

Pretreatment effect in the oxidative dehydrogenation of ethane on magnesia in the presence and absence of tetrachloromethane

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Abstract

The effects of a small addition of tetrachloromethane (TCM) into the feedstream for the oxidative dehydrogenation of ethane have been investigated over magnesia at reaction temperatures between 723 and 1098 K. Both the conversion of ethane and the selectivity to ethylene at reaction temperatures of 723–823 K were markedly increased on addition of TCM, while at temperatures between 998 and 1098 K little or no changes in these quantities were observed. Pretreatment experiments in which MgO was exposed to TCM + O₂ or TCM + O₂ + H₂O prior to introduction of the reactant stream showed that the chlorided surface which formed during the pretreatment contributed to the aforementioned improvement. The concentration of surface chloride, in whatever form, produced during the pretreatment was influenced by the introduction of water but showed no dependence on the temperature, the partial pressure of TCM in the pretreatment gas or the duration of exposure. Excess chlorination of the surface tended to reduce the beneficial effect especially in the presence of TCM in the feedstream.

Keywords: Magnesia; Ethane; Oxidation; Dehydrogenation; Magnesium Chloride; Tetrachloromethane

1. Introduction

The advantageous effects of the introduction of a small amount of a chlorinated compound such as tetrachloromethane (TCM) to the feedstream in the partial oxidation and oxidative

coupling of methane have been reported on a wide variety of catalysts [1–7]. In particular, the earlier work has shown that the selectivity to ethylene in the oxidative coupling process is increased on the addition of TCM but that to ethane is decreased, although the overall C₂₊ selectivities are generally increased. Since it is commonly believed that ethane is the precursor to ethylene in the coupling process further investigations of this aspect appeared to be war-

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ranted. Recently, the oxidative dehydrogenation of ethane to ethylene over $\text{Mg}_3(\text{PO}_4)_2$ [8] and MgSO_4 [9] has been investigated in our laboratories in order to obtain information on the source of the improved selectivity to ethylene when TCM is present in the feedstream. Over both catalysts, the selectivity to ethylene was improved by the introduction of TCM at lower temperatures, where purely homogeneous reactions are insignificant, but little or no improvement was observed at higher temperatures, where gas-phase reactions contributed substantially to the process. The results indicated that the chloride species deposited from TCM on the surface of both catalysts contributed to the alterations in selectivity observed, particularly at the lower temperatures. Regardless of the introduction of TCM, the catalytic activities on the phosphate were higher than those on the sulphate at the lower temperatures probably due to the disadvantageous effects of the acidic sites contained on the sulphate. However higher activities on the sulphate as compared with the phosphate were observed at the higher temperatures, apparently as a consequence of the presence of MgO formed from the reaction of the sulphate with carbon deposits on the surface.

Earlier work has also shown that the effects produced on addition of TCM in the methane coupling reaction are dependent on the composition of the catalyst, in particular the nature of the anion [5,6]. Since much of the work previously reported in the literature on the coupling reaction has been concerned with oxides [10–13], it is of interest to examine the activities for the oxidation dehydrogenation of ethane in the presence of TCM over MgO. Most recently the introduction of HCl to the feedstream in the oxidative dehydrogenation of ethane on Li/MgO has been shown to have a deleterious effect on the formation of ethylene [14].

In the present study, the oxidative dehydrogenation of ethane on MgO has been investigated in the presence and absence of TCM. The surface chlorination of the oxide during the reaction in the presence of TCM and the effect

of pretreatment of the oxide with $\text{TCM} + \text{O}_2$ and $\text{TCM} + \text{O}_2 + \text{H}_2\text{O}$ have also been studied.

2. Experimental

Magnesia (MgO) was obtained from Wako Pure Chemicals, Osaka, as a special grade and used as supplied. The oxide was kneaded for 1 h with a given amount of water. The paste was dried overnight at 353 K and calcined at 1048 K for 5 h. Particles of 0.85–1.70 mm were employed in the present work. The BET surface area and apparent density of the oxide were $11 \text{ m}^2/\text{g}$ and $0.55 \text{ g}/\text{cm}^3$, respectively.

The catalytic experiments were performed in a fixed-bed continuous flow quartz reactor operated at atmospheric pressure. Details of the reactor design and catalyst packing have been described previously [6]. Prior to reaction, the catalyst (0.7 g) was pretreated in situ in an oxygen flow (12.5 ml/min) at 1048 K for 1 h unless otherwise noted. The reaction conditions were as follows: $F = 15 \text{ ml}/\text{min}$, $T = 723\text{--}1098 \text{ K}$, $P(\text{CH}_4) = 27.1 \text{ kPa}$, $P(\text{O}_2) = 6.8 \text{ kPa}$, and $P(\text{TCM}) = 0$ or 0.17 kPa ; helium provided the balance to atmospheric pressure. In the pretreatment experiments, a gas mixture of $\text{TCM} + \text{O}_2$ or $\text{TCM} + \text{O}_2 + \text{H}_2\text{O}$ was employed in place of the oxygen flow.

The reactants and products were analyzed with an on-stream gas chromatograph (Shimadzu GC-8APT) equipped with a thermal conductivity detector and integrator (Shimadzu C-R6A). The columns used in the present study and the calculations of conversion and selectivity have been described previously [6].

Surface analyses by XPS were carried out at room temperature with a Shimadzu ESCA-1000AX using unmonochromatized Mg K α radiation. The samples were mounted on a sample holder in air and set into the spectrometer. After measurement of the surface, an argon-ion etching of the sample was carried out (2 kV, 1 min), and the spectra were measured again after etching. The sputtering rate was estimated as ap-

proximately 2 nm/min for SiO₂. Charge correction of the XPS data was accomplished by assuming that the binding energy of the C 1s peak resulting from contaminant carbon was 285.0 eV.

3. Results and discussion

3.1. The effects of TCM on the oxidative dehydrogenation of ethane on MgO and comparison with those on Mg₃(PO₄)₂ and MgSO₄

Since the contribution of the homogeneous oxidation of ethane becomes significant at higher temperatures [8,15], the oxidation on MgO was examined for two ranges of reaction temperatures, 723 to 823 K and 998 to 1098 K, in the former of which purely homogeneous reactions

are insignificant while in the latter gas phase reactions contribute substantially to the process.

The results in the presence and absence of TCM at temperatures between 723 and 823 K are described in Fig. 1. In the absence of TCM (Fig. 1(A)), the conversion of ethane increased with increase of the reaction temperature but the selectivity to each product showed little or no sensitivity to the temperature. On addition of TCM into the feedstream (Fig. 1(B)), the conversion increased by a factor of 2–3 in comparison with that observed in the absence of TCM and increased with the time-on-stream at 773 and 823 K, in contrast to the results obtained at 723 K, at which temperature the reaction was slightly retarded by the introduction of TCM. However the selectivity to ethylene increased at each temperature on addition of TCM and increased as the time-on-stream increased while that to C₁ products followed a reciprocal pattern.

At reaction temperatures between 998 and 1098 K (Fig. 2), the apparent effects of the introduction of TCM, such as those observed at the lower temperatures, were not found although small increases of the conversion of ethane and selectivity to ethylene were observed together with the reciprocal changes for CO₂. A number of interpretations are possible for these results. TCM cannot, for whatever reason, produce the beneficial effects at the higher temperatures which are produced at lower temperatures. Since earlier work has shown that, with both methane and ethane processes, TCM appears to interact with the catalyst surface producing favourable compositional and/or structural changes, it is conceivable that at the higher temperatures such interactions either do not occur to any appreciable extent or are disadvantageously reversible.

Table 1 shows the results of XPS analyses of the near surface region of MgO previously employed in the C₂H₆ reaction in the presence of TCM (see Figs. 1 and 2). With the exception of catalysts used in reactions at 1048 and 1098 K, the signals due to Mg 2s, O 1s and Cl 2p were

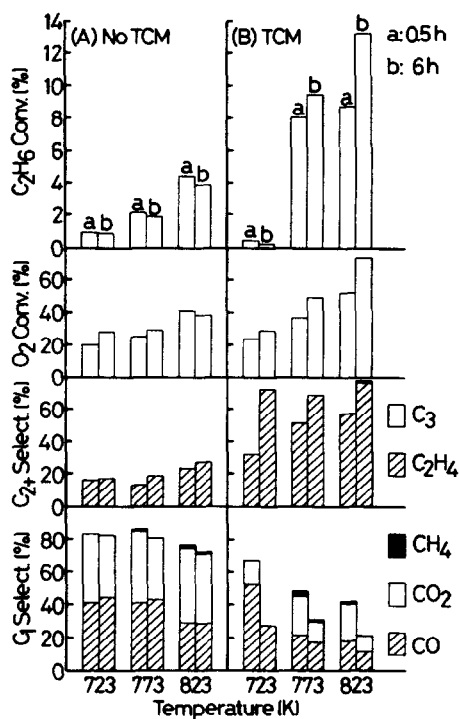


Fig. 1. Ethane oxidation on MgO in (A) absence and (B) presence of TCM at reaction temperatures between 723 and 823 K. Reaction conditions: C₂H₆ = 27.1 kPa, O₂ = 6.8 kPa and TCM 0.17 kPa (when present) diluted with He. Total flow rate = 15 ml/min. Weight of catalyst = 0.7 g.

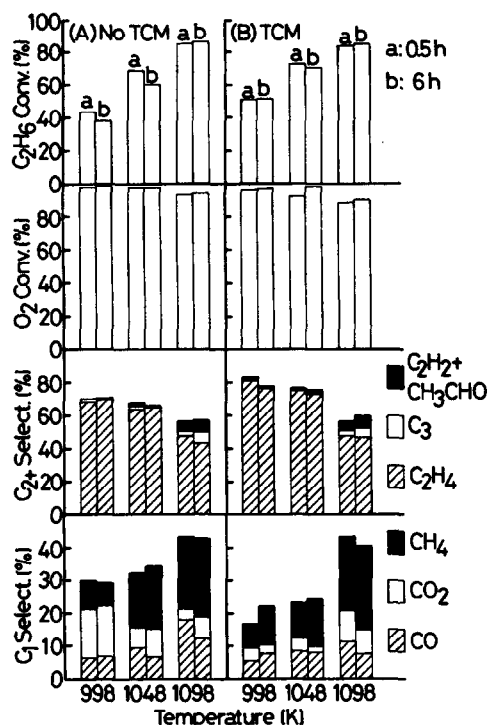


Fig. 2. Ethane oxidation on MgO in (A) absence and (B) presence of TCM at reaction temperatures between 998 and 1098 K. Reaction conditions: as in Fig. 1 except for reaction temperatures.

detected at approximately 88, 530 and 199 eV, respectively. The detection of the Cl 2p signal shows that chlorine is taken up by the surface of the catalyst presumably in the form of the chloride or oxychloride during the reaction at 723 K

[5]. The binding energy detected with the catalysts used at 1048 and 1098 K was not corrected because the C 1s signal resulting from carbon contamination overlapped with that of carbon deposits formed during the reaction. The uncorrected signals are expected to shift to higher values by ca. 2 eV, based on that of the lattice oxygen signal of O 1s. It should be noted that the Cl/Mg ratio was essentially constant between 773 and 998 K. At temperatures higher than 1048 K, surface chlorine could not be detected since the surface of the catalyst was completely covered with carbon deposits.

It is instructive to compare the activities on MgO with those on $Mg_3(PO_4)_2$ [8] and $MgSO_4$ [9] under the same reaction conditions, together with that in the absence of the catalyst [8]. The conversion of ethane at reaction temperatures between 723 and 823 K in the absence of TCM follows the order $Mg_3(PO_4)_2 > MgO > no-catalyst > MgSO_4$. Since the C–H bond scission of methane is believed to occur on basic sites [11,16–19] the low conversion on an acidic $MgSO_4$ [20,21] is not unexpected. It is interesting that the order of the conversion of ethane on magnesia and the phosphate contrasts with that in the oxidative coupling of methane at 1048 K [5,6] although the abstraction of hydrogen atoms from ethane or methane would be expected to take place on the same sites. The effects of the

Table 1
XPS analyses of MgO used in the presence of TCM^a

	Reaction temperature (K)					
	723	773	823	998	1048 ^b	1098 ^b
Mg 2s (eV)	87.5 (87.8)	88.0 (88.8)	88.3 (88.8)	88.1 (88.5)	90.4 (90.4)	89.9 (89.6)
O 1s (eV)	529.4 (529.7)	530.5 (530.7)	530.5 (530.8)	530.7 (530.4)	532.3 (532.3)	532.5 (531.3)
Cl 2p (eV)	198.2 (198.7)	198.8 (199.8)	199.0 (199.5)	198.4 (199.5)	– –	– –
O/Mg (–)	1.04 (0.93)	1.10 (1.04)	1.06 (0.97)	1.20 (0.98)	1.12 (0.65)	1.03 (0.99)
Cl/Mg (–)	0.03 (0.03)	0.08 (0.04)	0.06 (0.05)	0.05 (0.06)	– –	– –

^a Values in parentheses () are after argon etching for 1 min.

^b Binding energy was not corrected due to overlap of C 1s signal resulting from carbon contamination with that of carbon deposits.

introduction of TCM on the oxidative dehydrogenation of ethane on MgO, particularly as observed at 773 and 823 K, were quite contrary to the expectations resulting from the oxidative coupling of methane on the catalyst [5], where the conversion of methane was little influenced by the addition of TCM and only the selectivity to the dehydrogenation product of C_2H_4 was improved. In contrast, the effect of the addition of TCM on the oxidative dehydrogenation of ethane on the phosphate and sulphate could be expected from the results of the oxidative coupling of methane since, on addition of TCM, enhancements of the selectivities to C_2H_4 on the sulphate at the lower reaction temperatures were observed both in the oxidation of ethane [8,9] and of methane [6]. At higher reaction temperatures (above 998 K), the introduction of TCM into the feedstream in the oxidative dehydrogenation of ethane showed little or no influence on the activities over MgO, $Mg_3(PO_4)_2$ [8] and $MgSO_4$ [9], but the order of the conversion of ethane at 998 K under the same reaction conditions follows as no-catalyst > $MgSO_4$ > MgO > $Mg_3(PO_4)_2$. This observation may be interpreted variously. The sorption of chlorine, in whatever form, may be reduced at the higher temperatures. More probably, the concentration

of chlorine held on the surface may be diminished at these temperatures. Alternatively, the participation of the homogenous reaction, including the C–H bond scission, may be more substantial than that occurring on the surface of the catalyst.

3.2. Effects of pretreatment with TCM

In order to examine the interaction between MgO and TCM, experiments were performed in which MgO was exposed to TCM (0, 0.20, 0.39 or 0.55 kPa) and O_2 (12.5 ml/min) for various pretreatment durations and temperatures followed by XPS analyses of the pretreated samples (Table 2). Since ethane was not contained in the pretreatment gas, the carbon deposits were not formed on the surface and no significant differences in the binding energies of Mg 2s, O 1s and Cl 2p were observed regardless of the pretreatment conditions and etching time. The detection of Cl 2p shows that the surface has been chlorided under all of the pretreatment conditions [5]. It is of interest to note that the values of Cl/Mg (atom/atom) on the surface were virtually identical regardless of the partial pressure of TCM, temperature and duration of pretreatment. After argon-ion etching, the

Table 2
XPS analyses of MgO pretreated with TCM + O_2 ^a

Temp.: ^b	973	1048	1048	1048	1123	1123	1123
Time: ^c	1	1	3	6	1	1	1
TCM: ^d	0.20	0.20	0.20	0.20	0.20	0.39	0.55
Mg 2s (eV)	87.6 (88.0)	88.1 (88.5)	87.7 (88.3)	87.7 (88.5)	87.7 (88.5)	88.2 (88.2)	88.3 (88.3)
O 1s (eV)	528.9 (529.7)	529.9 (530.2)	529.7 (530.1)	529.8 (530.2)	530.2 (530.4)	530.0 (530.0)	530.4 (530.5)
Cl 2p (eV)	198.0 (199.0)	198.2 (199.0)	197.9 (198.9)	198.2 (199.5)	198.5 (199.4)	199.0 (199.5)	198.7 (199.1)
O/Mg (-)	0.82 (0.93)	1.06 (0.98)	1.02 (0.89)	0.96 (0.91)	0.98 (0.92)	0.87 (0.94)	1.03 (0.99)
Cl/Mg (-)	0.09 (0.02)	0.08 (0.04)	0.06 (0.02)	0.07 (0.03)	0.07 (0.06)	0.07 (0.03)	0.09 (0.06)

^a Values in parentheses () are after argon etching for 1 min.

^b Pretreatment temperature (K).

^c Pretreatment time (h).

^d The partial pressure of TCM in pretreatment gas: O_2 (12.5 ml/min) + TCM. Weight of the pretreated MgO: 0.7 g.

Cl/Mg ratio decreased with all pretreatment conditions. These observations indicate that the interaction of TCM with MgO occurs mainly on the surface of the oxide which evidently becomes readily saturated with chlorine under a variety of conditions.

The pretreated oxide when employed as a catalyst in the oxidative dehydrogenation of ethane at 773 K, produced higher conversions of ethane and selectivities to ethylene in either the absence or presence of feedstream TCM (Fig. 3). With the catalysts which had not been exposed to TCM during the pretreatment the conversion of ethane was increased from approximately 2 to 8% when TCM was added to the feedstream and the C_2H_4 selectivity was increased by a factor of three. In the absence of feedstream TCM the TCM-pretreated samples showed both higher conversions and C_2H_4 se-

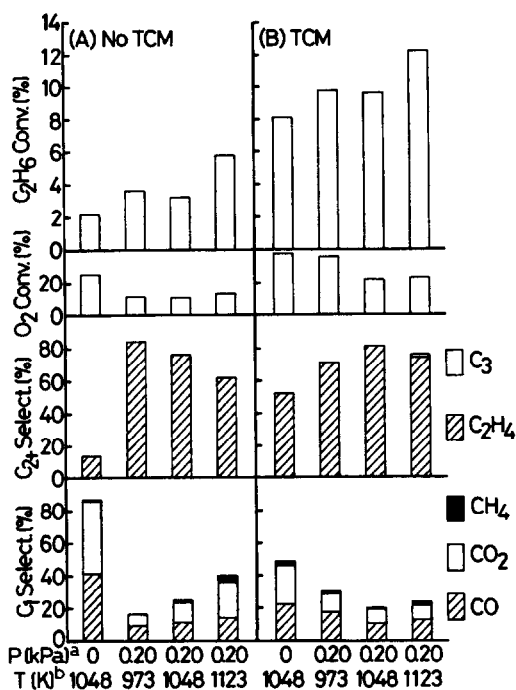


Fig. 3. Effect of pretreatment with TCM and O_2 prior to ethane oxidation in (A) absence and (B) presence of TCM at 773 K. Catalyst was pretreated with TCM and O_2 (12.5 ml/min) for 1 h before the reaction. Reaction conditions: as in Fig. 1 except for reaction temperatures. a: Partial pressure of TCM in the pretreatment gas (kPa). b: Pretreatment temperature (K). Data were collected at 0.5 h on-stream.

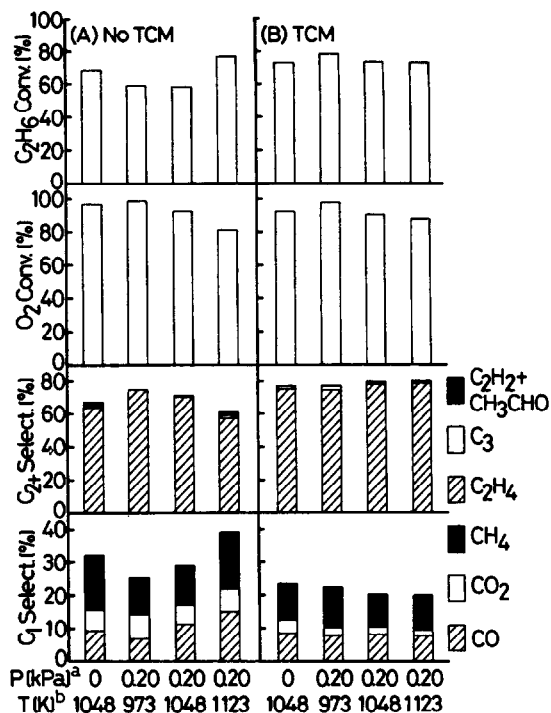


Fig. 4. Effect of pretreatment with TCM and O_2 prior to ethane oxidation in (A) absence and (B) presence of TCM at 1048 K. Pretreatment procedures, reaction conditions and symbols: as in Fig. 3 except for reaction temperatures. Data were collected at 0.5 h on-stream.

lectivities in the conversion of ethane. The TCM-pretreated catalysts when employed with TCM in the feedstream produced significantly higher conversions of ethane but the measured C_2H_4 selectivities were little different from those found with TCM absent from the feedstream. These results indicate that pretreatment of the catalyst with TCM produces not only a beneficial effect on the C_2H_4 selectivity but one which is essentially the same whether or not TCM is present in the reaction feedstream, whereas the presence of TCM in the feedstream appears to be necessary to optimize the conversion of ethane. The data in Fig. 3 also show that, at least from 973 to 1123 K, the effect of the temperature of pretreatment is relatively small, as would be expected from the results of XPS analyses of the pretreated catalysts (Table 2). At a reaction temperature of 1048 K (Fig. 4), the surface chloride and gas-phase TCM show

little or no effect on either the conversions or selectivities probably due to the substantial contributions of homogeneous reactions.

3.3. Effects of pretreatment with TCM together with H₂O

As described above, the formation of the surface chloride is not influenced by the partial pressure of TCM in the feed and pretreatment time and temperatures. It has been reported that relatively large quantities of the chloride were detected on MgO after the oxidative coupling of methane under extreme reaction conditions of 1123 K and 0.69 kPa of TCM [5]. Under such extreme conditions, it may be expected that a substantial quantity of water would be produced in the reaction. Therefore pretreatment experiments were carried out in which MgO was exposed to TCM (0.20 kPa), H₂O (1.6 kPa) and O₂ (12.5 ml/min). The results of XPS analyses of the pretreated MgO are shown in Table 3. It is apparent that, in general, the chloriding of the surface is favoured in the presence of H₂O. Furthermore a larger quantity of the surface chloride was also detected after the argon-ion etching. Thus it appears that introduction of H₂O together with TCM and O₂ promotes the

chloriding process in both the surface and the near-surface region, suggesting that the OH group on the oxide plays an important role in the introduction of chlorine on the surface.

Aliquots of MgO pretreated with one or more of O₂, TCM and H₂O were employed as catalysts at 773 and 1048 K in the presence and absence of TCM (Fig. 5). Although both the conversion of ethane and selectivity to ethylene at 773 K were increased on pretreatment of the catalyst with O₂, TCM and H₂O only the conversion increased and the selectivity to ethylene suffered a slight decrease when TCM was introduced into the feedstream with the aforementioned catalyst. In contrast to the observations at the lower temperature, little or no effect of the introduction of TCM, either in pretreatment or in the feedstream was seen at 1048 K.

Lunsford et al. reported that the introduction of 0.24 kPa of gas-phase chlorine (HCl) into the feedstream for the oxidative dehydrogenation of ethane on Li⁺-MgO had a negative effect on the formation of ethylene at 923 K and excess chloride on the surface resulted in a lower activity [14]. If HCl is used as a gas-phase additive, the basic sites, believed to be those responsible for the abstraction of hydrogen from the hydrocarbon, would presumably be destroyed by the

Table 3
XPS analyses of MgO pretreated with TCM + O₂ + H₂O^{a,b}

Temp.: ^c	973	973	1048	1048	1123	1123
Time: ^d	1	3	1	3	1	3
Mg 2s (eV)	87.8 (88.0)	87.9 (88.4)	88.3 (88.1)	88.1 (88.3)	87.9 (88.4)	87.9 (88.3)
O 1s (eV)	529.8 (530.2)	530.0 (530.2)	530.0 (530.1)	530.1 (530.2)	530.1 (530.4)	529.8 (530.3)
Cl 2p (eV)	198.1 (198.9)	198.1 (199.5)	198.7 (198.9)	198.4 (199.7)	198.2 (199.4)	198.3 (198.6)
O/Mg (-)	0.99 (0.07)	1.34 (1.31)	0.97 (0.89)	0.96 (0.92)	0.86 (0.92)	0.95 (0.90)
Cl/Mg (-)	0.09 (0.07)	0.15 (0.07)	0.10 (0.06)	0.15 (0.07)	0.09 (0.08)	0.10 (0.06)

^a Values in parentheses () are after argon etching for 1 min.

^b Pretreatment gas: O₂ (12.5 ml/min) + TCM (0.20 kPa) + H₂O (1.6 kPa). Weight of the pretreated MgO: 0.7 g.

^c Pretreatment temperature (K).

^d Pretreatment time (h).

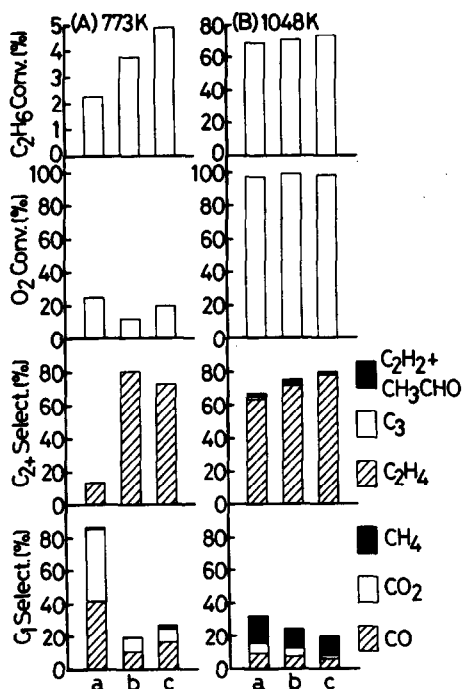


Fig. 5. Effect of pretreatment with TCM, H_2O and O_2 prior to ethane oxidation in the absence and presence of TCM at (A) 773 and (B) 1048 K. a: After the catalyst (0.7 g) was pretreated with O_2 (12.5 ml/min) for 1 h at 1048 K, the feedstream of C_2H_6 (27.1 kPa) and O_2 (6.8 kPa) diluted with He was introduced. b: After the catalyst was pretreated with O_2 (12.5 ml/min), TCM (0.2 kPa) and H_2O (1.6 kPa) for 3 h at 1048 K, the same feedstream as in a was introduced. c: After the same pretreatment as in b, the feedstream of C_2H_6 (27.1 kPa), O_2 (6.8 kPa) and TCM (0.17 kPa) diluted with He was introduced. Data were collected at 0.5 h on-stream.

adsorption of the acid thus producing a disadvantageous result. TCM would not be expected to have a similar deleterious effect on basic sites.

At the present any explanation of the effect resulting from the addition of TCM and the promotional effect of H_2O can only be largely speculative. However the presence of a partial negative charge on the chlorine atoms of TCM may result in an attractive coulombic interaction with the positively charged magnesium ions of MgO leading to a perturbation of electron density in the C–Cl bond of TCM and its ultimate scission, with the chlorine atom retained on the surface Mg. The surface chlorine atom may

then serve as a preferential site for the conversion of methane into methyl radicals and/or as promoter for the basic oxygen atoms. The observation that the beneficial effect of TCM does not continuously increase with increase in the concentration of surface chlorine atoms appears to suggest that the latter hypothesis is more probable.

MgO has a face-centred cubic lattice as found in sodium chloride and consequently each Mg ion on the surface of MgO will have four oxygen ions as nearest neighbours. Since the apparent effective charge on chlorine is less than that on oxygen it is expected that substitution of oxygen atoms attached to magnesium by chlorine will not be a facile process. The introduction of water presumably will lead to the formation of hydroxyl groups on the surface of the catalyst at least in part resulting from the binding of protons to the surface oxygen species. The replacement of hydroxyl groups by chlorine atoms appears to be more probable at least from an electrostatic viewpoint than the substitution of surface oxygen ions.

Not surprisingly, in view of the observations from a number of oxidation processes [see for example, [22,23]], evidence for the existence of structure sensitivity in the oxidative coupling of methane has also been reported [24,25]. Although the interaction of TCM with the surface of a solid may be dependent on the exposed crystallographic planes, each of the aliquots of magnesia employed in the present work undoubtedly display the same statistical distribution of surface planes and consequently the variation of morphology can presumably be discounted.

Regardless of the nature of the incorporation of chlorine into the surface of MgO the experimental results provide indisputable evidence for the existence of chlorine on the catalyst after exposure to TCM. However it is also clear that a definitive statement concerning the nature of the chlorine compounds thus formed cannot be expected. In part, as a consequence of the energetic and geometric heterogeneity of the surface

of MgO and partly as a result of the modification of this surface by the interaction with TCM, some localized regions may more closely resemble magnesium chloride structurally while others may appear as magnesium oxychloride. It is clear, however, that the substantial electronegativity of chlorine plays an important role in its effect on the methane conversion process.

4. Conclusion

1. At reaction temperatures of 723–823 K, the selectivity to C_2H_4 on MgO was enhanced by the introduction of TCM. The conversion of C_2H_6 was increased at 773 and 823 K but decreased at 723 K by the addition of TCM.
2. At reaction temperatures above 998 K, the introduction of TCM had little effect on the dehydrogenation.
3. A chlorided surface resulted from the pretreatment with TCM + O_2 or TCM + O_2 + H_2O under a variety of partial pressures of TCM, temperatures and pretreatment duration.
4. Pretreatment with TCM + O_2 + H_2O is not advantageous in the conversion of ethane.
5. Over the pretreated oxide regardless of the presence of H_2O in the pretreatment gas, the conversion of C_2H_6 and selectivity to C_2H_4 at 773 K were increased in the presence and absence of TCM in the feedstream of the ethane dehydrogenation. However the enhancement does not continuously increase with increase in the concentration of surface chloride.
6. At 1048 K, pretreatment of MgO produced little or no changes in the conversion or selectivities.

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