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Palladium supported on aminopropyl-functionalized polymethylsiloxane microspheres: Simple and effective catalyst for the Suzuki–Miyaura C–C coupling

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ABSTRACT

A palladium catalyst, obtained in the reaction of $PdCl_2(MeCN)_2$ with microspheric aminopropyl polymethylsiloxane, was used in the Suzuki–Miyaura cross-coupling of various aryl bromides with phenylboronic acids. Catalytic reactions, performed at 80 °C in a 2-propanol/water mixture, led to high yields of non-symmetric biphenyls. In recycling experiments, excellent results (up to 100%) were obtained in ten subsequent runs. Efficient separation of the catalyst from organic products was achieved by simple filtration due to the properties of microspheres.

1. Introduction

Heterogenized palladium-based catalytic systems, widely used for the carbon–carbon bond formation reactions, have been attracting more and more attention because of increasing environmental requirements [1–7].

In the context of green chemistry, the advantage of immobilization consists in the efficient separation of the catalyst and its recycling in the next several runs to increase its productivity. As a result, a lower cost of the catalytic process and the minimization of the metal content in the final organic product can be achieved. This aspect is especially very important in pharmaceutical applications, where the final product is predominantly in contact with living organisms.

Palladium complexes bonded to differently functionalized polymers have been used in catalysis [8–21], including the Suzuki–Miyaura reaction [22–30]. Pd(0) stabilized on polyvinylpyrrolidone [31–37], polyvinylpyridine [38,39] or other polymers has been widely applied [40–43]. However, very few reports have presented on the application of functionalized silicone polymers [44] as catalyst supports. At the same time, polysiloxane-supported palladium has recently been successfully used in the Heck reaction [45,46] and the Suzuki–Miyaura coupling [47,48].

Although palladium catalysts supported on siloxanes functionalized with imidazole and triazole groups have been successfully recycled [47,48], the separation step has been rather complicated in these systems due to the very small diameter of the beads formed by polysiloxane. Centrifugation has not been efficient and very careful filtration through a thick filter allowed to solve the problem of catalyst recovery.

Therefore, we decided to examine the catalytic activity of palladium supported on aminopropyl-functionalized polymethoxysiloxane in the form of microspheres [49,50]. It was expected that palladium supported on polymethoxysiloxane microspheres would be active in the Suzuki–Miyaura reaction and, in addition, its recyclability would be improved. It is also worth noting that polymethoxysiloxanes are chemically and thermally resistant non-toxic materials.

This article aims to report on the application of NH_2-modified siloxane polymers as supports for palladium catalysts in Suzuki–Miyaura carbon–carbon coupling reactions.

2. Results and discussion

2.1. Structural studies

Coordination of palladium to aminopropyl polymethoxysiloxane resulted in a change of the composition and a decrease in N,

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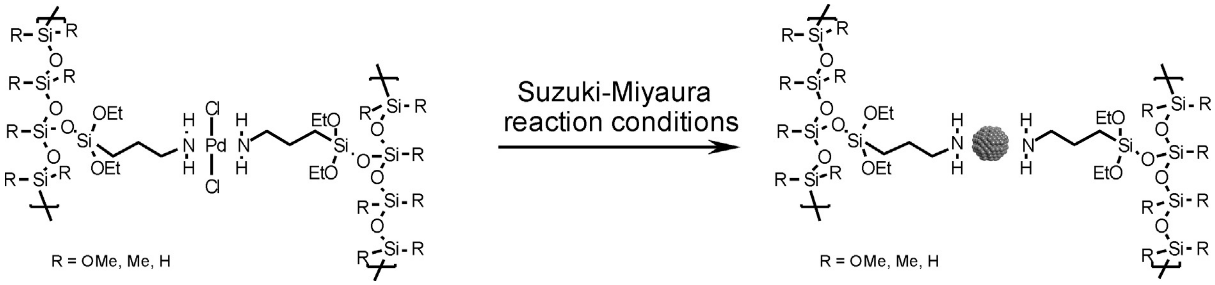


Fig. 1. Representation of the catalyst structure.

C, and H amounts in comparison with the free support, which is one of the proofs of palladium connection to the carrier surface. The Pd/N ratio, calculated from the N and Pd contents (measured by ICP), indicated that there were 10% of amino groups coordinated to the palladium ion. The most probable structure of [Pd], containing palladium bonded to two NH_2 groups and two chloride ions, is shown in Fig. 1.

Because of the insolubility of the polymer in organic solvents, ^{13}C and ^{29}Si NMR spectra were measured in the solid state.

The SEM analysis shows that palladium is evenly distributed on the surface of the spheres, and its amount does not differ for samples before and after the catalytic reaction (Table 1). Negligible differences in the amounts of palladium between samples can show the lack of leaching of the metal from the support during the reaction. This demonstrates the very strong and stable bond of palladium to the NH_2 groups. During the reaction Pd(II) is reduced to Pd(0) nanoparticles. Functional groups (NH_2) of the polymer play a role of stabilizers preventing agglomeration of nanoparticles. The observed interactions can be described as coordination to the palladium metallic surface due to the Lewis base properties of the polymer NH_2 groups, similarly as it was discussed in [36]. In this form it can be consistently observed very strong metal support interaction, which prevents the elution of the Pd and the unwanted entry into the reaction products.

The SEM picture of the catalyst sample analyzed after the Suzuki reaction performed with KOH as the base showed some structural changes (Figs. 4 and 5) indicating the partial decomposition of the support.

The reaction mixture under these conditions is very basic, which leads to the destruction of the polymer in the fragments where there are no functional groups. In particular, the fragment where there are free H or OMe groups can be attacked (Figs. 2–5). It appears that the amino group linked to the palladium remains intact, and this was also confirmed by the solid state NMR analysis of the support before and after the reaction, which showed that the chemical shifts of the representative carbons and silicones did not change much. TEM microscopy evidenced the presence of palladium nanoparticles bonded to the organic matrix, most probably by functional groups extended from the surface of the spheres (Figs. 6 and 7). Thus, during the catalytic reaction, Pd(II) was reduced to Pd(0) nanoparticles, similarly as it was observed for other catalysts supported on polysiloxane polymers (Fig. 1) [47,48].

Table 1
Average palladium content on the sample surface measured with EDS.

Sample	palladium content in the sample (weight% +/− 0.01)
Before reaction	0.25
After reaction with $KHCO_3$ as a base	0.23
After reaction with KOH as a base	0.26

2.2. *Suzuki–Miyaura cross-coupling reactions*

The Suzuki–Miyaura reaction of aryl bromides with substituted phenylboronic acids was selected as a model catalytic reaction for testing a new palladium catalyst (Fig. 8).

Due to the heterogeneous nature of the catalyst, it was required to carry out the reaction at a higher temperature such as 80 °C to obtain optimum conversion in a satisfactory time and to prolong the reaction time to 6 h.

For testing reactions, two different bases (KOH and $KHCO_3$) were chosen. Potassium hydroxide is a strong base, while potassium hydrocarbonate is considered a medium or even a weak base. However, both are known for their outstanding performance in palladium-catalyzed coupling reactions. As a solvent, a mixture of water and 2-propanol was used, regarded to be safe to use and environmentally friendly.

Test reactions were performed for different aryl halides with phenylboronic acid, in order to select the most reactive substrates and then to check their coupling with other substituted boronic acids. The obtained conversions of aryl halides are presented in Table 2.

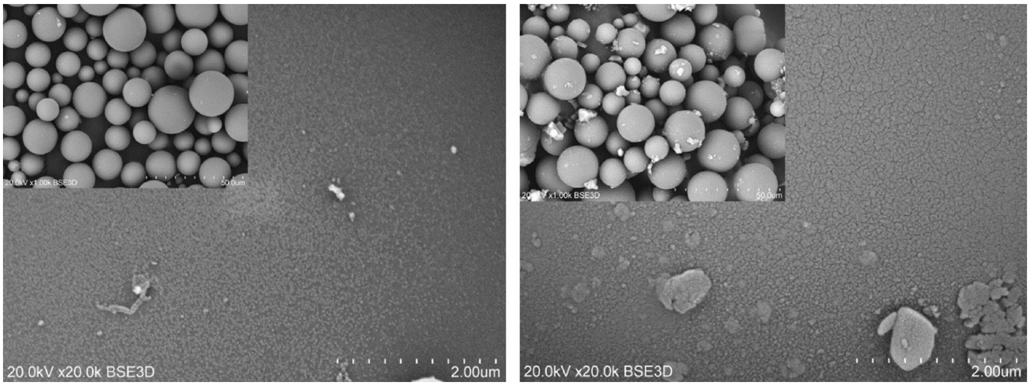
Generally, both the bases turned out to be good. The reaction yields were comparable, but in most of the reactions KOH was slightly better and made it possible to achieve higher halide conversions, up to 100%.

Reactions with different halides and phenylboronic acid showed conversions from 0% for 2-bromoacetophenone to 100% for bromobenzene and 3-bromobenzaldehyde. The highest conversions, up to 100%, were obtained for halides with OH, NH_2, NO_2, or CN substituents in the phenyl ring. Substrates with only methyl or methoxy groups were a little less reactive. Conversions for them ranged from 42% for 4-bromotoluene to 66% for 2-bromotoluene and 2-bromo-3-xylene.

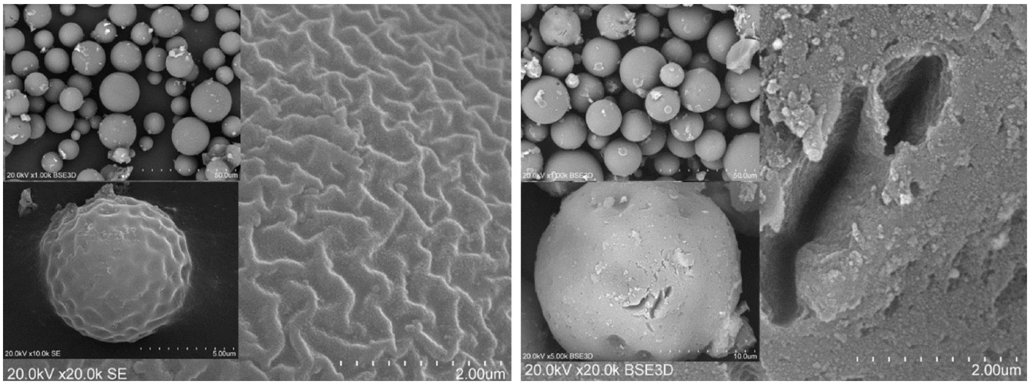
For further studies, 4-bromobenzaldehyde was selected as a representative halide. Reactions with substituted boronic acids showed conversions from 30% for 2-isopropyl-6-methoxyphenyl boronic acid to 100% for 4-*tert*-butylphenyl and naphthalene boronic acid derivatives. In this case, there is no effect of the specific substituent on the reaction yield. Generally, yields were very good to excellent. It should also be noted that during all the performed reactions only traces (up to 3%) of homo-coupling of the boronic acid product were observed. Quantity of biphenyl was determined by GC-FID, and estimated from the ratio of the signals areas of the main and the side products.

2.3. *Reuse and recycling of the catalyst*

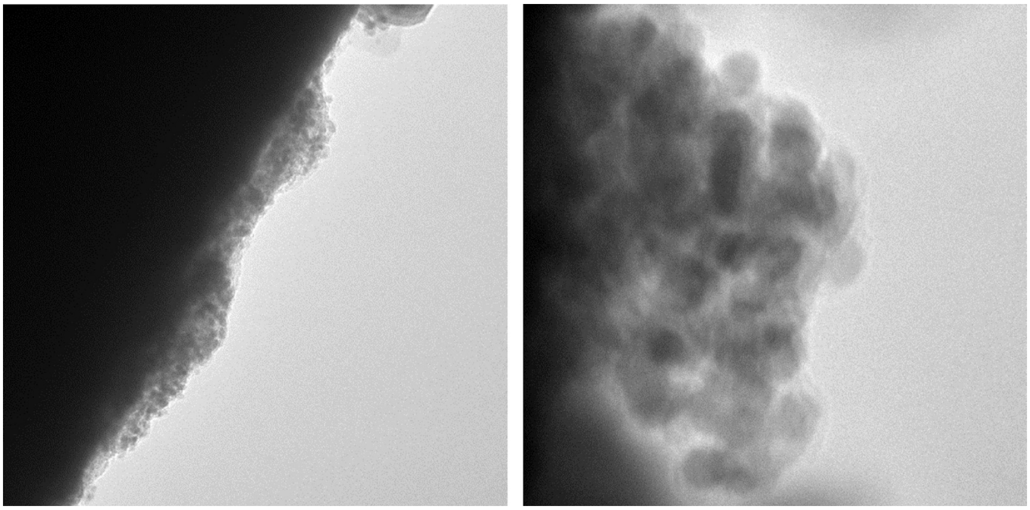
The most important feature of heterogenized catalysts is their ability to be reused, so-called recycling. During the research, such a test was also carried out. The catalyst was easily reused due to the fact that it floated on the surface of the water phase of a biphasic catalytic mixture. At the end of the catalytic reaction, the



Figs. 2 and 3. Catalyst surface (SEM) before (left) and after (right) one reaction with $KHCO_3$ as the base.



Figs. 4 and 5. Catalyst surface (SEM) after one and ten reactions with KOH as the base.



Figs. 6 and 7. Catalyst surface (TEM mag. 180 K, 930 K) after one reaction with KOH as the base.

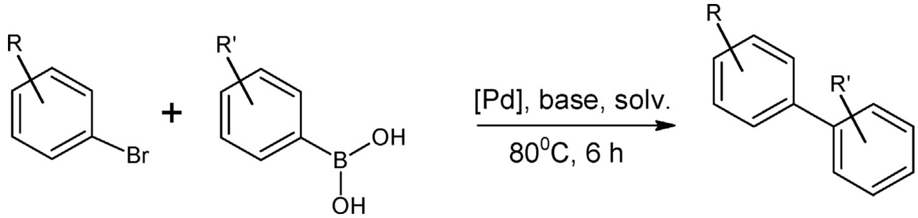
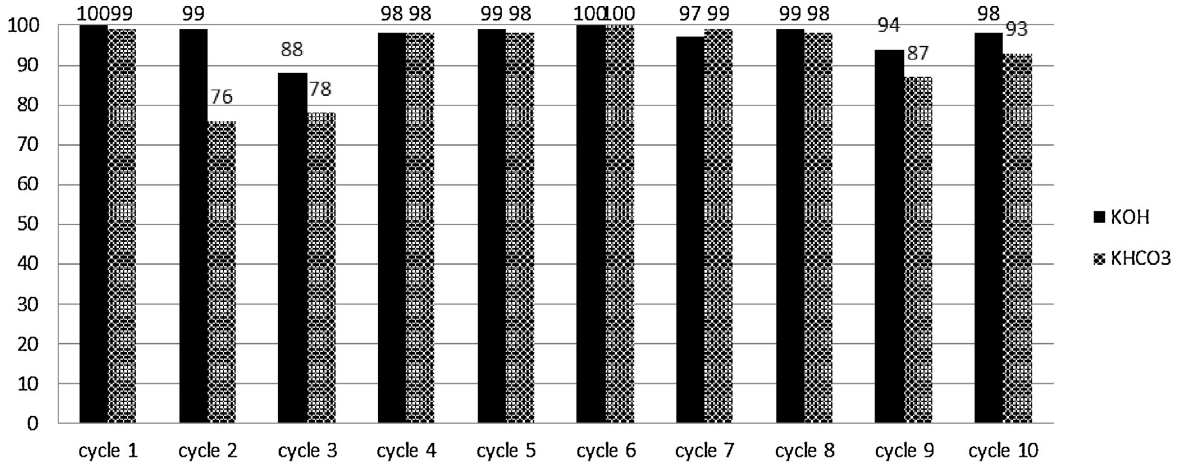


Fig. 8. Suzuki–Miyaura C–C coupling reaction scheme.



Reaction conditions: 4-bromobenzaldehyde (1 mmol), phenylboronic acid (1.2 mmol),[Pd] (2 mol%, 0.02 mmol Pd), base (2 mmol), solvent (2-propanol/water- 1:1, 5 mL), temperature 800C, time 6h.

Fig. 9. Catalyst reuse.

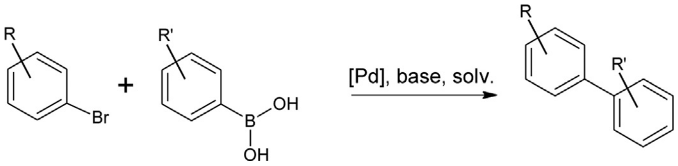
organic phase was separated, and a new portion of the substrates was added. The test made it possible to carry out ten consecutive reaction cycles without a significant reduction of the activity of the catalyst (Fig. 9).

The second series of recycling was performed using the catalyst separated from the reaction mixture and used for the coupling of 4-bromobenzaldehyde with phenylboronic acid. The catalyst also showed great activity in this experiment, making it possible to obtain a 100% conversion of the substrates.

It should also be underlined that the recovery of the catalyst from the reaction mixture is very simple and requires only filtration on a medium dense filter.

Under the operating reaction conditions, a two-phase system is formed (Fig. 10). One phase is composed of water-soluble components, i.e., the base and the boronic by-products of the reaction. The other phase contains the organic reactants and the reaction products. The solid catalyst is at the interface between

Table 2
Suzuki-Miyaura coupling reaction of aryl bromides [2] with arylboronic acids.

Entry	R	R'	KOH Conv.[%]	$KHCO_3$ Conv.[%]
				
1	4-NH_2	H	98	99
2	4-OH	H	100	85
3	2-Me	H	61	66
4	4-Me	H	53	42
5	2-OMe	H	64	46
6	2,5-Me	H	66	54
7	2-Ac	H	0	0
8	H	H	100	94
9	3-CHO	H	100	58
10	4-CHO	H	100	99
11	3-NO2	H	94	99
12	4-NO2	H	96	99
13	2,5-Me, 4-NO_2	H	100	86
14	2-CN	H	100	61
15	4-CN	H	99	36
16	4-CHO	2-iPr, 6-OMe	33	30
17	4-CHO	4-Vinyl	40	42
18	4-CHO	H, Pinacol ester	76	72
19	4-CHO	4-COOH	89	67
20	4-CHO	4-CHO	90	77
21	4-CHO	4-Ac	95	97
22	4-CHO	3,5-OMe	98	99
23	4-CHO	4-Boronic acid	99	78
24	4-CHO	4-Me, 1-Nap	100	99
25	4-CHO	1-Nap	100	99
26	4-CHO	4-tBu	100	100

Reaction conditions: aryl halide (1 mmol), arylboronic acid (1.2 mmol), [Pd] (2 mol%, 0.02 mmol Pd), base (2 mmol), solvent (2-propanol/water- 1:1, 5 mL), temperature 80 °C, time 6 h.

Fig. 10. Two-phase reaction system.

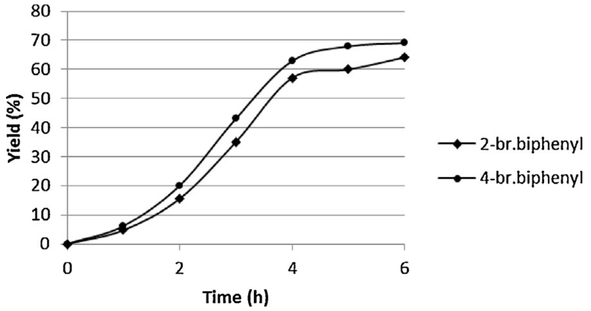


Fig. 11. Kinetic studies of the Suzuki–Miyaura reaction.

these two liquid phases in such a system. Microspheres do not have direct contact with the magnetic stirring element, so they are not mechanically damaged. The reaction requires vigorous stirring in order for the mixture to be evenly homogenized and for the contact of the reactants to be facilitated.

ICP studies of the reaction mixture and the post-reaction product extracts were done in order to assess the possible presence of palladium leached from the carrier. The content of palladium in the reaction products was below the detection limit.

2.4. *Kinetic studies*

To follow the kinetic properties of the Suzuki–Miyaura reaction, two of the slowest reacting substrates (2-bromotoluene and 4-bromotoluene) were selected (Fig. 11).

During these studies, the standard course of the reaction was observed. After 4 h of the reaction, a ca. 60% conversion was reached. To that point, the reaction was fast. After 4 h, the reaction slowed down, reaching a ca. 70% conversion after 6 h. It should be noted that, in the course of the reaction due to the necessity of sampling, the ratio between the substrates and the catalyst changed. After every hour, 1/6 of the substrate was lost, but the amount of the catalyst did not change. These differences, however, had very little effect on the reaction, and, after 6 h, a slightly higher conversion of the substrates was obtained, but it was still close to that obtained in the standard Suzuki–Miyaura reaction, 53% and 61%.

3. Experimental

3.1. *Synthesis of the palladium catalyst*

Polymer microspheres (1.00 g) were placed in a 50 mL flask, and 10 mL of MeCN was added. In another flask, a solution containing 0.10 g of $PdCl_2(MeCN)_2$ in 10 mL of MeCN was prepared. The solution of the palladium complex was slowly added to the stirred suspension of the polymer. When the entire amount of the solution was added, the reaction was left stirred for 24 h at room temperature. After that time, the product was filtered off, washed with MeCN, DEE, and dried in vacuo.

The palladium content estimated by ICP was 0.0125 weight%, which means that 10% of all nitrogen atoms in the sample are associated with palladium.

3.2. *Suzuki–Miyaura standard reaction procedure*

Suzuki–Miyaura reactions were performed in a Schlenk tube. Weighed amounts of the solid reactants: phenylboronic acids (1.1 mmol), base (2. mmol), catalyst (20.00 mg), aryl bromide (1 mmol), and 5 mL of the solvent (2-propanol/water mixture) were introduced to the Schlenk tube. Next, the Schlenk tube was sealed with a rubber septum and introduced into an oil bath preheated to 80 °C. The reaction mixture was magnetically stirred at a given temperature for 6 h and, after that time, left for several minutes to cool down. Next, the organic products were separated by extraction with 10 mL of diethyl ether. The extracts (10 mL) were GC-FID analyzed with dodecane (0.050 mL) as an internal standard to determine the conversion of aryl bromide. The products of the reaction were determined by GC–MS.

3.3. *Suzuki–Miyaura kinetic studies reaction procedure*

Suzuki–Miyaura reactions were performed in a Schlenk tube. Weighed amounts of the solid reactants: phenylboronic acids (3.3 mmol), base (4.0 mmol), catalyst (20.00 mg), aryl bromide (1 mmol), and 12 mL of the solvent (2-propanol/water mixture) were introduced to the Schlenk tube. Next, the Schlenk tube was sealed with a rubber septum and introduced into an oil bath preheated to 80 °C. The reaction mixture was magnetically stirred at a given temperature for 6 h. After each 1 h, 2 mL of the reaction mixture was taken and extracted with 5 mL of diethyl ether. The extracts were GC-FID analyzed with dodecane (0.010 mL) as an internal standard to determine the conversion of aryl bromides.

3.4. *Reuse of catalyst procedure*

Because the catalyst floats on the surface of the water, it was possible to remove the post-reaction remains (mainly residues of boronic acids and bases) by pipetting. Subsequently, a new portion of the starting materials was added to the Schlenk tube, and the reaction was carried out under the conditions described above. The recycling was performed ten times in a row for both bases.

3.5. *Separation of the catalyst for analysis and recycling procedure*

After several reactions, the catalyst was separated by filtration. A pale gray solid was washed several times with water and diethyl ether to remove all the reaction material and dried in an N_2 flow. For the recycling procedure, the catalyst recovered from five reactions was weighed (20 mg) and added to the Suzuki–Miyaura reaction under standard conditions. The catalyst was collected after the reuse procedure and used for SEM and TEM analyses.

3.6. *TEM*

TEM measurements were performed using a FEI Tecnai G^2 20 X-TWIN electron microscope with LaB_6 catode providing 0.25 nm resolution. To the small sample of catalyst 2 mL of methanol were added and the resulted mixture was ultrasonically treated for 5 min. Specimens for TEM studies were prepared by putting a droplet of a colloidal suspension on a copper microscope grid followed by evaporating the solvent under IR lamp for 15 min.

3.7. *GC*

GC-FID and GC–MS spectra of organic products were obtained using HP 5890 (Hewlett Packard) instrument with mass detector 5971 A. Capilary column HP 5 was used with non-polar liquid phase containing 95% of dimethyl- and 5% of diphenyl-polysiloxane.

3.8. *ICP*

ICP measurements of palladium content were performed using spectrometer ARL model 3410. Before analysis a weighted samples of palladium catalyst were mineralized with 2 mL of aqua regia, left for 7 days and diluted next to 10 mL with distilled water.

3.9. *SEM*

SEM measurements were carried out using Hitachi S-3400N instrument with EDS Thermo Scientific Ultra Dry 129 eV detector.

4. Conclusions

It was demonstrated that palladium supported on polymethoxysiloxane microspheres functionalized with propylamine groups efficiently catalyzed the Suzuki–Miyaura reaction in an environmentally friendly mixture of solvents (2-propanol/water).

The catalyst showed very good recyclability, demonstrated by the performance of ten successive runs with almost no decrease in catalytic activity. Another important advantage of this catalyst is its high mechanical strength and low density. The catalyst is floating on the surface of the water phase, and that prevents it from being crushed by a magnetic stirrer as it is observed for oxide-type supports. Thus, it becomes very easy to separate from the reaction mixture even after several cycles [3].

This work is certainly a step forward compared to the previous one [48] in which a triazolyl-functionalized polysiloxanes were used. Although in this studies higher amount of catalyst was used (2 mol% versus 0.23 mol% in [48]) the system is much easier to operate and, in particular, separation step is improved.

The studies of the catalyst separated after the Suzuki–Miyaura reaction showed the presence of Pd(0) nanoparticles bonded to the polymer. During the reaction with KOH as a base, we noted the partial degradation of the support surface. However, this did not affect catalytic activity, which remained high. There was no leaching of palladium from the carrier to the solution at the time of the reaction, which shows a very strong interaction between the metal and the support surface. This gives a chance for the potential use of this support, for example, for the production of pharmaceuticals.

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