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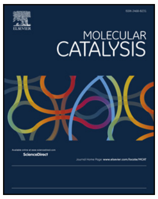

Highly active SBA-15-confined Pd catalyst with short rod-like micro-mesoporous hybrid nanostructure for *n*-butylamine low-temperature destruction

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ABSTRACT

Catalytic destruction of nitrogen-containing volatile organic compounds (NVOCs) is rarely reported although they can make great harm to the environment and public health. In the present work, a series of short rod-like micro-mesoporous composite SBA-15 materials (SBA-15-r) with developed porosity and enhanced mass transfer performance were rationally designed and synthesized, and highly dispersed and thermally stable Pd nanoparticles were successfully introduced into the mesopore channels of SBA-15-r *via* an extraordinary incipient wetness impregnation with the assistance of furfuryl alcohol and trimethylbenzene. The correlation between catalyst property and catalytic performance in *n*-butylamine destruction was elucidated. ^{29}Si MAS NMR and FT-IR results show that phosphorus is incorporated into the skeleton of SBA-15-r through a P—O—Si connection, altering the structural property of support. All Pd/SBA-15-r materials are highly active and stable catalysts with *n*-butylamine totally converted at 280 °C. Amongst, Pd/S-5 possesses the best *n*-butylamine oxidation activity and lowest NO_x formation rate ascribable to the largest surface area and highest porosity which can promote the dispersion of Pd active sites and accelerate the oxidation process and product diffusion, inhibiting the formation of reaction byproducts. Moreover, the structural micropores over Pd/SBA-15-r catalysts play an important positive role in NO_x formation control. The *n*-butylamine destruction mechanism were further discussed according to the results of gas chromatography and *in situ* DRIFTS. We believe that the present work provides new insights into the design and application of high-efficient catalysts based on hierarchical materials in NVOC elimination.

1. Introduction

Volatile organic compounds (VOCs) are main precursors of ozone and photochemical smog, which can make serious damage to the environment and human health [1,2]. Nitrogen-containing VOCs (NVOCs) such as amines, amides, nitro-compounds, and nitrile are one type of representative VOCs mainly emitted from industrial processes [3]. *N*-butylamine is widely used in pharmaceutical industrial and production of pesticide, causing great irritation to our eye, skin, and respiratory system. Nowadays, various methods have been developed for VOC removal such as adsorption, thermal combustion, photocatalytic decomposition, and catalytic combustion [4]. Amongst, the catalytic combustion is regarded as the most efficient and economical approach for the removal of VOCs with low concentrations [5]. Different from combustion of other kinds of VOCs, the yield of byproduct NO_x should be specially concerned and controlled in catalytic combustion of NVOCs to avoid the secondary pollution [2,6,7]. However, the catalytic combustion of NVOCs is rarely studied at present.

Noble metals are often used in VOC catalytic combustion due to their superior low-temperature activity. Amongst, platinum and palladium have been the most studied [8]. Compared with Pt, Pd is cheaper and has better resistance to thermal sintering and toxic compounds [9]. As such, Pd-based material is a promising catalyst for VOC combustion as the cost and stability are two of the most crucial factors determining the potential practical applications of a catalyst. The Pd particle size, active phase dispersion, preparation method, and palladium precursor type can influence the activity of Pd-based catalysts [1,10–12]. It is generally accepted that the support nature plays an important role in

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the improvement of catalytic oxidation efficiency. In general, material with high surface area, ordered pore channel, and developed porosity should be a desired support candidate. High surface area can enhance the dispersion of noble metal and increase the amount of active sites, and abundant ordered pores can accelerate reactant diffusion, enhance active site accessibility, and reduce the retention time of reaction products in catalyst [13].

Mesostructured SBA-15 has been widely used as catalyst support because of its high surface area, ordered pore structure, narrow pore size distribution, excellent hydrothermal stability, and potential ability to inhibit active particles growth and aggregation in its pores [14,15], appearing to be one of the best supports for Pd-loaded catalysts. However, conventional fiber-like SBA-15 possesses a 2D mesoporous structure with long and curved pore channels (even more than 100 μm) and densely packed secondary morphology, greatly limited the diffusion of large molecules within their pore channels and suppressed the mass transfer in catalytic reactions [16]. As such, modified SBA-15 with shorter pore channles in the form of films, spheres, rods, or platelets has been developed through the addition of salts/cosurfactants into the precursor solution or change preparation conditions [16–19]. For instance, Yu et al. [19] synthesized the rod-like SBA-15 with pore channel length of 1–2 μm by adding KCl into the synthesis system. Significantly, there exists residual micropores in the inorganic walls of the mesoporous structure, forming a 3D connected pore network which could promote mass transfer and reaction efficiency. The synthesis of SBA-15 with 3D micro-mesoporous composite structure has attracted increasing interests in recent years. Zhong et al. [20] prepared micro-mesoporous composite SBA-15 with various contents of residual micropores. Colilla et al. [21] adjusted the micropore volume in SBA-15 by adding different amounts of phosphoric acid into the precursor mixture. Zhu et al. [22] enhanced the content of micropore in SBA-15 by introducing poly vinyl alcohol (PVA) to the synthesis mixture and proved that the material with high micropore volume had better catalytic efficiency.

Previous work suggested that noble metal confined catalysts possess high catalytic activity and stability as the pore channels of supports have the potential ability to inhibit active particles growth and aggregation during reactions. Various strategies were developed for incorporating metal nanoparticles into mesoporous silica, such as chemical vapor deposition, wet impregnation, and ion exchange [23–26]. However, the aforementioned approaches could not ensure the encapsulation of Pd nanoparticles inside the mesoporous channels, and hence large metal aggregates would form on the external surface of supports during thermal treatments or reactions. Noteworthily, researchers suggested that post grafting approach can control the location and size of metal nanoparticles [27]. However, the grafting method is relatively complicated and requires many expensive coupling agents. As a consequence, the exploring and developing a simple and efficient protocol for the preparation of noble metal confined catalysts is of great significance.

In this work, a series of short rod-like micro-mesoporous composite SBA-15 supports with adjustable microporosity were synthesized in order to facilitate the diffusion of reactants and products. Moreover, we adopt a novel and economical incipient wetness impregnation approach, which allows the preparation of highly dispersed Pd nanoparticles within silica mesopores using $Pd(acac)_2$ as Pd source and furfuryl alchohol (FA) and trimethylbezene (TMB) as co-solvent. It is regarded as that this is an universal protocol for the preparation of silica-confined metal catalysts. The aim of this research is to comprehensively investigate the catalytic properties (activity, selectivity, and stability) and mechanism of these novel Pd-confined catalysts in *n*-butylamine (a typical NVOCs) destruction, and emphatically illuminate the relationship between the material phsicochemical properties and catalytic performance. The application of synthesized micro-mesoporous composite materials in other regions such as catalysis, separation, and adsorption can be reasonably anticipated.

2. Experimental

2.1. Material preparation

2.1.1. Synthesis of short rod-like SBA-15 support

Typically, 3.2 g P123 ($EO_{20}PO_{70}EO_{20}$) and 5.9 g KCl were dispersed in a solution contained 140 g of deionized water, 13.5 g HCl (36.5%), and a certain amount of H_3PO_4 (85%) under stirring at 38 °C. When the P123 and KCl were completely dissolved, 9.0 mL tetraethyl orthosilicate (TEOS) was added dropwise. The mixture was reacted under a static condition at 38 °C for 24 h and then aged in a sealed Teflon container at 100 °C for 24 h. The solid was filtered and washed with deionized water thoroughly and dried at 60 °C for 12 h. Template was removed by a two-step calcination, that is, heating at 350 °C for 3 h and then at 550 °C for 4 h (heating rate of 5 °C/min). According to the mole ratio of $H_3PO_4/HCl = 0, 1/3, 1/2, 1/1, 2/1, 3/1$, the SBA-15-r supports were labeled as S-1, S-2, S-3, S-4, S-5, and S-6, respectively.

2.1.2. Synthesis of Pd-confined catalysts

A certain amount of $Pd(acac)_2$ was dispersed in a mixed solution of furfuryl alcohol (FA) and trimethylbenzene (TMB). The volume ratio of FA: TMB is 2. Above mixture was used to infiltrate SBA-15 *via* an incipient wetness impregnation. Then, the sample was sequently heated at 60 and 80 °C (each for 12 h) for polymerization of FA. After drying at 60 °C for 12 h under vacuum, the powder was calcined at 550 °C for 6 h in N_2 for carbonization of FA, then at 550 °C for 6 h in air to remove the carbon to obtain the Pd-confined catalyst. The sample was reduced in a pure H_2 stream for 2 h at 480 °C. The obtained samples were labeled as Pd/S-1, Pd/S-2, Pd/S-3, Pd/S-4, Pd/S-5, and Pd/S-6. The theoretical Pd loading of these catalysts is 0.3 wt.%.

2.2. Material characterizations

X-ray diffraction (XRD) measurements were performed on a powder diffractometer (PANalytical, Netherlands) equipped with Cu-Ka radiation in the 2θ range of 0.8–8° (scanning rate of 0.5°/min) and 10–80° (scanning rate of 4°/min), respectively. The tube voltage was 45 kV and the current was 40 mA. N_2 adsorption/desorption isotherms were measured on a Builder SSA-6000 apparatus at liquid N_2 temperature. The samples were pretreated at 300 °C under vacuum for 3 h. The specific surface area of the samples were calculated from the adsorption isotherm ($P/P_0 = 0.05–0.30$) by the Brunauere-Emmette-Telle (BET) method. The mesopore size distribution was got by the Barrette-Joynere-Halenda (BJH) method and the micropore size distribution was got by the Horvathe-Kawazoe (HK) method. Morphology of the samples were observed on a field emission scanning electron microscopy (FE-SEM, JEOL-7800F) operating at an acceleration voltage of 15 kV and high resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 F30, USA) operating at an acceleration voltage of 300 kV. Fourier transform spectroscopy (FT-IR) adsorption spectra of samples were recorded in a Tensor 37 (Bruker, Germany) FT-IR spectrometer in 4000–400 cm^{-1}. ^{29}Si MAS NMR was performed on a Bruke AVANCE III 400WB. X-ray photoelectron spectroscopy (XPS) were collected on a AXIS ULtrabld instrument (Kratos, UK) operated at 250 W using Mg-Kα radiation at 1253.6 eV. Binding energies (BE) were calibrated relative to the C 1s peak (284.8 eV). The actual Pd content over samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a PerkinElmer OPTIMA 7000 DV. The temperature-programmed reduction (H_2-TPR) experiments were carried out on a PCA-1200 (Builder, China) equipped with a thermal conductivity detector (TCD). Typically, 75 mg samples were pretreated at 300 °C for 2 h in a flow of argon (40 mL/min). Then, the samples were reduced from room temperature to 400 °C at a heating rate of 10 °C/min in a flow of 5% H_2/Ar (50 mL/min). The hydrogen in the effluent was continuously monitored by the TCD.

The Pd dispersion was determined by CO pulse chemisorption.