



Short Communication

Preparation, characterization and application of sulfated Ti-SBA-15 catalyst for oxidation of benzyl alcohol to benzaldehyde

Rajesh V. Sharma, Kapil K. Soni, Ajay K. Dalai*

Catalysis and Chemical Reaction Engineering Laboratories, Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, SK, Canada S7N 5A9

ARTICLE INFO

Article history:

Received 22 June 2012

Received in revised form 1 September 2012

Accepted 22 September 2012

Available online 28 September 2012

Keywords:

Ti-SBA-15

Sulfation

Oxidation reaction

Benzyl alcohol

Catalyst acidity

ABSTRACT

Benzaldehyde is an important chemical and has tremendous application in cosmetics, perfumery, food, dyestuff, agrochemical and pharmaceutical industries. In the present investigation, threefold increase in oxidative property of mesoporous Ti-SBA-15 was observed by treatment with chlorosulfonic acid. Physio-chemical properties of this catalyst were analyzed by BET surface area, X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), FTIR, and NH₃-temperature programmed desorption (TPD) techniques. The super acidic nature of the catalyst is shown by NH₃-TPD profile. Enhanced acidity of the catalyst increases benzyl alcohol conversion from 20 to 62% without affecting benzaldehyde selectivity (95%).

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The major area of organic synthesis deals with selective oxidation of alcohols to aldehydes. Among these, aromatic aldehydes are important chemicals for the preparation of fragrances and flavors, hence, lots of attention are given to their effective production. Liquid phase oxidation of benzyl alcohol to benzaldehyde has widely attracted the research because it has tremendous application in cosmetics, perfumery, food, dyestuff, agrochemical and pharmaceutical industries, and is considered as the second most important aromatic molecule after vanillin [1,2]. Benzaldehyde is conventionally produced by oxidation of toluene and hydrolysis of benzal chloride [3,4]. The major limitation of toluene oxidation process is low selectivity, while benzal chloride process often leads to traces of chloride in the product [3,5]. The vapor phase oxidation of benzyl alcohol has been studied to overcome the above limitation [6–8]. However, high temperature is required for vapor phase reaction that leads to formation of carbon dioxide from benzyl alcohol [5,9,10]. Liquid phase oxidation of benzyl alcohol by using hydrogen peroxide is more convenient because the oxidant has high content of active oxygen and is cheap, mild and environmentally benign [11]. Soni et al. [12] reported modification of SBA-15 framework with titania, which provides additional stability to the silica framework. To the best of our knowledge, there has been no report about sulfated Ti-SBA-15 for oxidation reaction. In the present work, Ti-SBA-15 with different Si/Ti ratios have been prepared and further, catalyst was acidified with chlorosulfonic acid treatment to obtain sulfated Ti-SBA-15 catalyst. A comparative activity study of sulfated and non-sulfated catalyst has

been done. It is found that catalytic activity is increased to three fold by treatment with chlorosulfonic acid. The prepared catalysts were characterized by BET surface area, X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), FTIR, and NH₃-temperature programmed desorption (TPD) techniques, and the catalyst properties are correlated with their activities and product selectivities.

2. Experimental section

2.1. Chemicals and reagents

The following chemicals were procured from Sigma-Aldrich (Saskatoon, Canada) and used without further purifications: tetraethylorthosilicate (TEOS), titanium isopropoxide (Ti(OⁱPr)₄), pluronic P123, chlorosulfonic acid, titanium oxide (TiO₂), methylene dichloride, benzyl alcohol, hydrogen peroxide (30% w/v), acetonitrile, p-chlorobenzyl alcohol, p-methoxybenzyl alcohol, 4-nitrobenzyl alcohol, styrene, p-bromostyrene and cinnamyl alcohol.

2.2. Catalyst preparation

Ti-SBA-15 and sulfated Ti-SBA-15 with different Si/Ti ratios were synthesized by sol-gel method. The molar gel composition of the mixture was 0.988 TEOS:0.024–0.05 Ti(OⁱPr)₄:0.016 P123:0.46 HCl:127 H₂O. Typically Ti-SBA-15 with Si/Ti = 10 was synthesized by mixing 9.28 g of pluronic P123 to 228.6 g of water. After stirring for 2 h at 40 °C, a clear solution was obtained. Thereafter, 4.54 g of HCl (37%) was added and the solution was stirred for another 2 h. Then, mixture of 20.83 g of tetraethylorthosilicate and 2.84 g of titanium isopropoxide were added and the mixture was stirred for 24 h at 40 °C. The resulting gel

* Corresponding author. Tel.: +1 306 966 4771; fax: +1 306 966 4777.
E-mail address: ajay.dalai@usask.ca (A.K. Dalai).

was kept at 100 °C for 24 h in Teflon bottle for hydrothermal treatment. The solid product was recovered by filtration, washed with water, and dried overnight at 100 °C. Finally, the product was calcined at 550 °C for 6 h to remove the template. The samples were labeled as Ti-SBA-15 (10), where 10 denotes Si/Ti ratio in the sample. Sulfation of Ti-SBA-15 (10) was done by treating 0.5 M solution of chlorosulfonic acid (in methylene dichloride) per gram of catalyst. Further, catalyst was calcined at 550 °C for 3 h. It is noted as sulfated Ti-SBA-15 (10).

2.3. Catalyst characterization

Fourier transform infrared (FTIR) spectra were obtained with Perkin Elmer (Wellesley, MA, USA). The spectra for each analysis was averaged over 16 scans with a nominal 4 cm⁻¹ resolution by using spectroscopic grade potassium bromide (KBr) cell in the range of 375–4000 cm⁻¹ wave numbers. Nitrogen adsorption isotherm of the catalysts was obtained by using Micromeritics ASAP 2000 equipment. Catalysts were degassed at 200 °C and subjected to physical N₂ adsorption/desorption at -196 °C. Specific surface areas were determined through Brunauer–Emmett–Teller (BET) isothermic method, and mean pore diameter was calculated by the Barret–Joyner–Hallenda (BJH) method. Further, catalysts were characterized by powder X-ray diffraction with a D8 diffractometer using Cu K α radiation and a Bruker Smart 6000 CCD detector. X-ray diffractograms were obtained with a step rate of 0.005° with 300 s/step from 0.5 to 10° and 10–100°. NH₃-temperature programmed desorption (NH₃-TPD) of the catalyst was carried out using TPD/TPR Quantachrome (USA) instrument. 200 mg of the catalyst was purged with helium at 550 °C for 1 h. Then, the catalyst was cooled to 35 °C in flowing helium and saturated with 1% NH₃/N₂ (v/v) mixture at a flow rate of 30 ml/min for 120 min. TPD was carried out by heating the sample with 10 °C/min from 35 to 550 °C. TPD profile was recorded with a thermal conductivity detector. External morphology and surface elemental composition of the catalysts were recorded by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) by Hitachi-S4700 equipment.

2.4. Catalytic activity

Oxidation reactions were carried out in 50 ml capacity borosilicate glass reactor equipped with a six-blade pitched turbine impeller and

a reflux condenser. The standard experiment was carried out at a temperature of 60 °C with 0.01 mol benzyl alcohol, 0.04 mol of hydrogen peroxide (30% w/v), 0.5 g of catalyst and 20 ml of acetonitrile as solvent. Samples (~1 ml) were withdrawn periodically with a regular interval of 30 min and analyzed by gas chromatography equipped with flame ionizing detector. The stabilwax capillary column with 30 m length and 0.25 mm inside diameter with 0.5 μ m film thickness was used for analysis. The oven temperature was set at 80 °C for 4 min and ramped to 240 °C at 10 °C/min with the final holding time of 5 min. 1 μ l of the sample was injected with a split ratio of 10:1. Helium was used as the carrier gas. All experiments were performed in duplication and have \pm 5% error. The products were confirmed by GC–MS. Conversion and product selectivity were calculated as follows.

$$\text{Conversion(\%)} = \frac{(\text{Initial moles of reactant} - \text{final moles of reactant})}{\text{Initial moles of reactant}} \times 100$$

$$\text{Product selectivity(\%)} = \frac{\text{Moles of product formed}}{\text{Total moles of all products formed}} \times 100$$

3. Results and discussion

FTIR technique was used to interpret the nature of Ti in the silica based framework and linkage of sulfate group (Fig. 2). The band at 966 cm⁻¹ is due to Si–O–Ti vibration and the intensity of this band increases with increasing the titanium content in the framework [12–14]. The broad band in the range of 3700–3300 cm⁻¹ is due to the presence of surface hydroxyl group and physisorbed water. Sulfate moiety form covalent bond with surface hydroxyl group of the catalyst during sulfation, which can be chelated or in bridged form [15]. After treatment with chlorosulfonic acid, catalyst absorbed water and the band in the range of 1600–1700 cm⁻¹ is attributed to vibration of adsorbed water molecule [16,17]. The intensity of these band increases with decrease in Si/Ti ratio for the catalysts. It was observed from FTIR spectrum that all the sulfated catalysts have peak at 1388 cm⁻¹, which is attributed to sulfate vibration. This peak represents the amount of sulfate present in the catalyst in the chelate form [15,18]. It was also observed that the peak intensity at 1388 cm⁻¹ is increased with increase in titanium content in the catalyst i.e., for sulfated Ti-SBA-15 (80) to sulfated Ti-SBA-15 (10).

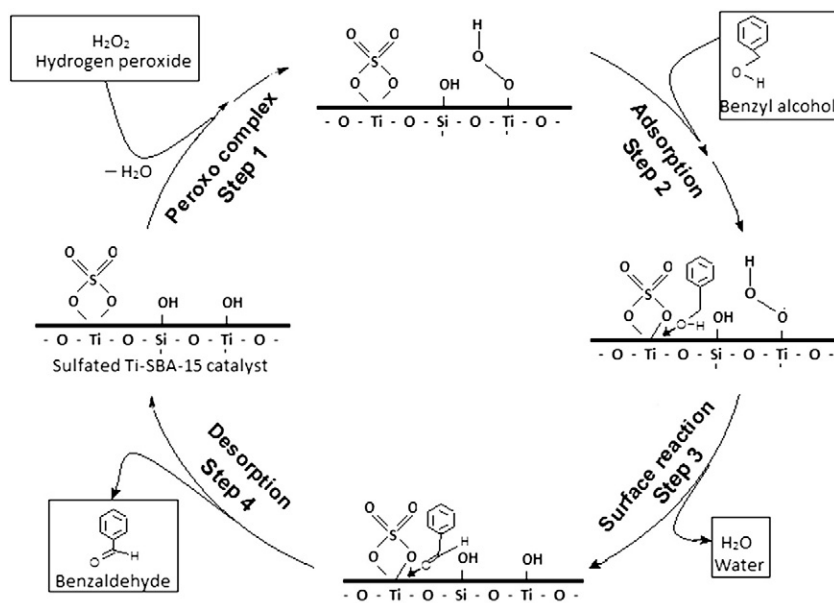


Fig. 1. The plausible mechanism for oxidation of benzyl alcohol on sulfated Ti-SBA-15 catalyst.

Download English Version:

<https://daneshyari.com/en/article/49841>

Download Persian Version:

<https://daneshyari.com/article/49841>

[Daneshyari.com](https://daneshyari.com)