

A New Solid Superacid Catalyst Prepared by Doping ZrO₂ with Ce and Modifying with Sulfate Simultaneously

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A new solid superacid catalyst, Ce-ZrO₂/SO₄²⁻, having high surface area and thermal stability even after calcination at temperatures of 650–700 °C, is prepared simply by doping ZrO₂ with Ce and modifying with sulfate simultaneously. The role of Ce is to form a thermally stable solid solution with zirconia and consequently to give high surface area of the sample.

Many kinds of solid acids have been found; their acidic properties, their catalysis, and the structure of acid site have been elucidated and those results have been reviewed by several workers.^{1–3} The preparation and use of solid superacid catalysts are active areas of research for isomerization, cracking, hydrocracking, dehydration, acylation, and a process from methanol to gasoline, etc.² Zirconium oxide, ZrO₂ is a very interesting material because of its thermal stability, its mechanical properties, and its basic, acidic, reducing, and oxidizing properties.⁴ The potential for a heterogeneous catalyst has yielded many papers on the catalytic activity of sulfated zirconia materials.^{1–3,5} Sulfated zirconia doped with Fe and Mn has been shown to be highly active for butane isomerization, catalyzing the reaction even at room temperature.⁶ However, it is known that for zirconia-supported catalyst its surface area and catalytic activity are decreasing under the severe reaction condition such as high temperature above 600 °C. In this paper we report a new solid superacid catalyst prepared by doping ZrO₂ with Ce and modifying with sulfate simultaneously to improve catalytic activity and thermal stability. For the acid catalysis, the cumene dealkylation was used as a test reaction.

The precipitate of Zr(OH)₄ was obtained by adding aqueous ammonia slowly into an aqueous solution of zirconium oxychloride (Junsei Chemical Co.) at room temperature with stirring until the pH of mother liquor reached about 8. The preparation of catalyst doped with Ce and modified with sulfate simultaneously was carried out by adding an acidic aqueous solution of cerium sulfate [Ce(SO₄)₂·4H₂O] to the Zr(OH)₄ powder followed by drying and calcining at high temperatures for 2 h in air. 5Ce-ZrO₂/SO₄²⁻ indicates the catalyst containing 5 wt % Ce(SO₄)₂. Chemisorption of ammonia was also employed as a measure of the acidity of catalysts.⁷ Cumene dealkylation was carried out at 400 °C in a continuous flow, fused quartz reactor having an internal diameter of 11 mm. Catalytic activity for cumene dealkylation was represented as mole of benzene converted from cumene per gram of catalyst.

In general, metal oxides modified with sulfate ion,^{7,8} followed by evacuating above 400 °C, exhibit a strong band assigned to an S=O stretching frequency at 1390–1370 cm⁻¹. The infrared spectrum of self-supported 5Ce-ZrO₂/SO₄²⁻ after evacuation at 500 °C for 1 h was examined. There was an intense

band at 1390 cm⁻¹ accompanied by broad and intense bands below 1200 cm⁻¹ due to the overlapping of the ZrO₂ skeletal vibration, thereby, indicating the presence of differently adsorbed species depending on the treatment conditions of the sulfated sample.^{7,8}

The strong intense band at 1390 cm⁻¹ after evacuation at 500 °C is related to the superacidic property,^{7,8} which is attributable to the double-bond nature of the S=O in the complex formed by the interaction between Ce-ZrO₂ and sulfate. The acid strength of Ce-ZrO₂/SO₄²⁻ samples after evacuation at 500 °C for 1 h was also examined by color change method, using Hammett indicator in sulfuryl chloride.⁹ The samples were estimated to have H₀ ≤ -14.5, indicating the formation of superacidic sites. The infrared spectra of ammonia adsorbed on 5Ce-ZrO₂/SO₄²⁻ sample evacuated at 500 °C for 1 h showed two characteristic bands (1444 and 1620 cm⁻¹) of ammonia adsorbed on both Brönsted and Lewis acid sites, indicating the presence of both Brönsted and Lewis acid sites. So, we suggest a model structure for the acid sites on Ce-ZrO₂/SO₄²⁻ as following scheme.

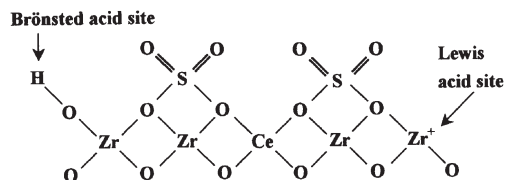


Figure 1 shows the BET surface areas of 5Ce-ZrO₂/SO₄²⁻ and 10Ce-ZrO₂/SO₄²⁻ as a function of calcination temperature. It was found surprisingly that the surface areas of catalysts cal-

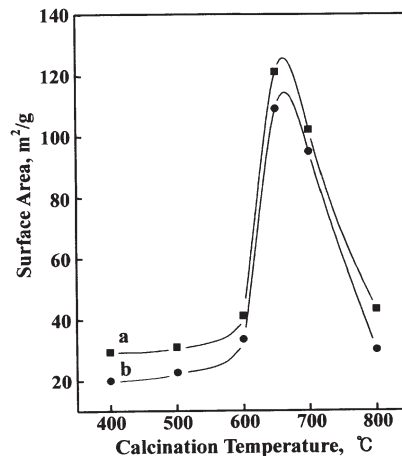


Figure 1. Variations of surface area of 5Ce-ZrO₂/SO₄²⁻ (a) and 10Ce-ZrO₂/SO₄²⁻ (b) as a function of calcination temperature.

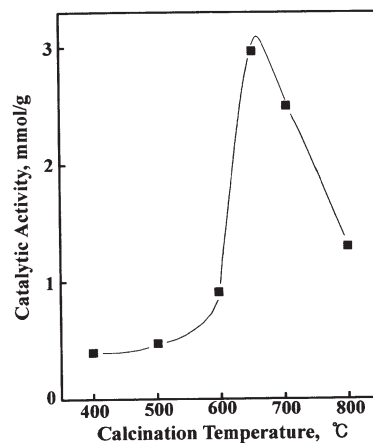
Table 1. Specific surface area and acidity of 5Ce-ZrO₂/SO₄²⁻ catalysts calcined at different temperatures

Calcination temperature /°C	Surface area /m ² g ⁻¹	Acidity /μmol g ⁻¹
400	29.4	46.2
500	31.0	51.3
600	41.2	57.4
650	121.2	129.3
700	102.1	107.2
800	48.3	62.3

calcined at 650–700 °C are very high compared to those calcined at 400–600 °C. This high surface area of Ce-ZrO₂/SO₄²⁻ is due to the doping effect of Ce which makes zirconia a stable tetragonal phase¹⁰ as confirmed by XRD. It was also reported that a small amount of rare-earth elements in zirconia powder can stabilize the tetragonal and cubic phases over a wide range of temperatures.¹¹ The surface area of 5Ce-ZrO₂/SO₄²⁻ calcined at 650 °C is 121.2 m²/g (Table 1), whereas those of undoped pure ZrO₂ and only sulfated ZrO₂ are 38 and 56 m²/g, respectively. However, the phase of catalyst calcined at 400–600 °C was mainly amorphous or poorly crystalline of tetragonal phase. The role of Ce in the catalysts is to form a thermally stable solid solution^{10,11} with zirconia and consequently to give their high surface area.

It is interesting to examine how the catalytic activity of acid catalyst depends on the acidic property. The catalytic activities of 5Ce-ZrO₂/SO₄²⁻ catalyst for the cumene dealkylation are measured and the results are illustrated as a function of calcination temperature in Figure 2, where reaction temperature is 400 °C. In view of Table 1 and Figure 2, the variation in catalytic activity for cumene dealkylation is well correlated with the change of their acidity measured by the ammonia chemisorption method,⁹ showing the highest activity and acidity for 5Ce-ZrO₂/SO₄²⁻ calcined at 650 °C. It has been known that cumene dealkylation takes place on relatively strong acid site of the catalysts.⁹ Good correlations have been found in many cases between the acidity and the catalytic activities of solid acids.^{2,9} The activity increased with the calcination temperature, giving a maximum at 650 °C and then the activity decreased. Comparing Figure 2 and Table 1, catalytic activity closely correlates to the acidity of 5Ce-ZrO₂/SO₄²⁻ catalysts calcined at different temperatures. The decrease of catalytic activities above 700 °C can be probably attributed to the fact that the surface area and acidity above 700 °C decrease with the calcination temperature.

In summary, we prepared a new solid superacid having high surface area and thermal stability even after calcination at tem-

**Figure 2.** Variation of catalytic activity of 5Ce-ZrO₂/SO₄²⁻ for cumene dealkylation as a function of calcination temperature.

peratures of 650–700 °C by doping ZrO₂ with Ce and modifying with sulfate simultaneously. The role of Ce in the catalysts is to form a thermally stable solid solution with zirconia and consequently to give high surface area of Ce-ZrO₂/SO₄²⁻.

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