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Tungstated Zirconia- A Solid Acid Catalyst

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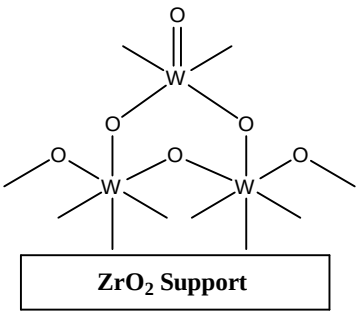
Abstract:

Tungstate modified zirconia is good alternative to sulfated zirconia. This catalyst can be prepared by precipitation followed by impregnation method. Tungstated zirconia has been successfully utilized for various organic synthesis and transformation reactions in liquid phase as well as vapor phase.

Keywords: Modified zirconia, Tungstated zirconia, Solid acid.

Introduction

Zirconia, when modified with tungstate oxide forms a highly acidic catalyst that exhibits superior catalytic activity in many reactions. Tungstated zirconia is monoclinic and tetragonal phases with H_0value – 14.6 (Hammett acidity), which is responsible for enhanced catalytic activity.[1]Based on several characterization results, it is generally believed that tungstate oxide could exist on zirconia surface in the form of polytungstate cluster.[2,3]



The tungstated zirconia catalyst has been mostly employed for various-vapour phase reactionsnamely, *tert*-butylation of *p*-cresol[4],tert-butylation of phenol[5],production of biodiesel fuel[6] and isomerization[7]. This catalyst also exhibits excellent activity for various liquid-phase organic reactions as complied in this article.

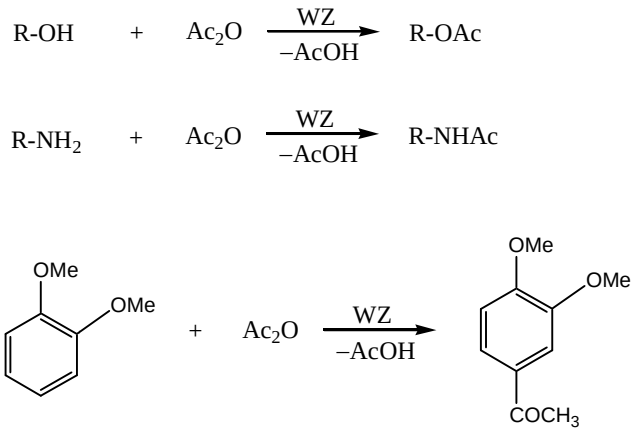
Preparation of Tungstated Zirconia (WZ)

Generally, WZ is prepared by an impregnation method[8]. $Zr(OH)_4$, $ZrOCl_2 \cdot 8H_2O$, and $Zr(NO_3)_4$ are normally used as zirconia precursors, and ammonium tungstate is used as a source of tungstate.

The requisite quantity of ammonium metatungstate (BDH Chemical Ltd., ARgrade) was dissolved in doubly distilled water and to this clear solution the desiredquantity of oven dried $Zr(OH)_4$ was added and the excess water was evaporated on awater-bath. The resulting cake was oven dried at 120 °C for 24 h and calcined at 800 °C for 6 h in a flow of oxygen.

Applications of Tungstated Zirconia (WZ)

(A) Acylation is a fundamental process in organic synthesis. WZ shows good catalytic activity for acetylation of phenols and alcohols using acetic anhydride as the acetylating agent. Amines also underwent *N*-acetylation to give *N*-acylated products in good yields[9]. Sakthivel*et al.*[10] and Bordoloi*et al.*[11] employed WZ catalyst for acetylation of anisole and veratrole with acetic anhydride respectively to produce 2- and 4-methoxyacetophenone and 3, 4-dimethoxy acetophenone in high yields.



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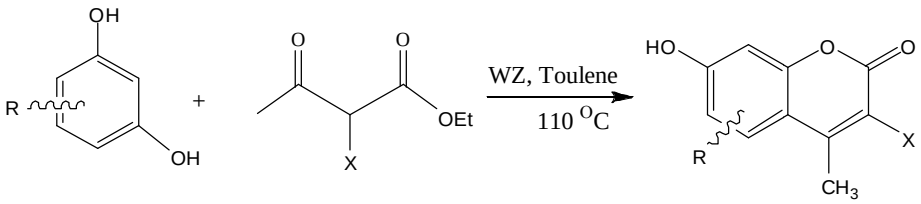
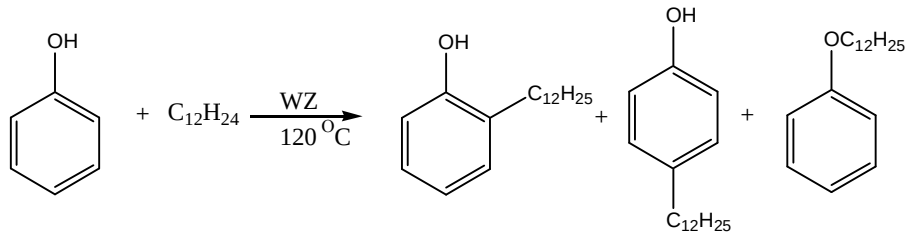
(B)Coumarins have been extensively investigated and widely used but still generate much interest. Manycoumarins and coumarin derivatives exhibit high level of biological activity.Tungstated zirconia shows good activity towards synthesis of substituted coumarins from resorcinol and substituted resorcinol withethyl acetoacetate and ethyl α-methylacetoacetate at 110 °C and toluene as a solvent[12].

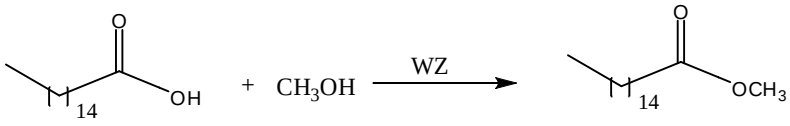


R= H, CH_3, OH X= H, CH_3

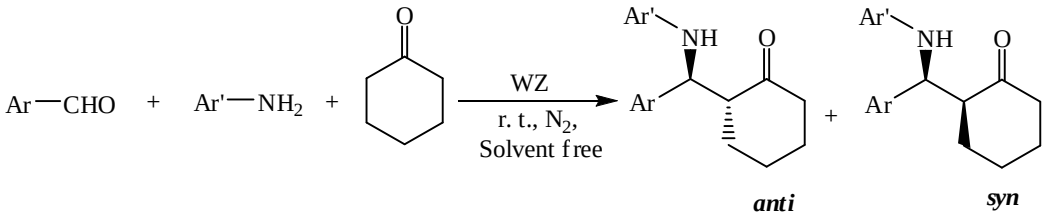
(C) Alkylation of phenol and alcohols with olefins is an industrially important process for the production of a variety of products. Tungstated zirconia has been employed for alkylation of phenol with long chain olefins (1-octane, 1-decene, 1-dodecene)[13]. 15wt. % WO_3 catalyst exhibited a maximum conversion at 70°C reaction temperature and selectivity for ether is high at low reaction temperature and decreased with increase in temperature and disappeared at 120°C.Bordoloi*et al.*also reported alkylation of toluene with 1-dodecene using WZ catalyst [11].

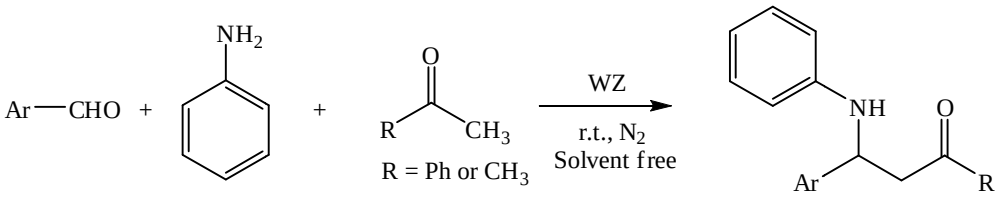


(D)WZ solid acid catalysts prepared by both impregnation and co-precipitation methods is employed for esterification of palmitic acid with methanol, the tungsten loading (2.5-25%) and calcination temperature were varied. It is found that the catalyst with 5% loading shows maximum catalytic activity[14].



(E)The Mannich reaction is a classical method for the preparation of β-amino ketones and aldehydes, and has been one of the most important basic reactions in organic chemistry for its use in natural product and pharmaceutical syntheses. Tungstated zirconia shows good activity towards synthesis of β-amino ketones by a three-component Mannich-type reaction of an aromatic aldehyde, aromatic amine and ketone in the liquid phase under solvent-free conditions at ambient temperature[15].





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