IR Study of the Secondary Reaction of Ethylene Oxide over Silver Catalyst Supported on Mesoporous Material

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Abstract–The secondary reaction of ethylene oxide over silver catalyst supported on MCM-41 mesoporous material was investigated by the in-situ IR method. MCM-41 mesoporous material with a large content of hydroxyl group was very active in catalyzing the isomerization of ethylene oxide to acetaldehyde. The reduction of hydroxyl group by silane treatment or silver loading suppressed the isomerization of ethylene oxide. The selectivity for ethylene oxide in the partial oxidation of ethylene is enhanced by silane modification, revealing the acceleration of the consumption of ethylene oxide on the hydroxyl group.

Key words : Ethylene Oxide, Partial Oxidation, Silver Catalyst, MCM-41 Mesoporous Material, Silane Modification

INTRODUCTION

Partial oxidation of ethylene on silver catalyst is very particular in the aspects of active species and support. Silver is a unique active metal for selective partial oxidation due to its specific adsorption form of oxygen [Kilty and Sachtler, 1974; Rah et al., 1978; Yong et al., 1991], and the other thing is the use of α-alumina with very low surface area as a support. The activity of the silver catalyst is strongly dependent on the exposed silver atom, so it is reasonable to use a porous support with a large surface area in order to prepare the silver catalyst with many silver atoms capable of participating in the catalytic reaction [Lee et al., 1988]. However, the acceleration of the secondary reaction of ethylene oxide by an acidic porous support is too severe to use γ-alumina or silica as a support. The secondary reaction of ethylene oxide significantly reduces the yield of ethylene oxide, the desired product of the partial oxidation of ethylene, so α-alumina without any acid-base properties is used as a support for the silver catalyst [Yong et al., 1991; Bulushev et al., 1995].

Ethylene oxide interacts with the hydroxyl group via an oxygen atom having high electron density, forming various secondary reaction products. Three routes of the secondary reaction are proposed : (1) decomposition of ethylene oxide to ethylene and adsorbed oxygen ; (2) isomerization of ethylene oxide to acetaldehyde ; (3) formation of glycol species on the catalyst surface [Bulushev et al., 1995]. Though the preference of the reaction path is varied with the catalyst type and reaction condition, it is important to suppress the secondary reaction to achieve a high yield of ethylene oxide. Among the secondary reactions,

the isomerization of ethylene oxide on the hydroxyl group is considered the most reliable path for the consumption of ethylene oxide. Modification of the silver catalyst with sodium or cesium and an addition of water vapor were suggested to be effective for the enhancement of ethylene oxide yield by inactivation of the hydroxyl group [Mao and Vannice, 1995; Jingfa et al., 1992]. However, the catalytic role of the hydroxyl group, which is to accelerate the isomerization or the consumption of ethylene oxide, is not examined systematically.

The chemical states of hydroxyl groups are usually very complex for porous support ; i.e., hydroxyl groups such as external, internal and acidic ones are observed even on zeolite which has the best regularity among acidic porous supports. This fact suggests that it is not easy to investigate the interaction between ethylene oxide and hydroxyl group on acidic porous supports [Chen et al., 1995]. On the other hand, the evacuated mesoporous material shows a very sharp absorption band of hydroxyl group at 3,740 cm⁻¹, since mutual interactions among the hydroxyl group and structure effect on the hydroxyl group are minimized by its uniform and large pores. Therefore, mesoporous material is suitable to investigate the adsorption of ethylene oxide on the hydroxyl group by IR spectroscopy. Furthermore, the reduction of the hydroxyl group by silane treatment [Jung et al., 1997] is helpful to confirm the contribution of the hydroxyl group to the secondary reaction.

The selectivity for ethylene oxide in the partial oxidation of ethylene is considered to be influenced by the particle size of silver as well as the amount of the hydroxyl group on the support. If silver impregnated on mesoporous material is located mainly in its pore, the effect of particle size may be excluded due to its homogeneous pore size. Thus, the catalytic role of the hydroxyl group to the secondary reaction of ethylene oxide can be investigated more clearly on the mesoporous material.

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In this paper, we report the conversion of ethylene oxide on silver-loaded mesoporous material catalysts. The catalytic role of hydroxyl group in the secondary reaction of ethylene oxide is examined by *in-situ* IR spectroscopy, and the suppression of the secondary reaction by silane modification is also discussed.

EXPERIMENTAL

1. Synthesis of MCM-41 Mesoporous Material

MCM-41 mesoporous material was synthesized using hexadecyltrimethyl-ammonium chloride (HTACl ; 25 wt%, Aldrich) as a template following Ryoo's procedure [Ryoo and Kim, 1995]. Colloidal silica (Ludox HS 40, Du Pont ; 39.5 wt% SiO_2, 0.4 wt% Na_2O, 60.1 wt% H_2O) was used as a silica source. The synthesizing gel composition was 4 SiO_2: 1 HTACl : 1 Na_2O : 0.15 $(NH_4)_2O$: 350 H_2O, and crystallization was carried out at 98 °C for 1 day. After cooling to room temperature, the pH of the gel was adjusted to 11.0 by the addition of a 30 % acetic acid solution. Crystallization and pH adjustment steps were repeated twice. Washed filtrate was heated to 550 °C in a nitrogen atmosphere, and calcined in an air atmosphere of 550 °C for 4 h. Aluminium-containing MCM-41 (AlMCM-41) mesoporous material with a Si/Al ratio of 20 was also synthesized by a procedure similar to that for MCM-41 mesoporous material [Jung et al., 1997].

The X-ray diffraction patterns of the calcined mesoporous materials were in agreement with that reported previously [Kresge et al., 1992], and BET surface areas obtained from N_2 adsorption isotherms were about 1,000 $m^2 \cdot g^{-1}$.

2. Silane Treatment

MCM-41 mesoporous material, dehydrated at 300 °C for 4 h in a nitrogen flow of 10 $ml \cdot min^{-1}$, was exposed to chlorotrimethylsilane (CTMS ; Aldrich, 98 %) vapor diluted in a nitrogen flow at 50 °C for 1 h. After removing the physically adsorbed silane by pure nitrogen for 1 h, the sample was calcined at 500 °C in an air flow for 2 h (Si-MCM-41). Since the additional loading amount of silica with silane treatment on silica-form MCM-41 mesoporous material could not be determined by chemical analysis, it was estimated from the increase of silicon to aluminium ratio of AlMCM-41 mesoporous material (Si/Al=20) treated as the same procedure. The additional loading amount of silica on Si-MCM-41 by the silane treatment was estimated as 1.0 wt%.

3. Preparation of Silver Catalyst

A silver catalyst (Ag/MCM-41) supported on MCM-41 mesoporous material was prepared by impregnation with a silver nitrate solution on MCM-41. A silver nitrate-loaded MCM-41 was calcined at 250 °C for 4 h. The loading amount of silver was adjusted to 50 wt% of MCM-41 mesoporous material. This amount corresponds to filling 25 % of mesopore of MCM-41 by silver metal. This loading amount was the maximum, because the decrease in the crystallinity of mesoporous material was severe when the loading amount of silver exceeded 50 wt%. The silver catalyst (Ag/Si-MCM-41) supported on Si-MCM-41 was prepared by the same procedure as the preparation of Ag/MCM-41 catalyst.
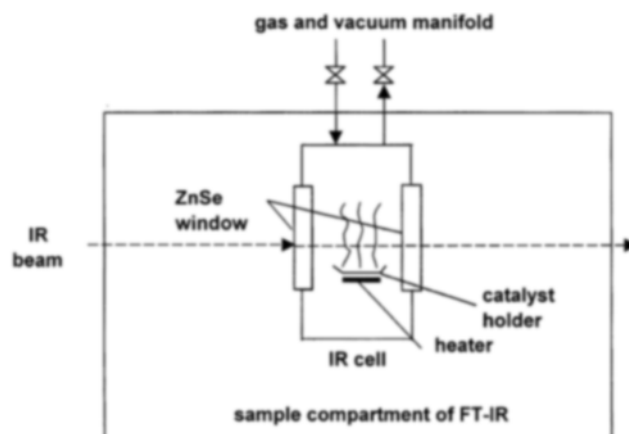

Fig. 1. Schematic diagram of *in-situ* cell for IR experiment.

4. FT-IR Investigation of Secondary Reaction of Ethylene Oxide

IR spectra were recorded on a BIORAD FT-IR spectrometer (model FTS 175C) with an *in-situ* cell made by GREASEBY SPECAC. The cell is composed of a catalyst holder, a heater, a pair of ZnSe windows and a connection port to gas and vacuum manifolds as shown in Fig. 1. The pressed sample of 10 mg was charged in the catalyst holder and evacuated at 250 °C for 1 h. Ethylene oxide of 3 kPa was admitted onto the
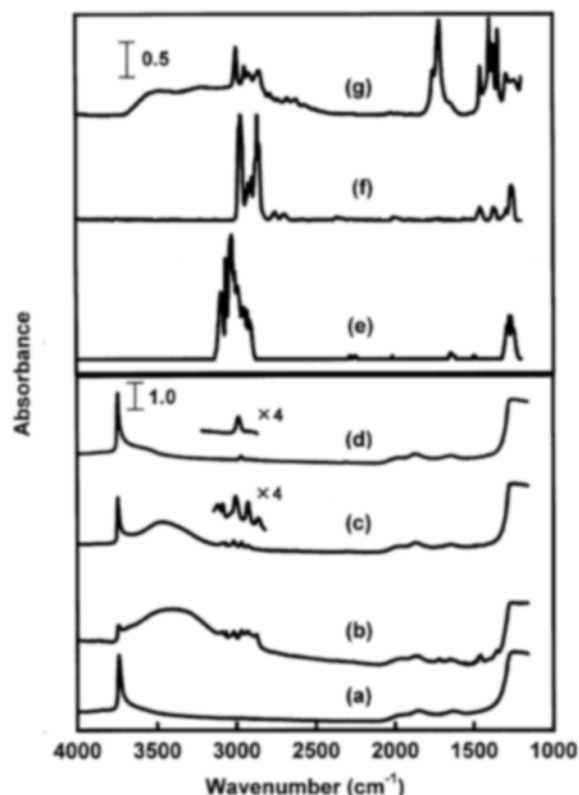

Fig. 2. IR spectra of MCM-41 evacuated and exposed to ethylene oxide.
(a) MCM-41 evacuated at 550 °C, (b) exposed to ethylene oxide of 3 kPa, (c) evacuated at 25 °C, and (d) at 350 °C. (e), (f) and (g) are gas phase IR spectra of ethylene oxide, dioxane and acetaldehyde, respectively.

catalyst at 50 °C. Upon heating to 500 °C for 18 min, the IR spectra of the gas phase were recorded at 400-4,000 cm^{-1} with 8 cm^{-1} resolution. The IR spectra of the catalyst after evacuation at 550 °C for 1 h were also recorded by a reflection device.

RESULTS AND DISCUSSION

The IR spectra of MCM-41 mesoporous material which was evacuated and exposed to ethylene oxide are shown in Fig. 2. Evacuated MCM-41 shows a sharp absorption band at 3,740 cm^{-1} (Fig. 2a). This band at zeolite is assigned to the isolated external hydroxyl group [Weglarski et al., 1996]. Therefore, a single sharp band at 3,740 cm^{-1} on mesoporous material is ascribed to the hydroxyl group located separately on its pore wall. This single band is not to differentiate between external and internal hydroxyl groups because of its large pore compared to zeolite. Since Brönsted acid sites are not formed on silica-form mesoporous material, the type of the hydroxyl group is also limited.

The 3,740 cm^{-1} band of MCM-41 disappears with exposure to ethylene oxide of 3 kPa, and a new broad band is observed at 3,200-3,600 cm^{-1} accompanied by several bands related to the C-H bond (Fig. 2b). The disappearance of the 3,740 cm^{-1} band indicates that the hydroxyl groups work as adsorption sites of ethylene oxide. The 3,740 cm^{-1} band is restored to 80 % by evacuation at 25 °C, showing that the interaction between ethylene oxide and the hydroxyl group is not strong (Fig. 2c). The chemical bond formation between ethylene oxide and the hydroxyl group may be expected, but easy desorption of ethylene oxide points out the low possibility of a chemical bond formation. Upon evacuation at 350 °C, the original spectrum of mesoporous material is restored with a trace of C-H absorption band at 2,950 cm^{-1} (Fig. 2d).

A small amount of ethylene oxide is retained on MCM-41 after evacuation at 25 °C. The IR spectra of ethylene oxide adsorbed are in accord with neither the gas phase of ethylene oxide (Fig. 2e), dioxane (Fig. 2f) and acetaldehyde (Fig. 2g), nor those of adsorbed states. If ethylene oxide is adsorbed via hydrogen bonding, the changes in wavenumber of absorption bands related to C-H bond are expected to be very small. However, the differences in the absorption bands between the ethylene oxide retained on MCM-41 (Fig. 2c) and the gas phase of ethylene oxide (Fig. 2e) strongly suggest that some changes occurred in the chemical configuration of ethylene oxide with adsorption on the hydroxyl group of MCM-41.

The amount of the hydroxyl group on MCM-41 is varied with silver impregnation or silane treatment as shown in Fig. 3. The hydroxyl group is not observed from the silane-treated samples of Si-MCM-41 (Fig. 3b) and the Ag/Si-MCM-41 (Fig. 3d). It is expected to reduce surface hydroxyl group by silane treatment. Silver loading also reduces the hydroxyl group because of surface masking, but a small amount of the hydroxyl group is retained (Fig. 3c).

The secondary reaction of ethylene oxide on the mesoporous material catalysts was investigated from the gas phase IR spectra of ethylene oxide. Formations of acetaldehyde and carbon dioxide can be easily detected because of their char-
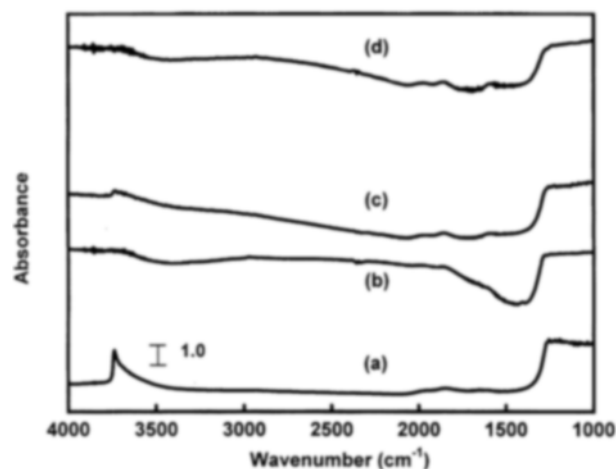

Fig. 3. IR spectra of various MCM-41 mesoporous materials evacuated at 550 °C for 1 h.
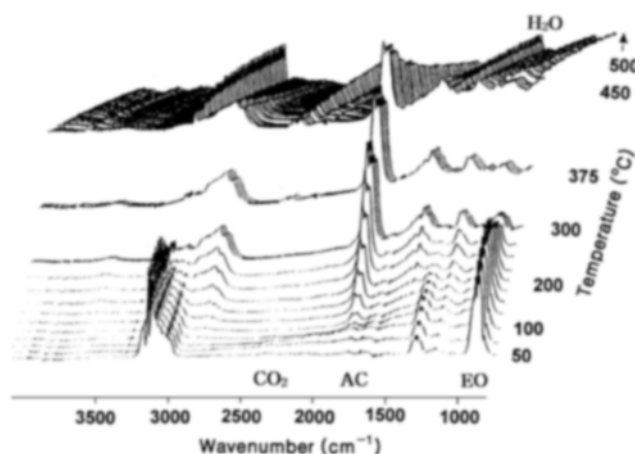(a) MCM-41, (b) Si-MCM-41, (c) Ag/MCM-41 and (d) Ag/Si-MCM-41.

Fig. 4. Secondary reaction of ethylene oxide over MCM-41 catalyst in absence of oxygen traced by IR spectra.

acteristic absorption bands. Fig. 4 shows the gas phase IR spectra recorded on the cell containing ethylene oxide of 3 kPa on the MCM-41 catalyst. These spectra were recorded in 1 min intervals in order to trace the chemical reaction of ethylene oxide. The temperature of the catalyst holder increased from 50 °C to 500 °C with a ramp of 25 °C·min^{-1}, and then remained constant at 500 °C for 40 min. The change in the composition of the gas phase deduced from IR spectra cannot be used as kinetic data directly, because the effect of mass transfer on the reaction rate in the cell is not eliminated. But the composition profiles of the gas phase represent the reaction path on the catalyst, and give a qualitative activity comparison for the given catalysts.

The IR spectra of the gas phase contacting with MCM-41, recorded at 50 °C, are identical to that of ethylene oxide, indicating no reaction proceeding at this temperature. When the catalyst temperature reaches 125 °C, new bands at 2,716, 1,747, 1,395 and 1,200 cm^{-1} are observed. The positions of these bands are in good accord with those of acetaldehyde (Fig. 2g), and are
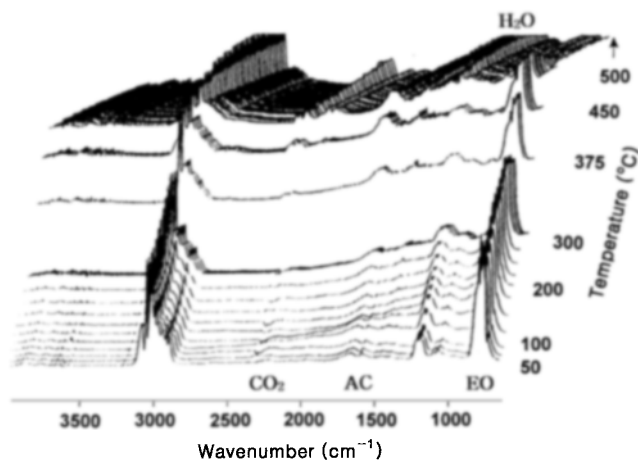
Fig. 5. Secondary reaction of ethylene oxide over Si-MCM-41 catalyst in absence of oxygen traced by IR spectra.

Fig. 6. Variation of gas composition in the secondary reaction of ethylene oxide over various MCM-41 catalysts in absence of oxygen.

accompanied by a decrease in the bands of ethylene oxide. The acetaldehyde bands increase with increasing temperature. When the catalyst is heated to 400 °C, absorption bands of carbon dioxide and water are observed. Upon heating to 500 °C and remaining constant at this temperature, acetaldehyde converts to carbon dioxide and water. These sequential spectra show consecutive chemical reactions on the MCM-41 catalyst from ethylene oxide to carbon dioxide and water via acetaldehyde, while some of the carbon is deposited as coke on the catalyst.

Si-MCM-41, whose hydroxyl group was diminished by the silane treatment, shows different catalytic behavior in the secondary reaction of ethylene oxide compared to the MCM-41 catalyst (Fig. 5). Absorption bands of acetaldehyde appeared when temperature reached above 400 °C. This temperature is much higher compared to that on the MCM-41 catalyst. Formations of carbon dioxide and water are observed above 500 °C.

The composition change with temperature in the cell can be calculated from the sequential IR spectra by integration of the characteristic band area of each component with a sensitivity compensation. Fig. 6 shows the secondary reaction of ethylene oxide over various MCM-41 catalysts. Water and carbon dioxide are formed as deep oxidation products, but the concentration of water is not shown in Fig. 6, because it is not possible to measure quantitatively due to condensation on the glass part of the IR cell.

The formation temperature of acetaldehyde varied with the catalyst used. Acetaldehyde is formed at 125 °C on the MCM-41 catalyst, but at 400 °C on the Si-MCM-41 catalyst. Silane modification considerably suppresses the isomerization of ethylene oxide to acetaldehyde. The temperature for acetaldehyde formation also shifts upward to 275 °C on the Ag/MCM-41 catalyst. Silane treatment and silver loading reduce the hydroxyl group as shown in Fig. 3, so the onset temperature for the isomerization shifts to a higher temperature due to the loss of an active site.

On the other hand, onset temperatures for carbon dioxide formation are almost the same as 400 °C on the MCM-41, Ag/MCM-41 and Ag/Si-MCM-41 catalysts. Since oxygen is not
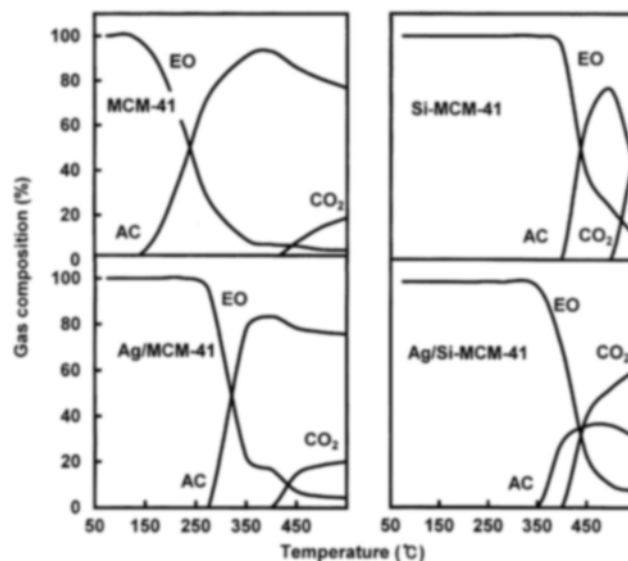
supplied in this study, this finding indicates that the decomposition of ethylene oxide or acetaldehyde takes place at 400 °C over these catalysts with the hydroxyl group and/or silver particle. On the Si-MCM-41 catalyst, however, carbon dioxide is formed at 500 °C, which is considerably higher compared to other catalysts. Since the Si-MCM-41 catalyst has neither a silver particle nor a hydroxyl group, the decomposition of ethylene oxide or acetaldehyde starts at a very high temperature. These findings indicate that the silver particle and the hydroxyl group also catalyze the decomposition of ethylene oxide or acetaldehyde.

Suppression of the secondary reactions of ethylene oxide to acetaldehyde and carbon dioxide must be required in order to achieve the high yield of ethylene oxide in the partial oxidation of ethylene. Actually, we reported that only silver loading mesoporous material showed very low selectivity for ethylene oxide [Jung et al., submitted]. But the selectivity for ethylene oxide was significantly increased by silane modification, because of the considerable reduction of the hydroxyl group. Therefore, a silane-treated silver catalyst supported on mesoporous material whose hydroxyl group is largely reduced, is sufficient as the catalyst for the partial oxidation of ethylene, if the dispersion of silver is proper to achieve a comparable conversion to a silver catalyst supported on α-alumina.

CONCLUSIONS

We conclude as follows : Ethylene oxide interacts strongly with the hydroxyl group of MCM-41 mesoporous material. The hydroxyl group catalyzes the isomerization of ethylene oxide to acetaldehyde, thus accelerating consumption of ethylene oxide. The in-situ IR studies on the secondary reactions of ethylene oxide show that the isomerization of ethylene oxide to acetaldehyde over Ag/Si-MCM-41 mesoporous material is suppressed due to reduction of the hydroxyl group by

silane treatment.

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