

Synthesis of Co/N doped microporous carbon using Co/2-methylimidazole anchored zeolite Y

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Introduction

Recently, zeolite-templated carbons (ZTCs) have been widely investigated as three-dimensional carbon materials with highly ordered channels; the structures of zeolites transferred by nanocasting the ingredients into sacrificial template-zeolites. [1] Some ZTCs exhibit uniform micropores (c.a. 1.2 nm) and large surface areas ($\sim 4000 \text{ m}^2 \text{ g}^{-1}$), which are beneficial especially for the applications in catalytic processes because they improve the accessibility of reactants to the active centers. [2]

Besides, currently intensive research efforts to extend the versatility of ZTCs doped with heteroatoms [3] and/or metal nanoparticles [4]. The outstanding catalytic performance of ZTCs doped with heteroatoms and/or metal nanoparticles comparing to conventional materials is likely to originate from their highly developed porosity and good mass transport property.

In our recent work, Co/N-C with highly dispersed Co species was synthesized by using a commercial ion exchange resin Amberlyst 15, as a support for Co/2-methylimidazole complex. [5] In this method, 2-methylimidazole works as a N source for CoN_x complexes directly formed after carbonization as active sites, and it efficiently suppresses the aggregation of Co atoms. In the present work, we propose a new method to synthesize Co/N-ZTC catalysts with high surface areas and highly dispersed CoN_x species; Co/2-methylimidazole complex is introduced into Y zeolite with 12-membered ring as the sources of Co and N and removal of Y zeolite after carbonization. Moreover, we actually investigated ORR catalytic performance of the obtained Co/N-ZTC.

Results and Discussion

We synthesized Co/N-ZTCs according to **Figure 1**. The first step is to anchor Co/2-methylimidazole complex into HY zeolite as a precursor of Co/N-ZTC by complexing Co ion with 2-methylimidazole in HY zeolite. The next step is chemical vapor deposition (CVD) using methanol as a carbon source, followed by carbonization process. The last step is base and acid treatments to remove HY zeolite and aggregated Co particles. As a control experiment, the same CVD process was also conducted for HY, Co/HY and NaY as zeolites.

We characterized Co/N-ZTC. Firstly, we carried our XRD measurement for Co/N-ZTC. XRD measurement for Co/N-ZTC confirms that Co/N-ZTC has the ordered structure derived from Y zeolite. Then, we measured N_2 adsorption isotherm of Co/N-ZTC to evaluate its porosity. Co/N-ZTC has uniform micropores with a size of around 1.2 nm and high surface area (ca. $2000 \text{ m}^2/\text{g}$). Next, we performed STEM observation for Co/N-ZTC. STEM image shows that Co/N-ZTC has single atomic Co. Furthermore, we investigated local chemical structure of Co using XANES

measurement. XANES spectra indicates that Co species of Co/N-ZTC is CoN_x species. Thus, Co/N-ZTC has single atomic Co in CoN_x moieties. Finally, we investigated catalytic performance of Co/N-ZTC on ORR in alkaline media. Co/N-ZTC shows high onset potential and limiting current density. The high catalytic performance of Co/N-ZTC is due to single atomic Co in CoN_x moieties and high surface.

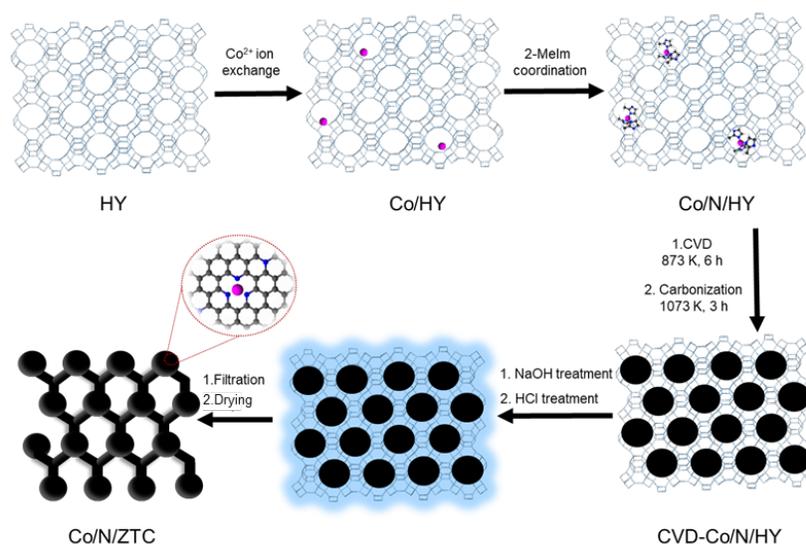


Figure 1. Synthetic strategy for Co/N-ZTC.

Conclusions

We synthesized Co/N-ZTC with a high surface area and highly dispersed CoN_x species by complexing Co ion with 2-methylimidazole in Y zeolite as a template. Co/N-ZTC shows excellent catalytic performance on ORR due to its high microporosity and single atomic Co species in CoN_x moieties. Our synthetic strategy can be applied to synthesize other TM/Het-ZTCs. Thus, this work provides a new direction for the design of ZTCs and expands the further utilization of ZTCs.

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