

## Heterogenization of molecular catalysts: C–H activation and dehydrogenation

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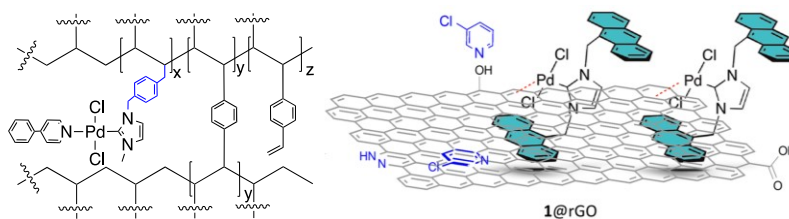
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Direct one step conversion of unreactive carbon-hydrogen bonds into bonds with a desired functional group is a highly effective and rational way of producing bulk and fine chemicals, but it still remains a fundamental challenge in synthetic chemistry. Most examples include homogeneous catalysts, but heterogeneous TM catalysts are in demand, not only because these supported systems are recyclable and easy to separate from the reaction mixture, but also for their potential to introduce novel chemical reactivity.

In this contribution we report two approaches to heterogenization of C–H activation catalysts. The first is based on a polymeric material derived from co-polymerization of polymerizable arms in an N-heterocyclic carbene palladium complex and divinylbenzene (Figure 1).[1] This material is stable towards reduction and recyclable with no or little loss in activity. In addition, it is applicable under flow conditions; this is a rare example of such a reaction and the catalyst tolerates up to six days of continuous flow conditions in a packed-bed reactor giving excellent yields and selectivities.[2] Both directed and undirected C–H activations were developed and the catalysts were characterised before and after catalysis using a combination of XRD, XPS and TEM.

We also set out to modify our Pd(II) system to include a  $\pi$ -stacking capability by installing two anthracene moieties in the backbone of the NHC ligand to give the Pd complex to the right in Figure 1. This modified complex was supported on reduced graphene oxide (rGO) and the so obtained system was applied in the undirected C–H acetoxylation.[3] We have also studied the reaction mechanism of this reaction by elucidating the palladium species and their oxidation states over the course of the C–H acetoxylation of benzene catalyzed by **1**@rGO using in situ XAS spectroscopy. [4]

Examples on heterogenized iridium catalysts for dehydrogenation reactions in flow will also be presented. [5]



**Figure 1.** Palladium catalysts for C–H activation based on co-polymerisation (left) and rGO  $\pi$ -stacking (right) .

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