Acidic Properties and Catalytic Activities of Sol–gel Derived Zn_2SiO_4

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The ZnO–SiO_2 binary oxides prepared by sol–gel method were calcined at various temperatures in order to reveal the relations between the surface properties as acid catalysts and the bulk structures. It was found that the catalytic activities and the acid amounts remarkably increased when the Zn_2SiO_4 phase was just formed by the calcination at 1173 K.

Binary oxides, such as SiO_2–Al_2O_3 and TiO_2–SiO_2, have been widely applied as acid catalysts for some catalytic reactions because they have strong acid sites on the surfaces.[1,2] The ZnO–SiO_2 binary oxides have been also reported to have Lewis acid sites though ZnO or SiO_2 showed little acidities.[3] The binary oxides with such acid sites have been observed to be almost noncrystalline or microcrystalline by X-ray diffraction measurements.[2] Therefore, the acid sites on the binary oxides have been accepted to be due to the charge imbalance at locally formed structural imperfections on the surface.[4] The authors have also reported that the acid properties on pure metal oxides, such as TiO_2 and ZrO_2, depended on the crystalline sizes.[5] The amounts of the surface imperfections increase with the decreases of the particle sizes.

The charge imbalances attributed the imperfections of the surface structures, however, would appear even when the bulk structures of the binary oxides are transformed by the solid-phase reactions arising out of the calcinations at high temperatures. Especially, the finely divided particles are readily prepared by the sol–gel processes, so that the solid reactions resulting in the complex oxides occur at much lower calcination temperatures than those of the traditional solid phase reaction processes.[6,7]

It has been known that the binary oxides composed of ZnO and SiO_2 provide the Zn_2SiO_4 complex oxide by the calcination at about 1173 K if the binary oxide is prepared by the sol–gel method.[6] The purpose of the present work is to evaluate the effects of the Zn_2SiO_4 formation upon the surface acidities and the catalytic properties of the binary oxides.

The binary oxides consisting of ZnO and SiO_2 were prepared by the sol–gel method, using zinc nitrate ($Zn(NO_3)_2$ $6H_2O$, Wako Chemical Co.) and ethyl orthosilicate ($Si(OC_2H_5)_4$, Kishida Chemical Co.) 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 the solution was refluxed for hydrolysis at 353 K with stirring until a gel-like condition was led. The gel-like object thus obtained was evaporated under the 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 was fixed to 2/1.

In Figure 1 are shown the X-ray diffraction patterns of the ZnO–SiO_2 binary oxides prepared by the calcinations at various temperatures, with the specific surface areas measured by BET method. The diffraction patterns assignable to ZnO phase were only observed at the temperatures lower than 1073 K, indicating that the binary oxides were composed of ZnO crystalline phase and noncrystalline SiO_2 phase. However, the β-Zn_2SiO_4 crystalline phase slightly appeared in the binary oxide once calcined at 1073 K, and then the Zn_2SiO_4 (willemite) phase occupied most above 1173 K. The specific surface areas were also observed to suddenly reduce at 1173 K. These results indicate that the binary oxides change from the mixture of ZnO and SiO_2 particles to the Zn_2SiO_4 complex oxide at about 1173 K.

In general, the phase diagram[8] depicts that the Zn_2SiO_4 phase is formed by the solid-phase reaction, which is caused at very high calcining temperatures around 1573 K. However, the sol–gel derived Zn_2SiO_4 is elaborated by the calcination at the lower temperatures, as shown in Figure 1. Because the sol–gel technique readily offers the finely divided particles as well as the homogeneously dispersed particles, the Zn_2SiO_4 phase must be formed at the temperature lower than 1573 K.[6]

Figure 2 shows the amounts of acid sites on the unit surface area of the ZnO–SiO_2 binary oxides obtained by the calcinations at various temperatures. The acid amounts were estimated from the amounts of ammonia gas adsorbed at 423 K on the samples which are pretreated in flowing He gas at 673 K for 1 h.[5] The maximum acid amount was observed with the calcina-

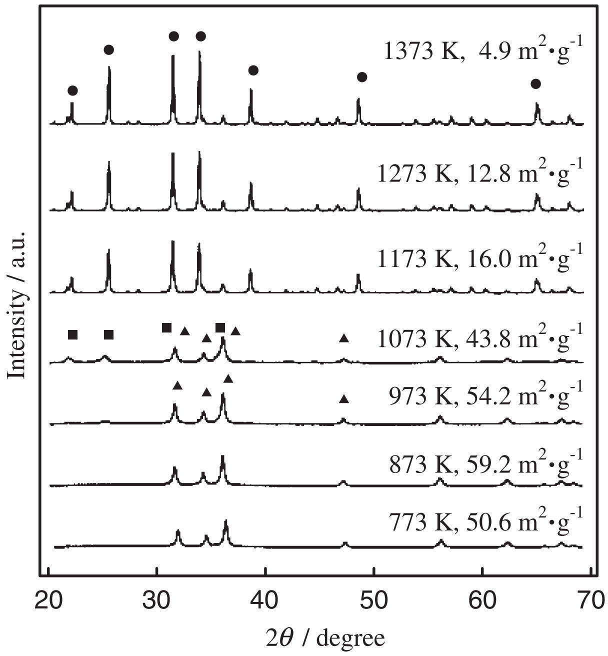

Figure 1. X-ray diffraction patterns and surface areas of ZnO–SiO_2 calcined at various temperatures. ●: Zn_2SiO_4(willemite), ■: β-Zn_2SiO_4, ▲: ZnO.

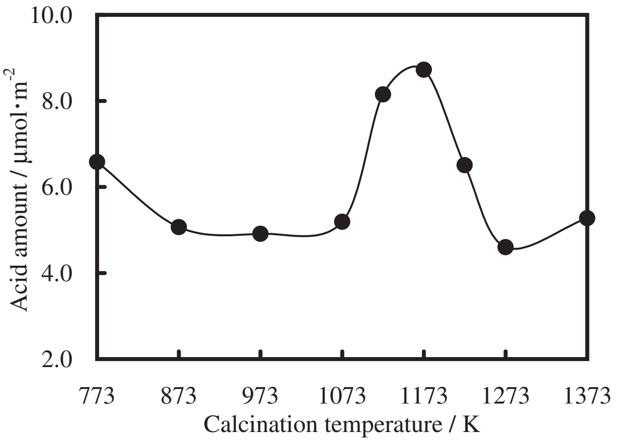

Figure 2. Change in the acid amount of ZnO–SiO_2 with the calcination temperature.

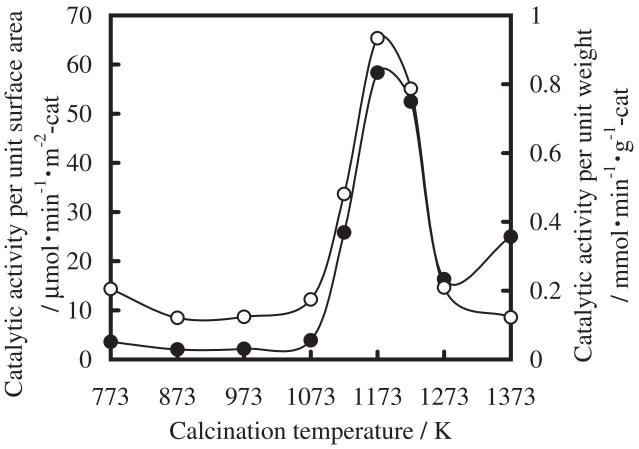

Figure 3. Changes in the catalytic activities per unit surface area (●) and unit weight (○) of ZnO–SiO_2 with the calcination temperatures.

tion at 1173 K. This indicates that the acid sites are generated on the surface of the ZnO–SiO_2 sample calcined around 1173 K, at which the Zn_2SiO_4 phase is clearly formed, as shown in Figure 1.

The catalytic activities for 1-butene isomerizations on the ZnO–SiO_2 binary oxides as an acid catalyst were measured in order to characterize the acid sites generated on the surfaces. The catalytic reactions were carried out at 523 K, using the closed circulation reactor made of glass, in which 0.1 g of the catalysts was packed. The catalyst samples were recalcined in air for 0.5 h at 673 K and followed by the treatment in vacuo for 1 h at the same temperature prior to the reactions. The catalytic activities were calculated by the isomerization rates per the unit surface area or weight of the catalysts.

The effect of the calcination temperatures on the catalytic activities of the binary oxides is shown in Figure 3. The catalytic activity on the binary oxide calcined at 1173 K was proved to be noticeably higher. This tendency accords with the change in the acid amounts with the calcination temperatures, as shown in Figure 2. The activity for 1-butene isomerization is known to increase by the existence of acid sites on the catalysts.[9] These results also indicate that the quantities of acid sites are generated on the surface when the sol–gel derived Zn_2SiO_4 was formed by the calcination around 1173 K. However, in the case of the calcination above 1273 K, the considerable acid sites disappeared from the surface of the Zn_2SiO_4 complex oxides. The surface imperfections which contribute to the acid sites can be regarded to rapidly decrease with the crystalline growth of the Zn_2SiO_4 at the higher temperatures.

The ratios of *cis*- to *trans*-2-butene of the reaction products were slightly dependent upon the calcination temperature; the cis/trans ratios were 1.2–1.4 at the temperatures lower than 1073 K, but those were 1.7–2.0 above 1123 K. Note that few basic sites were on the surface of the samples since the *cis*/*trans* ratios were always between 1 and 2.[10]

In addition, the activation energies for the isomerizations were obtained by the Arrenius plots. Although the activation energies on the binary oxides calcined at 773 and 973 K were 70.2 and 62.9 kJ·mol^{-1}, respectively, the lower value of 27.1 kJ·mol^{-1} was observed when the binary oxide was calcined at 1173 K. This indicates that the strength of the Lewis acid sites, which newly appear on the Zn_2SiO_4 complex oxide obtained at 1173 K, are comparatively strong.

It have been already reported that the Lewis acid sites are generated on the surface of the finely divided particles because the amounts of the structural imperfections on the surface increase with the decrease in the particle sizes.[5] But the surface imperfections are also expected to be created with the solid reactions between different metal oxide particles. The surface properties will be affected by the changes of the bulk structures. In this work, when the sol–gel derived Zn_2SiO_4 was just formed by the solid reaction of ZnO and SiO_2 particles around 1173 K, very high catalytic activities and large amounts of acid sites were observed.

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