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Article

Superior performance of Co-N/m-C for direct oxidation of alcohols to esters under air

Ning Li [a,b], Sensen Shang [b], Lianyue Wang [b], Jingyang Niu [a,*], Ying Lv [b], Shuang Gao [b,#]

[a] *Henan Key Laboratory of Polyoxometalate Chemistry, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, Henan, China*
[b] *Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China*

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ABSTRACT

A convenient, expeditious, and high-efficiency protocol for the transformation of alcohols into esters using a Co-modified N-doped mesoporous carbon material (Co-N/m-C) as the catalyst is proposed. The catalyst was prepared through direct pyrolysis of a macromolecular precursor. The catalyst prepared using a pyrolysis temperature of 900 °C (labeled Co-N/m-C-900) exhibited the best performance. The strong coordination between the ultra-dispersed cobalt species and the pyridine nitrogen as well as the large area of the mesoporous surface resulted in a high turnover frequency value (107.6 mol methyl benzoate mol^{-1} Co h^{-1}) for the direct aerobic oxidation of benzyl alcohol to methyl benzoate. This value is much higher than those of state-of-the-art transition-metal-based nanocatalysts reported in the literature. Moreover, the catalyst exhibited general applicability to various structurally diverse alcohols, including benzylic, allylic, and heterocyclic alcohols, achieving the target esters in high yields. In addition, a preliminary evaluation revealed that Co-N/m-C-900 can be used six times without significant activity loss. In general, the process was rapid, simple, and cost-effective.

1. Introduction

Esters are extensively utilized as building blocks in organic synthesis, and they can also be utilized in fine chemicals, agrochemicals, and pharmaceuticals [1]. Conventionally, esterification strategies are based on the reaction of carboxylic acids, anhydrides, acyl halides, or ketenes with alcohols. However, these complicated reaction processes are usually accompanied by reagent waste and the production of a large number of undesired byproducts [1–5]. During recent decades, an enormous amount of effort has been focused on the development of cost-effective and environmentally friendly strategies for ester synthesis [6–14]. Of all the established methodologies, single-step direct oxidative esterification of alcohols, in which readily available alcohols are used as the starting materials instead of acids or their derivatives, is garnering increasing attention [15–21]. Catalysts for the direct transformation of alcohols to esters are mostly based on noble metals (e.g., ruthenium, palladium, and gold) [22–30]. However, owing to the limited amounts of precious metals, the development of non-noble-metal-based catalysts for the direct oxidative esterification of alcohols is crucial from the perspectives of economic development and environmental protection. Moreover, with regard to catalyst separation and recycling, the employment of heterogeneous catalysts is more sustainable than that of homogeneous catalysts.

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[*] Corresponding author. Tel/Fax: +86-371-23886876; E-mail: jyniu@henu.edu.cn
[#] Corresponding author. Tel/Fax: +86-411-84379248; E-mail: sgao@dicp.ac.cn

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In recent years, carbon materials have become widely applied in many fields, including materials chemistry, chemical catalysis, and electrochemical catalysis, owing to their low costs, high stabilities, and excellent electrochemical performance [31–37]. Furthermore, the introduction of exotic atoms and metals can enhance the catalytic performance of pure carbon materials. This strategy is used to tune material compositions, entire electronic structures, and surface physicochemical properties to some extent, constructing new active sites and extending the application of carbonaceous materials to a wider range of organic syntheses [38–51]. Accordingly, cobalt-based N-doped carbon materials have been proposed as potential cost-effective and environmentally benign catalysts for the direct aerobic oxidation of alcohols to esters [31,40,52,53].

In 2013, Beller et al. [53] prepared Co_3O_4-N@C with Co_3O_4 nanoparticle sizes in the range 2–80 nm by pyrolyzing cobalt salts and 1,10-phenanthroline adsorbed on Vulcan XC72R. This catalyst achieved the target reaction using 2.5 mol% Co in 24 h. In 2015, Jiang et al. [31] and Li et al. [52] almost simultaneously but separately employed ZIF-8-derived Co@C-N containing 15 mol% Co to complete the synthesis of esters, with the latter group achieving base-free esterification at room temperature in 96 h. Very recently, Li et al. [40] reported the preparation of a Mott-Schottky-type Co@NC catalyst through direct polycondensation of simple organic molecules and inorganic metal salts in the presence of g-C_3N_4 powder. However, the active cobalt species were poorly dispersed owing to the poor thermal stability of the small organic compounds and their random location on the carbon support. This unavoidable agglomeration of active cobalt species during pyrolysis greatly decreased the atomic catalytic efficiency of the resultant material. Notably, porous carbon materials are better catalytic carriers than non-porous materials owing to their large surface areas and diverse porous structures, which facilitate access to active sites and promote the transport of active oxygen species [54–56].

The design and preparation of efficient catalysts are essential activities in our field. Accordingly, we have previously fabricated mesoporous carbon materials derived from macrocyclic compounds and vitamin B_{12} that showed high activity in the formation of imines [57,58]. We also achieved the synthesis of nitriles using cobalt-modified N-doped mesoporous carbon materials [59].

Encouraged by these results, in the present study we have applied cobalt-modified N-doped mesoporous carbon (Co-N/m-C) to the aerobic oxidative esterification of alcohols with air as a benign oxidant, achieving excellent catalytic activity, selectivity, and catalyst recyclability. This outstanding performance can be attributed to the robust ligand bridge that separates the cobalt ions and anchors them at the molecular level in the precursor, allowing uniform active-site distribution in the resultant catalyst at the sub-nano- or atomic scale. We demonstrate that the Co-N/m-C-900 catalyst, i.e., that prepared with pyrolysis at 900 °C, is the most active for the target reaction. Moreover, the results of a preliminary recycling evaluation are reported, revealing that Co-N/m-C-900 can be used six times without significant loss of activity, thus demonstrating its excellent recyclability.

2. Experimental

2.1. Materials

11,11'-bis(Dipyrido[3,2-a:2',3'-c]phenazinyl (bidppz), and other reagents were obtained from commercial sources and used without further purification.

2.2. Preparation of the Co-N/m-C catalyst

To prepare the Co-N/m-C catalyst, 270 mg bidppz and 122 mg $Co(OAc)_2\cdot4H_2O$ were added to 40 mL DMF under vigorous stirring. The mixture was then refluxed at 160 °C for 2 h. Then, 400 mg SiO_2 (40 wt% Ludox HS-40 colloidal silica) was added into the above mixture, which was vigorously stirred for another 3 h. After evaporating the solvent at 180 °C, a composite of Co-bidppz and the template was obtained and then pyrolyzed at the desired temperature for 2 h under flowing nitrogen. The heating rate was 5 $°C\cdot min^{-1}$. Generally, Co-N/m-C catalyst was obtained upon removal of the template by washing with HF (10 wt%) for 24 h under ambient atmosphere at room temperature.

2.3. Characterization of catalysts

N_2 adsorption-desorption isotherms were measured using a QuadraSorb SI4 Station at −196 °C, and the samples were degassed at 300 °C for 6 h before measurement. Transmission electron microscopy (TEM) images were obtained using a JEM-2100 microscope. Scanning electron microscopy (SEM) images were obtained using a JSM-7800F microscope with an acceleration voltage of 20 kV. The Co loadings of the catalysts were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin-Elmer OPTIMA 3300DV. The detection limit was 1.0×10^{-7}. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku/Max-3A X-ray diffractometer using Cu K_α radiation (λ = 1.54178 Å). X-ray photoelectron spectroscopy (XPS) analysis was conducted using a Thermo Scientific ESCALAB 250Xi with Al K_α radiation anode ($h\nu$ = 1486.6 eV).

2.4. Process for the synthesis of methyl benzoate

A mixture of 22 mg Co-N/m-C-900 catalyst (0.44 mol% Co), 1 mL methanol, 0.5 mmol of the corresponding alcohol, and 0.1 mmol potassium carbonate was added to a 10-mL vial. The vial was placed into an autoclave, then the autoclave was filled with air to 1 bar. The mixture was stirred at 60 °C for 2 h. After the reaction, the autoclave was removed and cooled to ambient temperature. The air inside the autoclave was discharged and the vial was removed from the autoclave, then biphenyl was added to the vial as a standard. The reaction solution was diluted with methanol, and then centrifuged and analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) quantitatively and qualitatively.

2.5. Recycling of Co-N/m-C-900