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A Comparative Study of the Oxides of Lanthanum, Cerium, Praseodymium, and Samarium as Catalysts for the Oxidative Dehydrogenation of Methane in the Presence and Absence of Carbon Tetrachloride

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The catalytic oxidative coupling of methane to ethane and ethene has been investigated on the rare earth oxides, i.e., La_2O_3, CeO_2, Pr_6O_{11}, and Sm_2O_3. Addition of a small amount of tetrachloromethane (TCM) to the reactant stream improves the catalytic activity of these oxides. In particular, the praseodymium catalyst yields high selectivity to the C_2 compounds comparable to La_2O_3 or Sm_2O_3 when TCM is present in the feedstream. The X-ray diffraction patterns for these catalysts after the reaction with TCM show the presence of the oxychlorides in the catalysts except for the cerium catalyst, for which the selectivity to C_2 compounds is very low even in the presence of TCM. The oxychlorides can be generated on La_2O_3, Sm_2O_3, or Pr_6O_{11} by preheating under a stream including TCM. The product distribution of the reaction with these catalysts in the absence of TCM is similar to that with the oxides in the presence of TCM, while Pr_6O_{11} pretreated with TCM is unstable with no TCM in the feedstream. It appears that the improvement of the activity of the rare earth catalysts with TCM in the feedstream is primarily due to the formation of the oxychlorides during the reaction.

INTRODUCTION

The oxidative dehydrogenation of methane generally produces selectivities to the preferred products, ethane and ethylene, and conversions and yields of methane which are less than desirable (*1*). A variety of approaches to improve the results has been explored by a number of researchers. Work in this laboratory has examined the effect of the addition of small quantities of chlorine (primarily in the form of carbon tetrachloride) into the catalyst or the feedstream (*2*), and work in other laboratories has focused on chlorine-promoted catalysts (*3*). With many but not all of the oxygen-containing catalysts it is found that both the conversion of methane and the total selectivity to C_{2+} hydrocarbons is increased on addition of as little as 0.1% of tetrachloromethane (TCM) to the feedstream. In addition, the selectivity to ethylene is increased while that to ethane is diminished.

Earlier studies with the metal–oxygen cluster compounds, 12-molybdophosphoric and 12-tungstophosphoric acids, supported on silica, have shown that selectivities to methyl chloride of 80% or higher can be obtained on the latter catalyst at 570°C (*4–6*). Furthermore a pretreatment of these catalysts with TCM followed by reaction of methane in the absence of TCM from the feedstream initially yields selectivities and conversions similar to those expected where a small quantity of TCM is added continuously to the feedstream (*6*). A simi-

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lar observation has been recorded with a number of supported oxides (*7*). Evidently the TCM is interacting with and altering the surface of the catalyst and is not simply functioning in the gas phase, although its participation in the gas-phase reactions cannot be excluded. Although there have been a number of studies concerned with the effect of the introduction of halogens to the catalyst and/or the feedstream, the source of the effect of such introductions is not yet clear.

The oxides of lanthanum, cerium, praseodymium, and samarium have received considerable attention as catalysts in the conversion of methane (*8–40*), with that of lanthanum being the most widely studied of these catalysts (*8–21*). Samarium oxide, while less frequently studied than lanthanum oxide, has nevertheless attracted considerable interest as a catalyst for the conversion of methane (*27–40*), while reports on the application of both cerium (*22–24*) and praseodymium (*25–27*) oxides have been relatively few in number.

The present work is concerned with a comparison of the oxides of the four lanthanides La, Ce, Pr, and Sm for the conversion of methane and, in particular, with an evaluation of the effect of the addition of small quantities of carbon tetrachloride to the feedstream for the purpose of providing further information on the nature and source of the effect of this additive.

EXPERIMENTAL

La_2O_3 (99.999%, surface area 2.1 m^2/g), CeO_2 (99.9%, surface area 12.7 m^2/g), Pr_6O_{11} (99.9%, surface area 1.6 m^2/g), and Sm_2O_3 (99.9%, surface area of 9.0 m^2/g), were obtained from Aldrich and used without further purification.

The catalytic experiments were performed in a fixed-bed continuous flow reactor operated under atmospheric pressure. The reactor was designed to minimize the free volume in the hottest zone to reduce the contribution of noncatalytic homogeneous reactions. The reactor consisted of a quartz tube of 7 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 20 cm. The catalyst was held in place in the enlarged portion of the reactor by two quartz wool plugs. In those experiments in which carbon tetrachloride (TCM) was added, the additive was introduced to the main flow of reactants (CH_4 or C_2H_6, O_2, and diluent helium) by saturating a separate stream of helium with TCM at 0°C. The reactor was usually charged with an aliquot of 0.7 g and the total flow rate was kept constant (at 15.0 ml min^{-1}). In all experiments, the temperature of the catalyst was raised to 775°C while maintaining a continuous flow of He and was then conditioned at this temperature under a 12.5 ml min^{-1} flow of O_2 for 1 h unless otherwise stated. The reactor was then purged with He and adjusted to the reaction temperature before introduction of the reactant gas mixture of CH_4, O_2, TCM (when present), and He (total flow rate, 15 ml min^{-1}).

The reactants and products were analyzed with an on-stream HP 5880 gas chromatograph equipped with a TC detector and integrator. Two columns, one Porapak T (5.4 m) and the other Molecular Sieve 5A (0.4 m), were employed in the analyses. The conversions and selectivities were calculated on the basis of the amount of reaction products formed as determined by the GC analysis.

Blank experiments conducted with CH_4 or C_2H_6 absent from the feed (O_2 + He + TCM) indicated that TCM undergoes oxidation producing CO and/or CO_2. The data reported were corrected by running duplicate experiments with CH_4 or C_2H_6 absent under otherwise identical sets of values of the process variables.

Powder X-ray diffraction patterns (XRD) were recorded on a Siemens Model D500 diffractometer using nickel-filtered Cu*Kα* radiation. Patterns were recorded over the range $2\theta = 5–70°$. The samples were supported in a sampler holder with depth of 1 mm.

TABLE 1

Methane Conversion over Lanthanide Oxides in the Presence and Absence of TCM[a]

Catalyst[b]	Time-on-stream (h)	Conversion		Selectivity (%)				
		CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	C_3
Pr_6O_{11} in absence of TCM	0.5	6.5	98	4.4	62.5	9.7	22.1	1.2
	6.0	6.1	100	5.6	67.2	7.4	18.6	1.2
Pr_6O_{11} in presence of TCM	0.5	11.9	99	10.5	65.3	11.4	11.8	1.1
	3.0	15.7	100	22.9	40.9	19.7	15.0	1.4
	6.0	17.2	100	25.0	31.8	28.1	13.2	2.0
Sm_2O_3 in absence of TCM	0.5	17.0	100	8.1	38.3	27.0	23.8	2.8
	6.0	17.2	100	9.3	38.5	26.7	22.8	2.8
Sm_2O_3 in presence of TCM	0.5	12.0	99	23.5	29.9	27.6	16.8	2.3
	3.0	11.4	100	28.4	20.4	31.6	17.0	2.5
	6.0	11.2	100	26.3	19.6	32.8	18.5	2.9
La_2O_3 in absence of TCM	0.5	14.3	100	5.0	29.3	26.1	35.8	3.9
	6.0	13.7	100	9.1	27.1	27.0	33.7	3.1
La_2O_3 in presence of TCM	0.5	15.4	100	10.9	31.0	25.8	29.4	2.9
	3.0	15.2	100	21.0	22.4	24.3	29.1	3.2
	6.0	14.9	100	21.0	22.4	24.3	29.1	3.2
CeO_2 in absence of TCM	0.5	13.5	100	70.8	29.2	0.0	0.0	0.0
	6.0	13.9	100	63.1	36.9	0.0	0.0	0.0
CeO_2 in presence of TCM	0.5	13.9	100	63.2	36.8	0.0	0.0	0.0
	3.0	13.6	100	59.9	40.1	0.0	0.0	0.0
	6.0	13.8	100	55.7	44.2	0.0	0.1	0.0

[a] Reaction conditions: catalyst, 0.7 g; CH_4, 215 Torr; O_2, 30.4 Torr; TCM, 1.3 Torr (when present); total flow rate, 15 ml min^{-1}; reaction temperature, 750°C.

[b] Pretreatment: O_2 (12.5 ml min^{-1}) for 1 h at 775°C.

RESULTS

Methane Conversion over Lanthanide Oxides with TCM Addition

The results for the conversion of methane on each lanthanide oxide, Pr_6O_{11}, Sm_2O_3, La_2O_3, and CeO_2, at 750°C under the standard conditions ($CH_4/O_2 = 7$) are summarized in Table 1. The principal products on Pr_6O_{11}, Sm_2O_3, and La_2O_3 were CO, CO_2, C_2H_4, and C_2H_6 both in the presence and absence of TCM. C_3 species were also detected on these three catalysts but the amount was small. On CeO_2, the principal products were CO and CO_2 plus a very small amount of C_2H_6 during 6 h on-stream in the presence of TCM. Water and hydrogen were produced on each catalyst. In the absence of TCM, Pr_6O_{11} produced low selectivities to C_{2+} compounds, while the activity remained stable over a 6-h period on-stream as previously reported (*25–27*). However, addition of TCM to the feedstream resulted in an increase in the C_{2+} selectivity during the reaction. While the selectivity to C_{2+} compounds was only 24.3% after 0.5 h on-stream, it increased to 43.3% over 6 h on-stream. The conversion of methane after 0.5 h on-stream was 11.9%, approximately twice that found in the absence of TCM, although the conversions of oxygen in the presence and in the absence of TCM were both nearly 100%. The amount of hydrogen produced in the reaction could not be determined quantitatively, however, that in the presence of TCM was significantly larger than that in the absence of TCM. It is noteworthy that over the 6 h on-stream with TCM present the C_2H_4/C_2H_6 ratio increased from 1.0 to 2.1. After reaction in the presence of TCM, the colour of the catalyst in the inlet portion of the bed was found to have been converted from the original black to white-green. The amount of the white-green portion was approximately 0.2 g and the main peaks in its XRD pattern were at 25.6°, 31.2°, and 34.4° in 2θ and were identical with that of PrOCl (*41*).

As expected from earlier reports in the literature (*27–39*), Sm_2O_3 displayed both high activity and stability in the absence of TCM. On introduction of TCM into the feedstream both the conversion of CH_4 and the C_{2+} selectivity decreased, the former from 17.0 to 12.0% in 0.5 h and the latter from 53.6 to 46.7% in the same time, while the C_2H_4/C_2H_6 ratio increased from 1.1 to 1.6 (see Table 1). Similar to the observations of the formation of PrOCl with Pr_6O_{11} as noted above, peaks attributed to SmOCl were also observed in the XRD pattern of Sm_2O_3 (*41*) after the reactions with TCM. The main peak for the oxychloride appeared at 25.7°, 31.5°, and 34.7° in 2θ. The selectivity to C_{2+} hydrocarbons was quite stable over La_2O_3 both in the presence and absence of TCM. Somewhat surprisingly, however, with TCM in the feedstream the selectivity to CO increased from 11 to 21%, while that to CO_2 decreased from 31 to 22% over 6 h on-steam. The peaks attributed to PrOCl were also observed in the XRD pattern of La_2O_3 after the reaction with TCM at 25.0°, 30.5°, and 33.7° (*41*). On CeO_2, the selectivity to C_2 species was insignificant with or without TCM and the conversion of CH_4 remained essentially unchanged at 14% after addition of TCM. However, as with the former three lanthanide oxides, the selectivity to CO_2 decreased on addition of TCM to the feedstream. Although formation of oxychlorides was observed over Pr_6O_{11}, Sm_2O_3, and La_2O_3, no peaks attributed to CeOCl were observed in the XRD pattern of CeO_2 after the reaction with TCM (*41*).

Effect of TCM Addition on Pr_6O_{11}

The addition of TCM to the feedstream produced a remarkable improvement in the catalytic activity of Pr_6O_{11}. In the presence of TCM, the conversion of CH_4 and selectivity to C_{2+} compounds increased with reaction temperature up to 800°C (Fig. 1). Somewhat surprisingly, the conversion of CH_4, the selectivity to C_{2+} and the C_2H_4/C_2H_6 ratio all increased with time-on-stream at each temperature. As noted above the inlet portion of the catalyst bed was observed to change to a white-green colour except for the catalyst employed in the reaction at 850°C, while the formation of a small amount of PrOCl was confirmed from its XRD pattern.

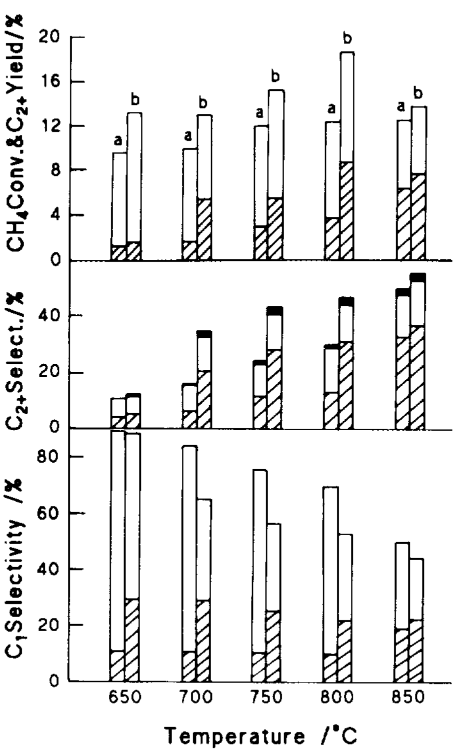

FIG. 1. The effect of temperature in the conversion of CH_4 and selectivities of C_1 and C_{2+} on Pr_6O_{11} in the presence of TCM (O_2 conversion ≥99%). Reaction conditions: CH_4, 215 Torr; O_2, 30.4 Torr; TCM, 1.3 Torr (when present); total flow rate, 15 ml min^{-1}; weight of catalyst, 0.7 g. Symbols: (a) 0.5 h on-stream; (b) 6 h on-stream; ▤, CH_4 conversion; ▨, C_{2+} yield, C_{2+} selectivities: ▨, C_2H_4; □, C_2H_6; ■, C_3; C_1 selectivities: ▨ CO; □, CO_2; ■, CH_3Cl.

The behaviour of the catalyst during an

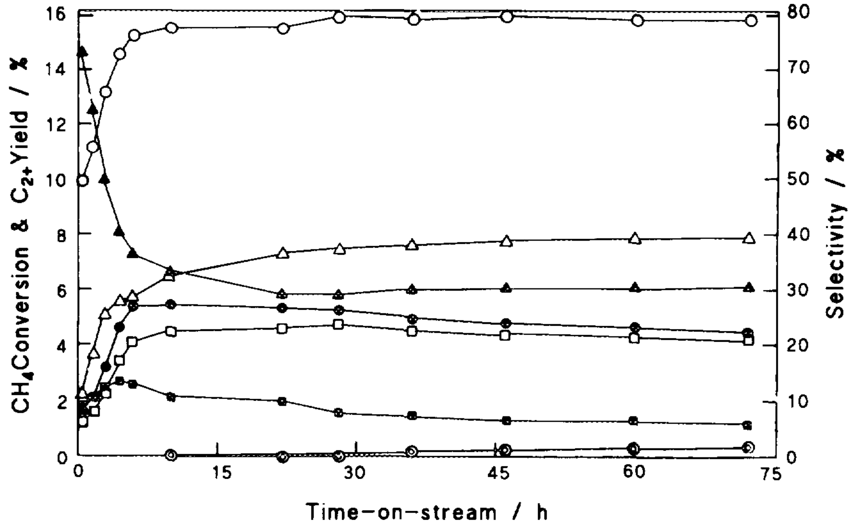

FIG. 2. Extended time-on-stream effects in the conversion of CH_4 on Pr_6O_{11} at 700°C in the presence of TCM (O_2 conversion ≥97%). Reaction conditions: CH_4, 215 Torr; O_2, 30.4 Torr; TCM 1.3, Torr (when present). Total flow rate, 15 ml min^{-1}; weight of catalyst, 0.7 g. Symbols: ○, CH_4 conversion; □, C_2H_4 selectivity; ■, C_2H_6 selectivity; △, CO selectivity; ▲, CO_2 selectivity; ●, C_{2+} yield; and ◎, CH_3Cl selectivity.

extended time-on-stream in the presence of TCM is reported in Fig. 2 (reaction temperature, 700°C). After the first 6 h on-stream, during which the conversion of CH_4 and the selectivities to C_2^+ compounds and CO increased sharply, the conversion remained approximately constant while the C_2H_4/C_2H_6 ratio increased with the time-on-stream. Interestingly, the selectivity to CH_3Cl increased with time-on-stream, but over 72 h did not reach values higher than 2%. After this time the colour of the catalyst bed was completely changed to white-green and the mass of the catalyst of this colour was now approximately 0.8 g.

With increase in the CH_4/O_2 ratio the conversion of CH_4 decreased while the C_{2+} selectivity increased (Fig. 3). The C_{2+} yield remained approximately constant for values of CH_4/O_2 equal to 3.5 and 7.1 and decreased with further increase of CH_4/O_2 from 7.1 to 14.2. As expected the C_2H_4/C_2H_6 ratio decreased with increasing CH_4/O_2 ratio (C_2H_4/C_2H_6 equal to 1.5 and 2.2 at CH_4/O_2 values equal to 14.2 and 3.5, respectively, after 6 h on-stream). The quantity of catalyst undergoing a colour change was approximately 0.2 g regardless of the CH_4/O_2 ratio after 6 h on-stream.

The effect of changes in the concentration of TCM in the feedstream is shown in Fig. 4. For four concentrations of TCM, a maximum in the conversion of methane is found at 1.3 Torr of TCM. The highest ratio of C_2H_4/C_2H_6 was found at 2.6 Torr. The selectivities to CO increased with increasing TCM concentration while those to CO_2 decreased. The quantity of recovered catalyst which had undergone a colour change was dependent on the concentration of TCM (0.0, 0.2, and 0.5 g at 0.65, 1.3, and 2.6 Torr, respectively).

Pretreatment of Pr_6O_{11} with TCM for Extended Periods of Time

In order to obtain further information on the participation of TCM in the conversion process two series of experiments in which the catalyst was pretreated for extended periods of time were carried out. The first con-

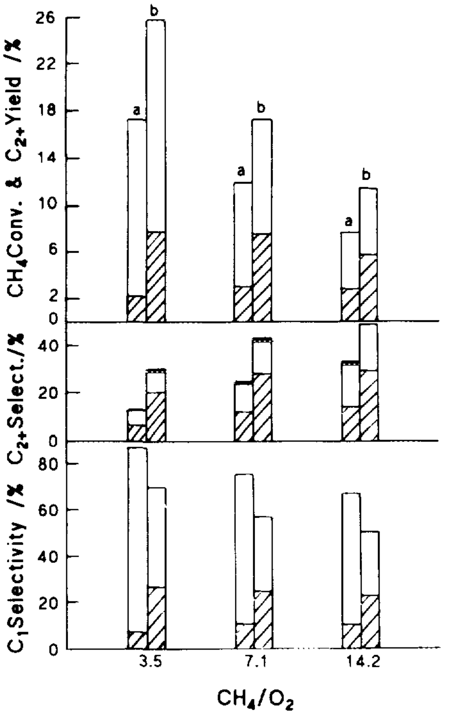

FIG. 3. The effect of CH$_4$/O$_2$ in the conversion of methane on Pr$_6$O$_{11}$ in the presence of TCM (O$_2$ conversion ≥99%). Reaction conditions and symbols as in Fig. 1 except for the partial pressure of O$_2$.

sisted of pretreatment with 2.6 Torr of TCM diluted with He for 15 h at 775°C, while the second employed 2.6 Torr of TCM and 30.4 Torr of O$_2$ again diluted with He. Subsequent to each of these experiments separate aliquots of the catalysts were employed in methane conversion experiments in the presence and in the absence of TCM in the feedstream.

Methane conversion in the absence of feedstream TCM on the TCM-pretreated praseodymium catalyst displayed a significantly different behaviour as compared with that found after the usual pretreatment [see Fig. 5(II) and Table 2]. After 0.5 h on-stream, the conversions of CH$_4$ and O$_2$ were relatively low (4.4 and 24%, respectively) but the C$_2$H$_4$/C$_2$H$_6$ ratio was approximately 9. Interestingly, the selectivity to CH$_3$Cl after this time period was very high (20.7%). However, after 1.75 h on-stream, the conversions of CH$_4$ and O$_2$ had increased to 12.6 and 91%, respectively, while the conversion of O$_2$ after 6 h on-stream had increased to 99%. At 1.75 h on-stream the conversion of CH$_4$ reached a maximum of 12.6% and decreased with additional time-on-stream. The high value for selectivity to CH$_3$Cl at 0.5 h on-stream decreased to a trace at 1.75 h, while the C$_2$H$_4$/C$_2$H$_6$ ratio decreased to less than 1 and finally at 6 h the selectivity to CO and CO$_2$ was as high as 82%. After the reaction the inlet portion of the catalyst was black, while the remainder of the catalyst had become white-green. With 1.3 Torr of TCM in the freedstream and a TCM-pretreated catalyst [Fig. 5 (I)] the methane conversion process was quite stable in contrast with that where the usual

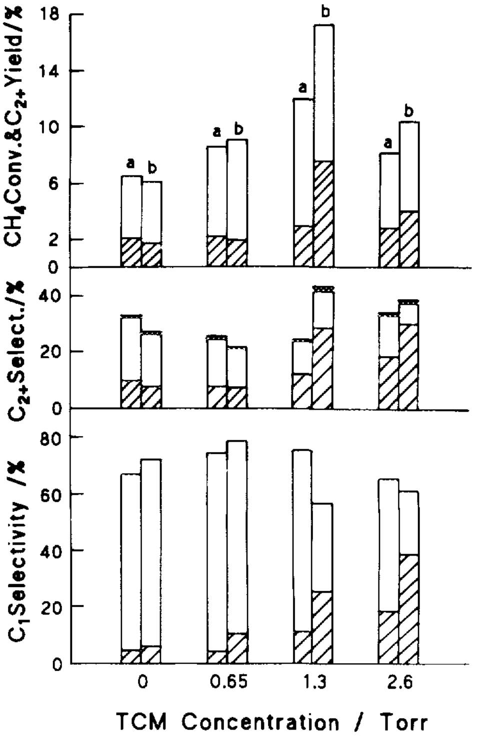

FIG. 4. Conversions and selectivities on Pr$_6$O$_{11}$ for various feedstream concentrations of TCM (O$_2$ conversion ≥98%). Reaction conditions and symbols as in Fig. 1.

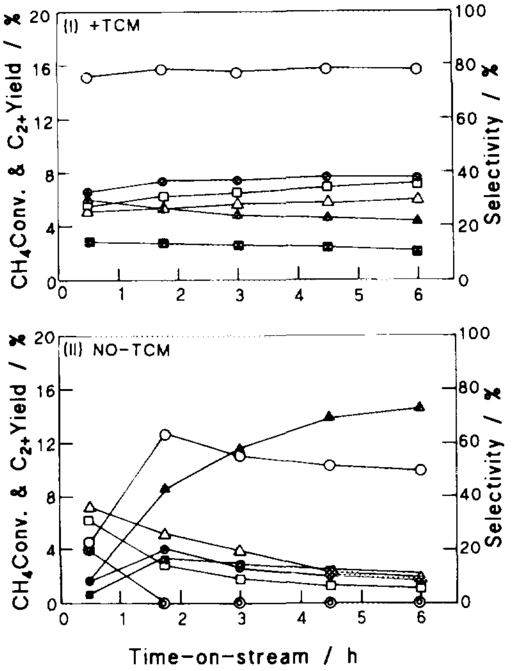

FIG. 5. The conversion and selectivities from CH_4 in the presence (I) and absence (II) of TCM on Pr_6O_{11} pretreated with TCM for 15 h (O_2 conversion ≥99% except (II); see text). Reaction conditions and symbols as in Fig. 2. Pretreatment: TCM 2.6 Torr diluted with He (total flow rate, 15 ml min^{-1}) for 15 h at 775°C.

pretreatment had been employed (see Table 1). Approximately the same conversion and selectivity were obtained after 6 h on-stream in the presence of TCM with a catalyst which had been subjected to the usual pretreatment. After the reaction the outlet portion of the catalyst was black and the quantity of the white-green portion at the reactor inlet was 0.5 g, while the whole catalyst had become white-green just after the pretreatment. Powder XRD patterns of the white-green catalyst after the extended pretreatment with TCM were identical with that of PrOCl *(41)*.

After the extended pretreatment with TCM and O_2, subsequent use in the conversion process on the praseodymium catalyst produced relatively different results in the absence of TCM [Fig. 6 (II)]. The conversion of CH_4 decreased gradually from 16.5 to 11.7% over 6 h on-stream and the C_{2+} yields at each time-on-stream were higher than those found with a TCM-only-pretreated catalyst. In contrast with the TCM-only-pretreated catalyst with which an appreciable selectivity to CH_3Cl was initially observed, with the catalyst pretreated with TCM and O_2 no CH_3Cl was observed at any time during the reaction.

In the presence of TCM, the conversion of CH_4 and selectivities to the various products with the catalyst pretreated with TCM and O_2 were again quite stable, similar to those found for the TCM-only-pretreated catalyst [cf. Fig. 5 (I) and 6 (I)]. Traces of CH_3Cl were found after 1.75 h on-stream. After the reaction, the whole catalyst was found to be white-green.

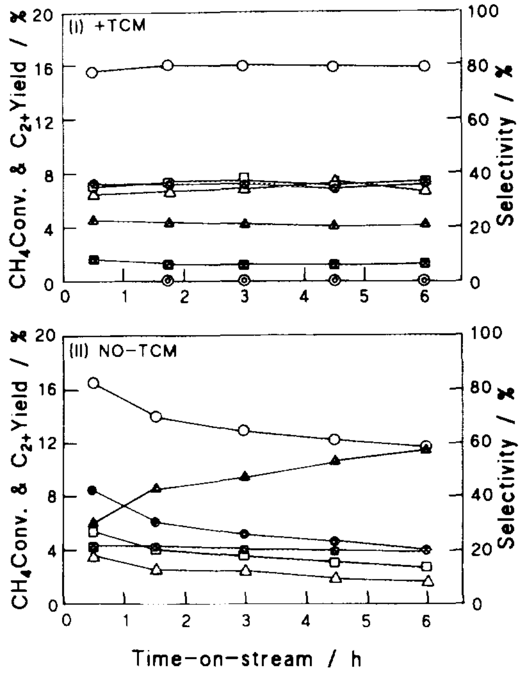

FIG. 6. The conversion and selectivities from CH_4 in the presence (I) and absence (II) of TCM on Pr_6O_{11} pretreated with TCM + O_2 for 15 h (O_2 conversion ≥98%). Reaction conditions and symbols as in Fig. 2. Pretreatment: TCM, 2.6 Torr, and O_2, 30.4 Torr, diluted with He (total flow rate 15 ml min^{-1}) for 15 h at 775°C.

TABLE 2

Methane Conversion over Lanthanide Oxides Free from TCM and over Oxides Pretreated with TCM and O_2[a]

Catalyst[b]	Conversion (%)		Selectivity (%)				
	CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	C_3
Pr_6O_{11} (O_2) in absence of TCM	6.9	99	1.6	69.6	5.9	20.0	2.7
Pr_6O_{11} (TCM, O_2) in presence of TCM	12.3	63	29.1	20.1	28.3	17.8	3.5
Sm_2O_3 (O_2) in absence of TCM	9.6	67	36.6	12.2	19.3	19.5	2.9
Sm_2O_3 (TCM, O_2) in presence of TCM	4.8	22	19.3	8.1	28.1	36.2	5.4
La_2O_3 (O_2) in absence of TCM	12.9	68	23.2	16.8	21.5	33.5	4.9
La_2O_3 (TCM, O_2) in presence of TCM	4.6	20	23.5	13.7	22.4	30.2	4.9

[a] Reaction conditions: catalyst, 0.7 g; CH_4, 215 Torr; O_2, 30.4 Torr; TCM, 1.3 Torr (when present); total flow rate, 15 ml min^{-1}; reaction temperature, 750°C.

[b] Pretreatment: (O_2), O_2 (12.5 ml min^{-1}) for 1 h at 775°C; (TCM), TCM 1.3 Torr diluted with He (total flow rate, 15 ml min^{-1}) for 15 h at 775°C.

To compare the catalytic activity with and without TCM at low O_2 conversion, the conversion of CH_4 was carried out over a small amount of catalyst. With 0.5 g of Pr_6O_{11} pretreated with TCM and O_2 for 15 h, O_2 conversion was 63% after 0.5 h on-stream in the presence of TCM (Table 2). The C_2H_4/C_2H_6 ratio was 1.6, while with 0.70 g of Pr_6O_{11} pretreated under TCM and O_2 flow this ratio was approximately 4 (see Table 3). The O_2 conversion remained at 99% with only 0.02 g of Pr_6O_{11} pretreated under oxygen flow and the result was similar to that with 0.70 g of the oxide while selectivity to CO was significantly lower (Table 2). The low CO selectivity may be due to the participation of the gas-phase reaction because the volume of the catalyst was very small compared with that of the reactor.

In contrast with the aforementioned observations, the main product in a reaction employing a catalyst pretreated with liquid TCM at room temperature was CO_2 (approximately 80% selectivity) and the conversion of methane was slightly increased.

It is of interest to examine the behaviour of the Pr_6O_{11} catalysts after the various pretreatments in the conversion of CH_4 with no oxygen present (Table 4). As expected the conversion of CH_4 is low in all examples. However, catalysts pretreated with TCM and O_2 produced higher CH_4 conversions than the catalyst pretreated with only TCM.

Effect of TCM Pretreatment on Sm_2O_3 and La_2O_3

To determine the contribution of TCM in the conversion process, similar experiments to those with Pr_6O_{11} were performed with Sm_2O_3 and La_2O_3. These catalysts were pretreated with 1.3 Torr of TCM and 30.4 Torr of O_2 diluted with helium for 15 h at 775°C. Methane conversion was carried out in the presence or absence of feedstream TCM (Table 3). Neither of these catalysts displayed significantly large changes in the catalytic activity during the reaction. The XRD patterns for the catalysts just after the 6 h on stream were recorded. The patterns for Sm_2O_3 after the reaction showed peaks for the oxychloride, oxide, and the intensity ratios of the peaks for oxychloride (at 25.7° in 2θ) vs that for oxide (at 28.0°) were 0.26 ($SmOCl/Sm_2O_3$) in the presence of feedstream TCM and 0.10 in the absence of TCM, while that for Sm_2O_3 after the reaction with TCM following the pretreatment under an oxygen flow was 0.10. In the case of La_2O_3 the peak ratio were 0.93 in the presence of feedstream TCM and 0.20 in the absence of TCM, while that after the reaction with TCM following the oxygen pre-

TABLE 3

Methane Conversion over Lanthanide Oxides Pretreated with TCM and O_2 in the Presence and Absence of TCM[a]

Catalyst[b]	Time-on-stream (h)	Conversion (%)		Selectivity (%)				
		CH_4	O_2	CO	CO_2	C_2H_4	C_2H_6	C_3
Pr_6O_{11} in absence of TCM	0.5	16.5	99	18.3	30.2	27.1	21.7	2.7
	6.0	11.2	100	8.6	57.2	13.9	18.9	1.4
Pr_6O_{11} in presence of TCM	0.5	15.6	98	32.2	22.2	35.0	8.1	2.5
	6.0	15.9	98	33.2	21.2	36.9	6.3	2.1
Sm_2O_3 in absence of TCM	0.5	17.9	99	23.6	25.1	31.2	17.4	2.7
	3.0	17.3	100	23.1	26.8	30.6	16.7	2.6
	6.0	16.8	100	24.9	25.7	30.5	16.4	2.6
Sm_2O_3 in presence of TCM	0.5	18.8	99	30.0	21.4	34.1	12.2	2.2
	3.0	16.8	99	29.0	19.8	35.0	13.8	2.3
	6.0	16.7	99	29.1	19.4	35.2	13.9	2.4
La_2O_3 in absence of TCM	0.5	15.5	96	16.5	35.5	20.6	25.0	2.5
	3.0	15.3	95	22.8	28.4	20.1	25.8	3.0
	6.0	14.9	95	23.4	27.9	20.0	26.2	2.3
La_2O_3 in presence of TCM	0.5	15.4	98	5.0	31.1	26.9	35.0	3.0
	3.0	15.2	98	7.2	27.1	27.6	34.3	3.7
	6.0	14.9	98	7.7	27.0	27.8	34.0	3.4

[a] Reaction conditions: catalyst, 0.7 g; CH_4, 215 Torr; O_2, 30.4 Torr; TCM, 1.3 Torr (when present); total flow rate, 15 ml min^{-1}; reaction temperature, 750°C.

[b] Pretreatment: TCM 1.3 Torr except for Pr_6O_{11} (2.6 Torr) diluted with He (total flow rate, 15 ml min^{-1}) for 15 h at 775°C.

treatment was 0.07 (the peak for LaOCl, 33.7°; for La_2O_3, 25.7°).

With 0.05 g of Sm_2O_3 and La_2O_3 pretreated with TCM and O_2, the oxygen conversion was quite low in the reaction with TCM while the same quantity of the catalysts pretreated with oxygen produced higher CH_4 and O_2 conversions in the absence of TCM (see Table 2).

The pretreatment with only 1.3 Torr of TCM at 775°C for 15 h produced results similar to those obtained following pretreatment with TCM and O_2.

DISCUSSION

Effect of TCM on Pr_6O_{11}

The conversion of methane and the selectivities to the various products on the four catalysts studied in this work showed significant differences for each of these solids both in the absence and presence of TCM. Under the reaction conditions employed CeO_2 in the least selective catalyst to C_{2+} hydrocarbons, with essentially all of the methane being converted to CO and CO_2, while La_2O_3 is the most selective to the desired products.

Remarkable differences in the effects of the addition of TCM to the feedstream are observed between the various catalysts. The addition of TCM with CeO_2 produced relatively little changes in the selectivities or conversion, except for a decrease in CO_2. With La_2O_3 on addition of TCM the conversion of methane increased slightly and the C_{2+} selectivity by approximately 20%. With Sm_2O_3 in the presence of TCM in the feedstream both the conversion and C_{2+} selectivity decreased while the C_2H_4/C_2H_6 ratio increased by approximately 50%.

The addition of TCM to the feedstream produces a remarkable increase in the C_{2+} selectivity of Pr_6O_{11}. The selectivity to CO_2, initially not too dissimilar from that in the

TABLE 4

Reduction of Pr_6O_{11} with Methane at 750°C[a]

Pretreatment	Time-on-stream (h)	CH_4 conv. (%)	Selectivity (%)					
			CO	CO_2	H_2CO	C_2H_4	C_2H_6	C_3
With O_2 at 775°C	0.5	0.57	48.4	27.6	0.0	8.0	15.9	0.0
for 1 h	6.0	0.13	71.9	6.0	0.0	4.4	17.7	0.0
With TCM at 775°C	0.5	0.03	14.8	0.0	0.0	17.9	67.4	0.0
for 15 h[b]	6.0	0.01	0.0	0.0	0.0	41.6	58.4	0.0
With TCM + O_2 at	0.5	0.70	98.9	1.1	0.0	0.0	0.0	0.0
775°C for 15 h[c]	6.0	0.10	90.0	5.1	0.0	1.9	3.0	0.0

[a] Reaction conditions: Pr_6O_{11}, 0.7 g; CH_4, 215 Torr diluted with He (total flow rate, 15 ml min^{-1}).

[b] TCM (2.6 Torr) was diluted with He (total flow rate, 15 ml min^{-1}).

[c] TCM (2.6 Torr) and O_2 (30.4 Torr) were diluted with He (total flow rate, 15 ml min^{-1}).

absence of TCM, decreases with time-on-stream (see Table 1). Concomitantly the selectivity to C_2H_4, again initially similar to that observed in the absence of TCM, increases with time-on-stream and, after 6 h, attains a value approximately three times larger with TCM present.

From the XRD pattern (not shown) it is evident that the white-green portion of the catalyst formed after the reaction with TCM present in the feedstream is PrOCl. At reaction temperatures in excess of 750°C the quantity of PrOCl decreased suggesting that at such temperatures Pr_6O_{11} is thermodynamically more stable than PrOCl. In the absence of feedstream TCM, Pr_6O_{11} previously heated under a stream of O_2 and TCM for 15 h displayed a high C_{2+} selectivity in the initial stages of the reaction [see Fig. 6 (II)]. These results suggest that the oxychloride is formed from TCM in the feedstream, either in the presence or absence of CH_4 and further that the oxychloride has a superior C_{2+} selectivity to the oxide, although in the absence of TCM from the feedstream, the oxychloride is deactivated. However, after preheating the Pr_6O_{11} with oxygen-free TCM for 15 h, the resulting catalyst displayed a low activity during the initial stages of the reaction, although PrOCl was also formed in this pretreatment [Fig. 5 (II)]. Although the catalyst pretreated in this manner produced a low conversion of CH_4, nevertheless the selectivity to C_2 hydrocarbons was high, suggesting the existence of active surface oxygen sites on PrOCl, although these appear to be small in number subsequent to the pretreatment with TCM in the absence of O_2 (Table 4). The formation of a considerable quantity of CH_3Cl during the initial stages of the reaction with the catalyst preheated only with TCM and the formation of a black compound on the inlet portion of the reactor suggested that dechlorination takes place from the surface oxygen-deficient PrOCl [Fig. 5 (II)]. The restoration of the catalytic activity of these species presumably results from the reoxidation of this surface oxygen-deficient oxychloride during the initial stages of the reaction [Fig. 5 (II)]. From isotopic studies Ekstrom and Lapszewicz showed that lattice oxygen is involved with Pr_6O_{11} in methane oxidation but did not play a role with Sm_2O_3 (*27*). Hence, the results obtained with small quantities of the catalyst (Table 2) suggest that the lattice oxygen in Pr_6O_{11} is much more active than that in PrOCl although the site mainly produces carbon oxides. Increased quantities of TCM in the feedstream reduce the catalytic activity in spite of the production of increased quantities of PrOCl (see Fig. 4 and text). It may be deduced that an excess of TCM reacts with the active oxygen sites and interferes in the conversion of methane. When TCM was present in the feedstream, significant amounts of the oxide were observed after the reaction with the catalyst pretreated with TCM but not with O_2 [Fig. 5 (I)], although no black portion was found just after the pretreatment. The mechanism for formation of the oxide during the reaction is not clear, but it is possible that the C_{2+} compounds formed assist dechlorination of PrOCl, which would be unstable as a result of the deficiency of surface oxygen.

Effect of TCM on Sm_2O_3, La_2O_3, and CeO_3

Addition of TCM to the feedstream of reaction or to the stream for pretreatment generates a small amount of SmOCl on Sm_2O_3. It is of interest to note that Burch *et al.* have found that Sm_2O_3 and SmOCl have comparable activities for the methane conversion process, although the activity of SmOCl cannot be retained without a supply of chlorine (*42*). As can be seen in their report, the catalyst containing SmOCl produces higher C_2H_4/C_2H_6 ratio at a lower space velocity than Sm_2O_3 free from the oxychloride although activity is lower than that of the oxide. In the absence of TCM in the reaction stream, the catalyst pretreated with TCM and O_2 contained a smaller quantity of SmOCl and produced lower C_2H_4/C_2H_6 ratios than the catalyst obtained in the presence of TCM in the feedstream (see Table 3), while the addition of TCM in the reaction of Sm_2O_3 pretreated in O_2 produced almost the same quantity of SmOCl and C_2H_4/C_2H_6 ratio after 6 h on-stream (see Table 1 and text). These results suggest that the ratio depends predominantly on the quantity of SmOCl, while TCM plays a major role as a generator of SmOCl on Sm_2O_3 as with Pr_6O_{11}.

With the lanthanum catalyst formation of LaOCl also suppresses the activity, while the catalyst containing LaOCl produces similar selectivities toward C_{2+} compounds to the catalyst free from LaOCl. Lattice oxygen may not be involved in the oxidation because there is no significant change between the catalysts pretreated with only TCM and with TCM and oxygen; if the lattice oxygen were active, TCM would react with the oxygen and the number of the oxygen sites would be small immediately after the pretreatment as observed with Pr_6O_{11}.

TABLE 5

Heat of Formation at 298°C for the Rare Earth Oxychlorides from the Corresponding Oxide (*43–49*)

Oxychloride	ΔH_f (kcal mol^{-1}) (298°C)
LaOCl	−41.4
PrOCl	−33.4
SmOCl	−32.3
CeOCl	−8.0

With the cerium catalyst no CeOCl was observed from XRD measurements. However, a small amount of C_2H_6 was detected in the products from CH_4 after 6 h on-stream in the presence of TCM (Table 1). This suggests that a small amount of CeOCl may have formed on CeO_2 and that CeOCl has a catalytic activity in the methane conversion process. The contrast between the behaviour of the cerium catalyst and the remaining catalysts may be rationalized from the examination of thermodynamic data (Table 5). The heats of formation of the oxychlorides from the oxides, and hence at least approximately, the free energies of formation are negative for the four rare earths, but the magnitudes of the values are largest and smallest for LaOCl and CeOCl, respectively. Although this data is strictly applicable to 25°C, nevertheless this suggests that the formation of CeOCl is the most difficult of the four oxychlorides.

CONCLUSION

The results presented here suggest that the addition of TCM to the feedstream in the conversion of methane alters the activity and C_{2+} selectivity primarily as a result of the interaction of the TCM with the catalyst, although the possibility of a gas-phase effect cannot be entirely eliminated. Furthermore, the observation that the oxychloride is formed on the catalyst through the introduction of TCM, at least with the oxides of praseodymium, samarium, and lanthanum, provides indirect evidence for the advantageous catalytic properties of the oxychloride in the oxidative coupling process. This is supported by the contrasting results with the three aforementioned oxides in comparison with cerium, with which the oxychloride does not form under the conditions employed in the present work.

Nevertheless, it is also clear that although the formation of the oxychloride may be a necessary condition for the enhancement of the activity and selectivity of the oxides in the conversion of methane, the presence of the oxychloride is not a sufficient condition for the enhancement effect. The contrasting behaviours of the praseodymium and samarium catalysts in the presence of TCM imply that the participation of lattice oxygen in the methane conversion process is required in order to benefit from the formation of the corresponding oxychloride.

The observation that less oxygen is consumed in the presence of TCM may be interpreted as implying that the catalyst suffers a smaller loss of oxygen when TCM is added. While a number of explanations for this are possible, it is tempting to believe that as a consequence fewer methyl peroxy species are formed.

The observation of optimum levels for TCM suggests that, while the presence of TCM is necessary to produce the oxychloride, surplus quantities may block the active sites. Thus the weight of evidence appears to favour surface oxygen as the site for the methane activation process. The presence of TCM would be expected to convert these to oxychlorides, although the activation is anticipated to continue to occur on the surface oxygen species. It is to be noted, however, that the electronic properties of the surface oxygen species in the oxychloride will be altered from those originally present in the oxide. It should be noted in this context that the corresponding chlorides do not possess the advantageous catalytic properties enjoyed by the oxychlorides.

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