# Selective Dehydrogenation of Ethanol over Highly Dehydrated Silica

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Silica dehydrated above ca. 1000 K selectively converts ethanol to acetaldehyde, and the dehydrogenation proceeds according to Langmuir–Hinshelwood kinetics. Measurement of phosphorescence spectra confirmed that new sites are formed on silica by preheating above ca. 1000 K, but the dehydrated silica showed no acidity or basicity which might have been responsible for the dehydrogenation activity. Infrared spectra indicated dissociative adsorption of ethanol on the dehydrated silica and we infer that the adsorption site is an active Si–O–Si oxygen bridge formed by the dehydration of silica at high temperature, and that the reaction intermediate is formed by the dissociative adsorption of ethanol accompanying cleavage of that oxygen bridge. © 1989 Academic Press, Inc.

## INTRODUCTION

Generally, basic sites have been considered to be the active sites for catalytic dehydrogenation of alcohols on oxide supports that do not contain transition metals (1–5) and therefore silica was believed to be a poor catalyst for this reaction because its surface is neutral or perhaps slightly acidic (6–9). However, we have observed recently that ethanol can be dehydrogenated to make acetaldehyde and hydrogen in the presence of silica samples heated to at least 870 K (10). The activity is not that of a simple base since these samples are quite selective for the dehydrogenation reaction and do not display the usually concomitant reactivity of bases toward alcohol dehydration (11). To elucidate the active sites, we have studied the kinetics of the reaction and the changes in surface properties of the silica with preheating temperatures.

## EXPERIMENTAL METHODS

### Materials

Silica was prepared from ethyl orthosilicate to obtain a pure sample. Ethyl orthosilicate purified by distillation was hydrolyzed to silica gel in a 5 $M$ nitric acid solution (G. R. grade). The obtained hydrogel was dried at ca. 400 K in air, washed with water, and then heated at 670 K in air for 5 h. Analysis by atomic absorption spectroscopy revealed that the only observable impurities were nickel (4 ppm) and sodium (4 ppm). After the sample was heated at 1270 K in vacuo for 1 h the XRD pattern was the same as that of the sample without preheating.

Ethanol was dehydrated by refluxing over magnesium just before the reaction.

Ammonia and carbon dioxide were high-purity grade supplied by Takachiho Kagaku Kogyo and were used without further purification.

### Ethanol Conversion

Ethanol conversion was carried out mainly in a pulse microcatalytic reactor at 520–670 K. The silica sample (0.050 g) was sandwiched with quartz wool (ca. 0.01 g) in a quartz reaction tube of 6-mm inner diameter. It was confirmed that the contribution of quartz wool (packing material) was very small or negligible. In the following reported results, the contribution was corrected. The catalyst bed was preheated at 770–1270 K for 1 h in a flow of helium gas
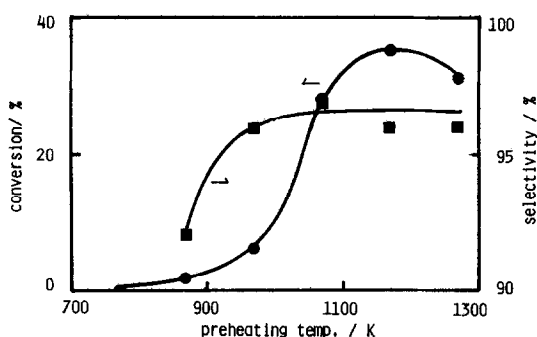
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FIG. 1. Dependence of catalytic activity of silica on preheating temperature. Reaction temperature, 670 K.

(the carrier gas; flow rate, $60 \times 10^{-6}$ m$^3$ min$^{-1}$) and then a pulse of $1 \times 10^{-9}$ m$^3$ of ethanol was injected into the catalyst bed. During the preheating, desorption of water from the silica was observed and the amount was measured. The reaction products were analyzed by gas chromatography. A Porapak Q (1 m) column was used for normal analyses.

To study the kinetics of the reaction, initial rates at different ethanol pressures were measured in a closed system equipped with a calibrated Pirani gauge. The pure silica sample (0.025 or 0.050 g) in a quartz reactor was preheated at 1170 K *in vacuo* for 30 min. Initial pressure of ethanol was below 2 Torr, and the reaction was stopped by abrupt cooling of the reactor before ethanol conversion reached 5%; then, the rate of dehydrogenation was determined from the amount of hydrogen produced during the reaction. By analysis of the products with gas chromatography, it was confirmed that the amount of hydrogen corresponded well to the amount of acetaldehyde produced.

## Measurement of Surface Properties

The silica sample was heated *in vacuo* at 770–1270 K for 1 h and the surface area was measured *in situ* by the BET method using nitrogen physisorption at 77 K.

Adsorption of ammonia or carbon dioxide on the sample was measured by a constant-volume method.

Infrared spectra were recorded with a

Nicolet 5DX Fourier transform infrared spectrometer. The silica samples (0.01 g) were pressed into self-supporting wafers and placed into an *in situ* IR cell that allowed heating under vacuum. The samples were heated *in vacuo* at 770–1270 K for 1 h. IR spectra of adsorbed ethanol were recorded at room temperature after ethanol vapor (ca. 20 Torr) was allowed to contact the preheated wafers at room temperature for 20 min and evacuated at a desired temperature for 30 min.

Phosphorescence spectra were recorded with a modified Hitachi 650-10S fluorescence spectrophotometer at 77 K (slit width of emission, 5 nm; slit width of excitation, 5 nm). The silica sample (0.3 g) had been preheated at 770–1270 K *in vacuo* for 1 h in a quartz tube cell (inner diameter, ca. 6 mm; outer diameter, ca. 8 mm). The effect of adsorption of oxygen or ethanol was examined on the spectra of preheated silica.

### RESULTS AND DISCUSSION

#### Conversion of Ethanol

Figure 1 shows the change in activity and selectivity with preheating temperature for ethanol conversion over dehydrated silica. Activity decreased gradually with pulse number. The results in Fig. 1 and Table 1 are those for the first pulse of ethanol. No reaction was observed over the pure silica sample preheated at 770 K. However, acetaldehyde was produced over samples pre-

TABLE 1

Ethanol Conversion over Dehydrated Silica[a]

| Run | Reaction temperature (K) | Selectivity (%) | | | Conversion of EtOH (%) |
|---|---|---|---|---|---|
| | | C$_1$ | C$_2$H$_4$ | CH$_3$CHO | |
| 1 | 520 | — | — | — | 0 |
| 2 | 570 | 0 | 0 | 100 | 4 |
| 3 | 620 | 1 | 1 | 98 | 16 |
| 4 | 670 | 2 | 2 | 96 | 35 |
| 5[b] | 670 | 2 | 2 | 96 | 26 |

[a] Preheating temperature, 1170 K.
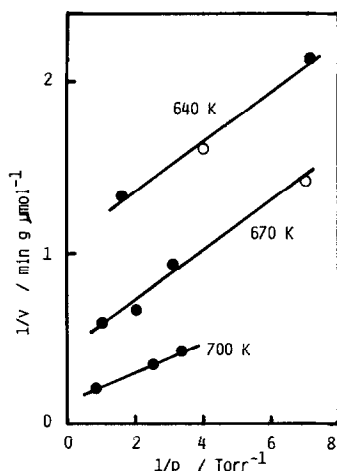[b] Before the reaction, the catalyst was injected with $1 \times 10^{-9}$ m$^3$ of H$_2$O.

FIG. 2. Change in the initial rate of dehydrogenation with ethanol pressure. Before the reaction, the pure silica sample was heated *in vacuo* at 1170 K for 30 min. $v$ = initial rate, $p$ = ethanol pressure. Catalyst: ●, 0.025 g; ○, 0.050 g.

heated to at least 870 K. The catalytic activity for ethanol conversion increased steeply with preheating above ca. 1000 K, and reached a constant value as shown in Fig. 1. Small amounts of ethylene, water, and $C_1$ compounds were also observed as products. Ethanol dehydrogenation proceeded at reaction temperatures above ca. 550 K over the sample preheated at 1170 K as presented in Table 1.

When ca. $1 \times 10^{-9}$ m³ of water was injected into the sample preheated at 1170 K before the reaction, a decrease in catalytic activity was observed (run 5 in Table 1); more deactivation was not observed when the water dose was repeated. When injection of ethanol into the sample preheated at 1170 K was repeated, the catalytic activity decreased gradually and reached to the same activity as that of the sample after the water dose. Thus, the deactivation can be ascribed to the trace amount of water produced in the reaction.

*Kinetics of Dehydrogenation*

To clarify the mechanism of ethanol dehydrogenation, kinetic studies were carried

out by using a closed reaction system and the catalyst preheated at 1170 K, which showed the maximum activity (Fig. 1). As shown in Fig. 2, the reaction rate obeys the equation $r = kKp/(1 + Kp)$, where $r$ is a reaction rate, $k$ is a rate constant, $K$ is an adsorption equilibrium constant, and $p$ is the partial pressure of ethanol. The values of $k$ and $K$ are presented in Table 2. The same results were obtained for both silica samples preheated at 1170 K *in vacuo* under an oxygen atmosphere. A good linear relationship was found on the Arrhenius plots for the constants presented in Table 2. From the plots the activation energy and the heat of adsorption were estimated to be 130 and 100 kJ mol⁻¹, respectively.

*Acid–Base Properties of the Silica Surface*

Acidity of silanol sites on silica gel is so weak that the usual acid-catalyzed reactions do not proceed on silica gel (12). Comparable tests show that there are no strong basic sites on silica gel (8). However, silica preheated at a high temperature might generate acidic or basic sites in much the same way that new basic sites are produced on oxides such as calcium oxide by heating at high temperature (7).

To study acid–base properties of highly dehydrated silica, adsorption of ammonia and carbon dioxide was carried out. If acidic or basic sites were generated on the silica surface, strong adsorption of ammonia or carbon dioxide would be observed (13). However, on both pure silica samples

TABLE 2

Reaction Rate for the Dehydrogenation of Ethanol[a]

| Reaction temperature (K) | $k$ ($\mu$mol min⁻¹ g⁻¹) | $K$ (Torr⁻¹) |
|---|---|---|
| 640 | 0.9 | 7.4 |
| 670 | 2.3 | 3.4 |
| 700 | 7.7 | 1.5 |

[a] $r = kKp/(1 + Kp)$: $r$ = reaction rate ($\mu$mol min⁻¹ g⁻¹); $p$ = partial pressure of ethanol (Torr).
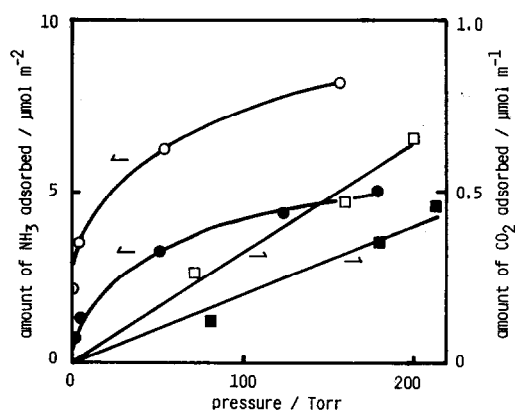
FIG. 3. Adsorption of ammonia and carbon dioxide on silica. Preheating temperature: ○, □, 770 K; ●, ■, 1170 K.

preheated at 770 and 1170 K, adsorption of ammonia and carbon dioxide was very weak and complete desorption was observed at room temperature. Thus, ammonia and carbon dioxide are only physisorbed on these samples. The amounts of physisorbed ammonia and carbon dioxide were different for these samples as shown in Fig. 3. The difference can be ascribed to the difference in concentration of surface hydroxyl groups. It is known that ammonia molecules are adsorbed to hydroxyl groups on the silica surface via hydrogen bonding (14). The ammonia uptake below 1 Torr was very steep and the amount corresponded to the amount of surface silanols determined in the following section. Thus, surface silanols are probably the sites responsible for the initial adsorption. The adsorption of carbon dioxide on the silica samples is very weak compared with that of ammonia, suggesting that the adsorption is caused mainly by van der Waals forces (15). Kiselev reported that the heat of physisorption for nitrogen on dehydroxylated silica was smaller than that on hydroxylated silica by ca. 30% because of a lack of "specific" interaction between the nitrogen molecules and the hydroxyl groups of silica (16). Probably, the decrease in carbon dioxide uptake by the dehydration of silica is

also due to the lack of "specific" interaction. Thus, we can conclude that effective acid–base sites do not exist in the silica sample and the active sites for dehydrogenation over silica are not acid–base sites.

## Surface Area and Concentration of Silanol Sites

When the silica sample was heated at high temperature, desorption of water was observed; the desorption of water is due to condensation of silanols (14,17), that is, $2Si-OH \rightarrow Si-O-Si + H_2O$. The catalytic activity of silica increases with an increase in the amount of water desorbed, and decreases after water adsorption on silica. The results suggest that the active sites are not surface silanols but might be the Si–O–Si sites. Thus, it is supposed that there is some inverse relationship between the activity and the concentration of surface silanols. The amount of surface silanols was estimated from the intensity of the silanol absorption band (at 3400–3800 $cm^{-1}$) in the IR spectra of the silica samples. Kondo et al. reported that a good linear relationship can be seen between the intensity and the amount of silanol determined by gravimetry (17). Table 3 presents surface silanol concentration and BET surface areas of the silica as a function of preheating temperature. The amount of water desorbed from the sample by heating corresponded to the silanol concentration. There is a close inverse

TABLE 3

Effect of Heat Treatment on Concentration of Surface Silanol and BET Surface Area of the Silica Sample

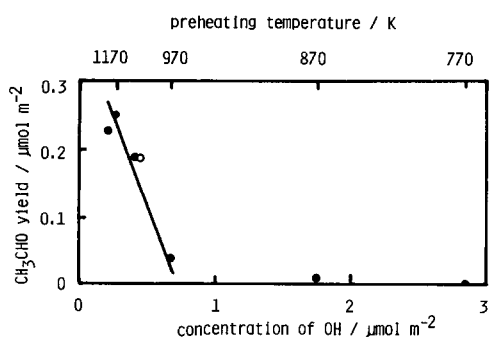| Preheating temperature (K) | Surface area ($m^2 g^{-1}$) | OH concentration ($\mu mol\ m^{-2}$) |
|---|---|---|
| 770 | 582 | 2.85 |
| 870 | 520 | 1.73 |
| 970 | 499 | 0.68 |
| 1070 | 482 | 0.41 |
| 1170 | 461 | 0.26 |
| 1270 | 451 | 0.22 |

FIG. 4. Relationship between activity of silica and concentration of hydroxyl groups on silica. The yield of acetaldehyde was determined from Fig. 1. The open circle shows the result for the silica-adsorbing water.

relationship between the activity change shown in Fig. 1 and the silanol concentration listed in Table 3. Figure 4 is a plot of the acetaldehyde yield normalized to surface area versus silanol concentration. The yield was negligible for the silica preheated below 900 K, which has substantial silanol groups. On the other hand, appreciable yield was observed for the silica preheated at 970–1270 K. A linear relationship can be observed between the yield and the silanol concentration for these samples, supporting the idea that the active sites might be the Si–O–Si sites. The active sites should be deactivated by water adsorption. The deactivation was confirmed by the following experiments. When the silica preheated at 1170 K was exposed to water vapor at 670 K and evacuated for 30 min at the same temperature, the amount of surface silanols was found to be 0.44 $\mu$mol m$^{-2}$. The yield of acetaldehyde was 0.19 $\mu$mol m$^{-2}$, and the value is on the straight line in Fig. 4 (open circle). Thus, the catalytic activity of silica is believed to relate mainly to the amount of the oxygen bridges newly generated by heating at temperatures above ca. 1000 K.

### Adsorption of Ethanol on Silica

The results of reaction kinetics suggest that chemisorption of ethanol proceeds on highly dehydrated silica in the reaction; therefore, an adsorbed state of ethanol on

silica was investigated by IR spectroscopy. In the case of the silica preheated at 770 K, adsorption of ethanol followed by evacuation at room temperature caused the absorption band assigned to hydroxyl groups (14) to shift to 3733 cm$^{-1}$ from 3742 cm$^{-1}$, where it was observed before adsorption (Fig. 5). After the adsorption, absorption bands at 2986, 2937, and 2913 cm$^{-1}$ were also observed on the spectrum. These bands were assigned to ethyl groups (14). After evacuation at 570 K following the adsorption, the band for hydroxyl groups was observed at the same position as before adsorption, but the intensity was discernibly reduced (see background-subtracted spectrum d in Fig. 5). The absorption bands at 2986, 2937, and 2913 cm$^{-1}$ remained after evacuation even at 570 K. Thus, these bands are not due to ethanol molecules but to ethoxyl groups formed by condensation between ethanol and silanol. It is known that methoxyl groups are also formed on the silica surface by condensation of methanol and surface silanol (14).

On the other hand, the bands for ethoxyl groups at 2986, 2937, and 2913 cm$^{-1}$ were also observed after ethanol adsorption in
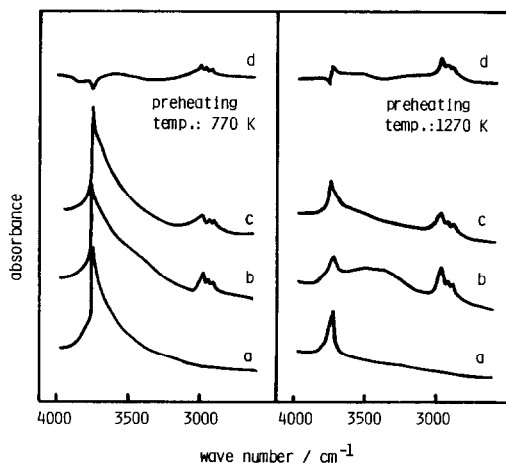


FIG. 5. Infrared spectra of ethanol adsorbed on the silica surface: (a) before adsorption; (b) after exposure to ethanol followed by evacuation at room temperature; (c) evacuation at 570 K; (d) background-subtracted spectra, c − a.
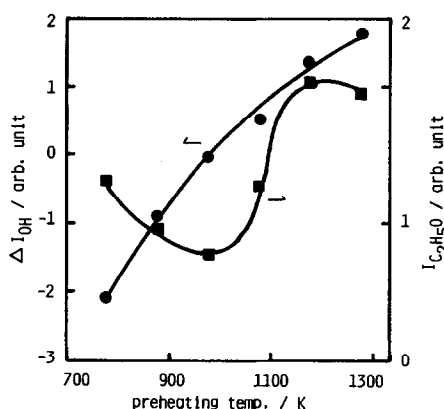
FIG. 6. Change in intensity of ethoxyl and hydroxyl groups on silica with ethanol adsorption followed by evacuation at 570 K.

the spectra of the silica preheated at 1270 K, even though the amount of surface silanols on the silica preheated at 1270 K was quite small. In this case, intensity of the silanol band at 3742 cm$^{-1}$ increased after evacuation even at 570 K, strongly suggesting dissociative adsorption of ethanol on the silica surface, that is, $C_2H_5OH + Si-O-Si^* \rightarrow Si-OH + Si-OC_2H_5$. Morterra and Low reported that a new absorption band at 2200–2300 cm$^{-1}$ assigned to Si–H appeared after activation of silica by pyrolysis of trimethylaluminum on the surface and that Si–O–O–Si species were formed on silica by the activation (18). However, we did not observe the new band, suggesting that the adsorption sites for ethanol are not the Si–O–O–Si species. Morrow et al. reported that dissociative adsorption of methanol occurs on the silica preheated at 1373 K and that the adsorption sites are probably distorted Si–O–Si oxygen bridges (19). Therefore, we believe that preheating of silica at high temperature causes formation of the active oxygen bridge on which dissociative adsorption of alcohol takes place.

The change in intensity of the silanol band after ethanol adsorption on silica depends on the preheating temperature of silica. As shown in Fig. 6, the intensity of the silanol band for the silica preheated at 770–

870 K was reduced after ethanol adsorption followed by evacuation at 570 K, whereas the intensity of the band for ethoxyl groups decreased with an increase in preheating temperature. The reduction in intensity of the silanol band is due to ethanol adsorption on the silanol groups because the adsorption causes a reduction in the amount of surface silanols. The decrease in intensity of the band for ethoxyl groups correlates with the surface silanol concentration of the silica sample before adsorption. On the contrary, in the case of the silica preheated at 1070–1270 K, the intensity of the silanol band was strengthened by ethanol adsorption, and that for ethoxyl groups increased with an increase in the preheating temperature, whereas the amount of surface silanol groups decreases with an increase in preheating temperature (see Table 3). Thus, we infer that the sites for dissociative adsorption of ethanol are effectively formed on silica by preheating above ca. 1000 K. It is noteworthy that the catalytic activity of silica correlates to the intensity of ethoxyl groups on silica preheated at 970–1270 K (Fig. 7). The finding suggests that the active sites for the dehydrogenation are the oxygen bridge on which dissociative adsorption of ethanol can take place. This is supported by the results that the catalytic activity of highly dehydrated silica depends on the amount of surface silanols (Fig. 4) because the amount of sil-
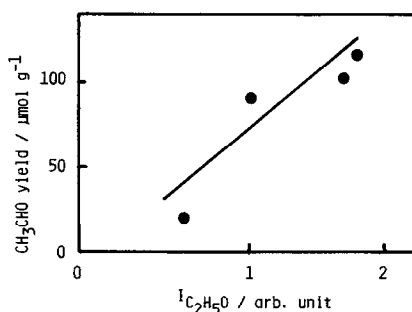


FIG. 7. Relationship between catalytic activity and IR intensity of ethoxyl group for silica preheated at 970–1270 K.
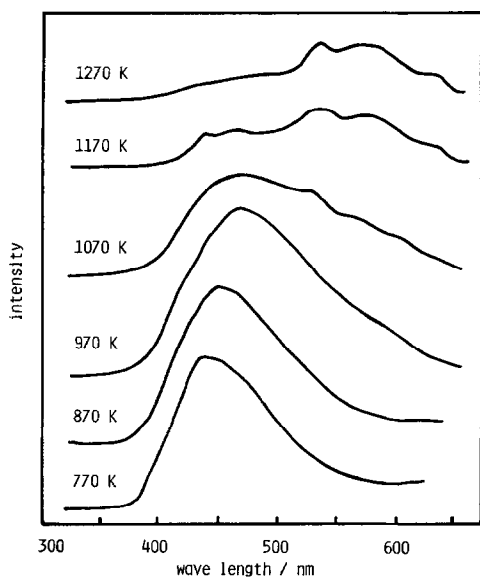
FIG. 8. Phosphorescence spectra of silica preheated at 770–1270 K (emission spectra at 77 K; excitation, 300 nm).

anols correlates to the amount of active oxygen bridge generated by heating.

### Phosphorescence of Silica

It has been recognized that phosphorescence spectroscopy is useful for clarification of surface active sites on oxides (20–22). Figure 8 shows the phosphorescence spectra for the silica samples preheated at 770–1270 K. In the case of a sample preheated at 770 K, a phosphorescence peak was observed at ca. 450 nm, and its life span was found to be 3.3 ms. Except for a discernible peak shift, no marked change was observed in the spectra for the samples preheated at 770–970 K. However, the intensity of the phosphorescence steeply decreased on preheating at 1070–1270 K and new phosphorescence peaks appeared above 500 nm. In the spectrum for the sample preheated at 1270 K, three phosphorescence peaks were observed at ca. 540, 580, and 640 nm, and the life span of the 540-nm phosphorescence was found to be 3.1 ms. The results strongly suggest that the surface structure of silica actually changes at

ca. 1000 K and new sites are formed by preheating above ca. 1000 K.

To assign the sites responsible for the phosphorescence, the phosphorescence spectra of the samples were recorded after adsorption of oxygen or ethanol on the samples preheated at 770 or 1270 K. The results are shown in Fig. 9 (A and B series are emission spectra; the C series shows excitation spectra). Since the phosphorescence above 500 nm appears on the silica preheated above ca. 1000 K and the intensity roughly correlates with the catalytic activity for dehydrogenation, the phosphorescence may be associated with the active sites. In the case of the sample preheated at 1270 K, adsorption of oxygen gave no definitive change in the phosphorescence
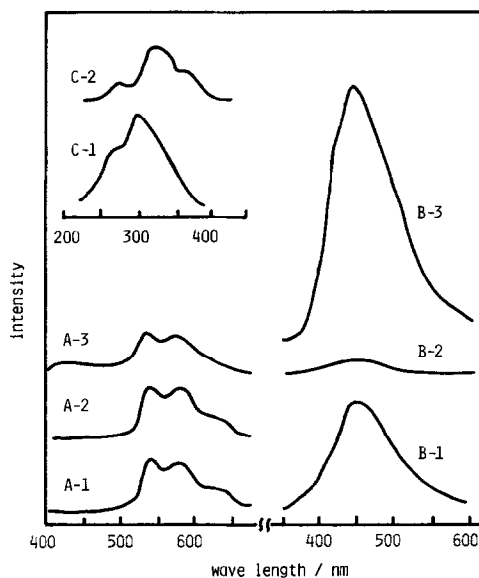


FIG. 9. Phosphorescence spectra of silica after adsorption of oxygen or ethanol. (A-1) emission spectrum at 77 K for silica preheated at 1270 K (excitation, 320 nm); (A-2) after adsorption of oxygen at 77 K; (A-3) after adsorption of ethanol at room temperature followed by evacuation at 570 K; (B-1) emission spectrum at 77 K for silica preheated at 770 K (excitation, 300 nm); (B-2) after adsorption of oxygen at 77 K; (B-3) after adsorption of ethanol at room temperature followed by evacuation at 570 K; (C-1) excitation spectrum for silica preheated at 770 K (emission, 420 nm); (C-2) excitation spectrum for silica preheated at 1270 K (emission, 550 nm).

above 500 nm, but ethanol adsorption discernibly reduced the phosphorescence. In addition, no change in lineshapes was observed in this case (Fig. 9A). On the silica preheated at 1270 K ethanol adsorption sites are probably the active Si–O–Si oxygen bridges which we believe to be the active sites for the dehydrogenation as described in the previous section. Thus, the result for ethanol adsorption strongly suggests that the phosphorescence above 500 nm is associated with the oxygen bridge on which dissociative adsorption of ethanol takes place.

On the other hand, the 450-nm phosphorescence of the silica preheated at 770 K was almost eliminated after adsorption of oxygen at 77 K (the amount of oxygen introduced onto the sample was ca. 10 $\mu$mol); on the contrary, for the sample adsorbing ethanol at room temperature and being evacuated at 570 K, the intensity was much stronger than that for the sample before adsorption (Fig. 9B). No change in lineshapes was observed on these emission and excitation spectra by the adsorption. Observation of phosphorescence of silica suggests that excited triplet states are produced on silica by UV irradiation. Ogata et al. reported that photooxidation of carbon monoxide proceeds on the silica preheated at 723 K under UV irradiation and that $O_3^-$ species are formed on the silica under UV irradiation in the presence of oxygen (23). This suggests that occurrence of charge transfer on the silica by UV irradiation. In the case of metal oxides such as magnesium oxide, an $O^-$ species is also formed on the oxide under UV irradiation caused by charge transfer from oxygen atom to metal atom, and its photoemission is observable (24). Thus, it can be supposed that the phosphorescence at 450 nm is associated with photoactive sites; quenching by oxygen can be accounted for through formation of $O_3^-$ species. As shown in Fig. 8, the phosphorescence peak diminished for the silica sample preheated above ca. 1000 K. As appreciable activity for ethanol dehydrogenation was

observed for samples preheated above ca. 1000 K, the sites responsible for the 450 nm phosphorescence peak are not associated with the active sites.

CONCLUSIONS

Since effective acid–base sites are not formed on highly dehydrated silica, the ethanol dehydrogenation observed here does not proceed on acid–base sites. On the other hand, there is an inverse relationship between the activity of the silica catalyst preheated above ca. 1000 K and the concentration of surface silanols, suggesting that the active sites are the oxygen bridge newly generated by heating above ca. 1000 K. The generation of new sites on highly dehydrated silica was also confirmed by measurement of the phosphorescence of silica. The new sites are probably the oxygen bridges on which dissociative adsorption of ethanol takes place as evidenced by the IR measurement. The results for reaction kinetics suggest that the dehydrogenation proceeds by the Langmuir–Hinshelwood mechanism. Thus, the reaction probably proceeds as

$$C_2H_5OH + Si-O-Si^* \rightleftarrows (Si-OH$$
$$+ Si-OC_2H_5)^* \rightarrow CH_3CHO + H_2$$
$$+ Si-O-Si^*.$$
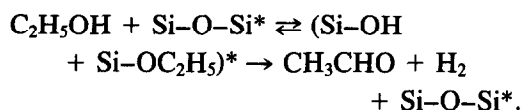
Molecular orbital calculations, reported elsewhere, support the idea that selective dehydrogenation can proceed via this intermediate (25).

REFERENCES

1. Schwab, G.-M. and Schwab-Agallidis, E., J. Amer. Chem. Soc. 71, 1806 (1949).
2. Niiyama, H., and Echigoya, E., Bull. Chem. Soc. Japan 44, 1739 (1971).
3. Kibby, C. L., and Hall, W. K., J. Catal. 29, 144 (1973).
4. Yashima, T., Suzuki, H., and Hara, N., J. Catal. 33, 486 (1974).
5. Wang, G.-W., Hattori, H., and Tanabe, K., Bull. Chem. Soc. Japan 56, 2407 (1983).
6. Parry, E. P., J. Catal. 2, 371 (1963).
7. Tanabe, K., in "Catalysis" (J. R. Anderson and M. Boudart, Eds.), Vol. 2, p. 231. Springer-Verlag, New York, 1981.

8. Malinowski, S., and Szczepańska, S., *J. Catal.* **2**, 310 (1963).

9. Tanaka, K., and Tamaru, K., *Bull. Chem. Soc. Japan* **37**, 1862 (1964).

10. Matsumura, Y., Hashimoto, K., and Yoshida, S., *J. Chem. Soc. Chem. Commun.*, 1987, 1599.

11. Winterbottom, J. M., *in* "Catalysis (Spec. Per. Rept)," Vol. 4, p. 141, Royal Society of Chemistry, London, 1980.

12. Benesi, H. A., and Winquist, B. H. C., *Adv. Catal. Relat. Subjects* **27**, 97 (1978).

13. Tanabe, K., "Solid Acids and Bases." Kodansha/Academic Press, Tokyo/New York, 1970.

14. Little, L. H., "Infrared Spectra of Adsorbed Species." Academic Press, New York, 1966.

15. Gregg, S. J., and Sing, K. S. W., "Adsorption, Surface Area and Porosity." Academic Press, New York, 1967.

16. Kiselev, A. V., *Disc. Faraday Soc.* **40**, 205 (1965).

17. Kondo, S., Muroya, M., and Fujii, K., *Bull. Chem. Soc. Japan* **47**, 553 (1974).

18. Morterra, C., and Low, M. J. D., *J. Catal.* **28**, 265 (1973).

19. Morrow, B. A., and Cody, I. A., *J. Phys. Chem.* **79**, 761 (1975).

20. Gritskov, A. M., Shvets, V. A., and Kazansky, V. B., *Kinet. Katal.* **15**, 1257 (1974).

21. Anpo, M., Tanahashi, I., and Kubokawa, Y., *J. Phys. Chem.* **84**, 3440 (1980).

22. Anpo, M., Nakaya, H., Kodama, S., Kubokawa, Y., Domen, K., and Onishi, T., *J. Phys. Chem.* **90**, 1633 (1986).

23. Ogata, A., Kazusaka, A., and Enyo, M., *J. Phys. Chem.* **90**, 5201 (1986).

24. Che, M., and Tench, A. J., *Adv. Catal. Relat. Subjects* **31**, 77 (1982).

25. Matsumura, Y., Hashimoto, K., and Yoshida, S., *Kagaku to Kogyo (Osaka)*, in press.