

## 황화합물로 개질된 $ZrO_2$ 의 초강산 성질

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## Superacidic Property of $ZrO_2$ Modified with Sulfur Compounds

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**요 약.**  $ZrO_2$ 의 표면을  $H_2SO_4$ 로 처리하거나  $SO_2$ ,  $H_2S$ ,  $CS_2$ 로 처리한 후 산화시킴으로 개질하였다. 처리된 황화합물의 산화종과 산화상태를 적외선분광법과 X-선광전자분광법으로 조사하였다. 처리된 황화합물을 산화시킨 후에는 사용된 황화합물의 종류에는 관계없이 개질된  $ZrO_2$ 는 모두 강한 산성질을 나타내었다. 개질된  $ZrO_2$ 가 초강산의 성질을 나타내는 것은 가장 높은 산화상태의 황( $SO_4^{2-}$ )에 기인하였다.

**ABSTRACT.**  $ZrO_2$  was modified by treating with  $H_2SO_4$  and by treating with  $SO_2$ ,  $H_2S$ , and  $CS_2$  followed by oxidation. The oxidized species and oxidation state of sulfur compounds were investigated by infrared and X-ray photoelectron spectroscopies. The generation of strong acidity of modified  $ZrO_2$  was independent of the sulfur source after oxidation. The sulfur ( $SO_4^{2-}$ ) in the highest oxidation state was responsible for the superacidic property of the modified  $ZrO_2$ .

### INTRODUCTION

Recently, it has been shown that  $NiO-TiO_2^{1-2}$  and  $NiO-ZrO_2^{3-4}$  modified with sulfate ion is very active for ethylene dimerization even at room temperature. Also,  $ZrO_2$  modified with sulfate ion exhibited high catalytic activity for the acid catalyzed reactions<sup>5-6</sup> like butene isomerization and butane skeletal isomerization. High catalytic activities in the above reactions attributed to the enhanced acidic properties of the modified catalysts, which originated from the inductive effect of S=O bonds of the complex formed by the interaction of oxides with sulfate ion.

However, it is necessary to test whether various

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sulfur compounds like  $H_2S$ ,  $CS_2$ , and  $SO_2$ , as sulfur source are effective for enhancing the acidic property, and to study the relationship between oxidation state of sulfur and acidic property. This paper deals with the influences of sulfur compounds and of the oxygen treatment on the oxidation state of sulfur and the acidic property of modified  $ZrO_2$ . Infrared spectroscopic technique was utilized on the  $ZrO_2$  treated with  $H_2S$ ,  $SO_2$ , and  $CS_2$  followed by oxidation, and XPS measurements were employed to examine the oxidation state of sulfur.

### EXPERIMENTAL

The precipitate of  $Zr(OH)_4$  was obtained by adding aqueous ammonia slowly into an aqueous

solution of zirconium oxychloride at room temperature with stirring until the pH of mother liquor reached about 8. The precipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected, and was dried at room temperature for 12 hr. The dried precipitate was powdered below 100 mesh and then the treatment with sulfate ion was performed by pouring 30ml of 1N  $H_2SO_4$  into 2g of the powdered sample on a filter paper and drying the sample in air. The dry solid powder decomposed in evacuation at  $400^\circ C$  was denoted by a symbol of  $ZrO_2/SO_4^{2-}$ .  $ZrO_2/SO_2-O_2$ ,  $ZrO_2/H_2S-O_2$ , and  $ZrO_2/CS_2-O_2$  were prepared by treating  $Zr(OH)_4$  evacuated at  $350^\circ C$  with 150 torr of  $H_2S$ ,  $CS_2$  and  $SO_2$  respectively, followed by oxidizing them with  $O_2$  at  $400^\circ C$  for 2hr.

The acid strength of the samples was measured qualitatively after the treatments using a series of the Hammett indicators. The sample treated with sulfur compounds followed by oxidation were evacuated in glass tube at  $400^\circ C$  for 1hr. They were cooled to room temperature and filled with dry nitrogen. The color changes of a series of indicators were observed for each sample by the spot test under dry nitrogen.

The infrared spectra were recorded in a heatable gas cell at room temperature using a Bruker FTIR spectrometer. Usually 4mg of sample was mixed with 150mg of KBr and pressed into a disk ( $600\text{ kg/cm}^2$ ). For adsorption experiment,  $Zr(OH)_4$  powder was attached on the both sides of KBr disk by pressing at about  $400\text{ kg/cm}^2$  to prevent the collapse of pure  $Zr(OH)_4$  disk. X-ray photoelectron spectroscopy was performed on a Hitachi 507 photoelectron spectrometer. Binding energies were referenced to the  $C_{1s}$  level at 285.0 eV.

## RESULTS AND DISCUSSION

The infrared spectra of  $ZrO_2$  treated with 1N

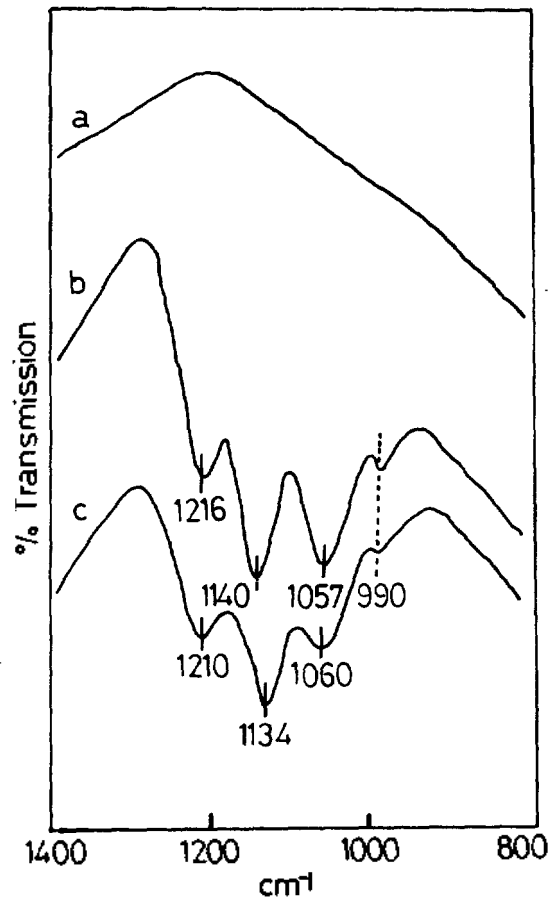


Fig. 1. Infrared spectra of  $ZrO_2$  modified with  $H_2SO_4$ : (a) back ground of  $Zr(OH)_4$  evacuated at  $300^\circ C$ ; (b)  $Zr(OH)_4$  modified with 1N  $H_2SO_4$ ; (c)  $Zr(OH)_4$  modified with 1N  $H_2SO_4$  followed by evacuation at  $400^\circ C$  for 1.5 hr.

$H_2SO_4$  are given in Fig. 1.  $ZrO_2/SO_4^{2-}$  showed infrared absorption bands at  $1216\sim 1210$ ,  $1134\sim 1140$ ,  $1057\sim 1060$ , and  $990\text{ cm}^{-1}$  which are assigned to the bidentate sulfate ion<sup>7</sup> coordinated to  $Zr^{+4}$ . The  $\nu$  SO spectra from the adsorbed sulfate in the  $\nu_1$  and  $\nu_3$  frequency region ( $900\sim 1400\text{ cm}^{-1}$ ) support a species of reduced  $C_{2v}$  symmetry with four bands<sup>8</sup> arising from  $\nu_1$  and splitting of the triply degenerate  $\nu_3$  vibration. Even after evacuation at  $400^\circ C$  for 1.5 hr, strong absorption bands of sulfate ion are left to indicate a very strong interaction between sulfate

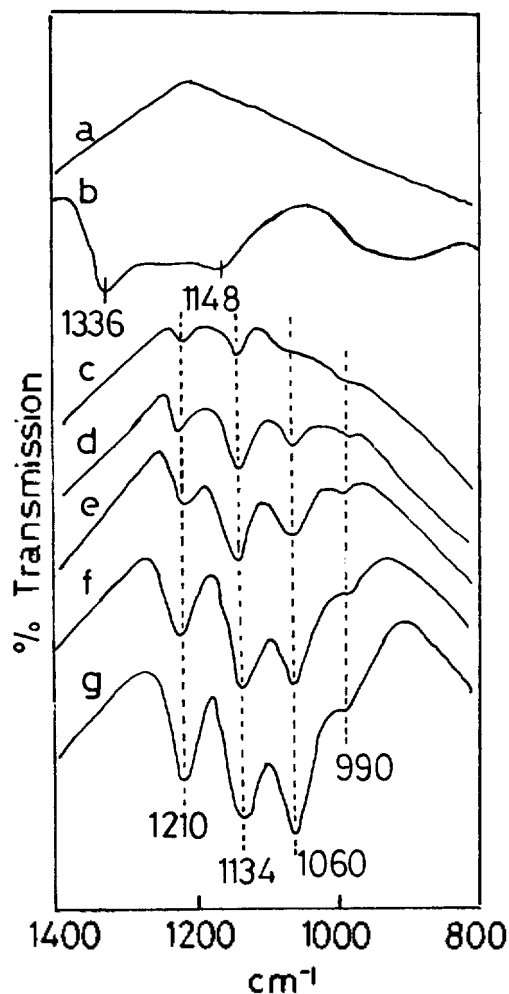


Fig. 2. Infrared spectral changes of  $ZrO_2$  modified with  $SO_2$  followed by oxidation at  $400^\circ C$ : (a) background of  $Zr(OH)_4$  evacuated at  $350^\circ C$ ; (b) exposed to 150 torr  $SO_2$  at room temperature; after evacuation at room temperature, (b) sample was oxidized with  $O_2$  at  $400^\circ C$  for 10 min (c), 20 min (d), 40 min (e), 1 hr (f), and 2 hr (g).

ion and  $ZrO_2$ . In fact, a loss of sulfur as gaseous  $SO_3$  above  $700^\circ C$  was confirmed by DTA-TG measurement<sup>9</sup>.

The adsorption of  $SO_2$  (150 torr) at room temperature on  $Zr(OH)_4$  evacuated at  $350^\circ C$  gave the bands at 1336 and  $1148\text{ cm}^{-1}$ , and a broad band at  $1000\text{--}850\text{ cm}^{-1}$  (Fig. 2). Since the bands

at  $1336$  and  $1148\text{ cm}^{-1}$  disappeared after evacuation at room temperature, these two bands can be ascribed to a weakly bound physically adsorbed species and can be assigned to the antisymmetric and symmetric S-O stretching vibrations.<sup>10</sup> A broad band at  $1000\text{--}850\text{ cm}^{-1}$  are assigned to the stretching frequencies of  $SO_3^{2-}$  species. Oxygen-bonded sulfite species<sup>7</sup> such as  $Tl_2[Cu(SO_3)_2]$  give  $902$  and  $862\text{ cm}^{-1}$  ( $\nu_3$ ) and  $989\text{ cm}^{-1}$  ( $\nu_1$ ) bands. The successive oxidation with  $O_2$  at  $400^\circ C$  gave new bands at 1210, 1134, 1060, and  $990\text{ cm}^{-1}$  whose intensities increased with the oxidation time as shown in Fig. 2. These bands in the shape and absorption position are very similar to those of  $ZrO_2/SO_4^{2-}$  in Fig. 1, indicating the formation of  $SO_4^{2-}$  species from the adsorbed  $SO_2$  species due to the oxidation process.

Similar oxidation experiments were performed using other sulfur compounds,  $H_2S$  and  $CS_2$ . Fig. 3. summarizes the spectral changes after the oxidation process at  $400^\circ C$  for 2 hr. The infrared spectral patterns of  $ZrO_2/SO_2\text{-}O_2$ ,  $ZrO_2/H_2S\text{-}O_2$ , and  $ZrO_2/CS_2\text{-}O_2$  in the region of  $900\text{--}1400\text{ cm}^{-1}$  are almost the same as that of  $ZrO_2/SO_4^{2-}$ . These results clearly indicate that the introduction of sulfur from  $SO_2$ ,  $H_2S$ , and  $CS_2$  leads to the formation of  $SO_4^{2-}$  species after the complete oxidation, regardless of the source of sulfur compounds.

For the sample treated with  $H_2S$ ,  $SO_2$ , and  $CS_2$  followed by oxidizing them with  $O_2$ , in view of infrared spectral results, the oxidation state of sulfur is considered to become the highest oxidation state,  $S^{+6}$  of  $SO_4^{2-}$ . To get more information about the oxidation state of sulfur, X-ray photoelectron spectroscopic investigation were performed. Fig. 4. shows the X-ray photoelectron spectra for the samples treated with sulfur compounds followed by oxidation. As expected, all samples gave the signal<sup>11</sup> attributed

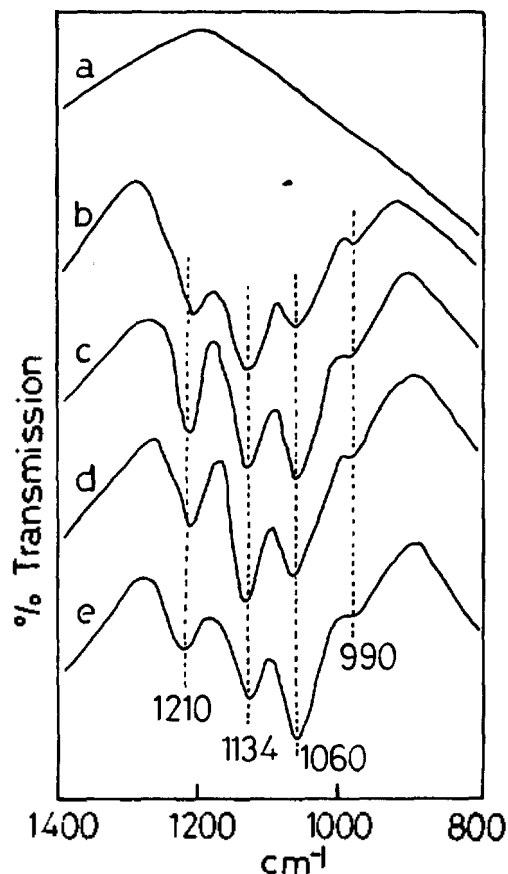


Fig. 3. Infrared spectra of ZrO<sub>2</sub> modified with sulfur compounds. (a) back ground of Zr(OH)<sub>4</sub> evacuated at 350 °C; (b) ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>; (c) ZrO<sub>2</sub>/SO<sub>2</sub>-O<sub>2</sub>; (d) ZrO<sub>2</sub>/H<sub>2</sub>S-O<sub>2</sub>; (e) ZrO<sub>2</sub>/CS<sub>2</sub>-O<sub>2</sub>.

to S<sup>+6</sup>. That is, the oxidation of all samples by O<sub>2</sub> at 400 °C resulted in oxidation to S<sup>+6</sup> state. The S<sub>2p</sub> binding energy of S<sup>+6</sup> was 168.8 eV referenced to the C<sub>1s</sub> level at 285.0 eV. However, ZrO<sub>2</sub>/H<sub>2</sub>S-O<sub>2</sub> and ZrO<sub>2</sub>/CS<sub>2</sub>-O<sub>2</sub> gave the weak S<sub>2p</sub> signal of S<sup>-2</sup> (Binding energy=161.5 eV).

It is interesting to examine the acid properties of ZrO<sub>2</sub> modified with sulfur compounds. It has been established that Brönsted and Lewis acid sites are distinguishable by infrared spectra of adsorbed pyridine<sup>12</sup>. Fig. 5. shows the infrared spectra of pyridine adsorbed on ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>. Both the pyridinium ion band at 1543cm<sup>-1</sup> and

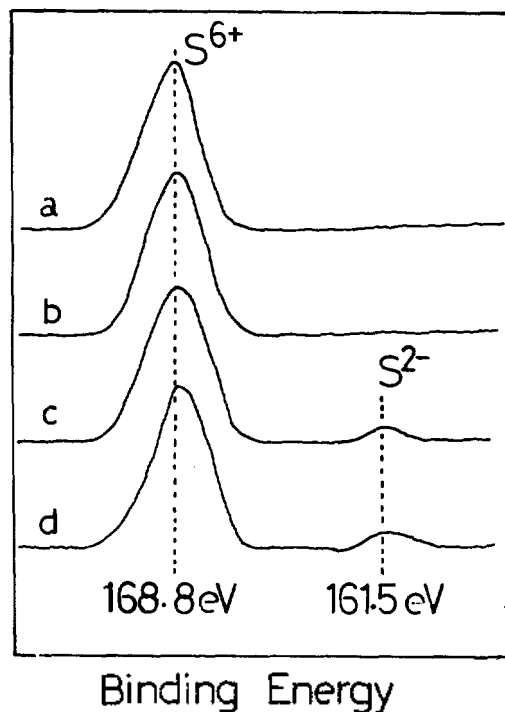


Fig. 4. Sulfur XPS spectra of ZrO<sub>2</sub> modified with sulfur compounds: (a) ZrO<sub>2</sub>/SO<sub>4</sub><sup>2-</sup>; (b) ZrO<sub>2</sub>/SO<sub>2</sub>-O<sub>2</sub>; (c) ZrO<sub>2</sub>/H<sub>2</sub>S-O<sub>2</sub>; (d) ZrO<sub>2</sub>/CS<sub>2</sub>-O<sub>2</sub>.

the coordinated pyridine band at 1450 cm<sup>-1</sup> are found with the sample evacuated at 300 °C, to indicate the presence of both Lewis and Brönsted acids. Other samples, ZrO<sub>2</sub>/SO<sub>2</sub>-O<sub>2</sub>, ZrO<sub>2</sub>/H<sub>2</sub>S-O<sub>2</sub>, and ZrO<sub>2</sub>/CS<sub>2</sub>-O<sub>2</sub> also showed similar infrared absorption bands.

The acid strength of the samples treated with sulfur compounds was examined by a color change method using Hammett indicators<sup>13</sup>, when a powdered sample was added to an indicator dissolved in dried benzene. The results are listed in Table 1. In this table, + means that the color of base form was changed to that of the conjugated acid form. Zirconium oxide prepared by evacuating zirconium hydroxide at 400 °C has the acid strength of H<sub>0</sub> ≤ -3.0. However, the acid strength of the other samples treated with sulfur compounds followed by oxi-

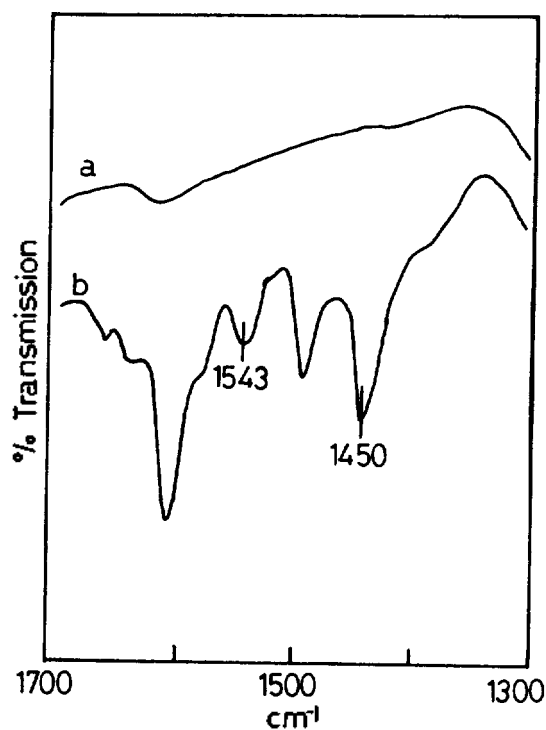


Fig. 5. Infrared spectra of pyridine adsorbed on  $ZrO_2/SO_4^{2-}$ : (a) back ground of  $ZrO_2/SO_4^{2-}$  after evacuation at  $300^\circ C$  for 1.5hr; (b) pyridine adsorbed on (a), where gas phase was evacuated at  $200^\circ C$  for 1hr after adsorption.

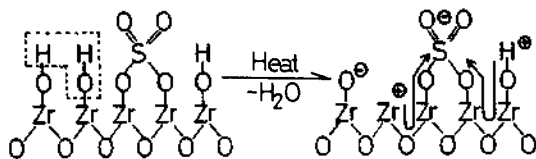


Fig. 6. A model of acid sites generated by the interaction with  $SO_4^{2-}$  ion.

ation was estimated to be  $H \leq -14.5$  as listed in Table 1. Therefore, it is very clear that the sulfur in the highest oxidation state of  $SO_4^{2-}$  is responsible for the superacidic property of the sample. It is remarkable that the acid strength of  $ZrO_2$  modified with sulfur compounds becomes as stronger as 11.5 by  $H_0$  unit than pure  $ZrO_2$ . The acid stronger than  $H_0 = -11.93$ , which corresponds to the acid strength of 100%

$H_2SO_4$ , is known as superacid.<sup>14</sup> Consequently, the present modified  $ZrO_2$  would be a solid superacid. Superacidic property is attributed to the double bond nature of  $S=O$  of the complex formed by the interaction of  $ZrO_2$  with sulfate ion. Both Lewis and Brønsted acid strength becomes stronger by the inductive effect of  $S=O$  in the complex as illustrated in Fig. 6. Enhancement of electron deficiency on Zr and OH bonds by the introduction of sulfate ion is the origin of superacidic properties.

### CONCLUSION

When  $ZrO_2$  was modified by treating with  $H_2SO_4$  and by treating with  $SO_2$ ,  $H_2S$ , and  $CS_2$  followed by oxidation, superacidic property developed. The generation of superacidity was independent of the starting sulfur compounds if the oxidation state of sulfur was brought to +6. Superacidic property is attributed to the double bond nature of  $S=O$  of the complex formed by the interaction of  $ZrO_2$  with  $SO_4^{2-}$ . Both Lewis and Brønsted acid strength becomes stronger by the inductive effect of  $S=O$  in the complex.

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