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Zirconia-supported heteropoly acids: Characterization and catalytic behavior in liquid-phase veratrole benzoylation

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Abstract

The liquid-phase benzoylation of veratrole with benzoic anhydride (BA) to 3,4-dimethoxy benzophenone was investigated using zirconia-supported silicotungstic acid (STA) as a catalyst. Catalysts with different STA loadings (5–25 wt%) and calcination temperatures (600–850 °C) were prepared by suspending zirconium oxyhydroxide in methanol solution of STA followed by drying and calcination. These catalysts were characterized by XRD, Raman spectroscopy, DTA, XPS, NH_3-TPD, FTIR pyridine adsorption, and DRUV–vis spectroscopy. XRD results indicated that the presence of STA retarded the crystallization of zirconia and stabilized ZrO_2 in tetragonal phase. Characterization of the catalyst with optimum STA loading (15%) by Raman spectroscopy showed the presence of zirconia-anchored mono-oxotungstate as the major tungsten species up to 750 °C. The catalysts showed both Brönsted and Lewis acidity, and 15% STA on zirconia calcined at 750 °C (15 SZ-750) had the highest Brönsted acidity and total acidity. The catalytic activity was found to depend on STA coverage, and the highest activity corresponded to the monolayer of silicotungstate on zirconia. Further, a comparison of the catalytic activity of 15 SZ-750 with zirconia-supported phosphotungstic acid (15%, calcined at 750 °C, 15 PZ-750) and silica-supported silicotungstic acid (15%, calcined at 300 °C, 15 SS-300) showed that silicotungstic acid and phosphotungstic acid supported on zirconia acted as efficient and stable solid acid catalysts, whereas silicotungstic acid supported on silica was leached into the reaction medium and catalyzed the reaction homogeneously. Under the reaction conditions of 120 °C and a veratrole-to-BA molar ratio of 5, the most active catalyst, 15 SZ-750, showed 99% BA conversion, and the deactivated catalyst could be regenerated by calcination without appreciable loss in activity.

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1. Introduction

Friedel–Crafts acylation reactions are of great importance in the industrial manufacture of aryl ketones and also are used extensively in the production of pharmaceuticals, insecticides, dyes, and other commercial products. Conventionally, these reactions are carried out in presence of aluminium chloride, using an acylating agent, such as acid chloride, in a volatile organic solvent [1]. Because of the complexation of the product ketone with aluminum chloride, stoichiometric excess of the catalyst must be used, which is then destroyed in the hydrolysis step required for product isolation. The large quantities of metal salt waste formed, as well as the production of HCl, have aroused much research interest in the development of new, cleaner technologies that generate minimal waste. A major step toward waste minimization would be to develop a truly catalytic process, using an acid anhydride, where the catalyst does not form a strong complex with product and is recyclable. At present, considerable efforts are being made to find efficient, sustainable, recyclable, and eco-friendly solid acid catalysts to serve as substitutes for current homogeneous Brönsted and Lewis acids. Various catalysts, including zeolites [2–5], heteropoly acids (HPAs) [6–9], and sulfated metal oxides [10–12], have been tested for this reaction.

HPAs are a unique class of materials active in both redox and acid catalysis [13–15]. These are polyoxometallates composed of heteropoly anions with metal–oxygen octahedra as the basic structural unit. The Keggin-type HPAs are the most important in

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catalysis, and 12-tungstophosphoric acid (phosphotungstic acid [PTA]) and 12-tungstosilicic acid (silicotungstic acid [STA]) are the usual catalysts of choice because of their high acidic strength, relatively high thermal stability, and lower oxidation potential compared with molybdenum HPAs. These are strong Brönsted acid catalysts, with a strength of acidity greater than that of conventional solid acids such as zeolites and mixed oxides [14].

HPAs can be used either directly as a bulk material or in supported form. The supported form is preferable because of its higher surface area compared with the bulk material (5–8 $m^2\,g^{-1}$) and better accessibility of reactants to the active sites. Acidic or neutral solids, which interact weakly with HPAs such as silica, active carbon, and acidic ion-exchange resin, have been reported to be suitable HPA supports [16]. A serious problem associated with these types of materials is their susceptibility to deactivation during organic reactions due to the formation of carbonaceous deposit (coke) on the catalyst surface. The thermal stability of HPAs is not sufficiently high to carry out conventional regeneration by burning coke at 500–550 °C, as is routinely used for zeolites and aluminosilicates [17]. HPAs are highly soluble in polar solvents and hence can leach from the catalyst surface to the reaction medium and catalyze the reaction homogeneously. Thus the preparation of HPA in supported form, which is active and stable at high temperature and in the presence of polar reactants, is essential to fully realize the potential of these materials as catalysts.

In recent years, zirconia has attracted much attention as both a catalyst and a catalyst support because of its high thermal stability and the amphoteric character of its surface hydroxyl groups [18,19]. Zirconia modified with anions like sulfate and tungstate act as strong solid acid catalysts [20,21]. In attempts to find suitable supports for HPAs, zirconia was found to be promising [22–24]. Recently, we have shown that zirconia can be used as an efficient support for HPAs [25–27].

The present study deals with the preparation of zirconia-supported silicotungstic acid and its characterization by XRD, Raman spectroscopy, DTA, XPS, NH_3-TPD, FTIR pyridine adsorption, and DRUV–vis spectroscopy. These catalysts were used in benzoylation of veratrole (1,2-dimethoxy benzene) with benzoic anhydride, and the activity of the most active catalyst 15 SZ-750 was compared with that of 15 PZ-750 and 15 SS-300.

2. Experimental

2.1. Materials

Zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) and ammonia (25%) were obtained from S.D. Fine Chemicals, Ltd., Mumbai. Veratrole (98%), 12-STA ($H_4SiW_{12}O_{40} \cdot nH_2O$), 12-PTA ($H_3PW_{12}O_{40} \cdot nH_2O$), tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$), and methanol were purchased from Aldrich. Benzoic anhydride (98%) was obtained from E. Merck India, Ltd., Mumbai. All chemicals were used as received without further purification.

2.2. Catalyst preparation

The catalysts were prepared by suspending a known amount of dried zirconium oxyhydroxide powder in a methanol solution of STA. Zirconium oxyhydroxide was prepared by hydrolysis of 0.5 M of zirconyl chloride solution by the dropwise addition of aqueous NH_3 (10 M) to a final pH of 10. The precipitate was filtered and washed with ammoniac water (pH = 8) until it was free from chloride ions as determined by the silver nitrate test. The zirconium oxyhydroxide thus obtained was dried at 120 °C for 12 h, powdered well, and dried for another 12 h. Each time, 4 ml of methanol per g of solid support was used, and the mixture was stirred in a rotary evaporator for 8–10 h. After stirring, the excess of methanol was removed at ca. 50 °C under vacuum. The resulting solid materials were dried at 120 °C for 24 h and ground well. A series of catalysts with different STA loadings (5–25%) were prepared by varying the STA concentration in methanol. The dried samples were then calcined in air. All samples were calcined in shallow quartz boats placed inside a 3-cm-diameter quartz tube in a tube furnace. The samples were heated at a rate of 5 °C min^{-1} to the final temperature and held for 4 h under static conditions, then cooled at a rate of 5 °C min^{-1} to room temperature. For comparison, catalysts with 15% PTA on zirconia (calcined at 750 °C; 15 PZ-750) and 15% STA on silica gel (calcined at 300 °C; 15 SS-300) were also prepared [28]. The support silica gel was prepared by the hydrolysis of TEOS in presence of HNO_3 followed by drying at 120 °C for 12 h, powdering, and further drying for another 12 h. The catalysts with STA on ZrO_2 are represented by xSZ-T, where x represents wt%, S represents STA, Z represents zirconia, and T denotes calcination temperature (°C).

2.3. Characterization

The specific surface areas of the catalysts were measured by N_2 physisorption at liquid nitrogen temperature using a Quantachrome Nova-1200 surface area analyzer and standard multipoint BET analysis methods. Samples were degassed in flowing N_2 for 2 h at 300 °C before N_2 physisorption measurements.

X-Ray diffraction (XRD) measurements of the catalyst powder were recorded using a Rigaku Geigerflex diffractometer equipped with Ni-filtered Cu-K_α radiation ($\lambda = 1.5418$ Å).

Raman spectra of the catalyst 15 SZ calcined at different temperatures were recorded on powder samples at room temperature with a Bruker IFS 66 spectrometer connected to a Raman module FRA 106. The 1.06-µm line of the NdYAG laser was used for excitation, and the spectral resolution was 3 cm^{-1}.

The ^{31}P MAS NMR spectrum of the catalyst 15 PZ-750 was recorded using a Bruker DSX-300 spectrometer at 121.5 MHz with high-power decoupling with a Bruker 4-mm probe head. The spinning rate was 10 KHz, and the delay between two pulses was varied between 1 and 30 s to ensure complete relaxation of the ^{31}P nuclei. The chemical shifts are given relative to external 85% H_3PO_4.

Differential thermal analysis (DTA) measurements were performed on a Pyris Diamond TG-DTA apparatus from room temperature to 1000 °C in flowing dry oxygen (ca. 50 ml min^{-1}),

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