Selective Dehydrogenation of Ethanol over Dehydrated Silica

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The selective dehydrogenation of ethanol to acetaldehyde proceeds at temperatures above *ca.* 550 K over highly dehydrated silica.

In terms of acid–base properties, the surface of silica is almost neutral.[1–3] Generally, the sites which are considered to be active for catalytic dehydrogenation of alcohols are basic, and the low activity of silica for this reaction was accounted for by the lack of basic sites on the silica surface.[4–8] However, we now report that ethanol is dehydrogenated over silica which had been dehydrated by heating to at least 870 K.

Silica was prepared from ethyl orthosilicate in order to obtain pure samples. Ethyl orthosilicate purified by distillation was hydrolysed to silica gel in 5 M nitric acid solution (guaranteed reagent grade). The hydrogel obtained was dried at *ca.* 400 K in air and washed with water, and then heated at 670 K in air for 5 h. Analysis by atomic absorption spectroscopy showed that the observable impurities were only nickel (4 p.p.m.) and sodium (4 p.p.m.). The silica was heated *in vacuo* at 770—1270 K for 1 h and the surface area was measured *in situ* by the Brunauer–Emmett–Teller (B.E.T.) method using nitrogen physisorption at 77 K. Adsorption of ammonia or carbon dioxide on the sample was measured by a constant volume method. I.r. spectra were recorded with a Nicolet 5DX Fourier-transform spectrometer. The silica samples (0.01 g) were pressed into self-supporting wafers and placed in an i.r. cell which could be heated under reduced pressure *in situ*. The samples were heated *in vacuo* at 770—1270 K for 1 h before the measurements at room temperature. Ethanol conversion was carried out in a pulse microcatalytic reactor. The silica sample (0.050 g) was sandwiched with silica wool (*ca.* 0.01 g) in a quartz reaction tube of 6 mm inner diameter. The catalyst bed was preheated at 770—1270 K for 1 h in a flow of helium carrier gas and then a pulse of 1×10^{-9} m^3 of ethanol was injected to the catalyst bed. Anhydrous ethanol was obtained by refluxing over magnesium just before the reaction. During the preheating, desorption of water from the silica was observed and the amount was measured. After the sample had been heated at 1270 K *in vacuo* for 1 h the *X*-ray powder diffraction pattern was measured; this was the same as that of the sample without preheating.

Ethanol conversion was not observed over the silica sample preheated at 770 K. However, acetaldehyde was produced over the catalyst preheated to at least 820 K. The catalytic activity for ethanol conversion increased steeply on preheating at temperatures above 1000 K, reaching a constant value (Table 1). Small amounts of ethylene, water, and C_1 compounds were also produced. Ethanol dehydrogenation proceeds at reaction temperatures above *ca.* 550 K over the sample preheated at 1170 K. It was confirmed that the

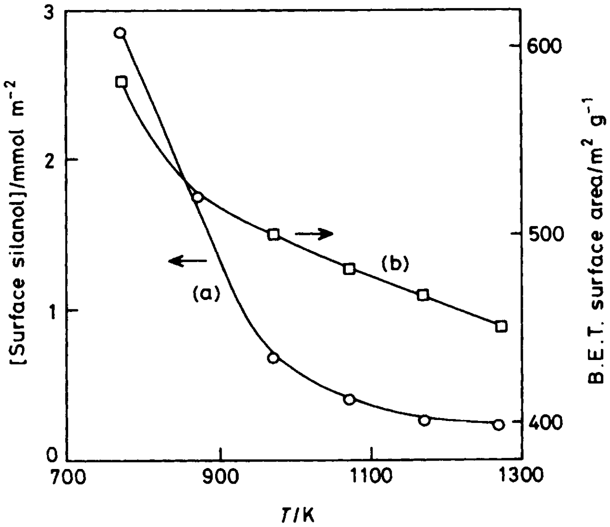

Figure 1. Dependence on temperature of preheating of (a) surface silanol concentration and (b) B.E.T. surface area of silica.

Table 1. Ethanol conversion over dehydrated silica.

Run	Preheating temp./K	Reaction temp./K	Selectivity/% C_1	C_2H_4	MeCHO	Conversion of EtOH/%
1	770	670	—	—	—	0
2	870	670	0	8	92	2
3	970	670	1	3	96	6
4	1070	670	1	2	97	27
5	1170	670	2	2	96	35
6[a]	1170	670	2	2	96	26
7	1270	670	2	2	96	31
8	1170	520	—	—	—	0
9	1170	570	0	0	100	4
10	1170	620	1	1	98	16

[a] Just before the reaction, the catalyst was injected with 1×10^{-9} m^3 of H_2O.

contribution of silica wool (packing material) was very small or negligible; the results in Table 1 have been corrected for the contribution of silica wool.

Only reversible adsorption of ammonia and carbon dioxide was observed at room temperature for all the samples investigated. Therefore, we conclude that acid–base sites do not exist in the silica sample,[7] and the dehydrogenation over silica does not result from acid–base sites. Figure 1 shows the surface silanol concentration and surface area of the silica as a function of preheating temperature; the silanol concentration was estimated from the intensity of the silanol i.r. absorption band (3400—3800 cm^{-1}) of the silica samples. Kondo *et al.* reported that there is a good linear relationship between the intensity and the amount of silanol determined by gravimetry.[9] In the case of the sample injected with water just before the reaction, a decrease in the catalytic activity was observed (run 6 in Table 1). The silanol concentration of 0.44 $\mu mol\ m^{-2}$ was based on i.r. measurements for the silica sample preheated at 1170 K followed by water adsorption at 670 K. The same amount of silanol is expected to exist in the silica used in run 6. The silanol concentration is almost the same as that of the sample preheated at 1070 K (see Figure 1) and the catalytic activity is also almost the same (*cf.* run 4 and 6 in Table 1). These results suggest that the catalytic activity may be correlated with the surface silanol concentration. Thus, we believe that the generation of the catalytic activity of silica is caused by elimination of hydroxyl groups on silica surface.

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