Journal of Colloid and Interface Science 517 (2018) 144–154

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Regular Article

Highly selective oxidation of styrene to benzaldehyde over a tailor-made cobalt oxide encapsulated zeolite catalyst

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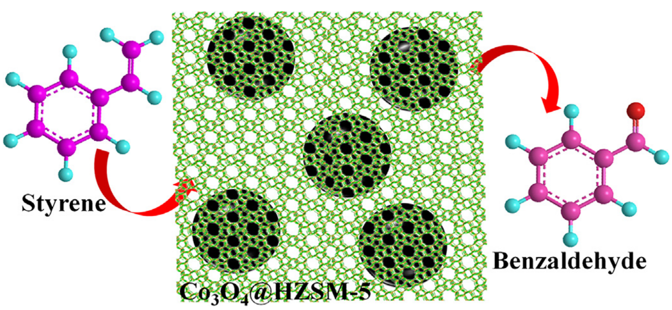
GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 October 2017
Revised 25 December 2017
Accepted 31 January 2018
Available online 2 February 2018

Keywords:
Styrene oxidation
Benzaldehyde
Cobalt oxide
Zeolite
Encapsulation

ABSTRACT

A tailor-made catalyst with cobalt oxide particles encapsulated into ZSM-5 zeolites (Co_3O_4@HZSM-5) was prepared via a hydrothermal method with the conventional impregnated Co_3O_4/SiO_2 catalyst as the precursor and Si source. Various characterization results show that the Co_3O_4@HZSM-5 catalyst has well-organized structure with Co_3O_4 particles compatibly encapsulated in the zeolite crystals. The Co_3O_4@HZSM-5 catalyst was employed as an efficient catalyst for the selective oxidation of styrene to benzaldehyde with hydrogen peroxide as a green and economic oxidant. The effect of various reaction conditions including reaction time, reaction temperature, different kinds of solvents, styrene/H_2O_2 molar ratio and catalyst dosage on the catalytic performance were systematically investigated. Under the optimized reaction condition, the yield of benzaldehyde can achieve 78.9% with 96.8% styrene conversion and 81.5% benzaldehyde selectivity. Such an excellent catalytic performance can be attributed to the synergistic effect between the confined reaction environment and the proper acidic property. In addition, the reaction mechanism with Co_3O_4@HZSM-5 as the catalyst for the selective oxidation of styrene to benzaldehyde was reasonably proposed.

1. Introduction

As the simplest aromatic aldehyde, benzaldehyde has been widely used as an important intermediate in the field of chemical industry [1–3]. Benzaldehyde can be synthesized via several methods including oxidation of benzyl alcohol, direct oxidation of toluene, hydrogenation of benzoic acid, indirect electrooxidation of toluene and hydrolysis of benzyl chloride [4–7]. However, these methods suffer from various disadvantages such as complex synthesis process, expensive raw material, severe environmental pollution, low catalytic convention and poor benzaldehyde selectivity. Recently, the direct oxidation of styrene to benzaldehyde using environmentally friendly oxidant has aroused much attention in

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https://doi.org/10.1016/j.jcis.2018.01.113

the academic community owing to its simple reaction procedure and pollution free feature [8–10].

Many kinds of catalysts, including homogeneous and heterogeneous catalysts, have been utilized for the oxidation of styrene to benzaldehyde. For the homogeneous catalysts, such as CoTPPS [11] and metal-schiff base complexes [12], the high cost, separation difficulty and poor recycling performance have severely limited their further application in the styrene oxidation process. Among the heterogeneous catalysts, zeolites modified with metals were mostly investigated such as Ti-MCM-41 [13], Co-ZSM-11 [14], Co-β [15], MCM-bpy-Mo [16], TM-MCM-48 (TM = Mn, V, Cr) [17], CoVSB-5 [18], Fe-Ti-SBA-15 [19], $H_3PW_{12}O_{40}$/SBA-15 [20], Ag/4A-zeolite [21]. However, these zeolite-based catalysts exhibited several insurmountable problems such as high cost, complicated or time-consuming preparation process and unsatisfactory reaction results. Furthermore, metal oxides, such as CeO_2 [22], Mn_3O_4 [23], Co_3O_4 [23], TiO_2 [24], $Mg_{0.5}Cu_{0.5}Fe_2O_4$ [25], were applied in the oxidation of styrene as well. These catalysts usually required expensive oxidant such as tert-Butyl hydroperoxide (TBHP) in the reaction procedure. Moreover, despite the good morphology and structure property of these metal oxide catalysts, they usually exhibited low conversion of styrene and poor selectivity of benzaldehyde.

In this study, based on our previous reports [26–29], we report on the facile synthesis of an intriguing cobalt oxide encapsulated zeolite catalyst (Co_3O_4@HZSM-5) which can function as a highly efficient and stable catalyst for the selective production of benzaldehyde from the oxidation of styrene with H_2O_2 as a green and economic oxidant. Various reaction parameters, including reaction time, reaction temperature, different kinds of solvents, styrene/H_2O_2 molar ratio and catalyst dosage on the catalytic performance were fully investigated to screen the optimum reaction condition. What's more, based on the characterization data and reaction results, the reaction mechanism with the Co_3O_4@HZSM-5 catalyst for the synthesis of benzaldehyde from the styrene oxidation process was rationally proposed.

2. Experimental

2.1. Materials

$Co(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, tetrapropylammonium hydroxide (TPAOH, 25%), ethanol, $NH_3{\cdot}H_2O$ (25–28%), acetonitrile, hydrogen peroxide (H_2O_2, 30%), N,*N*-dimethylformamide (DMF), styrene, CH_3OH and toluene were purchased from Sinopharm Chemical Reagent and used without further purification. The SiO_2 support (specific surface area 379 $m^2{\cdot}g^{-1}$, pore volume 1.018 $cm^3{\cdot}g^{-1}$ and mean pore size 6.9 nm) is commercially available.

2.2. Catalyst preparation

The precursor Co_3O_4/SiO_2 with 10 wt% cobalt loading was prepared via impregnating the SiO_2 support with an aqueous solution containing the required amount of $Co(NO_3)_2{\cdot}6H_2O$. After that, the sample was dried at 120 °C for 12 h before being calcined in air from room temperature to 500 °C for 2 h.

The Co_3O_4@HZSM-5 catalyst was prepared by a hydrothermal method with TPAOH as the structure-directing agent. In a typical process, $Al(NO_3)_3{\cdot}9H_2O$, served as Al source, was firstly dissolved by a mixture solution of H_2O and ethanol in a Teflon-lined stainless

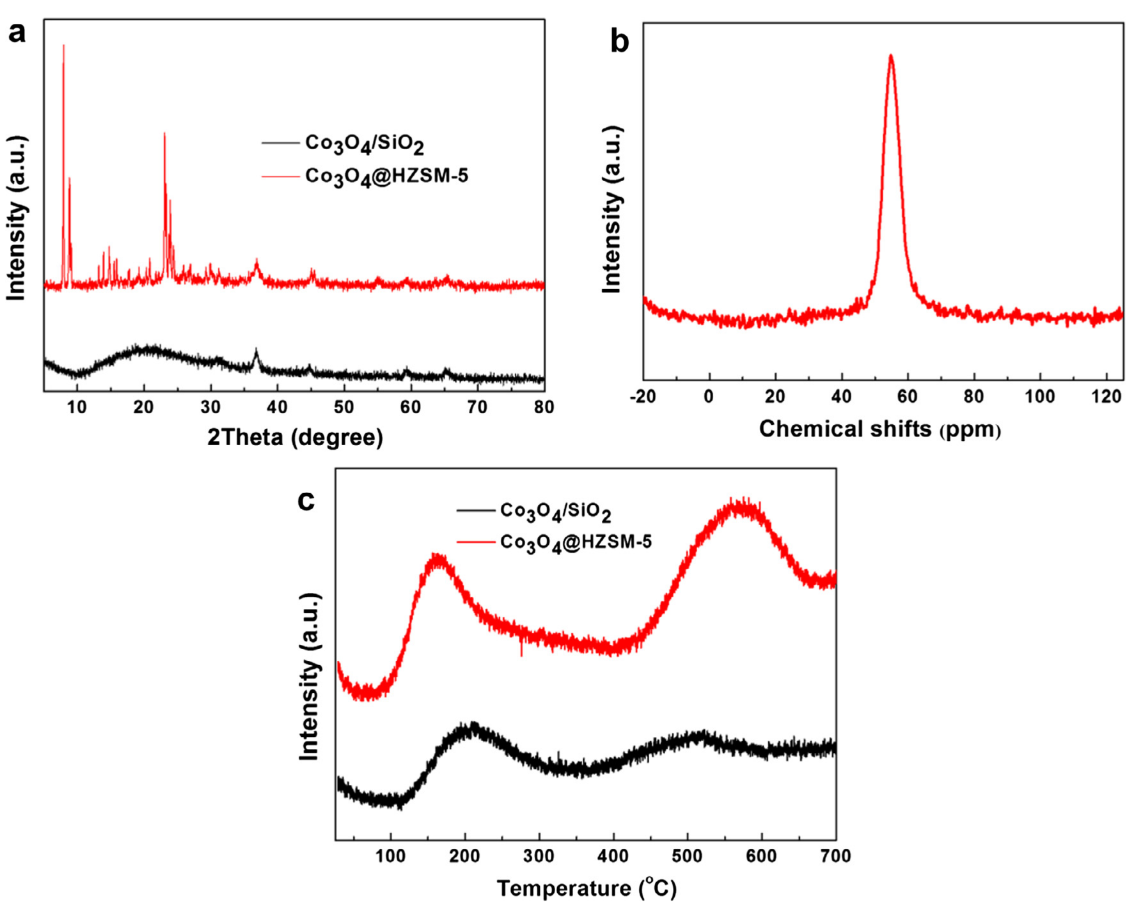

Fig. 1. (a) XRD patterns of the Co_3O_4/SiO_2 and Co_3O_4@HZSM-5 catalysts, (b) ^{27}Al-NMR spectrum of the Co_3O_4@HZSM-5 catalyst, and (c) NH_3-TPD profiles of the Co_3O_4/SiO_2 and Co_3O_4@HZSM-5 catalysts.