Direct Synthesis of Arylcarbamates from Amines, Alcohols and CO_2 over CeO_2 with 2-Cyanopyridine

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Abstract: We found that combination of CeO_2 and 2-cyanopyridine was effective for the direct conversion of CO_2 with aniline and methanol to methyl *N*-phenylcarbamate (MPC), which can be an important intermediate for the synthesis of polyurethane, and obtained high yield of MPC (97%) The catalyst system was applicable to the syntheses of various arylcarbamates from CO_2, alcohols and aniline derivatives, achieving high yields (up to >99%), which is far higher than those of the reported literatures.

Keywords: Cerium oxide, Carbo dioxide, Carbamate.

1. Introduction

Methyl *N*-phenylcarbamate (MPC) is a promising precursor for the synthesis of methylenediphenyl diisocyanate (MDI), which is an important intermediate of polyurethane. Conventionally, MPC is produced by using phosgene or CO, however, these reagents are hazardous and therefore greener methods are desired to be developed. Up to now, various alternative synthesis methods for MPC have been developed, and one-pot synthesis of MPC from aniline, methanol and CO_2 will be an eco-friendly method since water is an only byproduct, and cheap and abundant CO_2 can be used as a carbonyl source. However, it is difficult to obtain MPC in high yield due to the severe equilibrium limitation and low reactivity of aniline, and the reported yields of MPC was ≤10%. Therefore, development of effective methods for the direct MPC synthesis from CO_2, aniline and methanol is desirable. In our laboratory, we have investigated CeO_2-catalyzed CO_2 transformation to various valuable chemicals such as organic carbonates (1), ureas (2) and cyclic carbamate (3), and combination of CeO_2 and 2-cyanopyridine can work as an effective catalyst for the carbonate synthesis from CO_2 and alcohols and diols by removal of the produced H_2O via CeO_2-catalyzed hydration of 2-cyanopyridine to 2-picolinamide. Herein, we found that the combination of CeO_2 with 2-cyanopyridine was effective for the one-pot synthesis of MPC.

2. Experimental

CeO_2 was obtained by calcining CeO_2 (CeO_2-HS, Daiichi Kigenso Kagaku Kogyo Co., Ltd.) at 873 K for 3 h. Other metal oxides were also obtained by calcining commercial available ones or prepared ones at 873 or 773 K for 3 h. All the reactions were carried out in an autoclave reactor with inner volume of 190 ml. CeO_2 (1 mmol), aniline (5 mmol), methanol (75 mmol) and 2-cyanopyridine (75 mmol) were put into the autoclave together with a spinner, and then the reactor was purged with CO_2 (1 MPa) and pressurized with CO_2 (5 MPa) at room temperature. Then the reactor was heated to the reaction temperature (typically 403 K). After the reaction, the reactor was cooled down to room temperature, and the liquid products were collected by using methanol. Products in the liquid phases were analyzed by using GC-FID, GC/MS and HPLC.

3. Results and discussion

Direct MPC synthesis from aniline, methanol and CO_2 was carried out using various metal oxide and 2-cyanopyridine (Figure 1). Only 2-cyanopyridine or only CeO_2 hardly provided MPC, and *N*-phenyl-2-pyridinecarboxamidine, which is produced by the reaction of aniline and 2-cyanopyridine, was mainly obtained. In the case of CeO_2, SiO_2-Al_2O_3, Nb_2O_5, ZnO and SiO_2, MPC formation was observed, and among these metal oxides, CeO_2 provided the highest MPC selectivity with moderate conversion, and main other product was *N*,*N'*-diphenylurea (DPU), which can be produced from CO_2 and aniline. From these results, combination of CeO_2 and 2-cyanopyridine was effective for the reaction. Time-course of MPC synthesis from aniline, methanol and CO_2 using CeO_2 and 2-cyanopyridine was studied. The selectivity of DPU was high (~75%) at low conversion level, and decreased with increasing the reaction time and that of MPC increased. This result suggests that DPU was an intermediate for MPC formation. In addition, theoretical amount of 2-picolinanmide was observed, indicating that the produced H_2O was smoothly removed by the hydration of 2-cyanopyridine over CeO_2 catalyst, which will be responsible for high performance. At 8 h reaction time, MPC yield reached 97%, which is much higher than the reported MPC yields.

The catalyst system composed of CeO_2 and 2-cyanopyridine was applied to the arylcarbamate syntheses with various alcohols and aniline derivatives. Various substituted anilines were converted with methanol and CO_2 to the corresponding arylcarbamates in high yields, and moreover various primary and secondary alcohols were converted with aniline and CO_2 to the carbamates in high yields

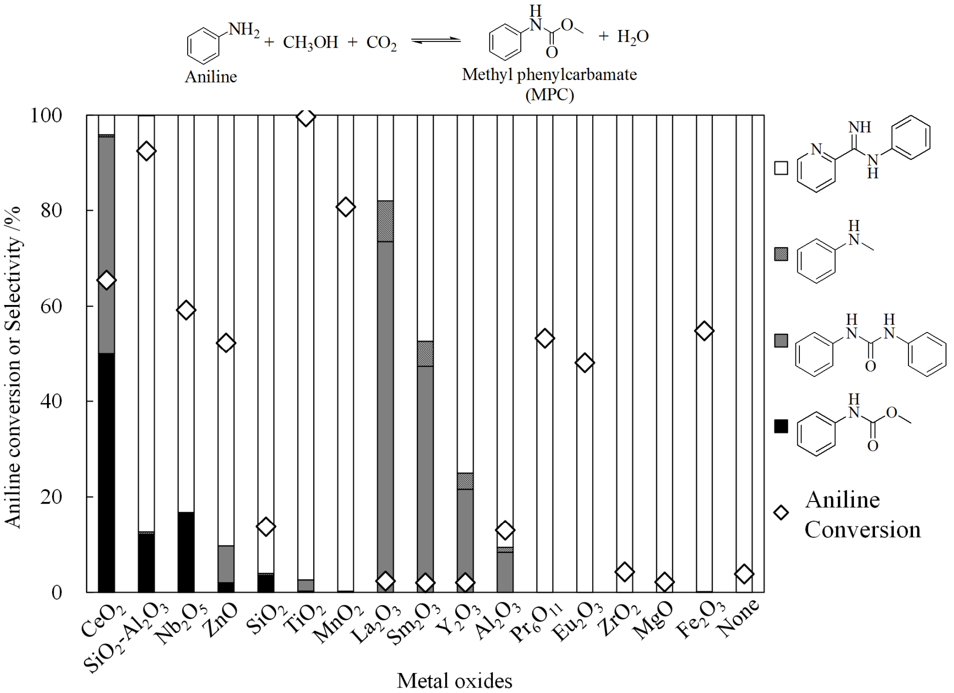

Figure 1. Catalyst screening for the synthesis of MPC from aniline, methanol and CO_2. Reaction conditions: metal oxides 0.34 g or 0 g, aniline 5.0 mmol, methanol 75 mmol, 2-cyanopyridine 75 mmol, CO_2 5 MPa (at rt), 403 K, 6 h.

4. Conclusions

The combination catalyst system of CeO_2 and 2-cyanopyridine was effective for the direct synthesis of MPC from aniline, methanol and CO_2, achieving high MPC yield (97%). Smooth removal of the produced H_2O by hydration of 2-cyanopyridine over CeO_2 catalyst led to the high yield of MPC. The catalyst system was applicable to the synthesis of various arylcarbamates from CO_2, alcohols and aniline derivatives.

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