

Acid Property of Sulfur-Promoted Zirconium Oxide on Silica as Solid Superacid

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An SO_3 -promoted $\text{ZrO}_2/\text{SiO}_2$ was found to be a solid superacid that had the acid strength of higher than $H_0 = -13.16$, regardless of the amount of ZrO_2 loaded. The sample of 3.5 mmol g^{-1} of ZrO_2 loaded on SiO_2 , which was the highest amount of loading tested here, showed the highest acid strength of $H_0 \leq -14.52$. A tetragonal form of ZrO_2 was found to grow extensively when the amount of ZrO_2 loaded became larger. Thus, it was concluded that the higher acid strength of thus prepared catalyst could be obtained after the crystal growth of supported oxide.

It has been reported recently that sulfur-promoted metal oxides such as SO_3/ZrO_2 , SO_3/TiO_2 , $\text{SO}_3/\text{Fe}_2\text{O}_3$, and SO_3/SnO_2 had stronger acid strength than a hundred percent of H_2SO_4 . This exhibited high catalytic activities for acid catalyzed reactions such as the skeletal isomerization of paraffin, the Friedel-Crafts' acylation of benzene with acyl chloride, the isomerization of cyclopropane, and the dehydration of 2-butanol.¹⁻³⁾ The structure of active site and the generation of acidic property of this type of catalyst has been described in our previous articles.⁴⁻⁷⁾ The dispersion of such a type of acid sites on a high surface area support may be of significance to investigate the relationship between the crystal growth and the generation of acid sites and to design a catalyst having higher amount of acid sites. Such a supported superacid will be important for practical use in industry from the view point of increase in mechanical strength and low cost of the solid superacid. This paper deals with the preparation of sulfur-promoted zirconium oxide on silica support ($\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$) by changing the amount of ZrO_2 loaded and the evaluation of the catalyst in terms of acidic properties, catalytic performances, and the crystal growth of ZrO_2 .

An $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ catalyst was prepared by impregnating a desired amount of $\text{ZrO}(\text{NO}_3)_2$ onto SiO_2 (Fuji-Davison type ID, 40-60 meshes; calcined at 773 K for 3 h; surface area = $299 \text{ m}^2 \text{ g}^{-1}$) from methanol solution, decomposing in air at 673 K for 3 h, admitting SO_3 gas at r.t, evacuating at 873 K for 2 h, and oxidizing at 573 K for 2 h.

The ring opening isomerization of cyclopropane was carried out at 373 K by using 0.5 g of catalyst in a closed recirculating system. The amounts of sulfur and zirconium were measured by X-ray fluorescence analysis. The crystallization

Table 1. Acid strength of $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$

Amount of ZrO_2 mmol g^{-1}	Acid strength in H_0 acidity scale			
	-11.35	-13.16	-13.75	-14.52
0.58	○	○	-	-
1.31	○	○	-	-
2.57	○	○	-	-
3.00	○	○	-	-
3.50	○	○	○	○
SO_3/SiO_2	-	-	-	-

of ZrO_2 on SiO_2 was examined by X-ray diffraction analysis using $\alpha\text{-Al}_2\text{O}_3$ as an internal standard. The acid strength of the catalysts was measured by the color development of organic indicators. The indicators used were p-nitrotoluene ($\text{pK}_a = -11.35$), m-nitrochlorobenzene ($\text{pK}_a = -13.16$), 2,4-dinitrotoluene ($\text{pK}_a = -13.75$), and 2,4-dinitrofluorobenzene ($\text{pK}_a = -14.52$). All the indicators were adsorbed from gas phase at the ambient vapor pressure at room temperature; no solvent was used.

Table 1 summarizes the acid strength found on the new type of solid acid. It is clear that all the samples exhibited the acid strength of $\text{H}_0 \leq -13.16$ and thus they are certainly the solid superacid. The SO_3 -mounted silica (SO_3/SiO_2) showed no pronounced acidity. It is worth mentioning that the sample that loaded 3.5 mmol g^{-1} of ZrO_2 had the remarkably high acid strength ($\text{H}_0 \leq -14.52$) among the sample tested here.

The catalytic performance of $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ with various amounts of ZrO_2 loaded is shown in Fig. 1. It is clear that the catalytic activity is increased proportionally to the amount of ZrO_2 loaded. $\text{ZrO}_2/\text{SiO}_2$ and SO_3/SiO_2 showed no activity. Since the X-ray diffraction analysis shows the exclusive presence of tetragonal structure of ZrO_2 , the relationship between the amount of ZrO_2 and the

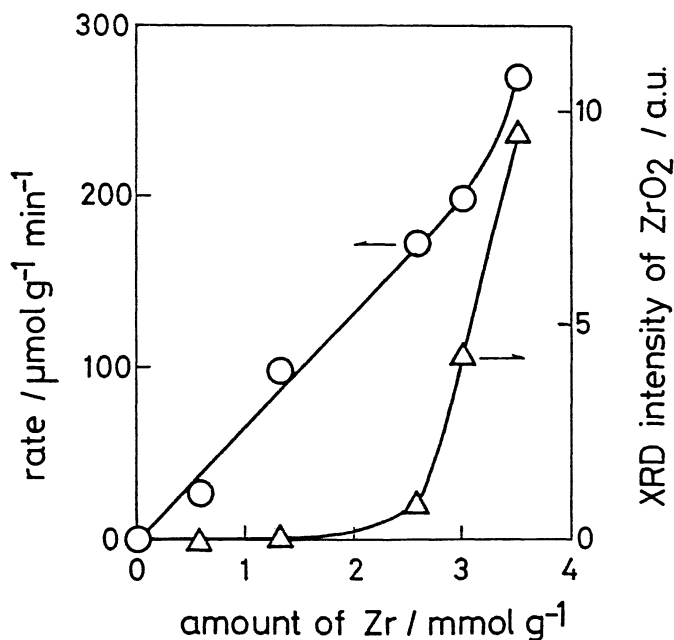


Fig. 1. The catalytic activity and amount of ZrO_2 crystal over $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$.

extent of crystallization to the tetragonal form in ZrO_2 is also plotted in Fig. 1. A diffraction from the tetragonal form first appeared at about 1.4 mmol g^{-1} of ZrO_2 loaded and the diffraction intensities increased markedly between 2.5 to 3.5 mmol g^{-1} .

Figure 2 shows the relationship between the amount of sulfur and that of zirconium loaded. The amount of sulfur first increased proportionally to the amount of ZrO_2 loaded up to 3.0 mmol g^{-1} , however, it abruptly decreased above 3.5 mmol g^{-1} of ZrO_2 . This indicates that the S/Zr ratio was kept constant up to 3.0 mmol g^{-1} but decreased at the highest amount of Zr loaded as shown in Fig. 2.

$\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ was prepared by the contact of SO_3 gas with $\text{ZrO}_2/\text{SiO}_2$ and no sulfate phase was found by the XRD investigation. Thus sulfur component may present on the surface of $\text{ZrO}_2/\text{SiO}_2$ and not in the bulk phase. If the $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ system produces bulk sulfate, amount of S should increase monotonously against the amount of Zr loaded and should not decrease over certain amount of Zr which was seen in Fig. 2.

Since the acid sites of this type of catalyst is composed of S and Zr, catalytic activity may be expressed in terms of the activity per unit amount of S. Thus the catalytic activity per unit amount of sulfur (turnover frequency; T.O.F.) over $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ was estimated and is shown in Fig. 3. It is clear that the T.O.F. was independent of the amount of ZrO_2 loaded except the sample with 3.5 mmol g^{-1} of ZrO_2 . Therefore it is considered that the

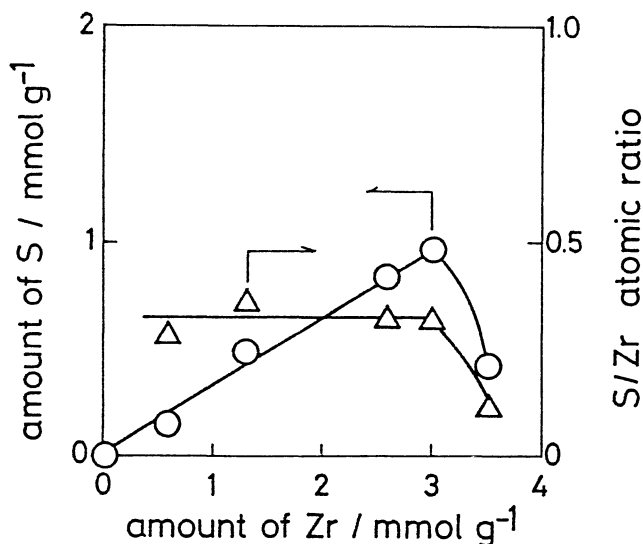


Fig. 2. The amount of sulfur and S/Zr ratio over $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$.

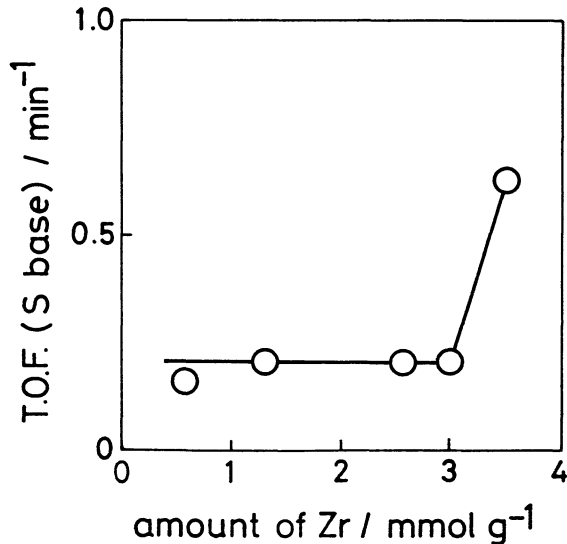


Fig. 3. T.O.F. vs. amount of ZrO_2 loaded over $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$.

amount of acid depends on the amount of sulfur rather than the amount of ZrO_2 . On the other hand, the T.O.F. on the sample of 3.5 mmol g^{-1} of ZrO_2 loaded was greater than the others. This sample had the highest amount of the tetragonal phase of ZrO_2 (Fig. 1) and the highest acid strength in all the samples (Table 1). Thus, it can be concluded that the acid strength of $\text{SO}_3/\text{ZrO}_2/\text{SiO}_2$ depends on the crystallization of ZrO_2 , though the amount of sulfur decreased by the crystallization.

The T.O.F. of unsupported catalyst was estimated to be 0.24 min^{-1} by using the data obtained on the SO_3/ZrO_2 catalyst containing 8 wt% of SO_3 , which was appeared in our previous article.⁵⁾ This value is almost the same as that of the supported catalyst having $0.58 - 3.0 \text{ mmol g}^{-1}$ of Zr, but the amount of Zr necessary to give a similar activity on the supported catalyst is much less than that of the unsupported one. The T.O.F. of the supported catalyst having 3.5 mmol g^{-1} of Zr is about 3 times higher than that of the unsupported one. The amount of Zr necessary to give this T.O.F. is still lower than that of the unsupported one. Thus the supported catalyst can give similar to higher T.O.F. than that of the unsupported one with respect to the total amount of Zr used.

To answer the question why the crystallization influenced the acidic properties, there may be several interpretations, however, we tentatively speculated that an ordered structure of ZrO_2 may be preferable to accomodate the charge around acidic sites when a basic molecule was adsorbed, since such an ordered structure may delocalize the charge more efficiently not only to S=O bonds,⁵⁾ but also to ZrO_2 network through periodical, continuous lattice than a disordered structure.

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