

Photooxidation of propene by O₂ over silica and Mg-loaded silica

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Silica and Mg/SiO₂ catalyse photooxidation of propene by molecular oxygen, and propylene oxide was produced.

Epoxides are very important intermediates for many chemicals, therefore, new heterogeneous catalytic systems producing epoxides directly from alkenes with gaseous oxygen are desirable. The production of ethylene oxide from ethene with gaseous oxygen over Ag catalysts was developed many years ago,¹ however, its application to propene has not yet succeeded. Ti-containing zeolites^{2–4} have recently attracted interest as catalysts for epoxidation; however, the system consumes hydrogen peroxide. Epoxidation of alkenes by gaseous oxygen over heterogeneous catalysts has rarely succeeded.

Recently, a spectroscopic study was reported on the production of propylene oxide from propene and O₂ over Ba Y-zeolite irradiated with visible light.⁵ We had already found that the formation of an epoxide intermediate in the photooxidation of alkenes over silica-supported vanadium oxide⁶ and that highly dispersed niobium oxide on silica can catalyse epoxidation of propene with gaseous oxygen under photoirradiation.⁷ Silica is often used as a support for photocatalysts but is usually inactive itself. However, it can function as a catalyst for some reactions,^{8–20} in particular when it is activated by photoirradiation.^{21–24} It has been found recently that silica showed unexpected potential for photocatalysis in metathesis reactions when it was evacuated at high temperatures.²⁵ In the present study, it is shown that the presence of gaseous oxygen leads to epoxidation and other partial oxidation products of propene over silica and Mg-loaded silica under UV irradiation.

The silica used was prepared from Si(OEt)₄ by the sol-gel method followed by calcination in air at 773 K.²⁶ Mg/SiO₂ (*x*MS; *x* is the mass% of MgO) samples were prepared by impregnating the silica in Mg(OMe)₂-methanol,^{27–29} followed by calcination at 773 K. Another silica employed was a Japan Reference Catalyst (JRC-SIO-4),^{30,31} which was supplied by the Committee on Reference Catalyst, Catalysis Society of Japan: this was re-calcined in air at 773 K for 5 h. MgO was obtained from hydrolysis of Mg(OMe)₂-methanol followed by calcination at 773 K.

Before reaction, tests of photooxidation, heating under an oxygen atmosphere and subsequent evacuation at 1073 K of the

samples were performed. The photooxidation of propene was carried out in a closed quartz reaction vessel (35 cm³) at room temperature for 2 h as the standard conditions. The reactants were propene (30 μmol) and oxygen (0–120 μmol). The catalyst (100 mg) was spread on the flat bottom (3.14 cm²) of the vessel. A 250 W ultra-high-pressure Hg lamp was used as the light source. Products were collected after reaction in a part of the closed system by a liquid-N₂ trap when the catalysts bed was under irradiation, and were analysed by GLC and GC-MS.

Table 1 shows the product yields in the photooxidation of propene in the presence of 60 μmol O₂ over silica, MgO and MS samples. The products were propylene oxide (PO; methyloxirane), ethanal (acetaldehyde; AA), propanal (propionaldehyde; PA), propanone (acetone; AC), prop-2-enal (acrolein; AL), and alcohols (methanol, ethanol and propan-2-ol), where the metathesis reaction as described in a previous study²⁵ was not detected in the presence of O₂.

On the silica samples (entry 1, prepared by sol-gel method; entry 2, JRC-SIO-4), AA was the main product with a selectivity of 40–50%, and the selectivity to PO was 25%. The production of AA, PA, AL has been reported previously in photooxidation over PVG.²⁴ However, partial oxidation to PO has not been reported. Thus, this is the first report of the partial oxidation of propene to PO by oxygen gas over silica.

Upon loading the catalyst with magnesium oxide, the oxidation activity was increased. The selectivity varied with the magnesium content. The lowest loading sample (1MS, entry 3) produced PO with the highest selectivity (50.8%) among the MS samples. Higher loading samples (4MS and 13MS, entries 4, 5) produced other products, predominantly AA. Over bulk MgO only little reaction occurred (entry 6).

In the high Mg-loading samples prepared by the present method, magnesium oxide is present as small crystallites in the typical rock-salt structure as clarified by X-ray absorption spectra.²⁹ The particle size is too small to be detected by XRD. In low-loading samples, *e.g.* 1MS, magnesium oxide is highly dispersed on the silica surface which exhibits a characteristic phosphorescent emission spectra with fine structures.²⁷ Recently, the emission site was suggested to be coordinatively unsaturated surface species; Mg(OSi)₃.^{28,32} The results in Table 1 indicate that crystallites of magnesium oxide on silica

Table 1 Results of the photooxidation of propene^a

Entry	Sample	Product yield (%) ^b							Total	Selectivity to PO (%)
		PO ^c	PA	AC	AL	AA	Alcohols			
1	SiO ₂	0.44	0.33	0.11	0.02	0.62	0.00	1.52	28.9	
2	SIO-4	0.45	0.04	0.14	0.00	0.93	0.30	1.86	24.2	
3	1MS	3.36	0.70	0.40	0.00	1.66	0.50	6.62	50.8	
4	4MS	0.23	0.82	1.11	0.07	2.25	1.43	5.91	3.9	
5	13MS	0.07	1.43	1.66	0.07	2.86	1.00	7.09	1.0	
6	MgO	0.03	0.03	0.00	0.03	0.03	0.00	0.12	25.0	
7	1MS ^d	0.02	0.03	0.03	0.02	0.15	0.04	0.29	6.9	
8	1MS ^e	0.00	0.04	0.01	0.11	0.12	0.20	0.46	0.0	

^a O₂/propene (Pr) mole ratio = 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 the Hg lamp in an electric furnace at 573 K for 1 h.

promote the oxidation to AA, AC and PA, while highly dispersed magnesium oxide species $\text{Mg}(\text{OSi})_3$ accelerate the oxidation to PO.

When the excitation light was limited by using a UV-cut filter ($\lambda_{\text{permittance}} > 310 \text{ nm}$), the reaction proceeded very slowly and the selectivity to PO was low (entry 7), indicating that the UV light is essential for the oxidation, especially for oxidation to PO. Oxidation in the dark (in a electric furnace) at 573 K proceeded very slowly and PO was not detected (entry 8).

The presence of O_2 is also essential for the photooxidation over the silica and Mg-loaded silica. Fig. 1 shows the dependence of the activity of IMS on the $\text{O}_2/\text{propene}$ ratio, where the amount of propene introduced was kept constant. Clearly, a high $\text{O}_2/\text{propene}$ ratio is favourable for the photooxidation. In the absence of O_2 , just a little oxidation to AA took place under irradiation over IMS. Photooxidation to PO progressed in the presence of O_2 . The optimal conditions for the highest selectivity of PO among the experiments studied was $\text{O}_2/\text{propene} = 2$, although an excess of oxygen seemed to promote other partial oxidation pathways.

In conclusion, it was found that under UV irradiation in the presence of O_2 , silica catalyses the partial oxidation of propene to ethanol and propylene oxide. Mg-loaded silica exhibits higher activity for partial oxidation than silica. Highly dispersed Mg on silica, $\text{Mg}(\text{OSi})_3$, promotes the oxidation of propene to propylene oxide by O_2 under irradiation, and magnesium crystallites on silica produce mainly ethanal.

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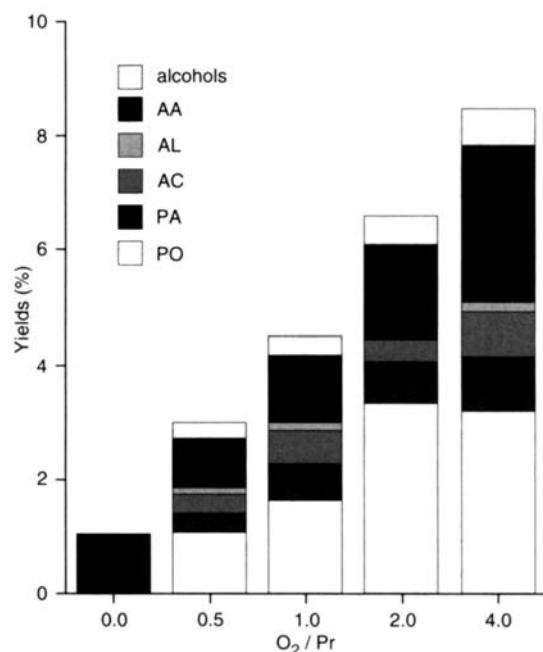


Fig. 1 Dependence of product yields on $\text{O}_2/\text{propene}$ ratio in the photooxidation of propene over IMS. Propene: $30 \mu\text{mol}$; irradiation time 2 h.

Footnote

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