

## SYNLETT Spotlight 109

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

### Sulfated Zirconia

Compiled by S. Z. Mohamed Shamshuddin

Mohamed Shamshuddin, S. Z., was born in Tumkur (Karnataka, India) in 1974. In 1997 he received his MSc degree in Chemistry (Inorganic Chemistry) from Bangalore University, Bangalore, India. He is currently working towards his PhD under the supervision of Prof. Nagaraju, N., at the Department of Chemistry, St. Joseph's Research Center, Bangalore, India. His present research interests focus on the synthesis of industrially important organic fine chemicals using environmentally benign solid acid catalysts.

Catalysis Research Laboratory, St. Joseph's Research Center, 46, Langford Road, Shanthinagar, Bangalore-560 027, India  
E-mail: Em\_Es@rediffmail.com



### Introduction

Zirconia, when modified with anions such as sulfate, forms a highly acidic or super-acidic catalyst that exhibits superior catalytic activity in many reactions.<sup>1</sup> Sulfated zirconia ( $\text{SO}_4^{2-}/\text{ZrO}_2$ , SZ) is a crystalline solid acid that has monoclinic and tetragonal phases with a super acidity of  $-16.04$  (Hammett acidity), which is responsible for its enhanced catalytic activity.<sup>2</sup>

A variety of organic reactions that are normally catalyzed by Brønsted or Lewis acids have been shown to take place more efficiently in the presence of sulfated oxides, especially sulfated zirconia even under milder reaction conditions. The reactions can take place in shorter time and with greater selectivity, and better yields. The range of reactions that have been successfully performed on SZ catalysts include alkylation, condensation, esterification, transesterification, nitration, cyclization and isomerization.<sup>3</sup>

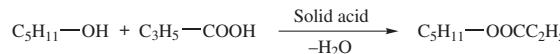
### Abstracts

(A) Catalytic activity of different solid acids such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and their sulfated forms has been investigated in a liquid phase esterification of isoamyl alcohol to prepare isoamyl propionate. The yield (%) of the ester was correlated with the total surface acidity and texture of the catalyst. Sulfated zirconia which exhibited the highest acidity among the other catalysts used in the study showed good activity towards the formation of the ester. The effect of sulfur loading on zirconia with respect to the total surface acidity and the texture was studied.<sup>5</sup> SZ also showed good activity towards the formation of benzyl acetate from benzyl alcohol.<sup>6</sup>

### Preparation of Sulfated Zirconia (SZ)

The catalytic property of SZ depends on many factors. The types of zirconia precursor, precipitating agent, and sulfating agent, as well as the method of preparation and calcination temperature, are all important factors.  $\text{Zr}(\text{OH})_4$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , and  $\text{Zr}(\text{NO}_3)_4$  are normally used as zirconia precursors, and  $\text{H}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{H}_2\text{S}$ , and  $\text{SO}_2$  as sulfating agents.

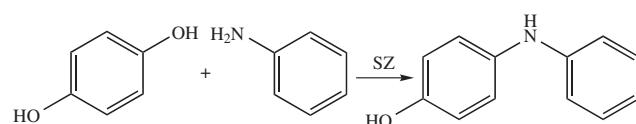
Generally, SZ is prepared by an impregnation method.<sup>4</sup>  $\text{Zr}(\text{OH})_4$  is first mixed thoroughly with 1 M  $\text{H}_2\text{SO}_4$  at room temperature for one hour. The resulting paste is dried at  $120^\circ\text{C}$  for twelve hours in an air oven and then calcined to  $550^\circ\text{C}$  in a furnace for five hours.



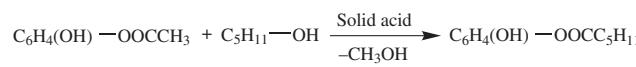
(B) Methane-ethylene mixtures react over super acidic sulfate-treated zirconia catalysts to yield higher hydrocarbons. SZ enables ethylene to undergo oligomerization at a rate which is at least 50 times higher than that found with zeolite (HZSM5). The demonstration of super acidity in SZ may be associated with thermal activation at temperatures (550 °C) at which substantial but incomplete recrystallization takes place.<sup>7</sup>



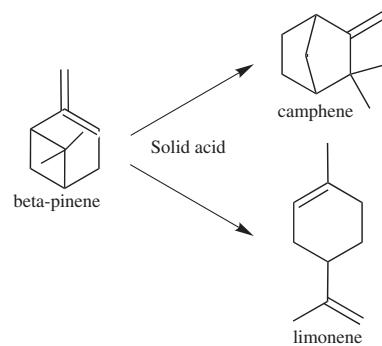
(C) Sulfated zirconia has also been employed for several condensation reactions. The use of SZ to catalyze the condensation of hydroquinone with aniline and substituted anilines has been investigated. SZ can catalyze this reaction under milder conditions.<sup>8</sup>



(D) The transesterification of methyl salicylate with isoamyl alcohol has been studied in vapor phase over oxides such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub> and their sulfated forms. Sulfated zirconia was found to be the efficient catalyst for the formation of isoamyl salicylate with good yields (60%) and selectivity (80%).<sup>9</sup>



(E) Sulfated zirconia shows good activity towards α-pinene isomerization under mild conditions. Conversion correlates with the number of Brønsted acid sites, while the selectivity towards mono-versus polycyclic depends on the corresponding acid site strength. Super acidity promotes limonene formation over camphene.<sup>2</sup>



## References

- (1) Hino, M. S.; Kobayashi, S.; Arata, K. *J. Am. Chem. Soc.* **1979**, *101*, 6439.
- (2) Ecormier, M. A.; Wilson, K.; Lee, A. F. *J. Catal.* **2003**, *215*, 57.
- (3) Yadav, G. D.; Nair, J. J. *Micropor. Mesopor. Mat.* **1999**, *33*, 1.
- (4) Hino, A.; Arata, K. *J. Chem. Soc., Chem. Commun.* **1980**, *24*, 1148.
- (5) Md Shamshuddin, S. Z.; Nagaraju, N. *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.* **2004**, *43*, 2060.
- (6) D'Souza, J.; Nagaraju, N. *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.* **2001**, *40*, 266.
- (7) Scurrell, M. S. *Appl. Catal.* **1987**, *34*, 109.
- (8) Kumbhar, P. S.; Yadav, G. D. *Chem. Engl. Sci.* **1989**, *44*, 2535.
- (9) D'Souza, J.; Nagaraju, N. *Indian J. Chem. Technol.* **2004**, *11*, 401.