Journal of Cleaner Production 185 (2018) 342–346

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Coconut agro-industrial waste in the production of catalyst containing palladium: The report of a mini-project for teaching of sustainable Suzuki-Miyaura reaction

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ARTICLE INFO

Article history:
Received 10 July 2017
Received in revised form
6 March 2018
Accepted 7 March 2018
Available online 8 March 2018

Keywords:
Coconut shell fiber
Agro-industrial waste
Pd catalyst
Suzuki-Miyaura cross-coupling

ABSTRACT

A four-week mini-project for teaching is described for an experimental physical chemistry or organic chemistry course. The activities included synthesis of a Pd catalyst, $PdCl_2$ supported on calcined coconut shell fiber, and its use in the preparation of 4-methylbiphenyl via Suzuki-Miyaura cross-coupling reaction. The technical skills and concepts that are typically presented in practical chemistry courses were covered, including notions of surface chemistry – development of new catalysts, modern organic synthesis, gas chromatography techniques, separation of mixtures, and stoichiometric calculations.

1. Introduction

The sustainable development in a society is only possible to be reached with the formation of a new global consciousness through the change of attitudes of all involved actors. For this purpose, the approach of the subject is fundamental in the varied levels of training of the individual from the professional qualification of workers (Sacchettini and Calliera, 2017) to the higher education (Sharma et al., 2017). The university has a crucial role in education for sustainable development, in which the interdisciplinary context of the theme can be approached directly or indirectly (Sharma et al., 2017). With reflexive attitudes developed in the academic environment, such as campaigns to reduce waste and awareness of recycling, the university forms a critical sense in its community (Fagnani and Guimarães, 2017). Thus, "pedagogy for sustainability" (Song et al., 2011) finds fertile ground in the academic medium and leads to the formation of more critical and responsible citizens with environmental issues, valuing the importance of the role of universities in this context. On the other hand, engineering courses related to the transformation industry are interdisciplinary in nature (Sharma et al., 2017), requiring practical classes that generate sustainability in an applied mode to the local reality (Chin et al., 2014). Project-based learning, applied in engineering courses from the constructivist point of view, helps to develop "engineer thinking" in undergraduates (Frank et al., 2003). Thus, our research group has reported the development mini-projects for teaching applied in engineering course in order to familiarize students with chemistry cutting edge topics (Dalmás et al., 2013; Vargas et al., 2016; Oliveira et al., 2015). Nevertheless, the report of new practical chemistry classes on catalysis for engineering undergraduates, focusing on sustainability through the use of local agro-industrial waste, is still scarce. In this context, the rational use of natural resources and the reduction of waste are good lines of research for mini-projects for teaching topics of sustainability (Chin et al., 2014). For example, the coconut industry produces a large amount of shell and fiber waste with little added value. The shell can be converted into activated carbon (Lakshmanan and Murugesan, 2016) and in the formulation of composites (Chun et al., 2012); however,

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https://doi.org/10.1016/j.jclepro.2018.03.082
0959-6526/

coconut shell fiber has its use almost restricted to agriculture (Carrijo et al., 2002) or burning. In coconut shell fiber burning to generate thermal energy, a calcined product is obtained and this is the object of investigation in this work: its evaluation for use as support of $PdCl_2$ for cross-coupling catalyst production.

Suzuki–Miyaura cross-coupling is a versatile reaction in organic chemistry that is typically catalyzed by palladium salts with auxiliary ligands (Negishi, 2002). Particularly, supported ligand-free Pd catalysts have a greater industrial appeal because they are readily recycled (Alvarenga et al., 2016). Thus, herein is reported a new proposal for a teaching mini-project that aims at the synthesis, characterization and application (in the Suzuki-Miyaura cross-coupling) of a new eco-friendly catalyst containing $PdCl_2$ supported on calcined coconut shell fiber (CCSF), named Pd/CCSF. To provide students with this experience, a four-week experiment (lab period = 4 h/week) is described, with the reaction between phenylboronic acid (**1**) and 4-iodotoluene (**2**) catalyzed by Pd/CCSF to synthesize 4-methylbiphenyl (**3**) being chosen to measure the catalytic efficiency (Fig. 1).

The main objective of this mini-project proposal is to give a new technological purpose of greater added value to a local agro-industrial waste (calcined coconut shell fiber). In addition, it is expected that the students involved will have greater contact with catalysis and develop skills inherent to the technique (laboratory routines domain). Approaches similar to this are extremely desirable as these themes (sustainable organic synthesis) are still barely explored in practical undergraduate classes. At the end of this mini-project students are expected to reflect on the valorization of agro-industrial waste based on the potential use of these materials. In addition, it is also expected that the Suzuki-Miyaura cross-coupling will be introduced with all its specificity through the use of a sustainable and low-cost catalyst.

2. Experiment

The proposal described below was tested with a working group of three students; despite, adjustments can be made according to laboratory working conditions. Prior to the initial laboratory period, students read journal articles related to the experiment - Pd catalyst production and Suzuki-Miyaura cross-coupling (Vargas et al., 2016; Alvarenga et al., 2016). During week one, a quick introduction to calcination technique and the elemental composition of coconut shell fiber was transmitted. The working group calcined the coconut shell fiber *in natura*, and then incorporated $PdCl_2$ into the solid obtained (see Supplementary Material). At the end of the first week of work, each group sent samples of the Pd/CCSF produced for quantification of supported Pd (Inductively Coupled Plasma - Optical Emission Spectrometry, ICP-OES), morphological analysis of the solid (Scanning Electron Microscopy, SEM) and qualitative elemental composition (Electron Dispersive Spectroscopy, EDS) by the FURG Analytical Center.

During week two, the results obtained in the SEM, EDS and ICP-OES analyses were discussed with the professor. With the exact mass of $PdCl_2$ incorporated in the Pd/CCSF known, it was possible to calculate the mass of catalytic precursor that would be necessary for its evaluation in the Suzuki-Miyaura reaction. Thus, at the end of this work week, the students organized the cross-coupling reaction of phenylboronic acid with 4-iodotoluene catalyzed by Pd/CCSF.

Week three was focused on the previously planned 4-methylbiphenyl synthesis via the Suzuki-Miyaura cross-coupling reaction catalyzed by Pd/CCSF. Phenylboronic acid (1.5 mmol), 4-iodotoluene (1.0 mmol), Pd/CCSF (279 mg, 0.5 mol% of Pd), K_2CO_3 (2.0 mmol), and 2 mL of ethanol were refluxed in a 25 mL Schlenk flask under an argon atmosphere. After 3 h of reaction, the students separated a sample of the reaction mixture to evaluate the conversion of 4-iodotoluene, via Gas Chromatography – Flame Ionization Detector (GC-FID).

Finally, in the last week the students isolated the 4-methylbiphenyl from the initial reaction mixture and characterized it by Gas Chromatography – Mass Spectrometry (GC-MS). The detailed procedures are in the Supplementary Material.

Hazards: Acetone, ethanol, and diethyl ether are flammable. NaOH and aqua regia are corrosive. $PdCl_2$ is dangerous. 4-Iodotoluene is harmful if inhaled. The 4-methylbiphenyl, biphenyl (by-product), and potassium carbonate are irritants. A small amount of by-product is generated during the proposed catalytic reaction (Suzuki-Miyaura cross-coupling) that is of low toxicity to the students. All experiments are conducted with students wearing eye protection, lab coats, nitrile gloves, and fume hoods (for harmful reagents).

3. Results and discussion

The mini-project was tested with 24 students in 2015–2016 in an upper-division undergraduate course, Physical Chemistry II, Agro-industrial Engineering Course, with an emphasis on agro-chemistry, at Universidade Federal do Rio Grande (FURG). The course covered the basic techniques of catalysis that are applied in organic synthesis of bioactive compounds.

The agro-industrial waste chosen for the work (calcined the coconut shell fiber) was elected due to the FURG *campus* being located in a city with a large chain of coconut-based handmade sweets. It is estimated that about 80–85% by weight of the green coconut is discarded as residue (Carrijo et al., 2002). Thus, there is a concern of the local agro-industries in minimizing the costs with the disposal of the waste generated. As already mentioned, the dry residue can be burned in boilers, however, it still generates ashes without added value.

Students were surprised at the idea of the research proposal: to produce a Pd catalyst using coconut shell fiber. The theme of agro-industrial waste is very prevalent in their training, but not its use in catalysis, so this idea created uneasiness in the working group. In addition, the cutting edge analytical techniques always have a strong motivation for students, leading them to a greater commitment to the proposed activities.

The group of students started the activity with coconut shell fiber calcination. After 4 h, 2 g of the coconut shell fiber was fully converted to ash. Inquiries regarding the composition of the ash and the analytical technique employed for its determination were carried out by the professor.

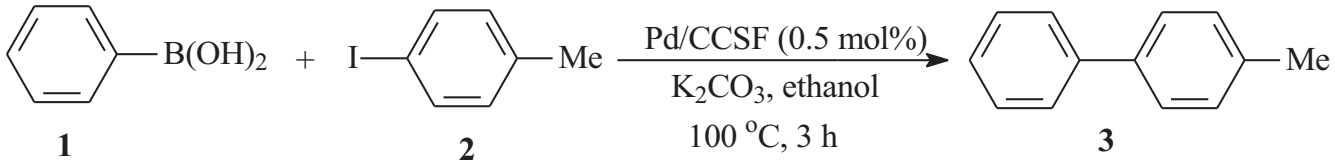

Fig. 1. Suzuki-Miyaura cross-coupling test.