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Reductive dehalogenation of aryl halides over palladium catalysts deposited on SBA-15 type molecular sieve modified with amine donor groups

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ABSTRACT

Supported palladium catalysts prepared from palladium(II) acetate and SBA-15 type molecular sieve modified with N-[2-(diethylamino)ethyl]-3-aminopropyl donor groups efficiently catalyse reductive dehalogenation of various bromo- and iodobenzenes with *in situ* formed triethylammonium formate as the hydrogen source. Since the corresponding chlorobenzenes react at considerably lower rates while fluorobenzenes remain unaffected, the catalytic system can be utilised for selective dehalogenations of multiply halogenated substrates. Compared with Pd/C tested earlier [N.A. Cortese, R.F. Heck, J. Org. Chem. 42 (1977) 3491], the catalysts deposited over modified SBA-15 are more reactive. Besides, they exert rather minor leaching of the metal component (8.4% during *five* consecutive runs with 0.5 mol.% Pd with respect to the substrate) and maintain their high activity during repeated use.

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1. Introduction

Halogenated aromatic hydrocarbons are valuable synthetic intermediates finding manifold use in common laboratory praxis and in chemical industry. Their massive use and improper disposal led to global contamination of the environment and, consequently, stimulated interest in processes leading to degradation of these chemically persistent pollutants. The methods utilised to decompose haloaromatic compounds are often based on reductive cleavage of the halogen–carbon bonds. Apart from their environmental significance, these methods hold considerable synthetic potential, particularly when allowing for selective modifications of multiply functionalised aromatic molecules.

The dehalogenation reactions are typically performed with reagents combining low-valent transition metal compounds – either defined or generated *in situ* from suitable precursors (typically carbene [1] or phosphine [2] complexes) – and reducing agents such as hydrides [3], alkali metals [4], zinc metal [5], or Grignard reagents [6]. As practically more convenient alternatives, however, appear to be systems based on a combination of finely dispersed catalytically active metal and reducing agents. Typically, these reducing systems involve Ni or Pd as the metal component and various hydrogen sources. The systems based on Al–Ni nanoparticles/NaH/*t*-BuOH [7], silica-supported Ni/H_2 [8], Ni over C with various H-sources [9] or D_2 [10] and, mainly, various forms of supported Pd catalysts (e.g., Pd over MCM-41 [11], Pd over PM2 with formate or 2-propanol [12], Pd over C with H_2 [13], D_2 [10], N_2H_4·HCl [14], NEt_3/MeOH [15], or 2-propanol/alkali metal hydroxide [16] as the hydrogen source, Pd on polystyrene–poly(ethylene glycol) resin/formate [17]) can serve as typical examples. Systems exploiting unsupported [18] or supported rhodium [16,19] particles, deposited platinum/H_2 [20], or a mixed metal Pd–Rh/H_2 system [21] have been reported, too.

Recently, we have prepared a series of palladium catalysts supported by siliceous materials modified with various aminoalkyl groups at the surface and demonstrated the superiority of the N-[2-(diethylamino)ethyl]-3-aminopropyl donor group [22]. The generally good catalytic performance of these catalysts in C–C bond forming reactions (Suzuki-Miyaura, Heck, and Sonogashira [22,23]) led us to explore their catalytic potential also in other Pd-catalysed reactions. Considering the applications of deposited palladium catalysts mentioned above, we decided to test our catalysts in reductive dehalogenation of aryl halides. In this contribution, we describe reductive dehalogenation of several model substrates with triethylammonium formate (HCO_2H/NEt_3) [13b] in the presence of Pd catalysts supported by SBA-15 type molecular sieve functionalised with the N-[2-(diethylamino)ethyl]-3-aminopropyl groups.

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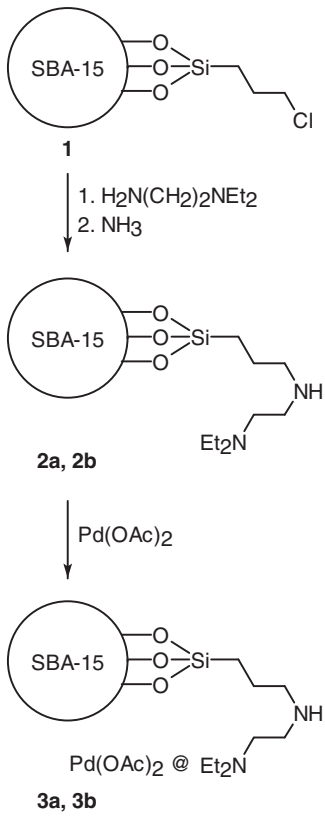


Scheme 1. Preparation of materials **1**–**3**.

2. Results and discussion

2.1. Preparation of the catalysts

The support required for the preparation of the catalysts was obtained in two steps (Scheme 1). At first, all-siliceous SBA-15 type mesoporous molecular sieve modified with 3-chloropropyl groups in the walls (material **1**) was prepared by acid-induced co-condensation of sodium silicate and (3-chloropropyl)triethoxysilane (ca. 8 mol.% of total Si in the reaction mixture) in the presence of a non-ionic polar, triblock alkene-oxide copolymer Pluronic P123 as the structure directing agent [24]. While trying to optimise the synthesis of material **1**, we found that the key properties of this support, namely the amount of incorporated modifying groups (chlorine content) and textural properties, change greatly with the duration of hydrothermal treatment (Fig. 1).

As the optimal reaction time we chose seven days (at 90 °C under autogenous pressure). During this time the chlorine content, reflecting the amount of anchored 3-chloropropyl groups, modestly increased while prolonged reaction times led to its sharp drop. A similar though less pronounced trend was noted also for BET surface areas. The surface areas of material **1** increased during the first ca. 5 days, then levelled-off (till ca. 15 days) and, finally, decreased. It appears likely that extended reaction times lead to a (partial) deterioration of the support, which is reflected by a decrease in the amount of chlorine and the BET surface areas. The powder X-ray diffraction patterns of material **1** prepared over different periods of the hydrothermal treatment (Fig. 2) all showed a strong diffraction peak above $2\theta = 1°$ and a pair of relatively weaker peaks in the range of $2\theta = 1.3–1.8°$. The patterns observed for individual samples did not differ much from each other and, above all, they confirmed that

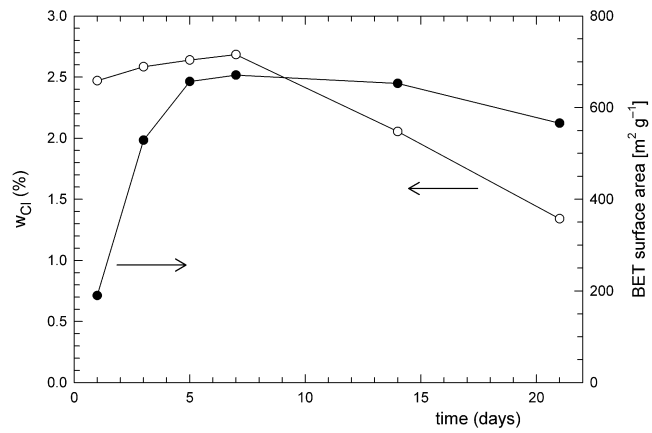


Fig. 1. Changes in the amount of incorporated 3-chloropropyl groups (expressed as w_{Cl}; open circles) and BET surface areas (filled circles) of material **1** with the reaction time.

the structure of pristine SBA-15 [25] remained largely unaffected upon the incorporation of the modifying groups.

In the next step, support **1** was reacted with an excess of 2-(*N*,*N*-diethylamino)ethylamine in dry toluene (at 100 °C for 24 h) and the resulting material was converted to a free amine form by treatment with ammonia in a water–ethanol mixture [22]. Comparison of the analytical data obtained for supports resulting from two independent runs revealed the amination step to be rather sensitive to the reaction conditions. Based on the residual chlorine content, 67% of the 3-chloropropyl groups reacted in material **2a** (nitrogen content: 1.11 mmol g^{-1}), while the data for material **2b** suggested ca. 81% conversion (nitrogen content: 1.36 mmol g^{-1}). As the last step, the amine-modified sieves were metalated with palladium(II) acetate. Support **2a** was used for the preparation of a metal-saturated catalyst **3a** via treatment with an excess of palladium(II) acetate (1 mmol Pd per 1 g of the support, reaction in dichloromethane) and subsequent removal of some loosely bound metal precursor by Soxhlet extraction. Material **2b** was treated with only 0.1 mmol $Pd(OAc)_2$ per 1 g of the solid support to give catalyst **3b**. According to elemental analysis, only 56% of the starting palladium(II) acetate was deposited in material **3a** (Pd: 0.56 mmol g^{-1}; molar Pd:N ratio = 1:1.8) while, in the case of **3b**, the metal component was deposited quantitatively (Pd: 0.11 mmol g^{-1}; molar Pd:N ratio = 1:12).

Powder X-ray diffraction patterns confirmed that the mesoporous structure of the supports remains virtually unaffected

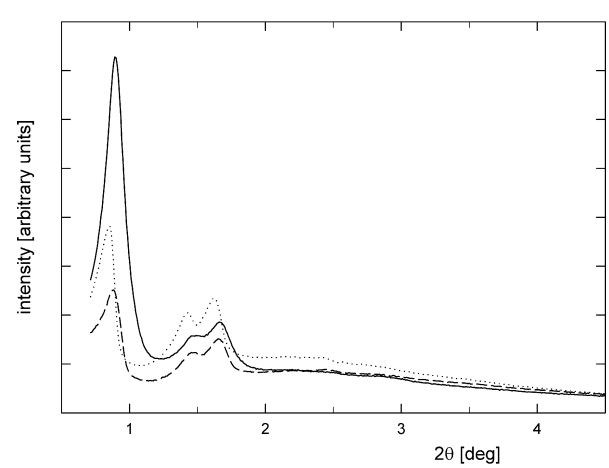


Fig. 2. X-ray diffraction patterns of material **1** obtained after one (dotted line), three (dashed line) or seven days (solid line) of the solvothermal treatment.

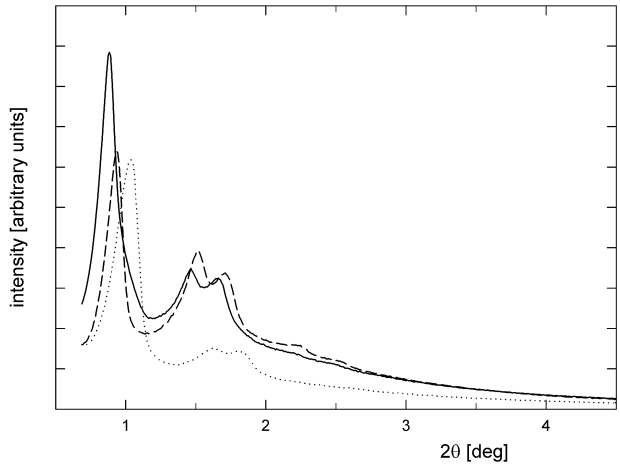


Fig. 3. Comparison of X-ray diffractions patterns of material **1** (dotted line), material **2a** (dashed line), and catalyst **3a** (solid line).

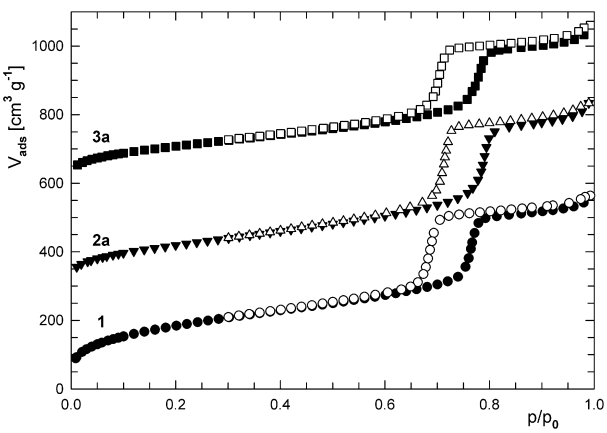
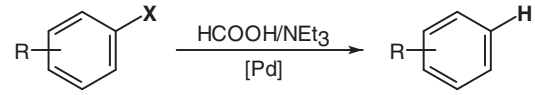


Fig. 4. Nitrogen adsorption–desorption isotherms for materials **1** (●), **2a** (▲), and **3a** (■). The isotherms of **2a** and **3a** are onset by 300 and 600 $cm^3\,g^{-1}$, respectively, to avoid overlaps (filled symbols = adsorption, empty symbols = desorption).

during the amination and metalation steps (Fig. 3). The nitrogen adsorption isotherms for materials **1**–**3** revealed favourable textural characteristics (Table 1) as it is typical for well-ordered mesoporous structure of this kind. The isotherms (Fig. 4) showed an increase in the adsorbed amount of nitrogen in the p/p_0 range ca. 0.65–0.75, being characteristic for mesoporous molecular sieves with narrow pore size distributions. The calculated textural parameters (Table 1) indicate a considerable decrease in the BET surface areas upon amination. Although the subsequent metalation had a less pronounced effect, the BET surface areas determined for catalyst **3a** and **3b** still differed considerably reflecting the amount of deposited palladium (cf. 491 $m^2\,g^{-1}$ for **3b** and 397 $m^2\,g^{-1}$ for the metal-saturated material **3a**; relative difference ca. 20%). On the other hand, all materials showed similar void volumes



Scheme 2. General scheme of the reductive dehalogenation reaction (X = halide).

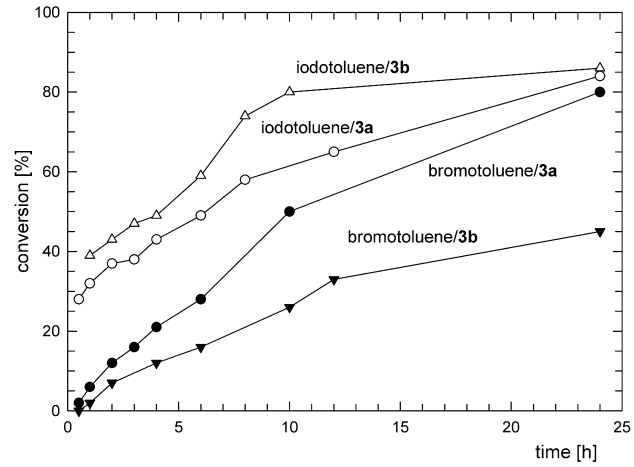


Fig. 5. Kinetic profiles for dehalogenation of 4-bromo- (filled symbols) and 4-iodotoluene (empty symbols) over **3a** (circles) and **3b** (triangles). *Conditions*: 0.5 mol.% Pd, 5 equiv. HCO_2H, 80 °C.

(0.7–0.8 $cm^3\,g^{-1}$) and pore diameters (around 7 nm). Finally, it should be noted, that the data available do not offer any evidence for a particular mode of interaction between the anchored palladium and the surface, and for the role (coordination) of the nitrogen groups.

2.2. Catalytic tests

For an initial catalytic testing in reductive dehalogenation (Scheme 2) we chose a complete series of 4-halotoluenes as simple model substrates. Initial attempts to combine our catalysts with 2-propanol/NaOH as a conventional hydrogen source were unsuccessful. The dehalogenation reaction did not proceed even with the more reactive halides (bromide and iodide) while the siliceous support was completely destroyed. Stimulated by the work of Cortese and Heck [13b], we then decided to test our catalysts in combination with triethylammonium formate generated *in situ* from formic acid and an excess of triethylamine.

Activity of the catalysts was thus studied in dehalogenation of 4-halotoluenes in a mixture of triethylamine and formic acid (5 equiv. HCO_2H with respect to the substrate) with 0.5 mol.% Pd at 80 °C. The reactions with 4-fluoro- and 4-chlorotoluene did not proceed appreciably within 24 h. On the other hand, those employing the more reactive 4-bromo- and 4-iodotoluene showed good conversions with 4-iodotoluene being expectedly faster dehalogenated than the bromo derivative with both catalysts (Fig. 5). Notably, the catalysts showed significant differences in their relative activities:

Table 1
Analytical data and textural parameters for materials and catalysts **1**–**3**.[a]

Material/catalyst	Pd content ($mmol\,g^{-1}$)	Cl content ($mmol\,g^{-1}$)	N content ($mmol\,g^{-1}$)	BET surface area ($m^2\,g^{-1}$)	BJH void volume ($cm^3\,g^{-1}$)	BJH pore diameter (nm)
1	n.a.	0.72	n.a.	668	0.80	6.4
2a	n.a.	0.24	1.11	443	0.84	7.3
2b	n.a.	0.14	1.36	477	0.79	6.9
3a	0.56	0.22	0.98	397	0.71	7.3
3b	0.11	0.17	1.36	491	0.79	6.9

[a] n.a. = not applicable.

Table 2
Optimisation of the reactions conditions in the dehalogenation of 4-bromotoluene as the model substrate.[a]

Entry	Pd loading [mol.%]	Amount of HCOOH [equiv.]	T [°C]	Conversion [%]
1	0.2	5	80	28
2	0.5	5	80	46
3	1.0	5	80	81
4	2.0	5	80	94
5	5.0	5	80	90
6	0.5	1	80	10
7	0.5	2	80	25
8	0.5	5	80	42
9	0.5	10	80	33
10	0.5	20	80	36
11	0.5	5	60	4
12	0.5	5	65	11
13	0.5	5	70	19
14	0.5	5	75	32
15	0.5	5	80	47

[a] The reaction time was 12 h in all experiments.

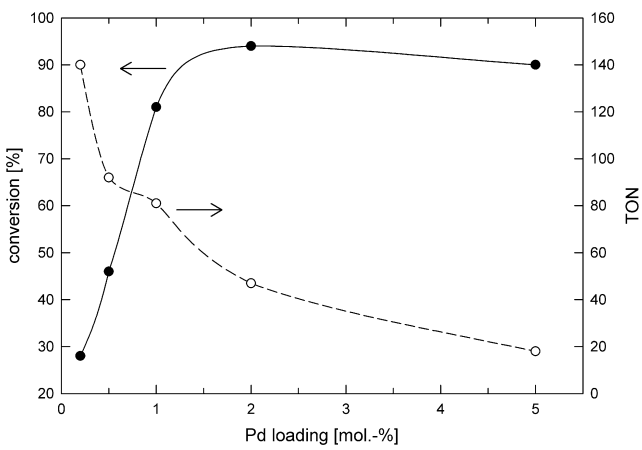


Fig. 6. Influence of the Pd loading on the conversion and turnover numbers.

whereas the metal saturated catalyst **3a** performed rather similarly with both substrates, particularly at the later stages of the reaction, its less metalated counterpart **3b** showed considerably different reactivity towards bromo and iodotoluene (I ≫ Br).

In the next step, the reaction conditions were optimised with catalyst **3a** by changing the amounts of the metal catalyst and the reducing agent (triethylammonium formate, which is generated *in situ* from HCO_2H and NEt_3), and the reaction temperature. The results summarised in Table 2 expectedly revealed the conversion to increase with the metal loading up to 90% for 5 mol.% of the metal catalyst (Table 2, entries 1–5) while the overall turnover numbers decreased (TONs; Fig. 6). As a compromise, we chose 0.5 mol.% metal loading (i.e., 0.5 mol.% of Pd with respect to substrate) for all other experiments. Changing the amount of the reducing agent (Table 2, entries 6–10) revealed a clear optimum corresponding to 5 molar equivalents of the acid with respect to the substrate (i.e., 5 mmol per 1 mmol of substrate in 5 mL of triethylamine as the solvent). With higher amounts of the acid the reaction proceeded still quite well. In contrast, the use of 2 or only 1 equiv. of HCO_2H resulted in considerably lower conversions. Finally, changing the reaction temperature (Table 2, entries 11–15) showed a very strong influence (approximately exponential) of this reaction parameter on the conversion. For instance, increasing the temperature from 60 to 80 °C resulted in a more than ten-fold increase in the conversion (4 → 47%).

Table 4
Recyclation tests with catalyst **3a**.[a]

Catalytic run	Conversion [%]	Pd in the liquid phase [ppm]	Fraction of total Pd [%]
1	69	4.1	3.0
2	82	1.1	0.8
3	86	1.4	1.0
4	100	3.8	2.8
5	100	1.1	0.8

[a] *Conditions*: dehalogenation of 4-bromotoluene (1.0 mmol), 0.5 mol.% Pd (catalyst **3a**), 5 equiv. HCO_2H, 5 mL triethylamine, 80 °C/12 h.

Applying the optimised reaction conditions (catalyst **3a**, 0.5 mol.% Pd, 5 equiv. HCO_2H, 80 °C), dehalogenation of several halide substrates was tested. The results collected in Table 3 show that extended reaction times (12 or 24 h) are required for achieving satisfactory conversions with bromobenzenes bearing electron-donating substituents (2-, 3- and 4-Me, 4-MeO; deactivated substrates). In contrast, electron-withdrawing substituents facilitate the halogen removal, which is reflected by very good conversions at considerably shorter reaction times (cf. the data for 4-bromoacetophenone and 4-bromobenzonitrile) [26]. However, this activation is not sufficient to allow for an efficient reductive dehalogenation of aryl chlorides (Table 3). Apart from the mentioned substrates, two asymmetric 1,4-dihalobenzenes were included in testing to examine the possibility of selective dehalogenation of multiply halogenated arenes. Both 1-bromo-4-chlorobenzene and 1-iodo-4-chlorobenzene reacted selectively at the site bearing the more reactive (heavier) halogen. For the former compound, a 69% conversion to chlorobenzene was achieved within 24 h. The latter, more reactive substrate was deiodinated almost completely within 2 h. Products resulting from chlorine loss (i.e., bromo- or iodobenzene) were not detected by GC analysis.

In order to assess the possibility of catalyst recycling, another series of experiments was carried out using catalyst **3a** and 4-bromotoluene as the substrate. The data presented in Table 4 clearly demonstrate favourable properties of this catalyst as it not only remained active (the conversion substantially increased upon repeated use!) but also did not suffer from any massive leaching of the deposited metal (max. 3% of total palladium per one catalytic run, cumulative loss ca. 8.4% in five runs). Notably, the amount of leached-out metal did not increase much when the reaction time was prolonged. For instance, the reaction with catalyst **3a** and 4-bromo- and 4-iodotoluene proceeded with 80%

Table 3
Reactivity of catalyst **3a** towards different haloaromatic compounds.[a]

Substrate	Conversion [%][b]	Substrate	Conversion [%][b]
2-Bromotoluene	6 (27/62)	4-Bromotoluene	12 (28/80[c])
3-Bromotoluene	5 (39/91)	4-Bromoanisole	4 (21/55)
1-Bromo-4-chlorobenzene	16 (33/69)	1-Iodo-4-chlorobenzene	87 (95/n.d.)
4-Bromoacetophenone	78 (86/n.d.)	4-Chloroacetophenone	6 (28/53)
4-Bromobenzonitrile	97 (n.d.)	4-Chlorobenzonitrile	18 (n.d.)

[a] *Conditions*: 1 mmol of substrate in 5 mL of triethylamine, 5 equiv. HCO_2H, 0.5 mol.% Pd catalyst, 80 °C.
[b] Conversion after 2 h (conversions achieved after 6/12 hours are given in parentheses if not specified otherwise). n.d. = not determined.
[c] Conversion after 24 h.

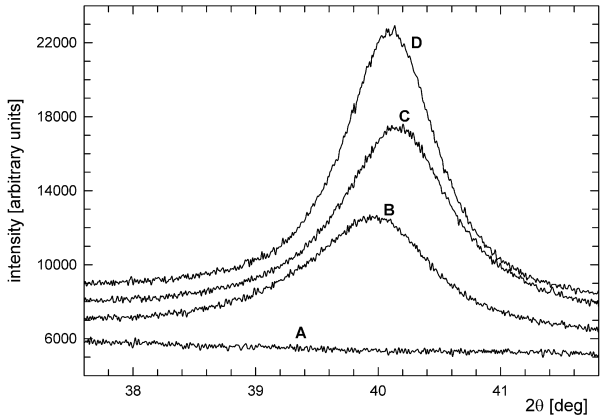


Fig. 7. Powder X-ray diffraction patterns in the region of Pd (1 1 1) diffraction as recorded for fresh catalyst **3a** (A) and the catalyst recovered from dehalogenation experiments with 4-bromotoluene (B: *five* runs of 12 h each, C: one run for 24 h) and 4-iodotoluene (D: one run for 24 h). *Conditions*: 1 mmol substrate, 0.5 mol.% Pd, 5 equiv. HCO_2H, 5 mL triethylamine, 80 °C. *Note*: The diffractograms are onset along the *y*-axis to avoid overlaps.

and 84% conversions, respectively, with only 4.3% and 3.2% of total palladium in the liquid phase after 24 h. The data obtained during the recyclation experiments further indicate that the catalyst develops during the reaction and repeated use. It appears likely that palladium(II) initially deposited is reduced (with formate) to form active Pd(0) species.

X-ray powder diffraction measurements (Fig. 7) revealed no differences in the region of low diffraction angles ($2\theta < 5°$), thus suggesting that the structure of the support remains unaffected during the dehalogenation reaction. However, they clearly implicated a formation of palladium metal particles. All materials recovered after dehalogenation experiments exerted broad diffraction line around $2\theta = 40°$ corresponding to (1 1 1) diffraction of palladium metal [27], while fresh catalyst **3a** (measured prior to catalytic use) did not show any detectable peak in this region.

3. Conclusions

Deposited palladium catalysts prepared from palladium(II) acetate and SBA-15 type molecular sieve bearing N-[2-(diethylamino)ethyl]-3-aminopropyl donor groups at the surface as the support efficiently promote reductive dehalogenation of bromo- and iodobenzenes with triethylammonium formate. The corresponding chlorobenzenes react at considerably slower rates while fluorobenzenes remain unaffected. Such different reaction rates allow for selective dehalogenations of multiply halogenated substrates. Compared to the commonly used Pd/C, the tested catalysts are more active. In addition, they exert practically negligible leaching of the metal component (8.4% during five consecutive runs at 0.5 mol.% Pd loading) and remain active during repeated use (at least for five consecutive runs).

4. Experimental

4.1. Materials and methods

Tri-block copolymer poly(ethylene oxide)$_{20}$(propylene oxide)$_{70}$(ethylene oxide)$_{20}$ (Pluronic P123, Aldrich), $Na_2SiO_3 \cdot 9H_2O$ (Aldrich), HCl (35%, Lach-Ner), (3-chloropropyl)triethoxysilane (Aldrich), 2-(*N*,*N*-diethylamino)ethylamine (Aldrich), palladium acetate (Aldrich), *p*-fluorotoluene (Aldrich), *p*-chlorotoluene (Fluka), *p*-bromotoluene (Fluka), *p*-iodotoluene (Aldrich), 2-propanol (Penta), triethylamine (Acros), dioxane (Riedel-de Haën), mesitylene (Fluka), formic acid (Lachema), sodium hydroxide (Lach-Ner) were used as received. Toluene (Lach-Ner) was dried by standing over sodium metal and distilled. Dichloromethane (Lach-Ner) was dried over anhydrous K_2CO_3 and distilled.

X-ray powder diffractograms were recorded with a Bruker D8 X-ray instrument using graphite-monochromatized Cu Kα radiation (λ = 1.5412 Å) and a position-sensitive detector Våntec-1 in Bragg–Brentano arrangement. Adsorption isotherms of N_2 were determined with a Micromeritics 2020 instrument at −196 °C. Prior to the measurement, the samples were degassed by heating to 130 °C and then evacuated till a pressure of 1 mPa was attained (at least for 24 h).

The content of palladium was determined by optical emission spectroscopy with inductively coupled plasma (ICP-OES) on an IRIS Interpid II instrument (Thermo Electron) using axial plasma and an ultrasonic nebuliser CETAC U-5000AT+ (plasma power: 1150 W, pressure in the nebuliser: 25.0 psi, auxiliary gas flow: 1 mL min^{-1}, sample uptake: 2.40 mL min^{-1}, wavelength used for spectrophotometric analysis: 324.270 nm). The samples were dissolved in a mixture of concentrated HNO_3 and HF (2:3, both Suprapure, Merck; 50 °C/15 min) and the solutions were diluted with redistilled water. C, H, N, and Cl were determined by a conventional combustion analysis.

4.2. Preparation of the catalysts

Material **1**. Commercial copolymer P123 (10.0 g) and $Na_2SiO_3 \cdot 9H_2O$ (27.35 g, 96.23 mmol) were dissolved in demineralised water (256 mL) by stirring in a polyethylene flask at room temperature overnight. Concentrated aqueous HCl was added (65 mL 35%, ca. 740 mmol) and the resulting mixture was heated in a bath kept at 45 °C and stirred at 400 rpm. After 30 min, neat (3-chloropropyl)triethoxysilane (1.96 g, 8.14 mmol; 7.6% of total Si) was introduced and stirring was continued at 45 °C for 1 h. Then, the reaction mixture was transferred to a pre-heated oven and allowed to react at 90 °C for seven days. The separated product was filtered off, washed thoroughly with distilled water (until the washings were neutral) and ethanol, and dried in the air. The crude product was Soxhlet extracted with ethanol over 24 h and dried in the air to afford **1** as a fine white powder. Powder X-ray diffraction ($2\theta/°$): 1.04 (s), 1.64 (w), 1.81 (w). Elemental analysis (mmol g^{-1}): C 7.37, H 26.0, Cl 0.72.

Material **2a**. An oven-dried reaction flask was charged with material **1** (6.5 g) and a stirring bar, and flushed with argon. Dry toluene (140 mL) and 2-(*N*,*N*-diethylamino)ethylamine (2.4 mL, 17 mmol) were introduced successively and the resulting mixture was stirred at 100 °C for 24 h. The solid was collected on a glass frit, washed with ethanol and dried in the air. The intermediate was suspended in a mixture of ethanol (100 mL) and aqueous ammonia (25 mL 25%) and the suspension was stirred at room temperature for 2.5 h. The solid was filtered off, washed with water until the washings were neutral and then with ethanol and, finally, dried in the air to give material **2a** as a white powdery solid. Powder X-ray diffraction ($2\theta/°$): 0.94 (s), 1.52 (m), 1.71 (m). Elemental analysis (mmol g^{-1}): C 7.09, H 20.0, N 1.11, Cl 0.24. Material **2b** was prepared in exactly the same manner. Elemental analysis (mmol g^{-1}): C 9.43, H 27.5, N 1.36, Cl 0.14.

Catalyst **3a**. An oven-dried flask was charged with material **2a** (4.9 g), flushed with argon and sealed with a septum. Palladium(II) acetate (1.101 g, 4.9 mmol; 1.0 mmol per 1 g of the support) was dissolved in dry dichloromethane (10 mL) and the solution was filtered through a 0.45 μm PTFE syringe filter directly to the solid support. The resulting slurry was diluted with dichloromethane (40 mL) and stirred under argon for 2 h. The solid was filtered off, extracted with dichloromethane in a Soxhlet apparatus for 24 h to remove loosely bonded palladium(II) acetate and, finally, dried in the air, afford-

ing catalyst **3a** as a grey-orange powder. Powder X-ray diffraction ($2\theta/^{\circ}$): 0.88 (s), 1.49 (w), 1.70 (w). Elemental analysis (mmol g^{-1}): C 8.03, H 20.6, N 0.98, Cl 0.22, Pd 0.56.

Catalyst **3b** was obtained similarly starting from material **2b** (4.8 g) and palladium(II) acetate (108 mg, 3 mmol; 0.10 mmol per 1 g of the support) in dichloromethane (10 + 40 mL). The product was filtered off, washed with dichloromethane (250 mL) and dried in the air to give **3b** as a yellowish powder. Powder X-ray diffraction ($2\theta/^{\circ}$): 0.88 (s), 1.46 (w), 1.66 (w). Elemental analysis (mmol g^{-1}): C 9.01, H 25.8, N 1.36, Cl 0.17, Pd 0.11.

4.3. Catalytic tests

Catalytic tests were performed with a Heidolph Synthesis I device allowing for 16 parallel reactions. The reaction vessel was charged with aryl halide (1.0 mmol), triethylamine (solvent; 4.0 mL), formic acid (5.0 mmol), mesitylene (1.0 mmol; internal standard) and an appropriate amount of catalyst. For tests with alcoholate reducing system, the reaction mixture consisted of aryl halide (1.0 mmol), NaOH (2.0 mmol), 2-propanol (5.0 mL), mesitylene (1.0 mmol; internal standard) and catalyst **3a** (0.5 mol.% Pd). The reactions were monitored by withdrawing small aliquots of the liquid phase, which were centrifuged at 4000 rpm for 10 min and then analysed with Agilent 6850 gas chromatograph equipped with a DB-5 column (0.18 mm diameter × 20 m, 0.18 μm film thickness) and a FID detector.

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[27] PDF card 5-0681: Palladium, cubic, space group Fm-3m (no. 225), a = 3.8898 Å at 26 °C; $h\,k\,l$ 1 1 1, d = 2.246 Å, relative intensity = 100, $2\theta \approx 40^{\circ}$ at Cu Kα.