Direct carbamates synthesis from CO_2, amines and alcohols using CeO_2 and 2-cyanopyridine

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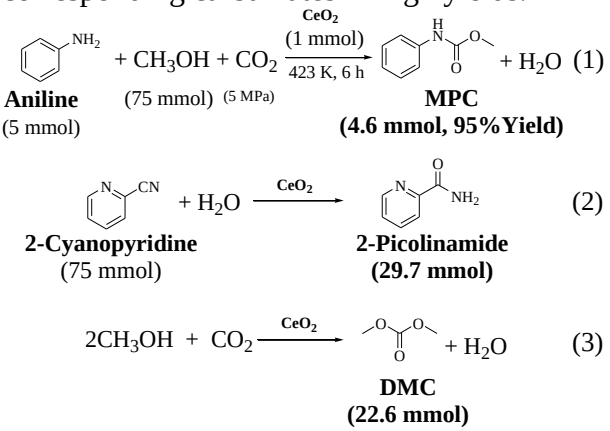
Carbamates are compounds of great interest owing to their application in organic synthesis. Methyl-*N*-phenylcarbamate (MPC) is an important intermediate for the synthesis of polyurethane. Among various synthesis methods of MPC, direct synthesis of MPC from CO_2, aniline and methanol will be an eco-friendly process because this process uses cheap and abundant CO_2 as a carbonyl source and H_2O is the only byproduct. Generally, the MPC yield is very low in this reaction due to the severe equilibrium limitation and the low reactivity of aniline [1]. Recently, we found that CeO_2 + 2-cyanopyridine catalyst system is effective for direct synthesis of organic carbonates from CO_2 and alcohols [2]. In this study, we applied this catalyst system to the direct synthesis of carbamates.

MPC synthesis from CO_2, aniline and methanol was investigated with 2-cyanopyridine as a reaction promotor and various metal oxides catalysts, which showed that CeO_2 was the most effective metal oxide among the metal oxides tested. With combination of CeO_2 and 2-cyanopyridine, high MPC yield of 95% was achieved at 423 K for 6 h. In this reaction, dimethyl carbonate (DMC) and 2-picolinamide were coproduced as main byproducts by carboxylation of methanol with CO_2 and hydration of 2-cyanopyridine, respectively (Scheme 1). The produced amount of 2-picolinamide was comparable to the produced amount of H_2O by MPC and DMC formation. This result showed that 2-cyanopyridine efficiently worked as a dehydrating agent and shifted the chemical equilibrium to the carbonate and carbamate side.

Fig. 1 shows the time-course of the MPC synthesis over CeO_2 with 2-cyanopyridine. High *N*,*N*`-diphenylurea (DPU) selectivity of 74% was detected at 0 h and the selectivity decreased with the reaction time. At the same time, MPC selectivity increased from 26% at 0 h to 97% at 8 h. This result suggested that MPC was produced via formation of DPU.

In addition, the combination of CeO_2 and 2-cyanopyridine was applied to reactions of various alcohols and amines affording the corresponding carbamates in high yields.



Scheme 1 MPC synthesis from CO_2, aniline and methanol by CeO_2 + 2-cyanopyridine system: (1) carboxylation of CO_2, aniline and methanol, (2) hydration of 2-cyanopyridine to 2-picolinamide, (3) carboxylation of methanol with CO_2.

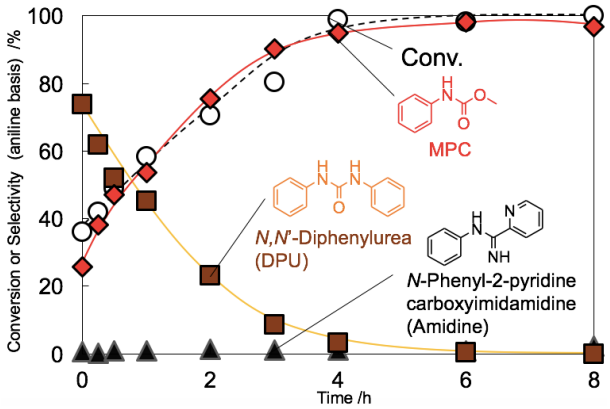


Fig. 1 The direct synthesis of MPC from CO_2, aniline and methanol using CeO_2 and 2-cyanopyridine. Reaction condition: aniline 5 mmol, methanol 75 mmol, 2-cyanopyridine 75 mmol, CO_2 5 MPa, CeO_2 1 mmol, reaction temperature 423 K.

REFERENCES

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[2] M. Honda, M. Tamura, Y. Nakagawa, K. Nakao, K. Suzuki and K. Tomishige, J. Catal., 318 (2014) 95.