CeO_2-catalyzed synthesis of 1,3-dialkylureas from amines and CO_2

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Abstract: CeO_2 was the most effective catalyst for the direct conversion of CO_2 and *n*-butylamine to 1,3-dibutylurea (DBU) among the metal oxides as follows; CeO_2, ZnO, Sm_2O_3, ZrO_2, La_2O_3, Pr_6O_{11}, γ-Al_2O_3, Y_2O_3 and MgO. The solvent in this reaction was very important, and *N*-methylpyrrolidone (NMP) was the most effective for this reaction among various solvents. The combination of CeO_2 catalyst and NMP solvent was applicable to the reactions of various amines such as linear primary alkylamines or branched primary alkylamines.

Keywords: Urea, Carbon dioxide, Cerium oxide

1. Introduction

Direct conversion of CO_2 to chemicals is promising because CO_2 is non-toxic, abundant and inexpensive C1 source. Traditionally, urea derivatives have been prepared by phosgene method[1], however, it has problems such as toxicity of phosgene and co-production of large amount of salts by the neutralization. Direct conversion of CO_2 and amines to urea derivatives will be promising because the by-product in the reaction is only water. In our laboratory, we reported that CeO_2 showed activity for the direct conversion of CO_2 to organic compounds such as dialkyl carbonates and carbamates[2, 3]. In this study, CeO_2 catalyst was efficient for the synthesis of 1,3-disubstituted ureas from amines and CO_2, and NMP was the most effective solvent for this reaction among the solvents tested[4].

2. Experimental

Preparation of pure CeO_2 was calcining cerium oxide for 3 h at 873 K. Preparation of other metal oxides was as follows: ZrO_2, calcination of $Zr(OH)_4$ at 873 K for 3 h; MgO, calcination of commercial MgO at 873 K for 3 h. Y_2O_3, La_2O_3, Pr_6O_{11} and Sm_2O_3 were prepared by the precipitation method. $Y(NO_3)_3 \cdot nH_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Pr(NO_3)_3 \cdot nH_2O$, $Sm(NO_3)_3 \cdot 6H_2O$ were used as precursors. A precursor (25 g) was dissolved in water (100 ml) and NH_3 *aq* (1 M) was dropped with stirring. The pH of the solution was set to 10, resulting in a precipitate. The precipitate was filtered and washed with water, followed by drying at 383 K overnight (12 h) and calcining under air at 873 K (673 K for La_2O_3) for 3 h.

Activity tests were performed in a 190 ml autoclave reactor. Reaction conditions were as follows: CeO_2 2 mmol, *n*-butylamine 20 mmol, *N*-methylpyrrolidone (NMP) 8 ml (81 mmol), CO_2 5 MPa, 433 K, 4 h. The products were analyzed by a gas chromatograph. Conversion and selectivity to each product in the reaction of CO_2 and amines were calculated on the basis of the amine amount.

3. Results and discussion

The result of catalyst screening for the synthesis of 1,3-dibutylurea (DBU) from CO_2 and *n*-butylamine in NMP solvent is shown in Table 1. Without any catalysts (entry 10), *n*-butylamine was converted to give 15% DBU yield with 96% selectivity (entry 10). Similar conversion and selectivity were obtained with ZrO_2, La_2O_3, Pr_6O_{11}, γ-Al_2O_3, Y_2O_3 and MgO (entries 4-9). They provided slightly higher conversion than that of the blank result. On the other hand, CeO_2, ZnO and Sm_2O_3 provided relatively higher conversion than other metal oxides (entries 1-3). Among them, CeO_2 showed the highest conversion (73 %) with 99% selectivity. CeO_2 also showed the highest TOF (2.4 h^{-1}) (entry 1).

The result of the solvent effect is shown in Figure 1. NMP, dimethyl sulfoxide (DMSO), acetonitrile and *N,N*-dimethylformamide (DMF) showed higher conversion (>70%) than the other solvents tested.

However, DMSO, acetonitrile and DMF showed low DBU selectivity because many by-products were formed by the reaction of *n*-butylamine with solvent. On the other hand, NMP provided few by-products and high selectivity to DBU (99%), therefore NMP is the most effective solvent for this reaction.

The substrate scope of amines was also investgated using CeO_2 in NMP at 433 K. Linear amines reacted to give the 1,3-dialkylureas in high yields. Branched primary alkylamines also reacted to provide the corresponding 1,3-dialkylureas. However, secondary amine hardly reacted, which will be due to the bulkiness of secondary amine.

Table 1. Catalyst screening for the synthesis of 1,3-dibutylurea (DBU) from CO_2 and *n*-butylamine in NMP.

Entry	Metal oxide	S^a (m^2g^{-1})	Conv. (%)	Sel. (%)	Yield (%)	TOF^b (h^{-1})
1	CeO_2	88	73	99	72	2.4
2	ZnO	66	42	97	41	0.3
3	Sm_2O_3	38	31	94	29	0.2
4	ZrO_2	46	23	98	23	0.09
5	La_2O_3	28	23	94	22	0.08
6	Pr_6O_{11}	30	19	97	18	0.04
7	γ-Al_2O_3	97	20	95	19	0.05
8	Y_2O_3	70	21	97	20	0.06
9	MgO	46	24	94	23	0.09
10	None	-	16	96	15	-

Reaction conditions: metal oxide 2 mmol (based on metal), *n*-butylamine 20 mmol, NMP 8 ml, CO_2 5 MPa (at r.t.), 433 K, 4 h.

[a] Specific surface area determined by BET method.

[b] TOF (h^{-1}) = {(amount of urea, mmol) – (amount of urea at 0 h, mmol)}/{(catalyst, mmol) × (reaction time, h)}.

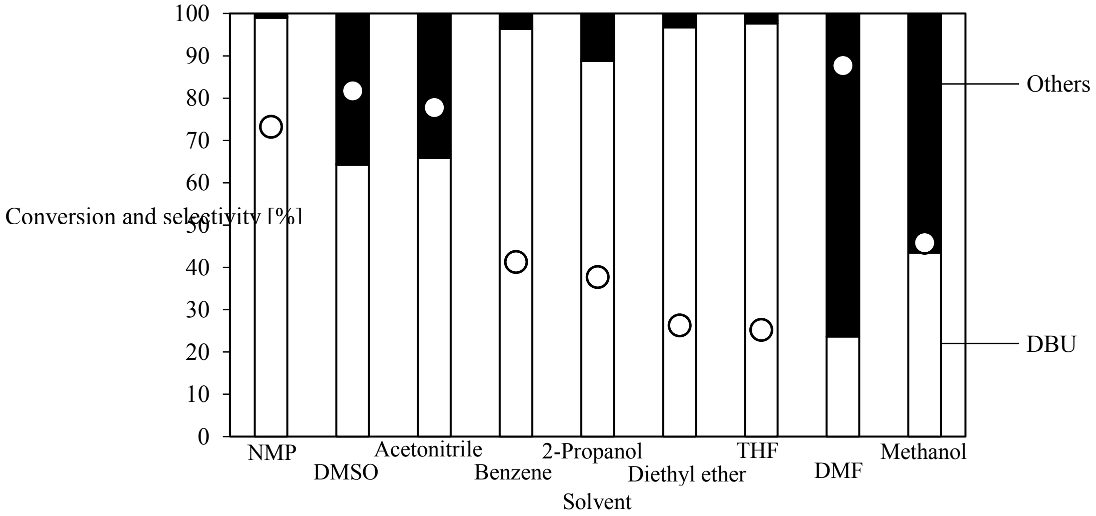

Figure 1. Solvent effect in the synthesis of DBU from CO_2 and *n*-butylamine over CeO_2.

Reaction conditions: CeO_2 2 mmol, amine 20 mmol, solvent 8 ml, CO_2 5 MPa (at r.t.), 433 K, 4 h. NMP : *N*-Methylpyrrolidone, DMSO : Dimethyl sulfoxide, THF : Tetrahydrofuran, DMF : *N,N*-Dimethylformamide. ○ Conversion.

4. Conclusions

CeO_2 was the most effective catalyst for the direct conversion of CO_2 and *n*-butylamine to 1,3-dibutylurea (DBU) among the metal oxides tested. The selection of solvent is very important and NMP was the most effective from the viewpoints of activity and selectivity in the synthesis of DBU over CeO_2. The combination of CeO_2 catalyst and NMP solvent was applicable to the reactions of various amines such as linear primary alkylamines and branched primary alkylamines.

References

1. F. Bigi, R. Maggi, G. Sartori, Green Chem. 2 (2000) 140.
2. M. Tamura, M. Honda, Y. Nakagawa, K. Tomishige, J. Chem. Technol. Biotechnol. 89 (2014) 19.
3. M. Honda, M. Tamura, Y. Nakagawa, K. Tomishige, Catal. Sci. Technol. 4 (2014) 2830.
4. M. Tamura, K. Ito, Y. Nakagawa, K. Tomishige, J. Catal. 343 (2016) 75.