Catalysis Letters 58 (1999) 217–223

Influence of electronic properties of Na_2O/CaO catalysts on their catalytic characteristics for the oxidative coupling of methane

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Received 7 December 1998; accepted 3 March 1999

For Na_2O/CaO catalysts of different sodium content the adsorption of oxygen and their electrical properties were studied by transient experiments and measurements of contact potential differences (CPD) as well as electrical conductivity. CPD results show a change of the mechanism of oxygen activation with increasing sodium concentration due to changing the type of ionic conductivity from cationic to anionic. Anion vacancies are formed by incorporation of sodium into the CaO lattice. As CPDs show, the cation conductivity promotes an accumulation of oxygen species on the catalyst surface resulting in a decrease of C_2 product selectivity for the catalyzed oxidative coupling of methane. The anion conductivity favors a dissociation of molecular adsorbed oxygen and a subsequent incorporation into the oxide lattice, hereby, decreasing its concentration on the catalyst surface which favors in term selective formation of ethane and ethylene.

Keywords: oxidative coupling of methane, work function as mean of catalyst-surface characterization, electrical conductivity of Na_2O-doped calcium oxide

1. Introduction

The first successful works [1–3] on the production of higher hydrocarbons from methane were carried out during the earlier 1980s. Achievements in this field of catalytic chemistry have been demonstrated in a number of reviews [4–7] on the subject. The main demerit of such process scheme is the fact that conversion and selectivity result in C_2 (ethane and ethylene) yield of generally $<25\%$. Usually, this limitation is attributed to undesired carbon oxides formation by either homogeneous phase reactions or heterogeneous catalytic processes. The concomitant gas-phase reactions can be potentially quenched [8,9]. As shown in many works [3,7,10–16], the active oxygen species and structural defects of OCM catalysts play an important role in the heterogeneous reactions. It has been reported that the OCM reaction medium influences the defect structure of the catalysts which determines the selective course of the reaction [17,18]. In addition, many selective catalysts possess a high mobility of lattice oxygen anions that is proposed to be important for formation of selective oxygen species [6,16,19,20]. Besides anion conductivity the selective catalysts exhibit p-conductivity, which results in the formation of negatively charged oxygen species [21]. Thus, it is obvious that the defect structure of catalysts and the type of active oxygen species may be a key-feature in the selective oxidation of methane to C_2 hydrocarbons.

Previously [22] we have shown that contact potential differences (CPD) between the catalyst studied and a reference gold electrode can be used to assess differences in the extent of oxygen adsorption and incorporation into the lattice of pure and SrO-doped Nd_2O_3. The aim of the present work is to compare the adsorption process of oxygen on Na_2O/CaO catalysts of different sodium concentration and to understand the favorable effect of sodium on C_2 selectivity in OCM. For this purpose the CPD was measured. This technique provides also information about the nature of the negatively charged oxygen species adsorbed on the catalyst surface. These results are correlated with catalytic performances, electrical conductivity and O_2 adsorption as determined by transient experiments using a temporal analysis of products (TAP) reactor. The catalysts were chosen since they are active and selective for OCM and their catalytic properties depend on sodium concentration [11,12,23–25].

2. Experimental

2.1. Catalyst preparation

Na_2O/CaO catalysts were prepared from $CaCO_3$ and $NaHCO_3$ of high purity. $CaCO_3$ was calcined at 1273 K for 10 h to decompose carbonates. After calcination the calcium oxide was impregnated with an aqueous solution of $NaHCO_3$ followed by drying at 400 K for 2 h and calcination at 1273 K for 2 h. After calcination the actual sodium concentration was determined by ICP-OES (inductively coupled plasma optical emission spectroscopy). The concentration of sodium is put inside brackets in the catalyst formula: Na(0.001 at%)/CaO, Na(1.2 at%)/CaO and Na(6.4 at%)/CaO.

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The BET surface areas of the catalysts amounted to 6.3 m^2/g for Na(0.001 at%)/CaO, 2.9 m^2/g for Na(1.2 at%)/CaO and 2 m^2/g for Na(6.4 at%)/CaO.

2.2. CPD measurements

The contact potential difference between the samples and a reference gold electrode was measured by applying the vibrating condenser method. Details of the apparatus have been reported elsewhere [22]. A catalyst disk with a diameter of 7 mm and a thickness of ca. 0.4–0.5 mm was placed on the measuring electrode in a vacuum chamber connected to a gas-supply system controlling the partial pressure of oxygen. The interaction of oxygen with the catalyst sample was studied in the temperature range of 623–723 K applying oxygen partial pressure between 2.5×10^{-4} and 5×10^{-3} Pa. Information on the charge of surface oxygen species may be derived according to Barbaux et at. [27] in a metal-oxide/oxygen system from equation (1):

$$\mathrm{CPD} = \frac{kT}{ae}\ln(p_{\mathrm{O_2}}) + \mathrm{const.} \tag{1}$$

The slope of a straight line obtained by plotting CPD versus $\ln(p_{\mathrm{O_2}})$ at constant temperature gives the a value. This value shows the type of the adsorbed oxygen species:

$$a = 1 \quad \mathrm{O_2 + e \leftrightarrow O_2^-} \tag{2}$$

$$a = 2 \quad \mathrm{O_2 + 2e \leftrightarrow 2O^-} \tag{3}$$

$$a = 2 \quad \mathrm{O_2 + 2e \leftrightarrow O_2^{2-}} \tag{4}$$

$$a = 4 \quad \mathrm{O_2 + 4e \leftrightarrow 2O^{2-}} \tag{5}$$

2.3. Electrical conductivity

The total conductivity of the catalysts studied at 673–1023 K was determined using the ac method with two platinum electrodes [28], between which the catalyst sample was placed. As an equivalent circuit a parallel connection of a condenser and an ohmic resistance was applied [29]. The catalyst sample has been pressed to a disk of 7 mm diameter and of ca. 1 mm thickness. To minimize contact resistance the catalyst disc was covered by a platinum paste on each side and was then treated in air oxygen for 30 min at 1023 K. To separate the various types of conductivities (p-type, n-type and ion type), the total conductivity was measured at different oxygen partial pressures (0.5–30 kPa). The relation of these three different types of conductivities with respect to oxygen partial pressures can be derived from equation (6) [28]:

$$n = \left(\frac{\partial \ln(\sigma)}{\partial p_{\mathrm{O_2}}}\right)_{T=\mathrm{const}}; \tag{6}$$

$n = 1/4$ for p-type, $n = -1/4$ for n-type and $n = 0$ for ion type.

2.4. Catalytic testing

The catalytic tests were carried out in a fixed-bed reactor made of quartz. The reactor was immersed into a fluidized sand bed serving as a source or sink of heat. The reactant gas stream consisted of 2–15 vol% oxygen and 30 vol% methane in nitrogen. The total flow rate was fixed at 60 cm^3/min and the reaction temperature range was 973–1023 K. For comparison of selectivities at similar degrees of methane conversion, the tests were performed with different amounts of catalyst from 0.03 to 0.140 g. The methane conversion data for all the catalytic runs are presented in table 1. The products and reagents were analyzed by using a micro gas chromatograph (Chrompack CP-2002) equipped with Poraplot Q and Molsiev 5 columns.

2.5. TAP measurements

The set-up of the TAP-2 reactor system has been described in detail elsewhere [13]. The catalyst (100 mg, particle size 250–355 μm) was packed between two layers of quartz of the same particle size in the fixed-bed reactor made of Inconel. Before each experiment the catalyst was treated by an O_2 flow (30 ml/min) at 823 K for ca. 1 h. Then, the reactor was evacuated at 873 K to 10^{-4} Pa for 20 min. After the vacuum treatment the temperature of the catalyst was set to the desired temperature (623–873 K). Subsequently, the reaction mixture ($\mathrm{O_2 : Ne} = 1:1$) was pulsed over the catalysts. The TAP measurements consisted of two series of multi-pulse experiments, each at constant temperature. The number of pulses in one series was varied from 50 to 100. After the first series of pulses the catalyst was kept under vacuum condition for 10 min and in the second series the reaction gas mixture was pulsed again over the catalyst to examine whether the adsorbed oxygen of the first series was desorbing.

Table 1
Methane conversion depending on initial oxygen partial pressure and temperature (initial concentration of methane is 30 vol%).

Catalyst	2 vol%			5 vol%			15 vol%		
	1023 K	998 K	973 K	1023 K	998 K	973 K	1023 K	998 K	973 K
Na(0.001 at%)/CaO	10	8	6.5	13	10	9	14	12	8
Na(1.2 at%)/CaO	10.5	8.5	6.5	11	7	6	12	10	7
Na(6.4 at%)/CaO	8	7.5	4	12	10	7.5	11	8	5

Table 2
Selectivity of formation of OCM products over Na_2O/CaO catalysts at various temperatures and oxygen concentrations. Concentration of methane is constant (30 vol%) for all tests.

T (K)	Na(0.001 at%)/CaO			Na(1.2 at%)/CaO			Na(6.4 at%)/CaO		
	C_2	CO	CO_2	C_2	CO	CO_2	C_2	CO	CO_2
Concentration of oxygen 2 vol%									
973	52.9	25.1	22.0	60.2	14.4	25.4	70.3	3.5	26.2
998	60.0	21.5	18.5	68.3	11.2	20.5	77.2	3.2	19.6
1032	65.8	17.2	17.0	74.3	7.6	18.1	81.1	3.5	15.4
Concentration of oxygen 5 vol%									
973	33.8	34.7	31.5	53.5	6.1	40.4	53	9.8	37.2
998	43.5	28.1	28.4	60.5	4.2	35.3	63.4	6.9	29.7
1032	50.4	23.3	26.3	65.4	4.1	30.5	70.8	5.0	24.2
Concentration of oxygen 15 vol%									
973	13.7	6.1	80.2	19.7	7.5	72.8	30.2	6.7	63.1
998	20.3	10.6	69.1	28.2	7.2	64.6	41.5	5.7	52.8
1032	25.8	14.9	59.3	33.8	7.6	58.6	49.5	5.1	45.4

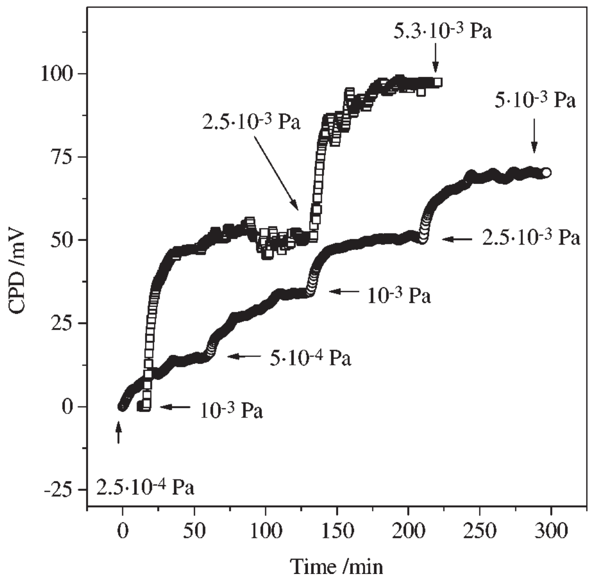

Figure 1. Contact potential difference (CPD) as a function of time (t) for Na(1.2 at%)/CaO (○) at 673 K and for Na(6.4 at%)/CaO (☐) at 723 K after change of oxygen partial pressure.

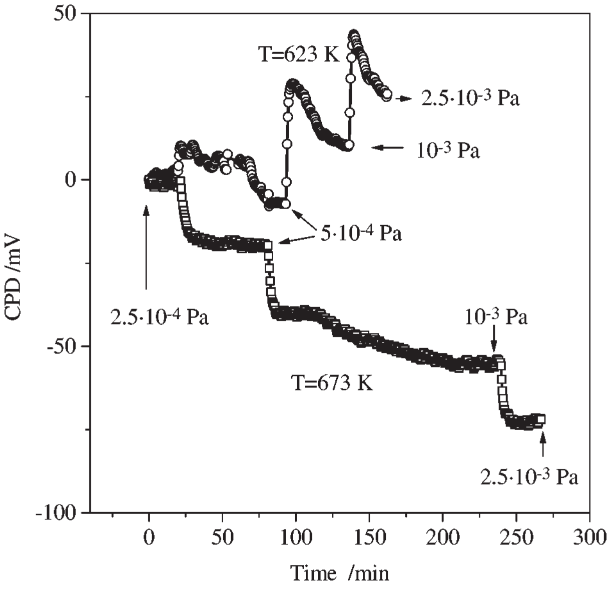

Figure 2. Contact potential difference (CPD) as a function of time (t) for Na(0.001 at%)/CaO after change of oxygen partial pressure at different temperatures: (○) $T = 623$ K, (☐) $T = 673$ K.

3. Results and discussion

3.1. Catalytic properties

The catalytic data are presented in table 2. Selectivity of C_2 products (ethane + ethylene) increases with increasing sodium concentration, temperature and decreasing oxygen partial pressure at constant partial pressure of methane. The results obtained agree well with earlier results published elsewhere [11,12,23–26,30,31]. The promoting effect of the alkali promoter was ascribed to dissociation of molecular adsorbed oxygen on the structural defects [12]. To substantiate this earlier assumption, the CPD of Na_2O/CaO with respect to a gold electrode was measured; the results are presented below.

3.2. Contact potential difference

The dependence of CPD on oxygen partial pressure for all the catalysts tested at different temperatures is presented in figures 1 and 2. Based on these results, the catalysts studied can be devided into two groups that differ by their properties:

Group I – Na(1.2 at%)/CaO and Na(6.4 at%)/CaO. An increase of oxygen partial pressure leads to an increase of CPD as a function of time and, finally, the CPD reaches a constant value (figure 1).

Group II – Na(0.001 at%)/CaO. An increase of oxygen pressure at 350 °C (upper part of figure 2) results in an increase and then a decrease of CPD with time. At high temperature CPD decreases if partial pressure of oxygen increases (low part of figure 2).

Table 3
Coefficient a for Na(1.2 at%)/CaO and Na(6.4 at%)/CaO at different temperatures.

T (K)	Na(1.2 at%)/CaO	Na(6.4 at%)/CaO
623	1.4 ± 0.2	
673	2.4 ± 0.1	1.76 ± 0.1
723	4.7 ± 0.2	1.64 ± 0.1

For group I catalysts, an increase of CPD with the growth of oxygen partial pressure means formation of negatively charged oxygen species due to adsorption of oxygen and stabilization of these species on a catalyst surface. From equation (1) information on the charge of surface oxygen species can be derived according to Barbaux [27] and by the a values which are listed in table 3 for the catalysts of group I. The values increase from 1.4 ± 0.2 to 4.7 ± 0.23 with temperature for Na(1.2 at%)/CaO. This pattern can be interpreted in such a way that adsorbed oxygen is transformed from O_2^- to O^{2-}. Such a change of a with increasing temperature was also observed by Cherrak et al. [32] on pure Sm_2O_3 and by Gayko et al. [22] on SrO-doped Nd_2O_3. For Na(6.4 at%)/CaO, a becomes practically constant over 400–450 °C temperature region and equals 1.76. This value indicates the presence of either atomic single-charged species (O^-) or molecular double-charged species (O_2^{2-}) as the dominant.

For group II catalyst the time dependence of CPD during increasing oxygen pressure (figure 2) may be interpreted in the term of a slow ionic transport in the oxide lattice. When an interaction between a lattice oxide and gas phase takes place then the surface charge caused by oxygen adsorption decreases as a result of oxygen incorporation and accompanying propagation of the surface charge into the deeper lattice layers leading to decreasing CPD (figure 2). The oxygen incorporation may be considered either as a diffusion of cation vacancies into the lattice (in the case of cation-deficient oxides) or an outward diffusion of anion vacancies (in the case of anion-deficient oxides).

Thus, the results of CPD studies show that the addition of an alkali promoter, i.e., sodium oxide, into the CaO lattice influences both the mechanism of oxygen adsorption and the type of oxygen associated with the catalysts.

To further elucidate the differences between two groups of catalysts the total conductivity of the catalysts was studied giving information on the type and a value of both ionic and p-conductivity.

3.3. Conductivity

The Arrhenius dependence of σ at a partial pressure of 10 kPa O_2 is presented in figure 3. The total conductivity of all catalysts studied increases with increasing sodium concentration and temperature. This dependence is different in the low (673–773 K) and high (773–1023 K) temperature ranges resulting in two different apparent activation energies.

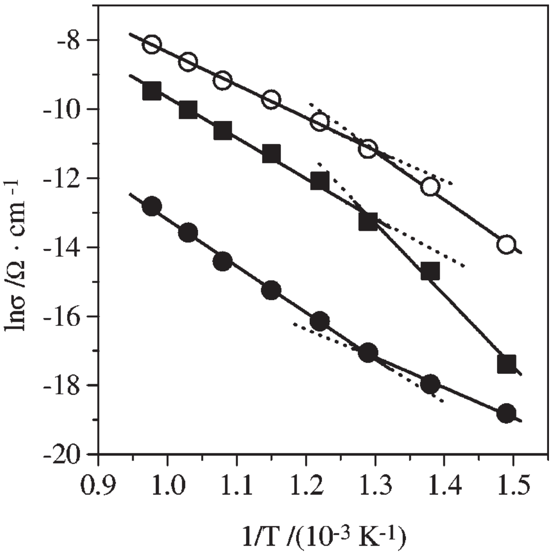

Figure 3. Arrhenius plot of total electrical conductivity for different catalysts: (○) Na(6.4 at%)/CaO, (■) Na(1.2 at%)/CaO, (●) Na(0.001 at%)/CaO.

Table 4
Exponent n for Na(0.001 at%)/CaO, Na(1.2 at%)/CaO and Na(6.4 at%)/CaO catalysts at different temperatures.

Catalyst	T (K)					
	723	823	873	923	973	1023
Na(0.001 at%)/CaO	79.4	33.6	11.7	10.6	9	8.2
Na(1.2 at%)/CaO	4.2	10.3	14.8	14.6	17	20.3
Na(6.4 at%)/CaO	4.2	6.5	6	6.2	7.5	11.8

Oxygen pressure was varied between 10^{-3} Pa and 30 kPa over a temperature range from 673 to 1023 K. As mentioned above the dependence of total conductivity on oxygen partial pressure can be characterized by the exponent n (equation (4)) that indicates the type of conductivity. For all catalysts, the total conductivity increases with partial pressure from 2 to 30 kPa. The variations of exponent n are presented in table 4. For Na(0.001 at%)/CaO n decreases with growing temperature, while for Na(1.2 at%)/CaO and Na(6.4 at%)/CaO n increases. This behavior may be caused by changing the ion transport in an oxide lattice. To separate the ion type of conductivity from the p-conductivity, we used an equation proposed by Etsel et al. [33]:

$$\sigma_{\text{total}} = \sigma_{\text{p}} + \sigma_{\text{ion}} = kp_{O_2}^{1/4} + \sigma_{\text{ion}}. \qquad (7)$$

We have found an increase of both p-conductivity and ion conductivity with increasing sodium concentration. The ratios of $\sigma_{\text{ion}}/\sigma_{\text{total}}$ are presented in table 5 for different temperatures and various oxygen concentrations. This ratio increases with decreasing temperature for Na(0.001 at%)/CaO and decreases for Na(1.2 at%)/CaO and Na(6.4 at%)/CaO. This means that for Na(1.2 at%)/CaO and Na(6.4 at%)/CaO the ion conductivity increases with temperature stronger compared to the p-conductivity, while for Na(0.001 at%)/CaO the p-conductivity is more temperature-dependent.

Table 5

Percent ratio of $\sigma_{\text{ion}}/\sigma_{\text{total}}$ as a function of temperature and oxygen concentration.

p_{O_2}	Na(0.001 at%)/CaO			Na(1.2 at%)/CaO			Na(6.4 at%)/CaO		
(kPa)	723 K	873 K	1023 K	723 K	873 K	1023 K	723 K	873 K	1023 K
1	95.7	75.7	63.4	10.4	83.1	84.3			
2							18.7	35.6	78.3
5	88.3	70.8	51.7	6.1	68.7	78.2	15.1	29.8	66.5
10	83.1	63.9	46.1	7.7	71.2	76.7	14.6	30.7	64.7
20							10.3	23.1	64.1
30	81.2	56.1	41.1	4.6	63.7	70.7			

Earlier, Miffot [34] and Kummar et al. [35] found that the p-conductivity of pure CaO and MgO decreased with temperature more pronounced than the ion conductivity. They proposed that Me^{2+} migration was responsible for the ion current. Based on the analysis of experimental and literature data, we suppose that Na(0.001 at%)/CaO is both p- and cation conductor. These data agree well with the CPD measurements, which showed that the ion mobility into the oxide lattice overcame the p-conductivity at low temperatures (section 3.2). For the catalysts with high concentration of sodium, the incorporation of Na^+ into the cationic sublattice results in creation of anion vacancies in the anionic sublattice and, therefore, in increasing both O^{2-} conductivity and p-conductivity.

Thus, the ion conductivity of CaO with a very low amount of sodium does not differ from that of pure CaO and is cationic in nature. The addition of an alkali promoter into CaO results in a change of the type of ion conductivity from cation to anion and an increase of both p-type conductivity and ion conductivity. The measurements of conductivity also support the CPD results concerning an incorporation of oxygen and electron transfer to the oxygen species due to doping.

3.4. Oxygen adsorption

The typical responses of a multi-pulse experiment are shown in figure 4. The area of the individual oxygen responses increases for the first pulses and remains subsequently constant for all catalysts. This is valid for the whole temperature range. The initial lower oxygen signals are attributed to oxygen adsorption with the catalyst surface. This adsorbed oxygen desorbs completely on a time scale of 10 min at 873 K, as was shown from the second series of multi-pulse experiment (see section 2). With decreasing temperature the oxygen uptake during the second series of pulses was decreasing. This means that adsorbed oxygen was not desorbing after the first series of oxygen pulses. Adsorption data obtained between 623 and 723 K could be used to estimate the amount of irreversibly adsorbed oxygen. The results of adsorption measurements are presented in figure 5. An increasing concentration of alkali promoter in CaO influences the amount of adsorbed oxygen in the same manner as the anion conductivity. The amount of irreversibly adsorbed oxygen was used to estimate the initial surface concentration of anion vacancies.

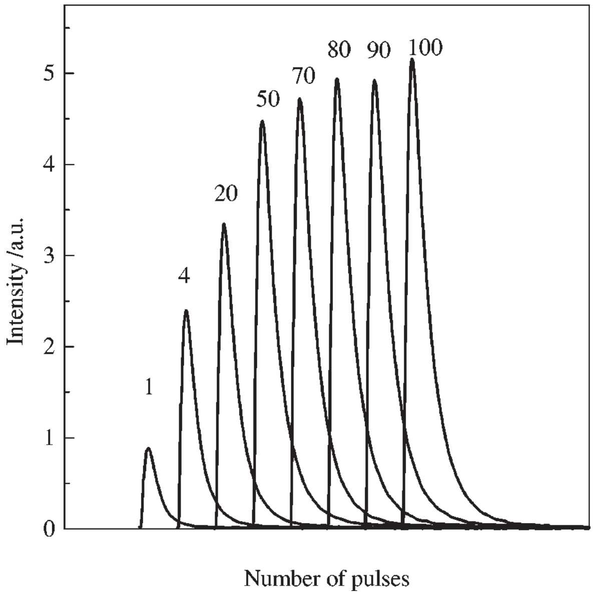

Figure 4. Change of outlet concentration of oxygen with increasing number of subsequent pulses when pulsing O_2–Ne mixture over Na(6.4 at%)/CaO at $T = 873$ K.

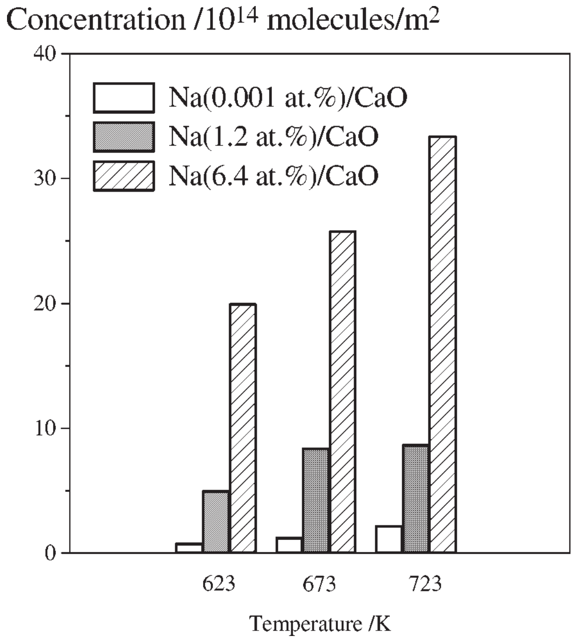

Figure 5. Concentration of irreversibly adsorbed oxygen versus temperature for different Na_2O/CaO catalysts.

Thus, the results on oxygen adsorption have proven the role of alkali dopant for the formation of anion vacancies and also the change of the type of ionic conductivity from cationic to anionic.

3.5. Relationship between catalytic and electronic properties

The catalysts show marked differences in selectivity for formation of ethane plus ethylene. It is necessary to note that the catalytic runs were made at a close conversion of methane (table 1). The differences found can not only be explained by a change of surface basicity or acidity, since there are different mechanisms of oxygen activation over the catalysts. It is well known [6,7,12,15,21] that oxidant activation on the catalyst surface is one of the important steps for the heterogeneous oxidation of light paraffins. As catalytic results show, Na(0.001 at%)/CaO has the lowest C_2 selectivity among all the catalysts. The total conductivity of this catalyst consists of both cation type and p-type. Low concentration of anion vacancies influencing O^{2-} conductivity was confirmed by oxygen adsorption results. It was also demonstrated that the CPD decreases with increasing oxygen partial pressure (see section 3.2). This is caused by diffusion of cation vacancies into the lattice for the cation conducting catalyst. From this it may be concluded that adsorbed oxygen species do not migrate into the oxide bulk, but stay and accumulate on the oxide surface. A comparison of the temperature dependence of the selectivity of C_2-product formation with cation conductivity shows, that the lower the ratio of $\sigma_{\text{ion}}/\sigma_{\text{total}}$ is, the more selective is the Na(0.001 at%)/CaO catalyst (tables 2 and 5).

Thus, the negative effect of cation conductivity may be rationalized in the following manner: cation vacancies do not favor a transformation of adsorbed oxygen into the lattice oxygen. This leads to a relatively high concentration of adsorbed oxygen on the surface and, therefore, to the total oxidation of methane or C_2 hydrocarbons.

Changing from cationic to anionic conductivity improves catalytic performance of Na(1.2 at%)/CaO and Na(6.4 at%)/CaO catalysts (table 2). In contrast to Na(0.001 at%)/CaO, the lower the ratio of $\sigma_{\text{ion}}/\sigma_{\text{total}}$ is, the less selective are these catalysts. From decreasing the oxygen partial pressure an increase of selectivity of C_2 products results for all catalysts, but anion-conducting catalysts are more selective as compared to cation-conducting ones (table 2). The improvement of the catalytic performances of anion-conducting catalysts is explained by reducing the concentration of oxygen surface species because of high concentration of anion vacancies. Oxygen anion vacancies facilitate the oxygen dissociation and its incorporation into the oxide lattice. This was directly seen by CPD results. The positive effect of a high oxygen-anion conductivity was previously found by our group [16] over La_2O_3 doped with different cations (Sr^{2+}, Zn^{2+}, Ti^{4+}, Nb^{5+}).

4. Conclusions

The study of catalytic performances, measurements of contact potential difference and conductivity as well as TAP measurements of oxygen adsorption permits to conclude that the positive effect of alkali dopant is caused by changing the process of oxygen activation and the state of surface oxygen species.

It was shown that Na(0.001 at%)/CaO is a mixed conductor with cation and p-conductivity. Increasing concentration of sodium in CaO results in the creation of anion vacancies and, hence, in the change of type of ion conductivity from cationic to anionic. The formation of anion vacancies in Na_2O/CaO was proven by measurements of oxygen adsorption in the TAP reactor. As shown by the CPD measurements, a cation-conducting catalyst does not make possible oxygen dissociation and its incorporation into an oxide lattice. For this reason the concentration of oxygen species on the catalysts is high resulting in the pour selectivity of ethane + ethylene formation. The high concentration of anion vacancies favors both the oxygen adsorption and its subsequent dissociation followed by incorporation into the lattice. Hence, the coverage of the surface with molecular oxygen species is reduced resulting in a selectivity growth.

Acknowledgement

EVK thanks Alexander von Humboldt Foundation for a postdoctoral fellowship to work at the Insitut für Angewandte Chemie Berlin-Adlershof e.V.

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