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ARTICLE TYPE

Palladium Nanoparticles Supported on Ionic Liquid Modified, Magnetic Nanobeads – Recyclable, High-Capacity Catalysts for Alkene Hydrogenation

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Magnetic hybrid materials have been synthesized as recyclable catalysts for alkene hydrogenation. The materials consist of magnetic nanobeads functionalized with imidazolium-based ionic liquids and optional polymer shells. Palladium nanoparticles (NPs) were synthesized on the surface of these supports by two different methods and evaluated as catalysts for alkene hydrogenation. Deposition of palladium(0) onto the magnetic nanobeads by microwave decomposition of $Pd_2(dba)_3{\cdot}CHCl_3$ leads to more efficient catalysts than the reduction of a Pd(II) precursor. Reactivity, recycling ability and ease of separation of the catalysts are compared. A hybrid material without polymer shells and a quite flexible ionic liquid was identified as the most promising for stabilizing Pd NPs resulting in a catalyst that shows high activity (TOF up to 330 h^{-1}), good recycling ability, and minor metal leaching into the product. Notably, the activity of this catalyst increases with an enhanced Pd loading, contrasting related systems for which a decrease of activity is observed due to agglomeration. Therefore, this recyclable, high-capacity system is especially attractive for large-scale applications, requiring just a minimal amount of supporting material for the recycling of expensive Pd that is readily achieved by magnetic decantation.

Introduction

Pd-catalyzed reactions are widely applied in today's organic synthesis.[1] The variety of reactions is enormous ranging from alkylations, oxidations and carbonylations to coupling reactions or hydrogenations. Especially palladium promoted hydrogenations[2] and coupling reactions[3] play a very important role in pharmaceutical, agrochemical and fine chemical industries. Therefore, the reuse and recycling of palladium and other expensive metals like platinum or gold is a major concern in organic chemistry and especially in industry.[4]

In recent years, the application of palladium nanoparticles became of strong interest owing to their extremely high surface to volume ratio compared to the bulk phase. Metal nanoparticles exceed the catalytic activity of the bulk metal by far, and consequently, the use of nanoparticles as catalysts can reduce the amount of metal needed in organic synthesis. However, aggregation of the nanomaterial to the bulk phase often causes problems during catalysis. To overcome these difficulties, nanoparticles can be stabilized by their immobilization on solid supports[5,6] or their coating with ionic liquids (ILs).[7] Additionally a combination of both strategies is also possible using supported ionic liquids (SILs).[8]

Ionic liquids can stabilize nanoparticles electrostatically or by coordination of the metal.[9] During recent years, palladium NPs were frequently stabilized by ILs applying either sole ILs,[10] supported ionic liquid phases (SILPs)[11] or ILs covalently supported on polymers,[12] silica,[13] and carbon nanotubes.[14] Activity and recycling ability of these Pd NPs is often significantly increased. However, the ease of recycling often suffers from the need of cost- and time-intensive filtration methods. One concept to solve this problem is the application of magnetic supports allowing the recovery of Pd NPs by simple magnetic decantation.[15] We recently reported Pd NPs deposited on magnetic carbon coated cobalt nanoparticles as catalysts for alkene hydrogenation. However, these catalysts suffered from agglomeration of the Pd NPs on the carbon surface of the magnetic support over time, allowing only small loadings of Pd (<1 wt%) to achieve high activity. Moreover, a significant decrease of activity of these catalysts was observed upon recycling and reuse.[16] Hence, the overall aim of this study is to generate a high-loading Pd nanocatalyst by the introduction of stabilizing IL groups and, furthermore, to take advantage of a magnetic support allowing simple magnetic separation.

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† Electronic Supplementary Information (ESI) available: Materials and methods, nomenclature of the nanobeads, ICP-OES analysis, TEM pictures, IR, GC, XRD and NMR data. See DOI: 10.1039/b000000x/

Herein, we describe the synthesis of novel hybrid systems consisting of a magnetic core (carbon-coated Co nanobeads), covalently attached imidazolium ILs and Pd nanoparticles immobilized on the surface. The attachment of ILs on the particles was performed in three different ways: (i) directly on the surface of the nanobeads; (ii) on a polymer coating the nanobeads; (iii) on a flexible spacer which is attached to the nanoparticles (Fig. 1). Our study includes the synthesis and characterization of the novel hybrid materials, comparison of different Pd sources for the nanoparticle synthesis, influence of the different materials on activity/recycling ability, leaching tests, and recycling studies.

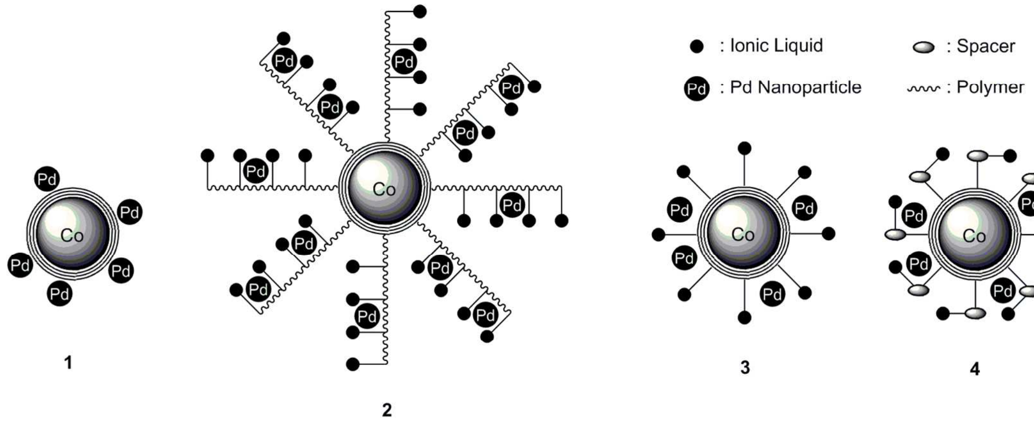
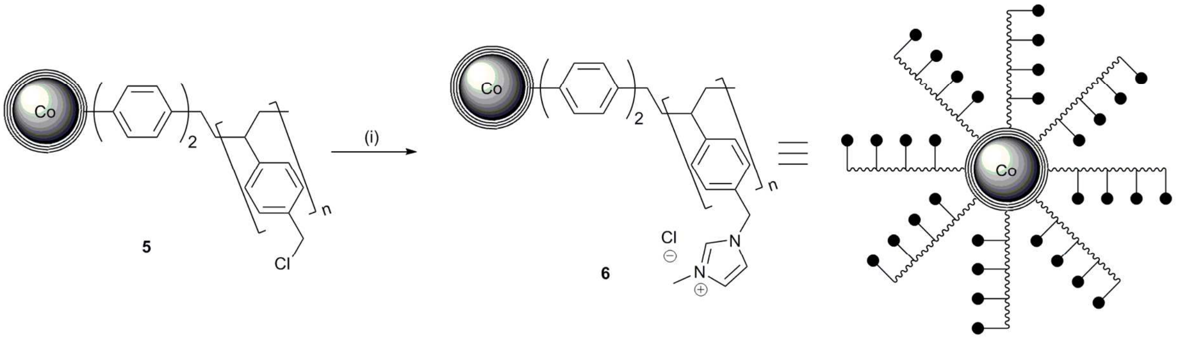


Fig. 1 Novel Pd@Co/C hybrid systems: Pd@Co/C **1**,[22] Pd@PS-IL@Co/C **2**, Pd@Bz-IL@Co/C **3**, and Pd@Spacer-IL@Co/C **4**.



Scheme 1 Synthesis of PS-IL@Co/C **6** from poly(benzyl-chloride)styrene functionalized Co/C NPs **5**. Reagents and conditions: (i) methyl imidazole, toluene, microwave heating, 150 °C, 30 min.

Results and discussion

Carbon-coated cobalt nanobeads (Co/C) were used as magnetic support for our studies. The highly magnetic material (158 emu/g) is synthesized on large scale via reducing flame spray pyrolysis (> 30 g/h).[17] The graphene-like coating of the beads provides high stability against acids, air/moisture, high temperature and, furthermore, enables facile functionalization of the surface analogous to carbon nanotubes (CNTs). We successfully demonstrated covalent as well as non-covalent methods to immobilize catalysts,[18] scavengers,[19] reagents[19,20] or fluorescent dyes[21] on the graphene-like surface. While the loading via direct immobilization is limited to ≈ 0.2 mmol/g,[18] the introduction of polymer-shells can lead to a higher loading of up to 3 mmol/g.[22] This reduces the amount of required support and can even lead to higher activities due to a dendritic-like effect.[22b] Most recently, we reported the deposition of Pd nanoparticles on the carbon surface of Co/C NPs.[16] This novel material (Fig. 1, **1**) showed extremely high activity in alkene hydrogenation reactions (TOF up to 11095 h^{-1}) and exceeded other Pd catalysts, especially common Pd/C catalysts, by far. These catalysts could be reused for six consecutive runs, however, a loss of activity was observed from the second run indicating agglomeration of the nanoparticles deposited on the Co/C support. Furthermore, a quite large amount of supporting material is needed due to the necessity of low palladium loading onto the support in order to achieve high catalytic activities.

Synthesis of Co/C-supported ionic liquids

Since ILs are known to effectively stabilize metal nanoparticles through electrostatic interactions and coordination of the metal,[8] Co/C-supported ILs could serve as a stabilizing material for Pd nanoparticles and therefore enhance the recycling ability of Pd catalysts. Hence, we synthesized different Co/C nanobeads with ILs covalently bound to the surface: PS-IL@Co/C **6** having a polymer shell between the Co/C beads and the IL (Scheme 1), Bz-IL@Co/C **9** bearing an IL directly on the Co/C surface, and Spacer-IL@Co/C **12**, having a small, flexible spacer between the Co/C core and the IL (Scheme 2).

The synthesis of PS-IL@Co/C **6** started from poly(benzylchloride)styrene functionalized Co/C NPs **5** (3.1 mmol/g chloride)[22] via microwave reaction with methyl imidazole (Scheme 1). The loading of IL on the surface was determined by elemental micro-

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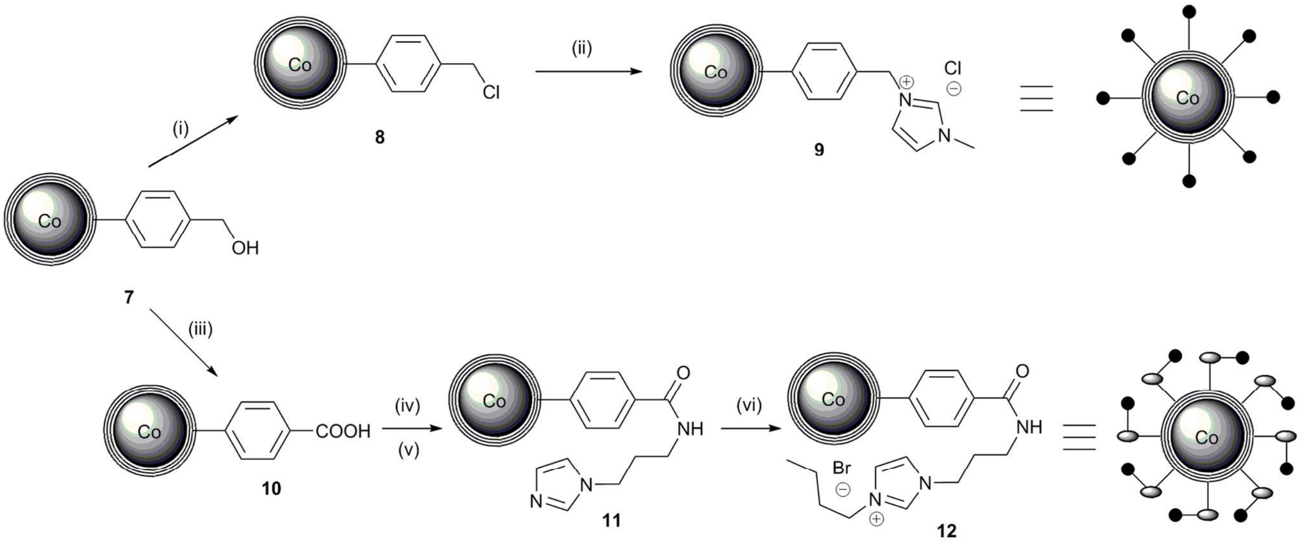
analysis as 2.1 mmol/g, indicating 88% displacement of chloride with the imidazolium moiety.



Scheme 2 Synthesis of Bz-IL@Co/C **9** and Spacer-IL@Co/C **12** from benzyl-alcohol functionalized Co/C NPs **7**. Reagents and conditions: (i) $SOCl_2$, DMF, DCM, 0 °C → rt, 12 h; (ii) methyl imidazole, toluene, microwave heating, 150 °C, 30 min; (iii) $KHSO_5$, $MeCN/H_2O$, reflux, 24 h; (iv) $SOCl_2$, reflux, 24 h; (v) amino propyl imidazole, 120 °C, 24 h; (vi) bromo butane, 80 °C, 24 h.

Table 1 Synthesis of Pd@PS-IL@Co/C **2**, Pd@Bz-IL@Co/C **3** and Pd@Spacer-IL@Co/C **4** with varying Pd loadings.

Entry	Index	Pd source	Method of synthesis[a]	Mass ratio[b]	Pd incorporated [%][c]	Pd loading [mmol/g][c]	Pd content [wt%][c]
1	**2a**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:1	56	2.6	28
2	**2b**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.6	64	2.3	24
3	**2c**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.2	74	1.2	12
4	**2d**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.1	69	0.6	6
5	**2e**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.01	81	0.08	0.8
6	**2f**	Na_2PdCl_4	B	1:1	100	4.8	50
7	**2g**	Na_2PdCl_4	B	1:0.6	90	3.2	34
8	**2h**	Na_2PdCl_4	B	1:0.2	85	1.3	14
9	**3a**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:1	91	4.3	45
10	**3b**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.6	83	2.9	31
11	**3c**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.2	100	1.6	17
12	**3d**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.1	86	0.7	8
13	**3e**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.01	96	0.09	0.9
14	**4a**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:1	86	4.0	43
15	**4b**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.6	90	3.2	34
16	**4c**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.2	81	1.3	14
17	**4d**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.1	90	0.8	8
18	**4e**	$Pd_2(dba)_3{\cdot}CHCl_3$	A	1:0.01	100	0.09	1

[a] Method A: heating under microwave irradiation; method B: reduction with H_2. [b] Mass ratio of NPs to Pd employed in the synthesis. [c] Determined by ICP-OES.

Bz-IL@Co/C **9** and Spacer-IL@Co/C **12** were synthesized from benzyl-alcohol functionalized Co/C NPs **7** (Scheme 2).[17a] Benzyl-chloride modified Co/C NPs **8** were generated by substitution reaction of **7** (0.11 mmol/g benzyl alcohol) with $SOCl_2$. To obtain Bz-IL@Co/C **9**, **8** was subsequently heated under microwave irradiation with methyl imidazole. The loading of IL on the surface was 0.09 mmol/g, reflecting 83% of the maximum loading. Spacer-IL@Co/C **12** were synthesized by oxidation of **7**, followed by amide formation of the benzoic acid functionalized Co/C NPs **8** with 1-(3-aminopropyl)imidazole. After substitution with 1-bromobutane following the lead of Lee et al.[14] Spacer-IL@Co/C **12** were generated with a loading of 0.05 mmol/g, reflecting 47% of the maximum loading after three steps.

Synthesis of Pd@IL@Co/C with varying Pd loadings

In a second step palladium NPs were deposited on IL modified Co/C NPs (IL@Co/C). Different mass ratios of palladium to IL@Co/C were used in the synthesis to determine an effect of the palladium loading on the catalytic activity.

The deposition of palladium NPs on IL@Co/C was carried out using two different methods. Urriolabeitia *et al.*[6] reported a procedure to immobilize palladium NPs on CNTs using

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$Pd_2(dba)_3{\cdot}CHCl_3$ as Pd(0) source in dry toluene under microwave heating in just two minutes. Alternatively Lee *et al.*[14] reported a procedure reducing Na_2PdCl_4 under hydrogen atmosphere to deposit palladium NPs on ionic liquid functionalized CNTs.

The tendency of $Pd_2(dba)_3{\cdot}CHCl_3$ to rapidly form Pd NPs upon decomposition was recently intensely discussed by the group of Ananikov.[23] The nanoparticles are not just formed under heating conditions, but also at room temperature upon storing for longer time. The amount of decomposed complex furthermore depends on the commercial source or the applied method of synthesis, respectively. The nanoparticles formed at room temperature were found to have a size of 60-200 nm with minor amounts of smaller ones (10-20 nm). The complex we used for our studies was commercially available (see supporting information), which was determined by the method of Ananikov to contain 68% of $Pd_2(dba)_3{\cdot}CHCl_3$ along with Pd-NPs, being in good agreement with the results reported for commercial sources.[23]

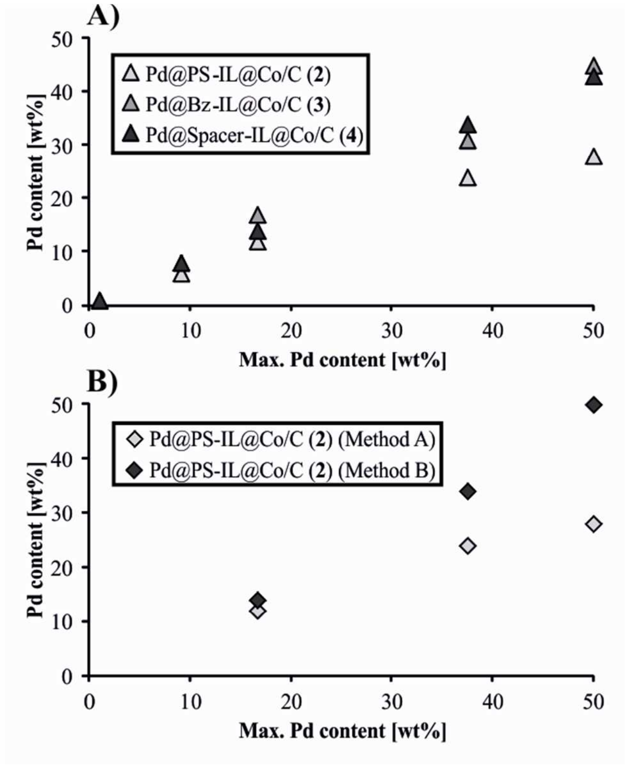

Fig. 2 Comparison of Pd incorporation depending on A) the support (Method A) and B) the deposition method.

Applying the two described methods we synthesized catalysts with varying palladium loadings for PS-IL@Co/C **6**, Bz-IL@Co/C **9**, and Spacer-IL@Co/C **12** (Table 1). For PS-IL@Co/C **6** dry toluene was replaced by a mixture of dry toluene/MeOH in order to increase the swelling of the polystyrene coating. The amount of palladium used in the synthesis is given as the mass ratio of ionic-liquid functionalized Co/C NPs to Pd. E.g. a mass ratio of 1:0.1 means 100 mg NPs to 10 mg Pd. The Pd content for the resulting hybrid materials was determined by ICP-OES analysis.

Thus, hybrid materials were obtained with Pd contents ranging from 0.8-50 wt% (Pd@PS-IL@Co/C, **2a-h**), 0.9-45 wt% (Pd@Bz-IL@Co/C, **3a-e**) and 1-43 wt% (Pd@Spacer-IL@Co/C, **4a-e**). The palladium incorporation into the polystyrene coated platforms PS-IL@Co/C **6** is not as effective as the deposition on Bz-IL@Co/C **9** and Spacer-IL@Co/C **12** (Fig. 2A). Especially with an increasing amount of palladium used in the synthesis the gap of Pd incorporation between polymeric and non-polymeric NPs is increasing. Furthermore, the results with PS-IL@Co/C **6** show that the palladium incorporation starting from a Pd(II) source is much more effective than starting from a Pd(0) source (Fig. 2B). This is probably due to the higher polarity of the solvent used in the synthesis, being consistent with the synthesis of **2** starting from $Pd_2(dba)_3{\cdot}CHCl_3$, where a solvent mixture of dry toluene/MeOH leads to a better swelling and dispersibility than in pure toluene.

The novel hybrid materials were characterized using transmission electron microscopy (TEM) and x-ray powder diffraction (XRD) techniques. TEM pictures clearly show the existence of Pd nanoparticles (5-15 nm) on the surface of the Co/C nanobeads (see supporting information), while XRD proves the presence of Pd and Co both in oxidation state ±0: For Co(0) the characteristic peaks at 2θ of 44.25°, 51.5°, and 75.81° and for Pd the characteristic peaks at 2θ of 40.06°, 46.49°, 67.94°, and 81.85° were observed (see supporting information). However, at Pd contents lower than 10 wt% the characteristic Pd(0) peaks could not be distinguished from the background any longer.

As the nanoparticles we observed on the surface of the supports are between 5-15 nm, we can conclude that Pd NPs which were already present in the $Pd_2(dba)_3{\cdot}CHCl_3$ complex (10-200 nm)[23] were crushed under the high temperature microwave conditions applied.

Hydrogenation of *trans*-stilbene

To evaluate the activity of the different catalysts and the effects of varying Pd loading the hydrogenation of *trans*-stilbene with molecular hydrogen was chosen as test reaction. The amount of catalyst was adjusted to ensure either 0.1 mol% or 1 mol% of Pd in each reaction.

Table 2 shows the results of the catalytic tests. Starting with catalyst **2**, we observed a higher activity of those stemming from the Pd(0) source.[24] For example, comparing catalyst **2c** (12 wt% Pd, Table 2, entry 4) with **2h** (14 wt% Pd, Table 2, entry 9) the activity is almost four times higher in case of the material prepared from the Pd(0) precursor. In both cases the activity of the materials increases with a higher Pd content on the surface which is opposite to what was observed in case of carbon stabilized Pd NPs (Pd@Co/C).[22] The maximum turn over frequency for the polymeric material **2** was 100 h^{-1}.

Using the non-polymer coated catalyst Pd@Bz-IL@Co/C **3** we observed an increase in activity by a factor of nine (Table 2, entry 14) and could even reach a turn over frequency of 4000 h^{-1} applying a hydrogen pressure of 10 bar (Table 2, entry 15). The loading/activity relationship in this case is reversed compared to the polystyrene coated catalyst **2**. The material with the lowest loading shows the highest activity in the hydrogenation (Table 2, entry 14). The activity of Pd@Spacer-IL@Co/C **4** turned out to be in between **2** and **3**, the maximum TOF was observed for **4a** (333 h^{-1}, Table 2, entry 16). Activity increases again with an increase in loading as previously seen for the polystyrene coated particles **2**.

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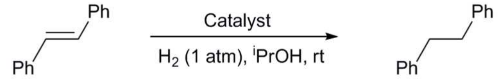
Generally, we observed also differences during the catalytic tests regarding the ease of separation of the materials (Fig. 3). Magnetic separation in case of polystyrene coated particles **2**, especially the ones with high Pd content, took several minutes applying a 1.2 T neodymium based magnet (Fig. 3A). However, hybrid materials **3** (Fig. 3B) and **4** (Fig. 3C) were separated from the reaction mixture within seconds.

Table 2 Hydrogenation of *trans*-stilbene using Pd@PS-IL@Co/C **2**, Pd@Bz-IL@Co/C **3** and Pd@Spacer-IL@Co/C **4**.[a]



Entry	Catalyst	Pd [wt%]	Catalyst [mol%]	t [min]	Conversion [%]^b	TOF [h^{-1}]^c
1	**2a**	28	1.0	60	87	87
2	**2b**	24	1.0	60	100	100
3	**2b**	24	0.1	60	5	50
4	**2c**	12	1.0	60	91	91
5	**2d**	6	1.0	60	52	52
6	**2e**	0.8	1.0	60	1	1
7	**2f**	50	1.0	60	48	48
8	**2g**	34	1.0	60	22	22
9	**2h**	14	1.0	60	23	23
10	**3a**	45	0.1	60	15	150
11	**3b**	31	0.1	60	19	190
12	**3c**	17	0.1	60	33	330
13	**3d**	8	0.1	60	61	610
14	**3e**	0.9	0.1	60	88	880
15^d	**3e**	0.9	0.1	15	100	4000
16	**4a**	43	0.1	90	50	333
17	**4a**	43	1.0	75	100	80
18	**4b**	34	0.1	90	34	200
19^d	**4b**	34	0.1	90	58	387
20	**4b**	34	1.0	120	100	50
21	**4c**	14	0.1	90	16	107
22	**4d**	8	0.1	90	10	93
23	**4e**	1	0.1	90	1	7

[a] Stilbene (2 mmol) in ^{i}PrOH (20 mL) was hydrogenated by 2 µmol (0.1 mol%) or 20 µmol (1 mol%) of catalyst using dodecane as internal GC standard. [b] Determined by GC analysis using internal standard. [c] Mol of substrate transformed per mol catalyst per hour. [d] 10 bar of H_2 pressure.

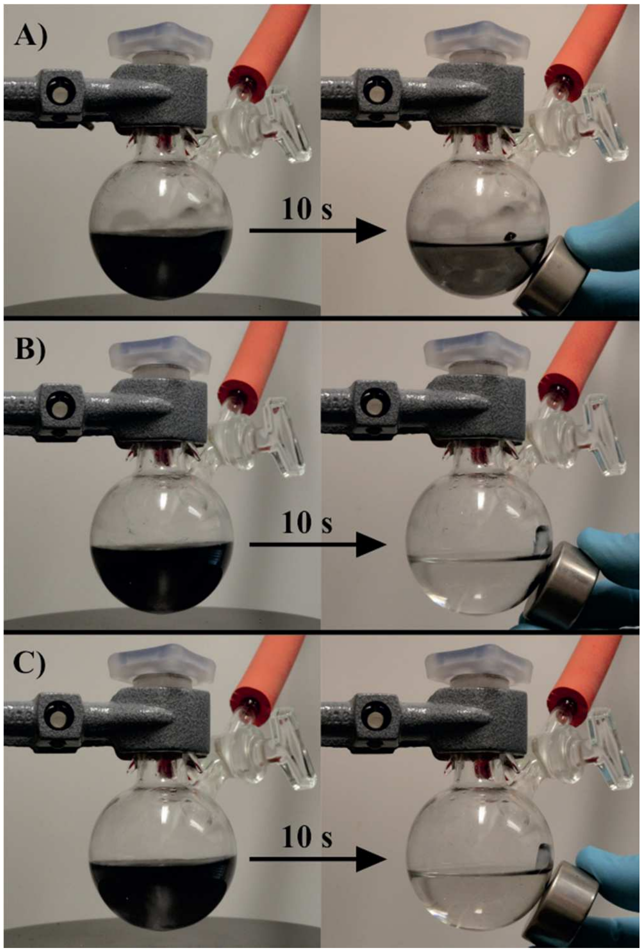


Fig. 3 Collecting the nanocatalysts from the reaction mixture by an external magnet. A) Pd@PS-IL@Co/C **2b**, B) Pd@Bz-IL@Co/C **3b**, C) Pd@Spacer-IL@Co/C **4b**.

Recycling studies

We next investigated the recycling ability of the three different hybrid materials (Fig. 4). Recycling experiments in all cases were performed with the two high-loading catalysts of each material, i.e. with Pd@PS-IL@Co/C **2a** and **2b**, Pd@Bz-IL@Co/C **3a** and **3b**, and Pd@Spacer-IL@Co/C **4a** and **4b**. Reactions were carried out with an initial palladium amount of 1 mol% and stopped in each case after reaching full conversion in the first run. For further runs the reaction time was held constant. In cases of **2** and **3** a drop of activity is observed after the first or the second run, respectively. This indicates that these materials are not effectively stabilizing the Pd NPs on the surface resulting in aggregation of the Pd NPs and/or leaching of Pd. However, the material with the more flexible ionic liquid on the surface shows much better results. In case of **4a** we also see a decrease in yield after the first run, whereas for **4b** recycling is possible for at least five runs without loss of activity demonstrating the efficient stabilization of Pd NPs on the surface of the hybrid material. The observation of a slight decrease for catalyst **4a** is probably caused by agglomeration due to higher Pd contents. From now on **4b** was used as catalyst for further leaching/recycling studies.

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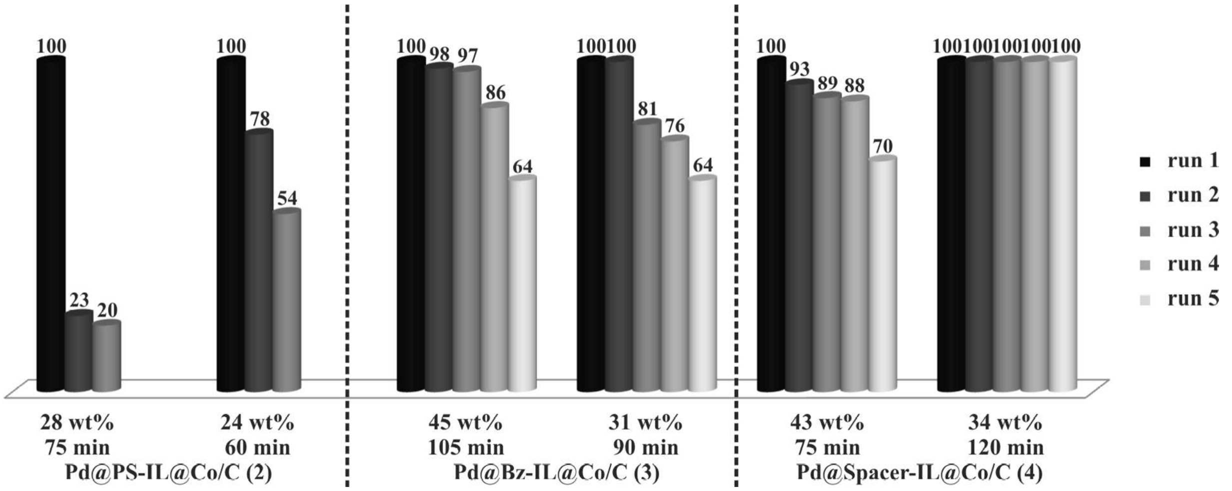

Fig. 4 Recycling studies with Pd@PS-IL@Co/C (**2a**, **2b**), Pd@Bz-IL@Co/C (**3a**, **3b**) and Pd@Spacer-IL@Co/C (**4a**, **4b**). Reaction times are given below the columns; yields in % are given above every single column.

Table 3 Recycling studies of Pd@Spacer-IL@Co/C (34 wt%, **4b**) in the hydrogenation of *trans*-stilbene.[a]

Run	Reaction time to full conversion [min][b]	Pd leaching [ppm][c]	Co leaching [ppm][c]
1	120	9	17
2	120	11	9
3	120	20	13
4	120	11	8
5	120	16	17
6	120	28	14
7	120	19	17
8	120	8	21
9	120	11	14
10	120	28	13
11	120	64	22
12	150	48	15

[a] Stilbene (2 mmol) in ^{i}PrOH (20 mL) was hydrogenated by 20 μmol (1 mol%) of catalyst **4b**. [b] Reaction was monitored by GC analysis and stopped at full conversion. [c] In μg per g of product. Determined by ICP-OES.

Next, another reaction batch with **4b** was run without internal standard in order to determine the contents of Pd and Co in the product by ICP-OES analysis (Table 3). Contamination of the product is possible either by leaching of Pd or Co from the catalyst or by particles that are not separated from the reaction mixture effectively. The material was recycled for 11 runs without any need of increasing the reaction time (120 min). In run 12 the reaction time had to be increased to 150 min to reach full conversion. After these 12 runs the Pd retained on the hybrid material was determined as 87% of the starting value. TEM pictures do not show any significant change of the nanocatalysts (see supporting information). The Pd and Co contents in the products were in the first 10 runs between 8 and 28 ppm, whereas the Pd content increases in run 11 and 12 to 64 and 48 ppm.

We also carried out leaching studies with **4b** using 0.1 mol% Pd under additional 10 bar of hydrogen pressure (Table 4). The particles could be recycled for 10 consecutive runs with reactions times from 180 to 300 mins. In this case, we observed Pd contents of < 10 ppm and Co contents of < 8 ppm with two exceptions (17 ppm Pd in run 7 and 14 ppm Co in run 8). These results are also promising for industrial uses as the acceptable palladium limits are reported to be between 10 and 20 ppm.[25]

Catalyst **4b** is additionally attractive due to its very high capacity in palladium, requiring only little amounts of supporting material, which is also important for the recycling of expensive metals like Pd. For experiments using a Pd content of 0.1 mol% only 0.7 mg of catalyst **4b** were needed in order to generate 20 mmol of product within 10 runs. This would in scale up lead to 30 mol of product (or 5 kg in case of *trans*-stilbene) applying 1 g of catalyst **4b**.

Table 4 Recycling studies of Pd@Spacer-IL@Co/C (34 wt%, **4b**) in the hydrogenation of *trans*-stilbene under 10 bar H_2-pressure.[a]

Run	Reaction time to full conversion [min][b]	Pd leaching [ppm][c]	Co leaching [ppm][c]
1	180	10	2
2	180	2	1
3	180	4	2
4	210	6	3
5	210	6	4
6	210	5	3
7	210	17	7
8	240	8	14
9	240	3	4
10	300	6	7

[a] Stilbene (2 mmol) in ^{i}PrOH (20 mL) was hydrogenated by 2 μmol (0.1 mol%) of catalyst **4b** under 10 bar of H_2-pressure. [b] Reaction was monitored by GC analysis and stopped at full conversion. [c] In μg per g of product. Determined by ICP-OES.

Recycling experiments varying the substrate

We also investigated the scope of the reaction with catalyst **4b** by reusing the particles and changing the substrate after each run (Table 5). Various styrene derivatives were hydrogenated in short reaction times of 15-60 minutes (Table 5, run 2-6) bearing elec-

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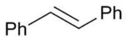
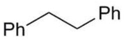
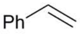
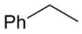
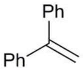
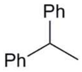
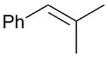
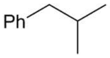
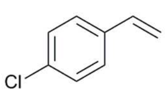
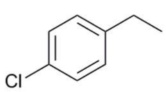
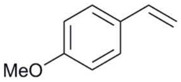
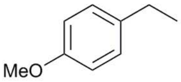
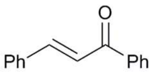
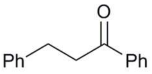
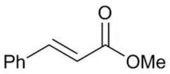
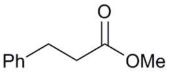
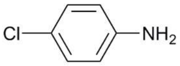
tron withdrawing (Table 5, run 5) as well as electron donating functional groups (Table 5, run 6). Additionally, chalcones and cinnamic esters were hydrogenated selectively (Table 5, run 7+8), which was additionally proved by ^{1}H-NMR and ^{13}C-NMR. Furthermore, strained compounds like norbornene were hydrogenated in very short reaction times (Table 5, run 9) as well as nitro compounds bearing electron donating (Table 5, run 10) or electron withdrawing groups (Table 5, run 11).

Conclusion

In this report, we successfully developed novel hybrid materials consisting of magnetic ionic liquids and stabilized Pd nanoparticles. The catalyst with a quite flexible ionic liquid on the surface turned out to be the most promising regarding the stabilization of Pd NPs. It showed high activity in the hydrogenation of *trans*-stilbene, is easily separable, and furthermore was recycled for at least 11 runs without significant loss of activity. Furthermore, we could show that the leaching of Pd and Co into the product was not noticeably high if a Pd amount of 0.1 mol% was used. Recycling of the catalyst was also possible varying the substrate after each run.

This novel catalyst is especially interesting regarding the point of sustainability as one can recycle expensive Pd with a very small amount of supporting material. This makes it especially attractive for industry where not only costs of catalyzing metal but also of supporting material play an important role.

Table 5 Recycling of catalyst Pd@Spacer-IL@Co/C (34 wt%, **4b**) in the hydrogenation of olefins and nitro compounds.[a]

Run	Substrate	Product	t [min]	Conversion [%][b]
1			120	100
2			15	100
3			50	100
4			60	100
5			15	100
6			15	100
7			420	100
8			40	100
9			10	100
10			20	100
11			20	100

[a] Substrate (2 mmol) in iPrOH (20 mL) was hydrogenated by 20 μmol (1 mol%) of catalyst **4b** using dodecane as internal GC standard. [b] Determined by GC analysis using internal standard.

Experimental

Benzyl-chloride functionalized carbon coated cobalt nanoparticles (8, Bz-Cl@Co/C)

450 mg (0.12 mmol/g) Bz-OH@Co/C (**7**) and 1.4 μL (18 μmol) dry DMF were predispersed in 4.5 mL dry dichloromethane for 10 min under N_2-atmosphere using an ultrasonic bath. The dispersion was cooled to 0 °C and 65.3 μL (0.9 mmol) $SOCl_2$ was added slowly. The reaction mixture was allowed to warm to rt and stirred over night. After magnetic decantation the particles were washed with dichloromethane (5 x 5 mL) and dried in vacuo to obtain Bz-Cl@Co/C (440.8 mg, 0.11 mmol/g).
IR (ν/cm^{-1}): 1676, 1596, 1503, 1263, 1015, 778; elemental microanalysis (%): C, 8.54; H, 0.14; N, 0.07; Cl, 0.40.

Benzyl-methyl imidazolium chloride functionalized carbon coated cobalt nanoparticles (9, Bz-IL@Co/C)

400 mg (0.12 mmol/g) Bz-Cl@Co/C (**8**) and 4 mL dry toluene

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were introduced to a microwave vial and sonicated for 10 min under N_2-atmosphere using an ultrasonic bath. After adding 24 µL (0.3 mmol) *N*-methyl-imidazole the reaction mixture was heated in a focused microwave oven to 150 °C for 30 min. After removing the supernatant by magnetic decantation the particles were washed with toluene (5 x 5 mL), and dichloromethane (3 x 5 mL) and dried under vacuum at 80 °C yielding **9** (397.6 mg, 0.09 mmol/g).

IR (ν/cm^{-1}): 2920, 2852, 2363, 1214, 1161, 1014, 814, 654; elemental microanalysis (%): C, 8.98; H, 0.16; N, 0.23; Cl, 0.27.

Poly(benzyl-methyl imidazolium chloride)styrene functionalized carbon coated cobalt nanoparticles (6, PS-IL@Co/C)

500 mg (3.1 mmol/g) PS-Cl@Co/C (**5**) and 5 mL dry toluene were introduced to a microwave vial and sonicated for 10 min under N_2-atmosphere using ultrasonic bath. 309 µL (3.88 mmol) *N*-methyl-imidazole was added and the reaction mixture heated in a focused microwave oven to 150 °C for 30 min. After magnetic decantation the particles were washed with toluene (5 x 5 mL), dichloromethane (3 x 5 mL) and dried under vacuum at 80 °C yielding **6** (637.2 mg, 2.1 mmol/g).

IR (ν/cm^{-1}): 3373, 2927, 2851, 1562, 1511, 1449, 1422, 1158, 1018; elemental microanalysis (%): C, 43.95; H, 4.62; N, 5.75; Cl, 7.41.

Benzoic acid functionalized carbon coated cobalt nanoparticles (10, Ph-COOH@Co/C)

1.3 g (0.26 mmol of benzylalcohol units) Bz-OH@Co/C (**7**) were sonicated in 30 mL MeCN/H_2O (1:1) for 10 min using an ultrasonic bath. After adding 479.5 mg (0.78 mmol) oxone the mixture was refluxed for 24 h. Another portion of oxone (479.5 mg, 0.78 mmol) was added after 12 h. After magnetic decantation the particles were washed with MeCN/H_2O (3 x 20 mL), MeCN (3 x 20 mL) and dried under vacuum to obtain Ph-COOH@Co/C (1.18 g).

IR (ν/cm^{-1}): 2358, 2330, 1731, 1360, 1219; elemental microanalysis (%): C, 8.71; H, 0.28; N, 0.30.

(*N*-Imidazole)propyl-benzamide functionalized carbon coated cobalt nanoparticles (11)

1.0 g Ph-COOH@Co/C (**10**) were stirred in 5.0 mL $SOCl_2$ under N_2-atmosphere for 24 h. After magnetic decantation the particles where washed with dry THF (5 x 5 mL) and dried under vacuum. Subsequently 5.0 mL 1-(3-aminopropyl)imidazole were introduced under N_2-atmosphere and the mixture heated to 120 °C for another 24 h. After magnetic decantation the particles were washed with THF (3 x 5 mL), 1M HCl (1 x 5 mL), saturated $NaHCO_3$ solution (1 x 5 mL), H_2O (1 x 5 mL) and EtOH (3 x 5 mL). After drying the particles in vacuo **11** (934.7 mg, 0.07 mmol/g) was obtained.

IR (ν/cm^{-1}): 2893, 2840, 1564, 973, 867, 848, 835, 819, 752, 698, 689, 656; elemental microanalysis (%): C, 9.32; H, 0.19; N, 0.60.

Benzamidopropyl-butyl-imidazolium bromide functionalized carbon coated cobalt nanoparticles (12, Spacer-IL@Co/C)

900 mg (0.063 mmol of imidazole units) of **11** were sonicated in 15 mL freshly distilled 1-bromobutane under N_2-atmosphere using an ultrasonic bath. The reaction mixture was stirred for 24 h at 80 °C. The particles were separated by an external magnet and washed with dry THF (5 x 10 mL) and dried under vacuum to obtain **12** (909.2 mg, 0.05 mmol/g).

IR (ν/cm^{-1}): 2913, 2850, 1738, 1455, 1366, 1222, 1217, 1160, 753; elemental microanalysis (%): C, 9.40; H, 0.24; N, 0.51.

Representative procedure for the microwave deposition of Pd nanoparticles on PS-IL@Co/C nanobeads (Method A)

100 mg PS-IL@Co/C (**6**) and 1 mL of a mixture dry toluene/MeOH were introduced to a microwave vial and sonicated in an ultrasonic bath for 10 min under N_2-atmosphere. 4.9 mg (4.7 µmol) $Pd_2(dba)_3{\cdot}CHCl_3$ was added and the reaction mixture heated in a focused microwave oven to 110 °C for 2 min. After magnetic decantation the particles were washed with dichloromethane (5 x 5 mL) and dried under vacuum to obtain Pd@PS-IL@Co/C (**2e**) (96.9 mg). The loading of Pd was determined by ICP-OES (0.08 mmol/g, 81%).

Representative procedure for the microwave deposition of Pd nanoparticles on Bz-IL@Co/C nanobeads (Method A)

100 mg Bz-IL@Co/C (**9**) and 1 mL dry toluene were introduced to a microwave vial and sonicated in an ultrasonic bath for 10 min under N_2-atmosphere. 4.9 mg (4.7 µmol) $Pd_2(dba)_3{\cdot}CHCl_3$ was added and the reaction mixture heated in a focused microwave oven to 110 °C for 2 min. After magnetic decantation the particles were washed with dichloromethane (5 x 5 mL) and dried under vacuum to obtain Pd@Bz-IL@Co/C (**3e**) (99.8 mg). The loading of Pd was determined by ICP-OES (0.089 mmol/g, 96%).

Representative procedure for the microwave deposition of Pd nanoparticles on Spacer-IL@Co/C nanobeads (Method A)

50 mg Spacer-IL@Co/C (**12**) and 1 mL dry toluene were introduced to a microwave vial and sonicated in an ultrasonic bath for 10 min under N_2-atmosphere. 2.5 mg (2.4 µmol) $Pd_2(dba)_3{\cdot}CHCl_3$ was added and the reaction mixture heated in a focused microwave oven to 110 °C for 2 min. After magnetic decantation the particles were washed with dichloromethane (5 x 5 mL) and dried under vacuum to obtain Pd@Spacer-IL@Co/C (**4e**) (50.1 mg). The loading of Pd was determined by ICP-OES (0.093 mmol/g, 100%).

Representative procedure for the deposition of Pd nanoparticles on PS-IL@Co/C nanobeads by H_2-reduction (Method B)

To a schlenk tube 20 mg PS-IL@Co/C (**6**) and 4 mL of a freshly prepared Na_2PdCl_4 solution (Pd conc. 1 mg/mL) were introduced. The reaction mixture was stirred vigorously for 30 min followed by 30 min under 1 atm H_2 pressure (balloon). After magnetic decantation the particles were washed with H_2O (5 x 3 mL), MeOH (3 x 3 mL), and acetone (2 x 3 mL) and dried under vacuum to obtain Pd@PS-IL@Co/C (**2h**) (15.8 mg). The loading of Pd was determined by ICP-OES (1.3 mmol/g, 85%).

General procedure for the hydrogenation using Pd@IL@Co/C catalysts

To a schlenk tube Pd@IL@Co/C (1 mol% Pd, 20 µmol), substrate (2 mmol), iPrOH (20 mL), and dodecane (1 mmol) as internal standard were introduced. The reaction mixture was sonicated in an ultrasonic bath for 10 min and subsequently stirred vigorously under 1 atm H_2-pressure (balloon). The progress of the reaction was monitored by GC analysis. For recycling experiments the particles were separated by an external magnet and after magnetic decantation washed with ^{i}PrOH (2 x 5 mL) and dichloromethane (2 x 5 mL). After drying in vacuo the catalyst was reused for further runs.

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Palladium Nanoparticles Supported on Ionic Liquid Modified, Magnetic Nanobeads – Recyclable, High-Capacity Catalysts for Alkene Hydrogenation

TOC one sentence

Ionic liquid modified magnetic nanobeads allow the support of high concentrations of palladium nanoparticles (34 wt%) with consistent high activity in alkene hydrogenations.