Sulfur and nitrogen-doped porous cobalt carbon catalyst for high efficient aerobic oxidation of hydrocarbons

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ARTICLE INFO

ABSTRACT

The selective oxidation of hydrocarbons to corresponding ketones under green reaction conditions is of more and more important in chemical processes due to environmental and economic pressure. In this respect, we successfully prepared high efficient sulfur and nitrogen-doped porous cobalt carbon catalyst through a simple but efficient one-pot method. Potassium thiocyanate (KSCN) is using as sulfur source and complexing agent, what's more, KSCN also acts as pore-forming agent to create larger specific surface area. In addition, the as-obtained catalyst shows high catalytic performance for oxidation of hydrocarbons under solvent-free and oxygen as oxidant conditions, especially for ethylbenzene, the conversion is up to 82% with 88% of selectivity for acetophenone, which is an exciting result due to the relative low activity of oxygen in comparison with tert-butyl hydroperoxide as oxidant. This is due to structure defect and Co_4S_3 by the doping of KSCN in CoNC catalysts, which may result in the improvement of the catalytic performance of the catalysts.

1. Introduction

The selective oxidation of hydrocarbons which has drawn great attention is one of the challenging and fundamental organic reactions in green chemistry since the main products of ketones are important intermediates and fine chemicals in perfume, pharmaceutical, cosmetics industries and so on [1,2]. Under the strict pressure of environmental regulation, researchers have developed many environmentally benign, low cost, and facile methods to reduce or end use of a massive glut of toxic and expensive stoichiometric metal oxidants [3]. Recently, an increasing effort has been made to replace those unsustainable technologies by using air or molecular oxygen (O_2) under solvent-free conditions [4–6]. For example, Xu et al. took advantage of a strong base-type catalyst to oxidize ethylbenzene to corresponding acetophenone using O_2 as oxidant under mild reaction conditions, which exhibited about 29% of conversion and 71% of selectivity [7]. However, Ma et al. reported that ethylbenzene was almost completely converted to acetophenone with tert-butyl hydroperoxide (TBHP) as oxidant under water solvent and the help of N-doped graphitic catalysts [8]. Thus, the most challenging part for O_2 remains limited catalytic performance compared to other liquid-phase processes. The development of efficient green catalyst would have a significant impact on the process of aerobic oxidation under solvent-free condition.

Recent studies have demonstrated that nitrogen doped metal carbon materials (MNC) have attracted considerable attention due to their pronounced catalytic performance, which is likely to result from metal coordinated with nitrogen to generate M–N active sites [9–11]. MNC have been widely researched and show excellent catalytic performance whether in heterogeneous catalysis, electrocatalysis or photocatalysis [11–15]. Scientists have put their attention to other heteroatoms (e.g., B, S, P and I) based on MCN [16–19]. It is an effective strategy that the introduction of heteroatoms into carbon frameworks for improving its catalytic performance, arising from the variations in charge and spin densities of carbon atoms adjacent to doped heteroatoms, as demonstrated by theoretical calculation and experimental studies [8,17,20]. Sulfur and nitrogen-doped carbon catalysts have performed excellent performance in electrocatalysis and batteries, which maybe ascribe to active sites surrounded by sulfur species [19]. As far as we know, however, sulfur and nitrogen-doped carbon catalysts are seldom applied into heterogeneous catalysis. Due to the presence of extensive studies for nitrogen doped carbon based catalysts with or without metals [5,8,21], sulfur atom which properties (defect, synergistic effect, charge transfer, etc.) are similar to nitrogen atom is recognized as a novel and efficient doped atom for heterogeneous catalysis. Thus, developing cheap and effective sulfur and nitrogen-doped carbon catalysts is promising and necessary to enhance catalytic efficiency of heterogeneous catalysis.

KSCN is widely used as poisoning agent in catalysis due to its strong complexing ability for transition metal ions. Meanwhile, KSCN is a good dopant to prepare catalyst containing nitrogen and sulfur elements

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because of its excellent characteristics of rich nitrogen and sulfur as well as strong complexing ability [22]. Herein, we report one-pot method to successfully prepare sulfur and nitrogen-doped porous cobalt carbon catalyst (S–CoNC), in which 1,10-phenanthroline is used as carbon and nitrogen source and KSCN is mainly using as sulfur source and pore-forming agent. The high specific surface area of S–CoNC is produced under the assistance of KSCN and significantly higher than carbon based materials synthesized by pyrolyzing directly 1,10-phenanthroline with other special pore-forming agent or support. In comparison with the reported catalysts for aerobic oxidation of saturated hydrocarbons, the novel S–CoNC exhibited significantly higher catalytic performance, and the catalytic active site is studied in detail.

2. Materials and methods

2.1. Materials and reagents

1,10-Phenanthroline (99.0%), KSCN (98.0%), cobalt nitrate hexahydrate (99.0%), mercapto acetic acid (MMA) (98.0%) and all solvents were of commercially available analytical reagent and used without further purification.

2.2. Catalyst preparation

1 mmol of cobalt nitrate hexahydrate and 2 mmol of 1,10-phenanthroline were dissolved into 30 mL of absolute ethanol by sonication. The mixed solution was stirred at 60 °C for 0.5 h, in which a large amount of yellow precipitation was formed at the beginning. After that, 3 mmol of KSCN was quickly added into this mixture, and then continue to stir at the same temperature for 2 h. It is remarkable that the precipitation quickly changed from yellow to pink in few seconds after the addition of KSCN. The mixture was cooled down to room temperature after stirring 2 h and suction filtration. During the process of materials preparation, the following reactions could occur [23]:

$$Co^{2+} + 2\ Phen = Co(Phen)_2^{2+}$$

$$Co(Phen)_2^{2+} + 2\ SCN_- = Co(Phen)_2(SCN)_2$$
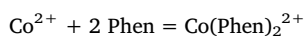
The pink precipitate was washed for several times by absolute ethanol and dried at 80 °C for overnight. The obtained product (69% of yield calculated from the mass ratio of obtained to added) was grinded and transferred to crucible, and then pyrolysis was conducted at 800 °C under N_2 for 2 h at the heating rate of 3 °C/min. The final catalyst was collected by grinding, denoted as S–CoNC.

For the control groups, S–CoNC-700 and S–CoNC-900 were only changed pyrolysis temperature; CoNC and S–CoNCm were prepared at the same procedure except for the addition of KSCN and mercapto acetic acid (MMA) as S source, respectively; S–CoNC was treated with HCl solution at 80 °C for 4 h and then S–CN was synthesized.

2.3. Characterizations

Structure and morphology characterization: The morphology and structure of catalyst were investigated by field emission scanning electronic microscopy (SEM, JSM-6700F microscope) and transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN instrument). The structure and phase purity of catalyst were examined by X-ray diffraction (XRD, Japan XRD-6100 diffractometer) equipped with Ni-filtered Cu Kα radiation (50 kV, 10 mA). Raman spectrum was recorded with LabRAM Aramis micro Raman spectrometer (laser wavelength 633 nm) using a 50× optical objective with an average spot size of around 2 μm. Nitrogen adsorption–desorption isotherms were obtained on Quantachrome NOVA-1000e at 77 K. Prior to the measurement, the samples were degassed at 200 °C for 3 h with a gas flow of N_2. The surface composition and oxidation state of catalyst were further investigated by X-ray photoelectron spectroscopy (XPS) on PHI 5000C

ESCA system (PerkinElmer) with an Al Kα (1486.6 eV) X-ray source, and all binding energies were referred to the C 1s peak (284.5 eV) arising from the C−C bonds.

2.4. Catalytic performance test

The selective aerobic oxidation of hydrocarbons was carried out in Teflon stainless steel autoclave, in which the ethylbenzene oxidation is the model reaction. In this process, 82 mmol of substrate and 30 mg of catalyst were added in reactor, which was sealed and filled with 0.8 MPa of O_2 then kept at 120 °C for 5 h with continuous magnetic stirring. The reacted solution was separated through centrifugation, meanwhile the catalyst was collected and washed for 3 times with absolute ethanol, and then dried for overnight. The mixture includes internal standard of 1,4-dichlorobenzene and bromobenzene, the as-obtained reacted solution as well as absolute ethanol was analyzed quantitatively by gas chromatography (GC) with a HP–5 ms capillary column (30 m, DF = 0.25 mm, 0.25 mm i.d.). The recycle performance was investigated under the same reaction conditions, however, the recycled catalyst was obtained via reannealing reacted catalyst at the same temperature.

3. Results and discussion

S–CoNC was prepared through a one-pot method as illustrated in Scheme 1. Cobalt nitrate hexahydrate and 1,10-phenanthroline (mole ratio of 1:2) were dissolved into absolute ethanol by sonicating to form homogeneous solution. There was a large amount of yellow precipitate ($Co(Phen)_2^{2+}$) after a period of stirring. KSCN has strong complexing ability besides rich nitrogen and sulfur. The yellow precipitate was immediately transformed to pink precipitate upon adding KSCN into this solution. It was noteworthy that the generated pink precipitate was ($Co(Phen)_2(SCN)_2$). The final pink product after filtration and drying was pyrolyzed at 800 °C for 2 h to obtain S–CoNC.

The crystallographic phases of samples were investigated by X-ray diffraction (XRD), as shown in Fig. 1a. According to the diffractogram of S–CoNC, there is a broad peak ascribed to graphite-type carbon at *ca.* 25°, while many sharp peaks appeared at 29.9°, 31.1°, 36.2°, 39.5°, 47.6°, and 54.6° are indexed to the (311), (222), (400), (331), (511), and (531) planes of hexagonal Co_4S_3 (JCPDS No. 02-1338), respectively, which suggest that cobalt has been sulfured via a simple heating treatment. Moreover, the pattern of S–CoNC also gives two weak peaks
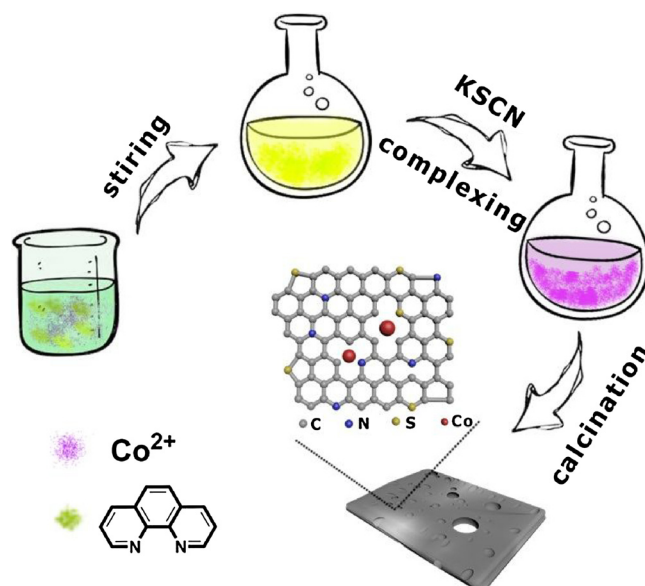
Scheme 1. Scheme illustration of preparation of S–CoNC.