

Metallic diselenides as Novel Heterogeneous Catalysts for Reductive Carbonylation of Nitroarenes for Carbamates

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Carbamates are important precursors for preparing isocyanates, a key monomer for polyurethane, since the carbamates can be transformed into isocyanates and alcohols by thermal cracking. Carbamates have been commercially produced by reacting phosgene with corresponding amines, which has fatal drawbacks such as difficulties in removing corrosive hydrogen chloride as a secondary product.

Herein, we present the synthesis and characterization of MSe_2 ($M = Fe$ and Se) and its supported system, and the catalytic activities for the reductive carbonylation of NB as a model substrate. It would be the first time to report that Se_2^{2-} (Se^-) can catalyze NB to generate methyl-*N*-phenyl carbamate (MPC) very selectively. Unlike the Pd-based catalyst, MSe_2 is heterogeneous, and thus leads to easy catalyst separation. It can be synthesized from 1st transition metal and non-expensive main group element, implying an escape from precious noble metals in the reductive carbonylation. In additions, the plausible reaction mechanism is proposed using this heterogeneous catalyst system, specifically invoking the importance of $CuSe_2(\mu-CO)$ species.