Anaerobic oxidation of isobutane
II. Catalysis by Mg–V complex oxides

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Abstract

Anaerobic oxidation of isobutane was studied using MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$. Isobutene, a small amount of CO_x, and trace amount of oxygen containing compounds were formed. CO_2 was formed mainly at the beginning of the reaction and decreased with reaction time. Catalytic activity of $Mg_2V_2O_7$ was slightly higher than that of MgV_2O_6 but the CO_x formation over MgV_2O_6 was more than over $Mg_2V_2O_7$. $Mg_3V_2O_8$ was the least active. Therefore, $Mg_2V_2O_7$ is the most suitable for oxidative hydrogenation of isobutane under the anaerobic reaction conditions. The equilibration between $^{16}O_2$ and $^{18}O_2$ over MgV_2O_6 was faster than over $Mg_2V_2O_7$ or $Mg_3V_2O_8$ at 673 K. The rate of equilibration between $^{18}O_2$ and lattice oxygen over MgV_2O_6 was similar to that over $Mg_2V_2O_7$, which was faster than over $Mg_3V_2O_8$. Highest yield of isobutene formation over $Mg_2V_2O_7$ would come from the character of $Mg_2V_2O_7$, in which mobility of the lattice oxygen is great but surface reaction of isobutane was not so fast. Higher activity for isobutene formation may come from the nature of $Mg_2V_2O_7$, of which mobility of the lattice oxygen is great but surface reaction of isobutane was not so much fast. Mn, Cr, Fe, Ni and Co can be introduced into $Mg_2V_2O_7$ to give a single phase. Substitution of Co, Cu and Cr for Mg increased the activity of $Mg_2V_2O_7$ for isobutane oxidation and substitution of Ni and Mn scarcely affected the activity but substitution of Fe and Zn decreased the activity. Substitution of all the metal ions slightly increased the isobutene selectivity. MgO, MgV_2O_4 and $Mg_3V_2O_8$ were observed in the sample after the anaerobic oxidation of isobutane. Cu containing catalyst was reduced to give Cu metal.
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1. Introduction

Selective oxidation of alkanes is a challenging topic because products are easily oxidized than alkanes and even if selective oxidation is achieved, products are easily oxidized to deeply oxidized products. So far, a lot of studies have been carried out and some efficient catalyst systems were reported [1–12]. The authors have studied the oxidation of isobutane over metal phosphates. For example, $Ni_2P_2O_7$, in which the mobility of the lattice oxygen ions is very low, catalyzes oxidative dehydrogenation of isobutane at 723–823 K [13–20]. When an oxygen poor (5 mol%) and isobutane rich (75 mol%) feed gas is introduced, isobutene was selectively formed in selectivity higher than 85%.

In this catalytic reaction, supply of the oxygen from gas phase is limited and oxygen ions are hardly supplied from the bulk and many isobutane molecules attack surface oxygen ions in the low concentration. However, this reaction system requires 823 K to obtain sufficient reaction rates.

To obtain higher activity and selectivity, the authors have studied the oxidation of alkanes in the absence of oxygen in the feed. After selective oxidation of alkanes is achieved, reduced catalysts might be oxidized to the initial state in a separate reactor. The previous paper [20] showed that single oxides and complex oxides of V, Nb, and Ta were active and relatively selectively formed isobutene, and the activity of Na_2MoO_4 and Ag_2MoO_4 was very low. Reaction temperatures suitable for these oxides were significantly lower than those for $Ni_2P_2O_7$. The order of the activity for the anaerobic oxidation of isobutane of MV_2O_x type oxides was $CuV_2O_6 \gg CoV_2O_6 > MgV_2O_6 > ZnV_2O_6 \gg ZrV_2O_7 > CaV_2O_6$ [20]. MgV_2O_6 was the most selective for

isobutene formation. CuV_2O_6 was active but not selective. Combination of vanadium and easily redoxable metal ions tends to accelerate deep oxidation [21]. Catalysis is not so simple because MgV_2O_6, which contains not easily redoxable Mg^{2+} ions, has relatively high activity and high selectivity but CaV_2O_6, which also contains not easily redoxable Ca^{2+} ions, are less active.

V–Mg–O systems have been reported to be effective catalysts for the oxidative dehydrogenation of light alkanes. According to the phase diagram, three stable phases exist in this system; they are magnesium orthovanadate ($Mg_3V_2O_8$), magnesium pyrovanadate ($Mg_2V_2O_7$), and magnesium metavanadate (MgV_2O_6). Most of the previous studies focused on the oxidation in the presence of gaseous oxygen. So that, anaerobic oxidation of isobutane over Mg–V complex oxides and the role of gaseous oxygen were studied in this paper. The modification of Mg–V complex oxides by other elements was also studied.

2. Experimental

2.1. Preparation of catalysts

Complex oxides were prepared as follows. An aqueous solution of ammonium metavanadate was mixed with an aqueous solution of $Mg(NO_3)_2 \cdot 3H_2O$ or the corresponding metal nitrates with stirring and the mixture was stirred and heated to dryness on a hot plate. Resultant powder was pressed, crashed, and sieved to 14–32 mesh. Finally, the catalysts were calcined in air at 923 K for 15 h except for 973 K ($Mg_{1.8}Fe_{0.2}V_2O_7$) and 823 K ($Mg_{1.8}Co_{0.2}V_2O_7$).

Specific surface areas of the catalysts before reaction were 2.0 m^2/g ($Mg_2V_2O_7$), 4.0 m^2/g ($Mg_{1.8}Cr_{0.2}V_2O_7$), 3.0 m^2/g ($Mg_{1.8}Mn_{0.2}V_2O_7$), 3.0 m^2/g ($Mg_{1.8}Fe_{0.2}V_2O_7$), 5.2 m^2/g ($Mg_{1.8}Co_{0.2}V_2O_7$), and 4.0 m^2/g ($Mg_{1.8}Ni_{0.2}V_2O_7$), respectively.

2.2. Catalytic reaction

Isobutane oxidation under anaerobic conditions were conducted at atmospheric pressure in a fixed-bed flow reactor using a feed gas of 30 mol% isobutane and 70 mol% N_2. The feed gas rate was 1.22 mmol/min (30 cm^3/min at 298 K). The experimental apparatus was described in the previous paper [19].

The products were analyzed using gas chromatography and GC-MS. In a blank test, catalyst zone of the reactor was filled with silicon carbide instead of catalyst; no conversion of isobutane could be detected.

2.3. Characterization of catalysts

The structure of the catalysts was characterized by XRD (Rigaku RINT4500). BET surface areas were measured by N_2 adsorption at liquid N_2 temperature. 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 the 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

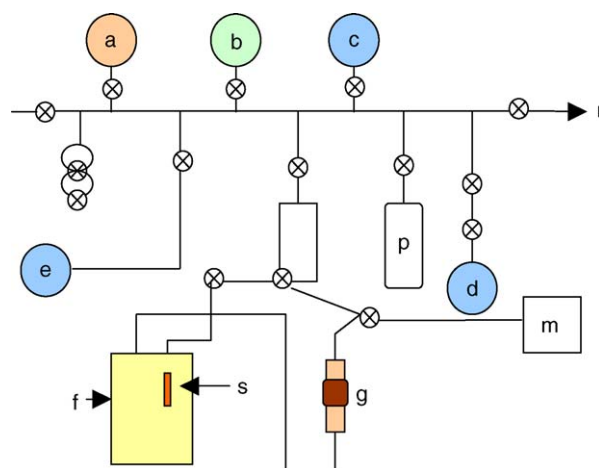Fig. 1. Schematic diagram of the circulated reaction system: a: CO_2, b: He, c: $^{16}O_2 + {}^{18}O_2$, d: $^{16}O_2$, e: $^{18}O_2$, f: furnace, g: gas circulation pump, m: MS, p: pressure gauge, r: evacuation system, s: sample. Volume (s + g): 43.6 cm^3.

to ambient temperature and then it was flashed by a mixed gas of 4.88% H_2 and 95.12% N_2. After the base line was stabilized, the sample was heated to 823 K at the rate of 10 K/min.

2.4. Tracer studies

Oxygen isotope equilibration was carried out using an apparatus depicted in Fig. 1. The samples were evacuated at 823 K for 0.25 h and O_2 (13,332 Pa) was introduced for 0.5 h and then the temperature was cooled to 673 or 773 K by 1 K/min. The samples were then evacuated at the same temperature for 0.5 h. A mixture of $^{16}O_2$ and $^{18}O_2$ or concentrated $^{18}O_2$ gas was introduced the circulation system and equilibration was commenced. Gaseous oxygen was analyzed by MS.

3. Results and discussion

3.1. Comparison of MgV_2O_6, $Mg_2V_2O_7$ and $Mg_3V_2O_8$

In our previous paper, we reported that MgV_2O_6 showed higher isobutene yield in anaerobic oxidation of isobutane than MV_2O_6 (M = Cu, Co, Zn, Zr, and Ca). Therefore, three complex oxides composed of Mg and V were studied. Results per unit weight and unit surface area of catalysts are shown in Figs. 2 and 3. The initial rate of isobutane consumption per unit weight was the highest over MgV_2O_6. The formation rate was slightly increased, attained a maximum at 100 min and then decreased. In contrast, the initial rate over $Mg_2V_2O_7$ was slightly lower than that over MgV_2O_6 but the rate increased relatively sharply until 360 min after momentary decrease within 20 min. It began to decrease again at 360 min. The total amounts of isobutane consumption over MgV_2O_6 and $Mg_2V_2O_7$ were similar to each other. The initial rate over $Mg_3V_2O_8$ was much lower than that over the other catalysts; therefore, the reacted amount of isobutane was much smaller than that over the other catalysts. Since the structure of these catalysts changes with the progress of the reaction, activity of the catalysts was compared at the beginning of the oxidation. Obviously the order of the activity of
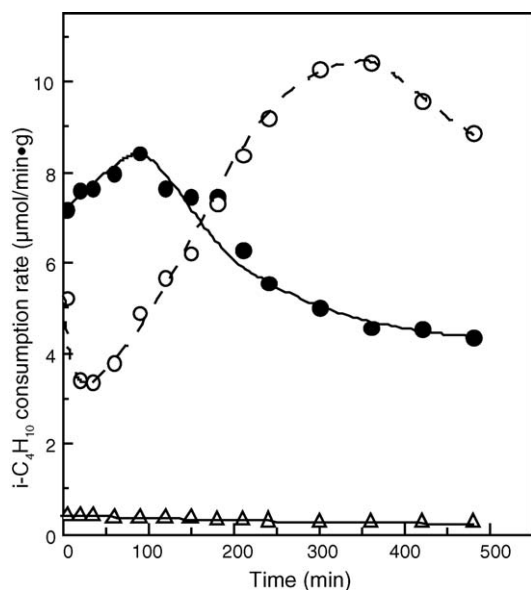
Fig. 2. Catalytic activity per unit weight of Mg–V oxides for anaerobic oxidation of isobutene: (●) MgV_2O_6; (○) $Mg_2V_2O_7$; (△) $Mg_3V_2O_8$; 673 K.

the three complex oxides is $MgV_2O_6 > Mg_2V_2O_7 > Mg_3V_2O_8$. The specific surface area (SSA) of these catalysts were $4 m^2/g$ (MgV_2O_6), $3 m^2/g$ ($Mg_2V_2O_7$), and $2 m^2/g$ ($Mg_3V_2O_8$), respectively. The SSA of the catalysts also changed with the progress of the reaction. Although the changes in SSA during the reaction were not known, the consumption rates were tentatively calculated using the initial SSA and the results are shown in Fig. 2. According to this figure, the amounts of the isobutane consumption over unit surface area were the same over MgV_2O_6 and $Mg_2V_2O_7$. The initial rate at 5 min over $Mg_2V_2O_7$ was higher than that over MgV_2O_6. Since no crystal growth in a special direction was observed in these catalysts, average amounts of exposed V ions of MgV_2O_6 should be larger than those of

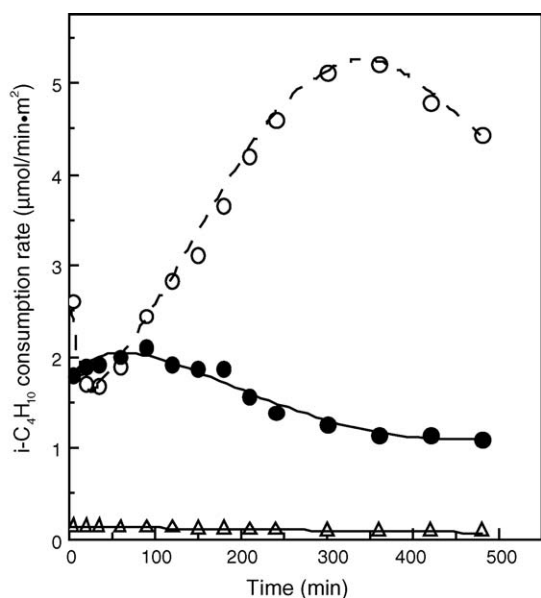Fig. 3. Catalytic activity per unit surface area of Mg–V oxides for anaerobic oxidation of isobutene: (●) MgV_2O_6; (○) $Mg_2V_2O_7$; (△) $Mg_3V_2O_8$; 673 K.
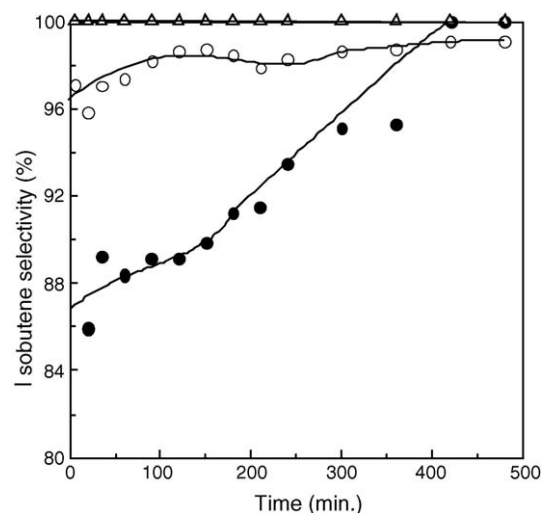

Fig. 4. Selectivity of isobutene in the anaerobic oxidation of isobutene: (●) MgV_2O_6; (○) $Mg_2V_2O_7$; (△) $Mg_3V_2O_8$; 673 K.

$Mg_2V_2O_7$ in contrast to the experimental results. Therefore, the differences in the catalytic activity may reflect the character of the oxides. In anaerobic oxidation of isobutane, the major product was isobutene. The formation of CO_2 was observed in the initial stage of the oxidation over active catalysts. The selectivity for isobutene over the catalysts is shown in Fig. 4. Over MgV_2O_6, isobutene selectivity was about 86–89% until initial 30 min, increased gradually with time and approached 100% at 420 min. Isobutene selectivity was 100% over less active $Mg_3V_2O_8$ throughout the experiment. The selectivity as high as about 97% was observed over $Mg_2V_2O_7$, which showed slightly smaller activity than MgV_2O_6. It increased with time; however, it never reached 100% until 480 min. Relatively high rate of formation of hydrogen was observed over MgV_2O_6. Ratio of H_2/isobutene was gradually increased with time, as 1.22 and 22.2% at 60 and 210 min, respectively. But the ratio was sharply increased to 60 and 90% at 300 and 420 min. Therefore, oxidative dehydrogenation of isobutane was dominant until 270 min and the essential reaction changed to simple dehydrogenation over MgV_2O_6. However, very small amount of hydrogen was formed over the other catalysts. The ratio was less than 5.0% until 120 min and never exceeded 10.0% over $Mg_2V_2O_7$ and the ratio over $Mg_3V_2O_8$ was less than 3.0% until 480 min. These results suggest that oxidative dehydrogenation was the major reaction over $Mg_2V_2O_7$ and $Mg_3V_2O_8$.

The total amount of formed isobutene until 480 min over $Mg_2V_2O_7$ is higher than that over MgV_2O_6 and the rate over $Mg_2V_2O_7$ is about twice as high as that over MgV_2O_6. Therefore, in terms of selective isobutene formation, $Mg_2V_2O_7$ is the most suitable catalyst among these oxides.

In order to examine the nature of the catalysts, oxygen isotope equilibration was carried out using a mixture of $^{16}O_2$ (46.7 atomic%) and $^{18}O_2$ (53.3 atomic%) at 673 K where no isotope exchange reaction between lattice oxygen and gaseous oxygen could proceed. It was confirmed that the concentration of ^{18}O in the gas phase was constant during the reaction. The rate of decrease in $^{18}O_2$ concentration is shown in Fig. 5. The rates were
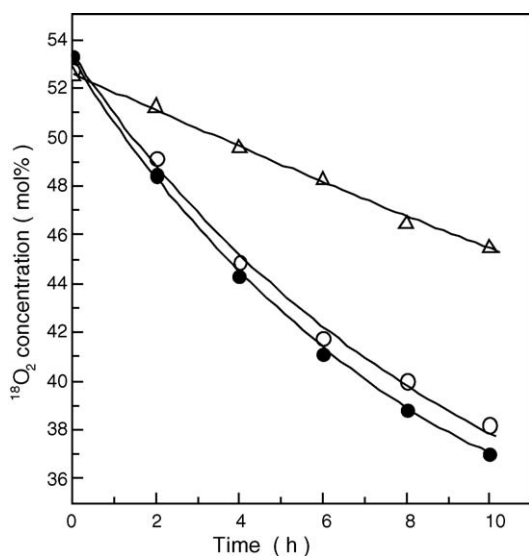
Fig. 5. Oxygen isotope equilibration between $^{16}O_2$ and $^{18}O_2$ over Mg–V oxides: (●) MgV_2O_6; (○) $Mg_2V_2O_7$; (△) $Mg_3V_2O_8$; 673 K.

Fig. 6. Oxygen isotope equilibration between $^{18}O_2$ and lattice oxygen, $Mg_3V_2O_8$, 773 K: (●) MgV_2O_6; (○) $Mg_2V_2O_7$; (△) $Mg_3V_2O_8$.

dependent on the deviation from equilibrium $^{18}O_2$ concentration by first order; therefore, the rate constants were determined and summarized in Table 1. The rate constant of MgV_2O_6 is somewhat larger than that of $Mg_2V_2O_7$ and that of $Mg_3V_2O_8$ is significantly small. This may suggest that the concentration of oxygen sites, which can be used for the equilibration, or the rate of adsorption–desorption rate for oxygen molecules over MgV_2O_6 and $Mg_2V_2O_7$ are higher than that over $Mg_3V_2O_8$.

Next the equilibration of oxygen isotope between gaseous oxygen and lattice oxygen was studied using concentrated $^{18}O_2$ at 773 K. The sample used was 0.50 g, which contained 6750 μmol of oxygen for MgV_2O_6, 6667 μmol for $Mg_2V_2O_7$, 6604 μmol for $Mg_3V_2O_8$, respectively. 13,332 Pa of $^{18}O_2$ was introduced to the circulation system 43.6 cm^3 in volume, which was 233 μmol. On introducing $^{18}O_2$ to the catalysts, evolution of $^{16}O^{18}O$ appeared as shown in Fig. 6. Under the assumption that the formation rate of $^{16}O^{18}O$ depends on the deviation from equilibrium concentration by first order, rate constants of $^{16}O^{18}O$ formation were calculated, which are summarized in Table 2. As can be seen from the table, rate constant of MgV_2O_6 is nine times as large as that of $Mg_2V_2O_7$, which is only twice as large as that of $Mg_3V_2O_8$. These rate constants are composed of the rate constant for oxygen exchange between gas and solid phases and/or that for the migration rate in the bulk. In the isobutane oxidation, lattice oxygen may migrate from the bulk to the surface and the oxide catalysts are totally reduced. On the other hand, in

this equilibration experiments, lattice oxygen ions migrate in the bulk under the fully oxidized state. If single crystal or well dense samples can be obtained, self-diffusion constant of oxygen for Mg–V oxides can be determined by measuring depth profile of ^{18}O concentration of the samples after equilibration. So that the preparation of dense samples were attempted but no dense samples was obtained. However, the results in Tables 1 and 2 suggest that oxygen ions in the bulk of MgV_2O_6 is easily moved to the surface when surface oxygen ions are removed. Although the oxygen ions of $Mg_2V_2O_7$ and $Mg_3V_2O_8$ are somewhat similar to each other, but the former is suitable for isobutane oxidation because the mobility of lattice oxygen ions is larger than that of the latter.

As for the active phases for catalytic oxidation of light alkanes under aerobic conditions, inconsistent conclusions have been reported by different researchers. Oganowski and Mista [22] and Chaar et al. [23,24] attributed the most active phase to $Mg_3V_2O_8$. On the other hand, Siew Hew Sam et al. [25] suggested that $Mg_2V_2O_7$ is the most active phase and that $Mg_3V_2O_8$ caused complete oxidation. Catalytic performance not only depends on the composition and structure of catalyst, but also depends on the alkane feed. In the previous paper, we studied the catalytic performance over these three magnesium vanadate for the oxidative dehydrogenation of isobutane to isobutene in the presence of gaseous oxygen and reported that the order of catalytic activity at 673–723 K was $Mg_2V_2O_7 > MgV_2O_6 > Mg_3V_2O_8$ and that $Mg_2V_2O_7$ was the most selective for isobutene [19]. Also in anaerobic oxidation, $Mg_2V_2O_7$ had a slightly higher activity than MgV_2O_6, and the isobutene selectivity over $Mg_2V_2O_7$ was higher than that over MgV_2O_6. $Mg_3V_2O_8$ had the lowest activity in the three magnesium vanadium oxides. $Mg_2V_2O_7$ was the most active phase for oxidative dehydrogenation of isobutane to isobutene.

In the oxidation of isobutane under the anaerobic conditions, the isobutene selectivity was much higher than that under the aerobic conditions. However, the general trend was similar to

Table 1
Rate constants for $^{16}O_2$–$^{18}O_2$ and $^{18}O_2$-lattice oxygen equilibration

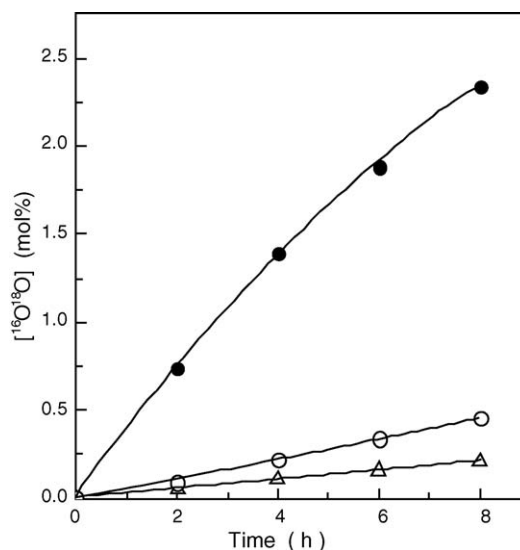| Equilibration	Temperature (K)	Rate constant (m^{-2} h^{-1})		
		MgV_2O_6	$Mg_2V_2O_7$	$Mg_3V_2O_8$
$^{16}O_2$–$^{18}O_2$	673	0.112	0.089	0.033
$^{18}O_2$-lattice oxygen	773	0.125	0.014	0.0076

Catalyst: 0.50 g.

Table 2
Activity and structure of the modified catalysts

	XRD		SSA m²/g (after)	TPR		Isobutane oxidation		Degree of Reduction (%)
	Before	After the reaction		H_2 consump. (μmol)	Commencing temp. (K)	Total i-C'_4 consump.	Total i-C'_4 select. (%)	
Mg	Single phase	$Mg_2V_2O_7$ (400), MgO (1150), $MgV_2O_4 + Mg_3V_2O_8$ (400)	2.0 (32)	7.8	653	3717	98.6	16.3
Cr	Single phase	$Mg_2V_2O_7$ (300), MgO (1500), $Mg(V,Cr)_2O_4$ (500)	4.0 (33)	119.6	513	4144	99.5	16.5
Mn	Single phase	$Mg_2V_2O_7$ (700), MgO (1000), $MgV_2O_4 + Mg_3V_2O_8$ (700)	3.0 (20)	60.5	523	3608	99.6	14.8
Fe	Single phase	$Mg_2V_2O_7$ (400), MgO (1300), $MgV_2O_4 + Mg_3V_2O_8$ (1000)	3.0 (24)	153	593	3011	99.0	13.2
Co	Single phase	$Mg_2V_2O_7$ (600), MgO (820)	5.2 (30)	242	553	4721	99.0	19.5
Ni	Single phase	$Mg_2V_2O_7$ (600), MgO (2000), MgV_2O_4 (400)	4.0 (24)	412.8	473	3883	99.6	15.7
Cu	$Mg_2V_2O_7$ (900), $Cu_2V_2O_7$ (250), $CuVO_3$ (50)	MgO (1000), Cu (400), $Mg_3V_2O_8$ (400)	2.1	–	–	4342	99.3	21.6
Zn	$Mg_2V_2O_7$(1500), MgV_2O_6(150)	MgO (1400), MgV_2O_4 (300)	2.8	–	–	2358	99.8	10.0

each other. Yield of isobutene formation was the highest over $Mg_2V_2O_7$. This would come from the character of $Mg_2V_2O_7$, in which mobility of the lattice oxygen is great but the surface reaction of isobutane was not so fast. Relatively high CO_x selectivity over MgV_2O_6 may be due to the consecutive oxidation of isobutene by a great mobility of oxide ions in MgV_2O_6. When the initial rate and the rate at 480 min for the reduction of the catalysts were plotted against the rate of lattice oxygen migration estimated from the rate of exchange reaction, no proportional correlation was observed. In this isotope equilibration experiments, we can obtain neither the rate constants for the exchange between gaseous O_2 and the catalyst surface nor the diffusion constants of oxygen ions in the bulk of the oxides. Since both constants can be obtained separately from analysis of the depth profile of ^{18}O of the specimen, which is treated with $^{18}O_2$, preparation of dense specimen is helpful.

We considered the mobility of O^{2-} in the Mg–V oxides using bond length between O^{2-} and surrounding metal ions in Table 3. O^{2-} ion in the $Mg_3V_2O_8$ is surrounded by many metal ions or strongly bounds to V ion, suggesting that O^{2-} is hard to migrate in the bulk. This well agreed with low catalytic activity of the $Mg_3V_2O_8$. As for MgV_2O_6, O3 ion is surrounded by three V ions with intermediate and long bond lengthes. O5 and O7 of the $Mg_2V_2O_7$ were surrounded by two Mg^{2+} ions with long distances and V ion with intermediate length. Therefore, these O^{2-} ions could be capable of fast migration in the bulk and cause the high catalytic activity of MgV_2O_6 and $Mg_2V_2O_7$.

3.2. Relation between aerobic and anaerobic oxidation of isobutane

As reported in the previous paper, oxygen in the feed gas seems to contribute to the CO_x formation in aerobic oxidation of isobutene [15]. In contrast, oxidative dehydrogenation of isobutane proceeds selectively under anaerobic reaction conditions.

Isobutane concentration of 30% has been taken in anaerobic reaction conditions in the previous sections. To avoid the effect of isobutane concentration on the reaction, anaerobic oxidation of isobutane was carried out using the feed gas containing 75 mol% isobutane, which is the same as the isobutane concentration for aerobic oxidation, and the results are shown in Fig. 7. The shape of the rate curve was similar to that of 30% isobutane concentration but the formation rate of isobutene was significantly increased. Surprisingly, the formed amount of isobutene (5978 μmol) until 360 min in the case of 75% isobutane in the feed was 2.5 times of that in the case of 30 mol% isobutane in the feed. Namely, the formation rate of isobutane was increased to 2.5 times by the 2.5-fold increase in the isobutane concentration in the feed. This suggests that the oxygen supplied sufficiently
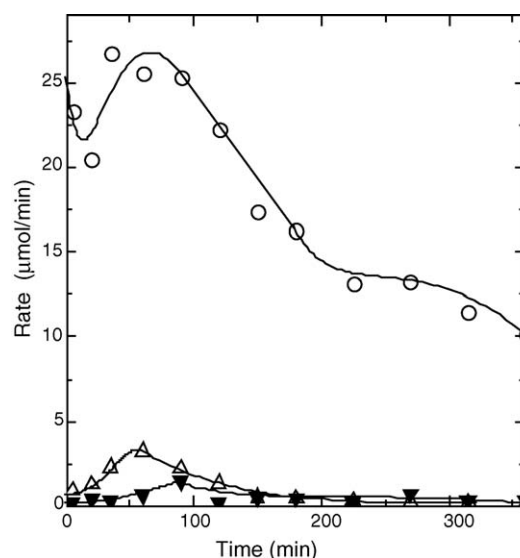
Fig. 7. Anaerobic oxidation of isobutane over MgV_2O_6; 673 K, feed gas: 75 mol% isobutane, 25 mol% N_2: (○) isobutene; (△) CO_2; (▼) H_2.

Table 3
Bond distances between O ions and surrounded ions

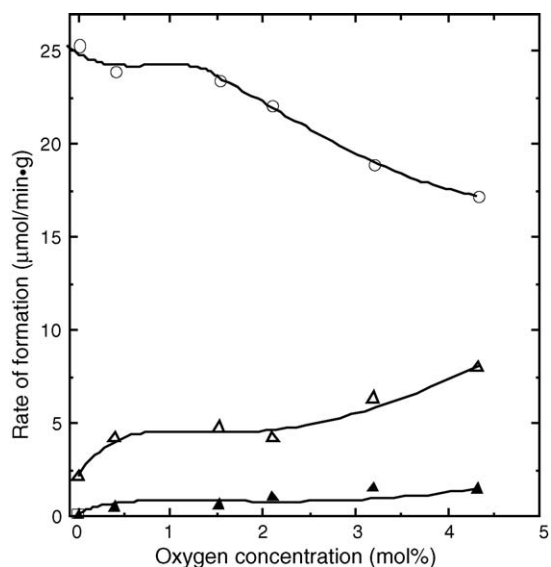|	MgV_2O_6	
O1	V1	0.1671
	Mg1	0.2198
	Mg2	0.2198
O2	V1	0.1665
	Mg1	0.2024
O3	V1	0.1853
	V2	0.1853
	V3	0.2111
	$Mg_2V_2O_7$	
O1	V1	0.1817
	V2	0.1785
	Mg2	0.2221
O2	V2	0.1744
	Mg	0.2083
	Mg	0.2090
	V	0.2440
O3	V1	0.1629
	Mg1	0.1992
O4	V2	0.1682
	Mg1	0.2050
	Mg1	0.2246
O5	V1	0.1702
	Mg2	0.2049
	Mg2	0.2104
O6	V2	0.1665
	Mg1	0.2098
	Mg2	0.2143
O7	V1	0.1710
	Mg2	0.2081
	Mg2	0.2094
	$Mg_3V_2O_8$	
O1	V1	0.1716
	Mg2	0.2022
	Mg2	0.2022
	Mg1	0.3444
O2	V1	0.1809
	Mg1	0.2035
	Mg2	0.2135
	Mg2	0.2135
O3	V1	0.1695
	Mg2	0.2118
	Mg1	0.2130
	V_2O_5	
O1	V1	0.1576
	O3	0.2651
	O2	0.2736
	O2	0.2736
	V1	0.2793
O2	V1	0.1878
	V1	0.1878
	V1	0.2018
O3	V1	0.1778
	V1	0.1778

Fig. 8. Effect of oxygen concentration in the feed gas; MgV_2O_6: (○) isobutene; (△) CO_2; (▲) CO; 673 K.

from the bulk. CO_x (mainly CO_2) formation, however, was slightly decreased compared to low isobutane concentration. The results of aerobic and anaerobic oxidation are summarized in Fig. 8. The rate at zero oxygen concentration is taken by the initial reaction rate of isobutane in anaerobic oxidation. According to this figure, the rate curve seems to be continuous; therefore, the anaerobic oxidation can be thought to be an extension of aerobic oxidation.

3.3. Reoxidation of reduced catalysts and regeneration of anaerobic oxidation of isobutane

The Mg–V oxide catalysts were reduced after the oxidation of isobutane. Mg–V oxides were reduced by 19.6, 16.3, and 1.18% for MgV_2O_6, $Mg_2V_2O_7$, and $Mg_3V_2O_8$, respectively, until 480 min as shown in Fig. 2. To be catalysts, the oxides after the reaction should be regenerated to the initial state and the activity should be also recovered. XRD spectra of the $Mg_2V_2O_7$ before and after the isobutane oxidation and the used catalysts after the reoxidation are shown in Fig. 9. Although the analysis of the catalyst after the isobutane oxidation is difficult, a part of $Mg_2V_2O_7$ seems to transform into MgO and MgV_2O_4, which contains reduced V^{3+} ions. After the calcination at 723 K for
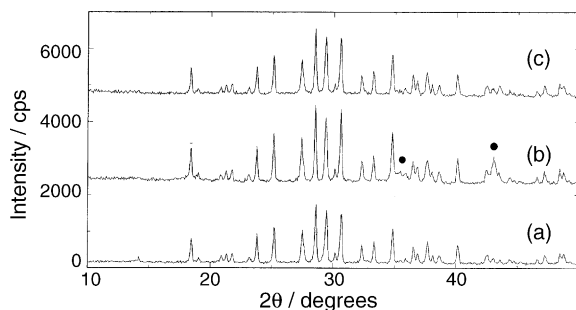

Fig. 9. XRD pattern of $Mg_2V_2O_7$ (a) before and (b) after the reaction and (c) after the reoxidation: (●) MgV_2O_4.
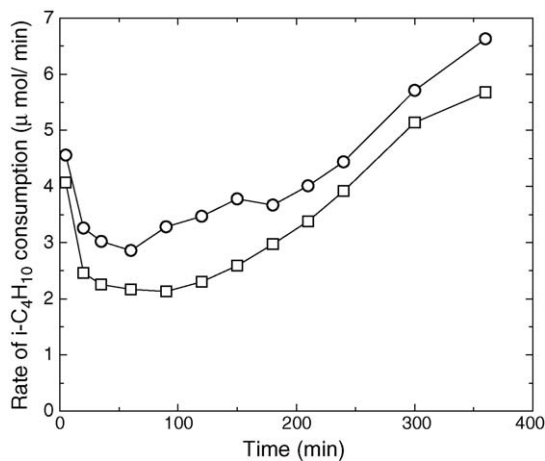
Fig. 10. Catalytic performance of regenerated $Mg_2V_2O_7$ catalyst for isobutane oxidation: (◯) 1st run; (□) 2nd run (regenerated catalyst).

5 h, the reduced catalyst seemed to recover the initial structure. The oxidation of isobutane was carried out using the reoxidized catalyst and the result is shown in Fig. 10. Although the reaction rate was decreased in the 2nd run, the shape of the isobutane consumption rate curve is quite similar to that of the initial $Mg_2V_2O_7$ catalyst, and isobutene was formed selectively. This suggests that $Mg_2V_2O_7$ acts as a catalyst for anaerobic oxidation of isobutane.

3.4. Modification of $Mg_2V_2O_7$ by other elements

In the previous section, it is clarified that $Mg_2V_2O_7$ is the most suitable catalyst for anaerobic oxidation of isobutane. Therefore, we chose $Mg_2V_2O_7$ as the basic catalyst, substitution of some metal ions for Mg ion in the lattice position was attempted to modify physicochemical property of $Mg_2V_2O_7$. The oxides containing Cr, Co, Fe, Ni, and Mn were composed of a single phase. Ionic radius of Cr^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, and Mn^{2+} are 0.069, 0.072, 0.074, 0.069, and 0.080 nm, respectively. Since ionic radius of Mg^{2+} is 0.066 nm, Co^{2+}, Fe^{2+} and Mn^{2+} seem to be too large to be substituted for Mg^{2+} (0.066 nm). In these complex oxides, Co^{3+} (0.063), Fe^{3+} (0.064) or Mn^{3+} (0.066), which has smaller ionic radius, may be introduced into the lattice accompanied with the formation of V^{4+}. Co containing oxides was identified carefully because $Co_2V_2O_7$ gives the diffraction peaks at similar positions to $Mg_2V_2O_7$. It was concluded that Co containing oxide was composed of a single phase of $Mg_2V_2O_7$. On the other hand, two catalysts containing Cu and Zn were not a single phase. Cu containing oxide showed weak diffraction peaks at $d = 3.0816$ and 2.1229, which were attributed to $Cu_2V_2O_7$ (blossite) and a small peak at $d = 2.7282$ to $CuVO_3$ in addition to the peaks of $Mg_2V_2O_7$. Zn containing oxide showed the diffraction peaks due to MgV_2O_6 with intensities of 1/10 of those for $Mg_2V_2O_7$. Ionic radius of Cu^{2+} and Zn^{2+} are 0.072 and 0.071 nm. Crystallinity of the oxides evaluated by the intensity of the most strong diffraction peaks was the same as that of $Mg_2V_2O_7$.

Subsequently, the authors studied the isobutane oxidation over these catalysts under the anaerobic reaction conditions.

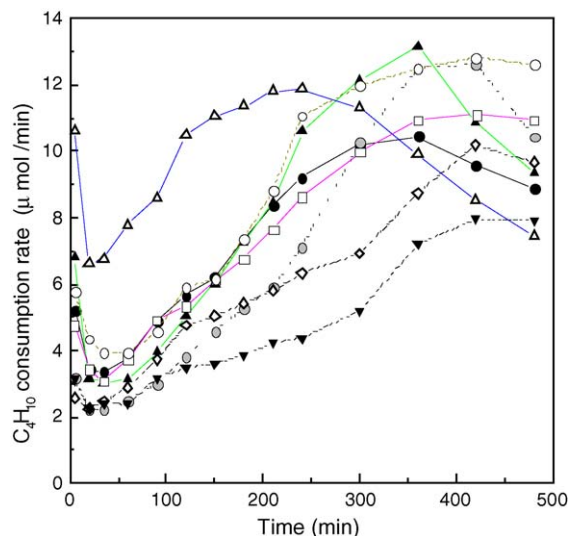Fig. 11. Isobutane oxidation over modified $Mg_2V_2O_7$. $Mg_{1.8}M_{0.2}V_2O_7$, M: (●) none ($Mg_2V_2O_7$); (◉) Mn; (▲) Cr; (△) Co; (◇) Fe; (□) Ni; (▼) Zn; (◯) Cu; 673 K.

Results are shown in Figs. 11 and 12. $Mg_{1.8}Co_{0.2}V_2O_7$ showed a highest initial activity. The initial rate of isobutane consumption over the other catalysts ranged from 2.5 to 7.0 µmol/min g. The rates of all catalysts were once decreased until 20–40 min and then increased. The rate of Cu containing catalyst achieved a maximum at 200–250 min and then decreased. The other catalysts also showed similar shapes having a maximum except for Zn containing catalyst. It is clear from Fig. 11 that the substitution of Co, Cu and Cr for Mg increased the activity of $Mg_2V_2O_7$. In contrast, substitution of Fe and Zn decreased the activity. The major product in the anaerobic oxidation was isobutene and a small amount of CO, CO_2 and a very small amount of oxygenated compounds, methanol, acrolein, methacrolein, acetaldehyde and acetic acid, were also obtained. Most of CO
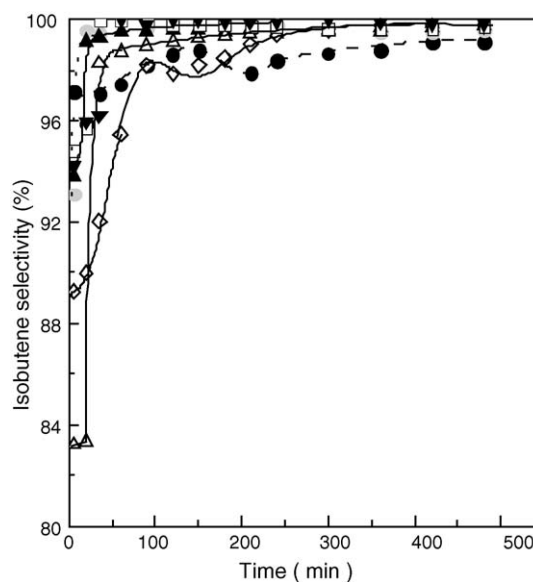

Fig. 12. Isobutene selectivity in anaerobic oxidation of isobutane over modified $Mg_2V_2O_7$. $Mg_{1.8}M_{0.2}V_2O_7$, M: (●) none ($Mg_2V_2O_7$); (◉) Mn; (▲) Cr; (△) Co; (◇) Fe; (□) Ni; (▼) Zn; (◯) Cu; 673 K.
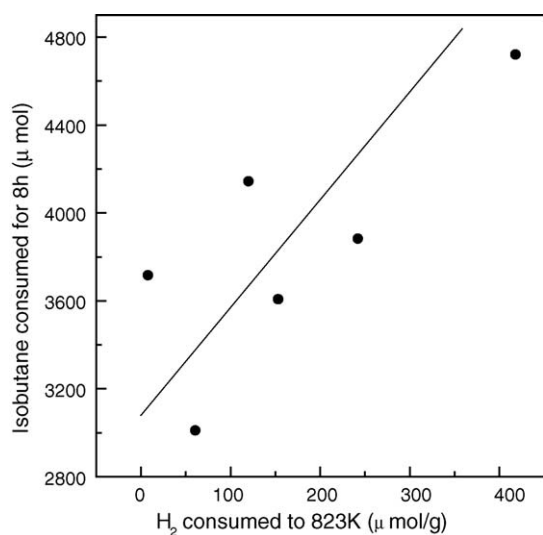
Fig. 13. Relation between catalytic activity for anaerobic oxidation of isobutane and TPR of the catalysts.

and CO_2 were formed just after the commencing oxidation over every catalyst. As can be seen from Fig. 12, initial CO_x formation was dominant over Co, Cu, and Fe containing catalysts: initial selectivity for isobutene was 78–89%. Although CO_x formation was also observed over the other catalysts, initial isobutene selectivity was as high as 93–97%. As for the initial selectivity, $Mg_2V_2O_7$, which has no substituted metal showed the highest selectivity. Total selectivity for isobutene until 480 min was calculated and shown in Table 2. Since formation of CO_x was sharply decreased during about initial 100 min, total selectivity for isobutene was strictly high over every catalyst. The selectivity for $Mg_2V_2O_7$ was 98.6%, and that for the other catalysts was in the range of 99.0% (Fe) to 99.8% (Zn). So that, it can be said that substitution of metals increase the isobutene selectivity of $Mg_2V_2O_7$.

The order of the catalytic activity, which is evaluated from the total isobutene formation, is Co > Cu > Cr > none > Ni > Mn > Fe > Zn. This order is not agreement with the order of acid amounts of the catalysts, which was reported in the previous paper [19]: Cr > none > Co > Fe > Ni > Mn. The amounts of isobutane during the anaerobic oxidation for 480 min was plotted in Fig. 13 against the amounts of hydrogen consumed to 823 K in TPR. There is a linear relation between them. Therefore, TPR results may be a measure for evaluation of the catalytic activity of a series of modified catalysts as $Mg_{1.8}M_{0.2}V_2O_7$.

Formation of hydrogen was observed but the formation rate was very small. H_2 formation over $Mg_2V_2O_7$ was very small throughout the experiment; it increased from 240 min but it was 0.94 μmol/min g at 480 min. The highest initial rate was 0.41 μmol/min g over the Co containing catalyst, rates were once decreased, achieved a minimum at 90 min and then increased monotonously. The rates of hydrogen formation at 480 min were (5.54 μmol/min g) for $Mg_{1.8}Cu_{0.2}V_2O_7$; (3.03 μmol/min g) for $Mg_{1.8}Co_{0.2}V_2O_7$; (2.0 μmol/min g) for $Mg_{1.8}Ni_{0.2}V_2O_7$; (1.66 μmol/min g) for $Mg_{1.8}Cr_{0.2}V_2O_7$; (1.11 μmol/min g) for $Mg_{1.8}Fe_{0.2}V_2O_7$; (0.94 μmol/min g) for $Mg_2V_2O_7$; (0.92 μmol/min g) for $Mg_{1.8}Mn_{0.2}V_2O_7$; and

(0.24 μmol/min g) for $Mg_{1.8}Zn_{0.2}V_2O_7$. Maximum contribution of simple dehydrogenation was 44.1% at 480 min over the Cu containing catalyst, in which Cu metal may catalyze the dehydrogenation. It is clear from the comparison to the rate of isobutene formation that the essential reaction for isobutene formation is oxidative dehydrogenation over all catalysts.

The catalysts after the reaction were examined by XRD. The results are summarized in Table 2. The catalysts after the reaction were composed of MgO and some Mg–V oxides. $Mg_2V_2O_7$ after the reaction was composed of MgO, MgV_2O_4 and $Mg_3V_2O_8$. Most of the diffraction peaks of MgV_2O_4 are overlapped with those of $Mg_3V_2O_8$. Cr containing catalyst after the reaction was composed of MgO and $Mg(VCr)_2O_4$, in which V and Cr occupied the same sites and V may be reduced V^{3+}. Mn and Fe containing catalysts were quite similar in the phase to $Mg_2V_2O_7$. MgO was observed in the XRD pattern of Co and Zn containing catalysts after the reaction. Cu catalyst was reduced deeply and showed the diffraction peaks due to Cu metal in addition to MgO and $Mg_3V_2O_8$; however, it is not clear which compounds was transformed to Cu metal because Cu catalyst before the reaction was composed of $Mg_2V_2O_7$, $Cu_2V_2O_7$, and $CuVO_3$.

4. Conclusion

It is concluded from the results that Mn, Cr, Fe, Ni and Co can be introduced into $Mg_2V_2O_7$ and a single phase was obtained. After the anaerobic reaction, catalysts are reduced to form MgO, MgV_2O_4 and $Mg_3V_2O_8$, but Cu containing catalyst is reduced to give Cu metal. Substitution of Co, Cu and Cr for Mg increases the activity for isobutane oxidation and substitution of Ni and Mn scarcely affects the activity but substitution of Fe and Zn decreases the activity. Substitution of the metal ions slightly increases the isobutene selectivity. TPR may be a measure for evaluation of the catalytic activity of a series of modified catalysts.

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