



Contents lists available at ScienceDirect

Particuology

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



Mesoporous carbon-supported cobalt catalyst for selective oxidation of toluene and degradation of water contaminants

Yuan Zhuang^a, Qisong Lin^a, Li Zhang^b, Lianshun Luo^a, Yuyuan Yao^{a,*}, Wangyang Lu^a, Wenxing Chen^a

^a National Engineering Lab of Textile Fiber Materials & Processing Technology, Zhejiang Sci-Tech University, Hangzhou 310018, China

^b School of Material Science and Chemical Engineering, Ningbo University, Ningbo 315211, China

ARTICLE INFO

Article history:

Received 9 March 2015
Received in revised form 8 May 2015
Accepted 20 May 2015
Available online xxx

Keywords:

Mesoporous carbon
Cobalt
Bifunctional catalyst
Toluene oxidation
Dye degradation

ABSTRACT

Mesoporous carbon-supported cobalt (Co-MC) catalysts are widely applied as electrode materials for batteries. Conversely, the development of Co-MC as bifunctional catalysts for application in organic catalytic reactions and degradation of water contaminants is slower. Herein, the catalyst displayed high activity in the selective oxidation of toluene to benzaldehyde under mild conditions, attaining a high selectivity of 92.3%. Factors influencing the catalytic reaction performance were also investigated. Additionally, Co-MC displayed remarkable catalytic activity in degrading dyes relative to the pure metal counterpart. Moreover, the catalyst exhibited excellent reusability, as determined by the cyclic catalytic experiments. The paper demonstrates the potential of Co-MC as a bifunctional catalyst for both toluene selective oxidation and water contaminant degradation.

© 2015 Chinese Society of Particuology and Institute of Process Engineering, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

Introduction

Catalytic oxidation is a fundamental reaction occurring in nature as well as a key conversion reaction employed in the synthesis and degradation of organics (Ding et al., 2012; Piera & Bäckvall, 2008). Over the past decades, considerable research efforts have been devoted to design and develop economically feasible and efficient catalysts (Boppana & Jiao, 2011; Huang, Xiang, Li, Jiang, & Guo, 2011; Liang et al., 2011). Transition metals, as a class of promising catalysts, have been applied to catalyze various oxidation reactions based on their multiple oxidation states, particularly in the field of organic catalytic reactions and degradation of water contaminants (Dhakshinamoorthy, Alvaro, & Garcia, 2011; Long, Liu, Wu, Liao, & Li, 2013; bin Saiman et al., 2012; Yan, Li, Zhao, & Chen, 2012; Zhang et al., 2013; Zou et al., 2012). Two groups of transition metal-based catalysts, including noble metal catalysts (Pd, Pt, and Au) and base metal catalysts (Mn, Co, Cu, Fe, and Ni), are used widely. Noble metal catalysts are typically employed because of their high catalytic activity; however, their low abundance and high cost hinder their wide application (Chuang, Liu, Lu, & Wey,

2009). Consequently, base metal catalysts have been increasingly investigated as potential alternatives for oxidation reactions.

Among the base metal catalysts studied, cobalt catalysts are promising for use in catalytic oxidation reactions (Jiao & Frei, 2010; Popova et al., 2014). To enhance the stability and dispersion of the active metal, supports, such as SiO₂ (Eggenhuisen, Breejen, Verdoes, Jongh, & Jong, 2010; Szegedi, Popova, Mavrodinova, & Minchev, 2008), Al₂O₃ (Rane, Borg, Rytter, & Holmen, 2012), TiO₂ (Yang, Choi, & Dionysiou, 2007; Shukla, Wang, Sun, Ang, & Tadé, 2010a), MgO (Zhang et al., 2010), and zeolite (Shukla, Wang, Singh, Ang, & Tadé, 2010b), are generally employed. Unfortunately, the interaction between cobalt and SiO₂ or Al₂O₃ leads to lower catalytic activity because of the formation of mixed compounds during catalyst preparation and reaction (Zhang et al., 2009a). In contrast, the use of TiO₂, MgO, or zeolite supports is limited owing to the unavailability of a suitable approach to recover the nanosized cobalt particles, thereby potentially causing secondary environmental problems (Shukla et al., 2010a; Yang et al., 2007; Zhang et al., 2010). The use of suitable supports would offer excellent catalytic performance (Huang, Bao, Yao, Lu, & Chen, 2014). Therefore, selection of the support is very important toward preparing supported cobalt catalysts with appealing performance and extensive applications.

In contrast to the abovementioned supports, mesoporous carbon (MC) has received extensive attention as an excellent support

* Corresponding author. Tel.: +86 571 86843810; fax: +86 571 86843255.
E-mail addresses: yyy0571@126.com, yyy@zstu.edu.cn (Y. Yao).

for catalysts because of its attractive features, i.e., high surface area (up to 2500 m²/g), large specific pore volume, narrow pore size distribution (2.0–50 nm), and chemical inertness (Almeida, Melo, & Airoidi, 2013; Li, Fu, & Su, 2012; Sun et al., 2012). Furthermore, their open porous network reduces mass transfer limitations when compared with traditional microporous activated carbons (Deng et al., 2010; Wang et al., 2013). Hence, several researchers have investigated mesoporous carbon-supported cobalt for various applications. For instance, Yang et al. (2012) reported the use of ordered mesoporous carbon-supported cobalt-based catalysts for Fischer–Tropsch synthesis, and investigated the influence of the amount of carbon precursor on catalytic performance. Dai & Vogt (2012) reported the synthesis of mesoporous carbon–cobalt composite for the removal of methylene green; the composite catalyst exhibited excellent capacity. Based on these studies, the integration of cobalt into MC holds great potential in developing cobalt catalysts with highly accessible active sites and stable characteristics while retaining the individual functionality. Furthermore, the MC support is expected to provide a good anchoring platform to trap the nanoparticles and prevent catalyst aggregation during catalytic oxidation reactions.

To our knowledge, mesoporous carbon-supported cobalt (Co-MC) catalysts have been widely applied as negative electrode materials for lithium batteries (Hou, Ndamanisha, Guo, Peng, & Bai, 2009; Liu et al., 2008). In contrast, the use of Co-MC as a bifunctional catalyst for organic catalytic reactions and degradation of water contaminants has been rarely reported.

Herein, toluene and various dyes were employed as model compounds to investigate the bifunctional catalytic properties of Co-MC. The results showed that the Co-MC catalyst exhibited high activity toward the selective oxidation of toluene and excellent potential toward the degradation of dyes. Furthermore, compared with free cobalt catalyst, the introduction of MC support into cobalt catalyst system led to a significant enhancement in catalytic activity, and the composite catalyst displayed convenient magnetic separability and excellent reusability. This research offers a new strategy to design catalysts with integrated functions for various advanced applications in organic synthesis, green chemistry, and environmental treatment.

Experimental

Materials

Poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) triblock copolymer Pluronic F127 (PEO₁₀₆PPO₇₀PEO₁₀₆) was purchased from Sigma-Aldrich Co., Ltd. (Shanghai, China). Phenol, formaldehyde, sodium hydroxide, hydrochloric acid, toluene, hydrogen peroxide, acetonitrile, and ethanol were purchased from Gaojing Chem. Co., Ltd. (Hangzhou, China). Cobalt (II, III) oxide (Co₃O₄) and peroxymonosulfate (PMS; Oxone) were purchased from Aladdin Co., Ltd. (Shanghai, China). Reactive Red M-3BE (RR M-3BE), Acid Red1 (AR 1), Acid Orange 7 (AO 7), Reactive Brilliant Orange K-GN (RBO K-GN), Basic Green (BG), and Weak Acid Pink BS (WAP BS) were commercial compounds (Shinyang Samwoo Fine Chemical Co. Ltd., Hangzhou, China). All chemicals were used as received without any further purification. Doubly distilled water was used in all experiments.

Preparation of Co-MC catalyst

Soluble resol precursors were prepared using phenol and formaldehyde in a base-catalyzed process according to Sun et al. (2012). The detailed synthesis procedure is available in the Supplementary Material. The Co-MC composite was synthesized through

simple Co₃O₄ doping in mesoporous carbon. Typically, 2 g Pluronic F127 was dissolved in 15 ml absolute ethanol at 40 °C. Then, 4.87 g resol precursor solution (51.3 wt% in ethanol) was gradually added, and the mixture was stirred for 10 min, after which 1.47 g Co₃O₄ powder was added. After further stirring for 30 min at 40 °C, the mixture was transferred into Petri dishes that were lined with silicon paper to avoid detachment issues. Subsequently, ethanol in the mixture was evaporated for 8 h at 35 °C. The resulting sticky film was subjected to curing at 100 °C. Finally, the obtained solid product was ground into powder. The powder sample was then pyrolyzed in a tube furnace at 800 °C for 4 h under N₂ atmosphere (heating rate: 1 °C/min) to decompose the triblock copolymer template and carbonize the resol precursor to finally generate cobalt and its metal oxide.

Characterization of catalyst

The catalyst samples were characterized by X-ray diffraction (XRD, XTRA, Thermo ARL, Switzerland), transmission electron microscopy (TEM, JEM-2100, JEOL, Japan), Brunner–Emmet–Teller (BET) surface area analysis (3H-2000PS1, Beishide Instrument Technology Co. Ltd., China). The magnetic properties of the Co-MC composite catalyst were investigated using a vibrating sample magnetometer (VSM, 7410, Lake Shore, USA). The toluene final reactant and product mixtures were analyzed by gas chromatography mass spectrometry (GC-MS, 6890 N/5973i, Agilent, USA) using bromobenzene as internal standard. The degradation efficiency of the dyes was determined by UV–visible absorption spectroscopy (U-3010, Hitachi, Japan).

Catalytic studies

The catalytic performance of the Co-MC composite toward the selective oxidation of toluene was examined under atmospheric pressure. Briefly, 3 ml toluene and 15 ml 35% aqueous H₂O₂ in acetonitrile (20 ml) were added to an appropriate amount of catalyst in a reaction vessel under continuous vigorous stirring at the desired temperature. After a given reaction time, excess H₂O₂ was quenched with sodium thiosulfate (Na₂S₂O₃), and the reaction mixture was separated by a magnet to remove the catalyst, followed by extraction with ethyl acetate. The final reactant and product mixtures were analyzed by GC-MS using bromobenzene as an internal standard. The yield of benzaldehyde and its selectivity was calculated using the following equations:

$$\text{Conversion (\%)} = \frac{\text{PhCHO}}{\text{PhMe}_{\text{all}}} \times 100, \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\text{PhCHO}}{\text{PhMe}_{\text{in}}} \times 100, \quad (2)$$

where PhCHO is the molar content of benzaldehyde, PhMe_{in} is the molar content of toluene that participated in the reaction, and PhMe_{all} is the initial molar content of toluene that was added to the reaction system.

The catalytic degradation of the dyes (RR M-3BE, AR 1, AO 7, RBO K-GN, BG, and WAP BS) was performed in 100 ml glass beakers at a set temperature of 25 °C using a constant temperature shaker water bath. In all experiments, a reaction volume of 50 ml was used. A typical reaction mixture comprised RR M-3BE dye (50 μM), unless specified otherwise, Co-MC (0.2 g/L), Co₃O₄ (0.2 g/L), and PMS (120 μM). pH adjustments were undertaken at the start. At given time intervals, the degradation efficiency of the dyes were determined by UV–vis spectrometer.

The residual and removal percentages of the dyes were calculated as follows:

$$\text{Residual percentage dyes (\%)} = C/C_0 \times 100 = A/A_0 \times 100, \quad (3)$$

Download English Version:

<https://daneshyari.com/en/article/671821>

Download Persian Version:

<https://daneshyari.com/article/671821>

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