

## Oxidative Dehydrogenation of Propane on Magnesium Vanadates in the Presence of Tetrachloromethane

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(Received August 13, 2001)

The oxidative dehydrogenation of propane to propene on active catalysts such as magnesium vanadates ( $\text{MgV}_2\text{O}_6$ ,  $\text{Mg}_2\text{V}_2\text{O}_7$ , and  $\text{Mg}_3\text{V}_2\text{O}_8$ ) has been investigated in the presence and absence of tetrachloromethane (TCM) at 723 K. The introduction of a small amount of TCM into the feedstream did not influence the selectivity to propene while the conversion of propane was improved on those catalysts. The conversion was enhanced by approximately twice on  $\text{Mg}_2\text{V}_2\text{O}_7$  upon addition of TCM. It has been shown that the effects of TCM on lattice oxygen in those catalysts mainly control the enhancement. The formation of an excess amount of the chlorinated species on the surface of the catalysts resulted in a decrease of the conversion.

Since magnesium vanadates have been proposed as efficient catalysts for the oxidative dehydrogenation of butane<sup>1</sup> and propane,<sup>2</sup> extensive papers on those catalysts<sup>3–9</sup> and the related catalysts<sup>10–20</sup> have been published. It has been generally accepted that the V=O and/or V–O–V bonds participate in the activation of  $\text{C}_3\text{H}_8$ , resulting in the remarkable activities for the oxidative dehydrogenation of propane on those catalysts.<sup>21</sup> Most researchers have focused on the combination of vanadates and other solid elements to prepare active catalysts. There are rather few reports on the enhancement of the activities for the oxidative dehydrogenation of propane by the introduction of gaseous additive into the feedstream. It has been shown that the activities for the partial oxidation of methane can be improved on various catalysts by the addition of gaseous chlorinated species, such as tetrachloromethane (TCM), into the corresponding feedstream.<sup>22–24</sup> Although participation of TCM in the gas-phase reaction cannot be excluded,<sup>25</sup> it has been suggested that the formation of structural or nonstructural chlorinated species on the catalyst surface would contribute to the enhanced activities in the partial oxidation with TCM. It seems to be rather strange that there are few reports<sup>26,27</sup> on the effects of TCM on redox behaviors of catalysts since the oxidative dehydrogenation of alkanes should be strongly influenced by the participation of lattice oxygen in the catalysts to the oxidation. Since TCM is not easily decomposed under ambient conditions<sup>28</sup> and is a suspected human carcinogen and an Environmental Protection Agency priority pollutant,<sup>29,30</sup> a wide variety of studies on the decomposition of TCM have been carried out in aqueous- and gas-phases. Since the elimination of TCM as proposed in these techniques requires the input of substantial quantities of energy,<sup>31–34</sup> the development of decomposition methods which produce usable products is desirable from practical points of view. Since propane conversion processes are, at least in principle, attractive for the generation of precursors for economically important chemicals, the possibility of decomposing TCM while generating value-added prod-

ucts from propane is practically attractive.

In the present paper, we report the oxidative dehydrogenation of propane on magnesium meta-, pyro-, and ortho-vanadates in the presence and absence of TCM. Further enhancement of the activities for the oxidative dehydrogenation on those catalysts by the introduction of TCM into the feedstream will be demonstrated.

### Experimental

Magnesium meta-, pyro-, and ortho-vanadates ( $\text{MgV}_2\text{O}_6$ ,  $\text{Mg}_2\text{V}_2\text{O}_7$ , and  $\text{Mg}_3\text{V}_2\text{O}_8$ , respectively) were prepared from  $\text{Mg}(\text{OH})_2$  and  $\text{NH}_4\text{VO}_3$  according to the procedure reported by Volta et al.<sup>3</sup> In preparing magnesium meta-vanadate, the resulting solids were dried at 383 K overnight, followed by the calcination at 773 K for 6 h and at 873 K for 6 h. In the calcination for the synthesis of magnesium ortho-vanadate, the calcination temperature was adjusted at 823 K for 6 h, at 898 K for 49 h, at 913 K for 49 h, at 913 K for 60 h, at 1023 K for 15 h, at 1023 K for 15 h, and then again at 1073 K for 15 h. The calcination procedure for magnesium pyro-vanadate was given in our previous report.<sup>27</sup> Each solid was finely ground between calcinations. After the final calcination, XRD patterns of magnesium meta-, pyro-, and ortho-vanadates matched  $\text{MgV}_2\text{O}_6$  (JCPDS 45-1050),  $\text{Mg}_2\text{V}_2\text{O}_7$  (JCPDS 31-0816), and  $\text{Mg}_3\text{V}_2\text{O}_8$  (JCPDS 37-0351), respectively, and were essentially identical to those reported by Volta et al.<sup>3</sup> ICP analysis (Shimadzu ICPS-5000) of magnesium meta-, pyro-, and ortho-vanadates found wt%Mg and wt%V to be 11.0 and 46.2, 18.9 and 38.8, and 25.2 and 33.9, respectively, which corresponded to the calculated values of 10.9 and 45.9, 18.5 and 38.8, and 24.1 and 33.7 for  $\text{MgV}_2\text{O}_6$ ,  $\text{Mg}_2\text{V}_2\text{O}_7$ , and  $\text{Mg}_3\text{V}_2\text{O}_8$ , respectively. Particles of 0.85–1.70 mm were employed as the catalyst. Surface area and apparent density of  $\text{MgV}_2\text{O}_6$ ,  $\text{Mg}_2\text{V}_2\text{O}_7$ , and  $\text{Mg}_3\text{V}_2\text{O}_8$  were 2.0 and 1.11, 3.5 and 1.06, and 1.1  $\text{m}^2/\text{g}$  and 0.98  $\text{g}/\text{cm}^3$ , respectively. The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor operated at atmospheric pressure. The reactor consisted of a quartz tube, 9 mm i.d. and 35 mm in length, attached at each end to 4 mm i.d. quartz tubes to produce a total

length of 25 cm. The catalyst charge was held in place in the enlarged portion of the reactor by two quartz wool plugs. 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 flow of oxygen for 1 h. No homogeneous oxidation of propane was observed at 723 K under the present conditions. The reaction was monitored with an on-stream Shimadzu GC-8APT gas chromatograph with a TC detector and integrator (Shimadzu C-R6A). Two columns, one Porapak Q (6 m  $\times$  3 mm) and the other Molecular Sieve 5A (0.2 m  $\times$  3 mm), were employed in the analyses. The conversion of propane was calculated from the products and the propane introduced into the feed. The selectivities were calculated from the conversion of propane to each product on a carbon basis. Blank experiments conducted with propane absent from the feed (TCM + O<sub>2</sub> + He) indicated that TCM undergoes oxidation while producing carbon oxides. Although the quantities of carbon oxides relative to propane present 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  $\pm$  5%. The reaction rates per unit of surface area were estimated as the rate ( $r = FC_0X_A/W$ , in which  $F$ ,  $C_0$ ,  $X_A$ , and  $W$  were flow rate, initial concentration of C<sub>3</sub>H<sub>8</sub>, conversion of C<sub>3</sub>H<sub>8</sub>, and catalyst weight) per the catalyst surface area. 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. <sup>51</sup>V MAS NMR was obtained with a Bruker AVANCE DSX300, with an external reference of 0.16 M NaVO<sub>3</sub> solution at -574.28 ppm at room temperature and a spinning rate of 30 kHz.

## Results and Discussion

**Catalytic Activities with and without TCM.** In order to compare the selectivities and to examine the effect of the introduction of TCM into the feedstream for the oxidative dehydrogenation of propane on three magnesium vanadates, we adjusted the reaction conditions to afford the similar conversion of propane in the absence of TCM (Fig. 1A). Under these conditions, the selectivities to propene on MgV<sub>2</sub>O<sub>6</sub> and Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> were essentially identical, while that to CO<sub>2</sub> on Mg<sub>3</sub>V<sub>2</sub>O<sub>8</sub> was rather greater than those on MgV<sub>2</sub>O<sub>6</sub> and Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub>. The reaction rate per unit of catalyst surface area on MgV<sub>2</sub>O<sub>6</sub> was ap-

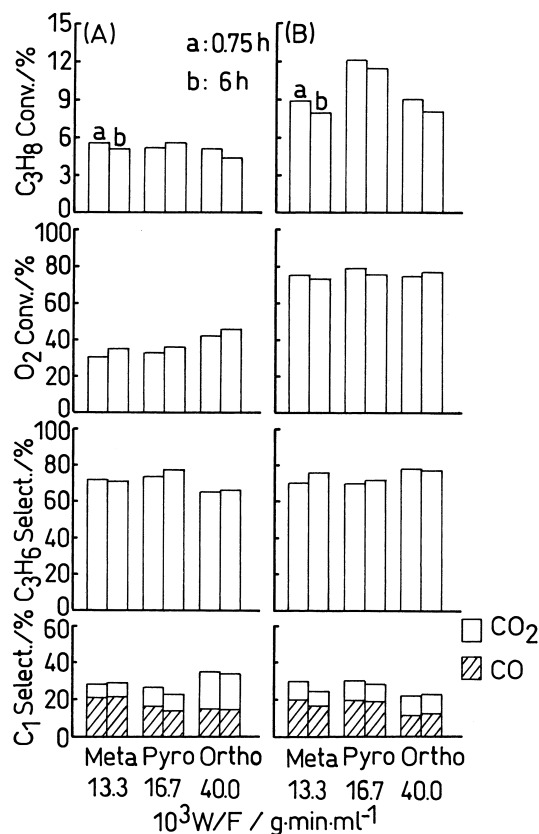


Fig. 1. The oxidative dehydrogenation of propane on MgV<sub>2</sub>O<sub>6</sub> (Meta-), Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> (Pyro-), and Mg<sub>3</sub>V<sub>2</sub>O<sub>8</sub> (Ortho-) in the absence (A) and presence (B) of TCM at 723 K. Reaction conditions: Wt = 0.4, 0.5 and 1.2 g for MgV<sub>2</sub>O<sub>6</sub>, Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub>, and Mg<sub>3</sub>V<sub>2</sub>O<sub>8</sub>, respectively.  $F = 30$  mL/min,  $P(\text{C}_3\text{H}_8) = 14.4$  kPa,  $P(\text{O}_2) = 4.1$  kPa,  $P(\text{TCM}) = 0$ , and 0.17 kPa.

proximately twice those on Mg<sub>2</sub>V<sub>2</sub>O<sub>7</sub> and Mg<sub>3</sub>V<sub>2</sub>O<sub>8</sub> (Table 1). Upon addition of TCM ( $P(\text{TCM}) = 0.17$  kPa, Fig. 1B), the conversion of propane (Fig. 1B) and the reaction rate (Table 1) were improved, while the selectivity to propene was essentially identical to that in the absence of TCM on three catalysts. Although deactivation with increasing time-on-stream was

Table 1. Reaction Rates per Unit of Catalysts Surface Area under Various Reaction Conditions ( $P(\text{C}_3\text{H}_8) = 14.4$  kPa,  $F = 30$  mL/min,  $T = 723$  K, and 0.75 h on-stream)

| Catal. | Wt/g | $P(\text{O}_2)$ /kPa | $P(\text{TCM})$ /kPa | Rate/mol min <sup>-1</sup> m <sup>-2</sup> |
|--------|------|----------------------|----------------------|--------------------------------------------|
| Meta   | 0.4  | 4.1                  | 0                    | 12.5 $\times 10^{-6}$                      |
| Meta   | 0.4  | 4.1                  | 0.17                 | 19.8 $\times 10^{-6}$                      |
| Meta   | 0.5  | 4.1                  | 0                    | 11.0 $\times 10^{-6}$                      |
| Meta   | 0.5  | 4.1                  | 0.17                 | 16.1 $\times 10^{-6}$                      |
| Meta   | 0.5  | 4.1                  | 0.34                 | 23.6 $\times 10^{-6}$                      |
| Meta   | 0.5  | 8.2                  | 0.51                 | 23.5 $\times 10^{-6}$                      |
| Pyro   | 0.5  | 4.1                  | 0                    | 5.3 $\times 10^{-6}$                       |
| Pyro   | 0.5  | 4.1                  | 0.17                 | 12.4 $\times 10^{-6}$                      |
| Pyro   | 0.5  | 4.1                  | 0.34                 | 14.5 $\times 10^{-6}$                      |
| Pyro   | 0.5  | 8.2                  | 0.34                 | 27.8 $\times 10^{-6}$                      |
| Ortho  | 1.2  | 4.1                  | 0                    | 6.9 $\times 10^{-6}$                       |
| Ortho  | 1.2  | 4.1                  | 0.17                 | 12.2 $\times 10^{-6}$                      |

sometimes observed in the oxidation of alkanes with TCM on some catalysts,<sup>24</sup> stable activities on three catalysts continued up to 6 h on-stream. It is of interest to note that such an improvement of the activities with TCM for the oxidative dehydrogenation of propane was not observed on  $V_2O_5$  catalyst. Since similar effects of the introduction of TCM were observed on magnesium meta-, pyro-, and ortho-vanadates, it may be suggested there are similar circumstances in those catalysts. It is of interest to note that  $^{51}V$  MAS NMR revealed that the signal at approximately  $-550$  ppm was similarly observed from three catalysts together with those at  $-613$  and  $-565$  ppm from  $MgV_2O_6$  and that at  $-606$  ppm from  $Mg_2V_2O_7$  (Fig. 2). Volta et al. observed  $^{51}V$  MAS NMR at a slower spinning rate of  $2.5$  kHz to detect the signals at  $-550$  and  $-615$  ppm for  $Mg_2V_2O_7$  and  $-550$  ppm for  $Mg_3V_2O_8$  while they could not obtain high-resolution NMR from  $MgV_2O_6$  due to a high quadrupolar interaction.<sup>6</sup> Therefore the vanadium species in three catalysts, for which a  $^{51}V$  NMR signal was observed at approximately  $-550$  ppm, indicate that the vanadium species possess similar electron densities. This may contribute to the enhancement of the activities in the presence of TCM. On the other hand, a  $^{51}V$  NMR signal at  $-609$  ppm was observed from  $V_2O_5$ , whose activities were not improved by the addition of TCM. The  $^{51}V$  NMR signal at  $-609$  ppm observed from  $V_2O_5$  indicates that vanadium species in the oxide are more anionic than those in three magnesium vanadates, from which the signal at approximately  $-550$  ppm was similarly observed. This may reveal that the nearest oxygen species around the vanadium in magnesium vanadates are more anionic than that in  $V_2O_5$ . Therefore it seems to be rea-

sonable that the activities on magnesium vanadates are greater than that on  $V_2O_5$  due to advantageous hydrogen abstraction from  $C_3H_8$  on the anionic oxygen species. It is evident that the anionic oxygen species contribute to the effects of TCM on magnesium vanadates, although it should be noted that various factors, partly described below, together with the anionic oxygen species, undoubtedly contribute to the advantageous effects of TCM. It is of interest to note that a few  $^{51}V$  NMR peaks are observed from  $MgV_2O_6$  and  $Mg_2V_2O_7$  while just one signal is observed from  $Mg_3V_2O_8$ , indicating that the effects of TCM may be evident from the synergism of several vanadate species in the former two magnesium vanadates. Since, for the three magnesium vanadates examined, the evident influence of the introduction of TCM on the activity is observed on  $Mg_2V_2O_7$  and the largest reaction rate in the absence of TCM is obtained on  $MgV_2O_6$ , the remainder of this report will be concerned with these two magnesium vanadates.

**Effects of the Partial Pressure of TCM.** The conversion of propane and the corresponding reaction rate increased with increasing  $P(TCM)$  on both  $MgV_2O_6$  and  $Mg_2V_2O_7$ , while the selectivity to propene was essentially insensitive to  $P(TCM)$  (Fig. 3 and Table 1). However, it should be noted that the increments of the conversion of propane and the reaction rate from  $P(TCM) = 0.17$  to  $0.34$  kPa particularly on  $Mg_2V_2O_7$  were rather small, probably because the conversion of  $O_2$  reached approximately 100% at  $P(TCM) = 0.34$  kPa. XRD patterns of  $MgV_2O_6$  employed in obtaining the results shown in Fig. 3A but at  $P(TCM) = 0$  and  $0.17$  kPa (Fig. 4A) were essentially identical to that of fresh  $MgV_2O_6$ , while that used at  $P(TCM) = 0.34$  kPa (Fig. 4B) showed that the catalyst

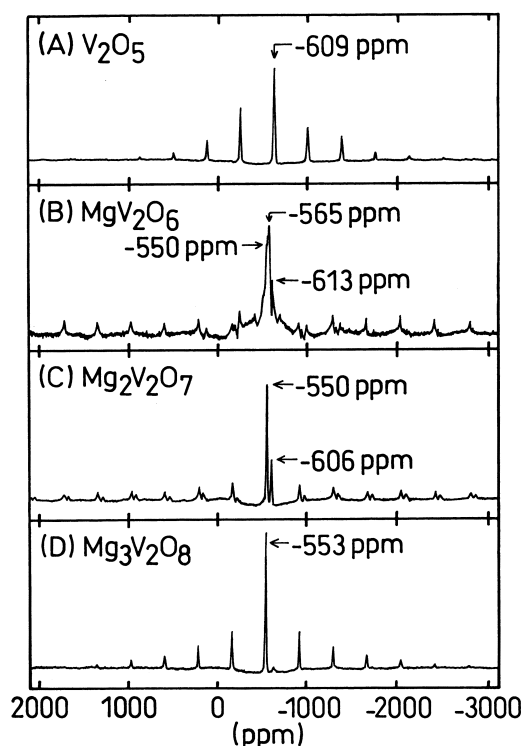


Fig. 2.  $^{51}V$  MAS NMR of  $V_2O_5$  (A),  $MgV_2O_6$  (B),  $Mg_2V_2O_7$  (C), and  $Mg_3V_2O_8$  (D).

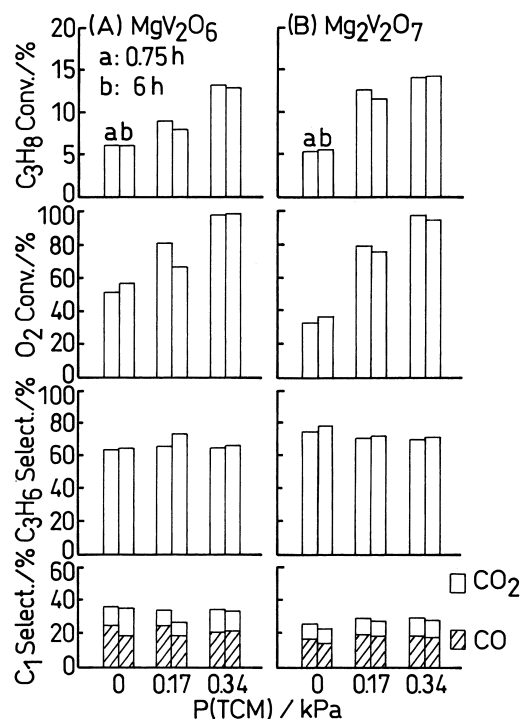


Fig. 3. Effects of  $P(TCM)$  on  $MgV_2O_6$  and  $Mg_2V_2O_7$  at 723 K. Reaction conditions: as in Fig. 1 except  $P(TCM)$  but  $Wt = 0.5$  g.

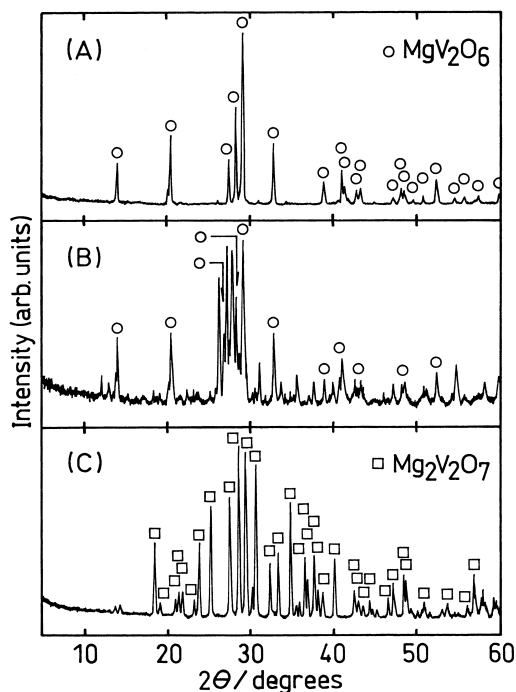


Fig. 4. XRD patterns of  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  previously employed in obtaining the results shown in Fig. 3 but after 6 h on-stream.

(A) and (B):  $\text{MgV}_2\text{O}_6$  used at  $P(\text{TCM}) = 0.17$  and  $0.34$  kPa, respectively.

(C):  $\text{Mg}_2\text{V}_2\text{O}_7$  used at  $P(\text{TCM}) = 0.34$  kPa.

changed, probably due to the employment of this catalyst under oxygen-limiting conditions. XRD patterns of  $\text{Mg}_2\text{V}_2\text{O}_7$  previously employed in obtaining the results shown in Fig. 3B

were insensitive to  $P(\text{TCM})$  and were in agreement with reference patterns for  $\text{Mg}_2\text{V}_2\text{O}_7$  (Fig. 4C). It is of interest to note that the structure of  $\text{Mg}_2\text{V}_2\text{O}_7$  used under the oxygen-limiting conditions at  $P(\text{TCM}) = 0.34$  kPa is retained even after oxidation, indicating that the effect of the introduction of TCM on the role of lattice oxygen in  $\text{Mg}_2\text{V}_2\text{O}_7$  may be different from that in  $\text{MgV}_2\text{O}_6$ .

#### Effects of the Introduction of TCM on Lattice Oxygen.

It has been suggested by various research groups that the ease of removal of lattice oxygen from magnesium vanadates explains the great activities for the oxidative dehydrogenation of propane.<sup>4,35,36</sup> In order to examine the role of lattice oxygen in  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  in the presence of TCM, the conversion of propane was observed in the absence of oxygen on both catalysts. In the absence and presence of TCM on  $\text{MgV}_2\text{O}_6$  (Figs. 5A and B, respectively), the conversion of propane decreased with increasing time-on-stream regardless of the addition of TCM, while the selectivities to the partial oxidation products,  $\text{C}_3\text{H}_6$  and  $\text{CO}$ , were evidently influenced by the introduction of TCM. It should be noted that the conversion of propane in the absence of TCM was greater than that in the presence of TCM. In the absence of TCM with  $\text{Mg}_2\text{V}_2\text{O}_7$  (Fig. 5C), the conversion of  $\text{C}_3\text{H}_8$  and the selectivity to  $\text{C}_3\text{H}_6$  decreased sharply and increased, respectively, with increasing time-on-stream. In contrast, the low conversion and the high selectivity to  $\text{C}_3\text{H}_6$  continued for 6 h on-stream in the presence of TCM on  $\text{Mg}_2\text{V}_2\text{O}_7$  (Fig. 5D). These results on both magnesium vanadates appear to indicate that lattice oxygens in both  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  directly contribute to the conversion of  $\text{C}_3\text{H}_8$ . Furthermore, the contribution of the lattice oxygen to the conversion of  $\text{C}_3\text{H}_8$  is controlled by the introduction of TCM. XRD patterns of  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  used without both oxygen and TCM showed that both catalysts were completely

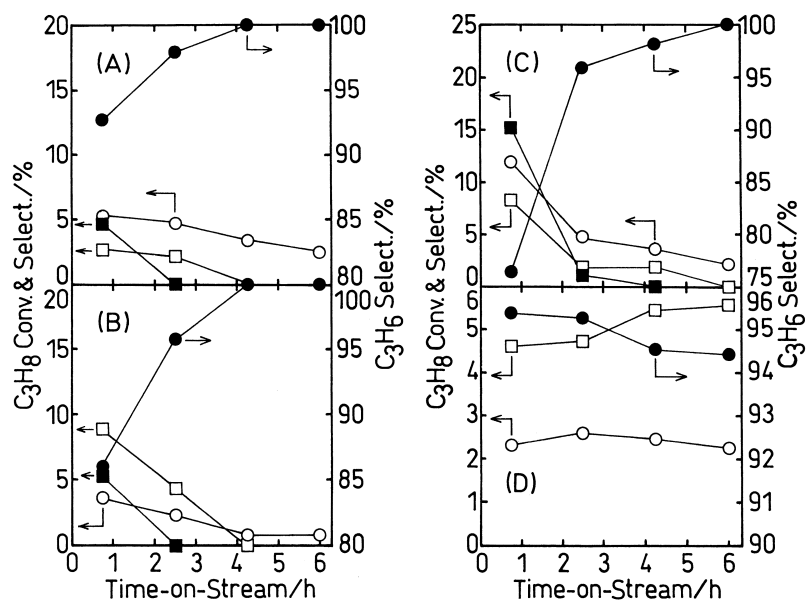


Fig. 5. Effects of TCM on the conversion of  $\text{C}_3\text{H}_8$  in the absence of  $\text{O}_2$  on  $\text{MgV}_2\text{O}_6$  (A and B) and  $\text{Mg}_2\text{V}_2\text{O}_7$  (C and D) at 723 K.

Reaction conditions:  $\text{Wt} = 0.5$  g,  $P(\text{C}_3\text{H}_8) = 14.4$  kPa,  $P(\text{O}_2) = 0$  kPa, and  $P(\text{TCM}) = 0$  for (A) and (C) and  $0.17$  kPa for (B) and (D).

Symbols; Open circle =  $\text{C}_3\text{H}_8$  conversion. Closed circle =  $\text{C}_3\text{H}_6$  selectivity.

Open square =  $\text{CO}$  selectivity. Closed square =  $\text{CO}_2$  selectivity.

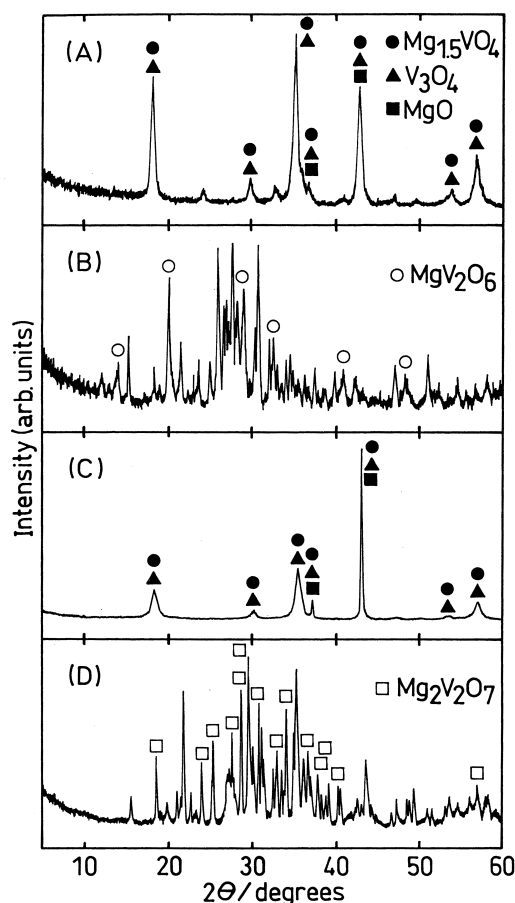


Fig. 6. XRD patterns of  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  previously employed in obtaining the results shown in Fig. 5 but after 6 h on-stream.

(A) and (B):  $\text{MgV}_2\text{O}_6$  used at  $P(\text{TCM}) = 0$  and  $0.17$  kPa, respectively.

(C) and (D):  $\text{Mg}_2\text{V}_2\text{O}_7$  used at  $P(\text{TCM}) = 0$  and  $0.17$  kPa, respectively.

converted to other phases (Figs. 6A and C, respectively), while  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  still remained in both catalysts after propane conversion in the presence of TCM (Figs. 6B and D, respectively). XRD patterns of Figs. 6A and C showed that these catalysts after propane conversion without TCM consisted of  $\text{Mg}_{1.5}\text{VO}_4$  (JCPDS 19-0778),  $\text{MgO}$  (JCPDS 34-0615), and  $\text{V}_3\text{O}_4$  (JCPDS 45-0946). Oxygen content calculated from  $\text{Mg}_{1.5}\text{VO}_4$ ,  $\text{MgO}$ , and  $\text{V}_3\text{O}_4$  are 42.3, 39.7, and 29.5 wt%, respectively, and such values are evidently smaller than those from  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  (43.2 and 42.7 wt%, respectively). Therefore lattice oxygen in both  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  is removed from the catalyst in the absence of TCM, while it remains in the structure in the presence of TCM. XPS analyses of  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  employed in propane conversion in the presence of TCM revealed that no chlorinated species were formed on the surface. It seems rather strange that the loss of lattice oxygen from both magnesium vanadates is reduced by TCM while no TCM residue appears in any form on the surface of the catalysts. It is possible, of course, that a trace amount of chlorinated species exists on the surface, which cannot be detected by XPS.

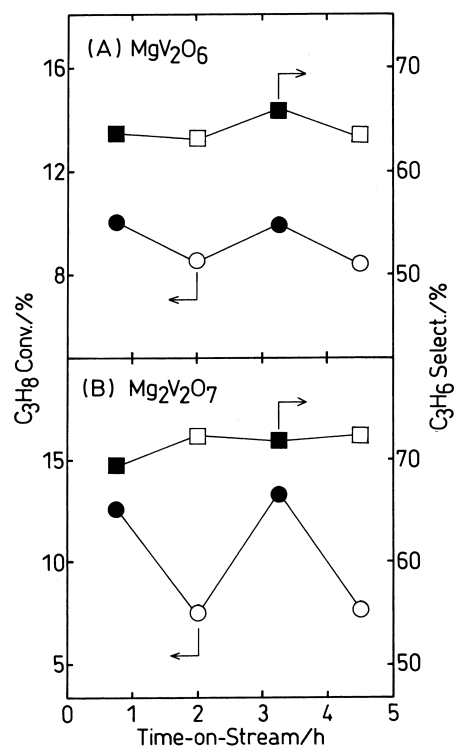


Fig. 7. Effects of the chlorinated species on the surface of the catalysts and/or in gas-phase at 723 K.

Reaction conditions:  $\text{Wt} = 0.5\text{ g}$ ,  $F = 30\text{ mL/min}$ ,  $P(\text{C}_3\text{H}_8) = 14.4\text{ kPa}$ ,  $P(\text{O}_2) = 4.1\text{ kPa}$ , and  $P(\text{TCM}) = 0.17\text{ kPa}$ .

Symbols; Circle =  $\text{C}_3\text{H}_8$  conversion.

Square =  $\text{C}_3\text{H}_6$  selectivity.

Closed symbols: Data with the chlorinated species on the surface of the catalysts and in gas-phase.

Open symbols: Data with the chlorinated species on the surface of the catalysts.

**Pretreatment with TCM.** In order to separate the effects of gaseous TCM from those of chlorinated species on the surface of the catalysts, pretreatment effects of  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$  with TCM were examined (Fig. 7). In Fig. 7, the feedstream from 0 to 0.75 and from 2.0 to 3.25 h on-stream contained  $\text{C}_3\text{H}_8$  (14.4 kPa),  $\text{O}_2$  (4.1 kPa) and TCM (0.17 kPa) diluted with He. In contrast,  $\text{C}_3\text{H}_8$  (14.4 kPa) and  $\text{O}_2$  (4.1 kPa) diluted with He were contained into the feedstream from 0.75 to 2.0 and from 3.25 to 4.5 h on-stream. Therefore closed symbols show data both with the surface chlorinated species and gaseous TCM, while open symbols show data just with the surface chlorinated species on the catalysts. On  $\text{MgV}_2\text{O}_6$  (Fig. 7A), the conversions of  $\text{C}_3\text{H}_8$  in the presence of TCM were always greater than those in the absence of TCM. However the effect of the presence of TCM on the selectivity to  $\text{C}_3\text{H}_6$  was rather small. On  $\text{Mg}_2\text{V}_2\text{O}_7$  (Fig. 7B), the conversion of  $\text{C}_3\text{H}_8$  was similarly influenced by TCM, as observed on  $\text{MgV}_2\text{O}_6$ , while the selectivity to  $\text{C}_3\text{H}_6$  was rather insensitive to the presence or absence of TCM. This may indicate that the presence of gaseous TCM, which controls the removability of lattice oxygen, is important for the enhancement of the catalytic activities. The contribution of the surface chlorinated species to the enhancement by TCM should not be overestimated in the present systems.

In conclusion, TCM controls the removability of lattice oxygen in  $\text{MgV}_2\text{O}_6$  and  $\text{Mg}_2\text{V}_2\text{O}_7$ , that is, redox behaviors of these catalysts. This results in the enhancement of the activities of both catalysts for the oxidative dehydrogenation of propane. It is generally accepted that formation of surface chlorinated species contributes to the enhancement of the activities for the oxidation of alkanes in the presence of TCM. However the present results reveal that control of removability of lattice oxygen in the catalysts with TCM seems to be important for activity improvement.

This work was partly funded by a Grant-in-Aid for Scientific Research No.13126215 to HH from the Ministry of Education, Science, Sports and Culture, to which our thanks are due.

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