Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# Highly efficient synthesis of novel bio-based pentamethylene dicarbamate via carbonylation of pentanediamine with ethyl carbamate over well-defined titanium oxide catalyst

Xiang Hui [a,b,c], Liguo Wang [a,b,c,e*], Yan Cao [a], Shuang Xu [a], Peng He [a], Huiquan Li [a,b,c,d]

[a] Key Laboratory of Green Process and Engineering, National Engineering Research Center of Green Recycling for Strategic Metal Resources, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China.

[b] Sino-Danish College, University of Chinese Academy of Sciences, Beijing, 100049, China

[c] Sino-Danish Center for Education and Research, University of Chinese Academy of Sciences, Beijing, 100049, China

[d] School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China

[e] Dalian National Laboratory for Clean Energy, Dalian, 116023, China

Corresponding Authors: lgwang@ipe.ac.cn

**Table S1.** Texture properties of $TiO_2$-101 and $TiO_2$-110

| Entry | Catalysts | $S^{BET}$ /($m^2g^{-1}$) | Pore diameter /(nm) | Pore volume ($cm^3g^{-1}$) |
|---|---|---|---|---|
| 1 | $TiO_2$-101 | 6.76 | 25.60 | 0.039 |
| 2 | $TiO_2$-110 | 70.91 | 10.80 | 0.25 |

**Table S2.** The amounts of acidic sites of catalysts

| Catalyst | Peak position (℃) | Quantity (μmol $g^{-1}$) | Peak position (℃) | Quantity (μmol $g^{-1}$) | Total acidity (μmol $g^{-1}$) |
|---|---|---|---|---|---|
| $TiO_2$-101 | 167 | 103.6 | 296 | 276.6 | 370 |
| $TiO_2$-110 | 167 | 50.6 | 333 | 34.7 | 85 |

**Table S3.** Performance of different catalysts for the syntheses of carbamates

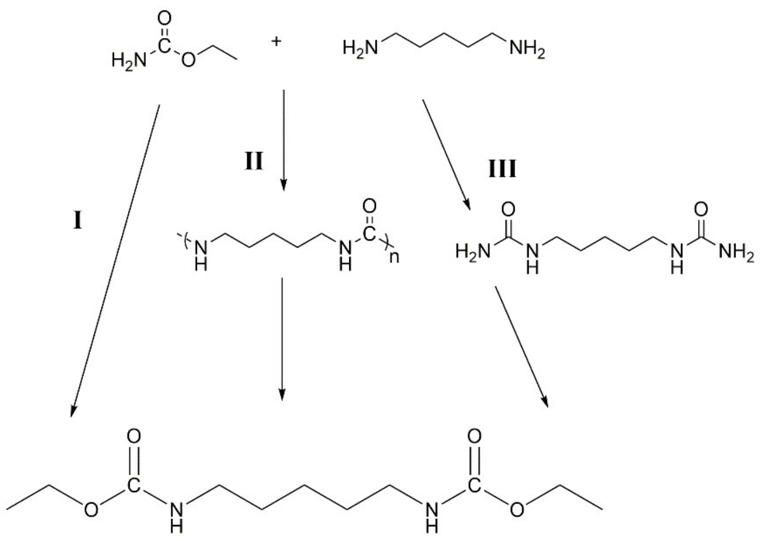
| Entry | Catalysts | Product | Conversion of amines (%) | Selectivity of amines (%) | TOF ($g\cdot g^{-1}h^{-1}$) [a] | Reference |
|---|---|---|---|---|---|---|
| 1 | PbO | MDC | 100 | 83 | 6.86 | 8 |
| 2 | $PbO_2$ | HDC | 100 | 93 | 3.27 | 10 |
| 3 | $Ni/Fe_3O_4$ | HDC | 100 | 98 | 4.82 | 13 |
| 4 | $TiO_2$ | PDC | 100 | >99 | 5.60 | This work |

[a] TOF: g of carbamates per g of catalyst per hour

**Table S4.** The catalytic performances of various catalysts for the synthesis of PDC

| Catalyst | Conversion of PDA/ % | Yield of PDC/% |
|---|---|---|
| ZSM-5 | 100 | 64 |
| HY | 100 | 84 |
| $TiO_2$ | 100 | 90 |

Reaction conditions: molar ratio of ethanol, EC to PDA= 25:4:1, reaction temperature = 190 °C, reaction time = 2 h.




**Scheme S1.** Possible pathways for the synthesis of PDC from PDA and EC

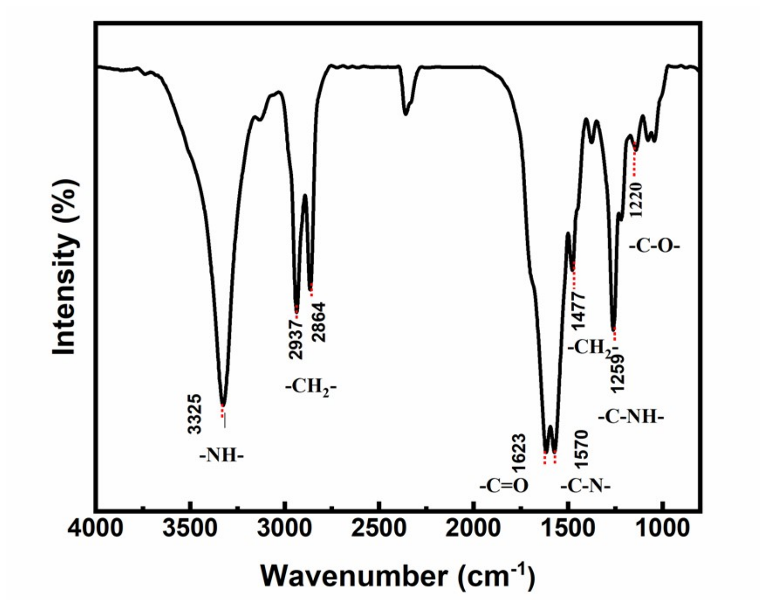



**Fig. S1** The FT-IR spectrum of solid product

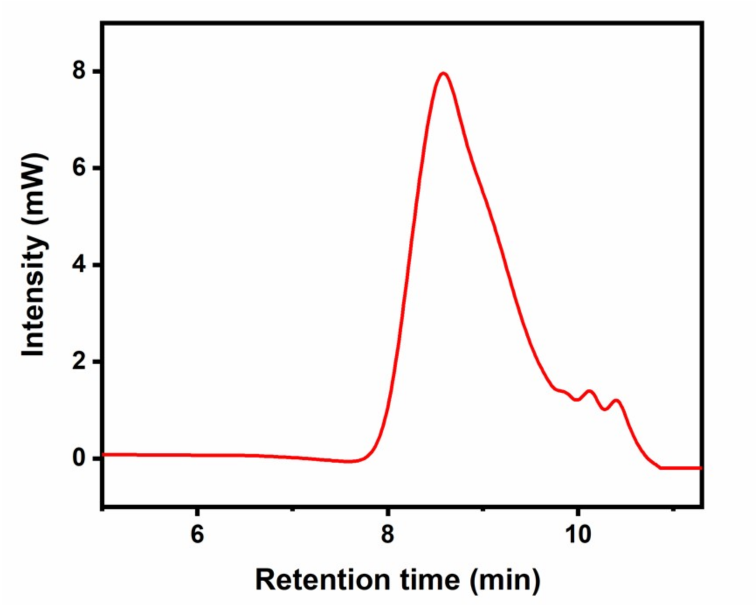



**Fig. S2** GPC curve of intermediate

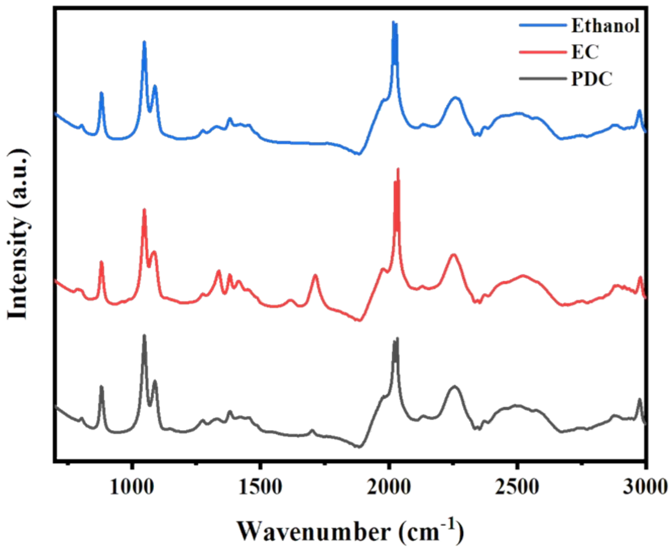



**Fig. S3** FTIR spectra of ethanol, EC, and PDC

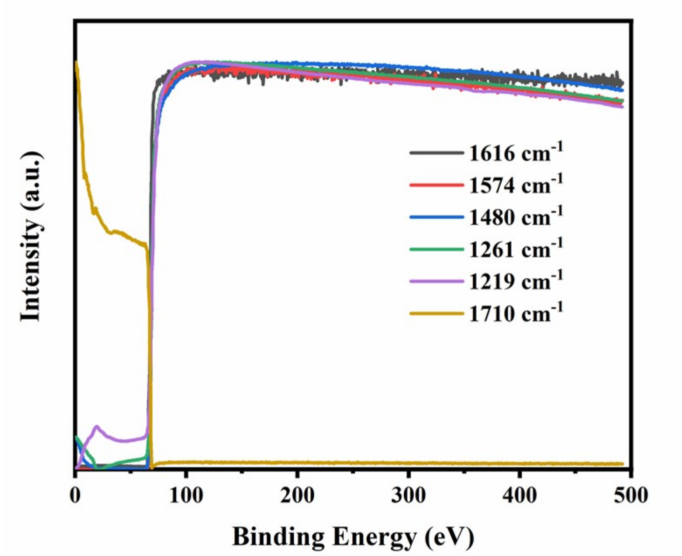



**Fig. S4** Trends of formation for polyurea and PDC without catalyst in a real time concluded from FTIR spectra

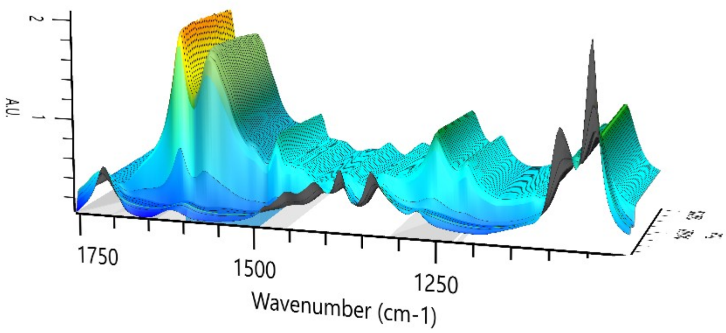
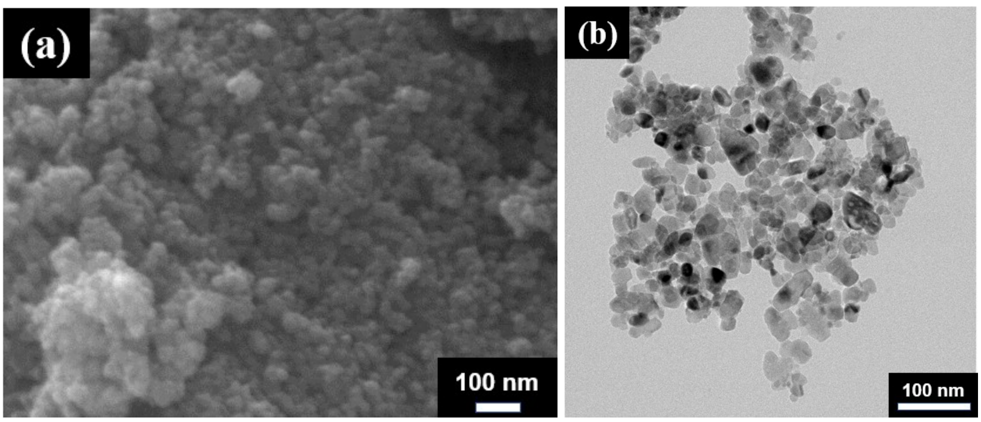



**Fig. S5** The FTIR spectrum of polyurea and three-dimensional surface monitoring of the formation of polyurea without catalyst



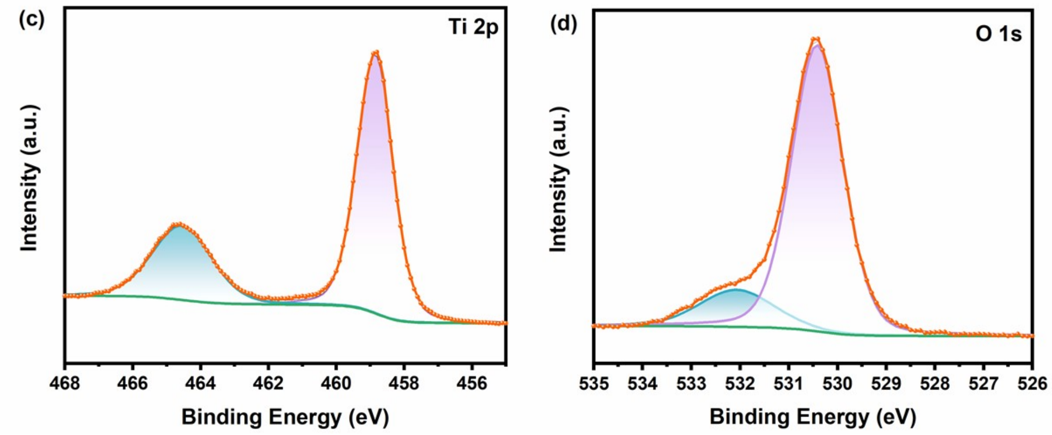



**Figure S6.** SEM (a) and TEM (b) images. XPS spectra of Ti 2p (c) and O 1p (d) for recycled catalyst