Supporting Information

Catalytic degradation of polyurea: Synthesis of N-substituted carbamates with CuO-ZnO as the catalyst

Qinghe Li, Peixue Wang, Liu Shimin, Yuqing Fei and Youquan Deng*

State Key Laboratory for Oxo Synthesis and Selective Oxidation, State Key Laboratory of Solid Lubrication, Qingdao Center of Resource Chemistry & New Materials, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

Table of contents

I. $^1$H NMR characterization results of products............................................................S2
II. TGA characterization results of product........................................................................S6
III. $^3$N$_2$ adsorption-desorption analysis of as-prepared catalysts................................S6
IV. TGA analysis of Cu(Im)$_2$......................................................................................S7
V. GC-MS copies of carbamate products........................................................................S7
VI. TGA, XPS, SEM, AFM and FT-IR characterization results of catalysts.........................S10
VII. $^1$H and $^{13}$C NMR of EHDC obtained from the degradation of PU-HDA for 2 and 18 h.............................................................................................S12
VIII. The thermal properties of the isolated and pure EHDC.............................................S14
I. $^1$H NMR characterization results of products

$^1$H NMR spectra of the carbamates spectra were measured using an INOVA NMR system at 400 MHz. All spectra were recorded in CD$_3$OD and chemical shifts ($\delta$) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks.

1) Dimethyl-hexane-1, 6-diyl dicarbamate

$$\begin{align*}
\text{O} & \text{H} \text{N} \text{O} \\
\text{O} & \text{H} \text{N} \text{O} \\
\text{H} & \text{N} \text{O} \\
\end{align*}$$

$^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 4.86 (s, 1H), 3.63 (s, 3H), 3.08 (m, 2H), 1.47 (m, 2H), 1.33 (m, 2H).

2) Diethyl-hexane-1, 6-diyl dicarbamate

$$\begin{align*}
\text{H} & \text{N} \text{O} \\
\text{H} & \text{N} \text{O} \\
\text{H} & \text{N} \text{O} \\
\end{align*}$$

$^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 4.87 (s, 1H), 4.04 (q, 2H), 3.06 (t, 2H), 1.47 (m, 2H), 1.31 (m, 2H), 1.21 (t, 3H).
3) Dibutyl-hexane-1, 6-diyl dicarbamate

$\text{\textsuperscript{1}H NMR (400 MHz, CD}_3\text{OD): } \delta 4.86 (s, 1H), 4.00 (t, 2H), 3.06 (t, 2H), 1.58 (m, 2H), 1.47 (m, 2H), 1.38 (m, 2H), 1.34 (m, 2H), 0.93 (t, 3H).$

4) Diethyl-4, 4'-methylenebis (cyclohexane-4, 1-diyl) dicarbamate
1H NMR (400 MHz, CD_{3}OD): \( \delta \ 4.86 \text{ (s, 1H), 4.03 (q, 2H), 3.60 (m, 2H), 1.89 (m, 1H), 1.72 (m, 1H), 1.56 (m, 1H), 1.23 (m, 1H), 1.15 (t, 3H), 1.07 (m, 1H), 0.95 (dd, 2H).} \\

5) 3-(aminomethyl)-3, 5, 5-trimethylcyclohexylcidicarbamate \\

1H NMR (400 MHz, CD_{3}OD): \( \delta \ 4.86 \text{ (s, 1H), 4.05 (q, 2H), 3.75 (m, 1H), 2.83 (d, 1H), 1.59 (d, 1H), 1.22 (dd, 1H), 1.16 (dd, 1H), 1.03 (d, 1H), 1.00 (t, 3H), 0.98 (d, 1H), 0.94 (s, 3H), 0.87 (s, 3H).}
6) Dimethyl 2-methyl-1, 4-phenylenedicarbamate

$^1$H NMR (400 MHz, CD$_3$OD): $\delta$ 7.52 (s, 1H), 7.16 (s, 1H), 7.07 (d, 1H), 4.86 (d, 1H), 3.72 (s, 3H), 2.12 (s, 3H).

Figure S1. $^1$H NMR copies of the carbamate products
II. TGA Characterization results of product

Figure S2. TGA copy of the carbamate products

III. N$_2$ adsorption-desorption analysis of as-prepared catalyst

Figure S3. N$_2$ adsorption-desorption analysis result of various catalysts.
IV. TGA analysis of Cu(Im)$_2$

![TGA analysis of Cu(Im)$_2$](image)

Figure S4. TGA analysis of Cu(Im)$_2$

V. GC-MS copies of carbamate products

![GC-MS copies of carbamate products](image)

- Dimethyl hexane-1,6-diyl dicarbamate
  - $m/z = 232$

- Diethyl hexane-1,6-diyl dicarbamate
  - $m/z = 260$
Figure S5. GC-MS copies of carbamate products
Figure S6. GC-MS copies of carbamate products
VI. TGA, XPS, SEM, AFM and FT-IR characterization results of catalysts

Figure S7. TGA analysis of CuO-ZnO catalysts, (a) CuO-ZnO-700, (b) CuO-ZnO-500, (c) 2CuO-ZnO-500, (d) CuO-2ZnO-500, and (e) CuO-ZnO-300.

Figure S8. X-ray photoelectron spectroscopy (XPS) characterization of CuO-ZnO-500.

Figure S9. Scanning electron microscope (SEM) characterization of CuO-ZnO-500
Figure S10. Atomic force microscope (AFM) characterization of CuO-ZnO catalysts, (A) CuO-ZnO-300, (B) CuO-ZnO-700, (C) 2CuO-ZnO-500, (D) CuO-2ZnO-500, (E) CuO-ZnO-500, (F) 3D analysis of CuO-ZnO-500. Insert: Roughness analysis of the corresponding samples.

Figure S11. Fourier transform infrared spectroscopy (FT-IR) characterization conducted with pyridine as the alkaline adsorbate. (a) CuO-ZnO-300, (b) CuO-ZnO-500, (c) CuO-ZnO-700, (d) 2CuO-ZnO-500 and (e) CuO-2ZnO-500. Full reference lines shown for Lewis acid sites (1616 cm\(^{-1}\), 1457 cm\(^{-1}\)), Lewis or Brønsted acid sites (1575 cm\(^{-1}\)), Brønsted acid sites (1540 cm\(^{-1}\)).
Figure 12 a) $^1$H NMR (400 MHz, CD$_3$OD) of EHDC obtained from the degradation of PU-HDA for 2 h: $\delta$ 4.85 (s, 1H), 4.07 (q, 2H), 3.09 (t, 2H), 1.47 (m, 2H), 1.34 (m, 2H), 1.24 (t, 3H).

Figure 12 b) $^{13}$C NMR (101 MHz, CD$_3$OD) of EHDC obtained from the degradation of PU-HDA for 2 h: $\delta$ 157.81, 60.16, 40.19, 29.47, 26.09, 13.63 ppm.
Figure 12 c) $^1$H NMR (400 MHz, CD$_3$OD) of EHDC obtained from the degradation of PU-HDA for 18 h: $\delta$ 4.85 (s, 1H), 4.07 (q, 2H), 3.08 (t, 2H), 1.49 (m, 2H), 1.38 (m, 2H), 1.24 (t, 3H).

Figure 12 d) $^{13}$C NMR (101 MHz, CD$_3$OD) of EHDC obtained from the degradation of PU-HDA for 18 h: $\delta$ 157.82, 60.16, 40.19, 29.67, 26.08, 13.62 ppm. The peaks at 29.99 and 39.50 ppm might be assigned to the PU-HDA.
Figure S13. The thermal properties of the isolated and pure EHDC