# Enhancement of the activities with feedstream doping by tetrachloromethane in the oxidative dehydrogenation of propane on $\alpha$-magnesium pyrovanadate

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The oxidative dehydrogenation of propane to propylene has been investigated on $\alpha$-magnesium pyrovanadate ($Mg_2V_2O_7$) at 723 K in the presence and absence of tetrachloromethane (TCM). Under the present conditions, the conversion of propane and the selectivity to propylene were 5.0 and 74.5%, respectively, in the absence of TCM while those were 14.0 and 70.2%, respectively, upon addition of a small amount of TCM ($P(\mathrm{TCM}) = 0.34$ kPa) into the feedstream on the catalyst. The conversion of propane on $Mg_2V_2O_7$ without oxidant in the presence and absence of TCM revealed that a contribution of lattice oxygen in the catalyst to the oxidation was strongly controlled by the addition of TCM, resulting in the enhancement of the activity with TCM.

**KEY WORDS:** $\alpha$-magnesium pyrovanadate; tetrachloromethane; propane oxidation

## 1. Introduction

It has been generally accepted that the addition of a small amount of chlorinated species such as tetrachloromethane (TCM) into the feedstream for the partial oxidation of light alkanes improves the catalytic activities. Since the advantageous effect of the continuous introduction of TCM into methane conversion feedstream was first reported from Moffat's laboratory in 1988 [1], the role of chlorinated species on the partial oxidation of methane was also reported by some groups [2,3]. Although participation of TCM in the gas-phase reaction cannot be excluded [4], it has been suggested that the formation of structural or non-structural chlorinated species on the catalyst surface would contribute to the enhanced activities in the partial oxidation in the presence of TCM [5]. Nozaki and Iimori have found that the introduction of TCM into the feedstream for the dehydrogenation of alcohol results in a rapid decrease in the dehydrogenation activities, indicating that TCM may control basic properties on the catalyst [6]. Recently in our laboratory the effect of the addition of TCM on the oxidative dehydrogenation of propane has been examined and the advantageous effect of TCM was also observed on $Sm_2O_3$ [7]. Unfortunately, the advantageous effect of TCM on the partial oxidation of methane, which has been most extensively observed among the oxidation of light alkanes, has not been observed on most active catalysts such as Li–MgO [8,9], $La_2O_3$ and $Sm_2O_3$ [10–13]. Furthermore, although a role of lattice oxygen in the catalyst should be a most important factor for the oxidation, to the best of our knowledge, an evident contribution of TCM to the lattice oxygen has not been reported.

In the present paper, the oxidative dehydrogenation of propane on $\alpha$-magnesium pyrovanadate is shown in the presence and absence of TCM. $\alpha$-magnesium pyrovanadate is one of the most active catalysts for the oxidative dehydrogenation of propane [14,15].

## 2. Experimental

$\alpha$-magnesium pyrovanadate ($Mg_2V_2O_7$) was prepared from $Mg(OH)_2$ and $NH_4VO_3$ according to the procedure reported by Volta et al. [14]. The resulting solid was calcined at 383 K overnight, followed by the calcination at 823 K for 6 h, 873 K for 6 h, 923 K for 6 h, 973 K for 17 h and then again 973 K for 17 h. The solid was finely ground after each calcination. Although, after the calcination at 823 K, the solid consisted of $MgV_2O_6$ and $Mg_2V_2O_7$, XRD patterns of the catalyst after the second calcination at 923 K matched with $Mg_2V_2O_7$ (JCPDS 31-0816). ICP analysis (Shimadzu ICPS-5000) of the catalyst found wt% Mg and wt% V as 18.86 and 38.84, respectively, which correspond to the calculated values of 18.52 and 38.81 for $Mg_2V_2O_7$. The particle size of 0.85–1.70 mm was employed as the catalyst. The surface area and apparent density of $Mg_2V_2O_7$ were 3.5 $m^2$ g and 1.06 $g\,cm^{-1}$, respectively. The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure. Details of the reactor design have been described elsewhere [13]. In all experiments, the catalyst was heated to the reaction temperature while maintaining a continuous flow of helium and was held at this temperature under a 25 $ml\,min^{-1}$ flow of oxygen for 1 h. No homogeneous oxidation of propane was observed at 723 K under the present conditions [16]. Column systems and definitions of the conversion and selectivity were

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reported previously [16]. Turnover rate using the catalyst surface area was estimated as the rate ($r = FC_0X_A/W$, in which $F$, $C_0$, $X_A$ and $W$ are flow rate, initial concentration of $C_3H_8$, conversion of $C_3H_8$ and catalyst weight [17]) per catalyst surface area. Blank experiments conducted with propane absent from the feed ($O_2$ + TCM + He) indicated that TCM is converted to carbon oxides. Although the quantities of carbon oxides produced in the blank experiments were small, all of the data reported were corrected by performing duplicate experiments with propane absent under otherwise identical values of the process variables. The carbon mass balances were 100 ± 5%. Decomposition behaviours of TCM were examined using the same procedure described elsewhere [18]. In the absence of the catalyst, no decomposition of TCM was observed under the present conditions. Powder X-ray diffraction (XRD) patterns were recorded with a Rigaku RINT 2500 X, using monochromatized Cu K$\alpha$ radiation. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) used Mg K$\alpha$ radiation. The binding energies were corrected using 285 eV for C 1s as an internal standard.

## 3. Results and discussion

Figure 1 showed the effects of $P$(TCM) on the conversion and the selectivity on $Mg_2V_2O_7$ at 723 K. Although the selectivity to $C_3H_6$ slightly decreased from 74.5 to 70.2% with increasing $P$(TCM) from 0 to 0.34 kPa, the conversion of $C_3H_8$ evidently improved from 5.0 to 14.2%, indicating that the introduction of TCM into the feedstream for the oxidation of $C_3H_8$ further enhances the great activities of $Mg_2V_2O_7$. The present great activities kept, at least, for 6 h on-stream. Turnover rates at $P(\mathrm{TCM}) = 0$, 0.17 and 0.34 kPa were estimated to be $5.1 \times 10^{-6}$, $13.1 \times 10^{-6}$ and $14.5 \times 10^{-6}$ $\mathrm{mol\,min^{-1}\,m^{-2}}$, respectively. XRD patterns described no conversion of the catalyst during the oxidation regardless to the addition of TCM (figure 2 (A) and (B)). Furthermore XPS analyses of the catalyst employed for the oxidation in the presence of TCM revealed that no chlorinated species were formed on the surface. Therefore, it is rather difficult to suggest that the enhancement of the activities with the introduction of TCM mainly attributes to the formation of bulk and/or surface chlorinated species. In order to check the conversion of TCM, the decomposition of TCM was examined under the same reaction conditions employed for the oxidation of $C_3H_8$ but $P(\mathrm{TCM}) = 0.51$ kPa. The conversion of TCM was 100% and no $C_xH_yCl_z$ ($x = 1$, 2 and 3) were detected, indicating that TCM converted to inorganic chlorinated species such as HCl, as observed in the decomposition of TCM under methane oxidation conditions [18]. Therefore, the formation of $C_3H_6$ may not be through those chlorinated organic species. Since $Mg_2V_2O_7$ can be formally described as $2MgO + V_2O_5$, the oxidation of $C_3H_8$ on MgO and $V_2O_5$ in the presence and absence of TCM was carried out under the same conditions

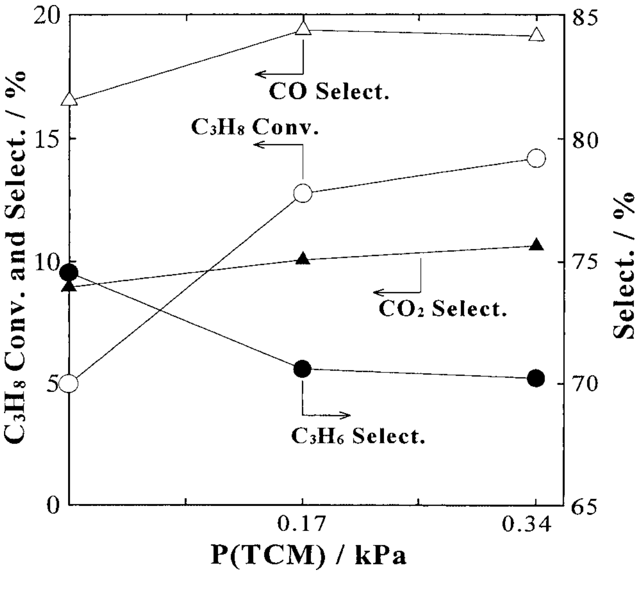

Figure 1. Effects of the partial pressure of TCM on the oxidative dehydrogenation of propane on $Mg_2V_2O_7$ at 723 K. Reaction conditions: $W = 0.5$ g, $P(C_3H_8) = 14.4$ kPa, $P(O_2) = 4.1$ kPa and $P(\mathrm{TCM}) = 0$, 0.17 and 0.34 kPa. Catalysts were pretreated with $O_2$ (25 $\mathrm{ml\,min^{-1}}$) at 723 K for 1 h. Data were collected at 0.75 h on-stream.

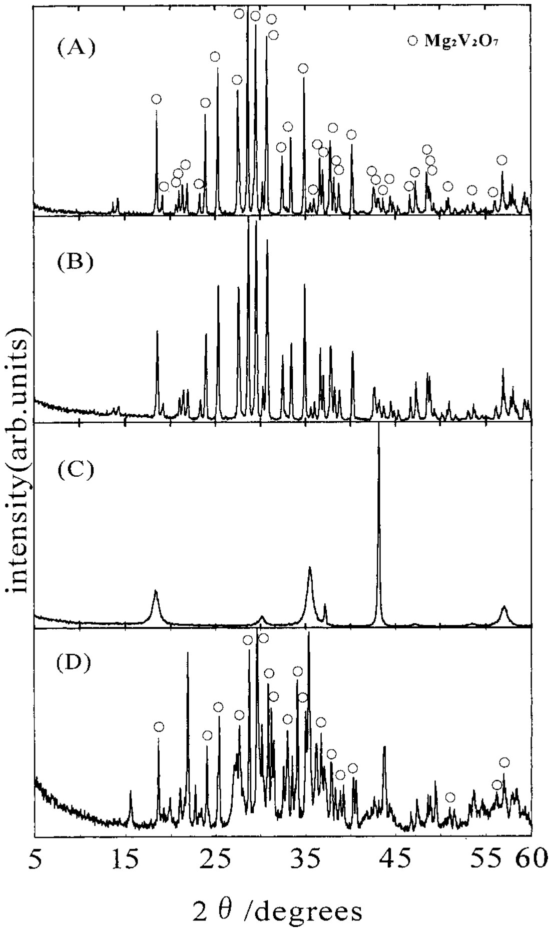

Figure 2. XRD patterns of $Mg_2V_2O_7$ previously employed for the conversion of propane for 6 h on-stream. (A) $P(O_2) = 4.1$ kPa and $P(\mathrm{TCM}) = 0$ kPa, (B) $P(O_2) = 4.1$ kPa and $P(\mathrm{TCM}) = 0.34$ kPa, (C) $P(O_2) = 0$ kPa and $P(\mathrm{TCM}) = 0$ kPa, (D) $P(O_2) = 0$ kPa and $P(\mathrm{TCM}) = 0.17$ kPa.

Table 1
Effects of the addition of TCM into the feedstream for propane oxidation on MgO and $V_2O_5$ at 723 K.

| Catal. | TCM[a] | Conversion (%) | | Selectivity (%) | | | | | TOR[b] |
|---|---|---|---|---|---|---|---|---|---|
| | | $C_3H_8$ | $O_2$ | CO | $CH_4$ | $CO_2$ | $C_2H_4$ | $C_3H_6$ | |
| MgO | A | 0.1 | $\sim 0$ | 55.3 | 0 | 44.7 | 0 | 0 | $0.1 \times 10^{-6}$ |
| | P | 1.0 | 9 | 15.3 | 0 | 19.5 | 11.4 | 53.9 | $1.0 \times 10^{-6}$ |
| $V_2O_5$ | A | 9.8 | 99 | 27.5 | 0.6 | 44.5 | 0 | 27.4 | $6.2 \times 10^{-6}$ |
| | P | 8.6 | 98 | 44.7 | 0 | 24.5 | 0 | 30.8 | $5.5 \times 10^{-6}$ |

[a] A: absence of TCM, P: presence of TCM.
[b] Turnover rate using the catalyst surface area (mol $min^{-1}$ $m^{-2}$).

as those employed for oxidation of $C_3H_8$ on $Mg_2V_2O_7$ (table 1). The surface areas of MgO and $V_2O_5$ were 3.5 and 5.6 $m^2$ $g^{-1}$, respectively. Upon addition of TCM on MgO, the conversion of $C_3H_8$ and the selectivity to $C_3H_6$ increased from 0.1 and 0% to 1.0 and 53.9%, respectively, while the activity was rather low regardless of the presence of TCM. Although the selectivities to CO and $CO_2$ were strongly influenced by the addition of TCM on $V_2O_5$, the conversion and the selectivity to $C_3H_8$ were insensitive to the introduction of TCM. Surface analysis of MgO and $V_2O_5$ previously employed for the oxidation with TCM showed that a small amount of chlorinated species was formed on the MgO surface (Cl/Mg = 0.07) while a trace amount of chlorinated species was detected on $V_2O_5$ by XPS. These results show that the enhancement observed on $Mg_2V_2O_7$ in the presence of TCM depends on the nature of the catalyst but not that of the corresponding single oxides. In order to examine the role of lattice oxygen in $Mg_2V_2O_7$ in the presence of TCM, the conversion of propane was observed in the absence of oxygen (figure 3). In the absence of TCM, the conversion of $C_3H_8$ and the selectivity to $C_3H_6$ extremely decreased and increased, respectively, with increasing time-on-stream. A qualitatively similar observation for the conversion of $C_3H_8$ in the absence of oxygen on $Mg_2V_2O_7$ has been already reported by Volta et al. [14]. In contrast, the low conversion of $C_3H_8$ and the high selectivity to $C_3H_6$ remained for 6 h on-stream in the presence of TCM. This appears to indicate that a lattice oxygen in $Mg_2V_2O_7$ directly contributes to the conversion of $C_3H_8$ even in the absence of oxygen. Evidently a contribution of lattice oxygen to the conversion of propane is strongly controlled by the introduction of TCM. XRD patterns of the catalysts employed in the absence of the oxidant showed that the catalyst completely converted to another species after the conversion without TCM while $Mg_2V_2O_7$ still remained in the catalysts after conversion with TCM (figure 2 (C) and (D)). XRD patterns of figure 2(C) show that the catalyst after the conversion without TCM consisted of $Mg_{1.5}VO_4$ (JCPDS 19-0778), MgO (JCPDS 34-0615) and $V_3O_4$ (JCPDS 45-0946). Oxygen contents in $Mg_{1.5}VO_4$, MgO and $V_3O_4$ are 42.3, 39.7 and 29.5 wt%, respectively, and evidently smaller than that in $Mg_2V_2O_7$ (42.7 wt%). Therefore, based on figure 2 (C) and (D) and figure 3, lattice oxygen in $Mg_2V_2O_7$ is removable from the structure in the absence of TCM while rather fixed in the structure in the presence of TCM. Although the solid previously employed in obtaining the XRD patterns shown in figure 2(C) was again treated in an oxygen flow at 523 K, the solid was not converted to $Mg_2V_2O_7$ but to a complex mixture which could not be identified by XRD. It seems rather strange that the loss of lattice oxygen from the catalyst is reduced by species which do not subsequently appear in any form on the surface of the catalyst. It should be noted that it is possible to suggest a formation of a trace amount of chlorinated species on the surface, which cannot be detected by XPS. Finally, we compared the present results with a relationship between conversions and selectivities, most of which were obtained at reaction temperatures greater than 763 K [19]. The present results are certainly included in the relationship although the present results were obtained at 723 K.

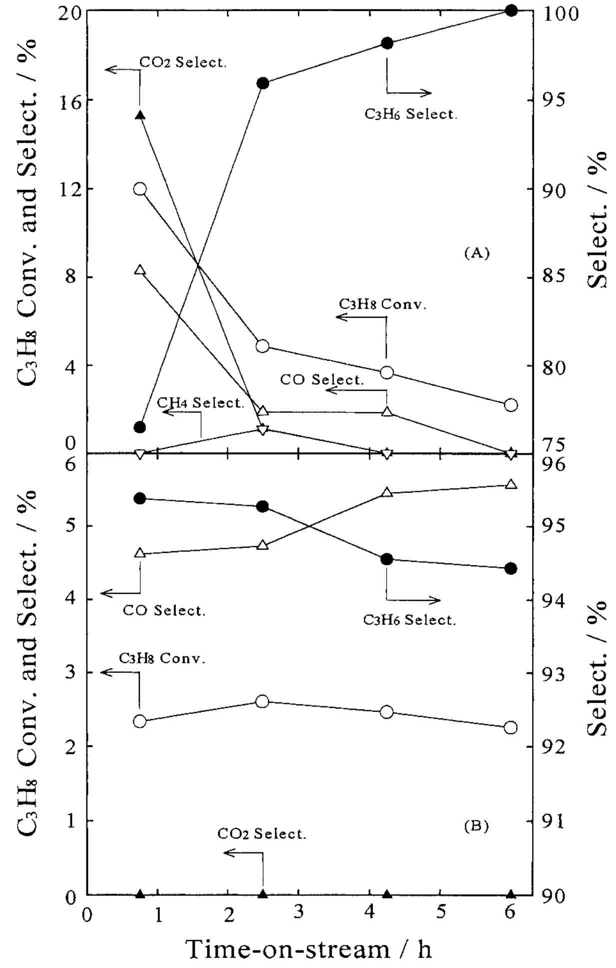

Figure 3. Effects of TCM on the conversion of $C_3H_8$ in the absence of $O_2$ on $Mg_2V_2O_7$ at 723 K. Reaction conditions: $W = 0.5$ g, $P(C_3H_8) =$ 14.4 kPa, $P(O_2) = 0$ kPa and $P(\mathrm{TCM}) = 0$ kPa for (A) and 0.17 kPa for (B). Catalysts were pretreated with $O_2$ (25 ml $min^{-1}$) at 723 K for 1 h.

In conclusion, TCM controls the removability of lattice oxygen in $Mg_2V_2O_7$, resulting in the enhancement of the activity of the catalyst for the oxidative dehydrogenation of propane. To the best of our knowledge, this appears to be a first observation on the direct contribution of chlorinated species to lattice oxygen during the oxidation of light alkanes in the presence of TCM. Further work is now in progress.

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