



The effect of the hydrotalcite structure and nanoparticle size on the catalytic performance of supported palladium nanoparticle catalysts in Suzuki cross-coupling

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ARTICLE INFO

Keywords:

Hydrotalcites
Palladium nanoparticles
'in-situ' preparation methodologies
Heterogeneous catalysis
Suzuki cross-coupling reaction

ABSTRACT

An uncalcined HT supported Pd-NP catalyst was synthesized via co-precipitation, i.e., PdHT_100RED_20, and benchmarked against a Pd impregnated HT catalyst, i.e., Pd@HT_500RED_20. TEM analysis pointed out that the largest NPs (6.5 nm) were found in the co-precipitated catalyst because of its weaker steric NP confinement, compared to the benchmark catalyst (3.2 nm). The PdHT_100RED_20 had a significantly higher catalytic performance (60% conversion, 1.85% leaching) than Pd@HT_500RED_20 (19%, 0.98%) due to lack of calcination resulting in an ordered, and thus, more accessible HT structure in combination with its high support basicity. Both catalysts showed low Pd leaching confirming the suitability of HTs as NP support.

Focusing on PdHT_100, the effect of the reduction temperature on the NP size and catalytic performance was investigated. NP size distribution analysis showed that the smallest NPs were found in PdHT_100RED_0 (5.3 nm), resulting in a higher catalytic performance (67%, 2.28%) when compared to PdHT_100RED_20 (6.5 nm). Performing the reduction at higher temperatures, i.e., at 60 °C (5.7 nm), caused an extremely low catalytic performance (13%, 0.20%) due to the less efficient reduction reaction with NaBH₄ at higher reduction temperatures.

Reusing PdHT_100RED_20, a decrease in catalytic performance (45%) was observed. However, this decrease was less pronounced (50%) when a re-activation of the catalyst with Na₂CO₃ between consecutive runs was performed. Moreover, it was shown that the leached Pd species were able to re-deposit onto the support if high conversions were obtained, and thus, an almost quantitatively recovery from the reaction mixture can be achieved with retention of its catalytic activity (> 99%).

1. Introduction

Carbon-carbon bond formations have a great significance in pharmaceutical and fine chemical industries [1,2]. The Suzuki-Miyaura cross-coupling reaction is a metal-catalysed organic reaction resulting in the production of biaryls. In that respect, the Suzuki reaction is one of the most efficient methods to form carbon-carbon bonds [3]. The reaction between aryl halides and aryl boronic acids is preferred compared to other cross-coupling reactions because of the mild reaction conditions and high variety and commercial availability of the boronic acids. In addition, the boronic acids are environmentally safer than their organometallic counterparts [3,4].

In industry, the Suzuki reaction is often carried out with

homogeneous Pd catalysts such as Pd(PPh₃)₄ [3]. However, an important drawback is the difficulty to separate and reuse the catalyst, from the reaction medium. As a result, the remaining amount of Pd can pollute the final products [5,6].

Therefore, supported Pd nanoparticle (Pd-NP) catalysts have been investigated. Due to their small size, nanoparticles have an increased surface to volume ratio and thus, very high surface area, compared to their corresponding bulk material, resulting in high catalytic activities. Moreover, they possess unique properties due to quantum confinement. However, nanoparticles as catalysts need to be stabilized against self-aggregation [7,8].

Various supports such as metal oxides [9–11], zeolites [12,13], carbon structures [14–17], polymers [18–22], mesoporous silicas

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[23–26], natural phosphates [27–29], etc. were used to immobilize the Pd-NPs. An emerging class of supports are Layered Double Hydroxides (LDHs) and derived materials due to (i) the cation-tunability of the brucite-like layers (e.g., Mg, Al, Ni, Cu, Mo, Co, Pd, Cr, Fe,...), (ii) their tunable surface basicity and (iii) the uniform dispersion of M^{2+} and M^{3+} cations in the layers allowing the formation of highly dispersed supported catalysts. The $M^{2+}:M^{3+}$ ratio can be modified between 2:1 and 4:1 [30–36]. By calcining the LDH between 400 °C and 550 °C, the interlayer water and anions are evaporated, causing the layered structure to collapse and mixed metal oxides (MMO) to be formed [37–40]. Exposing these MMO structures to air causes a reconstruction of the LDH structure (i.e., memory effect) due to adsorption of water and carbon dioxide [41–45]. In addition, hydrotalcites (HTs) are naturally occurring minerals of the layered double hydroxide (LDH) family, with the general formula $[(Mg_xAl_y(OH)_{14})^{2+}(CO_3^{2-})] \cdot 4H_2O$, in which the Mg/Al molar ratio is 3:1 and CO_3^{2-} ions are used to compensate the charge of the hydroxide layers created by the Al^{3+} [46–51].

HT supported Pd catalysts for the Suzuki reaction have been less studied in literature [52–56]. In 2008, Mora and co-workers reported the synthesis and catalytic performance of anionic clay based Pd^{2+} catalysts in the Suzuki cross-coupling reaction. Highly active HT supported Pd^{2+} catalysts were synthesized via different routes such as the intercalation of $PdCl_4^{2-}$ anions and the impregnation of Pd $(CH_3COO)_2Py_2$ or $PdCl_2$. Also, an LDH supported Pd^{2+} catalyst, synthesized via co-precipitation of $PdCl_2$, was studied. The intercalation method showed low conversions (13%) in combination with extremely high leaching (94%). The HT catalyst impregnated by $Pd(CH_3COO)_2Py_2$ exhibited the highest catalytic activity (52%), although it lost 27% of its initial Pd amount during reaction. The co-precipitated Pd^{2+} catalyst showed almost no conversion (< 1%) in combination with no leaching [57,58].

In 2014, Mora et al. reported the synthesis of a HT supported Pd-NP catalyst via impregnation of a Pd^{2+} salt (0.60 wt% Pd), followed by a reduction with cyclohexene. High conversion (92%) was obtained when the Suzuki reaction between iodobenzene and phenylboronic acid was carried out in an aqueous medium at 100 °C for 10 min. However, the data is determined at relatively high reaction temperatures (i.e., the energy efficiency is rather low since Suzuki reactions are mainly performed below 80 °C) and specific leaching results were not mentioned for this reaction. Considering the Suzuki reaction between chlorobenzene and phenylboronic acid (68%), a hot filtration test demonstrated that the catalytic reaction partly occurred in the homogeneous phase [59].

To our knowledge, a co-precipitated HT supported Pd-NP catalyst has never been studied in the Suzuki reaction. In this work, the effect of the HT structure on the NP size and catalytic performance of supported Pd-NP catalysts (0.01 mmol Pd) was thoroughly examined in the Suzuki cross-coupling reaction between iodobenzene and phenylboronic acid, in the presence of potassium carbonate as base and under mild reaction conditions. An uncalcined, co-precipitated HT supported Pd-NP catalyst, i.e., PdHT_100RED_20, was benchmarked against a Pd impregnated HT catalyst, i.e., Pd@HT_500RED_20. Besides studying the effect of the HT structure, the effect of the NP size on the catalytic performance of the PdHT_100RED_20 catalyst was investigated by varying the reduction temperature (0 °C–20 °C–60 °C). At last, the reusability of PdHT_100RED_20 was studied in a consecutive run. In that respect, a re-activation step with Na_2CO_3 was performed. Also, the conversion and Pd leaching were monitored as function of time. All Pd-NP catalysts were fully characterized by XRD, N_2 sorption, TPD- CO_2 , ICP OES and TEM.

2. Experimental section

2.1. Catalyst preparation

2.1.1. Preparation of palladium on hydrotalcite derived oxides by impregnation

For a 5 g synthesis, 116.4 mL 3:1 Mg/Al-solution (1 M) was prepared from the respective nitrate salts $Mg(NO_3)_2$ (> 98%, Carl Roth) and $Al(NO_3)_3$ (> 98%, Carl Roth), and was added dropwise to 116.4 mL basic solution of 0.15 M $NaCO_3$ (Carl Roth) and 2.2 M NaOH (Carl Roth) while sonicating (Elmasonic S100H instrument) at room temperature. The precipitates were repeatedly centrifuged (VWR Himac CT 6el centrifuge) for 3 min at 3000 rpm and washed with distilled water. Afterwards, it was pre-calcined for 4 h at 500 °C in air. The HT material is denoted as HT_500. Subsequently, an incipient wetness impregnation with an aqueous solution of $Pd(NO_3)_2$ (min. 32 wt%, Alfa Aesar) was performed to load 1 wt% (with respect to the catalyst amount) in HT_500. 1.2 mL Pd solution was slowly added to 1 g HT_500. Thereafter, the Pd@HT sample was calcined under the same conditions as the HT_500 material. The Pd^{2+} supported HT derived mixed oxide was chosen as benchmark catalyst and named as follows: Pd@HT_500.

XRD patterns and N_2 sorption measurements of the calcined pristine HT (i.e., HT_500) and the impregnated supported HT derived oxide (i.e., Pd@HT_500) can be found in the Supporting Information (Figs. S1 & S4).

2.1.2. Synthesis of PdMgAl LDHs and derived oxides

The PdMgAl LDHs were prepared by co-precipitation of $Pd(NO_3)_2$ (min. 32% Pd, Alfa Aesar). For a 5 g synthesis, 65.9 mL metal solution (1 M) with a Mg/Al molar ratio of 3:1 and a (Pd)/(Pd + Mg + Al) ratio of 0.01, was prepared from the respective nitrate salts $Mg(NO_3)_2$ (> 98%, Carl Roth), $Al(NO_3)_3$ (> 98%, Carl Roth) and $Pd(NO_3)_2$. This solution was added dropwise to 65.9 mL basic solution of 0.15 M Na_2CO_3 (Carl Roth) and 2.2 M NaOH (Carl Roth) while sonicating at room temperature. The precipitates were repeatedly centrifuged for 3 min at 3000 rpm and washed with distilled water. The solids were dried for 18 h at 100 °C and are denoted as PdHT_100. In order to fully comprehend the effect of the HT structure on the catalytic performance of Pd-NP catalysts, a PdHT_100 material was calcined for 4 h at 500 °C in air and is denoted as PdHT_500. To study the effect of the support basicity, also a PdHT_100 material with a Mg/Al molar ratio of 2:1, i.e., PdHT_100 (2:1) was prepared by co-precipitation.

XRD patterns and N_2 sorption measurements of the uncalcined pristine HT (i.e., HT_100) and the PdMgAl LDH (i.e., PdHT_100) and its derived oxide (i.e., PdHT_500) can be found in the Supporting Information (Figs. S1, S2, S4 & S5).

2.1.3. Catalyst reduction

All materials were washed with distilled water. Subsequently, 0.5 g Pd^{2+} containing support was converted into a HT supported Pd-NP catalyst using 25 mL 0.53 M of an aqueous $NaBH_4$ (ChemLab, > 95%) solution as reducing agent due to its very strong reducing character resulting in the desired NP size for high catalytic performances, i.e., below 10 nm [5,20,39]. The reduction temperature was generally set at 20 °C and was in addition evaluated at 0 °C and 60 °C for the PdHT_100 material. The reduction time was set at 18 h since at this point no more H_2 formation was observed. After reduction, the catalyst was separated by centrifugation from the solution, washed again with distilled water to remove any remaining $NaBH_4$ and eventually dried at 100 °C under inert atmosphere for 24 h. The reduced catalysts were stored under inert atmosphere to prevent oxidation of the metallic Pd and are denoted with RED_x, e.g., PdHT_100RED_20, i.e., PdHT_100 reduced at 20 °C.

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