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Visible light-induced photoepoxidation of propene by molecular oxygen over chromia–silica catalysts

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Highly dispersed chromate species on silica catalyse the selective epoxidation of propene to propene oxide (PO) by molecular oxygen under visible light irradiation with the same quantum yield as that under UV light irradiation.

Currently propene epoxidation is performed by two liquid phase processes: the chlorohydrin process and the hydroperoxide process.[1] These processes have some problems of by-products, wastes, *etc*. The direct gas phase epoxidation of propene by molecular oxygen, which is the most simple process without these problems, is desirable. Recently some workers reported new approaches for propene epoxidation using O_2 and H_2.[2] However, it is evident that using only O_2 is more advantageous, and many researchers have attempted epoxidation of propene using only O_2.[3]

On the other hand, 'photoepoxidation' of propene using only O_2 over TiO_2,[4] Ba-Y type zeolite,[5] Nb_2O_5/SiO_2,[6] MgO/SiO_2 and SiO_2[7] has been reported. However, these activities were low and it was not clear whether the reaction proceeded catalytically. We have found that isolated tetrahedral Ti species on titania–silica catalytically promoted the selective photoepoxidation of propene by molecular oxygen.[8] However, the isolated tetrahedral Ti species absorb only UV light (λ < 250 nm), and the reaction proceeded only under UV irradiation. Artificial UV light sources tend to be expensive, and the UV light component in sunlight reaching the surface of the earth is relatively small. Thus, it is significant to develop a visible light-driven photocatalyst for epoxidation of propene. It is known that Cr species have LMCT absorption in the visible light region, and recently NO decomposition and propane oxidation over Cr-containing mesoporous silica molecular sieves (Cr-HMS) under visible light irradiation have been reported.[9,10] In our previous screening study of silica-supported metal oxide catalysts for propene photoepoxidation, CrO_x/SiO_2 (1.5 mol% as Cr) showed high propene conversion, but low selectivity for PO.[11]

In the present study, we prepared chromia–silica catalysts containing a very small amount (0.1 mol%) of Cr by the sol–gel method or impregnation method, and examined the propene photoepoxidation activity and the dependence of the activity on the wavelength of photoirradiation.

CrO_x–SiO_2 binary oxide was prepared by hydrolysis of a mixed solution of $Si(OC_2H_5)_4$ and $Cr(NO_3)_3{\cdot}9H_2O$ dissolved in ethylene glycol followed by calcination at 773 K in flowing air for 5 h.[12] CrO_x/SiO_2 supported oxides were prepared by impregnation method with amorphous silica and $Cr(NO_3)_3{\cdot}9H_2O$ aqueous solution, followed by calcination in the same way.[11] CrO_x–SiO_2 and CrO_x/SiO_2 are denoted as Cr–Si(x) and Cr/Si(x) respectively, where x is mol% of Cr; $n_{Cr}/(n_{Cr} + n_{Si}) \times 100$. Prior to each reaction test and spectroscopic measurement, the sample was treated with 100 Torr oxygen at 773 K for 1 h, followed by evacuation at 673 K for 1 h. The photoepoxidation of propene was performed with a conventional closed system (123 cm^3) and 200 W Xe lamp in the same manner as previously reported.[8]The wavelength of photoirradiation light was limited by using TOSHIBA UV-cut glass filters: UV-31 and Y-43, which allow the transmission of light with λ > 310 nm and 430 nm, respectively. The distribution of the intensity of light from the Xe lamp was measured using a Hamamatsu Photonic Multi-Channel Analyzer C7473 with a CCD sensor. Diffuse reflectance UV-vis spectra of the pretreated samples were measured *in vacuo* on a JASCO V-570 spectrophotometer at room temperature.

Fig. 1 shows diffuse reflectance UV-vis spectra of Cr/Si(0.1), Cr–Si(0.1) and Cr/Si(1.5). All samples showed three absorption bands centred around 245, 330 and 460 nm, which were assigned to the LMCT (from O^{2-} to Cr^{6+} charge transfer) transitions of chromate species.[9] Cr/Si(1.5) and Cr–Si(0.1) showed an additional absorption band in the 580–800 nm region assigned to the d–d transition of octahedral Cr^{3+} in Cr_2O_3 clusters.[9] Weckhuysen *et al.* reported that monochromate and dichromate species existed over Cr/SiO_2 0.2 wt% (0.23 mol%), and, with increasing Cr loading, additional polychromate (trichromate, tetrachromate, *etc.*) species and Cr_2O_3 clusters were formed.[13] Since Cr/Si(0.1) contained 0.09 wt% of Cr and exhibited a spectrum without an absorption band at 580–800 nm, Cr/Si(0.1) would have dispersed chromate species (monochromate and/or dichromate) most abundantly. The additional very weak absorption band at 580–800 nm in the spectrum of Cr–Si(0.1) indicates that a very small amount of polychromate species and Cr_2O_3 clusters would also be formed on Cr–Si(0.1). Over Cr/Si(1.5), larger amounts of polychromate species and Cr_2O_3 clusters would exist, illustrated by the stronger band at 580–800 nm in the spectrum.

Table 1 shows the results of photooxidation of propene over chromia–silica catalysts. The major products were propene oxide (PO), ethanal, CO and CO_2. Small amounts of propanal, acetone, acrolein, 2-propanol, ethene and butene were also observed. Cr/Si(1.5) showed very high selectivity for CO_x and low selectivity for PO (run 1) as previously reported.[11] Cr/Si(0.1) and Cr–Si(0.1) showed much higher selectivity for PO than Cr/Si(1.5) when they were compared at similar conversion (runs 2 and 3). This indicates that chromia–silica catalysts containing a very small amount (0.1 mol%) of Cr were efficient for the photoepoxidation of propene. Cr–Si(0.1) showed slightly lower selectivity for PO and higher selectivity for ethanal than Cr/Si(0.1). These results on the photoreaction and the UV-vis spectra indicate that dispersed chromate species on SiO_2 should be effective in the photoepoxidation of propene, while polychromate species and Cr_2O_3 clusters should promote

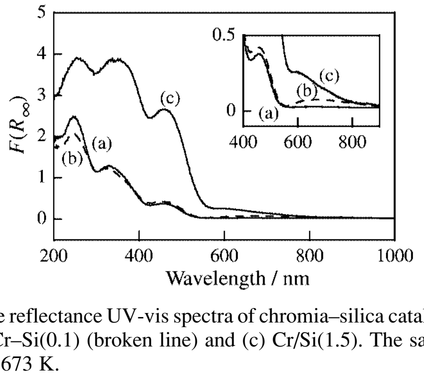

Fig. 1 Diffuse reflectance UV-vis spectra of chromia–silica catalysts. (a) Cr/Si(0.1), (b) Cr–Si(0.1) (broken line) and (c) Cr/Si(1.5). The samples were evacuated at 673 K.

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Table 1 Results of the photooxidation of propene over the chromia–silica catalyst[a]

							Selectivity[f] (C%)[e]						
Run	Catalyst	SA[b]/ m^2 g^{-1}	Filter	Time[c]/h	Conv.[d] (C%)	PO yield (C%)	PO	Propanal	Acetone	Acrolein	Ethanal	HC	CO$_x$
1	Cr/Si(1.5)[g]	573	no	1	16.9	0.6	3.7	1.7	1.9	4.8	15.2	8.9	61.5
2	Cr/Si(0.1)	537	no	2	16.7	7.3	44.0	2.7	5.8	4.3	17.9	3.7	19.6
3	Cr–Si(0.1)	382	no	2	17.8	5.7	32.0	4.6	5.3	4.8	22.2	5.2	19.5
4	Cr–Si(0.1)	382	UV-31	2	12.5	4.2	33.9	9.2	3.5	5.0	30.7	2.4	14.8
5	Cr–Si(0.1)	382	Y-43	2	7.7	2.5	31.8	9.2	3.0	5.8	30.8	3.3	15.7

[a] Catalyst 0.2 g, propene 100 μmol, O$_2$ 200 μmol, reaction time 2 h. [b] BET surface area. [c] Reaction time. [d] Conversion. [e] Based on introduced propene. [f] PO, propene oxide; HC, ethene + butenes; CO$_x$, CO + CO$_2$. A very small amount of 2-propanol was also observed, but is not shown here. [g] From ref. 11.

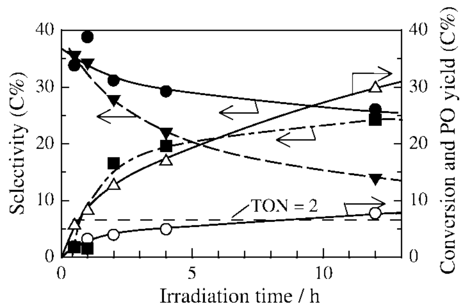

Fig. 2 Time course of photooxidation of propene over Cr–Si(0.1). Conversion (△), PO yield (○), and selectivity to propene oxide (●), ethanal (▼) and CO + CO$_2$ (■).

the oxidation of propene to by-products such as ethanal and CO$_x$. In addition, the turnover number, TON = (the amount of produced PO) / (the amount of Cr on sample), exceeded 2 after 12 h irradiation over Cr–Si(0.1) (Fig. 2), which indicated that this reaction proceeded catalytically.

The effective wavelength for photoepoxidation of propene over the Cr–Si(0.1) catalyst was examined using UV cut-off filters (Table 1, runs 4 and 5). Even under visible light (λ > 430 nm) irradiation (run 5), the conversion and PO yield almost reached half of the run without the filter (run 3). This means that visible light is sufficient to promote photoepoxidation of propene over chromia–silica catalysts. By using the UV cut-off filters, selectivity for PO was not significantly changed, but ethanal selectivity increased and CO$_x$ selectivity decreased. As shown in Fig. 2, in the range of conversion 7–18% (1–4 h) ethanal selectivity decreased and CO$_x$ selectivity increased with increasing conversion, but selectivity to PO was not so affected by the conversion. The differences in ethanal and CO$_x$ selectivity among runs 3–5 can be attributed to the difference in conversion, not in the wavelength of light. In other words, the product distribution would not be affected by the wavelength of light, which suggests that the chromate species excited by UV or visible light catalyse the photoepoxidation of propene *via* the same mechanism, regardless of the absorbed wavelength. The relative amount of photons absorbed by Cr–Si(0.1) was estimated from summing the products of absorption intensity of Cr–Si(0.1) and light intensity irradiated from the Xe lamp through UV cut-off filters at each wavelength. With increasing the relative amount of photons absorbed by Cr–Si(0.1), the conversion and PO yield increased linearly (Fig. 3). This result means that chromate species excited by UV or visible light would be equally efficient in the photoepoxidation of propene; that is, the quantum yield of photoepoxidation under visible light would be equal to that under UV light. Thus, exclusion of UV light changed neither the selectivity nor the quantum yield of propene photoepoxidation over chromate species. Therefore, it is suggested that chromate species excited by UV or visible light identically catalyse the photoepoxidation of propene, although the energy of photons was different at each wavelength. This should mean that the energy of visible light is sufficient to promote photoepoxidation of propene, that is, to activate oxygen and/or propene on the catalyst.

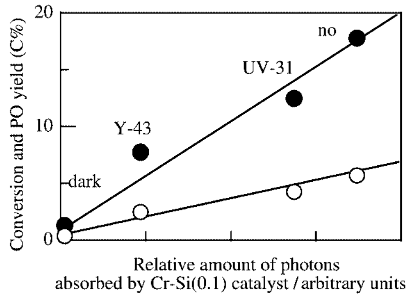

Fig. 3 The plot of conversion (●) and PO yield (○) in photooxidation of propene over Cr–Si(0.1) against the relative amount of photons absorbed by Cr–Si(0.1).

In conclusion, highly dispersed chromate species on SiO$_2$ were found to catalyse propene epoxidation by molecular oxygen under photoirradiation, and even under visible light irradiation. Chromate species excited by visible light would promote propene epoxidation identically to those excited by UV light.

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