Photooxidation of Propene by Molecular Oxygen over FSM-16

Hisao Yoshida,* Chizu Murata, Yoshitaka Inaki, 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 July 31, 1998; CL-980584)

Mesoporous silica (FSM-16) was found to exhibit a much higher activity for propene photooxidation than amorphous silica and to give different products distribution from those on silica, thus proposing FSM-16 as a new type of photooxidation catalyst.

Silica is a common material often used as not only a catalyst support but also a catalyst. Photocatalytic activities of silica have also been reported; e.g. isomerization of 2-butene,[1] olefin photooxidation,[2-4] CO photooxidation [5] and photometathesis.[6,7] Since mesoporous silica materials such as FSM-16 [8,9] and MCM-41 [10,11] were reported, they have attracted a great deal of attention as new materials for catalysts or support of catalysts. It was recently found that FSM-16 catalyzed metathesis reaction of propene under photoirradiation and that the activity was higher than amorphous silica.[12] In the present study, we examined the photooxidation of propene by gaseous oxygen over FSM-16.

FSM-16 were prepared by the reported methods.[8] Amorphous silica (AMS) was prepared by the sol-gel method.[13] The structure of sample was confirmed by XRD. Impurities were determined by ICP spectroscopy.

Before the photoreaction, the samples were heated in air up to 1073 K, and then evacuated. Subsequently the samples were treated with 100 Torr oxygen (1 Torr = 133.3 Nm^{-2}) at 1073 K for 1 h, followed by evacuation at 1073 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 as standard. The temperature of catalyst bed was elevated by ca. 20 K from room temperature by the photoirradiation. The reactants were propene (110 μmol) and oxygen (220 μmol). The catalyst (200 mg) was spread on a flat bottom (12.6 cm^2) of the vessel. A 250 W Xe lamp was used as a light source. Products in gas phase and products desorbed by photoirradiation for 10 min were analyzed by gas chromatography, followed by analysis of desorbed products by heating at 573 K. The results presented here are the sum of each product yield.

The synthesized FSM-16 and the FSM-16 evacuated at 1073 K showed almost the same XRD pattern as reported,[8,9] indicating that the synthesized sample had the same mesoporous hexagonal structure as the reported one, and the structure was maintained after the evacuation at high temperature such as 1073 K. BET surface area and amount of Al impurity of the samples were listed in Table 1.

Table 1. Surface area and amount of impurity of samples

Samples	BET surface area / m^2g^{-1}		Al impurity
	after calcination	after reaction	wt / %
AMS	654	526	0.005
FSM-16	1032	956	0.125

Table 2 shows the results in photooxidation of propene over AMS and FSM-16. The main products on these materials were partially oxygenated compounds, hydrocarbons, CO and CO_2. Partially oxygenated compounds were acetaldehyde (AA; ethanal), propylene oxide (PO; methyloxirane, or 1,2-epoxypropane), propionaldehyde (PA; propanal), acetone (AC; propanone), acrolein (AL; prop-2-enal), and alcohols (ROH; methanol, ethanol, and propan-2-ol). AMS (run 1) exhibits the conversion of 4.3% of propene; the main products were PO and AC. On the other hand, FSM-16 (run 2) showed nine times higher conversion (36.1%) than AMS. On FSM-16, a large amount of CO_2 was produced. Taking into account the specific surface area of these materials listed at Table 1, it was clearly shown that FSM-16 has a specific activity of about five times higher than AMS. In the dark, the oxidation of propene did not occurred on FSM-16 (run 4), indicating that the oxidation on FSM-16 is promoted by photoirradiation. From these results, it was clarified for the first time that FSM-16 has much higher activity for photooxidation of propene by gaseous oxygen than amorphous silica.

The photooxidation selectivities on the FSM-16 and AMS were compared at the same level of the conversion (runs 1 and 3). The products distribution was quite different from each other; main oxidized products on AMS were AC (selectivity, 25.1%) and PO (24.4%), while those on FSM-16 were AA (36.6%) and CO_2 (18.7%). AC and PO are produced by oxygenation of propene, while AA and CO_2 are obtained via bond fission of propene. The clear difference on products selectivity indicates that the photooxidation mechanism over FSM-16 was distinguishable from that of amorphous silica, and that FSM-16 has different type of active sites from amorphous silica.

The high activity for propene conversion and the unique selectivity of FSM-16 could result from the unique wall

Table 2. Results in photooxidation of propene over AMS and FSM-16

Run	Sample	Irradiation time / h	Conversion / %	Selectivity / %										
				AA[a]	PO	PA	AC	AL	ROH	C_2H_4	C_4H_8	others[b]	CO	CO_2
1	AMS	2	4.3	13.7	24.4	0.3	25.1	1.5	4.9	4.0	6.8	2.7	3.3	13.3
2	FSM-16	2	36.1	12.8	6.0	1.3	16.1	0.6	1.5	2.6	1.5	0.6	3.5	53.5
3	FSM-16	0.5	3.2	36.6	5.5	10.9	4.1	1.8	0.9	7.4	10.2	3.6	0.3	18.7
4	FSM-16	0[c]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] See text. [b] Hydrocarbons. [c] In the dark for 2 h.

structure which was reported to be double SiO_2 layers,[14] although the difference in the amount of Al impurity listed in Table 1 also might affect the conversion and selectivity. The details on the active sites on FSM-16 and amorphous silica are under investigation.

In conclusion, FSM-16 was found to have a much higher activity for photooxidation of propene by gaseous oxygen than amorphous silica. Since the products selectivity on the FSM-16 were different from that on amorphous silica, it is proposed that there are a new type of active sites on FSM-16.

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

References

1 A. Morikawa, M. Hattori, K. Yagi, and K. Otsuka, *Z. Phys. Chem. NF*, **104**, 309 (1977).
2 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 (1980), Vol. B, p. 1170.
3 H. Yoshida, T. Tanaka, M. Yamamoto, T. Funabiki, and S. Yoshida, *Chem. Commun.*, **1996**, 2125.
4 H. Yoshida, T. Tanaka, M. Yamamoto, T. Yoshida, T. Funabiki, and S. Yoshida, *J. Catal.*, **171**, 351 (1997).
5 A. Ogata, A. Kazusaka, and M. Enyo, *J. Phys. Chem.*, **90**, 5201 (1986).
6 H. Yoshida, T. Tanaka, S. Matsuo, T. Funabiki, and S. Yoshida, *J. Chem. Soc., Chem. Commun.*, **1995**, 761.
7 T. Tanaka, S. Matsuo, T. Maeda, H. Yoshida, T. Funabiki, and S. Yoshida, *Appl. Surf. Sci.*, **121/122**, 296 (1997).
8 S. Inagaki, Y. Fukushima, and K. Kuroda, *J. Chem. Soc., Chem. Commun.*, **1993**, 680.
9 S. Inagaki, A. Koiwai, N. Suzuki, Y. Fukushima, and K. Kuroda, *Bull. Chem. Soc. Jpn.*, **69**, 1449 (1996).
10 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, and J. L. Schlenker, *J. Am. Chem. Soc.*, **114**, 10834 (1992).
11 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature*, **359**, 710 (1992).
12 H. Yoshida, K. Kimura, Y. Inaki, and T. Hattori, *Chem. Commun.*, **1997**, 129.
13 S. Yoshida, T. Matsuzaki, T. Kashiwazaki, K. Mori, and K. Tarama, *Bull. Chem. Soc. Jpn.*, **47**, 1564 (1974).
14 S. Inagaki, Y. Sakamoto, Y. Fukushima, and O. Terasaki, *Chem. Mater.*, **8**, 2089 (1996).