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Epoxidation of Propene by Gaseous Oxygen over Silica and Mg-Loaded Silica under Photoirradiation

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Silica was found to promote the photooxidation of propene by molecular oxygen, yielding acetaldehyde, propylene oxide, and propionaldehyde. The yield of and selectivity to propylene oxide were improved significantly by modification of silica with 1 wt% magnesium oxide loading. The product selectivity was affected by the amount of magnesium and the preparation method. Mg *K*-edge XANES and phosphorescence spectra indicated that the active sites on the Mg-loaded silica for epoxidation of propene are highly dispersed and isolated magnesium oxide species. The photoactive sites on bare silica are briefly discussed. © 1997 Academic Press

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INTRODUCTION

Epoxides are very important intermediates for many chemicals. Therefore, new heterogeneous catalytic processes producing epoxides directly from alkenes with gaseous oxygen are desirable. Epoxidation of ethene with gaseous oxygen over Ag catalysts was developed many years ago (1), but the same reaction with propene has not been successful. Although Ti-containing zeolites (2–4) have recently attracted much interest as catalysts for epoxidation, the system must consume hydrogen peroxide as an oxidant. Gaseous oxygen is a more desirable oxidant for industrial use than hydrogen peroxide.

Silica is generally used as a support for catalysts and is usually regarded as a catalytically inactive material. However, it can function as a catalyst for some reactions (5–8), in particular, when it is activated by photoirradiation (9–11). Some silica-based materials containing nontransition metal oxides were also found to be photoactive; e.g., highly dispersed magnesium oxide supported on silica has a function of photooxidation of CO (12, 13) and silica–alumina binary oxides are also photoactive (14). These materials show photoemission spectra with fine structures similar to those of vanadium oxide dispersed on silica (15). Tanaka *et al.* had already reported that an epoxide intermediate is formed in the photooxidation of light alkenes with O_2 over silica-supported vanadium oxide (16) and that highly dispersed niobium oxide on silica can catalyze the epoxidation of propene with gaseous oxygen under photoirradiation (17). In addition, a spectroscopic study was recently reported on the production of propylene oxide from propene and O_2 over Ba Y-zeolite irradiated with visible light (18). These silica-based systems have some common factors; heteroatom species are highly dispersed and they become photoactive sites.

Previously, we found that silica showed an unexpected photocatalysis in metathesis reactions of light alkenes when it was evacuated at high temperatures (19), and successively we discovered that the presence of gaseous oxygen causes partial oxidation of propene including epoxidation (20). Furthermore (20), we pointed out that the selectivity for propylene oxide was doubled by loading magnesium oxide on the silica. However, the details on the promotion effect by loading Mg ions on silica have not been discussed. In the present study, we focus on the local structure of the active sites in Mg-loaded silica prepared by two different methods and discuss the correlation between the structure of the active sites and the epoxidation activity. The active sites of the bare silica are also discussed. The structure of magnesium species was studied by photoluminescence and Mg *K*-edge XANES spectra.

EXPERIMENTAL

The silica employed was prepared from $Si(OC_2H_5)_4$ by a sol-gel method, followed by calcination in air at 773 K (21). BET surface area was 556 $m^2\ g^{-1}$. Mg-loaded silica was prepared by two methods as follows: (i) After impregnating the silica with a solution of $Mg(OCH_3)_2$ in methanol (12), the mixture was filtered and the precipitation was dried at 343 K for 24 h, followed by calcination at 773 K in air for 5 h. (ii) After impregnating the silica with an aqueous

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$Mg(NO_3)_2$ solution, it was evaporated to dryness in water bath, followed by drying at 343 K for 24 h and calcination at 773 K in air for 5 h. These samples were referred to as (i) *x*MS-M (*x* stands for weight percent of MgO) and (ii) *x*MS-W hereafter. The magnesium oxide loadings were determined by XRF measurement. Bulk MgO was obtained from hydrolysis of a solution of $Mg(OCH_3)_2$ in methanol followed by calcination at 773 K.

Photoluminescence spectra were recorded at 77 K with a Hitachi F-3010 fluorescence spectrophotometer using a UV filter ($\lambda_{\text{transmission}} > 300$ nm) to remove scattered light from the UV source (Xe lamp), where the fluorescence emission was cut off mechanically to record phosphorescence spectra. Before recording the spectra, the sample was treated with 60 Torr (1 Torr = 133.3 N m^{-2}) oxygen for 1 h at 1073 K, followed by a 1-h evacuation at 1073 K. The optical cell was made of quartz, 5 mm diameter. The amount of the sample in the cell was ca. 150 mg.

X-ray absorption experiments were carried out on beamline BL-7A at UVSOR, Institute for Molecular Science, Okazaki, Japan, with a ring energy of 750 MeV and a stored current of 80–200 mA. Spectra were recorded at room temperature, using a beryl two-crystal monochromator in the total electron yield mode. The sample calcined at 1073 K was mixed with active carbon in dry hexane and was put on the first photocathode made of Cu–Be in the electron multiplier (22, 23). We obtained only the spectra of higher-loaded samples with a loading above 5 wt% MgO since low-loaded samples showed small ratios of signal to background (S/B) or signal to noise (S/N) in their spectra.

Before reaction, the samples were heated under an oxygen atmosphere and subsequently evacuated at 1073 K. The photooxidation of propene (20) was carried out in a closed reaction vessel made of quartz (35 cm^3) at room temperature for 2 h as the standard condition. The reactants were propene (30 μmol) and oxygen (0–120 μmol; 60 μmol as standard). The catalyst (100 mg) was spread on the flat bottom (3.14 cm^2) of the vessel. A 250-W ultrahigh-pressure Hg lamp was used as a light source. The temperature of the catalyst bed was elevated by ca. 10 K from room temperature by the photoirradiation. Products were collected in a part of the closed system by a liquid–N_2 trap when the catalyst bed was under irradiation. After that, the catalyst was heated in the dark to collect the adsorbed products on catalyst surface. Products were analyzed by GLC and GC-MS.

RESULTS

Phosphorescence Spectra

Figure 1 shows phosphorescence spectra of the silica and Mg-loaded silica samples. Silica (Fig. 1a) exhibited a broad emission centered around 440 nm, which can be assigned to surface hydroxy groups (13). The 1 wt% MgO-loaded silica prepared from a solution of $Mg(OCH_3)_2$ in methanol, 1MS-M (Fig. 1b), showed an emission spectrum with fine structure centered at 525 nm. In the previous study (12, 13), the site exhibiting the emission with fine structure was assigned to highly dispersed magnesium oxide species on the silica surface. For this sample, 1MS-M, the broad band resulting from the surface hydroxy groups had disappeared, indicating that magnesium ions replace almost all the silanols remaining after evacuation at 1073 K (13).

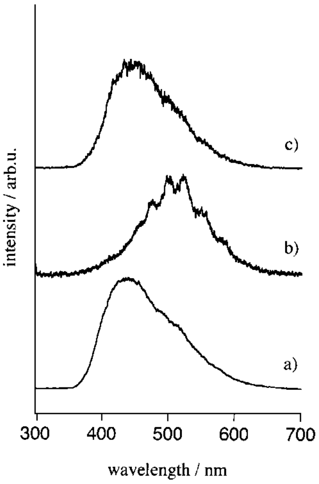

FIG. 1. Phosphorescence spectra of silica (a) and Mg-loaded silica, 1MS-M (b), and 6MS-M (c). The excitation wavelength was 240 nm.

In the sample with high Mg loading, 6MS-M (Fig. 1c), the fine structure disappeared and a broad band centered at 450 nm appeared instead, indicating that the magnesium oxide species in the sample are not highly dispersed. The peak position of the broad band of 450 nm was slightly different from that of hydroxy groups on silica of 440 nm. Since bulk MgO shows broad luminescence spectra (24–27), the broad spectrum would result from crystallites or islands of magnesium oxides on silica.

In Fig. 2, the spectra of Mg-loaded silica samples prepared from aqueous solution (*x*MS-W samples) are shown. Fine structure on the spectrum resulting from the highly dispersed magnesium oxide species was observed most clearly in the 5 wt% loaded sample, 5MS-W (Fig. 2b). The sample with low Mg loading, 1MS-W (Fig. 2a), showed a spectrum similar to that of silica; however, the spectrum contains a weak fine structure, indicating that there are both silanols and highly dispersed magnesium species on 1MS-W. A high-loaded sample, 20MS-W (Fig. 2c), shows only a broad emission centered at 460 nm. This broad spectrum is however different from that of 6MS-M in the line shape and peak position; the shape of the spectrum of 20MS-W is a little sharper than that of silica or 6MS-M, and the peak position shifts by ca. 10 nm to a higher wavelength than that of 6MS-M.

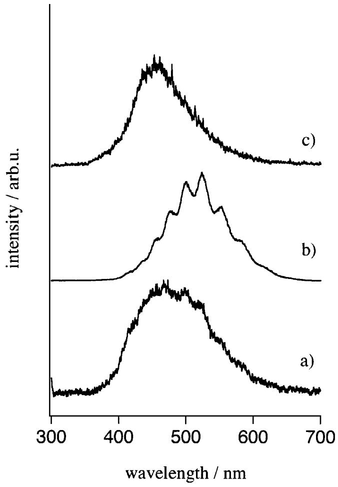

FIG. 2. Phosphorescence spectra of Mg-loaded silica, 1MS-W (a), 5MS-W (b), and 20MS-W (c). The excitation wavelength was 240 nm.

XANES Spectra

The structure of magnesium oxide species in this system could not be analyzed by X-ray diffraction because no definite diffraction lines were detected. On the other hand, XANES spectra can offer us information about the local structure of highly dispersed Mg species (28).

Some normalized XANES spectra of MS-M and MS-W samples calcined at 1073 K are shown in Fig. 3. The XANES of 20MS-M (Fig. 3b) is identical to that of bulk MgO of typical rock salt structure (22, 23, 29), indicating that Mg ions exist in MgO particles; i.e., the Mg ion is surrounded by an oxygen octahedron. The XANES spectrum of 5MS-M (Fig. 3a) is almost the same as that of MgO although the peak at 1315 eV is slightly larger. The *x*MS-M samples, prepared from a solution of $Mg(OCH_3)_2$ in methanol, exhibited almost the same XANES spectrum as that of MgO, indicating that MgO crystallites are formed on silica in this preparation method (22, 28).

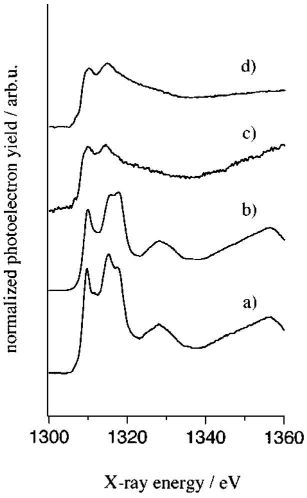

FIG. 3. Normalized Mg *K*-edge XANES spectra of Mg-loaded silica samples calcined at 1073 K; 5MS-M (a), 20MS-M (b), 5MS-W (c), and 20MS-W (d).

On the other hand, the XANES spectra of 5MS-W (Fig. 3c) and 20MS-W (Fig. 3d), samples prepared from a $Mg(NO_3)_2$ aqueous solution, are completely different from those of *x*MS-M samples, MgO, and other compounds such as $Mg(OH)_2$, Mg_2SiO_4, $MgSiO_3$, and $Mg_2Si_3O_8$ (22, 28). This type of XANES spectra was assigned to highly dispersed magnesium oxide species on the silica surface (28). Other *x*MS-W samples below the amount corresponding to a monolayer coverage (up to 30 wt% MgO) show also the same spectra. This indicates that impregnation with an aqueous solution of $Mg(NO_3)_2$ is more advantageous to disperse the magnesium ions on the silica surface than impregnation with a solution of $Mg(OCH_3)_2$ in methanol (28).

Photooxidation

Table 1 shows the product yields in the photooxidation of propene in the presence of 60 μmol O_2 over silica, Mg-loaded silica samples, and MgO. The products were propylene oxide (PO; methyloxirane, or 1,2-epoxypropane), acetaldehyde (AA; ethanal), propionaldehyde (PA; propanal), acetone (AC; propanone), acrolein (AL; prop-2-enal), and alcohols (methanol, ethanol, and propan-2-ol). Although metathesis of propene takes place in the absence of gaseous oxygen over silica (19), the presence of gaseous oxygen inhibited the metathesis reaction completely. Heating the samples was necessary to desorb the

TABLE 1

The Photooxidation of Propene[a]

		Product yield[b] (%)							Selectivity to PO
Entry	Sample	PO[c]	PA	AC	AL	AA	Alcohols	Total	(%)
1	SiO_2	0.44	0.33	0.11	0.02	0.62	0.00	1.52	28.9
2	1MS-M	3.36	0.70	0.40	0.00	1.66	0.50	6.62	50.8
3	4MS-M	0.23	0.82	1.11	0.07	2.25	1.43	5.91	3.9
4	13MS-M	0.07	1.43	1.66	0.07	2.86	1.00	7.09	1.0
5	0.3MS-W	2.02	0.40	0.91	0.17	1.20	0.80	5.50	36.7
6	1MS-W	3.13	0.83	1.03	0.17	2.33	0.30	7.79	40.2
7	3MS-W	2.05	0.70	0.76	0.06	1.61	0.84	6.02	34.1
8	6MS-W	1.68	0.86	1.33	0.07	2.01	0.99	6.94	24.2
9	13MS-W	0.25	0.85	1.15	0.11	2.36	0.97	5.69	4.4
10	MgO	0.03	0.03	0.00	0.03	0.03	0.00	0.12	25.0
11	1MS-M[d]	0.02	0.03	0.03	0.02	0.15	0.04	0.29	6.9
12	1MS-M[e]	0.00	0.04	0.01	0.11	0.12	0.20	0.46	0.0
13	1MS-M[f]	1.93	0.48	0.45	0.06	1.11	0.28	4.30	44.9

[a] O_2/Pr (mol ratio of O_2 to propene) = 2, irradiation time, 2 h.

[b] Based on initial amount of propene.

[c] See text.

[d] By using a UV cut filter. See text.

[e] Performed without Hg lamp in an electric furnace at 573 K for 1 h.

[f] Photoirradiation for 1 h in the presence of gaseous oxygen was carried out before starting the standard reaction experiment.

products for full collection: in some cases, the adsorbed products amounted to half the total product yield. The yields listed in Table 1 are the sum of the adsorbed and gaseous products.

On the silica sample (entry 1), acetaldehyde was main product with 0.62% yield, while propylene oxide was produced with 0.44% yield and the selectivity for propylene oxide was 28.9%. The production of acetaldehyde, propionaldehyde, and acrolein had been reported in the photooxidation over a kind of silica, porous Vycor glass (30). However, the epoxidation of propene by gaseous oxygen over silica has not been reported.

Upon loading magnesium oxide on the silica, the oxidation activity (total yield) was enhanced ca. four times, regardless of the Mg-loading method and loading amount (entries 2–9). The selectivity to propylene oxide varied considerably with the loading amount and loading method. The highest yield of propylene oxide was 3.36% on 1MS-M (entry 2) and 3.13% on 1MS-W (entry 6). The best selectivity to propylene oxide in this study is 50.8% on 1MS-M sample (entry 2). The Nb_2O_5/SiO_2 system also produces propylene oxide in the photooxidation of propene (17), while the highest selectivity to propylene oxide was 33%.

On high-loaded samples prepared with a solution of $Mg(OCH_3)_2$ in methanol, 4MS-M and 13MS-M (entries 3, 4), acetaldehyde was predominantly produced rather than propylene oxide. In the *x*MS-W samples prepared by an aqueous solution, the lower-loaded sample (entry 5) and the higher-loaded samples (entries 7–9) than 1MS-W showed lower selectivity to propylene oxide. The high-loaded sample such as 3MS-W, 6MS-W, and 13MS-W (entries 7–9) exhibited higher selectivity to propylene oxide than the corresponding samples prepared in the other method such as 4MS-M and 13MS-M (entries 3 and 4). On bulk MgO, the reaction hardly occurred (entry 10), suggesting that large particles of magnesium oxide are not efficient for photooxidation.

When the irradiation light was limited by using a UV cut filter ($\lambda_{\text{transmission}} > 310$ nm), the reaction proceeded very slowly and the selectivity to propylene oxide was low (entry 11). This indicates that the UV light is essential for the oxidation, particularly for oxidation to propylene oxide. Oxidation in the dark at 573 K proceeded very slowly, where propylene oxide was not detected (entry 12).

The presence of O_2 was also essential for the photooxidation over the silica and Mg-loaded silica. Figure 4 shows the dependence of the activity of 1MS-M on the O_2/propene ratio, where the amount of propene introduced was constant. Clearly, a high O_2/propene ratio is favorable for the photooxidation. In the absence of O_2, only oxidation of propene to acetaldehyde took place at a very slow rate under irradiation over 1MS-M, although metathesis reaction proceeded (the result is not shown). Photooxidation to propylene oxide progressed just in the presence of O_2. The optimal condition for the highest selectivity to propylene oxide in this study was $O_2/\text{propene} = 2$, although an excess oxygen seemed to promote other partial oxidation pathways.

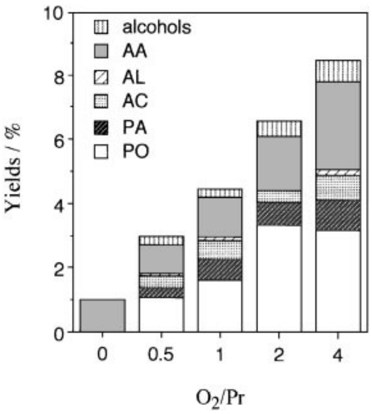

FIG. 4. Dependence of product yields on O_2/propene ratio in the photooxidation of propene over 1MS-M. Propene, 30 μmol constant; irradiation time, 2 h.

To examine the oxygen photoactivation, the following test (entry 13) was carried out; after the pretreatment, the sample was irradiated for 1 h in the presence of gaseous oxygen without propene and subsequently the reaction was started by the introduction of propene into the reactor. In comparison with the standard condition (entry 2), the yields of propylene oxide and others were not increased, or rather slightly decreased, suggesting that the first step in the reaction mechanism is the activation of propene by the photoexcited site rather than the activation of oxygen molecules. The activation of propene is supported by the activity for metathesis reaction over irradiated silica.

The dependence of product yields on the irradiation time was studied on the 1MS-M sample (Table 2). A fresh sample was used for each run. The conversion, the total product yields, increased at longer reaction time, although it was not proportional to irradiation time. It would be caused by the products adsorption on the active sites. The appropriate reaction time for the production of propylene oxide would be around 2 h in these conditions. The reduction of the selectivity for propylene oxide after the irradiation for

TABLE 2

Dependence of Product Yields on UV Irradiation Time over the 1MS-M Sample[a]

Irradiation time (h)	Product yields[b] (%)							Selectivity to PO (%)
	PO[c]	PA	AC	AL	AA	Alcohols	Total	
1	2.12	0.49	0.40	0.11	1.56	0.28	4.95	42.8
2	3.36	0.70	0.40	0.00	1.66	0.50	6.62	50.8
8	2.77	1.24	1.79	0.26	1.98	5.06	13.09	21.1

[a] O_2/Pr (mol ratio of O_2 to propene) = 2.

[b] Based on initial amount of propene.

[c] See text.

8 h (Table 2) indicated that produced propylene oxide was converted to other products successively. To examine the reactivity of propylene oxide, propylene oxide (10 μmol) was introduced with oxygen (60 μmol) over 1MS-M sample. After irradiation for 2 h, 35% of the propylene oxide was converted into propionaldehyde (selectivity 33.5%), propene (22%), and others (ethene, acetaldehyde, acetone, etc.). This result confirmed that the produced propylene oxide was subsequently converted into other products. A large part of the propionaldehyde yield might come from secondary isomerized product from propylene oxide.

DISCUSSION

Mg Loading by Using a $Mg(OCH_3)_2$ in Methanol Solution

The preparation method using $Mg(OCH_3)_2$ in methanol solution, leads to the formation of small crystallites on silica (22, 28) and zeolite (31). In this study, the high-loaded samples prepared in this method (xMS-M, $x > 5$) contain magnesium oxide crystallites, as indicated by XANES (Figs. 3a and 3b) and the broad phosphorescence spectrum (Fig. 1c) assigned to the MgO crystallites on which the hydroxy groups and/or unsaturated Mg–O pair emit (24–27). The $Mg(OCH_3)_2$ should aggregate on the silica surface and MgO crystallites should be formed by calcination.

In the low-loaded sample such as 1MS-M, judging from the highest conversion and selectivity to propylene oxide and the phosphorescence spectrum with fine structure, the structure of magnesium species should be different from the MgO crystallites mentioned above. Although we cannot record XANES spectrum of such a low-loaded sample, we could presume that the structure, i.e., magnesium oxide, should be highly dispersed on the silica surface. On the spectrum of 1MS-M, the broad band resulting from silanols (13) as shown in Fig. 1a disappeared completely while only the emission with fine structure as shown in Fig. 1b was observed instead, indicating that almost all the hydroxy groups on silica react with the $Mg(OCH_3)_2$ and that no aggregation of magnesium species occurs. The loading of MgO in 1MS-M corresponds to 0.25 mmol g^{-1}, and the population of residual hydroxy groups on silica calcined at 773 K was evaluated to be 0.211 mmol g^{-1} (13). These values correspond to 0.3 nm^{-1} on the silica surface. Therefore, the magnesium species on 1MS-M should be highly dispersed and isolated. Since the spectrum with the fine structure is observed when it is evacuated at high temperature, the emission site is suggested to be coordinatively unsaturated surface magnesium oxide species (13, 14).

Since $Mg(OCH_3)_2$ easily reacts with water, $Mg(OCH_3)_2$ should react with surface hydroxy groups on silica in dry methanol:

$$Mg(OCH_3)_2 + [Si]{-}OH \rightarrow Mg(OCH_3){-}O{-}[Si] + CH_3OH. \quad [1]$$

When the number of $Mg(OCH_3)_2$ molecules is comparable to (or less than) that of [Si]–OH, highly dispersed species would be formed on silica.

When there are more $Mg(OCH_3)_2$ molecules than [Si]–OH groups, they would be weakly adsorbed on silica surface under impregnation. By successive drying and calcination in air, the adsorbed magnesium species could aggregate. Magnesium oxide crystallites would be formed on the surface after calcination.

In conclusion we can state that the local structures of magnesium oxide species in a low-loaded sample are different from the high-loaded ones; magnesium oxide species on xMS-M samples are small crystallites of MgO of rock salt structure in the high-loaded samples ($x > 5$) and highly dispersed and isolated in a low-loaded sample ($x = 1$).

Mg Loading by Using a $Mg(NO_3)_2$ Aqueous Solution

In the Mg-loaded silica samples prepared by using an aqueous solution of $Mg(NO_3)_2$, the dispersion of the magnesium oxide species is high as shown by the XANES spectra (Figs. 3c and 3d). The local structure of magnesium oxide species was not changed with loading below the amount corresponding to a monolayer coverage (up to 30 wt% MgO). Although we cannot obtain XANES spectrum of 1MS-W, it is a reasonable assumption that the local structure of these magnesium oxide species is also the same as in the other xMS-W samples, that is, highly dispersed. The local structure of the highly dispersed magnesium oxide species is strongly affected by silica tetrahedral structure, if the species is epitaxially constructed.

Phosphorescence emission spectra, however, varied with the magnesium oxide loading. The 1MS-W sample shows a broad emission accompanied by a spectrum with fine structure (Fig. 2a), indicating that there are both silanol and highly dispersed magnesium oxide species on the surface. Since the xMS-W samples were prepared by using an aqueous solution, the number of the surface hydroxy groups on the silica soaked in the impregnating solution would be larger than that in a nonaqueous solution. Therefore, while in the 1MS-M preparation (nonaqueous solution), $Mg(OCH_3)_2$ molecules replace all the silanols that remain after evacuation at 1073 K (13), the same number of Mg ions can replace only part of the silanols formed in the 1MS-W preparation because of a larger number of silanols formed in the aqueous solution. To exchange all such silanols completely by Mg ions in the aqueous impregnating solutions, in other words to prepare the sample exhibiting the phosphorescence spectrum with the fine structure (Fig. 2b), an amount of Mg ions corresponding to 5 wt% as MgO would be demanded. In this aspect, the local structure of magnesium oxide species in 1MS-W and 5MS-W are similar to each other, but the Mg ions in 1MS-W are more scattered and isolated than in 5MS-W.

The phosphorescence spectrum of the high-loaded sample exhibited a broad band (Fig. 2c), although the local structure of Mg is the same as the highly dispersed species, as shown in the XANES spectra (Figs. 3c and 3d). We suppose that there are islands or raft-like arrays of magnesium oxide species whose local structure is identical to that in the highly dispersed species. In this preparation method, the magnesium cations would be adsorbed on the silica surface, and the sintering of magnesium oxide species would not occur even under calcination. It is suggested that the luminescence is sensitively affected also by their second neighboring atoms of the sites; only the isolated magnesium species on the silica surface would exhibit the fine structure.

Activity and Local Structure of Magnesium Oxide Species

The photooxidation activities of silica and Mg-loaded silica are reproduced in Fig. 5 from Table 1 to discuss the correlation between the local structures of magnesium oxide species and the activities. The results of the *x*MS-M samples (Fig. 5a) show that only 1MS-M produced propylene oxide dominantly and that higher-loaded samples than 4 wt% produced mainly acetaldehyde. The results suggest that highly dispersed magnesium oxide species accelerate the oxidation to propylene oxide, while aggregated species and crystallites of magnesium oxide on silica are not responsible for the epoxidation. In the case of *x*MS-W (Fig. 5b), even 13MS-W produced appreciable amounts of propylene oxide. Since the magnesium oxide species in *x*MS-W samples are highly dispersed, *x*MS-W samples are available for the production of propylene oxide. Among *x*MS-W samples, the higher-loaded samples showed lower activities for epoxidation than 1MS-W, indicating that the highly dispersed and isolated magnesium oxide species are active for epoxidation. On the other hand, the species which existed as islands or raft-like arrangements are not so active for epoxidation; e.g., in 13MS-W, there would only be a small amount of isolated species which are active for photoepoxidation. Among the *x*MS-W samples, the local structure of the magnesium species is similar, but the scattering of the species (isolated or not) affects the selectivity for epoxidation. Judging from the photooxidation activity and the selectivity for propylene oxide, the local structure and dispersion of the magnesium oxide species on 1MS-W would be the same as that on 1MS-M; highly dispersed, isolated, and coordinatively unsaturated.

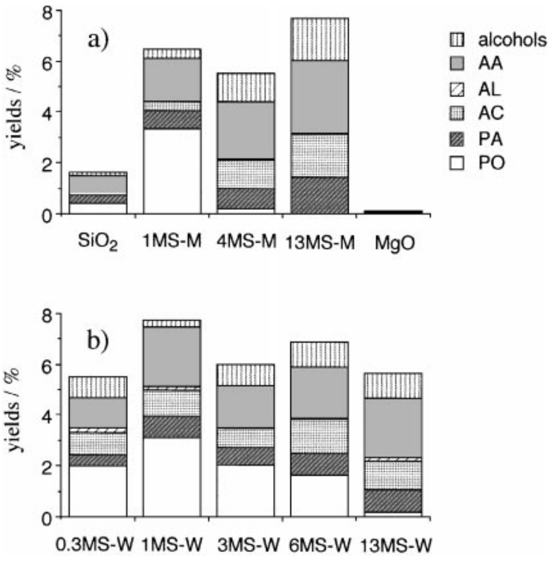

FIG. 5. Product yields over silica, *x*MS-M samples and MgO (a) and *x*MS-W samples (b).

It is important aspect that the isolated magnesium species which is put in silica network rather promote the epoxidation activity of the bare silica.

Highly dispersed niobium oxides supported on silica also produce propylene oxide in the photooxidation of propene (17). In this system, highly dispersed species are responsible for propylene oxide production and aggregated species predominantly produce acetaldehyde. The correlation between the dispersion of metal oxide species and the selectivity in the niobium–silica system is similar to the present case of Mg-loaded silica. Highly dispersed heteroatoms on silica seem to be active site for propylene oxide production.

Active Sites of Silica Surface

Silica is usually used as a catalyst support, since silica itself is considered to be inactive for catalytic reactions; in the studies of silica-supported catalysts (16, 17, 32, 33), the photooxidation on pure silica was not reported. Supported vanadium (16, 32, 33) or niobium oxides (17) were activated by lower pretreatment temperature such as 673 K. On the other hand, catalytic activities of silica for photooxidation (20) and for photometathesis (19) were generated when the silica samples were evacuated at a higher pretreatment temperature (873 or 1073 K). The key of the discovery seems to be evacuation at high temperature; e.g., in the previous study (19) the activity of silica for metathesis was found to increase with increasing pretreatment temperature. In this study, the metathesis reaction hardly occurs in the presence of gaseous oxygen. Therefore, the active sites which are produced by evacuation at high temperature are the same in the two reactions, photometathesis and photooxidation.

Silica is known to exhibit broad photoemission spectra (13, 14, 34, 35). The employed silica evacuated at 1073 K also exhibited a broad phosphorescence spectrum as shown in Fig. 1a, which results from surface hydroxyl groups (13). Although the active sites for the photooxidation might emit a specific luminescence, the spectrum would be concealed with the large broad spectrum resulting from silanols. On the other hand, when heteroatoms such as magnesium (12, 13) or aluminum (14) are on/in the silica matrix, they easily show the phosphorescence spectra with the fine structure.

We treat here the heteroatoms as a clue to determine the active sites for the photooxidation on pure silica surface. The spectra of Mg-loaded silica and silica–alumina were only clearly observed on samples evacuated at high temperature, such as 1073 K. The activation by evacuation at high temperature for photocatalysis (19) or photoluminescence (12–14) is explained by desorption of water molecules or hydroxyl groups on the surface. The desorption of hydroxyl groups would produce coordinatively unsaturated sites on the surface, and the sites would be concerned with photoexcitation. The photoexcitation sites on Mg-loaded silica and silica–alumina were proposed to be coordinatively unsaturated Mg and Al sites on the surface of the tetrahedral silica network (13, 14). By analogy, in the case of silica surface, coordinatively unsaturated surface sites such as $Si-(O-Si)_3$ are suggested to be the photoactive sites. The spectrum of silica evacuated at 1073 K might seem to be slightly overlapped with the fine structure in the higher wavelength region (Fig. 1a). If the $M-(O-Si)_3$ site model is acceptable, the differences on the photoactivity might be explained by the difference of the central atom of the $M-(O-Si)_3$ unit.

CONCLUSION

It was found that silica catalyzed the partial oxidation of propene to acetaldehyde and propylene oxide under photoirradiation in the presence of O_2. Mg-loaded silica exhibited a higher activity for photooxidation than silica. Highly dispersed and isolated magnesium oxide species on silica, the local structure of which is proposed to be tetrahedral, promoted the epoxidation of propene by O_2 under irradiation selectively, while crystallites or island structure of magnesium oxide on silica promoted the photooxidation to acetaldehyde predominantly. The local structures of magnesium oxide species were controlled by the preparation method and loading amount of magnesium. The active sites on the bare silica would be coordinatively unsaturated sites which were produced by evacuation at high temperatures. The active sites are the same in photometathesis as well as photooxidation.

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REFERENCES

1. Lefort, T. E., French Patent 729,952 (1931).
2. Clerici, M. G., Bellussi, G., and Romano, U., *J. Catal.* **129**, 159 (1991).
3. Romano, U., Esposito, A., Maspero, F., Neri, C., and Clerici, M. G., *Stud. Surf. Sci. Catal.* **55**, 33 (1990).
4. Notari, B., *Stud. Surf. Sci. Catal.* **37**, 413 (1987).
5. Armor, J. N., *J. Catal.* **70**, 72 (1981).
6. Kastanas, G. N., Tsigdinos, G. A., and Schwank, J., *Appl. Catal.* **44**, 33 (1988).
7. Matsumura, Y., Hashimoto, K., and Yoshida, S., *J. Catal.* **117**, 135 (1989).
8. Parmaliana, A., Frusteri, F., Miceli, D., Mezzapica, A., Scurrell, M. S., and Giordano, N., *Appl. Catal.* **78**, L7 (1991).
9. Morikawa, A., Hattori, M., Yagi, K., and Otsuka, K., *Z. Phys. Chem. N.F.* **104**, 309 (1977).
10. Anpo, M., Yun, C., and Kubokawa, Y., *J. Catal.* **61**, 267 (1980).
11. Ogata, A., Kazusaka, A., and Enyo, M., *J. Phys. Chem.* **90**, 5201 (1986).
12. Tanaka, T., Yoshida, H., Nakatsuka, K., Funabiki, T., and Yoshida, S., *J. Chem. Soc. Faraday Trans.* **88**, 2297 (1992).
13. Yoshida, H., Tanaka, T., Funabiki, T., and Yoshida, S., *J. Chem. Soc. Faraday Trans.* **90**, 2107 (1994).
14. Yoshida, H., Tanaka, T., Satauma, A., Hattori, T., Funabiki, T., and Yoshida, S., *Chem. Commun.* 1153 (1996).
15. Gritscov, A. M., Shvets, V. A., and Kazansky, V. B., *Chem. Phys. Lett.* **35**, 511 (1975).
16. Tanaka, T., Ooe, M., Funabiki, T., and Yoshida, S., *J. Chem. Soc., Faraday Trans. 1* **82**, 35 (1986).
17. Tanaka, T., Nojima, H., Yoshida, H., Nakagawa, H., Funabiki, T., and Yoshida, S., *Catal. Today* **16**, 297 (1993).
18. Blatter, F., Sun, H., and Frei, H., *Catal. Lett.* **35**, 1 (1995).
19. Yoshida, H., Tanaka, T., Matsuo, S., Funabiki, T., and Yoshida, S., *J. Chem. Soc., Chem. Commun.* 761 (1995).
20. Yoshida, H., Tanaka, T., Yamamoto, M., Funabiki, T., and Yoshida, S., *Chem. Commun.* 2125 (1996).
21. Yoshida, S., Matsuzaki, T., Kashiwazaki, T., Mori, K., and Tarama, K., *Bull. Chem. Soc. Jpn.* **47**, 1564 (1974).
22. Yoshida, H., Tanaka, T., Nakatsuka, K., Funabiki, T., and Yoshida, S., *Stud. Surf. Sci. Catal.* **90**, 473 (1994).
23. Yoshida, T., Tanaka, T., Yoshida, H., Funabiki, T., Yoshida, S., and Murata, T., *J. Phys. Chem.* 10890 (1995).
24. Tench, A. J., and Pott, G. T., *Chem. Phys. Lett.* **26**, 590 (1974).
25. Coluccia, S., Deane, A. M., and Tench, A. J., *J. Chem. Soc. Faraday Trans. 1* **74**, 2913 (1978).
26. Duley, W. W., *J. Chem. Soc., Faraday Trans. I* **80**, 1173 (1984).
27. Anpo, M., Yamada, Y., Kubokawa, Y., Coluccia, S., Zecchina, A., and Che, M., *J. Chem. Soc., Faraday Trans. 1* **84**, 751 (1988).
28. Yoshida, H., Yoshida, T., Tanaka, T., Funabiki, T., Yoshida, S., Abe, T., Kimura, K., and Hattori, T., *J. Phys. IV* **7**(C2), 911 (1997).
29. Yoshida, T., Tanaka, T., Yoshida, H., Takenaka, S., Funabiki, T., Yoshida, S., and Murata, T., *Phys. B* **208 & 209**, 581 (1995).
30. Kubokawa, Y., Anpo, M., and Yun, C., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), Vol. B, p. 1170. Elsevier, Amsterdam, 1981.
31. Tsuji, H., Yagi, F., Hattori, H., and Kita, H., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi, and P. Tetenyi, Eds.), Vol. B, p. 1171. Akadémiai Kiadó, Budapest, 1993.
32. Yoshida, S., Magatani, Y., Noda, S., and Funabiki, T., *J. Chem. Soc., Chem. Commun.* 601 (1981).
33. Yoshida, S., Tanaka, T., Okada, M., and Funabiki, T., *J. Chem. Soc., Faraday Trans. 1* **80**, 119 (1984).
34. Yun, C., Anpo, M., and Kubokawa, Y., *J. Chem. Soc., Chem. Commun.* 665 (1977).
35. Anpo, M., Yun, C., and Kubokawa, Y., *J. Chem. Soc., Faraday Trans. I* **76**, 1014 (1980).