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Effect of tetrachloromethane as a gas-phase additive on the oxidative dehydrogenation of ethane over magnesium phosphate

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Abstract

The oxidative dehydrogenation of ethane to ethylene on $Mg_3(PO_4)_2$ has been investigated in the presence and absence of tetrachloromethane (TCM). The homogeneous reaction proceeded extensively at temperatures above 998 K, while the heterogeneous reaction on the phosphate occurred at temperatures below 823 K. Selectivity to ethylene in the presence of TCM between 723 and 823 K was six times higher than that in the absence of TCM with a concomitant decrease in the conversion of ethane under the present reaction conditions, while no effects of TCM were observed at temperatures between 998 and 1098 K. Chlorinated species were detected on the surface of the used catalysts after contact with TCM even at temperatures as low as 723 K. The ratio of Cl/Mg measured by XPS after the ethane reaction was strongly influenced by both the relative amounts of C_2H_6 and O_2 in the reactant stream and the reaction temperature.

Keywords: Chloride; Ethane; Magnesium; Oxidation; Phosphate; Tetrachloromethane

1. Introduction

The effects of the introduction of small quantities of tetrachloromethane (TCM) as a gas-phase additive into the feedstream during the oxidative coupling of methane over oxides, sulphates, phosphates and supported catalysts have been studied in our laboratories [1–8]. The features observed on the addition of TCM are summarized as:

(1) The improvement of the conversion of methane.

(2) The improvement of the selectivity to C_2 compounds.

(3) The increase of the selectivity to ethylene with the decrease of that to ethane.

The former two points have been investigated in detail by our groups [1–10] and the Burch group [11] and the improvement of the catalytic activities by the introduction of TCM is attributed to the formation of the corresponding chlorides [5,7,8,11] or oxychlorides [2,3] species during the reaction. However little or no studies of the effect of TCM on the oxidative dehydrogenation of ethane to ethylene have been reported.

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Research on the oxidation of ethane is of fundamental value in providing further information on oxidation processes in general and of practical value since products such as acetaldehyde and ethylene have applications as precursors for commercial materials. Since the purely homogeneous oxidation of ethane begins to compete with the analogous catalytic reaction temperatures of the oxidative coupling of methane above 973 K [12], most of the studies of the oxidation of ethane have been investigated at temperatures below 923 K [13–23]. In some reports, N_2O has been used as the oxidant instead of O_2 at the reaction temperatures [24–30]. However there have been reports on the heterogeneously catalyzed oxidation of ethane at reaction temperatures similar to those employed for the oxidative coupling of methane [31–35], although ethylene is believed to form via secondary reactions of ethane in the oxidative coupling of methane. Conway and Lunsford have reported that $Li^+ - MgO - Cl^-$ catalysts and those promoted with metal oxides display both excellent stability and a high selectivity to ethylene at reaction temperatures similar to those employed in the oxidative coupling of methane [33,34]. Burch and Tsang have also reported that $LiCl/MnO_x$ yields a high selectivity to ethylene at a relatively wide range of reaction temperatures between 673 and 1023 K [35]. Both groups emphasize that chlorine species as a solid-phase additive play an important role in the selective catalytic conversion of ethane to ethylene.

In the oxidative coupling of methane, a wide variety of oxide catalysts has been investigated, but it is important in understanding the mechanism of the catalytic process to have information on solids possessing anions other than oxygen. Our recent results on the oxidative coupling of methane on oxides, sulphates and phosphates in the presence of TCM show that the interaction between TCM and the catalysts is dependent, not only on the composition of the catalysts, but in particular on the nature of the anion species [4,6–8].

In this paper, the oxidative dehydrogenation of ethane to ethylene on $Mg_3(PO_4)_2$ has been inves-

tigated in the presence and absence of TCM as a gas-phase additive at reaction temperatures between 723 and 1098 K. Magnesium has been selected as a cation since anion effects in the oxidative coupling of methane in the presence of TCM on the phosphate, oxide and sulphate of magnesium [7,8] and a considerable number of studies employing magnesium oxide in the methane coupling process have been reported [36,37].

2. Experimental

2.1. Catalyst and procedure

Reagent $Mg_3(PO_4)_2 \cdot 8H_2O$ was purchased from Wako Pure Chemicals, Osaka, and used as received. The hydrate was kneaded for 1 h with a quantity of water. The paste was dried overnight at 353 K and calcined at 1048 K for 5 h. Particles of 10–20 mesh were employed as a catalyst in the present work. The catalytic experiments were performed in a fixed-bed continuous flow quartz reactor at atmospheric pressure [5]. The catalyst (0.7 g) was heated to 1048 K while maintaining a continuous flow of helium and was then conditioned at this temperature under a 12.5 ml/min flow of oxygen for 1 h unless otherwise reported. In those experiments in which TCM was contained in the feedstream, the additive was introduced to the main flow of reactants (C_2H_6 , O_2 and diluent He) by saturating a separate stream of He with TCM at 273 K. Experiments in the absence of $Mg_3(PO_4)_2$ have been also performed with conditions similar to those employed with the catalyst was present. The carbon mass balances in the reaction were $100 \pm 5\%$.

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 N (6 m \times 3 mm, programmed 318–423 K), the other Molecular Sieve 5A (20 cm \times 3 mm, 318 K) were employed in the

analyses. The conversion of ethane was calculated on an account-for-carbon basis. The selectivity was calculated as a mole percent of the products. Blank experiments conducted with C_2H_6 absent from the feed ($O_2 + He + TCM$) 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 [5].

2.3. Characterization of the catalyst

The surface area of $Mg_3(PO_4)_2$ after calcination ($7.7 \text{ m}^2/\text{g}$) was measured with a conventional BET nitrogen adsorption apparatus (Shibata P-700). Surface analyses by X-ray photoelectron spectroscopy (XPS) were carried out with a Shimadzu ESCA-1000 AX using unmonochromatized $MgK\alpha$ radiation at room temperature without any additional surface treatment. The binding energies were corrected by using the 1s

level (285.0 eV) for contaminant carbon as an initial standard.

3. Results

3.1. Effect of TCM on the homogeneous reaction

In the oxidative coupling of methane in the presence of TCM, it is sometimes suggested that chlorine radicals produced from TCM in the gas phase may contribute to the improvement of the catalytic activity [5,38]. Since the homogeneous oxidation of C_2H_6 easily proceeds at a reaction temperature similar to that for the oxidative coupling of methane, the oxidative dehydrogenation of C_2H_6 in the absence of a catalyst and in the presence and absence of TCM was first investigated in the present work (Table 1). The reaction proceeded at temperatures greater than 723 K, but below 773 K the conversion was relatively low. The main product in the absence of TCM at temperatures less than 773 K was CO_2 while the selec-

Table 1
Conversion and selectivity at various temperatures in the empty reactor in the presence and absence of TCM

Temp. ^a	TCM ^b	Conv. (%)		Selectivity (%)						
		C_2H_6	O_2	CO	CO_2	CH_4	C_2H_4	C_2H_2	CH_3CHO	C_3
723	A	0.3	3	–	99.3	0.7	–	–	–	–
	P	+ ^c	15	–	–	100	–	–	–	–
763	A	1.5	2	–	69.4	29.0	1.6	–	–	–
	P	0.5	17	–	–	0.5	99.4	–	–	–
773	A	0.6	6	–	83.3	15.1	1.5	–	–	–
	P	1.4	33	2.1	–	1.5	96.3	–	–	–
803	A	21	86	22.2	3.1	12.3	60.0	–	–	2.5
	P	14	86	9.3	–	4.5	81.8	–	2.7	1.7
823	A	21	88	18.4	–	12.5	61.1	–	3.0	5.0
	P	13	82	10.2	–	13.0	63.6	–	5.1	8.1
998	A	67	94	12.1	0.4	17.0	61.2	4.2	0.3	4.9
	P	64	92	20.9	1.1	18.0	58.4	–	0.4	1.2
1048	A	82	91	15.4	8.6	18.7	48.3	7.6	–	1.4
	P	84	94	15.7	0.8	20.7	54.7	5.5	–	2.5
1098	A	89	90	9.9	–	38.3	42.6	8.2	–	1.1
	P	90	84	6.3	9.0	24.8	47.4	9.1	–	3.5

^a Reaction temperature (K).

^b A; Absence of TCM, P; presence of TCM.

^c Trace. Reactant gas: C_2H_6 27.1 kPa, O_2 6.8 kPa and TCM 0.17 kPa (when present) diluted with He. Flow rate 15 ml/min.

tivity to CO exceeded that to CO₂ at higher temperatures. On the introduction of a small partial pressure of TCM at 763 and 773 K, the selectivity to C₂H₄ significantly increased while that to CO₂ and CH₄ decreased. In contrast, the selectivity to CH₄ was increased by the addition of TCM at 723 K. At temperatures higher than 803 K relatively little or no changes in the conversions and selectivities were observed on introduction of TCM.

Although C₂H₂ was not observed, in the absence of the catalyst, at temperatures up to 823 K, at higher temperatures selectivities to C₂H₂ greater than 5% were generally obtained with little or no effect due to the addition of TCM. Acetaldehyde is observed at temperatures between 803 and 998 K but is probably decomposed at higher temperatures. C₃ hydrocarbons begin to appear at 803 K but with these compounds no systematic effect of the addition of TCM is evident.

It is evident that in the absence of a catalyst the effect of the addition of TCM is most apparent at the lowest temperatures and gradually dissipates as the temperature is increased until, at 1098 K, the differences are relatively small. Thus the presence of a catalyst is not required for TCM to be effective in the ethane conversion process. This suggests that, at least in the homogeneous reaction, gas phase chlorine-containing radicals may be participating in the conversion process. The ethane conversion process in which chlorine-containing species are participating is selective for the production of ethylene. At the lower temperatures the rate of this process is greater than that of the process operating in the absence of TCM but as the temperature increases the rate of the latter process increases more substantially than that of the former process. Thus the activation energy of the chlorine-enhanced process should be smaller than that of the process in which chlorine is absent.

3.2. Effect of TCM on the thermal pyrolysis of C₂H₆ to C₂H₄

The conversion of ethane in the presence and absence of TCM without oxygen was investigated

Table 2
Conversion and selectivity at various temperatures in the empty reactor in the presence and absence of TCM without O₂

Temp. ^a	TCM ^b	Conv. (%)	Selectivity (%)				
			C ₂ H ₆	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₃
773	A	0	–	–	–	–	–
	P	0.3	–	100	–	–	–
823	A	0.9	–	100	–	–	–
	P	0.9	2.4	97.6	–	–	–
998	A	36	5.3	93.8	–	0.9	
	P	38	5.7	92.9	–	1.4	
1048	A	70	16.3	70.6	8.1	5.0	
	P	72	17.1	72.3	8.2	2.4	
1098	A	87	37.5	50.5	9.1	2.9	
	P	88	38.0	51.1	8.8	2.0	

^a Reaction temperature (K).

^b A; Absence of TCM, P; presence of TCM. Reactant gas: C₂H₆ 27.1 kPa and TCM 0.17 kPa (when present). Total flow rate: 15 ml/min.

in the empty reactor in order to clarify the contribution of oxygen to those gas phase reactions where TCM is present (Table 2). In the absence of TCM, the reaction proceeded at temperatures higher than 823 K, approximately 100 degrees above that in the presence of oxygen. As can be seen from the data in Table 2, at a given temperature both the conversions and selectivities to the various products are little influenced by the presence of TCM.

These results, as with those from experiments in which oxygen was present, may be interpreted in terms of the relative rates and their temperature coefficients of those reactions with and without TCM where oxygen is not present. There is, however, an additional possible interpretation, namely that the formation of the advantageous chlorine-containing species cannot take place in the absence of oxygen. Although this latter conclusion cannot be ruled out it appears, at least intuitively, to be less probable than the former.

3.3. Effect of TCM on the oxidative dehydrogenation of C₂H₆ on Mg₃(PO₄)₂

3.3.1. Effect of the reaction temperatures

As described above, the contribution of the homogeneous reactions to the ethane conversion process was appreciably less significant at lower

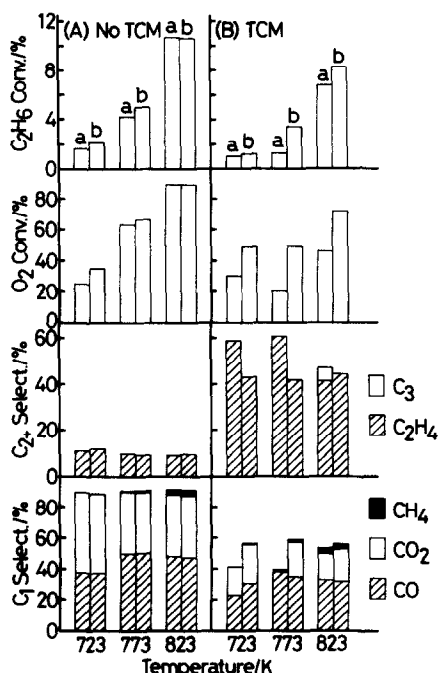


Fig. 1. Ethane oxidation on $\text{Mg}_3(\text{PO}_4)_2$ in the presence and absence of TCM at reaction temperatures between 723 and 823 K. (a) 0.5 h on-stream. (b) 6 h on-stream. Reaction conditions: $\text{C}_2\text{H}_6 = 27.1$ kPa, $\text{O}_2 = 6.8$ kPa and TCM = 0.17 kPa (when present) diluted with He. Total flow rate = 15 ml/min. Weight of catalyst = 0.7 g.

temperatures. Therefore the effect of temperature on the oxidation on $\text{Mg}_3(\text{PO}_4)_2$ was examined under the same partial pressure of each reactant and total flow rate for two ranges of reaction temperatures, 723 to 823 K and 998 to 1098 K, where the former is the range in which purely homogeneous reactions are not significant and the latter is that in which gas phase reactions contribute substantially to the process. The results in the presence and absence of TCM at lower temperatures are described in Fig. 1.

In the absence of TCM, the conversions of C_2H_6 at 723 and 773 K on $\text{Mg}_3(\text{PO}_4)_2$ are higher than those in the absence of the catalyst. At these temperatures, selectivity to C_2H_4 was ca. ten times greater than that in the empty reactor. Meanwhile, the conversion of C_2H_6 and the selectivity to C_2H_4 at 823 K were lower than those found with the empty reactor.

On addition of a small quantity of TCM to the feedstream at 723–823 K, the selectivity to C_2H_4 on the catalyst was increased by a factor of five as

compared with that in the absence of TCM, with the slight decrease in the conversion of C_2H_6 . Since an increase in the selectivity to C_2H_4 on addition of TCM is observed in the homogeneous reactions, the extent of the participation in the catalytic process of species formed on the catalyst from TCM is not evident from these results. The catalytic activity was relatively stable in the absence of TCM during 6 h on-stream, but depended on the reaction temperatures in the presence of TCM.

Although acetaldehyde was produced at temperatures of 803–1098 K in the reactions in which the catalyst was absent this compound was not observed with the catalyst between 723 and 823 K. Acetylene was also not observed at these latter temperatures with the catalyst, nor was it found in the absence of the catalyst. C_3 hydrocarbons were found at 823 K in the presence of TCM but not in its absence.

At the higher reaction temperatures, between 998 and 1098 K (Fig. 2), the conversion of ethane

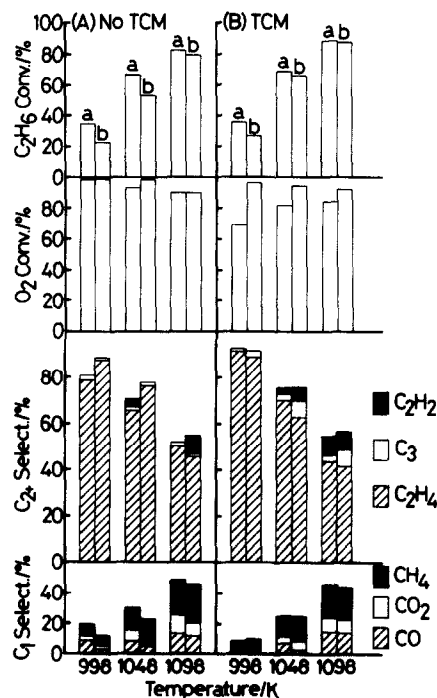


Fig. 2. Ethane oxidation on $\text{Mg}_3(\text{PO}_4)_2$ in the presence and absence of TCM at reaction temperatures between 998 and 1098 K. (a) 0.5 h on-stream. (b) 6 h on-stream. Reaction conditions: as in Fig. 1 except reaction temperatures.

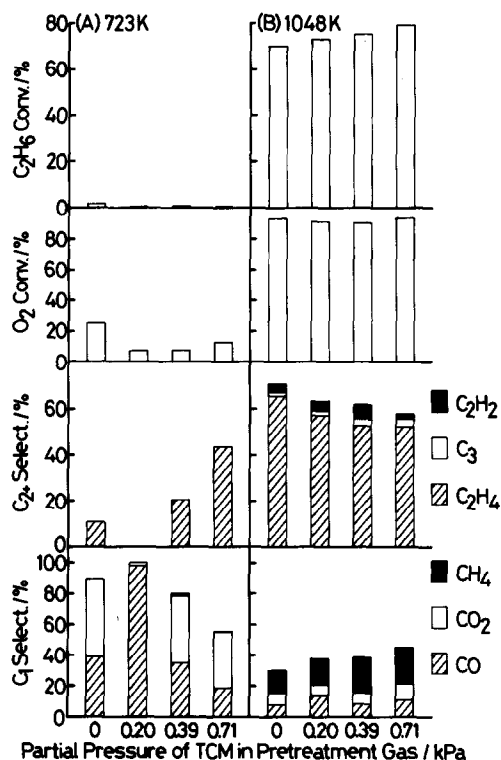


Fig. 3. Effect of pretreatment with TCM prior to ethane oxidation in the absence of TCM at 723 and 1048 K. Catalyst was pretreated with TCM and O_2 (12.5 ml/min) at 1048 K for 1 h before the reaction. Reaction conditions: $C_2H_6 = 27.1$ kPa and $O_2 = 6.8$ kPa diluted with He. Total flow rate = 15 ml/min. Weight of catalyst = 0.7 g. Data were collected at 0.5 h on-stream.

on the catalyst in the absence of TCM was lower than observed with the empty reactor, but the selectivity to C_2H_4 was higher than found with the empty reactor. At 1098 K the conversion of C_2H_6 and of O_2 and the total selectivities to C_{2+} and C_1 were similar with and without the catalyst. At the higher reaction temperatures (998–1098 K) the selectivity to C_3 hydrocarbons in the presence of TCM increases with increase in the time-on-stream, whereas in the absence of TCM no such effect is observed.

3.3.2. Effect of TCM pretreatment

In order to examine the role of the catalyst in the presence of TCM, experiments were performed in which separate aliquots of $Mg_3(PO_4)_2$ were exposed to TCM (0, 0.20, 0.39 or 0.71 kPa) and O_2 (12 ml/min) for 1 h at 1048 K prior to the

introduction of the reactant stream, which did not contain TCM (Fig. 3). It is evident that the selectivity to C_2H_4 at 723 K after the pretreatment with TCM increased with the partial pressure of TCM in the pretreatment gas (except TCM = 0.20 kPa) although TCM was absent from the feedstream. However, the conversion of C_2H_6 at 723 K was very small and little influenced by the pretreatment. At 1048 K, the selectivity to C_2H_4 decreased slightly, while the conversion of C_2H_6 increased somewhat with the partial pressure of TCM in the pretreatment gas.

3.3.3. Effect of C_2H_6/O_2

The conversion of C_2H_6 was examined under a constant partial pressure of TCM (0.17 kPa) at 723 and 1048 K and for a number of C_2H_6/O_2 ratios (Fig. 4). As expected, the selectivity to

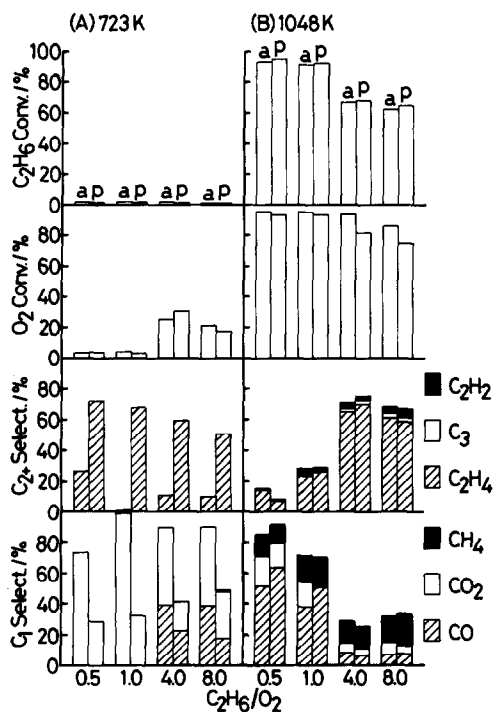


Fig. 4. Effect of C_2H_6/O_2 ratio in the presence and absence of TCM at 723 and 1048 K. A: absence of TCM. P: presence of TCM. Reaction conditions: as in Fig. 1 except partial pressure of C_2H_6 and O_2 . (C_2H_6 13.5 kPa and O_2 27.1 kPa at $C_2H_6/O_2 = 0.5$, C_2H_6 27.1 kPa and O_2 27.1 kPa at $C_2H_6/O_2 = 1.0$, C_2H_6 27.1 kPa and O_2 6.8 kPa at $C_2H_6/O_2 = 4.0$, and C_2H_6 54.0 kPa and O_2 6.8 kPa at $C_2H_6/O_2 = 8.0$. Helium dilution as described in text.) Data were collected at 0.5 h on-stream.

C_2H_4 at 723 K was increased by the introduction of TCM regardless of the C_2H_6/O_2 ratio, while the increase was not observed at 1048 K and, in contrast, the selectivity at $C_2H_6/O_2=0.5$ decreased on addition of TCM.

3.4. Surface analyses of the used phosphate catalysts by XPS

The formation of chlorine-containing species on catalysts previously employed in the oxidative coupling of methane at 1048 K in the presence of TCM has previously been shown by XPS and/or XRD [2,3,5,7,8]. In the present work the catalysts previously employed in the experiments whose results are reported in Fig. 4 were analyzed by XPS and the results are summarized in Table 3. Binding energies of Mg 2s, P 2p and O 1s and the atomic ratio of O/Mg and P/Mg at each reaction condition were virtually identical regardless of the reaction temperature and C_2H_6/O_2 ratio. Somewhat surprisingly, the chlorinated species were detected on the used phosphates at 723 K at the

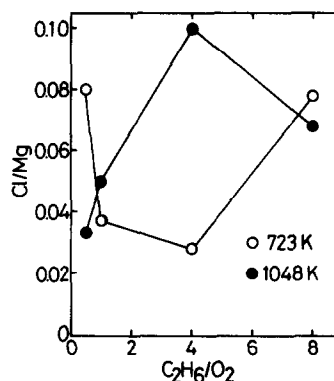


Fig. 5. The relationship between the atomic ratio of Cl/Mg on the catalyst surface after reaction as measured by XPS and C_2H_6/O_2 of feedstream during reaction.

binding energy of 199 eV, which was the same as those found on the used catalysts at 1048 K. As shown in our previous papers [7,8], the chlorine species on the magnesium phosphate catalysts is apparently magnesium chloride [39]. Fig. 5 shows the relationship between the atomic ratio of Cl/Mg and the molar ratio of C_2H_6/O_2 in the feedstream. It is of interest to note that the amounts

Table 3
XPS analyses of phosphates^a

Temp. ^b	C_2H_6/O_2 ^c	TCM ^d	Binding energy (eV)				O/Mg ^e	P/Mg ^e
			Mg 2s	P 2p	O 1s	Cl 2p		
723	8.0	A	88.7	133.5	531.5	–	2.3	0.74
723	8.0	P	89.6	133.8	532.0	198.9	2.3	0.76
723	4.0	A	88.7	133.1	531.2	–	2.4	0.83
723	4.0	P	89.2	133.7	531.8	198.5	2.0	0.69
723	1.0	A	89.4	133.9	532.1	–	2.2	0.72
723	1.0	P	89.4	133.6	531.8	198.7	2.0	0.65
723	0.5	A	89.3	133.8	531.8	–	2.2	0.71
723	0.5	P	89.3	133.7	532.0	198.8	1.9	0.72
1048	8.0	A	89.1	134.0	531.8	–	2.3	0.75
1048	8.0	P	89.9	133.9	531.6	199.5	2.3	0.74
1048	4.0	A	89.3	135.6	533.5	–	2.1	0.68
1048	4.0	P	88.5	133.0	531.0	198.4	1.9	0.70
1048	1.0	A	89.5	134.0	532.3	–	2.3	0.70
1048	1.0	P	89.2	133.6	531.7	198.7	2.2	0.77
1048	0.5	A	89.0	133.3	531.6	–	2.4	0.74
1048	0.5	P	89.3	133.4	531.8	198.3	2.0	0.68

^a Previously employed in obtaining the results reported in Fig. 4, but after 6 h on-stream.

^b Reaction temperature (K).

^c Ratio of partial pressures.

^d A; Absence of TCM, P; presence of TCM. See Fig. 4 for partial pressures.

^e Atom/atom.

of the chloride at 723 and 1048 K are of the same order and the maximum of Cl/Mg at 1048 K is found at the same C_2H_6/O_2 ratio of 4 as the minimum at 723 K.

4. Discussion

The results of the experiments performed in the absence of a catalyst clearly demonstrate that TCM participates in the homogeneous conversion of ethane. At the lower temperatures employed in the present work TCM can be seen to direct the selectivity from the deep oxidation to the dehydrogenation product while having relatively little effect on the conversion of ethane. At the higher temperatures the influence of TCM is less apparent. It is well known that chlorinated methanes decompose, at elevated temperatures, to generate chlorine radicals which are themselves capable of inducing the formation of ethyl radicals through the extraction of hydrogen from ethane. Such radicals are presumably the precursors of ethylene. At the higher temperatures the rate of the production of these radicals, unassisted by TCM, is sufficiently high that the effect of TCM becomes less apparent.

The experiments with catalysts pretreated in TCM and subsequently employed in the conversion of ethane demonstrate that a significant portion of the TCM interacts with the solid catalyst. Of course this does not preclude the concomitant participation of TCM in the gas phase process. As with the homogeneous process, with the catalyst present the TCM evidently serves as a selectivity director with little influence on the conversion. At the highest temperature, as also observed in the homogeneous reaction, the participation of TCM is less evident.

The XPS results provide supporting evidence for the interaction of TCM with the catalyst, although the nature of the species formed is unclear. The relative quantities of the chlorine-containing species formed on the surface of the catalyst, or at least remaining there after the conclusion of the reaction, show a dependence on the

C_2H_6/O_2 ratio, but there is no unambiguous relationship between these amounts and the results from the corresponding reactions.

Both the results reported earlier for the effects of TCM in the partial oxidation and oxidative coupling of methane and those presented in the present work on the similar effects in the conversion of ethane provide evidence, albeit indirect, for the participation of TCM, or its decomposition products, in the generation of radicals which are precursors to propitious products. Although processes leading to undesirable products are also dependent on the production of such radicals the rates of these processes appear to be lower than those of the former reactions at least at the lower temperatures employed in the present work.

As in the partial oxidation and oxidative coupling of methane the catalysts employed in the conversion of ethane evidently function primarily, but not entirely, as vehicles for the dissociation of the hydrocarbon, since the conversion is seen to increase on introduction of the catalyst.

It is also clear that TCM is capable of enhancing both the gas-phase and the heterogeneous processes. However it is not clear that the chlorinated methane produces these improvements via the same mechanism in both the homogeneous and heterogeneous processes in spite of the common factor of chlorine. Although the evidence is not conclusive it appears that magnesium chloride is formed on the interaction of TCM with magnesium phosphate but it is conceivable that, whatever the chlorinated species formed on the catalyst, these species may play both a direct and indirect role in the enhancement of radical production by the catalyst.

Finally, it should be noted that the introduction of TCM suppresses the formation of carbon dioxide, although not of carbon monoxide. There is growing evidence, at least in the methane conversion process, of the deleterious action of carbon dioxide. Although it is tempting to suggest a connection between these two sets of observations, the evidence to this date remains circumstantial.

5. Conclusion

1. The selectivity to ethylene in the homogeneous reaction of ethane is increased by the introduction of a small amount of TCM at temperatures below 773 K, while the influence is less apparent at temperatures above 803 K.
2. At temperatures of 723–834 K the selectivity to ethylene in the oxidative dehydrogenation of ethane on $\text{Mg}_3(\text{PO}_4)_2$ in the presence of TCM was a factor of five higher than that in the absence of TCM but little or no improvement was observed at temperatures of 998–1098 K.
3. Experiments in which the catalyst is subjected to a pretreatment with TCM show that the chlorinated methane interacts with the solid to produce modifications which are advantageous for the subsequent ethane conversion.
4. The species formed on the catalyst surface, apparently magnesium chloride, appears to be independent of the reaction temperature, although strongly dependent on the relative quantities of ethane and oxygen.

Acknowledgements

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