Synergistic effect of a boron-doped carbon-nanotube-supported Cu catalyst for selective hydrogenation of dimethyl oxalate to ethanol

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Abstract: Herein, a series of boron-doped carbon nanotubes supported Cu catalysts (Cu/xB-CNTs) were prepared for the hydrogenation of dimethyl oxalate (DMO) to ethanol. The structure and chemical properties of boron doped catalysts revealed that doping boron into CNTs supports improved the Cu dispersion, strengthened the interaction of Cu species with CNTs support, introduced more surface acid sites, and increased the surface area of Cu^0 and especially Cu^+ sites. Consequently, the catalytic activity and stability of the catalysts were greatly enhanced by boron doping.
Keywords: Carbon nanotubes 1, Boron doping 2, Hydrogenation 3.

1. Introduction

Ethanol, that is combustible and can easily power engines, has been pushed to the center stage of clean and renewable energy.[1] As an alternative route, the efficient production of ethanol from syngas (CO/H_2) with DMO as the intermediate has gained increasing attention in recent years.[2] Currently, silica-supported Cu catalysts have been widely investigated for hydrogenation of DMO due to their high catalytic activity for DMO hydrogenation to ethanol.[3] Nevertheless, the use of silica as support could be a fatal flaw in the DMO hydrogenation process because of leaching of the silica.[4] In previous works, carbon nanotubes (CNTs) have been found to be outstanding catalyst supports because of their unique features, including well-defined nano-channels, graphene-like tube walls, and sp^2-hybridized carbon frameworks.[5] Moreover, heteroatom-doped CNTs usually exhibit outstanding performance for specific purposes. Consequently, boron-doped carbon nanotubes were prepared and utilized as supports for Cu-based catalysts.

2. Experimental

Prior to doping, multi-walled carbon nanotubes were treated in 65 wt% HNO_3 solution to eliminate impurities and open the caps of CNTs. The boron-doped CNTs supports were prepared by thermal annealing of a mixture of CNTs and boric acid (weight ratios of boric acid with CNTs is 0.05:1, 0.1:1, 1:1 and 2:1, respectively). For comparison, CNTs supports were also treated by the same thermal annealing procedure of xB-CNTs without adding boric acid, and denoted as CNTs-T. Cu/xB-CNTs catalysts were prepared by a sonication-assisted impregnation method with a constant Cu loading of 15 wt%. For comparison, Cu/CNTs and Cu/CNTs-T catalysts with pristine CNTs and CNTs-T as supports were also prepared by the same synthetic procedure.

Catalyst evaluation in DMO hydrogenation was conducted in continuous-flow mode in a stainless steel fixed-bed reactor. The products were condensed in a cold trap and then analyzed by a gas chromatograph equipped with a flame-ionization detector, in which 2-propanol was employed as the internal standard.

3. Results and discussion

The FE-SEM images were taken to examine the morphologies of CNTs, CNTs-T and xB-CNTs, as shown in Figure 1(a-e). The CNTs-T and xB-CNTs exhibited similar tube structure with CNTs, indicating that the structure of CNTs did not be damaged during the thermal treatment and boron doping process. The similar result could be also obtained by XRD characterization in Figure 1f.

Surface characterization by nanoscale elemental STEM-EDX mapping (Figure 2) was used to determine the distribution of B species in the 1B-CNTs support. The distribution domain of B species was

clearly located on the wall of CNTs, demonstrating that the B species were successfully doped into the outer and inner wall of 1B-CNTs support.
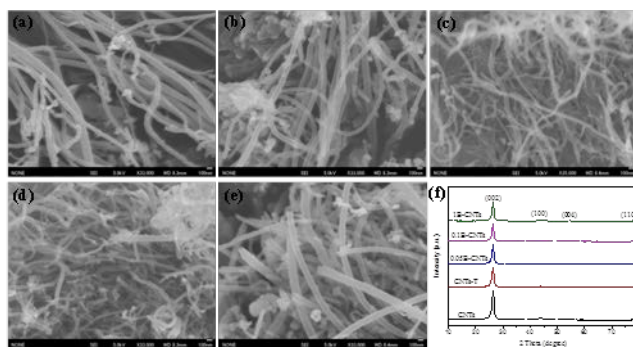

Figure 1. FE-SEM images of (a) CNTs, (b) CNTs-T, (c) 0.05B-CNTs, (d) 0.1B-CNTs, (e) 1B-CNTs and (f) XRD patterns of all samples.
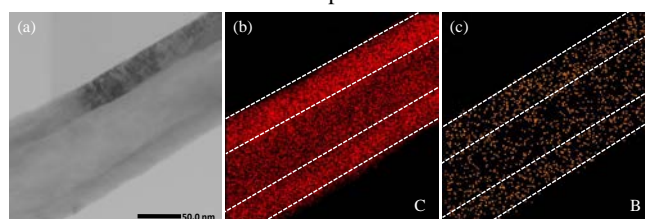
Figure 2. STEM-EDX images of 1B-CNTs support.

The catalytic activity for DMO hydrogenation versus Cu/xB-CNTs with different boron content was plotted in Figure 3a. DMO conversion was close for all catalysts, while the best ethanol selectivity of 78.1% was obtained over the Cu/1B-CNTs catalyst. The catalytic stability over the boron-free Cu/CNTs and boron-doped catalysts was also investigated as in Figure 3b. The result indicated that boron doping on Cu/xB-CNTs catalysts had remarkable influence on the enhanced ethanol selectivity and catalytic stability of DMO hydrogenation reaction.
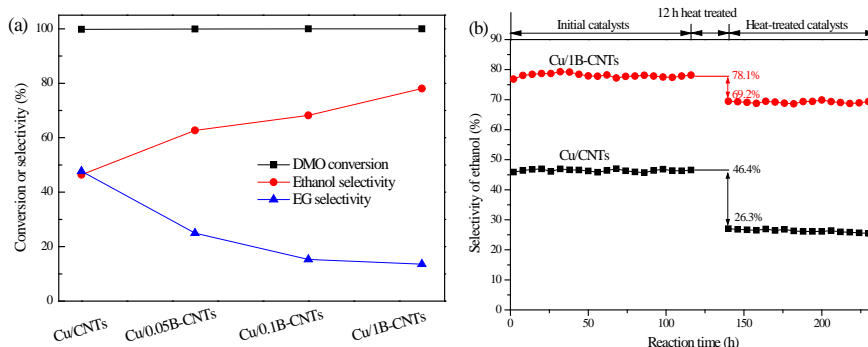
Figure 3. The catalytic activity and stability of catalysts.

4. Conclusions

In summary, boron-doped CNTs supported Cu catalysts exhibited superior catalytic performance in the hydrogenation of DMO to ethanol. The Cu/1B-CNTs catalyst achieved the highest ethanol selectivity and DMO conversion, which could be attributed to high copper dispersion, enhanced interaction of Cu species with CNT support, appropriate Cu^0 and Cu^+ distribution and suitable surface acidity. [6, 7]

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