

Direct Mechano catalysis: Palladium as Milling Media and Catalyst in the Mechanochemical Suzuki Polymerization

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Abstract: The milling ball is the catalyst. We introduce a palladium-catalyzed reaction inside a ball mill, which makes catalyst powders, ligands, and solvents obsolete. We present a facile and highly sustainable synthesis concept for palladium-catalyzed C–C coupling reactions, exemplarily showcased for the Suzuki polymerization of 4-bromo or 4-iodophenylboronic acid giving poly(*para*-phenylene). Surprisingly, we observe one of the highest degrees of polymerization (199) reported so far.

The formation of C–C bonds is an important tool in organic^[1,2] and polymer chemistry.^[3–5] There are many cross-coupling reactions established to create those bonds such as Negishi,^[6,7] Mizoroki–Heck,^[8,9] Sonogashira,^[10] and Suzuki–Miyaura^[5,11] coupling. In all these, palladium species are required as a catalyst, mainly brought in as complexes such as tetrakis(triphenylphosphine)palladium(0).^[1] In most cases, the catalyzed reactions are run homogeneously, although there are discussions and studies in the literature about heterogeneous analogues.^[12–14] In the recent past, several of the aforementioned reactions have been performed in a solvent-free manner in ball mills.^[15–19] These mechanochemical reactions proved advantageous, being extremely swift and consuming less energy while the solvent-free reaction environment significantly reduces the amount of waste produced and circumvents any possible solubility issues.^[20,21] However, often the catalyst salts used in these solvent-free protocols are

still the same as those in conventional solution-based processes.

Utilizing this pathway, we have recently demonstrated that a mechanochemical Suzuki polymerization is possible even with simple palladium(II) acetate catalyst.^[22] This solid-state approach yielded poly(*para*-phenylene) (PPP) much faster than by solution or electrochemical synthesis. In addition, the reached degree of polymerization (DP) was greatly elevated.^[22] These materials are promising conducting polymers in opto- and microelectronics.^[23,24]

In this contribution, we advance the system of a mechanochemical Suzuki polymerization considerably by using the milling equipment itself as the catalyst. This represents a considerable advance since processing steps are reduced and separation is greatly simplified. This concept which we will call “direct mechanocatalysis” was motivated by pioneering work of the Mack group, who replaced copper(I) iodide in a Sonogashira coupling by using a milling vessel made of copper and copper balls.^[25] They also developed a rapid and efficient azide–alkyne-type click reaction that does not require any copper(I) salt in the reaction mixture.^[26] Moreover, they also extended the range of possible metals by using nickel pellets as milling balls, which proved to be an excellent catalyst in the cycloaddition of alkynes yielding cyclooctatetraenes.^[27] Other groups picked up the methodology and showed that even stainless steel milling equipment could serve as a catalyst for hydrogen generation^[28] and the reduction of organic compounds.^[29] Herein, we demonstrate that milling balls made out of palladium metal (one of the most frequently used transition metal catalysts^[30]) catalyze the Suzuki cross-coupling reaction. No additional catalyst powder, no ligands, and no solvent has to be applied.

With this goal in mind, we proceeded stepwise by adapting the well-known Pd(OAc)₂-catalyzed Suzuki polymerization of 4-bromophenylboronic acid yielding poly(*para*-phenylene), by first applying Pd⁰ black metal powder, and finally solid Pd milling balls (Scheme 1). In detail, we looked at how the milling material, milling time, catalyst concentration, halide function of the monomer, and mill type influenced the reaction yield and DP.

In our standard synthesis we used 1.454 g (7.2 mmol) 4-bromophenylboronic acid, 8.510 g (61 mmol) K₂CO₃ as a base, and 4.7 mol% (0.34 mmol) catalyst in a planetary ball mill (PBM) with 22 ZrO₂ milling balls (10 mm diameter, 3.19 g each) placed in a 45 mL ZrO₂ milling vessel. The milling time ranged from 2 to 6 hours (see Table 1). The resulting reaction mixture was washed and dried overnight (for characterization see Section 2 in the Supporting Information).

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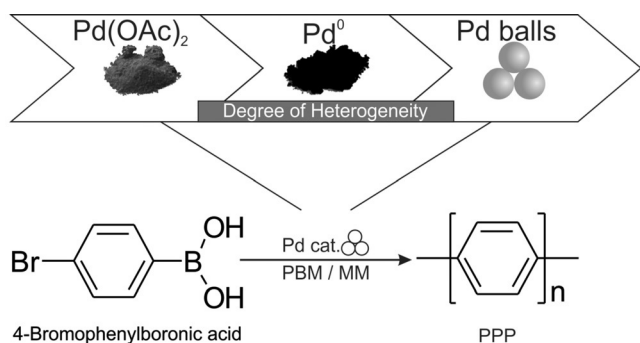
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Scheme 1. Mechanochemical Suzuki polymerization reaction of 4-bromophenylboronic acid to give poly(*para*-phenylene) (PPP). The Pd catalyst was subsequently advanced and simplified from a Pd salt to Pd black and finally to simply Pd milling balls.

First, we conducted the reference reaction using Pd(OAc)₂ with milling balls and vessel made from ZrO₂ and obtained PPP_{PBM}-Ref in 47% yield and with a DP of 69 after 30 min milling time.^[22] After that we switched to Pd⁰ black metal powder as the catalyst. The resulting material (in the following exemplarily shown for PPP_{PBM}-6) was crystalline (see powder X-ray diffraction (PXRD) pattern in Figure 1A),^[48] the C/H ratio obtained by elemental analysis is close to the theoretical value (see Table S2), and the material showed the characteristic Fourier transform infrared (FTIR) spectrum of PPP (Figure 1B and Figure S2). FTIR spectroscopy was used to determine the degree of polymerization (DP) by measuring the ratio of the band at 690 cm⁻¹ (attributed to terminal phenyl rings) to that at 805 cm⁻¹ (principal band of *para*-substituted benzene rings)^[31,32] (for further information see Section 1.1 in the Supporting Information). The materials were also investigated via Raman spectroscopy (Figure 1C and Figure S3) where characteristic bands were observed at 1220 cm⁻¹ (ν_{intra-ring}(C-C)), 1280 cm⁻¹ (ν_{inter-ring}(C-C)), and 1600 cm⁻¹ (δ_{in-plane}(C-H)).^[33] Fitting the spectral peaks by a Lorentzian function^[34] and comparing the

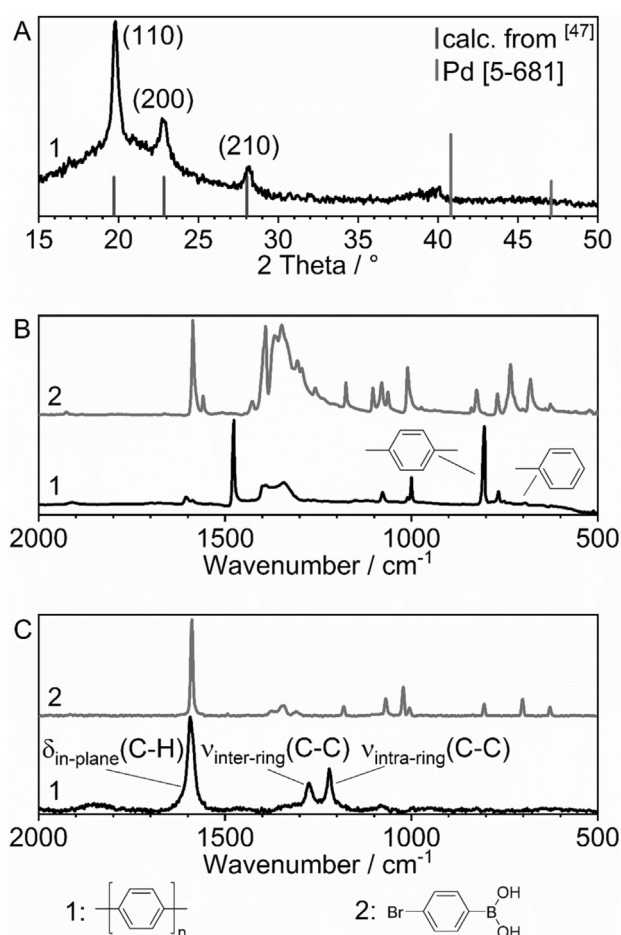


Figure 1. Spectra of sample PPP_{PBM}-6 (1) and the respective monomer (2). A: PXRD pattern of polymer, reference calculated from ref. [47]. B: FTIR spectra of monomer and polymer. C: Raman spectra of monomer and polymer.

intensities of the peaks at 1220 cm⁻¹ and 1280 cm⁻¹^[35] validated qualitatively the high degree of polymerization as

Table 1: Poly(*para*-phenylene) obtained by mechanochemical Suzuki polymerization in a planetary ball mill with Pd(OAc)₂ and Pd black as catalysts.

	Sample code	Vessel/ ball material	Reaction time [h]	Amount of catalyst	DP	Yield of insoluble polymer [%] ^[a]	Halide function of monomer
Reference PBM	PPP _{PBM} -Ref ^[22]	ZrO ₂	0.5	9.3 mol% Pd(OAc) ₂	69	47	Br
Pd black/PBM	PPP _{PBM} -1	ZrO ₂	4	4.7 mol% Pd black	18	59	Br
	PPP _{PBM} -2	steel	4	4.7 mol% Pd black	13	56	Br
	PPP _{PBM} -3	WC	4	4.7 mol% Pd black	10	81 ^[b]	Br
	PPP _{PBM} -4	Si ₃ N ₄	2	4.7 mol% Pd black	34	19	Br
	PPP _{PBM} -5	Si ₃ N ₄	3	4.7 mol% Pd black	45	14	Br
	PPP _{PBM} -6	Si ₃ N ₄	4	4.7 mol% Pd black	56	22	Br
	PPP _{PBM} -7	Si ₃ N ₄	5	4.7 mol% Pd black	40	19	Br
	PPP _{PBM} -8	Si ₃ N ₄	6	4.7 mol% Pd black	32	34	Br
	PPP _{PBM} -9	Si ₃ N ₄	4	2.3 mol% Pd black	55	20	Br
	PPP _{PBM} -10	Si ₃ N ₄	4	0.5 mol% Pd black	48	5	Br
	PPP _{PBM} -11	Si ₃ N ₄	4	4.7 mol% Pd black	0	0	Cl
	PPP _{PBM} -12	Si ₃ N ₄	4	4.7 mol% Pd black	79	66	I

DP and yield measured five times with a standard deviation of ± 5% [a] Yield calculated from the mass of insoluble polymer after washing with water, 10 wt% HCl, ethanol, and acetone. In the organic washing solutions, smaller oligomers could be detected (see Section 1.2 in the Supporting Information). [b] Overestimated due to impurities from WC abrasion. Densities of the milling materials and weight of the milling balls: ZrO₂ 5.7 g cm⁻³, 3.19 ± 0.05 g, steel 7.7 g cm⁻³, 4.02 ± 0.02 g, WC 14.3 g cm⁻³, 7.20 ± 0.26 g, Si₃N₄ 3.25 g cm⁻³, 1.94 ± 0.03 g.

calculated from FTIR. However, quantification was not possible with this technique, since the polymers were already too long (for further information see Section 4 in the Supporting Information).^[32]

The samples PPP_{PBM}-1, -2, -3, -6 were milled with ZrO₂, steel, tungsten carbide (WC), and Si₃N₄ milling balls/vessels, respectively. The higher density of the milling equipment resulted in higher yield but lower DP after 4 h milling (Table 1). The higher density and thus higher mass of the milling balls correspond to an increased kinetic energy during ball impacts ($E_{kin} = 0.5 mv^2$), which increased the conversion efficiency of the polymerization. In turn, a higher ball impact led to a fracturing of growing polymer chains, resulting in a lower DP (see fracturing tests, Section 1.2 in the Supporting Information).^[36,37]

The highest DP was achieved using milling equipment made of Si₃N₄, so we continued to use it and investigated the influence of the milling time (PPP_{PBM}-4 to -8 in Table 1) on yield and DP. Going from 2 to 5 h of milling did not change the yield drastically, while after 6 h the yield increased to 34%. On the other hand, the DP reached a maximum of 56 after 4 h (PPP_{PBM}-6, characterization shown in Figure 1), with further milling leading to fracturing and lower DP.

Subsequently, we reduced the amount of Pd black catalyst. With 2.3 mol % (PPP_{PBM}-9) the yield was nearly the same, but with 0.5 mol %, it was drastically reduced to 5% (PPP_{PBM}-10). The amount of catalyst did not affect the DP, meaning that the equilibrium of polymer chain growth and fracture was mainly dependent on the density of the milling balls as mentioned above (Section 2 in the Supporting Information; considerations about mechanism in Section 7). Thereafter, we examine the halide function of the monomer due to its known influence in Suzuki couplings. PPP was not obtained with 4-chlorophenylboronic acid (PPP_{PBM}-11), whereas 4-iodophenylboronic acid gave the highest yield (66%) and DP (79) (Table 1). The literature supports the observed trend of increasing reactivity on going from chloride to bromide and iodide.^[22,38] For further experiments, we thus continued with 4-iodophenylboronic acid as the monomer.

To verify the catalytic nature of the reaction, we also performed the reaction without Pd catalyst or with the base replaced by NaCl as an inert bulking material. In both cases,

no product was formed, confirming the need for a catalyst and a base in this reaction.

In the third step, we tested Pd milling balls as the catalyst. We had to change the milling setup since using 22 Pd milling balls, as in all other PBM experiments, was too expensive. As an alternative approach, we used a mixer ball mill (MM). Recently, several publications have shown how a Suzuki coupling reaction can be transferred from PBM to MM without affecting the reaction outcome.^[39-41] As additional evidence, we first showed that yield and DP of two reference materials synthesized by MM with Pd(OAc)₂ (PPP_{MM}-Ref-1) and Pd black (PPP_{MM}-Ref-2) as catalysts were comparable to the results obtained in a PBM with 4-bromophenylboronic acid (PPP_{PBM}-Ref and PPP_{PBM}-1) as well as with Pd black catalyst and 4-iodophenylboronic acid (PPP_{PBM}-12) (Table 2). However, in the case of MM longer milling time was necessary due to the lower energy input and a different mixing regime compared to PBM.

For direct mechanocatalysis, the standard synthesis in the MM involved 496 mg (2.00 mmol) of 4-iodophenylboronic acid and 2.504 g (18.12 mmol) of K₂CO₃ with one or two palladium milling balls (10 mm diameter) in a 25 mL ZrO₂ milling vessel. The reaction mixture was milled at 30 Hz (for characterization see Section 3 in the Supporting Information).

The reaction with one Pd milling ball (3.6 g) resulted in a low yield (6%) but a high DP (115) (PPP_{MM}-1, see Table 2). The high energy impact with one milling ball had a high conversion efficiency but only a few possibly reactive collisions occurred. Also, inefficient mixing of the reaction mixture with one ball may have caused the poor yield. Adding a second milling ball (PPP_{MM}-2) improved the mixing and increased the number of possible reactive collisions but decreased the average velocity and therefore the impact energy of the milling balls because of the reduced free path. As a result, the yield increased (31%) to a level closer to that of PPP_{PBM}-1, while the DP of 99 was comparable to that obtained with one Pd milling ball. As this setup gave the best results so far, we repeated approach PPP_{MM}-2 another two times, finding a deviation in DP of $\pm 5\%$ and in yield of $\pm 2\%$. This also addresses a good reproducibility of the direct mechanocatalytic Suzuki polymerization.

Table 2: Poly(*para*-phenylene) obtained by mechanochemical Suzuki polymerization of 4-iodophenylboronic acid in a mixer ball mill using Pd(OAc)₂, Pd black, and Pd milling balls as catalysts.

	Sample code	Vessel/ ball material	Reaction time [h]	Amount of catalyst	DP	Yield of insoluble polymer [%] ^[a]
Reference MM	PPP _{MM} -Ref-1	ZrO ₂	8	4.7 mol % Pd(OAc) ₂	50	50
	PPP _{MM} -Ref-2	ZrO ₂	8	4.7 mol % Pd black	52	6
Pd balls/MM	PPP _{MM} -1	ZrO ₂ /Pd	8	1 Pd ball	115	6
	PPP _{MM} -2	ZrO ₂ /Pd	8	2 Pd balls	99	31
Leaching	PPP _{MM} -3	ZrO ₂ /Pd	8	2 Pd balls	199 ^[b]	18 ^[b]
In situ Raman	PPP _{MM} -4	PMMA/ZrO ₂	8	4.7 mol % Pd black	123	100
	PPP _{MM} -5	PMMA/Pd	14	2 Pd balls	118	50

DP and yield measured five times with a standard deviation of $\pm 5\%$ [a] Yield calculated from the mass of insoluble polymer after washing with water, 10 wt % HCl, ethanol, and acetone. In the organic washing solutions, smaller oligomers could be detected (see Section 1.2 in the Supporting Information). [b] DP and yield measured three times, with a standard deviation of $\pm 15\%$. Densities of the milling materials and weight of the milling balls: ZrO₂ 5.7 g cm⁻³, 3.19 \pm 0.05 g, Pd 12.0 g cm⁻³, 3.6 g.

In order to establish the heterogeneous nature of the reaction protocol, we performed the reaction and removed a 100 mg sample of the reaction mixture every two hours. After 4 h the reaction was briefly stopped and the Pd milling balls were replaced with ZrO₂ balls of the same size. We then continued the reaction and sampling. While monitoring the reaction, we found that it had significantly slowed down (4 % additional yield over the next 4 hours of milling without Pd balls compared to additional 18 % yield when milled with Pd balls). The continued reaction in the absence of Pd milling balls can be explained by the minor abrasion of Pd from the balls in the first phase of the reaction (for characterization see Section 5 in the Supporting Information). Interestingly, since the ZrO₂ milling balls are less dense than the Pd milling balls, the polymer fracturing was reduced, resulting in a higher DP (199 compared to 99 for PPP_{MM}-2; for detailed results see Section 5 in the Supporting Information). Moreover, we could not identify any soluble Pd species, supporting a heterogeneous reaction pathway.

In additional experiments, we added common complexation ligands such as triphenylphosphine and 1,5-cyclooctadiene to the reaction mixture with the aim of Pd stabilization (see Section 5 in the Supporting Information).^[42] Unexpectedly, this did not lead to PPP material. We assume that the ligands were coordinated to the Pd surface of the milling balls and therefore blocked the catalyst sites making them inaccessible for the monomer. This again indicates a heterogeneous reaction at the surface of the Pd.

Finally, we monitored the reaction course by in situ Raman spectroscopy^[43,44] and by in situ synchrotron PXRD^[44-46] at the DESY/PETRA III beamline P02.1 (see Section 6 in the Supporting Information). We conducted the reaction according to PPP_{MM}-Ref-2 and PPP_{MM}-2 in a transparent poly(methyl methacrylate) (PMMA) milling vessel and compared Pd black to Pd milling balls as catalysts.

As seen in Figure 2B the conversion of the monomer could be followed by the decreasing Raman band of the monomer at 1580 cm⁻¹ (Figure 2B right). The intensity of the main PPP band at 1600 cm⁻¹ was too low for following reaction kinetics. Potassium carbonate showed a band at 1060 cm⁻¹ that decreased with ongoing reaction. The intensity of the main band from the PMMA milling vessel at 810 cm⁻¹ was nearly constant during the whole milling time and therefore suitable as an internal reference.

The in situ Raman data for PPP_{MM}-4 (Section 6.2 in the Supporting Information) showed a fast reaction, in which the monomer was completely depleted after a few minutes. The in situ PXRD pattern of PPP_{MM}-4 (Figure 2A) was consistent with the Raman monitoring and therefore provided qualitative proof of the monomer conversion. The resulting polymers from PPP_{MM}-4 were much longer (DP = 123) than those obtained in the ZrO₂ milling vessel (PPP_{MM}-Ref-2, 6 %, DP = 52) with significantly higher yield (100 % compared to 6 %).

According to the in situ Raman data, the reaction proceeded slower with Pd milling balls (PPP_{MM}-5, Figure 2B). After 2 h of milling, the monomer was almost fully converted, whereas the yield of insoluble polymer was much lower, indicating the formation of smaller oligomers that were soluble in ethanol or acetone. This was supported by GCMS

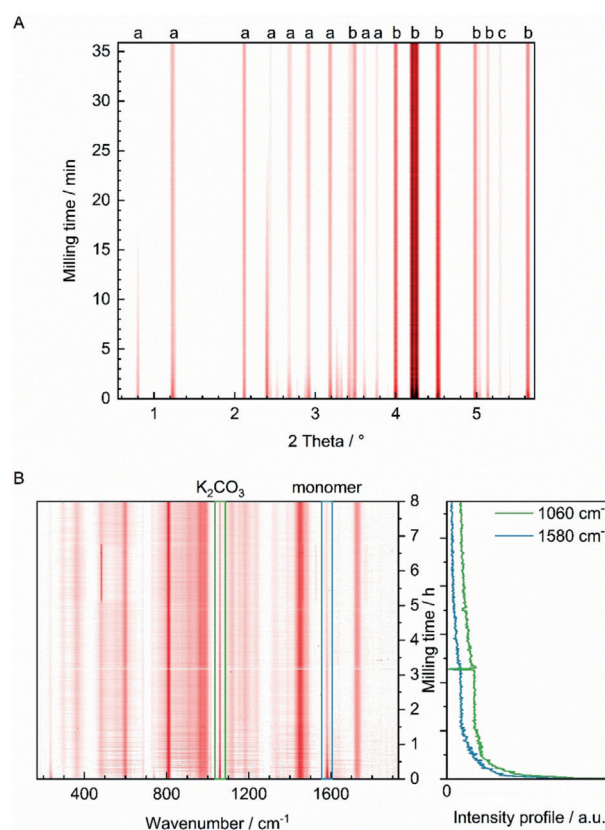


Figure 2. A: In situ PXRD pattern of reaction PPP_{MM}-4. a: commercial monomer containing 4-iodophenylboronic acid and anhydride. b: K₂CO₃ (PDF-2 [16-820]). c: Pd (PDF-2 [5-681]). B: In situ Raman spectroscopic monitoring of reaction PPP_{MM}-5. At 3 h 10 min the laser had to be switched off briefly such that one acquisition is missing. For experimental details see Section 1.2 in the Supporting Information.

analysis of organic washing solutions in which traces of iodobenzene, iodobiphenyl, and iodoterphenyl were identified (see Section 1.2 for detailed information). Comparing PPP_{MM}-5 with PPP_{MM}-2, the yield and DP of insoluble polymer increased from 31 % to 50 % and from 99 to 118, respectively (Table 2).

In the end, the softer PMMA milling vessel seemed more suitable for the reaction, since the respective samples gave the highest yield, whereas even the light but hard Si₃N₄ milling material with the higher energy input in PBM fractured the PPP significantly. Also, the total abrasion of Pd milling balls in the PMMA vessel was nearly a third (120 mg) of that of PPP_{MM}-2 (ZrO₂ vessel, 290 mg), yet gave a higher yield. Again, this indicated a heterogeneous reaction at the surface of the milling ball without the need of a certain amount of abraded Pd.^[49] Lastly, the overall results showed a decreased reaction velocity on going from Pd(OAc)₂ to Pd black and the Pd milling ball catalyst. Longer reaction times led to the fracturing of the formed polymer chains when hard milling equipment, such as ZrO₂ and Pd, was used, whereas in soft PMMA milling vessel high yields and DPs could be achieved.^[50]

In summary, the solvent-free environment of a ball mill makes it possible to directly use palladium milling equipment or Pd black catalyst, instead of conventional Pd^{II} salts or Pd

complexes, as we have shown here for the Suzuki polymerization of *para*-substituted phenylboronic acids to produce poly(*para*-phenylene). With 4-iodophenylboronic acid as the monomer, a good yield and high DP were achieved in PBM using Si₃N₄ milling material, while full conversion to long-chain polymers was obtained in MM using a softer PMMA vessel. In addition, the DPs achievable by this method surpassed those obtained by solution or electrochemical processes, which is beneficial for PPP application in opto- and microelectronics. In situ Raman and PXRD investigations were used to monitor the conversion of monomer. Our results indicate a most likely heterogeneous reaction, which was not improved by using established ligands from solution-based homogeneous procedures.

We also expect the concept of “direct mechanocatalysis” presented here will be used in other palladium-catalyzed cross-coupling reactions under solvent-free conditions beyond the Suzuki cross-coupling.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: heterogeneous catalysis · mechanochemistry · poly(*para*-phenylene) · sustainable chemistry · Suzuki cross-coupling

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- [48] Please note that the Pd black catalyst remained as an impurity in the sample but could be removed by washing with 37 wt % HCl, water, and ethanol. The Pd impurity could be entirely removed without modification of PPP (see Figure 1A). No abrasions of milling material were found according to PXRD and EDX (Figures S1 and S4). Only tungsten carbide (WC) milling equipment showed high abrasion and therefore remained as an impurity (PPP_{PBM-3}).
- [49] We reviewed and quantified the sustainability of our solvent free approaches from Pd(OAc)₂ to Pd black and finally Pd milling ball catalyst by calculating green metrics. Also a possibility to use recycled catalyst was tested and proved suitable to obtain PPP materials. For details see Section 8 in the Supporting Information.
- [50] The mechanochemical Suzuki coupling could also be conducted for the synthesis of 1,3,5-triphenylbenzene from phenylboronic acid and 1,3,5-tribromobenzene. This has even a higher potential in organic chemistry because of the solubility of starting materials and product and easy catalyst handling without weighing. For details see Section 9 in the Supporting Information.

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