Effects of chlorine additives in the gas- and solid-phases on the oxidative dehydrogenation of ethane over praseodymium oxide

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Abstract

The oxidative dehydrogenation of ethane in the presence and absence of tetrachloromethane (TCM) as a gas-phase additive has been investigated on Pr_6O_{11}, $PrCl_3/Pr_6O_{11}$ and Pr_6O_{11} pretreated with TCM at 773 and 973 K. The conversion of C_2H_6 was little influenced but the selectivity to C_2H_4 was significantly improved by the introduction of TCM at 773 K. In contrast, at 973 K the addition of TCM produced increases in the conversion but little or no improvement in the selectivity to C_2H_4. Although in the absence of TCM and at 773 K the selectivity to C_2H_4 increased markedly on loading of $PrCl_3$ on the oxide, both the conversion and selectivity deteriorated with increasing time-on-stream. With TCM present in the feedstream the latter effect was suppressed. At 973 K, the addition of $PrCl_3$ had little or no effect on either the conversion or selectivities regardless of the presence or absence of TCM. However little or no enhancement of the activities was observed on Pr_6O_{11} pretreated with TCM, on which PrOCl was formed, at 773 or 973 K.

Keywords: Oxidative dehydrogenation; Ethane; Praseodymium oxide; Praseodymium chloride; Praseodymium oxychloride; Tetrachloromethane

1. Introduction

The oxidative coupling of methane (OCM) with tetrachloromethane (TCM) as a feedstream additive has previously been investigated with Sm_2O_3, La_2O_3, CeO_2 and Pr_6O_{11} as heterogeneous catalysts [1,2]. While the conversion of methane and the selectivities to C_2H_4 and CO

were increased on Pr_6O_{11} on introduction of the chlorine-containing additive, with the remaining rare earth oxides little or no differences were observed. The beneficial effects resulting from the introduction of TCM were attributed to the oxychloride, formed during the methane reaction. Others have recently noted the high activities of some oxychlorides as catalysts in the OCM [3].

Studies of the oxidative dehydrogenation of ethane are consequently of value in examining

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and comparing the effects of TCM on this molecule with those of methane, to provide further information on the mechanism of the process, to investigate the relative participation of the chlorine-containing species in the homogeneous and heterogeneous processes, and to provide information on the identity of the chlorine-containing species formed on the surface. The results of recent work from our laboratories which was concerned with the oxidative dehydrogenation of ethane on magnesium compounds (4-6) have been found useful in comparisons with the OCM process on similar catalysts where in the presence of TCM magnesium chloride is formed [7,8].

In the present study, the oxidative dehydrogenation of ethane on Pr_6O_{11} has been examined in the presence and absence of TCM at 773 and 973 K, at the former of which the contribution of the gas-phase oxidation of ethane was negligible while at the latter of which ethane oxidation proceeds extensively in the gas-phase [4], and compared with the results of the oxidative coupling of methane [1]. Furthermore, the effects of the loading of $PrCl_3$ on Pr_6O_{11} and the pretreatment of Pr_6O_{11} with TCM on the oxidative dehydrogenation of ethane have also been investigated in order to compare the role of the chloride and oxychloride in the Pr_6O_{11} systems. The results of studies of the oxidative dehydrogenation of ethane in the absence of TCM on rare earth oxides have been reported earlier [9].

2. Experimental

2.1. Catalyst and procedure

Reagent Pr_6O_{11} (99.9%) was purchased from Wako Pure Chemicals, Osaka, and was used as received. Praseodymium chloride supported on Pr_6O_{11} (denoted as wt% $PrCl_3/Pr_6O_{11}$) was prepared by impregnation of Pr_6O_{11} with an aqueous solution of $PrCl_3 \cdot 7H_2O$ (Nacalai Tesque, Kyoto, 99.9%) followed by drying in

Table 1
BET surface areas and the apparent densities of unsupported and supported Pr_6O_{11}.

	Loading of $PrCl_3$ (wt%)			
	0	2	5	10
Surface area (m^2/g)	3.2	3.8	7.3	7.7
Bulk density (g/cm^3)	1.75	1.41	1.63	1.75

air at 373 K overnight and calcination for 3 h at 1048 K. 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 all catalysts employed in the present study are summarized in Table 1. The catalytic experiments were performed in a fixed-bed continuous flow quartz reactor at atmospheric pressure. The reactor consisted of a quartz tube, 9 mm i.d. and 35 mm in length, sealed at each end to 4 mm i.d. quartz tubes to produce a total length of 25 cm. The catalyst charge (0.7 g) was held in place in the enlarged portion of the reactor by two quartz wool plugs. In all experiments except those in which the effect of pretreatment was studied, the temperature of the catalyst was raised to 1048 K, while maintaining a continuous flow of helium, and was conditioned at this temperature under a 12.5 ml/min flow of oxygen for 1 h. The reactor was then purged with helium while its temperature was adjusted to that for the reaction, prior to the introduction of the reactant gas mixture (15 ml/min) consisting of ethane (27.1 kPa), oxygen (6.7 kPa) and helium (diluent), unless otherwise stated. These reaction conditions were selected to permit comparison with the results obtained earlier on ethane oxidation [4–6] in which similar conditions were employed. In those experiments in which TCM was contained in the feedstream the additive was introduced to the main flow of reactant (C_2H_6, O_2 and He) at a partial pressure of 0.17, 0.34 or 0.51 kPa by saturating a separate stream of He with TCM at 273 K. The carbon mass balances in the reaction were 100 ± 5%.

2.2. Analysis

The reactants and products were analyzed with a 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 conversion of C_2H_6 was calculated on a carbon-account-for basis. The selectivities were calculated as mole percents of the products. Blank experiments conducted with C_2H_6 absent from the feed (O_2 + TCM + He) indicated that TCM undergoes oxidation producing CO and CO_2. The quantities of CO and CO_2 were negligibly small compared to those produced when C_2H_6 was present in the feed. Nevertheless, the data reported were corrected by running duplicated experiments with C_2H_6 absent under otherwise identical sets of process variables.

2.3. Characterization of the catalyst

The surface areas were measured with a conventional BET nitrogen adsorption apparatus (Shibata P-700). Powder X-ray diffraction (XRD) patterns were recorded with Rigaku CN-2011, using monochromatized Cu Kα radiation. Patterns were recorded over the 2θ range from 5–60°. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) used monochromatized Mg Kα radiation. The binding energies were corrected using 285 eV for C 1s as an internal standard. Argon-ion etching of the catalyst was carried out at 2 kV for 1 min with a sputtering rate estimated as ca. 2 nm/min for SiO_2.

3. Results and discussion

3.1. Effect of the partial pressure of O_2 on the ethane oxidation on Pr_6O_{11}

Fig. 1 shows the effect of the partial pressure of O_2 on the oxidative dehydrogenation of C_2H_6
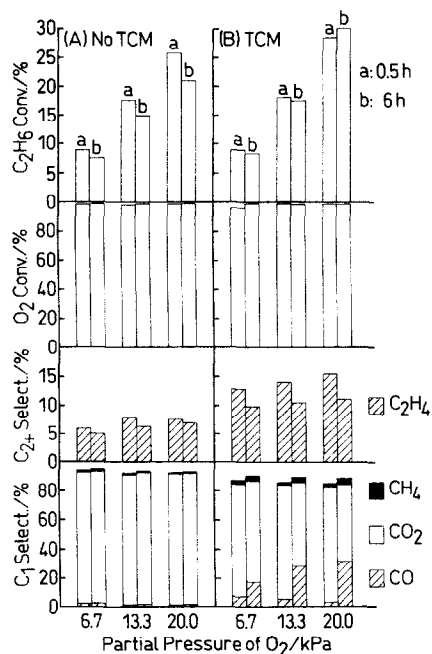

Fig. 1. Effect of partial pressure of O_2 on ethane oxidation on Pr_6O_{11} in the presence and absence of TCM at 773 K: (a) 0.5 h on-stream. (b) 6 h on-stream. Reaction conditions: $P(C_2H_6) =$ 27.1 kPa. $P(O_2) = 6.7$. 13.3 or 20.0 kPa, and $P(TCM) = 0.17$ kPa (when present) diluted with He. Total flow rate = 15 ml/min. Weight of catalyst = 0.7 g.

on Pr_6O_{11} in the presence and absence of TCM at 773 K, at which the homogeneous reaction is negligible [5]. The conversion of C_2H_6 in the absence of TCM increased with increasing $P(O_2)$, as expected, while the selectivities showed little or no dependence on this variable. With TCM in the feedstream, the selectivity to C_2H_4 at 0.5 h on-stream was significantly larger than that in its absence at all three values of $P(O_2)$, although decreases occurred with time-on-stream. The conversion of C_2H_6 remained relatively unchanged on the introduction of TCM, except at the highest $P(O_2)$. Particularly noteworthy is the increase in selectivity to CO with $P(O_2)$ when TCM is present. These observations of the effect of TCM are semiquantitatively similar to those made in the OCM on Pr_6O_{11}. It may be concluded, at least tentatively, that TCM functions, at least in part, as an inhibitor of the oxidation of CO.

At 973 K, at which the oxidation of ethane in

the gas phase is significant, the conversion of C_2H_6 and the selectivity to C_1 compounds, particularly to CO_2, increased in the absence of TCM while that to C_2H_4 decreased with $P(O_2)$, confirming the dependence of the oxidation to CO_2 on the concentration of O_2 in the feedstream (Fig. 2). Since the homogeneous oxidation of C_2H_6 at 973 K occurs readily with small selectivities to CO_2 [5], the heterogeneous reaction apparently contributes to the formation of CO_2 via secondary reactions of C_2H_4 or CH_4 during the oxidative dehydrogenation of C_2H_6. In contrast to observations at the lower temperature, at 973 K the conversions of C_2H_6 at 6.7 and 13.3 kPa of O_2 increased on introduction of TCM while that at 20.0 kPa was somewhat suppressed, the latter apparently due, in part, to the increased contribution of the homogeneous reaction at the higher temperature and oxygen partial pressure [5]. Although the selectivities to C_2 compounds remained relatively unchanged on addition of TCM, the increased selectivities to CH_4 and CO concomitant with the decrease of that to CO_2 provides additional evidence for
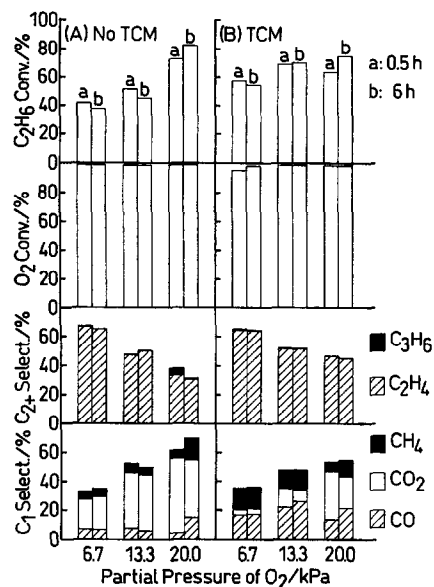

Fig. 2. Effect of partial pressure of O_2 on ethane oxidation on Pr_6O_{11} in the presence and absence of TCM at 973 K. Conditions and symbols as in Fig. 1 except reaction temperature.

the inhibition of secondary oxidation processes by TCM. The formation of C_3H_6 was observed in the absence of TCM at 973 K and 20.0 kPa

Table 2
XPS analyses of Pr_6O_{11} [a].

$P(O_2)$ [b] (kPa)	RT [c] (K)	ET [d] (min)	Binding energy [e] (eV)		Cl 2p	Atomic ratio	
			O 1s	Pr $3d_{5/2}$		Pr/O	Cl/Pr
6.7	773	0	531.3, 529.0 (5.7:1.0)	934.1, 929.8 (1.0:0.2)	198.3	0.33	1.10
		1	530.8, 528.8 (0.4:1.0)	933.4, 928.9 (1.0:0.3)	198.3	0.68	0.51
20.0	773	0	531.7, 529.3 (2.6:1.0)1	933.9, 929.2 (1.0:0.4)	198.5	0.17	2.09
		1	531.7, 529.7 (0.5:1.0)	934.0, 929.1 (1.0:0.4)	199.1	0.30	1.13
6.7	973	0	531.3, 529.2 (1.2:1.0)	933.4, 928.8 (1.0:0.5)	198.5	0.40	2.50
		1	531.7, 530.1 (0.3:1.0)	934.6, 929.7 (1.0:0.5)	199.4	0.64	0.15
20.0	973	0	531.8, 529.4 (1.9:1.0)	934.0, 929.7 (1.0:0.4)	198.5	0.32	1.71
		1	532.0, 529.7 (0.3:1.0)	934.2, 930.2 (1.0:0.5)	198.8	0.52	0.90

[a] Previously employed in obtaining results reported in Fig. 1(B) and Fig. 2(B).
[b] Partial pressure of O_2 in the feedstream.
[c] Reaction temperature.
[d] Etching time.
[e] Values in parentheses show intensity.

of O_2 but the selectivity to this hydrocarbon was diminished on introduction of TCM.

XRD patterns of each catalyst employed in ethane oxidation in the presence of TCM at 773 and 973 K show that PrOCl is formed in increasing quantities with increases in the partial pressure of O_2 in the feedstream (not shown). The carbonate is also formed but only at 773 K and 20.0 kPa of $P(O_2)$. With Pr_6O_{11} which had been used in ethane oxidation without TCM the carbonate was again detected under the aforementioned conditions but, as expected, no oxychloride was found (not shown).

The binding energies for O 1s, Pr $3d_{5/2}$ and Cl 2p, as determined from XPS analyses, are found to be invariant under the conditions employed in the present work (Table 2). Argon-ion sputtering produced substantial decreases in the intensities of the O 1s signal at ca. 531 eV [2,10] which were reflected in increases in the Pr/O atomic ratio. Such changes in the oxygen intensities probably result from the migration of oxygen to the surface where reaction with ethane can occur [11]. In contrast the XPS and XRD data suggest that the surface, in the presence of TCM, is first chlorinated and the chlorine penetrates into the bulk to form PrOCl.

3.2. Effect of the partial pressure of TCM and the pretreatment with TCM on the ethane oxidation of Pr_6O_{11}

At 773 K (Fig. 3(A)), the conversion of C_2H_6 remained virtually unchanged with increasing P(TCM) while the selectivities to C_2H_4 and to CO, the latter of which increased with increasing time-on-stream, increased on introduction of TCM at a partial pressure of 0.17 kPa but remained constant for higher pressures. In contrast, the selectivity to C_2H_4 at 973 K was not influenced by the introduction of TCM while the conversion of C_2H_6 and the selectivities to CH_4 and CO increased but, as at the lower temperature, showed little or no dependence on the partial pressure of TCM (Fig. 3(B)). At 973 K trace amounts of C_3H_6 were
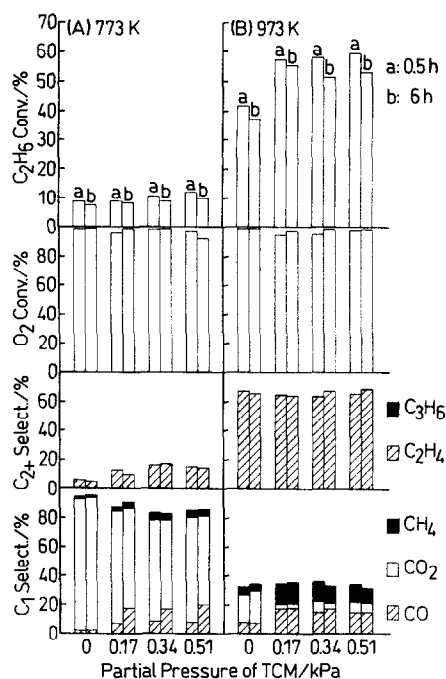

Fig. 3. Effect of partial pressure of TCM on ethane oxidation of Pr_6O_{11} at 773 and 973 K. Conditions and symbols as in Fig. 1Fig. 2 except the partial pressures of oxygen and TCM.

obtained in the presence of TCM but these were little influenced by the partial pressure of TCM. XRD patterns of catalysts previously employed in ethane oxidation both at 773 and 973 K showed that the quantities of PrOCl formed were strongly influenced by the partial pressure of TCM in the feedstream but were essentially independent of the reaction temperature (not shown).

To provide information on the contribution of the chlorinated catalyst to the ethane conversion process experiments were performed in which Pr_6O_{11} was pretreated with a mixture of TCM and O_2 prior to exposure to the reactant stream, the latter without TCM. At 773 K (Fig. 4(A)) the conversion of C_2H_6 and the selectivities to C_2H_4 increased slightly with the duration of pretreatment, providing evidence for the participation of the chlorinated surface, as PrOCl, in the ethane oxidation process. It should be noted that the aforementioned effect is considerably less significant than that observed in the OCM reaction [1,2]. The results obtained at 973 K
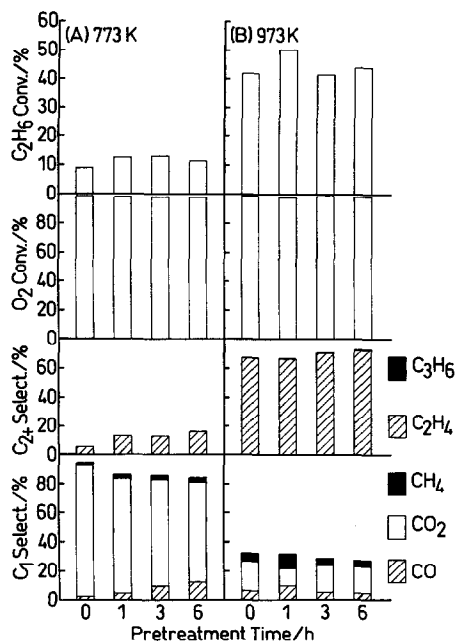
Fig. 4. Ethane oxidation in the absence of TCM at 773 and 973 K on Pr_6O_{11} pretreated with TCM. Data were collected at 0.5 h on-stream. Catalysts were pretreated with TCM (0.20 kPa) diluted with O_2 (total flow rate: 12.5 ml/min) at 1048 K for a given time. Conditions and symbols as in Fig. 1Fig. 2 except the partial pressure of O_2.

show little or no dependence on the TCM pre-treatment (Fig. 4(B)). The results obtained from C_2H_6 conversion at 773 K and at various times-on-stream with Pr_6O_{11} which had been pre-treated with TCM show decreases in the conversion and selectivity to C_2H_4 with the first increases in time-on-stream while that to CO increases (Fig. 5). In contrast at 973 K the changes in conversion and selectivities are probably insignificant. Although a definitive interpretation of these observation is not available at this time, it may tentatively be concluded that the contribution of TCM and the chlorinated surface diminishes as the temperature increases and concomitantly the homogeneous reaction plays a greater role.

3.3. Ethane oxidation in the presence and absence of TCM on $PrCl_3/Pr_6O_{11}$

Since it has been already reported that the chloride, not the oxychloride, formed on the

surface of the catalyst contributes to the improvement of the catalytic activities for the oxidative dehydrogenation of C_2H_6 in the presence of TCM on magnesium salts [5–7], it is of interest to investigate the catalytic activities of Pr_6O_{11} doped with the corresponding chloride, $PrCl_3$, for the ethane oxidation.

The introduction of $PrCl_3$ leads, at low times-on-stream, to increases in both the conversion of C_2H_6 and the selectivity to C_2H_4 at 773 K, regardless of the loading (Fig. 6(A)). The addition of TCM to the feedstream produces no further increment in the aforementioned results but either with or without TCM some diminution is observed with time-on-stream, although this is not as severe in the presence of TCM (Fig. 6(B)).
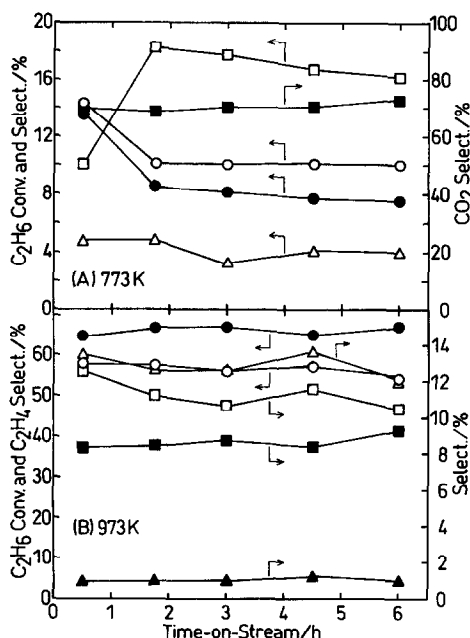
In contrast to the results at 773 K, those at

Fig. 5. Time-on-stream effects in ethane oxidation in the absence of TCM at 773 and 973 K on Pr_6O_{11} pretreated with TCM. Catalysts were pretreated with TCM (0.80 kPa), diluted with O_2 (total flow rate: 12.5 ml/min) at 1048 K for 1 h. Conditions as in Fig. 1Fig. 2 except the partial pressure. Symbols: open circles: conversion of C_2H_6; open squares: selectivity to CO; open triangles: selectivity to CH_4; filled squares: selectivity to CO_2; filled circles: selectivity to C_2H_4; filled triangles: selectivity to C_3H_6.
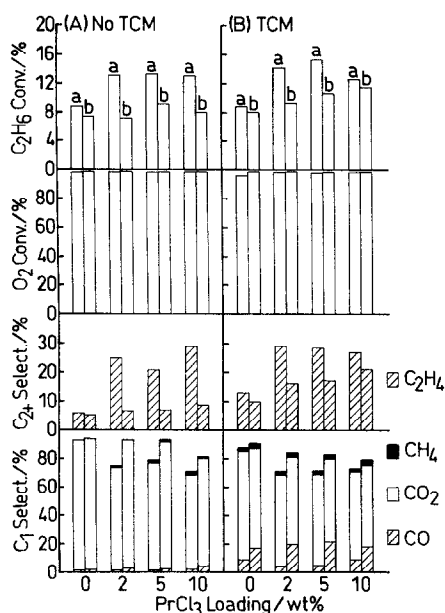
Fig. 6. Ethane oxidation in the presence and absence of TCM on $PrCl_3/Pr_6O_{11}$ at 773 K. Conditions and symbols as in Fig. 1 except the partial pressure of O_2.

973 K show no effect of the addition of $PrCl_3$, regardless of the loading (not shown). On addition of TCM to the feedstream, the conversion and selectivities to CH_4 and to CO increase while that to CO_2 decreases.

3.4. Effect of chlorinated species in the solid-and gas-phase

The results reported in the present work clearly show the advantageous effects of the introduction of TCM into the ethane/O_2 feedstream with Pr_6O_{11} at 773 K. Such enhancements are, however, largely absent at 973 K at which temperature homogeneous reactions are permanently dominant.

Results from XRD, XPS and reactions in which the catalyst had been pretreated with TCM before use but employed in the absence of TCM demonstrate that TCM is interacting with the catalyst. Although such interactions must initially involve the surface of the solid, as seen from XPS, evidently the chlorine is migrating into the bulk to form PrOCl, as observed from the XRD data. Unfortunately, however, it is

difficult, if not impossible to demonstrate, from the XPS results, that PrOCl is forming on the surface.

Although similar observations were made with TCM in the OCM reaction, these enhancements were quantitatively more significant than those found with ethane, presumably as a consequence of the relative ease of the latter reaction in comparison with the former [1].

It is of interest to speculate on the nature of the participation of chlorine in the ethane conversion process. At least two possibilities exist, one direct, one indirect. Although oxygen is frequently suggested as the site for activation of the C–H bond in the OCM reaction, the nature of the oxygen species is not yet known. However, such species are inevitably negatively charged. The presence of chlorine ions in the vicinity of these oxygen species may induce a perturbation of electron densities which is beneficial to the C–H scission process in both CH_4 and C_2H_6. It is also possible, of course, that Cl^- may itself act as the site for C–H bond scission.

4. Conclusions

1. The effects resulting from the addition of TCM to the feedstream in the conversion of C_2H_6 are considerably smaller than those observed in the oxidative coupling of methane.
2. The predominant effect seen on introduction of TCM with C_2H_6 is an increase in conversion and selectivity to C_2H_4 and CO while that to CO_2 decreases.
3. The aforementioned changes are evident at 773 K but are considerably diminished at 973 K.
4. XPS analysis shows that the surface of Pr_6O_{11} is chlorinated during C_2H_6 conversion with TCM present in the feedstream.
5. XRD analysis demonstrates that PrOCl is formed from TCM during the ethane conversion reaction.

6. The results from experiments in which Pr_6O_{11} was pretreated with TCM prior to use in the C_2H_6 reaction show that, at least at 773 K, the chlorinated surface contributes to changes in the conversion and selectivities.
7. Experiments with $PrCl_3/Pr_6O_{11}$ provide further evidence for the involvement of the chlorinated surface at 773 K but, in addition demonstrate that the attribution of the effect to a specific surface compound is not yet possible.
8. The effects of TCM in the C_2H_6 reaction and the participation of the chlorinated surface are more evident at 773 K at which temperature the heterogeneous reaction plays a more important role. However at 973 K, at which temperature the gas phase reaction is dominant, the contribution of TCM is less evident.

Acknowledgements

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