Development of Zn Complex Catalyzed Organic Carbamate Synthesis Using Orthosilicates from 1 Atmosphere of CO_2

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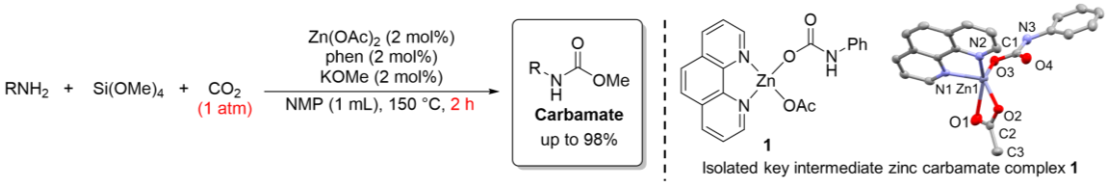
Polyurethanes are very important materials in industry, but the use of toxic phosgene in their synthesis has been a problem. Therefore, as an alternative route that does not involve the use of toxic reagents, the use of organic carbamates (RHNCOOR') derived from CO_2 and amines as raw materials for polyurethane has been proposed. Based on these backgrounds, our research group has previously reported an environmentally friendly synthesis method for organic carbamates from amines and CO_2 using tetramethyl orthosilicate ($Si(OMe)_4$), which is recyclable reactant, in the presence of $Zn(OAc)_2$/phen catalyst.[1] However, since this previous method requires high CO_2 pressure (50 atm) and long reaction time (24 hours at 150 °C), a significant improvement in reaction efficiency is needed for industrialization. In this study, we have improved this carbamate synthesis reaction based on the reaction mechanism assumed by the isolation and reactivity analysis of the reaction intermediate and DFT calculations, and have achieved a significant increase in reaction efficiency.[2]

First, we successfully isolated and characterized the reaction intermediate zinc carbamate complex Zn(OAc)(OC(=O)NHPh) (**1**). Then, stoichiometric reactions of **1** with MeOH or $Si(OMe)_4$ were performed to investigate the reaction mechanism. As results, under the same reaction condition, desired carbamate was only obtained when using $Si(OMe)_4$ as a reactant. Further investigation of the reaction pathway by DFT calculations indicated that the reaction of **1** with $Si(OMe)_4$ is the rate-limiting step of the catalytic cycle. Therefore, in order to accelerate this rate-limiting step, KOMe as an additive and used an excess amount of $Si(OMe)_4$, and the CO_2 pressure and reaction time were significantly reduced. By optimizing the reaction conditions, we found that carbamates could be obtained with a very high reaction efficiency (1 atm of CO_2 pressure, 2 h of reaction time for 150 °C). In addition, this method can also be applied to the synthesis of dicarbamates, industrially important polyurethane raw materials.



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