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Oxidative Coupling of Methane over CaO–CeO$_2$ Catalysts: Effect of Oxygen-Ion Conductivity on C$_2$ Selectivity

Oxidative coupling of methane generally proceeds only at temperatures above ca. 900 K with satisfactory selectivity to C_{2+} hydrocarbons. Although the intrinsic reason for requiring such high temperatures is still unclear, it is well known that at these temperatures mobility of lattice oxygen in an oxide catalyst becomes significant. The importance of the oxygen-anion mobility with respect to C_2 formation has received only little attention (*1–5*). In the present work, CaO–CeO$_2$ mixed oxides which form solid solutions with highly mobile lattice oxygen are applied as model catalysts to evaluate the influence of oxygen mobility on C_2 formation. A marked advantage of this catalyst system is the possibility of varying oxygen-ion conductivity in a controllable way by changing the CaO content; electron conductivity is negligible compared to anion conductivity for this solid material (*6, 7*).

CaO–CeO$_2$ catalysts were prepared by the coprecipitation method as described in (*8*). For comparison, CaO–CeO$_2$ catalysts were also prepared by mechanical mixing. X-ray diffraction patterns of the catalysts were recorded on a Siemens D 500 powder diffractometer by applying Cu$K\alpha$ radiation. The surface compositions were determined by XPS (Leybold Heraeus LHS-10 spectrometer, Al$K\alpha$-ray source). The specific surface areas were measured by the BET method using N_2 adsorption at 77 K.

Catalyst characterization. The BET surface areas were in the range of from 1.3 to 2.1 m^2/g for CeO$_2$ containing catalysts and were ca. 8.6 m^2/g for the pure CaO catalyst. For the samples prepared by mechanical mixing, XRD lines characteristic of CaO could be clearly detected when the Ca content (=100 Ca/(Ca + Ce)) was above ca. 5 at.%; for the samples prepared by the coprecipitation method, only XRD lines characteristic of CeO$_2$ were detected at low Ca contents whereas XRD lines characteristic of calcium compounds (including CaO, Ca(OH)$_2$, and CaCO$_3$) were only detected when the Ca content was above 20 at.% (cf. Table 1). It was noted that the CeO$_2$ lines were well centered to those due to fluorite-type structure CeO$_2$, but some major lines of CeO$_2$ did show a broadening effect after adding CaO. These results suggest that a certain amount of Ca^{2+} ions is incorporated into the CeO$_2$ matrix to form a fluorite-type CaO–CeO$_2$ solid solution with a solubility limit of around 20 at.% (*9–10*). The surface composition determined by XPS is also presented in Table 1. Over the entire composition range, the surface concentration was approximately equal to the bulk; this result indicates that CaO and CeO$_2$ are homogeneously mixed by using the coprecipitation method. There was a small enrichment of calcium on the surface at low Ca content, however, this small amount most probably did not result in the formation of any separated calcium crystallites.

Catalytic performance. Oxygen conversion was above 95% for all the CeO$_2$-containing catalysts but was only ca. 70% for the pure CaO catalyst when a contact time of 0.36 s g/ml was applied. Pure CaO and CeO$_2$ resulted in C_2 selectivities of 29 and 3.0%, respectively. The addition of CaO to CeO$_2$ has a marked positive effect on C_2 selectivity of the catalyst: with increasing Ca content C_2 selectivity first increased markedly and then decreased; a maximum of C_2 selectivity (55–60%) existed at a Ca content of 20–25 at.%. Also at low degrees of oxygen conversion (20 to 70%, except

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TABLE 1

Effect of the Ca Concentration on the Performance (X_{O_2}, Oxygen Conversion; S_i, Selectivity) of CaO–CeO$_2$ Catalysts

Ca/(Ca + Ce)/at.%		Cryst. phase[c]	X_{O_2}[d] %	S_i[d]/%			
Bulk[a]	Surf.[b]			C_2H_4	C_2H_6	CO	CO_2
0	not examined	—	99.2	0.3	2.7	9.9	87.0
			90.0[e]	0.2	3.5	10.1	85.8
2	4.9	—	99.0	0.7	4.0	11.6	83.4
5	7.2	—	99.2	3.8	22.2	5.0	68.8
5[f]	not examined	CaO	94.3	2.0	9.2	17.8	71.0
10	12.2	—	94.6	9.7	34.1	2.5	54.2
			72.0[e]	3.1	27.3	12.0	58.1
20	23.1	—	97.0	11.4	37.8	2.3	48.5
25	26.8	CaO[g]	99.2	12.0	40.0	2.0	45.8
			64.7[e]	8.6	36.0	12.1	41.0
25[f]	24.6	not examined	90.3	1.3	11.0	8.5	78.9
50	48.9	CaO, Ca(OH)$_2$	99.1	10.5	35.1	5.0	49.9
			52.0[e]	4.1	23.0	17.5	55.4
70	73.0	not examined	99.0	7.5	30.0	5.0	58.0
100	not examined	not examined	72.1	4.2	24.5	28.2	42.7
			20.0[e]	2.1	18.0	35.0	45.0

[a] According to catalyst preparation.

[b] Determined by XPS.

[c] In all the samples fluorite-type CeO$_2$ lines were detected.

[d] T = 1013 K, CH_4/O_2 = 13.2, m/V = 0.36 s g/ml, P_{tot} = 0.1 MPa, no diluent was used.

[e] Data obtained at 0.036 s g/ml.

[f] Catalysts were prepared by mechanical mixing.

[g] The reflex peaks were very weak.

for the pure CeO$_2$) which were obtained by reducing the contact time to 0.036 s g/ml the dependence of C$_2$ selectivity on the CaO content was similar to that observed at 0.36 s g/ml, although on a lower level (see Table 1). The effect of the two different preparation procedures, i.e., coprecipitation and mechanical mixing for Ca contents of 5 and 25 at.%, on catalytic performance is also shown in Table 1. It is evident that the more homogeneous mixture of CaO and CeO$_2$ resulting from the coprecipitation method leads to much higher activity and selectivity than those in the less homogeneous mixture prepared by mechanical mixing. This is a rather significant result, indicating that the homogeneous mixture of CaO and CeO$_2$ is the key factor in reducing the total oxidation channel of CeO$_2$ in favor of the selective one.

The marked differences in C$_2$ selectivity of the various catalysts are certainly not due to their textural properties, since the specific surface areas of the CaO–CeO$_2$ catalysts did not differ significantly. The fact that the maximum C$_2$ selectivity obtained over the CaO–CeO$_2$ mixture is much larger than that for the pure compounds leads to the suggestion that selectivity is governed by a synergistic interaction between CaO and CeO$_2$. In referring to the different catalytic results when applying the two different preparation procedures, it appears that such a synergistic interaction is related to the homogeneous mixing of CaO and CeO$_2$. This observation is tentatively explained in the following. Previous studies showed (*6, 7, 9–11*) that both pure CaO and CeO_2 have rather low oxygen-ion conductivities; however, when both are homogeneously mixed, the oxygen-ion conductivity is significantly increased due to the substitution of Ce^{4+} ions by Ca^{2+} ions in the lattice. Oxygen-ion conductivity of the solid solution varies with the Ca content and the temperature within the composition range of the solid solution:

$$\sigma_{\text{ion}} = \frac{\sigma^0_{\text{ion}}}{T}(n_{\text{CaO}}) \exp\left(-\frac{E}{RT}\right) \quad (1)$$

(σ^0_{ion}, a constant; T, temperature; n_{CaO}, the content of Ca dissolved; and E, the activation energy).

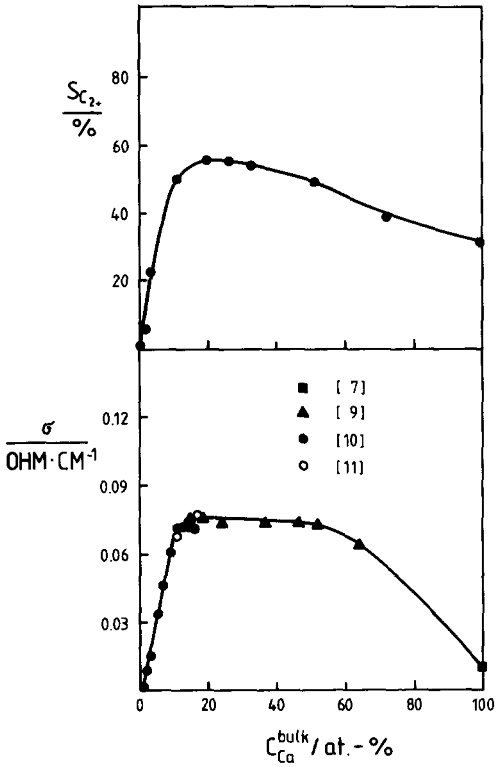

FIG. 1. Dependences of C_2 selectivity and the oxygen-ion conductivity on the Ca content in CaO–CeO_2 catalysts (reaction conditions: T = 1013 K; P_{tot} = 0.1 MPa, P_{O_2} = 7 kPa, P_{CH_4} = 93 kPa, $m/\dot{V}$ = 0.36 s g/ml).

The composition corresponding to maximum conductivity is around the solubility limit; if the Ca content exceeds the solubility limit, the conductivity will decrease gradually due to the formation of additional calcium oxide crystallites, which results in the oxygen ions becoming much less mobile. An illustration of the relationship between oxygen-ion conductivity and Ca content along with the corresponding C_{2+} selectivity is given in Fig. 1. Assuming that a CaO–CeO_2 solid solution is formed in the present CaO–CeO_2 samples, no crystalline CaO phase should be expected and only small changes in the lattice parameters of the CeO_2 matrix should occur when the amount of CaO is within the solubility limit. The XRD results are in good agreement with this supposition considering that the solubility limit of CaO in CeO_2 is approximately 20 mol%; this value is within the range reported in previous studies (*9–11*). Thus, it is reasonable to expect that a relationship between oxygen-ion conductivity and the Ca content similar to that shown in Fig. 1 also exists for the CaO–CeO_2 catalysts applied in the present work. In applying this reasoning to the catalytic results obtained over CaO–CeO_2 catalysts, it appears that the dependence of C_2 selectivity and oxygen-ion conductivity on the Ca content follows a similar pattern, i.e., they both first increase and then decrease with increasing Ca content, having a maximum at a Ca content of around 20–25 at.% (see Fig. 1). Thus, the synergistic interaction resulting in larger C_2 selectivity may be tentatively ascribed to the increasing oxygen-ion conductivity of the CaO–CeO_2 catalysts. When relating selectivity to bulk composition, which is approximately equal to the surface composition (see Table 1), it becomes obvious that the maximum C_2 selectivities are around the solubility limit of CaO in the CeO_2 matrix (20–25 at.%) where maximum oxygen-ion conductivity exists. In the methane oxidative coupling reaction, methane reacts but does not adsorb or only weakly adsorbs onto the surface (*12*), this is to say that the type of activated oxygen species that is mainly affected by the electronic property of the catalytic solid governs the selective processes on the surface. Thus, the relationship between oxygen-ion conductivity and C_2 selectivity appears reasonable, considering that the oxygen-ion conductivity dominates the entire electronic conductivity of the $CaO-CeO_2$ solid solution (*6, 7*).

A good catalyst for the oxidative methane coupling reaction should have the capability of creating a high concentration of methyl species and also of inhibiting the deep oxidation of these species and of C_2 hydrocarbons formed by coupling. Reactive oxygen species (e.g., O^-, O_2^-, O_2^{2-}) may be suited to activate methane by hydrogen abstraction, but they may also favor nonselective oxidation by interacting with methyl species (*2, 4*). Surface lattice oxygen species (O^{2-}) that can also activate methane efficiently at elevated reaction temperatures (>900 K) minimize nonselective surface reactions (*2, 13, 14*). Thus, the basic O^{2-} sites (most probably with low coordination) may be more favorable in view of the selective reaction. Since catalytic solids with highly mobile oxygen defects have a high capability of transforming any surface oxygen species into lattice oxygen (*1–3, 6*), the positive effect of high oxygen-ion conductivity on C_2 formation may be reasoned in the following. A catalyst with high oxygen-ion conductivity favorably forms a surface with a relatively small amount of weakly adsorbed oxygen species, thereby reducing the nonselective surface reactions of methyl species and C_2 hydrocarbons caused by the interaction with such weakly adsorbed oxygen species. It must be emphasized that in addition to oxygen-ion conductivity, other properties of catalytic solids (e.g., basicity/acidity and p-conductivity) also affect the selectivity and activity of the reaction. Thus, the dependence of C_2 selectivity on the Ca content, which has been currently explained in terms of oxygen-ion conductivity, may also be due to other contributing factors; however, it is believed that the factor of oxygen-ion conductivity plays a major role in the present $CaO-CeO_2$ catalysts.

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