Photocatalytic epoxidation of propene by molecular oxygen over highly dispersed titanium oxide species on silica

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Highly dispersed titanium oxide species on silica prepared by the sol-gel method catalyse selective epoxidation of propene by molecular oxygen upon photoirradiation.

Propene epoxidation is of industrial importance. The mixed oxide of Ti and Si has been recognized as a catalyst for the epoxidation of olefins with hydroperoxides and is employed industrially to produce propene oxide (PO) from propene.[1] TS-1, titanium-containing crystalline silica, is known to catalyse epoxidation of propene using H_2O_2.[2] However, employing oxygen as oxidant would be the most economical way of carrying out the oxidation.[1] The discovery of catalysts for the epoxidation of propene by molecular oxygen is highly desirable. One of the most promising systems for this reaction should be photocatalysis on silica-supported systems, since PO was obtained as a product over Nb/SiO_2,[3] Mg/SiO_2 and even over bare amorphous silica[4,5] with significant selectivity. However, the PO yield in these systems was still low, and it is not clear whether the reaction proceeds catalytically or not.

In the present study, we prepared highly dispersed titanium oxide species on silica by two methods, impregnation and sol-gel methods, and examined their photocatalytic activity for propene epoxidation using molecular oxygen.

Amorphous silica was prepared from $Si(OEt)_4$ by the sol-gel method followed by calcination in a flow of air at 773 K for 5 h.[6] The bulk titanium oxide employed was a Japan Reference Catalyst (JRC-TIO-4; equivalent to P-25). A silica-supported titanium oxide sample containing 0.1 mol% Ti (Ti/Ti + Si), referred to as T/S(0.1), was prepared by the impregnation method.† A TiO_2–SiO_2 mixed oxide sample containing 0.34 mol% Ti, T-S(0.34), was prepared by the sol-gel method.‡ The Ti content was determined by inductively coupled plasma (ICP) measurements. A diffuse reflectance UV-VIS absorption spectrum of the sample *in vacuo* was recorded at room temperature with a JASCO V-570 spectrophotometer after the same pretreatment as for the photoreaction test.

Before the photoreaction, the samples were heated in air up to 673 K, and then evacuated. Subsequently the samples were treated with 100 Torr oxygen (1 Torr = 133.3 N m^{-2}) at 673 K for 1 h, followed by evacuation at 673 K for 1 h.§ 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 was elevated by *ca.* 20 K from room temperature by the photoirradiation. The reactants were propene (100 μmol, 15 Torr) and oxygen (200 μmol, 30 Torr). The catalyst (200 mg) was spread on the flat 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 1 h were analyzed separately by gas chromatography, followed by analysis of the desorbed products by heating at 573 K. The results presented here are the sum of each product yield. The products were propene oxide (PO), propanal (PA), acetone (AC), acrolein (AL), acetaldehyde (AA), alcohols (MeOH, EtOH and Pr^{i}OH), hydrocarbons (ethene and butenes; HC) and CO and CO_2 (CO_x).

Fig. 1 shows diffuse reflectance UV-VIS spectra of the samples. Bare silica showed no large absorption band [Fig. 1(*a*)], while bulk TiO_2 showed a large absorption band below the band gap [Fig. 1(*d*)]. Both T/S(0.1) and T-S(0.34) exhibited a narrow band centred at *ca.* 210 nm [Fig. 1(b),(*c*)] which is assigned to the ligand-to-metal charge transfer band of highly dispersed tetrahedral titanium species.[7] This means that T/S(0.1) and T-S(0.34) consist of predominantly highly dispersed tetrahedral titanium species on silica.

Table 1 shows the results of photooxidation of propene by molecular oxygen on the samples. Bare silica (entry 1) exhibited almost the same conversion (1.53%) and propene oxide selectivity (22.3%) as previously reported.[4,5] The conversion to CO_x was not significant. Other major by-products are AC, AL and AA. Bulk TiO_2 (entry 2) showed high photooxidation activity; the conversion of propene was 14.1% when irradiated for 1 h (half of the standard irradiation time). However, the

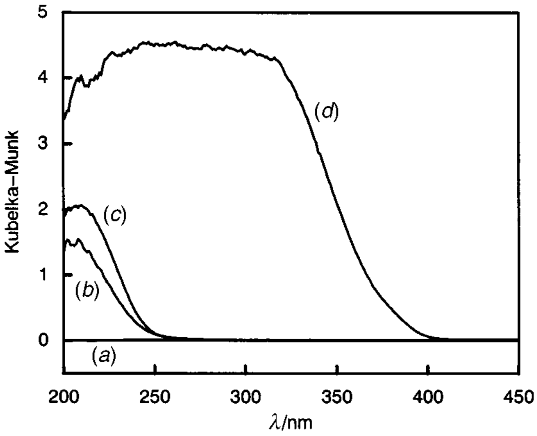

Fig. 1 Diffuse reflectance UV-VIS spectra of (*a*) silica, (*b*) T/S(0.1), (*c*) T-S(0.34) and (*d*) TiO_2.

Table 1 Results of the photooxidation of propene

Entry	Sample	BET surface area/ $m^2\ g^{-1}$	Irradiation time/h	Conversion of propene (%)	PO yield (%)	Selectivity (%)							
						PO	PA	AC	AL	AA	Alcohol	HC	CO_x
1	SiO_2	558	2	0.7	0.2	27.1	1.4	26.7	8.9	16.8	6.0	8.8	4.3
2	TiO_2	34	1	14.1	0.0	0.0	0.0	1.3	0.0	0.8	0.0	1.7	96.2
3	T/S (0.1)	477	2	9.1	3.7	40.8	3.3	11.3	4.2	24.5	3.6	2.3	10.0
4	T-S (0.34)	423	2	9.2	5.3	57.5	2.7	5.8	1.2	21.1	0.0	5.1	6.6

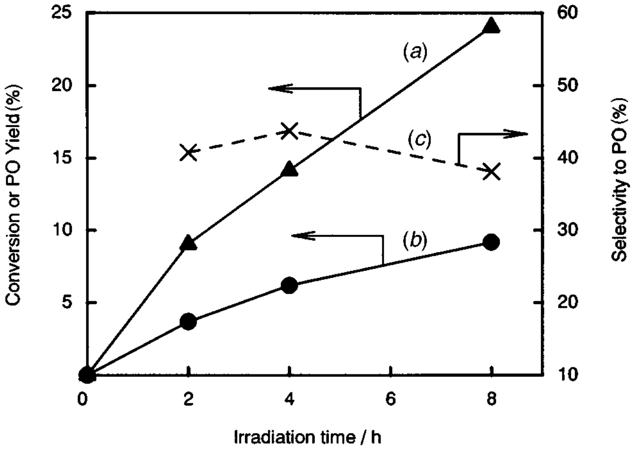

Fig. 2 Time course of (*a*) propene conversion, (*b*) PO yield and (*c*) PO selectivity in the photooxidation of propene by molecular oxygen on T/S(0.1).

major product (96.2%) was CO_x; no propene oxide was observed.

On the other hand, the silica-supported titania sample T/S(0.1) (entry 3) exhibited higher selectivity to PO (40.8%) than bare silica and bulk TiO_2. The conversion of propene on T/S(0.1) was much higher than on bare silica, while selectivity to CO_x was considerably lower than bulk TiO_2. Therefore, it was found that dispersed titanium oxide on silica has a moderate ability to produce PO from propene and molecular oxygen upon photoirradiation.

T-S(0.34) prepared by the sol-gel method showed almost the same conversion as T/S(0.1); therefore, an accurate comparison of product selectivity was allowed. Obviously the PO selectivity on T-S(0.34) was higher than that on T/S(0.1); it was also higher than the selectivities previously reported in the literature.[3–5] The conversion to CO_x was also suppressed more than that of T/S(0.1). It is thus indicated that T-S(0.34) has excellent properties for this photoepoxidation; sol-gel methods should be advantageous for producing active sites for selective photoepoxidation of propene using molecular oxygen.

Fig. 2 presents the time course of propene conversion, PO yield and PO selectivity in the photooxidation on T/S(0.1). The conversion of propene and yield of PO increased with increasing irradiation time. The selectivity was not affected significantly by the conversion at least until a conversion of 24.1%. After 8 h photoirradiation, the yield of PO achieved was 9.2% of the initial amount of propene. The amount of PO produced was 9.2 μmol, and the calculated amount of titanium ions in the reactor was 3.33 μmol. Even if all the titanium ions were active sites, the turnover number¶ would be 2.8, indicating that the photoepoxidation of propene on titanium oxide species on silica proceeded catalytically. This is the first report of the catalytic photooxidation of propene to propene oxide by molecular oxygen.

In conclusion, highly dispersed titanium oxide species were found to catalyse the photooxidation of propene to propene oxide by molecular oxygen at room temperature. The selectivity to propene oxide on titanium oxide species on silica was affected by the preparation method; the sol-gel method was superior to conventional impregnation methods. Titania–silica prepared by the sol-gel method in the present study showed higher selectivity to propene oxide than those previously reported in the literature. It is expected that fine-tuning of the preparation method, the amount of titanium oxide and the reaction conditions should further enhance their activities.

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Notes and references

† Calcined silica was impregnated by aqueous solutions of ammonium titanyl oxalate, dried at 383 K for 12 h and calcined at 773 K in a flow of air for 5 h.

‡ A mixture of $Si(OEt)_4$, EtOH, H_2O and HNO_3 (1, 3.8, 1, and 0.085 mol, respectively) was stirred at 353 K for 3 h and cooled down to room temperature. An Pr^iOH solution of titanium isopropoxide was added dropwise and stirred at 293 K for 2 h, followed by very slow addition of an aqueous solution of HNO_3 [1 and 0.085 mol respectively, the amount of this acid solution was equivalent to that of $Si(OEt)_4$ used]. Two weeks later, the obtained gel was heated at a rate of 0.2 K min^{-1} up to 338 K and dried for 5 h. After drying for an additional 5 h at 373 K, the TiO_2–SiO_2 mixed oxide was obtained by calcination at 773 K in a flow of air for 8 h.

§ This treatment temperature was lower than that of the previous reports (refs. 4,5) because low temperature (673 K, even room temperature) was found to be sufficient to activate the sample.

¶ Turnover number is defined as (the amount of produced PO)/(the amount of catalytic active sites).

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