Gas-Phase Epoxidation of Propylene to Propylene Oxide on a Supported Catalyst Modified with Various Dopants

Shigeru Sugiyama [1,*], Yasuhiro Sakuwa [2], Tomoyasu Ogino [2], Naotaka Sakamoto [2], Naohiro Shimoda [1], Masahiro Katoh [1] and Nobuhiro Kimura [3]

[1] Department of Applied Chemistry, Graduate School of Technology, Industrial and Social Science, Tokushima University, Minamijosanjima, Tokushima-shi, Tokushima 770-8506, Japan

[2] Department of Applied Chemistry, Graduate School of Technology, Industrial and Social Science, Tokushima University, Minamijosanjima, Tokushima-shi, Tokushima 770-8506, Japan

[3] Pilot Testing Group, Fuels Research Laboratory, Central Technical Research Laboratory, JXTG Nippon Oil & Energy Corporation, 8, Chidoricho, Naka-ku, Yokohama 231-0815, Japan

* Correspondence: sugiyama@tokushima-u.ac.jp; Tel.: +81-88-656-7432

Abstract: In the present study, the production of propylene oxide (PO) from propylene via gas-phase epoxidation was investigated using various catalysts. Although Ag is known to be a highly active catalyst for the epoxidation of ethylene, it was not active in the present reaction. Both Al and Ti showed high levels of activity, however, which resulted in confusion. The present study was conducted to solve such confusion. Although the employment of MCM-41 modified with Ti and/or Al was reported as an active catalyst for epoxidation, the combination resulted in the formation of PO at a less than 0.1% yield. Since this research revealed that the acidic catalyst seemed favorable for the formation of PO, versions of ZSM-5 that were both undoped and doped with Na, Ti, and Ag were used as catalysts. In these cases, small improvements of 0.67% and 0.57% were achieved in the PO yield on H–ZSM-5 and Ti–ZSM-5, respectively. Based on the results of the Ti-dopant and acidic catalysts, Ag metal doped on carbonate species with a smaller surface area was used as a catalyst. As reported, Ag–Na/$CaCO_3$ showed a greater yield of PO at 1.29%. Furthermore, the use of $SrCO_3$ for $CaCO_3$ resulted in a further improvement in the PO yield to 2.17%. An experiment using CO_2 and NH_3 pulse together with SEM and TEM examinations for Ag–Na/$CaCO_3$ revealed that the greatest activity was the result of the greater particle size of metallic Ag rather than the acid–base properties of the catalysts.

Keywords: epoxidation; propylene; propylene oxide; Ag; alkaline carbonates

1. Introduction

Propylene oxide (PO) is a major raw material of functional chemicals such as polyester resins, urethane foams, pigments, pharmaceutical intermediates, and disinfectants. Various industrial production processes are used to produce PO. Currently, the two main processes for the industrial production of PO in a liquid phase are the chlorohydrin process and the Halcon process [1]. The former epoxidation process is not an oxidative process, while the latter is an oxidative process using peroxide. However, these processes suffer from a load of wastewater in the first case and an excessive amount of various by-products in the latter, with a market value that is lower than that of PO [1,2]. In order to suppress the formation of various by-products, the cumene method was developed as a "PO-only Process" that is based on the Halcon process [2]. However, persistent problems include complex process management and an excess use of peroxide [2]. Against such a background, the development of a new PO production method is desired. One of the most plausible

candidates examined for the production of PO is the oxidative epoxidation of propylene using gaseous O_2 on solid catalysts (Equation (1)). The employment of this heterogeneous catalytic system results in an easy separation of the solid catalyst from the gaseous reactant and product. Furthermore, the use of gaseous O_2 together with propylene as a reactant decreases the cost of PO production and improves safety. Since the epoxidation of an alkene has been put to practical use in the reaction between ethylene and oxygen on Ag-based catalysts, Ag was the first choice of a solid catalyst that was applied to the reaction between propylene and oxygen. However, Ag/α-Al_2O_3 has been reported as unsuitable for the epoxidation of propylene due to the highly active allylic C–H bonds in propylene [3], which suppress the selective formation of PO. This is why some researchers have declared that this epoxidation cannot be realized. In fact, propylene oxide has recently been reported to inhibit propylene epoxidation [4], highlighting the difficulty of this reaction. To overcome this difficulty, special efforts have been made, such as using high pressure [5,6] and using N_2O instead of O_2 [7]. However, when considering practical applications, it is better to avoid such special efforts if possible.

These circumstances seem to require a different perspective for the selection of a catalytically active species and support. Based on this viewpoint, we focused on two types of supported catalyst systems. One was a catalyst system prepared from a unique combination of supports such as MCM-41 (Mobil composition of matter 41) or a high-silica zeolite (HSZ) and catalytically active species such as Ti and/or Al. The other was a unique silver catalyst system supported on carbonate. From the former catalyst systems, PO yields far exceeded the yields achieved thus far (5.3% on Ti–Al–MCM-41, 20.4% on 15%Ti/HSZ at 523 K and 14.6% on Ti–Al–HSZ at 523 K), as reported by the same group [8–12]. From the latter catalyst systems, $Ag/CaCO_3$ doped with K [3,13] or Na [11] was tested and returned an unimpressive PO yield of 1.2% at 533 K [11]. The large difference between the two supported catalyst systems suggested that the Ag catalyst, which has been accepted as having high activity in the past, may have been misjudged, while the success of the Ti and/or Al system may have been overestimated.

In the present study, in order to eliminate such confusion in the development of a high level of activity, MCM-41 doped with Ti and/or Al, high- or low-silica zeolites doped with Ti, Na and Ag, and sodium-modified Ag catalysts supported on various alkaline carbonates ($CaCO_3$, basic $MgCO_3$ and $SrCO_3$) were employed for the epoxidation of propylene to propylene oxide. Carbonates are known to undergo thermal decomposition to release CO_2. Therefore, its use as a support may be inconvenient. However, the decomposition temperatures of $CaCO_3$, $MgCO_3$, and $SrCO_3$ were reported as 1192 K [14], 683 K [15], and 1323 K or higher [16], respectively, indicating that they are thermally stable and can be used as a support.

$$\text{---}\diagup^{CH_3} + 0.5O_2 \quad \Rightarrow \quad \triangledown\diagup^{CH_3} \qquad (1)$$
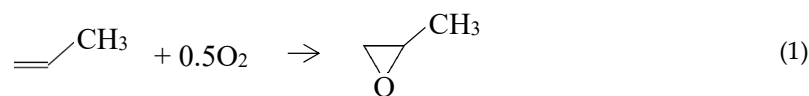
2. Results and Discussion

2.1. Catalytic Performances on MCM-41 Doped and Undoped with Al and/or Ti

Since it is generally believed that the active catalyst used in epoxidation was the Ag-based catalyst used in the reaction of ethylene to ethylene oxide [17,18], it is easy to understand why silver catalysts are being deployed in the epoxidation of propylene to propylene oxide [19]. Therefore, the employment of Al and/or Ti instead of Ag for this epoxidation of propylene is undoubtedly unique and worth considering in detail since there has been no verification by researchers other than the group that proposed this catalyst system [8–12]. Table 1 shows the results obtained after the epoxidation of propylene on MCM-41, Ti–MCM-41 (Si/Ti = 95), Al–MCM-41 (Si/Al = 75), Al–Ti–MCM-41 (Si/Ti = 24), and Al–Ti–MCM-41 (Si/Ti = 910) under the reaction conditions of W/F = 2.5×10^{-2} g·min/mL, T = 623 K, $P(O_2)$ = 8.6 kPa, and time-on-stream = 1.75 h. The partial pressure of C_3H_6 was adjusted to 16.7 kPa and 33.4 kPa for MCM-41 and other catalysts, respectively. As shown

in Table 1, MCM-41 (Catal. A) showed no activity for the epoxidation of propylene to mainly produce CO_x (CO + CO_2). Then, the partial pressure of propylene was increased from 16.7 kPa to 33.4 kPa in order to suppress the production of CO_x to examine the activity on MCM-41 modified with Ti and/or Al. The use of Ti–MCM-41 (Si/Ti = 95) (Catal. B in Table 1) again resulted in no activity for the epoxidation of propylene due to the main production of CO_x, while a certain formation of propionaldehyde (PA) could be detected. In contrast, the use of Al–MCM-41 (Si/Al = 75) (Catal. C in Table 1) resulted in an evident suppression of CO_x formation, while PO was certainly detected, indicating that the modification of MCM-41 using Al rather than Ti may be more suitable for the production of PO. The reaction was examined under the same conditions shown in Table 1, with the exception of the reaction temperature (523 K), to reveal, in the present catalyst system, the best PO yield of 0.095% with PO selectivity of 1.19% on Al–Ti–MCM-41 (Si/Ti = 910). The advantageous effect of Al rather than Ti may further support the notion that an excess addition of Ti into Al–Ti–MCM-41 decreased the PO selectivity from 0.35% on Al–Ti–MCM-41 (Si/Ti = 910) (Catal. E in Table 1) to 0.06% on Al–Ti–MCM-41 (Si/Ti = 24) (Catal. D in Table 1). Furthermore, it should be noted that the excess addition of Ti into Al–Ti–MCM-41 resulted in an enhancement of the formation of CO_x, as shown in the results using Al–Ti–MCM-41 (Si/Ti = 24) (Catal. D in Table 1).

Table 1. Catalytic activities on MCM-41 and related catalysts.

Catal.[1]	Conv.[%]	Selectivity [%]			Yield [%]	
	C_3H_6	CO_x	PO	PA	PO	PA
A	9.6	97.7	0	0	0	0
B	4.0	97.0	0	1.4	0	0.054
C	7.0	28.2	0.37	1.0	0.026	0.069
D	5.1	88.2	0.06	1.8	0.003	0.093
E	7.2	30.9	0.35	1.7	0.025	0.122

Catal.[1]: MCM-41 (**A**), Ti–MCM-41 (Si/Ti = 95) (**B**), Al–MCM-41 (Si/Al = 75) (**C**), Al–Ti–MCM-41 (Si/Ti = 24) (**D**) and Al–Ti–MCM-41 (Si/Ti = 910) (**E**).

Table 2. Information concerning the structure, surface properties, and acidity of MCM-41 and related catalysts.

Catal. [1]	2θ from (100) [2] [°]	Surface Area [3] [m²/g]	Total Pore Volume [4] [cm³/g]	Acidity [5] [mmol/g]
A	2.52	908	0.82	0.006
B	-	335	0.47	0.026
C	-	490	0.69	0.179
D	-	137	0.39	0.164
E	-	479	0.78	0.070

Catal.[1]: MCM-41 (**A**), Ti–MCM-41 (Si/Ti = 95) (**B**), Al–MCM-41 (Si/Al = 75) (**C**), Al–Ti–MCM-41 (Si/Ti = 24) (**D**) and Al–Ti–MCM-41 (Si/Ti = 910) (**E**). [2] Diffraction angle obtained from XRD due to (100) plane of MCM-41. [3] BET surface area. [4] Total pore volume estimated using N_2 adsorption/desorption isotherms. [5] Concentration of acid sites estimated using NH_3–TPD.

The XRD pattern of MCM-41 showed characteristic peaks at 2θ = 2.52° due to the hexagonal structure of MCM-41 while the catalysts modified with Ti and/or Al did not show a characteristic peak (Table 2). This indicated that the modification resulted in structural destruction. Since MCM-41 mainly produced CO_x (Table 1), the structural destruction of MCM-41 due to the modification with Ti and/or Al may be suitable for the formation of PO. It should be noted that the relatively greater surface areas of 490 and 479 m²/g, greater acid amounts such as 0.179 and 0.070 mmol/g, and a greater acid strength (ca. 503 K for NH_3 desorption temperature from both catalysts compared with ca. 473 K from MCM-41) detected from Al–MCM-41 (Si/Al = 75) and Al–Ti–MCM-41 (Si/Ti = 910), respectively, resulted in an evident formation of PO, as shown in Catal. C and E in Tables 1 and 2.

Finally, it may be worthwhile to mention that the employment of other modification procedures for MCM-41 with Ti and/or Al such as an incipient wetness method resulted in PO yields of less than 0.095% (not shown in Table 1). Therefore, the present study shows that the role of Ti and/or Al in the epoxidation of propylene to propylene oxide should not be overestimated.

2.2. Catalytic Performances on H–ZSM-5 Doped and Undoped with Na, Ti, or Ag

As described above, the acidic nature of the catalyst may be one of the key factors in the enhancement of the epoxidation of propylene to propylene oxide. Furthermore, it has already been reported that high-silica zeolite (HSZ) and related systems show excellent PO yield [8,11]. Therefore, as one of the typical zeolites, ZSM-5 was selected as a catalyst for epoxidation, and the activity was discussed using their acidic natures. Table 3 lists the results obtained after the epoxidation of propylene on H–ZSM-5(23.8), H–ZSM-5(37), H–ZSM-5(1880), Na–ZSM-5(23.8), Ti–ZSM-5(23.8) and Ag–ZSM-5(23.8) under reaction conditions of W/F =2.5 × 10^{-2} g·min/mL, T = 523 K, P(C_3H_6) = 33.4 kPa, and time-on-stream = 0.5 h.

Table 3. Catalytic activities and acid properties on H–ZSM-5 and related catalysts.

Catalyst	Conv. [%]	Select. [%]		Yield [%]	Acid amount	Temp.[3]
	C_3H_6	COx	PO	PO	[mmol/g]	[K]
H–ZSM-5(23.8) [1]	90.7	-	0.71	0.64	0.803	513
H–ZSM-5(23.8) [2]	91.5	8.2	0.73	0.67	0.686	743
H–ZSM-5(37) [1]	11.4	-	1.12	0.13	0.428	505
					0.431	713
H–ZSM-5(1880) [1]	13.8	-	1.35	0.19	0.296	528
Na–ZSM-5(23.8) [2]	6.5	36.9	1.05	0.07	0.857	555
Ti–ZSM-5(23.8) [2]	68.3	3.2	0.84	0.57	0.395	510
					0.082	694
Ag–ZSM-5(23.8) [2]	5.1	-	1.31	0.07	0.341	550
					0.094	726

[1] P(O_2) = 8.4 kPa. [2] P(O_2) = 16.4 kPa. [3] Temperature at which each peak was shown to be at a maximum.

In contrast to the catalytic activity of MCM-41 doped or undoped with Al and/or Ti, the conversion of oxygen at less than 3% and the selectivity to COx were almost negligible while the conversions of C_3H_6 were relatively greater than those on MCM-41 and related catalysts. This indicates that the oxidation reaction hardly proceeded on H–ZSM-5 and related catalysts since it is generally accepted that these catalysts are active for cracking, aromatization, isomerization, and successive reactions via these three reactions [20–22]. Therefore, since these catalyst systems did not possess the ability for an oxidation reaction, the small amount of PO that was produced did not suffer from deep oxidation to COx to show a relatively greater yield of PO of up to 0.67% on H-ZSM-5(23.8) at P(O_2) = 16.4 kPa.

It is evident that various reactions such as cracking, aromatization, and isomerization proceed on acidic sites of H–ZSM-5 and related catalysts. Since the epoxidation of propylene should be undoubtedly influenced by those reactions, the acidic properties of those catalysts were analyzed using NH_3-TPD (Figure 1).
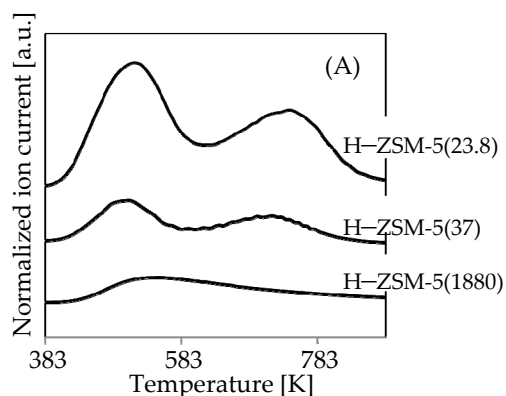
Figure 1. NH_3–TPD spectra of various H–ZSM-5 and those ion-exchanged with Na, Ti, and Ag.

As expected, the acid amount was decreased with an increase in the Si/Al ratio in H-ZSM-5 while the shape of the spectra was not influenced by the Si/Al ratio (Figure 1A). Upon the ion-exchange of protons in H–ZSM-5 with Na, Ti and Ag, the intensity of the NH_3-TPD peak detected at higher temperature regions of approximately 743 K was evidently decreased (Figure 1B). Furthermore, the TPD shape was strongly influenced by the ion exchange. Table 3 shows the acid amount and a temperature at which each peak was maximum, both of which were calculated using the data described in Figure 1. As shown in Table 3, a PO yield greater than 0.57% was detected on H-ZSM-5(23.8) and Ti–ZSM-5(23.8). Therefore, the presence of a TPD peak at a higher temperature region of approximately 743 K shows that the presence of a stronger acidic site may not be correlated to the formation of PO. Furthermore, the presence of a broader TPD peak detected at a lower temperature region of approximately 550 K detected from Na–ZSM-5(23.8) and Ag–ZSM-5 (23.8) may not be suitable for the formation of PO. The results shown in Figure 1 and Table 3 reveal that PO formation from epoxidation is strongly influenced by the balance between acid amount and acid strength in order to suppress the catalytic activity for the deep oxidation of PO to COx by shifting to reactions such as cracking, aromatization, isomerization of propylene, and successive reactions via these three reactions on the acid site on the present catalysts. Finally, it is worthwhile to mention that the negligible PO yield of 0.093% on Al–Ti-MCM-41 (Si/Ti = 910) could be improved to 0.67% on H-ZSM-5(23.8).

*2.3. Catalytic Performances on Ag Metal Doped on Carbonates*

Silver-based catalysts, which are industrial catalysts for the epoxidation of ethylene, have been repelled against the epoxidation of propylene due to the highly active allylic C–H bonds in propylene. However, it was reported that a catalyst with $CaCO_3$ as a support and a significantly increased level of silver loading was effective for the epoxidation of propylene to PO [23]. According to ARCO patent [24], some interesting reports have been reported for the epoxidation of propylene to propylene oxide on $Ag/CaCO_3$ prompted with alkali metal [13,25], indicating that the epoxidation activity was extensively enhanced with increase of Ag content from 1 wt % to 56 wt %, and $CaCO_3$ itself was ineffective for the further conversion of propylene oxide to unwanted products. This indicates that the very great catalytic activity of silver for the allylic C–H bonds in propylene may be reduced by decreasing the dispersion of silver, and as a result, PO can be suitably obtained. In the present study, we confirmed this result and examined further improvements in the PO yield. Table 4 shows the catalytic activities on various Ag catalysts supported on alkaline carbonate ($CaCO_3$, basic $SrCO_3$ or $MgCO_3$) modified or unmodified with Na under the reaction conditions at W/F = 2.5 x 10^{-2} g·min/mL, T = 573 K, $P(C_3H_6)$ = $P(O_2)$ = 33.4 kPa and time-on-stream = 0.5 h. The catalyst pretreatment was carried out with 10 mL/min of C_3H_6 diluted with He ($P(C_3H_6)$ = 33.4 kPa) at 673 K for 1 h before the evaluations of catalytic activity. Since some examples using carbonates as the support for this reaction have already been reported in papers and patents, the activity of the support itself was not examined [13,23–25].

Table 4. Catalytic activities on various Ag–Na/MCO₃ (M = Ca, Sr, or Mg).

Catalyst	Conversion [%]	Selectivity [%]		Yield [%]
	C_3H_6	COx	PO	PO
Ag(56)/CaCO₃	33.1	99.0	0.1	0.03
Ag(56)-Na(1)/CaCO₃	10.6	87.7	12.2	1.29
Ag(5.6)-Na(1)/CaCO₃	3.5	88.0	11.7	0.41
Ag(56)-Na(0.5)/CaCO₃	13.2	92.9	6.6	0.87
Ag(56)-Na(2)/CaCO₃	11.2	91.4	8.2	0.92
Ag(56)-Na(1)/SrCO₃	17.4	86.9	12.5	2.17
Ag(56)-Na(1)/MgCO₃	22.0	98.0	0.7	0.15

Based on the selectivity to COx, the oxidation of propylene certainly proceeded on the present catalyst system, in contrast to that on H-ZSM-5 and related catalysts. It should be noted that the removal of surface carbonate at temperatures below that of the decomposition is certainly possible. However, the COx selectivity and carbon balance reported in the present study would alleviate that concern. Although PO was slightly formed on Ag(56)/CaCO₃ (PO yield = 0.03%), an addition of 1% Na to this catalyst resulted in an evident enhancement of the PO yield of up to 1.29%. This PO yield is reasonable based on the results reported by Lu et al. [23], indicating that there is no problem in our experimental method. Both the decreased loading of Ag to 5.9% and the change of Na content to either 0.5 or 2% in the catalyst resulted in a decreased PO yield. The employment of basic MgCO₃ as a support resulted in an evident decrease in the PO yield to 0.15%, while that of SrCO₃ led to a further enhancement of the PO yield to 2.17%, which was the best PO yield in the present study.

The difference in PO yield between Ag(56)-Na(1)/CaCO₃, and Ag(5.6)-Na(1)/CaCO₃ should be strongly influenced by the dispersion of silver on the catalyst. Therefore, the silver presence was analyzed using XRD and FE-SEM. Figures 2A,B showed XRD patterns of Ag(5.6)-Na(1)/CaCO₃ and Ag(56)-Na(1)/CaCO₃, respectively. Although peaks due to CaCO₃ (PDF 00-005-0586) and Ag (PDF 01-087-0597) were evidently detected from Ag(5.6)-Na(1)/CaCO₃ and Ag(56)-Na(1)/CaCO₃, respectively, information on the dispersion of Ag is not yet clear.
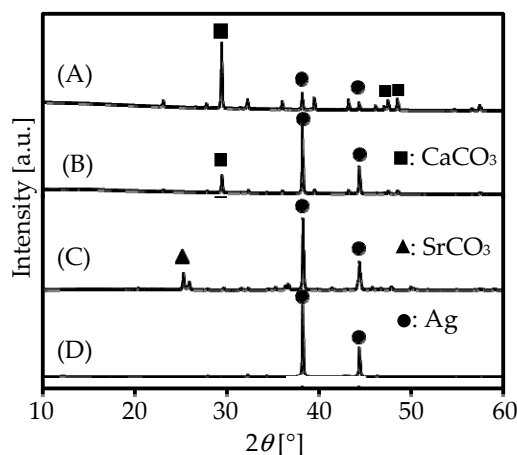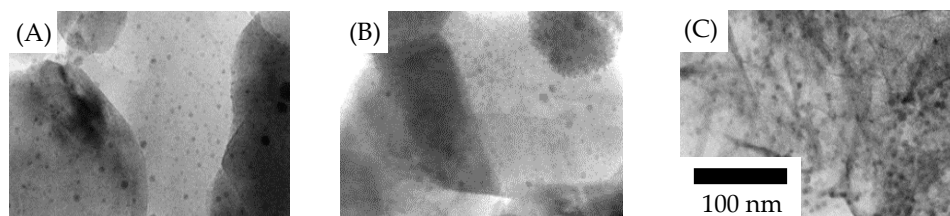

Figure 2. XRD patterns of (**A**) Ag(5.6)-Na(1)/CaCO₃, (**B**) Ag(56)-Na(1)/CaCO₃, (**C**) Ag(56)-Na(1)/SrCO₃, and (**D**) Ag(56)-Na(1)/MgCO₃.
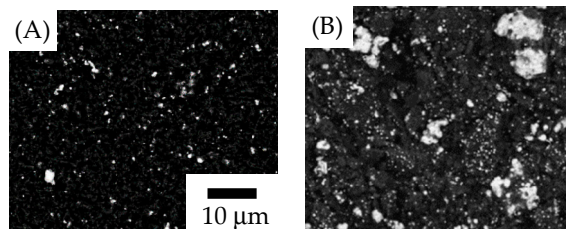
Figure 3. BSE images of Ag over Ag(5.6)-Na(1)/CaCO$_3$ (**A**) and Ag(56)-Na(1)/CaCO$_3$ (**B**). The scale of these figures is the same.

Therefore, both catalysts were analyzed using FE-SEM. Figure 3 displays a backscattered electron (BSE) image on Ag detected using FE-SEM to reveal that the particle size of Ag on Ag(56)-Na(1)/CaCO$_3$ was evidently greater than that on Ag(5.6)-Na(1)/CaCO$_3$, as expected. This indicates that a lower dispersion and a greater particle size makes Ag a more catalytically active site, in contrast to the conventional catalyst systems.

As shown in Table 4, PO yields on Ag(56)-Na(1)/MCO$_3$ (M = Ca, Sr, and Mg) were strongly influenced by the support, while the yield did not depend on the specific surface areas of these catalysts (4, 25 and 2 m^2/g, respectively). Since the particle size of Ag on those catalysts could not be explained by XRD (Figure 2), those catalysts were analyzed using TEM (Figure 4) to reveal that similar particles of Ag were detected, regardless of the supports. In using these TEM data, the particle size distribution of Ag on each catalyst was estimated and the results are summarized in Figure 5.

Figure 4. TEM images of (**A**) Ag(56)-Na(1)/CaCO$_3$, (**B**) Ag(56)-Na(1)/SrCO$_3$ and (**C**) Ag(56)-Na(1)/MgCO$_3$. The scale of these figures is the same.
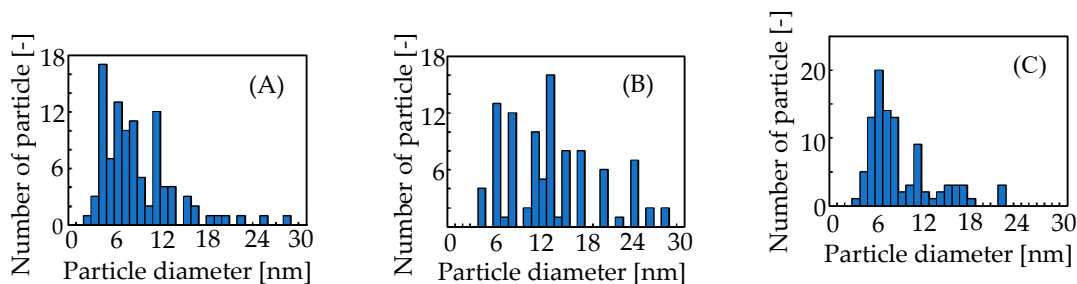

Figure 5. Particle size distribution of Ag on (**A**) Ag(56)-Na(1)/CaCO$_3$, (**B**) Ag(56)-Na(1)/SrCO$_3$, and (**C**) Ag(56)-Na(1)/MgCO$_3$.

The most active catalyst, Ag(56)-Na(1)/SrCO$_3$, showed a wider particle size distribution, while a sharp distribution was detected from the least active catalyst, Ag(56)-Na(1)/MgCO$_3$. The average particle sizes of Ag(56)-Na(1)/CaCO$_3$, Ag(56)-Na(1)/SrCO$_3$, and Ag(56)-Na(1)/MgCO$_3$ were 9.0, 13.9, and 10.1 nm, respectively. Therefore, it can be concluded once again that a lager particle of Ag would strongly influence the oxidative epoxidation of propylene to propylene oxide. It is worth noting that, in the case of the epoxidation of ethylene to ethylene oxide on Ab-based catalysts in the presence of

gaseous O_2, the better ethylene epoxidation performance was observed over lower Ag dispersions [26].

Finally, the acid–base properties of Ag(56)-Na(1)/CaCO$_3$, Ag(56)-Na(1)/SrCO$_3$, and Ag(56)-Na(1)/MgCO$_3$ were analyzed using NH$_3$- and CO$_2$-TPD, respectively (Figure 6A,B, respectively). As shown in Figure 6A, these three catalysts did not show an acidic nature regardless of supports. For CO$_2$-TPD from Ag(56)-Na(1)/MgCO$_3$, an evident broad peak was detected at approximately 483 K, due to the employment of basic MaCO$_3$ as a support, resulting in the lowest activities among Ag(56)-Na(1)/MCO$_3$ (M = Ca, Sr, and Mg). Furthermore, a desorption peak was evident at temperatures greater than ca. 683 K for Ag(56)-Na(1)/CaCO$_3$ and Ag(56)-Na(1)/SrCO$_3$ or 783 K for Ag(56)-Na(1)/MgCO$_3$. These desorption peaks were due to decarboxylation from the support, indicating that those three catalysts did not show the basic nature that contributed to the present catalysis regardless of supports. Therefore, in the case of a silver catalyst, the particle size may be one of the most important factors for the epoxidation of propylene, while acid base properties may not contribute to the enhancement of catalytic activity. Finally, it is worthwhile to mention that the negligible PO yield of 0.095% on Al–Ti–MCM-41 (Si/Ti = 910), followed by a better yield of 0.67% on H-ZSM-5(23.8) was further improved to 2.17% on Ag(56)-Na(1)/SrCO$_3$.
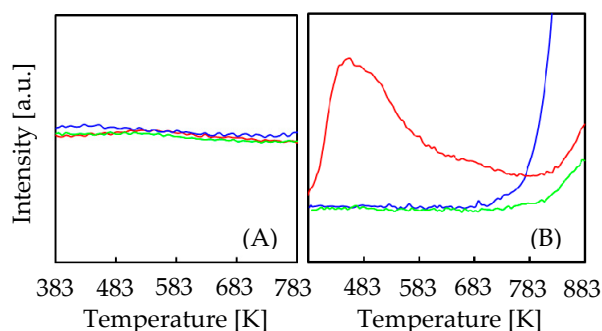
Figure 6. NH$_3$-TPD (**A**) and CO$_2$-TPD (**B**) spectra of Ag(56)-Na(1)/CaCO$_3$, Ag(56)-Na(1)/SrCO$_3$ and Ag(56)-Na(1)/MgCO$_3$ indicated by blue, green, and red lines, respectively.

3. Materials and Methods

3.1. Materials and Reagents

The reagents and the supports were of analytical grade and were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan except for colloidal silica, which was purchased from Nissan Chemical Ind. Tokyo, Japan, and ethylene diamine and ethanolamine, both from Kanto Chemical Co., Inc. Tokyo, Japan. All the reagents and the supports were used without further purification.

3.2. Preparation of Catalysts

Unmodified MCM-41 was prepared using a method similar to one previously reported [27,28]. Dodecyltrimethylammonium bromide (33.75 g, 109.5 mmol) dissolved in 96.21 g of distilled water was used as the surfactant template. Colloidal silica (45.95 g) was used as the silica source. Sodium hydroxide (1.74 g, 43.5 mmol) was dissolved in 18.82 g of distilled water to be used for the pH adjustment solution. Into the surfactant solution, colloidal silica and a sodium hydroxide solution were alternatively added dropwise for about 20 min, and the mixed solution was stirred at 313 K for 2 h. With this mixed solution, hydrothermal synthesis was carried out at 413 K for 48 h. The white wet solid thus obtained was filtered, washed with distilled water, and dried at 333 K for two days. Finally, MCM-41 was obtained by calcination at 873 K for 6 h.

According to a similar method previously reported [9], Ti-containing MCM-41 (Ti–MCM-41) was prepared by the drop-wise addition of a clear solution of tetraethyl orthosilicate (TEOS; 9.28 g, 44.6 mmol) in 2-propanol (22.7 g) to a stirred solution of hexadecyltrimethyl-ammonium chloride (11.3 g, 35.3 mmol), followed by addition of a solution of titanium tetraisopropoxide (TTIP; 0.134 g,

0.471 mmol) in 2-propanol (8 mL) and the successive addition of tetramethylammonium hydroxide (8.10 g, 44.7 mmol) in water (6.4 g)/2-propanol (29.4 g) mixture. The pH was adjusted to approximately 11.4 with diluted H_2SO_4. Then, H_2O (72.9 g) was added. Allowing the resulting gel to age for six days at 373 K produced the crystalline templated product. After filtration, the obtained samples were air-dried at 333 K for 24 h and calcined at 813K under air for 8 h to remove the structurally incorporated template of Ti–MCM-41 at a molar ratio of Si/Ti = 95 (Ti–MCM-41 (Si/Ti = 95)). The molar ratio was controlled by adjusting the ratio of TEOS to TTIP. The preparation of Al-containing MCM-41 (Al–MCM-41) followed the same procedure as Ti–MCM-41 except for the use of a solution of aluminum isopropoxide in 2-propanol other than that of a solution of TTIP in 2-propanol. For the preparation of Al–MCM-41 with a molar ratio of Si/Al = 75 (Al–MCM-41 (Si/Al = 75)), 0.12 g of aluminum isopropoxide (0.588 mmol) in 8 mL 2-propanol was employed in a preparation that was the same procedure as that of the Ti–MCM-41 for a TEOS solution. In MCM-41 that contained both Ti and Al (Al–Ti–MCM-41), the molar ratio of Si/Al was fixed at 75 and that of Si/Ti was adjusted using an amount of TTIP. Al–Ti–MCM-41 (Si/Ti = 24 or 910) was prepared from 8 mL 2-propanol solution containing either 0.53 g (1.86 mmol) or 0.014 g (0.049 mmol) of TTIP.

Various H-ZSM-5 catalysts, with ratios for Si/Al of 23.8, 378 and 1880 (H-ZSM-5(23.8), H-ZSM-5(37) and H-ZSM-5(1880), respectively), were supplied from Tosoh Corp., Tokyo, Japan. In order to prepare Na–ZSM-5(23.8), 10.0 g of H-ZSM-5(23.8) was added to 180 mL of a 1 M aqueous solution of $NaNO_3$. This solution was evaporated at 353 K under a vacuum to degas and then stirred at this temperature for 1.5 h at atmospheric pressure. The evaporation and stirring processes were repeated three times. Thus treated, the solid was filtered, washed with 600 mL of distilled water and dried at 333 K for 24 h, followed by calcination at 823 K for 6 h to produce Na–ZSM-5(23.8). This Na–ZSM-5(23.8) was treated in 20 mL of a 0.001 mol aqueous solution of titanium sulfate or silver nitrate at room temperature for 12 h. The resultant solid was washed, dried and calcined as above to produce either Ti–ZSM-5(23.8) or Ag–ZSM-5(23.8), respectively.

Sodium-modified silver catalysts supported on various forms of alkaline carbonate ($CaCO_3$, basic $MgCO_3$ or $SrCO_3$) were prepared using a method reported by Lu et al. [23]. A typical example would be the preparation procedure for Ag(56)-Na(1)/$SrCO_3$, in which the numbers in parentheses refer to the wt % loading of silver and sodium. Ethylene diamine (15.0 g, 250 mmol) was dissolved in distilled water (20.0 g). Then oxalic acid (10.1 g, 112 mmol) and $AgNO_3$ (8.90 g, 38.4 mmol) were slowly added to the solution with magnetic stirring until they were completely dissolved. After 1 h stirring, ethanolamine (1.80 g, 29.5 mmol) and NaCl (0.147 g, 2.51 mmol) were dissolved in 4 mL distilled water and added to the solution. The obtained mixture was stirred for an additional 1 h. Then 6.40 g of $SrCO_3$ were added to the solution to form a slurry. The slurry was stirred for 4 h, dried at 393 K for 2 h, and calcined at 633 K for 3 h to produce Ag(56)-Na(1)/$SrCO_3$.

3.3. Evaluation of Catalytic Performances

The catalytic activities were measured with a fixed-bed continuous flow reactor under atmospheric pressure. Each catalyst was pelletized and sieved to 0.85–1.70 mm. The catalysts (0.25 g) were then placed into a reactor. Unless otherwise stated, the catalyst pretreatment was carried out with 25 mL/min of O_2 gas flow at 673 K for 1 h before the evaluations of catalytic activity. The evaluations were carried out under 10 mL/min of a reactant gas flow, which consisted of propylene and oxygen diluted with helium. In the preset study, homogeneous reactions in the absence of the catalyst were not detected with the exception of a reaction at 623 K that showed a conversion of C_3H_6 of less than 0.01% at $P(C_3H_6) = P(O_2) = 33.4$ kPa. In this case, the data were corrected by subtracting the data obtained after homogeneous reaction in the absence of the catalyst from that after heterogeneous reaction in the presence of the catalyst. The reaction was monitored using two gas chromatographs (both GC-8APT, Shimadzu Corp., Kyoto, Japan) with a thermal conductivity detector (TCD) and a flame ionization detector (FID), together with a capillary gas chromatograph (GC-2010 Plus, Shimadzu Corp.) equipped with a flame ionization detector (FID). The columns in TCD-GC consisted of a Molecular Sieve 5A (0.3 m × Φ 3 mm) for the detection of O_2, CH_4, and CO and a Porapak Q (3 m × Φ 3 mm) for the detection of CO_2, C_2, C_3, and C_4 species. A Gaskuropak 55 (2

m × Φ 3 mm) was used for the detections of CH_4, C_2H_4 and C_3H_6. A Stabilwax (60 m × Φ 0.25 μm) was used as a capillary column to provide detailed analyses of C_3H_6, C_3H_8, acetaldehyde, PO, propionaldehyde (PA), acetone, and acrolein. The catalytic activities were estimated on a carbon basis. The carbon balance between the reactant and the products was within ± 5%.

3.4. Characterization of Catalysts

The X-ray diffraction (XRD) patterns were measured using a SmartLab/R/INP/DX (Rigaku Co., Tokyo, Japan) with a Cu Kα radiation monochromator at 45 kV and 150mA. After pretreatment at 473 K for 10 h under a vacuum, N_2 adsorption/desorption isotherms of the catalysts were measured using a BELSORP max12 (MicrotracBEL, Osaka, Japan) at 77 K, and then the specific surface areas were estimated via BET. The acidic or basic properties of the catalysts were measured for NH_3 and CO_2 temperature- programed desorption (TPD), respectively, using a BELCAT II (MicrotracBEL, Osaka, Japan). The desorbed NH_3 and CO_2 from the catalyst was monitored using a BELMass (MicrotracBEL, Osaka, Japan) quadruple mass spectrometer with a mass signal of m/e = 16 or 44 for NH_3 or CO_2, respectively. It should be noted that m/e = 17, which is the mass signal of an NH_3 parent peak, was strongly influenced by H_2O, and, therefore, m/e = 16 was used for the analysis of NH_3. In order to characterize the silver in Ag(56)-Na(1)/$SrCO_3$, which showed the highest activity among the catalysts examined in the present study, a field mission-scanning electron microscope (FE-SEM) (S4700, Hitachi High-Technologies Co., Tokyo, Japan) and transmission electron microscope (TEM) (JEM-2100F, JEOL Ltd., Tokyo, Japan) were used.

4. Conclusions

For the epoxidation of propylene to propylene oxide using O_2, it is concluded that the silver catalyst, which is used extensively in the industry for the epoxidation of ethylene, is inconvenient due to the highly active allylic C–H bonds in propylene on an Ag catalyst. As suggested above, the present re-examination of the catalytic activity employed in the previous reports revealed that the use of Al and/or Ti instead of silver as a catalytically active species resulted in almost no activity. In order to confirm that there was no problem with the experimental method of this study and develop a catalyst with high activity, the activity on Ag metal doped on carbonates was examined. The Ag(56)-Na(1)/$CaCO_3$ prepared in the present study showed similar activity to that reported previously under similar reaction conditions [23], which indicated that the reaction method used in the present study was not a problem. Furthermore, the use of $SrCO_3$ in place of $CaCO_3$ in Ag(56)-Na(1)/$CaCO_3$ resulted in an evident improvement in the PO yield of 1.29–2.17%. The present study revealed that the employment of a silver catalyst with a large particle size supported on various alkaline carbonates resulted in suitable activity for the epoxidation of propylene due to the suppression of the catalytic activity on the Ag catalyst. Although it is sometimes suggested that Ti and/or Al could be a suitable catalyst for the epoxidation of propylene, the present results revealed that the expectations for these elements were not met. It should be noted that, in a catalyst not containing silver, the acid nature of the catalyst is an important factor that contributes to this epoxidation.

Author Contributions: S.S. and N.K. conceived the experiments; S.S., N.S. (Naohiro Shimoda), M.K. and N.K. designed the experiments; Y.S. T.O., and N.S. (Naotaka Sakamoto) performed the experiments; All authors discussed the results; S.S. wrote and revised the manuscript. All authors read and approved the original and the revised manuscripts.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Nijhuis, T.A.; Makkee, M.; Moulijin, J.A.; Weckhuysen, B.M. The production of propene oxide: Catalytic processes and recent development. *Ind. Eng. Chem. Res.* **2006**, *45*, 3447–3459.

2. Tsuji, J.; Yamamoto J.; Ishino, M.; Oku, N. Development of new propylene oxide process. *Sumitomo Kagaku* **2006**, *1*, 4–10.

3. Palermo, A.; Husain, A.; Tikhov, M.S.; Lambert, R.M. Ag-Catalyzed epoxidation of propene and ethene: An investigation using electrochemical promotion of the effects of alkali, NOx, and chlorine. *J. Catal.* **2002**, *207*, 331–340.

4. Harris, J.W.; Arvay, J; Mitchell, G.; Delgass, W.N.; Ribeiro, F.H. Propylene oxide inhibits propylene epoxidation over Au/TS-1. *J. Catal.* **2018**, *365*, 105–114.

5. Ghosh, S.; Acharyya, S.S.; Tiwari, R.; Sarkar, B.; Singha, R.K.; Pendem, C.; Sasaki, T.; Bal, R. Selective oxidation of propylene to propylene oxide over silver-supported Tungsten oxide nanostructure with molecular oxygen. *ACS Catal.* **2014**, *4*, 2169–2174.

6. Lei, Y.; Chen, X.; Xu, C.; Dai, Z.; Wei, K. Enhanced catalytic performance in the gas-phase epoxidation of propylene over Ti-modified MoO_3-Bi_2SiO_5/SiO_2 catalysts. *J. Catal.* **2015**, *321*, 100–112.

7. Held, A.; Kowalska-Kuś, J.; Lapiński, A.; Nowińska, K. Vanadium species supported on inorganic oxides as catalysts for propene epoxidation in the presence of N_2O as an oxidant. *J. Catal.* **2013**, *306*, 1–10.

8. Murata, K.; Kiyozumi, Y. Oxidation of propene by molecular oxygen over Ti-modified silicate catalysts. *Chem. Commun*. **2001**, *15*, 1356–1357.

9. Murata, K.; Liu, Y.; Miura, N.; Inaba, M. Direct vapor phase oxidation of propylene by molecular oxygen over MCM-41 or MCM-22 based catalysts. *Catal. Commun*. **2003**, *4*, 385–391.

10. Murata, K.; Liu, Y.; Inaba, M.; Mimura, N. Effect of Ti-modified mesoporous materials on the direct epoxidation of propylene by molecular oxygen. *Catal. Taday*, **2004**, *91*, 39–42.

11. Liu, Y.; Murata, K.; Inaba, M.; Mimura, N. Mimura. Syntheses of Ti- and Al-containing hexagonal mesoporous silicas for gas-phase epoxidation of propylene by molecular oxygen. *Appl. Catal. A: Gen.* **2006**, *309*, 91–105.

12. Mimura, N.; Tsubota, S.; Murata, K.; Bando, K.; Bravo-Suárez, J.J.; Haruta, M.; Oyama, S.T. Gas-phase radical generation by Ti oxide clusters supported on silica: application to the direct epoxidation of propylene to propylene oxide using molecular oxygen as an oxidant. *Catal. Lett*. **2006**, *110*, 47–51.

13. Zemichael, F.W., Palermo, A.; Tikhov, M.S.; Lambert, R.M. Propene epoxidation over K-promoted Ag/$CaCO_3$ catalysts: the effect of metal particle size. *Catal. Lett.* **2002**, *80*, 93–98.

14. Ishizawa, N. On the thermal decomposition of calcite. *Annu. Rep. Adv. Ceram. Res. Cent. Nagoya Inst. Technol*. **2014**, *2*, 19–24.

15. Sawada, Y.; Uematsu, K.; Mizutani, N.; Kato, M. Thermal decomposition of basic magnesium carbonates. *J. Chem. Soc. Japan*; in Japanese, *Nippon Kagaku Kaishi,* **1979**, *1*, 57–63.

16. Kobayashi, Y.; Sumi, K.; Asai, T.; Kato, E. Fabrication of dense celsian ceramics by reaction of kaolin with $SrCO_3$ and $BaCO_3$. *J. Ceram. Soc. Jpn*. **1999**, *107*, 657–661.

17. Van Santen, R.A.; Kuipers, H.P.C.E. The mechanism of ethylene epoxidation. *Adv. Catal.* **1987**, *35*, 265–321.

18. Kestenbaum, H.; Lange de Oliveira, A.L.; Schmidt, W.; Schüth, F.; Ehrfeld, W.; Gebauer, K.; Löwe, H.; Richter, T.; Lebiedz, D.; Untiedt, I.; et al. Silver-catalyzed oxidation of ethylene to ethylene oxide in a microreaction system. *Ind. Eng. Chem. Res*. **2002**, *41*, 710–719.

19. Lei, Y.; Mehmood, F.; Lee, S.; Greeley, J.; Lee, B.; Seifert, S.; Winans, R.E.; Elam, J.W.; Meyer, R.J.; Redfern, P.C.; et al. Increased Silver Activity for Direct Propylene Epoxidation via Subnanometer Size Effects. *Science* **2010**, *328*, 224–228

20. Anderson, J.R.; Mole, T.; Christov, V. Mechanism of some conversions over ZSM-5 Catalyst. *J. Catal*. **1980**, *61*, 477–484.

21. Kitagawa, H.; Y. Sendoda, Y.; Ono, Y. Transformation of propane into aromatic hydrocarbons over ZSM-5 zeolite. *J. Catal*. **1986**, *101*, 12–18.

22. Hoang, T.Q.; Zhu, X.; Sooknoi, T.; Resasco, D.E.; Mallinson, R.G.A comparison of the reactivities of propanal and propylene on HZSM-5. *J. Catal*. **2010**, *271*, 201–208.

23. Lu, J., Bravo-Suárez, J.J.; Haruta, M.; Oyama, S.T. Direct propylene epoxidation over modified Ag/$CaCO_3$ catalysts. *Appl. Catal. A: Gin*. **2006**, *302*, 283–295.

24. Cooker, B.; Gaffney, A.M.; Jewson, J.D.; Kahn, A.P.; Pitchai, R. Epoxidation process using supported silver catalysts pretreated with organic chloride. *US Patent No. 5,770,746*, 20 May **1998**

25. Lu, J., Bravo-Suárez, J.J.; Takahashi, A.; Haruta, M.; Oyama, S.T. In situ UV-vis studies of the effect of particle size on the epoxidation of ethylene and propylene on supported silver catalysts with molecular oxygen. *J. Catal*. **2005**, *232*, 85–95.

26. Chongterdtoonskul, A.; Schwank, J.W.; Chavadej, S. Effects of oxide supports on ethylene epoxidation activity over Ag-based catalysts. *J. Mol. Catal. A: Chem*. **2012**, *358*, 58–66.

27. Iwamoto, M.; Abe, T.; Tachibana, Y. Control of bandgap of iron oxide through its encapsulation into SiO_2-based mesoporous materials. *J. Mol. Catal. A: Chem.*, **2000**, *155*, 143–153.

28. Ehiro, T.; Itagaki, A.; Misu, H.; Nakagawa, K.; Katoh; M., Katou, Y.; Ninomiya, W.; Sugiyama, S. Effects of acid treatment on the acidic properties and catalytic activity of MCM-41 for the oxidative dehydrogenation of isobutane. *J. Chem. Eng. Jpn*. **2016**, *49*, 152–160.