Oxidative dehydrogenation of ethane on rare earth oxides: effects of chlorine additives in gas and solid phase on the oxidation over cerium oxide

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The oxidative dehydrogenation of ethane in the presence and absence of tetrachloromethane (TCM) has been investigated on La_2O_3, Sm_2O_3, Pr_6O_{11} and CeO_2 at 773 and 973 K. Although the introduction of TCM into the ethane feedstream produced no significant changes with La_2O_3, Sm_2O_3 and Pr_6O_{11} at 773 K, the conversion of ethane and the selectivity to ethylene on CeO_2 were distinctly enhanced by the addition of the chlorinated additive. At 973 K, with all of the rare earth oxides studied the selectivities to CH_4 increased while those to CO_2 decreased, the latter particularly significantly, suggesting that the further oxidation of CO and/or CH_4 is suppressed by the addition of the chlorinated additive. XPS measurements provide evidence for the introduction of Cl into the surface of CeO_2, apparently forming CeOCl which is responsible for the enhancement observed in the reactions catalyzed by CeO_2.

Keywords: ethane; oxidative dehydrogenation; rare earth oxides; cerium oxide; tetrachloromethane

1. Introduction

Earlier work from our laboratories has shown that the introduction of small quantities (< 1 mol%) of tetrachloromethane (TCM) into the feedstream for the partial oxidation and oxidative coupling of methane generally has advantageous effects in increasing the conversion of methane and/or the selectivity to C_2 hydrocarbons, particularly ethylene [1,2]. Concomitantly the selectivity to ethane is observed to decrease, although to a lesser extent than the increase of that of ethylene. It is of interest to compare the effect of TCM on ethane with that on methane, particularly since ethylene is believed to form as a secondary product from ethane in the oxidative coupling of methane [3]. The oxidative dehydrogenation of ethane has been compared with and without TCM on several catalysts in our laboratories [4–7]. With 12-molybdophosphoric acid supported on silica the conversion is increased on addition of TCM to the feedstream while the C_2 selectivities are unaffected. In the oxidation of methane and of ethane on magnesium salts, where TCM is present, evidence for the formation of magnesium chloride has been found [6–10] and the effects of the addition of TCM on the conversion of ethane and the selectivity to ethylene appear to be dependent on the composition of the anions. The effects of the introduction of HCl on ethane conversion have also been studied [11].

In contrast to the observations of the oxidative coupling of methane on magnesium based catalysts, oxychlorides which have been found to form on rare earth oxides such as La_2O_3, Sm_2O_3, CeO_2 and Pr_6O_{11}, in the presence of TCM, apparently contribute to the enhancement of the catalytic properties of these solids, particularly with the latter oxide [12,13]. Rare earth oxides, for example, Sm_2O_3 and La_2O_3, have been shown to be highly active in the oxidative coupling of methane [12–15] and such oxides have been employed as catalysts in comparative studies of the oxidative coupling of methane (OCM) and the oxidative dehydrogenation of ethane (ODE) in the absence of TCM [16]. There are, however, no reports of the results of studies of the effect of the introduction of TCM on the latter reaction over rare earth oxides.

In the present work, the effect of the addition of small quantities of TCM into the ODE feedstream has been investigated on La_2O_3, Sm_2O_3, Pr_6O_{11} and CeO_2 at 773 and 973 K. In addition, the catalytic activity of CeO_2

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doped by solid-phase chlorine additives such as $CeCl_3$ and CeOCl has been examined in the presence and absence of TCM.

2. Experimental

Rare earth oxides La_2O_3 (99.5%), Sm_2O_3 (99.5%), Pr_6O_{11} (99.9%) and CeO_2 (99.9%) were obtained from Wako Pure Chemicals, Osaka, and used as received. Cerium chloride supported on CeO_2 was prepared by impregnation of CeO_2 with an aqueous solution of $CeCl_3 \cdot 7H_2O$ (Kishida, Osaka, 99%). The supported catalysts were dried in air at 373 K overnight and calcined for 3 h at 1048 K. After the calcination, XPS analyses showed that Cl/Ce ratios on the surface of 5 and 10 wt% $CeCl_3/CeO_2$ were 0.32 and 0.15, respectively, to be compared with 0.12 and 0.10, respectively, after argon-ion etching for 1 min, suggesting that $CeCl_3$ in the 5 wt% catalyst exists predominantly in the surface region while that in the 10 wt% catalyst has migrated into the bulk phase. All catalysts were pressed, crushed, and sieved to the particle size of 1.70–0.85 mm. BET surface areas and the apparent densities of the catalysts prior to use in a reaction are collected in table 1. The catalytic experiments were performed in a fixed-bed continuous flow quartz reactor operated at atmospheric pressure. Details of the reactor design and procedures have been described elsewhere [7,8,12]. The reaction conditions were selected to permit comparison with the results obtained earlier on ethane oxidation [6,7] in which similar conditions were employed. The reaction was monitored with an on-stream Shimadzu GC-8APT gas chromatograph with a TC detector and integrator (Shimadzu C-R6A). Two columns, one Porapak Q (6 m × 3 mm) the other Molecular Sieve 5A (0.5 m × 3 mm) were employed in the analyses. The conversions and selectivities were calculated on the basis of the amounts of reaction products formed as determined by the GC analyses [7,8]. The carbon mass balances were 100 ± 5%. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku CN-2011, using monochromatized Cu Kα radiation. Patterns were recorded from 5 to 60°. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) used monochromatized Mg Kα radiation. The samples were mounted on a sample holder in air and set into the analytical chamber. The binding energies were corrected using 285 eV for C 1s as an internal standard. Argon-ion etching of the catalysts was carried out at 2 kV for 1 min with a sputtering rate estimated as ca. 2 nm/min for SiO_2.

Table 1
BET surface areas and apparent densities

Catalyst	Surface area (m^2/g)	Apparent density (g/cm^3)
La_2O_3	4.6	1.40
Sm_2O_3	1.9	2.32
Pr_6O_{11}	3.2	1.75
CeO_2	11.2	1.74
5 wt% $CeCl_3/CeO_2$	7.2	2.33
10 wt% $CeCl_3/CeO_2$	5.3	2.34

3. Results and discussion

3.1. Effect of TCM on ethane oxidation on rare earth oxides

Fig. 1 shows the ODE results on La_2O_3, Sm_2O_3, Pr_6O_{11} and CeO_2 in the presence and absence of TCM at 773 K, at which the contribution of the homogeneous oxidation of C_2H_6 is negligible [6]. Although the conversion of C_2H_6 and the selectivities to C_2 hydrocarbons showed little or no dependence on the catalyst in the absence of TCM, the CO_x product compositions for La_2O_3 and Sm_2O_3 were approximately equally divided between CO and CO_2, while with Pr_6O_{11} and CeO_2 virtually all of the CO_x was CO_2. Although neither the conversion nor the selectivities to CO_x and C_{2+} obtained with La_2O_3 and Sm_2O_3 were appreciably altered on the introduction of TCM, the deep oxidation to CO_2 was

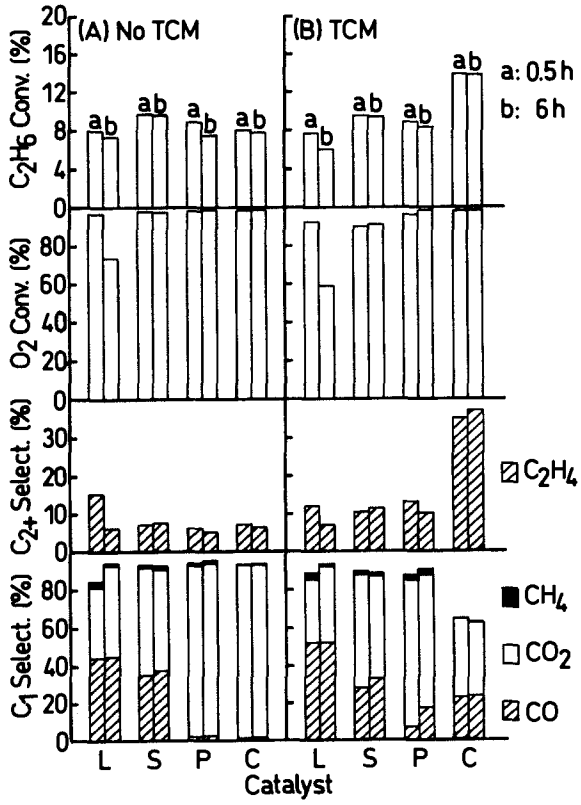

Fig. 1. Ethane oxidation on rare earth oxides in the presence and absence of TCM at 773 K. Conditions: $W = 0.7$ g, $F = 15$ ml/min, $P(C_2H_6) = 27.1$ kPa, $P(O_2) = 6.8$ kPa and P(TCM) = 0 or 0.17 kPa diluted with He. Catalysts were pretreated with O_2 (12.5 ml/min) at 1048 K for 1 h. Symbols: a, 0.5 h on-stream; b, 6 h on-stream; L, La_2O_3; S, Sm_2O_3; P, Pr_6O_{11}; C, CeO_2.

apparently suppressed on Pr_6O_{11} and CeO_2 and with the latter catalyst both the conversions and the C_{2+} selectivities were substantially increased.

In the oxidative coupling of methane, the conversion of methane and the selectivities to CO and C_2H_4 in the presence of TCM increased with increasing time-on-stream on Pr_6O_{11} [12]. In contrast with the remaining three catalysts, CeO_2, La_2O_3 and Sm_2O_3, the introduction of TCM to the methane feedstream produced little or no changes. Thus the mechanism through which TCM participates in the ODE is apparently not identical to that in OCM, at least on the rare earth catalysts. These comparisons also emphasize the predominant importance of the interaction of TCM with the catalyst as compared with the gas phase process at 773 K.

At 973 K, a temperature at which the homogeneous conversion of ethane has a significant rate [6], the introduction of TCM produces an increase in conversion on Pr_6O_{11} and CeO_2 but not on La_2O_3 and Sm_2O_3 and a small increase in selectivity to C_2H_4, particularly on CeO_2, while that to CO_2 decreased markedly (fig. 2). These results suggest that TCM functions, at least in part, as an inhibitor of the secondary oxidation processes. Since, of the four rare earth oxides examined, CeO_2 is the most strongly influenced by the introduction of TCM, the remainder of this report will be concerned with CeO_2.

3.2. Effect of the partial pressure of O_2 on CeO_2

As expected, either with or without TCM, the conversion on CeO_2 increases with the partial pressure of oxygen $P(O_2)$ at 773 K (fig. 3). However, on introduction of TCM, at all of the three values of $P(O_2)$ the selectivities to C_2H_4 are substantially increased, while those to CO_x decrease and the proportion of CO in the latter becomes significant.

At 973 K (fig. 4) the conversion of C_2H_6 at the lowest $P(O_2)$ is increased when TCM is present, but with increasing $P(O_2)$ the effect of TCM on the conversion is diminished and at the highest $P(O_2)$ leads to a decrease in the conversion. However, at this higher temperature the beneficial effect of TCM on the selectivity to C_2H_4 is again evident but the magnitude of the increase at this temperature is less than that observed at 773 K. While at 973 K the selectivity to CO changes relatively little on addition of TCM that to CO_2 is again reduced, but either

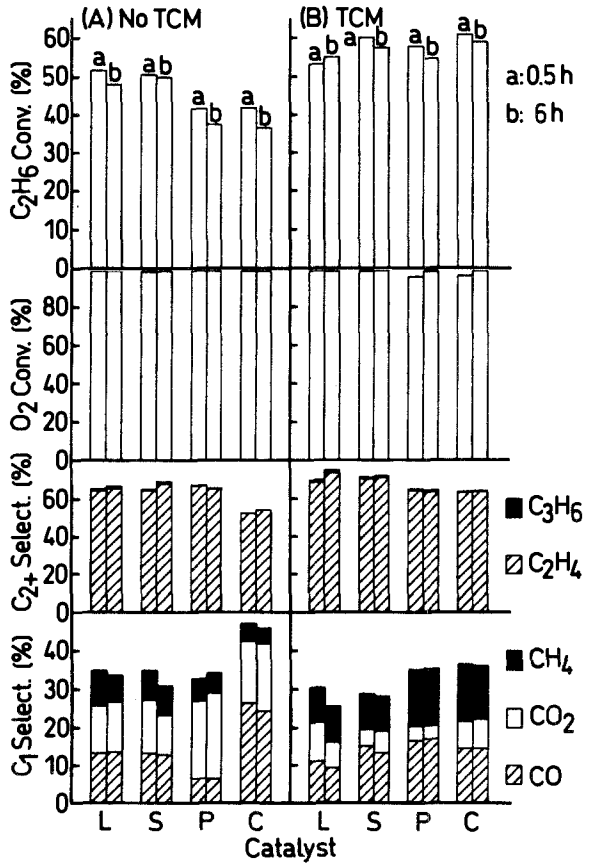

Fig. 2. Ethane oxidation on rare earth oxides in the presence and absence of TCM at 973 K. Conditions and symbols as in fig. 1.

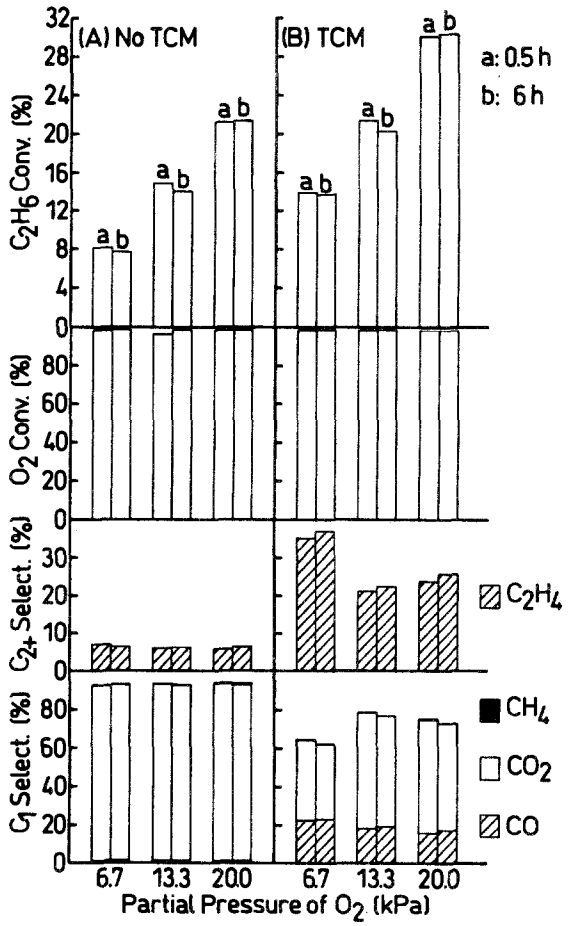

Fig. 3. Effect of partial pressure of O_2 on ethane oxidation in the presence and absence of TCM on CeO_2 at 773 K. Conditions and symbols as in fig. 1, except $P(O_2)$.

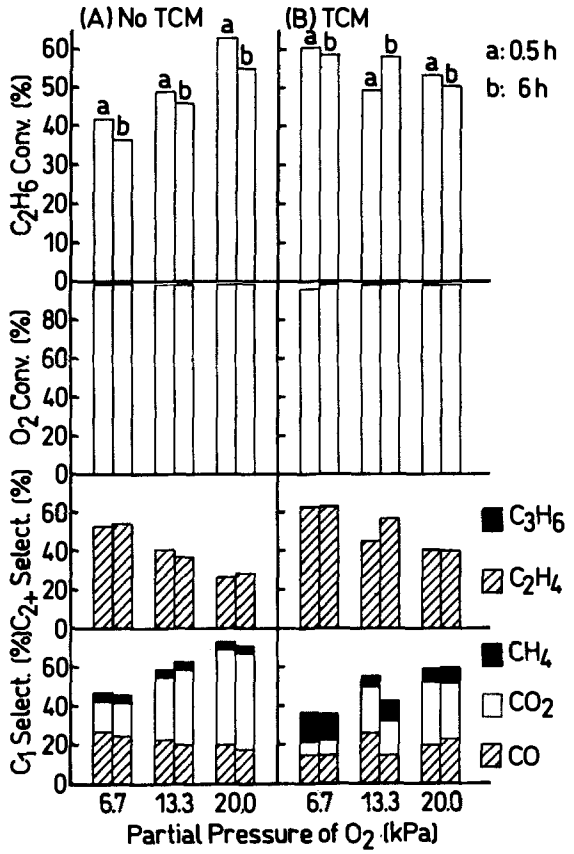

Fig. 4. Effect of partial pressure of O_2 on ethane oxidation in the presence and absence of TCM on CeO_2 at 973 K. Conditions and symbols as in fig. 2, except $P(O_2)$.

with or without TCM increases with $P(O_2)$ as does that to the total C_1 selectivities.

XRD patterns of CeO_2 previously employed in the oxidation process show that only CeO_2 is present (not shown), as found similarly with CeO_2 samples which had been used in the oxidative coupling of methane in the presence of TCM [12]. However, XP spectra show the presence of Cl 2p on CeO_2 after use in oxidation as well as the expected O 1s and Cl $3d_{5/2}$, the binding energies of which remain invariant with changes in $P(O_2)$, the introduction of TCM or argon-ion etching (table 2). The Ce/O ratio prior to etching was, under all experimental conditions, smaller than that found after etching, indicating the surface excess of oxygen existing after the oxidation process. In contrast the Cl/Ce ratio obtained from XPS decreased after etching as expected for a surface excess of chlorine produced during the reaction where TCM was present.

Although it is evident that chlorine is present in the interfacial region of CeO_2 after use in the ethane reaction, in the presence of TCM no chlorine, at least within the detection capabilities of XRD, is found in the bulk under the conditions employed in these experiments. Since the Cl/Ce ratios are reduced by factors as large as 3 after argon-ion etching for 1 min the chlorine is apparently predominantly held within the outer portion of the surface region. It is therefore improbable that the chlorine is distributed uniformly over the surface region of the catalyst particles, thus rendering the identification of the chlorided compound difficult, if not impossible. In view of the relatively small values found for Cl/Ce it is tempting to suggest that at least the localized form of the chlorided surface more closely resembles CeOCl rather than $CeCl_3$.

3.3. Effect of the partial pressure of TCM

At 773 K both the conversion of ethane and the selectivity to C_2H_4 increase with P(TCM) with relatively little change with time-on-stream (fig. 5). Concomitantly the C_1 selectivities decrease but, as expected from the earlier observations, the formation of CO_2 is suppressed and that of CO enhanced on the introduction of TCM at the lowest P(TCM). Somewhat similar results are found at 973 K although the conversion appears to reach a maxi-

Table 2
XPS analyses of CeO_2[a]

Temp. (K)	$P(O_2)$ (kPa)	P(TCM) (kPa)	Binding energy (eV)			Atomic ratio	
			O 1s	Ce $3d_{5/2}$	Cl 2p	Ce/O	Cl/Ce
773	6.7	0	529.6	883.0	–	0.23	–
			(529.5	882.9	–	0.32	–)[b]
773	6.7	0.17	530.0	883.3	198.8	0.28	0.39
			(529.8	883.1	198.8	0.38	0.14)
773	20.0	0.17	529.8	883.0	198.4	0.26	0.34
			(529.7	882.8	198.7	0.36	0.13)
973	6.7	0	529.6	882.7	–	0.17	–
			(529.6	882.7	–	0.29	–)
973	6.7	0.17	529.9	883.3	198.8	0.23	0.32
			(529.7	883.1	198.8	0.34	0.14)
973	20.0	0.17	529.4	882.8	198.1	0.20	0.27
			(529.5	882.7	198.4	0.26	0.19)

[a] Previously employed in obtaining results reported in figs. 3 and 4.
[b] Values in parentheses show those after argon-ion etching for 1 min.

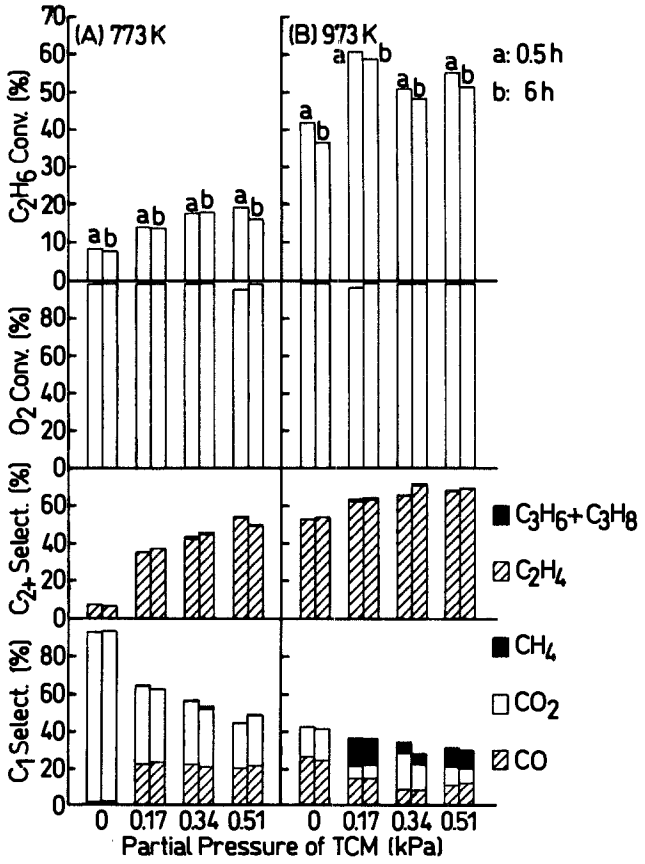

Fig. 5. Effect of partial pressure of TCM on ethane oxidation on CeO_2 at 773 and 973 K. Conditions and symbols as in figs. 1 and 2, except P(TCM).

mum and methane first appears at the lowest P(TCM), At the higher temperature the C_{2+} selectivities are higher while those of C_1 are lower than observed at the lower temperature.

Values for Cl/Ce of the catalysts previously employed in obtaining the results shown in fig. 5 show little or no dependence on the reaction temperature, but some dependence on P(TCM), not surprisingly, is evident (table 3). Since no correlation between these results and those obtained from the catalytic studies is evident, it may be concluded that even at the lowest P(TCM) employed in the present work sufficient of the chlorinated species, presumably CeOCl, is present to alter the course of the reaction.

3.4. Ethane oxidation on CeO_2 pretreated with TCM

Pretreatment of CeO_2 with TCM, in the absence of ethane, results in the chlorination of the surface of the catalyst apparently with the formation of CeOCl which may exist in the form of patches quite probably localized with respect to their depths and breadths (table 3). Since no dependence of the quantity of CeOCl formed on the duration of pretreatment is seen, rapid achievement of

Table 3
Atomic ratio of Cl/Ce in the near-surface region of CeO_2

Temp. (K)	P(TCM) (kPa)	Time[c] (h)	Cl/Ce	
			ET[d] = 0	ET[d] = 1
773[a]	0.17	–	0.39	0.14
773[a]	0.34	–	0.84	0.37
773[a]	0.51	–	0.38	0.21
973[a]	0.17	–	0.32	0.14
973[a]	0.34	–	0.47	0.20
973[a]	0.51	–	0.80	0.53
1048[b]	0.20	1	0.31	0.13
1048[b]	0.20	3	0.29	0.12
1048[b]	0.20	6	0.32	0.15

[a] Previously employed in obtaining results reported in fig. 5.
[b] CeO_2 pretreated with TCM at 1048 K but not employed in ethane oxidation.
[c] Pretreatment time (h).
[d] Etching time (min).

equilibrium with respect to the formation process is occurring.

In view of the XPS results on the pretreated catalysts it was expected that the catalytic reactions would show little or no dependence on the duration of the pretreat-

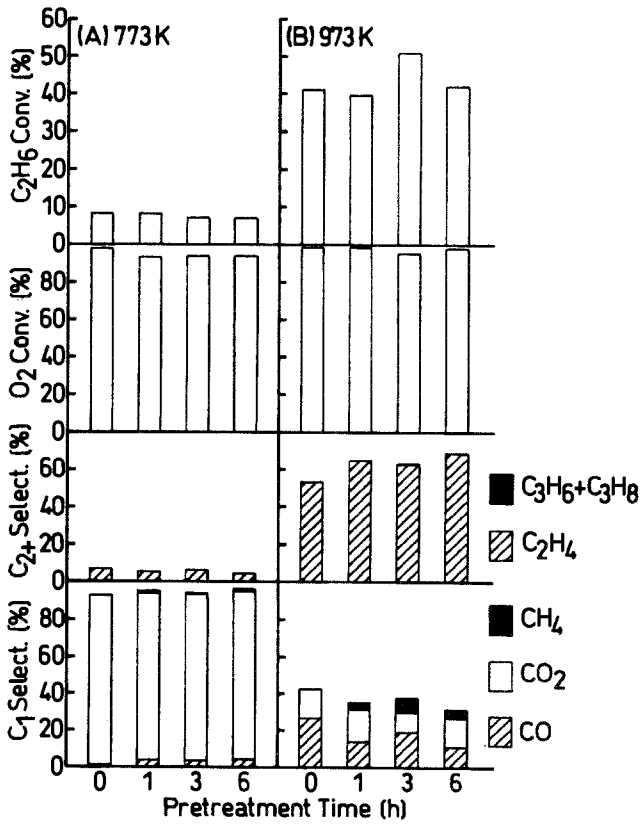

Fig. 6. Ethane oxidation in the absence of TCM at 773 and 973 K on CeO_2 pretreated with TCM. Data were collected at 0.5 h on-stream. Catalysts were pretreated with TCM (0.20 kPa) diluted with O_2 (total flow rate: 12.5 ml/min) at 1048 K for a given time. Conditions and symbols as in figs. 1 and 2, except pretreatment conditions.

ment. In the absence of TCM in the feedstream the conversion of ethane and the selectivities to C_1 and C_{2+} at 773 K remain unchanged with pretreatment time (fig. 6). This is almost equally so at 973 K except for the appearance of methane on the catalysts pretreated with TCM.

3.5. Ethane oxidation on $CeCl_3$ supported on CeO_2

Earlier work has shown that, with magnesium-containing catalysts, the introduction of TCM in the ODE results in the formation of the chloride, to which the enhancement in the reaction is ascribed [6–8]. To compare these earlier results with those in the present work catalysts with $CeCl_3$ loaded on CeO_2 were employed in the ODE. At both 773 and 973 K, in either the absence or presence of TCM, the introduction of $CeCl_3$ produced little or no changes in the conversion and selectivities, although the presence of TCM in the feedstream produced the expected advantageous results (figs. 7 and 8). Therefore it is concluded that the contribution of $CeCl_3$ to the catalytic properties of CeO_2 in the ODE is negligible.

Although it is not possible at this time to provide a definitive explanation of the nature of the effect produced by the introduction of chlorine into the ODE feedstream, the results from the present work add some additional pieces to the puzzle. While the participation of the chloride ion contained within the surface region could be direct or indirect, since large concentrations of this ion as found in $CeCl_3$ are apparently not beneficial it can be concluded that the effect is indirect rather than direct. The chloride ions may be perturbing the electron density of the surface oxygen ions or merely serving as a diluent for the latter species. In either case, however, the net effect is to produce an enhancement of the conversion of ethane and the selectivity to ethylene when the chlorided surface is available, thus implying a surface-dependence of both the conversion and the selectivity. Although the surface and its composition are undoubtedly important in the production of free radicals from ethane, the nature of the participation of the surface in enhancing the selectivity to ethylene is less evident. However, increases in the selectivity to ethylene apparently result from reductions in the selectivities to products which would result from the further oxidation of ethylene and consequently the chlorided surface appears to suppress this disadvantageous process. This is consistent with the results reported earlier on the suppression of the oxidation of CO by such surfaces.

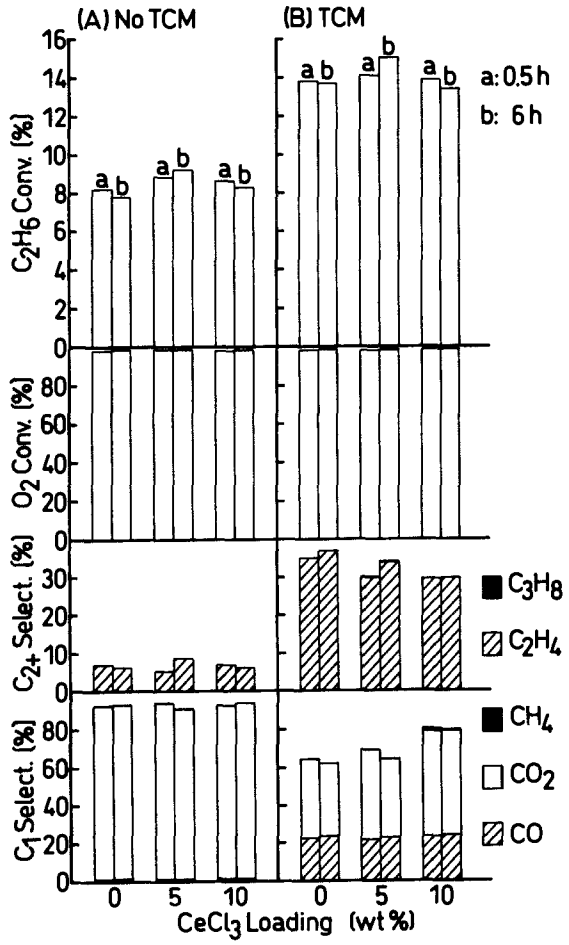

Fig. 7. Ethane oxidation in the presence and absence of TCM on $CeCl_3/CeO_2$ at 773 K. Conditions and symbols as in fig. 1.

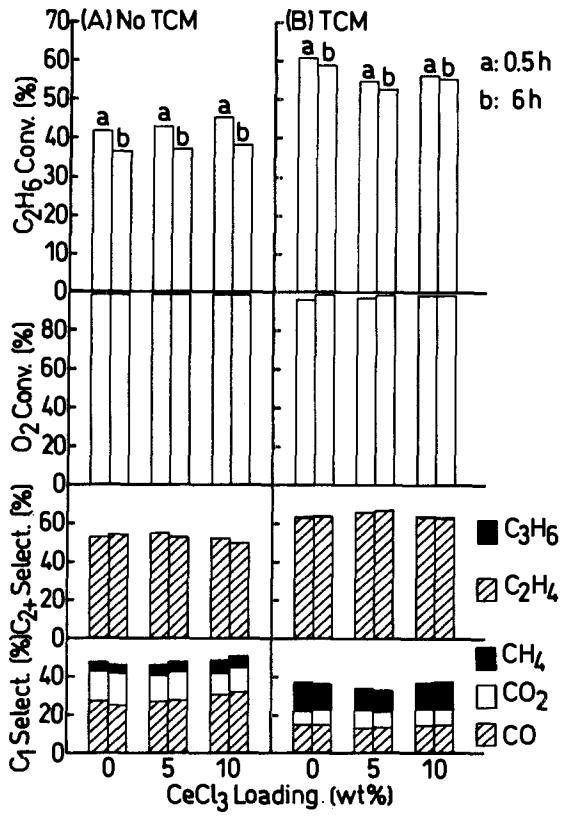

Fig. 8. Ethane oxidation in the presence and absence of TCM on $CeCl_3/CeO_2$ at 973 K. Conditions and symbols as in fig. 2.

4. Conclusion

In contrast to the earlier observations from the oxidative coupling of methane in the presence and absence of TCM, on rare earth oxides, the use of TCM in the ODE at 773 and 973 K produced beneficial effects on CeO_2 but not on the remaining three rare earth oxides examined. The addition of TCM to the ODE feedstream is shown from XPS to introduce surface Cl on the CeO_2, forming CeOCl which is apparently responsible for the enhancement observed in the reactions catalyzed with CeO_2. Since the homogeneous reaction participates in the ethane conversion process to a considerably greater extent at 973 K, the effects due to the chlorinated surfaces are diminished at this temperature.

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