

Article

Zn-Co@N-Doped Carbon Derived from ZIFs for High-Efficiency Synthesis of Ethyl Methyl Carbonate: The Formation of ZnO and the Interaction between Co and Zn

Ya-Nan Miao, Yuan Wang, Dong-Hui Pan, Xiang-Hai Song, Si-Quan Xu, Li-Jing Gao and Guo-Min Xiao *

School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, China; mmiaoynan@163.com (Y.-N.M.); wangyuan9108@126.com (Y.W.); ppandonghui@163.com (D.-H.P.); tju109@126.com (X.-H.S.); siquanxu@163.com (S.-Q.X.); gaolj@seu.edu.cn (L.-J.G.)

* Correspondence: xiaogm426@gmail.com; Tel./Fax: +86-25-5209-0612

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Abstract: In this work, a series of Zn-Co@N-doped carbon materials were prepared by pyrolysis of Co/Zn-ZIF precursors under a N₂ atmosphere and used for high-efficiency synthesis of ethyl methyl carbonate (EMC) from dimethyl carbonate (DMC) and diethyl carbonate (DEC). The Co to Zn molar ratio and calcination temperature were varied to study the physical and chemical properties of Zn-Co@N-doped carbon materials identified by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET), inductively coupled plasma (ICP), thermogravimetric analysis (TG) and temperature programmed desorption (TPD) analysis. It was deduced that the formation of a ZnO crystalline structure and the interaction between zinc and cobalt providing weak basic sites and strong basic sites, respectively, in different samples significantly affected their catalytic performance. The catalyst activated the reaction most effectively when the Co to Zn molar ratio was 1.0 and calcination temperature was 600 °C. With the DMC to DEC molar ratio controlled at 1:1, a superior yield of around 51.50% of product EMC can be gained over catalyst ZnCo/NC-600 at 100 °C with 1 wt% catalyst loading in 7 h.

Keywords: zeolitic imidazolate frameworks; Zn-Co@N-doped carbon; transesterification

1. Introduction

Ethyl methyl carbonate (EMC) is the simplest asymmetric ester and an important intermediate in organic synthesis. Recently, EMC has received extensive attention as an excellent co-solvent in the electrolyte of lithium ion batteries [1–5]. Considering security and environmental issues, the traditional method of producing EMC by methyl chloroformate and ethanol was abandoned. Instead, transesterification between dimethyl carbonate (DMC) and ethanol with mild reaction conditions and a high utilization rate of atoms is the most common method for the preparation of EMC [6–8]. However, the by-product methanol should be removed in a timely way to achieve high EMC yield, and the formation of an azeotropic system increases the difficulty of separation and energy consumption [9]. The disadvantages of the above route have contributed to the development of alternative methods, such as the transesterification reaction between dimethyl carbonate and diethyl carbonate (DEC), which is environmentally-friendly, with high atom utilization and mild reaction conditions. Moreover, in the transesterification system, reactants and products can be directly used as co-solvents in the electrolyte without further separation [10,11].

Initially, most catalysts applied to the transesterification reaction between DMC and DEC were homogeneous [12], bringing about separation problems. Subsequently, a number of more economical and environmentally friendly heterogeneous catalysts have been reported. A series of solid base catalysts, including MgO, ZnO, La₂O₃ and CeO₂, were prepared by Shen et al. [13], among which MgO showed best catalytic performance, followed by ZnO. However, the activity of a single metal oxide as the catalyst was not particularly good. Hence, supporter or new metals promoting the transformation of the composition or structure of the available catalyst were introduced to enhance catalytic activity. Zhao et al. [14] prepared carbon-supported catalysts (MgO/NC-2) with an impregnation method in which active sites were effectively dispersed on the surface of supporter, and the EMC yield reached up to 49.3% at optimum conditions. Furthermore, a few bimetallic catalysts were reported, presenting relatively higher EMC yields compared with single metal catalysts due to the interaction between different metals [15,16]. For instance, acid-base bifunctional mesoporous catalysts, which combined specific properties of the acid-base materials and the chemical stability of the mesoporous structure, were prepared with varying metal types (Mg or Al) and the catalysts promoted equilibrium of the transesterification reaction being approached in 30 min [17].

Recently, metal organic frameworks (MOFs) made up of metal ions and organic ligands have attracted widespread attention in different fields, such as gas adsorption and storage [18,19], molecular separation [20,21], catalysts [22,23] as well as drug delivery [24,25], due to their porous structures and high thermal stability [26–28]. Meanwhile, several groups applied MOF materials, in which metal ions acted as acid sites, to transesterification between DMC and DEC since the reaction was essentially an acid-base catalyzed process. Zhou et al. [29] reported that MOF-5 [Zn₄(O)(BDC)₃] (BDC = benzene-1,4-dicarboxylate) showed superior catalytic performance in this reaction, with 50.1% DEC conversion and almost 100% EMC selectivity. Moreover, zeolitic imidazolate frameworks (ZIFs) consisting of metal ions (Zn²⁺, Co²⁺), imidazole and derivatives were also active catalysts for the transesterification, providing not only acid sites but also basic sites compared with general MOF materials. Chizallet et al. [30] proved theoretically that Zn²⁺ performed as acid sites, combined with N[−] moieties and OH groups as basic sites, determining the catalytic performance of ZIF-8. For further experimental verification, Zhou et al. [31] found that ZIF-8 synthesized at room temperature showed excellent activity, selectivity and stability. The yield of the target product, EMC, reached 50.7% under moderate conditions (0.208 g catalyst, 100 °C and 3 h).

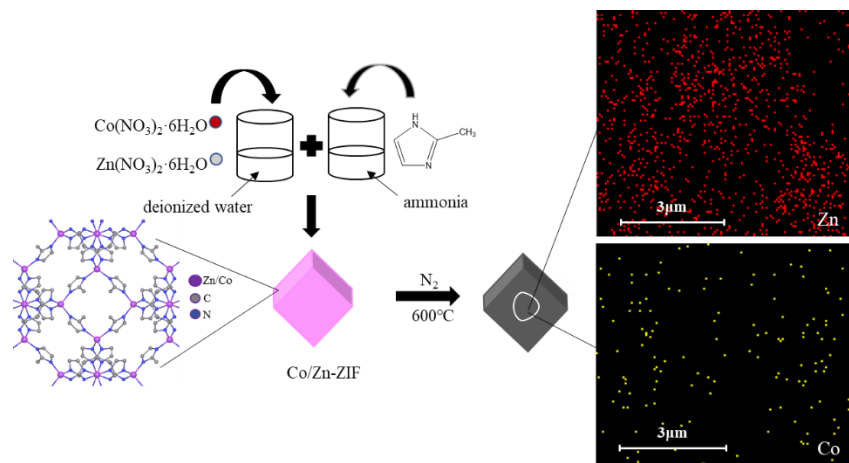
As reported, ZIF materials rich in metallic elements also act as precursors to prepare metal/C or metal oxide/C for further treatment [32–34]. For corresponding derivatives, the porous morphology of ZIF materials can be maintained after low-temperature pyrolysis under an inert atmosphere [35]. Besides, it has been proved that porous N-doped carbon derived from ZIF materials can be applied to alkali catalytic reactions due to the presence of basic sites [36]. Hence, we proposed a new material combining the structure, as well as the properties, of ZIFs and the coordination of two metals. In this study, bimetallic Co/Zn-ZIFs were firstly synthesized using the one-pot method and utilized as the precursor to prepare Zn-Co@N-doped carbon. A series of materials were prepared with different metal molar ratios and calcination temperatures to study the role of Zn and Co and their impact on the formation of active sites. Then, Zn-Co@N-doped carbon as a catalyst was applied to the transesterification reaction between DMC and DEC. Reaction conditions were optimized on the basis of EMC yield and selectivity.

2. Results and Discussion

2.1. Characterization of Catalysts

Zn-Co@N-doped carbon materials labeled as ZnCo_x/NC-T (*x* represents the molar ratio, T is the mark of calcined temperature) were synthesized at room temperature using a simple method, as shown in Scheme 1. In the preparation process, Co/Zn-ZIF with uniform cubic shapes was successfully obtained, as displayed in the SEM images in Figure S1. The XRD pattern of prepared

Co/Zn-ZIF shown in Figure S2 is consistent with the reported literature and there was no marked difference in the pattern of synthesized ZIF-8 [37], implying that the incorporation of cobalt resulted in hardly any destruction of the structure of the ZIF materials. Then, a pre-determined amount of the above light purple powder was transformed into bimetallic particles supported by porous carbon.



Scheme 1. Synthesis process of Zn-Co@N-doped carbon.

Characteristics of the calcined products were determined by XRD, and the patterns of catalysts calcined under N_2 atmosphere with different molar ratios and calcination temperature are shown in Figure 1. Clearly, $ZnCo_{0.6}/NC-600$ and $ZnCo_{1.4}/NC-600$ are amorphous (Figure 1A). The catalysts ($ZnCo/NC-550$, $ZnCo/NC-650$, $ZnCo/NC-700$) with calcination temperatures above or below $600\text{ }^{\circ}C$, and the molar ratio fixed at 1.0, also failed in the formation of crystalline structures, which agrees with a previous report [38]. Instead, a crystalline structure formed when the Co to Zn molar ratio was controlled from 0.8 to 1.2 with a calcined temperature of $600\text{ }^{\circ}C$. As shown in Figure 1B, the characteristic peak of ZnO with hexagonal wurtzite crystal structures (JCPDS card No. 36-1451) can be observed in all the crystalline samples. This suggests that zinc elements of the precursor have changed to zinc oxides after heat treatment, even under a nitrogen atmosphere, probably attributed to the higher electrode potential of Zn^{2+}/Zn than -0.27 eV [36]. More importantly, it was demonstrated that the ZnO crystalline structure is essential to the catalytic activity of Zn-Co materials (this will be discussed later). Although the molar ratio of Co to Zn was close to 1.0, no obvious signals of metallic cobalt and oxides of cobalt can be detected for catalysts $ZnCo_{0.8}/NC-600$ after local enlargement of patterns (Figure 1C). As the molar ratio increased up to 1.0, a weak peak at around 44.22° can be observed corresponding to the (1 1 1) plane of the metallic cobalt phase (JCPDS card No.15-0806). Further enhancement of the cobalt amount results in the stronger intensity of this catalyst $ZnCo_{1.2}/NC-600$. However, no peak assigned to oxides of cobalt can be found in any samples. These results suggest that the Co to Zn molar ratio in all samples was far lower than the theoretical value. Cobalt particles are probably uniformly distributed on the surface of the carrier. On the other hand, the crystallinity of cobalt is relatively low at $600\text{ }^{\circ}C$ [39]. It is also worth noting that the characteristic peaks (Zn 2p) of catalysts doped with cobalt shift to lower diffraction angles compared with calcined products of ZIF-8. This may be attributable to the interaction between zinc and cobalt [40].

Moreover, XPS analyses of catalysts were conducted to identify their chemical composition. The existence of elements including cobalt, zinc, carbon, oxygen and nitrogen was confirmed by XPS spectra (Figure 2A). Zn 2p patterns of catalysts with different metal molar ratios are shown in Figure 2B. Two peaks centered at the binding energy of 1044.9 eV and 1021.9 eV are apparent in the patterns, implying the presence of zinc oxides in accordance with XRD analysis. With the addition of cobalt

elements, the binding energy of Zn 2p_{1/2} and 2p_{3/2} increased a little, probably due to the chemical environment of zinc and the interaction between zinc and cobalt [40].

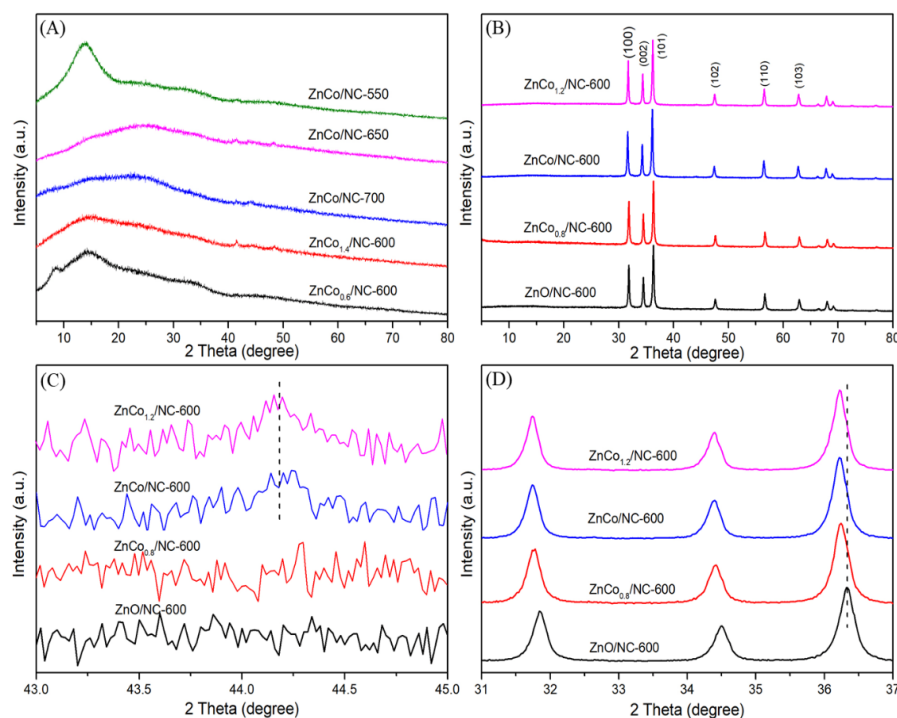


Figure 1. XRD patterns of: (A) catalysts with amorphous structure; (B) catalysts with crystalline structure. Local enlargement of XRD patterns: (C) 43–45°, (D) 31–37°.

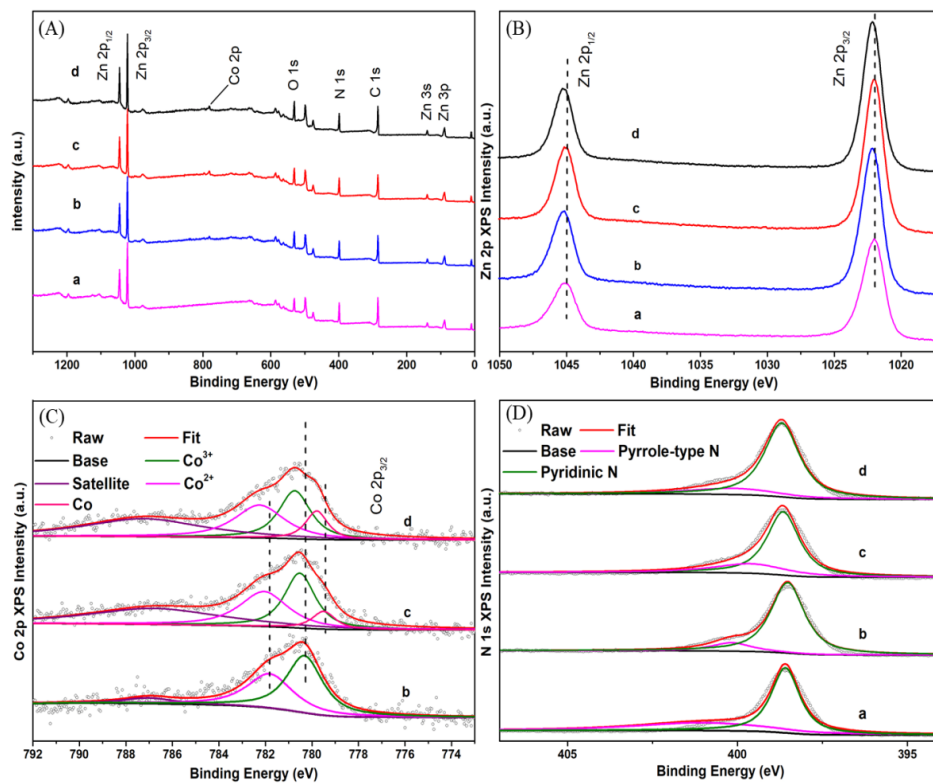


Figure 2. XPS spectra of (a) ZnO/NC-600, (b) ZnCo_{0.8}/NC-600, (c) ZnCo/NC-600 and (d) ZnCo_{1.2}/NC-600: (A) full range XPS spectra; (B) Zn 2p spectra; (C) Co 2p spectra; (D) N 1s spectra.

Calcined products display complicated valence states of cobalt in the Co 2p patterns (Figure 2C). Two peaks located at around 782 eV and 780.4 eV were detected in all samples, ascribed to the different valence states (Co^{2+} , Co^{3+}) of cobalt oxides. Meanwhile, the satellite peaks at around 786.9 eV in all samples also indicated the presence of cobalt oxides [41]. Banerjee et al. [42] proposed that only metal ions with their electrode potential higher than -0.27 V contained in MOFs could be reduced to zero-valent metals under an inert atmosphere. Thus, it is suggested that the neutral electrode potential of Co^{2+}/Co (-0.27 V) probably accounts for the complex valence states of cobalt. With the increase of Co elements in catalysts ZnCo/NC-600 and $\text{ZnCo}_{1.2}/\text{NC-600}$, the peak of metallic cobalt appears and the binding energy of cobalt in all valence states shown in Figure 2C, remarkably, shifts to higher positions [43]. Clearly, the cobalt incorporation leads to the shift of the characteristic peak both in Zn 2p and Co 2p patterns. Hence, the XRD and XPS results together illustrate that the interaction between zinc and cobalt may generate in calcined catalysts, and further are probably linked with catalytic performance.

Most nitrogen elements of the precursor Co/Zn ZIF were preserved after heat treatment under a nitrogen atmosphere. The N 1s spectra of different samples were decomposed into different peaks according to the different chemical states of N (Figure 2D). Apart from the peak centered at around 398.4 eV as evidence of pyridinic-N, a weak peak can also be observed at 400.4 eV implying that a pyrrolic-N exists in the catalyst [39]. Pels et al. [44] reported that pyrrolic-N (N-5) was stable at temperatures as high as 600°C and above that temperature N-5 disappeared, gradually converting to pyridinic-N (N-6) and quaternary-N (N-Q). Moreover, the preserved N not only acted as a carrier to avoid the agglomeration of particles but also bonded with metal atoms [39,45].

SEM was carried out to investigate morphology and microstructure characteristics of the bimetallic Zn-Co catalysts with different metal molar ratios. As can be seen from Figure 3A,B, the cubic structure of the precursor ZIF-8 was maintained after calcination at 600°C under a nitrogen atmosphere. The SEM patterns shown in Figure 3C,D of catalyst ZnCo/NC-600 cannot be well distinguished from the above ZnO/NC-600, indicating that the addition of the Co element apparently did not destroy the morphology and microstructure of the ZIFs. The preservation of N was further verified by SEM/EDX mapping (Figure S3 A-2) which displays the dispersion of different elements in catalyst ZnO/NC-600. Additionally, it is remarkable that the distribution density of cobalt was less than that of zinc (Figure S3 B-1,B-2), suggesting that the Co to Zn molar ratio was probably less than 1, in accordance with the XRD results. Combined with ICP analysis (Table S2), we speculate that cobalt nitrate may partly react with ammonia, producing cobalt ammine complexes during the catalyst preparation, which lead to the decrease of cobalt.

To further characterize particle dispersion and the average size of calcined catalysts, HRTEM experiments were also performed. Similar to the SEM results, Zn/Co bimetallic catalysts after thermal treatment also had cubic shapes dimly visible in the HRTEM images (Figure 4A). In ZnCo/NC-600, uniform dispersion of zinc and cobalt particles embedded in carbon matrix can be clearly observed (Figure 4B). Lattice spacings of 0.26 nm, 0.25 nm and 0.20 nm in Figure 4C correspond to the interplanar spacings of ZnO (0 0 2), ZnO (1 0 1) and Co (1 1 1), which correlates with the XRD analysis. Moreover, the particle size distribution image of ZnCo/NC-600 is listed in Figure 4D and the mean size is about 24 nm, which shows it undergoes an obvious increase compared with that of ZnO/NC-600 (Figure 4F).

The BET surface area, pore volume and average pore size of five samples are illustrated in Table 1 to identify the porosity of catalysts determined by nitrogen adsorption–desorption isotherms. The precursor Co/Zn-ZIF displays a relatively high BET surface area of around $1168.3\text{ m}^2/\text{g}$. After calcination, there is a sharp decline in BET surface area. Compared to ZnO/NC-600 (BET surface area $715.6\text{ m}^2/\text{g}$ and average pore size 5.38 nm), the incorporation of cobalt results in a decrease of BET surface area and the increase of average pore size. Furthermore, it (Entry 2–5) reveals a positive variation trend between BET surface area and Co loading amount, but a negative one between average pore size and Co loading amount, suggesting that excessive cobalt may lead to the collapse of the catalyst structure.

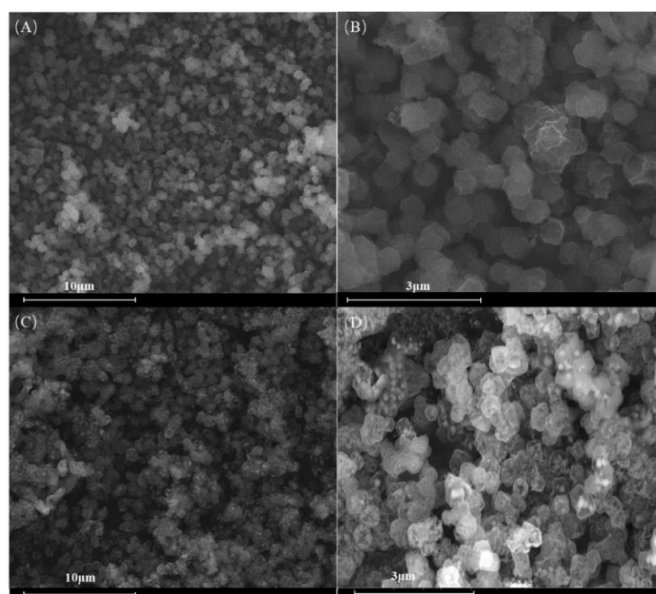


Figure 3. SEM images of: (A,B) ZnO/NC-600; (C,D) ZnCo/NC-600.

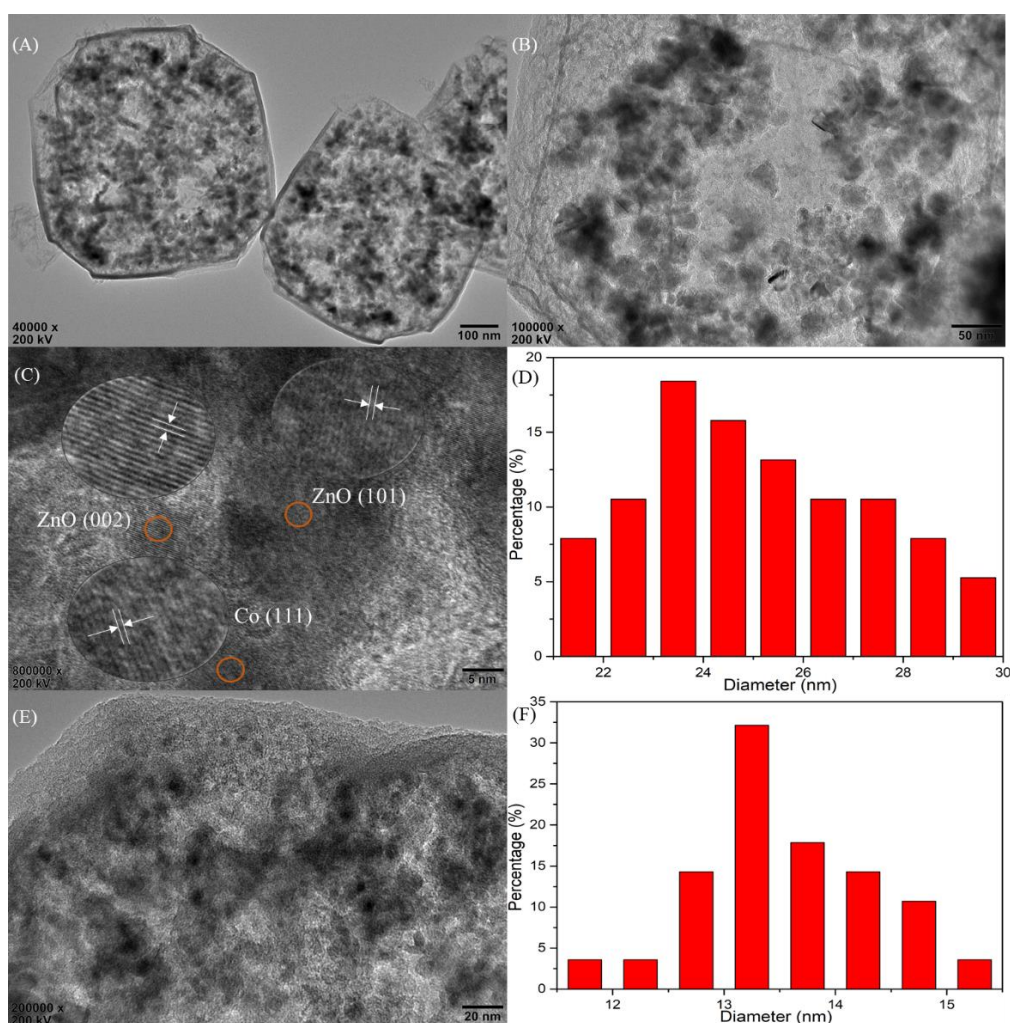


Figure 4. (A–C) HRTEM images of ZnCo/NC-600; (D) particle size distributions of ZnCo/NC-600; (E) HRTEM images of ZnO/NC-600; (F) particle size distributions of ZnO/NC-600.

Table 1. Surface area, pore volume and average pore size of catalysts.

Entry	Catalyst	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (nm)
1	Co/Zn-ZIF	1168.3	0.074	10.15
2	ZnO/NC-600	715.6	0.144	5.38
3	ZnCo _{0.8} /NC-600	275.0	0.295	11.15
4	ZnCo/NC-600	254.8	0.274	11.72
5	ZnCo _{1.2} /NC-600	200.8	0.535	12.18

The CO₂-TPD profiles of different samples to determine the base properties of catalysts are exhibited in Figure 5. As can be seen, curves of samples clearly drift upward over 500 °C, probably due to the decomposition of minor Co/Zn-ZIF. For further verification, a blank run of ZnO/NC-600 without CO₂ adsorption (Figure 5g) was investigated. It shows that the curve displays an up-trend with two peaks clearly centered between 400 °C and 500 °C, and around 746 °C, respectively. In addition, the TG curves of ZnCo/NC-600 obtained in N₂ reveal that the compound suffered from weight loss at a similar temperature (Figure S4). Hence, the above two peaks can be attributed to catalyst decomposition and should be ignored in TPD analysis. Extra peaks, with the exception of decomposition peaks, cannot be detected in the NH₃-TPD profiles (Figure S5), implying the absence of acid sites in the Zn-Co samples. For catalyst ZnO/NC-600 (Figure 5c), a single desorption peak appears around 100 °C and extends into a broad peak, indicating a single alkali type and weak basic sites. A peak centered at a similar temperature can also be observed in other samples (Figure 5c–f), which can be ascribed to the presence of ZnO [30]. With the incorporation of cobalt, the peak centered over 600 °C, as the symbol of strong basic sites, was detected. For comparison, samples calcined from single ZIF-67 and a mechanical mixture of ZIF-67 and ZIF-8 (1:1) were identified by TPD analysis and the results (Figure 5a,b) showed that the peak centered over 600 °C was missing. To sum up, strong basic sites over 600 °C cannot generate in the absence of Zn or Co, and the mechanical mixing of two elements also prevents their formation. Cosimo et al. [46,47] discovered in similar experimental research that Li/MgO exhibited the strongest basic properties, and further assumed that the appearance of these basic sites resulted from the addition of lithium, causing a structural promotion of the MgO sample by replacing the Mg²⁺ ions with Li⁺ in the MgO lattice. Based on this foundation, Song et al. [39] proposed a hypothesis that the strong basic sites in catalyst Li/ZnO originated from [Li⁺ O[−]] attributing to the substitution of Zn²⁺ by Li⁺ in the ZnO lattice. In this work, it has been proved in the above analysis that Co together with Zn simultaneously exist in the framework of the Co/Zn-ZIF precursor instead of simply being attached to the surface. Hence, it can be inferred that the interaction between Zn and Co in the lattice promotes the generation of strong basic sites. Furthermore, compared with ZnCo_{0.8}/NC-600 and ZnCo_{1.2}/NC-600, the peak ascribed to strong basic sites in ZnCo/NC-600 is located at the higher temperature. Hence, we speculate that ZnCo/NC-600 may show the best catalytic performance in the reaction between DMC and DEC, for the reason that stronger basic sites promote transesterification more effectively [39].

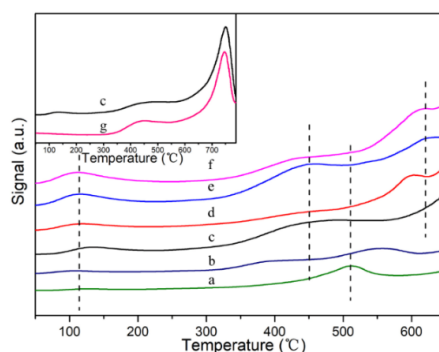


Figure 5. CO₂-TPD profiles of: (a) CoO_x/NC-600 calcined from ZIF-67; (b) CoZnO_x/NC-600 calcined from the mechanical mixture of ZIF-67 and ZIF-8 (1:1); (c) ZnO/NC-600; (d) ZnCo_{0.8}/NC-600; (e) ZnCo/NC-600; (f) ZnCo_{1.2}/NC-600; (g) ZnO/NC-600 without CO₂ adsorption.

2.2. Synthesis of EMC across Different Zn-Co@N-Doped Carbon Materials

Mild transesterification between dimethyl carbonate (DMC) and diethyl carbonate (DEC) was carried out, the reactants of which mainly convert into ethyl methyl carbonate (EMC). Table 2 shows EMC yield under unified conditions catalyzed by a series of catalysts with different metal molar ratios and calcination temperatures.

Table 2. Catalytic performance of different catalysts ^a.

Entry	Catalysts	n(DMC):n(DEC)	Yield (%)	Selectivity (%)
1	ZnO/NC-600	1:1	29.50	~100
2	ZnCo _{0.6} /NC-600	1:1	2.26	~100
3	ZnCo _{0.8} /NC-600	1:1	43.58	~100
4	ZnCo/NC-600	1:1	51.50	~100
5	ZnCo _{1.2} /NC-600	1:1	42.53	~100
6	ZnCo _{1.4} /NC-600	1:1	—	—
7	ZnCo/NC-550	1:1	0.91	~100
8	ZnCo/NC-650	1:1	9.33	~100
9	ZnCo/NC-700	1:1	1.82	~100

^a Reaction conditions: 100 °C, 7 h, 1 wt% catalyst amount.

With almost no by-product generated, the EMC selectivity can reach close to 100% when catalyzed by all samples displayed in the Table 2. Unsatisfactory EMC yield was obtained using the mono-metallic catalyst ZnO/NC-600 in which ZnO acted as the single alkali site, as confirmed by TPD results, although the 29.5% yield was a little higher than previously reported for ZnO catalysts probably due to the increase of surface area and the presence of N interacted with metals as active sites [13]. Afterwards, cobalt elements in the form of nitrate were added into the mother liquor for the reason that the synergy between different metals can improve the activity and selectivity of catalysts [48,49]. For catalyst ZnCo/NC-600, the EMC yield dramatically reached 51.5%, twice that of the reaction catalyzed by ZnO/NC-600. The TPD results show that the interaction between Zn and Co in the lattice promotes the generation of strong basic sites in Zn-Co catalysts, suggesting that apart from ZnO active sites, the interaction between zinc and cobalt can also remarkably enhance catalyst activity.

Metal molar ratios of Co to Zn were varied from 0.6 to 1.4 in order to achieve catalysts with superior catalytic performance. It deserves to be mentioned that the EMC yield decreased regardless of whether Co to Zn molar ratios increased or decreased from 1:1. Hence, adding a moderate amount of cobalt activated the catalyst, instead of simply assuming that the more cobalt loading the better the catalytic performance would be. It is probable that the basic sites of ZnO, which have been proved to be the main catalytic active sites, were covered with the improvement of cobalt elements. It can be seen from Table 2 that as Co to Zn molar ratios increased to 1.4 or decreased to 0.6, the EMC yield underwent a rapid decline from 51.5% to 2.26% even 0%.

Additionally, for different catalysts with the Co to Zn molar ratio fixed at 1.0 and calcined under temperatures from 550 °C to 700 °C, ZnCo/NC-600 has the best catalytic performance. Combined with XRD results, when catalysts with no crystalline structure formed on the surface of the carrier were added, the reaction suffered from an unexpectedly lower EMC yield. Based on the above experiments, it is reasonable to infer that the non-formation of a crystalline structure may be responsible for the less active performance of these catalysts, even compared to ZnO/NC-600 calcined directly from ZIF-8. Hence, the presence of zinc oxides, together with the interaction between zinc and cobalt, can be further proved to play the role of catalytic sites in these materials.

2.3. Effects of Reaction Conditions

In order to optimize reaction conditions, the effects of reaction time, temperature and catalyst loading on the yield of EMC were investigated over catalyst ZnCo/NC-600. As shown in Figure 6A,

the EMC yield increased steadily as the reaction time lengthened from 0 to 7 h and reached 51.5% in 7 h. However, no remarkable increase of EMC yield can be observed over 7 h, or even up to 10 h, suggesting that equilibrium can almost be reached in 7 h. Thus, the optimum reaction time is 7 h.

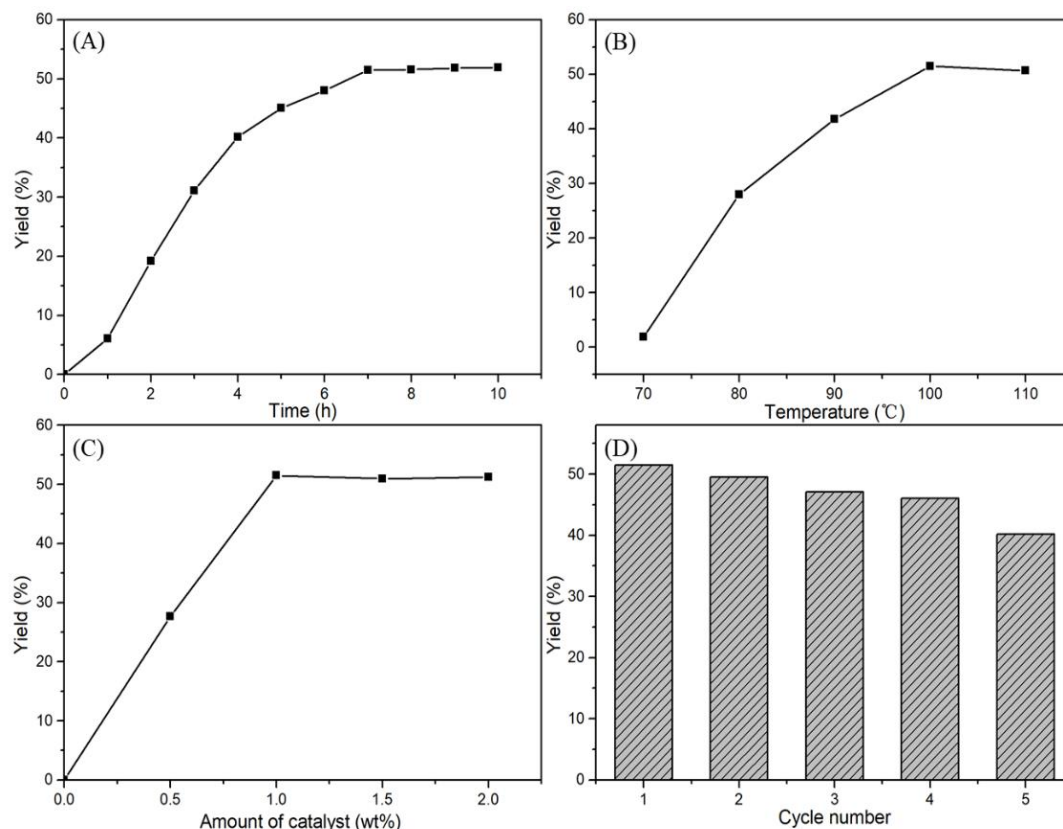


Figure 6. (A) Effect of time (100 °C, 1 wt% catalyst amount); (B) effect of temperature (7 h, 100 °C, 1 wt% catalyst amount); (C) effect of catalyst amount (7 h, 100 °C); (D) reusability of the catalyst ZnCo/NC-600 (7 h, 100 °C, 1 wt% catalyst amount).

The impact of temperatures ranging from 70 °C to 110 °C on the EMC yield was studied. Figure 6B illustrates that ZnCo/NC-600 performed unsatisfactory catalytic activity with the EMC yield lower than 5% at 70 °C. Also, it was found that the yield of EMC increased with the increase of the reaction temperature, and the maximum yield (51.5%) was obtained at 100 °C. However, the EMC yield declined slightly when the temperature was elevated to 110 °C. It is likely that sustained loss of DMC, due to its relatively low boiling point (90 °C), may result in the decrease of EMC yield with the raising of the reaction temperature.

As can be seen from Figure 6C, the yield of EMC was also strongly influenced by catalyst loading. Obviously, no EMC can be detected in the absence of any catalyst. With the lower addition of catalyst ZnCo/NC-600, 27.68% of EMC yield is achieved at the same reaction conditions. The yield of EMC increases sharply when the catalyst loading increases from 0.5 wt% to 1 wt%. However, the EMC yield undergoes a slight decline with further increasing of catalyst loading. It is reasonable to infer that excessive catalyst loading may influence the rate of mass transfer which resulted in the relatively slightly lower yield in 7 h. These results may suggest that sufficient catalytic sites provided by appropriate loading of catalyst promote the transesterification between DMC and DEC. Hence, 1 wt% catalyst of reactants is optimum for this reaction considering both EMC yield and industrial cost.

Figure S7 also presents the comparative results of different DMC to DEC molar ratios over catalyst ZnCo/NC-600. Consistent with theoretical analysis, the yield of EMC improved with the increase of the DMC to DEC molar ratio, and even rose to 81.56% with the ratio controlled at 5:1. This discovery

has great industrial significance by increasing the use of low-cost reactants to achieve higher product yield. However, the EMC percentage after reaction undergoes an obvious decline, which increases the difficulty of separation and purification. Hence, the above two results should be taken into consideration in combination.

2.4. Recycling of the Catalyst

Considering the cost, it is important to study the reusability of the heterogeneous catalyst in order to determine the applicability to industrial processes. After the completion of reaction, used catalyst was separated simply by filtration, washed with ethanol three times, and then dried at 80 °C in an oven overnight. Then, the reaction was conducted using 1 wt% amount of catalyst ZnCo/NC-600 at 100 °C for 7 h. The recycle process was conducted five times, and the catalytic performance of the reused catalyst is exhibited in Figure 6D. It reveals that the yield of EMC decreased from 51.5% to 40.19% after five cycles of reaction, indicating that ZnCo/NC-600 displayed relatively good stability during the recycles. Then, the used catalyst was characterized to verify the reasons for the small loss of EMC yield. As shown in Figure 7A, catalyst ZnCo/NC-600, after five recycles, has the same characteristic peaks ascribed to ZnO as the fresh one. Furthermore, combined with TG analysis (Figure S4), this suggests that the structure of the catalyst has not been damaged. However, local enlargement of the XRD (Figure 7A) shows that the characteristic peak of spent ZnCo/NC-600 shifts to a higher position, implying a decreased interaction between zinc and cobalt. Moreover, the intensity of peaks ascribed to ZnO, and the interaction between zinc and cobalt, becomes lower than the fresh catalyst (Figure 7B). Also, it can be proved from ICP analysis (Table S2) that Zn and Co suffered a nearly one-half mass loss after five cycles. Hence, the leaching of metal elements may lead to deactivation of the catalyst.

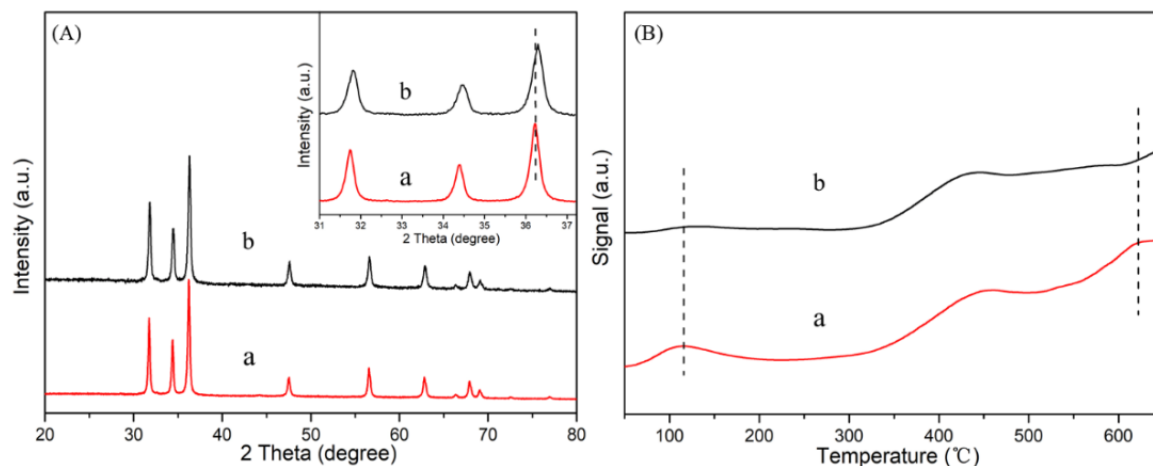


Figure 7. (A) XRD patterns of: (a) fresh ZnCo/NC-600 and (b) ZnCo/NC-600 after five cycles; (B) CO₂-TPD profiles of: (a) fresh ZnCo/NC-600 and (b) ZnCo/NC-600 after five cycles.

To further understand the reason for catalyst deactivation, a leaching experiment was performed. A transesterification process where the reaction was stopped after 3 h, and then continued after filtering out the solid catalyst, was conducted in comparison to another reaction with its equilibrium approached in 7 h. The results (Figure 8) illustrate that the EMC yield increased slightly, within 5%, for another 4 h in spite of the removal of catalysts, implying the presence of a small amount of active component in the reaction system. Hence, we further believe that the leaching of active sites may account for the deactivation of the catalyst in the reaction and recycle process.

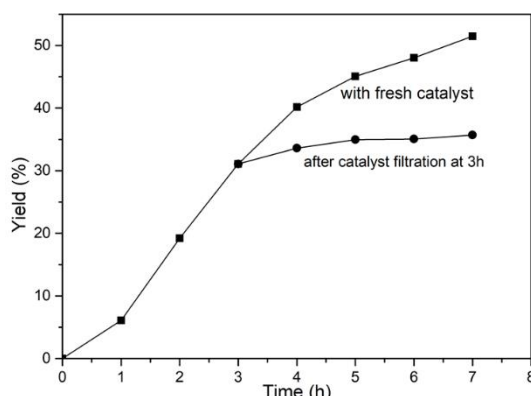
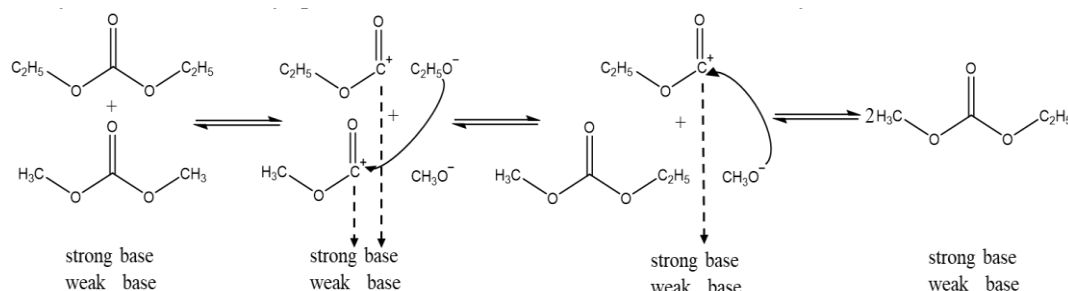


Figure 8. Leaching test in the transesterification of DMC with DEC over fresh ZnCo/NC-600 and after catalyst filtration at 3 h. Reaction conditions: 100 °C, 7 h, 1 wt% catalyst amount.

2.5. Reaction Mechanism

The mechanism of this reaction has been well-studied and reported in previous literature [10,29]. Based on the above analysis in this study, a possible reaction mechanism for the transesterification between DMC and DEC is proposed as shown in Scheme 2. DMC and DEC were firstly absorbed on the basic sites of Zn-Co catalyst, and then intermediates were formed on the surface. The carbonyl of DMC was attacked by ethoxy ion and the carbonyl of DEC was attacked by methoxy ion. The steps were affected by the base properties of the catalyst and other reaction conditions, such as temperature and catalyst amount. Finally, product EMC was detached from the catalyst surface.



Scheme 2. Possible reaction mechanism over Zn-Co@N-doped carbon.

3. Materials and Methods

3.1. Catalyst Preparation

All chemical reagents were of analytical grade and used as received without further purification. Co/Zn-ZIFs were synthesized from an aqueous solution according to the previous literature with a little modification [37]. Typically, 2 mmol mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 99\%$, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ($\geq 98.5\%$, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) with designed molar ratio, and 4 mmol 2-methylimidazole (99%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were separately dissolved in 3 mL deionized water and 4.2 mL ammonia (25–28 wt%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China). Then, two solutions were quickly mixed and changed into brown. The mixture was stirred continuously for 6 h at room temperature. After centrifugation, the product was washed with deionized water and methanol several times until pH of around 7 was reached, and dried at 80 °C overnight. Then, Co/Zn-ZIF was prepared.

In order to synthesize bimetallic Zn-Co@N-doped carbon materials, Co/Zn-ZIF was calcined in nitrogen for 2 h at a predefined temperature. The heating rate of the pipe furnace was set at 5 °C/min. After cooling to room temperature, a black solid was obtained and labeled $\text{ZnCo}_x/\text{NC-T}$, where x

represents the molar ratio of Co to Zn ranging from 0.6 to 1.4 and T is the mark of calcined temperature between 550 °C and 700 °C.

For comparison, ZIF-8 was synthesized by the same method and sent to the pipe furnace calcined at 600 °C to obtain ZnO/NC-600.

3.2. Characterization of Catalysts

X-ray diffraction (XRD) patterns of the catalysts were recorded on an X-ray diffractometer (Ultima IV, Rigaku, Kyoto, Japan) using Cu K α as the radiation source (40 kV and 40 mA). The scanning range (2 θ) was from 5° to 80°, with a scanning rate of 20°·min⁻¹.

The morphologies and microstructures of prepared catalysts were investigated using a FESEM scanning electron microscopy (SEM, FEI Inspect F50, Hillsborough, OR, USA) with an accelerating voltage of 15.0 kV. Additionally, the mapping of energy dispersive X-ray spectrometer (EDX, Quanta 250, Hillsborough, OR, USA) was conducted to measure the dispersion of different elements.

High-resolution transmission electron microscopy (HRTEM) was performed on a transmission electron microscopy (JEM-2100F, JEOL, Kyoto, Japan) operated at 200.0 kV.

The X-ray photoelectron spectroscopy (XPS) was recorded with a spectrometer (ESCALAB-250Xi, Thermo Scientific, Waltham, MA, USA) with Al K α (1486.6 eV) radiation. The obtained element binding energy was calibrated and corrected using the peak of C (1s) at 284.6 eV as references.

The nitrogen adsorption-desorption isotherms were recorded with an analyzer (3H-2000, Beishide, Beijing, China). Prior to measurement, the samples were degassed under vacuum at 200 °C for 12 h. The surface area was obtained using the multipoint Brunauer-Emmett-Teller (BET) method while pore volume and pore size were calculated using the Barrett-Joyner-Halenda (BJH) method.

The concentration of elements was measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, Varian 720-ES, Palo Alto, CA, USA).

Thermogravimetric analysis (TG) was conducted with a thermogravimetric analyzer (STA 449C FS, NETZSCH, Bavaria, Germany). The experiment was performed under N₂ atmosphere and the samples were heated from room temperature to 900 °C at a heating rate of 20 °C per minute.

Temperature programmed desorption (TPD) was carried out to determine the properties of the samples, using a catalyst analyzer (TP-5076, Xianquan, Tianjin, China) equipped with a thermal conductivity detector (TCD). Typically, 0.1 g sample was pretreated under an He atmosphere at 300 °C for 1 h to exclude moisture and other adsorbed gases at the flow rate of 30 mL·min⁻¹. After cooling to room temperature, the catalyst was exposed to pure CO₂ or ammonia gas to conduct the adsorption process for 0.5 h, and then flushed again with He flow (30 mL·min⁻¹) for at least 50 min to remove redundant and physically adsorbed gas. Then, the sample was heated to 800 °C at a rate of 10 °C min⁻¹ under a constant He flow to obtain the CO₂ or ammonia gas desorption curve.

3.3. Reaction Procedure

Interesterification between dimethyl carbonate (DMC) and diethyl carbonate (DEC) was carried out in a 50 ml three-necked flask equipped with a reflux condenser and a magnetic stirring. In a typical reaction, 9 g (0.1 mol) DMC (99.5%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China), 11.8 g (0.1 mol) DEC (99.5%, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) and 0.2 g (1 wt% of reactants) catalysts were mixed into the flask. Then the mixture was heated to a predetermined temperature with continuous stirring for the given time. After cooling to room temperature, the product was analyzed using a gas chromatograph (GC-6890, Ouhua, Shanghai, China) equipped with a flame ionization detector (FID) and a capillary column (SE-30, 30 m $\times$ 0.25 mm, Agilent, CA, USA). Used catalysts were separated by filtration, washed with ethanol several times and finally dried at 80 °C overnight. Then, the above reaction was repeated using the regenerated catalyst to examine the reusability of catalysts.

4. Conclusions

In summary, bimetallic Zn-Co catalysts carbonized by zeolitic imidazolate frameworks were prepared for high-efficient synthesis of ethyl methyl carbonate. It was demonstrated that the cobalt loading and calcined temperature had a great impact on the catalyst microstructure, particle size, chemical states and further catalytic performance. When the DMC to DEC molar ratio was controlled at 1:1, the best catalytic performance, with 51.50% EMC yield, was obtained over 1 wt% catalyst ZnCo/NC-600 of total reactants at a temperature of 100 °C for 7 h. Combined with the characterization results, it can be inferred that the superior catalytic performance is mainly attributed to the formation of a ZnO crystalline structure, and the interaction between zinc and cobalt providing weak basic sites and strong basic sites, respectively. Moreover, with a simple method, Zn-Co catalysts can be reused for five recycles with only a slight decline in the yield of EMC.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/1/94/s1>. Figure S1, SEM images of Co/Zn-ZIF; Figure S2, XRD patterns of different ZIF materials; Figure S3, SEM/EDX mapping of (A) ZnO/NC-600, (A-1) the dispersion of Zn, (A-2) the dispersion of N, (B) ZnCo/NC-600, (B-1) the dispersion of Zn, (B-2) the dispersion of Co, (C) samples calcined from mechanical mixture of ZIF-67 and ZIF-8, (C-1) the dispersion of Zn, (C-2) the dispersion of Co; Figure S4, the TG analysis of ZnCo/NC-600 catalysts, (a) fresh, (b) spent; Figure S5, NH₃-TPD profiles of ZnO/NC-600 and ZnCo/NC-600; Figure S6, the GC analysis of liquid products; Figure S7, effect of molar ratio of DMC to DEC:EMC yield, EMC molar percentage after reaction; Table S1, particle sizes calculated from XRD; Table S2, ICP results of the materials; Table S3, results of CO₂-TPD over catalysts.

Author Contributions: Y.-N.M. and Y.W. conceived and designed the experiments; Y.-N.M. performed the experiments; Y.-N.M. and X.-H.S. analyzed the data; S.-Q.X., L.-J.G. and D.-H.P. provided reagents, materials and analysis tools; Y.-N.M. mainly wrote the paper and all authors revised the paper. All authors have read the final version of the manuscript.

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