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Highly selective oxidation of benzyl alcohol over Pt-sulphated zirconia supported on SBA-15 catalyst by using a high-pressure fixed bed reactor

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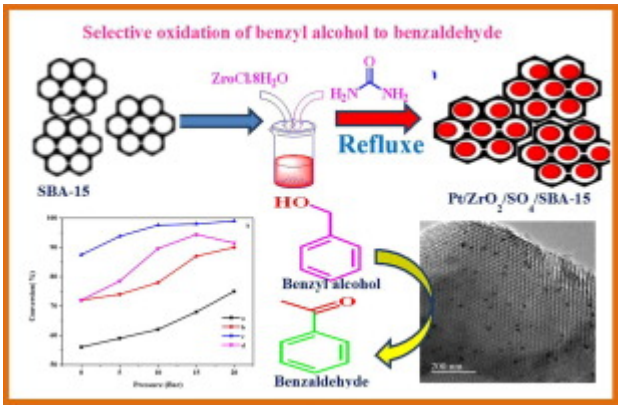
Abstract

An active platinum loaded sulphated zirconia supported SBA-15 catalyst ($Pt/SO_4/ZrO_2$-SBA-15) was synthesized and characterized using scanning electron microscope, transmission electron microscope, N_2adsorption-desorptionisotherms. The different percentage level (10, 20 and 30 wt.%) of ZrO_2 was loaded on SBA-15 by precipitation of zirconium oxychloride, calcined and sulfated with H_2SO_4. The sulphated zirconia supported SBA-15 catalyst were loaded with 0.5 wt.% of Pt and characterized by different characterization technique. The Pt-loaded catalysts were evaluated to the selective oxidation of benzyl alcohol to benzaldehyde by the continuous-flow reactor system. Also, the bulk sample of SO_4-ZrO_2 and Pt-SO_4-ZrO_2 was prepared for the comparison purposes. The supported catalysts, even at the lowest loading of 10% ZrO_2were more active than unsupported SO_4-ZrO_2. The catalyst containing 20% of ZrO_2 was most active for the selective oxidation of benzyl alcohol; the highest activity was obtained over this catalyst at a lower temperature (90 °C). The Pt/SZ-SBA-15 catalyst

showed very high catalytic activity and selectivity to benzyl alcohol oxidation. Besides, the long-term stability of the Pt/SZ-SBA-15 catalyst was excellent and there is no loss in catalytic activity or selectivity occurred during the time of continuous operation.

Graphical abstract

$Pt/SO_4/ZrO_2$-SBA-15 catalyst for highly selective oxidation of benzyl alcohol to benzaldehyde.



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Introduction

The selective oxidation of alcohols to aldehyde is one of the important reactions in organic synthesis because the corresponding aldehyde compound could be used in agriculture, pharmacy, and various chemical industries. Moreover, the selective oxidation reaction contributes to 30% of the total production of chemical products in the chemical industry [1], [2], [3], [4], [5]. Hence, the many key intermediates and chemicals such as ketones, alcohols, aldehydes, epoxides, and organic acids are produced via selective oxidation [6], [7]. Nowadays, many chemical industry processes carried out by oxidation process viz., selective oxidation of butane to maleic anhydride, ammoxidation of propylene to acrylonitrile, selective oxidation of the propene to acrolein, selective oxidation of methanol to formaldehyde and epoxidation of ethylene topropylene [8], [9], [10], [11].

Selective oxidation of benzyl alcohol has been investigated by both vapor and liquid phase [12]. The oxidations in the liquid-phase generally carried out at below 100 °C, while in vaporphase, the molecular oxygen generally required the temperatures above

200 °C resulting in the formation of CO_2 [13], [14]. Moreover, large variety of oxidants such as, dioxiranes, H_2O_2, TBHP, benzoyl peroxide, peroxy acids etc. can be utilized and make liquid phase reactions more attractive [15]. The heterogeneous and homogeneous catalysts have performed in the liquid phase selective oxidation of benzyl alcohol [16]. Besides, the heterogeneous catalysts have major advantages such as high thermal stability, multiple active sites, an ease of recovery (solid), and reusability than the homogeneous catalysts. The heterogeneous catalysts also alternatives to the conventional stoichiometric inorganic oxidants, which are generating large amounts of hazardous waste and expensive [17], [18], [19], [20], [21], [22]. Tert-butyl hydroperoxide (TBHP) used in the synthesis of peroxide derivatives, another catalytic oxidation reaction, epoxidation reactions, and also polymerization reactions in the free radical initiator. Moreover, the active oxygen in TBHP is a good oxygen supplier, safe to handle and reasonably thermally stable under reaction conditions [23], [24].

In recent times, SBA-15mesoporous silica has been recognized as a potential support for noble metals due to their ordered structure with pore diameters (in the range from 5 to 30 nm), higher surface area (more than 1000 m^2/g), high thermal stability, improved dispersion of metal particles, and metal-support interactions [25], [26], [27]. It is known that sulfated zirconia having both Lewis and Brønsted acid sites and are responsible for the high catalytic activity [28]. In many reactions, sulfated zirconia supported on SBA-15 showed high activity such as glycerol esterification with palmitic acid [29], cumene cracking [30], cellobiose hydrolysis [31], oxybromination [32], etherification of 5-hydroxymethyl-2-furfural (HMF) with ethanol [33].

The selective oxidation of aldehyde and alcohols are the important components of chemical industry fractions have been extensively investigated over zirconium sulphate SO_4–ZrO_2 and other catalysts [34]. Many reports available for oxidation of the benzaldehyde reaction over ZrO_2 supported on MCM-41 and ZSM-5. On the other hand, CeO_2 (Ce/Si = 0.38–2.32) loading MCM-41 exhibiting an excellent activity in the selective oxidation of benzyl alcohol [35], [36], [37]. As per the literature studies, the $Pt/SO_4/ZrO_2$ and $Pt/SO_4/ZrO_2$-SBA-15 supported catalyst has not been reported for the selective oxidation of benzyl alcohol in high-pressure fixed bed stainless steel reactor with TBHP. Hence this work presents the urea-assisted synthesis of SO_4/ZrO_2-SBA-15 and $Pt/SO_4/ZrO_2$-SBA-15 catalyst have been reported for the selective oxidation of benzyl alcohol. The preparation of the catalyst and the evaluation utilized with TBHP as the oxidant in the selective oxidation of benzyl alcohol. Moreover, the effects of temperature, pressure, and weight hourly space velocity (WHSV) have been investigated in detailed.

Section snippets

Preparation of catalysts

SBA-15 was synthesized in a Teflon-lined autoclave under autogenous pressure in an acidic medium (2 M HCl) following previously published article using Pluronic (P123) triblock copolymer (Mol. Wt. 5800) as the template and TEOS as the silica source [38]. The synthesized SBA-15 was dried at 373 K and calcined at 823 K after that, ZrO_2 (10–30 wt.%) was deposited over calcined SBA-15 by a urea hydrolysis method. In a typical synthesis (for 10 wt.% ZrO_2), 4.0 g of calcined SBA-15 was immersed in

X-ray diffraction studies

The low angle XRD patterns of SBA-15 and different ratio of the Pt-SZ/SBA-15 samples are presented in Fig. 1A. The SBA-15 sample exhibits the typical patterns expected for the sample, the intensity peaks are continuous decrease after loading of each of the catalyst components, viz. ZrO_2, SO_4, and Pt. This suggests that continuous loss in the orderliness of the mesoporous structure due to the sequential impregnation and calcination. A slight shift in the position of the lines towards larger

Conclusion

The Pt-SO_4-ZrO_2 supported on the high surface area SBA-15 possesses a higher catalytic activity in the of selective oxidation of benzyl alcohol to benzaldehyde than the bulk material. This is attributed to the good dispersion of ZrO_2 over the support. Even at 30% loading, ZrO_2 could not be detected by X-ray diffraction in the catalyst. Among the supported catalysts, the 20% catalyst is more active in the selective oxidation of benzyl alcohol to benzaldehyde, the maximum conversion and

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References (47)

R.V. Sharma *et al.*
Catal. Commun. (2012)

Y. Pérez *et al.*
J. Mol. Catal. A: Chem. (2012)

S. Ajaikumar *et al.*
J. Mol. Catal. A: Chem. (2008)

Y. Yu *et al.*
Chem. Eng. J. (2010)

M.D. González *et al.*
Microporous Mesoporous Mater. (2011)

N. Viswanadham *et al.*
Microporous Mesoporous Mater. (2006)

M. Boveri *et al.*
Catal. Today (2006)

K.-H. Chung
Microporous Mesoporous Mater. (2008)

M. Lenarda *et al.*
Inorg. Chim. Acta (2003)

Y. Guo *et al.*
Chem. Eng. J. (2011)

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...However, the selective oxidation of benzyl alcohol was generally applicable to homogenous catalysts. However, homogeneous catalysts have several drawbacks: strict separation, low reproducibility, lack of low conversion, cost-effectiveness, and releases of toxic by-products [1,2,4]. Though, heterogeneous catalysts have attracted much attention recently due to their huge advantages....

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Citation Excerpt :

...A method reported by Zhao et al followed for the synthesis of SBA-15 [26,34]. The SBA-15 was synthesized by following 1TEOS/0.54HCl/0.016P123/100H2O molar ratios [21]. The FSM-16 was synthesized by making use of kanemite (NaHSi2O5·3H2O) as a silica source and CTAB as a surfactant (Zym et al) [27]....

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...These noble metals are cost effective, needs high temperature and high pressure conditions.

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Citation Excerpt :

...Over the past two decades, noble metal (Pt, Au, Pd, etc.) has been widely applied as heterogeneous catalysts to oxidize alcohols to corresponding aldehydes [13–18]. Significantly, the heterogeneous catalysts have numerous advantages, such as high thermal stability, multiple active sites, an ease of recovery and reusability [19]. Wherein, researchers throughout the world have carried out considerable studies on Au-based catalysts to obtain high catalytic performance [20–24]....

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