Oxidative coupling of methane over some titanates based perovskite oxides

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A series of perovskites of the formula $Ca_{1-x}Sr_xTi_{1-y}M_yO_{3-\delta}$ (M = Fe or Co, $x = 0$–1, $y = 0$–0.6 for Fe, $y = 0$–0.5 for Co) were prepared and tested as the catalyst for the oxidative coupling of methane. The catalysts were stable under the reaction conditions. The catalysts of high p-type and oxide ionic conductivity afforded the high selectivity. Some catalysts containing Co on B-sites are thermally unstable and decomposed to metal oxide components at high temperature, giving rise to synthesis gas production.

Keywords: Perovskites; oxidative coupling of methane; $CaTiO_3$ based catalysts; sol–gel method; p-type conductivity

1. Introduction

Oxidative coupling of methane (CH_4) is an attractive process for producing C_2 hydrocarbons, and there have been done many studies in this field since Keller and Bhasin first demonstrated this possibility [1,2]. It is generally accepted that the initial step in the catalytic oxidative coupling of CH_4 involves the homolytic cleavage of a C–H bond on the catalyst surface to form $CH_3\cdot$ radicals which may undergo coupling to form ethane in the gaseous phase [3]. The intermediate radicals and the products may undergo deep oxidation to carbon oxides in the presence of molecular oxygen. It has therefore been frequently proposed to use the cyclic

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operation by feeding CH_4 and oxygen alternatively over the catalyst interspaced by a short purge of inert gas [2] or to use an oxygen permeable membrane [4].

The present study was performed as part of a search for a catalyst for electrochemical conversion of light alkanes, using a zirconia solid electrolyte membrane reactor [5,6]. A catalyst for this purpose should be a material with mobility for both electrons and oxide ions, and chemical and mechanical stability should be maintained during preparation and operation of the reactor. Furthermore, the catalyst should be able to activate light alkanes. The material characteristics mentioned are found among some perovskites, and titanates are among the most stable compounds of this class. However, only a few papers [7,8] have dealt with successful use of perovskites such as $BaCeO_{3-\delta}$, $BaPb_{1-x}Bi_xO_{3-\delta}$ and $CaTiO_3$ in the oxidative coupling of CH_4, even though many perovskites based on $LaCoO_{3-\delta}$ or $LaMnO_{3-\delta}$ are well known to be active for deep oxidation of hydrocarbons [9]. A recent report by Xu et al. [7] showed that $Ca_{0.9}Sr_{0.1}TiO_3$ has reasonably high catalytic activity for oxidative coupling of CH_4 in a fixed bed reactor. The lifetime of the catalyst was tested for 500 h with no significant loss of activity and, moreover, analyses showed no change in the catalyst structure during this period. This is an important feature of an industrial catalyst. In this respect, too, perovskites may have interesting properties compared to the catalysts containing alkaline and alkaline earth metals which have been widely used for the oxidative coupling of CH_4.

We recently reported that some of $LaCoO_{3-\delta}$ based perovskites oxides with Ba and Fe on A- and B-sites, respectively, in the lattice are active for the oxidative coupling of CH_4 when the reaction was carried out by TPR method and cyclic operation [10]. A number of $CaTiO_3$ based perovskite oxides were prepared and characterized as the catalyst for partial oxidation of light hydrocarbons [11], some of which were found to be active for the oxidative dehydrogenation of ethane to ethene [12]: $CaTi_{1-y}Fe_yO_{3-\delta}$, with $0 \leqslant y \leqslant 0.4$, or $SrTi_{1-y}Fe_yO_{3-\delta}$, with $0 \leqslant y \leqslant 1.0$, were used and the latter catalysts containing more basic Sr metal showed higher selectivity to ethene than the former catalysts containing Ca. Here, we have carried out the oxidative coupling of CH_4 over the region of $Ca_{1-x}Sr_xTi_{1-y}M_yO_{3-\delta}$ with M: Fe and Co on Ti-sites in the lattice, which were clarified to possess perovskite crystal structure [11].

2. Experimental

The materials used in the present study have the general formula $Ca_{1-x}Sr_xTi_{1-y}M_yO_{3-\delta}$ with M: Fe ($y \leqslant 0.6$) and Co ($y \leqslant 0.5$) on Ti-sites in the lattice. The structure, homogeneity range and stability, as well as the synthesis of the materials have been reported separately [11]; all of these materials possess perovskite crystal structure. An important feature to be kept in mind in the following discussion, is that the surface area of the titanates without doping on B(Ti)-sites was around 15 m^2/g, while the surface of catalysts containing M: Fe and Co was well below 5 m^2/g.

All materials have been tested in a mixture of air (0.28 ℓ/h) and CH_4 (1.5 ℓ/h, from Takachiko Chemical Industry Co. Ltd.) in the oxidative coupling reaction. 300 mg catalyst was dispersed in 2 ml of quartz wool to avoid sintering and clogging of the reactor. The quartz reactor used was U-shaped, with the catalyst bed near the bottom. The inner diameter of the inlet tube was 10 mm and the outlet was 4 mm. Above and below the catalyst bed the reactor was filled with quartz sand. The thermocouple was introduced from the top of the reactor, and placed in the middle of the catalyst bed. 0.5 ml of the product gases were sampled immediately after the reactor and injected into a gas chromatograph for analysis.

The catalytic tests in this study were performed on $Ca_{1-x}Sr_xTi_{1-y}Fe_yO_{3-\delta}$ samples that were previously used for oxidative dehydrogenation of ethane; the procedure and results of the experiments on ethane are given separately [12]. The results from these samples showed no difference from fresh samples heated directly for the oxidation of CH_4. Before the oxidation studies, the catalysts were calcined in an air stream in the reactor for 1 h at 973 K. The reactor was flushed with N_2 before introducing the reactants. No change in product distribution was observed after 15 min on line. All samples in the following are taken 15 min or more after establishing steady state of the reaction. The temperature was further elevated to 1023 and 1073 K for each catalyst. Finally, the whole reactor was quickly removed from the furnace with the reacting gases present, and quenched in cold water in order to preserve any phases stable only under reaction conditions.

Characterization of the catalyst was carried out as follows: the powder X-ray diffraction (XRD) diagrams were recorded by using MXP-18 (MAC Science Co.) with Cu Kα radiation. Thermal analyses (TGA/DTA) were carried out by using Shimadzu TGA 50 and DTA 50 containing electrobalance. Diffuse reflectance infrared spectra were recorded by using a JASCO FT/IR 7000 spectrometer.

3. Results and discussion

As a preliminary experiment, the reactor was filled with quartz sand and quartz wool, i.e. without catalyst, and was tested with the same gas mixture as used in the catalytic reactions. The oxygen conversion stayed below 10% even at the highest reaction temperature, while the oxygen conversion was always above 90% in catalytic tests. CH_4 conversion stayed below 1% in the quartz filled reactor where the main product was ethane ($>50\%$). The similar test on ethane showed some thermal activity above 973 K [12]; this is probably due to the lower activation energy for the ethane molecule.

3.1. OXIDATION OVER $Ca_{1-x}Sr_xTiO_3$

In the composition range between $CaTiO_3$ and $SrTiO_3$ in a flow of CH_4 (1.5 ℓ/h) and air (0.28 ℓ/h), the CH_4 conversion increased with temperature (973–1073 K) and Sr content. Typical values at 1073 K were 3.9% for $CaTiO_3$, 4.4% for $Ca_{0.9}Sr_{0.1}TiO_3$ and 4.7% for $SrTiO_3$. The measured oxygen conversion was above 95% in the whole range. The selectivities to C_2 compounds over the three catalysts were 2–10% and gradually increased with temperature and Sr content. The selectivities to CO and CO_2 were 10–50 and 40–90%, respectively, and $SrTiO_3$ alone showed a higher CO selectivity and a lower CO_2 selectivity compared to the other samples.

The results obtained above cannot be compared well to the study by Xu [7], even though the catalysts have been prepared by similar procedures and the temperature is the same. Xu obtained ethane and ethene selectivities of 21.6 and 33.7%, respectively, even with a lower methane/oxygen ratio (2.5 : 1) over $Ca_{0.9}Sr_{0.1}TiO_3$. Their CO_2 selectivity was 36.8%, compared to our value 75% over the same catalyst at 1023 K. The reason for this discrepancy is not clear. There was thus observed a fairly favourable effect of a high Sr content in the $Ca_{1-x}Sr_xTiO_3$ perovskite for the oxidative coupling of CH_4.

3.2. OXIDATION OVER $CaTi_{1-y}Fe_yO_{3-\delta}$

Catalytic features of materials with Fe substituted into B-sites of $CaTiO_3$, $CaTi_{1-y}Fe_yO_{3-\delta}$ ($y = 0$–0.4), were tested at the temperatures 973–1073 K. The oxygen conversion was measured to be above 95% for all the reactions. There was observed an increase in the CH_4 conversion with temperature, and an intermediate Fe content ($y = 0.3$) afforded the highest conversion of 8% at 1073 K. The selectivities to C_2 compounds increased monotonously with the Fe content and reached 20% at $y = 0.4$. The selectivities to CO and CO_2 showed a complex dependency on the composition (fig. 1). The CO_2 production decreased, while CO increased, with temperature. 5–20 and 50–90% were obtained for CO and CO_2 selectivities, respectively, with both $y = 0$ and 0.4, while both the selectivities largely changed with $y = 0.3$; CO increased from 6 to 65% and CO_2 decreased from 80 to 20% when increasing temperature from 973 to 1073 K. A substantial amount of CO suggests a synthesis gas production from CH_4 over $CaTi_{0.7}Fe_{0.3}O_{3-\delta}$ catalyst at 1073 K.

The p-type and oxide ionic conductivity calculated from a study by Iwahara et al. [13] has been previously reported [12]. p-type conductivity increases monotonously with Fe-content and temperature, while the mobility of oxide ions is the highest for intermediate compositions. The dependence of the oxidative coupling of CH_4 on p-type conductivity, as suggested by Dubois and Cameron [4], is clearly reflected in the product distribution in the present work. In our previous study on oxidative dehydrogenation of ethane [12], a similar dependence could not be seen. Thus, it seems likely that the primary reaction of ethane formation, and not the secondary dehydrogenation is dependent on p-type conductivity.

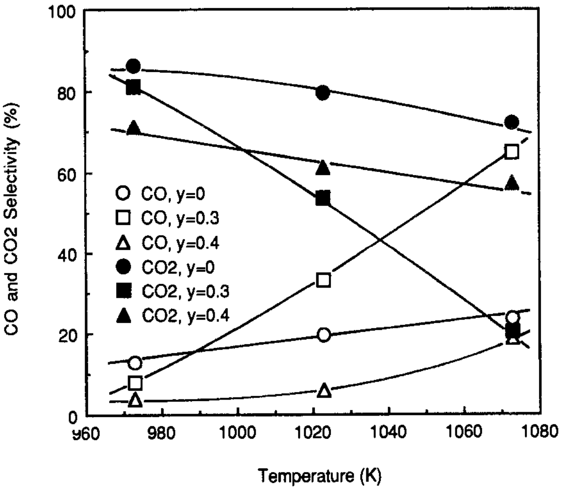

Fig. 1. Selectivity to CO and CO_2 as a function of temperature in a flow of CH_4 (1.5 ℓ/h) and air (0.28 ℓ/h) over various catalysts of formula $CaTi_{1-y}Fe_yO_{3-\delta}$.

The catalysts used above were studied by diffuse reflectance infrared spectroscopy before and after catalytic testing. None of the materials in the series $CaTi_{1-y}Fe_yO_{3-\delta}$ showed any change in XRD patterns during catalytic testing, but IR revealed changes in the surface. For intermediate Fe contents, an "IR-black" surface was seen after catalytic reactions. Carbonate band at 1450 cm^{-1} was also seen at the maximum at intermediate Fe contents. $CaTiO_3$ showed no carbonate band. The details and examples of spectra are given in the previous paper [12]. The presence of surface carbonate species has been suggested by Dubois and Cameron to be beneficial for the oxidative coupling of CH_4 [14]. In the present study, the absence of a carbonate band on $CaTiO_3$ is followed by the lowest C_2 selectivity in this series. However, there is no relationship between the magnitude of the carbonate band and the selectivity of the catalyst.

3.3. OXIDATION OVER $SrTi_{1-y}Fe_yO_{3-\delta}$

The conversions of O_2 and CH_4 over $SrTi_{1-y}Fe_yO_{3-\delta}$ catalysts stayed above 90 and at 5%, respectively, at all temperatures (973–1073 K). The selectivities to ethane and ethene in various compositions of the catalyst of $SrTi_{1-y}Fe_yO_{3-\delta}$ are shown in figs. 2 and 3, respectively. The former decreased, while the latter increased, with increasing temperature. This shows that ethane can be dehydrogenated to ethene at high temperature. Generally, the C_2 selectivities in total increased monotonously with the Fe content in the catalyst and reached 55% with $y = 1.0$. The selectivities to CO and CO_2 are shown in figs. 4 and 5, respectively. $SrTiO_3$ gave selectivities to CO and CO_2 which are independent of temperature. For the samples containing Fe the CO selectivity increased with temperature, while the CO_2 selectivity showed an inverse behavior. With $y = 0.2$ in $SrTi_{1-y}Fe_yO_{3-\delta}$

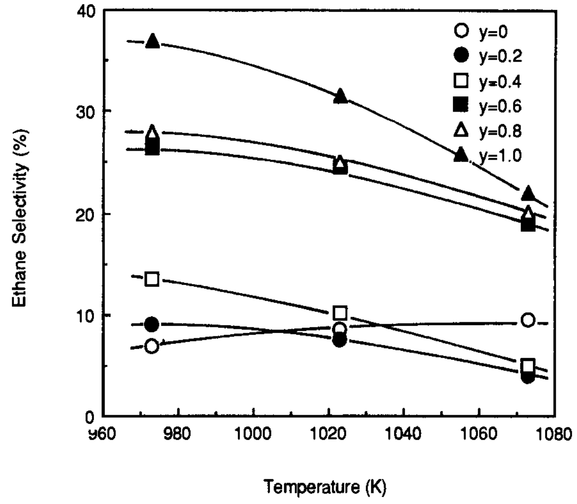

Fig. 2. Selectivity to ethane as a function of temperature in a flow of CH_4 (1.5 ℓ/h) and air (0.28 ℓ/h) over various catalysts of formula $SrTi_{1-y}Fe_yO_{3-\delta}$.

at 1073 K, very high selectivity to CO was observed together with low selectivity to CO_2. This suggests an occurring of synthesis gas production from CH_4 over the catalyst with $y = 0.2$ at high temperature.

To the knowledge of these authors, no study that can separate the various types of conductivities at elevated temperature has been published for the system $SrTi_{1-y}Fe_yO_{3-\delta}$. In the composition range $0 \leqslant y \leqslant 0.2$, Clevenger [15] found no Fe^{4+} ions in the lattice. Thus, the iron is probably compensated by oxygen vacancies, giving rise to increased oxide ionic conductivity in this range. For $0.2 < y \leqslant 1.0$, this

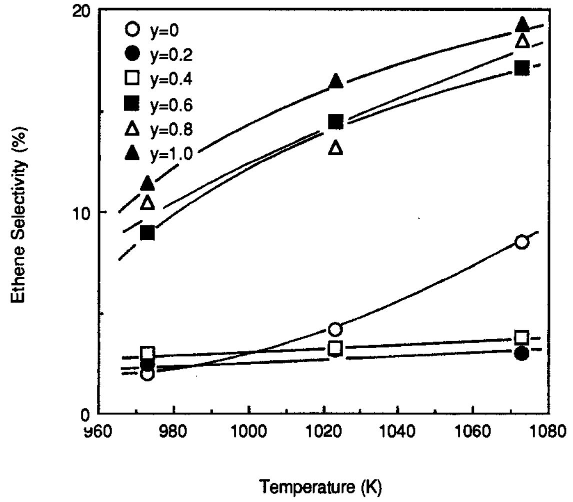

Fig. 3. Selectivity to ethene as a function of temperature in a flow of CH_4 (1.5 ℓ/h) and air (0.28 ℓ/h) over various catalysts of formula $SrTi_{1-y}Fe_yO_{3-\delta}$.

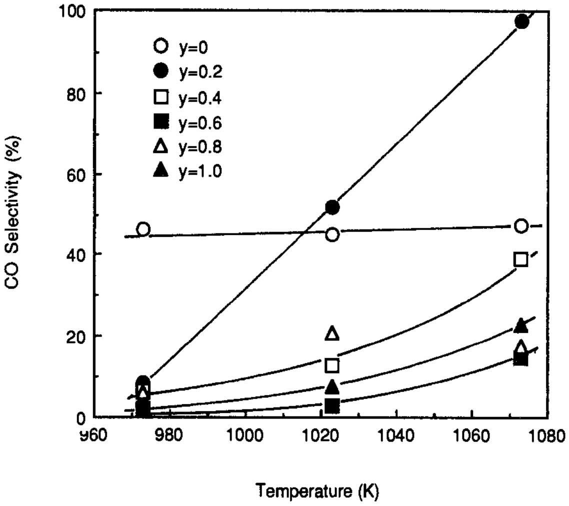

Fig. 4. Selectivity to CO as a function of temperature in a flow of CH_4 (1.5 ℓ/h) and air (0.28 ℓ/h) over various catalysts of formula $SrTi_{1-y}Fe_yO_{3-\delta}$.

oxide should still be a fairly good conductor for oxide ions, but p-type conductivity is dominating, and it is probably monotonously increasing with y and temperature [12,13,15]. If there is no conclusive evidence, one may indicate that in the region of low Fe content and temperatures above 973 K the C_2 selectivity decreases with oxide ionic conductivity. In the presence of hypervalent Fe^{4+} ions, the C_2 selectivity increases with the dopant level, and thus also with p-type conductivity. This is another example to support the suggestions of Dubois and Cameron [14] on the beneficial effect of p-type conductivity for the oxidative coupling of CH_4. The

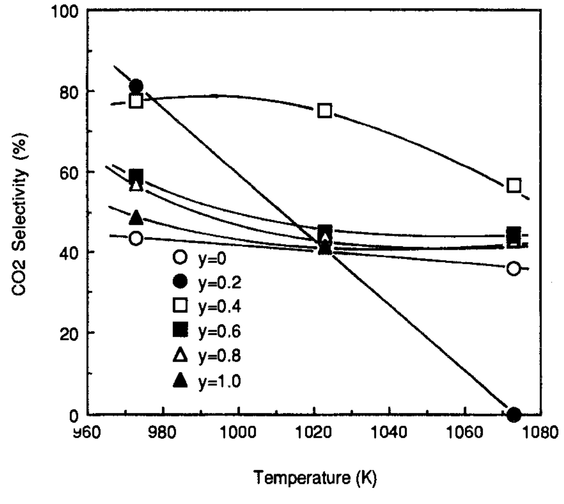

Fig. 5. Selectivity to CO_2 as a function of temperature in a flow of CH_4 (1.5 ℓ/h) and air (0.28 ℓ/h) over various catalysts of formula $SrTi_{1-y}Fe_yO_{3-\delta}$.

details about IR spectra before and after catalytic testing have been reported elsewhere [12]. In relation to the studies of Dubois and Cameron [14], it should just be noted that the presence of carbonate species on the surface was observed on all catalysts containing Fe. For $SrTiO_3$, the carbonate band could hardly be seen.

To localize the optimum reaction conditions for using $SrFeO_{3-\delta}$ which showed the highest selectivity to the C_2 compounds, a set of experiments on this catalyst was performed at variable temperatures and gas mixtures; the total gas flow was kept constant. Fig. 6 shows the conversions and selectivities for this catalyst at various temperatures. There seems to be a maximum in C_2 yield around 998 K, and the gas composition was varied at this temperature. The results of various gas mixtures at 998 K are shown in fig. 7. There might be a small decreasing in oxygen conversion in gas mixtures with the low CH_4/air ratio; otherwise this conversion was constant. The CH_4 conversion increased rapidly in the low CH_4/air ratio; the same was the fact for the CO_2 selectivity. CO selectivity was low for all mixtures, and C_2 selectivity increased with CH_4 content. The maximum C_2 yield under the conditions tested was 4.8% at a CH_4/air ratio of 1.7 at 998 K. The maximum yield under similar experiments on $SrTiO_3$ was 1.4% at 1073 K and CH_4/air ratio of 1.6; $SrTi_{0.4}Fe_{0.6}O_{3-\delta}$ gave a C_2 yield of 4.7% at 1023 K and a CH_4/air ratio of 1.7.

3.4. OXIDATION OVER $Ca_{1-x}Sr_xTi_{1-y}Co_yO_{3-\delta}$

$Ca_{1-x}Sr_xTi_{1-y}Co_yO_{3-\delta}$ catalysts containing Co on B-sites were tested; conversions and selectivities over $Ca_{0.4}Sr_{0.6}Ti_{0.4}Co_{0.6}O_{3-\delta}$ are shown in fig. 8. Oxygen conversion was high at all temperatures; CH_4 conversion increased with temperature. At 973 K, the CO_2 selectivity was 76%; at higher temperatures the CO selectivity was more than 90%. Substantial production of hydrogen was observed in GC analysis.

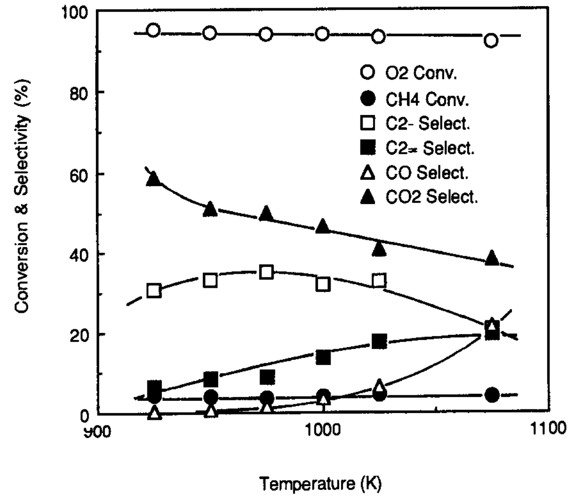

Fig. 6. Conversions and selectivities as a function of temperature in a flow of CH_4 (1.5 ℓ/h) and air (0.28 ℓ/h) over $SrFeO_{3-\delta}$.

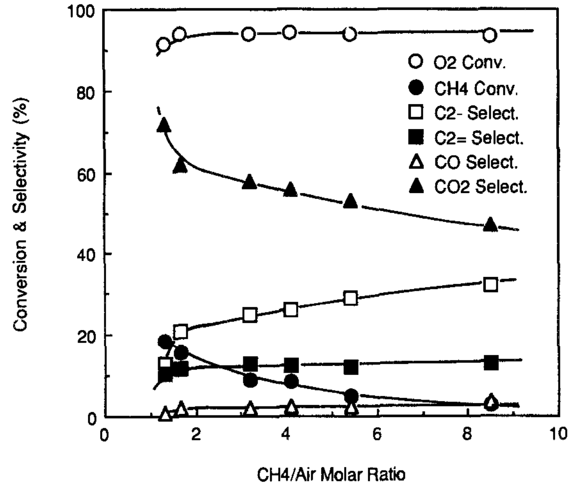

Fig. 7. Conversions and selectivities as a function of the CH_4/air ratio in a gas flow of 1.78 ℓ/h over $SrFeO_{3-\delta}$ at 998 K.

The features of this material as a partial oxidation catalyst from ethane to synthesis gas has been discussed in the previous paper [12]. Synthesis gas production started at 950 K in ethane and at 980 K in CH_4; this is probably due to the lower activation energy for the ethane molecule. A similar catalyst with 20% Co on B-sites showed the transition to synthesis gas production in CH_4 at 1050 K. The characterization of catalysts containing Co was reported previously [12], indicating that the change in catalytic activity is a consequence of phase transformations and decompositions in the catalyst.

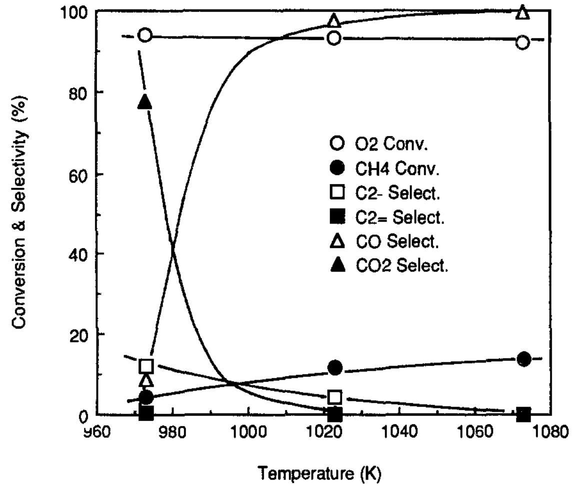

Fig. 8. Conversions and selectivities as a function of temperature in a flow of CH_4 (1.5 ℓ/h) and air (0.28 ℓ/h) over $Ca_{0.4}Sr_{0.6}Ti_{0.4}Co_{0.6}O_{3-\delta}$.

4. Conclusion

Calcium titanate based catalysts containing Sr and Fe on A(Ca)- and B(Ti)-sites, respectively, showed interesting properties for the oxidative coupling of CH_4. The catalyst is stable under the reaction conditions. The catalyst of high p-type and oxide ionic conductivity afforded the high activity for this oxidation. Some catalysts containing Co on B-sites are thermally unstable and decomposed to metal oxide components at high temperature, giving rise to synthesis gas formation.

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