Nickel-Functionalized Covalent Organic Framework NiCl@RIO-12 for Heterogeneous Suzuki-Miyaura Catalysis

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A series of nickel-functionalized Covalent Organic Frameworks (COFs) was prepared based on the COF RIO-12, obtained from the condensation reaction of 1,3,5-triformylresorcinol and hydrazine hydrate [1]. The nickel-functionalized COFs were prepared through the Post-Synthetic Modification method: reaction of $NiCl_2$ with pristine RIO-12 under basic conditions in order to afford NiCl@RIO-12 materials [2]. The nickel content was tunable from 3.6 wt.% to 25 wt.%, depending on the reaction conditions. Furthermore, the paramagnetic NiCl@RIO-12 retained its crystallinity in relation to RIO-12, SEM and TEM-EDS showed homogeneous nickel dispersion, and the BET surface area decreased due to nickel incorporation within the framework. Moreover, NiCl@RIO-12 presented promising catalytic activity in the heterogeneous Suzuki-Miyaura cross-coupling reaction of 4'-bromoacetophenone and phenylboronic acid under microwave heating (Figure 1). The conversions to 4-acetylbiphenyl were up to 34% in 15 minutes with no homocoupling product when employing 0.2 mol% of the catalyst. Combining (*i*) the importance of employing earth abundant metals as catalysts over precious metals, (*ii*) a thermal stability up to 270 °C, (*iii*) the absence of metal leaching, and (*iv*) a recyclability up to three cycles, the nickel-decorated COF NiCl@RIO-12 holds promising characteristics to be further explored. Therefore, we expect that despite the moderate yields, this study will highlight that Ni@COF materials, which are still in their infancy, have a bright future of applications in catalysis.

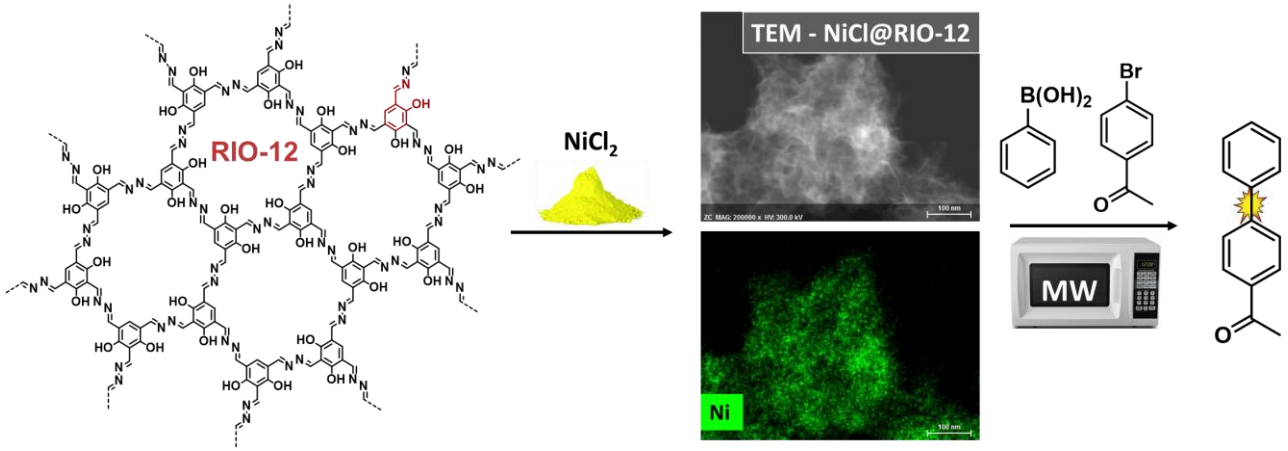

Figure 1 : Nickel functionalization of COF RIO-12 to afford NiCl@RIO-12 and its employment in Suzuki-Miyaura cross-coupling assisted by microwave.

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[2] Maia, R. A., Berg, F., Ritleng, V., Louis, B., Esteves, P. M., *Chem. Eur. J.* doi :10.1002/chem201904845 (2019).