Effects of the enhancement of the abstraction of lattice oxygen from magnesium vanadates incorporated with copper(II) cations on the oxidative dehydrogenation of propane

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Abstract

The influences of the incorporation of copper(II) cations into MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$ on the catalytic activities and the mobility of lattice oxygen in those catalysts have been investigated to observe the contribution of lattice oxygen in magnesium vanadates to the oxidative dehydrogenation of propane. The incorporation of Cu^{2+} into those magnesium vanadates resulted in the decrease of the selectivity to propylene, while the evident enhancement of the reaction rate per unit of the surface area was observed. In order to examine the mobility of lattice oxygen in those Cu^{2+} incorporated catalysts, those magnesium vanadates incorporated with Cu^{2+} at the atomic ratios of $Cu/[Mg + Cu] = 0$ and 0.10 were employed for the oxidative dehydrogenation in the absence of oxygen for 2.25 h, followed by the addition of gaseous oxygen into the feed-stream. After the addition of gaseous oxygen under the present conditions, oxygen in the effluent gas was detected at approximately 36, 7 and 2 min with MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$ while no oxygen was detected from those catalysts incorporated with Cu^{2+} even 60 min after the addition of gaseous oxygen. Therefore, the incorporation of Cu^{2+} into those magnesium vanadates results in the enhancement of the abstraction of lattice oxygen from the catalysts. ^{51}V MAS NMR and XPS revealed that redox of vanadium and copper species in those catalysts contributed to the abstraction of the lattice oxygen from the corresponding catalysts.
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1. Introduction

It is generally accepted that magnesium meta-, pyro-, and ortho-vanadates (MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$, respectively) are active catalysts for the oxidative dehydrogenation of propane to propylene [1–4]. It has been suggested that the V=O and/or V−O−V bonds in those magnesium vanadates participate in the activation of propane [5,6]. Particularly, it should be noted that the ease of removal of lattice oxygen from those binary oxide catalysts explains the great activities for the oxidative dehydrogenation [7,8]. Based on

the structure of those magnesium vanadates [2], lattice oxygen in $Mg_2V_2O_7$ and $Mg_3V_2O_8$ is shared with both the VO_4 tetrahedron and the MgO_6 octahedron, while part of the lattice oxygen in MgV_2O_6 is shared with only VO_6 octahedron. It should be noted that the lattice oxygen shared with V species is more easily abstracted than that with Mg species since V^{5+} is more reducible than Mg^{2+}. As expected from those structures, it has been found out that the removal of lattice oxygen from MgV_2O_6 is more favorable than that from $Mg_2V_2O_7$ and $Mg_3V_2O_8$ [9]. Furthermore, it has been also reported that the partial substitution of Mg^{2+} with Ca^{2+} in those magnesium vanadates results in little effects on the removability in meta-vanadates while evident those in both pyro- and ortho-vanadates [10]. It should be noted that the ionic radius of Ca^{2+}

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Table 1
Calcination conditions for the preparation of magnesium vanadates incorporated with Cu^{2+}

Catalyst	Calcination temperature			
	First	Second	Third	Fourth
MgV_2O_6	773 K for 6 h	873 K for 12 h	–	–
$Mg_{0.95}Cu_{0.05}V_2O_6$	773 K for 6 h	873 K for 6 h	–	–
$Mg_{0.90}Cu_{0.10}V_2O_6$	773 K for 6 h	873 K for 6 h	–	–
$Mg_2V_2O_7$	823 K for 6 h	973 K for 17 h	–	–
$Mg_{1.90}Cu_{0.10}V_2O_7$	823 K for 6 h	873 K for 6 h	923 K for 12 h	–
$Mg_{1.80}Cu_{0.20}V_2O_7$	823 K for 6 h	873 K for 6 h	923 K for 12 h	–
$Mg_3V_2O_8$	823 K for 6 h	898 K for 49 h	1023 K for 15 h	1073 K for 6 h
$Mg_{2.85}Cu_{0.15}V_2O_8$	823 K for 6 h	898 K for 26 h	973 K for 6 h	1023 K for 6 h
$Mg_{2.70}Cu_{0.30}V_2O_8$	823 K for 6 h	898 K for 26 h	973 K for 6 h	1023 K for 6 h

(1.14 Å) is different from that of Mg^{2+} (0.86 Å), resulting in the difficulty of the substitution of Mg^{2+} with Ca^{2+} in those magnesium vanadates.

In the present study, we prepared Cu^{2+} incorporated MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$ as the catalysts for the oxidative dehydrogenation of propane. Ionic radius of Cu^{2+} (0.87 Å) is essentially identical to that of Mg^{2+} that may be favorable for the substitution of Mg^{2+} in those magnesium vanadates with Cu^{2+}. Furthermore, Cu^{2+} is more reducible than Mg^{2+}, probably resulting in the dissimilar redox behaviors to those observed on Ca^{2+}-incorporated catalysts. Those Cu^{2+} incorporated catalysts were employed for the examination of the effects of the incorporation of Cu^{2+} on the mobility of the lattice oxygen together with the activities. The catalytic activities of $Cu_2V_2O_7$, which is produced from the complete substitution of Mg^{2+} in $Mg_2V_2O_7$ with Cu^{2+}, for the oxidative dehydrogenation of butane [11] and propane [12] have been already reported. For the oxidative dehydrogenation of butane, the activities on $Cu_2V_2O_7$ at 573 and 723 K were higher and lower, respectively, than those on $Mg_2V_2O_7$ [11]. The influences of the divalent cation on the activities of lattice oxygen were suggested for the oxidation on $Cu_2V_2O_7$ [11]. The oxidative dehydrogenation of propane on $Cu_2V_2O_7$ was a little bit more selective than that on $Mg_2V_2O_7$ while no comments on the role of lattice oxygen were described in the paper [12]. The present paper will be particularly concerned with the influences of the incorporation of Cu^{2+} into magnesium vanadates on the mobility of lattice oxygen.

2. Experimental

Magnesium meta-, pyro-, and ortho-vanadates incorporated with Cu^{2+}, which are denoted as $Mg_{1-x}Cu_xV_2O_6$, $Mg_{2-x}Cu_xV_2O_7$ and $Mg_{3-x}Cu_xV_2O_8$, were prepared from $Mg(OH)_2$ (Wako Pure Chemicals, Osaka), $Cu(OH)_2$ (Wako) and NH_4VO_3 (Wako). The preparation procedure was essentially identical to that reported by Sam et al. for those parent magnesium vanadates [2,9,10]. Fine powders of $Mg(OH)_2$ and $Cu(OH)_2$ were added to 1% ammonia solution of NH_4VO_3, in which the amounts of those reagents were ad-

justed to the atomic ratio of the corresponding catalysts. The suspension was evaporated to dryness while being stirred and then finally dried at 383 K. The resulting solid was ground into a fine powder and calcined at higher temperatures for different duration. Based on the examination with XRD (Rigaku RINT 2500X using monochromatized Cu Kα radiation), the calcination conditions described in Table 1 were employed. Each solid was finely ground between calcination. Particles of 0.85–1.70 mm were employed in a fixed-bed continuous flow reactor operated at atmospheric pressure. The reactor consisted of a quartz tube, 9 mm i.d. and 35 mm length, attached at each end to a 4 mm i.d. quartz tube to produce a total length of 25 cm. The catalyst was held in place in the enlarged portion of the reactor by two quartz wool plugs. In all experiments, the catalyst (0.5 g) was heated to the reaction temperature (723 K) while maintaining a continuous flow of helium and was held at this temperature under a 25 mL/min flow of oxygen for 1 h. The reaction conditions were as follows unless otherwise stated: $P(C_3H_8) = 14.4$ kPa, $P(O_2) = 4.1$ or 0 kPa and $F = 30$ mL/min. No homogeneous oxidation of propane was observed 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 × 3 mm) and the other Molecular Sieve 5A (0.2 m × 3 mm), were employed in the analyses. The conversion of propane was calculated from the products and from the propane introduced into the feed-stream. The selectivities were calculated from the conversion of propane to each product on a carbon basis. The carbon mass balances were $100 \pm 5\%$. The reaction rates per unit of surface area were estimated as the rate ($r = FC_0X/W$, in which F, C_0, X and W were flow rate, initial concentration of C_3H_8, conversion of C_3H_8 and catalyst weight, respectively) per catalyst surface area [13]. For the continuous analyses of the reaction, an effluent gas from the reactor was introduced into the quadrupole mass spectrometer (Pfeiffer-Hakuto OmniStar-s). ^{51}V MAS NMR was obtained from a Bruker AVANCE DSX300, with an external reference of 0.16 M $NaVO_3$ solution at −574 ppm at room temperature and a spinning rate of 25 kHz. X-ray photoelectron spectroscopy (XPS, Shimadzu ESCA-1000AX) for the analysis of Cu species used Al Kα radiation [14,15]. The surface

areas were calculated from adsorption isotherms obtained with a nitrogen adsorption apparatus (Belsorp18 Plus, BEL, Japan). The apparent densities of the catalysts (particles of 0.85–1.70 mm) were determined by the dry mass per apparent volume.

3. Results and discussion

3.1. Preparation of magnesium vanadates incorporated with Cu^{2+} and the catalytic activities for the oxidation of propane

It has been already reported that Ca^{2+} can be incorporated by 10% (atomic ratio of $100 \times Ca/[Ca + Mg]$) into MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$. Since ionic radius of Cu^{2+} is smaller than that of Ca^{2+} while similar to that of Mg^{2+}, it is expected that the incorporation with Cu^{2+} into those magnesium vanadates is more favorable than that with Ca^{2+}. Therefore, $Mg_{1-x}Cu_xV_2O_6$, $Mg_{2-x}Cu_xV_2O_7$ and $Mg_{3-x}Cu_xV_2O_8$, in which, the atomic ratios of $100 \times Cu/[Cu + Mg]$ were 0, 5 and 10%, were prepared as the catalysts in the present study. XRD patterns of $Mg_{1-x}Cu_xV_2O_6$ and $Mg_{2-x}Cu_xV_2O_7$, in which the atomic ratios were 0, 5 and 10%, were essentially identical to those of MgV_2O_6 (JCPDS 45-1050) and $Mg_2V_2O_7$ (JCPDS 31-0816), respectively (not shown). However, XRD patterns of $Mg_3V_2O_8$ (JCPDS 37-0351), $Mg_{2.85}CuO_{0.15}V_2O_8$ and $Mg_{2.70}Cu_{0.30}V_2O_8$ reveal that the intensity of two peaks at $2\theta = 26.3°$ and $28.0°$ was enhanced proportionally with increasing the amount of Cu^{2+} incorporated (Fig. 1(A), (B) and (C), respectively). Those peaks were not matched with the reference data for Cu (JCPDS 4-0836), Cu_2O (JCPDS 5-0667) and CuO (JCPDS 45-0937). Therefore, those two peaks were detected probably due to the incorporation of Cu^{2+} into $Mg_3V_2O_8$ but not phase separation of other Cu compounds. The apparent density and the surface area are summarized in Table 2. It is evident that those are not correlated with the Cu^{2+}-contents in those catalysts.

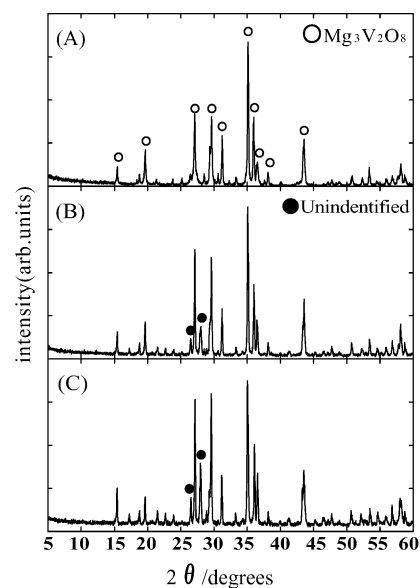Fig. 1. XRD patterns of $Mg_3V_2O_8$ (A), $Mg_{2.85}Cu0_{0.15}V_2O_8$ (B) and $Mg_{2.70}Cu_{0.30}V_2O_8$ (C).

Since the stable catalytic activities for the oxidative dehydrogenation of propane on those catalysts were observed by 6 h on-stream, the conversion, the selectivity and the reaction rate per unit surface area at 3 h on-stream were shown in Table 2. As reported by Sam et al. [2], who suggested that great activities on $Mg_2V_2O_7$ were related to its activities to stabilize V^{4+} associated with lattice oxygen, the conversion of propane and the reaction rate followed the order $Mg_2V_2O_7 > MgV_2O_6 > Mg_3V_2O_8$. Upon addition of Cu^{2+} into those magnesium vanadates, the selectivity to C_3H_6 and the reaction rate were decreased and increased, respectively, indicating that the formation of CO_x was enhanced by the introduction of Cu^{2+}. It should be noted that the effects of the Cu^{2+} introduced on meta- and pyro-vanadates were dissimilar to those on ortho-vanadates. With increase in the amount of Cu^{2+} in the former two vanadates, the conversion of C_3H_8

Table 2
Apparent density, surface area and catalytic activities of magnesium vanadates incorporated with Cu^{2+}

Catalyst	AD[a]	SA[b]	Conversion (%)		Selectivity (%)			Rate[c]
			C_3H_8	O_2	C_3H_6	CO	CO_2	
MgV_2O_6	1.15	3.0	11.9	96	47.4	33.6	19.1	14.2×10^{-6}
$Mg_{0.95}Cu_{0.05}V_2O_6$	1.14	1.6	8.7	94	39.3	26.9	33.8	19.5×10^{-6}
$Mg_{0.90}Cu_{0.10}V_2O_6$	1.14	1.6	9.3	96	32.9	28.3	38.8	20.8×10^{-6}
$Mg_2V_2O_7$	0.97	2.8	14.0	88	51.0	29.3	19.8	17.9×10^{-6}
$Mg_{1.90}Cu_{0.10}V_2O_7$	1.06	1.7	8.8	96	34.5	34.2	31.3	18.5×10^{-6}
$Mg_{1.80}Cu_{0.20}V_2O_7$	1.08	1.3	7.3	88	32.0	32.6	35.5	20.1×10^{-6}
$Mg_3V_2O_8$	0.97	3.4	3.9	21	58.1	16.9	25.1	4.1×10^{-6}
$Mg_{2.85}Cu_{0.15}V_2O_8$	1.02	1.6	9.6	95	10.4	1.0	88.6	21.5×10^{-6}
$Mg_{2.70}Cu_{0.30}V_2O_8$	1.03	1.2	3.7	60	22.0	5.2	72.8	11.0×10^{-6}

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 3 h on-stream.

[a] Apparent density (g/cm^3).
[b] Surface area (m^2/g).
[c] Reaction rate per unit of catalyst surface area (mol min^{-1} m^{-2}).
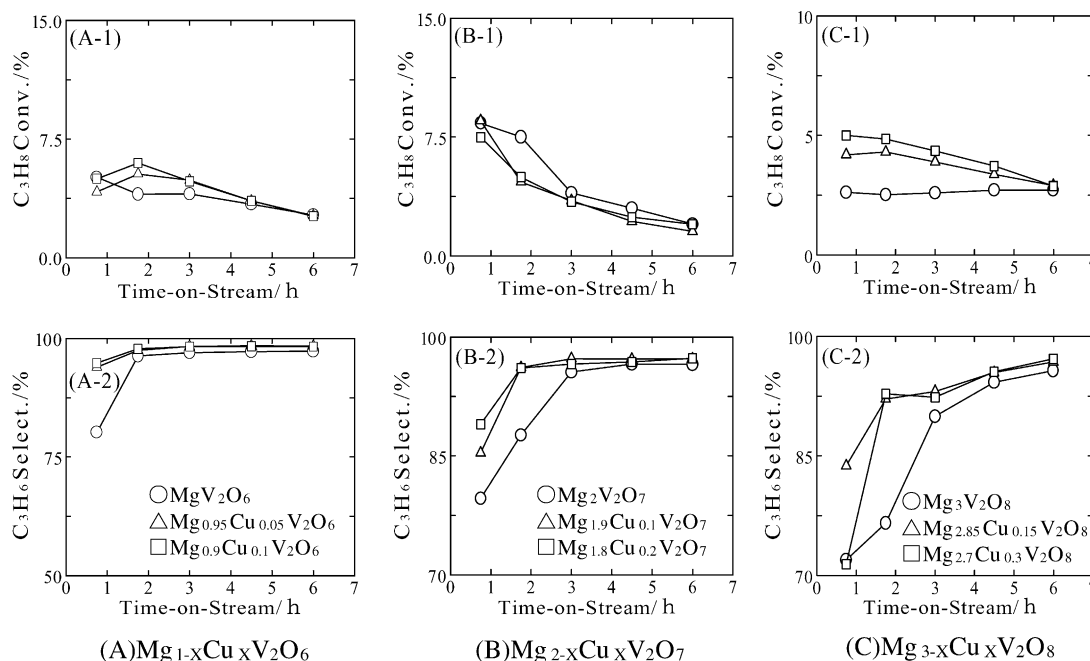
Fig. 2. The conversion of C_3H_8 and the selectivity to C_3H_6 obtained from propane conversion in the absence of oxygen in the feed-stream on $Mg_{1-x}Cu_xV_2O_6$ (A), $Mg_{2-x}Cu_xV_2O_7$ (B) and $Mg_{3-x}Cu_xV_2O_8$ (C). Reaction conditions: the same as those described in Table 2 except $P(O_2) = 0$ kPa.

and the selectivity to C_3H_6 decreased while the selectivity to CO_2 increased. The selectivities to CO on those two catalysts were rather insensitive to the Cu^{2+}-contents. However, those trends with Cu^{2+}-contents were broken with the ortho-vanadates. On the ortho-vanadates, the conversion and the selectivities were not related with Cu^{2+}-content, while the catalysts incorporated with Cu^{2+} seemed to favor the formation of CO_2 over CO, which was somewhat contrast to the other vanadates. Those parent catalysts, that is, magnesium meta-, pyro- and ortho-vanadates were well characterized [2]. Magnesium meta-vanadate consists of VO_6 octahedra joined by edges and connected together through MgO_6 octahedra [2,16]. Magnesium pyro-vanadate consists of rows of V_2O_7 groups with long V–O bridges within three groups. Each terminal oxygen atoms of the V_2O_7 groups are shared with two Mg ions [2,17]. Magnesium ortho-vanadate consists of nearly cubic closest packing of oxygen atom layers with the Mg ions in octahedral sites and the V ions in tetrahedral sites [2,18]. Based on the structural information, it may be rather reasonable that the catalytic activities on those catalysts are related with the amount of Cu^{2+} after the exchange of Mg^{2+} with Cu^{2+} in those catalysts, as observed on meta- and pyro-vanadates incorporated with Cu^{2+}. Together with those effects of the amount of Cu^{2+} in the catalysts, the unidentified species detected in the Cu^{2+} incorporated ortho-catalysts may contribute to the effects of the amount of Cu^{2+} species on ortho-vanadates. It is generally accepted that copper shows favorable redox behaviors between Cu^{2+} and Cu^0 through Cu^+, indicating that the incorporation and abstraction of lattice oxygen in the catalysts are strongly influenced

by the nature of Cu^{2+} incorporated into magnesium vanadates together with that of vanadium species [9,10].

3.2. Oxidative dehydrogenation of propane in the absence of O_2 into the feed-stream

The oxidative dehydrogenation of propane on magnesium vanadates proceeds extensively with the abstraction of lattice oxygen from the oxide catalysts, when gaseous oxygen is not introduced into the feed-stream for the oxidation [9]. In our previous paper on the oxidation in the absence of gaseous oxygen in the feed-stream on those magnesium vanadates and those incorporated with Ca^{2+}, the effects of time-on-stream on MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$ were dissimilar to those on the catalysts incorporated with Ca^{2+} [10]. In those systems, the abstraction of lattice oxygen with the reduction of V^{5+} to V^{4+} together with the nature of Mg^{2+} and Ca^{2+} contributed to those reaction behaviors [9,10]. It should be noted that those V^{4+}, Mg^{2+} and Ca^{2+} cations still bond to the remained lattice oxygen in those catalysts. Therefore, the nature of those cations should be reflected on the activity of the remained lattice oxygen. However, the conversion of C_3H_8 and the selectivity to C_3H_6 on MgV_2O_6 after 1.75 h on-stream essentially matched to those on $Mg_{0.95}Cu_{0.05}V_2O_6$ and $Mg_{0.90}Cu_{0.10}V_2O_6$ (Fig. 2(A-1) and (A-2)) while after 3 and 6 h on-stream for $Mg_{2-x}Cu_xV_2O_7$ (Fig. 2(B-1) and (B-2)) and $Mg_{3-x}Cu_xV_2O_8$ (Fig. 2(C-1) and (C-2)) systems. Thus, it was rather strange that the incorporated Cu^{2+} did not afford any evident influences on the activities on those

catalysts after the mentioned time-on-stream. It may be reasonable to suggest that Cu species does not play important role on the oxidative dehydrogenation on those catalysts when Cu^{2+} in those catalysts is reduced particularly to Cu^0, since Cu^0 does not bond to the lattice oxygen. Therefore, further examination on the redox behaviors of Cu species together with those of vanadium species is needed to the present catalyst systems. A certain amount of copper in those catalysts should be needed for obtaining information on redox behaviors of Cu species. Therefore, the remainder of this paper will be concerned with $Mg_{0.90}Cu_{0.10}V_2O_6$, $Mg_{1.80}Cu_{0.20}V_2O_7$ and $Mg_{2.70}Cu_{0.30}V_2O_8$.

Fig. 3 shows XRD patterns of fresh $Mg_{0.90}Cu_{0.10}V_2O_6$ (A-1), $Mg_{1.80}Cu_{0.20}V_2O_7$ (B-1) and $Mg_{2.70}Cu_{0.30}V_2O_8$ (C-1) and those (Fig. 3(A-2), (B-2) and (C-2), respectively) previously employed for obtaining the results described in Fig. 2. It was evident from Fig. 3 that those catalysts were converted to different phase during the conversion of propane without gaseous oxygen, probably due to the abstraction from the corresponding catalysts of lattice oxygen that was supplied as oxidant for the conversion of propane. The abstraction of lattice oxygen from those catalysts should directly contribute to the reduction of V^{5+} and Cu^{2+} species in $Mg_{0.90}Cu_{0.10}V_2O_6$, $Mg_{1.80}Cu_{0.20}V_2O_7$ and $Mg_{2.70}Cu_{0.30}V_2O_8$. In order to examine the reduction behaviors of V^{5+} and Cu^{2+} species in those catalysts, ^{51}V MAS NMR and XPS were employed, respectively. It should be noted that diamagnetic V^{5+} species

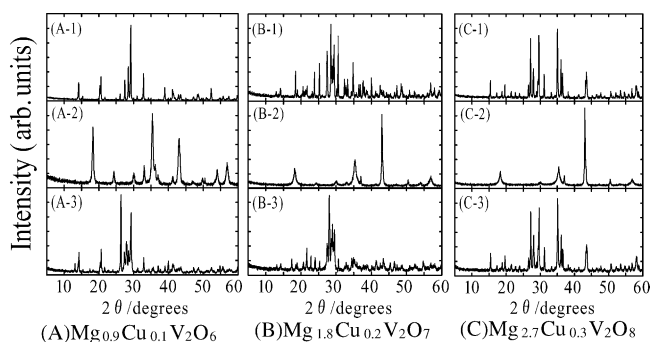Fig. 3. XRD patterns of $Mg_{0.90}Cu_{0.10}V_2O_6$ (A), $Mg_{1.80}Cu_{0.20}V_2O_7$ (B) and $Mg_{2.70}Cu_{0.30}V_2O_8$ (C) employed for the observation of redox behaviors. (A-1), (B-1) and (C-1): fresh catalysts; (A-2), (B-2) and (C-2): after employed for obtaining the results shown in Fig. 2; (A-3), (B-3) and (C-3): after re-oxidation with oxygen flow (30 mL/min) at 723 K for 2 h of the samples employed for obtaining the results shown in Fig. 2.

afford evident NMR signals while paramagnetic V^{4+} affords a broad and weak signal [9,10]. Furthermore, with regard to the redox behaviors of Cu species, it has been reported that XPS signal due to Cu $2p_{3/2}$ from Cu^{2+} species affords a satellite peak with a great intensity, while no satellite peaks are observed from Cu^+ and Cu^0 species [14,15]. As shown in Fig. 4(A-1), (B-1) and (C-1), evident ^{51}V NMR signals were observed from fresh $Mg_{0.90}Cu_{0.10}V_2O_6$, $Mg_{1.80}Cu_{0.20}V_2O_7$ and $Mg_{2.70}Cu_{0.30}V_2O_8$, respectively, indicating that V^{5+} was
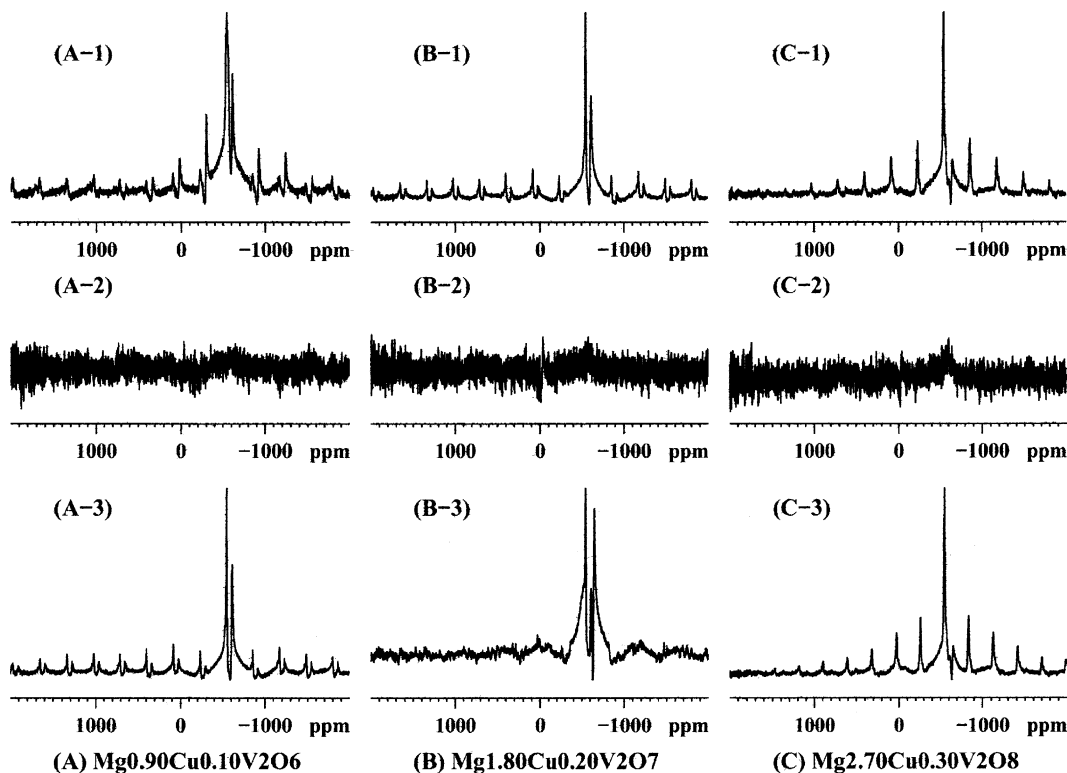
Fig. 4. ^{51}V MAS NMR of $Mg_{0.90}Cu_{0.10}V_2O_6$ (A), $Mg_{1.80}Cu_{0.20}V_2O_7$ (B) and $Mg_{2.70}Cu_{0.30}V_2O_8$ (C) employed for the observation of redox behaviors. (A-1), (B-1) and (C-1): fresh catalysts. (A-2), (B-2) and (C-2): after employed for obtaining the results shown in Fig. 2. (A-3), (B-3) and (C-3): after re-oxidation with oxygen flow (30 mL/min) at 723 K for 2 h of the samples employed for obtaining the results shown in Fig. 2.

certainly present in those fresh catalysts. However, signals with quite poor S/N ratio were detected from those catalysts used in the conversion of propane in the absence of gaseous oxygen in the feed-stream (Fig. 4(A-2), (B-2) and (C-2)). Thus, the reduction of V^{5+} to V^{4+} together with the evident abstraction of lattice oxygen from the corresponding catalysts proceeds easily during the conversion of propane without gaseous oxygen in the feed-stream. It should be noted that the reduction of V^{5+} to V^{4+} on magnesium vanadates incorporated with Cu^{2+} proceeds more extensively than that on the corresponding parent catalysts [9] and those incorporated with Ca^{2+} [10]. Therefore, the introduction of reducible Cu^{2+} into magnesium vanadates may result in the enhancement of the reduction of V^{5+} during the conversion of propane without gaseous oxygen, followed by the enhancement of the abstraction of lattice oxygen from the corresponding catalysts. Fig. 5 shows XPS signals due to Cu $2p_{3/2}$ from $Mg_{0.90}Cu_{0.10}V_2O_6$ (A), $Mg_{1.80}Cu_{0.20}V_2O_7$ (B) and $Mg_{2.70}Cu_{0.30}V_2O_8$ (C). From those fresh catalysts (Fig. 5(A-1), (B-1) and (C-1)), the evident satellite peak was detected between 940 and 948 eV, together with main peak at approximately 933 eV, indicating that Cu^{2+} was present in those catalysts. As shown in Fig. 5(A), (B) and (C), more than two kinds of Cu species may be present. If Cu^{2+} is exchanged with Mg^{2+} that was present on different sites in the unit cell, the results shown in those figures are possible. Since the binding energy obtained from Cu-species is rather insensitive to the valent of Cu-species [19] and the active sites are believed to be the lattice oxygen in those vanadates [5,6], those species are not further identified. Although the signals due to Cu $2p_{1/2}$ were also detected, the intensity was rather weaker than that from Cu $2p_{3/2}$. Therefore, the signals due

to Cu $2p_{3/2}$ together with the corresponding satellite peaks were described in Fig. 5. It should be noted that the ratios of the intensity of the satellite peak against that of Cu $2p_{3/2}$ peak were approximately 0.40, 0.36 and 0.43 for Fig. 5(A-1), (B-1) and (C-1), respectively. After those catalysts were employed for the conversion of propane in the absence of gaseous oxygen, the ratios of the satellite peak against that of Cu $2p_{3/2}$ decreased (0.25, 0.17 and 0.21 for Fig. 5(A-2), (B-2) and (C-2), respectively), indicating that some of Cu^{2+} was reduced during the conversion. Therefore, reduction of Cu^{2+} together with that of V^{5+} proceeds upon abstracting the lattice oxygen from those catalysts. It is expected that more lattice oxygen can be abstracted from the catalysts incorporated with Cu^{2+} than the parent [9] and Ca^{2+}-added catalysts [10] since Cu^{2+} is easily reducible species.

3.3. Re-oxidation of the catalysts employed for the conversion of propane in the absence of gaseous oxygen in the feed-stream

As mentioned above, the reduction of V^{5+} and Cu^{2+} species in $Mg_{0.90}Cu_{0.10}V_2O_6$, $Mg_{1.80}Cu_{0.20}V_2O_7$ and $Mg_{2.70}Cu_{0.30}V_2O_8$ resulted in the formation of oxygen vacancy due to the abstraction of lattice oxygen from those catalysts. It was expected that more lattice oxygen was abstracted from those Cu^{2+} incorporated catalysts than from MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$. Therefore, the re-oxidation behaviors of those reduced catalysts should be dependent on the presence and absence of Cu^{2+} in those catalysts. 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 gaseous oxygen for 2.25 h on-stream, when oxygen at 4.1 kPa was introduced into the feed-stream. In Fig. 6, the oxygen responses after the introduction of gaseous oxygen on MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$, respectively, were described, and $t = 0$ min in the figure corresponded to the above-described 2.25 h on-stream. In our previous papers [9,10], the oxygen responses were monitored by $t = 18$ min,
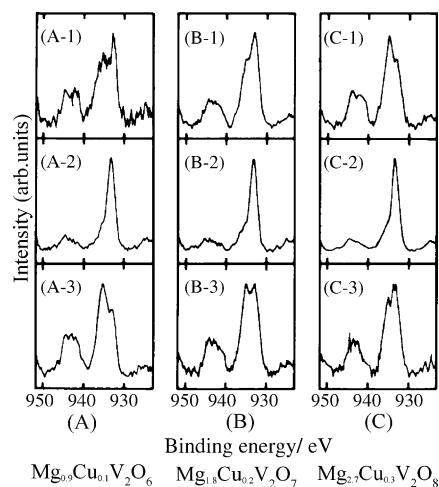

Fig. 5. XPS signals due to Cu $2p_{3/2}$ of $Mg_{0.90}Cu_{0.10}V_2O_6$ (A), $Mg_{1.80}Cu_{0.20}V_2O_7$ (B) and $Mg_{2.70}Cu_{0.30}V_2O_8$ (C) employed for the observation of redox behaviors. (A-1), (B-1) and (C-1): fresh catalysts. (A-2), (B-2) and (C-2): after employed for obtaining the results shown in Fig. 2. (A-3), (B-3) and (C-3): after re-oxidation with oxygen flow (30 mL/min) at 723 K for 2 h of the samples employed for obtaining the results shown in Fig. 2.
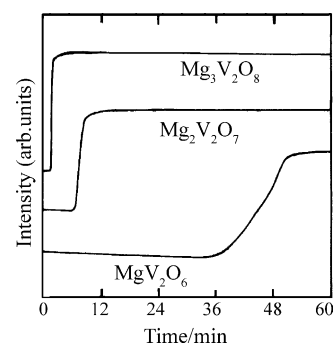

Fig. 6. Oxygen response in the effluent gas from MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$. Reaction conditions: before and after $t = 0$ min, the catalysts were exposed to the reactant gas under the same conditions described in Table 2 except $P(O_2) = 0$ and 4.1 kPa, respectively.

while $t = 60$ min was employed in the present study since an excess amount of oxygen may be needed for the sufficient oxidation of the corresponding Cu^{2+}-added catalysts. Although it has been reported in our previous papers [9,10] that oxygen is not detected by 18 min on MgV_2O_6, oxygen was certainly detected at approximately 36 min in the present study (Fig. 6). The order of the oxygen-effluent time from $Mg_2V_2O_7$ and $Mg_3V_2O_8$ followed same order reported in our previous papers [9,10]. These results revealed that the number of oxygen vacancy formed during the conversion of propane in the absence of gaseous oxygen, that was corresponded to the order of the reducibility, followed the order $MgV_2O_6 > Mg_2V_2O_7 > Mg_3V_2O_8$. However, no oxygen response was observed from $Mg_{0.90}Cu_{0.10}V_2O_6$, $Mg_{1.80}Cu_{0.20}V_2O_7$ and $Mg_{2.70}Cu_{0.30}V_2O_8$ by 60 min (not shown). From those Cu^{2+} incorporated catalysts, lattice oxygen was extensively abstracted from those catalysts during the conversion of propane without gaseous oxygen since reducible Cu^{2+} together with V^{5+} was present in those catalysts. Therefore, the present results revealed that an excess amount of gaseous oxygen was needed for the sufficient re-oxidation.

In order to obtain information on structure of those Cu^{2+} incorporated catalysts and valent of vanadium and copper species after re-oxidation, $Mg_{0.90}Cu_{0.10}V_2O_6$, $Mg_{1.80}Cu_{0.20}V_2O_7$ and $Mg_{2.70}Cu_{0.30}V_2O_8$, that were employed for obtaining the results shown in Fig. 2, were re-oxidized with oxygen flow (30 mL/min) at 723 K for 2 h and those re-oxidized catalysts were analyzed with XRD, ^{51}V MAS NMR and XPS. XRD analyses reveals that the regeneration was observed from $Mg_{2.70}Cu_{0.30}V_2O_8$ after the re-oxidation (Fig. 3(C-3)) while the conversion to dissimilar phases from $Mg_{0.90}Cu_{0.10}V_2O_6$ and $Mg_{1.80}Cu_{0.20}V_2O_7$ was observed (Fig. 3(A-3) and (B-3), respectively). It should be noted that the reduction of the parent pyro-$Mg_2V_2O_7$ and ortho-$Mg_3V_2O_8$ is more favorable than that of ortho-$Mg_3V_2O_8$, indicating that the nature of the fresh ortho-species may be reflected on that of the solid obtained after the conversion of propane without gaseous oxygen (Fig. 3(C-2)). Although the structural regeneration was observed only from $Mg_{2.70}Cu_{0.30}V_2O_8$, the regeneration of V^{5+} and Cu^{2+} from the corresponding reduced forms of $Mg_{0.90}Cu_{0.10}V_2O_6$, $Mg_{1.80}Cu_{0.20}V_2O_7$ and $Mg_{2.70}Cu_{0.30}V_2O_8$ was confirmed with the detection of evident ^{51}V MAS NMR signals (Fig. 4(A-3), (B-3) and (C-3), respectively) and that of evi-

dent satellite peaks together with main Cu $2p_{3/2}$ XPS signals (Fig. 5(A-3), (B-3) and (C-3), respectively).

4. Conclusion

The incorporation of Cu^{2+} into MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$ resulted in the enhancement not only of the activities for the oxidation of propane but also of the formation of CO_x species. It may be suggested that the partial oxidation to CO or the deep oxidation to CO_2 proceeds more favorably than the oxidative dehydrogenation to propylene, since the introduction of reducible Cu^{2+} in those magnesium vanadates enhances the abstraction of the lattice oxygen from the catalysts to form oxygen vacancy together with the incorporation of gaseous oxygen into the oxygen vacancy.

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