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Short communication

The synthesis of N, S-codoped ordered mesoporous carbon as an efficient metal-free catalyst for selective oxidation of arylalkanes

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ABSTRACT

The N, S-codoped mesoporous carbon catalysts are prepared with a template method by using SBA-15 as the hard template, and phenanthroline and KSCN as the nitrogen and sulfur precursors. The catalyst calcined at 900 °C with relatively high specific surface areas and uniform pore sizes displays the highest catalytic performance among the obtained catalysts for selective oxidation of ethylbenzene, which is attributed to the unique architectures and the synergistic effect of pyridinic-N, graphitic-N, and thiophene-S. The excellent catalytic performance and facile preparation process enable the catalyst to be a promising metal-free substitute for selective oxidation of arylalkanes.

1. Introduction

Phenyl ketones have drawn great attention because they are important raw materials for the production of esters, resins, alcohol, perfumes, aldehydes, and pharmaceuticals [1]. Generally, the main ways to synthesize phenyl ketones are based on the selective oxidation of arylalkanes [2]. Therefore, various metal-based catalysts, for instances, Mn₃O₄ nanoparticles [3], Co₃O₄ nanocrystals [4], NiAl hydrotalcite [5], and Metal-N-C catalysts [6,7], have been employed in this process to improve the conversion and selectivity. However, the majority of these catalysts containing metals suffer from several drawbacks such as the waste of resources, high cost, and potentially detrimental to environment, which hampers their wide application [8,9]. In the past few years, materials based on nonmetallic atoms such as N, S, B, and P have been widely used for electrocatalysis [10]. Furthermore, compared with single-atom doping, the doped with multiple heteroatoms can further enhance the catalytic performance of catalysts [11,12]. However, the catalytic performance of these metal-free catalysts still has large promotion space for selective oxidation of saturated C–H bond. Toward this end, the development of cheap, environmentally friendly, efficient, stable and metal-free catalysts for selective oxidation of arylalkanes is highly desirable.

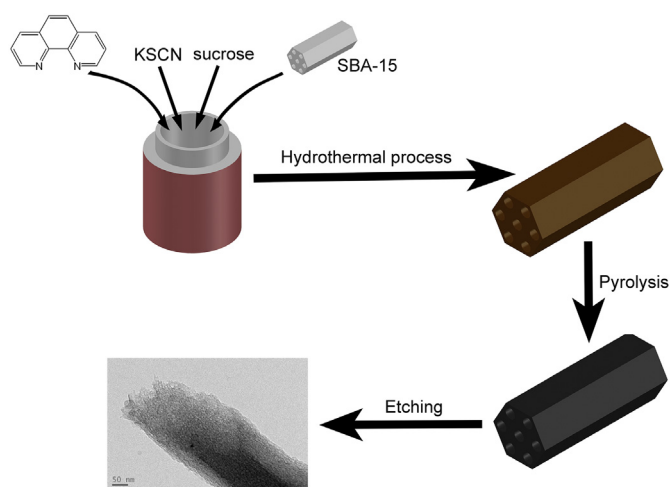
Recently, carbonaceous materials have been investigated, such as mesoporous carbon [13], graphene [14], activated carbon [15], etc. In these carbonaceous materials, ordered mesoporous carbon materials have stimulated special interest and have been applied in fields of catalysis [16], sensors [17], energy storage [18], electrochemistry [19],

et al., due to their tunable pore structures, uniform pore sizes, and large specific surface areas [20]. Generally, the ordered mesoporous carbon materials are synthesized via template method, sol-gel synthesis, and chemical blowing [21]. Among these methods, the template method has been extensively investigated to fabricate ordered mesoporous carbon materials to meet the characteristics of multifarious porous frameworks, various chemical functionalities, and well-defined morphologies [22,23]. However, most of mesoporous carbon materials have a high hydrophobic surface and limited active sites which hinder its development [24]. It is found that the incorporation of heteroatoms into the carbon framework can significantly improve the electrical properties and catalytic performance of carbon materials. For example, the ordered mesoporous carbon materials decorated with nitrogen atoms have been reported and show excellent catalytic performance in electrocatalysis and organocatalysis [24,25]. Therefore, the heteroatoms doped mesoporous carbon materials with the superiority of porous structures and heteroatoms doping effects are expected to be the cheap, efficient, and environmentally friendly metal-free catalysts.

Herein, as shown in Scheme 1, the N, S-codoped ordered mesoporous carbon materials are prepared under different pyrolysis temperature with SBA-15 as the template, and phenanthroline and KSCN as the nitrogen and sulfur precursors. Additionally, the control samples which lack one of the precursors are also prepared through the similar process. The selective oxidation of ethylbenzene is conducted to investigate the catalytic performance of the as-prepared catalysts. Moreover, the relationship between structures and performance of the samples are analyzed in detail by techniques such as N₂ adsorption-

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Scheme 1. Schematic illustration of the preparation of N, S-codoped catalysts.

desorption, TEM, SEM, XRD, XPS, and Raman.

2. Experimental sections

2.1. Synthesis of catalysts

The N, S-codoped ordered mesoporous carbon was prepared with one-pot method. Briefly, a mixture containing water (5 mL), phenanthroline (0.5 g), concentrated sulfuric acid (0.2 mL), KSCN (0.5 g), sucrose (0.5 g), and SBA-15 (0.5 g, the details for the synthesis of SBA-15 were shown in supporting information) was heated at 80 °C and 150 °C in a drying oven for 4 h, respectively. Subsequently, the dried mixture was carbonized in a tube furnace at 600 °C, 700 °C, 800 °C, 900 °C or 1000 °C under N₂ atmosphere for 2 h with a heating rate of 5 °C/min. Finally, the samples were etched in 4 M NH₄HF₂ at room temperature for 24 h, followed by filtered, washed and dried in vacuum at 100 °C. The final samples were named as S-N-C-T (T represents the heating temperature). For comparison, the N-C and S-C were also prepared through the similar process as described above but without KSCN and 1, 10-Phenanthroline hydrate, respectively.

3. Results and discussion

3.1. Catalyst characterization

The morphology and structures of SBA-15 and the as-prepared catalysts are characterized by TEM. As shown in Fig. S1a, the SBA-15 has a typical rod-like morphology and an obvious ordered mesoporous structure. Generally, the porous structure can enhance the surface area of the materials and benefit supporting more active sites, which is desirable to get the catalysts with an effective catalytic performance [26]. Similar rod-like morphology and clear dimensional channels are also observed in S-N-C-900 and other control samples, indicating that the ordered mesoporous structures of samples are replicated from the templates after the etching (Fig. 1a, Fig. S1b–d). Apparently, the materials with an ordered and numerous mesopores texture can provide a large surface area to support active species, suppress the accumulation of active species, and enhance the mass transfer of reactants [27]. In addition, the SEM image of S-N-C-900 exhibits a well-developed nanorod constructed by porous structures, which is in good agreement with the observation in TEM (Fig. S1e).

To further investigate the porosity of the catalysts, N₂ adsorption-desorption isotherms have been conducted and illustrated in Fig. 1b. There is a typical characteristic of shape and sorption type IV (according to the IUPAC classification) and a clear condensation step at P/P₀ = 0.5–0.9 in N₂ adsorption-desorption isotherm in the sample,

suggesting the presence of mesoporous [25,28]. The pore size distribution (inset of Fig. 1b) revealed that the as-prepared S-N-C-900 with a narrow pore size distribution mainly centered at 5.4 nm. The details of the Brunauer-Emmett-Teller (BET) specific surface area and average pore diameter of the samples are summarized in Table S1. According to Table S1, the specific surface areas of the S-N-C-T samples range from 359.9 m²/g to 708.3 m²/g, and the pore sizes range from 5.4 nm to 7.0 nm, showing high specific surface areas and uniform pore sizes of these samples. In addition, the control samples of S-C-900 and N-C-900 also exhibit relatively high surface areas (Table S1). Generally speaking, the highly accessible specific surface area and uniform pore sizes of catalysts are desirable for optimizing the catalytic performance of ordered mesoporous materials [26].

The structures of the as-prepared catalysts have been identified by XRD and Raman. As demonstrated in Fig. S4, the XRD patterns of S-N-C-T are similar with each other, with two distinct diffraction peaks centered at 24° and 44°, which are corresponding to the (002) and (100) plane of graphitic carbons [29]. The wide peak of the (002) plane suggests that a great amount of amorphous carbon exist in these materials [30], and the intensity of (100) peak in the samples enhances slightly with the increase of the heating temperatures, indicating a higher degree of graphitization in the high temperature. Furthermore, the I_D/I_G of S-N-C-T samples increases from 1.28 to 1.91 when the temperature is below 900 °C, and then decreases to 1.76 as the temperature rises to 1000 °C (Fig. S5). Moreover, the I_D/I_G values for S-C-900 and N-C-900 (Fig. S6) are also smaller than that of S-N-C-900. The highest I_D/I_G of S-N-C-900 may be ascribed to the increase of structural defects originating from the incorporation of heteroatoms [31].

X-ray photoelectron spectroscopy (XPS) measurement has been performed to investigate the surface composition and chemical environment of these samples. The XPS survey spectra (Fig. S7) of S-N-C-T indicate the presence of C, N, S, and O, demonstrating the successful incorporation of heteroatoms. The doping level of N and S represented by N/C ratio and S/C ratio in the samples are summarized in Table S2. It is found that the N/C ratio decreases from 0.085 to 0.020 as the heating temperatures increase, while an opposite trend from 0.033 to 0.076 is observed in S/C ratio, suggesting a higher content of doping S atoms can be obtained in a high temperature. Previous studies indicated that the doping level of N and S is not the only determinant for the catalytic performance of catalysts, and the type of bonds formed between dopant and graphitic carbon structures are also crucial [25,32].

The high-resolution C1s spectra have been fitted into five peaks, namely, the main peak is assigned to C–C at 284.5 eV, indicating that most of the carbon atoms still remain in the graphite system. The peaks at 283.9 eV and 286.1 eV can be attributed to C–S and C–N, respectively, which are further confirmed the incorporation of S and N atoms. Moreover, the other two peaks can be fitted into C–O at 286.8 eV and C=O at 287.5 eV (Figs. S8a–S11a) [31]. Although the signal of N1s is not of good quality because of the low content, four peaks at 398.4, 399.5, 400.8, and 403.5 eV, corresponding to pyridinic-N, pyrrolic-N, graphitic-N, and pyridinic-N⁺–O[–], respectively, can be observed in the N1s spectra (Fig. 2a, Figs. S9b–S11b) [31]. Likewise, in terms of S2p spectra, the peaks at 163.8 and 165.1 eV are belong to C–S–C (thiophene-S), and the other two peaks at 167.3 and 168.6 eV are ascribed to the oxidized sulfur species of C–SO_x–C (Fig. 2b, Figs. S9c–S11c) [31]. In addition, the peaks located at 531.2, 532.3, 532.6, and 533.5 eV in O1s spectra can be attributed to C=O, O–C–O/C–OH, O–S, and O–C=O, respectively (Figs. S8b, S9d–S11d) [33,34]. It has been reported that pyridinic-N, graphitic-N, and thiophene-S can bring more catalytic activities in reaction than other bonds [31,35]. The total contents of pyridinic-N and graphitic-N of S-N-C-800 are similar with S-N-C-900 (Table 1), while the content of thiophene-S in S-N-C-800 is obvious lower (Table 1). Combined with the much higher specific surface area of S-N-C-900 and S-N-C-800 than other samples (Table S1), it can be speculated that a superior catalytic performance may be obtained in S-N-C-900. Furthermore, the total contents of pyridinic-N and graphitic-N

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