Flow chemistry: a tool to make rhodium catalyst recyclable in carbene insertion reactions

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In organic synthesis many important transformations rely on the use of late-transition metal catalysts due to their unique and superior activity.[1] Rhodium catalysts largely dominates in terms of efficiency for carbene insertion reactions, but remains a very rare and expensive metal.[2] Here we will present the extremely simple immobilization of the Rh-based catalyst, which allows its use in continuous flow for the transfer of carbene from methyl diazoacetate (MDA) precursor with several substrates. Two different methods to heterogenize the catalyst in a column reactor were applied (using sand or silica). Different X−H (X = O, S, Si, CH) were successfully functionalized (Figure 1) and the cyclopropenation was carried out under very mild continuous flow conditions. Following these promising results, catalyst recycling experiments using both methodologies were carried out in which up to 10 consecutive cycles with different substrates were carried out without loss of catalytic activity, thus allowing the production of families of compounds in a simple, secure and efficient way.[3]

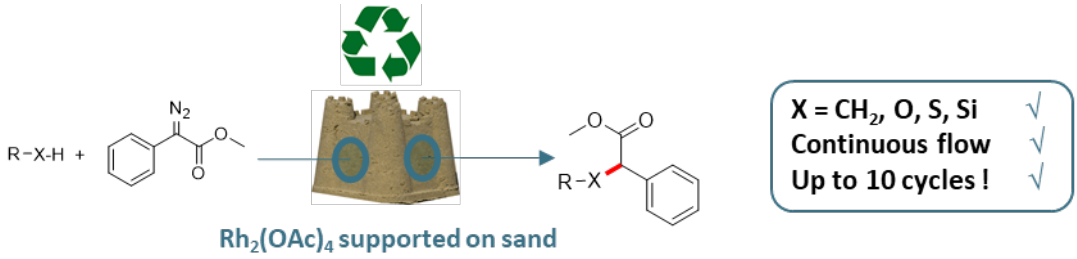

Figure 1. general scheme of our heterogeneous rhodium catalyzed X-H bond functionalization

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3 T. A. C. A. Bayrakdar, C. Lescot, *ChemSusChem* **2023**, 16, e202300596.