

Supporting information

Methoxycarbonylation of 1,6-hexanediamine with dimethyl carbonate to dimethylhexane-1,6-dicarbamate over Zn/SiO₂ catalyst

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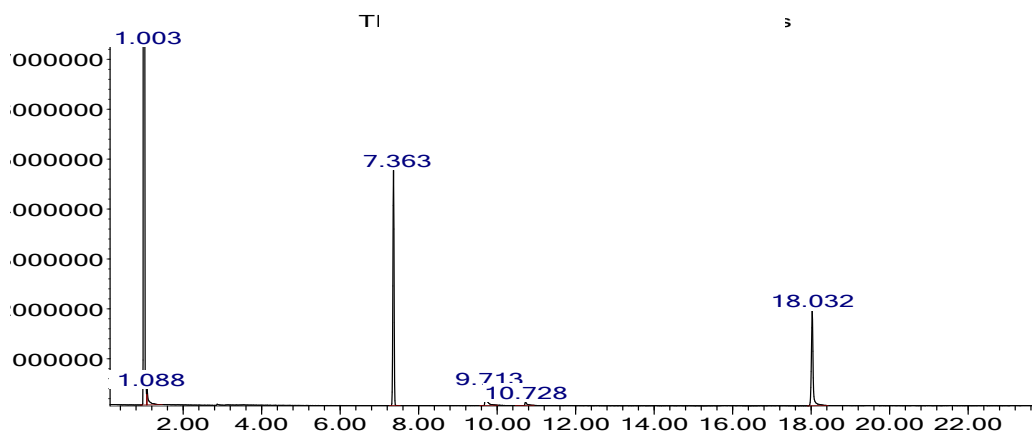
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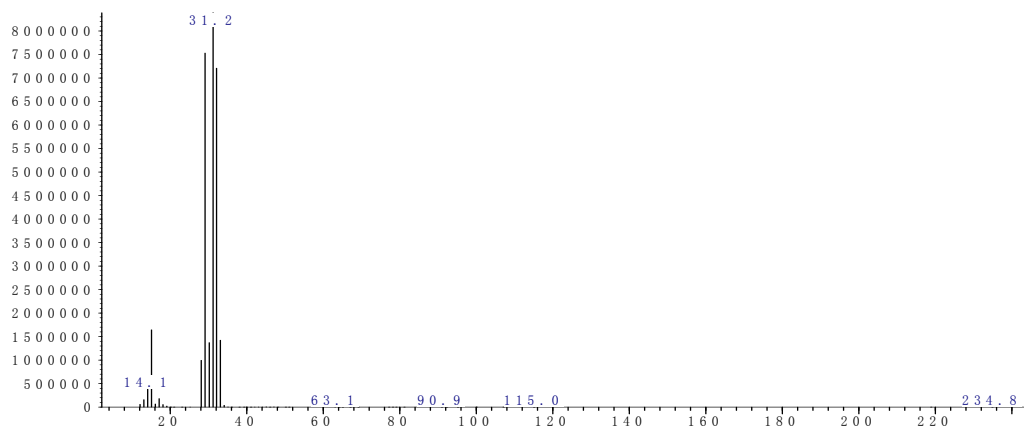
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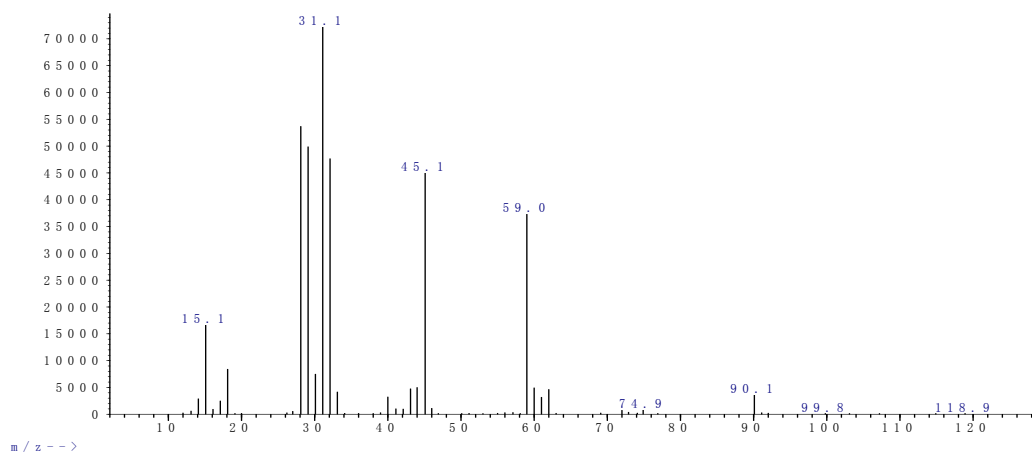
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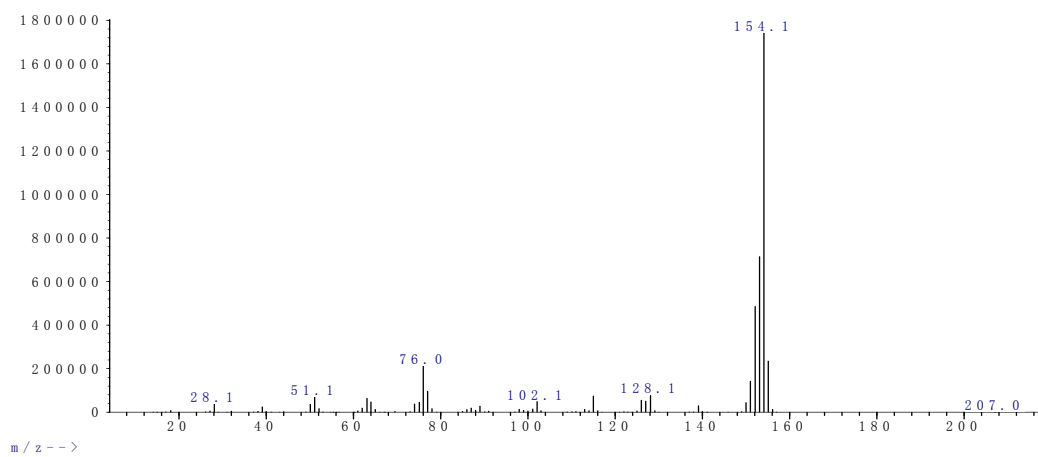
(a)



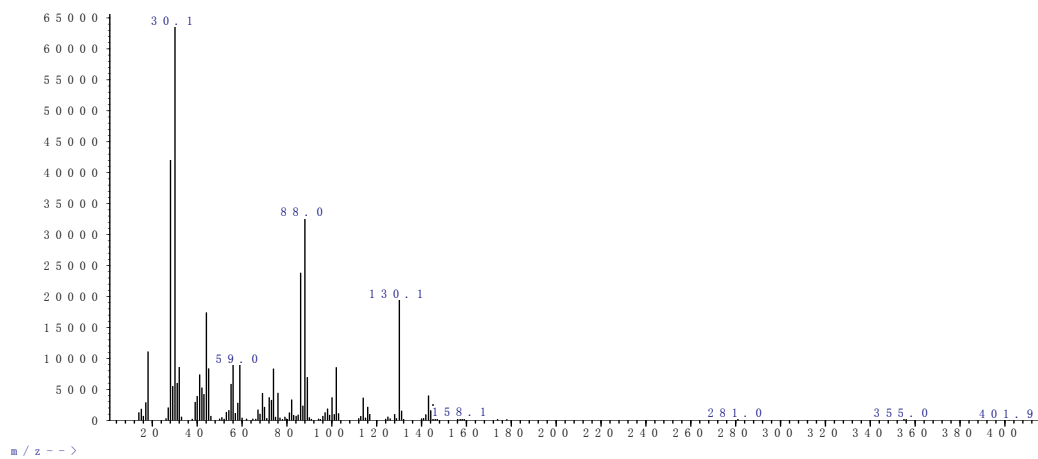
(b)



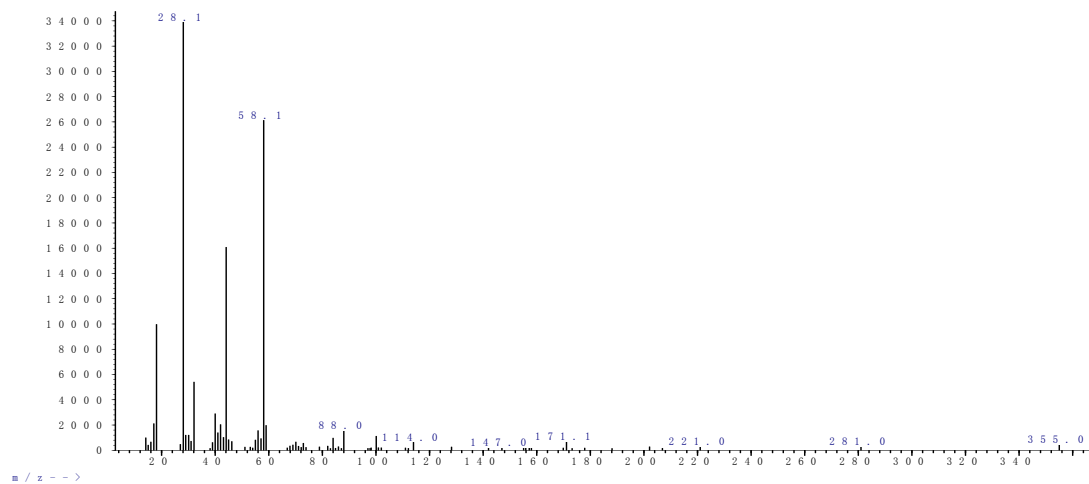
(c)



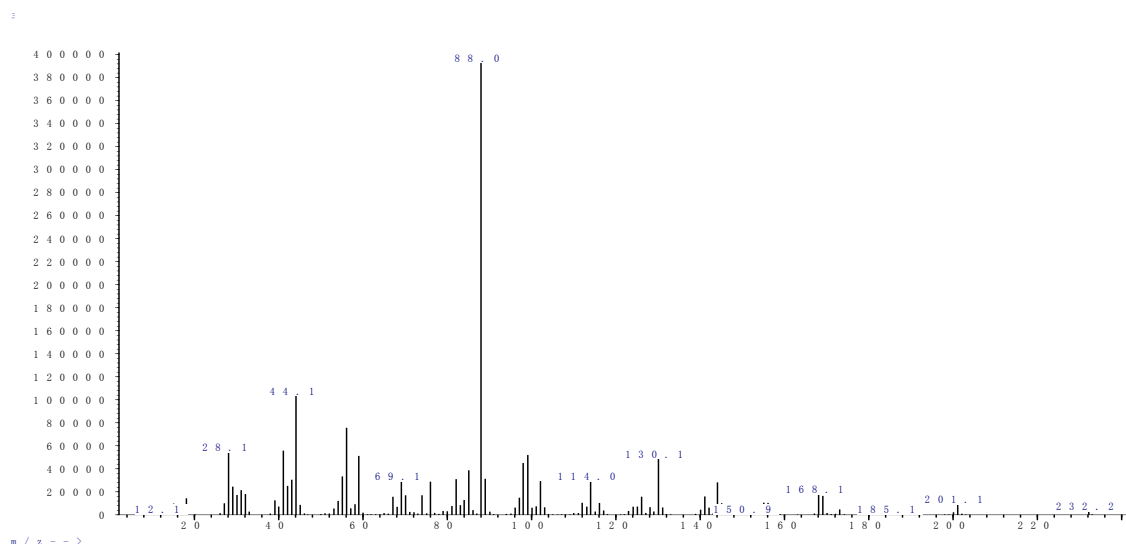
(d)



(e)



(f)



(g)

Fig. S1 GC-MS chromatogram of the products mixture

(a) TIC; (b)-(g) MS spectra of the peaks at 1.003, 1.088, 7.363, 9.713, 10.728 and 18.032 min in the TIC, respectively

The qualitative identities of the products were confirmed by Agilent 7890A-5975C GC-MS equipped with a capillary column Agilent HP-5 (30m×0.32mm×0.25um), which was linked to a mass detector. The gasification temperature was 280 °C and the mass spectrometer detection temperature was 240 °C. The column temperature was program-controlled as followed: the initial column temperature was 160 °C, increased to 240 °C at a rate of 5 °C/min, and then maintained for 10 min.

The GC-MS chromatogram of the products mixture is shown in Fig. S1. Six peaks at 1.003, 1.088, 7.363, 9.713, 10.728 and 18.032 min in the total ion chromatogram (TIC) can be found. The corresponding MS spectra of each peak are scanned to qualitative identify the product. The peaks at 1.003 and 7.363 min are obviously attributed to the solvent CH₃OH and the internal standard biphenyl. According to the reported data, the peak observed at 1.088 and 18.032 min are assigned to the reactant HDA and the main product HDC respectively. The remaining two peaks at 9.713 and 10.728 min can be identified as the intermediate NH₂(CH₂)₆NHCOOCH₃ and the by-products (CH₃)₂N(CH₂)₆NHCOOCH₃ by

analyzing the fragment ions detected.

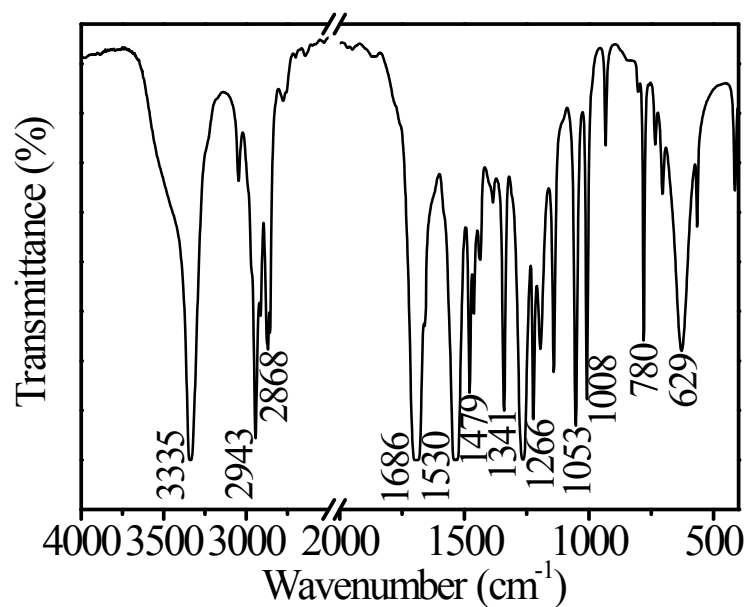


Fig. S2 FTIR spectra of HDC

The main product HDC is obtained by the recrystallization of the crude product with water according to the report of Sun *et al*[1]. HDC is grinded together with KBr in a weight ratio of 1:200 and press into a thin disk for IR spectra measurement (Fig. S2).

[1] D.L. Sun, S.J. Xie, J.R. Deng, C.J. Huang, E. Ruckenstein, Z.S. Chao, CH₃COONa as an effective catalyst for methoxycarbonylation of 1,6-hexanediamine by dimethyl carbonate to dimethylhexane-1,6-dicarbamate, *Green Chem.*, 12 (2010) 483-490.

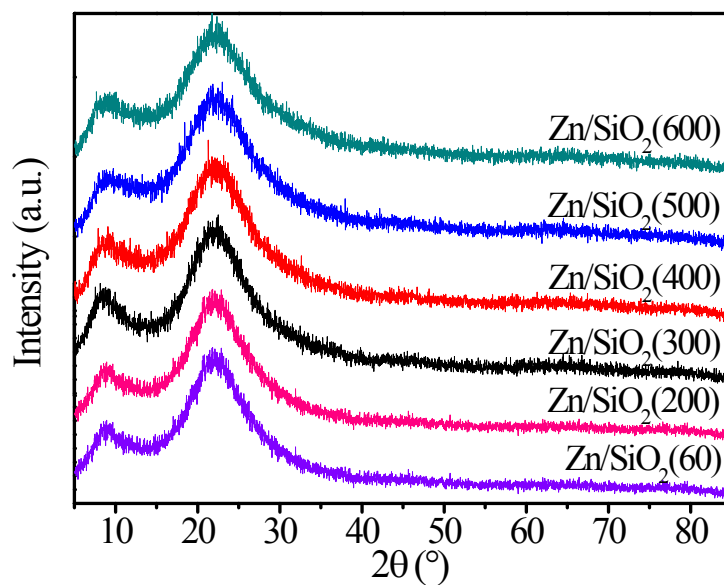


Fig. S3 XRD patterns of different catalysts

X-ray diffraction (XRD) spectroscopy was performed on a Bruker D2 diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm) at 30 kV and 10 mA in the 2θ range of 5 to 85 ° at a rate of 4 °/min.

Fig. S3 displays the XRD patterns of the catalysts calcined at different temperature. There are only SiO₂ support diffraction peaks and no Zn species diffraction peaks, indicating the active component is highly dispersed on the surface of SiO₂ as a monolayer.

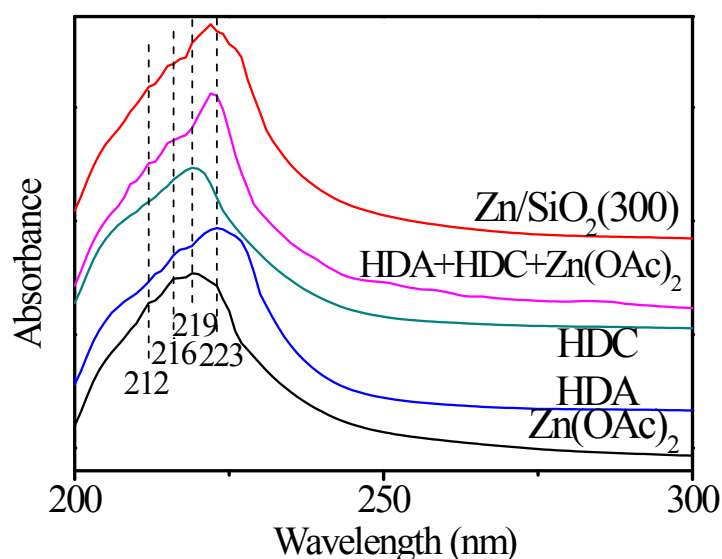


Fig. S4 UV–Vis absorption spectra of the standard samples and the product solution catalyzed by Zn/SiO₂(300)

UV–Vis absorption spectroscopy (UV–Vis) was carried out on PERSEE TU-1901 double-beam UV-Vis spectrophotometer scanning from 200 to 350 nm.

Fig. S4 presents the UV–Vis absorption spectra of the product solution catalyzed by Zn/SiO₂(300). In order to confirm the existence of Zn(OAc)₂ in the product solutions, the standard solutions are prepared by dissolving Zn(OAc)₂, HDA, HDC and all above reagent in CH₃OH as a reference. The spectra of Zn(OAc)₂ standard solution shows absorptions at 212, 216, 219 and 223 nm, which are appeared in the spectra of the product solution catalyzed by Zn/SiO₂(300). Furthermore, the spectral shape of product solution is similar to that of the HDA+HDC+Zn(OAc)₂ standard solution, indicating that the Zn specie in homogeneous reaction system is in the form of Zn(OAc)₂.

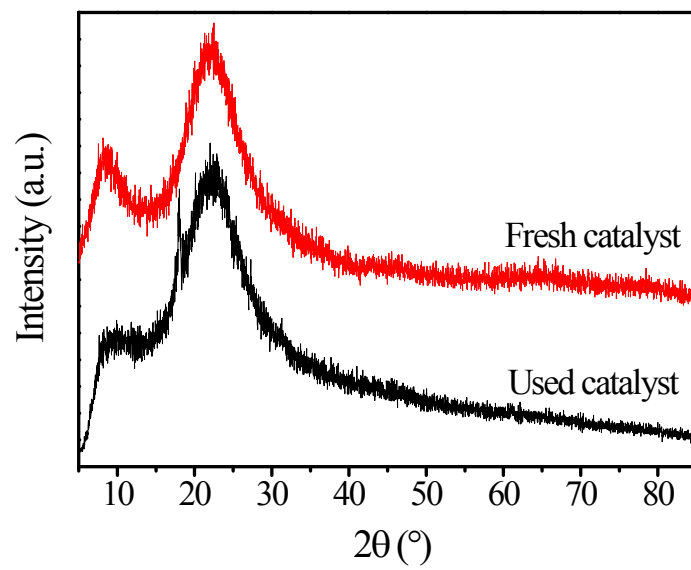


Fig. S5 XRD patterns of different catalysts

Fig. S5 presents the XRD patterns of the fresh and used catalysts. It can be seen that no ZnO diffraction peaks appear in the XRD pattern of the used catalyst.