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CeO_2-catalyzed direct synthesis of dialkylureas from CO_2 and amines

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ABSTRACT

CeO_2 showed higher activity for the direct synthesis of 1,3-dibutylurea (DBU) from CO_2 and *n*-butylamine than the metal oxides tested. The solvent largely influenced the reaction over CeO_2, and *N*-methylpyrrolidone (NMP) was preferable among various solvents tested from the viewpoints of activity and selectivity. The catalyst system composed of CeO_2 catalyst and NMP solvent (CeO_2 in NMP) was applicable to the reactions of various amines such as linear primary alkylamines or branched primary alkylamines, although *tert*-butylamine afforded low conversion. In contrast, secondary amines and aniline provided no yield of the ureas. The combination of 2-cyanopyridine with CeO_2 in NMP (CeO_2 in NMP with 2-cyanopyridine) promoted the transformation of the unreactive amines, showing that *tert*-butylamine and aniline were converted to the corresponding ureas in 82% and 80% yields, respectively. These yields are much higher than those reported in the previous literatures, indicating that CeO_2 in NMP with 2-cyanopyridine drastically promoted transformation of amines with low reactivity.

1. Introduction

CO_2 is an abundant, non-toxic, non-flammable and inexpensive C1 source [1–3]. Many methods for direct conversion of CO_2 to chemicals have been developed [4–16]. Compared with reductive transformation of CO_2 to chemicals such as methanol and formic acid [4–13], non-reductive transformation to chemicals such as carbonates, carbamates and ureas [3,14–16] is preferable from the viewpoint of energy input, while the direct transformation of CO_2 is generally difficult because CO_2 is very stable due to the very strong double bonds [3]. Urea derivatives are an important class of carbonyl compounds and can be used for many applications as intermediates for the synthesis of pharmaceuticals or agrochemicals, and also used as additives for fuels [17].

Urea derivatives have been traditionally prepared with phosgene or its derivatives [17]. However, the phosgene process has considerable drawbacks such as toxicity of phosgene and co-production of large amount of salts by the neutralization. Other various methods for the synthesis of urea derivatives have been also studied, such as oxidative carbonylation of amines with CO, reductive carbonylation of amines with CO, transamidation of ureas with amines, reaction of carbonates with amines, and reaction of CO_2 and amines [17–19]. Among these methods, direct reaction of CO_2 with amine to urea derivatives will be promising because only water is produced. Homogeneous catalysts and catalyst systems were reported such as CsOH, Cs_2CO_3, [BMIm]OH, Co$(acac)_3$ and $TBA_2[WO_4]$ [20–24]. However, heterogeneous catalysts or non-catalyst systems are more desirable than homogeneous ones from the industrial, environmental, and economical viewpoints. Deng and co-workers reported that polymer supported Au nanoparticles (Au/Poly), which showed the high activity ($TOF = 2900\ h^{-1}$) using cyclohexylamine among the reported heterogeneous catalysts, although the catalyst has drawbacks such as use of the precious metal of Au [25]. KOH/PEG catalyst and Mg–Al hydrotalcite catalyst were also reported [26,27], and these catalysts however have some problems such as low selectivity, cumbersomeness of catalyst preparation and/or narrow scope of substrate. Zhao and co-workers reported non-catalyst and non-solvent system; however, low activity and narrow scope of substrates were problems to be solved [28].

Recently, CeO_2-catalyzed organic reactions have been vigorously studied [29,30] such as transformation of nitriles [31–33], transformation of CO_2 to carbonate derivatives [34–57], reduction of alkynes and carboxylic acids [58,59], and transamidation and transesterification of amides or esters [60–69]. In our laboratory, it was firstly reported that CeO_2 showed activity for the activation of CO_2, and applied CeO_2 catalyst to transformation of CO_2 to organic carbonates such as dialkyl carbonates and cyclic carbonates, and carbamates such as methyl benzyl carbamate and cyclic carbamates [15,16,36–49]. It was also reported that CeO_2 is efficient for the direct synthesis of cyclic ureas from CO_2 and diamines [37]. In this report, CeO_2 catalyst was applied to the synthesis of

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1,3-disubstituted ureas from CO_2 and amines, and CeO_2 showed higher activity than the metal oxides tested. NMP is a preferable solvent for the reaction and enhances the activity of CeO_2.

2. Experimental

2.1. Catalysts and reagents

Preparation of pure CeO_2 catalyst was carried out by calcining cerium oxide HS (Daiichi Kigenso, Japan) for 3 h in air at 873 K, which is the optimized calcination temperature of CeO_2 according to the result of DMC synthesis for CO_2 and methanol [41]. The specific surface area (BET method) of the CeO_2 was 84 m^2/g. The purity of the CeO_2 is 99.97%. All the chemicals for organic reactions were commercially available and were used without further purification. Other metal oxides were commercially available, supplied from the Catalysis Society of Japan or synthesized by the precipitation method: ZrO_2 (Daiichi Kigenso Kogyo Co., Ltd., $Zr(OH)_4$ was calcined under air at 873 K for 3 h), MgO (Ube Industries, Ltd., MgO 500A, 873 K, 3 h), TiO_2 (Nippon Aerosil Co., Ltd., P-25), γ-Al_2O_3 (Nippon Aerosil), ZnO (FINEX-50, Sakai Chemical Industry Co., Ltd.), and SiO_2 (Fuji Silysia Chemical Ltd., 773 K, 1 h). Y_2O_3 La_2O_3, Pr_6O_{11} and Sm_2O_3 were prepared by the precipitation method. $Y(NO_3)_3{\cdot}nH_2O$ (Wako Pure Chemical Industries Ltd., >99.9%), $La(NO_3)_3{\cdot}6H_2O$ (Wako Pure Chemical Industries Ltd., >99.9%), $Pr(NO_3)_3{\cdot}nH_2O$ (Wako Pure Chemical Industries Ltd., >99.5%) and $Sm(NO_3)_3{\cdot}6H_2O$ (Wako Pure Chemical Industries Ltd., >99.5%) were used as precursors. A precursor (25 g) was dissolved in water (100 ml) and NH_3aq (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 by 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.

2.2. Catalytic test

All the reactions were carried out in an autoclave reactor with an inner volume of 190 ml. The standard procedure of the 1,3-dibutylurea (DBU) synthesis from CO_2 and *n*-butylamine was as follows: CeO_2 (0.34 g, 2 mmol), *n*-butylamine 1.46 g (20 mmol) and *N*-methylpyrrolidone (NMP) 8 ml (81 mmol) were put into the autoclave together with a spinner, and then the reactor was purged with 1 MPa CO_2 (Shimakyu Co., Ltd., >99.5%) three times. The autoclave was pressurized with CO_2 to the desired pressure (typically 5.0 MPa) at room temperature, and then the autoclave was heated to 433 K, where the CO_2 pressure was about 12 MPa. In the experiments for determination of the reaction rates, the autoclave with substrate, solvent and catalyst was first purged with 1 MPa Ar (Taiyo Nippon Sanso Corporation >99.9999%) three times and pressured with Ar to 0.1 MPa. The autoclave was heated to 433 K and was pressured with CO_2 to 5.0 MPa (CO_2 + Ar). The time when the temperature reached 433 K was set as 0 h. The mixture was constantly stirred during the reaction. After the reaction time, the reactor was cooled in water bath to room temperature. Methanol (10 ml) was added to the liquid phase as a solvent, and 1-hexanol (~0.2 ml) was also added as an internal standard substance for a quantitative analysis. The reactor was washed with methanol, and the liquids used in washing were added to the reaction mixture. The products were analyzed by a gas chromatograph equipped with an FID using a CP/Sil 5 CB capillary column (Agilent Technologies Inc., length = 50 m, I.D. = 0.25 mm, df = 0.25 μm). The following operating conditions were used: carrier gas: N_2, initial flow rate: 0.86 ml/min (pressure control mode), split ratio: 55:1, injection temperature of 573 K, column temperature program: 313 K (7 min), 20 K/min to 433 K (4 min), 20 K/min to 473 K (10 min), and 20 K/min to 573 K (26 min), detection temperature of 573 K. The qualitative analysis of the products was conducted by a gas chromatograph equipped with a quadrupole mass spectrometer (GC–MS) using the same capillary column.

Conversion and selectivity to each product in the reaction of CO_2 and amines were calculated on the basis of the amine amount as follows:

$$Conversion\ (\%) = \left(1 - \frac{\text{Amount of amine after the reaction}}{\text{Amount of amine before the reaction}}\right) \times 100$$

$$Selectivity\ (\%) = \frac{\text{Product amount based on alkyl moiety of the substrate}}{\text{Amount of reacted amine}} \times 100$$

The products that were not identified by GC–MS are denoted as “Others”. The selectivity of “Others” was calculated as follows:

$$Selectivity\ of\ others\ (\%) = \frac{\text{Amount of reacted amine} - \text{Amount of identified products}}{\text{Amount of reacted amine}} \times 100$$

The urea formation rate per catalyst gram (V_1, mmol h^{-1} g^{-1}) and the urea formation rate per specific surface area (V_2, mmol h^{-1} m^{-2}) were calculated as follows:

$$\begin{aligned} V_1\ (\text{mmol h}^{-1}\text{g}^{-1}) = {} & [\{(\text{amount of urea, mmol}) - (\text{amount of urea at 0 h, mmol})\}/(\text{reaction time, h}) \\ & - \{(\text{amount of urea without catalyst, mmol}) \\ & - (\text{amount of urea at 0 h without catalyst, mmol})\}/(\text{reaction time, h})]/(\text{catalyst, g}) \end{aligned}$$

$$V_2\ (\text{mmol h}^{-1}\text{m}^{-2}) = (V_1,\ \text{mmol h}^{-1}\text{g}^{-1})/(\text{specific surface area, m}^2\ \text{g}^{-1})$$

The procedure of the reverse reaction of DBU synthesis was as follows: CeO_2 (0.34 g, 2 mmol), DBU 1.72 g (10 mmol), H_2O 0.18 g (10 mmol) and *N*-methylpyrrolidone (NMP) 8 ml (81 mmol) were put into the autoclave together with a spinner, and then the reactor was purged with 1 MPa CO_2 (Shimakyu Co., Ltd., >99.5%) three times. The autoclave was pressurized with CO_2 to 5.0 MPa at room temperature, and then the autoclave was heated to 433 K. The mixture was constantly stirred during the reaction. After the reaction time, the reactor was cooled in water bath to room temperature. The analysis of the products was conducted similar to that in the synthesis of DBU from CO_2 and *n*-butylamine.

The reusability test of CeO_2 was conducted as follows: After the reaction, the used catalyst was collected by decantation. The collected catalyst was washed with ethanol and dried at 383 K for 12 h. After the treatment, the recovered catalyst is applied to the next reaction. The catalyst was more or less lost during the