

Oxidative Coupling and Partial Oxidation of Methane over Solid Catalysts in the Presence and Absence of Tetrachloromethane as a Gas-Phase Additive

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Oxidative Coupling and Partial Oxidation of Methane over Solid Catalysts in the Presence and Absence of Tetrachloromethane as a Gas-Phase Additive

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Our recent studies on the oxidation of methane in the presence and absence of tetrachloromethane (TCM) over a variety of solid catalysts have been summarized together with those of the oxidation of related hydrocarbons. The catalytic activities were generally improved by the addition of TCM and the improvement was strongly dependent on the chlorine species formed over the surface of the catalysts during the oxidation with TCM. However no effects of the introduction of TCM into the feedstream were observed on highly active catalysts such as Li/MgO, Sm₂O₃, and La₂O₃. Various X-ray analyses of the catalysts previously employed in the oxidation are also described in order to clarify the nature and source of the introduction of TCM.

Introduction

The catalytic conversion of natural gas to value-added products continues to occupy the attention of a significant number of researchers. Since methane is the major component of natural gas, the oxidative coupling of methane to form ethane and ethylene^{1,2)} and the partial oxidation to carbon monoxide³⁾ are, at least in principle, an attractive process for the generation of precursors for economically important chemical process.

Since the advantageous effect of the continuous addition of a small partial pressure of tetrachloromethane (TCM) into the methane conversion feedstream was first reported in 1988,⁴⁾ the role of chlorine in the partial oxidation of methane have also been reported by some groups.^{5,6)}

In the present paper, the results of our studies on the effect of TCM on the methane oxidation are described together with those on the oxidative dehydrogenation of ethane to ethylene in the presence and absence of TCM on some catalysts since ethylene is believed to form *via* secondary reactions of ethane in the oxidative coupling of

methane.

Results and Discussion

Effect of the Introduction of TCM on Methane Oxidation. Oxidative Coupling of Methane over Salts of Alkali and Alkaline Earth Metals

Since Lunsford *et al.* reported lithium-doped magnesia as an effective catalyst for methane coupling,^{2,7,8)} alkali-doped alkaline earth oxides⁸⁾ and related catalysts^{8,9,10)} have been examined. Since the C-H bond scission of methane is believed to occur on basic sites over solid catalysts,⁸⁾ acidic catalysts such as sulfate¹¹⁾ were not employed to the methane oxidation. However acidic alkali sulfates revealed apparent activities for the oxidative coupling of methane in the absence of TCM at 1108 K (Fig. 1),¹²⁾ in which the weight of catalyst (*W*) and total flow rate (*F*) of the feedstream ($P(\text{CH}_4)=28.7$ kPa and $P(\text{O}_2)=4.1$ kPa diluted with He) were 1.4 g and 30 ml/min, respectively. The conversion of methane increased in the order $\text{Li}_2\text{SO}_4 < \text{Na}_2\text{SO}_4 < \text{K}_2\text{SO}_4 < \text{Cs}_2\text{SO}_4 < \text{Rb}_2\text{SO}_4$, approximately inverse to the electronegativity of

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Dedicated to Professor Hitoshi Takeshita on the occasion of his retirement

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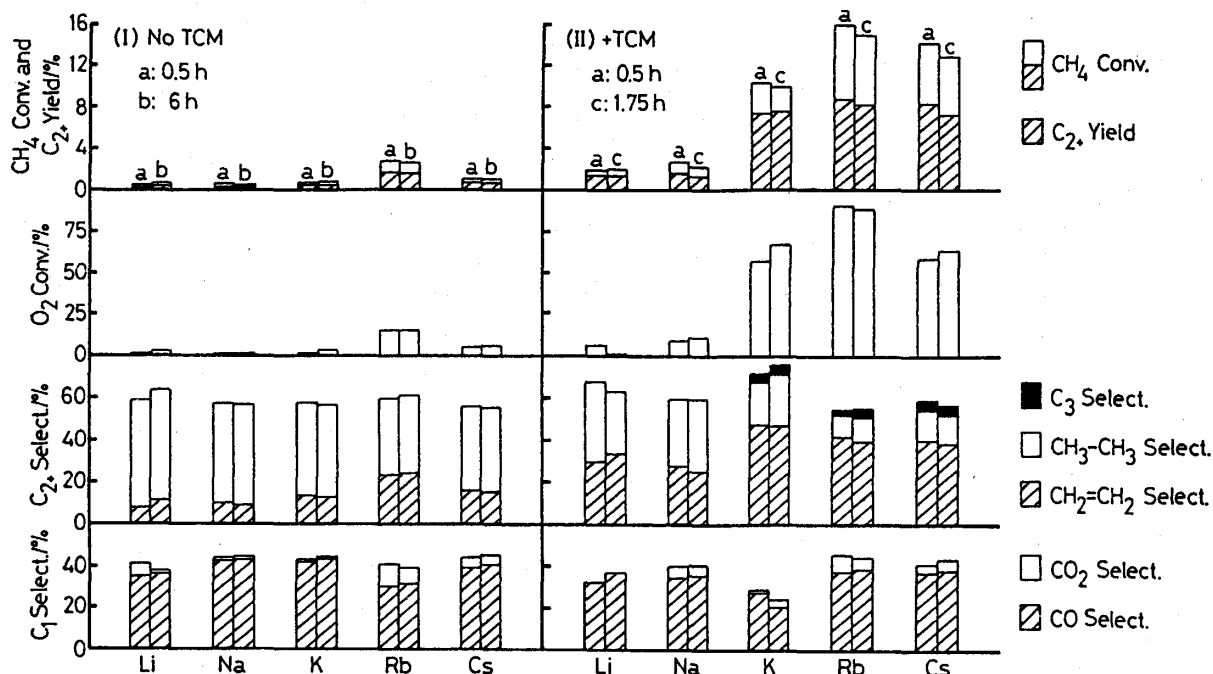


Fig.1 Methane oxidation on alkali sulfates at 1108 K.

alkali cations. The similar correlation between the conversion and the electronegativity of cations was also observed on alkaline earth sulfate.¹³⁾ The perturbation of the electron density of the anion by neighbouring cations may decrease with decrease in the electronegativity of the cations and consequently the effective charge on the oxygen atoms of the sulfate anion should be higher for cations of lower electronegativity. This appears to be consistent with the ability of the oxygen atoms to assist in the dissociation of a C-H bond of methane by perturbation of the electron density and the subsequent scission of the bond. On addition of a small quantity of TCM (0.17 kPa) on both sulfates, the conversion of methane and the selectivity to ethylene were distinctly improved with a concomitant decrease in the selectivity to ethane. Since chlorine radicals catalyze the formation of ethane from methane in a gas phase at high temperature, the beneficial effect of the introduction of TCM may arise from the chain reactions.¹⁴⁾ However the conversion of methane after the pretreatment of K_2SO_4 with TCM was evidently higher than that observed without the pretreatment.¹²⁾ Therefore the surface chlorinated species (KCl)¹²⁾ may contribute to the oxidation in the presence of TCM.

Three magnesium salts were examined as catalysts in the methane oxidation. In the absence of TCM at 1048 K, the conversions of methane followed the order $MgO > Mg_3(PO_4)_2 > MgSO_4$ while the selectivities to C_2 compounds were in the

order $MgSO_4 > MgO > Mg_3(PO_4)_2$.^{15,16)} The introduction of TCM had relatively little effect on the conversion of methane on MgO and $Mg_3(PO_4)_2$.^{15,16)} Although the selectivity to ethylene was enhanced both on the oxide and the phosphate by the addition of TCM, the selectivity was independent on the partial pressure of TCM and the reaction temperature.^{15,16)} In contrast, the conversion of methane on $MgSO_4$ increased with increase in the partial pressure of TCM and reaction temperature.¹⁶⁾ The selectivity to ethylene on $MgSO_4$ increased on addition of 0.17 kPa of TCM but decreased with further increase in the partial pressure of TCM.¹⁶⁾ Therefore the role of TCM on the surface of basic MgO and $Mg_3(PO_4)_2$ is different from that of acidic $MgSO_4$. Little or no chlorinated species were detected by XRD and XRF of each used magnesium salts.^{15,16)} However a certain amount of the chlorinated species was detected by XPS analyses. Thus the chlorinated species are formed only on the catalyst surface and the improvement by the addition of TCM on each magnesium salt may be attributed to the presence of these chlorinated species on the surface. Based on thermal stabilities of the chloride,¹⁵⁾ the formation of $MgCl_2$ on each magnesium salt appears to be more probable. It is of interest to note that a trace amount of MgO was detected only in XRD of $MgSO_4$ previously employed in the oxidation in the presence of TCM, indicating that the decomposition of $MgSO_4$ to MgO is enhanced by the addition of TCM. If basic MgO is formed on the surface of acidic $MgSO_4$, the

conversion of methane would be improved as observed on MgSO_4 in the presence of TCM. The decomposition of MgSO_4 to MgO was further supported by the observation of the oxidation in the presence of TCM on binary MgSO_4 - MgO catalysts.¹⁷⁾

The introduction of TCM had little or no enhancement effect with Li/MgO while a distinct improvement both of the conversion and the selectivity to ethylene with TCM was observed on MgO doped by K and Rb . In contrast, the conversion of methane and the selectivity to ethylene were enhanced by the introduction of TCM on $\text{Mg}_3(\text{PO}_4)_2$ and MgSO_4 doped by those alkali carbonates.¹⁸⁾ Therefore the effect of the addition of TCM on the doped MgSO_4 and $\text{Mg}_3(\text{PO}_4)_2$ appears to be primarily the result of the interaction with the anions of the alkaline earth compounds, but not the alkali-dopants.¹⁸⁾

Oxidative Coupling of Methane over Rare Earth Oxides and Related Catalysts.

It has been suggested that an important difference between the rare earth oxide^{8,19)} and alkali/alkaline earth oxide^{8,20)} catalysts is that the active oxygen species on the rare earth oxides are a sorbed form of oxygen whereas those in the latter catalysts are a part of the lattice, while Ekstrom showed later that the lattice oxygen was involved with Pr_6O_{11} in methane oxidation but did not play a role with Sm_2O_3 .²¹⁾

Figure 2 described the effect of TCM on the oxidative coupling of methane on Pr_6O_{11} , Sm_2O_3 , La_2O_3 and CeO_2 at 1023 K.^{22,23)} In the absence of TCM, the conversion of methane followed the order $\text{Sm}_2\text{O}_3 > \text{La}_2\text{O}_3 \geq \text{CeO}_2 > \text{Pr}_6\text{O}_{11}$ at 1023 K while, at 873 K (not shown)²⁴⁾ $\text{Sm}_2\text{O}_3 > \text{La}_2\text{O}_3 > \text{Pr}_6\text{O}_{11} > \text{CeO}_2$. The latter order agreed with that for the oxidative coupling of benzene at the same reaction conditions as those employed for the methane coupling.²⁴⁾ Upon addition of TCM, the conversion of methane on Sm_2O_3 decreased while little or no effect was observed on La_2O_3 and CeO_2 . In contrast, the conversion and the selectivity to C_2H_4 were enhanced by the introduction of TCM on Pr_6O_{11} , both of which further increased with increasing time-on-stream.^{22,23)} The XRD patterns of Pr_6O_{11} , Sm_2O_3 and La_2O_3 previously used in the methane oxidation with TCM showed the formation of the corresponding oxychloride but no CeOCl was detected in CeO_2 . No formation of CeOCl appears to lead to no effect of TCM on CeO_2 . The contrasting behaviours on Pr_6O_{11} in the presence of TCM imply that the participation of lattice oxygen in the methane oxidation is required in order to

benefit from the formation of the oxychloride.^{22,23)}

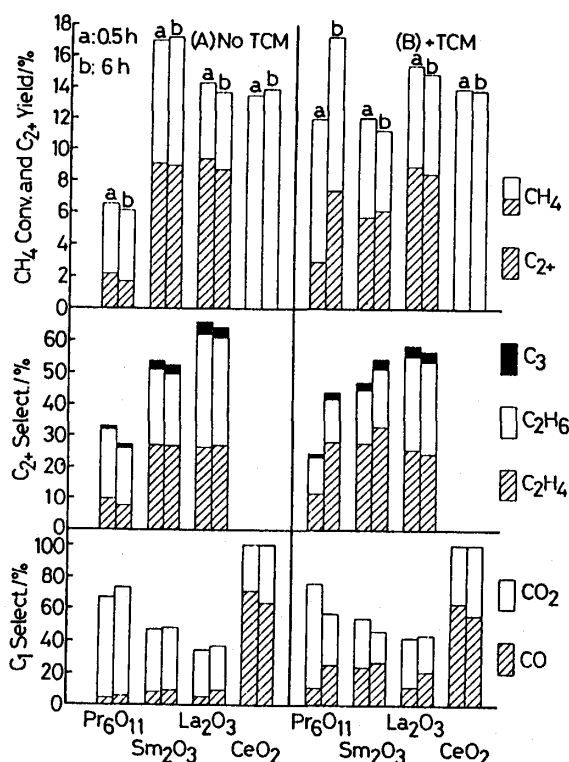


Fig.2 Methane oxidation on rare earth oxides at 1023K.

When La_2O_3 , LaPO_4 and $\text{La}_2(\text{SO}_4)_3$ were used for the oxidative coupling of methane in the absence of TCM at 1108 K, the conversion of methane followed order $\text{La}_2\text{O}_3 > \text{LaPO}_4 > \text{La}_2(\text{SO}_4)_3$.²⁵⁾ The same order in the conversion on oxide, phosphate and sulfate of magnesium for the methane coupling was obtained as described above.^{15,16)} It may be assumed that the ability of the catalyst to bring about the scission of the C-H bond in methane is dependent on the magnitude of the negative charge on the oxygen atoms of the solid. The semi-empirical electronegativity obtained for oxygen in La_2O_3 , LaPO_4 and $\text{La}_2(\text{SO}_4)_3$ are -0.49, -0.30 and -0.21, respectively, which corresponds to the order followed by the methane conversion.²⁵⁾ The effect of TCM was very small on La_2O_3 , as described above, in contrast with LaPO_4 and $\text{La}_2(\text{SO}_4)_3$. By the addition of TCM, methane conversion on LaPO_4 decreased distinctly but relatively little change in the selectivity was observed.²⁵⁾ In contrast, the conversion of CH_4 and the selectivity to C_2H_4 dramatically improved on $\text{La}_2(\text{SO}_4)_3$ in the presence of TCM and were strongly influenced by the partial pressure of TCM in the feedstream.²⁵⁾ It is of interest to note that the loading of LaCl_3 to the sulfate produce relatively little change from the

results obtained with $\text{La}_2(\text{SO}_4)_3$ alone either in the presence or in the absence of TCM.

Partial Oxidation of Methane over Hydroxyapatites

Calcium hydroxyapatites have shown to be bifunctional catalysts, with acidic or basic properties, depending on their composition [$\text{Ca}_{10-z}(\text{HPO}_4)_2(\text{PO}_4)_{6-z}(\text{OH})_{2-z}$; $z=0$ ($\text{Ca/P}=1.67$), stoichiometric form; $0 < z \leq 1$ ($1.51 \leq \text{Ca/P} < 1.67$), non-stoichiometric form].²⁶⁻²⁸ Calcium hydroxyapatites ion-exchanged with lead has been shown to catalyse the selective coupling of methane²⁹⁻³¹ while with calcium hydroxyapatites itself^{32,33} and strontium hydroxyapatites³⁴ the principal products are carbon oxides.

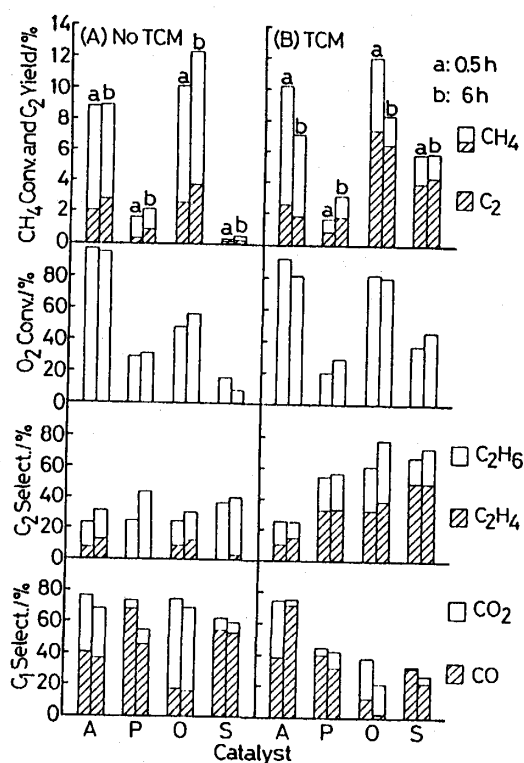


Fig. 3 Methane oxidation on $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (A), $\beta\text{-Ca}_3(\text{PO}_4)_2$ (P), CaO (O) and CaSO_4 (S) at 973K.

The conversion, selectivities and yields on $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, $\beta\text{-Ca}_3(\text{PO}_4)_2$, CaO and CaSO_4 at 973 K are summarized in Fig. 3.^{35,36} In the absence of TCM, the conversion of methane followed the order $\text{CaO} > \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 > \beta\text{-Ca}_3(\text{PO}_4)_2 > \text{CaSO}_4$. The same order of oxide, phosphate and sulfate was also observed in the methane coupling on magnesium¹⁶ and lanthanum²⁵ salts. On introduction of TCM, the conversion on CaSO_4 increased, but showed little or no change on $\beta\text{-Ca}_3(\text{PO}_4)_2$ and CaO . The selectivity to ethylene increased on those three catalysts. In contrast, the

introduction of TCM on $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ produced quite different changes. While the selectivity to C_2 compounds remains unchanged on the addition of TCM, that to CO increased with time on-stream. On each calcium salts previously used in the oxidation with TCM, chlorinated species were detected by XPS at the binding energy of 199 eV due to $\text{Cl} 2p$.³⁶

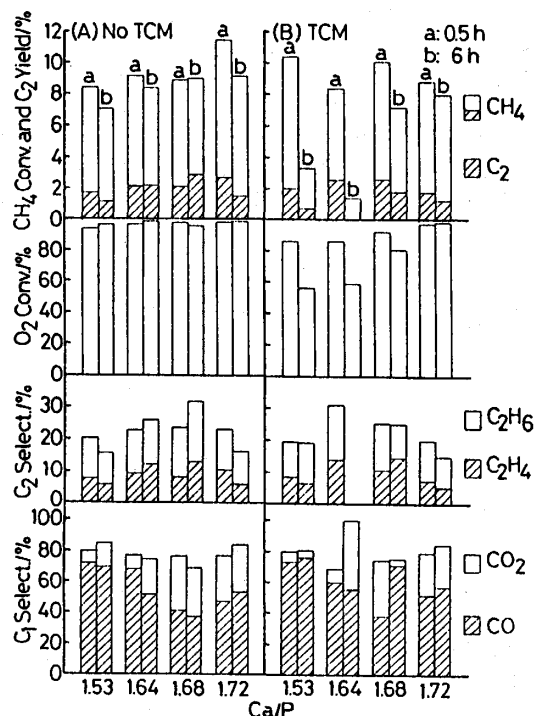


Fig. 4 The effects of the Ca/P ratio of calcium hydroxyapatites on methane oxidation at 973K.

The X-ray diffraction patterns of the bulk phase of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ showed the complete conversion of the hydroxyapatite to the chlorapatite [$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$] during the oxidation with TCM while no chlorinated species were detected with CaO and CaSO_4 .³⁶ Furthermore, the formation of small quantities of chlorapatite was found with $\beta\text{-Ca}_3(\text{PO}_4)_2$ previously used in the oxidation with TCM.³⁶ Since the values obtained for Cl/Ca in the bulk phase are smaller than those found by XPS, diffusion of the chlorine into the bulk phase is evidently.³⁶ Based on the results on magnesium salts,^{15,16} the increase of the selectivity to ethylene by the introduction of TCM on $\beta\text{-Ca}_3(\text{PO}_4)_2$, CaO and CaSO_4 was attributed to a chlorinated surface, nominally in the form of calcium chloride, since the possibility that a small quantity of CaCl_2 cannot be discounted on $\beta\text{-Ca}_3(\text{PO}_4)_2$.³⁶

The effect of changes in the Ca/P value of calcium hydroxyapatites (Ap) on the methane

oxidation at 973 K were described in Fig. 4 in the presence and absence of TCM. The conversion of methane in the absence of TCM was little influenced by the value of Ca/P in each calcium hydroxyapatite, while the selectivity to CO was in the order $Ap_{1.72} > Ap_{1.68} < Ap_{1.64} < Ap_{1.53}$. Over calcium-deficient hydroxyapatite ($Ap_{1.64}$ and $Ap_{1.53}$), a sharp decrease on the conversion was observed on addition of TCM while a substantial increase of the selectivity to carbon monoxide occurred on the stoichiometric calcium hydroxyapatite ($Ap_{1.68}$). On $Ap_{1.72}$, minor increases in the selectivity to carbon monoxide on addition of TCM were observed, particularly at shorter space time (not shown).³⁷⁾ Since the XRD patterns of the four fresh samples of calcium hydroxyapatite are essentially the same,³⁷⁾ no correlations with catalytic activity can be deduced with XRD. Consequently, it may be possible to view each sample as stoichiometric calcium hydroxyapatite containing an excess of either calcium or phosphorous. Analyses by X-ray absorption fine structure (EXAFS) were applied to clarify the bond distance and the local structure around the calcium atoms. The results of EXAFS are shown in Table 1. The nearest-neighbour distances of the Ca-O bond of each apatite are in the order of $Ap_{1.72} > Ap_{1.68} \leq Ap_{1.64} < Ap_{1.53}$. It may be of interest to compare the order of the Ca-O bond with that of the selectivity to carbon monoxide in the oxidation of methane in the absence of TCM. The properties of the catalysts appear to be more strongly influenced by the bond lengths of the fresh catalyst.

Table 1. Results of EXAFS analysis

Catalyst	$r/\text{\AA}^a$	N^b	$r/\text{\AA}^{2c}$	E_0/eV^d	$R/(\%)^e$
$Ap_{1.73}$	2.41	5.5	0.1042	6.741	7.7
$Ap_{1.68}$	2.37	4.8	0.0999	3.961	8.1
$Ap_{1.64}$	2.38	4.6	0.0975	4.480	6.7
$Ap_{1.53}$	2.39	4.2	0.0705	5.018	6.1

^a Distance; estimated maximum deviation (± 0.01).

^b Coordination number; estimated maximum deviation (± 0.1), except for 4.8 which is fixed.

^c Debye-Waller factor.^d Threshold increment.

^e Reliability factor.

The high selectivity (90%) to carbon monoxide on strontium hydroxyapatite ($Sr_{10}(PO_4)_6(OH)_2$) was observed even in the absence of TCM during the initial 6 h on-stream at 873 K.³⁸⁾ However the selectivity decreased after 78 h on-stream,

concomitantly with a gradual increase in the selectivity to CO_2 . The XRD patterns of $Sr_{10}(PO_4)_6(OH)_2$ after used in the oxidation for 6 h on-stream revealed a trace amount of $Sr_3(PO_4)_2$ but, after 78 h on-stream, the apatite was completely converted to $Sr_3(PO_4)_2$, which appeared to contribute to the retardation. Although the conversion of methane on strontium hydroxyapatites decreased in the presence of TCM during 6 h on-stream the selectivity to CO approached 100%. At a higher temperature of 973 K in the presence of TCM on stoichiometric and non-stoichiometric strontium hydroxyapatites, the selectivities to carbon monoxide and those to C_2 compounds were increased while the conversion of methane was decreased.³⁹⁾ Since the hydroxyapatite was easily converted to $Sr_3(PO_4)_2$ at 973 K, the catalytic properties of the apatite and phosphate appear to contribute to the enhancement of both selectivities.³⁹⁾

Effect of the Introduction of TCM on Ethane Oxidation

The results of the oxidative dehydrogenation of ethane on MgO ,⁴⁰⁾ $Mg_3(PO_4)_2$,⁴¹⁾ and $MgSO_4$ ⁴²⁾ at 773 K in the absence and presence of TCM are summarized in Fig. 5, in which the reaction conditions were adjusted to $W=0.7$ g and $F=15$ ml/min ($P(C_2H_6)=27.1$ kPa, $P(O_2)=6.8$ kPa and $P(TCM)=0.17$ kPa (when present) diluted with He).

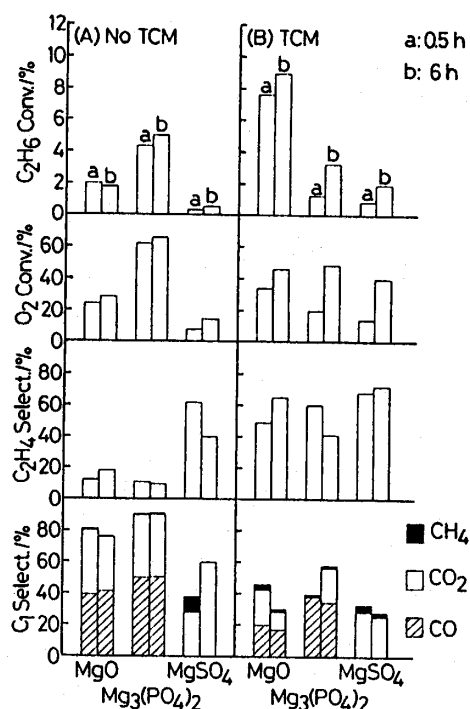


Fig. 5 Ethane oxidation on salts of magnesium at 773K.

In the absence of TCM, the conversion of ethane followed the order phosphate > oxide > sulfate, which was different from that for methane oxidation on salts of magnesium^{15,16} and lanthanum²⁵) and that of benzene on lanthanum salts.²⁴) Therefore the role of the catalyst for the abstraction of hydrogen appears to be strongly dependent on the nature of the reactant. On addition of TCM, the conversion of ethane on MgO and MgSO₄ was distinctly enhanced in contrast to the decrease on Mg₃(PO₄)₂. The selectivity to ethylene on MgSO₄ was little influenced by the introduction of TCM while those on MgO and Mg₃(PO₄)₂ were improved. Those effects of TCM were quite contrast to those on methane oxidation. Since the chlorinated species on the surface of each salts of magnesium previously used in ethane oxidation with TCM were detected by XPS as those used on methane oxidation, the contribution of the chlorinated species on the surface and in the gas-phase would be dependent on the bond strength of C-H bond of the reactant.

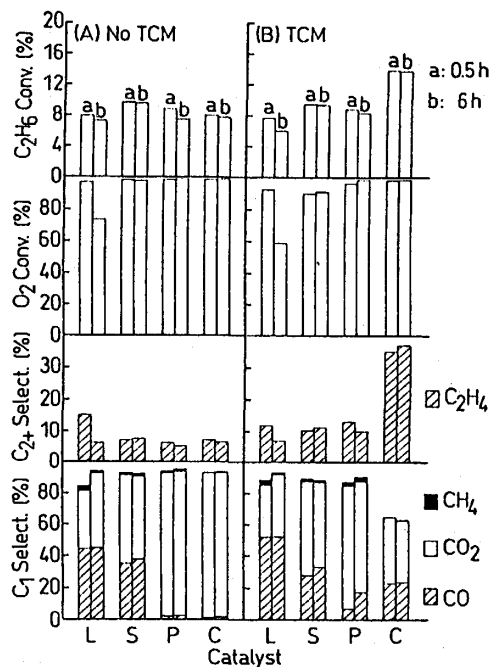


Fig.6 Ethane oxidation on La₂O₃ (L), Sm₂O₃ (S), Pr₆O₁₁ (P) and CeO₂ (C) at 773 K.

The effect of TCM on the oxidation of ethane was also observed on lanthanum oxides as shown in Fig. 6.^{43,44}) The conversion of ethane and the selectivity to ethylene were improved by the addition of TCM on CeO₂, on which no TCM effect was observed on the oxidation of methane, while little effects were observed on Pr₆O₁₁, on which the introduction of TCM resulted in the distinct

improvement of the catalytic activities for methane oxidation. When Pr₆O₁₁ was doped by PrCl₃, the catalyst revealed higher ethane conversion and ethylene selectivity regardless to the addition of TCM than the undoped oxide.⁴⁴) Therefore the mechanism through which TCM participates in the oxidative dehydrogenation of ethane is apparently not identical to that in the oxidative coupling of methane, at least magnesium salts and the rare earth oxides. These comparisons also emphasize the predominant importance of the interaction of TCM with the catalyst as compared with the gas phase process.

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