Synthesis of Urethanes via the Reductive Carbonylation of Nitroarenes over CuSe₂/CeO₂

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Urethanes (carbamates) are raw material for producing polyurethane products and regarded as important precursors of isocyanate. The conventional process for the production of urethanes involves the usage of toxic phosgene, which delivers the corrosive hydrogen chloride as a secondary product. Accordingly, there have been enormous efforts for the manufacture of urethanes via phosgene-free way. One of the promising approaches is the reductive carbonylation of aromatic nitro compounds with carbon monoxide in the presence of alcohol and a proper catalyst, which has attracted much attention as a phosgene-free alternative route to urethane. In our study, we found that the $\text{CuSe}_2/\text{CeO}_2$ catalyst is a cheap and novel heterogeneous catalyst for producing various mono- and di-urethanes via the reductive carbonylation of nitroarenes. Furthermore, we firstly report that Se_2^{2-} (Se^-) can act as an active species, and it forms asymmetric semi-bridging carbonyl copper diselenide during the carbonylation reaction.