

Mechanistic studies of the Suzuki-Miyaura reaction with aryl bromides using Pd supported on micro- and mesoporous activated carbons

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ABSTRACT

The Suzuki-Miyaura reaction has been studied using palladium supported on modified activated carbons as catalysts. Two kinds of supports (micro- and mesoporous) have been prepared from plum stones and oak wood, and subsequently modified with different agents (HNO₃, (NH₄)₂S₂O₈, air or ammonia) in order to produce new or alter the existing surface functional groups. The selectivity changes in the competitive Suzuki-Miyaura reaction indicate a substantial contribution of the heterogeneous catalysis to the reaction mechanism. Thus, the data obtained are not consistent with the widely accepted point of exclusive homogeneous catalysis of the Suzuki-Miyaura reaction.

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1. Introduction

The Suzuki-Miyaura reaction of aryl halide and arylboronic compound (Fig. 1) catalysed by palladium is intensively studied field of organic chemistry [1]. In spite of great progress in the area of development of highly active catalytic systems for this process, some fundamental aspects of the reaction have remained unclear. For instance, the key problem concerning the nature of the active catalyst (homogeneous or heterogeneous) has not been solved as yet.

There are a lot of contradictory results of various tests on homogeneity-heterogeneity including: hot filtration, three-phase test, poisoning and kinetic studies [2,3]. The complex dynamics of transformation of some potentially active palladium species (Fig. 2), presented in the reaction mixture during the process, seems to be the main cause of these contradictions. Unfortunately, the conventional tests on reaction homogeneity-heterogeneity do not allow excluding a possible influence of this transformation on the test results [2]. The study of differential selectivity of a catalyst can be used as a method to establish the nature of active species and is not sensitive to the effects of catalyst transformation because

of differential selectivity does not depend on the concentration of active species [2,4].

As pointed out above, there is no common standpoint on the nature of active species in the Suzuki-Miyaura catalysis as yet. Some scientists claim the homogeneous nature of the true catalyst [5–19] but according to others the catalyst is of heterogeneous character (e.g. catalysis on the Pd nanoparticles surface) [20–32]. There are some significant data pointing to the homogeneous mechanism of the reaction. For example palladium leaching was detected during the Suzuki-Miyaura coupling reaction with the use of insoluble catalyst precursors (including Pd nanoparticles) [6,7,9,12,13,15,33,34]. Also there was a correlation between the activity and the amount of dissolved Pd [12,15,33]. In addition, homogeneous character of the Suzuki-Miyaura catalysis is indicated by the specific TOF (turnover frequency, that is mol product per mol Pd per h) dependence on the palladium amount [5], effects of catalytic poisons addition [7] and changes in the size and shape of catalyst precursor particles during the reaction [14]. On the other hand, there are convincing evidences for heterogeneous catalysis in Suzuki-Miyaura reaction, obtained by the operando spectroscopy technique [22,23].

The inconsistency of the above results and their implications illustrate the complexity of the distinction between homogeneous and heterogeneous catalyses in the Suzuki-Miyaura reaction. A similar long lasting discussion has been taking place in literature on the

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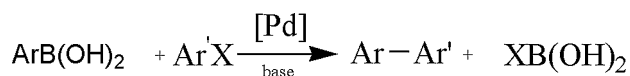


Fig. 1. The Suzuki-Miyaura reaction of aryl halide and arylboronic compound catalysed by palladium.

Mizoroki-Heck reaction until recently [3,35–37], and as a result most scientists agreed upon true homogeneous catalysis of the reaction regardless of the catalyst precursor nature. Apparently, the main cause of such problems are permanent interconversions of different palladium compounds generated from a catalyst precursor [2,22,23,36] (Fig. 2) which are very often not taken into account when planning the experiment. These interconversions lead to ambiguous interpretations of the results of conventional tests on the reaction homogeneity-heterogeneity. In general, it is attributed to appearance of the “compensating effect”, i.e. a response of the catalytic system to a removal of some form of catalyst by implementation of the test procedure, e.g. using a poison or removal of solid catalyst by filtration, (like Le Chatelier’s principle in equilibrium systems). Also the most complicated case, when the reaction is catalysed by homogeneous and heterogeneous active species simultaneously is impossible to be excluded. This possibility for the Suzuki-Miyaura reaction was formulated in a few papers only [38–41]. Relative contributions of homogeneous and heterogeneous catalyses to the total substrate conversion may vary in the course of the reaction, and so interpretation of test results can depend on many factors that are usually not controlled by experimenters. In addition, the conclusion about homogeneous catalysis based on test results is made with no account taken of the presence of “soluble” palladium nanoparticles that can also catalyse the reaction. The in situ nanoparticles formation was detected using soluble [42–44] as well as heterogeneous catalyst precursors [45,46]. Thereby in spite of existence of much evidence for the homogeneous catalysis nature of the Suzuki-Miyaura reaction it is impossible to eliminate the alternate heterogeneous mechanism of the reaction.

In this work the kinetic approach is taken consisting of checking the relationship between the conversion rates of competing

substrates in the Suzuki-Miyaura reaction. If changes in the selectivity are observed when the reaction conditions are capable of provoking changes in different palladium species distribution, the evidence will be obtained for a change in active catalyst nature. The nature of catalyst precursor is one of the factors influencing apparently the palladium transformation paths. Therefore we performed a set of experiments with varying catalyst precursors similar in chemical composition but substantially different in textural properties of the catalyst support (activated carbons).

2. Experimental

2.1. Preparation of catalyst support samples

The activated carbons used as supports for Pd phase were prepared from waste materials (plum stones or oak wood) and modified in different ways to change the character of their chemical or textural properties. Detailed sample preparation procedure is presented below.

To obtain microporous activated carbons the plum stones were ground and sieved to a uniform size range ≤ 0.4 mm. The starting material was then chemically activated with solid potassium hydroxide (the weight ratio of the precursor to KOH was 1:1) at 800 °C for 45 min. The material obtained was washed with a 5% solution of HCl, then with distilled water and dried overnight at 120 °C. The initial activated carbon prepared (S) was modified with different agents: concentrated HNO₃ at 60 °C for 8 h, (NH₄)₂S₂O₈ (APS) at 30 °C for 24 h, or air at 300 °C for 8 h.

The procedure applied for preparation of mesoporous activated carbons was based on the method proposed by Juárez-Galán et al. [47]. The oak wood was ground to the grain size below 0.4 mm, impregnated with 7% aqueous solution of CaCl₂ at 85 °C for 7 h. The material obtained was then carbonised at 800 °C for 1 h and activated with CO₂ at 800 °C for 0.5 h. The product was demineralised with HCl, washed with distilled water and dried overnight at 120 °C. After that the initial carbon (TD) was modified with ammonia at three different temperatures (750, 850 or 950 °C) for 4 h.

All the activated carbon samples prepared were labelled according to the scheme: type of precursor (S or TD)- modifying agent- modification temperature- modification time.

2.2. Characterisation of support samples

Textural properties of the carbons prepared were determined on the basis of N₂ adsorption/desorption isotherms obtained at –196 °C with a Micromeritics Sorptometer ASAP 2010 Apparatus. The apparent surface area (S_{BET}) was calculated using BET equation, whereas external surface areas (S_{ext}) and micropore volumes (V_{micro}) were determined using *t*-plot method [48]. The total pore volumes (V_{tot}) were obtained from the N₂ amount adsorbed at a relative pressure close to unity. CHNS elemental analyses were made on an Elemental Analyser Vario El III.

2.3. Preparation of catalysts

Pd/C (C is micro- or mesoporous carbon: S, S-HNO₃-60 °C-8 h, S-AIR-300 °C-8 h, S-APS-30 °C-24 h, TD, TD-NH₃-750 °C, TD-NH₃-850 °C, TD-NH₃-950 °C) was prepared using Pd(OAc)₂ at a Pd loading of 4 wt%. The support material (1 g) was suspended in 20 ml of toluene. Pd(OAc)₂ was added and the suspension was stirred for 30 min at 95 °C. Completeness of Pd(OAc)₂ adsorption was controlled by observation of changes in intensity of absorption band in solution at 300 nm. Then 0.04 ml of formic acid was added to reduce palladium on carbon surface and the suspension was stirred for 20 min until discoloration occurred. Resulting catalyst was filtered

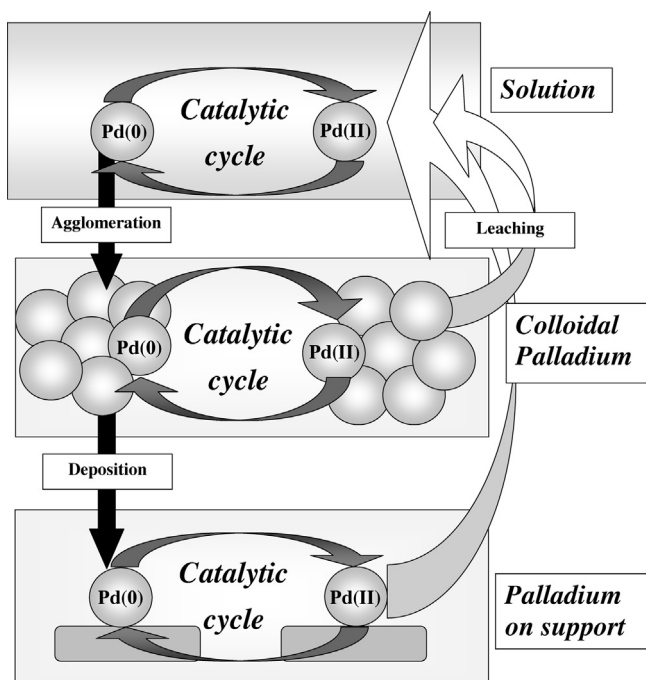


Fig. 2. Pd transformations in the Suzuki-Miyaura reaction.

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