Redox behaviors of magnesium vanadate catalysts during the oxidative dehydrogenation of propane

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In order to examine the mobility of lattice oxygen in magnesium vanadates, these catalysts were employed for the oxidative dehydrogenation of propane in the absence of oxygen for 2.25 h, followed by the addition of gaseous oxygen into the feedstream. Depending on the degree of the abstraction of lattice oxygen from these catalysts during the oxidation in the absence of the gaseous oxidant, oxygen in the effluent was detected at approximately 1.4 and 9 min with $Mg_3V_2O_8$ and $Mg_2V_2O_7$ respectively, after the addition of gaseous oxygen under the present reaction conditions. However, no oxygen was detected with MgV_2O_6 even after 18.5 min from the addition of gaseous oxygen. ^{51}V MAS NMR was also employed for the observation of redox behaviors of vanadium species in these catalysts during the reaction.

KEY WORDS: propane oxidation; lattice oxygen; redox; ^{51}V MAS NMR.

1. Introduction

Magnesium vanadates (MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$) have been known as efficient catalysts for the oxidative dehydrogenation of propane to propylene [1–6]. It has been suggested that the V = O and/or V–O–V bonds participate in the activation of C_3H_8 [7,8] and the ease of abstraction of these lattice oxygens from magnesium vanadates explains the remarkable activities of the oxidative dehydrogenation [3,9,10]. Indeed, in our previous papers [11,12], it was reported that the oxidative dehydrogenation of propane to propylene on these magnesium vanadates proceeded with the direct contribution of lattice oxygen and the mobility of the lattice oxygen was related to the activities. However, unfortunately, we could obtain information on the abstraction of lattice oxygen from these catalysts [11,12] but could not obtain information on the redox behaviors of the catalysts. In the present paper, abstraction and incorporation of lattice and gaseous oxygen from and into these magnesium vanadate catalysts, respectively, are examined with a quadrupole mass spectrometer for the oxidation of propane on the catalysts in the absence of oxygen, followed by the addition of gaseous oxygen into the feedstream. Furthermore, high-resolution solid-state ^{51}V MAS NMR at a high spinning rate of 25 kHz is employed for the analysis of redox behaviors of vanadium species in these catalysts during the oxidation.

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2. Experimental

Magnesium meta-, pyro-, and ortho-vanadates (MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$, respectively) were prepared from $Mg(OH)_2$ and NH_4VO_3 according to the procedure as previously reported [11,12], except the calcination conditions. The calcination conditions were as follows: 773 K for 6 h and 873 K for 4 h to MgV_2O_6; 823 K for 6 h and 973 K for 17 h to $Mg_2V_2O_7$; 823 K for 6 h, 913 K for 49 h, and 1023 K for 15 h to $Mg_3V_2O_8$. As shown in the following text, these improvements resulted in the enhancement of the activities. X-ray diffraction (XRD) patterns of these magnesium vanadates prepared in the present study (figure 1(A), (B), and (C)) matched MgV_2O_6 (JCPDS 45-1050), $Mg_2V_2O_7$ (JCPDS 31-0816), and $Mg_3V_2O_8$ (JCPDS 37-0351), respectively, and were essentially identical to those previously reported [2,11,12]. Particles of 0.85–1.70 mm were employed as catalysts. Surface area and apparent density of MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$ were 3.0 m^2/g and 1.15 g/cm^3, 3.2 m^2/g and 0.97 g/cm^3, and 3.4 m^2/g and 0.97 g/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, the procedure of the catalytic experiments and the calculation methods of the conversion, and the selectivity and turnover rates have been described in [11,12]. No homogeneous oxidation of propane was observed at 723 K under the present conditions. The carbon mass balances were $100 \pm 5\%$. The reaction was monitored with an onstream Shimadzu GC-8APT gas chromatograph with a TC detector and integrator (Shimadzu C-R6A). Two columns, one

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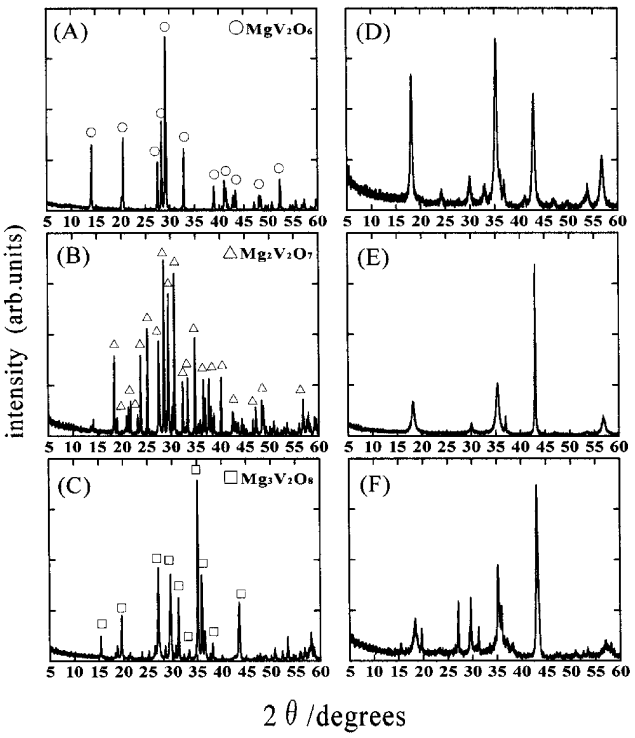

Figure 1. XRD patterns of magnesium vanadates before and after the conversion of propane in the absence of oxygen in the feedstream. (A), (B), and (C): Fresh MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$ respectively. (D), (E), and (F): MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$ previously used for the conversion respectively.

Porapak Q (6 m × 3 mm) and the other Molecular Sieve 5A (0.2 m × 3 mm), were employed in the analyses. For the continuous analyses of the reaction, an effluent gas from the reactor was introduced into the quadrupole mass spectrometer (Pfeiffer OmniStar-s). Powder XRD patterns were recorded with a Rigaku RINT 2500 X, using monochromatized Cu Kα radiation. ^{51}V MAS NMR was obtained with a Bruker AVANCE DSX300, with an external reference of 0.16 M $NaVO_3$ solution at −574.28 ppm at room temperature and a spinning rate of 25 kHz. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) used monochromatized Mg Kα radiation. The binding energies were corrected using 285 eV for C 1s as an internal standard.

3. Results and discussion

Table 1 shows the catalytic activities for the oxidative dehydrogenation of propane at 1.75 h on-stream on MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$. The stable activities were observed for 6 h on-stream, and both the conversion of C_3H_8, the yield of C_3H_6, and the turnover rate using the surface area followed the order $Mg_2V_2O_7 > MgV_2O_6 > Mg_3V_2O_8$, which was identical to the order of the selectivity to C_3H_6 at isoconversion of C_3H_8 [2,8]. These results essentially supported those reported by Sam *et al.* [2], who suggested that the highest activities of $Mg_2V_2O_7$ were related to its abilities to stabilize V^{4+} ions associated with oxygen vacancies [2,8]. In order to examine the contribution of V^{4+} species, which were formed through the reduction of V^{5+} species in these catalysts, the conversion of propane in the absence of oxygen was observed on magnesium vanadates (figure 2). Results shown in figure 1 were obtained under the same conditions employed in obtaining the results shown in table 1 while oxygen was not introduced into the feedstream. The selectivities to C_3H_6 and CO_2 increased and decreased on three magnesium vanadates with increasing time on-stream when suddenly changed from 0.75 to 1.75 h on MgV_2O_6 (figure 2(A)), gradually changed from 1.75 to 4.5 h on $Mg_2V_2O_7$ (figure 2(B)), and monotonously changed by 6 h on-stream on $Mg_3V_2O_8$ (figure 2(C)). These results show that lattice oxygen, which is supplied as an oxidant for the conversion of propane, is abstracted from the corresponding catalysts and the ability of the abstraction depends on these catalysts. The signals obtained from solid-state ^{51}V MAS NMR showed that the intensity of the signals due to MgV_2O_6 and $Mg_2V_2O_7$ recovered after the conversion of propane in the absence of oxygen at 6 h on-stream revealed to be rather weak (figure 3(D) and (E), respectively) while the NMR signals due to fresh catalysts were detected with sufficient intensity as observed in our previous study (figure 3(A) and (B) respectively), [12]. However, $Mg_3V_2O_8$ afforded evident ^{51}V MAS NMR signals before and even after the conversion of propane in the absence of O_2 (figure 3(C) and (F), respectively). It is generally known that diamagnetic V^{5+} species affords evident NMR signal while paramagnetic V^{4+} affords a

Table 1
Catalytic activities on MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$

Catalyst	Conversion (%)		Selectivity (%)			Yield (%) C_3H_6	Turnover rate (mol min^{-1} m^{-2}
	C_3H_8	O_2	C_3H_8	CO	CO_2		
MgV_2O_6	13.1	78	46.5	29.5	24.0	6.1	15.6×10^{-6}
$Mg_2V_2O_7$	14.9	89	50.0	29.7	20.3	7.5	16.7×10^{-6}
$Mg_3V_2O_8$	3.9	19	58.3	16.9	24.8	2.2	4.1×10^{-6}

Note: Reaction conditions: $P(C_3H_8) = 14.4$ kPa; $P(O_2) = 4.1$ kPa; F = 30 mL/min; W = 0.5 g, and T = 723 K. Data were collected at 1.75 h on-stream.

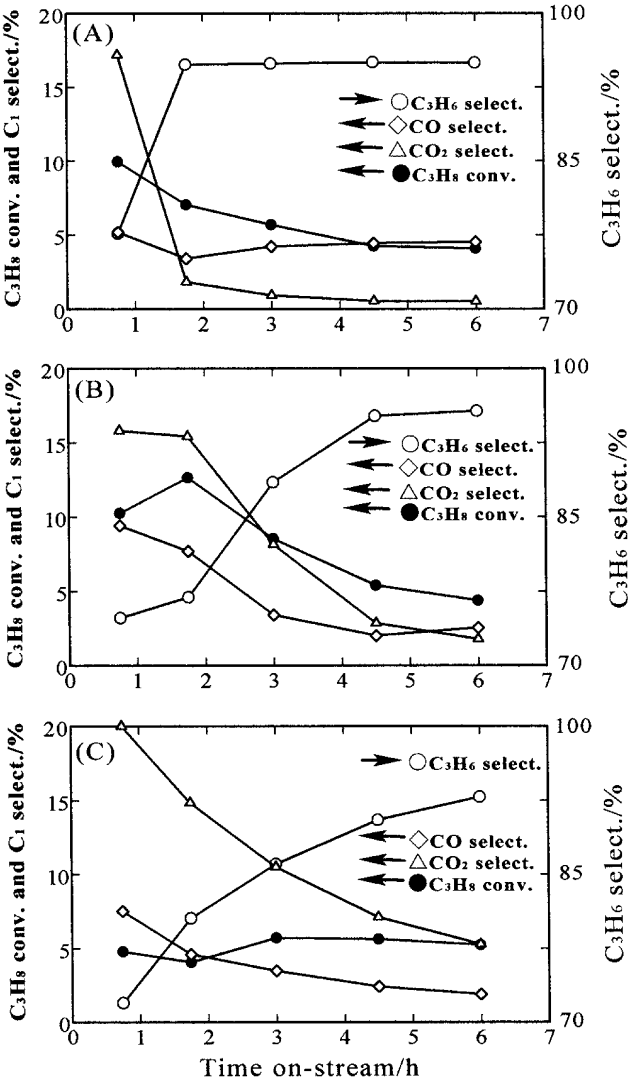

Figure 2. The conversion of propane in the absence of oxygen in the feedstream on MgV_2O_6 (A), $Mg_2V_2O_7$ (B), and $Mg_3V_2O_8$ (C). Reaction conditions: same as those described in table 1 but $P(O_2) = 0$ kPa.

broad and weak signal. Therefore, these NMR results reveal that V^{5+} in MgV_2O_6 and $Mg_2V_2O_7$ can be easily reduced to V^{4+} together with ease abstraction of lattice oxygen as shown in figure 3(D) and (E), while V^{5+} species in $Mg_3V_2O_8$ cannot be easily reduced to V^{4+} species (figure 3(F)). It should be noted that ^{51}V MAS NMR of these fresh magnesium vanadates were essentially identical to those previously reported [12]. In order to obtain further evidence on the reduction of V^{5+} species, XPS was employed for the analyses of the catalysts before and after the conversion of propane without oxygen (table 2). XPS signals due to V $2p_{3/2}$ from fresh MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$ appeared at 517.5 eV, 517.8 eV, and 517.5 eV, while those binding energies after the conversion of propane without oxygen were unexceptionally lowering to 517.1 eV, 517.3 eV, and 517.2 eV. Since a similar shift of the binding energy due to Mg 2s and O 1s was not observed as described in table 2, the shifts of the V $2p_{3/2}$ signal may further afford evidence on the reduction of V^{5+} species after the conversion of propane in the absence of oxygen. XRD patterns of these catalysts, recovered after obtaining the results shown in figure 2, showed that the original structure of these three catalysts could not be kept under the conditions (figure 1(D), (E), and (F)). It is evident that the reduction of V^{5+} to V^{4+} in these magnesium vanadates results in the formation of oxygen vacancy due to the abstraction of lattice oxygen in these catalysts. On the basis of redox of these catalysts, reoxidation of these reduced catalysts should be dissimilar. The quadrupole mass spectrometer was employed for the analyses of the oxygen response in the effluent gas from those catalysts that were employed for the conversion of propane in the absence of oxygen for 2.25 h onstream, when oxygen at 4.1 kPa was introduced into the feedstream. In figure 4(A), (B), and (C), the oxygen responses after the introduction of oxygen on MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$ respectively, were described, and $t = 0$ in these figures corresponded to the above-described 2.25 h onstream. As shown in these figures, oxygen was detected at approximately 1.4 and 9 min after the addition of oxygen on $Mg_3V_2O_8$ and $Mg_2V_2O_7$ while oxygen could not be detected at 18.5 min on MgV_2O_6. These results revealed that the number of oxygen vacancy formed during the conversion of propane in the absence of oxygen followed the order $MgV_2O_6 > Mg_2V_2O_7 > Mg_3V_2O_8$. On the basis of these results obtained in the present study, redox between V^{5+} and V^{4+} together with the oxidation and formation of oxygen vacancy in these catalysts, respectively, followed the order $MgV_2O_6 > Mg_2V_2O_7 > Mg_3V_2O_8$. Therefore, as suggested by Sam *et al.* [2,8], the evident contribution of V^{4+} species, which was observed on MgV_2O_6 and $Mg_2V_2O_7$, should be needed for the activation of propane. However, it should be noted that extensive reduction to V^{4+} species resulted in the decrease of the activities as observed on MgV_2O_6. Finally, the catalysts that were employed for obtaining the results shown in figure 2, were reoxidized with oxygen flow (30 mL/min) at 723 K for 2 h and these

Table 2
Binding energies of each element in fresh and used[a] catalysts

Catalyst	Fresh or used[a]	Binding energy (eV)		
		Mg 2s	V $2p_{3/2}$	O 1s
MgV_2O_6	Fresh	88.8	517.5	530.3
	Used	88.6	517.1	530.4
$Mg_2V_2O_7$	Fresh	88.8	517.8	530.6
	Used	88.9	517.3	530.7
$Mg_3V_2O_8$	Fresh	88.6	517.5	530.3
	Used	88.6	517.2	530.7

[a]Previously used for the conversion of propane in the absence of oxygen.

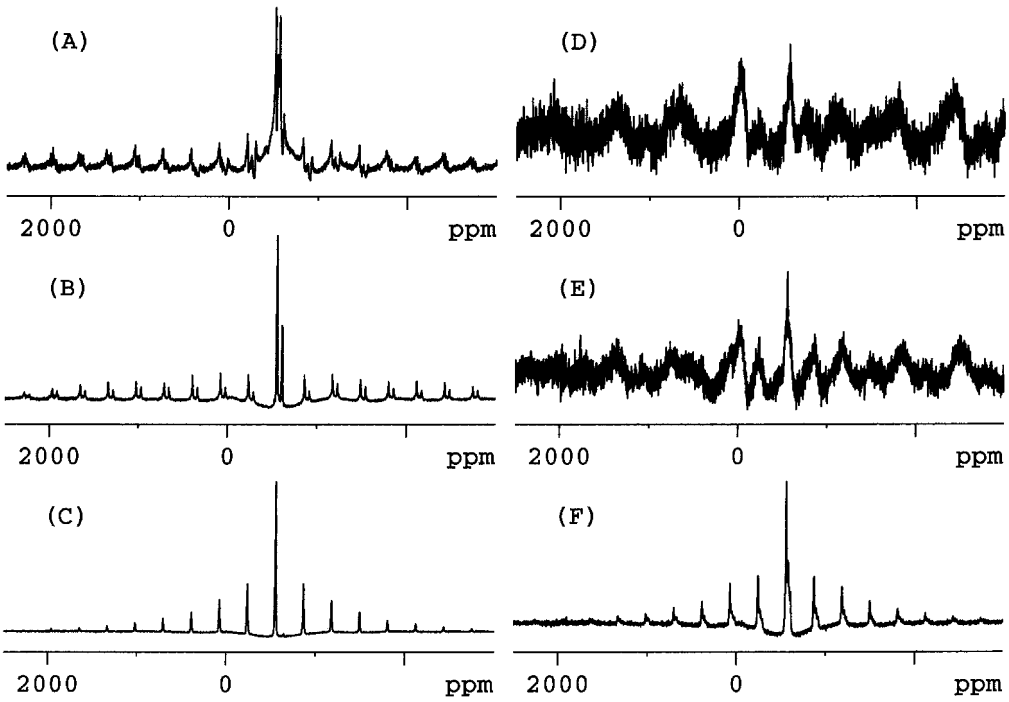

Figure 3. ^{51}V MAS NMR of magnesium vanadates before and after the conversion of propane in the absence of oxygen in the feedstream. (A), (B), and (C): Fresh MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$, respectively. (D), (E), and (F): MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$, previously used for the conversion respectively.

catalysts were analyzed with XRD. Complete and partial regeneration of $Mg_3V_2O_8$ and MgV_2O_6, respectively was observed with XRD (figure 5(C) and (A)), while a dissimilar phase to the corresponding fresh catalyst was detected (figure 5(B)) after the reoxidation

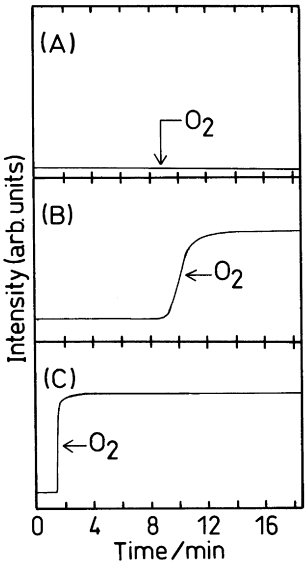

Figure 4. Oxygen response in the effluent gas from MgV_2O_6 (A), $Mg_2V_2O_7$ (B), and $Mg_3V_2O_8$ (C). Reaction conditions: Before and after $t = 0$ min, the catalysts were exposed with the reactant gas under the same conditions shown in table 1 but $P(O_2) = 0$ and 4.1 kPa, respectively.

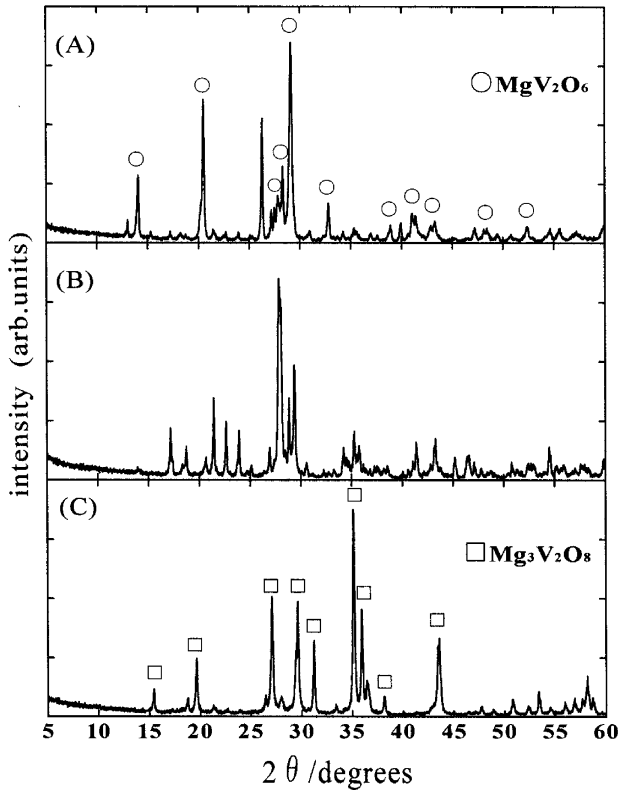

Figure 5. XRD patterns of MgV_2O_6 (A), $Mg_2V_2O_7$ (B), and $Mg_3V_2O_8$ (C), which were previously employed for obtaining the results shown in figure 2, followed by the reoxidation with oxygen flow (30 mL/min) for 2 h at 723 K.

of $M_2V_2O_7$, as reported in our previous paper [11]. Therefore, the combination of the most favorable redox behaviors of $Mg_2V_2O_7$ and its keeping nature of the original structure during the oxidative dehydrogenation may result in the great activities of the catalyst.

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