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Pd and Pd2Sn nanoparticles synthesis for the Suzuki-Miyaura cross-coupling reaction

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PURPOSE OF THE ABSTRACT

The Suzuki-Miyaura cross-coupling reaction allowing the creation of a simple C-C bond between a (pseudo)-halogenated compound and a boron reactant has been known for over 40 years and was rewarded by a Nobel Prize in 2010 but it is still a major area of research. Despite a lot of promising and innovative work based on non-noble metals such as iron, nickel or cobalt performed these past years, palladium remains the benchmark thank due to its outstanding performances. It has also been demonstrated that Pd nanoparticles are not always a way of deactivation of molecular complexes but could be seen as a catalyst or a pre-catalyst, acting as an active species reservoir.

A tremendous challenge is the lessening of the Pd amount involved in the cross-coupling reaction as the Pd amount in active pharmaceutical ingredients (API) should be lower than 10 ppm due to no known biological role, hence a bio-accumulation could be deleterious as well as a possible coordination to every molecules or macromolecules containing binding site such as DNA, proteins and metallo-proteins. Also, the scarcity of palladium makes it a critical resource because of its extensive use in catalytic converters, electronics, hydrogen fuel cells, hydrogenation reactions (for margarine production for instance) and fine chemistry. As a result, it is now more expensive than platinum or gold, transforming it into a rising threat of shortage.

From these data, we have developed mono- and bi-metallic particles based on Pd and Pd2Sn alloy for the Suzuki-Miyaura cross-coupling reaction. Several protocols were optimized to produce, under mild conditions at room temperature, crystalline Pd and selectively Pd2Sn nanoparticles with very narrow size distributions centered at 1.5 nm of diameter which were extensively characterized (TEM, IR, UV-vis...).

The catalytic activity of these nanoparticles was investigated in a benchmark Suzuki-Miyaura reaction implying 4'-iodoacetophenone and phenylboronic acid in ethanol at 60°C. While at 2·10-3 mol% of total Pd, NPs yielded 90% conversion of 4'-iodoacetophenone (limiting reagent) which translates into a TON of 45'000 with a complete selectivity toward the cross-coupling product in 4.5 h and an activity of 11'000 h-1, the Pd2Sn alloy gave, with the same Pd loading, a full conversion (TON = 50'000) and full selectivity towards the cross-coupling product in 1.5 h with an increased activity of 45'000 h-1, showing the beneficial role of tin addition.

From this promising data on Pd2Sn nanoparticles, a decrease of catalytic loading to 2·10-4 mol% of total Pd allowed to reach up a TON of 497000. Regarding the amount of Pd compared to the limiting reagent, a charge of 0.9 ppm was reached, well below the current specifications, while it corresponds to 13 ppb compared to the whole mass of solution contained in the batch reactor.

FIGURES

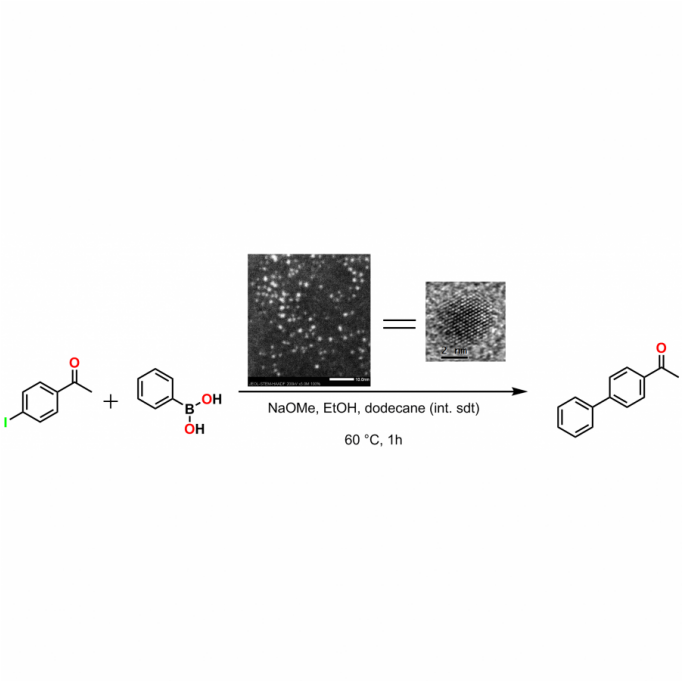

FIGURE 1

Suzuki-Miyaura coupling with Pd2Sn NPs

STEM and HRTEM of Pd2Sn NPs able to catalyze at very low concentration a fully selective Suzuki-Miyaura cross-coupling reaction

FIGURE 2

KEYWORDS

BIBLIOGRAPHY