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Selective Dehydrogenation of Ethanol to Acetaldehyde over Silicalite-1

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Silicalite-1 catalyzes ethanol dehydrogenation to acetaldehyde. On the basis of the IR spectra of ethanol adsorbed on its surface, the active sites are believed to be the active oxygen bridges on which dissociative adsorption of ethanol can take place. The active sites are stable compared with the active oxygen bridges on highly dehydrated silica, which also catalyze the selective ethanol dehydrogenation. Since there were trace amounts of acid site on the silicalite-1, simultaneous ethanol dehydration was observed. However, almost all the acid sites disappeared by heating at 1070 K in the case of silicalite-1 containing 0.7 wt% of sodium ions, and ethanol was selectively converted to acetaldehyde. In this treatment, the sodium ions partly poison the active sites for dehydrogenation, but their activity is restored by leaching excess sodium ions from the silicalite-1 under reflux in water.

INTRODUCTION

The catalysts containing transition-metal elements are active for ethanol dehydrogenation to acetaldehyde. In particular, copper–chromium oxides are known to catalyze the reaction very well, but in the high conversion range considerable amounts of ethyl acetate are produced by the reaction of formed acetaldehyde with ethanol over those catalysts. Since the active sites for the ethyl acetate formation are supposed to be the same sites for ethanol dehydrogenation, inhibition of the ethyl acetate formation is difficult. Hence, compounds that do not include transition-metal elements are preferable as catalysts for selective ethanol dehydrogenation to acetaldehyde. Alcohol dehydrogenation proceeds over acid–base catalysts which do not contain transition-metal elements, but dehydration of alcohol proceeds simultaneously (*1–5*). We recently found that a highly dehydrated silica catalyzes ethanol dehydrogenation and that the active sites are the oxygen bridges newly generated by condensation of hydroxyl groups on the silica surface at temperatures above ca. 1000 K (*6, 7*). Over these active oxygen bridges ethanol is selectively converted to acetaldehyde. However, these oxygen bridges are easily deactivated in the presence of water because they are converted to stable silanol groups (*7*). Silicalite-1, which is an extremely aluminum-deficient ZSM-5-type zeolite (*8*), is regarded as a silica having the structure of ZSM-5 (*9*). Since there are internal silanol groups in silicalite-1 (*10*), it is possible that new oxygen bridges are generated by condensation of these silanol groups. If the oxygen bridges can catalyze ethanol dehydrogenation, the lifetime of the bridges would be longer than that for silica preheated at high temperatures because the oxygen bridges would be stable in the crystalline structure of silicalite-1 compared with those in silica. Thus, we tried ethanol conversion over silicalite-1 and found the catalytic activity of silicalite-1 for the dehydrogenation. The lifetime of silicalite-1 was longer than that of highly dehydrated silica; however, ethanol dehydration to ethylene was also observed because there are trace amounts of acid sites in the silicalite-1 used.

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To obtain higher selectivity to acetaldehyde, we carried out sodium modification of silicalite-1 and also investigated the activity of the sodium-modified silicalite-1.

EXPERIMENTAL

Materials

Silicalite-1 was synthesized by the patented method (*11*). The main starting materials of silicalite-1 (SL) were tetraethyl orthosilicate (purified by distillation) and tetra-*n*-propylammonium hydroxide (TPAOH). After hydrothermal reaction at 440 K for 3 days in a Teflon tube inserted in a stainless-steel autoclave, the precipitate was heated in air at 770 K to remove organic components. A sodium-modified silicalite sample (Na-SL) was prepared by addition of sodium nitrate to the starting material of the synthesis. The preparation conditions were the same as those of SL except for the presence of sodium nitrate. Sodium content of Na-SL was analyzed to be 0.7 wt% by an atomic absorption method. The Si/Al ratio of these samples was found to be ca. 4000 by chelatometric titration. Some of the sodium ions can be leached out by refluxing in water (*12*). The extent of leaching depends on the calcination temperature of Na-SL. A leaching process (three times reflux in water for 2 h each) was applied to three samples calcined in air for 0.5 h at 770, 1070, and 1270 K. The obtained samples will be referred to as LL-SL, L-SL, and LH-SL and the sodium contents were found to be 0.1, 0.4, and 0.6 wt%, respectively.

The pure silica sample used here was the same as that used in Refs. 6 and 7.

Ethanol Conversion

Ethanol conversion was carried out in a fixed-bed continuous flow reactor at 670 K under atmospheric pressure. A catalyst (0.100 g) was sandwiched with quartz wool (ca 0.01 g) in a quartz reaction tube of 6-mm inner diameter. Ethanol was fed in a stream of helium gas (flow rate, 1.8 liter h^{-1}; ethanol fed, 1.3 mmol h^{-1}). The catalyst bed was preheated at 770–1270 K for 0.5 h in a flow of helium gas and then the reaction gas was fed. The reaction products were analyzed on-line by gas chromatography (separation column: Porapak Q, 1 m). Since quartz wool (packing material) discernibly contributes to the reaction, the results of the reaction have been corrected for the contribution of quartz wool.

Infrared Spectroscopy

IR spectra were recorded with a Nicolet 5DX FTIR spectrometer. The samples (0.01 g) were pressed into self-supporting wafers and placed into an *in situ* IR cell allowing heating under vacuum. After the wafers were heated *in vacuo* for 0.5 h, ethanol vapor (ca. 10 Torr) was contacted with these wafers at 420 K for 0.5 h and evacuated at the same temperature. Then, IR spectra of adsorbed ethanol were recorded at room temperature.

Adsorption of Ethanol

Adsorption of ethanol on the samples was measured by gravimetry using a Cahn 2000 microbalance. Before the measurement, the samples (ca. 0.03 g) were heated *in vacuo* at 770–1270 K for 0.5 h.

X-Ray Diffraction

XRD patterns of the samples were recorded with a Rigaku Denki Corp. Geigerflex. The samples were first heated *in vacuo* at 770–1270 K for 0.5 h, and then were contacted with air. They were mounted on sample boards as quickly as possible and the measurements were carried out immediately.

RESULTS AND DISCUSSION

Ethanol Conversion

The catalytic activity of SL for ethanol conversion was compared with that of silica. The activity changed with preheating temperature of the samples. Figures 1a and 1b show the results of the reaction after a

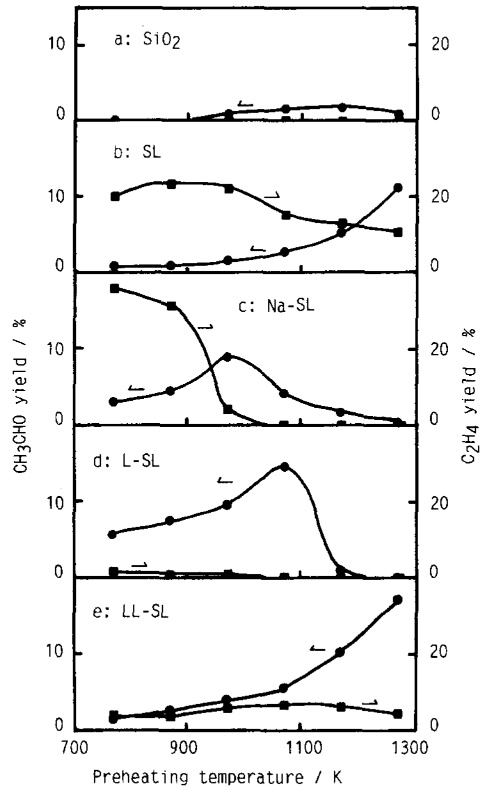

FIG. 1. Relationship between catalytic activity and preheating temperature. Time on stream, 1 h. Reaction conditions: catalyst, 0.100 g; temperature, 670 K; flow rate, 1.8 liter h^{-1}; ethanol fed, 1.3 mmol h^{-1}.

lapse of 1 h. The products detected were acetaldehyde, ethylene, hydrogen, water, and trace amounts of C1 compounds. Since the silicalite-1 sample used is a high-silica ZSM-5, production of aromatics or others was expected. However, these compounds were not detected. Though the silica preheated below 1000 K did not catalyze ethanol dehydrogenation (Fig. 1a), SL preheated even at 770 K catalyzed the reaction and its activity increased with increase in preheating temperature (Fig. 1b). Figure 2 shows a typical time course of the reaction. The activity of silica preheated at high temperatures decreased quickly at the initial stage of the reaction, whereas the deactivation of SL was significantly slower. This suggests that the active sites in silicalite-1 are stable compared with those in silica. After the reactions, the color of these samples were still white; hence, the deactivation is not due to coke formation.

In the case of SL the selectivity to acetaldehyde was low because of simultaneous ethylene production. Kitagawa *et al.* reported that the catalytic activity of NH_4-ZSM-5 for the transformation of propane into aromatic hydrocarbons, which is a typical acid-catalyzed reaction, depends on preheating temperature of the catalyst and NH_4-ZSM-5 preheated at 853 K exhibited a maximum activity (*13*). Dehydration of ethanol to ethylene is also catalyzed by acid sites (*14*), and SL preheated at 870 K showed a maximum activity for the dehydration (see Fig. 1b). Since SL exhibits the same acidic property as NH_4-ZSM-5, the ethanol dehydration is believed to be catalyzed over the strong acidic sites constituted of trace amounts of aluminum ion in SL (*15*). Anderson *et al.* reported that acidity of silicalite-1 doped with excess of sodium ions to the acid sites is small (*16*). Since silicalite-1 lacks ion-exchange capacity, introduction of large amounts of sodium ions to SL is impossible by the ion-

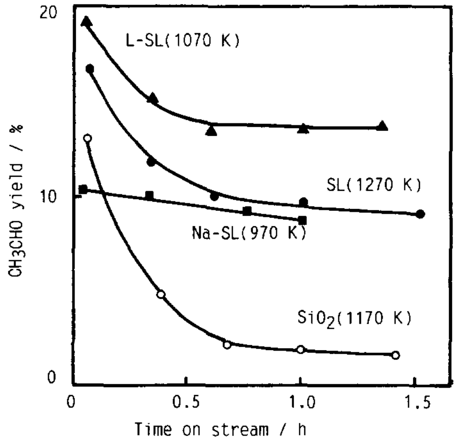

FIG. 2. Catalytic activity for ethanol dehydrogenation. In parentheses, preheating temperatures are presented. Reaction conditions: catalyst, 0.100 g; temperature, 670 K; flow rate, 1.8 liter h^{-1}; ethanol fed, 1.3 mmol h^{-1}.

exchange technique. However, when sodium ions are used as a raw material for the synthesis of silicalite-1, considerable amounts of sodium ions remain in the silicalite-1 as impurities and the ions disperse highly in the compound (*12*). The sodium-modified silicalite-1 sample (Na-SL), which is synthesized from a mixture including sodium ions, contains 0.7 wt% of sodium ions; thereby, we examined the sample. The results of the reaction with Na-SL are shown in Fig. 1c. In contrast to expectations, Na-SL preheated up to 870 K exhibited higher catalytic activity for the dehydration than that of SL. However, the catalytic activity steeply declined at the preheating temperature of 970 K and the production of ethylene was very small over Na-SL preheated at 1070–1270 K. It is noteworthy that the selectivity to acetaldehyde was higher than 99% over the sample preheated at 1070 K. In Na-SL, the amount of sodium ions greatly exceeds that of aluminum ions and the sodium ions are supposed to poison the acid sites constituted of aluminum ions. On the contrary, there are weak Brønsted acid sites on the outer surface of sodium-modified silicalite-1, and almost all the acid sites are removed by heating at 970 K (*12*). Thus, the activity of Na-SL preheated up to 870 K for ethanol dehydration is probably due to the weak acid sites.

In order to prevent ethanol dehydration, we must heat Na-SL at 1070 K or above, whereas the catalytic activity of Na-SL for ethanol dehydrogenation decreased at the preheating temperature of 1070 K (see Fig. 1c). This suggests that at 1070 K sodium ions poison the acid sites and excess amounts of sodium ion also poison the active sites for dehydrogenation. Thereby, a sodium-ion leached sample (L-SL) was prepared from Na-SL heated at 1070 K while L-SL contains 0.4 wt% of sodium ions. As shown in Figs. 1d and 2, satisfactory results were obtained with L-SL; that is, ethanol was converted selectively to acetaldehyde over the catalyst and the activity became stable after a lapse of 0.5 h. The catalytic activity was higher than that of Na-SL, and L-SL preheated at 1070 K showed a maximum activity and its selectivity to acetaldehyde was 94%.

The catalytic activity of other sodium-leached samples was examined. As shown in Fig. 1d, the catalytic activity of LL-SL prepared from Na-SL heated at 770 K for ethanol dehydration was notably lower than that of SL but the activity was not lost by preheating even at 1270 K. On the other hand, no reaction was observed over LH-SL prepared from Na-SL heated at 1270 K.

Structures of Silicalite-1 Preheated at High Temperatures

To investigate effects of preheating at high temperature on the structure of the silicalite-1 samples, the XRD patterns were recorded. Significant change was not observed in the patterns of SL and LL-SL preheated at 770–1270 K and the pattern is identical to that of silicalite-1 reported by Olson *et al.* (*17*). The patterns of Na-SL preheated at 770–970 K were the same as those of silicalite-1; however, after heating at 1070 K and above, the patterns changed as shown in Fig. 3. The pattern for Na-SL preheated at 1270 K is identical to that of cristobalite (*18*). No significant change was observed between the patterns for L-SL preheated at 770–1170 K and those for Na-SL preheated at 1070 K, but the pattern for L-SL preheated at 1270 K changed to that of cristobalite. Although almost all sodium ions in nonpreheated silicalite-1 can be leached out (*12*), considerable amounts of sodium ion in Na-SL preheated at 1070 K were not leached out. The finding suggests that these sodium ions are mainly distributed in the portions where the crystalline structure change occurred. While sodium ions in silicalite-1 exist as Na–O–Si in the structure (*19*), when heated at high temperature the sodium ions are supposed to be liberated and to break the oxygen bridges in silicalite-1. It is known that the stable structure of a high-silica SiO_2–Al_2O_3–Na_2O crystal is cristobalite and that the temperature for transition to cristobalite from other crystalline structures decreases with increases in the amount of sodium included in the high-silica crystal (*20*). Since sodium ions exist near aluminum ions in zeolites, the sodium density around aluminum ions in silicalite-1 is probably higher than that of other portions; that is, the transition to cristobalite could easily take place at the portions around aluminum ions compared with other portions. In the case of Na-SL, the change of crystalline structure and the disappearance of the catalytic activity for dehydration were simultaneously observed by preheating at 1070 K. Thus, the disappearance of the acid sites in Na-SL is probably due to the change in crystalline structure around aluminum ions. The activity of L-SL for dehydration of ethanol was very low. Since L-SL was prepared from Na-SL heated at 1070 K by reflux in water, the sample is rehydrated by water. Hence, the acid sites in Na-SL removed by the change in crystalline structure cannot be restored by rehydration of the sample.

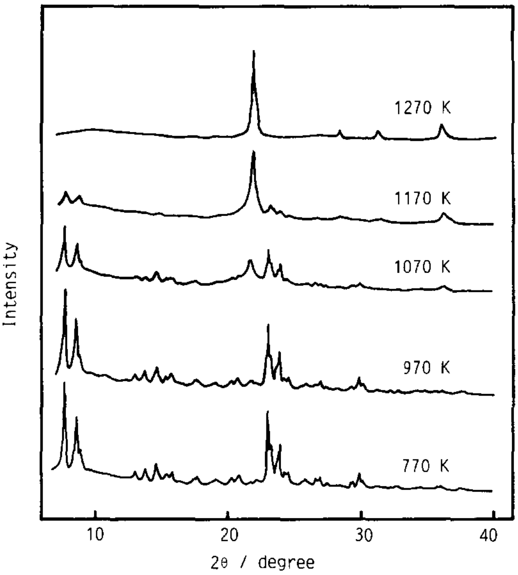

FIG. 3. Change of XRD patterns for Na-SL with preheating temperature.

Adsorption of Ethanol at Room Temperature

Ethanol adsorption was carried out over SL, Na-SL, and L-SL at room temperature. Since silicalite-1 is a good adsorbent for organic compounds (*9*), the adsorption would reflect the structural change of the silicalite samples by heating at high temperature. The adsorption was almost saturated at an ethanol pressure of ca. 10 Torr. Ethanol adsorption on SL preheated at 770–1270 K gave the same saturation amount of 2.4 mmol g^{-1}, *i.e.*, 0.14 ml g^{-1} in adsorption volume. Since the micropore volume of silicalite-1 determined by adsorption of oxygen at 90 K was 0.185 ml g^{-1} (*9*), ethanol adsorbed was condensed in the micropores. Thus, the value relates to the micropore volume of the sample. In the case of Na-SL preheated at 770–970 K, the amount was 2.1 mmol g^{-1} and the amount for Na-SL preheated at 1070 K was 2.2 mmol g^{-1}. The amount is discernibly smaller than that for SL suggesting that the micropore volume is smaller and the presence of sodium ions in Na-SL causes the smaller micropore volume. When Na-SL was heated at 1070 K, the silicalite-1 structure changed considerably to cristobalite. However, the amount of adsorbed ethanol was discernibly larger than that for the sample before the heating. The result strongly suggests that the micropore volume of Na-SL rather increases with preheating at 1070 K and that the structure of the micropores is maintained. Thus, Na-SL heated at 1070 K is a silicalite-like compound; in the structure, the size of each cristobalite portion is supposed to be very small. The amount of ethanol adsorbed on Na-SL heated at 1170 K was 0.01 mmol g^{-1}; that is, almost all of the micropores in Na-SL collapsed at 1170 K. In the case of the sodium-leached sample, L-SL, prepared from Na-SL heated at 1070 K, 0.3 wt% of sodium ions were leached out during the preparation. The amount of ethanol adsorbed on L-SL preheated at 770–1070 K was 2.4 mmol g^{-1}, although it showed the same crystalline structure as Na-SL pre-

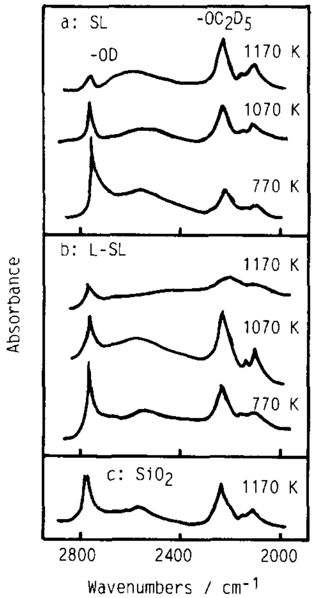

FIG. 4. IR spectra of C_2D_5OD adsorbed on SL, L-SL, and SiO_2 at 420 K (background-subtracted spectra).

heated at 1070 K. Since the amount is discernibly larger than that for Na-SL preheated at 1070 K and the same as that for SL, we can infer that the leached sodium ions had existed on the micropore surface of Na-SL preheated at 1070 K and the sodium ions remaining in L-SL exist inside the micropore surface. The crystal structure of Na-SL heated at 1270 K is cristobalite, and almost none of the sodium ions in that sample were leached out by reflux with water. Thus, sodium ions in L-SL are supposed to exist mainly in the portion of cristobalite located inside the micropore surface.

IR Spectra for Ethanol Adsorbed on Active Sites

In the case of highly dehydrated silica, the active sites for ethanol dehydrogenation are probably the oxygen bridges that have a distorted structure (*7*). Hunger *et al.* reported that there are defect centers composed of internal silanol groups and/or nonintact Si–O–Si oxygen bridges in ZSM-5-type zeolite or silicalite-1 synthesized from a solution including TPA ions (*19*). Since SL was prepared from a solution including TPA ions, the nonintact oxygen bridges exist in SL. The amount of the oxygen bridges is supposed to increase with an increase in preheating temperature of SL because condensation of the silanol groups is stimulated at high temperature and the oxygen bridges are supposed to be distorted in the defect. As shown in Fig. 1b, the catalytic activity of SL for ethanol dehydrogenation increased with an increase in preheating temperature. Hence, the nonintact oxygen bridges may be the active sites.

To confirm this, we carried out activated adsorption of C_2D_5OD on SL or L-SL at 420 K and monitored the IR spectra for the adsorption species. The spectra are shown in Figs. 4a and 4b (background-subtracted spectra); we observed the absorption bands at 2400–2700 and 2762 cm^{-1} assigned to $-OD$ groups and the bands at 2102, 2148, and 2231 cm^{-1} assigned to $-C_2D_5$ groups (*21*). In the case of silica preheated at 1170 K, these absorption bands were also observed in the IR spectrum (Fig. 4c). Before the adsorption, we observed the sharp absorption band at 3746 cm^{-1} assigned to isolated silanol groups in the spectra of the samples (*10, 21*), but the band almost disappeared after the adsorption. When the silanol group is deuterated, the IR band is expected to be near 2762 cm^{-1}; therefore, the band at 2762 cm^{-1} can be assigned to the isolated $-OD$ species generated by H–D exchange of the isolated silanols with C_2D_5OD. While the intensity of this band decreased with an increase in preheating temperature, that of the broad absorption band at 2400–2700 cm^{-1} rather increased in the case of SL, suggesting that most of the $-OD$ groups responsible for the broad band were not generated by H–D exchange. Since the intensities of the bands at 2100–2300 cm^{-1} for $-C_2D_5$ groups simultaneously increased with an increase in that of the OD band, generation of the $-OD$ groups responsible for the broad band is supposed to be associated with an adsorption species of C_2D_5OD. The intensities of these bands for L-SL also increased, but upon preheating at 1170 K their intensities decreased. The intensities of these bands relate to the catalytic activity for ethanol dehydrogenation; thus, the absorption bands can be ascribed to the active sites for ethanol dehydrogenation. Since ethanol dehydration is not catalyzed by L-SL, the bands are not ascribed to the active sites for the dehydration. Over the silica preheated above ca. 1000 K, hydroxyl and ethoxyl groups are generated by dissociative adsorption of ethanol accompanying cleavage of the active Si–O–Si oxygen bridges which are believed to catalyze ethanol dehydrogenation (*7*), *i.e.*, $Si{-}O{-}Si + C_2H_5OH \rightarrow Si{-}OH + Si{-}OC_2H_5$. Therefore, we assigned the bands at 2100–2200 cm^{-1} for the silica preheated at 1170 K to the $-OC_2D_5$ groups generated through dissociative adsorption of C_2D_5OD. Since the positions of the bands at 2100–2700 cm^{-1} for SL and L-SL are almost identical with those for the silica, the bands are assigned to the $-OD$ and $-OC_2D_5$ groups generated by dissociative adsorption of C_2D_5OD. Thus, we believe that there are active oxygen bridges on which dissociative adsorption of ethanol takes place in silicalite-1 and that these oxygen bridges are probably the active sites for ethanol dehydrogenation. Since we observed similar absorption bands in the case of Na-SL adsorbing C_2D_5OD, the active oxygen bridges exist also in Na-SL.

Effects of Sodium Modification to Silicalite-1 on Activity for Ethanol Dehydrogenation

The catalytic activity of Na-SL for ethanol dehydrogenation is notably higher than that of SL (cf. Figs. 1b and 1c). One can suppose that this high activity of Na-SL is due to generation of basic sites in silicalite-1 by sodium modification, but we confirmed that the amount of basic sites in sodium-modified silicalite-1 is very small (*12*) and that the function of the basic sites is negligible. It was also confirmed that the amount of silanol groups included in sodium-modified silicalite-1 is appreciably larger than that in nonmodified silicalite-1 (*12*). Since the active oxygen bridges are generated by condensation of the silanol groups in silicalite-1, the number of oxygen bridges probably depends on the number of silanol groups. Thus, the difference in the activity between SL and Na-SL would be caused by the difference in the number of active oxygen bridges.

To estimate the number of these oxygen bridges, we measured the amounts of ethanol irreversibly adsorbed on SL and Na-SL at 420 K. By the measurement of the IR spectra for ethanol adsorbed on the silicalite samples, it was confirmed that the number of the active oxygen bridges relates to the amount of ethanol irreversibly adsorbed. As shown in Fig. 5, the amount of ethanol adsorbed relates to the catalytic activity for dehydrogenation (see Figs. 1b and 1c). When SL preheated at 770 K was heated at 1270 K in a flow of helium gas, desorption of ca. 0.3 mmol g^{-1} of water was confirmed with a TCD detector. This amount is roughly the same as that of the adsorption sites newly generated by heating at 1270 K, strongly suggesting that generation of the sites is caused by condensation

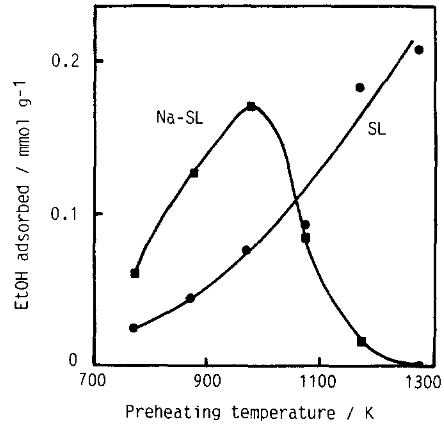

FIG. 5. Irreversible adsorption of ethanol on SL and Na-SL at 420 K.

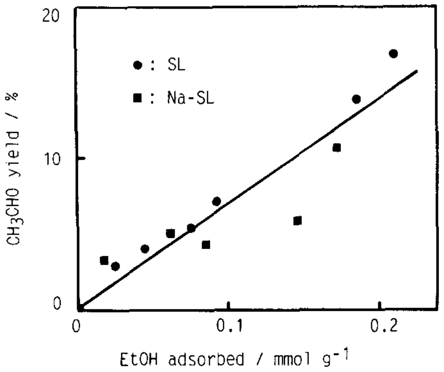

FIG. 6. Relationship between amount of ethanol irreversibly adsorbed on SL and Na-SL and initial activity for ethanol dehydrogenation.

of silanols in silicalite-1. Figure 6 shows the relationship between the amount of irreversibly adsorbed ethanol and the initial activity measured within 10 min after the starting of the feed. The data for SL and Na-SL gave one straight line; therefore, the active sites for the dehydrogenation in Na-SL are ascribed to be the active oxygen bridges and the catalytic activity depends only on the number of the oxygen bridges.

The catalytic activity of L-SL preheated at 1070 K for the dehydrogenation was notably higher than that of Na-SL preheated at 1070 K although the activity of both samples preheated at 970 K is roughly the same. The numbers of the active oxygen bridges in these samples can be estimated from the initial catalytic activity by using the relationship in Fig. 6, and the amounts are found to be ca. 0.08 mmol g^{-1} for Na-SL and ca. 0.26 mmol g^{-1} for L-SL. It is noteworthy that L-SL was prepared by leaching 0.13 mmol g^{-1} of sodium ions from Na-SL. Since the amount of the sodium ions leached agrees roughly with the difference of the amounts of the active oxygen bridges, in Na-SL preheated at 1070 K almost all the sodium ions on the micropore surface are supposed to poison these oxygen bridges.

Stability of Active Sites

In the case of the silica preheated at 1170 K, the amount of active oxygen bridges at the initial stage of the reaction is estimated to be ca. 0.1 mmol g^{-1} on the basis of the results for pulse reaction described in Ref. (*7*). Since the turnover number of these sites to each of the repeated pulse-reactions exceeded one (*7*), ethanol dehydrogenation over these active sites is not a stoichiometric one but a catalytic one. However, as shown in Fig. 2, 80% or more of the active sites were deactivated during the first half hour on the continuous flow reaction. The presence of water causes deactivation of the catalyst (*7*), but the amount of water produced during the first half hour of the reaction was estimated to be ca. 0.02 mmol g^{-1} from the amount of ethylene produced. The finding suggests that the active sites are not deactivated mainly by water. The reaction intermediate is probably the hydroxyl and ethoxyl groups formed via adsorption of ethanol on the active oxygen bridge (*7*). Since the surface structure of silica is supposed to be quite flexible, the intermediate would be converted to stable hydroxyl and ethoxyl groups under the reaction conditions and the number of effective active sites would decrease. The activity of silica preheated at 1170 K measured at the initial stage of this flow reaction is appreciably lower than that measured by the pulse reaction previously carried out by us (*6, 7*). Since the reaction in the pulse system proceeded over the fresh surface of the silica, the reaction was not affected by the deactivation due to presence of ethanol. On the other hand, the first point in Fig. 2 shows the activity after 5 min from the beginning of feed, and there should be some deactivation by ethanol.

The active sites in silicalite-1 are rather stable compared with those in silica as shown in Fig. 2, but these sites in silicalite-1 would be likewise deactivated via the same mechanism for deactivation of silica. Fyfe *et al.* reported that the pore structure of silicalite-1 is distorted by adsorption of six-membered ring compounds such as benzene (*22*). The finding suggests that the crystalline structure of silicalite-1 is discernibly flexible. In the case of Na-SL preheated at 970 K, the deactivation was appreciably slow (see Fig. 2), suggesting that the presence of sodium ions in silicalite-1 stabilizes the active sites. Sodium ions would keep the structure around the active sites from significant change. The sodium-leached samples, L-SL and LL-SL, were prepared from Na-SL by reflux in water. The reflux temperature probably suffices for rehydration of the active oxygen bridges presented in Na-SL because irreversible adsorption of ethanol occurs at a temperature near 400 K. Actually, the activity of LL-SL preheated at 770 K for dehydrogenation is lower than that of Na-SL preheated at 770 K (cf. Figs. 1c and 1e), suggesting that the active oxygen bridges in Na-SL are decomposed to rather stable silanols during reflux in water. On the other hand, the structure of cristobalite is rigid. Since Na-SL heated at 1070 K is a compound partly having the structure of cristobalite, its surface structure is supposed to be quite rigid and the active oxygen bridge would be appreciably stable. The activity of L-SL preheated at 770 K was considerably larger than that of Na-SL preheated at 770 K and roughly the same as the activity of Na-SL preheated at 1070 K (cf. Figs. 1c and 1d). This result enables us to suppose that the silanols produced by rehydration of the active oxygen bridges in Na-SL heated at 1070 K during reflux in water are unstable and are easily converted to active oxygen bridges even at 770 K; thus, L-SL heated at 770 K has a considerable number of active sites.

CONCLUSIONS

The catalytic activity of silicalite-1 for ethanol dehydrogenation to acetaldehyde is stable compared with that of highly dehydrated silica and the activity increases with an increase in preheating temperature of the catalyst in the range 770 to 1270 K. The active sites are probably the oxygen bridges in the defect center of silicalite-1, on which dissociative ethanol adsorption takes place. Since the silicalite-1 sample used contained as impurities small amounts of aluminum, which constitutes a strong acid site, simultaneous ethanol dehydration to ethylene proceeded over the acid sites. Dehydration also proceeded over the silicalite-1 catalyst containing 0.7 wt% of sodium ions when the catalyst was preheated at 770–970 K. However, after preheating at 1070 K almost all of its acid sites disappeared and selective ethanol dehydrogenation to acetaldehyde was observed. The disappearance of the acid sites is believed to be due to partial transformation of the sample from the silicalite-1 structure to cristobalite, although the sample heated at 1070 K maintained the pore structure of silicalite-1. The catalytic activity of the sample preheated at 1070 K for ethanol dehydrogenation was smaller than that of the sample preheated at 970 K, probably because by heating at 1070 K sodium ions in the sample are liberated and poison the active oxygen bridges. The sodium ions poisoning the active sites for ethanol dehydrogenation can be removed by refluxing the sample in water. The dehydrogenation activity of the sodium-leached sample preheated at 1070 K was notably larger than that of the sodium-modified sample preheated at 970 K, while its activity for ethanol dehydration was very small.

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