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Surface-Initiated Gas-Phase Epoxidation of Propylene with Molecular Oxygen by Silica-Supported Molybdenum Oxide: Effects of Addition of C_3H_8 or NO and Reactor Design

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Abstract The gas-phase epoxidation of propylene was studied over MoO_x/SiO_2 catalysts in a reaction system with a post-catalytic bed volume. In the reaction of a mixture of propylene and propane with oxygen below 578 K, propylene oxide (PO) was mainly formed from the oxidation of propylene. It was found that the oxidation reaction was very sensitive to the temperature of the post-catalytic space more than the temperature of the catalyst bed, strongly indicating that radical reactions occurring in the post-catalytic bed free space were responsible for the PO formation. The addition of NO increased propylene conversions and PO selectivity at low conversions, confirming that radical reactions were involved in the propylene reactions.

Keywords Epoxidation · Silica-supported molybdenum oxides · Post-catalytic reaction · Radical reaction

1 Introduction

Propylene oxide (PO) is an important chemical feedstock in the chemical industry, and is currently manufactured by multi-step methods, such as the chlorohydrin process, which uses Cl_2 and H_2O, or variants of the Halcon process which use organic hydroperoxides [1]. The above industrial processes are not only complex and costly, but also produce large amounts of side products or co-products. Thus, the development of a process for the one-step production of PO from propylene, especially using molecular oxygen as oxidant, is highly desirable.

Recently, we reported that a reactor having a post-catalytic bed volume, was effective in forming PO over silica-supported titanium oxide [2, 3] and molybdenum oxide [4, 5] catalysts using molecular oxygen as an oxidant. It was suggested that the metal oxide clusters present in these catalysts are effective for the generation of allyl radicals from propylene at relatively low temperature, and PO is produced through gas-phase chain reactions. It has been reported that the homogeneous gas-phase oxidation of a mixture of propane and propylene with molecular oxygen can produce PO with much higher efficiency than that with propane or propylene alone [6]. Co-feeding NO with C_3H_6 and O_2 enhanced both conversion and PO selectivity on supported silver catalysts. However, a silver catalyst containing molybdenum as a promoter had the same activity and selectivity with or without the addition of NO in the feed [7, 8].

In previous studies [2–5], we have reported that the post-catalytic bed space played an important role in the gas-phase epoxidation of propylene and that silica-supported titanium oxide and molybdenum oxide catalysts showed high catalytic activity. In the present work, we further investigated the role of the post-catalytic bed space

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on the gas-phase epoxidation of propylene with the use of a two-level reactor, in which the catalytic-bed temperature and the temperature of the post-catalytic bed space could be separately controlled by two heaters. Furthermore, the effects of propane and NO in the feed gas were studied.

2 Experimental

2.1 Catalyst Preparation

A silica-supported molybdenum oxide catalyst denoted as MoO_x/SiO_2 (0.255) where 0.255 denotes the loading amount of molybdenum oxide (mmol/g-SiO_2) was prepared by a simple impregnation method, as reported previously [4]. The precursor, H_2MoO_4 was dissolved in water and the pH was set to 1.0 by adding a dilute solution of HNO_3. A quantity of 3 g of SiO_2 support (Fuji Silysia Chemical LTD, CARIACT, Q-30, 75–500 μm, $S_{BET} = 127\ m^2\ g^{-1}$) was wet impregnated with aqueous solutions of the H_2MoO_4, and then the water was evaporated using a rotary evaporator. The obtained powders were dried at 373 K for 24 h and calcined in air at 873 K for 3 h.

2.2 Catalytic Testing

The catalysts were evaluated in two types of reactor. Reactor 1 was a conventional stainless steel down-flow reactor with an inner quartz tube sleeve. The quartz tube had a volume section (25 cm^3) following the catalyst bed that could be empty or could be filled with quartz chips.

Reactor 2 was a two-level flow reactor produced by Honma Riken (Saitama, Japan). The temperature of the catalytic bed and the post-catalytic bed space could be separately controlled by two heaters (Fig. 1). Three thermocouples were used, one in the inner reactor tube close to the catalyst bed, a second in the empty tube middle-zone, and a third in the empty tube bottom-zone. The post-catalytic bed volume in the quartz tube was 62.3 cm^3.

A quantity of 1.0 g of catalyst (75–500 μm) was mixed with 3.0 g of quartz sand (Nacalai Tesque) and placed in the catalytic bed section of the reactor. A bed of quartz chips was placed above the catalytic bed to preheat the reactants. Feed gases (C_3H_6, O_2, He, etc.) were delivered by mass flow controllers and the products were analyzed on-line by two gas chromatographs (Shimadzu GC-14). One was equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) and the other with two TCD's. An FFAP capillary column (0.32 mm × 60 m) and a Porapak Q column (3 mm × 2 m) were used to detect oxygenates (acetaldehyde, propylene oxide, acrolein, propionaldehyde, acetone, and alcohols (methanol, ethanol, and isopropanol)) and CO_2, respectively, while a MS-5A 60/80 compact column (3 mm × 2 m) and a Gaskuropak 54 84/100 compact column (3 mm × 2 m) were used to detect CO and hydrocarbons (methane, ethylene, ethane, propylene and propane), respectively.

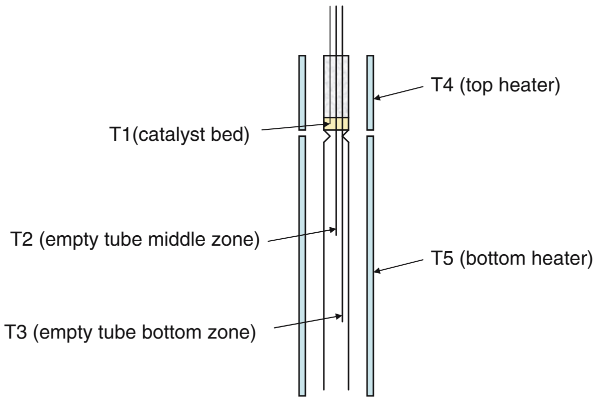

Fig. 1 Two-level reactor

3 Results and Discussion

3.1 Reaction of Propylene and Propane Mixture with Oxygen

Table 1 shows the results of oxidation of propane alone and oxidation of a mixture of propylene and propane using reactor 1. In the case of the oxidation of propane alone, no reactivity was measured at 573 K. When the reaction temperature was increased up to 593 K, a low conversion (0.5%) of propane was obtained. Above 600 K, the conversion of propane was as high as 20% but the PO selectivity was only about 1%. In the case of oxidation of the propylene and propane mixture, the overall conversion of propylene and propane was 7.0% and the PO selectivity was 28.2% at 573 K. Above this reaction temperature, the overall conversion of propylene and propane increased rapidly, but the PO selectivity decreased. It has been reported that the homogeneous gas-phase oxidation of a mixture of propane and propylene with molecular oxygen can produce PO with much higher efficiency than that with propane or propylene alone at 633–793 K and atmospheric pressure [6]. The plausible reaction scheme includes propylene formation by the oxidative dehydrogenation of propane and PO formation by the reaction between propylene and peroxy radical species, which are suggested as key intermediates originating from propane. If the PO could be produced from propane at a low temperature, it would be a considerable achievement. The overall conversion of propylene and propane listed in Table 1 was

Table 1 The gas-phase catalytic reaction of propylene and propane with oxygen using MoO_x/SiO_2 catalyst[a]

$C_3H_6/C_3H_8/O_2/He$ (cm^3 min^{-1})	Temp. (K)	Yield of PO (%)	Conv. of ($C_3H_6 + C_3H_8$) (%)	Sel. (%)[b]							
				AA	PO	AL	PA	AC	ALC	HC	CO_x
0/10/5/10	573	0	0	0	0	0	0	0	0	0	0
	593	0	0.5	20.8	0	0	0	0	0	26.4	0
	603	0.2	23.2	7.3	1.1	0.4	1.5	0	19.0	11.8	43.2
	606	0.3	26.5	6.6	1.0	0.4	1.3	0	19.7	11.1	44.5
5/5/5/10	556	0.05	0.08	0	61.9	0	38.1	0	0	0	0
	573	2.0	7.0	22.7	28.2	3.5	3.8	2.2	4.7	0.5	33.6
	578	2.4	22.9	14.4	10.5	1.4	1.6	0	12.3	5.6	51.6

[a] Reaction conditions: reaction pressure, 4.5 atm; catalyst bed, 1.0 g of catalyst mixed with 3.0 g of quartz sand; post-catalytic bed volume, 25 cm^3; products were analyzed after 30 min of reaction

[b] AA = Acetaldehyde, AL = Acrolein, PA = Propionaldehyde, AC = Acetone, ALC = Alcohol, HC = Hydrocarbon, $CO_x = CO_2 + CO$

calculated by a conventional external standard analysis method. Alone, it cannot be determined whether PO was formed from propane or from propylene formed from propane. Figure 2 shows the concentrations, C' of propane and C'' of propylene in the outlet gas vs. reaction temperature, respectively. The C' of propane in the outlet gas is defined as $C'_{\text{propane}} = 100 * C_{\text{propane}}/\Sigma C_i(1/3)N_i$, where C_{propane} = molecular concentration of propane in the outlet gas; C_i = molecular concentration of compound i in outlet gas; N_i = carbon number of compounds i.

The C'' of propylene in the outlet gas is defined similarly.

With an increase of the reaction temperature from 550 to 580 K, the C'' of propylene in the outlet gas decreased, while the C' of propane in the outlet gas was almost constant. This suggested that in the reaction of the mixture of propylene and propane with oxygen at these reaction conditions, the formation of propylene oxide came mainly from the propylene. The propane acted only as an inert gas because at low temperature the oxidative dehydrogenation of propane to propylene is very difficult even in the presence of the MoO_x/SiO_2 catalyst. These results are different with those in the previous report [6], but the latter were obtained at higher temperature (>673 K vs. <583 K in this study).

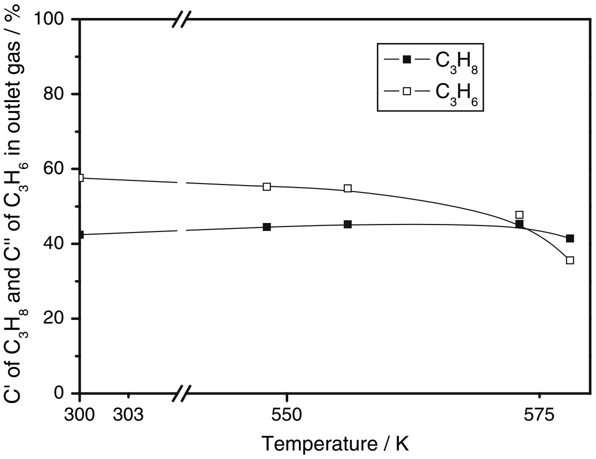

Fig. 2 C' of propane and C'' of propylene in outlet gas vs. reaction temperature. 1.0 g of catalyst was mixed with quartz sand 3.0 g; reaction pressure, 4.5 atm; PCBV (Post-catalytic bed volume) = 25 cm^3; Feed gas, $C_3H_6/C_3H_8/O_2/He$ = 5/5/5/10 cm^3 min^{-1}

3.2 Effect of NO Addition

Recently, several groups have reported that modified silica-supported iron oxides are effective for propylene epoxidation using N_2O as the oxidant [9–11]. However, a major disadvantage in the use of N_2O is that it is not commercially available in large quantities for an oxidation process. Here, NO was used to study the effect of a more available nitrogen oxide on the epoxidation of propylene (Table 2). It was also used to confirm that gas-phase free-radical reactions were important in the system.

The effect of NO was substantial. Both at 1 atm and 4.5 atm of reaction pressure NO increased conversion. For example, at 1 atm and 573 K the addition of NO (2% in He) increased the propylene conversion from 0 to 1.2% and the PO selectivity from 0 to 11.9%. (Table 2) The effect was even greater at 4.5 atm. At 558 K the presence of NO (2% in He) increased the propylene conversion from 1.1% to 2.2%, while maintaining the PO selectivity above 18%. At 573 K the conversion rose from 14% to 18.2%, although in this case the PO selectivity decreased from 32.3% to 18.6%. (Table 2) The increase in conversion is likely due to the initiation of radical reactions by the NO, which itself has an unpaired electron.

The results here differ from other effects of NO reported in the literature. Lambert et al. [12] have reported that for

Table 2 Effect of NO addition in the epoxidation of propylene[a]

No.	Pressure (atm)	Temp. (K)	Yield of PO (%)	Conv. (%)	Sel. (%)[d]							
					AA	PO	AL	PA	AC	ALC	HC	CO_x
1[b]	4.5	558	0.2	1.1	36.4	18.8	6.8	0	8.3	10.0	0	19.6
		573	4.5	14.0	17.7	32.3	2.6	2.7	2.7	5.5	0.5	35.5
		578	5.2	22.6	13.8	23.1	1.1	1.1	0.6	7.4	2.0	49.7
2[c]	4.5	523	0.09	1.1	44.4	8.0	0	0	6.8	0	0	40.9
		543	0.1	1.5	37.6	9.0	0	0	5.7	0	0	47.7
		558	0.4	2.2	35.5	18.6	0	0	4.6	0	0	41.3
		572	4.4	18.2	14.5	24.0	1.1	1.8	1.3	4.0	1.0	51.6
3[b]	1.0	573	0	0	0	0	0	0	0	0	0	0
		593	0	0.2	79.8	0	0	0	20.2	0	0	0
		623	3.1	25.0	21.2	12.5	2.6	2.0	2.0	7.7	4.2	45.4
4[c]	1.0	558	0.06	0.9	51.6	6.8	0	0	0	0	0	41.6
		573	0.1	1.2	48.6	11.9	0	0	0	0	0	39.4

[a] 1.0 g of catalyst was mixed with quartz sand 3.0 g; PCBV (Post-catalytic bed volume) = 25 cm^3

[b] Feed gas, $C_3H_6/O_2/He = 10/5/10\ cm^3\ min^{-1}$

[c] Feed gas, $C_3H_6/O_2/(2\%\ NO/He) = 10/5/10\ cm^3\ min^{-1}$

[d] Same definitions of AA, AL, PA, AC, ALC, HC, CO_x as in Table 1

the epoxidation of propylene, the presence of K and NO (0–60 ppm) decreased the PO selectivity over a Ag-based catalyst. The result differed from that observed in ethylene epoxidation, wherein the K and NO promoters led to a marked improvement in EO selectivity. For both ethylene and propylene epoxidation the role of the NO is to increase the atomic oxygen concentration on the surface of the silver. In the case of ethylene, atomic oxygen increases selectivity to ethylene oxide due to the formation of oxametallycles, but in the case of propylene, atomic oxygen reduces selectivity to the epoxide because it abstracts labile allylic oxygens. These cases are different from the situation in our system where NO promotes gas-phase radical reactions.

3.3 Propylene Epoxidation in the Two-Level Reactor

Table 3 shows the results of propylene epoxidation in the two-level reactor. First, the middle-zone temperature (T2) and end-zone temperature (T3) were fixed to 474 and 469 K, respectively. When the catalytic-bed temperature (T1) was increased from 560 to 583 K, the conversion of propylene was very low and increased slightly. Comparison with experiment No.1 for the empty reactor (without catalyst) which shows only trace conversion at 583 K (T1), experiments No. 2 and 3 show the positive action of the molybdenum oxide catalyst. Second, when the catalytic-bed temperature (T1) was fixed at 573 K while T2 was increased from 522 to 555 K, the conversion was observed to increase from 0.3% to 4.7% and the PO selectivity was observed to range between 20% and 30% in this temperature interval. When the catalytic-bed temperature (T1) was elevated to 577 K, the conversion increased to 13.8% and the PO selectivity to 33%. Further increase of T2 led to a decrease in the PO selectivity and an increase in the CO_x selectivity. On the basis of these results, we suggest that the oxidation reaction mainly proceeds in the post-catalytic space while the contribution of the oxidation reaction on the catalyst surface is small.

In the previous papers [2–5], we proposed a mechanism for the gas-phase oxidation of propylene with molecular oxygen. The equilibrium constant for the reaction of the allyl radical, $C_3H_5^{\bullet} + O_2 \rightleftharpoons C_3H_5O_2^{\bullet}$ is reported to be log-K_{eq} ($K_{eq} = [C_3H_5O_2^{\bullet}]/[C_3H_5^{\bullet}]\ [O_2]$) = 5.0, 0.75, and –0.97 at 300, 500, and 600 K, respectively [13]. The reaction shifts towards the right with a decrease in temperature. Therefore, low temperatures in the post-catalytic space is expected to yield high selectivity to PO. On the basis of the analyses of the results in Table 3, moderate temperatures in the catalytic bed and in the post-catalytic bed space are necessary. The possible formation of radical species and a plausible gas-phase radical chain reaction mechanism have been described in previous reports [2–5]. It is conjectured that radicals are generated on the surface of MoO_x/SiO_2, which are released to the gas phase to subsequently react with molecular oxygen. Higher temperatures in the

Table 3 Results of propylene epoxidation in two-level reactor[a]

No.	T1 (K)	T2 (K)	T3 (K)	Yield of PO (%)	Conv. (%)	Sel. (%)[b]							
						AA	PO	AL	PA	AC	ALC	HC	CO_x
1	583	504	499	0	Trace	0	0	0	0	0	0	0	0
2	560	474	469	0	0.07	100	0	0	0	0	0	0	0
	573	474	469	0	0.2	74.2	0	25.8	0	0	0	0	0
	578	475	469	0	0.2	63.0	0	20.3	0	16.7	0	0	0
	583	475	469	0.03	0.4	52.7	8.6	14.4	0	14.7	9.6	0	0
3	573	522	517	0.08	0.3	53.7	23.6	11.2	0	11.5	0	0	0
	573	542	538	0.2	0.8	34.2	27.4	4.5	0	6.3	0	0	27.6
	573	553	549	0.5	1.4	37.2	32.6	3.3	0	4.5	0	0	22.4
	573	555	561	1.4	4.7	21.5	30.2	0.9	0	2.6	1.7	2.0	41.5
	577	556	561	4.6	13.8	13.7	33.0	0	0.7	1.4	4.4	2.6	45.4
	577	561	563	4.6	18.9	12.0	24.6	0.8	0.6	0.2	6.2	3.8	53.0

[a] Post-catalytic bed volume = 62 cm^3; Reaction pressure: 4.5 atm

[b] Same definitions of AA , AL, PA, AC, ALC, HC, CO_x as in Table 1

No. 1: empty; Feed gas, $C_3H_6/O_2/He = 10/5/20\ cm^3\ min^{-1}$

No. 2 and No. 3: 1.0 g of catalyst was mixed with quartz sand 3.0 g; Feed gas, $C_3H_6/O_2//He = 15/7.5/17.5\ cm^3\ min^{-1}$

catalytic bed would lead to the generation of more radicals from the surface of MoO_x/SiO_2. The post-catalytic bed free space is very important for PO formation. For lower temperature in the free space, the PO selectivity was lower; for higher temperature in the free space, the conversion increased but, unfortunately, the PO selectivity decreased. It is believed that the transfer of oxygen from peroxy radicals to alkenes is the rate-determining step in the formation of epoxides ($k_2 \gg k_{-1}$), and that for a peroxy radical attacking a series of alkenes, the activation energy for the overall reaction correlates well with the ionization energy of the alkenes [14–16].

$$C_3H_5OO^\bullet + C_3H_6 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_3H_5OOC_3H_6^\bullet$$

$$C_3H_5OOC_3H_6^\bullet \xrightarrow{k_2} C_3H_5O^\bullet + C_3H_6O$$

It should be mentioned that surface-initiated gas-phase reactions have been documented extensively in the past [17]. An interesting possibility is the phenomenon of oxygen transient formation where the chemisorption of molecular oxygen on a metal surface produces “hot” atomic species ($O^{\delta-}_{(s)}$) which can activate gas-phase molecular species [18–20].

It is clear from the work presented here that radical species need to be present in the empty volume after the catalyst bed to produce selective oxidation products. The radicals may be surface-generated species or may be supplied from species such as NO. The importance of the free space was earlier pointed out in the oxidation of propane [21], ethane [22], and methane [23].

4 Conclusions

In the gas-phase epoxidation of propylene in the presence of propane, the formation of propylene oxide mainly originated from propylene, with the propane only acting as an inert gas. Addition of NO in the feed gas increased the conversion and moderately the PO selectivity at low conversions. Subsequent reactions, however, decreased PO yields at high conversions. A two-level reactor with separate catalyst-bed and empty post-catalytic volume sections was utilized, and it was found that the oxidation reaction was very sensitive to the temperature of the post-catalytic space but was not influenced greatly by the temperature of the catalyst surface.

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