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Adsorption of Ethylene Oxide on Cab-O-Sil Silica, Reactive Silica, and Oxygen-treated Reactive Silica

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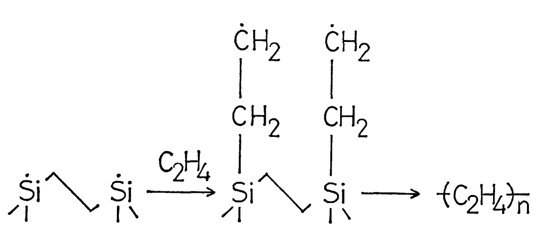
Ethylene oxide reacted with surface Si–OH of Cab–O–Sil silica to form Si–O–CH_2–CH_2–OH, while ethylene oxide was adsorbed on the silicon radicals of the reactive silica, and the oxygen radicals of the oxygen-treated reactive silica on which the adsorbed species polymerized to form $(-CH_2-O-CH_2-)_n$.

It is well known that ethylene oxide radicals are formed by pyrolysis[1] and photolysis,[2–4] and that these radicals can be easily polymerized without catalyst. The polymerization reaction of ethylene oxide occurs on various oxides, hydroxides and metal carbonates.[5–7] Furukawa *et al.*[5] have carried out a large number of experiments using solid catalysts. Ethylene oxide is easily polymerized under the influence of water and other substances containing labile hydrogen atoms such as amines and alcohols. The hydroxyl group appears to be the active centers in the polymerization reaction of ethylene oxide.[8] This polymerization occurs as an ionic type reaction.[9] On the other hand, a non-acid solid, for instance, silica gel with 5.6% of water bound on the surface is inactive in this polymerization.[9]

The polymerization product of ethylene oxide was studied by X-ray diffraction technique[10,11] and infrared spectroscopy,[12,13] and was confirmed to be a polyethylene glycol. In the presence of a strong acid or base catalyst the successive addition of ethylene oxide molecules yielded a polyethylene glycol. Aldehyde was presumably formed through oxyethylene biradicals.[14]

Reactive silica (RS) shows high reactivity in chemisorbing a variety of gases,[15–19] and it has been shown that acetylene, ethylene, several alkenes,[20,21] and ethylene oxide[22] are polymerized on its surface. Surface structure unlike those found on ordinary silica is formed. The high activity is thought to arise from the presence of unusual reaction center on the silica surface, *i.e.*, a pair of silicon radicals,[23] shown schematically in the following structure (I). Acetylene, ethylene, and several alkenes are adsorbed on silicon radicals of RS, and acetylene, ethylene and alkene radicals are formed as shown in structure (II). These radicals are easily polymerized[19–21] and these polymerization should be a radical type reaction.



(I) (II)

Polymerization of ethylene oxide on RS can be expected to be a radical type reaction. Therefore, the present author studied the adsorption of ethylene oxide on Cab–O–Sil silica, RS and oxygen-treated reactive silica(ORS), and tried to find the difference in the reaction mechanisms on these silicas and the mechanism of the polymerization reaction.

Experimental

RS was prepared from Cab–O–Sil silica (obtained from G. Carbot Co., Boston, Mass.). It was methoxylated by using methoxy-containing compounds,[18] of which trimethoxymethane (trimethyl orthoformate, TMM) was the most efficient.[19] The methoxylated samples were pyrolyzed and then degassed at high temperature.[16,17] ORS was obtained from RS by exposing it to dry oxygen.[17] The samples were treated in the cell described elsewhere[17] and the conventional high vacuum technique was employed. Infrared spectra were recorded on Perkin Elmer Models 421 and 621 spectrometers.

Ethylene oxide (Eastman Kodak "pure grade") was degassed at liquid nitrogen temperature and distilled several times prior to the use.

Results

Cab–O–Sil Silica. Ethylene oxide was added to Cab–O–Sil silica, which was treated in about 100 Torr of wet oxygen at 650 °C for 1 h and was degassed at 700 °C for 1 h. When the silica was exposed to ethylene oxide, infrared absorption bands appeared immediately at 3350, 3085, 3066, 3007, 2970, 2929, 2870, 2720, 1736, 1468, and 1455 cm^{-1}, in addition to the band at 3747 cm^{-1} due to OH stretching vibration attached to surface Si atoms (Si–OH)[15–17] as shown in Fig. 1(A). Figure 2 shows the changes in intensities of the bands at 3747, 3350, and 2929 cm^{-1} when ethylene oxide was added to the silica. The band intensity was determined after 20 min. The intensity of the 3747 cm^{-1} band decreased with the increase of pressure of ethylene oxide. On the other hand, the intensities of the bands at 3350 and 2929 cm^{-1} increased with the increase of the pressure. This result shows that these three bands strongly correlate with each other. Namely, this means that the surface OH of Cab–O–Sil silica was reacted with added ethylene oxide and that a new adsorbed species showing the bands at 3350 and 2929 cm^{-1} was formed.

The sample adsorbed with ethylene oxide was degassed for 5 min at room temperature and at 105 °C. The bands at 3085, 3066, 3007, 2970, 2720, and 1736 cm^{-1} disappeared completely by degassing, but the bands at 3747, 3350, 2955, 2925, 2878, 1468, and 1451 cm^{-1} were maintained as shown in Figs. 1(B) and (C), and they still remained at 400 °C (Fig.

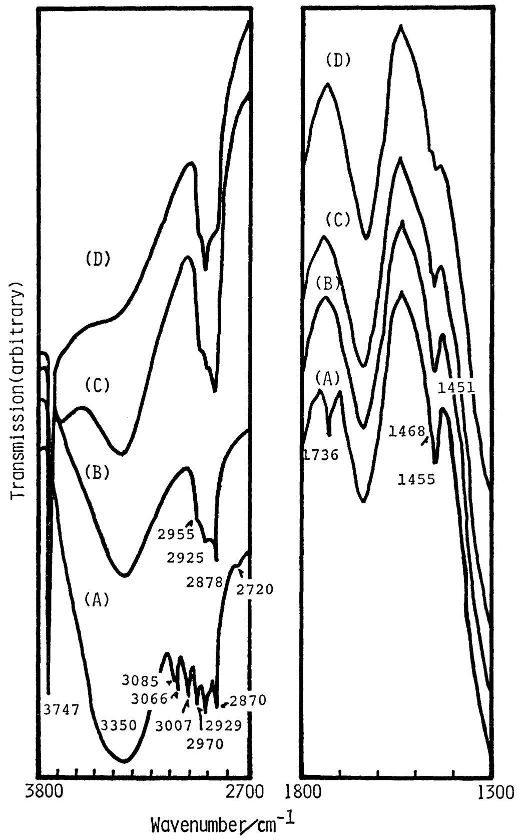


Fig. 1. IR spectra of ethylene oxide adsorbed on Cab–O-Sil silica.
A: 95 Torr† ethylene oxide at room temperature for 15 h, B: degassed at room temperature for 5 min, C: degassed at 105 °C for 5 min, D: degassed at 400 °C for 5 min.

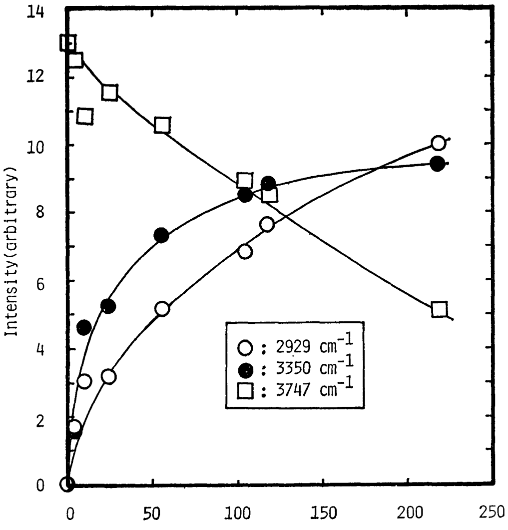


Fig. 2. Changes in intensities of the bands at 3747 (□), 3350(●), and 2929(○) cm^{-1} with pressure of ethylene oxide.

1(D)). The bands at 2720 and 1736 cm^{-1} are characteristic frequencies of aldehyde,24) which is weakly adsorbed. The bands at 3085, 3066, 3007, and 2970 cm^{-1} are identified with typical bands of gaseous ethylene oxide reported by Potts,25) which are CH_2 stretching vibration. The fact that the bands at 3085, 3066, 3007, and 2970 cm^{-1} disappeared easily by degassing at room temperature means that ethylene oxide kept its ring structure and was weakly adsorbed on Cab–O–Sil silica.

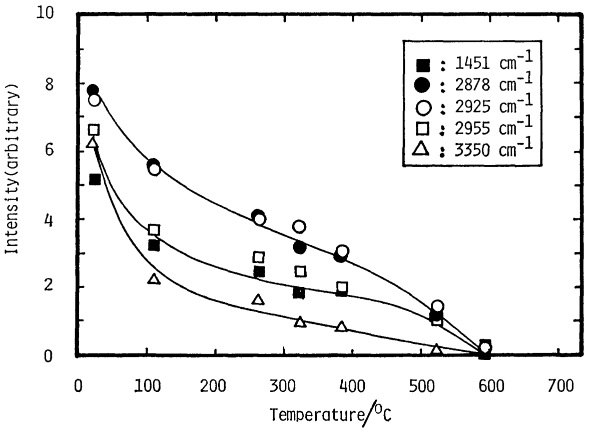


Fig. 3. Changes in intensities of the bands at 3350 (△), 2955(□), 2925(○), 2878(●), and 1451(■) cm^{-1} with evacuation temperature.

Figure 3 shows the change in band intensities by degassing at different temperatures. The band intensities at 3350, 2955, 2925, 2878, and 1451 cm^{-1} gradually decreased with elevation of degassing temperature. From Figs. 2 and 3, it is clear that the band at 3747 cm^{-1} correlates strongly with the bands at 3350, 2955, 2925, 2878, and 1451 cm^{-1}. Considering these results two types of adsorbed ethylene oxide are presumed, that is, one is the weakly adsorbed ethylene oxide molecules which keep a ring structure, and the other, the new adsorbed species reacts with surface OH which shows the band at 3350, 2955, 2925, 2878, and 1451 cm^{-1}.

RS (Reactive Silica). Sixty five Torr of ethylene oxide was added to RS. Figure 4(A) shows an infrared spectrum of ethylene oxide introduced on RS, which shows the bands at 3092, 3063, 3025, 3007, 2960, 2931, 2917, 2865, and 1450 cm^{-1}. Among these, the intensities of the bands at 3092, 3063, 3025, 3007, and 2917 cm^{-1} decreased as the time went on, on the other hand, the intensities of the bands at 2960, 2931, 2865, and 1450 cm^{-1} increased. Figure 5 shows the changes in intensities of the bands at 3063, 3007, 2931, 2865, and 1450 cm^{-1} by the same procedure. It is clear that the intensities of the bands at 2931, 2865, and 1450 cm^{-1} increased with the decrease of the band intensities at 3063 and 3007 cm^{-1}. The bands at 3063 and 3007 cm^{-1} are typical of ethylene oxide molecules.25) Namely, Fig. 5 shows that the weakly adsorbed ethylene oxide molecules were converted into the new adsorbed species on RS.

The sample exposed to ethylene oxide vapor was degassed at room temperature for 5 min. The bands due to ethylene oxide disappeared completely, the bands at 2960, 2876, and 1455 cm^{-1} were maintained and a new band at 1465 cm^{-1} appeared as shown in Fig. 4(B). No further change was observed by degassing at room temperature for 1 h. The band at 2876

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† 1 Torr≈133.322 Pa.

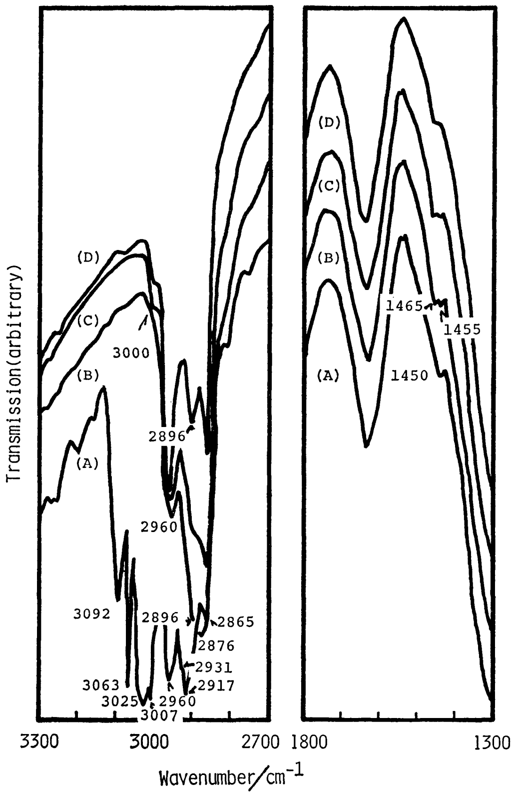


Fig. 4. IR spectra of ethylene oxide adsorbed on RS. A: 65 Torr ethylene oxide at room temperature, B: degassed at room temperature for 5 min, C: degassed at 200 °C for 5 min, D: degassed at 440 °C for 5 min.

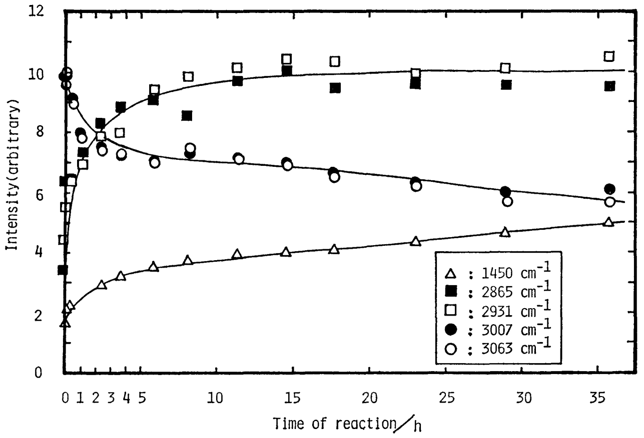


Fig. 5. Changes in intensities of the bands at 3063(○), 3007(●), 2931(□), 2865(■), and 1450(△) cm^{-1} with the time of reaction.

cm^{-1} split into two bands (2896 and 2865 cm^{-1}), and a new small band appeared at 3000 cm^{-1} by degassing at 200 °C and at higher temperatures even though the band intensities were changed as shown in Figs. 4(C) and (D).

As in the case of adsorption of ethylene oxide on Cab-O-Sil silica, the bands at 3092, 3063, 3025, 3007, and 2917 cm^{-1} disappeared easily and completely by degassing at room temperature. These bands due to gaseous ethylene oxide molecules having a ring structure as reported by Potts,[25] and by Lord and Nolin.[26]

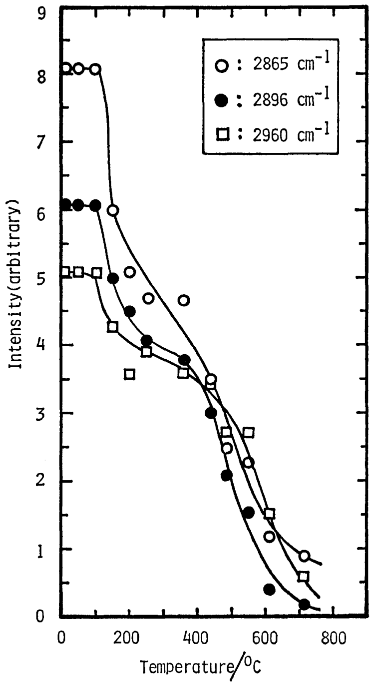


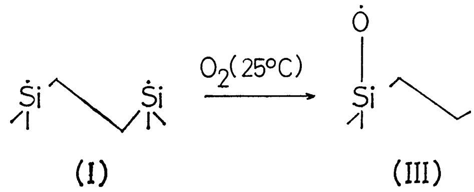
Fig. 6. Changes in intensities of the bands at 2960(□), 2896(●), and 2865(○) cm^{-1} with evacuation temperature.

This means that ethylene oxide is weakly adsorbed on RS.

Figure 5 shows the changes in intensities of the bands at 3063, 3007, 2931, 2865, and 1450 cm^{-1}. The intensities of the 3063 and 3007 cm^{-1} bands due to ethylene oxide molecules decreased at room temperature with the time of reaction. On the contrary, the intensities of the bands at 2931, 2865, and 1450 cm^{-1} increased. This result suggests that the weakly adsorbed ethylene oxide is converted into another new type of adsorbed species. While the intensities of both bands at 2931 and 2865 cm^{-1} increased similarly, but, as shown in Fig. 4, the band at 2931 cm^{-1} disappeared by degassing at room temperature, and the band at 2865 cm^{-1} was maintained even by degassing at 720 °C. Considering these results, there exist two different species showing the 2931 cm^{-1} band and the 2865 cm^{-1} band.

Figure 6 shows the changes in intensities of the bands (2960, 2896, and 2865 cm^{-1}) with evacuation temperature. No change was observed under 150 °C, but the intensities of three bands decreased above 150 °C. These bands were kept even at 720 °C. From Figs. 5 and 6, it is assumed that there are two kinds of adsorbed species on RS. One is the weakly adsorbed species, and the other, the strongly adsorbed one. Therefore, it is reasonable to consider that the weakly adsorbed species having the band at 2931 cm^{-1} was converted into another strongly adsorbed species having the bands at 2960, 2896, and 2865 cm^{-1}. Namely, the species having the band at 2931 cm^{-1} is assumed to be an intermediate on RS.

ORS (Oxygen-treated Reactive Silica). RS chemisorbs O_2 at room temperature, the reaction being complete within a few second. Oxygen-chemisorbed



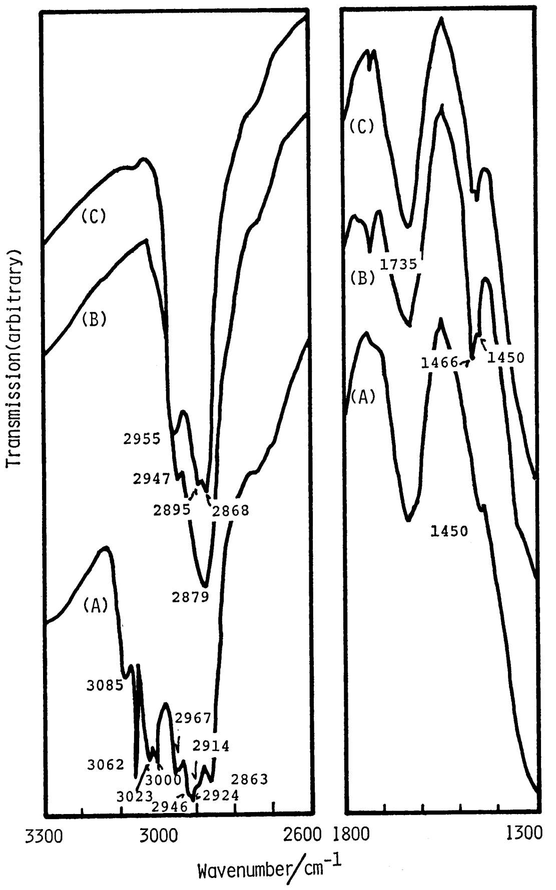


Fig. 7. IR spectra of ethylene oxide adsorbed on ORS. A: 71 Torr ethylene oxide at room temperature for 17 h, B: degassed at room temperature for 5 min, C: degassed at 460 °C for 5 min.

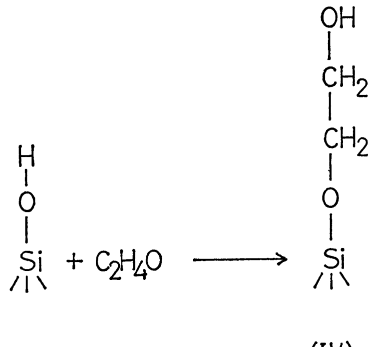
RS has a pair of oxygen radicals in structure (III).[17] It shows high activity and reacts with various gases as in the case of RS.[17]

Figure 7(A) shows the spectrum of ethylene oxide added to ORS at room temperature. The bands at 3085, 3062, 3023, 3000, 2967, 2924, 2914, 2863, 1735, and 1450 cm^{-1} were observed. Among these the bands at 3085, 3023, 3000, 2967, 2924, and 2914 cm^{-1} disappeared by degassing at room temperature, but the band intensity at 1735 cm^{-1} increased. The band at 1450 cm^{-1} split into two bands (1466 and 1456 cm^{-1}). By degassing at 460 °C, the band at 2947 cm^{-1} shifted to 2955 cm^{-1} and the band at 2879 cm^{-1} split into two bands (2895 and 2868 cm^{-1}) as shown in Fig. 7(C). These bands are similar to those in the case of RS except the one at 1735 cm^{-1}.

Discussion

Cab-O-Sil Silica. It is well known that the band at 3747 cm^{-1} is due to the surface OH(Si–OH).[15–17] The intensity of the 3747 cm^{-1} band decreased with the increase of those of the 3350 and 2929 cm^{-1} bands which were kept even by degassing at 600 °C as shown in Fig. 3. As mentioned above, this means that ethylene oxide reacts with surface OH. If the adsorbed species interacts with surface OH, the band due to OH shifts to lower frequencies by hydrogen bonding. In that case ethylene oxide should be adsorbed on the different site from surface OH, and this species was adsorbed weakly on Cab–O–Sil silica. This adsorbed species should be removed easily by degassing at room temperature. In the case of OH bonded to hydrocarbon such as alcohol (R–OH), the OH stretching vibration shifts to lower frequencies by hydrogen bonding and appears at near 3300 cm^{-1}.[8,27,28] The band at 3350 cm^{-1} just falls in this range and this may result from OH attached to the end of hydrocarbon. Therefore, it should be concluded that ethylene oxide reacted with the surface OH of Cab–O–Sil silica to form the new adsorbed species having the end OH group.

Considering that the ethylene oxide ring opens at C–O and fragment –CH$_2$–CH$_2$–O– reacts with surface ≡Si–OH, the reaction product should have structure (IV). This is what is called an ionic type reaction.



(IV)

Structure(IV) is very similar to ethylene glycol except for the fact that one of the end OH groups is replaced with Si atom. Kanbayashi and Nukada[29] reported that the bands due to ethylene glycol appeared at 2947, 2924, 2881, and 1462 cm^{-1}. The bands at 2955, 2925, 2878, and 1451 cm^{-1} observed in this work (Fig. 1(B)) show little shift from those of ethylene glycol. These differences result from strong adsorption on Si atom of Cab–O–Sil silica like structure(IV). Indeed, Fig. 3 proved the presence of the strong adsorption species.

The results and reasons mentioned above lead to the following conclusions; (i) Ethylene oxide is weakly adsorbed on Cab–O–Sil silica, forming a ring structure. That is, this is physical adsorption; (ii) Small amount of aldehyde is formed; (iii) Ethylene oxide reacts with the surface OH to form the adsorption species of structure (IV) which is similar to ethylene glycol. This is an ionic type reaction.

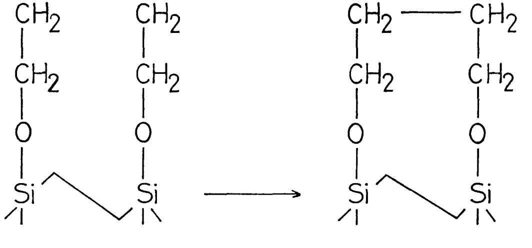
RS and ORS. As shown in Fig. 4, the bands at 3063 and 3007 cm^{-1} disappeared completely by degassing at room temperature, and at the same time the band at 2931 cm^{-1} also disappeared completely. The bands at 3063 and 3007 cm^{-1} are characteristic bands due to ethylene oxide having a ring structure, but the band at 2931 cm^{-1} is not. That is, the weakly adsorbed ethylene oxide molecule on RS is converted into the species having the band at 2931 cm^{-1}. On the other hand, the intensity of the band at 2931 cm^{-1} increases with the increase of the band intensities at 2865 and 1450 cm^{-1}, but the weakly adsorbed species having the band at 2931 cm^{-1} differs markedly from those having the bands at 2865 and 1450 cm^{-1} and also differs from the one resulted on Cab–O–Sil silica. Therefore, the author may safely predict that the species having the band at 2931 cm^{-1} is an intermediate of the reaction.

According to Markova,[30] adsorption species of ethylene oxide on $Mg(OH)_2$ showed three bands at 3055, 2925, and 2880 cm^{-1}. By degassing at room temperature the band at 3055 cm^{-1} disappeared completely and the band at 2925 cm^{-1} gradually disappeared by degassing at 180—200 °C. Only the band at 2880 cm^{-1} was kept. He proposed that the band at 3055 cm^{-1} was due to the characteristic of gaseous ethylene oxide which was physically adsorbed, and the bands at 2925 and 2880 cm^{-1} were due to valence vibration of CH_2 groups of the polymer molecule. Especially, he reported that the band at 2925 cm^{-1} was due to the band of the intermediate between ethylene oxide monomer and polymer.

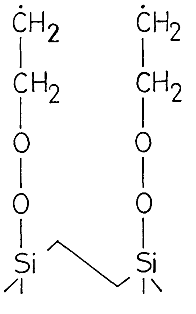
The intensities of the bands at 2931 and 2865 cm^{-1} increased as shown in Fig. 5. The band at 2865 cm^{-1} was kept by degassing at room temperature and even at higher temperatures as shown in Fig. 6, while the band at 2931 cm^{-1} disappeared by degassing at room temperature. It is clear that the species having the band at 2865 cm^{-1} was formed when the species having the band at 2931 cm^{-1} existed. Namely, the species having the band at 2931 cm^{-1} plays an important role in inducing the species having the band at 2865 cm^{-1}. In addition to the results by Markova,[30] this result leads to the conclusion that the species having the 2931 cm^{-1} band is the intermediate. This result was recognized in the case of ORS.

As shown in Fig. 6, the intensities of the bands at 2960, 2896, and 2865 cm^{-1} were kept by degassing under 200 °C, but those decreased above 200 °C. On the other hand, a new band appeared at 3000 cm^{-1} and the shoulder at 2896 cm^{-1} appeared clearly. Namely, as shown in Figs. 4(C) and (D), three strong bands at 2960, 2896, and 2865 cm^{-1} appeared clearly. The intensities of these bands decreased similarly by degassing above 200 °C, and these bands were kept even by degassing at 720 °C. This result means that the species was strongly adsorbed on RS. In the case of ethylene oxide adsorption on ORS, the band appeared at 1735 cm^{-1} by degassing at room temperature and was kept at higher temperatures as shown in Fig. 7. But the other bands behaved similarly as those of RS except the band at 3000 cm^{-1}.

Ethylene oxide ring opens in two ways as $-CH_2-CH_2-O-$(V) and $-CH_2-O-CH_2-$(VI). Usually, ethylene oxide reacts with hydrogen atoms such as alcohols, amines, hydroxyl groups and strong acids by cleavage at the C–O linkage and forms $-CH_2-CH_2-OH$ structure (V'). That is, this proceeds as an ionic type reaction. Indeed, as described above, in the case of Cab–O–Sil silica, ethylene oxide reacts with surface OH and forms $Si-O-CH_2-CH_2-OH$. RS and ORS have no hydrogen or hydroxyl group, but they have silicon radicals(I) and oxygen radicals(III). Therefore, it is easy to predict that reaction of ethylene oxide on RS and ORS differs from that on Cab–O–Sil silica. Low reported[16,17] that silicon radicals of RS and oxygen radicals of ORS reacted with various gases in the same way. Especially, radicals were formed on RS and ORS such as ethylene radicals (structure (II)) and these radicals were polymerized on them. Low also reported[21] that ethylene reacted with oxygen radicals of ORS to form species (VII) and then species (VIII). If species (V) reacted with silicon radicals(I), species (VII) should be formed and then species (VIII). But there was no evidence, *i.e.*, there was no band for which Low[21] assigned species (VII) and species (VIII). On the other hand, if species (V) reacted with oxygen radicals of ORS, a peroxide having structure (IX) should be formed. If peroxide (IX) was formed, the band due to CH vibration was expected to shift to lower frequencies than that of ethoxide by effect of oxygen atom, but there was no evidence of the shift as shown in Fig. 7. Namely, the bands due to vibration of CH_2 group show no difference between the cases of RS and ORS. Therefore, there is little probability that species (IX) exists.



(VII) (VIII)



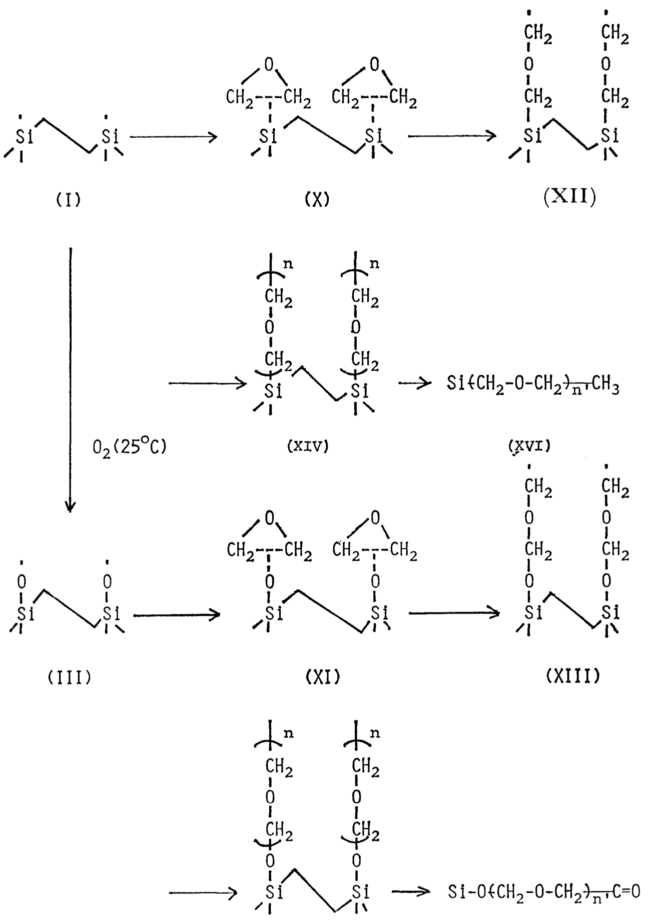
(IX)

Generally, CH stretching vibration in CH_2 groups appears at 2940—2915 and 2870—2845 cm^{-1}.[24,31–34]

But the bands due to CH_2 in ether as the structure of R–O–CH_2– shift to higher frequencies at 2955—2922 and 2878—2835 cm^{-1}.[31,34] According to Miyazawa *et al.*[13] polyethylene glycol has the –CH_2–O–CH_2– repeating unit and shows the bands at 2950, 2890, 1470, and 1453 cm^{-1}. Naccache *et al.*[9] reported that the polymer of ethylene oxide showed the bands at 2943, 2887, 1467, and 1455 cm^{-1}. The bands observed in the present work (Fig. 4(B): 2960, 2876, 1465, and 1455 cm^{-1}, and Fig. 7(B): 2947, 2879, 1466, and 1456 cm^{-1}) are very similar to those by Miyazawa *et al.*[13] and Naccache *et al.*[9] The structure of –CH_2–O–CH_2– is, therefore, expected.

The band at 2876(ORS;2879) cm^{-1} splits into two bands at 2896(ORS;2895) and 2865(ORS;2865) cm^{-1} by degassing at high temperature and these band intensities decreased similarly as shown in Fig. 6. From the result mentioned above, it is speculated that polymerization of ethylene oxide proceeds at high temperature. At the same time, a new band appeared at 3000 cm^{-1} on RS and 1735 cm^{-1} on ORS. The former predicts the existence of CH_3 group, and the latter C=O group. These groups should be formed by depolymerization at higher temperature.

Considering the above results, it is concluded as follows; (i) Ethylene oxide is weakly adsorbed on RS and ORS, forming a ring structure. This is physical adsorption; (ii) The intermediate is formed on silicon and oxygen radicals as species (X) and (XI), which are adsorbed weakly; (iii) Species (X) and (XI) open its ring at C–C bond as a radical type reaction to form species (XII) and (XIII), and, then, they are polymerized as species (XIV) and (XV), (iv) One of species (XIV) and/or (XV) depolymerizes at higher temperatures to form species (XVI) and/or (XVII).



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