Journal of Catalysis **202,** 427–429 (2001)
doi:10.1006/jcat.2001.3287, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

Partial Photooxidation of Ethylene with Water as Oxidant over Copper Oxide Supported on Silica

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Received January 2, 2001; accepted May 15, 2001; published online August 9, 2001

Ethylene can be photooxidized selectively with water as an oxidant via irradiation with UV light over copper oxide supported on silica after evacuation at 973 K. Ethylene oxide was formed by irradiation of UV-filtered light at a wavelength longer than 280 nm, and a high selectivity to ethylene oxide (82.5%) with an ethylene conversion of 1.6% was obtained at 278 K for 5 h of irradiation. However, irradiation of UV-unfiltered light results in the disappearance of ethylene oxide, while carbon dioxide, acetaldehyde, ethanol, ethane, and C_3 and C_4 hydrocarbons are formed. X-ray absorption near-edge structure (XANES) spectroscopy showed the presence of Cu^+ cations in the pore structure of the catalyst, suggesting that a mild oxidant can be generated from water on Cu^+ sites by UV light irradiation. © 2001 Academic Press

Key Words: **photooxidation of ethylene; partial oxidation; XANES; photocatalyst; copper oxide supported on silica; decomposition of water.**

INTRODUCTION

The selective oxidation of hydrocarbons to their respective oxygenates is one of the goals of chemical industries. However, the direct oxidation with molecular oxygen often results in low selectivity of the desired compounds. The process of using a photocatalyst offers a unique route to oxidation (1–4), but it is accompanied by over oxidation due to the high oxidation potential of the photocatalysts; such as TiO_2. In a photocatalytic system, the decomposition of water can occur, and it is known that hydrogen formation is promoted in the presence of organic compounds which consume oxygen from water. Taylor *et al.* reported the formation of methanol and carbon monoxide from methane in a photocatalytic decomposition of water and suggested the formation of the OH radical, which is considered to be a mild oxidant (5). Gonzalez *et al.* also showed that OH radical may be involved in the photooxidation of hydrocarbons over titanium oxide with molecular oxygen in the presence of water (6). Hence, water is expected to be an effective oxidant of hydrocarbons with photocatalysts and it may provide a new oxidation process. In the present study, we will show the possibility of selective photooxidation of ethylene, as a model reaction, using water without molecular oxygen over copper oxide supported on silica.

EXPERIMENTALS

Copper oxide supported on silica (Fuji Silicia, Cariact G-10; BET surface area, 176 $m^2\ g^{-1}$; mean pore diameter, 13.7 nm) was prepared by impregnation with an aqueous solution of $Cu(NO_3)_3$ (Wako Pure Chemical Industries). The solvent was removed by evacuation at ca. 330 K. The resulting wet solid was freeze-dried, then calcined in air for 5 h at 673 K. The sample will be designated as n wt% CuO_x/SiO_2, where n represents the content of copper ($n =$ 0.05, 0.1, 1, and 3).

The powder catalyst (150 mg) was spread on the flat bottom of a quartz reaction cell (12.5 cm^2) connected to a conventional vacuum line equipped with a Baratoron vacuum gauge. The photoreaction was carried out under a static condition. Prior to the reaction, the sample was heated in oxygen at 673 K for 1 h, then evacuated at 973 K for 1 h to 10^{-4} Pa. After introduction of ethylene (0.5 kPa, 18 μmol) and water (0.5 kPa, 18 μmol) in gas phase the catalyst was usually irradiated for 5 h with a high-pressure Hg lamp (100 W) through a water bath of which the bottom was a transparent quartz glass plate. In some experiments, the light shorter than 280 nm was cut off with a color filter (Hoya UV-28). The reactants were purified by vacuum distillation. The products were collected in a liquid nitrogen trap after the irradiation and analyzed using a gas chromatograph (Shimadzu GC-8A) equipped with a thermal conductivity detector with a helium carrier gas. Active

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0021-9517/01 $35.00

carbon (0.5 m) and Porapak Q (4 m) columns were employed in the analysis.

Profiles of X-ray absorption near-edge structure (XANES) for the samples were taken at room temperature in fluorescence mode for K-edges of Cu at beam-line BL01B1 of SPring-8. The sample was sealed with polyethylene films in nitrogen atmosphere.

RESULTS AND DISCUSSION

Ethylene was oxidized mainly to carbon dioxide (CO_2) along with a small amount of acetaldehyde (CH_3CHO) by UV light irradiation without the color filter over silica at 293 K in the presence of water (Table 1). This shows that water can function as an oxidant during UV light irradiation. Ethane (C_2H_6), C_3 and C_4 hydrocarbons, and hydrogen were also detected, but the quantification of hydrogen was impossible. No methane formation was detected.

The loading of copper oxide on silica resulted in an increase in the yield of acetaldehyde and the production of ethanol (C_2H_5OH). The conversion obtained with 0.05 wt% CuO_x/SiO_2 was similar to that of SiO_2, but the selectivity of acetaldehyde increased from 0.5 to 5.8%. The highest conversion was obtained with 0.1 wt% CuO_x/SiO_2 and the selectivity of acetaldehyde (19.6%) was relatively high. In the case of 1 wt% CuO_x/SiO_2, the conversion decreased, but the selectivity to acetaldehyde (14.2%) was still high. In the absence of water, C_4 hydrocarbons with the yield of 1.5% was mainly produced over 0.1 wt% CuO_x/SiO_2 by irradiation, and the yield of carbon dioxide by-produced was only 0.2%. This strongly suggests that water is the major oxidant in the photocatalysis.

The Cu K-edge X-ray absorption near-edge structure (XANES) of 0.1 wt% CuO_x/SiO_2 after evacuation at 973 K was rather similar to that of Cu_2O and dissimilar to that of CuO (Fig. 1). Since the concentration of copper is very low in the catalyst, almost all the copper particles are probably dispersed on the pore surface of the silica support (7). The presence of the pre-edge peak at 8984 eV is characteristic of the Cu^+ ion (8, 9). Hence, it can be assumed that Cu^+ ions are formed on 0.1 wt% CuO_x/SiO_2 during the evacuation at 973 K. No significant change in the spectrum of 0.1 wt% CuO_x/SiO_2 after irradiation of UV light in the presence of C_2H_4 and H_2O for 1 h (see Fig. 1b) showed that Cu^+ ions are not oxidized during the photooxidation.

TABLE 1

Product Distribution in the Photocatalytic Reaction of C_2H_4 and H_2O during Irradiation Using UV-Unfiltered Light for 5 h over CuO_x/SiO_2

Cu contents (wt%)	Conversion of C_2H_4 (%)	Selectivity (%)					
		C_2H_6	C_3	C_4	CO_2	CH_3CHO	C_2H_5OH
0	7.7	39.8	26.7	2.3	30.7	0.5	0
0.05	7.2	28.1	32.3	6.1	24.7	5.8	3.0
0.1	11.4	22.2	26.2	5.6	21.9	19.6	4.5
1	7.4	18.0	29.0	7.9	24.4	14.2	6.5
3	6.3	11.0	36.9	8.2	24.4	12.6	6.9

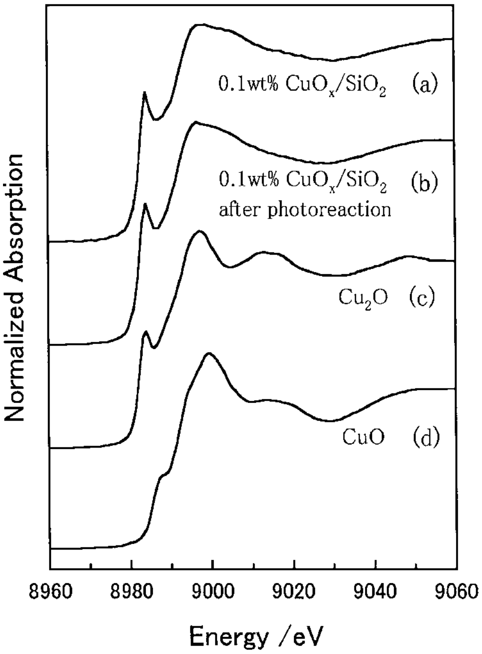

FIG. 1. XANES spectra of 0.1 wt% Cu/SiO_2 catalyst evacuated at 973 K (a) before reaction and (b) after photoreaction in the presence of ethylene and water for 1 h, (c) Cu_2O, (d) CuO.

Since the excitation band of the silica photoluminescence is around 250 nm and no excitation takes place with light longer than 280 nm (1, 10), the activity of silica was slight during the irradiation in the absence of the UV light shorter than 280 nm. However, the band gap energy of Cu_2O is ca. 2.0 eV (ca. 620 nm), the catalyst containing Cu^+ ions may work with light longer than 280 nm (11, 12). In practice the irradiation of light longer than 280 nm activated the CuO_x/SiO_2 catalysts as summarized in Table 2. Surprisingly, ethylene oxide (C_2H_4O) was produced during irradiation with light longer than 280 nm while the total conversion of ethylene decreased. No formation of C_3 hydrocarbons was observed. Since the production of hydrocarbons is drastically suppressed with the filtered light, it is supposed that the surface sites of the silica support mainly produce ethane and other hydrocarbons with the UV light shorter than 280 nm. The formation of C_3 hydrocarbons under UV light irradiation may be correlated to the formation of ethane because the cleavage of the C–C bonding in ethylene should be accompanied by the hydrogenation process. The conversions of ethylene decreased with an increase in the content of copper above 0.1 wt%, suggesting that high dispersion of copper is advantageous in the photoreaction with both the filtered and unfiltered light; the

TABLE 2

Product Distribution in the Photocatalytic Reaction of C_2H_4 and H_2O during Irradiation Using UV-Filtered Light ($\lambda > 280$ nm) over CuO_x/SiO_2

Cu contents (wt%)	Reaction temperature (K)	Conversion of C_2H_4 (%)	Selectivity/%					
			C_2H_6	C_4	CO_2	CH_3CHO	C_2H_4O	C_2H_5OH
0.05[a]	293	0.6	2.3	1.2	25.5	21.4	49.6	0
0.1[a]	293	1.1	1.0	0.4	39.6	16.4	42.6	0
1[a]	293	0.8	1.9	3.7	30.8	32.9	28.6	2.1
3[a]	293	0.4	3.9	6.3	13.3	39.5	32.9	4.1
0.05[a]	278	1.6	0.5	0.2	2.1	14.7	82.5	0
0.05[b]	278	2.5	0.4	0.4	1.8	14.7	81.7	1.0

[a] Period of photo irradiation, 5 h.
[b] Period of photo irradiation, 10 h.

interaction between copper and silica may stabilize the Cu^+ species.

When the reaction was carried out at 278 K over 0.05 wt% CuO_x/SiO_2 with light longer than 280 nm, the conversion of ethylene during a 5-h reaction was significantly higher than that at 293 K (see Table 2). It is noteworthy that the selectivity of ethylene oxide increased to more than 80% while that of carbon dioxide was only 2%. The product distribution of the reaction for 10 h was similar to that for the reaction of 5 h, while the conversion increased to 2.5%. It was also confirmed that the quantity of oxygen atoms in the products produced in the reaction for 2 days exceeded the number of copper ions in the 0.05 wt% CuO_x/SiO_2 catalyst. Thus, it is proved that the formation of ethylene oxide is a catalytic process and water is the oxidant. The color of the catalyst, which was yellowish after evacuation at 973 K, did not obviously change during the reaction. The reaction was repeatable with the spent catalyst, suggesting that carbon deposition during the reaction, if present, is small.

Although a detailed mechanism will be the subject of future work, we can emphasize that water is a possible oxidant for the selective oxidation of hydrocarbons in conjunction with copper oxide catalysts. Since the catalytic system in this study was designed as a model reaction to prove it, the reaction rate obtained was too low as an industrial standard. However, we believe that the performance can be improved by the further development of the catalyst, which probably contains a larger number of stable Cu^+ species, while justification of the reaction conditions such as reaction pressure, reaction temperature, and power of the light source is also important.

ACKNOWLEDGMENTS

The synchrotron radiation experiments were performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 1999A0030-NX-np).

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