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Anaerobic oxidation of isobutane: Catalytic properties of MgV_2O_6 and $Mg_2V_2O_7$ prepared by the molten method

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Abstract

The catalytic activity of MV_2O_6 and $M_2V_2O_7$ type oxides prepared by the molten method (MM) for anaerobic oxidation of isobutane was studied in order to construct a system for the selective oxidation of isobutene using a thin layer reactor. Isobutene, CO and CO_2 were formed by every catalyst tested. The activities for isobutene formation were $CuV_2O_6 > ZnV_2O_6$, NiV_2O_6, $CoV_2O_6 > MgV_2O_6 > MnV_2O_6 \gg CaV_2O_6$. Isobutene was a major product over $M_2V_2O_7$ (MM). $Co_2V_2O_7$ showed the highest activity and high isobutene selectivity exceeded 90%, demonstrating that $Co_2V_2O_7$ is a suitable oxide for a thin layer reactor for anaerobic oxidation of isobutane. Partial substitution of Mg by Cu in $Mg_2V_2O_7$ (MM) improved the activity. It is shown by the oxidation at low O_2 concentration as 2–3% that two types of oxidations occurred simultaneously: isobutene formation by the lattice oxygen ions diffused from the bulk, and CO and CO_2 formation by the oxygen species derived from molecular oxygen in the gas phase.

Keywords: Anaerobic oxidation; Isobutane conversion; MV_2O_6; $M_2V_2O_7$; Active oxygen species

1. Introduction

Alkanes are resistive to oxidation because there are no active functional groups in these molecules. Generally, products are more easily oxidized than reactant alkanes, so the selective oxidation of alkanes is a challenging topic. A number of studies have been carried out on the catalytic oxidation of lower alkanes over various catalysts such as Mg–V–O [1–14], V_2O_5/γ-Al_2O_3 [15], Pt/ceramic foam [16], $Ag_{0.01}Bi_{0.85}V_{0.54}$–$Mo_{0.45}O_4$ [17,18], Bi–Mo–O/TiO_2 [19], B–P–O [20], $V_2O_5/AlNbO_4$ [21], V_2O_5/TiO_2 [22], $ZnFe_2O_4$ [23], Mo–V–Sb [24,25], Fe/ZSM-5 [26], heteropolyacid [27,28], SbO/Fe_2O_3 [29], Mo–V–Nb–Te, Mo–V–Ta–Te [30], CrO/Al_2O_3 [31,32], Re–Sb–O [33], LaBaSm–O [34], K, Ca, P-doped $NiMoO_4$ [35] and composites of Bi–Mo–O and Nb_2O_5 [36].

The selective oxidation of isobutane to isobutene was found to occur over metal phosphate catalysts, which have less active lattice oxygen. For example, $Ni_2P_2O_7$ selectively catalyzed the oxidative dehydrogenation of isobutane at relatively high temperatures such as 723–823 K, because the lattice oxygen ions of $Ni_2P_2O_7$ move so slowly as to inhibit the successive oxidation of isobutene [37–45]. When an oxygen poor (5 mol%) and isobutene-rich (75 mol%) feed gas was introduced, isobutene was formed with a selectivity higher than 85%. Usually, gaseous oxygen in the feed gas is rapidly supplied to the oxygen vacancy formed by the oxidation of isobutane at the surface. Therefore, if gaseous oxygen is absent from the feed, oxidative dehydrogenation of isobutane would proceed selectively by surface lattice oxygen ions. Extending this concept in order to develop highly active and selective catalysts, we have studied the oxidation of isobutane over various catalysts in the absence of oxygen in the feed [44], a process named “anaerobic oxidation.” In anaerobic oxidation, no oxygen is supplied from the gas phase, so isobutane molecules attack the surface oxygen ions, which exist at a low concentration and diffuse from the bulk. Thus, a high selectivity of isobutene was achieved by this reaction system, but it required relatively high reaction temperatures such as 823 K in order to obtain sufficient diffusion rates of oxygen ions in the catalysts. In this reaction system, oxide catalysts are gradually reduced during the isobutane oxidation, therefore, reduced catalysts should be oxidized to a certain reduced state suitable for selective oxidation in the same or separate reactors.

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We studied isobutane oxidation over MV_2 type complex oxides in the absence of gaseous O_2, and reported in a previous paper [44] that the catalytic activity was in the order of $CuV_2O_6 \gg CoV_2O_6 > MgV_2O_6 > ZnV_2O_6 \gg ZrV_2O_7 > CaV_2O_6$. CuV_2O_6 and CoV_2O_6 were very active, but were not selective for isobutene formation. MgV_2O_6 was the most selective for isobutene formation.

Anaerobic oxidation of isobutane using $Cu_nV_2O_x$ ($n=0$–3, and 5) type complex oxides was also studied [45]. V_2O_5, CuV_2O_6, and $Cu_2V_2O_7$ showed high oxidizing activity, but $Cu_3V_2O_8$ and $Cu_5V_2O_{10}$ were less active. Over active catalysts, CO_2 was selectively formed only at the beginning of the reaction, and its formation decreased with reaction time. Isobutene formation became dominant 15–30 min after the beginning of the reaction. The order of the catalytic activity at 623 K was $V_2O_5 > CuV_2O_6, Cu_2V_2O_7 \gg Cu_3V_2O_8, Cu_5V_2O_{10}$. Since CO_2 forms at the beginning of the reaction, selective isobutene formation can be achieved under an appropriate degree of reduction. Although the reduction degree of the CuV_2O_6 and $Cu_2V_2O_7$ where isobutene selectivity reached 100% was as high as about 40%, it was concluded that CuV_2O_6 and $Cu_2V_2O_7$ are applicable to a thin layer reactor in which isobutane and oxygen are separately supplied to opposite sides of the layer.

To construct a thin layer reaction system, it is necessary to prepare a dense thin layer of the catalysts without voids, which is thought to be quite similar to that of the catalysts prepared by the molten method. Therefore, information about the oxidation of isobutane over the catalysts prepared by the molten method is helpful for estimating the results in a thin layer reactor. From this point of view, the catalytic properties of the catalysts prepared by the molten method were studied in this paper.

As for the reactor for the anaerobic oxidation of alkanes, it is practical that reduced catalysts are regenerated in the same reactor; however, catalytic oxidation should be stopped during the regeneration of catalysts. If very thin tubular reactors of oxygen conducting oxides can be prepared, and alkanes and air are supplied to both sides separately, consumed oxygen of the catalyst surface will be supplied from the bulk, and the consumed bulk oxide ion is supplied from air. Thus, the oxidation can continue for a long time. This type of reactor requires thin dense membranes of oxides. The surface of dense membranes may be the same as that of molten oxides. Therefore, the anaerobic oxidation of isobutane over MV_2O_6 type oxides prepared by the molten method was studied in this paper.

2. Experimental methods

2.1. Catalyst preparation

Preparation of $M_2V_2O_7$ (MM): A mixture of the component oxide powders was mixed in a mixing pot overnight, and then the obtained powder was melted in an alumina crucible. $Zn_2V_2O_7$, $Cu_2V_2O_7$, $Co_2V_2O_7$, $Mg_2V_2O_7$, and $Ca_2V_2O_7$ were melted at 1223, 1073, 1273, 1373, and 1423 K, respectively, and the samples were cooled to ambient temperature. The samples were cooled at a rate of 0.2 K/min at a temperature near the respective melting point. In the case of $Mn_2V_2O_7$, the sample in the pot was rapidly cooled by removing it from the furnace. Then, the formed lump of oxides was crushed and sieved. Granules of 16–32 mesh were used for the catalytic test. The catalysts prepared by the molten method are designated (MM). Partially substituted catalysts $Mg_{1.8}M_{0.2}V_2O_7$ were prepared by molten liquids at 1373 K.

Preparation of $M_2V_2O_6$ (WD): An aqueous solution of ammonium metavanadate was mixed with an aqueous solution of the corresponding metal nitrates, and the mixture was stirred and heated on a hotplate to evaporate the water. The resulting solid samples were calcined at 550 °C for 15 h in air. Catalysts prepared by this wet and dry method were designated (WD).

2.2. Characterization of catalysts

The structures of the catalysts were characterized by XRD (Rigaku RINT4500). BET surface areas were measured by N_2 and Ar adsorption at liquid N_2 temperatures. Temperature-programmed-reduction (TPR) measurement was performed on 0.2 g catalyst. After the sample was evacuated at 550 °C for 0.5 h, about 13,332 Pa of O_2 was introduced to a gas circulation system for 0.5 h to remove organic species on the surface of the samples, and then the sample was evacuated at 550 °C for 0.5 h. The sample was cooled to ambient temperature, and was then flashed by a mixed gas of 4.88% H_2 and 95.12% N_2. After the baseline was stabilized, the sample was heated to 823 K at a rate of 10 K/min.

2.3. Catalytic reaction

Isobutane oxidation under anaerobic conditions was conducted at atmospheric pressure in a fixed-bed flow reactor using a feed gas of 30 mol% isobutane and 70 mol% N_2 as an internal standard. The 14–32 mesh SiC granules were charged in the lower part of the reactor to avoid the homogeneous reaction taking place in the post-catalytic volume. The feed gas rate was 1.23 mmol/min (30 cm^3/min at 298 K). The reactant gas and effluent gas were analyzed by gas chromatography and GC–mass spectrometry (Shimadzu GCMS-QP5050). In a blank test, the catalyst zone of the reactor was filled with silicon carbide instead of catalyst; no conversion of isobutane could be detected.

3. Results and discussion

3.1. Anaerobic oxidation of isobutane over MgV_2O_6 catalysts prepared by the molten method

Mg–V oxides (WD) showed high catalytic activity and high isobutene selectivity among various complex oxides in the oxidation of isobutane in the presence of oxygen. Therefore, anaerobic oxidation of isobutane was carried out using the MgV_2O_6 (MM) catalyst at 673 K, and the results are shown in Fig. 1 along with the results of MgV_2O_6 (WD) for comparison. The specific surface area (SSA) of (MM) oxides was very small. Although MgV_2O_6 (MM) showed an SSA as small as 0.37 m^2/g, the reaction rate of isobutane was significantly fast. The shape of the rate of isobutene formation for MgV_2O_6 (MM)

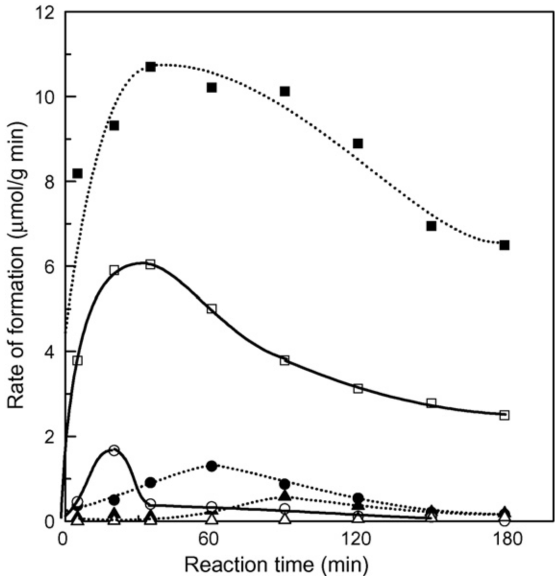

Fig. 1. Comparison of the catalytic activity of MgV_2O_6 catalysts prepared by the wet and dry method (WD) and the molten method (MM) for anaerobic oxidation of isobutane. WD: (■) isobutene, (●) CO_2, (▲) H_2; MM: (□) isobutene, (○) CO_2, (△) CO.

was very similar to that for MgV_2O_6 (WD); both curves have a maximum at 35 min. The maximum rate over MgV_2O_6 (MM) was about 57% of that over MgV_2O_6 (WD). The rate curves of CO_2 formation were slightly different from each other; the rate over MgV_2O_6 (WD) had a maximum of 1.3 µmol/g min at 60 min, and then decreased gradually; on the other hand, that over MgV_2O_6 (MM) had a maximum at 20 min and then sharply decreased with time. Selectivity for isobutene is one of the most important factors for isobutene production, so the selectivity for isobutene over both catalysts is plotted in Fig. 2. The selectivity over MgV_2O_6 (MM) at the initial stages was relatively small at 70–80%, but it increased sharply to 95% between 35 and 60 min. Then, it increased gradually and reached 100% at 225 min. Over MgV_2O_6 (WD), the initial selectivity was as high as 95%, but it decreased to 87% at 60 min due to the promotion of CO_2 formation, and then it recovered to 96% at 150 min.

Small amounts of H_2 formation were observed in the initial stages of the reaction over MgV_2O_6 (WD). This amount increased with time on stream, and after reaching a maximum at around 90 min, it decreased with reaction time. The rate was not much higher over MgV_2O_6 (WD). On the other hand, only very small amounts of H_2 were observed throughout the experiment over MgV_2O_6 (MM). The formation of H_2 suggested that simple dehydrogenation of isobutane was occurring. The contribution of simple dehydrogenation in isobutene formation reached only 5.7% over MgV_2O_6 (WD), but it was negligibly small over MgV_2O_6 (MM). It can therefore be predicted that isobutene would be formed by oxidative dehydrogenation on the surface of a thin layer of the catalyst.

A schematic diagram of a thin layer reactor using MgV_2O_6 is shown in Fig. 3. In this reactor, oxygen can be supplied from the oxidant chamber to the catalyst surface, and the oxygen ions diffuse through the oxide catalyst to the side of the reactant chamber. Since oxygen ions located at the surface can be calculated to be about 8 µmol/m^2 over MgV_2O_6 from the crystal structure, about 3 µmol/g of lattice oxygen will be located at the surface.

The amount of oxygen removed from MgV_2O_6 (MM) by the reaction with isobutane was about 200 µmol at 1.5% reduction. This suggests that lattice oxygen ions in the bulk of the catalyst can diffuse through reduced phases of MgV_2O_6. The selectivity of isobutene would depend on the degree of reduction of the catalyst at the surface of the reactant chamber, R2. Although the exact degree of reduction at the catalyst surface cannot be known, it can be seen from Fig. 2 that if the total degree of reduction of the catalyst were kept to more than 3.0%, isobutene would be obtained with a selectivity greater than 99%.

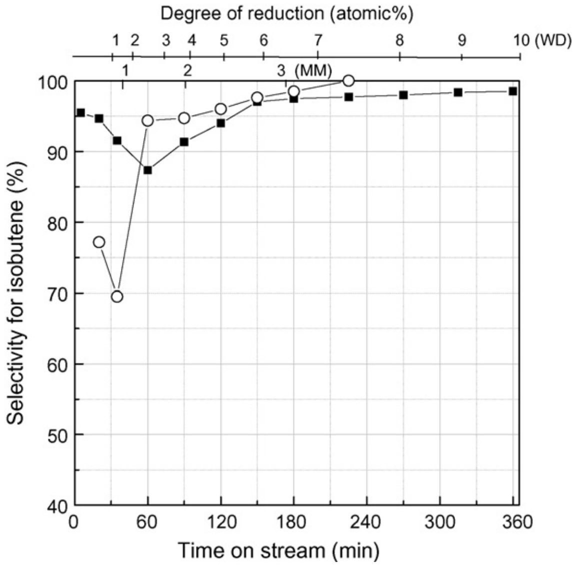

Fig. 2. Comparison of isobutene selectivity for MgV_2O_6 catalysts prepared by WD and MM methods: (■) MgV_2O_6 (WD), (○) MgV_2O_6 (MM).

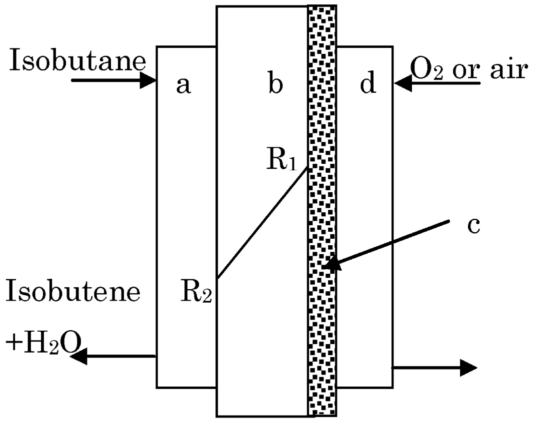

Fig. 3. Schematic expression of a thin layer reactor using MgV_2O_6: (a) reactant chamber; (b) thin layer; (c) porous heater; (d) oxidant chamber; R_1 and R_2: reduction degree of catalyst.

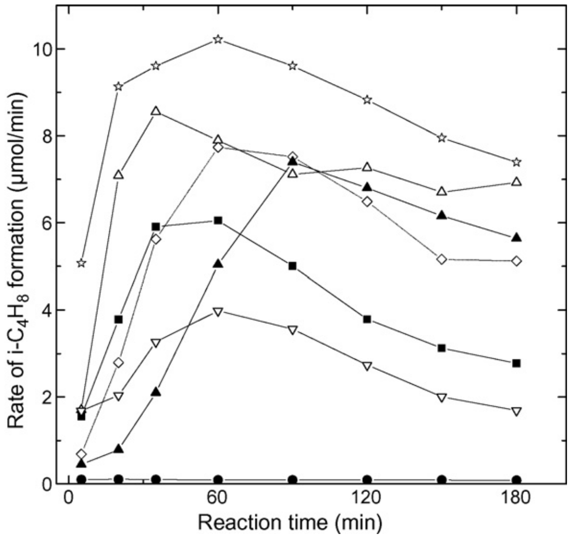

Fig. 4. Catalytic activity of MV_2O_6 catalysts prepared by the molten method for anaerobic oxidation of isobutene: (☆) CuV_2O_6, (△) ZnV_2O_6, (◇) NiV_2O_6, (▲) CoV_2O_6, (■) MgV_2O_6, (▽) MnV_2O_6, (●) CaV_2O_6.

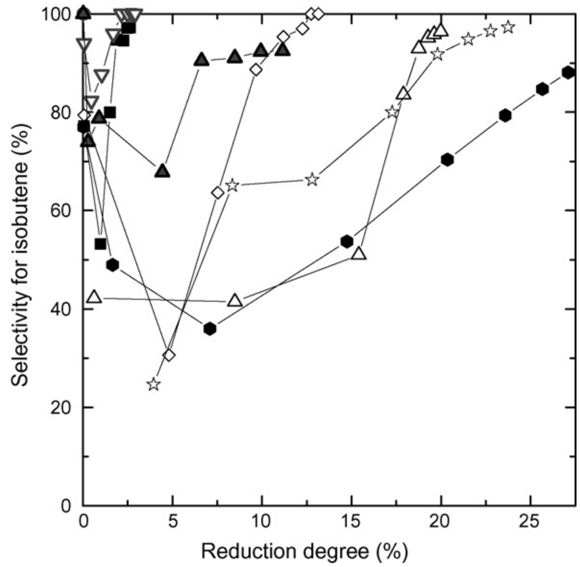

Fig. 5. Selectivity for isobutene over various MV_2O_6 catalysts: (☆) CuV_2O_6, (△) ZnV_2O_6, (◇) NiV_2O_6, (▲) CoV_2O_6, (■) MgV_2O_6, (▽) MnV_2O_6, (●) CaV_2O_6.

3.2. Anaerobic oxidation of isobutane over MV_2O_6 (MM) catalysts prepared by the molten method

The results of various MV_2O_6 catalysts prepared by the molten method are shown in Fig. 4. Isobutene, CO, and CO_2 were formed by every catalyst except for CaV_2O_6. The formation of H_2 was observed over ZnV_2O_6, CuV_2O_6, and V_2O_5. The rate of *i*-butene formation was the highest over CuV_2O_6, followed by ZnV_2O_6, NiV_2O_6, CoV_2O_6, MgV_2O_6, and MnV_2O_6, in this order. CaV_2O_6 was not active for this reaction. All catalysts reached a maximum reaction rate at 30–90 min. The maximum rate was achieved the fastest over ZnV_2O_6 at 35 min, and it appeared at 60 min over CuV_2O_6, NiV_2O_6, MgV_2O_6, and MnV_2O_6. The highest formation rate, 10 μmol/min g, was found over CuV_2O_6, and a high formation rate of about 8 μmol/min g was observed over ZnV_2O_6 and NiV_2O_6. The selectivity for isobutene over the catalysts is plotted against the degree of reduction of the catalysts in Fig. 5. It is of interest that MnV_2O_6 and CoV_2O_6, which contain easily redoxable metal ions, showed higher selectivity. This clearly suggests that the oxidizability of surface oxygen ions supplied from gaseous oxygen is different from lattice oxygen ions diffused from the bulk of the oxides. It can be seen that the isobutene selectivity was significantly small in the region of lower degrees of reduction over NiV_2O_6, ZnV_2O_6, and CuV_2O_6, and it increased with increasing reduction degree. The V_2O_5 catalyst also gave a selectivity curve similar to that of NiV_2O_6, ZnV_2O_6, and CuV_2O_6, suggesting that the lattice oxygen ions of V_2O_5 are not selective for the oxidation of isobutane. On one hand, MgV_2O_6, which contains ions which are not easily redoxable, also showed higher selectivity. These results suggest that the oxidizability of the oxygen ions of V_2O_5 was controlled by making a MV_2O_6 compound (WD) not with Mn, Co and Mg, but with Ni, Zn, and Cu. TPR of the MV_2O_6 catalysts (WD) were measured and reported in a previous paper [44], and are shown again in Fig. 6. Although the method of preparation is different, the starting temperature of reduction in TPR and the rate of isobutene formation at 60 min are tentatively plotted in Fig. 7. A linear relation was observed between these two variables, suggesting that the oxidizability of V_2O_5 was controlled by making MV_2O_6 compounds.

H_2 formation was observed over most of the MV_2O_6 catalysts. Therefore, the contribution of the simple dehydrogenation among the formed isobutene was calculated from the rate of H_2 formation, and these results are shown in Fig. 8. Simple dehydrogenation was dominant over the ZnV_2O_6 catalyst throughout the experiment. Over CuV_2O_6, MnV_2O_6, and CoV_2O_6, the contribution of simple dehydrogenation increased with an increasing degree of reduction of catalysts, and about 35% of the isobutene was formed by simple dehydrogenation at 180 min. The contribution of simple dehydrogenation was very small over MnV_2O_6 and MgV_2O_6.

Catalytic activity, isobutene selectivity of the catalysts, and the degree of reduction of MV_2O_6 (MM) catalysts until 180 min

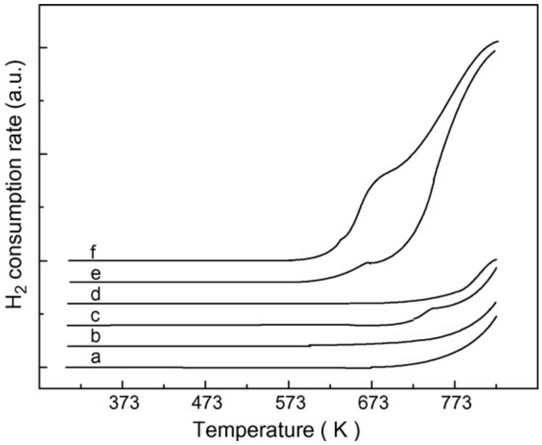

Fig. 6. TPR spectra of various complex oxides: (a) MgV_2O_6, (b) ZrV_2O_7, (c) ZnV_2O_6, (d) CaV_2O_6, (e) CoV_2O_6, (f) CuV_2O_6.

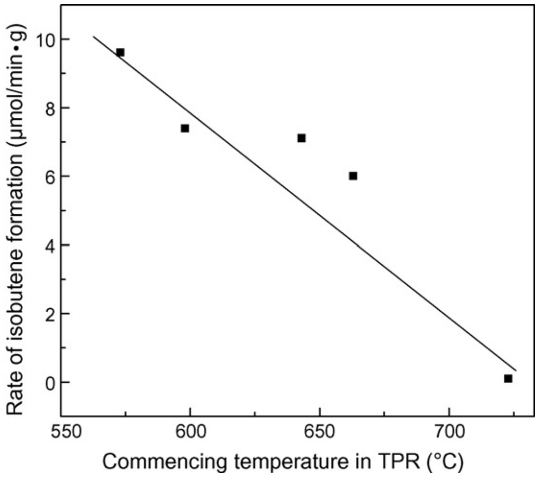

Fig. 7. Oxidizability of the MV_2O_6 catalysts and catalytic activity for isobutane oxidation.

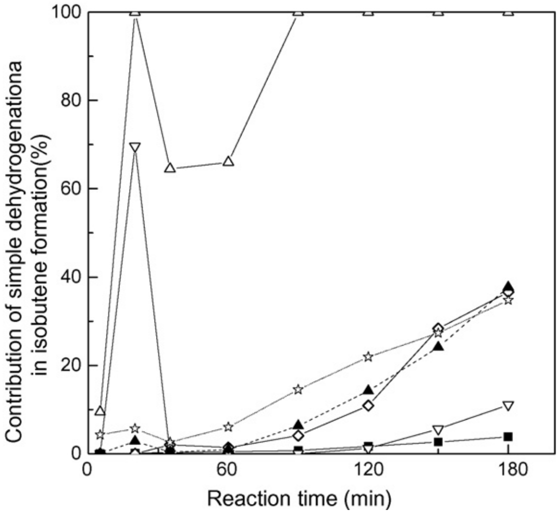

Fig. 8. Contribution of simple dehydrogenation in isobutene formation: (☆) CuV_2O_6, (△) ZnV_2O_6, (◇) NiV_2O_6, (▲) CoV_2O_6, (■) MgV_2O_6, (▽) MnV_2O_6, (●) CaV_2O_6.

are summarized in Table 1. Catalytic activity determined by isobutene formation was in the order of $CuV_2O_6 > ZnV_2O_6$, $V_2O_5 > NiV_2O_6 > CoV_2O_6 > MgV_2O_6 > MnV_2O_6 \gg CaV_2O_6$. Three types of crystal structures of MV_2O_6 type oxides were reported: brannerite type (B), pseudobrannerite type (P), and NiV_2O_6 type (N) [46]. These types of each oxide are also shown in Table 1. However, any correlation between this structural type and catalytic activity could not be determined.

If the catalysts are utilized for a thin layer reactor, in the region of the degree of reduction where no CO_2 is produced, selectivity for isobutene will be much improved over that displayed in Table 1.

3.3. Structural changes of MV_2O_6 by anaerobic oxidation of isobutane

After anaerobic oxidation, catalysts are reduced. The changes in the structure of the catalysts before and after the reaction were studied. A previous paper reported the examination of catalysts prepared by the WD method. XRD patterns of the MgV_2O_6 (WD) catalyst before reaction showed strong peaks attributed to MgV_2O_6 [44]. After reaction at 673 K, the structure of MgV_2O_6 (WD) was completely changed, and weak peaks appeared in the XRD pattern. Assignment of these peaks was very difficult, but we believe that $Mg_2V_2O_7$, $Mg_2V_6O_{17}$, V_3O_4, and V_3O_5 are present. CuV_2O_6 (WD) changed completely after the reaction and was comprised of Cu metal, $CuVO_3$, and V_2O_3. This shows that the catalyst was deeply reduced and contained Cu^0 and V^{3+}. Although $Cu_2V_2O_7$ is not a MV_2O_6 type oxide, it was estimated from XPS analysis that Cu^{2+}, not V^{5+}, may be initially reduced in the reduction of $Cu_2V_2O_7$ (WD) by isobutane [45]. In the case of CaV_2O_6 (WD), the intensity of the diffraction peaks was not very strong. Since anaerobic oxidation proceeded only slightly, the intensity of the peaks declined to 90% and no changes in crystal size were seen [44].

Some results of MV_2O_6 (MM) are shown in Figs. 9–11. Results for the catalysts prepared by the MM method were varied. CaV_2O_6 was almost composed of a single phase. MgV_2O_6 was composed of mainly MgV_2O_6, and a small amount of $Mg_2V_2O_7$ and V_2O_5 were present. In the case of Mn, MnV_2O_6 was the major product, and the product also contained a small amount of V_2O_5 and $Mn_2V_2O_7$. In the case of Zn, the product was composed of ZnV_2O_6 as the major product, along with a significant amount of $Zn_2V_2O_7$. In the case of Cu, CuV_2O_6 was the major product, but significant amounts of $Cu_{0.4}V_2O_5$ and small amounts of $Cu_2V_2O_7$ were also formed. In the cases of Ni and Co, strong diffraction peaks due to V_2O_5 were observed, and

Table 1
Anaerobic oxidation of isobutane over MV_2O_6 (MM)

Catalyst	SSA (m^2/g)	Formed amount (μmol/g)		Selectivity for i-C_4H_8 (%)	Degree of reduction (%)	Crystal structure[a]
		i-C_4H_8	Total			
CaV_2O_6	0.23	16.4	16.4	100	0.06	P
CuV_2O_6		1575	1918	82	23.7	B
ZnV_2O_6	0.37	1281	1648	78	20.0	B
CoV_2O_6		952	1097	87	11.1	N
MgV_2O_6	0.39	746	843	88	2.7	B
MnV_2O_6		488	506	96	2.9	B
NiV_2O_6		1052	1239	85	13.2	N
V_2O_5		1136	1681	68	27.1	

[a] B: brannerite type, P: pseudobrannerite type, and N: NiV_2O_6 type.

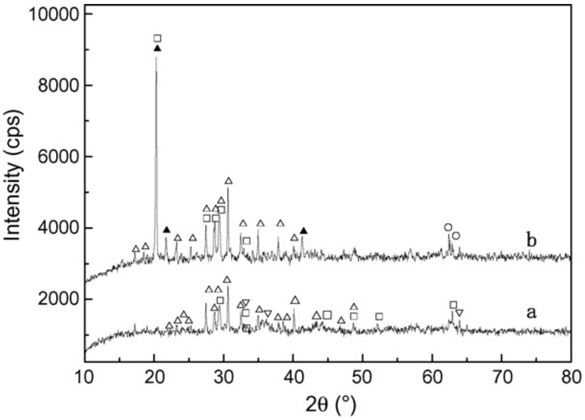

Fig. 9. XRD patterns of CoV_2O_6: (a) after the reaction and (b) before the reaction. (□) CoV_2O_6, (△) $Co_2V_2O_7$, (▽) V_2O_3, (▲) V_2O_5.

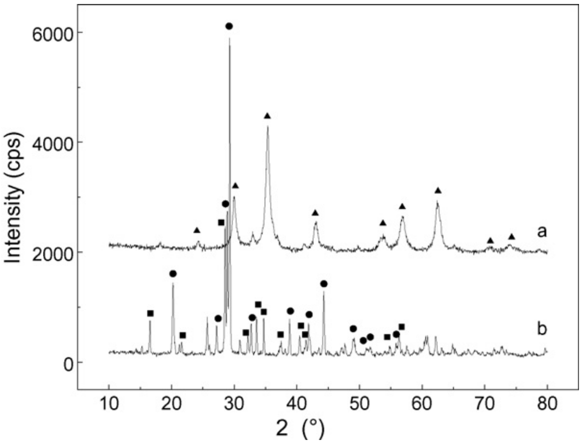

Fig. 10. XRD patterns of ZnV_2O_6 before and after the reaction: (a) after the reaction and (b) before the reaction. (●) ZnV_2O_6, (■) $Zn_2V_2O_7$, (▲) $Zn_3V_3O_8$.

weak diffraction peaks due to MV_2O_6 and $M_2V_2O_7$ type compounds were obtained. The cooling rate was varied; however, it had little effect on the composition of products.

After the anaerobic oxidation of isobutane, CaV_2O_6 (MM) was not changed because no anaerobic oxidation proceeded. The intensity of the peaks due to MgV_2O_6 largely decreased, and small peaks due to $Mg_2V_2O_7$ remained. No new reduced phases were observed. It may be suggested that MgV_2O_6 could be changed to $Mg_2V_2O_7$ and reduced phases of V oxides. After the reaction, small peaks due to V_2O_5 in the MnV_2O_6 (MM) disappeared, and the peaks due to MnV_2O_6 were unchanged. This may suggest that V_2O_5 as an impurity was reduced by isobutane. In the case of ZnV_2O_6 (MM) after the reaction, strong diffraction peaks due to ZnV_2O_6 disappeared, and the diffraction peaks due to $Zn_3V_3O_8$ appeared, which have intermediate strength and wide half width. $Zn_3V_3O_8$ has low valent Zn or V ions, therefore ZnV_2O_6 and small amounts of $Zn_2V_2O_7$ in the initial sample were reduced to form $Zn_3V_3O_8$ and perhaps low valent V oxides during the reaction. The XRD pattern of the CuV_2O_6 (MM) after the reaction was composed of strong diffraction peaks due to Cu metal, and very small peaks due to V_2O_3 and CuV_2O_6. Formation of $CuVO_3$, a reduced oxide phase, was observed in the CuV_2O_6 (WD) after the reaction; however, no formation of this phase was observed. The NiV_2O_6 (MM) catalyst after the reaction was composed of V_2O_3, which is a reduced phase and $Ni_3V_2O_8$, which is not a reduced phase. Ni metal was not found. The CoV_2O_6 (MM) catalyst after the reaction was composed of a large amount of $Co_2V_2O_7$ and a small amount of CoV_2O_6, which are not reduced phases, and only a small amount of V_2O_3 seems to be present. It can be concluded from the results that in anaerobic oxidation, MV_2O_6 compounds tend to form MVO_x type oxides, which have equivalent moles of M and V, and V_2O_3.

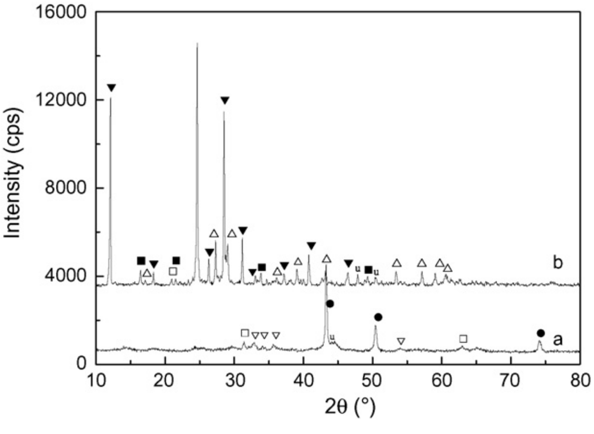

Fig. 11. XRD patterns of ZnV_2O_6 before and after the reaction: (a) after the reaction and (b) before the reaction. (□) CuV_2O_6, (▼) $Cu_{0.4}V_2O_5$, (■) $Cu_2V_2O_7$ (26–569), (△) $Cu_2V_2O_7$ (26–566), (●) Cu, (▽) V_2O_3, u: unknown.

3.4. *Anaerobic oxidation of isobutane over $M_2V_2O_7$ prepared by the molten method*

$Mg_2V_2O_7$ (WD) showed slightly higher selectivity for isobutene than MgV_2O_6 (WD) in aerobic oxidation of isobutane, although the catalytic activity was slightly smaller than that of MgV_2O_6 (WD) [45]. Similar to MgV_2O_6, catalysis of $M_2V_2O_7$ type metal oxides prepared by the molten method (MM) was studied, and the results are shown in Figs. 12 and 13.

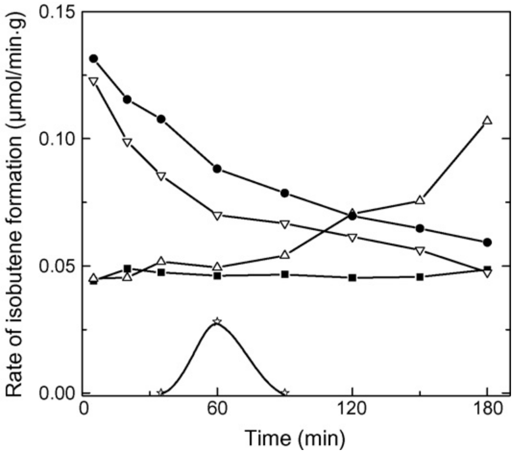

Fig. 12. Anaerobic oxidation of isobutane over $M_2V_2O_7$: (■) $Mg_2V_2O_7$, (△) $Zn_2V_2O_7$, (☆) $Cu_2V_2O_7$, (▽) $Mn_2V_2O_7$, (●) $Ca_2V_2O_7$.

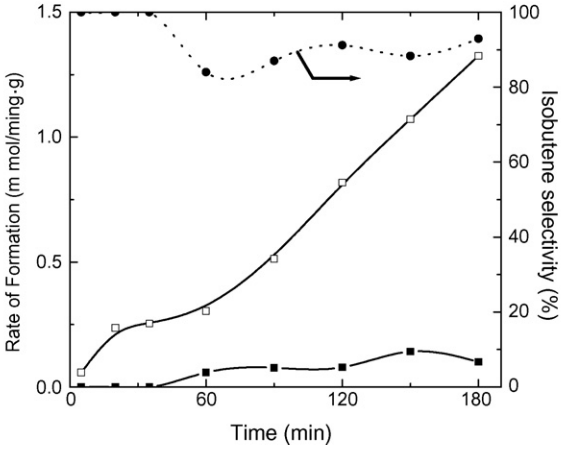

Fig. 13. Anaerobic oxidation of isobutane over $Co_2V_2O_7$: (□) isobutene formation, (■) CO_x formation, (●) selectivity for isobutene.

Isobutene was the only product obtained over every catalyst, and CO_x was only obtained over $Co_2V_2O_7$ and $Mn_2V_2O_7$. As can be seen from the figures, among the oxides, $Co_2V_2O_7$ showed significantly higher formation rates of isobutene with an activity an order of magnitude higher than the other oxides. A steady rate of about 0.05 μmol/min g was observed over the $Mg_2V_2O_7$ (MM) catalyst. The rates decreased with reaction time over $Mn_2V_2O_7$ and $Ca_2V_2O_7$; on the contrary, the rate increased with time over $Zn_2V_2O_7$, and isobutene formation was observed only at around 60 min over $Cu_2V_2O_7$. The activity of these oxides except for $Co_2V_2O_7$ was generally quite small. The selectivity of CO_x was 39.4% only at around 60 min over $Mn_2V_2O_7$. In the case of $Co_2V_2O_7$, which showed the highest activity, isobutene selectivity exceeded 90% over wide ranges of time. Therefore, it is concluded that $Co_2V_2O_7$ is a suitable oxide for a thin layer reactor for the anaerobic oxidation of isobutane.

In $Co_2V_2O_7$, the vanadium is in a tetrahedral environment. The cobalt atoms, in contrast, form isolated linear chains of CoO_6 octahedra, which are interconnected in zigzag chains [47,48]. It was reported that the crystal structure of α-$Zn_2V_2O_7$ contains only one type of metal site, which is five-coordinated by a somewhat distorted trigonal bipyramid of ZnO_5 [49] and $Cu_2V_2O_7$ [51]. β-$Mn_2V_2O_7$ adopts the thortveitite structure containing edge-sharing MnO_6 octahedra and corner-sharing $V_2O_7{}^{4-}$ divanadate groups, which have staggered conformation and linear $V–O_b–V$. The structure of α-$Mn_2V_2O_7$ differs from that of β-$Mn_2V_2O_7$ mainly by the bending of the $V–O_b–V$ moieties, as observed in the low-temperature forms of other thortveitite-like compounds [50]. $Mg_2V_2O_7$ is composed of VO_4 tetrahedra and MgO_6 octahedra, and Ca is surrounded by seven oxygen ions in the $Ca_2V_2O_7$ structure. The environment of each metal ion is different, however, no characteristic was found to relate the crystal structure of $M_2V_2O_7$ to the catalytic activity. Determination of the rate of oxygen ion transfer at the catalyst surface and the diffusion rate of oxygen ions in the bulk of the oxides will be helpful to understand the catalytic activity of $M_2V_2O_7$ for anaerobic oxidation of alkanes.

3.5. *The effect of substitution by metals to the Mg site in $Mg_{1.8}M_{0.2}V_2O_7$ prepared by MM*

The magnesium ion is not easily redoxable, so the improvement of the redoxability of the catalyst by the substitution of Mg ions with redoxable metal ions is considered here. Since it has been reported that $M_2V_2O_7$ type oxides can be easily mixed with each other, $Mg_{1.8}M_{0.2}V_2O_7$ oxides with 10 at.% of Mg ions in $Mg_2V_2O_7$ substituted were prepared by molten liquids at 1373 K and the effects of substitution were studied. All the catalysts gave intermediate strength diffraction patterns due to $Mg_2V_2O_7$. In the patterns of $Mg_{1.8}Zn_{0.2}V_2O_7$ (MM) and $Mg_{1.8}Fe_{0.2}V_2O_7$ (MM), several unknown peaks were observed below 10°. It was concluded that the added metal ions are occupying the Mg lattice sites because the *d* values of the main peaks in XRD were shifted higher in agreement with the substituted ion radii. The results of catalytic reactions over these catalysts are shown in Fig. 14. Substitution by Cu significantly increased the activity, substitution by Fe and Co slightly increased the catalytic activity, and substitution by Mn and Zn had less of an influence on the activity.

As can be seen from Fig. 13, the activity of simple $M_2V_2O_7$ (MM) was very low, especially that of $Cu_2V_2O_7$ (MM); however, it is clear that partial substitution of Mg with Cu in $Mg_2V_2O_7$ (MM) brought about a remarkable improvement in activity. CO_x formation was observed only at the initial stage of the reaction until 5 min over $Cu_2V_2O_7$ (MM). Optimization may lead to the development of a metal oxide suitable for a thin layer reactor.

3.6. *Active oxygen species in aerobic and anaerobic oxidations of isobutane*

In aerobic oxidation, molecular oxygen in the gas phase may supply oxygen ion defects when oxygen ions at the catalyst surface are consumed by the oxidation of alkanes. On the other hand, in anaerobic oxidation, oxygen ions in the bulk of the cat-

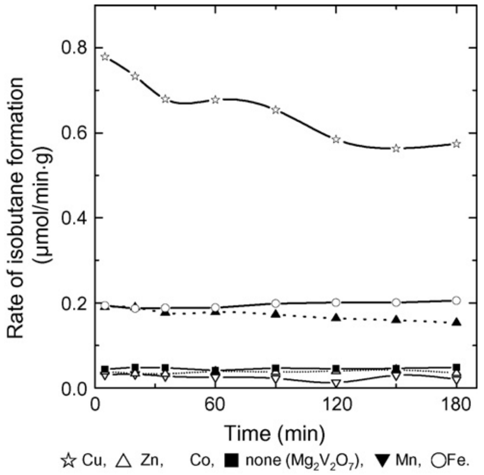

Fig. 14. The effects of the substitution of Mg sites of $Mg_2V_2O_7$ with redoxable ions on the catalytic activity: (☆) Cu, (△) Zn, (▲) Co, (■) none ($Mg_2V_2O_7$), (▽) Mn, (◯) Fe.

Table 2
Comparison of aerobic and anaerobic oxidation of isobutane

O_2 concentration in the feed gas (mol%)		0	2.1	3.2	4.3
O_2 feed rate (μmol/min)		0	25.0	38.3	52.9
Rate of O_2 introduced to products (μmol/min)	i-C_4H_8	11.7	11.0	9.5	8.6
	CO	2.3	4.8	6.9	6.7
	CO_2	6.1	27.5	41.4	52.0
	Total	20.1	43.4	57.8	67.0
Rate of diffused oxygen from the bulk of the catalyst (μmol/min)		20.1	18.4	19.5	14.5

Catalyst 2.50 g, feed gas concentration: isobutane 75 mol%, N_2 balance, 673 K.

alyst will diffuse to oxygen ion defects at the catalyst surface formed by the reaction with alkanes. When the concentration of oxygen in the gas phase is changed, it may be possible to distinguish the roles of these two kinds of oxygen in the oxidation of isobutane: molecular oxygen and diffused oxygen ions. Since anaerobic oxidation is not a steady reaction, the comparison of aerobic and anaerobic oxidations is difficult. However, aerobic oxidation of isobutane was carried out using various oxygen concentrations in the feed, and the results were compared to that of anaerobic oxidation of isobutane using MgV_2O_6 (WD). The results are summarized in Table 2. When no molecular oxygen was fed into the reactor, leading to anaerobic oxidation, the rate of oxygen introduced to products was calculated to be 20.06 μmol/min. This is the rate of oxygen diffusion from the bulk of the MgV_2O_6 catalyst at 673 K. In the experiments with 2.1–4.3% O_2 concentration, both aerobic and anaerobic oxidation occurred, and the carbon recovery was near 100%. The amount of oxygen required to form products exceeded the amount of O_2 supplied in the feed, and only a trace amount of hydrogen was formed, suggesting that no simple dehydrogenation proceeded. In the aerobic oxidation of isobutane using a feed gas containing 2.1 mol% O_2, the rate of O_2 introduced to the products was calculated to be 43.35 μmol/min. Since molecular O_2 was supplied at a rate of 25 μmol/min, the rate of oxygen diffusion from the bulk was estimated to be 18.35 μmol/min. Similarly, the rate was calculated for each run with varied oxygen concentration. At 2.1% and 3.2% oxygen, the calculated rates of diffused oxygen from bulk are very similar to each other, which suggest that the rates of diffused oxygen from the bulk are constant, and that the O_2 added in the feed is consumed to form CO and CO_2. When sufficient concentrations of molecular O_2 were supplied in the feed gas, such as 4.3%, a part of the formed isobutene seems to be successively oxidized to CO and CO_2 by reaction with oxygen species derived from molecular oxygen. In another case, isobutene formation by diffused oxygen anions might be decelerated because the complete oxidation by molecular oxygen was accelerated.

These experimental results are very important as an example where lattice oxygen ions and oxygen species derived from molecular oxygen play separate roles in the oxidation of alkane.

4. Conclusions

(1) MgV_2O_6 prepared by the molten method can react with isobutane to give isobutene selectively at 673 K suggesting that this compound can be utilized to thin layer oxidation reactor. If the total degree of reduction of the catalyst were kept to more than 3.0%, isobutene would be obtained with selectivity greater than 99%.

(2) No single phase of MV_2O_6 was obtained by molten method. However, catalytic activity determined by isobutene formation was in the order of $CuV_2O_6 > ZnV_2O_6$, $V_2O_5 > NiV_2O_6 > CoV_2O_6 > MgV_2O_6 > MnV_2O_6 \gg CaV_2O_6$ and some of these compounds would be utilized in thin layer reactor for selective isobutene formation by the choice of the conditions.

(3) Among $M_2V_2O_7$ (MM), $Co_2V_2O_7$ showed high catalytic activity but the activity of these oxides except for $Co_2V_2O_7$ was generally quite small.

(4) $Mg_2V_2O_7$ of which 10% of Mg is substituted by various metals prepared by molten method gave single phase. Substitution by Cu significantly increased the activity and substitution by Fe and Co slightly increased the catalytic activity.

(5) It is shown by the oxidation at low O_2 concentration as 2–3% that two types of oxidations occurred simultaneously: isobutene formation by the lattice oxygen ions diffused from the bulk, and CO and CO_2 formation by the oxygen species derived from molecular oxygen in the gas phase.

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