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Transformations of Carboxylic Acids Derivatives Using Heterogenous Acid-base Catalysts

(Summary)

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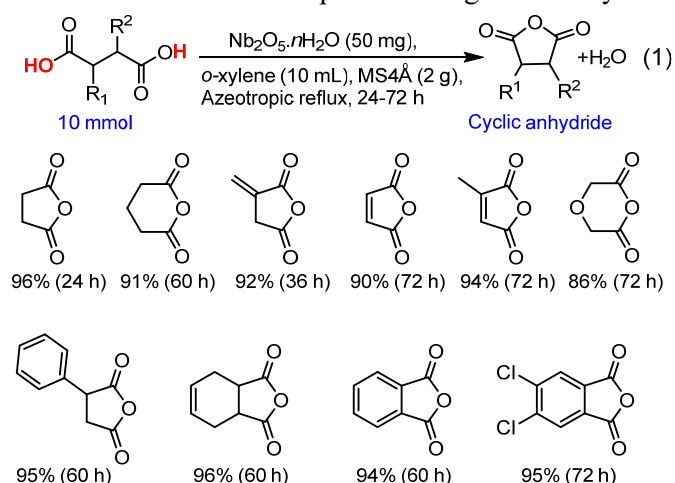
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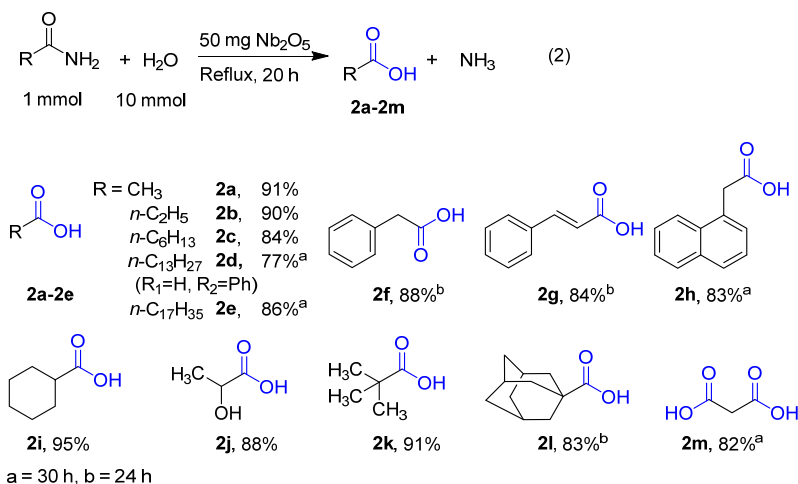
Carboxylic acids and their derivatives constitute important structural motifs that are frequently encountered in a vast array of natural products and pharmaceutical drugs. They are versatile starting materials and vital building blocks in organic synthesis. However, the synthetic applicability of carboxylic acids and amides is limited owing to delocalization of lone pairs into carbonyl moiety which makes them thermodynamically most stable bonds. The classical methods for the conversion of carboxylic acid derivatives suffer from use of excess amount of promoters (dehydrating agents, acids, or bases). Previously reported Lewis acid catalysts for transformations of carboxylic acid derivatives generally suffer from the deactivation by hard base (NH_3 , H_2O , amines) present as reactants or byproducts in the reaction mixture. The first target of this thesis is the development of heterogeneous Lewis acid catalysts for transformations of carboxylic acid derivatives workable in the co-presence of hard base (Chapters 2, 3). For transformation of the most stable carboxylic acid derivatives, amides, purely Lewis acidic catalysts may not show sufficient activity. The second target of this thesis is the development of heterogeneous catalysts having Lewis acid-base cooperative mechanism for transformation of amides (Chapters 4, 5).

Chapter 2 presents a development of heterogeneous Lewis acid catalyst for direct intramolecular dehydration of dicarboxylic acids, which has been unprecedented previously by conventional heterogeneous catalysts. I screened various water tolerant heterogeneous and homogeneous catalysts for this cyclization reaction. The result showed that a commercial niobic acid, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, gave the highest yield of the corresponding cyclic anhydride. Various dicarboxylic acids, which can be produced from biorefinery process, are transformed to the corresponding cyclic anhydrides as monomers for polyesters. The proposed catalytic system was applicable for gram-scale synthesis of anhydrides up to 96% isolated yields (Eqn. 1). Moreover, catalyst reusability and leaching study indicate that $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ possesses high durability for the reaction. In industry, cyclic anhydrides, as key intermediates of carbon-neutral and biodegradable polyesters, are currently produced from biomass-derived dicarboxylic acids by a high-cost multistep process. The simple synthetic method of cyclic anhydride developed in this work can simplify the current high-cost synthetic route to renewable polyesters.

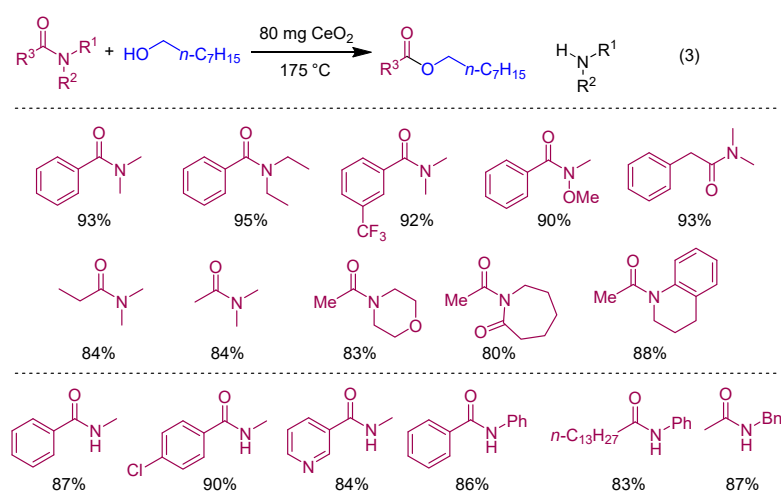


Chapter 3 highlights the structure-activity relationship of Nb_2O_5 catalysis for two challenging reactions: 1) hydrolysis of amides to carboxylic acids (Eqn. 2) and 2) amidation of carboxylic acids with NH_3 . The number of Lewis acid (LA) sites of Nb_2O_5 catalysts and

interaction between LA sites and carbonyl group of amides decreased with the calcination temperature. Low temperature calcined Nb2O5 (TT and/or T-Nb2O5 phases) were more reactive than that of high temperature calcined M- and/or H-Nb2O5 phases. The catalytic performance is attributed to the preferential activation of carbonyl group (soft base) by surface Nb(V) LA sites even in presence of hard bases (H2O and NH3). Detailed structure-activity relationship investigation for the present reactions was performed toward a rational design of catalysts.



Chapter 4 shows that CeO2 catalyzes esterification reaction of tertiary amides by alcohols (Eqn. 3), which has been unprecedented previously by conventional heterogeneous catalysts. CeO2 was found to promote ester forming alcoholysis reactions via direct cleavage

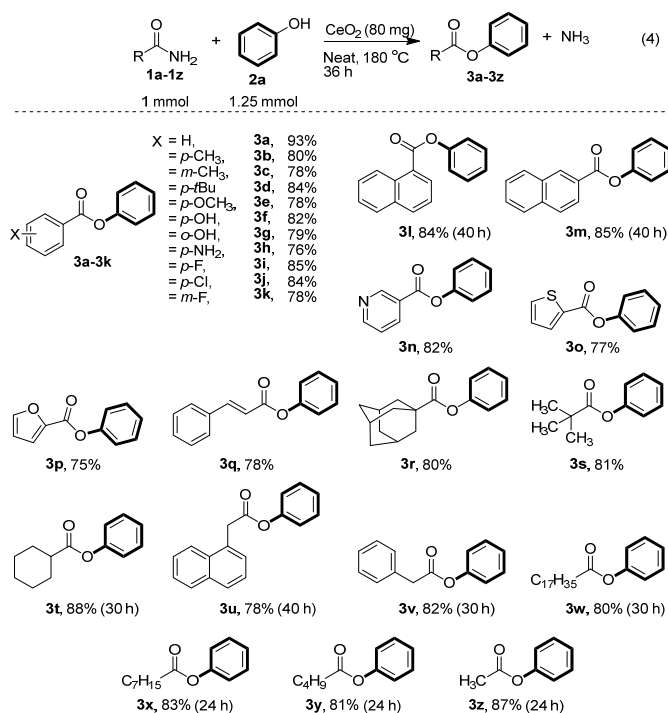


of amide's C–N bonds. The catalytic method was operationally simple, recyclable, and it did not require any additives. In situ FT-IR and temperature programmed desorption using probe molecules demonstrated that both acidic and basic sites of CeO2 were important for the reaction. Based on DFT and in situ FT-IR studies, I propose a possible reaction mechanism, in which nucleophilic attack of surface oxygen of CeO2 to the carbonyl group of the acetamide adsorbed on Ce(IV) LA site is the rate limiting step.

Chapter 5 describes that more challenging reaction, phenolysis of amides, can be achieved by CeO2 (Eqn. 4). Catalyst screening study showed that CeO2 was the best catalyst for the reaction. Various functionalized amides and phenols were converted to the corresponding phenolic esters. Results of kinetic studies afforded mechanistic insights; the cooperation of the acid-base functions of the CeO2 catalyst is of importance for the efficient progression of the C–

N bond breaking process. Consequently, CeO₂ showed the best catalytic performance among the catalysts explored.

Chapter 6 demonstrates general conclusions of the thesis. Chapters 2, 3 conclude that a solid Lewis acid, Nb₂O₅, effectively catalyzes three challenging reactions of carboxylic acids derivatives: 1) direct intramolecular dehydration of dicarboxylic acids, 2) hydrolysis of amides to carboxylic acids, 3) amidation of carboxylic acids with NH₃. The key feature in these



catalytic systems is the activation of carbonyl group (soft base) even in presence of hard bases (H₂O and NH₃). Chapters 4, 5 conclude that CeO₂ promotes two catalytic transformation of amides, 1) esterification reaction of tertiary amides by alcohols and 2) phenolysis of amides, which have been unprecedented by previous heterogeneous catalysts. The key feature in these catalytic systems is cooperation of Ce(IV) Lewis acid sites (for coordination of carbonyl oxygen) and adjacent basic oxygen (nucleophilic oxygen).