Journal of Catalysis **194,** 364–372 (2000)
doi:10.1006/jcat.2000.2952, available online at http://www.idealibrary.com on IDEAL®

Screening Study of Silica-Supported Catalysts for Photoepoxidation of Propene by Molecular Oxygen

Hisao Yoshida,*[,1] Chizu Murata,* and Tadashi Hattori†

*Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan; and †Research Center for Advanced Waste and Emission Management, Nagoya University, Nagoya 464-8603, Japan

Received February 10, 2000; revised May 25, 2000; accepted May 30, 2000

To find systems that are effective for the photocatalytic epoxidation of propene by molecular oxygen, 50 types of silica-supported metal oxides were screened for photooxidation activity. Many elements on silica were found to be active for photooxidation, and the samples were classified according to activity. High selectivity for propene oxide (PO), but with a conversion as low as that of the silica, was observed on silica loaded with alkali metals (Li, and Na), alkaline-earth metals (Mg, Ca, Sr, and Ba), and rare-earth elements (Y and La). It seems that moderate electron negativity of elements improve the epoxidation selectivity on silica. Some elements (such as Ti, Zn, Pb, and Bi) on silica gave high yields of PO. The most effective systems, with high PO yields and low CO_x selectivity, were silica-supported Ti and Zn systems under the experimental conditions. Furthermore, photoepoxidation proceeds *catalytically* on the silica-supported Ti sample. High dispersion of metal oxides on the silica surface is an important factor for PO production in these systems.

Key Words: **photooxidation; propene oxide; silica-supported catalyst; screening study.**

INTRODUCTION

The heterogeneous catalytic process for the production of propene oxide (PO) is of industrial importance. TS-1 is known to catalyze the epoxidation of propene with H_2O_2 (1–6), and the H_2–O_2 system, employing metal catalysts, has also attracted much attention (7, 8). However, the desired direct epoxidation of propene with molecular oxygen (1) has not yet been achieved.

Photocatalysis is another possibility for achieving the epoxidation of propene. Pichat *et al.* (9) reported that propene was photocatalytically oxidized by molecular oxygen over various semiconducting oxides such as TiO_2, ZnO, and SnO_2, and that a very small amount of PO was produced; however, complete oxidation to CO_2, which is not desirable, was the predominant reaction. On the other hand, it was found that photocatalytically inactive V_2O_5 became active when supported on silica and efficiently promoted the partial photooxidation of propene (10, 11) via the formation of the epoxide intermediate (12), although PO was not obtained as a product. Complete oxidation did not occur. PO was recently obtained as a product under photoirradiation over Nb_2O_5/SiO_2 (13) and MgO/SiO_2 (14, 15). In addition, it was found that this photoepoxidation occurs even over bare amorphous SiO_2 (14, 15). On the other hand, the Ba Y-zeolite system resulted in the adsorption of PO species (16, 17) as well as the production of PO (18). These results imply that the silica matrix is important in designing photoepoxidation catalysts. While silica is generally used as a support for catalysts and is usually considered to be a catalytically inactive material, it promotes not only some thermal reactions (19–22), but also photoreactions (14, 15, 23–31) including photooxidation (14, 15, 23–26).

In the silica-supported systems, the added elements, supported on silica, would become the photocatalytic sites for the photooxidation or might assist the silica sites. Although the function of the added element on silica has been investigated in each of the systems mentioned above, no studies have compared these elements, supported on silica, under the same conditions. In addition, in these silica-supported and ion-exchanged zeolite systems, the conversion was insufficient to determine whether or not the reaction proceeds catalytically in these systems. In the present study, we screened 50 samples of silica-supported metal oxides in order to establish guidelines for designing effective systems for the synthesis of PO in the photooxidation of propene by molecular oxygen. Almost all the elements that can be used for heterogeneous catalysts were tested under the same conditions as those in this study.

EXPERIMENTAL

Amorphous SiO_2 was prepared from tetraethylorthosilicate ($Si(OEt)_4$) using the sol–gel method described in Ref. (32). $Si(OEt)_4$ (Kishida Chemicals) was distilled before

---

[1] To whom correspondence should be addressed. Fax: +81-52-789-3193. E-mail: yoshidah@apchem.nagoya-u.ac.jp.

0021-9517/00 $35.00

use. H_2O was ion-exchanged and distilled before use. The mixture of $Si(OEt)_4$ (200 ml), EtOH (400 ml, Kishida Chemicals), and H_2O (300 ml) was heated and stirred while increasing the temperature ($1\,K\,min^{-1}$) to 351 K to obtain white sol through hydrolysis. The sol was successively heated; H_2O was added dropwise in an amount equivalent to that of the EtOH vapor that was extracted from the system by means of a condenser. The sol temperature was elevated to 373 K ($4\,K\,h^{-1}$) and gelation proceeded. The wet gel was filtered by means of suction, dried in an electric oven at 393 K, ground, and calcined in a flow of air at 773 K for 5 h to yield the amorphous SiO_2 powder.

Silica-supported metal oxide samples were prepared by impregnation; SiO_2 powder (0.8 g) was impregnated with aqueous solutions of each precursor (50 ml) and heated and magnetically stirred until it was dry. The obtained powder was dried in an electric oven at 383 K for 12 h and calcined at 773 K in a flow of dry air for 5 h. The precursors used were mainly nitrate salts, while ammonium titanyl oxalate, zirconyl nitrate dihydrate, ammonium metavanadate, niobium oxalate, tantalum oxalate, ammonium molybdate tetrahydrate, ammonium paratungstate pentahydrate, ammonium platinous nitrate, germanium(IV) chloride, tin(II) chloride dihydrate, and phosphoric acid were used as precursors for Ti, Zr, V, Nb, Ta, Mo, W, Pt, Ge, Sn, and P samples, respectively. With respect to the sample which was prepared from chloride (Ge and Sn), the Cl^- ion was removed from the calcined sample using a 4 N aqueous ammonia followed by calicination at 773 K. The metal ion (1.5 mol% ($n_M/n_{Si} + n_M$), calculated from the amount of the start materials) was equivalent to the most suitable loading reported for the MgO/SiO_2 system (14, 15). In the present study, the supported sample is referred to as MO_x/SiO_2, since it was assumed that most of the samples would be oxidized, and the oxidation states were not confirmed experimentally. Another sample was 0.1 mol% TiO_x/SiO_2 (33), referred to as TiO_x (0.1)/SiO_2, and was prepared in the same way. The bulk metal oxide samples employed were TiO_2 (a Reference Cata-lyst from Japan, JRC-TIO-4, 99.5% (34), equivalent to P-25), ZnO (Kishida, 99.0%), and Nb_2O_5 (Mitsuwa, 99.9%).

The specific surface area of BET was calculated from the amount of desorbed N_2 which adsorbed on the samples at 77 K in a flow (200 ml min^{-1}) of a mixture of N_2 (30%) and He (70%). Before the measurement, the sample was heated in a flow of He (30 ml min^{-1}) at 673 K for 30 min. The amount of N_2 adsorbed was determined by gas chromatography (GC).

Before the photoreaction, the samples were heated in air to 673 K and then evacuated. The samples were then treated with 100 Torr oxygen (1 Torr $= 133.3\ N\,m^{-2}$) at 673 K for 1 h and evacuated at 673 K for 1 h. With the exception of specially indicated cases, the photooxidation of propene was carried out in a closed reaction vessel made of quartz ($123.6\ cm^3$) for 2 h. The temperature of the catalyst bed rose to 318 ± 5 K as a result of photoirradiation. The reactants were propene (100 μmol, 15 Torr) and oxygen (200 μmol, 30 Torr). The catalyst (200 mg) was spread on the bottom ($12.6\ cm^2$) of the vessel. A 200 W Xe lamp was used as the light source. Products in the gas phase and products desorbed by photoirradiation for 10 min were analyzed separately by GC followed by analysis of the desorbed products after heating to 573 K. The sum of each product yield is presented. Propene oxide (PO), propanal (propionaldehyde, PA), propanone (acetone, AC), prop-2-enal (acrolein, AL), ethanal (acetaldehyde, AA), alcohols (methanol, ethanol, and propan-2-ol), hydrocarbons (ethene and butenes, HC), and CO, CO_2 (CO_x) were detected.

RESULTS

Catalyst Screening for Photoepoxidation Activity

Table 1 shows the results of the screening of various silica-supported samples for the photoepoxidation of propene using molecular oxygen and the specific surface area (*SA*) of representative samples. Since the surface area values of the supported samples, with the exception of the bare silica, were almost the same (standard deviation was only 11%), the comparison of the conversion and the PO yield, based on the raw values, could be used as such in the present screening study. Propene conversion, PO yield, and PO selectivity on the bare SiO_2 and silica-supported samples are presented in Figs. 1a to 1c. The bare SiO_2 (Table 1, entry 1) exhibited almost the same conversion and propene oxide selectivity as reported previously (14, 15).

The elements in the 1A group exhibited low conversion but high PO selectivity (Figs. 1a and 1c). The conversion and PO yield did not increase after the addition of alkaline metal ions. In the 1A group (Table 1, entries 2–6), only LiO_x/SiO_2 exhibited higher PO selectivity than the bare SiO_2. The major product varied with the ions added; Li and Na mainly promoted the production of PO, while Rb and Cs promoted the formation of AC.

The elements in the 2A group (entries 7–10) increased PO selectivity by as much as 22 to 37%, which was the highest PO selectivity of all the groups studied. MgO_x/SiO_2 (entry 7) showed higher conversion and a higher PO yield than bare SiO_2 (14, 15), although the PO selectivity did not increase.

In the 3A group (entries 11–23), Y and La (entries 12 and 13) were effective for PO production; reasonable selectivity and conversion were observed. Other elements in this group were not effective because of low PO selectivity.

The samples in the 4A–6A group (entries 24–31) showed high propene conversion (Fig. 1a). TiO_x/SiO_2 resulted in the highest yield of PO (Fig. 1b): 4.7% yield (Table 1, entry 24) was the highest value compared with literature results for photoepoxidation (13–15). Though the PO selectivity was

TABLE 1

Results of Screening Silica-Supported Samples for the Photooxidation of Propene

Group	Entry	Sample	SA[a]/ $m^2\,g^{-1}$	Conversion[b]/ %	PO yield/ %	Selectivity/%							
						PO	PA	AC	AL	AA	Alcohols	HC	CO_x
—	1	SiO_2	654	1.5	0.3	22.3	3.5	25.8	15.2	18.1	0.0	10.0	5.1
1A	2	Li_xO/SiO_2	495	0.8	0.3	37.9	2.4	23.6	18.5	6.9	3.1	3.1	4.5
	3	NaO_x/SiO_2	533	1.1	0.2	22.8	2.9	20.8	12.2	5.3	13.4	5.7	16.9
	4	KO_x/SiO_2	429	1.5	0.2	15.5	6.1	18.9	13.3	5.4	7.5	6.4	26.9
	5	RbO_x/SiO_2	435	1.1	0.2	15.9	7.4	31.2	6.8	5.5	12.7	12.8	7.7
	6	CsO_x/SiO_2	428	1.2	0.2	13.2	7.9	35.2	10.9	6.7	10.0	6.5	9.6
2A	7	MgO_x/SiO_2		4.7	1.1	22.8	15.8	16.3	8.4	15.9	4.6	6.4	9.8
	8	CaO_x/SiO_2	569	1.7	0.5	32.7	7.1	14.2	7.9	9.8	3.2	15.1	10.0
	9	SrO_x/SiO_2		1.2	0.4	37.0	3.4	18.5	11.0	6.7	9.0	1.2	13.2
	10	BaO_x/SiO_2		1.4	0.4	26.2	2.5	21.7	19.0	6.7	8.8	2.0	13.1
3A	11	ScO_x/SiO_2		6.1	0.4	7.2	18.0	14.6	9.2	18.5	9.2	9.7	13.6
	12	YO_x/SiO_2		4.9	1.1	23.4	15.0	18.4	9.0	18.0	5.4	3.1	7.7
	13	LaO_x/SiO_2	584	2.5	0.8	32.1	17.3	15.3	0.6	17.0	4.1	4.3	9.3
	14	CeO_x/SiO_2		4.8	0.4	9.2	4.1	13.3	5.2	22.7	2.5	1.5	41.5
	15	PrO_x/SiO_2		1.2	0.1	5.3	11.3	26.0	14.2	5.8	8.8	11.1	17.5
	16	NdO_x/SiO_2		1.1	Tr.	3.8	13.0	25.1	9.9	17.4	6.8	5.6	18.4
	17	SmO_x/SiO_2		0.7	Tr.	2.5	11.5	31.0	12.9	20.4	14.2	7.5	0.0
	18	EuO_x/SiO_2		1.8	0.1	8.0	15.9	13.8	11.2	22.4	9.3	4.7	14.7
	19	GdO_x/SiO_2		2.8	0.4	13.3	16.5	17.3	10.2	14.6	11.0	5.8	11.3
	20	TbO_x/SiO_2		1.8	Tr.	2.5	8.1	33.6	15.0	8.8	8.6	9.3	14.1
	21	DyO_x/SiO_2		1.2	Tr.	2.7	10.7	30.6	10.5	15.3	8.1	10.9	11.2
	22	ErO_x/SiO_2		1.5	Tr.	2.9	13.2	26.0	8.4	18.9	9.8	17.6	3.2
	23	YbO_x/SiO_2		1.8	0.1	4.5	16.4	19.4	10.0	20.5	8.8	11.1	9.1
4A	24	TiO_x/SiO_2	620	24.4	4.7	19.2	17.6	9.3	8.7	21.5	7.2	2.4	14.1
	25	ZrO_x/SiO_2	620	12.2	0.9	7.0	19.9	14.1	6.5	14.9	10.1	11.7	15.8
5A	26	VO_x/SiO_2	554	19.2	0.1	0.6	6.6	9.2	26.7	32.9	1.4	2.7	19.9
	27	NbO_x/SiO_2		7.7	0.2	2.1	14.3	14.5	4.3	39.1	4.8	2.5	18.4
	28	TaO_x/SiO_2		11.3	0.4	3.7	8.1	19.2	3.9	27.1	5.8	8.5	23.7
6A	29	CrO_x/SiO_2	573	34.4	1.6	4.5	3.2	4.5	6.3	20.3	4.3	8.9	48.0
	30	MoO_x/SiO_2		14.0	0.2	1.3	10.2	12.0	19.9	32.7	1.6	3.5	18.8
	31	WO_x/SiO_2		17.8	0.6	3.1	17.7	13.8	4.5	32.7	4.9	1.9	21.4
7A	32	MnO_x/SiO_2	531	0.7	N.d.	0.0	0.0	11.3	33.7	13.1	0.0	2.2	39.7
8A	33	FeO_x/SiO_2		1.1	N.d.	0.0	4.3	22.3	13.6	17.2	4.0	9.4	29.2
	34	CoO_x/SiO_2	583	0.7	Tr.	0.9	4.2	25.3	39.5	3.4	7.6	10.2	8.9
	35	RhO_x/SiO_2		6.6	Tr.	0.4	0.0	3.4	0.0	0.0	0.0	0.9	95.3
	36	NiO_x/SiO_2	589	0.8	Tr.	2.0	5.1	33.9	33.8	7.0	5.5	2.4	10.3
	37	PdO_x/SiO_2		4.0	Tr.	0.3	1.1	3.3	2.2	0.4	0.1	4.7	87.9
	38	PtO_x/SiO_2		25.2	N.d.	0.0	0.0	4.0	0.0	0.0	0.1	0.2	95.7
1B	39	CuO_x/SiO_2	585	4.0	0.0	1.1	1.2	7.0	59.9	4.3	1.8	2.7	22.0
	40	AgO_x/SiO_2		0.7	Tr.	3.4	1.7	36.4	29.6	3.8	2.1	11.6	11.4
2B	41	ZnO_x/SiO_2	592	8.6	2.9	33.4	11.4	11.2	5.1	17.9	4.0	6.2	10.8
3B	42	AlO_x/SiO_2	592	10.3	0.4	3.9	15.7	14.0	0.0	21.1	2.6	21.9	20.8
	43	GaO_x/SiO_2		8.3	0.2	1.8	19.9	16.5	2.9	25.4	3.3	17.8	12.4
	44	InO_x/SiO_2	585	3.6	0.1	2.5	14.5	14.4	11.7	14.8	3.6	9.7	18.8
4B	45	GeO_x/SiO_2		0.9	0.2	27.2	2.3	20.9	10.7	17.2	0.0	16.3	5.4
	46	SnO_x/SiO_2		1.8	Tr.	0.9	19.1	17.4	13.3	35.2	0.3	3.2	10.6
	47	PbO_x/SiO_2		8.2	2.2	26.9	1.5	16.8	3.9	11.3	2.2	1.4	36.1
5B	48	PO_x/SiO_2	593	1.4	0.1	3.8	16.3	26.5	16.2	19.5	1.5	8.9	7.3
	49	BiO_x/SiO_2		18.7	3.8	20.2	2.2	16.2	3.3	15.6	5.8	1.2	35.5

[a] BET surface area.

[b] Irradiation time was 2 h. Tr. = trace; n.d. = not detected.

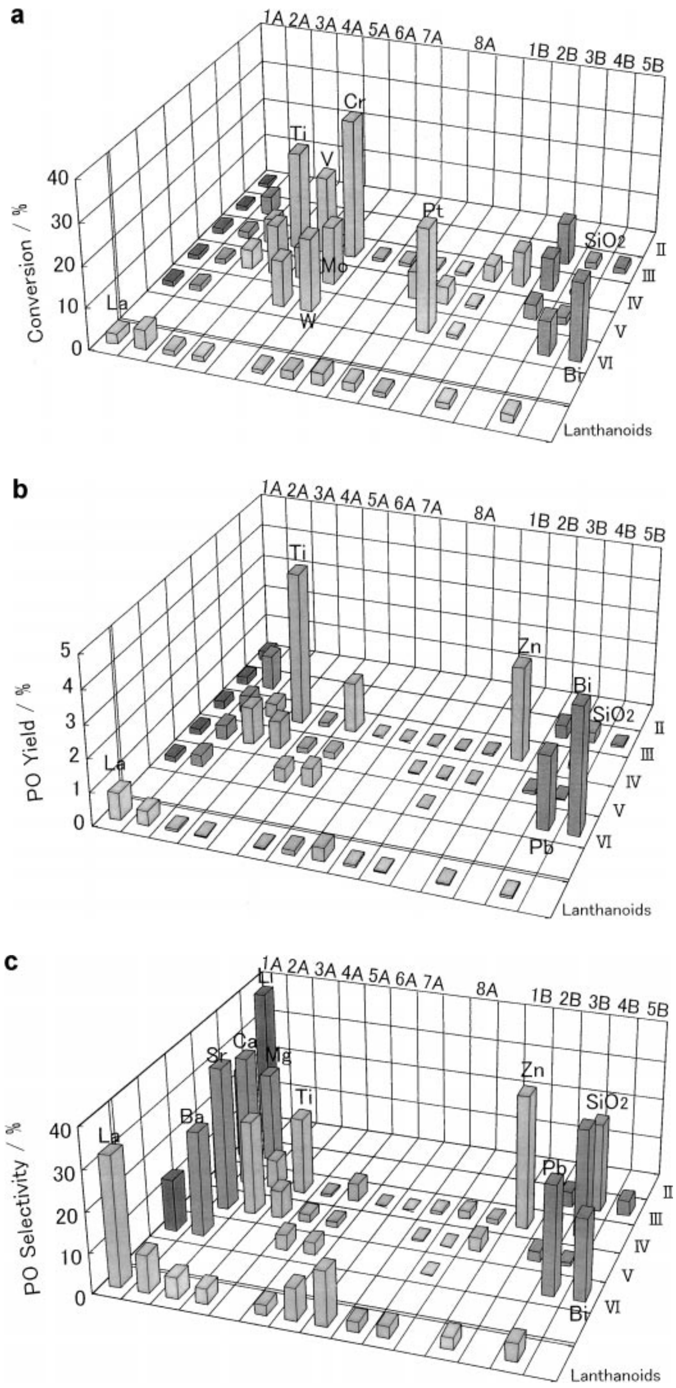

FIG. 1. Propene conversion (a), PO yield (b), and PO selectivity (c) on various silica-supported samples and on bare silica in the photooxidation of propene by molecular oxygen. Irradiation time was 2 h.

almost the same as that of bare SiO_2, the high propene conversion resulted in the highest PO yield. ZrO_x/SiO_2 in the same 4A group was not a suitable catalyst for producing PO under these conditions, whereas PA was produced. Characteristic features of the 5A and 6A groups (entries 26–31) are high AA selectivity, high conversion, and low PO selectivity. CrO_x/SiO_2 exhibited a high PO yield (1.6%), but it was accompanied by a high yield of CO_x.

The elements in groups 7A, 8A, and 1B (entries 32–40) produced little PO (Fig. 1b). Complete oxidation of propene occurred on RhO_x/SiO_2, PdO_x/SiO_2, and PtO_x/SiO_2 upon photoirradiation. However, at the same temperature (328 K) but in the dark, the conversion of propene on PtO_x/SiO_2 was 8.4% and the CO_x selectivity was 91.0%. Further experiments are required to clarify whether or not this was photocatalytic oxidation.

ZnO_x/SiO_2 in the 2B group (entry 41) exhibited a high PO yield (2.9%) with high PO selectivity (33.4%) and low CO_x selectivity (35). Although the high selectivity (higher than 30%) was also observed on samples such as LiO_x/SiO_2, CaO_x/SiO_2, SrO_x/SiO_2, and LaO_x/SiO_2, these samples showed a very low PO yield (less than 1%). This shows the advantage of using ZnO_x/SiO_2 for photoepoxidation.

The main feature of the 3B group (entries 42–44) is low selectivity; PA, AA, and hydrocarbons were observed. In the 4B and 5B groups, PbO_x/SiO_2 and BiO_x/SiO_2 showed a high PO yield (entries 47 and 49), although these samples also produced a larger amount of CO_x than of PO. GeO_x/SiO_2 (entry 45) showed high PO selectivity. SnO_x/SiO_2 (entry 46) exhibited lower PO selectivity than GeO_x/SiO_2 and PbO_x/SiO_2 in the same 4B group.

The PO selectivity on each sample was plotted against the propene conversion (Fig. 2). The group plotted on the upper left side, which exhibited higher selectivity than bare SiO_2 without an increase in conversion (less than 5%), consisted mainly of alkali metals, alkaline-earth metals, and rare-earth elements. Some elements, such as Ti, Zn, Pb,

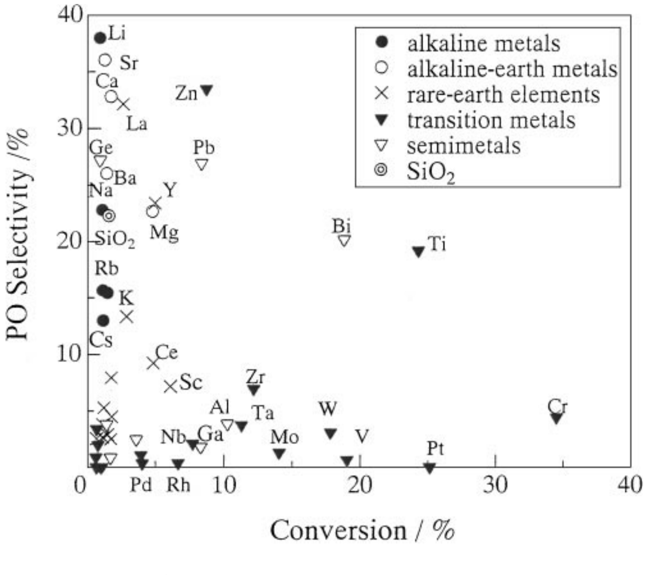

FIG. 2. Plots of PO selectivity vs propene conversion on various silica-supported samples and on bare silica in the photooxidation of propene by molecular oxygen. Irradiation time was 2 h.

TABLE 2

Results of Photooxidation of Propene on Silica-Supported Samples and Bulk Oxides

Entry	Sample	SA^a/m^2 g^{-1}	Time/h	Conversion/%	PO yield/%	Selectivity/% PO	PA	AC	AL	AA	Alcohol	HC	CO$_x$
1[b]	CaO$_x$/SiO$_2$	569	2	1.7	0.5	32.7	7.1	14.2	7.9	9.8	3.2	15.1	10.0
2	CaO$_x$/SiO$_2$		24	16.0	5.8	35.9	2.2	9.3	2.6	4.6	11.9	6.0	27.5
3	TiO$_x$/SiO$_2$	620	1	12.6	1.8	14.3	23.1	9.5	7.1	24.9	5.7	4.1	11.3
4[b]	TiO$_x$/SiO$_2$		2	24.4	4.7	19.2	17.6	9.3	8.7	21.5	7.2	2.4	14.1
5	CrO$_x$/SiO$_2$	573	0.5	16.9	0.6	3.7	1.7	1.9	4.8	15.2	2.3	8.9	61.5
6[b]	CrO$_x$/SiO$_2$		2	34.4	1.6	4.5	3.2	4.5	6.3	20.3	4.3	8.9	48.0
7	TiO$_x$(0.1)/SiO$_2$	477[c]	2	9.1	3.7	40.7	3.3	11.3	4.2	24.5	3.6	2.3	10.1
8	TiO$_x$(0.1)/SiO$_2$		8	24.1	9.2	38.1	1.3	12.8	3.0	14.6	2.1	1.6	26.5
9	TiO$_2$	34	1	14.1	0.0	0.0	0.0	1.3	0.0	0.8	0.0	1.7	96.2
10	ZnO	12	2	1.3	0.0	1.9	0.0	20.8	8.1	6.2	6.9	4.2	51.9

[a] Specific surface area.
[b] The results are also listed in Table 1 for comparison.
[c] Another amorphous silica (558 m^2 g^{-1}) was employed as a support.

and Bi, showed higher conversion and higher or comparable selectivity to SiO$_2$. Many transition metals, such as Cr, Pt, and V, gave higher conversion but lower PO selectivity than SiO$_2$.

It is assumed that PO selectivity was reduced by consecutive oxidation. The influence of propene conversion on PO selectivity is shown in Table 2 (entries 1–8); samples which exhibited high, moderate, and low PO selectivity are regarded as being representative examples. For example, there was 1.7% conversion and 32.7% selectivity on CaO$_x$/SiO$_2$ after 2 h of irradiation (entry 1) and 16.0% conversion and 35.9% selectivity after 24 h of irradiation (entry 2). PO selectivity did not decrease with time, at least not in these cases (entries 1–8). To the contrary, PO selectivity increased slightly with time on some samples (entries 1–6). Thus, the distribution presented in Fig. 2 was not particularly affected by the consecutive oxidation of PO.

TiO$_x$(0.1)/SiO$_2$, which is a TiO$_x$/SiO$_2$ sample containing 0.1 mol% Ti only (entry 8), yielded 9.2% PO after 8 h of irradiation. This indicates that the photoepoxidation of propene on TiO$_x$/SiO$_2$ proceeded catalytically, as will be discussed below.

Dispersion of Metal Oxides on the Silica Surface

Under the experimental conditions, silica-supported Ti and Zn systems may be effective systems for PO production, because they result in a high PO yield and low CO$_x$ selectivity (Table 1). Bulk TiO$_2$ (Table 2, entry 9) showed high photooxidation activity; the conversion of propene was 14.1%, even after 1 h of irradiation. However, the major product was CO$_x$; PO was not observed. On bulk ZnO (Table 2, entry 10), the main product was CO$_x$ even when the conversion was low. These results indicate that a silica support is essential. PO selectivity after 2 h of irradiation on the Ti/SiO$_2$ sample containing 1.5 mol% of Ti (standard) was 19.2% (entry 4), while that on TiO$_x$(0.1)/SiO$_2$ was 40.7% (entry 7), indicating that a lower loading of Ti was better for PO selectivity.

Figure 3 shows diffuse reflectance UV–vis absorption spectra of TiO$_x$/SiO$_2$, ZnO$_x$/SiO$_2$, and NbO$_x$/SiO$_2$ samples and of the corresponding bulk oxides and bare SiO$_2$. Bulk ZnO showed a wide absorption band below the band gap at about 390 nm (Fig. 3a). Bulk TiO$_2$ and Nb$_2$O$_5$ also showed wide absorption bands below the band gap (Figs. 3b and 3c, respectively). On the other hand, the edges of the absorption bands of NbO$_x$/SiO$_2$ (Fig. 3d), TiO$_x$/SiO$_2$ (Figs. 3e, 3f),

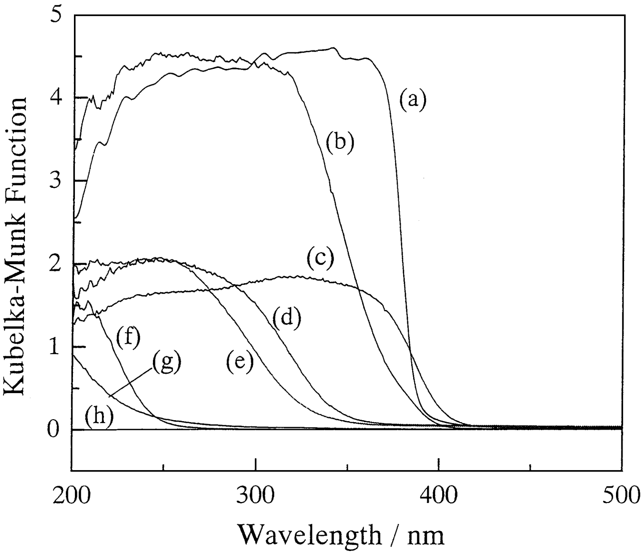

FIG. 3. Diffuse reflectance UV–vis spectra of ZnO (a), TiO$_2$ (b), Nb$_2$O$_5$ (c), NbO$_x$/SiO$_2$ (d), TiO$_x$/SiO$_2$ (e), TiO$_x$ (0.1)/SiO$_2$ (f), ZnO$_x$/SiO$_2$ (g), and bare SiO$_2$ (h).

and ZnO_x/SiO_2 (Fig. 3g) appeared clearly at a shorter wavelength than bulk Nb_2O_5, TiO_2, and ZnO, respectively, while such apparent absorption bands were not observed on bare SiO_2 (Fig. 3h). It is clear that these oxide species, supported on silica, were dispersed on the silica surface as small species and that their electron structures were different from those of bulk oxides. In addition, $TiO_x(0.1)/SiO_2$ (Fig. 3f) showed an absorption band at a much shorter wavelength, indicating that the Ti oxide species in $TiO_x(0.1)/SiO_2$ were dispersed to a greater extent than those on the 1.5 mol% sample (Fig. 3e) (36). Thus, the higher PO selectivity on $TiO_x(0.1)/SiO_2$ is due to the presence of the highly dispersed Ti species.

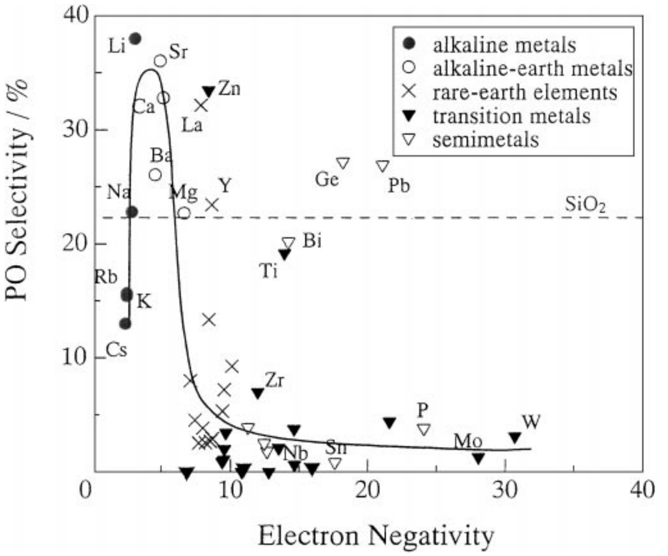

FIG. 4. Plots of PO selectivity vs electronegativity of cation (Tanaka, K., and Ozaki, A., *J. Catal.* **8**, 1 (1967)) on various silica-supported samples (symbols) and on bare silica (broken line) in the photooxidation of propene by molecular oxygen. Irradiation time was 2 h.

DISCUSSION

Classification of the Silica-Supported Samples

The active silica-supported samples can be divided into several classes on the basis of their PO selectivity and conversion (Table 3). High propene conversion and high PO selectivity were shown by the samples in the first group (Class A), which consists of the oxides of Ti, Zn, Pb, and Bi. High PO selectivity but low conversion, close to that on the bare SiO_2, were found on the samples in the second group (Class B) that contained alkali metals, alkaline-earth metals, and rare-earth elements such as Li, Na, Mg, Ca, Sr, Ba, Y, and La.

The other three groups showed low PO selectivity. Partial oxidation products other than PO were predominant on transition metals such as Zr, V, Nb, Ta, Cr, Mo, and W, which are considered to be active elements in selective oxidation catalysts (Class C). High selectivity for PA, AA, and hydrocarbons were observed on Al and Ga (Class D).

Electron Negativity and Photooxidation Activity (Class B)

Class B consists of alkali metals, alkaline-earth metals, and rare-earth elements. The element such as alkali metal is often used as a promoter: the element electronically affects the active sites and improves activity. In the present study, the silica itself was photoactive for epoxidation, and the element in Class B only slightly affected the photooxidation selectivity in comparison with that on the silica. Thus, it seems that the elements in Class B have an electronic effect on the photoactive sites on the silica surface. We then plotted the PO selectivity versus electronegativity of the cation (Fig. 4). The electronegativity of the cation was calculated according to the equation (37)

$$\chi_\iota = (1 + 2i)\chi_p, \qquad [1]$$

where χ_ι is the electronegativity of the cation, i the valence of the cation, and χ_p the electronegativity of the metal. The PO selectivity of bare SiO_2 (22.3%) is shown as a broken line. Most of the plots are on a curve, the maximum of which is around an electronegativity of 5. The group 2A and 3A elements have maximum activity. Adding these electronegative elements would modify the electronic property of the

TABLE 3

Classification of Active Silica-Supported Samples in the Photooxidation of Propene

Photooxidation activity				
Selectivity	Conversion	Class	Elements on silica	Category
High PO selectivity (19–33%)	High (8–24%)	A	Ti, Zn, Pb, Bi	
High PO selectivity (23–38%)	Low (<5%)	B	Li, Na Mg, Ca, Sr, Ba Y, La	Alkali metals Alkaline-earth metals Rare-earth elements
Low PO selectivity (<5%)	High (8–34%)	C	Zr, V, Nb, Ta, Cr, Mo, W	Transition metals
Low oxidation selectivity (HC selectivity, 18–22%)	High (8–10%)	D	Al, Ga	3B group

photoactive sites on the silica surface and improve PO production: it is proposed that electron donation by the element reduces the oxidative ability of the hole formed at the photoexcitation sites, possibly at lattice oxygen, on silica.

Some of the samples in group 3A exhibited high PO selectivity, while other samples in this group did not, although they have similar electronegativity. Other factors, such as dispersion on the silica surface, apparently play a role, as discussed below.

Photooxidation Activity of Class A Samples

Conversion and product distribution on the samples of Class A, PbO_x/SiO_2, BiO_x/SiO_2, and TiO_x/SiO_2, were quite different from those on samples in Class B. They exhibited high conversion (8–24%) and high PO selectivity (19–33%) (Table 3). In addition, they are not on the curve in Fig. 4. Therefore, these samples should be placed in Class A, not in class B. The added elements would become the active sites and exhibit a unique activity that is different from that of Class B samples. For example, it was reported that highly dispersed titanium oxide species on silica, which is different from a solid semiconductor such as bulk TiO_2, receive photoenergy to form an excited complex $[Ti^{3+}–O^{-}]^*$ and play a significant role in the photocatalytic reaction (38). In propane oxidation, the titanium oxide species are suggested to govern the photocatalytic reaction, since the local structure of these species affects the photocatalytic properties (39, 40).

In Class A, only ZnO_x/SiO_2 seems to be on the curve (Fig. 4). Zn has one of the lowest electronegativities of the transition metal elements. The product distribution on ZnO_x/SiO_2 was similar to that on the alkaline-earth metal samples; the mechanism of photoepoxidation on ZnO_x/SiO_2 might, therefore, be similar to that of the alkaline-earth metal samples. However, ZnO_x/SiO_2 exhibited a clearly higher conversion than the Class B samples. In the present study, ZnO_x/SiO_2 was tentatively classified as Class A; further experiments are in progress.

In Class A samples, PbO_x/SiO_2 and BiO_x/SiO_2 also produced large amounts of CO_x. Thus, TiO_x/SiO_2 and ZnO_x/SiO_2 were the most effective systems for PO production in this study.

Certification of Catalytic Reaction

We confirmed that the photoepoxidation proceeded catalytically on the most effective sample, $TiO_x(0.1)/SiO_2$, which showed a 9.2% yield of PO after 8 h of irradiation (Table 2, entry 8). The amount of PO produced was 9.2 μmol. If the silica surface maintains its original activity, the PO yield on silica (Table 1, entry 1) should be 1.2 μmol after 8 h of irradiation, in which case the PO yielded by Ti ion would be 8.0 μmol. The calculated amount of Ti ions in the reactor was 3.33 μmol. Even if all of the Ti ions are active sites, the turnover number over the Ti ion (TON_{Ti}) is defined as

$$TON_{\mathrm{Ti}} = \text{(the amount of PO produced on Ti ions)}/\text{(the amount of Ti ions)}. \quad [2]$$

Thus, the TON_{Ti} will be 2.4. If all the PO is assumed to be produced on Ti sites, then the TON_{Ti} will be 2.8. In any case, the number is higher than 1, indicating that the photoepoxidation of propene on TiO_x/SiO_2 proceeded catalytically. This is the first time (33) that catalytic photooxidation of propene to propene oxide by molecular oxygen has been observed. TS-1 is known to be a catalyst for propene epoxidation by H_2O_2, as mentioned above (1–6). It is assumed that, upon addition of hydroperoxides to titanium, silicates form titanium peroxo complexes as the intermediate (1). The present photoepoxidation on TiO_x/SiO_2 might proceed in the same way.

Dispersion and Photooxidation Activity of Class C Metal Oxides on Silica

In this study NbO_x/SiO_2 exhibited lower PO selectivity than that reported in the literature (13). The best concentration of Nb on silica for PO production is reported to be 0.1 wt% (13), i.e., 0.04 mol%, which is much lower than in the present study (1.5 mol%). It has been reported that only highly dispersed monomeric tetrahedral niobium oxide species, obtained through equilibrium adsorption, provide the highest PO selectivity (13, 41). The monomeric tetrahedral species exhibit an absorption band below 300 nm in the UV–vis spectrum (13). NbO_x/SiO_2 exhibited an absorption band below 350 nm (Fig. 3), indicating that the Nb species in NbO_x/SiO_2 were not sufficiently dispersed. This explains why the present NbO_x/SiO_2 exhibited low PO selectivity.

In the case of TiO_x/SiO_2 and ZnO_x/SiO_2, which exhibited the highest performance for PO production in the present study, the supported oxide species on the silica surface showed UV–vis spectra very different from those of the bulk oxides (Fig. 3). This indicates that the active Ti and Zn species are well dispersed on silica. In addition, the lower loading sample, $TiO_x(0.1)/SiO_2$, was shown by UV–vis spectra to be more highly dispersed than the 1.5 mol% sample and revealed a higher PO selectivity. NbO_x/SiO_2, TiO_x/SiO_2, and ZnO_x/SiO_2, used as examples, clearly demonstrate that the presence of highly dispersed species on the silica surface is of great importance when designing the best catalysts for PO production in the photooxidation of propene by molecular oxygen.

In the case of NbO_x/SiO_2, it is reported that, although samples with highly dispersed species show high PO selectivity, samples with species that are not as well dispersed exhibit high AA selectivity (13). Some of the silica-supported transition metal oxides in Class C also exhibited high AA selectivity. Therefore, metal oxide species on these systems are probably not sufficiently dispersed and, thus, do not show the best performance. We predict that some of these catalysts can be further optimized to become Class A catalysts.

Photooxidation Activity of Class D Samples

High selectivity for hydrocarbons was observed on AlO_x/SiO_2 and GaO_x/SiO_2 (Class D) (Table 1). The study of propene photoconversion in the absence of oxygen on zeolites (27) suggested that propene was polymerized by the acid sites on the zeolite. In the present study, polymerization may have occurred on the surface of these samples during photooxidation, since incorporation of Al or Ga into the silica matrix is expected to produce acid sites on the surface. We also observed high selectivity to aldehydes. The production of PA will be discussed in the next section.

Possibility of Thermal Isomerization

Most of the products in the photooxidation were collected through thermal desorption at 573 K *in vacuo*. Although the results in Table 2 show that consecutive photoreaction did not take place, thermal reactions might occur during the thermal desorption process. It has been reported that PO is isomerized to PA on acid sites or AC on basic sites at 533 K (42). PA was observed in the cases of Mg, Y, La, Ti, Zr, Mo, W, Zn, Al, Ga, and Sn, the oxides of which were mixed with silica and are reported to possess acid sites (43). On the other hand, a high AC selectivity of more than 30% was observed on RbO_x/SiO_2 and CsO_x/SiO_2 and may be due to their basic properties. In this respect, several rare-earth metal samples, such as ScO_x/SiO_2, YO_x/SiO_2, LaO_x/SiO_2, EuO_x/SiO_2, GdO_x/SiO_2, and YbO_x/SiO_2, would have basic properties and several samples, such as PrO_x/SiO_2, NdO_x/SiO_2, SmO_x/SiO_2, TbO_x/SiO_2, DyO_x/SiO_2, and ErO_x/SiO_2, would have acid properties. These random properties, which do not seem to have any relation to the periodic table, are probably due to the differences in the dispersion of the metal oxide species on silica, as discussed above. In this category, only a few samples (e.g., LaO_x/SiO_2) exhibited high PO selectivity. Highly dispersed species with neutral properties on silica might be suitable for PO production in the photooxidation of propene by molecular oxygen.

CONCLUSIONS

The following guidelines were established for designing effective catalysts for PO synthesis in the photooxidation of propene by molecular oxygen:

(1) TiO_x/SiO_2 and ZnO_x/SiO_2 (Class A) are the most effective systems for PO production from propene and molecular oxygen upon photoirradiation. Photoepoxidation proceeds *catalytically* on TiO_x/SiO_2.

(2) Photoactivity of silica for PO production was improved by adding elements with moderate electronegativity (Class B). The moderate donation of electrons from these elements modifies the photoactivity of silica.

(3) The presence of highly dispersed metal oxide species on the silica surface is an important factor in PO production. Acid–base properties might disturb PO production.

ACKNOWLEDGMENTS

This work was supported by a grant-in-aid from the Japanese Ministry of Education, Science, Art, Sports, and Culture and by Nippon Sheet Glass Foundation for Materials Science and Engineering.

REFERENCES

1. Notari, B., *Adv. Catal.* **41**, 253 (1996).
2. Neri, C., Anfossi, B., and Buonomo, F., European Patent 100,118, 1984.
3. Neri, C., Esposito, A., Anfossi, B., and Buonomo, F., European Patent 100,119, 1984.
4. Notari, B., *Stud. Surf. Sci. Catal.* **37**, 413 (1987).
5. Romano, U., Esposito, A., Maspero, F., Neri, C., and Clerici, M. G., *Stud. Surf. Sci. Catal.* **55**, 33 (1990).
6. Clerici, M. G., Bellussi, G., and Romano, U., *J. Catal.* **129**, 159 (1991).
7. Hayashi, T., Tanaka, K., and Haruta, M., *J. Catal.* **178**, 566 (1998).
8. Meiers, R., Dingerdissen, U., and Hölderich, W. F., *J. Catal.* **176**, 376 (1998).
9. Pichat, P., Herrmann, J. M., Disdier, J., and Mozzanega, M. N., *J. Phys. Chem.* **83**, 3122 (1979).
10. Yoshida, S., Magatani, Y., Noda, S., and Funabiki, T., *J. Chem. Soc., Chem. Commun.* 601 (1981).
11. Yoshida, S., Tanaka, T., Okada, M., and Funabiki, T., *J. Chem. Soc., Faraday Trans. 1* **80**, 119 (1984).
12. Tanaka, T., Ooe, M., Funabiki, T., and Yoshida, S., *J. Chem. Soc., Faraday Trans. 1* **82**, 35 (1986).
13. Tanaka, T., Nojima, H., Yoshida, H., Nakagawa, H., Funabiki, T., and Yoshida, S., *Catal. Today* **16**, 297 (1993).
14. Yoshida, H., Tanaka, T., Yamamoto, M., Funabiki, T., and Yoshida, S., *Chem. Commun.* 2125 (1996).
15. Yoshida, H., Tanaka, T., Yamamoto, M., Yoshida, T., Funabiki, T., and Yoshida, S., *J. Catal.* **171**, 351 (1997).
16. Blatter, F., Sun, H., and Frei, H., *Catal. Lett.* **35**, 1 (1995).
17. Blatter, F., Sun, H., Vasenkov, S., and Frei, H., *Catal. Today* **41**, 297 (1998).
18. Xiang, Y., Larsen, S. C., and Grassian, V. H., *J. Am. Chem. Soc.* **121**, 5063 (1999).
19. Armor, J. N., *J. Catal.* **70**, 72 (1981).
20. Kastanas, G. N., Tsigdinos, G. A., and Schwank, J., *Appl. Catal.* **44**, 33 (1988).
21. Matsumura, Y., Hashimoto, K., and Yoshida, S., *J. Catal.* **117**, 135 (1989).
22. Parmaliana, A., Frusteri, F., Miceli, D., Mezzapica, A., Scurrell, M. S., and Giordano, N., *Appl. Catal.* **78**, L7 (1991).
23. 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.
24. Anpo, M., Yun, C., and Kubokawa, Y., *J. Catal.* **61**, 267 (1980).
25. Ogata, A., Kazusaka, A., and Enyo, M., *J. Phys. Chem.* **90**, 5201 (1986).
26. Yoshida, H., Murata, C., Inaki, Y., and Hattori, T., *Chem. Lett.* 1121 (1998).

27. Yoshida, H., Kimura, K., Inaki, Y., and Hattori, T., *Chem. Commun.* 129 (1997).
28. Tanaka, T., Matsuo, S., Maeda, T., Yoshida, H., Funabiki, T., and Yoshida, S., *Appl. Surf. Sci.* **121**/**122**, 296 (1997).
29. Yoshida, H., Tanaka, T., Matsuo, S., Funabiki, T., and Yoshida, S., *J. Chem. Soc., Chem. Commun.* 761 (1995).
30. Anpo, M., *Stud. Surf. Sci. Catal.* **47**, 119 (1989).
31. Morikawa, A., Hattori, M., Yagi, K., and Otsuka, K., *Z. Phys. Chem., N.F.* **104**, 309 (1977).
32. Yoshida, S., Matsuzaki, T., Kashiwazaki, T., Mori, K., and Tarama, K., *Bull. Chem. Soc. Jpn.* **47**, 1564 (1974).
33. Yoshida, H., Murata, C., and Hattori, T., *Chem. Commun.* 1551 (1999).
34. Uchijima, T., "Catalytic Science and Technology," Vol. 1, p. 393. Kodansha, Tokyo VCH, Weinheim, 1991.
35. Yoshida, H., Murata, C., and Hattori, T., *Chem. Lett.* 901 (1999).
36. Marchese, L., Gianotti, E., Dellarocca, V., Maschmeyer, T., Rey, F., Coluccia, S., and Thomas, J. M., *Phys. Chem. Chem. Phys.* **1**, 585 (1999).
37. Tanaka, K., and Ozaki, A., *J. Catal.* **8**, 1 (1967).
38. Anpo, M., Aikawa, N., Kubokawa, Y., Che, M., Louis, C., and Giamello, E., *J. Phys. Chem.* **89**, 5017 (1985).
39. Yoshida, S., Takenaka, S., Tanaka, T., Hirano, H., and Hayashi, H., *Stud. Surf. Sci. Catal.* **101**, 871 (1996).
40. Yoshida, S., Takenaka, S., Tanaka, T., and Funabiki, T., *J. Phys. IV Fr.* **7**, C2-859 (1997).
41. Yoshida, H., Tanaka, T., Yoshida, T., Funabiki, T., and Yoshida, S., *Catal. Today* **28**, 79 (1996).
42. Okamoto, Y., Imanaka, T., and Teranishi, S., *Bull. Chem. Soc. Jpn.* **46**, 4 (1973).
43. Tanabe, K., Misono, M., Ono, Y., and Hattori, H., "New Solid Acids and Bases." Kodansha, Tokyo Elsevier, Amsterdam, 1989.