

Supporting Information for
Heterogeneous CeO₂ catalyst for one-pot synthesis of organic carbamates
from amines, CO₂ and alcohols

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The detail procedure of dibenzylurea synthesis

Benzylamine solution (Benzylamine 4.82 g (45 mmol) + toluene 20 ml) was dropped into the solution of *N, N'*-carbonyldiimidazole (*N, N'*-carbonyldiimidazole 3.23 g (20 mmol) + toluene 20 ml), and the mixture was stirred for 3 h under air atmosphere.

After the reaction, 30 ml of 10% HCl_{aq} was added and the reaction mixture was separated. Then the reaction mixture was washed and dried by Na₂SO₄ all night long. Dibenzylurea, the white crystal, was filtrated and obtained with 39% yield.

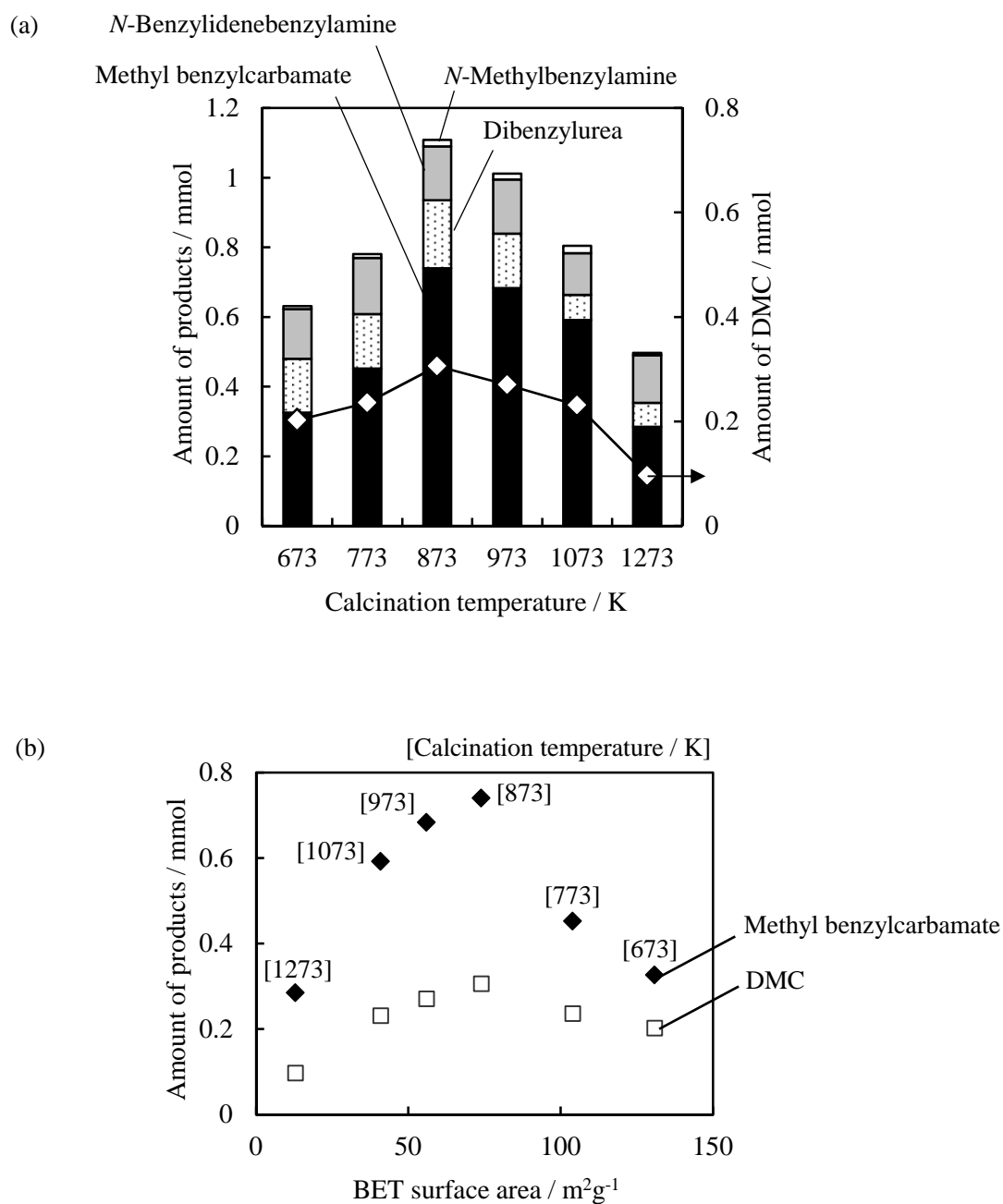


Figure S1. Results of the reaction of $C_6H_5CH_2NH_2 + CO_2 + CH_3OH$ over CeO_2 calcined at various temperatures (a) Relation between the amount of products and the calcination temperature, (b) Relation between the amount of products and BET surface area of CeO_2 .

Reaction conditions: CeO_2 0.03 g, $C_6H_5CH_2NH_2 : CH_3OH = 5 \text{ mmol} : 500 \text{ mmol}$, CO_2 5 MPa, 423 K, 2 h.

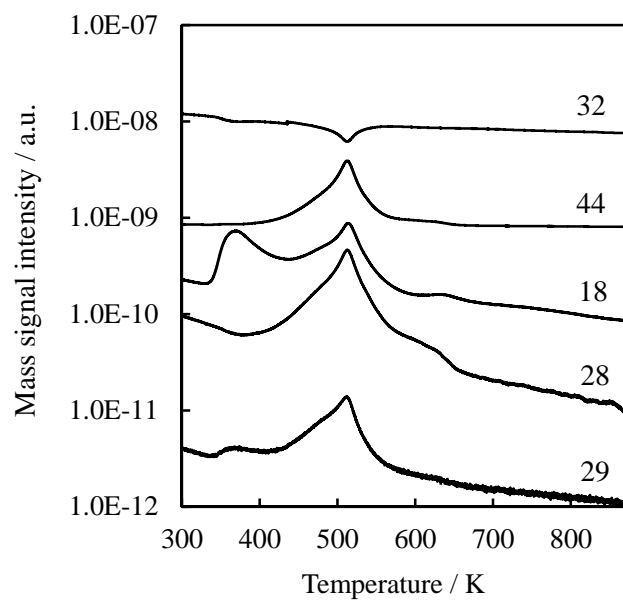


Figure S2. TPO profile of the CeO₂ after the reaction of C₆H₅CH₂NH₂ + CO₂ + CH₃OH

Heating rate 10 K/min., Sample 100 mg.

Reaction conditions: CeO₂ 0.17 g, C₆H₅CH₂NH₂ : CH₃OH = 5 mmol : 500 mmol, CO₂ 5 MPa, 423 K, 2 h.

Table S1. Results of the reaction of $C_6H_5CH_2NH_2 + CO_2 + CH_3OH$ over various catalysts

Catalyst	Amount of products / mmol				
	Methyl benzylcarbamate	Dibenzylurea	<i>N</i> -Benzylidene- benzylamine	<i>N</i> -Methyl- benzylamine	DMC
none	0.00	0.00	0.07	0.05	0.00
CeO ₂	4.1	0.05	0.26	0.06	0.69
CeO ₂ *	2.3	0.53	0.21	0.06	0.17
Cs ₂ CO ₃	0.00	0.07	0.10	0.03	0.00
Cs ₂ CO ₃ *	0.03	0.01	0.01	0.01	0.00
ZrO ₂	0.09	0.03	0.09	0.09	0.03
ZrO ₂ *	0.03	0.06	0.13	0.01	0.00
SnO ₂	0.00	0.00	0.09	0.05	0.00
MgO	0.00	0.00	0.09	0.04	0.00
SiO ₂	0.00	0.00	0.06	0.07	0.00
α -Al ₂ O ₃	0.00	0.00	0.03	0.05	0.00
γ -Al ₂ O ₃	0.00	0.00	0.05	0.04	0.00
HSZ (Si/Al=72)	0.00	0.00	0.10	0.10	0.00
HY4.8 (Si/Al=5.2)	0.00	0.00	0.12	0.04	0.00
TiO ₂	0.00	0.00	0.08	0.04	0.00
CuO	0.00	0.00	0.13	0.05	0.00
Cu ₂ O	0.00	0.00	0.12	0.10	0.00
Y ₂ O ₃	0.00	0.00	0.07	0.05	0.00
FeO	0.00	0.00	0.05	0.02	0.00
Fe ₂ O ₃	0.00	0.00	0.05	0.03	0.00
Fe ₃ O ₄	0.00	0.00	0.07	0.03	0.00
CoO	0.00	0.00	0.15	0.10	0.00
Co ₃ O ₄	0.00	0.00	0.07	0.06	0.00
NiO	0.00	0.00	0.08	0.05	0.00
Mn ₂ O ₃	0.00	0.00	0.04	0.04	0.00
WO ₃	0.00	0.00	0.07	0.04	0.00
La ₂ O ₃	0.00	0.00	0.09	0.07	0.00
Pr ₆ O ₁₁	0.00	0.00	0.06	0.08	0.00
Nd ₂ O ₃	0.00	0.00	0.09	0.05	0.00
Sm ₂ O ₃	0.00	0.00	0.07	0.03	0.00
Eu ₂ O ₃	0.00	0.00	0.04	0.11	0.00
Gd ₂ O ₃	0.00	0.00	0.05	0.02	0.00
Tb ₄ O ₇	0.00	0.00	0.05	0.02	0.00

Dy ₂ O ₃	0.00	0.00	0.06	0.05	0.00
Ho ₂ O ₃	0.00	0.00	0.05	0.02	0.00
Er ₂ O ₃	0.00	0.00	0.05	0.05	0.00
Yb ₂ O ₃	0.00	0.00	0.05	0.08	0.00
Yb ₂ O ₅	0.00	0.00	0.05	0.03	0.00

Reaction conditions:

Catalyst (Metal = 1 mmol), C₆H₅CH₂NH₂ : CH₃OH = 5 mmol : 500 mmol, CO₂ 5 MPa, 423 K, 12 h.

* Catalyst (Metal = 1 mmol), C₆H₅CH₂NH₂ : CH₃OH = 5 mmol : 200 mmol, CO₂ 5 MPa, 423 K, 12 h.

Table S2. Relative molar sensitivity of all the products toward 1-hexanol

Reactants or products	Relative molar sensitivity
Benzylamine	1.32
Aminomethylcyclohexane	1.15
Aniline	1.05
Aniline	0.99 ^{a)}
Methanol	0.15
Ethanol	0.33
1-Propanol	0.75
1-Propanol	0.49 ^{a)}
2-Propanol	0.42
Methyl benzylcarbamate	1.30
Ethyl benzylcarbamate	1.28
<i>n</i> -Propyl benzylcarbamate	1.52
<i>iso</i> -Propyl benzylcarbamate	1.52 ^{b)}
Methyl <i>N</i> -(cyclohexylmethyl)carbamate	0.83
Ethyl <i>N</i> -(cyclohexylmethyl)carbamate	1.39
<i>n</i> -Propyl <i>N</i> -(cyclohexylmethyl)carbamate	1.54
Methyl methylcarbamate	0.26 ^{c)}
Methyl phenylcarbamate	0.86
Ethyl phenylcarbamate	1.37
<i>n</i> -Propyl phenylcarbamate	0.78
Dibenzylurea	0.32
<i>N</i> -Benzylidenebenzylamine	2.78
<i>N</i> -Methyl benzylamine	1.59
<i>N</i> -Ethyl benzylamine	1.56
<i>N</i> -Propyl benzylamine	2.04
Dimethyl carbonate	0.19
Diethyl carbonate	0.61
Dipropyl carbonate	1.25

a) TC-WAX was used as a capillary column.

b) *n*-Propyl benzylcarbamate was used.

c) Ethyl carbamate was used.