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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

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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.[1] Sulfated zirconia (SO_4^{2-}/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.[2]

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.[3]

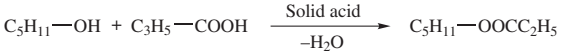
Preparation of Sulfated Zirconia (SZ)

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. $Zr(OH)_4$, $ZrOCl_2 \cdot 8H_2O$, and $Zr(NO_3)_4$ are normally used as zirconia precursors, and H_2SO_4, $(NH_4)_2SO_4$, H_2S, and SO_2 as sulfating agents.

Generally, SZ is prepared by an impregnation method.[4] $Zr(OH)_4$ is first mixed thoroughly with 1 M H_2SO_4 at room temperature for one hour. The resulting paste is dried at 120 °C for twelve hours in an air oven and then calcined to 550 °C in a furnace for five hours.

Abstracts

(A) Catalytic activity of different solid acids such as Al_2O_3, SiO_2, 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.[5] SZ also showed good activity towards the formation of benzyl acetate from benzyl alcohol.[6]



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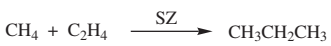
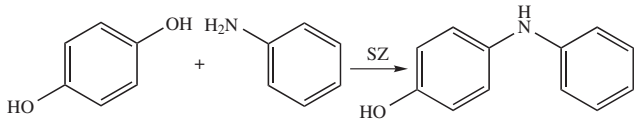
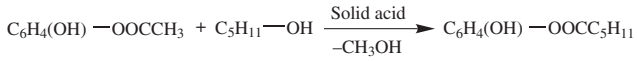
(B) Methane-ethylene mixtures react over super acidic sulfate-treated zirconia catalysts to yield higher hydrocarbons. SZ enables ethylene to undergo oligomerization at a rate which is at least 50 times higher than that found with zeolite (HZSM5). The demonstration of super acidity in SZ may be associated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



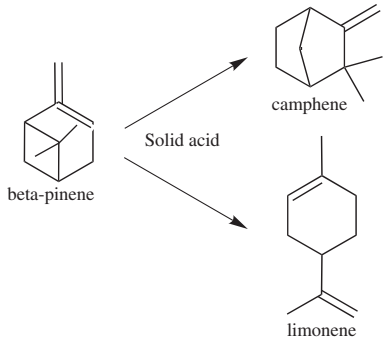
(C) Sulfated zirconia has also been employed for several condensation reactions. The use of SZ to catalyze the condensation of hydroquinone with aniline and substituted anilines has been investigated. SZ can catalyze this reaction under milder conditions.[8]



(D) The transesterification of methyl salicylate with isaomyl alcohol has been studied in vapor phase over oxides such as Al_2O_3, SiO_2, ZrO_2 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%).[9]



(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.[2]



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