc. Chem. Commun. (1988) 1593;
T. Tsunoda, T. Hayakawa, Y. Imai, T. Kameyama, K. Takehira and K. Fukuda, Denki Kagaku 60 (1992) 212.
[3] H. Nagamoto, K. Amanuma, H. Nobutomo and H. Inoue, Chem. Lett. (1988) 237;
Y. Inoue, H. Sano and K. Sato, J. Mater. Sci. Lett. 8 (1989) 17;
Y. Xu, H. Lui, J. Huang, Z. Lin and X. Guo, *Proc. of the 3rd China–Japan Symp. on Coal and C1 Chemistry*, Kunming, Oct. 29–Nov. 1, 1990, p. 449.
[4] D.B. Meadowcroft, Nature 226 (1970) 847;
R.J.H. Voorhoeve, J.P. Remeika, P.E. Freeland and B.T. Matthias, Science 177 (1972) 353;
H.M. Zhang, Y. Shimizu, Y. Teraoka, N. Miura and N. Yamazoe, J. Catal. 121 (1990) 432.
[5] J.-L. Dubois and C.J. Cameron, Appl. Catal. 67 (1990) 49; Chem. Lett. (1991) 1089;
T. Norby and A.G. Andersen, Appl. Catal. 71 (1991) 89.
[6] M.P. Pechini, US Patent 3,330,697 (1967);
M.S.G. Baythoun and F.R. Sale, J. Mater. Sci. 17 (1982) 2757.
[7] M. Ceh, D. Kolar and L. Golic, J. Solid State Chem. 68 (1987) 68.
[8] H. Iwahara, T. Esaka and T. Mangahara, J. Appl. Electrochem. 18 (1988) 173.
[9] T.R. Clevenger Jr., J. Am. Ceram. Soc. 46 (1963) 207.
[10] L.H. Brixner, Mater. Res. Bull. 3 (1968) 299.
[11] J.B. MacChesney, R.C. Sherwood and J.F. Potter, J. Chem. Phys. 43 (1965) 1907.
[12] Y. Takeda, R. Kanno, T. Takada, O. Yamamoto, M. Takano and Y. Bando, Z. anorg. allg. Chem. 540/541 (1986) 259.
[13] Y. Takeda, K. Kanno, T. Takada, O. Yamamoto, M. Takano, N. Nakayama and Y. Bando, J. Solid State Chem. 63 (1986) 237.
[14] S. Shin, Mater. Res. Bull. 16 (1981) 299.