

Application of a Microreactor in the Oxidative Dehydrogenation of Propane to Propylene on Calcium Hydroxyapatite and Magnesium *ortho*-Vanadate Doped and Undoped with Palladium

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A microreactor was employed for the oxidative dehydrogenation of propane to propylene in order to suppress a deep oxidation of the resultant propylene to CO and CO₂. Magnesium *ortho*-vanadate, doped and undoped with palladium, and calcium hydroxyapatite, were used as catalysts while the reaction temperature was controlled by steady- and unsteady-state conditions. The enhancement of the selectivity to propylene was the most advantageous effect from using the microreactor, and it occurred when calcium hydroxyapatite was used under an unsteady-state. For example, the selectivity to propylene was 0 and 73.0% using a fixed-bed continuous-flow reactor and the microreactor, respectively, under almost identical propane conversion of 3.1 and 3.2%, respectively. The advantageous effect was also achieved, although to a lesser degree, when magnesium *ortho*-vanadate was used undoped with palladium under both steady- and unsteady-state conditions. However these advantageous effects of the microreactor were not observed with magnesium *ortho*-vanadate doped with palladium. With regard to the selectivity to propylene, the redox nature of the catalysts seemed to influence the performance of the microreactor.

Introduction

Propylene mainly obtained by naphtha cracking is an important raw material for the petrochemical industry. Since the demand of propylene derivatives has recently exceeded that of ethylene, a lack of propylene is a concern for the middle to long term (Suwa, 2004). Therefore, the development of another technology for the production of propylene is desired. The oxidative dehydrogenation of propane on solid catalysts is one of the most attractive reactions for the production of propylene. In our laboratory, calcium hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂; CaHAp) and palladium-doped magnesium *ortho*-vanadate (Mg₃V₂O₈ doped with Pd; Pd-MgVO) have shown relatively greater catalytic activity for the oxidative dehydrogenation of propane to propylene, while magnesium *ortho*-vanadate (MgVO) itself has shown rather low activity (Sugiyama *et al.*, 2008a, 2008b). Although Pd-MgVO in particular has shown great catalytic activity during the oxidative dehydrogenation of propane, a deep oxidation of propylene to CO and CO₂ (CO_x) could not be avoided when using a typical fixed-bed continuous-flow reactor. Therefore, a

different reactor system for the suppression of deep oxidation had to be developed.

In the present study, a microreactor under steady-state operation was employed to suppress the deep oxidation of propylene to CO_x as an enhancement of the selectivity to propylene. As a catalyst, CaHAp, Pd-MgVO and MgVO were employed. We also examined the effect of unsteady-state operation, defined by heating (on) and cooling (off) of the power supply, on oxidative dehydrogenation. Furthermore, the catalytic activity of the microreactor was compared with a typical fixed-bed continuous-flow reactor.

1. Experimental

Precursor sols of CaHAp, Pd-MgVO and MgVO, which were used for the preparation of a catalyst bed in the microreactor, were prepared as shown in our previous papers (Sugiyama *et al.*, 2008b, 2009). The microreactor used in the present study consisted of a T union (quartz tube, $\phi = 6$ mm) and electrodes (stainless wire, $\phi = 0.3$ mm) connected to Pt wire ($\phi = 0.1$ mm) (**Figure 1**) (Sotowa *et al.*, 2008). In this microreactor, propylene formed on the catalyst coated over two alumina tubes and was easily separated from the hottest

zone to avoid the formation of deep oxidation products. Therefore, catalytic activity for the formation of propylene may be improved.

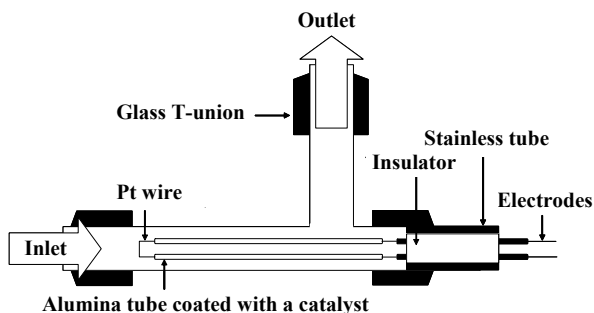


Fig. 1 Microreactor employed in the present study

The precursor sols of CaHAp, Pd-MgVO and MgVO were coated over alumina tubes, followed by drying at room temperature for 1 h. The loading of Pd in Pd-MgVO was 5 wt% in the present study. Then, the tube coated with CaHAp was calcined at 773 K for 3 h, while the tube coated with Pd-MgVO or MgVO was calcined at 823 K for 6 h, followed by an additional calcination at 973 K for 10 h. X-ray diffraction patterns of the three catalysts were matched to data reported in our previous papers (Sugiyama *et al.*, 2008a, 2008b). The coated tubes thus prepared were set in the microreactor. The reaction temperature in the microreactor was estimated by comparing the results obtained from a blank test of the microreactor and the fixed-bed continuous-flow reactor (see Section 2.1). In the heating mode, power of 256 μ s was supplied to the electrodes. The rate of heat release was adjusted to 27.3, 39.1, 46.9 and 58.6%. At 58.6% of the rate of heat release, approximately 31 W of electric power was supplied into the microreactor. The alumina tubes coated with the catalysts were heated to the reaction temperature in the microreactor under a continuous flow of helium and then pretreated under a 25 mL/min flow of oxygen for 1 h. The reaction conditions employed for both the microreactor and the fixed-bed continuous-flow reactor were as follows: $P(\text{C}_3\text{H}_8) = 14.4$ kPa, $P(\text{O}_2) = 4.1$ kPa, and $F = 15$ mL/min. The reaction was monitored with an online gas chromatograph (GC-8APT, Shimadzu Corp.). No homogeneous reaction was observed under these conditions. In employing the unsteady-state operation of the microreactor, two parameters were used to control the reaction temperature (Sotowa *et al.*, 2008). One was the cycle time, wherein a heating mode (on) and a cooling mode (off) were altered by switching the power supply. The other was a cycle split, which was defined as a rate of “heating time/cycle time.” In the present study, the cycle split was adjusted to 0.5, while the rate of heat release was fixed at 39.1%. At this rate of heat release, approximately 10 W was supplied into the microreactor. In using the fixed-bed continuous-flow reactor operated at atmospheric pressure

(Sugiyama *et al.*, 2008a, 2008b), CaHAp (0.15 g), Pd-MgVO (0.16 g) and MgVO (0.10 g) particle size of 0.85 - 1.70 mm were heated to the reaction temperature (723 K) under a continuous flow of helium, and were then preheated at 723 K under a 25 mL/min flow of oxygen for 1 h. In order to confirm the reproducibility of the activity and the mass balance, each reaction was repeated at least twice.

2. Results and Discussion

2.1 Blank test for an estimation of the reaction temperature in the microreactor

As shown in Figure 1, there was no thermometer in the microreactor. It should be noted that use of a typical thermometer such as a thermocouple cannot detect the reaction temperature over the catalyst and it is very difficult to detect the reaction temperature directly in the microreactor. In order to estimate the reaction temperature, a comparative study using the microreactor and a fixed-bed continuous-flow reactor in the absence of catalysts, a blank test, was carried out.

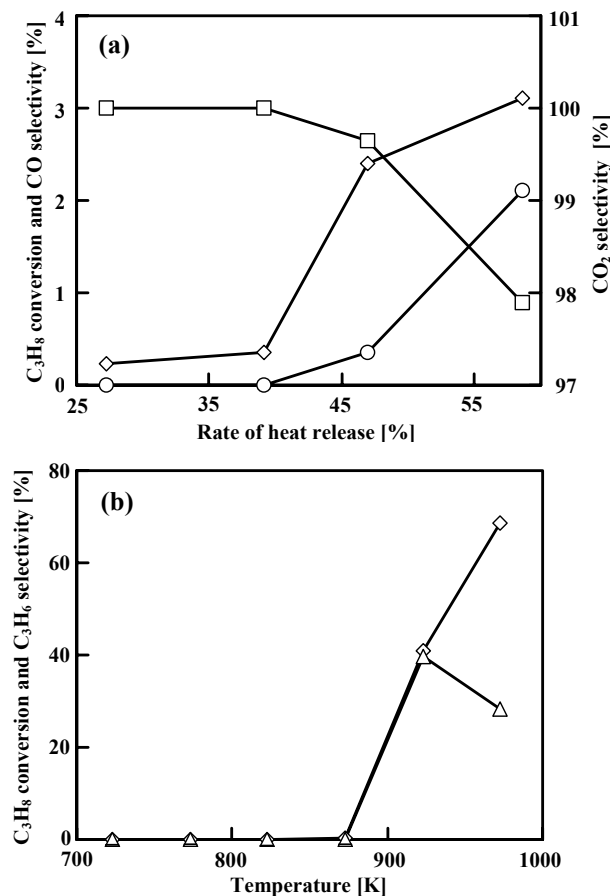


Fig. 2 Results obtained from the blank test using the microreactor (a) and the fixed-bed continuous-flow reactor (b). Symbols: \diamond , C_3H_8 Conversion; \triangle , \square and \circ , Selectivity to C_3H_6 , CO_2 and CO , respectively

The results of the blank test using the microreactor and that using the fixed-bed continuous-flow reactor are shown in **Figure 2**. When using the microreactor, the conversion of C_3H_8 was negligible at 39.1% of the rate of heat. Similarly, the conversion of C_3H_8 was negligible at 873 K in the fixed-bed reactor. Therefore, the contribution of the homogeneous reaction was negligible at those two points. As described later, 39.1% of the rate of heat release in the microreactor was typically used, particularly under the unsteady-state operation in the present study. Therefore, it should be noted that 39.1% (rate of heat release) in the microreactor roughly corresponded to 873 K (reaction temperature) in the fixed-bed reactor.

2.2 Steady- and unsteady-state operations on CaHAp using the microreactor

First the oxidative dehydrogenation of propane was examined on CaHAp. It was previously reported that the catalytic active-site was the OH group in CaHAp (Sugiyama *et al.*, 2003) and that the oxygen species in CaHAp was fixed in the unit cell showing a negligible redox nature (Sugiyama *et al.*, 2008b). **Figure 3** shows catalytic activities at 0.25 h on-stream on CaHAp under steady-state operation. When the rate of heat release increased, the conversion of C_3H_8 and the selectivity to CO_2 also tended to increase, while the selectivity to C_3H_6 decreased. The best catalytic activity, that is, the best yield of C_3H_6 , was obtained at 39.1% of the rate of heat release under steady-state operation. The conversion of C_3H_8 and the selectivity to C_3H_6 on CaHAp were obtained at 4.7 and 48.1%, respectively, at 39.1% of the rate of heat release. Thus, the C_3H_6 yield was 2.3% under these conditions, and no homogeneous reaction proceeded. In order to additionally suppress the deep oxidation of C_3H_6 , unsteady-state operation using the microreactor was examined.

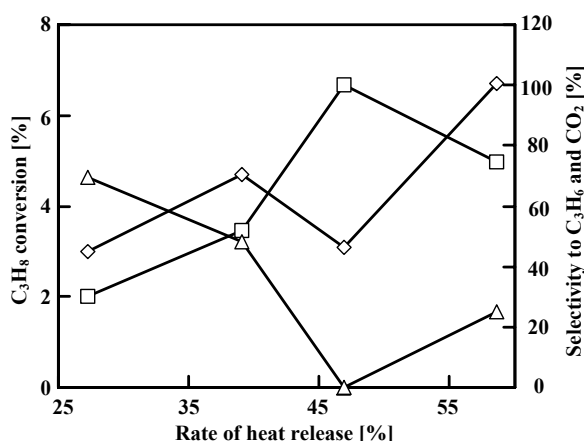


Fig. 3 Catalytic activity on CaHAp under steady-state operation. Symbols: \diamond , C_3H_8 Conversion; \triangle and \square , Selectivity to C_3H_6 and CO_2

Figure 4 shows catalytic activities at 0.25 h on-stream on CaHAp under unsteady-state operation. When the cycle time was increased, the conversion of C_3H_8 and the selectivity to C_3H_6 tended to decrease while the selectivity to CO_2 increased. The maximum yield of C_3H_6 was observed at 39.1% the rate of heat release and at a cycle time of 3 s. At this point, the conversion of C_3H_8 , the selectivity to C_3H_6 , and the maximum yield of C_3H_6 were 3.2, 73.0 and 2.3%, respectively. The conversion of C_3H_8 and the selectivity to C_3H_6 under unsteady-state operation on CaHAp decreased at a cycle time of longer than 5 s. Therefore, the selectivity to CO_2 increased with the increasing cycle time. Consequently, suppression of the deep oxidation of C_3H_6 was not observed at the longer cycle time. Although the same optimum yield of C_3H_6 (2.3%) was obtained under both steady- and unsteady-state operation, it should be noted that the selectivity to C_3H_6 under unsteady-state operation (73.0%) was evidently greater than that under the steady-state operation (48.1%).

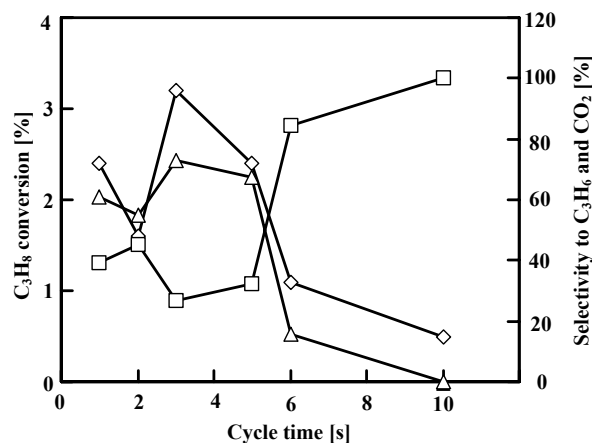


Fig. 4 Catalytic activity on CaHAp under unsteady-state operation. Symbols: \diamond , C_3H_8 Conversion; \triangle and \square , Selectivity to C_3H_6 and CO_2

2.3 Steady- and unsteady-state operations on MgVO using the microreactor

The oxidative dehydrogenation of propane was examined on MgVO ($Mg_3V_2O_8$, magnesium *ortho*-vanadate). Magnesium vanadates (MgV_2O_6 , $Mg_2V_2O_7$ and $Mg_3V_2O_8$) are known as active catalysts for the oxidative dehydrogenation of propane. $Mg_3V_2O_8$ (MgVO) showed the lowest activity among magnesium vanadates (Sam *et al.*, 1990; Kung, 1994), while the stability of MgVO was the highest among the three vanadates (Sugiyama *et al.*, 2007). The ease of removal of the lattice oxygen in these magnesium vanadates explains their level of activity in the oxidative dehydrogenation of propane (Pepera *et al.*, 1985; Kung, 1994; Yoshimura, 1998). The nature of removal of lattice oxygen in MgVO shows that the redox nature of

MgVO is evidently greater than that of CaHAp. **Figure 5** shows the catalytic activities at 0.25 h on-stream on MgVO under steady-state operation. In contrast to the results shown in Figure 3 for CaHAp, the conversion and the selectivity were rather insensitive to the rate of heat release. The best catalytic activity, i.e. the yield of C_3H_6 , was again obtained at 39.1% the rate of heat release under steady-state operation. The conversion of C_3H_8 , the selectivity to C_3H_6 , and the yield of C_3H_6 on MgVO were 1.7, 30.9 and 0.5%, respectively, at 39.1% the rate of heat release.

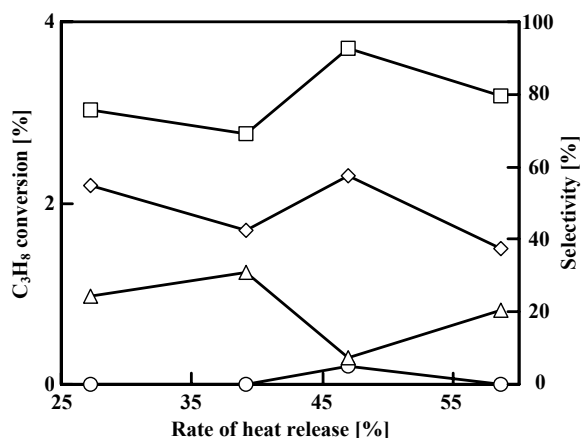


Fig. 5 Catalytic activity on MgVO under steady-state operation. Symbols: \diamond , C_3H_8 Conversion; \triangle , \circ and \square , Selectivity to C_3H_6 , CO and CO_2 .

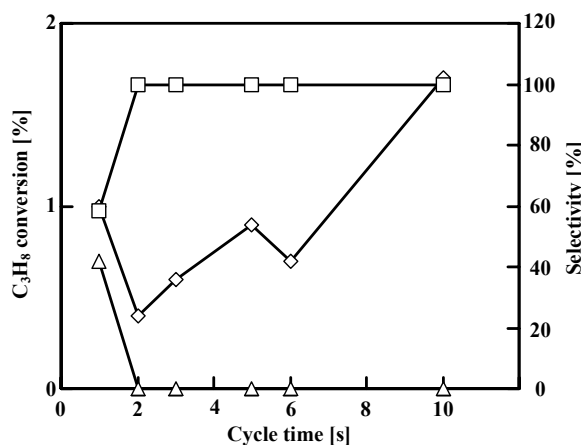


Fig. 6 Catalytic activity on MgVO under unsteady-state operation. Symbols: \diamond , C_3H_8 Conversion; \triangle and \square , Selectivity to C_3H_6 and CO_2

Figure 6 shows catalytic activities at 0.25 h on-stream on MgVO under unsteady-state operation. In this case, the selectivity to CO_2 was almost 100%, with the exception of a cycle time of 1 s, although the conversion of C_3H_8 increased as the cycle time increased. The maximum yield of C_3H_6 was observed at 39.1% the rate of heat release and cycle time of 1 s. At

this point, the conversion of C_3H_8 , the selectivity to C_3H_6 , and the yield of C_3H_6 were 1.0, 41.8 and 0.4%, respectively. It should be noted that the maximum activity on CaHAp was evidently greater than that on MgVO, although the activity on MgVO was generally greater than that on CaHAp when using a typical fixed-bed continuous-flow reactor under our standard conditions for the reactor (Sugiyama *et al.*, 2008a, 2008b). We paid attention to the effect of the ease of the removal nature of lattice oxygen from the catalyst, i.e. the redox nature of the activity when using the microreactor.

2.4 Steady- and unsteady-state operations on Pd-MgVO using the microreactor

Results of the present study showed that the catalyst possessing an ease of removal of lattice oxygen from the catalyst showed no evident enhancement from use of the microreactor. To confirm this conclusion, palladium-doped magnesium *ortho*-vanadate ($Mg_3V_2O_8$ doped with Pd; Pd-MgVO) was employed for the oxidative dehydrogenation of propane using the microreactor. According to previous reports, Pd-MgVO showed great catalytic activity for the oxidative dehydrogenation of propane using a typical fixed-bed continuous-flow reactor due to an improvement in the ease of removal of lattice oxygen from MgVO by doping with palladium (Sugiyama *et al.*, 2008b). **Figure 7** shows the catalytic activities on Pd-MgVO under steady-state operation.

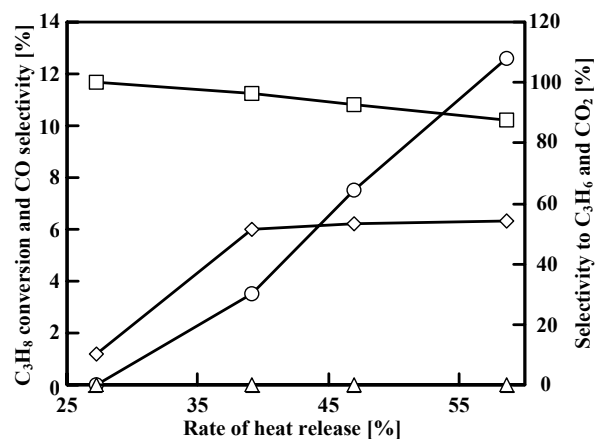


Fig. 7 Catalytic activity on Pd-MgVO under steady-state operation. Symbols: \diamond , C_3H_8 Conversion; \triangle , \circ and \square , Selectivity to C_3H_6 , CO and CO_2

When using Pd-MgVO, propylene was not detected, probably due to the deep oxidation of C_3H_6 to a CO_x species since the conversion of oxygen was almost 100% at 27.3% the rate of heat release. As a result, a high selectivity to CO_2 was obtained from the deep oxidation of C_3H_6 . In the present steady-state operation, the reaction temperature was always set as in

a typical fixed-bed continuous-flow reactor while the doping of palladium species in the catalyst resulted in great ease of the removal of lattice oxygen from the catalyst, which showed great activity. Therefore, deep oxidation of C_3H_6 to CO_x proceeded. Unfortunately, no advantageous effect from employment of the microreactor under steady-state operation was observed on Pd-MgVO. With regard to reaction temperature, unsteady-state operation using the microreactor was studied for an improvement in catalytic activity on Pd-MgVO.

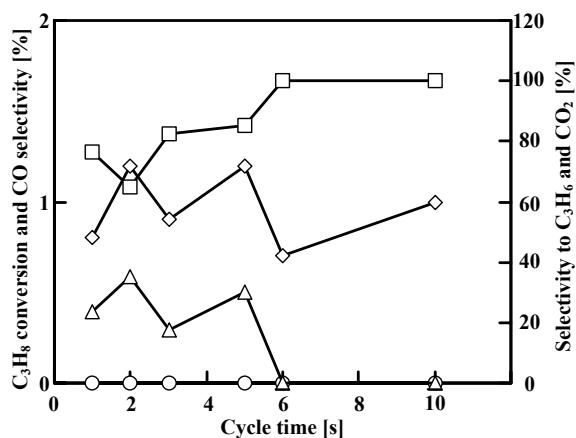


Fig. 8 Catalytic activity on Pd-MgVO under unsteady-state operation; Symbols: ◇, C_3H_8 Conversion; △, ○ and □, Selectivity to C_3H_6 , CO and CO_2

Figure 8 shows the catalytic activity on Pd-MgVO at 0.25 h on-stream under unsteady-state operation. The maximum yield of C_3H_6 was observed at 39.1% the rate of heat release and at a cycle time of 2 s. At this point, the conversion of C_3H_8 , the selectivity to C_3H_6 , and the

yield of C_3H_6 were 1.2, 35.2 and 0.4%, respectively. C_3H_6 was detected at a rather shorter cycle time. As a result, the suppression of the deep oxidation of C_3H_6 to CO_x was observed at a relatively shorter cycle time. It should be noted that selectivity to C_3H_6 was certainly enhanced under unsteady-state operation. On the other hand, catalytic activities at a rather longer cycle time were similar to those under steady-state operation, i.e. no formation of C_3H_6 . Therefore, high selectivity to CO_2 was observed due to the deep oxidation of C_3H_6 at the rather longer cycle time. Based on the results shown for the oxidative dehydrogenation on Pd-MgVO together with those on CaHAp and MgVO, employment of the microreactor seems to be more suitable for a catalyst in which lattice oxygen is rather fixed as in CaHAp, but not suitable for a catalyst in which lattice oxygen can be easily removed.

2.5 Comparison of activities obtained using microreactor and fixed-bed continuous-flow reactor

Catalytic activity obtained by using a microreactor was compared to that by the typical fixed-bed continuous-flow reactor. **Table 1** lists the catalytic activities using both reactors under essentially identical conditions, except for the space-time and the reaction temperature. The space-time and the reaction temperature using the fixed-bed continuous-flow reactor were adjusted as the conversion of C_3H_8 on the same catalyst became almost equal except in the case of Pd-MgVO. On CaHAp and MgVO, the selective formation of C_3H_6 was observed using the microreactor due to the suppression of the deep oxidation of C_3H_6 to CO_x . In the microreactor, C_3H_6 formed on these catalysts can be removed from the hottest zone over the catalyst surface. Therefore, the conversion of C_3H_6 to CO and CO_2 can be avoided in the present system, resulting in the enhancement of the selectivity to C_3H_6 .

Table 1 Comparison of catalytic activity on CaHAp, MgVO and Pd-MgVO under various operations

Catalyst	Temperature [K]	Rate of heat release [%]	Cycle time [s]	Conversion [%]		Selectivity [%]			Yield [%]
				C_3H_8	O_2	C_3H_6	CO	CO_2	C_3H_6
CaHAp (A)	723	-	-	3.1	45	0.0	44.3	55.7	0.0
CaHAp (B)	-	39.1	-	4.7	30	48.1	0.0	51.9	2.3
CaHAp (C)	-	39.1	3	3.2	16	73.0	0.0	27.0	2.3
MgVO (A)	723	-	-	1.1	17	0.0	41.6	58.4	0.0
MgVO (B)	-	39.1	-	1.7	23	30.9	0.0	69.1	0.5
MgVO (C)	-	39.1	1	1.0	19	41.8	0.0	58.2	0.4
Pd-MgVO (A)	723	-	-	6.4	100	0.0	16.6	83.4	0.0
Pd-MgVO (B)	-	39.1	-	6.0	100	0.0	3.5	96.5	0.0
Pd-MgVO (C)	-	39.1	2	1.2	27	35.2	0.0	64.8	0.4

A: Fixed-bed continuous-flow reactor

B: Microreactor under steady-state operation

C: Microreactor under unsteady-state operation

In particular, the selectivity to C₃H₆ was further improved using the microreactor under unsteady-state operation. Under unsteady-state operation, the reaction temperature was controlled by temperature cycling, such as altering the heating mode (on) and cooling mode (off) by switching the power supply. It is generally expected that the cooling mode, a low temperature, is favorable for the adsorption of the reactant on the catalyst surface. By contrast, the heating mode, a high temperature, is favorable for the reaction of the reactant adsorbed on the catalyst surface, followed by the desorption of the product from the catalyst surface (Sotowa, 2006). Furthermore, as described above, the ease of the removal of lattice oxygen from the catalyst reflects the enhancement of the selectivity to the desired product. Unfortunately, the conversion of C₃H₈ on Pd-MgVO using the microreactor under unsteady-state operation could not increase the corresponding conversion using the other two conditions. As described above, the lattice oxygen in Pd-MgVO was easily removed from the catalyst, indicating that the removal rate should be strongly influenced by the reaction temperature. Under unsteady-state operation, the thermal energy was not sufficiently supplied to the catalyst, resulting in lower activity on the catalyst.

Conclusions

In conclusion, employment of the microreactor, which was designed for the suppression of deep oxidation of C₃H₆ to CO_x, resulted in enhancement of the selectivity to C₃H₆ in the oxidative dehydrogenation of C₃H₈. In particular, the employment of unsteady-state operation such as temperature cycling between the heating mode and the cooling mode resulted in a remarkable improvement in the selectivity to C₃H₆. A catalyst having lattice oxygen that is rather tightly fixed seems to be favorable for the microreactor.

Acknowledgements

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