Cu immobilized on hierarchically porous N-doped carbon derived from ZIF-8 for oxy-carbonylation of methanol to dimethyl carbonate

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Abstract: Nitrogen-containing carbons (NCs) have attracted considerable attention for their outstanding physicochemical properties including effects of electricity and basicity. The supported metal catalysts using the NCs with proper nitrogen content and structure as carriers can usually present enhanced performance through intensified metal–support interactions. Herein, we report the preparation and catalytic performance of supported Cu catalysts on hierarchically porous NCs derived from ZIF-8 for the oxy-carbonylation of methanol to dimethyl carbonate with molecular oxygen. Compared with pristine carbon-supported Cu catalysts, the present NCs-supported ones show superior performance for the target reaction. The structure–activity correlations are investigated by extensive characterizations.

Keywords: Nitrogen-doped carbon, Supported Cu catalyst, oxy-carbonylation of methanol.

1. Introduction

Carbon supported metal catalysts have been viewed as one of the most important and common catalysts over past decades due to a carbon-based support normally showing high specific surface area, large pore volume, good electricity and thermal conductivity, and low cost of manufacture. However, the surface of carbon materials is relatively inert for anchoring catalytically active metallic nanoparticles (NPs), resulting in inferior stability at elevated reaction temperature. An altered carbons surface with heteroatoms, such as nitrogen, sulfur, or phosphorus, exhibit the various properties and benefit the intensified interaction of metal and supports, which may be expressed a reinforced catalytic combined with the anchoring effect and electronic variation of host metal NPs. Specifically, replacing C with N atoms in carbon surface can lead to an enhanced electron density of states near the Fermi level, which can yield a positive effect to the catalyst and become a novel support for loading metal NPs.

In this work, we have prepared supported Cu catalysts with hierarchically porous NCs derived from ZIF-8 for the oxy-carbonylation of methanol to dimethyl carbonate (DMC) with molecular oxygen. We show that, compared with pristine carbon-supported metal catalysts, the ZIF-8 derived NCs-supported ones can afford superior performances for the target reactions. The structure–activity correlations will be discussed by extensive spectroscopic studies.

2. Experimental

The microporous ZIF-8 was prepared according to the reference.[1] The porous N-doped carbon materials were fabricated using ZIF-8 as a self-sacrificed template by calcinating ZIF-8 under an atmosphere of Ar at the different temperatures. The resultants were marked as NCs-*T* (*T* represents the calcination temperature). The supported Cu catalysts then were obtained by using NCs-*T* as the carrier and copper salts as the precursor through a conventional impregnation method, labeling as Cu/NCs-*T*. The oxy-carbonylation of methanol was evaluated in a fixed-bed reactor-GC combined system. The structure of the catalysts was characterized by means of by elemental analysis, XPS, ESR, HAADF-STEM, and so on.

3. Results and discussion

Figure 1 shows the XRD patterns of Cu/NCs-*T* catalysts. For Cu/NCs-600 and Cu/NCs-700, only a peak at 24.0° can be observed, corresponding to the (002) carbon diffraction.[2] For Cu/NCs-800, Cu/NCs-

900 and Cu/NCs-1000, another peak at 43.6° was observed. The peak was assigned to the (101) carbon diffraction.[2] Compared with the Cu/NCs-*T*, the Cu/ZIF-8 had the same diffraction peaks as the pure ZIF-8. In all catalysts, there were no diffraction peaks of Cu species. To investigate the microstructure of the catalysts, the TEM images were taken as displayed in Fig. 2. The NCs-*T* inherited the original morphology of pure ZIF-8 crystal. However, with the increase of calcination temperature, the NCs-*T* surfaces became rough and the entities became thinner in thickness. The N amount, BET surface area (S_{BET}), and typical catalytic performance of the Cu/NCs-*T* samples are listed in Table 1. The S_{BET} value of the Cu/NCs-*T* increased from 40.0 to 879.3 m^2/g with the increase of calcination temperature from 600 °C to 1000 °C. The Cu/NCs-1000 catalyst showed the highest catalytic activity, affording a conversion of methanol above 67.0% with 98.4% selectivity to DMC.

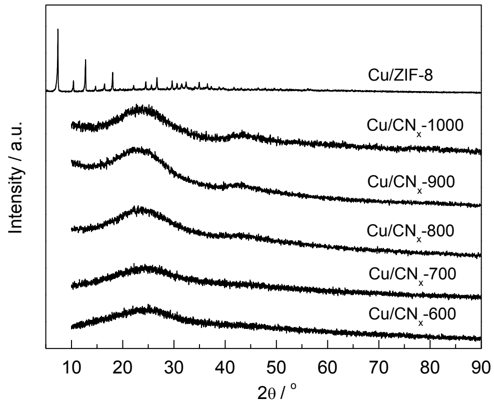

Fig. 1. The XRD patterns of catalysts.

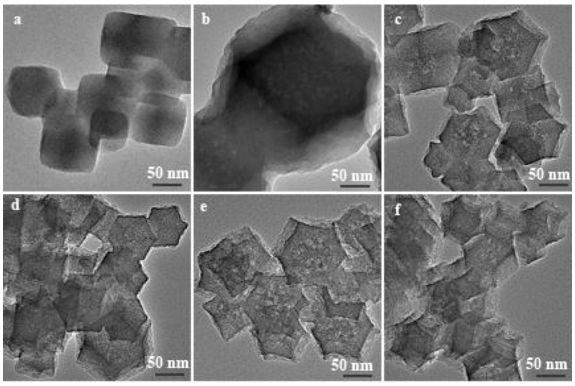

Fig. 2. The TEM images of (a) ZIF-8, (b) NCs-600, (c) NCs-700, d) NCs-800, (e) NCs-900, and (f) NCs-1000.

Table 1 The physiochemical property and oxy-carbonylation performance of several catalysts

Catalyst	Cu loading / wt%	S_{BET} / m^2/g	C/N / weight ratio	Content / wt %			MeOH conv. / %	DMC selec. / %
				N	C	H		
Cu/ZIF-8	12.1	722.6	1.7	*15.3*	25.9	3.6	4.2	89.5
Cu/NCs-600	12.2	40.0	2.4	*21.3*	38.7	2.5	trace	trace
Cu/NCs-700	11.6	477.6	2.0	*20.4*	43.6	2.5	1.9	68.0
Cu/NCs-800	7.6	665.0	2.9	*17.8*	51.1	2.1	2.4	68.9
Cu/NCs-900	4.3	711.3	6.3	*9.9*	62.3	2.0	4.5	90.0
Cu/NCs-1000	10.9	879.3	13.4	*5.1*	68.5	1.5	67.0	98.4

Reaction conditions: T = 110 °C, P = 1.1 MPa, GHSV = 5190 h^{-1}, 0.2 g catalyst.

4. Conclusions

We have prepared a series of hierarchically porous NCs-*T* materials using ZIF-8 as the precursor. These NCs-*T* materials inherited the octahedral structure of ZIF-8. The NCs-*T*-supported Cu catalysts thus prepared with NCs-*T* materials as carriers were employed for the oxy-carbonylation of methanol to produce DMC. The results showed that Cu/NCs-1000 had the highest activity and DMC selectivity compared with the Cu/ZIF-8 and Cu/C counterparts. The catalyst performance was very stable. The studies on the correlation of catalytic performance and structure are under way of progress.

References

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