



Atom economical Michael addition of indole with methyl vinyl ketone over novel solid acid catalyst sulfated zirconia on silica tubes



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ABSTRACT

Porous structures of inorganic oxides with different morphology are being paid a great deal of attention because of their potential for providing ultra large specific surface areas, exceptionally fine inner pores, and catalytic surface properties. A facetted silica tube functionalized with sulfated zirconia was prepared and used to catalyze Michael addition reaction of indole with methyl vinyl ketone. The effect of mesoporous tubular structure in generation of mild acidic sites on silica is discussed. The reaction is 100% atom economical. The silica tubes were prepared by using tetraethylorthosilicate and (dl)-tartaric acid in basic medium. The support and catalyst were well characterized by XRD, FT-IR, ASAP, SEM and EDXS. The activity was also compared through benzylation of toluene in liquid phase with reference to sulfated zirconia. Several other catalysts were also evaluated. The effects of various parameters on the rate of reaction were investigated. Based on the experimental data, a suitable mechanism was developed and kinetic model deduced.

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1. Introduction

Indoles are one of the most important nitrogen containing heterocyclic compounds which find numerous applications in natural product formulations, pharmaceuticals and polymeric materials [1,2]. The 3-position in indole is the preferred site for electrophilic substitution and thus 3-alkyl or acyl indoles can be synthesized as versatile intermediates for preparation of a wide range of derivatives. 3-Substituted indoles are useful building blocks for the synthesis of biologically active compounds as well as natural products [3,4]. Since β -indolylketones are commercially valuable, their synthesis has been reported using various homogeneous catalysts such as $\text{Bi}(\text{OTf})_3$ [5], $\text{Sc}(\text{OTf})_3$ [6], CAN [7], InBr_3 [8], PTSA [9], pyridinedicarboxylic acid [10], FPA [11], $\text{Cu}(\text{OTf})_3$ [12], I_2 [13], Ga_3 [14], HfCl_4 and ScCl_3 [15], NO^+BF_4^- [16], $\text{Zr}(\text{OtBu})_4$ [17]. Recently application of cyanuric chloride and chiral pybox-diph-Zn(II) complex for Michael addition reaction is reported [18,19].

Acid catalyzed electrophilic substitution of indole is beset with polymerization and reactions at N-centre and requires careful control of acidity to overcome these problems [1]. Many Lewis acids get deactivated or occasionally decomposed by nitrogen containing reactants such as indole and more than stoichiometric amount of

the Lewis acids are required [20]. The use of lanthanide triflates is promising but they are very expensive. For this reason, cheaper heterogeneous Lewis acid catalysts are desirable and development of solid acids which would not be deactivated and could lead to efficient synthesis of substituted indoles is required. In particular, the use of different supports would be attractive to incorporate acidic centers. This work is an attempt in that direction.

Over the past few years substantial attention has been paid to the synthesis of tubular materials based on transition metal oxides which possess unusual structure and remarkable properties. Template based synthesis of porous materials can be used to fabricate hierarchical materials with controlled porosity over micron to nanometer range, having structures with unique physical, optical, magnetic and semiconducting properties [21–24]. It has been reported that tartaric acid (racemic mixture) and citric acid exhibit unique aggregation in solution and hence can be used as structure directing agents to form facetted hollow silica tubes with wall thicknesses in nm range [25,26]. Silica tubes explored in these studies contained, in addition to the hollow silica tubes, other non-uniform structures such as spheres or ill-defined and unwanted non-porous morphologies. Incorporation of acidic centers in neutral silica tubes as supports will be useful. In recent years, a great deal of attention has been focused on sulfated zirconia in a number of industrial processes and our laboratory has added vastly to this area [27]. UDCaT series of catalysts have been used for green acylation, alkylation, nitration, condensation,

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Nomenclature

A	reactant species A indole
B	reactant species B methyl vinyl ketone
AS	chemisorbed indole
BS	chemisorbed methyl vinyl ketone
E	product species E, β -indolylketone
S	vacant site
C_A	concentration of A, mol/cm ³
C_{A0}	initial concentration of A in bulk liquid phase, mol/cm ³
C_{AS}	concentration of A at catalyst surface, mol/g-cat
C_B	concentration of B, mol/cm ³
C_{B0}	initial concentration of B in bulk liquid phase, mol/cm ³
C_{BS}	concentration of B at solid surface, mol/g-cat
C_C	concentration of C, mol/cm ³
C_{CS}	concentration of C at solid surface, mol/g-cat
C_S	concentration of vacant sites, mol/g-cat
C_T	total concentration of sites, mol/g-cat
k_{R2}	reaction rate constant, cm ⁶ mol ⁻¹ s ⁻¹ g-cat ⁻¹

w	catalyst loading, g/cm ³ of the liquid volume
X_A	fractional conversion of A
$-r_A$	rate of surface reaction, mol cm ⁻³ s ⁻¹
k_1	pseudo-first order rate constant, s ⁻¹

Abbreviation for catalysts

Cs-DTP/K10	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ supported on montmorillonite acid treated clay
K10	montmorillonite clay
PAZ	persulfated alumina and zirconia
SZ/ST	sulfated zirconia supported on silica tubes
S-ZrO ₂	sulfated zirconia
UDCaT-4	University Department of Chemical Technology catalyst-4
UDCaT-6	University Department of Chemical Technology catalyst-6

cyclization, esterification and rearrangement reactions. They are well designed and modified versions of zirconia using different precursors, supports and acidifying agents to impart acidity greater than S-ZrO₂ and they include UDCaT-1 (stronger than sulfated zirconia) [28,29], UDCaT-2 (shape selective and tunable) [30,31], UDCaT-4 (synergism of persulfated alumina and zirconia into HMS) [32,33], UDCaT-5 (stronger than UDCaT-1) [34], UDCaT-6 (mesoporous) [35,36]. Above 4% w/w sulfur loading, the tetragonal phase of zirconia is strongly affected [33]. UDCaT-5, a zirconia-based mesoporous solid acid catalyst was prepared by Yadav and Murkute [34], where they have used chlorosulfonic acid as a new source for incorporation of sulfate into zirconia with high sulfur content (9% w/w) which also led to preservation of the tetragonal phase of zirconia. Combustion synthesized zirconia sulfated with chlorosulfonic acid (fuel lean sulfated zirconia) was much better catalyst with 15% sulfur content [37]. It was thus thought worthwhile to prepare sulfated zirconia (SZ) supported on silica tube (ST) using the novel procedures developed in our lab with incorporation of high sulfur content to increase acidity of sulfated zirconia.

In the present work, we report preparation of silica tubes by sol-gel method using tetraethoxyorthosilicate as silica source on to which zirconia was loaded and sulfated to prepare an excellent acidic catalyst. It was fully characterized by various techniques such as FTIR, XRD, ASAP, SEM and EDXS to throw light on its activity and reusability. The activity of SZ/ST was demonstrated in comparison with other catalysts in the reaction of methyl vinyl ketone with indole to get β -indolylketone, which are valuable compounds as discussed earlier. Effect of various parameters on the rate of reaction was studied systematically and the mechanism and kinetics of reaction were established.

2. Experimental section

2.1. Chemicals

The following chemicals were procured from firms of repute and used without further purification. Zirconium oxychloride, aqueous ammonia solution, cesium chloride, dodecatungstophosphoric acid (DTP), chlorosulfonic acid, indole, methyl vinyl ketone, toluene and benzyl chloride were obtained from S.D. Fine Chem. Ltd., Mumbai, India. Tetraethyl orthosilicate and K-10 were obtained from Fluka Germany. Other reagents and solvents were purchased from S.D. Fine Chem Ltd. The catalysts used for the reaction were dried at 120 °C for 2 h before use., 20% w/w Cs_{2.5}H_{0.5}PW₁₂ O₄₀ (Cs-DTP/

K10 clay) [39], UDCaT-4 [32,33] UDCaT-5 [34], UDCaT-6 [35,36], persulfated alumina zirconia (PAZ) [32], and sulfated zirconia (S-ZrO₂) [38–41] were prepared by well established procedures reported from our laboratory.

2.2. Preparation of silica tubes

The method reported by Chaudhary et al. [42] was used to prepare silica tubes. In preparation of silica tube, tetraethyl orthosilicate (TEOS), meso-tartaric acid, water and ethanol were all maintained at 0 °C for 20 min before their use as reagents. Then the required amount of tartaric acid dissolved in 6 ml of water and 2.5 ml of ethanol was taken and ammonia vapors were bubbled through it to get a cloudy solution of ammonium tartarate; to which dropwise addition of 3 ml TEOS was made. After completion of addition, the solution was kept at 0 °C for another 2 h. It was filtered and washed 4 times with ethanol. The material was dried at 110 °C for 24 h. It was then calcined at 550 °C at a rate of 1 °C/min to remove tartaric acid.

2.3. Preparation of catalyst

Sulfated zirconia (SZ)/silica tube (ST), designated as SZ/ST was prepared by adding an aqueous solution of 2.5 g zirconium oxychloride to 5 g of precalcined ST by incipient wetness technique and it was dried in an oven at 120 °C for 24 h. The dried material was hydrolyzed by ammonia gas and washed with distilled water until no chlorine ions were detected which was confirmed by AgNO₃ test. This led to the formation of Zr(OH)₄/ST. It was further dried in an oven for 2 h at 120 °C. Zr(OH)₄/ST was immersed in 15 cm³/g of 0.5 M chlorosulfonic acid in ethylene dichloride as discussed earlier [34]. It was then allowed to stand without allowing any moisture to absorb. It was oven dried at 120 °C for 24 h. The sample was then calcined at 550 °C for 3 h to get the final acidic catalyst, SZ/ST.

2.4. Characterization of support and catalyst

Infrared spectra of the samples pressed in KBr pellets were obtained with a Perkin Elmer instrument at a resolution of 2 cm⁻¹ between 4000 cm⁻¹ and 350 cm⁻¹, and in each case samples were referenced against a blank KBr pellet. Powder X-ray diffraction (XRD) patterns were obtained by using (Bruker AXS, D8 Discover, USA) Cu K α radiation at $\lambda = 1.5406 \text{ \AA}$ from $2\theta = 5^\circ - 80^\circ$. Samples were scanned from 1 to 40 in 0.045 steps, with a stepping

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