Polypyrrole–palladium nanoparticles composite as efficient catalyst for Suzuki–Miyaura coupling

Tatiana V. Magdesieva [a,*], Oleg M. Nikitin [a,d], Oleg A. Levitsky [a], Veronika A. Zinovyeva [b], Igor Bezverkhyy [c], Ekaterina V. Zolotukhina [b], Mikhail A. Vorotyntsev [a,b,**]

[a] Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory, 1/3, Moscow 119991, Russia
[b] Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR-CNRS 5260, Université de Bourgogne, 9 Av. A. Savary, BP 47870, 21078 Dijon Cedex, France
[c] Laboratoire Interdisciplinaire Carnot de Bourgogne (ICB), UMR-CNRS 5209, Université de Bourgogne, 9 Av. A. Savary, BP 47870, 21078 Dijon Cedex, France
[d] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Science, Vavilova Str. 28, 119991, Moscow, Russia

ARTICLE INFO

ABSTRACT

Synthesis of a new hybrid material (Pd/PPy) composed of polypyrrole globules with uniformly incorporated Pd nanoparticles via direct redox reaction between pyrrole and $Pd(NH_3)_4Cl_2$ in water has been recently reported (V.A. Zinovyeva, M.A. Vorotyntsev, I. Bezverkhyy, D. Chaumont, J.-C. Hierso, Adv. Funct. Mater. 21 (2011) 1064–1075). In the actual study, this procedure has been extended to synthesize a series of Pd/PPy powders with variable palladium content and morphological parameters. Depending on the monomer-to-oxidant ratio in reaction mixture, average diameters of Pd and PPy particles may change in the ranges of 1.25–1.45 and 27–62 nm, respectively, the Pd concentration being within 33.5–42.0 wt.%. In general terms, decrease of the monomer-to-oxidant ratio led to formation of the Pd/PPy hybrid material with smaller diameters of both components and a higher Pd loading. The Pd/PPy composites have been studied in Suzuki–Miyaura coupling and showed high catalytic efficiency. Aryl iodides, bromides and chlorides are active. The reaction can be performed using arylboronic acids or tetraarylborates, both in organic solvents and in water, thus making the process ecologically friendly. The recycling of the catalyst is possible if its particles are immobilized on the graphite support. The comparison of two samples revealed that Pd/PPy nanocomposite with the diameter of PPy spheres of about 30 nm is more efficient in catalysis, as compared to the sample with bigger PPy spheres (about 60 nm), due to transport limitations for reagents inside the polypyrrole sphere in the latter case. For palladium/polypyrrole nanocomposites with the small diameter of PPy sphere, which are easily penetrable for the reagents and in which all Pd nanoparticles are active, Pd content in polypyrrole spheres does not influence the yield of biaryls: the more is the Pd content in polypyrrole spheres, the less amount of catalyst is necessary to obtain the same yield of biaryl.

1. Introduction

Palladium-catalyzed cross-coupling of aryl halides with arylboronic derivatives is a very convenient and widely used approach to $C(sp^2)$–$C(sp^2)$ bond construction and is the most popular for accessing biaryls [1]. Biaryl motif is often present in natural products, pharmaceuticals, herbicides and other useful molecules [2]. Plenty of catalysts for this reaction have been already developed, both homogeneous and heterogeneous [1,3]. Each of them has advantages and drawbacks, as well as limitations in application. The rapid development of the pharmaceutical and fine chemical industries dealing with complex multifunctional compounds brings to a focus new additional requirements. Namely, design and synthesis of new types of efficient and selective catalysts satisfying the requirements of sustainable chemistry, such as a possibility of recycling, small palladium loadings and replacement of hazardous organic solvents by water is still of primary importance. Most of the catalysts used in Suzuki–Miyaura coupling are based on palladium complexes with phosphine ligands [1,3–6] which are very efficient but economically and environmentally undesirable due to the difficulties with their recover and the formation of toxic phosphines as byproducts in the reaction. The latter can be overcome by using new types of ligands such as carbenes [7,8], pincer ligands [9] or palladacycles [10,11] which demonstrated excellent

* Corresponding author. Tel.: +7 495 939 3065; fax: +7 495 939 0290.
** Corresponding author at: Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR-CNRS 5260, Université de Bourgogne, 9 Av. A. Savary, BP 47870, 21078 Dijon Cedex, France. Tel.: +33 3 8039 6064; fax: +33 3 8039 6064.
E-mail addresses: tvm@org.chem.msu.ru (T.V. Magdesieva), mv@u-bourgogne.fr (M.A. Vorotyntsev).

catalytic results in Suzuki–Miyaura coupling. However, the recycling of the homogeneous catalyst is still an open question in the majority of cases. Besides, contamination of the products by palladium residues and losses of expensive palladium are common drawbacks of homogeneous catalysis.

Thus, one of the key goals in the design of a new catalyst is to combine high efficiency of the catalyst with its easy separation from the reaction products and the possibility of recycling; and in this aspect nanosize metallic catalysts in solid supports create a perspective type of catalytic materials. Its preparation is usually performed in ligand-free conditions and rather cheap inorganic precursors are used [12]. Catalysis is one of the principle applications of nanoscience and nanotechnology [13–16]. The use of nanoparticles provides a bridge between homogeneous and heterogeneous catalysis integrating the advantages of each form and this is the main reason for increasing interest in catalysis by metal nanoparticles.

However, the application of palladium nanocatalysts in Suzuki–Miyaura coupling is still not as wide as can be expected. In the majority of publications aryl bromides and aryl iodides were used [12,17–31], the examples of the efficient couplings of aryl chlorides are rarer [32–36]. The reactions can be performed in organic solvents, organic solvent/H_2O mixtures, or in pure water [19,23,24,26–31,37], which is of special interest in the context of green chemistry. Microwave irradiation can be used for enhancement of catalytic activity [35] though it often makes impossible a recycling of the catalyst. Various types of polymeric support were used for incorporation of nanosized Pd particles, such as polyvinylpyrrolidone [27,38,39], hypercrosslinked polystyrene matrix [32], zeolite [20,40], polyurea [21], epoxide-containing copolymers [36,41], copolymers of styrene with divinylbenzene [22], 4-vinylpyridine [26], vinylpyrrolidone [28] or methacrylic acid [28,31] and some others [23,29]. In [28] a strategy to facilitate reuse of palladium catalyst stabilized by block copolymer micelles was proposed. Following this strategy, the polystyrene-poly(4-vinyl pyridine) micelles were firstly anchored on the surface of polystyrene-*co*-poly(methyl acrylic acid) core–shell microspheres to form raspberry-like colloid. Then it was used as scaffold to support colloidal palladium catalyst and showed similar activity to the catalyst stabilized by block copolymer micelles but much improved recoverability [28]. Nanosized palladium on polyvinylpyrrolidone proposed in [27] also showed excellent recoverability. It was recycled for eight consecutive trials without significant loss of its activity in Suzuki–Miyaura coupling of aryl bromides and iodides.

Dendrimers also can behave as "molecular boxes" that can entrap and stabilize Pd nanoparticles especially if there are heteroatoms in the dendrimer interiors. The effect of the poly(amidoamine) dendrimer generation on the catalytic activity in Suzuki–Miyaura coupling was investigated in [42–44] and the 3rd and 4th generations turned out to be the most efficient. However, the form of Pd nanoparticles within the dendrimer is still not clear despite TEM studies [45], as well as the question if the nanospecies are really completely inside the dendrimer.

The high activity of Pd/PANI composites prepared by interaction of Pd(II) ions with reduced polyaniline (PANI) matrix in Suzuki–Miyaura coupling has been shown in several reports, that makes this class of composites, metal component/conducting polymer, perspective for catalytic studies [46–48].

Polypyrrole is also used for preparation of Pd nanocomposites. Electrochemical incorporation of palladium nanoparticles into electroactive polypyrrole matrices during electrochemical synthesis of PPy films [49]; electrodeposition of metal nanoparticles on preformed electrodes (surface of electrodes was coated with thin polymer films) [50–53]; absorption of metal ions by polymer film/particles from the solution of transition metal salts, with their subsequent chemical reduction [54,55] – these are common approaches. A few examples of direct chemical reduction of palladium ions during pyrrole oxidation have been also reported, namely the syntheses of a Pd/PPy composite in an inverse microemulsion medium [56] and in hydrochloric acid [57]; and bimetallic Cu/Pd/PPy composite formation in water [58].

Recently, we described a simple non-template one-step method for the synthesis of palladium nanoparticles encapsulated into polypyrrole globules (Pd/PPy) via direct redox reaction between various palladium(II) salts and pyrrole in aqueous and organic media [59,60]. This Pd/PPy composite has shown a high catalytic activity for direct arylation of heteroaromatics with bromoarenes [60]. The same synthetic procedure based on mixed aqueous solutions of pyrrole and $PdCl_2$ in the presence of KCl has also been used to deposit the Pd/PPy nanocomposite as a layer around micrometer-sized polystyrene (PS) latex spheres, with demonstration of their catalytic activity [61]. The formation of nano catalysts in redox-polymerization of heterocyclic precursor oxidized by metal ions is one of the approaches promising for catalytic application. It allows avoiding addition of surface stabilizers (as it is often the case in the preparation of stable nanosize systems) since the simultaneously formed conducting polymer matrix itself stabilizes nanoparticles and prevents their aggregation. Pd/PPy nanocomposites on the surface of PS latex particles are efficient catalysts for Suzuki–Miyaura-type coupling reactions in aqueous media [61]. Pd component for this 26 wt.% PPy–Pd nanocomposite system was represented by metal nanoparticles with a bimodal size distribution: 6.0 nm Pd nanoparticles forming about 130 nm Pd aggregates on the surface of the PPy shell and 1.8 nm Pd nanoparticles dispersed in the shell [61].

The influence of a size and morphology of nanocomposite on its catalytic properties is an important question. Consequently, the systems with tunable parameters, allowing to create an optimal catalyst, are of special interest. Recently we described synthetic protocol with the use of $Pd(NH_3)_4Cl_2$ as oxidant in water resulted in formation of small Pd nanoparticles (about 2.4 nm) uniformly distributed inside PPy spheres [60]. In a continuation of this investigation, we found that sizes of both Pd nanoparticles and PPy globules may be reliably controlled by the choice of the synthesis conditions, both geometrical parameters being uniform, with a low dispersion. In this context, we have extended the preparation method of Pd/PPy composites with the use of $Pd(NH_3)_4Cl_2$ as oxidant in aqueous medium by varying of initial reagent concentrations. In the present paper several types of Pd/PPy nanocomposites with different size of PPy globules and Pd content were synthesized, to establish the influence of polymerization conditions on chemical composition, morphological and then catalytic properties of composites. As a model catalytic reaction, Suzuki–Miyaura coupling of aryl halides with arylboronic acids or sodium tetraphenylborate in organic and aqueous media was chosen and it clearly demonstrated that the size of PPy globules should be considered as an important parameter determining the catalytic efficiency of the nanocomposite.

2. Experimental

2.1. Materials

$Pd(NH_3)_4Cl_2$ monohydrate (99%, Alfa Aesar) and ammonium carbonate (for analysis, Carl Roth) were used as received. Pyrrole (98+%, Alfa Aesar) was distilled under argon atmosphere before use. Aryl halides and sodium tetraphenyl borate were commercially available from Aldrich. Substituted arylboronic acids were synthesized via standard protocol [62]. N-methylpyrrolidone (NMP, Aldrich, spectroscopic quality) was stirred over CaH_2 for 3 h and distilled under reduced pressure. Acetonitrile (AN, Aldrich

spectroscopic quality, <0.02% water content) was refluxed over CaH_2 for 12 h and distilled. Water was distilled using aquadistillator BE-4 (Russia) for catalytic experiments.

2.2. Preparation of Pd/PPy nanocomposites

Pd/PPy nanocomposites were obtained via direct redox reaction between pyrrole and $Pd(NH_3)_4Cl_2$ in water (purified by means of GFL-2008 distiller) with the use of the synthetic procedure described in [60]. In typical synthesis equal volumes (500 ml) of aqueous solutions of $Pd(NH_3)_4Cl_2$ (2 mM) and pyrrole (varied concentration) were mixed under vigorous stirring to obtain the following molar ratios of oxidant to monomer: 1:10 (Pd/PPy-10), 1:100 (Pd/PPy-100) and 1:300 (Pd/PPy-300). The reaction mixture was treated in ultrasonic bath (48 kHz, output power 50 W; Bransonic 220, Germany) at $T = 40–50°C$ for 5 h per day during 5 days. The sedimentation of colloid was either spontaneous at the end of the 7th day, or provoked by addition of about 2 g of $(NH_4)_2CO_3$ to standardize the reaction time. The supernatant was decanted, and the dark precipitate was rinsed several times by water and acetonitrile, then dried under vacuum at 60 °C for 4 h.

2.3. Characterization

The chemical composition of Pd/PPy powders was determined by means of elemental analysis (detection of C, H, N, S; Flash EA 1112 Thermo Electron analyzer), inductively coupled plasma atomic emission spectroscopy (ICP-AES; analysis of Pd concentration in Pd/PPy composites) and energy-dispersive X-ray spectroscopy (EDX; Oxford Instruments EDX analyzer attached to the scanning electron microscope).

Morphology of the synthesized Pd/PPy nanocomposites was studied by scanning and transmission electron microscopies (SEM and TEM, respectively). SEM micrographs of dried powders were registered on a JEOL JSM-6400F device at 15 kV accelerating voltage. Due to the technical limitations of the accurate detection of small particles (less than 50 nm) by SEM method, the detailed analysis of the obtained SEM images of Pd/PPy samples is not provided. TEM images were obtained on a Jeol JEM-2100 TEM instrument with LaB6 source operating at accelerating voltage of 200 kV.

The particle size distribution (PSD) of Pd/PPy and Pd globules was determined by analysis of at least 100 particles using TEM images. On basis of these data, the average diameters of PPy and Pd components with corresponding confidence intervals (at the 95% confidence level) were calculated.

The description of Pd/PPy sample preparation for analyses is given in [60].

2.4. Suzuki–Miyaura cross-coupling reaction

2.4.1. Pd/PPy in solution

Pd/PPy (0.01 mmol of Pd) was suspended in 2 ml of NMP or CH_3CN using ultrasonication. A mixture of aryl halide (1 mmol),[1] $NaBPh_4$ (0.25 mmol) or arylboronic acid (1 mmol) and 2.5 mmol of Na_2CO_3 was added to the suspension. The reaction mixture was vigorously stirred under Ar atmosphere at 100 °C (NMP) or 82 °C (CH_3CN) for several hours. After cooling to room temperature, the reaction mixture was separated from Pd/PPy particles using centrifuge (*centrifuge 5424 Eppendorf AG, Hamburg,* 15,000 rpm, g-force = 20,238 rcf). 30 ml of H_2O saturated with NaCl was added to the reaction mixture in NMP and organic products were extracted with the diethyl ether (3 × 15 ml). In case of reaction performed in

acetonitrile, the solvent was evaporated under reduced pressure and the products were extracted from the residue with the diethyl ether. The ether extract was washed with water, dried over $MgSO_4$ and analyzed using GC–MS "Pegasus 4D" (LECO) with naphthalene as an internal standard.

2.4.2. Pd/PPy on the graphite support

To obtain an immobilized catalyst, 1 mg of Pd/PPy-100 was dispersed in 2 ml of NMP (or acetonitrile) using ultrasonication. 300 μl[2] (0.3 mol.% of Pd respectively to aryl halide) of suspension was carefully deposited on a graphite tissue (2 cm × 1 cm) with specific surface area of 12 m^2/g ("URAL", Russia). Afterwards the graphite tissue was dried in a Schlenk tube under reduced pressure (10 Torr) at 80 °C for 1 h.

Thus prepared immobilized Pd/PPy samples were used in the Suzuki–Miyaura coupling in NMP or in water according to the general procedure. A modified graphite tissue was placed in a reaction mixture containing 2 ml of a solvent (NMP or H_2O), 0.2 mmol of aryl halide, 0.05 mmol of $NaBPh_4$, and 0.5 mmol of a base – Na_2CO_3. The mixture was stirred with magnetic stirrer for several hours at 100 °C. Afterwards, the modified graphite tissue was taken off, washed with 5 ml of a solvent. When the reaction was performed in water, the joint solution was saturated with NaCl and the products were extracted with the diethyl ether (3 × 10 ml). When the solvent was NMP, before ether extraction of the products (3 × 15 ml), 30 ml of water saturated with NaCl was added to the reaction mixture. In both cases ether extracts were washed with water, dried over $MgSO_4$ and analyzed using GC–MS "Pegasus 4D" (LECO) with naphthalene as an internal standard.

For recycling experiments, after the first reaction was finished, the graphite tissue with the immobilized catalyst was taken off, washed with NMP and dried in a Schlenk tube under reduced pressure (10 Torr) at 80 °C for 1 h. Afterwards, the catalyst was used in the subsequent reaction runs with new portions of reagents without any additional treatment.

Mass-spectra for selected compounds:

Mes-Ph:
EI-MS m/z (I, %): 196 $[M]^+$ (62), 181 $[M–CH_3]^+$ (100), 165 $[M–2CH_3]^+$ (32), 119 $[M–Ph]^+$ (20), 76 $[M–MesH]^+$ (12)
4-NO$_2$C$_6$H$_4$Ph
EI-MS m/z (I, %): 199 $[M]^+$ (85), 153 $[M–NO_2]^+$ (100), 76 $[M–NO_2–PhH]^+$ (13)
4-CH$_3$OC$_6$H$_4$Ph
EI-MS m/z (I, %): 184 $[M]^+$ (100), 169 $[M–CH_3]^+$ (35), 153 $[M–CH_3O]^+$ (6), 76 $[M–CH_3O–PhH]^+$ (2)
2-CH$_3$C$_6$H$_4$Ph
EI-MS m/z (I, %): 168 $[M]^+$ (100), 153 $[M–CH_3]^+$ (32)
4-CH$_3$C$_6$H$_4$Ph
EI-MS m/z (I, %): 168 $[M]^+$ (100), 153 $[M–CH_3]^+$ (24)
2-Py-Ph
EI-MS m/z (I, %): 155 $[M]^+$ (100), 77 $[M–Ph–H]^+$ (9), 76 $[M–Py–H]^+$ (5)
4-BrC$_6$H$_4$Ph
EI-MS m/z (I, %): 232 $[M]^+$ (100), 153 $[M–HBr]^+$ (59), 76 $[M–HBr–Ph]^+$ (25)
4-ClC$_6$H$_4$Ph
EI-MS m/z (I, %): 188 $[M]^+$ (100), 153 $[M–HCl]^+$ (39), 76 $[M–HCl–Ph]^+$ (15)

---

[1] To carry out the test reactions one fifth amount of the reactants were used.

[2] The efficiency of the immobilized catalyst was tested in a model reaction (PhBr + $NaBPh_4$, NMP, 100 °C, 4 h) with three samples of graphite tissue with 0.5 mol.% (500 μl), 0.3 mol.% (300 μl) and 0.2 mol.% (200 μl) of the catalyst. The yields of Ph_2 were >99% in the first two cases and 88% in the third case. That is why in all consequent experiments 0.3 mol.% of Pd was used.

4-Diphenylbenzene
EI-MS m/z (I, %): 230 [M]$^+$ (100)

All these spectra are in complete agreement with the corresponding data in Wiley database.

3. Results and discussion

3.1. Pd/PPy nanocomposites

Elemental composition of the synthesized Pd/PPy materials was studied by means of a set of methods. The presence of four elements (carbon, nitrogen, oxygen and palladium) was revealed by EDX chemical analysis of Pd/PPy powders, while chlorine was not detected in our systems. These data point on the low oxidation state of polypyrrole in Pd/PPy composites, and they are in full conformity with our previous report [60] on the synthesis of the Pd/PPy material with the use of $Pd(NH_3)_4Cl_2$ as oxidant.

The results of CHNS elemental and ICP-AES analyses of Pd/PPy powders are summarized in Table 1. We have found that the decrease of the monomer to oxidant ratio in the reaction mixture leads to augmentation of the metal content in such materials: from 33.5 to 35.0 wt.% of Pd for Pd/PPy-100 and Pd/PPy-300 samples to 42.0 wt.% for Pd/PPy-10 composites.

The studies of morphology of Pd/PPy composites prepared with low initial oxidant concentration (1 mM) and various pyrrole contents (10, 100, 300 mM) in solution were carried out by TEM method after the reaction completing (Fig. 1 and Table 1). Similar morphologies were observed for samples Pd/PPy-10 and Pd/PPy-100: the polypyrrole matrix in such composite materials is represented by spherical globules, their average diameters (±confidence interval) being close to 27 ± 1 and 28 ± 1 nm, respectively (see Section 2 for details). The use of the high initial pyrrole concentration, 300 mM, resulted in increase of average diameter of polymer globules up to 62 nm (Fig. 1c). Inside all polymer globules, we have observed uniformly distributed dark spots of high contrast. These small particles are attributed to Pd component in agreement with our previous reports [59,60]. The observed diameters of *all* Pd particles in TEM images are very small, below 2.20 nm in synthesized Pd/PPy composites, and their PSD distributions are very narrow (Fig. 1d–f). One may note a slight increase of the average Pd particle size in Pd/PPy composites with increase of the monomer to oxidant ratio in the reaction mixture: 1.25 ± 0.05 nm (Pd/PPy-10), 1.40 ± 0.04 nm (Pd/PPy-100) and 1.45 ± 0.05 nm (Pd/PPy-300).

3.2. Catalytic Suzuki–Miyaura coupling of aryl halides

To be successfully used in catalysis, the composite materials must meet several key requirements:

- nano-size metal particles should be stable towards aggregation,
- they should be uniformly distributed inside the stabilizing matrix,
- the stabilizing matrix should be inert and penetrative for the reagents.

Our Pd/PPy system meets all these requirements. Moreover, as it was demonstrated in Section 3.1, it is possible to obtain particles with narrow size distributions of both PPy globules and Pd nanoparticles by varying monomer to oxidant ratio. For testing in catalytic applications, several Pd/PPy samples were prepared. The diameter of Pd nanoparticles in each sample falls within the interval of 1.2–1.4 nm. The following parameters were varied:

- The diameter of PPy spheres (27–28 nm for Pd/PPy-10 and Pd/PPy-100 and 62 nm for Pd/PPy-300).

- Palladium content in the PPy globule (33.5–35.0 wt.% for Pd/PPy-300 and Pd/PPy-100 and 42.0 wt.% for Pd/PPy-10).

Suzuki–Miyaura coupling (an interaction of aryl halides with boronic acid or tetraphenyl borate) was chosen as a test-reaction:
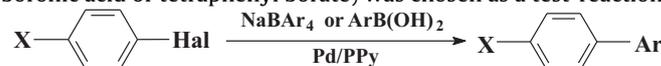
The yields of biaryls were determined using GC/MS. We started with the easier case and used organic solvents. Pd/PPy nanocomposites were suspended in acetonitrile or N-methylpyrrolidone (NMP) using ultrasonication. The initial screening of catalytic efficiency was performed using a Pd/PPy-300 sample. The comparison of two solvents (CH_3CN or NMP) and the screening of the reaction parameters are given in Table 1. For the optimization of the reaction conditions, a model reaction of PhBr with $NaBPh_4$ in acetonitrile in the presence of Na_2CO_3 as a base was chosen. The reaction time and amount of catalyst were varied. An increase in the reaction time from 2 h to 8 h at 82 °C increases the yield of biphenyl from 56% to 84%, but still 14% of the starting PhBr was detected in the reaction mixture (see entries 2–4 in Table 2). A gradual increase in the amount of the catalyst suspended in CH_3CN from 0.5 to 4 mol.% (as calculated to the starting aryl halide) does not influence the yields of biphenyl substantially (62% and 66%, respectively, see entries 1, 3, 5, 6 in Table 2). The reason for this is, probably, the low stability of the suspensions of the nanocomposite in acetonitrile. The significant part of the catalyst is precipitated soon after the ultrasonication is switched off. Contrary to CH_3CN, the suspensions of Pd/PPy in NMP are much more stable and, consequently, more efficient. Almost quantitative yield of biphenyl was obtained in 4 h in NMP with 4 mol.% of the catalyst (Table 2, entry 10). The investigation of the other model compound – mesitylboronic acid ($MesB(OH)_2$) revealed the same tendencies: an increase in the reaction time increases the yield of biaryl and NMP is much better solvent for the reaction, as compared to CH_3CN (compare entries 7, 8 and 7, 11 in Table 2). Evidently, an increase in temperature (when using NMP), in addition to the stability of dispersed catalyst, also contributes to the enhancement of the yield of the coupling product.

For estimation of the influence of geometrical parameters of the Pd/PPy nanocomposite on its catalytic efficiency, two samples were prepared, Pd/PPy-100 and Pd/PPy-300. They had similar Pd nanoparticles size distributions (see below on the absence of effects dependent on the Pd particle sizes), the same Pd content in the composite material and differ only in the diameter of the polypyrrole spheres. The comparison of the PPy nanocomposites with diameters of polymer spheres of 62 and 27–28 nm demonstrated a moderate but systematic increase in catalytic activity for smaller particles (Fig. 2). The possible reason might be transport limitations: in larger polymer spheres not all Pd works since it takes more time for the reagent to penetrate into the inner part of the sphere.

In order to explore the scope of the reactions catalyzed by this material, various boron derivatives and various aryl halides (Table 3) have been tested with the use of the catalyst with smaller diameter of PPy globules (Pd/PPy-100) which showed the best results in the preliminary screening. A variety of substituted aryl halides featuring an electron-releasing or an electron-withdrawing group were examined, the former are less active, as usual, but still the yields are not bad. Aryl chlorides are also active. 2-bromo- and 2-chloropyridines can be involved in the reaction leading to 2-phenylpyridine with high yield. Both arylboronic acids and tetraaryl borates can be used in the cross-coupling. In the latter case the addition of a base allows utilization of all four aryl groups which is in line with atom-economy strategy. Sterically hindered mesitylboronic acid gives smaller yields of biaryls, as it is usually

Table 1
Chemical composition (in wt.%) and morphological parameters (average diameters ± confidence interval, in nm) of Pd/PPy composites prepared with the use of $Pd(NH_3)_4Cl_2$ as oxidant.

System	C	N	H	Pd	Ash[a]	d(PPy)	d(Pd)
Pd/PPy-10	30.7	12.4	2.6	42.0 ± 2.1	12.3	27 ± 1	1.25 ± 0.05
Pd/PPy-100	33.0	13.3	3.4	33.5 ± 1.7	16.8	28 ± 1	1.40 ± 0.04
Pd/PPy-300	37.6	14.5	2.9	35.0 ± 1.8	10.0	62 ± 2	1.45 ± 0.05

[a] The ash of 10–17 wt.% is attributed to oxygen component in Pd/PPy composite.

observed. Besides biaryl, only certain amounts of the starting aryl halide were detected in the reaction mixtures. This means that no side reactions occur and the increase in the reaction time should increase the conversion of the aryl halide. The data given in the entries 4 and 5 (Table 3) and 2–4 (Table 2) confirm this conclusion.

Among possible concurrent reactions homo-coupling is of special importance since it often occurs in the experimental conditions discussed above. Investigation of substituted aryl halides allowed us not only to determine the activity of the catalyst but also to estimate the contribution of homo-coupling in the products formation. GC–MS analysis of the reaction mixtures obtained (using naphthalene as internal standard) revealed the presence of only traces of homo-coupling product (Ph_2) in the resulting solutions (Table 4); no Ar_2 was detected in any reaction mixture. This means that the
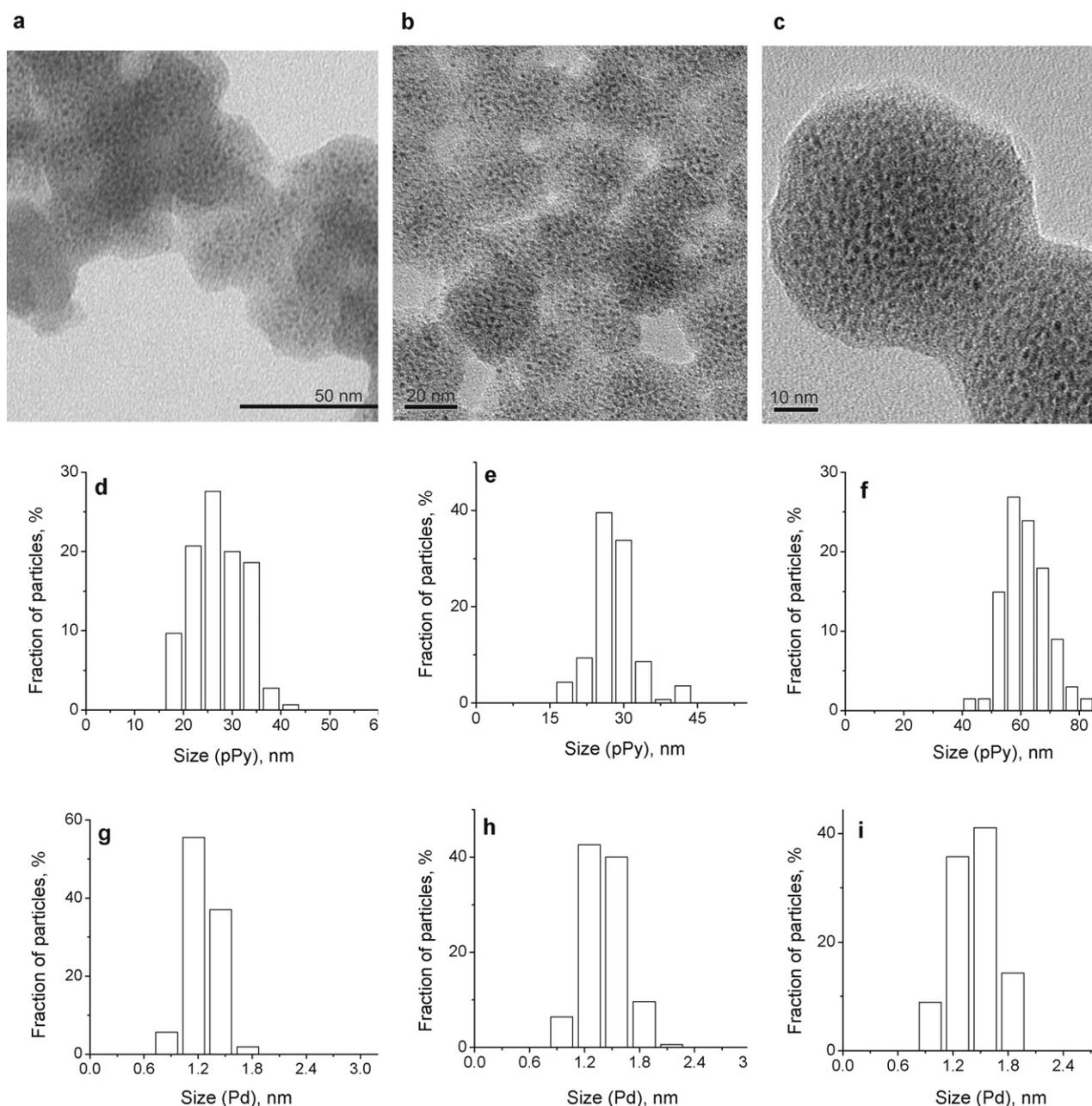

Fig. 1. TEM images of Pd/PPy composites obtained with the use of $Pd(NH_3)_4Cl_2$ as oxidant and the corresponding PSD histograms: (a, d, g) – Pd/PPy-10; (b, e, h) – Pd/PPy-100; (c, f, i) – Pd/PPy-300.

Table 2

Screening of the reaction parameters for Suzuki–Miyaura coupling (*Pd/PPy-300*, 0.1 M PhBr, 0.025 M NaBPh$_4$ or 0.1 M ArB(OH)$_2$, 0.5 M Na$_2$CO$_3$).

No.	Solvent, T (°C)	Reagent	Amount of catalyst (mol.%)	Time (h)	The yield of ArPh (%)	Starting PhBr (%)
1	CH$_3$CN, 82 °C	NaBPh$_4$	0.5	4	62	41
2	CH$_3$CN, 82 °C	NaBPh$_4$	1	2	56	47
3	CH$_3$CN, 82 °C	NaBPh$_4$	1	4	64	38
4	CH$_3$CN, 82 °C	NaBPh$_4$	1	8	84	14
5	CH$_3$CN, 82 °C	NaBPh$_4$	2	4	65	36
6	CH$_3$CN, 82 °C	NaBPh$_4$	4	4	66	33
7	CH$_3$CN, 82 °C	MesB(OH)$_2$	1	4	32	66
8	CH$_3$CN, 82 °C	MesB(OH)$_2$	1	8	64	38
9	NMP, 100 °C	NaBPh$_4$	1	4	82	19
10	NMP, 100 °C	NaBPh$_4$	4	4	97	3
11	NMP, 100 °C	MesB(OH)$_2$	1	4	69[a]	32
12	NMP, 100 °C[b]	NaBPh$_4$	1	4	68	31
13	NMP, 100 °C[b]	NaBPh$_4$	1	6	90	9

[a] 1.5% of Ph$_2$ was detected.

[b] NO$_2$C$_6$H$_4$Cl was used as a starting aryl halide and Pd/PPy-100 as a catalyst; no homo-coupling products were detected in the reaction mixture.
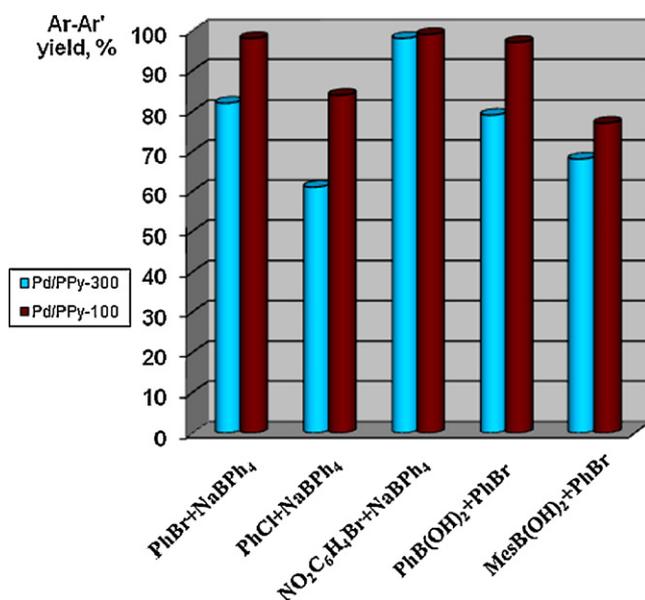
Fig. 2. Influence of the size of Pd/PPy spheres (*Pd/PPy-100 and Pd/PPy-300*) on the catalytic activity in Suzuki coupling (NMP, 100 °C, 4 h, 0.1 M ArHal, 0.025 M NaBPh$_4$ or 0.1 M ArB(OH)$_2$, 0.5 M Na$_2$CO$_3$, 1 mol.% of Pd).

Table 3

Various aryl halides and boron derivatives in Suzuki–Miyaura coupling (0.1 M ArHal, 0.025 M NaBPh$_4$ or 0.1 M ArB(OH)$_2$, 0.5 M Na$_2$CO$_3$, NMP, Pd/PPy-100, 1 mol.% Pd).

	ArHal	Reagent	t (h)	Ar′–Ar yield (%)	ArHal (%)
1	PhI	NaBPh$_4$	4	>99	–
2	PhBr	NaBPh$_4$	4	98[a]	1
3	PhBr[b]	NaBPh$_4$	4	95	2
4	PhCl	NaBPh$_4$	4	63	39
5	PhCl	NaBPh$_4$	6	84	16
6	4-NO$_2$C$_6$H$_4$Br	NaBPh$_4$	4	>99	–
7	4-NO$_2$C$_6$H$_4$Cl	NaBPh$_4$	6	90	9
8	4-CH$_3$OC$_6$H$_4$Br	NaBPh$_4$	4	71	31
9	4-CH$_3$C$_6$H$_4$Br	NaBPh$_4$	4	84	15
10	4-CH$_3$C$_6$H$_4$Br[b]	NaBPh$_4$	4	83	15
11	2-CH$_3$C$_6$H$_4$Br	NaBPh$_4$	4	39	63
12	2-Bromopyridine	NaBPh$_4$	4	96	6
13	2-Chloropyridine	NaBPh$_4$	6	81	22
14	PhBr	PhB(OH)$_2$	4	98	2
15	PhBr	MesB(OH)$_2$	4	77	22
16	4-IC$_6$H$_4$Br	NaBPh$_4$	4	11 (44% PhC$_6$H$_4$Ph)	41
17	4-IC$_6$H$_4$Cl	NaBPh$_4$	6	91 (4% PhC$_6$H$_4$Ph)	7

[a] The isolated yield was 90%.

[b] Pd/PPy-10 was used as a catalyst.

catalytic process is highly selective in favor of the cross-coupling route.

The investigation of two dihalobenzenes revealed that in case of p-IC$_6$H$_4$Cl it is possible to substitute one of halogen atoms (iodine) for phenyl group selectively (only 4% of PhC$_6$H$_4$Ph is formed when p-IC$_6$H$_4$Hal: NaBPh$_4$ molar ratio is 4:1). When the halogen activities differ not so dramatically (in case of p-IC$_6$H$_4$Br) the dominant product in the applied reaction conditions was PhC$_6$H$_4$Ph, in spite of deficiency of NaBPh$_4$ which was taken in ¼ molar ratio respectively to aryl dihalide, almost one half of which stayed unreactive. The yield of p-PhC$_6$H$_4$Br was only 11%.

The next step of our investigation was a comparison of catalytic activity of two samples (Pd/PPy-10 and Pd/PPy-100) having almost identical diameters of PPy spheres (27–28 nm), with close sizes of Pd nanoparticles (the size distribution graphs are given in Fig. 1d and e) but with different Pd contents (42 and 35 wt.%). Two different substrates were examined in the test reaction with NaBPh$_4$: phenyl bromide and p-tolyl bromide. It turned out that the yields of biaryls are almost equal (compare entries 2, 3 and 9, 10 in Table 3) if the total amount of the Pd catalyst used in the reaction is the same (1 mol.% in both cases). In other words, the higher is the Pd content inside polypyrrole spheres, the less amount of catalyst is necessary to obtain the same yield of the biaryl. This observation supports the expectation that small PPy spheres are completely penetrable for the reagents and all Pd nanoparticles are active.

When dealing with Pd-containing catalyst, an estimation of Pd leaching is very important, both from a mechanistic point of view and to prevent losses of precious metal. We performed a special investigation to clarify this aspect. For this aim a set of leaching tests was performed as described in [63]. The reaction NO$_2$C$_6$H$_4$Br + NaBPh$_4$ was selected as a model for leaching tests. The reaction was performed in NMP as described in Experimental but it was interrupted after 30 min of heating; the catalyst was centrifuged (15,000 rpm, g-force = 20,238 rcf), the solution was decanted from the solid precipitate and divided in two portions. One was analyzed using the standard catalytic procedure,

Table 4

The estimation of relative contribution of homo-coupling products (0.1 M ArHal, 0.025 M NaBPh$_4$, 0.5 M Na$_2$CO$_3$, NMP, Pd/PPy-100, 1 mol.% Pd).

ArHal	ArPh yield (%)	ArHal (%)	Ph$_2$ (%)
4-CH$_3$OC$_6$H$_4$Br	71	31	2
4-CH$_3$C$_6$H$_4$Br	84	15	1
2-CH$_3$C$_6$H$_4$Br	39	63	2
4-NO$_2$C$_6$H$_4$Br	>99	–	–
4-NO$_2$C$_6$H$_4$Cl	90	9	–
4-IC$_6$H$_4$Br	11 (44 PhC$_6$H$_4$Br)	41	–
4-IC$_6$H$_4$Cl	91 (4-PhC$_6$H$_4$Cl)	7	<0.5

Table 5
The recycling of the Pd/PPy-100 catalyst (NMP, 100 °C, 0.1 M PhBr, 0.025 M NaBPh$_4$, 0.5 M mol Na$_2$CO$_3$, 0.3 mol.% Pd).

Immobilization conditions	The yield of Ph$_2$, %		
	I run	II run	III run
NMP, us[a]	>99 (4 h)	74 (4 h)	71 (6 h)
CH$_3$CN, us[a]	>99 (4 h)	72 (4 h)	70 (6 h)

[a] Ultrasonication.

additional portion of the base (0.5 mmol Na$_2$CO$_3$) was added to the other and it was treated further for 3 h under the standard reaction conditions as described in the Experimental and then analyzed. GC–MS data obtained for the first (treated) and the second (non-treated) portions of solution were almost identical: NO$_2$C$_6$H$_4$Ph (53%), NO$_2$C$_6$H$_4$Br (46%) for the portion corresponding to 30 min conversion and NO$_2$C$_6$H$_4$Ph (52%), NO$_2$C$_6$H$_4$Br (46%) after additional treatment of the filtrate.

This observation is radically different from literature results [63,64] where a significant amount of Pd was found in the solution fraction after ultrafiltration or centrifugation experiments. In [63] it has been demonstrated that the catalytic activity was mainly due to leached Pd species. In [64] the solution turned out to be catalytically much more active than the deposited fraction, with respect to the subsequent reaction run. On the contrary, the above experimental data for our system do not show any noticeable catalytic activity of the solution fraction. Thus, one can conclude that the amount of solute Pd in the centrifuged solution for our system is probably too small to observe its catalytic activity, i.e. the presence of Pd/PPy composite is necessary for catalysis of these reactions. This specific feature of our system might be related to a stronger structure-forming properties of chemically synthesized PPy globules compared e.g. to polymeric micelles.

3.3. The recycling of Pd/PPy catalyst

The recycling of the catalyst is a very important aspect for its application prospects. Unfortunately, reuse of Pd/PPy catalyst in solution turned out to be less efficient (the yield of biaryl decreases in the second run from 80% to 17% for coupling of PhBr with NaBPh$_4$). The reason is not clear yet and further investigations are in progress. On the other hand, experiments with immobilized catalyst turned out to be rather promising. We immobilized Pd/PPy nanocomposite (Pd/PPy-100) on the graphite support by the deposition of Pd/PPy suspension in NMP or acetonitrile. Thus modified graphite support was used in a test Suzuki–Miyaura coupling of PhBr with NaBPh$_4$ (NMP, 100 °C, 4 h). As follows from Table 4, at least three consequent reactions with new portions of reagents are possible, with only small decrease in the catalytic activity. After each run the graphite support with the immobilized catalyst was washed with NMP and used for the next catalytic reaction without any additional treatment. Comparison of the yields of the coupling product in three subsequent runs for the catalysts immobilized using freshly prepared suspensions in NMP or in acetonitrile (Table 5) shows that the nature of the solvent used for the immobilization of the catalyst is not important, contrary to the solvent in which the reaction is performed (in both cases it was NMP). If the reaction with the immobilized catalyst is performed in acetonitrile, the yields of the coupling product are lower.

3.4. Suzuki–Miyaura coupling in water

Organic synthesis is routinely performed in non-aqueous solvents. In contrast, the nature, in its unique way, uses water for enzymatic transformations of all organic substrates. Current emphasis of green chemistry underscores the need for developing

Table 6
The yields of ArPh in water (_Pd/PPy-100_, 4 h, 100 °C, 0.1 M ArHal, 0.025 M NaBPh$_4$, 0.5 M Na$_2$CO$_3$, 0.3 mol.% Pd).

ArHal	Time (h)	ArPh (%)	ArHal (%)
PhI	4	>99	–
PhI	4[a]	92	7
PhBr	4	>99	–
PhCl	6	72	26
4-NO$_2$C$_6$H$_4$Br	5	96	2
4-CH$_3$C$_6$H$_4$Br	6	79	19
4-CH$_3$OC$_6$H$_4$Br	7	74	22

[a] Pd/PPy-300 was used as a catalyst.

catalytic reactions, especially involving precious metals as mediators, in aqueous medium.

Suspensions of Pd/PPy nanocomposites in water (which passed through the sedimentation stage, contrary to the relatively stable initial colloid solution) exhibit fast precipitation. However, Pd/PPy nanocomposites immobilized on the graphite support turned out to work very efficiently in water, thus making the process ecologically friendly. The reactions were performed at 100 °C in argon atmosphere, the reaction mixture was intensively stirred. The results obtained are given in Table 6. Comparison of Pd/PPy activity in water and organic solvents reveals (Tables 3 and 6) that the yields of biaryls are similar. In some cases a small decrease in the yields in water is observed but in the context of green chemistry it seems not very significant.

4. Conclusion

Palladium/polypyrrole nanocomposites synthesized via redox reaction of a Pd salt and pyrrole, have been tested as catalysts in Suzuki–Miyaura coupling and turned out to be very efficient. Aryl iodides, bromides and chlorides are active. The reaction can be performed both in organic solvents and in water, thus making the process ecologically friendly. The recycling of the catalyst is possible if its particles are immobilized at graphite tissue.

Our operationally simple synthesis procedure results in the Pd/PPy nanocomposite in the form of spherical polypyrrole globules with relatively uniform sizes. Another component, Pd, is distributed inside each globule as nanoparticles, also with close sizes. Both these geometrical parameters may be varied by means of synthesis conditions, the average polymer size being from 27 to 62 nm while the size of metal nanoparticles may be from 1.25 to 1.45 nm.

The comparison of two different samples revealed that Pd/PPy nanocomposite with the diameter of PPy spheres of about 30 nm is more efficient in catalysis, as compared to the sample with bigger PPy spheres (about 60 nm), due to transport limitations for reagents inside the polypyrrole sphere in the latter case. For palladium/polypyrrole nanocomposites with the small diameter of PPy sphere, which are easily penetrable for the reagents and in which all Pd nanoparticles are active, Pd content in polypyrrole spheres does not influence the yield of biaryls. As a consequence, the more is the Pd content in polypyrrole spheres, the less amount of catalyst is necessary to obtain the same yield of biaryl.

Acknowledgements

References

[1] A. Suzuki, in: D. Astruc (Ed.), Modern Arene Chemistry, Wiley-VCH, Weinheim, 2003, pp. 53–106.
[2] P.J. Hajduk, M. Bures, J. Prastgaard, S.W. Fesik, J. Med. Chem. 43 (2000) 3443–3447.
[3] A. De Mejere, F. Diederich, Metal-catalyzed Cross-coupling Reactions, Wiley-VCH, Weinheim, 2004.
[4] N. Miyaura, A. Suzuki, Chem. Rev. 95 (1995) 2457–2483.
[5] J. Hassan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, Chem. Rev. 102 (2002) 1359–1469.
[6] G.A. Molander, B.J. Biolatto, Org. Chem. 68 (2003) 4302–4314.
[7] R. Singh, M.S. Viciu, N. Cramareva, O. Navarro, S.P. Nola, Org. Lett. 7 (2005) 1829–1832.
[8] J.H. Kim, J.W. Kim, M. Shokouhimehr, Y.S. Lee, J. Org. Chem. 70 (2005) 6714–6720.
[9] F.E. Hahn, M.C. Jankhe, T. Pape, Organometallics 26 (2007) 150–154.
[10] C. Baleizao, A. Corna, H. Garcia, A. Leyva, Chem. Commun. (2003) 606–607.
[11] F. Zeng, Z. Yu, J. Org. Chem. 71 (2006) 5275–5277.
[12] D. Astruc, F. Lu, J.R. Aranzaes, Angew. Chem. Int. Ed. 44 (2005) 7852–7872.
[13] G. Schmid, Nanoparticles, Wiley-VCH, Weinheim, 2004.
[14] M.A. El-Sayed, Acc. Chem. Res. 34 (2001) 257–264.
[15] T. Yonezawa, N. Toshima, in: H.S. Nalwa (Ed.), Advanced Functional molecules and Polymers, Accelerated Development (Chapter 3), Overseas Publishers Association, Amsterdam, 2001.
[16] J. Grunes, J. Zhu, G.A. Somorjai, Chem. Commun. (2003) 2257–2260.
[17] Y. Kitamura, S. Sako, T. Udzu, A. Tsutsui, T. Maegawa, H. Monguchi, H. Sajiki, Chem. Commun. 506 (2007) 9–5071.
[18] T. Maegawa, Y. Kitamura, S. Sako, T. Udzu, A. Sakurai, A. Tanaka, Y. Kobayashi, K. Endo, U. Bora, T. Kurita, A. Kozaki, Y. Monguchi, H. Sajiki, Chem. Eur. J. 13 (2007) 5937–5943.
[19] H. Sakurai, T. Tsukuda, T. Hirao, J. Org. Chem. 67 (2002) 2721–2722.
[20] G. Artok, H. Bulut, Tetrahedron Lett. 45 (2004) 3881–3884.
[21] C. Ramarao, S. Ley, S. Smith, I. Shirley, N. DeAlmeidac, Chem. Commun. 113 (2002) 2–1133.
[22] Y. Monguchi, Y. Fujita, K. Endo, S. Takao, M. Yoshimura, Y. Takagi, T. Maegawa, H. Sajiki, Chem. Eur. J. 15 (2009) 834–837.
[23] M. Zhang, W. Zhang, J. Phys. Chem. C 112 (2008) 6245–6252.
[24] S. Sawoo, D. Srimani, P. Dutta, R. Lahiri, A. Sarkar, Tetrahedron 65 (2009) 4367–4374.
[25] Y. Lu, A. Wittemann, M. Ballauff, Macromol. Rapid Commun. 30 (2009) 806–815.
[26] F. Wen, W. Zhang, G. Wei, Y. Wang, J. Zhang, M. Zhang, L. Shi, Chem. Mater. 20 (2008) 2144–2150.
[27] L. Wang, Chin. J. Chem. 24 (2006) 770–774.
[28] X. Jiang, G. Wei, X. Zhang, W. Zhang, P. Zheng, F. Wen, L. Shi, J. Mol. Catal. A: Chem. 277 (2007) 102–106.
[29] K.S. Sivudu, N.M. Reddy, N.N. Prasad, K.M. Raju, Y.M. Mohan, J.S. Yadav, D. Shailaja, J. Mol. Catal. A: Chem. 295 (2008) 10–17.
[30] C. Desmarets, R. Omar-Amrani, A. Walcarius, J. Lambert, B. Champagne, Y. Fort, R. Schneider, Tetrahedron 64 (2008) 372–381.
[31] P. Zheng, W. Zhang, J. Catal. 250 (2007) 324–330.
[32] S.E. Lyubimov, A.A. Vasil'ev, A.A. Korlyukov, M.M. Ilyin, S.A. Pisarev, V.V. Matveev, A.E. Chalykh, S.G. Zlotin, V.A. Davankov, React. Funct. Polym. 69 (2009) 755–758.
[33] C.R. LeBlond, A.T. Andrews, Y. Sun, R. Sowa, Org. Lett. 13 (2001) 1555–1557.
[34] R.G. Heidenreich, K. Kohler, J.G.E. Krauter, J. Pietsch, Synlett (2002) 1118–1122.
[35] I. Baxendale, C. Griffiths-Jones, S. Ley, G. Tranmer, Chem. Eur. J. 12 (2006) 4407–4416.
[36] H. Hagio, M. Sugiura, S. Kobayashi, Org. Lett. 8 (2006) 375–378.
[37] M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, Adv. Synth. Catal. 352 (2010) 33–79.
[38] R. Narayanan, M.A. El-Sayed, J. Am. Chem. Soc. 125 (2003) 8340–8347.
[39] Y. Li, E. Boone, M.A. El-Sayed, Langmuir 18 (2002) 4921–4925.
[40] F. Durap, M. Rakap, M. Aydemir, S. Ozkar, Appl. Catal. A: Gen. 382 (2010) 339–344.
[41] Y.M.A. Yamada, K. Takeda, H. Takahashi, S. Ikegami, J. Org. Chem. 68 (2003) 7733–7741.
[42] Y. Li, M.A. El Sayed, J. Phys. Chem. B 105 (2001) 8938–8943.
[43] R. Narayanan, M.A. El-Sayed, J. Phys. Chem. B 108 (2004) 8572–8580.
[44] M. Pittelkow, K. Moth-Poulsen, U. Boas, J.B. Christensen, Langmuir 19 (2003) 7682–7684.
[45] M. Ooe, M. Murata, T. Mizugaki, K. Ebitani, K. Kaneda, Nano Lett. 2 (2002) 999–1002.
[46] B.J. Gallon, R.W. Kojima, R.B. Kaner, P.L. Diaconescu, Angew. Chem. Int. Ed. 46 (2007) 7251–7254.
[47] M.L. Kantan, M. Roy, S. Roy, B. Sreedhar, S.S. Madhavendra, B.M. Choudary, R.L. De, Tetrahedron 63 (2007) 8002–8009.
[48] B.M. Choudary, M. Roy, S. Roy, M.L. Kantan, B. Sreedhar, K.V. Kumar, Adv. Synth. Catal. 348 (2006) 1734–1742.
[49] R. Chepuri, K. Rao, D.C. Trivedi, Catal. Commun. 7 (2006) 662–668.
[50] G. Chen, Z. Wang, T. Yang, D. Huang, D. Xia, J. Phys. Chem. B 110 (2006) 4863–4868.
[51] N. Cioffi, L. Torsi, I. Losito, L. Sabbatini, P.G. Zambonin, T. Bleve-Zacheo, Electrochim. Acta 46 (2001) 4205–4211.
[52] I. Becerik, F. Kadirgan, Synth. Met. 124 (2001) 379–383.
[53] K.-M. Mangold, F. Meik, K. Juttner, Synth. Met. 144 (2004) 221–227.
[54] S.W. Huang, K.G. Neoh, C.W. Shih, D.S. Lim, E.T. Kang, H.S. Han, K.L. Tan, Synth. Met. 96 (1998) 117–122.
[55] G. Schmid, L.F. Chi, Adv. Mater. 10 (1998) 515–526.
[56] A. Drelinkiewicz, A. Waksmundzki, W. Makowski, J.W. Sobczak, A. Krol, A. Zieba, Catal. Lett. 94 (2004) 143–155.
[57] L. Li, E.T. Kang, K.G. Neoh, J. Nanosci. Nanotechnol. 6 (2006) 2571–2575.
[58] M.C. Henry, C.-C. Hsueh, B.P. Timko, M.S. Freund, J. Electrochem. Soc. 148 (2001) D155–D162.
[59] S.V. Vasilyeva, M.A. Vorotyntsev, I. Bezverkhyy, E. Lesniewska, O. Heintz, R. Chassagnon, J. Phys. Chem. C 112 (2008) 19878–19885.
[60] V.A. Zinovyeva, M.A. Vorotyntsev, I. Bezverkhyy, D. Chaumont, J.-C. Hierso, Adv. Funct. Mater. 21 (2011) 1064–1075.
[61] S. Fujii, S. Matsuzawa, Y. Nakamura, A. Ohtaka, T. Teratani, K. Akamatsu, T. Tsuruoka, H. Nawafune, Langmuir 26 (2010) 6230–6239.
[62] P. Brown, M.F. Mahon, K.C. Molloy, J. Chem. Soc., Dalton Trans. (1992) 3503–3510.
[63] L. Joucla, G. Cusati, C. Pinel, L. Djakovitch, Appl. Catal. A: Gen. 360 (2009) 145–153.
[64] I.P. Beletskaya, A.N. Kashin, I.A. Khotina, A.R. Khokhlov, Synlett (2008) 1547–1552.