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## Palladium Nanoparticles Supported on Poly(*N*-vinylimidazole-*co*-*N*-vinylcaprolactam) as an Effective Recyclable Catalyst for the Suzuki Reaction

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A recyclable and effective polymer-immobilized ligandless palladium catalyst for the Suzuki reaction has been investigated. Palladium nanoparticles are formed in situ and stabilized by poly(*N*-vinylimidazole-*co*-*N*-vinylcaprolactam). A series of aryl bromides have been studied in the reaction with phenylboronic acid under mild conditions with water–alcohol systems as a solvent that complies with "Green Chemistry" demands. The

#### Introduction

The Suzuki reaction (Nobel Prize in Chemistry, 2010)<sup>[1]</sup> is the mostly widely utilized cross-coupling technique for the synthesis of biaryls and other compounds with  $C_{sp^2}$ - $C_{sp^2}$  bonds.<sup>[2]</sup> It is also used as a model reaction (as the Heck reaction) to test palladium catalysts for their activity with different ligands under various conditions.<sup>[3]</sup> There have been attempts to replace relatively expensive palladium by cheaper alternatives, such as nickel,<sup>[4]</sup> but the major trend is to increase the efficiency of palladium catalysts and to decrease cost by multiple recycling steps. Recently, the focus of investigations into catalysts has shifted to the field of nanocatalysis, that is, catalysis by palladium nanoparticles (PdNPs), obtained by various methods and differently stabilized<sup>[5]</sup> (on solid supports, polymers, dendrimers, ionic liquids, etc.). The tremendous number of studies have resulted in a great variety of protocols, and some of them have achieved very interesting and useful results.<sup>[6]</sup> PdNPs possess activity that is often comparable to that of homogeneous complexes, and even higher sometimes, especially when using phosphine-functionalized polymers.<sup>[7]</sup> However, the advantage of PdNPs over homogeneous complexes is the ability to function without toxic phosphine ligands, even at the expense of activity. Additionally, PdNPs are capable of being recycled (allowing the catalyst to be separated from the products used multiple times). This allows us to approach the "ideal" catalyst in the context of Green Chemistry.

However, the use of a heterogeneous precursor, such as stabilized PdNPs, is not evidence for a heterogeneous mechanism catalyst can be recycled eight times without appreciable loss in activity and a low degree of palladium leaching. Kinetic studies reveal unusual behavior of the reaction; this can be explained on the basis of the observation of changes to the sizes of the particles during recycling, as determined by TEM results. The suggested mechanism of the reaction is in accordance with the concept of the role of leaching in the process.

of catalysis, although there are many reports providing solid arguments in its favor.<sup>[8]</sup> One of them was based on a very interesting investigation into PdNPs on several supports by using differences in their selectivity.<sup>[8j]</sup> Numerous other reports attempted to prove the opposite, namely, that "leaching" was responsible for catalysis and PdNPs provide molecular species, which form the true catalyst, that are homogeneous in nature.<sup>[5b, 9]</sup>

Surprisingly, different authors came to the opposite conclusions regarding the mechanisms, even upon using the same catalyst.<sup>[8e,10]</sup> The issues of the first stage of the reaction and causes of possible "leaching " are also disputed. In our opinion, it proceeds through heterogeneous palladium oxidation by ArHal on the surface of PdNPs.<sup>[11]</sup> Subsequent leaching could lead to numerous kinds of species ranging from monoatomic palladium complexes through a number of palladium clusters to PdNPs of different sizes and shapes. Such a variety of states that are intermediate between homogeneous and heterogeneous are called microheterogeneous; this hardly makes it possible to finalize a conclusion of the true mechanism, although one could certainly exclude the extreme points, such as atomic-level homogeneous and macro-level heterogeneous.

A clear understanding of the mechanism of PdNP-catalyzed reactions is essential for the development of recyclable catalysts. One of the major problems to solve is deactivation of the catalyst associated with changes to the PdNPs during the reaction.<sup>[11]</sup>

Herein, we aimed to investigate conditions for recycling PdNP-based catalysts in the Suzuki reaction. To achieve this, we needed to clarify the catalyst state during the reaction and during the process of recycling, and determine the causes of deactivation of the catalyst.

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## **Results and Discussion**

Previously, we developed a catalytic system of PdNPs supported on a soluble statistical copolymer of *N*-vinylimidazole with *N*-vinylcaprolacam (30%; PVI-PVCL), which revealed high activity and recyclability in the Heck reaction,<sup>[12]</sup> the cyanation of aryl halides,<sup>[13]</sup> and the carbonylation of aryl iodides.<sup>[14]</sup> Polymer PVI-PVCL successfully models natural enzymes on the basis of peptide macromolecules.<sup>[15,16]</sup> The advantage of PVI-PVCL is its solubility in aqueous solutions, wherein it forms aggregates. Hydrophobic reagents are concentrated in such aggregates and this leads to an increase in the rate of reactions by several orders of magnitude. The interfacial nanolayer of aggregates can be considered as a catalytic nanoreactor.

PVI-PVCL forms complexes with palladium dichloride owing to the ligand donor ability of imidazole fragments. Palladium(II) is easily reduced into a zero-valent palladium, which forms PdNPs that are stabilized by the polymer. Notably, PdNPs are obtained in situ both through the reduction of PdCl<sub>2</sub> with phenylboronic acid and through preliminary reduction by alcohol in the presence of the polymer. (The PdNPs obtained by the latter method are considerably larger.)

First, we tested different reaction conditions in the model reaction of *p*-bromoacetophenone with phenylboronic acid catalyzed by the PdCl<sub>2</sub>/PVI-PVCL (1:5) system through varying the solvent, base, and temperature (Table 1). The aim was to find conditions that provided not only high yields, but stable catalysts.

It appears that all three factors, solvent, base, and temperature, influence the reaction and also the possibility of recycling the catalyst. Some conditions gave excellent yields in the first cycle, but failed in the second. Undoubtedly, this confirmed a change in the catalyst state at the end of the first cycle. Sometimes that change was visible by eye as palladium black, so the degradation of the catalyst was clear.

A high yield of product was obtained in the system DMF/K<sub>2</sub>CO<sub>3</sub> at 120 °C (Table 1, entry 1); however, such a reaction needed a high temperature and long time (Table 1, entries 1 and 2). Upon decreasing the temperature to 100°C, the yield of product fell slightly (Table 1, entry 3). Surprisingly, Na<sub>2</sub>CO<sub>3</sub> in DMF gave a better result at 100  $^\circ C$  than at 120  $^\circ C$  (Table 1, entries 4 and 5). PVP, which is similar in nature to PVI and very popular in the Suzuki reaction, as a PdNP support gave worse results (Table 1, entries 9 and 10). A lower yield in the second cycle showed that the stability of PdNPs on PVI/PVCL was better than that on PVP. Recycling of the catalysts after the reactions in DMF, in all cases, led to a noticeable decrease in the yield. Thus, standard conditions for palladiumcatalyzed cross-coupling reactions (DMF at 100-120 °C) are not optimal for PdNPs immobilized on PVI-PVCL and PVP.

A number of reports presented ethanol as a promising green solvent for the Suzuki reaction. High yields were obtained in EtOH with both  $K_2CO_3$  and NaOH at 80 °C (Table 1, entries 11 and 12). The EtOH/K<sub>2</sub>CO<sub>3</sub> system gave excellent results in both cycles. However, in the EtOH/NaOH system, the yield sharply decreased (from 90 to 15%) in the second cycle (Table 1, entry 12). The catalyst was clearly degraded and rather large palladium particles were observed. "Green" aqueous medium was successfully used for the Suzuki reaction with water-soluble reagents.<sup>[11]</sup> Unfortunately, an attempt to perform the reaction under aqueous conditions with aryl bromide, which is insoluble in water, did not give positive results (Table 1, entries 15 and 16).

Aqueous organic solvents represent the optimal compromise. Water participates in the reaction and stabilization of PdNPs and the organic solvent allows dissolution of the substrates. Aqueous DMF was reported to be more efficient than pure DMF.<sup>[17]</sup> A more environmentally friendly 1:1 water/ethanol system was found to be optimal for the Suzuki reaction catalyzed by PdNPs in numerous reports published recently,<sup>[18]</sup> especially for aerobic conditions<sup>[18a]</sup> and catalyst recycling.<sup>[18b]</sup> The use of a mixture of EtOH/H<sub>2</sub>O (1:1) as a solvent and K<sub>2</sub>CO<sub>3</sub> as a base at 80 °C allowed the product to be obtained in close to quantitative yields, with both PdNPs generated in situ and those synthesized in advance (Table 1, entries 17 and 18).

We tested several typical bases for the Suzuki reaction. Among them, KF gave the worst results (Table 1, entries 6 and 13). Moreover, the addition of KF to  $K_2CO_3$  lowered the yields (Table 1, entries 7, 14, and 16). This could be possible owing to

Table 1. Screening of base, solvents, and temperature in the reaction of phenylboron- ic acid with <i>p</i> -bromoacetophenone. <sup>[a]</sup>										
	O F	PdCl <sub>2</sub> /p 3r + PhB(OH) <sub>2</sub> solv 80-12	olymer se ent, 20°C	°	$\succ$					
Entry	Base	Solvent	Т	t	Yield [%]					
		_	[°C]	[h]	Cycle 1	Cycle 2				
1 <sup>[b]</sup>	K₂CO₃	DMF	120	6	96	90				
2 <sup>[b]</sup>	K <sub>2</sub> CO <sub>3</sub>	DMF	120	2	88	69				
3 <sup>[b]</sup>	K <sub>2</sub> CO <sub>3</sub>	DMF	100	4	88	61				
4	Na <sub>2</sub> CO <sub>3</sub>	DMF	120	6	81	65				
5	Na <sub>2</sub> CO <sub>3</sub>	DMF	100	4	90	48				
6	KF	DMF	100	4	40	11				
7	K <sub>2</sub> CO <sub>3</sub> /KF	DMF	100	4	84	60				
8	Bu₃N	DMF	120	6	74	-				
9 <sup>[c]</sup>	K <sub>2</sub> CO <sub>3</sub>	DMF	120	6	96	84				
10 <sup>[c]</sup>	Bu₃N	DMF	120	6	52	14				
11	K <sub>2</sub> CO <sub>3</sub>	EtOH	80	4	95	92				
12	NaOH	EtOH	80	4	90	15				
13	KF	EtOH	80	4	50	50				
14	K <sub>2</sub> CO <sub>3</sub> /KF	EtOH	80	4	30	-				
15	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	100	4	50	-				
16	K <sub>2</sub> CO <sub>3</sub> /KF	H <sub>2</sub> O	100	4	27	-				
17	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (1:1)	80	4	>99	92				
18 <sup>[d]</sup>	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (1:1)	80	4	>99	93				
19	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (1:1)	80	0.75	97	91				
20 <sup>[e]</sup>	K <sub>2</sub> CO <sub>3</sub>	EtOH/H <sub>2</sub> O (1:1)	80	4	>99	75				

[a] Reaction conditions: PdCl<sub>2</sub> (1 mol%), PVI-PVCL (5 mol%, relative to the monomeric unit), *p*-bromoacetophenone (0.2 mmol), PhB(OH)<sub>2</sub> (0.22 mmol), base (0.4 mmol), solvent (0.5 mL). [b] Determined by <sup>1</sup>H NMR spectroscopy. [c] 20 mol% of poly(*N*-vinylpyridine) (PVP) as a polymer component. [d] PdNPs synthesized in advance. [e] PdCl<sub>2</sub> (0.1 mol%), *p*-bromoacetophenone (2.0 mmol), PhB(OH)<sub>2</sub> (2.2 mmol), base (4.0 mmol), solvent (5 mL).

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the ability of F<sup>-</sup> to form inactive boron-fluoride anionic complexes.<sup>[19]</sup> Bu<sub>3</sub>N was also inefficient (Table 1, entries 8 and 10), as noted previously for amines.<sup>[19]</sup> NaOH was successfully used before, but it promoted degradation of the catalyst for this particular system of PdNPs on PVI/PVCL (Table 1, entry 12). Mild and inexpensive K<sub>2</sub>CO<sub>3</sub> was also shown to be efficient. Thus, the optimal conditions for the Suzuki reaction were determined as follows: 1:1 EtOH/H<sub>2</sub>O with K<sub>2</sub>CO<sub>3</sub> at 80°C. The most important achievement was the highest stability of the catalyst under these conditions. The activity of the catalyst under the optimized conditions was higher; hence it allowed the reaction time to be shortened from 4 h to 45 min (Table 1, entry 19). A decrease in the palladium loading from 1 to 0.1 mol% did not lead to a decrease of the yield in the first cycle (fresh), but the yield sharply dropped in the second cycle (Table 1, entry 20).

Under the optimized conditions, the Suzuki reaction was performed for a range of aryl bromides containing electrondonor and -acceptor substituents (Table 2). Good yields of diaryls were observed in all cases. A mixture of mono-, di-, and trisubstituted products, of which the trisubstituted product was the major product, were formed in the reaction of tribromobenzene. Chloro derivatives, even upon activation, did not react under these conditions.

#### Recycling of the catalyst

Recycling of the catalyst was performed eight times for the model reaction of *p*-bromoacetophenone with phenylboronic acid; the yield in all eight cycles remained constant under the optimized conditions (Table 3). However, in an attempt to cut the reaction time (45 min instead of 4 h), the yield was not so constantly high and noticeably dropped in the eighth cycle. To shed some light on the catalyst state during the reaction, more studies were performed.

Images recorded by TEM (Figure 1) after the first and subsequent cycles showed a significant change to the distribution of the sizes of the particles, although the average size only slightly increased. The noticeable decrease in the amount of smaller particles with a simultaneous increase in the amount of larger particles was observed from first to the third and from the third to the eighth cycles (Figure 1 c). After the eighth cycle, the smallest particles (< 1.7 nm) vanished completely and the average size (2.1 nm) changed to 2.5 nm. The size of the nanoparticles synthesized before the reaction turned out to be much larger, and consequently, the change in the particle size during the reaction was also less, but the tendency to increase the average size remained (Figure 1 f).

Kinetic studies were performed at a lower temperature (40 °C) than the optimized conditions (80 °C) because the initial reaction rate was very high (Figure 2). It should be noted that there was no induction period, which was always present for other similar palladium(II)-catalyzed reactions (Heck, Sonogashira); this can be explained by the instant reduction of Pd<sup>II</sup> to Pd<sup>0</sup> with arylboronic acid. The kinetic behavior of the reaction was totally unexpected. The reaction proceeded extremely quickly at the beginning, so the conversion reached more than



monomeric unit), aryl bromide (0.2 mmol),  $PhB(OH)_2$  (0.22 mmol),  $K_2CO_3$  (0.4 mmol), EtOH (0.25 mL), water (0.25 mL), 80 °C. [b] Hetar = heteroatom. [c] Yield of product isolated. [d] EtOH (0.5 mL). [e] Determined by <sup>1</sup>H NMR spectroscopy. [f]  $PhB(OH)_2$  (0.62 mmol). [g] Overall yield.

<b>Table 3.</b> Catalyst recycling in the reaction of phenylboronic acid with <i>p</i> -bromoacetophenone. <sup>[a]</sup>								
Run	Yield [%]		Run	Yield [%]				
	45 min	4 h		45 min	4 h			
1	> 99	>99 (>99) <sup>[b]</sup>	5	92	> 99			
2	91	92 (93) <sup>[b]</sup>	6	95	>99			
3	96	99 (98) <sup>[b]</sup>	7	97	>99			
4	92	99	8	81	98			
[a] Reaction conditions: [Pd] = PdCl <sub>2</sub> /PVI-PVCL 1:5 (1 mol%; relative to the monomeric unit), <i>p</i> -bromoacetophenone (0.2 mmol), PhB(OH) <sub>2</sub> (0.22 mmol), K <sub>2</sub> CO <sub>3</sub> 0.4 mmol, EtOH (0.25 mL), water (0.25 mL), 80 °C. [b] PdNPs synthesized in advance.								

half after only 1 min, but then the rate sharply dropped and more than one hour was needed for full conversion. To the best of our knowledge, nobody has reported similar reaction behavior. These results were completely reproducible. The ki-

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**Figure 1.** TEM images of the catalytic system based on  $PdCl_2/PVI-PVC = 1:5$  after the reaction of phenylboronic acid with *p*-bromoacetophenone for 4 h, showing PdNPs after the first (a) and eighth (b) cycles; the particle size distribution of the PdNPs is also shown (c). TEM images of the PdNPs synthesized in advance before the reaction (d) and after the third cycle (e); the particle size distribution of the PdNPs is also shown (f).

netic curve apparently consists of two parts: the first part reflects a high rate constant that lasts until 1 min and the second part corresponds to a considerably lower rate of the reaction. The rate in the second cycle repeated the slower part of the first cycle. During the following consecutive cycles, the activity of the catalyst gradually decreased. The use of a higher



**Figure 2.** Quantity of *p*-bromoanisole as a function of the reaction time. Reaction conditions: [Pd] = PdCl<sub>2</sub>/PVI-PVCL 1:5 (1 mol%; relative to the monomeric unit), *p*-bromoanisole (0.4 mmol), PhB(OH)<sub>2</sub> (0.42 mmol), K<sub>2</sub>CO<sub>3</sub> (0.8 mmol), EtOH (1 mL), water (1 mL), 40 °C, and veratrol (0.2 mmol) as an internal standard.

temperature (80 °C instead of  $40^{\circ}$  C) allowed consistently high yields to be achieved in seven cycles, but completion of the reaction in the eighth cycle required a longer reaction time (4 h instead of 45 min; Table 3).

Such unusual behavior might be a consequence of the complex nature of the reaction catalyzed by PdNPs. An attempt to explain the kinetics is based on the observation of changes to the sizes of the particles during recycling. The very fast reduction of Pd<sup>II</sup> to Pd<sup>0</sup> at the beginning of the first cycle produced very active catalytic species, probably in the form of very small palladium metal particles and clusters. Soon after that, the active small particles took part in the reaction, and hence, were dissolved. Subsequently, palladium atoms leaving the reaction cycle precipitated to give only large, stable, and less active nanoparticles. Those particles were responsible for the lower reaction rate of the second part of the first cycle and all subsequent cycles. The active smaller particles disappeared from cycle to cycle accompanied by a gradual decrease in the reaction rate. It should be noted that small PdNPs can arise in the process of grinding large particles.<sup>[11]</sup> The ratio of the processes of grinding and dissolution of PdNPs determines the trend in their size distribution. Very active substrates, such as aryl iodides, were shown to react fast enough with all types of particles, including palladium black of micrometer particle sizes,<sup>[20]</sup> causing their grinding.<sup>[11]</sup> In this study, we used less active aryl bromides, the oxidation addition of which to palladium proceeded very slowly; therefore, they reacted more selectively and preferred smaller PdNPs, and consequently, the rate of dissolution of small particles was considerably higher than the rate of grinding of large particles, which resulted in the disappearance of small particles and an increase in the average size of the particles. PdNPs prepared in advance through the process of the slow reduction of Pd<sup>II</sup> by alcohol had a three times larger initial average size and did not contain smaller particles, and consequently, they were less active, but their low activity remained constant.

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However, this is only a part of characteristics of the mechanism. We performed a hot filtration test and found that only a small amount of palladium was contained in the solution (0.3%, much less than that expected for a homogeneous reaction based on leaching). The reaction did not proceed in this solution, although even homeopathic doses could catalyze the reaction.<sup>[21]</sup> Maybe this is not so surprising if we examine our kinetic curves, which show how fast the change in the activity of PdNPs occurred, even during the course of the reaction. We do not know if size and morphology are responsible. One can see that even small changes to the conditions do not allow us to recycle a successful reaction (see Table 1), and if we manage to recycle the catalyst, the kinetic behavior is different in the second cycle (see Figure 2). All of these observations clearly show that the mechanism of this rather simple reaction is far from being fully understood and needs to be studied further.

#### Conclusion

The Suzuki reaction is one of the mostly investigated catalytic processes: thousands of studies have been reported and the huge flow of articles has not stopped. This could be explained by the complex nature of the mechanism, the variety of results, difficulties in their interpretation, and problems with recycling of the catalyst. The results obtained herein revealed completely unexpected behavior for such a well-studied reaction. Kinetic results and changes to the sizes of the particles were in accordance with our view of the role of leaching in the course of the reaction and supported the homogeneous nature of the mechanism of the Suzuki reaction catalyzed by palladium nanoparticles. The suggested protocol allows the reaction of aryl bromides to be performed under mild conditions with a high yield in a green solvent and undoubtedly complies with Green Chemistry principles.

## **Experimental Section**

#### General

A copolymer of *N*-vinylimidazole and *N*-vinylcaprolactam (30%;  $M_r$  20000) was prepared by a method reported in the literature.<sup>[12]</sup> All reactions were performed under an argon atmosphere and were monitored by TLC on silica-gel Alugram SilG/UV254 plates (Macherey–Nagel). Column chromatography was performed on silica gel (60–200 nm) purchased from Alfa Aesar. <sup>1</sup>H NMR spectra were obtained by using a Bruker AMX-400 spectrometer at 400 MHz in CDCl<sub>3</sub> and a Bruker Avance III 600 spectrometer at 600 MHz. Qualitative <sup>1</sup>H NMR spectroscopy analysis was performed by using dimethyl terephthalate as an internal standard. TEM images were obtained on an LEO912 AB OMEGA transmission electron microscope.

#### Preparation of the PdNP-supported copolymer

A solution of copolymer (21.5 mg, 0.2 mmol) of *N*-vinylimidazole and *N*-vinylcaprolactam in EtOH (2 mL) was added to a stirred solution of Pd(OAc)<sub>2</sub> (8.98 mg, 0.04 mmol) in ethanol (6 mL). The mixture was stirred for 0.5 h at room temperature. The resulting solution of PdNPs was diluted with EtOH up to 10 mL;  $c(Pd) = 4 \times 10^{-3}$  mmol mL<sup>-1</sup>.

# General procedure for the Suzuki-Miyaura cross-coupling reaction

A  $2 \times 10^{-3}$  M solution (1 mL) of H<sub>2</sub>PdCl<sub>4</sub> in EtOH, prepared by a method reported previously,<sup>[11]</sup> was placed into the reactor and evaporated in vacuum. Then polymer (1.0 mg; 5 mol% in relation to aryl bromide), aryl bromide (0.2 mmol), base (2 equiv), phenylboronic acid (0.22 mmol), and solvent (0.5 mL) were added. The mixture was stirred at 80-120 °C. The product was then extracted with diethyl ether (3×2 mL; for reactions with EtOH/H<sub>2</sub>O as solvent), or diethyl ether (4 mL) was added and the reaction mixture was stirred for 5 min, the solution was separated, and the precipitate was washed with diethyl ether (2×2 mL; for reactions with DMF as the solvent). The combined ethereal extracts were passed through a silica filter, which then was washed with dichloromethane (5 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated in vacuum. The products were isolated by flash chromatography by using petroleum ether (fraction 40–70  $^{\circ}$ C) as the eluent. The structure of the products was determined by <sup>1</sup>H NMR spectroscopy.

#### Recycling of the catalyst

After completion of the reaction and cooling to room temperature, the reaction mixture was filtered; the precipitate was washed with water, EtOH, and diethyl ether; dried under air; and employed for the next cycle. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated in vacuum. The product was isolated by flash column chromatography on silica gel by using petroleum ether (fraction 40–70 °C) as the eluent. *p*-Acetodiphenyl yields were 97% after the first cycle and 98% after the second cycle.

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**Keywords:** cross-coupling · kinetics · nanoparticles · palladium · supported catalysts

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# **FULL PAPERS**

**Fast or slow?** Palladium nanoparticles immobilized on poly(*N*-vinylimidazole*co-N*-vinylcaprolactam) reveal unusual kinetic behavior in the Suzuki reaction. This can be explained on the basis of the observation of changes to the sizes of the particles during recycling, and is in accordance with the concept of leaching during the process.

PhB(OH)<sub>2</sub> + Ar-Br EtOH/H<sub>2</sub>O K<sub>2</sub>CO<sub>3</sub>

40-80 °C

Pd/polymer A.

År

A. V. Selivanova, V. S. Tyurin, I. P. Beletskaya\*



Palladium Nanoparticles Supported on Poly(*N*-vinyl-imidazole-*co*-*N*vinylcaprolactam) as an Effective Recyclable Catalyst for the Suzuki Reaction