Properties of Acid Sites Generated on Sol–Gel Derived Zn$_2$SiO$_4$

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ZnO–SiO$_2$ binary oxides prepared by the sol–gel method were calcined at various temperatures in order to reveal the relations between the surface properties as an acid–base catalyst and the bulk structures measured by X-ray diffraction. It was found that the acid amount and strength as well as the catalytic activity increased remarkably when the Zn$_2$SiO$_4$ phase was formed exclusively by the reactions between ZnO and SiO$_2$ particles at 1173 K. Changes in the bulk structures were suggested to affect the surface properties of the oxide particles.

Binary oxides, such as SiO$_2$–Al$_2$O$_3$ and TiO$_2$–SiO$_2$, have been widely applied as acid catalysts for some catalytic reactions because of their strong acid sites on the surfaces.[1,2] The ZnO–SiO$_2$ binary oxides have also been reported to have Lewis acid sites, though ZnO or SiO$_2$ have shown very little acidity.[3] The binary oxides with such acid sites have been observed to be almost non-crystalline or micro-crystalline structures by X-ray diffraction measurements.[2] Therefore, it has been accepted that the acid sites on the binary oxides are attributed to the charge imbalance locally formed by structural imperfections on the surfaces.[4] The authors have also reported that the acid properties of pure metal oxides such as TiO$_2$ and ZrO$_2$ depend on the crystalline sizes.[5–7] The amount of surface imperfections increases with a decrease of particle sizes.

The charge imbalances attributed to the imperfections of the surface structures appear even when the bulk structures of the binary oxides are transformed by the solid-phase reactions through calcination at high temperatures. Notably, finely divided particles are readily prepared by sol–gel processes so that the solid reactions occur with the result that the complex oxides are formed at much lower calcination temperatures than those formed by traditional solid-phase reaction processes.[8,9]

It is already known that the binary oxides composed of ZnO and SiO$_2$ are provided with the Zn$_2$SiO$_4$ complex oxide by calcination at about 1173 K when the binary oxide is prepared by the sol–gel method.[8] The purpose of the present work is to evaluate the effects of Zn$_2$SiO$_4$ formation on the surface acidities and the catalytic properties of the binary oxides.

Experimental

Preparation of Binary Oxides. Binary oxides consisting of ZnO and SiO$_2$ were prepared by the sol–gel method, where zinc nitrate (Zn(NO$_3$)$_2$·6H$_2$O, Wako Chemical Co.) and ethyl orthosilicate (Si(OC$_2$H$_5$)$_4$, Kishida Chemical Co.) were used as raw materials. 0.2 mol of zinc nitrate and 0.1 mol of ethyl orthosilicate were dissolved in 180 cm^3 of distilled water and drops of nitric acid were added to the solution until the pH was adjusted to 4.

Then, the solution was refluxed for hydrolysis at 353 K while stirring until the whole solution became viscous and gel-like. The gel-like substance obtained was evacuated under reduced pressure and then dried in an oven at 383 K for 12 h, followed by calcinations at 773–1373 K in air for 3 h. The molar ratio of ZnO/SiO$_2$ in the binary oxides prepared was set to be 2/1.

The structural differences in the binary oxides calcined at various temperatures were observed by X-ray diffraction (Rigaku Denki Co., RINT-1200), operated at 30 kV with a filament current of 20 mA for Cu Kα radiations. The specific surface areas were measured by the BET method using nitrogen at 77 K.

Measurements of Acidity and Basicity. The acid amounts on the binary oxides were estimated from the amounts of ammonia gas adsorbed at 423 K, using 0.50–1.05 g of sample powders treated by flowing He gas at 673 K for 1 h.[5] A given amount of ammonia was iteratively injected into the He carrier gas, which was introduced to the sample at 423 K until adsorption of ammonia was no longer observed. The temperature programmed desorption (TPD) of ammonia on the binary oxides was carried out using a He purge with a flow rate of 100 mL min^{-1} and a temperature rising rate of 10 K min^{-1}. The desorbed gas was detected by the TCD detector of a gas chromatograph. In order to observe the exact profile of the ammonia gas desorbed from the sample surface, the differential spectrum was obtained by removing the blank spectrum from the desorption spectrum.[7] Measurements of the base amount and a TPD were also performed using carbon dioxide instead of ammonia for the acidity measurements in the same way.

Isomerization of 1-Butene. The catalytic activities of the binary oxides for the isomerization of 1-butene were measured in order to characterize the acid sites generated on the binary oxides. The catalytic reactions were conducted in a closed circulating reactor made of glass, in which 0.1 g of the binary oxides were packed, at temperatures ranging from 483 to 583 K. The binary oxides as the catalysts were recalcined at 673 K in air for 0.5 h, followed by treatment under vacuum for 1 h at the same temperature prior to the reactions. The initial pressure of 1-butene introduced to the catalyst was about 110 Torr (14.7 × 10^3 Pa) and the products were *cis*- and *trans*-2-butene, as analyzed by a gas chromatograph (Hitachi Co., GC-163) with an FID detector using
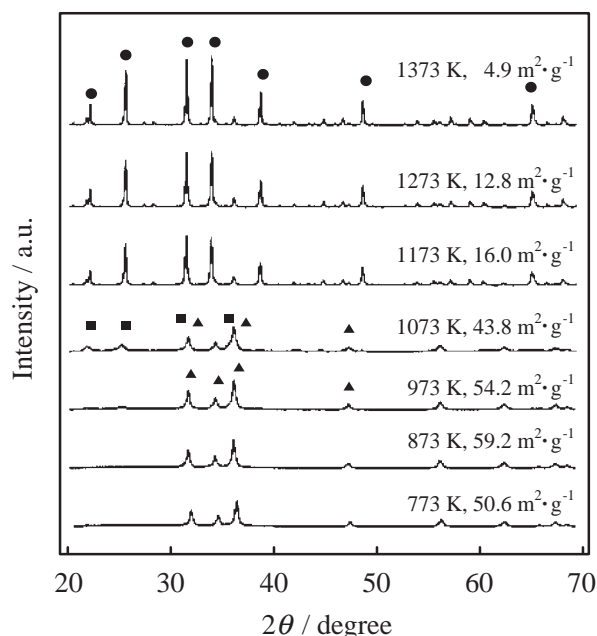
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Fig. 1.   X-ray diffraction spectra and surface areas of ZnO–SiO$_2$ calcined at various temperatures. ●: Zn$_2$SiO$_4$ (willemite), ■: β-Zn$_2$SiO$_4$, ▲: ZnO.

a column packed with Unicarbon A-400. The catalytic activities were calculated by the isomerization rates per unit weight or surface area of the catalysts.

Results and Discussion

The X-ray diffraction spectra of the ZnO–SiO$_2$ binary oxides prepared by calcination at various temperatures are shown in Fig. 1, with the specific surface areas measured by the BET method. The diffraction patterns assigned to the ZnO phase were observed only at temperatures lower than 1073 K, indicating that the binary oxides were composed of ZnO crystalline phase and non-crystalline SiO$_2$ phase. β-Zn$_2$SiO$_4$ crystalline phase patterns appeared slightly in the binary oxides calcined at 1073 K, the Zn$_2$SiO$_4$ (willemite) phase dominating above 1173 K. The sudden decrease in specific surface areas was also recognized at the calcination temperature of 1173 K. These results indicate that the binary oxides changed from a mixture of ZnO and SiO$_2$ particles to Zn$_2$SiO$_4$ complex oxides at about 1173 K.

In general, the phase diagram[10] shows that the Zn$_2$SiO$_4$ phase is formed by the solid-phase reaction, which occurs at very high calcining temperatures of around 1573 K. However, sol–gel derived Zn$_2$SiO$_4$ is proliferated by calcination at lower temperatures as shown in Fig. 1. Because sol–gel technique readily offers finely divided particles as well as homogeneously dispersed particles, the Zn$_2$SiO$_4$ phase is expected to be formed at temperatures lower than 1573 K.[8]

Figure 2 shows the amounts of acid sites and base sites on the unit surface areas of ZnO–SiO$_2$ binary oxides obtained by calcination at various temperatures. Very large amounts of acid sites were observed on the binary oxides calcined in the range of about 1123 to 1223 K, and the maximum acid amount peak was located at a calcination temperature of 1173 K. On the other hand, the base amounts tended to increase slightly
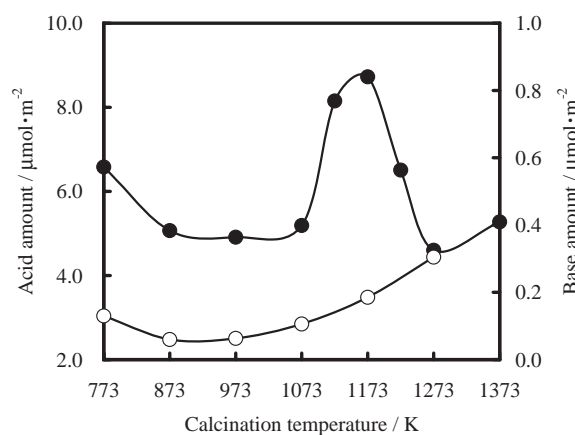

Fig. 2.   Changes in the acid and base amounts of ZnO–SiO$_2$ with calcination temperature. ●: Acid amount, ○: base amount.
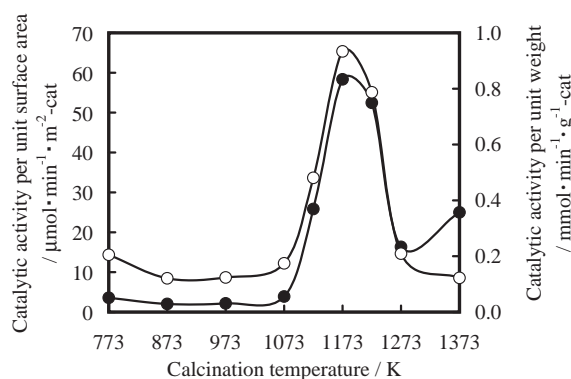

Fig. 3.   Changes in the catalytic activities per unit surface areas (●) and unit weights (○) of ZnO–SiO$_2$ with calcination temperature. The catalytic reactions were carried out at 523 K.

with an increase in calcination temperature. However, only small base amounts less than 1/10 of the acid amount were measured on all the samples. That means a relatively small number of base sites are present on the binary oxides. These results indicate that a lot of acid sites are generated on the surface of the ZnO–SiO$_2$ sample calcined at around 1173 K, at which temperature the Zn$_2$SiO$_4$ phase is clearly formed from the ZnO and SiO$_2$ particles as shown in Fig. 1, but the base sites are scarcely created even if the samples are calcined at various temperatures.

The effect of calcination temperature on the catalytic activities of the binary oxides is shown in Fig. 3. The activity for 1-butene isomerization is known to be increased by the existence of acid sites and/or base sites on the catalysts.[11] Therefore, the catalytic reaction has often been utilized for the estimation of surface acidity or basicity. As shown in Fig. 3, noticeably higher catalytic activities were observed when the binary oxides were calcined in the range of about 1123 to 1223 K, and the maximum activity was also obtained at a calcination temperature of 1173 K. This tendency is in accordance with the trend for change in acid amounts with calcination temperature in Fig. 2. It seems that the acid sites generated on the Zn$_2$SiO$_4$ surface mainly serve as the active sites for the reaction.
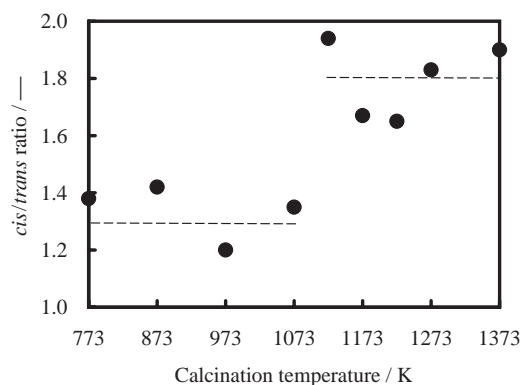
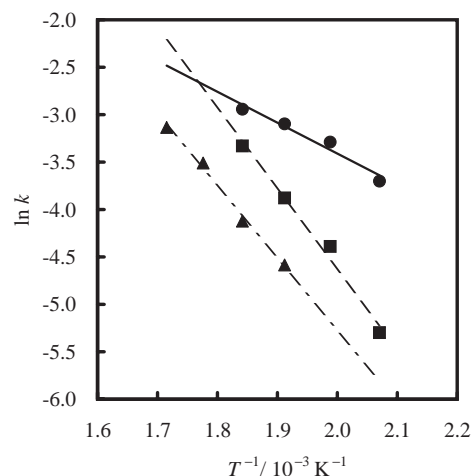Fig. 4. The ratios of *cis*-2-butene to *trans*-2-butene from 1-butene on ZnO–SiO₂ calcined at various temperatures.

Fig. 5. Arrhenius plots for 1-butene isomerizations on ZnO–SiO₂ calcined at various temperatures. ■: 773 K, ▲: 973 K, and ●: 1173 K.

Table 1. Activation Energies of 1-Butene Isomerizations on ZnO–SiO₂ Calcined at Various Temperatures, Catalytic Activities, and the Surface Areas

Calcination temperature /K	XRD pattern	Surface area /$m^2 \, g^{-1}$	Catalytic activity /$\mu mol \, min^{-1} \, m^{-2}$	Activation energy /$kJ \, mol^{-1}$
773	ZnO	50.6	3.57	70.2
973	ZnO	54.2	2.17	62.9
1173	Zn₂SiO₄	16.0	58.3	27.1

It is also known that the ratios of *cis*-2-butene to *trans*-2-butene of the reaction products from 1-butene are affected by the properties of the active sites on the catalysts. In Fig. 4, the *cis*/*trans* ratios of the 1-butene isomerizations on the binary oxides calcined at various temperatures are summarized. The *cis*/*trans* ratios were estimated by extrapolation to 0% conversion in the 1-butene isomarization. The ratios were also identified to depend slightly upon the calcination temperatures; the *cis*/*trans* ratios were 1.2–1.4 at temperatures lower than 1073 K, but were 1.7–2.0 above 1123 K. It is suggested that the properties of the acid sites, which act as the active sites on the Zn₂SiO₄ particles, differ between those of the mixture of ZnO and SiO₂ particles and Zn₂SiO₄ particles. Note that few basic sites were on the surface of the samples since the *cis*/*trans* ratios were always between 1 and 2.[12]

Moreover, the activation energies of the isomerizations were obtained by Arrhenius plots in order to inspect variations in the acidic properties of binary oxides having different structures. Figure 5 shows Arrhenius plots for the 1-butene isomerizations catalyzed by the binary oxides. The binary oxides calcined at 773, 973, and 1173 K were used for the reactions as catalysts. The activation energies calculated from the plots are listed in Table 1 along with the catalytic activities and the surface areas. Although the activation energies of the isomerizations on the binary oxides calcined at 773 and 973 K were 70.2 and 62.9 kJ mol^{-1}, respectively, a lower value of 27.1 kJ mol^{-1} was observed when the binary oxide was calcined at 1173 K. The activation energies are affected by the properties of acid sites acting as active sites on the catalysts. Consequently, the lowering of activation energy indicates that
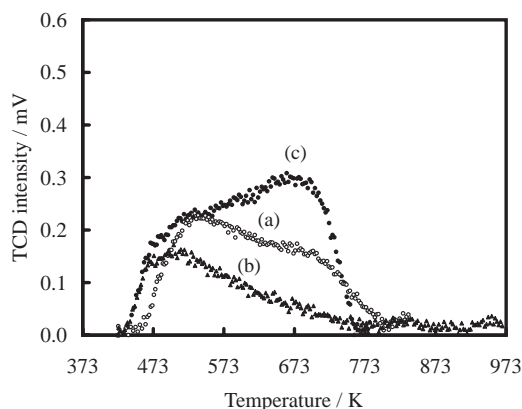
Fig. 6. NH₃–TPD spectra of ZnO–SiO₂ calcined at various temperatures. The amount of samples was adjusted to make the same surface area in all samples. (a): 773 K, (b): 973 K, and (c): 1173 K.

the strength of the newly generated acid sites on the Zn₂SiO₄ complex oxide obtained at 1173 K is comparatively strong.

The acid strength of the binary oxides was also confirmed by the measurements of the ammonia TPD spectra. Figure 6 shows the TPD spectra of ammonia adsorbed on typical samples calcined at the three different temperatures of 773, 973, and 1173 K. The quantity of each sample used for the TPD measurement was adjusted to be the same surface area in order to compensate for the differences in surface area. On the binary oxide consisting of Zn₂SiO₄ particles obtained by calcination at 1173 K, two large desorption peaks were observed at

around 673 and 513 K, indicating that two types of acid sites mainly exist on the surface of Zn_2SiO_4. The peak observed at the higher temperature of 673 K results from the presence of many strong acid sites on the binary oxide sample. The other peak around 513 K is caused by the existence of weaker acid sites. However, the binary oxides calcined at 773 K as well as at 973 K have major peaks at lower temperature; most of the acid sites have only weak strengths on the binary oxides consisting of ZnO and SiO_2 particles. These results also indicate that the appreciable amount of strong acid sites is generated on the surface when the sol–gel derived Zn_2SiO_4 is formed by calcination at around 1173 K.

Sol–gel derived Zn_2SiO_4 has been widely used as a host material for a green phosphor in electroluminescence devices.[13,14] The structures of the ZnO–SiO_2 binary oxide prepared by the sol–gel method have already been reported in earlier literature to be transformed from the mixed phase of ZnO and SiO_2 to the Zn_2SiO_4 phase by the solid-state reactions at around 1173 K.[8] The transformation by the solid-state reaction has also been confirmed in this work (Fig. 1). As mentioned previously, the finely divided particles and the homogeneously dispersed particles are readily prepared by sol–gel methods, so that the solid-state reactions between the component oxides can occur at low temperatures. The Zn_2SiO_4 particles thus formed at low temperatures have also been reported to be nano-sized particles.[15,16]

We have already reported that Lewis acid sites are generated on the surface of nano-sized metal oxide particles because the amount of structural imperfections on the surface increases with a decrease in particle size.[5] Since the sol–gel derived Zn_2SiO_4, which is formed at low temperatures, consists of very small-sized particles, strong acid sites may be generated on the surface. However, it is also expected that the surface imperfections are created together with the solid reactions between different metal oxide particles. Thus, conformational changes of the oxide particles are bound to have some influence on the surface properties, such as acidity or basicity. As shown in Figs. 2, 3, and 6, when the sol–gel derived Zn_2SiO_4 was formed solely by the solid reaction of ZnO and SiO_2 particles at around 1173 K, very high catalytic activities and large amounts of strong acid sites were observed. These indicate that the change of bulk structures results in an increase in the surface imperfections acting as strong Lewis acid sites and in turn, an improvement in catalytic activity.

Incidentally, in the case of calcination at above 1273 K, the considerable acid sites disappeared from the surface of the Zn_2SiO_4 complex oxides. The particles grow to be larger according to the increase in calcination temperature. As shown in Fig. 1, the diffraction peaks assigned to the Zn_2SiO_4 phase are observed to strengthen with a rise in calcination temperature, indicating that the particles grow. It can be regarded that the surface imperfections, which contribute to the acid sites, rapidly decrease with the crystalline growth of Zn_2SiO_4 at higher temperatures.

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