A Study of the Preparation Procedures of Sulfated Zirconia Prepared from Zirconia Gel. The Effect of the pH of the Mother Solution on the Isomerization Activity of *n*-Pentane

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Solid superacids of sulfated zirconia were prepared by the sulfation of zirconia gels, which were obtained from mother solutions with different pH values. The gel precipitated at pH = 8 gave the sulfated zirconia, which showed the highest catalytic activity and selectivity for the skeletal isomerization of *n*-pentane. The active superacid was obtained with high reproducibility upon heating the mother solution, followed by washing the precipitate with hot water; this preparation procedure provided the oxide of small particle size. The catalytic activity of sulfated zirconia could be estimated from the exothermal peak caused by crystallization of the zirconia gel in DTA.

Today, many studies have been reported concerning the solid superacid of sulfated zirconia, which exhibits a high catalytic activity for the skeletal isomerization of hydrocarbons, and so on.[1)] Commonly, it has been prepared following the procedures known to lead to superacidity: (i) preparation of an amorphous zirconia gel as a precursor from zirconium salts[1)] or propoxide;[2)] (ii) treatment of the amorphous substance with sulfate ion in contact with on H_2SO_4 solution or by impregnation with $(NH_4)_2SO_4$; (iii) calcination of the dry sulfated material at high temperature in air. The gel is usually prepared by precipitation from a zirconium solution by adding ammonia; the final pH of a mother solution is 8 in many cases.[1,3)] Some reports related to a solution different from pH 8 can be seen.[4,5)] It is known that the characteristics of zirconia gel as a precursor are greatly dependent on the pH of the mother solution when it is precipitated.[6—8)] This implies that the preparation procedure of the gel has a great influence on the superacidity of sulfated zirconia. However, little attention has been paid to the preparation conditions of zirconia gel.[4)]

This study was aimed at improving the reproducibility of the preparation of sulfated zirconia through an examination of the properties of various zirconia gels obtained from the mother solutions of different pH, as well as the influence of the pH on the activity and selectivity for the isomerization of *n*-pentane. Measurements of the thermogravimetric and differential thermal analyses together with X-ray diffraction were performed in order to analyze the properties of the zirconia gel and the crystalline structure of zirconia.

Experimental

The zirconia gel used as a precursor of the sulfated zirconia was prepared by three methods, described below:

[1]. One hundred grams of $ZrOCl_2\cdot 8H_2O$ were dissolved in 2 dm^3 of distilled water, followed by adding 28% NH_4OH dropwise with stirring; the final pH of the mother solution was made to vary from 4 to 10 by changing the amount of 28% NH_4OH. The precipitated product was washed 15 times with 1 dm^3 of distilled water for each, filtered with suction, and then dried at 373 K for more than 24 h.

[2]. Ammonia water (28%) was added dropwise into 25 g of $ZrOCl_2\cdot 8H_2O$ dissolved in 0.5 dm^3 of distilled hot water (323—333 K), the final pH being made to vary from 5 to 9 by changing the amount of 28% NH_4OH. The solution, including the precipitated product, was kept in a water bath warmed at 323—333 K for 2 h, followed by washing the precipitate 2 times with 0.25 dm^3 of hot water for each, filtering with suction, and finally drying at 373 K for more than 24 h.

[3]. An aqueous solution of 0.5 dm^3 containing 25 g of $ZrOCl_2\cdot 8H_2O$ and 18.8 g of urea was heated at temperatures above 363 K so as to precipitate the gel on a boiling-water bath for 3 h; the final pH of the mother solution was 7. The precipitate was filtered, dried at 373 K for more than 24 h, and then finely ground. The zirconia gels prepared by methods [1], [2], and [3] were labeled as normal, heat, and urea, respectively.

The treatment with sulfuric acid was performed as follows. Zirconia gel (2 g) was placed on a suction funnel, covered with 30 cm^3 of 0.5 $mol\,dm^{-3}$ H_2SO_4, and allowed to stand for 1 h. After the sample was filtered and left to air dry, it was calcined in air at 873 K for 3 h and stored in a sealed ampule until use. Some sample gel which was not treated with sulfate ion was also calcined in air at 773 or 873 K to give a reference zirconia.

The skeletal isomerization of *n*-pentane was performed at 273 K in a closed recirculation system. After the catalyst (0.8 g, 32—50 mesh) was set in a reactor and pretreated in vacuum at 523 K for 3 h, ca. 6.7 kPa of *n*-pentane was introduced into the reactor. The products were analyzed by GLC using a 3 m column packed with VZ-7 at room temperature.

Thermogravimetric and differential thermal analysis (TG-DTA) was carried out using a Rigaku model at a programmed rate of 10 K min^{-1}. An X-ray diffraction (XRD) was taken to determine the crystalline structure of zirconia calcined and sulfated zirconia calcined with a Rigaku X-ray diffractometer using Cu $K\alpha$ radiation over the range of $2\theta = 20$—80 degrees.

Results and Discussion

The isomerization of *n*-pentane was carried out over sulfated zirconia calcined at 873 K, whose precursor, zirconia gel, was obtained from the mother solution of different pH; the results are shown in Fig. 1. The products were predominantly *i*-pentane and *i*-butane, which were formed through skeletal isomerization. The formation of a small amount of methane was observed with a few kinds of catalysts. The conversion into *i*-pentane and *i*-butane was remarkably dependent on the pH of the mother solution. The maximum activity was observed at pH = 8 for both the normal and heat samples; a decrease in the activity was seen in the range of pH 8—9. The catalysts prepared by the heat method showed activity higher than those of the normal method over the entire pH range. The sample prepared by using the urea method gave a much low activity for this reaction. The acid strength of the sample by the heat method with pH 8 was estimated to be $H_0 \leq -16.12$ by the visual color-change method using Hammett indicators, the highest for the sulfated zirconia yet reported.[1]

Figure 2 shows the DTA profiles of zirconia gels precipitated at pH = 5 to 8 (normal and heat) in addition to the sample with urea. An exothermal reaction due to the crystallization of zirconia was observed around 703 K for both the normal and heat samples. The calorimetric values of the exothermal peak, calculated on the basis of the peak area, were almost constant, ca. 105 J g^{-1} in the average, for all samples, except for the normal samples with pH=4 and 5 as well as the urea one. The samples prepared by both methods with pH = 8 showed a crystallization peak that was the sharpest and highest as shown in Fig. 2.

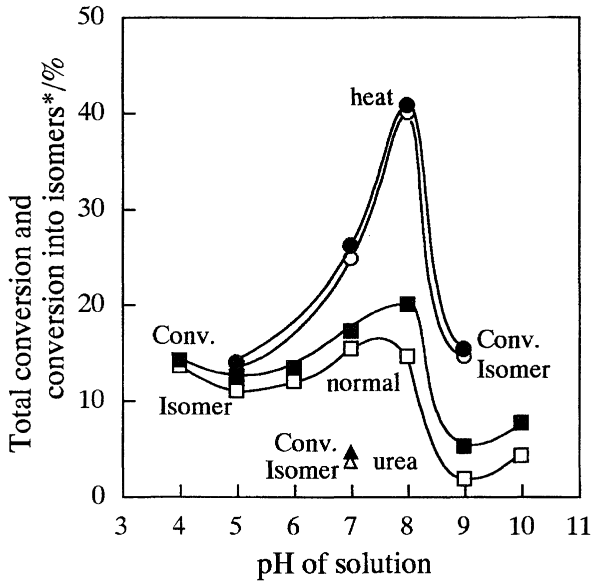

Fig. 1. Isomerization of *n*-pentane over sulfated zirconia at 273 K, an effect of pH of mother solution on catalytic activity. Catalyst weight: 0.8 g, *n*-pentane pressure: 6.7 kPa, reaction time: 3 h. *Total conversion into *i*-pentane and *i*-butane.

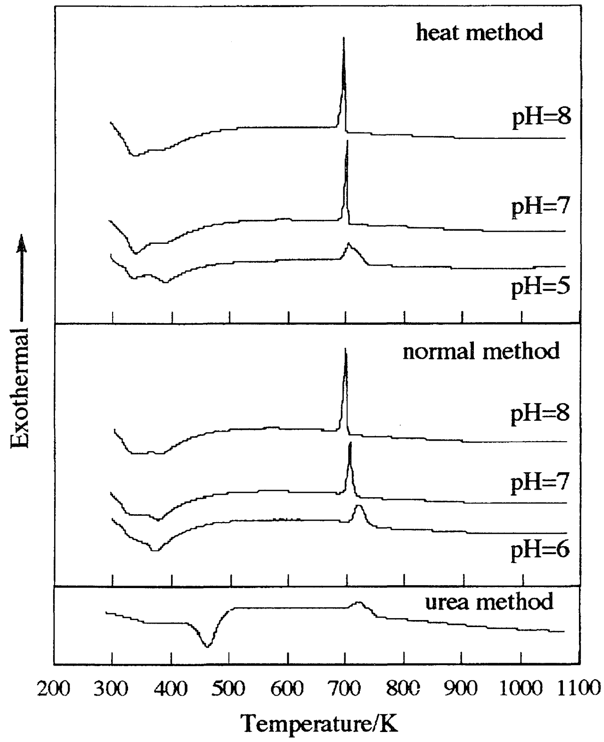

Fig. 2. DTA profiles of zirconia gels prepared by various methods.

The XRD spectra of zirconium oxides are given in Fig. 3. The samples were prepared from zirconia gels by the normal and heat methods, and calcined at 773 K in air for 3 h. It can be seen that the zirconias prepared by the normal method and calcined at 773 K produced the tetragonal phase predominantly with a lower degree of crystallization in the case of pH 8, which was the precursor of the sulfated zirconia showing higher activity. The transformation to the monoclinic phase, which is the stable form at high temperature, occurs in part. On the contrary, samples prepared using the heat method with pH 7 and 8 show mainly the monoclinic structure. This result assumed that the difference in the profile of the exothermal peak in DTA is responsible for the reactivity of the gel to crystallization. The crystallization progresses rapidly over a short range of temperatures giving the monoclinic structure, because of the high reactivity and small particle size of the gel substance, though the reaction of matter with a low reactivity occurs partially and gradually. Table 1 shows the particle size and crystalline structure of zirconia calcined and sulfated zirconia calcined together with the particle size of the zirconias obtained using the Scherrer's method. The particle size of the zirconias was 34 and 117 nm for samples with pH 8 by the heat and normal methods, respectively. The results given in Table 1 support the explanation mentioned above.

The XRD patterns of the sulfated zirconia are shown in

Table 1. Particle Size and Crystalline Structure of Zirconia and Sulfated Zirconia

Sample	Method	pH	Crystalline structure	Particle size/nm
ZrO_2[a]	Normal	6	Tetragonal	185
	Normal	7	Tetragonal	138
	Normal	8	Tetragonal	117
	Heat	5	Tetragonal	107
	Heat	7	Monoclinic	39
	Heat	8	Monoclinic	34
SO_4^{2-}/ZrO_2[b]	Normal	6	Tetragonal	85
	Normal	7	Tetragonal	95
	Normal	8	Tetragonal	126
	Heat	5	Tetragonal	66
	Heat	7	Amorphous	—
	Heat	8	Amorphous	—

a) Calcined at 773 K. b) Calcined at 873 K.

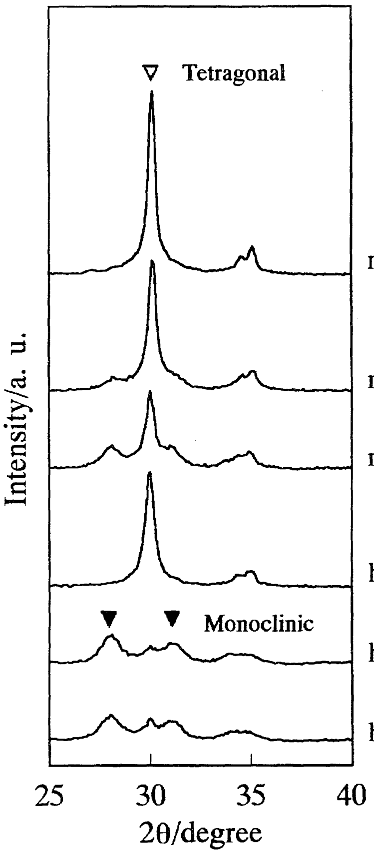

Fig. 3. XRD patterns of zirconia calcined at 773 K.

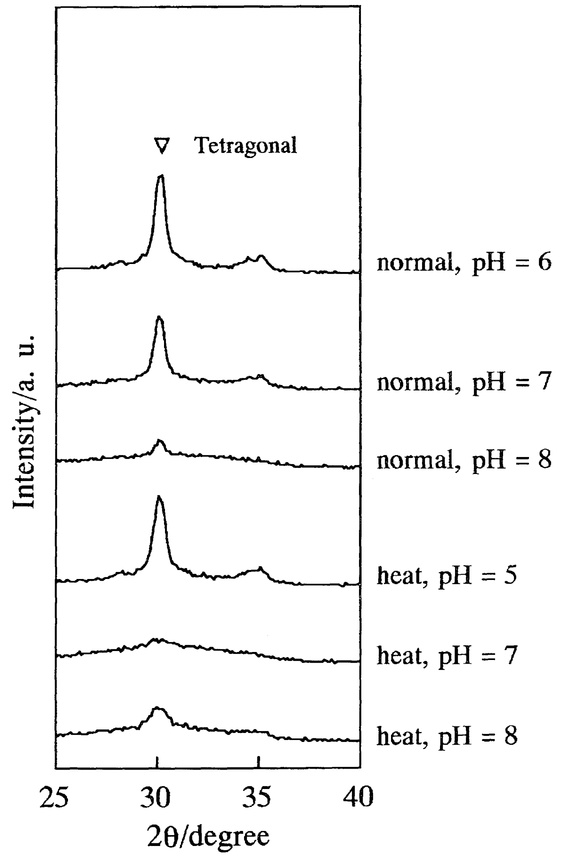

Fig. 4. XRD patterns of sulfated zirconia calcined at 873 K.

Fig. 4. Although the samples prepared by the heat method with pH 7 and 8 show a tetragonal structure, the degree of crystallization is low, close to that of the amorphous state. The crystallization of zirconia is inhibited by a strong interaction of the surface sulfate with the support, ZrO_2.[1] These results mean that the particle size of the heat sample is smaller than that of the normal sample, giving a higher reactivity with the sulfate species.

A high surface area of zirconia, calcined at 873 K, obtained by the heat method with pH 8, was observed (58 $m^2\ g^{-1}$), compared with 46 $m^2\ g^{-1}$ for a sample obtained by the normal method. After treating with sulfate ion and being calcined at 873 K, the surface area of the sulfated zirconia obtained by the heat method with pH 8 was the largest (137 $m^2\ g^{-1}$) among the prepared catalysts. The catalytic activity of sulfated zirconia was strongly dependent on the surface area, and a correlation can be seen between the catalytic activity and the surface area. This means that the increase in the number of active sites attended with an increase of the surface area improves the activity.

In conclusion, the pH of the mother solution of zirconia gel has a significant effect on the catalytic activity of the sulfated zirconia. The gel prepared at pH = 8 by the heat method shows the highest activity, and provides a sharp exothermal peak due to the crystallization in DTA, because of the small particle size of the gel; rapid crystallization occurs. On sulfated zirconia, the effect of the inhibition of crystallization is strong, the structure of the sulfated zirconia being almost amorphous. It is also proposed that the catalytic activity of sulfated zirconia can be judged from the DTA profile of the precursor, zirconia gel.

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