Photooxidation of Propene to Propene Oxide by Molecular Oxygen over Zinc Oxide Dispersed on Silica

Hisao Yoshida,* Chizu Murata, and Tadashi Hattori†
Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603
†Research Center for Advanced Waste and Emission Management, Nagoya University, Nagoya 464-8603

(Received June 8, 1999; CL-990490)

Dispersed zinc oxide species on silica, which exhibited different UV-vis absorption spectrum from bulk ZnO, promoted selective photooxidation of propene by molecular oxygen to propene oxide.

The development of catalysts for propene epoxidation by molecular oxygen is still challenging matter for the catalysis researchers. Photocatalysis is one of the promising systems for this reaction. Formation of epoxide intermediate on the surface was shown in the photooxidation of light alkenes on V_2O_5/SiO_2[1] and on Ba Y-zeolite,[2] though propene oxide (PO) as a gaseous product could not be obtained in these systems.[1-4] Gaseous PO was obtained under photoirradiation over Nb_2O_5/SiO_2,[5] MgO/SiO_2 and even over a bare amorphous silica[6,7] with significant selectivity but low yield, and it was proposed that the surface of silica matrix is necessary to design photoepoxidation catalysts with additive elements.

The present study aims at inquiring the possibility to improve PO yield by using silica-supported semiconductor oxides such as ZnO. It is reported that ZnO has catalytic activity for photooxidation of propene although the amount of produced propene oxide was not enough to discuss.[8]

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.[9] Commercially obtained ZnO (Kishida, 99.0%) was calcined in air at 773 K for 5 h. Silica-supported zinc oxide sample, ZnO/SiO_2, was prepared by impregnation method; calcined silica was impregnated by aqueous solutions of $Zn(NO_3)_2$, dried at 383 K for 12 h and calcined at 773 K in a flow of air for 5h. The amount of Zn ion was 1.5 mol% (Zn/Zn+Si). BET surface area of the samples was listed in Table 1.

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 Nm^{-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 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 a flat bottom (12.6 cm^2) of the vessel. A 200 W Xe lamp was used as a light source. Products in gas phase and products desorbed by photoirradiation for 10 min were analyzed separately by gas chromatography, followed by analysis of desorbed products by heating at 573 K. The results presented here are the sum of each product yields. The products were propene oxide (PO), propanal (propionaldehyde; PA), propanone (acetone; AC), prop-2-enal (acrolein; AL), ethanal (acetaldehyde; AA) alcohols (methanol, ethanol and propan-2-ol; ROH), hydrocarbons (ethene and butenes; HC) and CO, CO_2 (CO_x).

Diffuse reflectance UV-vis absorption spectrum of the sample *in vacuo* was recorded at room temperature with JASCO V-570 spectrophotometer after the same pretreatment as the photoreaction test.

Table 1 shows the results of photooxidation of propene by molecular oxygen on SiO_2, ZnO and ZnO/SiO_2. Bare SiO_2 (entry 1) exhibited almost the same conversion (1.53%) and propene oxide selectivity (22.3%) as reported.[6,7] The conversion to CO_x was not predominant. Other products are mainly carbonyl compounds such as AC, AL and AA; dominant product was AC (25.8%).

ZnO (entry 2) showed almost the same conversion of propene (1.25%); this low conversion should be due to small surface area of ZnO. However, more than half of propene was completely oxidized into CO_x (51.9%), the selectivity to PO was very low, and the main product was AC (20.8%). This selectivity is similar to the reported results in photooxidation of propene[8] or 2-butene.[10] It was confirmed that ZnO has photooxidation activity but it is not suitable for the selective oxidation to propene oxide.

On the other hand, ZnO/SiO_2 (entry 3) showed clearly the highest conversion of propene (8.6%) among them. The selectivity (33.4%) and PO yield (2.88%) were also the highest values. It is also noteworthy that complete oxidation to CO_x was suppressed about 10% selectivity. This means that ZnO/SiO_2 has excellent property for PO production with minimum amount of by-products.

Figure 1 shows UV-vis absorption spectrum of the samples in the range of 200-600 nm. Bulk ZnO showed a large absorption band below the band gap at ca. 390 nm (Figure 1a). On the other hand, ZnO/SiO_2 exhibited a small absorption band below ca. 270

Table 1. Results of the photooxidation of propene by molecular oxygen on the samples[a]

Entry	Sample	BET surface area / m^2g^{-1}	Conversion /%	PO yield /%	Selectivity /%							
					PO	PA	AC	AL	AA	ROH	HC	CO_x
1	SiO_2	654	1.53	0.34	22.3	3.5	25.8	15.2	18.1	0.0	10.0	5.1
2	ZnO	12.1	1.25	0.02	1.9	0.0	20.8	8.1	6.2	6.9	4.2	51.9
3	Zn/SiO_2	592	8.61	2.88	33.4	11.4	11.2	5.1	17.9	4.0	6.2	10.8

[a] In the case of SiO_2 and ZnO/SiO_2, major amount of the partially oxygenated products were obtained as thermal desorption products. On the other hand, in the case of ZnO, products were mainly observed in gaseous phase.

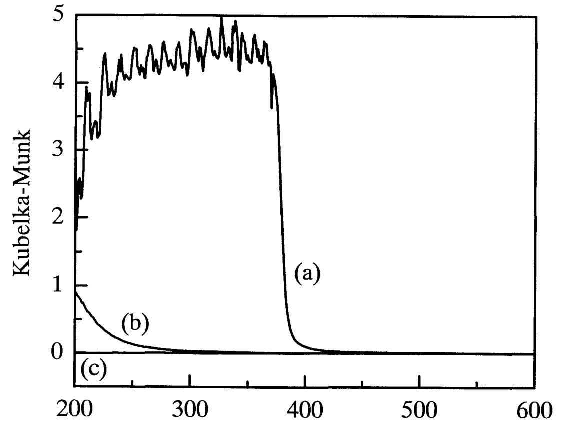

Figure 1. Diffuse reflectance UV-vis absorption spectra of ZnO (a), Zn/SiO_2 (b) and SiO_2 (c).

nm (Figure 1b), while such absorption band was not observed on bare silica (Figure 1c). It is clearly indicated that dispersed zinc oxide on silica had different electron structure from that of bulk ZnO. The excellent performance in photoepoxidation of ZnO/SiO_2 would be due to the dispersed zinc oxide species on silica which had such an electronic structure. However, it would be also possible that the addition of zinc oxide improved the performance of silica for PO production, since the bare SiO_2 also exhibited roughly similar products distribution.

In conclusion, it was found that selective photoepoxidation of propene can be greatly enhanced by using silica-supported ZnO, one of semiconductor oxide exhibiting photoactivity. Both propene conversion and PO selectivity on dispersed zinc oxide on silica were higher than those on bare silica and bulk zinc oxide. It is expected that fine tuning of their preparation method and of the reaction conditions should further enhance their activities.

This work was supported by a grant-in-aid from the Japan Ministry of Education, Science, Art, Sports and Culture.

References

1 T. Tanaka, M. Ooe, T. Funabiki, and S. Yoshida, *J. Chem. Soc., Faraday Trans. 1*, **82**, 35 (1986).
2 F. Blatter, H. Sun, and H. Frei, *Catal. Lett.*, **35**, 1 (1995).
3 S. Yoshida, Y. Magatani, S. Noda, and T. Funabiki, *J. Chem. Soc., Chem. Commun.*, **1981**, 601.
4 S. Yoshida, T. Tanaka, M. Okada, and T. Funabiki, *J. Chem. Soc., Faraday Trans. 1*, **80**, 119 (1984).
5 T. Tanaka, H. Nojima, H. Yoshida, H. Nakagawa, T. Funabiki, and S. Yoshida, *Catal. Today*, **16**, 297 (1993).
6 H. Yoshida, T. Tanaka, M. Yamamoto, T. Funabiki, and S. Yoshida, *Chem. Commun.*, **1996**, 2125.
7 H. Yoshida, T. Tanaka, M. Yamamoto, T. Yoshida, T. Funabiki, and S. Yoshida, *J. Catal.*, **171**, 351 (1997).
8 P. Pichat, J. M. Herrmann, J. Disdier, and M. N. Mozzanega, *J. Phys. Chem.*, **83**, 3122 (1979).
9 S. Yoshida, T. Matsuzaki, T. Kashiwazaki, K. Mori, and K. Tarama, *Bull. Chem. Soc. Jpn.*, **47**, 1564, (1974).
10 Y. Kubokawa, M. Anpo, and C. Yun, in "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," ed by T. Seiyama and K. Tanabe, Kodansha, Tokyo (1981), Vol. B, p. 1170.