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Microwave Irradiation Synthesized Cobalt-Loaded Nitrogen-Doped Active Carbon as an Efficient Catalyst for Selective Oxidation of Ethylbenzene

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Abstract. Microwave irradiation technology was used to dope nitrogen on the active carbon using dicyanodiamide as nitrogen source. The obtained nitrogen-doped active carbon was then modified by an ion impregnation method to load cobalt ions. The as-prepared cobalt-loaded nitrogen-doped active carbon (Co–N–AC) was characterized by techniques such as XRD, SEM, XPS, EA and AAS and the catalytic performance was evaluated via the selective oxidation of ethylbenzene under solvent-free condition using molecular oxygen as oxygen source. The results showed that 23.2 mol% conversion of ethylbenzene and 95.7% selectivity to acetophenone was obtained over 3%Co–N–AC, in which the excellent catalytic performance of the catalysts may be attributed to the stable doped N, the highly dispersed Co on the surface of AC and the structure of Co-N bond.

Keywords: microwave irradiation synthesis; nitrogen-doped carbon; oxidation of ethylbenzene

1. Introduction

Carbon materials, including traditional carbon materials such as activated carbon, graphite, carbon black, and many nano-carbon materials like carbon nanofibers, carbon nanotubes, and graphene are widely used as supports or catalysts in heterogeneous catalysis [1-4] due to the advantages of large specific surface area, good chemical stability, environmental-friendliness and easily accessible starting materials. In recent literature it was found that doping some heteroatoms such as N [5, 6], B [7, 8], P [8], S [9] could greatly improve the catalytic activity of the carbon materials. Among them, N-doped carbon materials have drawn much attention because of their unexpected catalytic activity [10-12] due to the redistribution of the charge of the carbon atoms influenced by the neighbor nitrogen dopants or the increased zigzag edges/defects of carbon materials [13-16], which may induce more active sites to the catalytic reaction.

Generally, the N-doped carbon materials were obtained by pyrolysis of the precursor containing C and N in an inert atmosphere, especially for some metal macrocyclic compounds which not only utilized as the precursor of N-doped carbon but also used as the source of the active metals in which it is facile to one-step synthesize M–N–C catalysts[17-20]. Fu et al. [18] synthesized cobalt catalysts embedded in N-doped carbon (Co–N–C) through heating cobalt (II) meso-tetraphenyl porphyrin (CoTPP) for the selection oxidation of ethylbenzene showed excellent catalytic performance with 13.4% conversion of ethylbenzene and 73.3% selectivity to acetophenone. Recently, using microwave synthesis technology to obtain N-doped carbon materials has aroused more and more attention. Compared to conventional heating methods, microwave irradiation technology has a several advantages of more effective, faster and more economical. In addition, the obtained products are

simpler and cleaner for the less side reactions due to selective heating in the microwave [21-22]. Nasini et al. used microwave technique to successfully synthesize nitrogen, phosphorous and oxygen enriched mesoporous carbon materials for supercapacitor with excellent electrochemical performance specific capacitance in both acidic and alkaline media [23]. Liu et al. reported a high-performance La-N-TiO$_2$/AC photocatalyst obtained via microwave irradiation with the highest degradation efficiency of 93.5% for naphthalene within 2 hours under visible light irradiation [24]. Bai et al. developed a strategy to in situ prepare functionalized ultra-microporous carbons by microwave irradiation which could be used as excellent adsorbents for uranium recovery [25].

Herein, a new strategy that utilizing microwave irradiation to directly dope nitrogen on the surface of active carbon (AC) using dicyanodiamide as N source and then modified cobalt by wet ion impregnation to obtain Co-N-AC materials is reported. The obtained Co-N-AC was characterized by the technologies of XRD, SEM, XPS, EA and AAS to gain the information of the structure and composition and then applied in the selective catalytic oxidation of ethylbenzene using molecular oxygen as oxidant to investigate the catalytic performances and stability.

2. Experimental

2.1. Materials
The main reagents used include cobalt (II) nitrate hexahydrate (Co(NO$_3$)$_2$•6H$_2$O, >99%), dicyanodiamide (C$_2$H$_4$N$_4$, >99%), urea (CH$_4$N$_2$O, 99%). AC was purchased from Shanhai Quanhu Active Carbon Co., Ltd. All the chemicals were used as received without further treatment. The water used throughout all experiments was purified through a Millipore system.

2.2. Preparation of Catalysts

2.2.1 Preparation of nitrogen-doped active carbon (N-AC).
Microwave irradiation was used to prepare nitrogen-doped active carbon. Briefly, 1.0 g of AC and 0.1g of nitrogen source dicyanodiamide were mixed and ground fully in a mortar, and then transfer to a 50 mL quartz three-necked flask placed in a carbon bath, which made of a quartz evaporating pan containing activated carbon, in a microwave oven (XH-100B, Beijing Xianghu). Before the microwave heating, the dry nitrogen was introduced to the three-necked flask via a nitrogen protection device. The black solid mixture was irradiated for 1 min by microwave with the power of 700 W, then cooled for 2 min and irradiated for another 1min, and so on. Five times later, the mixture was taken out and added another 0.1g of dicyanodiamide and ground, irradiated and so on. After three times of adding dicyanodiamide and irradiating, the obtained mixture was transfer into a round-bottled flask and 30 g of deionized water was added. The resulting suspension was refluxed in an oil bath at 100°C for 4 h to remove the unreacted dicyanodiamide. After the filtration, the obtained black solid was dried overnight at 80°C, designating as N-AC.

2.2.2 Preparation of cobalt-loaded nitrogen-doped active carbon (Co-N-AC).
Wet ion impregnation method was used to obtain cobalt-loaded nitrogen-doped active carbon. In a typical process, 2.0 g of the obtained N-AC were dispersed in 30 mL of deionized water. Then 0.264 g of Co(NO$_3$)$_2$•6H$_2$O (i.e., the amount of cobalt is 3% of that of N-AC) was added in the above mixture. The mixture was refluxed in an oil bath at 90°C for 8-9 h. After the filtration and washed several times with deionized water, the black solid powder was dried in an oven at 105°C for 8 h and cooled naturally, designating as 3%Co-N-AC.

2.3. Characterization
X-ray powder diffraction (XRD) was performed on a Rigaku MiniFlex 600 diffractometer with Cu Kα (λ=1.5418 Å) radiation operating at 30 kV and 10 mA. The scanning range was from 2θ =5 to 70° with a scanning speed of 2°/min. Scanning electron microscopy (SEM) was carried out on a JEOL JSM-6510A with a high resolution of 3.0 nm at 30 kV. Samples were grounded using aluminum stub. X-ray photoelectron spectroscopy (XPS) was recorded on a Perkin Elmer PHI 5400 ESCA system using Mg as the exciting source. Atomic absorption spectroscopy (AAS) was used to determine the

actual cobalt content in the samples on a TAS-990 atomic absorption spectrometer equipped with a cobalt hollow cathode lamp using flame atomization. Element analysis (EA) was conducted on an Elementar Vario Micro Cube analyzer.

2.4. Catalytic Reactions
The obtained black Co-N-AC solid powder was directly used as heterogeneous catalyst to investigate the catalytic performance with no further treatment. The selective catalytic oxidation of ethylbenzene was carried out in a 200 mL miniature magnetic autoclave (WCGF, Xi'An Taikang) as a batch reaction at 120°C. In typical batch experiment, 10 mL of ethylbenzene and 100 mg catalyst were loaded in the autoclave and then sealed and raised pressure to 0.8 MPa with O_2. Following that, the temperature was elevated to 120°C and kept for 4 h. After the system cooled, the catalyst was separated by high-speed centrifugation, and the liquid organic products were quantitatively analyzed using a gas chromatograph (GC) (Thermofisher Trace 1300) equipped with a FID detector and a TR-V1 capillary column (30 m×0.32 mm×0.18 μm), a programmed oven (temperature range 323-423 K), and N_2 as the carrier gas, using with bromobenzen as an internal standard. The solid obtained in the centrifugation was washed with ethanol and dried at 80°C in air. It would be reused in the stability experiments of the catalysts.

## 3. Results and Discussion

3.1. Structural Characteristics
The samples of AC, N-AC and 3%Co-N-AC were characterized by XRD analysis and the results were displayed in Figure 1. It is clearly noted that, the sample of AC, which was not treated further, presented two broad diffraction peak at around 2θ of 25° and 44°, respectively, corresponding to the (002) and (100) reflections associated with the presence of graphitic structures for AC[26, 27]. There were also some small sharp diffraction peaks with 2θ between 20° and 30°, which indicated that the AC used has a random layer of micro-crystal with graphite structure, although the crystallite is not regular. While the samples of N-AC showed very similar diffraction as that of AC except some sharp diffraction peaks reduced and other disappeared, showing that the doping of nitrogen in the heating of microwave irradiation has not changed the graphitic structures of AC but perturbed the sectional micro-crystal structure. As for the samples of 3%Co-N-AC, no evident new diffraction peaks were observed, especially the characteristic diffraction peaks of Co and CoO, indicating that cobalt is loaded on the surface of AC in amorphous form. On one hand, the reason is that the content of cobalt (3%) is very low. On the other hand, the presence of nitrogen on the carbon material would inhibit the cobalt ions from aggregation to a certain extent.
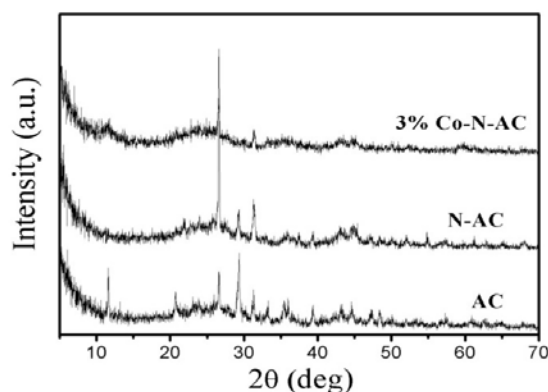
Figure 1. XRD patterns of AC, N-AC and 3%Co-N-AC, respectively.

The morphology of AC and the sample 3%Co-N-AC were then characterized by scanning electronic microscopy (SEM) and the results were displayed in Figure 2. As can be seen from Figure 2a, AC in the experiment is composed of irregular carbon particles or carbon sheets with different

sizes from 500 nm to 5 μm. The obvious interlayer structure indicated the higher surface area of AC. It also can be seen that, there are no evident differences for the morphology between AC and 3%Co-N-AC (Figure 2b). Even in the much clearer view (Figure 2c), no aggregated particles were found except the wrinkles on the surface of the carbon sheets. The reason, on one hand, is that the content of Co loaded on the surface of AC was very low, on the other hand, the loaded cobalt are homogeneously dispersed on the carbon support in the form of subnanometer clusters or single atom [28], which is consistent with the result of XRD analysis.
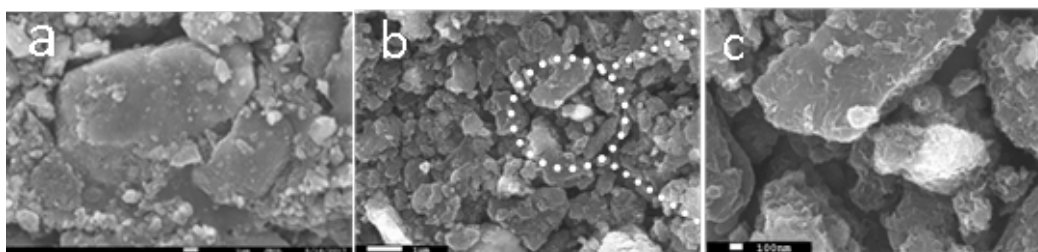
Figure 2. SEM images of AC (a) and 3%Co-N-AC (b, c) and the scales are 1μm (a, b) and 100 nm (c), respectively.

The samples of AC and 3%Co-N-AC were also characterized by the technique of X-ray photoelectron spectroscopy (XPS) to investigate the chemical states and the results were exhibited in Figure 3. Figure 3a showed the full survey spectra of AC and 3%Co-N-AC, respectively. The survey spectra of AC showed evident characteristic peaks of carbon and oxygen at 285.1 eV and 532.1 eV, respectively, revealing the existence of C and O in the sample of AC. While in the survey spectra of 3%Co-N-AC, the emergence of of characteristic peaks of nitrogen and cobalt at 398.6 eV and 782.1 eV, respectively, proved the success of nitrogen-doping and cobalt modification.
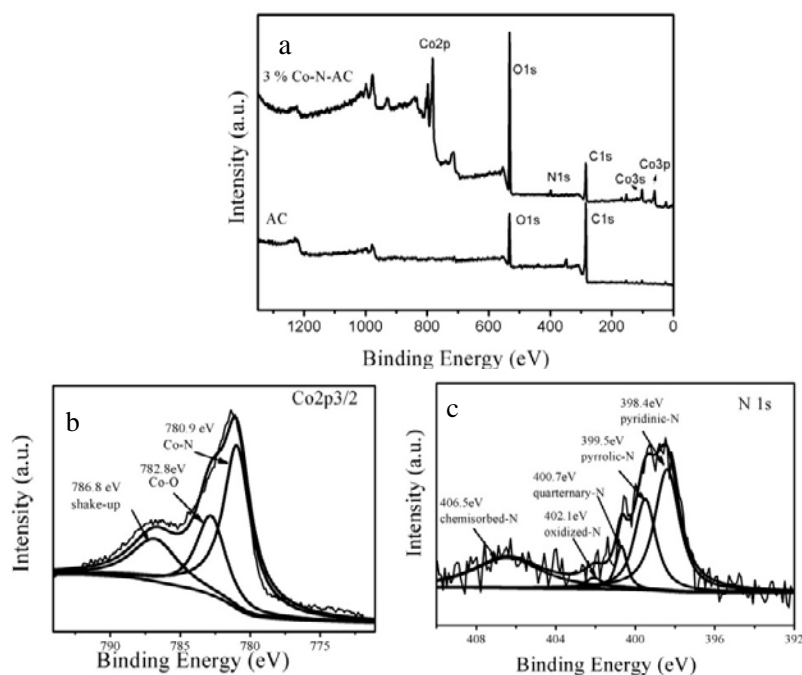
Figure 3. XPS spectra of the cobalt-loaded nitrogen-doped AC. (a) XPS survey spectra of AC and 3% Co-N-AC, respectively, (b) N1s XPS spectrum and (c) Co 2p3/2 XPS spectra of 3% Co-N-AC, respectively.

The high-resolution N 1s spectra (Figure 3b) indicate the existence of five main signals of doping N, including N_1 (pyridinic N, 398.3 eV), N_2 (pyrolic N, 399.2 eV), N_3 (graphitic N, 400.7 eV), N_4 (N-oxides, 402.1 eV) and N_5 (Chemisorbed-N, 406.5 eV). According to the literature, the pyridinic N was considered as the possible active sites in the oxidation of C-H bond reaction, which serving as coordination sites with the metal ions (Co-N) and generating high active sites in the catalytic reaction [28, 29]. Meanwhile, the graphitic N can be also used as active species in the catalytic oxidation of alkanes and alcohols [31]. Figure 3c displayed a more profound insight about the chemical state of Co in the catalyst of 3%Co-N-AC. The Co2p3/2 spectra could be fitted into two peaks at 780.9 eV of Co-N and 782.8 eV of Co-O respectively, while the shake-up satellite at around 786.8 eV from the spin-orbit component (Co^{2+} combined with O) [32, 33]. The Co-N moieties, which was originated from the interactions of Co with N are believed to serve as the potential active sites for oxidation reaction, and thus are responsible for improvement in catalytic performance of the 3%Co-N-AC catalysts [34, 35].

The samples of AC, N-AC and Co-N-AC with different content of cobalt were characterized by EA and AAS technique to investigate the content of various elements and the results were exhibited in Table 1. Evidently, the elements of C and O are the main components in all the tested samples. In the sample of AC, the content of N is very low (0.47%), while in the sample of N-AC, it increased to 6.78% after nitrogen doping, indicating microwave irradiation is a very effective technique to dope nitrogen in the AC. Additionally, the content of C reduced from 53.07% to 44.12%, further proving the substitution of C atom rather than other element by N atom during the doping process. When the nitrogen-doped carbon modified further by cobalt, the content of N decreased between 2.83% and 3.03%, which may due to the partial etching effect of ion impregnation on the doped N atom.

Table 1. Ratio analysis of various elements[a].

Entry	Catalyst	C (%)	O (%)	N (%)	Co[b] (%)	Other[c] (%)
1	AC	53.07	43.47	0.47	-	2.99
2	N-AC	44.12	47.68	6.78	-	1.42
3	1%Co-N-AC	50.42	44.36	2.93	0.81	1.48
4	3%Co-N-AC	47.90	45.24	2.83	2.35	1.68
5	5%Co-N-AC	48.31	43.01	2.88	4.03	1.77
6	10%Co-N-AC	49.14	38.36	3.03	7.72	1.75

[a] The content of C, N, O comes from the results of element analysis.
[b] The content of cobalt was obtained from the atomic absorption technique.
[c] Other represents H, S and other elements.

3.2. Selective Oxidation of Ethylbenzene

The selective catalytic oxidation of ethylbenzene by molecular oxygen at 120°C and 0.8 MPa pressure is chosen as the model reaction to measure the catalytic performance of as prepared Co-N-AC with different content of cobalt and the results are listed in Table 2. From Table 2, we can see that when directly using commercial AC as the catalyst in the reaction (Entry 1), the catalytic performance of both ethylbenzene conversion and acetophenone selectivity are very low, in which only 8.7 mol% of the substrate converted. Using N-AC as catalyst (Entry 2), the conversion of ethylbenzene slightly increased to 10.3 mol% although the selectivity of acetophenone still remained at around 73%. While Co-N-AC was used in the reaction (Entries 3-7 and 9-12), the catalytic performance was greatly improved, especially the selectivity of acetophenone increased significantly with the highest value to 97.2% (5% Co-N-AC). Thus, it can be speculated that the metal carbon nitrogen (Co-N-C) may play a vital role in the reaction, as was reported on the catalyst of Co-N-C/g-C_3N_4 [29]. When more cobalt was loaded (3-10% Co-N-AC) on AC, the conversion of ethylbenzene firstly reached a maximum value and then began to decline, which is due to a different degree of agglomeration of cobalt nanoparticles [36]. In order to further investigate the stability, the catalysts were separated by centrifugal separation and reused in another reaction cycle and the results were also shown in Table 2 (Entries 5, 6, 7, 10, 12). Evidently, the reused catalyst for a second time showed worse activity

comparing with that of the fresh catalyst, especially for the catalysts loaded with higher content of cobalt, in which the conversion of ethylbenzene decreased from 24.2 mol% to 19.9 mol % for 5%Co-N-AC and from 56.5 mol % to 31.3 mol % for 10%Co-N-AC, respectively. By comparing, the catalyst 3%Co-N-AC exhibits better recyclability even after recycling 4 times. It may due to the doped nitrogen on the catalysts surface which act as Lewis base sites and is expected to be more effective in retaining metal nanoparticles [37]. In order to further prove the effect of N in the sample, the sample of 3%Co-AC without doping N was prepared and used in the reaction. The results showed that only 12.5 mol% conversion of ethylbenzene and 78.8% selectivity to acetophenone was obtained. While for the prepared catalyst Co-N-ACs the content of doped-nitrogen is limited and can only support or retain a small amount of cobalt. So Co-N-AC catalysts with lower content of cobalt proved to have better stability than those with higher content of cobalt. To confirm the above conjecture, when the oxidation reaction was finished, the supernatant obtained after centrifugation was tested and found that the cobalt ions loaded on the catalysts had different degree of leakage into solution. For the fresh catalyst of 3%Co-N-AC, there was only about 4.3% of the total content of cobalt ions leaked into the solution. While for the catalyst of 10%Co-N-AC, there was nearly 21.2% of cobalt ions leaked. Here among all the samples 3%Co-N-AC was considered to be more stable than other catalysts.

Table 2. Catalytic performance of Co-N-AC for selective oxidation of ethylbenzene[a].

Entry	Catalysts	Conversion of ethylbenzene (mol%)	Selectivity of acetophenone (%)
1	AC	8.7	73.0
2	N-AC	10.3	72.7
3	1%Co-N-AC	13.3	81.9
4	3%Co-N-AC	23.2	95.7
5	3%Co-N-AC-II[b]	21.1	93.3
6	3%Co-N-AC- III[b]	20.6	94.8
7	3%Co-N-AC- IV[b]	21.9	91.7
8	3%Co-AC	12.5	78.8
9	5%Co-N-AC	24.2	97.2
10	5%Co-N-AC-II[b]	19.9	88.1
11	10%Co-N-AC	56.5	91.8
12	10%Co-N-AC-II[b]	31.3	80.1

[a] Reaction condition: ethylbenzene 10 mL, catalyst 100 mg, O_2 pressure 0.8 MPa, reaction time 4 h, temperature 120°C.
[b] Rome better represents the number of times the catalyst is reused.

4. Conclusion

To sum up, Co-N-AC was prepared by microwave irradiation nitrogen-doping and wet cobalt ions impregnation technology. A series of morphological characterizations, structural characterizations and elemental characterizations including XRD, SEM, XPS, EA and AAS revealed that microwave irradiation was an effective method in nitrogen-doping and the doped nitrogen existed mainly in the form of pyridinic N and pyrolic N; the loaded cobalt by ions impregnation was highly dispersed on the surface of AC. The selective aerobic oxidation of ethylbenzene under solvent-free condition was used as the model reaction to probe the catalytic performance and 3%Co–N–AC was proved to a good catalyst with better ethylbenzene conversion, acetophenone selectivity and better durability, in which the doped nitrogen played significant role in the sustain of cobalt and the formation of Co-N, the doped pyridinic nitrogen was the main reason for the excellent catalytic performance and the high stability. Therefore, Co-N-AC catalysts would have more hopeful prospects in catalytic oxidation of ethylbenzene.

5. Acknowledgments

6. References

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