



# Palladium catalysts deposited on silica materials: Comparison of catalysts based on mesoporous and amorphous supports in Heck reaction

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## ABSTRACT

Palladium catalysts supported on different silica-based materials were investigated in the Heck reaction of *n*-butyl acrylate with bromobenzene at 160 °C. The main objective was to understand the role of mesopores in the catalysts supported on SBA-15 functionalised with  $\equiv\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NEt}_2$  donor groups at the surface in comparison with the analogous silica gel-based catalysts. The results obtained evidence a crucial influence of the ratio of the anchoring groups to palladium (N/Pd): a higher excess of coordinating groups in the catalysts results in a higher catalytic activity, probably because such supports aid the deposition of the metal onto the support and, simultaneously, prevent aggregation of the 'active' metal species at high reaction temperatures. This is very important as the reactions with deposited palladium catalysts typically take place in solution with the metal first leaching out from the support and then returning back to the solid matrix. In contrast, the nature of the solid support (mesoporous vs. amorphous) seems to play a less important role. The differences in the activity of catalysts deposited on SBA-15 or silica gel can be accounted for a better availability of the active metal species.

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## 1. Introduction

Palladium-catalysed cross-coupling reactions are highly selective transformations that allow for assembling two different organic molecules into a new compound via creating new C–C or C–heteroatom bonds. One of the most often utilised cross-coupling reactions is the Heck reaction [1]. Despite its enormous synthetic potential, a wide practical implementation of Heck reaction is hindered mainly by the high cost of the noble metal catalysts. Therefore, in recent years, a great effort has been devoted to the design of highly efficient recyclable catalysts, among which heterogeneous systems play a prominent role.

The preparation of heterogeneous catalysts for Heck reaction typically relies on immobilisation of palladium species onto an inorganic solid support [2]. Typical approaches are deposition of palladium nanoparticles [3], covalent anchoring of palladium complexes [4], and immobilisation of donor groups followed by treatment with a palladium source [5]. However, it has been previously noted that even the rather inert inorganic supports are not entirely innocent and may influence the course of the cross-coupling reactions [6].

Since their first preparation in the early 1990s [7], mesoporous molecular sieves gained a considerable attention as solid supports suitable for heterogenisation of various catalytic systems. The main advantages of these siliceous or aluminosilicate materials are mainly their good thermal stability, high surface areas, narrow pore size distribution, and relatively easy covalent modification with organic or organometallic moieties [8]. Despite the frequent utilisation of mesoporous sieves as solid supports for palladium-based catalysts, the role of mesopores has not been systematically studied yet.

In our previous work we have demonstrated that SBA-15 mesoporous molecular sieves bearing  $\equiv\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NEt}_2$  donor groups at the surface are good supports for palladium(II) acetate and that the corresponding metalated materials efficiently mediate Suzuki and Heck reactions, serving as a source of active metal [9]. As an extension of this work, we decided to investigate the influence of the mesopores on the catalytic properties of analogous catalysts based on palladium(II) acetate anchored via the  $\equiv\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NEt}_2$  groups. In this contribution, we report the preparation of a series of catalysts from in-synthesis and post-synthesis modified mesoporous sieve SBA-15 and from analogous, amine-functionalised commercial silica gel. Catalytic properties of these materials were compared in the model Heck reaction of *n*-butyl acrylate with bromobenzene.

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## 2. Results

### 2.1. Preparation and characterisation of the catalysts

The series of catalysts to be investigated was designed to include both materials based on SBA-15 type mesoporous silica and the conventional amorphous silica gel (Scheme 1). The surface of these all-siliceous supports was modified with 3-[2-(*N,N*-diethylamino)ethylamino]propyl groups ( $\equiv\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NEt}_2$ ) either in-synthesis or post-synthetically. The choice of the organic modifying group was based on our previous comparative study that revealed the superiority of the  $\equiv\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NEt}_2$  moiety over other simple (e.g.,  $\equiv\text{Si}(\text{CH}_2)_3\text{NH}_2$ ,  $\equiv\text{Si}(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$ ) and some branched amine modifiers [10].

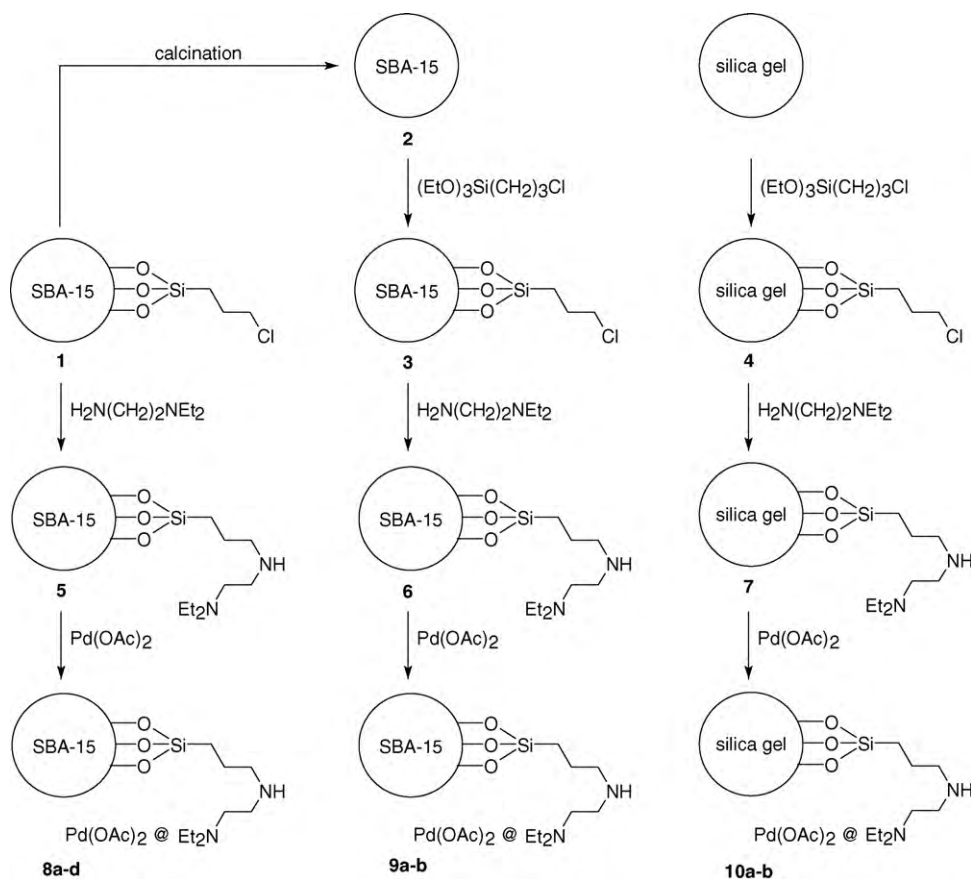
The starting, in-synthesis functionalised SBA-15 material **1** was prepared by direct template synthesis from sodium silicate using P123 tri-block copolymer as a structure-directing agent and (3-chloropropyl)triethoxysilane as the source of the surface modifying groups. Following the template removal by Soxhlet extraction, the intermediate 3-chloropropylated SBA-15 was converted to aminopropylated support **5** by reacting with *N,N*-diethyl-1,2-diaminoethane and then with ammonia in ethanol–water. Finally, material **5** was metalated with a solution of palladium(II) acetate in dichloromethane to afford a series of supported palladium catalysts with different metal loading, **8a–d**.

The corresponding post-synthesis functionalised materials were prepared (Scheme 1) from mesoporous SBA-15 (**2**), which resulted from material **1** after removal of all organic components by means of calcination at 550 °C. We used this convergent approach rather than the direct template synthesis of pristine

SBA-15 to ensure similar properties of the supports used for the preparation of in-synthesis and post-synthetically functionalised materials. Material **2** was subsequently re-functionalised by reacting with (3-chloropropyl)triethoxysilane to give material **3**, which was then converted to aminopropylated support **6** and, subsequently, to catalysts **9a–b** as described above. The related catalysts supported with silica gel were prepared similarly (Scheme 1) starting with the conventional, chromatographic grade silica gel (Fluka, 70–230 mesh). The silica gel was first calcined (550 °C/5 h) and then treated with (3-chloropropyl)triethoxysilane to give 3-chloropropylated material **4**. Subsequent introduction of the amine groups and metalation with palladium(II) acetate afforded catalysts **10a–b**.

Besides, material **11** possessing the larger multidonor  $\equiv\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{N}[(\text{CH}_2)_2\text{NH}_2]_2$  groups at the surface was prepared analogously by amination of support **1** with *N,N,N*-tris(2-aminoethyl)amine. Since the deposited palladium catalyst based on this support, namely  $\text{Pd}(\text{OAc})_2@11$ , does not show any catalytic activity in Heck reaction [10], material **11** was employed only as a catalytic poison. All materials were characterised by elemental analysis, IR spectroscopy, X-ray powder diffraction, and by nitrogen adsorption isotherms. Selected analytical data and textural parameters are summarised in Table 1.

From the results of chemical analysis it follows that the in-synthesis functionalised SBA-15 samples accommodate roughly twice as much anchored organic groups than the corresponding post-synthesis modified materials (see the chlorine and nitrogen content in materials **1/3** and **5/6**, respectively). Thus, the relative amount of modifying groups increased from the materials based on post-synthesis modified mesoporous sieves (**3**, **6**, and **9**) to those prepared from silica gel (**4**, **7**, and **10**) and further to materials based



Scheme 1. Preparation of catalysts 8–10.

**Table 1**  
Analytical data and textural parameters for materials and catalysts **1–11**<sup>a</sup>.

Material/catalyst	Pd content (mmol g <sup>-1</sup> )	Cl content (mmol g <sup>-1</sup> )	N content (mmol g <sup>-1</sup> )	N:Pd molar ratio	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Void volume (cm <sup>3</sup> g <sup>-1</sup> )	Pore size (nm)
<b>1</b>	n.a.	0.6	n.a.	n.a.	716	0.79	6.7
<b>2</b>	n.a.	n.a.	n.a.	n.a.	851	0.80	6.6
<b>3</b>	n.a.	0.2	n.a.	n.a.	733	0.74	6.4
<b>4</b>	n.a.	0.5	n.a.	n.a.	440	0.53	n.a.
<b>5</b>	n.a.	Traces	1.3	n.a.	n.d.	n.d.	n.d.
<b>6</b>	n.a.	Traces	0.56	n.a.	n.d.	n.d.	n.d.
<b>7</b>	n.a.	Traces	0.89	n.a.	n.d.	n.d.	n.d.
<b>8a</b>	0.60	Traces	1.3	2	452	0.63	6.8
<b>8b</b>	0.22	Traces	1.3	6	512	0.74	6.8
<b>8c</b>	0.11	Traces	1.4	13	502	0.72	6.9
<b>8d</b>	0.06	Traces	1.4	23	509	0.75	6.9
<b>9a</b>	0.14	0.1	0.53	4	380	0.67	6.9
<b>9b</b>	0.03	Traces	0.52	17	315	0.71	7.0
<b>10a</b>	0.40	Traces	0.81	2	324	0.43	n.a.
<b>10b</b>	0.06	Traces	0.87	15	353	0.52	n.a.
<b>11</b>	n.a.	Traces	3.0	n.a.	327	0.83	7.1

<sup>a</sup> n.a. = not applicable, n.d. = not determined.

on the in-synthesis functionalised SBA-15 (**1**, **5**, and **8**). The data also suggest that chloride substitution reaction is virtually complete in all materials (both SBA-15 type and silica gel-based) as the molar amount of incorporated nitrogen is approximately a double of the chlorine content in the parent chloropropylated supports. A deviation notable from this trend observed for the pair of materials **3** and **6** can be explained by a relatively lower precision of the determination of the chlorine content (N.B. there is less than 0.7 wt.% of chlorine in material **3**).

The concentrations of anchored palladium as determined in catalysts **8–10** by inductively coupled plasma optical emission spectroscopy (ICP OES) correspond well with the amount of palladium source used during the metalation step. Apparently, a simple treatment of the support with a solution of palladium(II) acetate is sufficient for a practically complete deposition of the metal component which, in turn, demonstrates a good metal scavenging ability of the N-functionalised supports. According to the data available, the maximum metal binding capacity of material **5** is ca. 0.6 mmol Pd per gram of the solid support.

The selective metalation also allowed for the preparation of materials having *different amounts* of the anchoring groups (nitrogen) per palladium. For instance, the N/Pd molar ratio in the in-synthesis modified SBA-15 catalysts **8a–d** varied over a range of 2.2–23. In the catalysts based on the post-synthesis modified SBA-15 and silica gel, the N/Pd molar ratio were 3.6 and 2.0 for the higher metalated catalysts **9a** and **10a**, while the corresponding catalyst containing less palladium, **9b** and **10b**, showed the N/Pd ratios of 17 and 15, respectively.

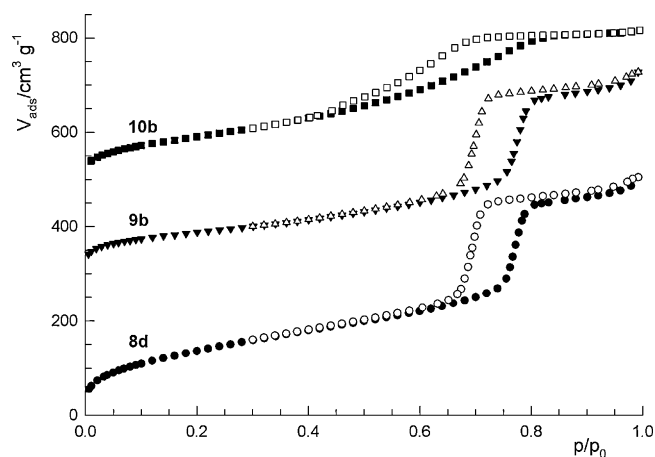
Nitrogen adsorption isotherms (Fig. 1) of the SBA-15 based materials confirm their well-ordered mesoporous structures and favourable textural characteristics. They all display a steep increase in the adsorbed amount of nitrogen in the  $p/p_0$  range ca. 0.65–0.80, which is typical for mesoporous molecular sieves with narrow pore size distribution. The calculated textural parameters (Table 1) further evidence good quality and ordered structure of the materials.

Upon converting material **1** into **2**, the BET surface area increases, very likely due to a removal of organic groups by calcination. The subsequent re-functionalisation leading to support **3** is expectedly accompanied by a decrease in the BET surface area, which then approaches the value of the parent material **1**. This evidences a good stability of the support under the conditions of treatment performed in this study. The amination and deposition of the metal source results in a blocking of the surface of the mesoporous supports and is consequently reflected by a lowering of the BET surface areas. For catalysts **8** prepared from the in-synthesis modified SBA-15, the lowest BET surface area is observed for **8a**

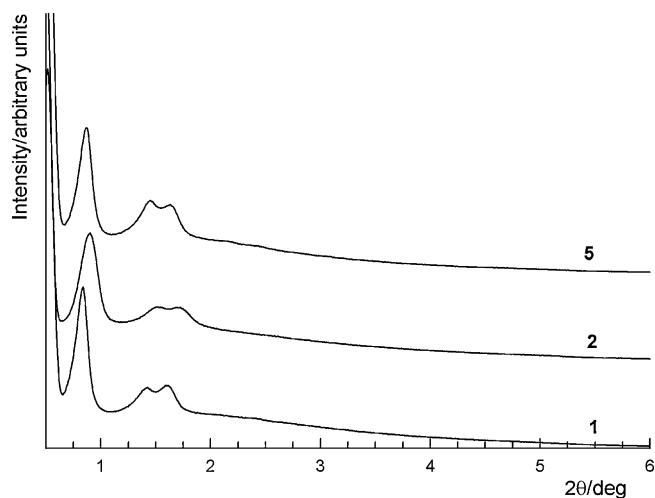
containing the highest amount of anchored palladium. However, among the related less metalated catalysts (**8b–d**) as well as in the pairs **9a/9b** and **10a/10b**, the differences in BET surface areas are rather minor or even negligible. The isotherms recorded for samples prepared from silica gel also showed some hysteresis during the adsorption–desorption cycle (Fig. 1). This can be accounted for by capillary condensation/evaporation of nitrogen in a porous fraction of this material.

X-ray powder diffraction patterns (Fig. 2) of SBA-15 based materials display three characteristic diffraction lines in the range  $2\theta < 3^\circ$ . Upon converting the 3-chloropropyl groups to ‘aminopropyl’ ones and after deposition of palladium, the diffraction patterns remain virtually unchanged: the positions of the diffraction peaks are practically the same while the diffraction intensity *slightly* decreases due to the presence of organic moieties inside the mesopores. This again suggests that the mesoporous structure remains largely unaffected by the surface modifications.

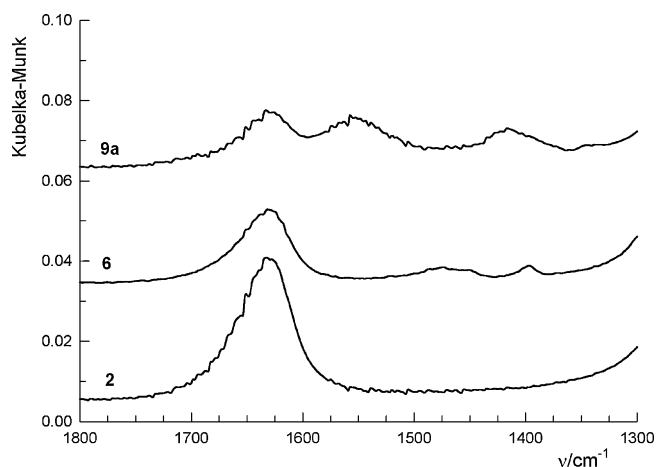
FTIR spectra (Fig. 3) are rather inconclusive, mainly due to relatively minor changes that reflect the low amounts of the anchored organic groups and palladium(II) acetate and the fact that the strongly dominant bands of the support (mainly due to O–H and Si–O bonds) remain invariant. Nevertheless, upon introduction of the 3-chloropropyl groups, there are observed several bands attributable to  $\nu_{C-H}$  at ca. 2850–2990 cm<sup>-1</sup>, whereas the subsequent amination is manifested via bands at ca. 1395 and 1465 cm<sup>-1</sup>,



**Fig. 1.** Nitrogen adsorption–desorption isotherms for materials **8d** (●), **9b** (▲), and **10b** (■). The isotherms of **9b** and **10b** are onset by 300 and 500 cm<sup>3</sup> g<sup>-1</sup>, respectively, to avoid overlaps (filled symbols = adsorption, empty symbols = desorption).



**Fig. 2.** Powder X-ray diffraction patterns of materials **1**, **2** and **5**. The diffractograms are shown with the same scale but are offset to avoid overlaps.

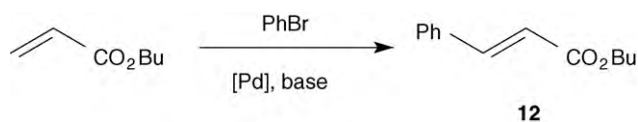


**Fig. 3.** Section of the IR spectra of materials **2**, **6**, and **9a**. The intensity is not scaled with the respect to the amount of material used. For clarity, the spectra are shifted along the y-axis.

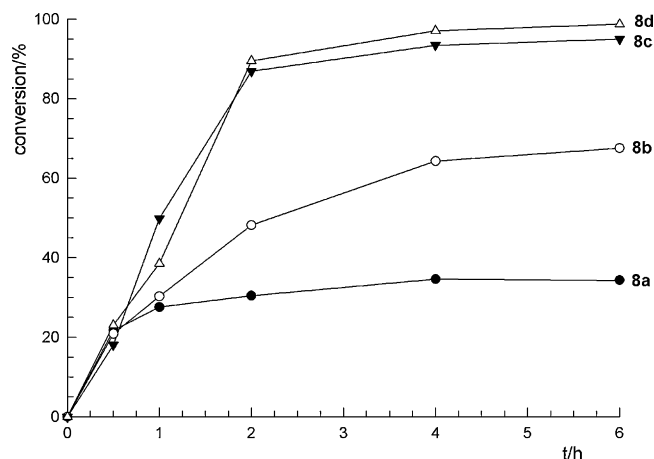
tentatively attributable to C–H bending vibration. Finally, the deposition of palladium(II) acetate results in a pair of relatively strong bands at ca. 1410 and 1560  $\text{cm}^{-1}$  due to acetate  $\nu_{\text{S}}$  and  $\nu_{\text{AS}}$  vibrations [9].

## 2.2. Catalytic tests

During the catalytic tests, we focused mainly on the role of the support (type of the support and the N/Pd ratio) on the catalytic performance of the deposited Pd-catalysts. Other issues such as optimal reaction conditions and catalyst recyclability have been studied earlier [9]. Thus, all catalytic tests have been carried out using the model Heck coupling of *n*-butyl acrylate with bromobenzene to give *n*-butyl cinnamate **12** (Scheme 2). The reaction was performed in the presence of sodium acetate as a base (1.5 equiv. vs. bromobenzene). The acrylate was also used in excess (1.5 equiv.)



**Scheme 2.** The model Heck reaction of *n*-butyl acrylate with bromobenzene to give *n*-butyl cinnamate (**12**).

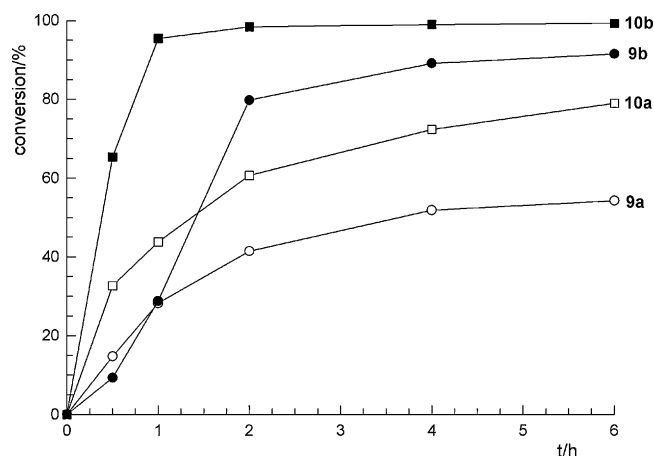


**Fig. 4.** Time-dependence of the conversion of bromobenzene for the model Heck reaction catalysed with catalysts **8** (1 mol% Pd).

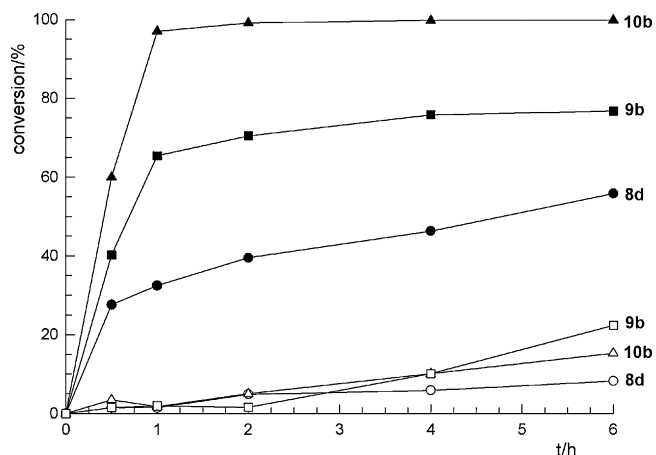
in order to suppress twofold arylation leading to *n*-butyl 2,2-diphenylacrylate. Neither this nor any other side product (e.g., biphenyl) was detected in significant amounts by GC–MS analysis of the reaction mixtures. This not only indicated the coupling reaction to proceed cleanly but also allowed to directly relate the amount of reacted bromobenzene with its conversion to **12**.

Initial reactions performed in the presence of in-synthesis modified catalysts **8a–d** (1 mol% palladium loading) at 160 °C (Fig. 4) confirmed the findings of our previous study [9] that the performance of otherwise similar catalysts is very strongly affected by the N/Pd ratio. At the relatively high reaction temperature used, the least-metallated catalyst **8d** (the highest N/Pd ratio) achieved practically complete conversion within ca. 4 h, whereas the catalyst showing the highest palladium loading **8a** led to only ca. 35% conversion by this time.

Having this feature in mind, we decided next to consider in parallel only catalysts having similar N/Pd ratios, namely **8a**, **9a**, and **10a** or, alternatively, **8c**, **9b**, and **10b**. When compared with the in-synthesis modified counterpart **8a**, catalysts **9a** and **10a** based on the post-synthesis modified supports (Fig. 5) performed considerably better, particularly the latter, silica gel-based material. A similar trend though with higher overall conversions was noted also in the series comprising the less metallated materials **8c**, **9b**, and **10b**. This again suggests that the N/Pd ratio plays a more important role in determining the catalyst efficacy than the total amount of anchored nitrogen groups. The catalysts featuring the highest



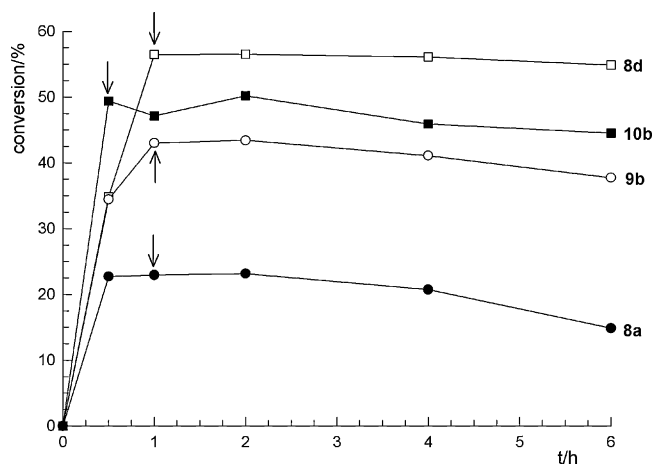
**Fig. 5.** Time-dependence of the conversion of bromobenzene for the model Heck reaction catalysed with catalysts **9** and **10** (1 mol% Pd).



**Fig. 6.** Time-dependence of the conversion of bromobenzene for the model Heck reaction catalysed with catalysts **8d** (circles), **9b** (squares), and **10b** (triangles) performed in the presence of 0.5 mol% (full symbols) or 0.1 mol% of palladium (empty symbols).

N/Pd ratios preserve their high activity even when used in lower amounts (0.5 mol% Pd; Fig. 6). In this case, there is clear the prevalence of the silica gel-based material **10b** over the in-synthesis modified catalyst **8d** and even the post-synthesis functionalised material **9b**. The trend observed at the palladium loading of 0.1 mol% (Fig. 6) is slightly different but gives a rather similar overall picture.

Based on the recent mechanistic investigations [11] and our previous results [9], it appears likely that the support serves only as a source of active palladium species (atoms, small metal clusters, or nanoparticles) [12], and that the reaction takes place in homogeneous phase being catalysed with the leached-out metal. To prove this assumption, several catalyst poisoning tests were carried out, using either elemental mercury or the highly functionalised mesoporous sieve **11** [10] as scavengers to the active metal. The results presented graphically in Fig. 7 for the latter poison clearly demonstrate that the reaction stops immediately after the addition of the metal scavenger regardless of the nature of the support used in the catalyst preparation. The mercury poisoning tests gave very similar results.



**Fig. 7.** Results of the catalyst poisoning tests performed with catalysts **8a**, **8d**, **9b**, and **10b** (1 mol% Pd). The time by which the poison, material **11**, was added to the reaction mixture is indicated by vertical arrows. For details, see Section 4.

### 3. Discussion and conclusions

The nature of active palladium species and its generation from the conventional and ‘heterogeneous’ pre-catalysts have been the subject of intense investigation in the recent past [12,13]. Likewise, the differences between catalysts for cross-coupling reactions supported with *mesoporous molecular sieves* and *amorphous silica* have been previously studied. However, the catalysts tested often differed more than only in the nature of the support, most typically in the ratio of the anchoring groups to palladium [14,15]. As far as chemically related catalysts are concerned, Corma and co-workers studied catalytic activity of an oxime carbapalladacycle anchored onto conventional silica and mesoporous MCM-41. The catalyst based on silica achieved a higher conversion of *p*-chloroacetophenone in Suzuki reaction with phenylboronic acid than its MCM-41 counterpart (91% vs. 43%) [16]. Shimizu et al. prepared catalysts based on palladium(II) acetate deposited at mercaptopropyl-modified FSM-16 or silica gel, and studied these materials in Suzuki reaction of *p*-bromoanisole with phenylboronic acid and in Heck reaction of *p*-bromoacetophenone with ethyl acrylate. In both cases the catalyst based on mesoporous sieve showed *higher conversions* (79% vs. 73%, and 92% vs. 84%, respectively) [17]. Finally, Crudden et al. synthesised palladium catalysts supported on SBA-15 and amorphous SiO<sub>2</sub> modified with 3-mercaptopropyl groups. These catalysts showed comparable (95–100%) yields in Suzuki reaction of *p*-bromoacetophenone with phenylboronic acid pinacol ester in a DMF/H<sub>2</sub>O mixture [18a,b]. However, in Suzuki cross-coupling of *p*-bromoacetophenone with phenylboronic acid in pure DMF the silica gel-based catalyst achieved only a 31% yield compared with 94% yield obtained with its mesoporous counterpart [18c]. In the later work, the same group observed degradation of the mesoporous support which, in the case of SBA-15 possessing linear cylindrical pores, led to a faster deactivation compared with catalyst based on KIT-6 support with a three-dimensional porous structure [19].

The present work clearly demonstrates the differences in the activity of catalysts deposited on amine-functionalised SBA-15 and silica gel. From the results collected, it follows that the nature of the solid support (mesoporous vs. amorphous) has only a minor influence on the overall catalytic activity. The differences in activity of the catalysts deposited on SBA-15 or silica gel reported in this work can be accounted for a better availability of the active metal from the latter support. Since the poisoning tests indicate that that reaction takes place in solution and not inside mesopores of the SBA-15 based catalysts (material **11** cannot enter the pores), the role of mesopores is probably limited only to altering the rate of diffusion of palladium species into the liquid phase (leaching).

On the other hand, the ratio of the anchoring groups to palladium (N/Pd ratio for the catalysts studied) appears to have crucial influence on the catalytic activity, at least at the relatively high reaction temperature used. An excess of coordinating groups in the less metalated catalysts cannot only aid the repeated deposition of the metal onto the support (‘nesting effect’) but may also prevent aggregation of the metal species, which are more widely dispersed on the support’s surface. This is very important in view of the recent data suggesting that the reaction with deposited palladium catalysts typically proceed in solution so that the active metal is first leached out from the support and then returns back (at least partially) to the solid matrix because a better dispersed metal particles can preserve their catalytic activity due to a suppressed aggregation. However, any generalisations should be taken with care as the catalytic results can be very significantly influenced by the reaction temperature, a low stability of the active metal species in insufficiently functionalised materials, and also by the total concentration of the leached-out palladium in the reaction mixture.

## 4. Experimental

### 4.1. Materials and methods

Palladium(II) acetate (Aldrich), mesitylene (Fluka), bromobenzene (Aldrich), *n*-butyl acrylate (Aldrich), *n*-butyl cinnamate (Alfa Aesar), dry *N,N*-dimethylacetamide (Aldrich), poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P123, Aldrich), 3-chloropropyltriethoxysilane (Aldrich), 2-(*N,N*-diethylamino)ethylamine (Aldrich) and *N,N,N*-tris(2-aminoethyl)amine (Aldrich) were used without further purification. Toluene was distilled from sodium under argon. Sodium acetate was freshly melted before use in order to remove traces of water.

Nitrogen adsorption isotherms were measured with a Micromeritics ASAP 2020 volumetric instrument at  $-196^\circ\text{C}$ . The samples were slowly heated up to  $110^\circ\text{C}$  (from room temperature to  $80^\circ\text{C}$  at  $0.5^\circ\text{C min}^{-1}$ , kept at  $80^\circ\text{C}$  for 1 h, and then heated to  $110^\circ\text{C}$  at  $1^\circ\text{C min}^{-1}$  and maintained at this temperature for 5 h) and then degassed until a pressure of  $10^{-3}$  Pa was reached (at least for 24 h). X-ray powder patterns were recorded using a Bruker D8 X-ray powder diffractometer equipped with a graphite monochromator and a position-sensitive detector (Väntec-1) using Cu  $K\alpha$  radiation ( $\lambda = 1.5412 \text{ \AA}$ ) in Bragg–Brentano arrangement. Infrared spectra were recorded in diffuse reflectance mode on Nicolet 7600 (Thermo Fisher Scientific) spectrometer ( $400\text{--}4000 \text{ cm}^{-1}$ , resolution  $4 \text{ cm}^{-1}$ ) using samples diluted with KBr.

The amount of deposited palladium was determined from ICP OES spectra with IRIS Intrepid Duo spectrometer (Thermo Fisher Scientific) equipped with axial plasma and ultrasonic nebuliser (conditions: plasma power 1150 W, sample uptake  $1.0 \text{ mL min}^{-1}$ ). The samples were mineralised in a mixture of concentrated HF and  $\text{HNO}_3$  (volume ratio 2/3; Suprapur Merck) at  $50^\circ\text{C}$  for 15 min and the diluted with redistilled water. The Pd content was determined from the intensity of a line at 324.270 nm. The content of carbon, hydrogen, nitrogen and chloride was determined by combustion analysis.

### 4.2. Preparation of materials 1–4

All-siliceous chloropropylated mesoporous molecular sieve (material **1**) was prepared by direct template synthesis. Commercial tri-block copolymer P123 (10.0 g) and sodium silicate nonahydrate (27.35 g, 0.0962 mol) were dissolved in water (256 mL) by stirring for several hours at room temperature. Then, 35% HCl (67.5 mL, 0.78 mol) was added, and the reaction vessel was immersed into a water bath kept at  $45^\circ\text{C}$ . After 30 min (3-chloropropyl)triethoxysilane (1.88 g, 7.8 mmol); this amount corresponds to 7.5% of all Si atoms in the mixture) was introduced, and the reaction mixture was stirred at  $45^\circ\text{C}$  for 1 h and then put into pre-heated oven at  $90^\circ\text{C}$  for 7 days. The resulting white powder was filtered off, washed thoroughly with water and ethanol, and extracted with ethanol in a Soxhlet apparatus for 24 h.

Characterisation data for material **1**: powder X-ray diffraction:  $2\theta = 0.8$  (s), 1.4 (m), 1.6 (m) $^\circ$ ; elemental analysis: C 9.4 mmol  $\text{g}^{-1}$ , Cl 0.6 mmol  $\text{g}^{-1}$ ; IR:  $\nu_{\text{max}} = 3371$  (br s), 2979 (w), 2939 (w), 1633 (m), 1456 (w), 1380 (w), 1394 (w), 1069 (s), 961 (s), 803 (s)  $\text{cm}^{-1}$ .

Preparation of mesoporous molecular sieve modified with 3-chloropropyl groups *after* the synthesis (material **3**) started from material **1**, which was firstly calcined at  $550^\circ\text{C}$  for 6 h (the calcination temperature was attained with a constant increase in temperature of  $1^\circ\text{C min}^{-1}$ ) to remove all organic modifiers and thus afford material **2**. Material **2** (1.0 g), freshly dehydrated at  $120^\circ\text{C}$  under oil-pump vacuum for 3 h, was suspended in dry toluene (25 mL). The suspension was treated with (3-chloropropyl)triethoxysilane (0.83 g, 3.5 mmol) and the mixture

was refluxed for 16 h under an argon atmosphere. The resulting white powder, material **3**, was filtered off and washed successively with toluene, acetone and pentane.

Characterisation data for material **2**: powder X-ray diffraction:  $2\theta = 0.9$  (s), 1.5 (m), 1.7 (m) $^\circ$ ; elemental analysis: C 0.2 mmol  $\text{g}^{-1}$ ; IR:  $\nu_{\text{max}} = 3400$  (br s), 1633 (m), 1073 (s), 962 (s), 800 (s)  $\text{cm}^{-1}$ . Characterisation data for material **3**: powder X-ray diffraction:  $2\theta = 0.9$  (s), 1.5 (m), 1.7 (m) $^\circ$ ; elemental analysis: C 5.3 mmol  $\text{g}^{-1}$ , Cl 0.2 mmol  $\text{g}^{-1}$ ; IR:  $\nu_{\text{max}} = 3400$  (br s), 1628 (m), 1073 (s), 962 (s), 804 (m)  $\text{cm}^{-1}$ .

The 3-chloropropyl modified silica, material **4**, was prepared by an analogous procedure as the post-synthetically modified mesoporous molecular sieve **3** starting from commercial, chromatographic grade silica (1.0 g, particle size 0.063–0.2 mm; calcined before use at  $550^\circ\text{C}$  for 5 h) and (3-chloropropyl)triethoxysilane (0.83 g, 3.5 mmol).

Characterisation data for **4**: powder X-ray diffraction:  $2\theta = 1.2$  (m) $^\circ$ ; elemental analysis: C 4.3 mmol  $\text{g}^{-1}$ , Cl 0.5 mmol  $\text{g}^{-1}$ ; IR:  $\nu_{\text{max}} = 3340$  (br s), 2981 (m), 2937 (w), 2900 (w), 1866 (s), 1704 (w), 1622 (s), 1446 (w), 1394 (w), 1034 (s), 803 (s)  $\text{cm}^{-1}$ .

### 4.3. Preparation of materials 5–7

Mixture of the chloropropylated material **1** (1.0 g) and 2-(*N,N*-diethylamino)ethylamine (1.98 g, 17 mmol) in 30 mL of dry toluene was stirred at  $100^\circ\text{C}$  under argon for 30 h. The solid was filtered off, washed with ethanol and dried. The resulting yellowish powder was stirred in mixture of 25% aqueous ammonia and ethanol (1:3, ca. 100 mL) for 3 h, the mixture was filtered off, and the residue was washed with ethanol and dried in air at room temperature. The resulting solid was characterised by elemental analysis and used directly in the next step (i.e., for the reaction with palladium(II) acetate; see the following sections).

Analytical data. Material **5**: elemental analysis: C 10.0 mmol  $\text{g}^{-1}$ , N 1.3 mmol  $\text{g}^{-1}$ , Cl traces; IR:  $\nu_{\text{max}} = 3300$  (br s), 2980 (w), 2943 (w), 2889 (w), 1635 (w), 1473 (w), 1396 (w), 1070 (s), 962 (m), 802 (s)  $\text{cm}^{-1}$ . Material **6**: elemental analysis: C 5.1 mmol  $\text{g}^{-1}$ , N 0.6 mmol  $\text{g}^{-1}$ , Cl traces; IR:  $\nu_{\text{max}} = 3290$  (br s), 1869 (w), 1631 (m), 1474 (w), 1397 (w), 1077 (s), 961 (s), 799 (s)  $\text{cm}^{-1}$ . Material **7**: elemental analysis: C 6.4 mmol  $\text{g}^{-1}$ , N 0.9 mmol  $\text{g}^{-1}$ , Cl traces; IR:  $\nu_{\text{max}} = 3300$  (br s), 2979 (w), 2945 (w) 1634 (m), 1474 (w), 1393 (w), 1085 (s), 966 (s), 801 (m), 688 (w), 563 (w)  $\text{cm}^{-1}$ .

### 4.4. Preparation of catalysts 8–10

Catalyst **8a** was prepared by mixing 1.0 g of amine-modified material **1** with 146 mg (0.65 mmol) of palladium(II) acetate dissolved in dry dichloromethane (30 mL). The mixture was stirred for 1 h at room temperature and then filtered off. The solid was thoroughly washed with dichloromethane and dried in air at room temperature.

Characterisation data for **8a**: powder X-ray diffraction:  $2\theta = 0.8$  (s), 1.4 (m), 1.6 (m) $^\circ$ ; elemental analysis: C 9.6 mmol  $\text{g}^{-1}$ , N 1.3 mmol  $\text{g}^{-1}$ , Cl traces; IR:  $\nu_{\text{max}} = 3230$  (br s), 2978 (w), 2936 (w) 1557 (m), 1411 (w), 1339 (w), 1073 (s), 966 (s), 799 (m), 688 (w), 563 (w)  $\text{cm}^{-1}$ .

Catalyst **8b** was prepared in an analogous manner using 0.2 mmol of palladium(II) acetate per gram of amine-modified material **1**. Characterisation data for **8b**: powder X-ray diffraction:  $2\theta = 0.9$  (s), 1.46 (m), 1.7 (m) $^\circ$ ; elemental analysis: C 9.0 mmol  $\text{g}^{-1}$ , N 1.3 mmol  $\text{g}^{-1}$ , Cl traces; IR:  $\nu_{\text{max}} = 3230$  (br s), 2981 (w), 2941 (w), 2890 (w), 1634 (w), 1558 (w), 1471 (w), 1413 (w), 1070 (s), 966 (s), 799 (s), 560 (w)  $\text{cm}^{-1}$ .

Catalyst **8c** was prepared similarly using 0.1 mmol of palladium(II) acetate per gram of amine-modified material **1**. Characterisation data for **8c**: powder X-ray diffraction:  $2\theta = 0.9$

(s), 1.5 (m), 1.7 (m)<sup>o</sup>; elemental analysis: C 8.6 mmol g<sup>-1</sup>, N 1.4 mmol g<sup>-1</sup>, Cl traces; IR:  $\nu_{\max}$  = 3290 (br s), 2980 (w), 2944 (w), 2893 (w), 1634 (w), 1557 (w), 1471 (w), 1413 (w), 1070 (s), 962 (s), 799 (s), 552 (w) cm<sup>-1</sup>.

Catalyst **8d** was prepared similarly to **8a** starting with 0.05 mmol of palladium(II) acetate per gram of amine-modified material **1**. Characterisation data for **8d**: powder X-ray diffraction:  $2\theta$  = 0.9 (s), 1.5 (m), 1.7 (m)<sup>o</sup>; elemental analysis: C 8.6 mmol g<sup>-1</sup>, N 1.4 mmol g<sup>-1</sup>, Cl traces; IR:  $\nu_{\max}$  = 3360 (br s), 2980 (w), 2944 (w), 2895 (w), 1632 (w), 1552 (w), 1474 (w), 1396 (w), 1073 (s), 962 (s), 796 (s), 549 (w) cm<sup>-1</sup>.

Catalyst **9a** was prepared similarly from amine-modified material **3** and 0.14 mmol of palladium(II) acetate per gram of the support. Characterisation data: powder X-ray diffraction:  $2\theta$  = 0.9 (s), 1.5 (m), 1.7 (m)<sup>o</sup>; elemental analysis: C 3.8 mmol g<sup>-1</sup>, N 0.5 mmol g<sup>-1</sup>, Cl 0.1 mmol g<sup>-1</sup>; IR:  $\nu_{\max}$  = 3310 (br s), 1633 (m), 1558 (m), 1417 (w), 1077 (s), 961 (s), 800 (s), 552 (w) cm<sup>-1</sup>.

Catalyst **9b** was prepared similarly using 0.03 mmol of palladium(II) acetate per gram of amine-modified material **3**. Characterisation data: powder X-ray diffraction:  $2\theta$  = 1.1 (s), 1.7 (m), 1.9 (m)<sup>o</sup>; elemental analysis: C 2.9 mmol g<sup>-1</sup>, N 0.5 mmol g<sup>-1</sup>, Cl traces; IR:  $\nu_{\max}$  = 3320 (br s), 1634 (m), 1081 (s), 958 (s), 800 (s) cm<sup>-1</sup>.

Catalyst **10a** was prepared by an analogous procedure starting from amine-modified material **4** and 0.45 mmol of palladium(II) acetate per gram of the solid support. Characterisation data: powder X-ray diffraction:  $2\theta$  = 1.1 (br)<sup>o</sup>; elemental analysis: C 5.6 mmol g<sup>-1</sup>, N 0.8 mmol g<sup>-1</sup>, Cl traces; IR:  $\nu_{\max}$  = 3230 (br s), 2980 (w), 2946 (w), 1865 (w), 1567 (m), 1405 (w), 1335 (w), 1084 (s), 803 (s), 687 (w) cm<sup>-1</sup>.

Catalyst **10b** was prepared similarly using 0.04 mmol of palladium(II) acetate per gram of amine-modified material **4**. Characterisation data: powder X-ray diffraction:  $2\theta$  = 1.1 (br)<sup>o</sup>; elemental analysis: C 4.7 mmol g<sup>-1</sup>, N 0.9 mmol g<sup>-1</sup>, Cl traces; IR:  $\nu_{\max}$  = 3380 (br s), 2980 (w), 2945 (w), 2894 (w), 1876 (w), 1633 (m), 1558 (w), 1472 (w), 1395 (w), 1081 (s), 804 (s) cm<sup>-1</sup>.

#### 4.5. Preparation of material **11**

Mesoporous molecular sieve surface-modified with  $-(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{N}[(\text{CH}_2)_2\text{NH}_2]_2$  groups (material **11**) was prepared by stirring the chloropropylated SBA-15 sieve **1** (1.0 g) and *N,N,N*-tris(2-aminoethyl) amine (17 mmol) in dry toluene (20 mL) at 100 °C for 28 h under argon. After cooling, the solid product was filtered off, washed with ethanol and dried. The resulting yellowish powder was stirred with a mixture of 25% aqueous ammonia and ethanol (1:3, ca. 100 mL) for 4 h, the solid was filtered off, with ethanol and dried in air at room temperature.

Characterisation data for material **11**: powder X-ray diffraction:  $2\theta$  = 0.8 (s), 1.4 (m), 1.6 (m)<sup>o</sup>; elemental analysis: C 8.9 mmol g<sup>-1</sup>, N 3.0 mmol g<sup>-1</sup>, Cl traces; IR:  $\nu_{\max}$  = 2940 (br s), 1635 (w), 1558 (w), 1471 (w), 1062 (s), 962 (s), 791 (m), 548 (w) cm<sup>-1</sup>.

#### 4.6. Catalytic tests

Catalytic experiments were performed with Heidolph Synthesis I (system of 16-parallel reactions). The reaction mixture consisted of *n*-butyl acrylate (64 mg, 0.75 mmol), bromobenzene (78.5 mg, 0.5 mmol), sodium acetate (63 mg, 0.75 mmol), mesitylene (50 mg, 0.42 mmol), DMA (2.5 mL) and catalyst (1 mol% with respect to *n*-butyl acrylate). The reaction vessel was thoroughly flushed with nitrogen prior to the reaction. Reaction temperature was 160 °C.

The progress in the reaction was monitored by gas chromatography (Agilent 6890 chromatograph equipped with a flame ionisation detector and HP-1 column or Agilent 6850 chromatograph equipped with a flame ionisation detector and HP-5 column). The identity of the reaction product was checked by GC-MS analysis (Thermo Focus DSQ equipped with Thermo TR-5MS column). Poisoning tests were performed as the reaction experiments except that 1 mL of mercury or 100 mg of material **11** was introduced at the given time.

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