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Preparation and characterization of a new bis-layered supported ionic liquid catalyst (SILCA) with an unprecedented activity in the Heck reaction

Nemanja Vucetic[a,*], Pasi Virtanen[a], Ayat Nuri[a,b], Ida Mattsson[c], Atte Aho[a], Jyri-Pekka Mikkola[a,d] and Tapio Salmi[a]

[a] Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering, Biskopsgatan 8, FI-20500, Turku, Finland. E-mail: nvucetic@abo.fi

[b] University of Mohaghegh Ardabili, Faculty of Science, Department of Applied Chemistry, Ardabil 56199-11367, Iran.

[c] Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Laboratory of Organic Chemistry, Biskopsgatan 8, FI-20500, Turku, Finland.

[d] Umeå University, Chemical-Biological Centre, Department of Chemistry, Technical Chemistry, SE-90187 Umeå, Sweden.

ABSTRACT

A new bis-layered supported ionic liquid catalyst (SILCA) loaded with palladium was designed and successfully applied for the Heck reaction of iodobenzene and methyl acrylate. The silica modified catalyst with first ionic liquid layer consisting of covalently anchored imidazolium bromide up on which attached second layer made of pyridine-carboxylic acid balanced with tetramethylguanidinium cation raised a catalyst with high activity. High turnover frequencies of 22 000 were achieved in reactions with a low palladium loading as 0.009 mol % indicating on palladium dimerization when higher amounts were used. The TMG cation had a purpose to recapture and stabilize the Pd nanoparticles thus followed a release and catch mechanism. In order to get a full understanding of the catalyst structure and behaviour, the catalyst was characterized by means of nitrogen physisorption, thermal gravimetric analysis, infrared spectroscopy, scanning electron and transmission electron microscopes, solid-state NMR, X-ray photoelectron spectroscopy and inductively coupled plasma spectroscopy. The catalyst preserved good activity in six cycles.

Keywords: Heck reaction; Supported ionic liquid catalyst; Palladium; Turn-over frequency; Catalyst characterization

1 Introduction

Growing demands for different kinds of molecules in fine-chemical industry and drug production cannot be any more satisfied from natural sources, and the question is should it be considered that today technologies can offer alternative routes to different chemicals. From economical aspect, extraction and isolation of molecules that preserve certain functionalities is cumbersome, much cheaper is just to produce them, favorably in–situ. The Heck reaction catalyzed by the palladium and conducted in the presence of base presents a significant tool in synthetic chemistry. It was firstly introduced by Mizoroki [1] and described by Heck [2] almost half a century ago. The Heck reaction is C-C coupling reaction between various olefins and aryl, vinyl or allyl halides, triflates or acetates to yield the molecule with preserved olefin double bond. It is usually conducted in polar solvents at elevated temperatures, in slight excess of base and alkene in order to compensate their losses due to the evaporation [2,3].

As well as many other organic reactions, the Heck reaction faces a challenge to abound volatile organic solvents and transfer the reaction into more ecologically acceptable and controllable environment. Ionic liquids (ILs) have emerged and with the time evolved into something that can replace bulk solvents and provide many other advantages in processes involved with reactions, separation, electrochemistry *etc.* In the very beginning [4–8] ionic liquids were ignored and for the first time acknowledged a century ago [9], at which time they were described as salts, therefore purely consistent of ions that are in liquid state at temperatures below 100 °C and with no significant vapor pressure. From that

moment on, they slowly started to draw attention of the scientific society and got a huge swing 30 years ago when few research groups started to study and promote them [10–20]. Ionic liquids are characterized to be polar, water immiscible, thermally stable, non-volatile, non-flammable and task-specific compounds with wide liquidus range. However, in line with recent studies these too generalized properties which were mainly derived for most popular ILs based on imidazolium cation had to be updated [21]. Features as such cannot be prescribed to complete order of these organic compounds, especially when one becomes aware of the tremendous number of ILs that can be designed. Even though each group of ILs has to be separately defined, there are few features which unify all of them: they consist of ions only, their melting temperature is lower than the decomposition temperature and they can be 'task-specified' to meet specific requirements. Furthermore they can be utilized in catalyst design.

The first Heck reaction in ionic liquids was conducted in tetraalkylammoinum and phosphonium salts without addition of phosphonium ligands [22]. Compared to usual organic solvents for this reaction such as DMF, DMA, NMP or acetonitrile, the ionic liquid $[Bu_4N]Br$ was found to be a good medium, giving competitive results [23,24]. Commonly used imidazolium $[C_4mim]PF_6$ and n-hexylpyridinium $[C_6Pyr]PF_6$ ionic liquids also present an attractive alternative [25]. Based on these findings during the next decade new compounds like tetramethylguanidine acetate and hexafluorophosphate ([HTMG]OAc, $[HTMG]PF_6$) [26], pyridyl-functionalized imidazolium-based [27] and ethanolamine-functionalized [28–30] ionic liquids were synthesized and applied

in different Heck reactions with various palladium catalysts and alkaline compounds. It was concluded that ionic liquids are beneficial for the product isolation and with ability to act as a base and ligand in Heck chemistry.

Parallel to ILs development, new ligands for Pd were investigated giving C, N, C pincer bis-carbene complexes [31] and pyrimidine-functionalized N-heterocyclic carbenes [32,33] as alternative replacement for toxic and expensive phosphine-containing ligands.

In chemical engineering the ubiquitous interest is to heterogenize catalytically assisted reactions and diminish the use of expensive materials whether it is metal, ligand or solvent. In conjunction with this concept, ionic liquids and metals can be deposited on carrying materials, forming a supported ionic liquid catalyst or SILCA. Within SILCA the amount of ionic liquid is kept on such a low level that the mass transfer limitations due to viscosity are avoided, but still sufficiently enough to preserve their bulky characteristics. In this way the supported ionic liquid that interacts with the active metal, is the phase where reaction takes place, while the bulk solvent is used to deliver and overtake reactants/products.

Soon after introducing this inspiring concept [34–37] it was employed for Heck reaction of iodbenzene and acrylate in $[C_4mim]PF_6$ layer immobilized on silica with n-decane [38] and H_2O [39] as a solvents. The interesting aspect was the simplicity of the impregnation method for a reactions which proceed in a liquid phase. The ability of imidazolium ion to act as an N-heterocyclic carbene ligand was then used to affix Pd for the support. In this case, silylated

methylimidazoium chloride was covalently anchored on the SiO_2 [40] and SBA-16 [41] surface. On the other hand, if it is preferred first to functionalize silica, metal can be introduced just by dissolving it with IL and re-layering [42] or again with help of covalently anchored IL [43].

In this article we report synthesis of a new type of SILCA with bis- ionic liquid layer grown up one on another. The layer contains N-heterocyclic carbene palladium complex in its primary ionic liquid layer upgraded by pyridine linker with acidic head which is balanced with tetramethylguanidinium cation in a secondary layer. The catalyst gave rise to a huge activity in the Heck reaction and one of the best turnover frequencies reported in literature till now. The separation and recyclability was simple without any significant loss of the activity after five cycles.

2 Experimental

2.1 Chemicals

Iodobenzene, methyl acrylate, triethanolamine, dimethylformamaide, (3-chloropropyl)trimethoxysilane and palladium(II) chloride were purchased from Alfa Aesar. N-methyl-2-pyrrolidone, imidazole, 6-bromo-nicotinic acid, 1,1,3,3-tetramethylguanidine, sulfuric acid, sodium hydroxide, sodium bicarbonate and dimethyl ether were supplied by Sigma Aldrich. Other chemicals were obtained from common commercial sources. All the chemicals were used as obtained, without further purification.

2.2 General Heck reaction procedure

All the experiments were performed in flat bottom glass vial tubes (8 ml volume) with Teflon cup screw and magnetic stirrer. The vials were heated up in oil bath, submerged in it just above the level of the reaction mixture leaving the upper part of the vial not heated. Temperature of the oil was monitored and reported as a temperature of the reaction with assumption that the temperature differences were minimal due to small volumes and good stirring. In a typical experiment, the determined amount of SILCA and 1 ml of solvent was introduced directly into vials, followed by the addition of 1 mmol of aryl halide, base (1.5 mmol) and olefin (1.5 mmol). The starting point of the reaction was set as the point when the temperature reached the preset value and the reaction was let to run until completion or it was quenched at a certain time by submerging the vial into the ice bath.

The progress of the reactions was monitored with TLC and analyzed by GC. All the experiments were repeated at least two times, and the average values are reported. The experimental error was ± 2 %.

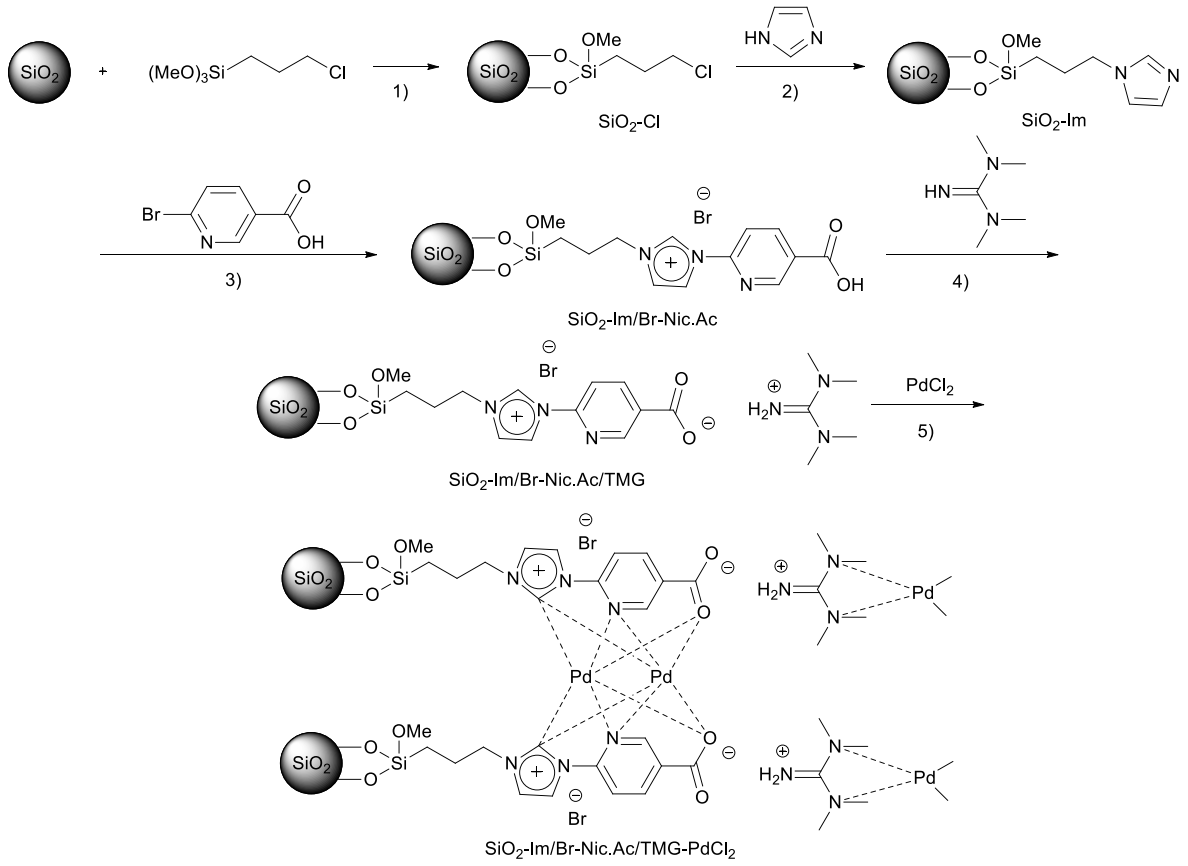
2.3 Products extraction and catalyst recovery

The reaction slurry was firstly diluted with DMF and separated from the catalyst with a centrifuge leaving organic layer rich with products. To remove all formed salts and products deposited on the catalyst we continued with washing the catalyst with DMF and centrifuging. At the end all the DMF was combined to give 4 vol. % diluted aliquot.

To recover the catalyst it was flushed with diethyl ether and dried in air at 100 °C for 30 min. This catalyst was reused in next cycle without removal from the vial or stored at ambient conditions for characterization.

2.4 Catalyst synthesis

Bis-layered SILCA consisted of 3-imidazolbromide nicotinic tetramethylguanidinium ionic liquid on SiO_2 loaded with palladium (SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$) was synthesized according to Scheme 1.



Scheme 1. Synthesis of SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$.

2.4.1 Silica functionalization

In a first step calcined SiO_2 was functionalized with a procedure reported in literature [44]. In a round bottom flask, under nitrogen atmosphere, (3-chloropropyl)trimethoxysilane was reacted with support in refluxing toluene for a 24 h. A modifying agent was introduced dropwise in a ratio of 5 mmol per 1 g of support. The obtained material (SiO_2-Cl) was washed with ethanol in a Soxhlet apparatus, vacuum dried at 80 °C for 8 h and dried at 100 °C for 3 h.

This 3-chloropropylated silica was further immobilized with imidazole. In a round bottom flask well grinded imidazole (20 mmol, 1.3616 g) was first dissolved in 30 ml of anhydrous toluene at 90 °C. To a stirred solution 2 g of modified

support was added and let to react for 24 h under reflux conditions and N_2 atmosphere. The material was then separated by filtration in a Soxhlet nimble, flushed with hot toluene and washed with ethanol for 24 h in the Soxhlet apparatus to yield white solid (SiO_2-Im). The procedure is presented as reaction 1) and 2), respectively, Scheme 1.

2.4.2 Synthesis of (3-imidazoliume propylated nicotinic acid) bromide supported SiO_2

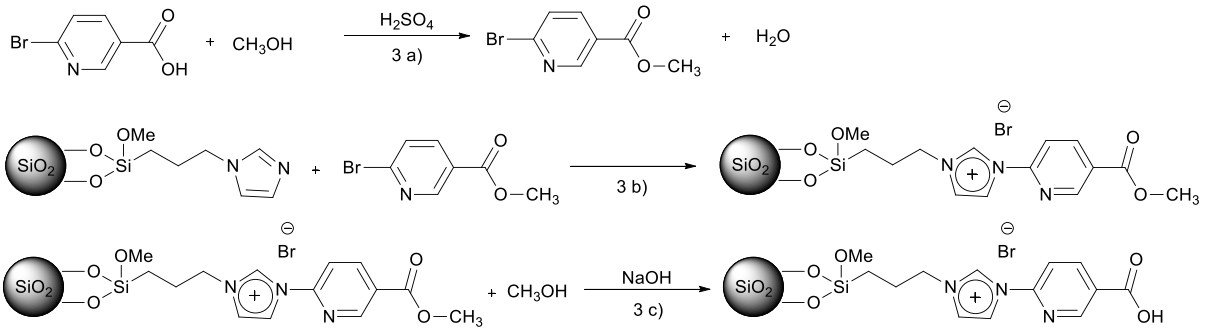
6-Bromo-nicotinic acid was anchored to functionalized SiO_2 via multistep route presented in Scheme 1 (reaction 3) and Scheme 2.

Fischer esterification of 6-bromo-nicotinic acid (Scheme 2, 3a). This synthesis is slightly modified literature procedure [45]. In the glass batch reactor with dean-stark apparatus and magnetic stirrer 6-bromo-nicotinic acid (3 mmol, 0.606 g) was dissolved in 10 ml of methanol. The mixture was cooled in ice bath and added dropwise 1.5 ml of concentrated H_2SO_4. The suspension was than heated to refluxing conditions and under vigorous stirring reacted overnight. After cooling down, 5 ml of H_2O was added and then to neutralize the acid, saturated $NaHCO_3$ solution was added. The mixture was transferred to a separation funnel and the product was extracted with dichloromethane (3*30 ml) as a bottom layer. Dichloromethane was evacuated in rotary evaporator at room temperature to obtain 6-bromo-nicotinic acid methyl ester as a white solid (0.43 g, 66 %) with m.p. 65-67 °C. ^{1}H-NMR (500.20 MHz, $CDCl_3$, 25 °C): δ = 8.97 (dd, $J_{H2,H4}$ = 2.4 Hz, $J_{H2,H5}$ < 1 Hz, 1 H, pyH^2), 8.13 (dd, $J_{H4,H5}$ = 8.3 Hz, 1 H, pyH^4), 7.59 (dd, 1 H, pyH^5), 3.96 (s, 3 H, -OCH_3). ^{13}C-NMR (125.8 MHz, $CDCl_3$, 25 °C):

δ = 165.1 (-CO_2CH_3), 151.4 (pyC^2), 146.9 (pyC^6), 139.2 (pyC^4), 128.1 (pyC^5), 125.3 (pyC^3), 52.6 (-OCH_3) (for more detailed see Supplementary material).

Functionalization of 3-imidazolepropylated SiO_2 with 6-bromo-nicotinic acid methyl ester (Scheme 2, 3b). The reaction of 6-bromo-nicotinic acid methyl ester with imidazole groups was done in refluxing DMF. The reaction itself was inspired by the reaction of bulky imidazole and chloro-sibling compound performed by others [46], while the workup and extraction was simplified to correspond the heterogeneity of new system [47,48]. In the glass batch reactor with dean-stark apparatus and magnetic stirrer 6-bromo-nicotinic acid methyl ester (3 mmol, 0.6481 g) was dissolved in 30 ml of DMF followed with addition 2 g of SiO_2-Im. The mixture was heated to refluxing conditions and the reaction kept for 24 h under N_2 atmosphere and vigorous stirring. The solid product was separated and repeatedly washed with dichloromethane and ethanol to remove non-reacted ester followed with drying at 70 °C for 3 h.

Hydrolysis of 3-imidazolbromide nicotinic methyl ester functionalized SiO_2 (Scheme 2, 3c). All the material synthetized in the previous step was dissolved in 30 ml of methanol. Followed by dropwise addition of 2.5 ml of 1 M NaOH. The suspension was heated to refluxing conditions and under vigorous stirring reacted overnight. After cooling, the slurry was acidified with 1M HCl untill pH=2-3. The solid product was separated with a centrifuge and repeatedly washed with H_2O and ethanol to remove the non-reacted ester. The final solid was then dried at 70 °C for 3 h and then at 100 °C prior to the use in the next step. The obtained supported ionic liquid layer of 3-imidazolbromide nicotinic acid on SiO_2 was a white solid (SiO_2-Im/Br-Nic.Ac).



Scheme 2. 3a) esterification of 6-bromo-nicotinic acid, 3b) synthesis of 3-imidazolbromide nicotinic methyl ester functionalized SiO_2, 3c) hydrolysis of 3-imidazolbromide nicotinic methyl ester functionalized SiO_2.

2.4.3 Synthesis of tetramethylguaindinum ionic liquid layer on SiO_2-Im/Br-Nic.Ac

Reaction 4 presented in Scheme 1 is supposed to simulate the common route in the ionic liquid synthesis where a simple neutralization takes place and yields salt. For the heterogeneous reasons three equivalents of base were used instead of the equimolar ratio.

To the 30 ml ethanol solution of 1,1,3,3-tetramethylguanidine (10 mmol, 1.5118 g) 2 g of SiO_2-Im/Br-Nic.Ac (all obtained from previous step was slowly added). The reactor was then sealed and repeatedly washed with diethyl ether to remove non-reacted TMG. The final solid was dried at 70 °C for 3 h and then at 100 °C for 3 h. Obtained was supported ionic liquid layer of 3-imidazolbromide nicotinic tetramethylguanidinium on SiO_2 (SiO_2-Im/Br-Nic.Ac/TMG).

2.4.4 Palladium impregnation

In glass batch reactor 0.2 mmol of $PdCl_2$ (0.03547 g) was dissolved in 150 ml of methanol. Followed with addition of 2 g SiO_2-Im/Br-Nic.Ac/TMG (all obtained

from previous step). Reactor was sealed and slurry stirred 8 h at room temperature. After reaction completion solid product was separated with centrifuge and repeatedly washed with ethanol and diethyl ether to remove physical absorbed $PdCl_2$. Final solid was dried at 70 °C for 3 h and at 100 °C for 3 h. Pale yellow SILCA powder SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$ was obtained (Scheme 1, reaction 5).

2.5 Catalyst characterization

The thermogravimetric analysis (TGA) of the catalyst was done on CHAN D-200 instrument in the temperature range of 20 - 700 °C with a heating rate of 10 °C min^{-1} under Ar atmosphere. The specific surface area and pore volume measurements were done by means of nitrogen physisorption with Carlo-Erba instrument, 1990 Sorptometer. The BET equation and Dollimore-Heal method were used for calculations. Prior to the analysis, samples were outgassed for 3 h at 150 °C. The surface modification of the support was monitored with infrared spectroscopy (FT-IR) on ATI Mattson FTIR. Samples were pressed into pellets and dried at 100 °C. Elemental analysis was performed with energy-dispersive X-ray spectroscopy (EDX), while the morphology and palladium deposition were followed with scanning electron microscopy (SEM). Coupled EDX-SEM analyses were done on a Zeiss Leo Gemini 1530 with a Thermo-NORAN vantage X-ray detector. Imaging of the catalyst was performed with transmission electron microscopy (TEM) on JEM 1400 plus (120 kV, 0.38 nm) equipped with OSIS Quemesa 11 Mpix bottom mounted digital camera. The solution state ^{1}H and ^{13}C NMR spectra were recorded at 298 K with a Bruker Avance-III HD 500 MHz spectrometer equipped with a Bruker SmartProbe™.

As the solvent, deuterated chloroform with 0.03 % tetramethylsilane (TMS) as internal standard was used. CP MAS ^{13}C and ^{29}Si NMR spectra were obtained with a Bruker AVANCE-III HD 400 MHz spectrometer. The powdered sample was spin at 5 kHz spin rate in a Bruker ^{1}H broadband double-resonance 4 mm CP MAS probe. For ^{13}C, the proton 90° high-power pulse was 2.9 µs and contact time 2 ms. The recovery delay time was set to 2 s and 10000 scans were accumulated. For ^{29}Si, the proton 90° high-power pulse was 2.5 µs and contact time 2 ms.

The binding energies of all compounds and oxidation state of palladium in ionic liquid was investigated with X-ray photoelectron spectroscopy (XPS). A Perkin-Elmer PHI 5400 spectrometer with monochromatized Mg Kα 945 was used; the X-ray source operated at 14 kV and 200 W. The pass energy of the analyzer was 35.5 eV and the energy step 0.1 eV. Samples were outgassed overnight in high vacuum ($8*10^{-9}$ mbar) before scanning. The peak fitting was performed with the program XPS Peak 4.1. The background was corrected with the Shirley function. The metal content at the catalyst was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with Optima 4300 DV optical atomic emission spectrometer. The recovery delay time was set to 90 s and 1000 scans were accumulated.

The Heck reaction progress was analyzed with GC system HP 6890 Series with HP-5, 5 % Phenyl methyl siloxane capillary column (30.0 m * 320 µm, 0.25 µm) equipped with FID. The injector temperature was 280 °C while gas flow was 9.5 ml min^{-1}. Column was heated from 40 °C to 250 °C with 10 °C min^{-1} heating rate

and at the other end detector was at the constant temperature of 300 °C. Hexadecane was used as internal standard.

3 Results and discussion

FT-IR was used as a first tool for catalyst study during the preparation process and obtained spectra are presented in Figure 1. The most evident peaks are the ones at 470, 810, 1090 and 1215 cm^{-1} denoted to SiO_2, as well as those at 1635 and 3450 corresponding to Si-OH and H-OH stretching of adsorbed water. After the first reaction where (3-chloropropyl)trimethoxysilane was anchored on the SiO_2 surface, peaks at 1635 and 3450 disappeared which indicates that the silanol groups were occupied with modifying agent. In following step, chlorine was exchanged with imidazole ring and this reaction broth changes in signal at 1670 cm^{-1} which is assigned to C=C stretching. With nicotinic acid peak at 1575 cm^{-1} belonging to C=N vibration of pyridine ring confirmed new ionic liquid layer formed, together with a very broad acidic CO-H peak that dominated at around 3400 cm^{-1}. The disappearance of this peak was obvious when TMG was introduced and protonated (light blue line in Figure 1, a). However, this peak was recovered after the $PdCl_2$ introduction implying on hydrogen migration between the acidic head of the IL layer and TMG (Figure 1, a).

Spectrum of the catalyst recovered after Heck reaction did not show difference compared to the fresh one indicating that layer is firmly bonded and stable in reaction conditions (see Figure 1, b).

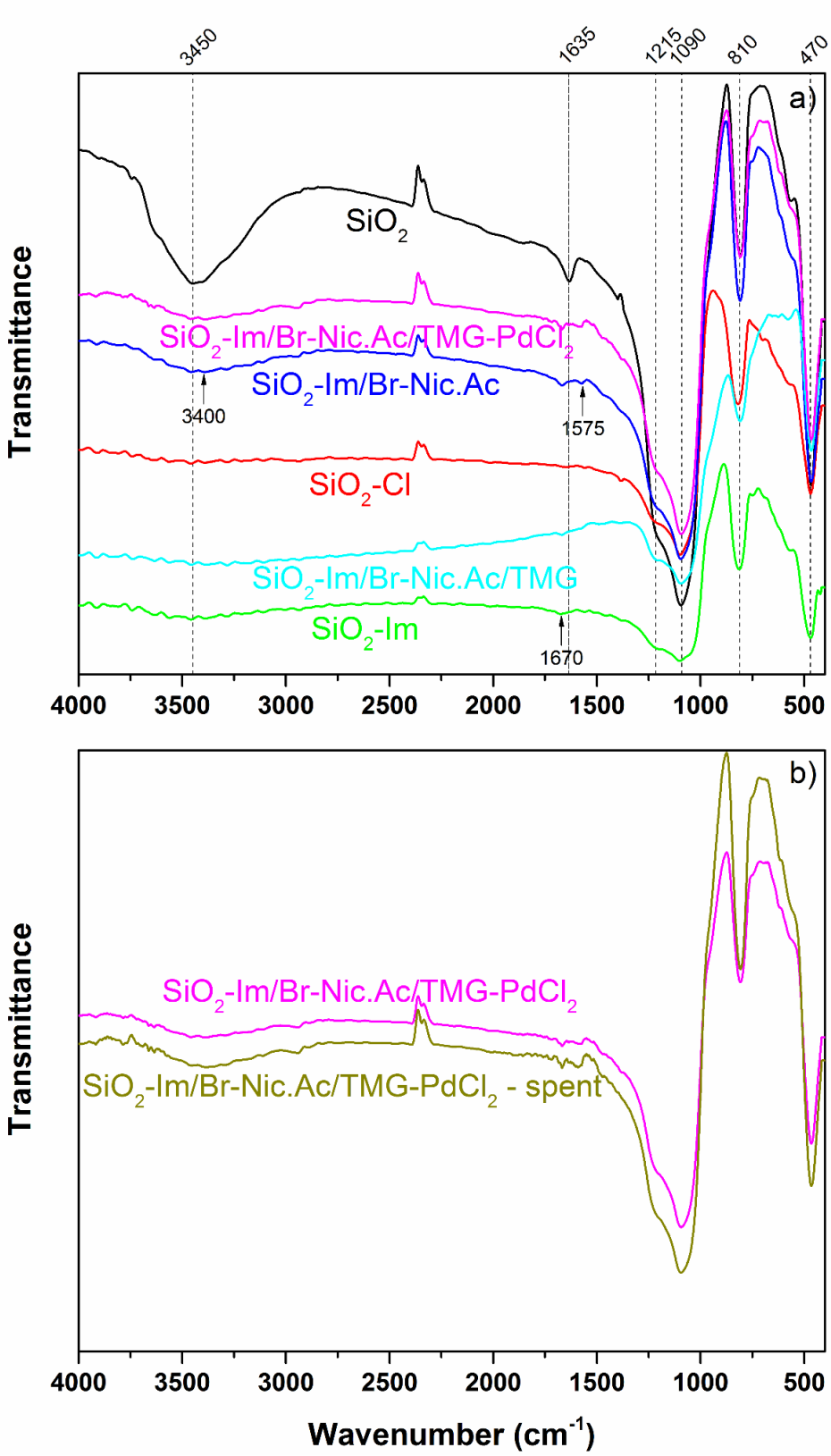


Figure 1. FT-IR spectra of catalysts on different preparation stages (a) and after one reaction cycle (b).

Elemental analysis of fresh and recycled catalysts gave information of catalyst content. As presented in Figure 2. Carbon, nitrogen, oxygen and bromine were present as a part of the formed IL layer, and they retained even after reaction. Palladium was loaded and detected as a $PdCl_2$ salt; nevertheless, these chlorine anions were exchanged with iodine in the first Heck cycle. The elemental percentages were calculated without the carbon content due to limitation introduced with the analytic practice. This disallows a quantitative study of the catalyst, but still based on the results listed in Table 1 it is indicated that the IL layer is stable during the reaction because nitrogen, oxygen and bromine amount did not change significantly. Traces of fluorine appeared as an impurity.

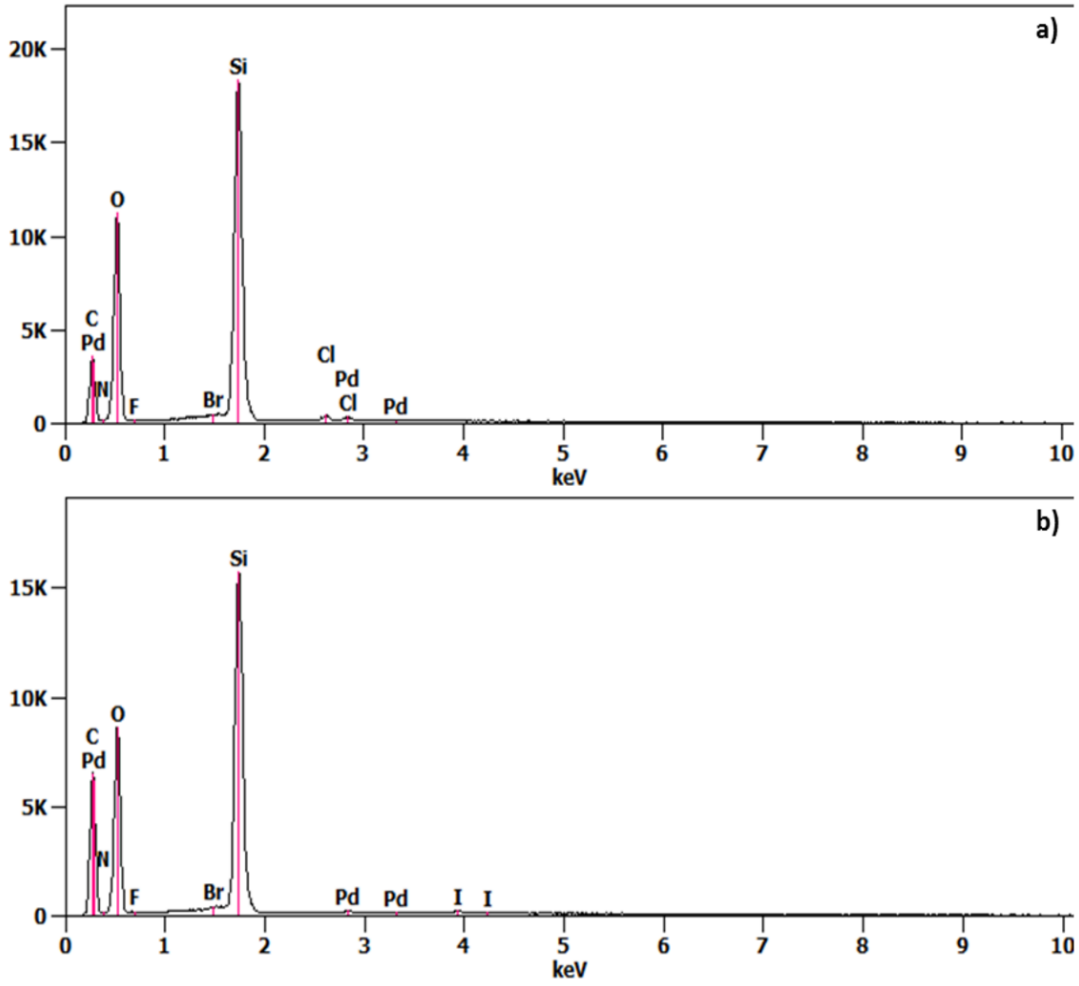


Figure 2. EDX analysis of fresh (a) and recycled catalysts (b).

Table 1. Elemental analysis of fresh and used catalysts.

	N	O	F	Si	Cl	Br	Pd	I
Sample				**atom %**				
SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$	13.86	68.76	0.00	16.85	0.27	0.09	0.17	0.00
SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$ - spent	15.44	65.76	1.00	17.44	0.00	0.09	0.07	0.21

The decomposition temperature of solid samples were analyzed with TGA and illustrated in Figure 3. The initial weight loss in the range from room temperature

to 220 °C was attributed to physically absorbed water in the catalyst pores and also some other volatiles (for the spent catalyst). In case of fresh and used catalyst this was 2.5 % and 6.0 % of the catalyst weight while in case of pristine silica this was about 1.5 %. The organic moieties in the IL layer start to decompose at the 265 °C and continue to do so until 510 °C. At 450 °C the decrease of weight was assigned to the decomposition of the methoxy side groups [49]. A similar thermal behavior of modified silica has been reported elsewhere [50]. From TGA thermogram the loading of IL can be estimated to be 8 wt % which corresponds to 0.1621 mmol g^{-1} grafted amount.

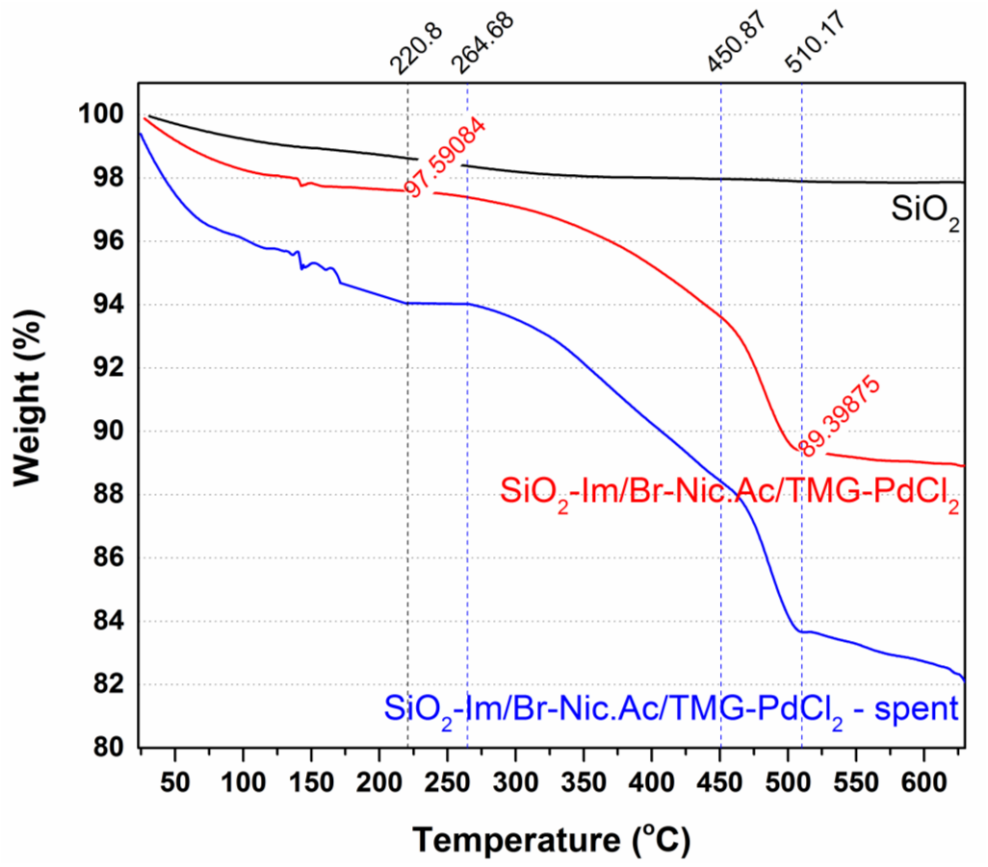


Figure 3. TGA of fresh SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$ and spent catalysts.

The surface area measurements are presented in Table 2. With the modification surface area decreased from 414.65 m^2 g^{-1} to 333.66 m^2 g^{-1} which is still a

relatively high value. The modification also affected the pore volume and diameter that decreased from 0.58 cm^3 g^{-1} (6.60 nm) to 0.33 cm^3 g^{-1} (5.46 nm) indicating that the organic groups were successfully anchored inside the pores of the pristine material and the mesoporosity was preserved. After the first Heck reaction, the recycled catalyst did not show any significant decrease in the surface area; however, the pore volume was drastically diminished. In our opinion, this indicates on catalyst poisoning due to the formation of salts from the Heck cycle. A moderate increase in the nitrogen amount after the reaction can also indicate on the salt formation (Table 1). Thus, for catalyst recycling repeated washing with a polar solvent is necessary.

Table 2. BET surface area and pore characteristics of support and catalyst.

Sample	**S_{BET} (m g^{-1})[a]**	**V_p (cm^3 g^{-1})[b]**	**d_p (nm)[c]**
SiO_2	414.65	0.58	6.60
SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$	333.66	0.33	5.46
SiO2-Im/Br-Nic.Ac/TMG-$PdCl_2$ - spent	329.82	0.16	4.92

[a] Specific surface area, [b] Pore specific volume, [c] Average pore diameter.

The successful propylation of the SiO_2 surface was confirmed with ^{29}Si NMR and results are presented in Figure 4. The peak at -57.9 ppm (T^3 band) confirmed that most of the alkane chains were anchored to the surface via two Si-O-Si bonds. Additionally some of the chains was connected to the surface trough one and three bonds (peaks at -50.7 and -67.1 ppm). However, the large peak at -101.3 ppm pointed out that many of the silanol groups (Q^3 units) stayed unchanged and this was expected because the IL loading was 8 % (estimated with TGA). Similar results have been reported in literature [50].

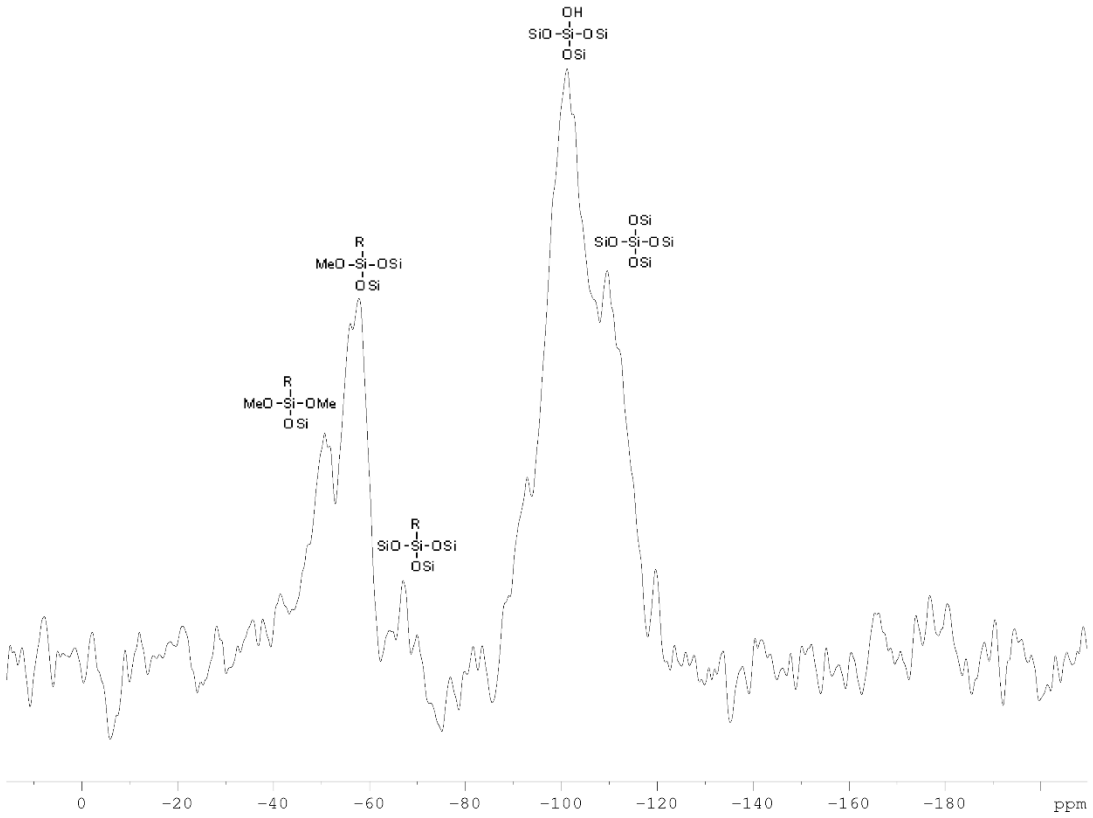


Figure 4. ^{29}Si CP MAS NMR spectra of propylated surface of silica.

To have a final proof of the IL layer formations we performed solid state ^{13}C NMR. The carbon atoms originally belonging to the 3-chloroprpylated chain have peaks at 7.7, 23.0 and in 49.7 ppm region (see Figure 4). The imidazole carbon coordinated with N atoms showed up at 136.2 and two other carbons are overlapping in 122.0 ppm region [41]. The carbon atoms belonging to the nicotinic acid were detected downfield with the most polarized carbon belonging to the acid group appeared at 171.4 ppm due to the deshielding in the presence of the tetramethylganidinium cation in vicinity of oxygen atom. Those carbons bonded to nitrogen are at 151.8 and a stronger peak at 143.8. The peak at 137.6 ppm was assigned to the carbon opposite to the nitrogen atom in pyridine

ring. As showing Figure 4, carbon no. 11 is expected to give week signal that is overlapping with signal of imidazole carbons (136.2 ppm region) which would be in agreement with theoretical predictions and earlier studies [51]. The carbon atoms belonging to TMG cation are detected at 160.9 ppm and 37.5 ppm, later one belonging to the methyl groups. In addition to these two, at 157.4 ppm one more peak was detected after the TMG immobilization. We assume that this one belongs to the fraction of TMG that eventually forms ionic liquid with bromine as anion. Which indicate that TMG is not strictly attached to end chain of grafted IL layer but that there is a free flow in between the two different anions appearing in site.

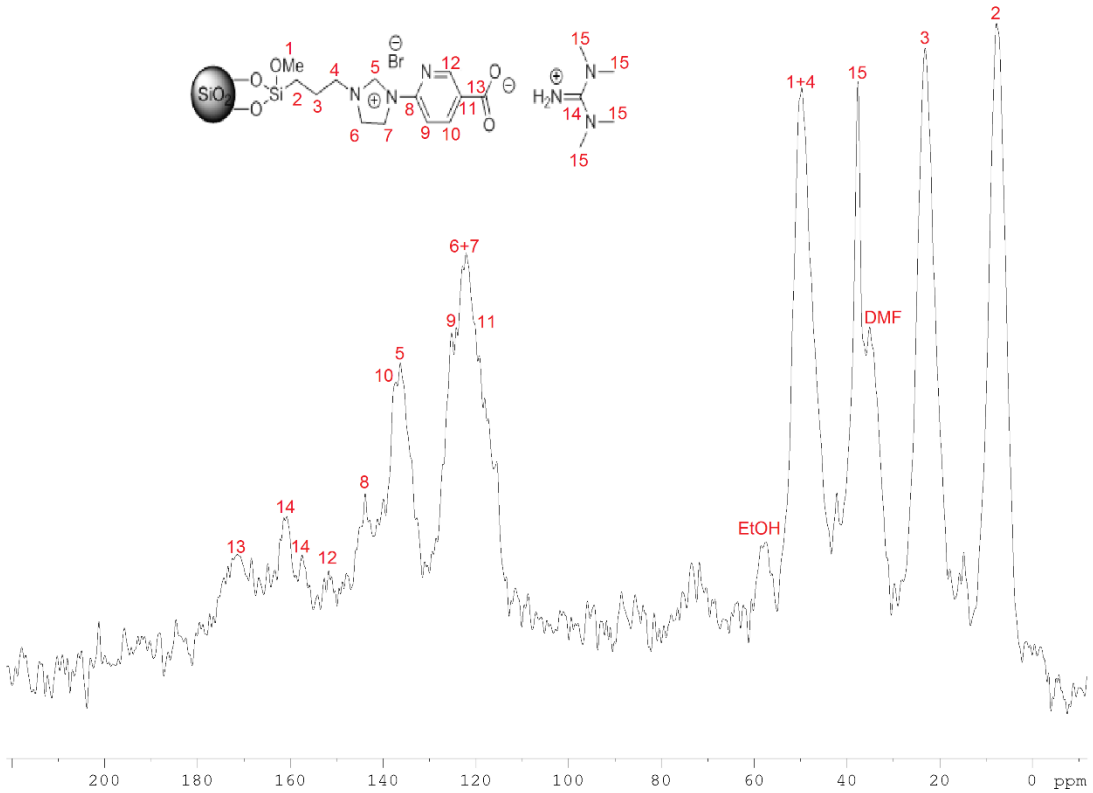
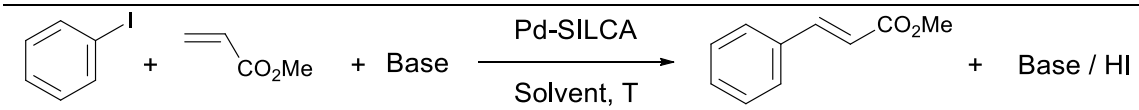


Figure 5. ^{13}C CP MAS NMR spectra of SiO_2-Im/Br-Nic.Ac/TMG.

Before going deeper in the catalyst characterization, the prepared catalytic material was screened under different conditions in the benchmark reaction of iodobenzene and methylacrylate to give methyl cinnamate as the main product. In the first study the solvent, base and temperature were optimized. When reaction was performed without solvent (Table 3, entry 1), only a small amount of the product was detected. Different solvents showed that the reaction proceeds much better in polar aprotic solvents (entries 2-8) compare to protic ones (entries 9, 12, 13) and their mixtures (entries 10 and 11), while nonpolar solvents almost hindered reaction (entries 14, 15, 16). To distinguish between the DMA and NMP as best solvents, the raction was conducted with a reused catalyst for additional three cycles, and in the third cycle, NMP showed a much better performance giving 70 % yield of cinnamate. In the following stage, we studied the influence of different organics (entries 18-27) and inorganic bases (entries 28-32) and their mixture (entry 33). As expected the use of a base was necessary (entry 17). Tertiary amines gave the best results out of which triethanolamine outperformed the other ones (entry 21) resulting in complete conversion in the second Heck cycle and, therefore, became an obvious choice. To inspect the temperature influence the reaction was tested at room temperature and at 50, 80 and 120 °C, respectively (entries 34-37). At temperatures less than 100 °C, the reaction could not proceed. On the other hand, the reaction was completed in 5 minutes at 120 °C, so in further experiments this was fixed as the reaction temperature.

Table 3 Reaction condition optimization for Heck reaction of iodobenzene and methylacrylate.



Entry[a]	Solvent	Base	T (°C)	time (min)	Yield (%)[b]
1	/	Et_3N	100	15	5
2	DMF	Et_3N	100	15	92
3	DMSO	Et_3N	100	15	52
4	DMA	Et_3N	100	15	100 (98, 87, 12)[c]
5	Acetonitrile	Et_3N	100	15	11
6	NMP	Et_3N	100	15	100 (100, 87, 70)[c]
7	THF	Et_3N	100	15	4
8	Et_3N	Et_3N	100	15	2
9	H_2O	Et_3N	100	15	3
10	DMF+H_2O (4:1)	Et_3N	100	15	29
11	DMF+H_2O (1:4)	Et_3N	100	15	5
12	$(EtOH)_3N$	Et_3N	100	15	32
13	EtOH	Et_3N	100	15	2
14	Toluene	Et_3N	100	15	2
15	Heptane	Et_3N	100	15	1
16	Decane	Et_3N	100	15	2
17	NMP	/	100	10	1
18	NMP	Et_3N	100	10	100 (29)[d]
19	NMP	Pr_3N	100	10	100 (91)[d]
20	NMP	Bu_3N	100	10	100 (88)[d]
21	NMP	$(EtOH)_3N$	100	10	100 (100)[d]
22	NMP	Pyridine	100	10	0
23	NMP	Imidazole	100	10	8

24	NMP	TMG	100	10	1
25	NMP	Bu-TMG	100	10	1
26	NMP	DBU	100	10	0
27	NMP	DBN	100	10	0
28	NMP	K_2CO_3	100	10	30
29	NMP	Na_2CO_3	100	10	83
30	NMP	$NaHCO_3$	100	10	2
31	NMP	NaOAc	100	10	5
32	NMP	NaOH	100	10	30
33	NMP	$Et_3N+Na_2CO_3$ (1:1)	100	10	100
34	NMP	$(EtOH)_3N$	r.t.	30	0[e]
35	NMP	$(EtOH)_3N$	50	30	0[e]
36	NMP	$(EtOH)_3N$	80	30	0[e]
37	NMP	$(EtOH)_3N$	120	5	100

[a] Reaction conditions: iodobenzene 1.0 mmol, methylacrylate 1.5 mmol, base 1.5 mmol, Pd 0.09 mol % (detected by ICP-OES), solvent 1 ml. [b] Isolated yield of main product based on iodobenzene, detected with GC. [c] 2nd, 3rd and 4th reaction cycle (reaction time 30 min, temperature 120 °C). [d] 2nd reaction cycle (reaction time 10 min, temperature 120 °C). [e] Monitoring with TLC.

Under the optimized reaction conditions, we studied the amount of catalyst and the reaction versatility as summarized in Table 4. In the first set of experiments (entries 1-5), the reaction was initially catalyzed with Pd loading as low as 0.00009 mmol (0.009 mol % related to iodobenzene) and further with a higher Pd content up to 0.0018 mmol (0.18 mol %). Catalyst appeared to be highly active for iodobenzene with different alkenes, while a decline of activity was observed for bromo- and chlorobenzene due to their thermodynamic restrictions (entries 6-13). Turnover frequency for our benchmark reaction was calculated to

be about 22 000 h^{-1} for low loading and around 16 000 h^{-1} for higher catalyst loading. In our opinion the reason for deviation from first order kinetic in this case can be due to formation of Pd dimers that slowly agglomerate as palladium black. On the other hand, when small amount of palladium is used, all the Pd is utilized in the reaction cycle and the activity is preserved. This deviation from 1st order kinetics was also hypothesized in other studies [52] where it was found out that the reaction rate depends on the catalyst amount and is between half and first order, depending on the substrate ratios. Beside the fact that the best activity was achieved with 0.009 - 0.018 mol % of Pd (1 - 2 mg of catalytic material), we decided to conduct our study with higher loadings of palladium (0.09 mol % Pd, 10 mg of catalytic material) in order to decrease the influence of experimental errors.

The catalyst activities are presented as the turnover frequencies. When compared with similar catalytic systems found in literature and gathered in Table 5, our catalyst showed the best performance. In our opinion the reason for such a high activity is the stability of palladium species in the ionic liquid layer, where they are firmly bonded via NHC, CO and TMG ligands. Exposing the catalyst in close presence of halide activates Pd and releases it from the surface, where it is immediately recaptured after the reaction. Therefore we would also propose that a release and catch mechanism takes a place on our catalyst.

Table 4 Catalyst amount optimization and reaction versatility tests.

Entry[a]	**Aryl halide**	**Alkene**	**Pd (mmol)[b]**	**Product (mmol)[c]**	**time (min)**	**TOF (h^{-1})[d]**

1	Iodobenzene	Me. Acrylate	0.00009	1.0000	30	22222
2	Iodobenzene	Me. Acrylate	0.00018	1.0000	15	22222
3	Iodobenzene	Me. Acrylate	0.00045	0.9371	8	15618
4	Iodobenzene	Me. Acrylate	0.0009	0.9762	4	16270
5	Iodobenzene	Me. Acrylate	0.0018	0.9479	2	15798
6	Iodobenzene	Bu. Acrylate	0.0009	0.916	60	1018
7	Iodobenzene	Styrene	0.0009	0.71	60	789
8	Bromobenzene	Me. Acrylate	0.0009	0.02	60	22
9	Bromobenzene	Bu. Acrylate	0.0009	0.02	60	22
10	Bromobenzene	Styrene	0.0009	0.02	60	22
11	Chlorobenzene	Me. Acrylate	0.0009	0	60	0
12	Chlorobenzene	Bu. Acrylate	0.0009	0	60	0
13	Chlorobenzene	Styrene	0.0009	0	60	0

[a] Reaction conditions: arylhalide 1.0 mmol, alkene 1.5 mmol, base 1.5 mmol, solvent 1 ml, temperature 120 °C. [b] Pd content detected by ICP-OES. [c] Isolated yield of main product based on aril halide, detected with GC. [d] Calculated as mmol of product per mmol of Pd in unit of time.

Table 5. TOF numbers for similar catalytic systems found in literature for reaction of iodobenzene and methyl acrylate.

Entry	**Catalyst**	**Pd (mmol %)[b]**	**T (°C)**	**TOF (h^{-1})[c]**
1	SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$[a]	0.009	120	22222
2	SBA-TMG-Pd [53]	0.01	140	8400
3	SBA-15-SIL-$Pd(OAc)_2$ [42]	1.0	120	29
4	Pd/SBA-15 nanocomposite [54]	0.04	140	2500
5	SiO_2-BisILs[$PdCl_4^{2-}$] [55]	0.5	100	8
6	SiO_2 -Im. Cross Linked-Pd [56]	0.1	90	46
7	Silica-Supported NHC-Pd/IL [40]	0.05	140	380
8	PDVB-IL-Pd [57]	0.02	120	1212
9	Pd–g-SILLP [58]	0.02	130	9375[d]

[a] This work. [b] Amount related to iodobenzene. [c] Calculated as mmol of product per mmol of Pd in unit of time. [d] TOF calculated at 50 % of conversion.

To visualize the state of the catalyst, SEM and TEM imaging was recorded on fresh and recycled catalysts in one Heck cycle. From the SEM scans displayed in Figure 6 it is clear that the palladium particles were uniformly dispersed on the silica surface before the reaction while after being exposed to reaction conditions these particles were agglomerated. Looking deeper into the catalyst morphology by studying TEM images (Figure 7) it was found that before reaction, palladium particles were in the range of 12-18 nm but after the first reaction cycle this changed to the 32-52 nm range. The activity of reused catalyst was still extremely high. This renders us believe that during the course of the reaction, active Pd particles are released from the surface of the catalyst and when the reaction is finished, they are redeposited on the surface. Recaptured palladium assemble dimerized particles in grape-like formations. Since the activity of this palladium is still extremely high, we consider that the dimerized form represent a reservoir of the active species.

The release and catch mechanism for the Heck reaction was already reported [56] and it comes from the ability of the moiety to retake Pd. In our case, the nitrogen containing and mainly the TMG molecule has a function to harvest leached Pd in the form of nanoparticles. To confirm this hypothesis, we prepared a catalyst in same manner as described above but without the TMG appendix. This catalyst was equally efficient in the first reaction cycle, however, when reused this catalyst completely lost its activity. The SEM analysis showed that Pd agglomerated into inactive nanoparticles with a particle size exceeding

100 nm (Fig.7, c). This indicates that positively charged nitrogen atoms in the imidazolium and pyridinum rings are able to keep the palladium metal in smaller clusters [58]. Nevertheless, after Pd is dimerized into more negative charges only tetramethylguanidinium cations are capable to keep Pd anions tight enough. This ability of TMG to behave as a ligand and stabilize Pd during the Heck reaction was demonstrated in bulk ionic liquids [59] and in the heterogenized form [53].

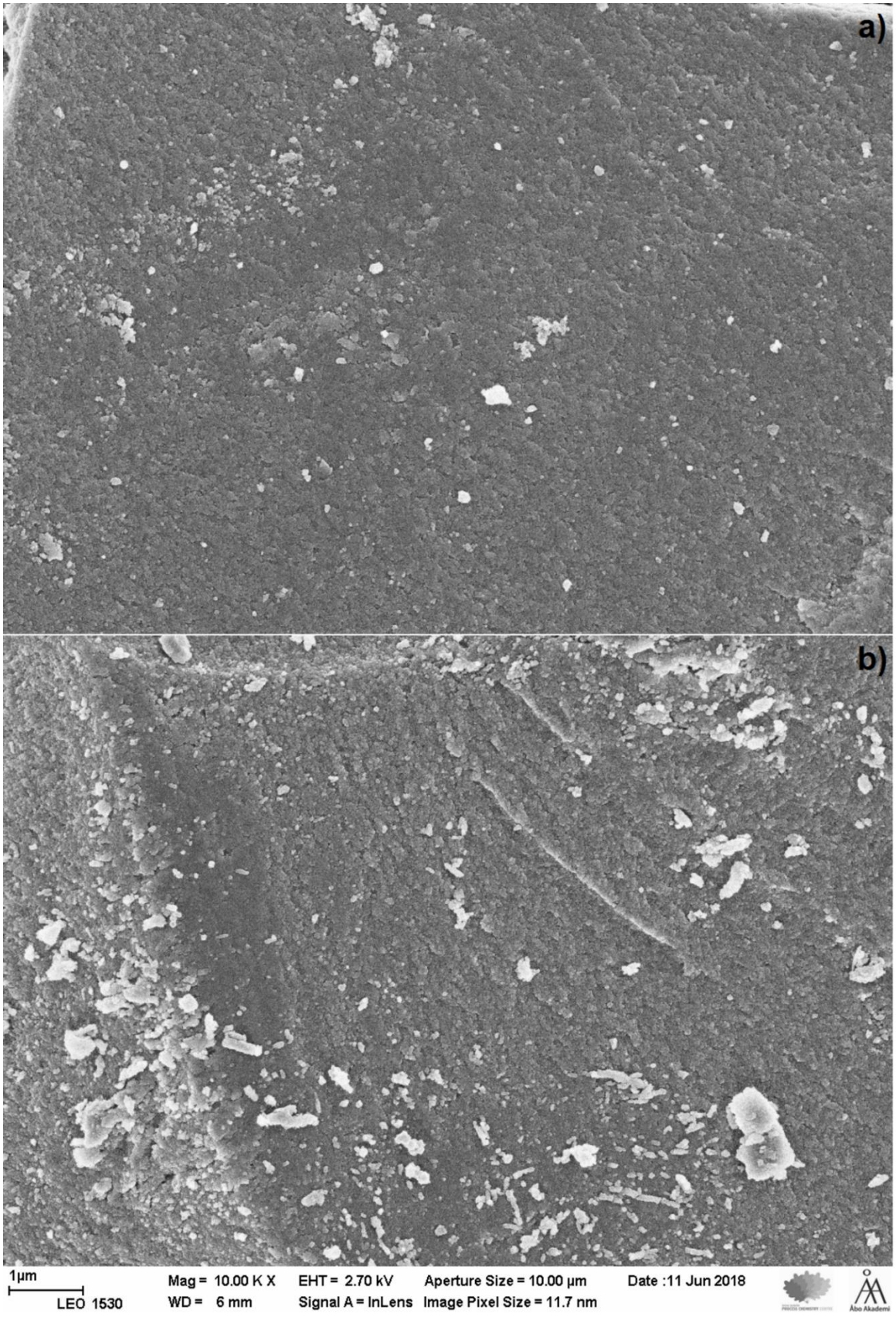


Figure 6. SEM images of fresh (a) and spent catalyst (b).

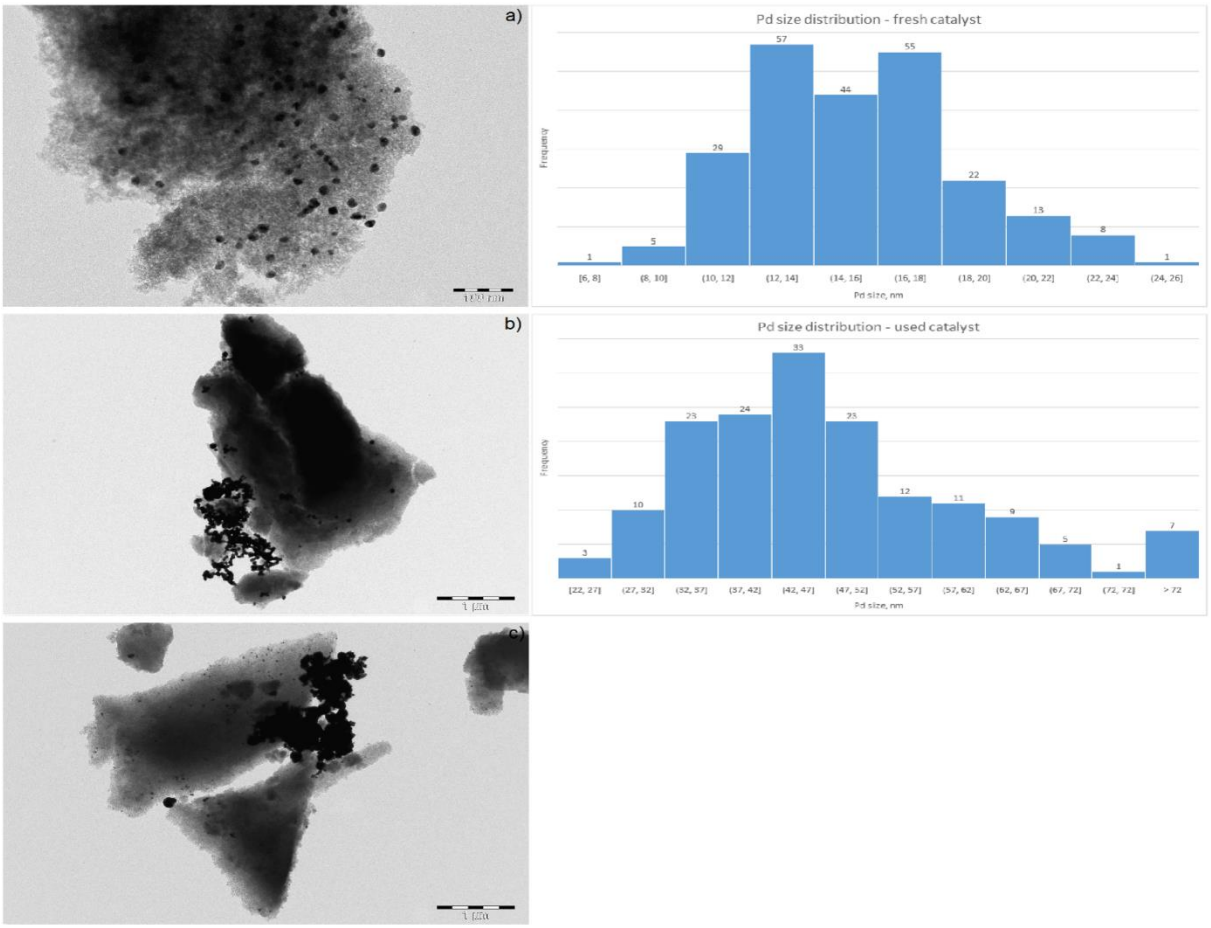


Figure 7. TEM images and particle size distribution for fresh catalyst (a) and recycled catalyst (b). Recycled catalyst synthetized without TMG moiety (c).

The ICP-OES tests showed that a fresh catalyst had a Pd loading of 0.96 wt. % or 0.090 mmol g_{cat}^{-1} which means that 90 % of the palladium that was used for the synthesis ended up immobilized in the catalyst, however we believe that not all of it was chemically bonded. After the reaction, recycled catalyst showed a decrease in Pd amount to 0.77 wt. % (0.085 mmol g_{cat}^{-1}), and this leached palladium was detected in the solvent. We consider that the palladium leached during the reaction was the one that was physically absorbed on the catalyst surface as well as one that did not found the way back to the to the anchoring places on the catalyst surface because of possible contamination with salts formed in the Heck cycle. The catalyst prepared without TMG showed similar

results with initial Pd loading of 0.88 wt. % (0.083 mmol g_{cat}^{-1}) and 0.77 wt. % (0.072 mmol g_{cat}^{-1}) after the reaction. This implies that the role of TMG was merely to hinder formation of huge agglomerates and not just to retake released metal.

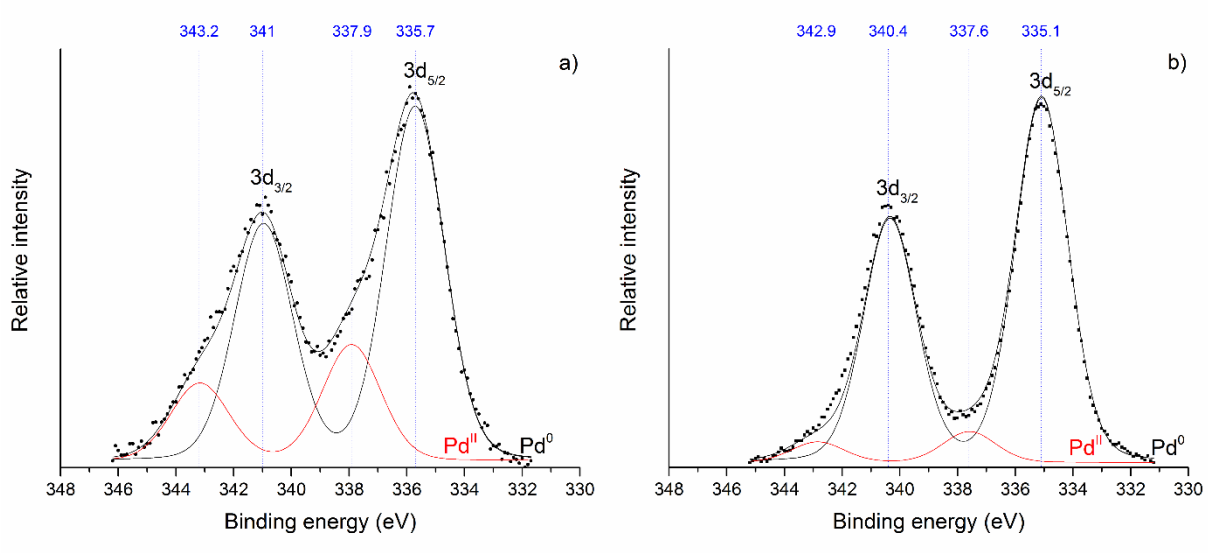


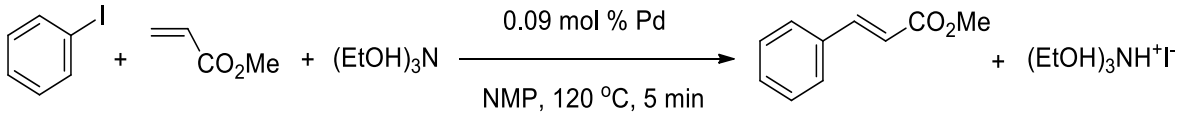
Figure 8. XPS spectrum of Pd 3d of fresh SiO_2-Im/Br-Nic.Ac/TMG-$PdCl_2$ (a) and spent catalyst (b).

The physical state of palladium in fresh and spent catalysts was determined by X-ray photoelectron spectroscopy. As displayed in Figure 8 both Pd(II) and metallic Pd(0) were detected in the catalyst. If the ratio of ionic to metallic palladium was compared before versus after reaction (Fig. 8, a) and b)) it is evident that after the reaction most of Pd(II) was reduced to Pd(0). This was ascribed to the abundance of nitrogen in ionic liquid layer.

To investigate the catalyst recyclability we repeated the reaction of iodbenzene and methylacrylate in presence of 0.09 mol % of Pd and $(EtOH)_3N$ base in NMP, like presented in Table 4, entry 4. After each cycle the catalyst was washed with DMF to extract all the products, followed with diethyl ether washing

and drying. After drying, the catalyst was reused in the reaction (Table 6). A high activity was maintained in five cycles before the activity started to decrease and prolonged reaction times were needed to reach comparable conversion.

Table 6. Catalyst amount optimization and reaction versatility tests.



Entry[a]	Cycle	Yield (%)[b]
1	1	100
2	2	100
3	3	100
4	4	100
5	5	100
6[c]	6	100

[a] Reaction conditions: iodobenzene 1.0 mmol, methylacrylate 1.5 mmol, triethanolamine 1.5 mmol, NMP 1 ml. [b] Isolated yield of main product based on iodobenzene, detected with GC. [c] Reaction time 7 min.

Although a general opinion is that the agglomeration is responsible for the decrease in the activity of the palladium supported catalysts, we believe that this is not a primary reason, because in that case the catalyst might be deactivated after the first cycle, as agglomeration occurs. We consider that the decrease of the activity after five cycles indicates on catalyst leaching as well as poisoning of some kind. To gain more information we performed the studies at lower conversion by suppressing reaction before full conversion, this leaded to complete catalyst deactivation in following cycle, once more confirming the release and catch mechanism. As long as iodobenzene is present in slurry,

palladium will be in its homogenous form therefore not recovered by physical removal of the solid. Nevertheless, the catalyst deactivation mechanism is speculative at this level and would require more detailed analysis which will be conducted in upcoming studies.

4 Conclusions

In the current study we disclosed a new catalytic system for the Heck reaction. Supported ionic liquid catalyst showed by far the best activity reported in literature for the reaction of iodobenzene and methyl acrylate, achieving TOFs of 22 000 h^{-1}. The high activity was denoted to the multiple anchoring points in the ionic liquid layer that can stabilize active palladium via NHC, CO and TMG ligands. The mostly influential were the TMG ligands which were able to stabilize the Pd nanoparticles and limit the agglomeration to the 52 nm particle size or less. These particles are considered to be the reservoirs of the active Pd that catalyzes reaction via a release and catch mechanism. Extremely small amounts of palladium (0.009 mol %) were able to catalyze the reaction in a short time; on the other hand when this amount was increased the catalyst started to loss the activity probably due to the dimerization of Pd. Considering the Pd amount used in this study, the metal deposition was efficient and the utilization reached 90 %. For the upcoming studies the results will bring significant savings in the production costs. The described catalyst synthesis procedure gave SiO_2 functionalized with nicotinic acid as an intermediate which can lead to new applications. The work provides solid ground for further investigations with bis-layered catalysts with different metals, building blocks and reactions.

5 Conflicts of interest

There are no conflicts to declare.

6 Acknowledgments

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7 Notes and references

[1] T. Mizoroki, K. Mori, A. Ozaki, Arylation of Olefin with Aryl Iodide Catalyzed by Palladium, Bull. Chem. Soc. Jpn. 44 (1971) 581–581. doi:10.1246/bcsj.44.581.

[2] R.F. Heck, J.P. Nolley Jr, Palladium-catalyzed vinylic hydrogen substitution reactions with aryl, benzyl, and styryl halides, J. Org. Chem. 37 (1972) 2320–2322.

[3] R.F. Heck, Palladium Catalyzed Reactions of Organic Halides with Olefins, Acc. Chem. Res. 12 (1979) 146–151.

[4] W. Ramsay, On picoline and its derivatives., Philos. Mag. (1878).

[5] P. Murrill, Halides and perhalides of the picolines., J. Am. Chem. Soc. 21 (1899) 828–854. doi:10.1021/ja02060a002.

[6] H.O. Jones, A study of isomerism and optical activity of quinquevalent nitrogen compounds., J. Chem. Soc. Trans. 83 (1903) 1400–1421. doi:10.1039/CT9038301400.

[7] H.O. Jones, Optically active nitrogen compounds. d- and l-Phenylbenzylmethylethylammonium salts., J. Chem. Soc. Trans. 85 (1904) 223–234. doi:10.1039/CT9048500223.

[8] A.W. Harvey, A note on phenyldimethylallylammonium compounds., J. Chem. Soc. Trans. 85 (1904) 412–414. doi:10.1039/CT9048500412.

[9] P. Walden, Molecular weights and electrical conductivity of several fused salts., Bull. l'Academie Imp. Des Sci. St.-Petersbg. (1914) 405–422.

[10] J.S. Wilkes, M.J. Zaworotko, Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids., J. Chem. Soc. Chem. Commun. (1992) 965–967. doi:10.1039/c39920000965.

[11] J.D. Holbrey, K.R. Seddon, Ionic Liquids, Clean Prod. Process. 1 (1999) 223–236. doi:10.1007/s100980050036.

[12] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy and synthesis., Inorg. Chem. 21 (1982) 1263–1264. doi:10.1021/ic00133a078.

[13] K.R. Seddon, Ionic Liquids for Clean Technology, J. Chem. Technol. Biotechnol. 68 (1997) 351–356. doi:10.1002/(SICI)1097-4660(199704)68:4<351::AID-JCTB613>3.0.CO;2-4.

[14] R. Hagiwara, Y. Ito, Room temperature ionic liquids of alkylimidazolium cations and fluoroanions, J. Fluor. Chem. 105 (2000) 221–227. doi:10.1016/S0022-1139(99)00267-5.

[15] P. Wasserscheid, W. Keim, Ionic Liquids—New “Solutions” for Transition Metal Catalysis, Angew. Chemie. 39 (2000) 3772–3789. doi:10.1002/1521-3773(20001103)39:21<3772::AID-ANIE3772>3.0.CO;2-5.

[16] T. Welton, Room-Temperature Ionic Liquids. Solvents for Synthesis and Catalysis., Chem. Rev. (Washington, D. C.). 99 (1999) 2071–2083. doi:10.1021/cr980032t.

[17] C.L. Hussey, Room temperature haloaluminate ionic liquids. Novel solvents for transition metal solution chemistry., Pure Appl. Chem. 60 (1988) 1763–1772. doi:10.1351/pac198860121763.

[18] C.L. Hussey, Room-temperature molten salt systems., Adv. Molten Salt Chem. 5 (1983) 185–230.

[19] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Ionic Liquid (Molten Salt) Phase Organometallic Catalysis., Chem. Rev. (Washington, DC, United States). 102 (2002) 3667–3691. doi:10.1021/cr010338r.

[20] Y. Chauvin, H. Olivier-Bourbigou, Nonaqueous ionic liquids as reaction solvents., Chemtech. 25 (1995) 26–30.

[21] R. Feng, D. Zhao, Y. Guo, Revisiting Characteristics of Ionic Liquids: A Review for Further Application Development, J. Environ. Prot. (Irvine,. Calif). 01 (2010) 95–104. doi:10.4236/jep.2010.12012.

[22] D.E. Kaufmann, M. Nouroozian, H. Henze, Molten salts as an efficient medium for palladium-catalyzed C-C coupling reactions., Synlett. (1996) 1091–1092. doi:10.1055/s-1996-5658.

[23] W.A. Herrmann, V.P.W. B?hm, Heck reaction catalyzed by phospha-palladacycles in non-aqueous ionic liquids, J. Organomet. Chem. 572 (1999) 141–145. doi:10.1016/S0022-328X(98)00941-3.

[24] V.P.W. Bohm, W.A. Herrmann, Coordination chemistry and mechanisms of metal-catalyzed C-C coupling reactions; Part 12 nonaqueous ionic liquids: superior reaction media for the catalytic Heck-vinylation of chloroarenes., Chem. - A Eur. J. 6 (2000) 1017–1025. doi:10.1002/(SICI)1521-3765(20000317)6:6<1017::AID-CHEM1017>3.0.CO;2-8.

[25] A.J. Carmichael, M.J. Earle, J.D. Holbrey, P.B. McCormac, K.R. Seddon, The Heck Reaction in Ionic Liquids: A Multiphasic Catalyst System., Org. Lett. 1 (1999) 997–1000. doi:10.1021/ol9907771.

[26] S. Li, Y. Lin, H. Xie, S. Zhang, J. Xu, Brønsted guanidine acid-base ionic liquids: Novel reaction media for the palladium-catalyzed heck reaction, Org. Lett. 8 (2006) 391–394. doi:10.1021/ol052543p.

[27] R. Wang, J.-C. Xiao, B. Twamley, J.M. Shreeve, Efficient Heck reactions

catalyzed by a highly recyclable palladium(II) complex of a pyridyl-functionalized imidazolium-based ionic liquid., Org. Biomol. Chem. 5 (2007) 671–678. doi:10.1039/b616529j.

[28] L. Wang, H. Li, P. Li, Task-specific ionic liquid as base, ligand and reaction medium for the palladium-catalyzed Heck reaction, Tetrahedron. 65 (2009) 364–368. doi:10.1016/j.tet.2008.10.042.

[29] Z.D. Petrović, D. Simijonovišć, V.P. Petrović, S. Marković, Diethanolamine and N,N-diethylethanolamine ionic liquids as precatalyst-precursors and reaction media in green Heck reaction protocol, J. Mol. Catal. A Chem. 327 (2010) 45–50. doi:10.1016/j.molcata.2010.05.010.

[30] Z.D. Petrović, S. Marković, V.P. Petrović, D. Simijonović, Triethanolammonium acetate as a multifunctional ionic liquid in the palladium-catalyzed green Heck reaction, J. Mol. Model. (2012). doi:10.1007/s00894-011-1052-1.

[31] J.A. Loch, M. Albrecht, E. Peris, J.W. Faller, R.H. Crabtree, Palladium Complexes with Tridentate Pincer Bis-Carbene Ligands as Efficient Catalysts for C - C Coupling, (2002) 700–706. doi:10.1021/cr050004s.

[32] D. Meyer, M.A. Taige, A. Zeller, K. Hohlfeld, S. Ahrens, T. Strassner, Palladium Complexes with Pyrimidine-Functionalized N-Heterocyclic Carbene Ligands: Synthesis, Structure and Catalytic Activity, Organometallics. 28 (2009) 2142–2149. doi:10.1021/om8009238.

[33] F. Schroeter, J. Soellner, T. Strassner, Cross-Coupling Catalysis by an Anionic Palladium Complex, ACS Catal. 7 (2017) 3004–3009. doi:10.1021/acscatal.6b03655.

[34] C.P. Mehnert, E.J. Mozeleski, R.A. Cook, Supported ionic liquid catalysis investigated for hydrogenation reactions, Chem. Commun. (2002) 3010–3011. doi:10.1039/b210214e.

[35] C.P. Mehnert, R. a Cook, N.C. Dispenziere, M. Afeworki, Supported ionic liquid catalysis--a new concept for homogeneous hydroformylation catalysis., J. Am. Chem. Soc. 124 (2002) 12932–12933. doi:10.1021/ja0279242.

[36] P. Virtanen, H. Karhu, G. Toth, K. Kordas, J.P. Mikkola, Towards one-pot synthesis of menthols from citral: Modifying Supported Ionic Liquid Catalysts (SILCAs) with Lewis and Brønsted acids, J. Catal. 263 (2009) 209–219. doi:10.1016/j.jcat.2009.02.005.

[37] P. Mäki-Arvela, J.-P. Mikkola, P. Virtanen, H. Karhu, T. Salmi, D. Yu. Murzin, Supported Ionic Liquid Catalyst (SILCA) in the Hydrogenation of Citral, Sci. Bases Prep. Heterog. Catal. 162 (2006) 87–94. doi:https://doi.org/10.1016/S0167-2991(06)80894-3.

[38] H. Hagiwara, Y. Sugawara, K. Isobe, T. Hoshi, T. Suzuki, Immobilization

of Pd(OAc)2 in ionic liquid on silica: Application to sustainable Mizoroki-Heck reaction, Org. Lett. (2004). doi:10.1021/ol049343i.

[39] H. Hagiwara, Y. Sugawara, T. Hoshi, T. Suzuki, Sustainable Mizoroki–Heck reaction in water: remarkably high activity of Pd(OAc) 2 immobilized on reversed phase silica gel with the aid of an ionic liquid, (2005). doi:10.1039/b502528a.

[40] B. Karimi, D. Enders, New N-heterocyclic carbene palladium complex/ionic liquid matrix immobilized on silica: Application as recoverable catalyst for the Heck reaction, Org. Lett. (2006). doi:10.1021/ol060129z.

[41] H. Yang, X. Han, G. Li, Y. Wang, N-Heterocyclic carbene palladium complex supported on ionic liquid-modified SBA-16: an efficient and highly recyclable catalyst for the Suzuki and Heck reactions, Green Chem. (2009). doi:10.1039/b904136b.

[42] J.Y. Jung, A. Taher, H.J. Kim, W.S. Ahn, M.J. Jin, Heck reaction catalyzed by mesoporous SBA-15-supported ionic liquid-Pd(OAc)2, Synlett. (2009). doi:10.1055/s-0028-1087488.

[43] X. Shi, X. Han, W. Ma, J. Fan, J. Wei, A PdCl 2-ionic liquid brush assembly: An efficient and reusable catalyst for Mizoroki-Heck reaction in neat water, Appl. Organomet. Chem. (2012). doi:10.1002/aoc.1857.

[44] J. Yang, T. Zeng, D. Cai, L. Li, W. Tang, R. Hong, T. Qiu, Supported ionic liquids as green catalyst for 2-butanol synthesis from transesterification of sec-butyl acetate, Asia-Pacific J. Chem. Eng. 11 (2016) 901–909. doi:10.1002/apj.2024.

[45] B.V.L. Potter, J. Dowden, A. Galione, WO2005054198A2, 2005.

[46] J. Liao, Y. Hong, Y. Wang, T.W. Von Geldern, K.E. Zhang, WO2011094890A1, 2011.

[47] M. Li, P.J. Pham, C.U. Pittman, T. Li, SBA-15-supported ionic liquid compounds containing silver salts: Novel mesoporous π-complexing sorbents for separating polyunsaturated fatty acid methyl esters, Microporous Mesoporous Mater. 117 (2009) 436–443. doi:10.1016/j.micromeso.2008.07.017.

[48] S.K. Gupta, D. Ghorai, J. Choudhury, A new type of palladium-pincer complexes generated via hydrolytic ring-opening of imidazole-2-ylidenes, Organometallics. 33 (2014) 3215–3218. doi:10.1021/om500362x.

[49] V. Antochshuk, M. Jaroniec, Functionalized mesoporous materials obtained via interfacial reactions in self-assembled silica-surfactant systems, Chem. Mater. 12 (2000) 2496–2501. doi:10.1021/cm000268p.

[50] Q. Wang, G.A. Baker, S.N. Baker, L.A. Colón, Surface confined ionic

liquid as a stationary phase for HPLC, Analyst. 131 (2006) 1000–1005. doi:10.1039/B607337A.

[51] D. Brunel, A. Cauvel, F. Fajula, F. DiRenzo, MCM-41 type silicas as supports for immobilized catalysts, Stud. Surf. Sci. Catal. 97 (1995) 173–180. doi:10.1016/S0167-2991(06)81887-2.

[52] T. Rosner, J. Le Bars, A. Pfaltz, D.G. Blackmond, Kinetic studies of heck coupling reactions using palladacycle catalysts: Experimental and kinetic modeling of the role of dimer species, J. Am. Chem. Soc. 123 (2001) 1848–1855. doi:10.1021/ja003191e.

[53] X. Ma, Y. Zhou, J. Zhang, A. Zhu, T. Jiang, B. Han, Solvent-free Heck reaction catalyzed by a recyclable Pd catalyst supported on SBA-15 via an ionic liquid, Green Chem. 10 (2008) 59–66. doi:10.1039/b712627a.

[54] P. Han, X. Wang, X. Qiu, X. Ji, L. Gao, One-step synthesis of palladium/SBA-15 nanocomposites and its catalytic application, J. Mol. Catal. A Chem. 272 (2007) 136–141. doi:10.1016/j.molcata.2007.03.006.

[55] X. Shi, X. Han, W. Ma, J. Fan, J. Wei, A PdCl2-ionic liquid brush assembly: An efficient and reusable catalyst for Mizoroki-Heck reaction in neat water, Appl. Organomet. Chem. 26 (2012) 16–20. doi:10.1002/aoc.1857.

[56] C. Pavia, F. Giacalone, L.A. Bivona, A.M.P. Salvo, C. Petrucci, G. Strappaveccia, L. Vaccaro, C. Aprile, M. Gruttadauria, Evidences of release and catch mechanism in the Heck reaction catalyzed by palladium immobilized on highly cross-linked-supported imidazolium salts, J. Mol. Catal. A Chem. 387 (2014) 57–62. doi:10.1016/j.molcata.2014.02.025.

[57] G. Liu, M. Hou, J. Song, T. Jiang, H. Fan, Z. Zhang, B. Han, Immobilization of Pd nanoparticles with functional ionic liquid grafted onto cross-linked polymer for solvent-free Heck reaction, Green Chem. 12 (2010) 65–69. doi:10.1039/b913182e.

[58] M.I. Burguete, E. García-Verdugo, I. Garcia-Villar, F. Gelat, P. Licence, S. V. Luis, V. Sans, Pd catalysts immobilized onto gel-supported ionic liquid-like phases (g-SILLPs): A remarkable effect of the nature of the support, J. Catal. 269 (2010) 150–160. doi:10.1016/j.jcat.2009.11.002.

[59] S. Li, Y. Lin, H. Xie, S. Zhang, J. Xu, Brønsted Guanidine Acid − Base Ionic Liquids : Novel Reaction Media for the Palladium-Catalyzed Heck Reaction, Tetrahedron. (2006) 2003–2006.