

Iron-based pre-catalyst supported on polyformamidine for C–C bond formation

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Received 10th November 2011, Accepted 30th December 2011

DOI: 10.1039/c2py00540a

In the present study the incorporation of iron into an organic polymer, composed of formamidine subunits [R–N=C(H)–NH–R], has been examined. The catalytic ability of the recyclable material was investigated in the iron-catalyzed formation of C–C bonds. After optimization of the reaction conditions, excellent yields and chemoselectivities were feasible.

Introduction

The direct functionalization of aromatic C–H bonds is one of the key transformations for industry as well as academia to access organic compounds with higher values starting from low cost materials.¹ In this regard, one of the most frequently applied methodologies for C–C bond formations is the Friedel–Crafts reaction. The impact of this method is outlined by several applications in the synthesis of bulk-, fine- or agrochemicals. Classically, aluminium chloride is used to force the reaction towards the C–C bond formation.² However, several difficulties arise with the use of AlCl₃, e.g., problematic separation and recovery, corrosion, toxicity, and moisture sensitivity.³ Recently, manifold alternatives have been accounted, because of modern requirements for higher efficiency, better selectivity and a greener chemistry.^{3,4} Within those improvements the application of iron as a catalyst seems to be a promising tool to accomplish several of those requests. For instance, the low price, the availability, the low toxicity and the biocompatibility of iron sources are favourable aspects.⁵ Indeed, during the past years a number of Friedel–Crafts reactions has been established based on iron catalysts.^{6,7} However, those methods apply homogeneous systems, which do not allow an easy recovery or reuse of the catalyst. Therefore, the incorporation of the catalyst on supporting materials can be a choice to solve this problem. Manifold approaches have been reported for the heterogenization,

recycling and catalytic application of iron-based materials, e.g., metal–organic frameworks, mesoporous materials, montmorillonite, and ionic liquids.^{8,9} On the other hand, the embedding of ligands in a heterogeneous matrix allows the coordination/fixation of metals, tuning of the catalyst abilities and, as a consequence, recycling of the catalyst. However, this interesting access has not been accounted for those reactions. Based on this heterogeneous ligand concept, novel materials for immobilization of metal catalysts are highly desired. More recently, some of us studied the application of well-defined formamidine ligands in the iron-catalyzed oxidation of carbon–carbon double bonds and their use as synthons for the construction of molybdenum based dimensional networks.^{10,11} Due to the straightforward synthesis and great availability of the starting materials, an attractive ligand class can be provided. In addition, they can be easily incorporated into polymers containing the formamidine unit as the key motif (Fig. 1).¹²

Herein, we report on our initial studies on the application of iron supported on polyformamidine based polymers in the iron-catalyzed C–C bond formation.

Results and discussion

For the synthesis of polyformamidine a procedure was performed in accordance with the protocol reported by Böhme and co-workers with slight modifications.¹² A dimethylsulfoxide

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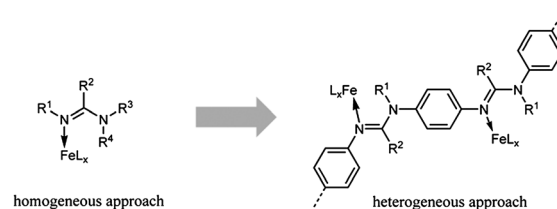
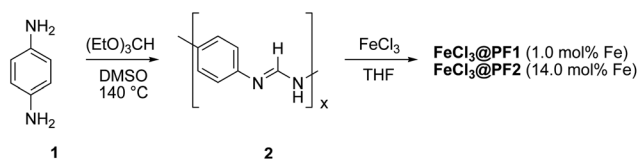


Fig. 1 Catalyst strategy based on homogeneous and heterogeneous formamidine ligands.

solution of *para*-phenylene diamine (**1**) and triethyl orthoformate was stirred at 140 °C for 24 hours under non-inert conditions (Scheme 1). After work-up a yellow-orange powder was obtained, which is highly stable up to a temperature of 300 °C. Noteworthy, the compound is highly insoluble in various organic solvents (*e.g.*, DMSO, THF, toluene, CH₂Cl₂). Applying the ¹³C NMR chemical shift of the [N=C(H)-N] group as a probe, we found for the polyformamidine **2** a chemical shift of 146.4 ppm, which is in agreement with well-defined formamidine ligands (*e.g.*, *N,N'*-bisphenylformamidine, δ = 149.5 ppm).¹³ For **2**, ¹³C {1H} CP/MAS NMR was applied, due to the poor solubility, resulting in broad overlapping signals. In case of the FT-IR for the *N,N'*-bisphenylformamidine (1679 cm⁻¹) and **2** (1665 cm⁻¹), a shift of 19 cm⁻¹ for the band of the C=N functionality was detected. Furthermore, attempts to elucidate the molecular weight (MALDI TOF MS) of the polymeric compound failed due to the poor solubility.

To support iron on the polyformamidine, **2** was refluxed for 24 hours in THF with different loadings of FeCl₃ (Scheme 1). After work-up a color change from yellow to brown was observed correlating with the amount of iron. The obtained FeCl₃@PF composites were investigated with several analytical tools. In case of the FT-IR, the band for the C=N functionality in FeCl₃@PF2 was shifted to 1674 cm⁻¹, while the unmodified polyformamidine resulted in a band at 1665 cm⁻¹. This increase can probably be attributed to the coordination of iron to the C=N of the formamidine subunit. In case of the FeCl₃@PF1 material a small shoulder (1665 cm⁻¹) of the band at 1674 cm⁻¹ was observed, which can be assigned to the uncoordinated formamidine units. Whereas for FeCl₃@PF2 the band at 1674 cm⁻¹ is broad and probably overlaps the band for the free formamidine. Moreover, the existence of iron in the polymer was determined by energy dispersive X-ray (EDX) spectroscopy. Applying the nitrogen content as a probe, we clearly see an increased incorporation at higher loadings, which was additionally approved by elemental analysis. Electron microscopy of the doped and undoped polymeric materials showed large agglomerates of differently sized particles in the range of approximately 100 nm to 5 μm. Comparing the SEM image of the undoped polymer (Fig. 2a) to the FeCl₃@PF2 composite (Fig. 2b) demonstrates that the loading process does not have a significant influence on the morphology of the polymer and thus underlines its intrinsic stability during the loading process. A SEM-element-mapping shows that iron is dispersed almost homogeneously in the material (Fig. 2c). The intrinsic stability of the polymer was furthermore approved by X-ray diffraction measurements (Fig. 3) of the doped and undoped polymeric material. The received values are in agreement with the WAXS pattern of the homopolymer reported in the literature.^{12a}



Scheme 1 Synthesis of polyformamidine **2** and iron supported on polyformamidine **2**.

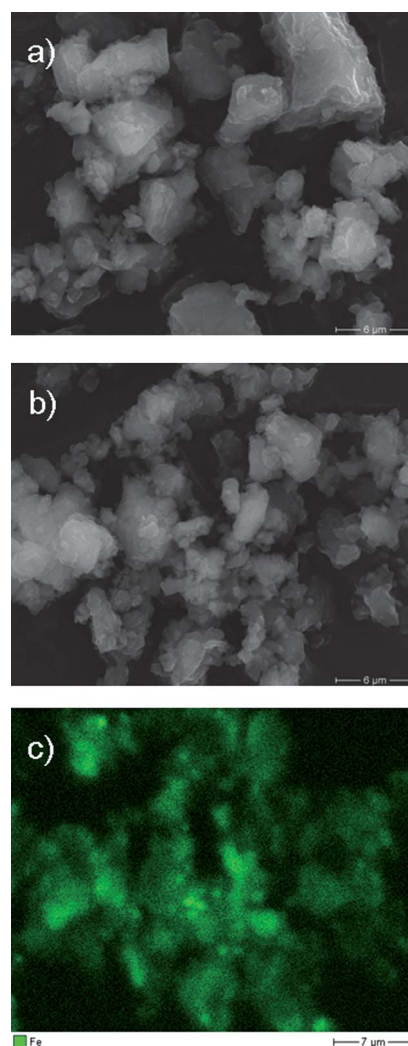


Fig. 2 SEM: (a) **2**, (b) FeCl₃@PF2, and (c) iron mapping.

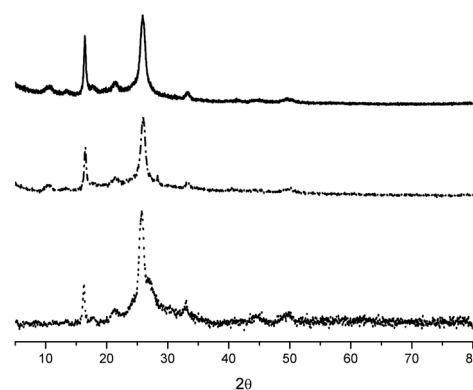


Fig. 3 XRD: **2** (solid curve), FeCl₃@PF1 (dash-dotted curve), and FeCl₃@PF2 (dotted curve); curves are normalized to the reflex at 25.9°.

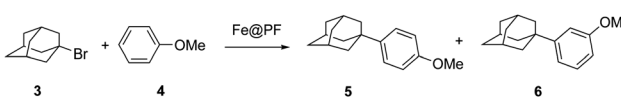
Apparently, the crystallinity and crystallite size remained unchanged during the FeCl₃ loading procedure. As no diffraction peaks of FeCl₃ could be identified, one can assume that all the iron in the sample is in a coordination state. The shoulder of the reflex at 25.9°, at 28.3° for FeCl₃@PF1 and 27.1° for

FeCl₃@PF2, respectively, has an increasing intensity and a shift to smaller angles with higher FeCl₃ content was observed. This effect can be probably attributed to coordinated FeCl₃ and its influence on the crystallization of the polymer. This could be further evidenced by TEM, as no iron hydroxide or iron oxide nanoparticle formation was observed. To evaluate the surface area of the catalysts, nitrogen adsorption/desorption measurements were performed both on unloaded and loaded polymers. From BET analysis the obtained polymers have surface areas in the range of 20–50 m² g⁻¹.

With the material in hand we became interested in the catalytic abilities. As a model reaction the Friedel–Crafts alkylation was chosen. Initial studies on the influence of the reaction conditions were carried out with an excess of anisole (**3**) and 1-bromoadamantane (**4**) under solvent free conditions for one hour at 100 °C (Table 1). First, unmodified FeCl₃ was applied as a pre-catalyst resulting in an excellent yield (>99%) with a regioselectivity of 85% to the formation of the *para*-substituted isomer **5** (Table 1, entry 1).

In addition, a combination of catalytic amounts of FeCl₃ and *N,N'*-bisphenylformamidine was tested in a “homogeneous approach” to investigate the influence of the formamidine unit on the reaction outcome. A significantly lower yield (19%) was obtained compared to unmodified FeCl₃ (Table 1, entries 1 and 2). In contrast, FeCl₃@PF2 was tested with a catalyst loading of 1.0 mol%, resulting in a good yield (84%) and an excellent regioselectivity (97%) (Table 1, entry 4). This result shows clearly the advantages of the heterogeneous approach in comparison to unmodified FeCl₃ and the homogeneous approach. For FeCl₃@PF1 with only 1.0 mol% Fe lower yields were obtained; hence, further studies were carried out with FeCl₃@PF2. The metal-free polymer was tested as catalyst for the C–C bond formation (Table 1, entry 3), and showed no activity as expected.

Table 1 FeCl₃@PF-catalyzed alkylation of anisole (**4**)^a



Entry	Catalyst (mol%)	T/°C	Conv. (%)	Select. (5) (%)	Yield (5) (%)
1	FeCl ₃ (1.0)	100	>99	85	85
2 ^b	FeCl ₃ (1.0)	100	19	>99	19
3	2	100	<1	<1	<1
4	FeCl ₃ @PF2 (1.0)	100	87	97	84
5	FeCl ₃ @PF2 (2.5)	100	92	97	89
6	FeCl ₃ @PF2 (5.0)	100	88	97	85
7 ^c	FeCl ₃ @PF2 (5.0)	100	>99	97	97
8	FeCl ₃ @PF2 (5.0)	80	<1	<1	<1
9 ^d	FeCl ₃ @PF2 (5.0)	120	95	97	92
10 ^e	FeCl ₃ @PF2 (2.5)	100	28	>99	28
11 ^f	FeCl ₃ @PF2 (2.5)	100	53	99	53
12 ^g	FeCl ₃ @PF2 (5.0)	100	26	85	22

^a Reaction conditions: 0.48 mmol 1-bromoadamantane, 1.85 mmol anisole, 20 mg FeCl₃@PF2, 1 h. The conversion and yield were determined by GC (30 m Rxi-5ms column, 40–300 °C) using dodecane as internal standard. ^b 0.41 mmol *N,N'*-bisphenylformamidine. ^c 24 h. ^d Reaction time: 30 min. ^e **3** : **4** 1 : 1. ^f **3** : **4** 1 : 2. ^g 1-Chloroadamantane instead of **3**.

However, with increasing the catalyst loading towards 2.5 and 5.0 mol% a slight improvement of the reaction outcome was seen (Table 1, entries 5 and 6). Performing the reaction for 24 hours led to full conversion (>99%) and an excellent selectivity (97%) (Table 1, entry 7). Subsequently, the effect of the reaction temperature was studied. Decreasing the temperature (80 °C) resulted in no product formation, while for an increased temperature (120 °C) nearly full conversion was observed within 30 minutes with comparable regioselectivity (Table 1, entries 8 and 9).

Since an excess of anisole (**4**) (~3.9 equiv) was applied the effect of the amount of anisole was studied under solvent free conditions. Reducing the amount of anisole to a ratio of 1 : 1 (anisole : 1-bromoadamantane) the yield of the product **5** decreased significantly to 28%, while the selectivity for the *para*-isomer is excellent with >99% (Table 1, entry 10). Changing the ratio to 2 : 1 (**3** : **4**) the yield increased to 53% accompanied by an excellent selectivity (Table 1, entry 11).

Additionally, the outstanding Lewis acid zinc(II) triflate was supported on polyformamidine and the corresponding material [Zn(OTf)₂ loading 14.0 mol%] was tested as a catalyst (5.0 mol%) under conditions in accordance with Table 1, entry 6.¹⁴ However, the obtained yields (35%) and regioselectivities (76%) are significantly lower than the results achieved with iron, demonstrating the excellent abilities of FeCl₃@PF2.

Noteworthy, FeCl₃@PF2 is insoluble in the starting materials (**3** and **4**) and in the reaction mixture after the reaction is completed and cooled to room temperature, due to an excess of **4**. This fact allows the easy separation of FeCl₃@PF2 from the reaction mixture and a potential reuse of the catalyst compared to the homogeneous approach. Indeed, the material was recycled four times and subjected to catalysis with a small loss of activity, but with constant selectivity (Fig. 4). In more detail, FeCl₃@PF2 was filtered after catalysis, washed with acetone and dried in vacuum before resubmission. In contrast, Zn(OTf)₂@PF showed full depletion of the activity after the first run. To push this concept further, a stationary catalyst phase was built up. The polymer was placed on the top of a filter and catalytic amounts of FeCl₃ were added. After addition of anisole (**3**) and

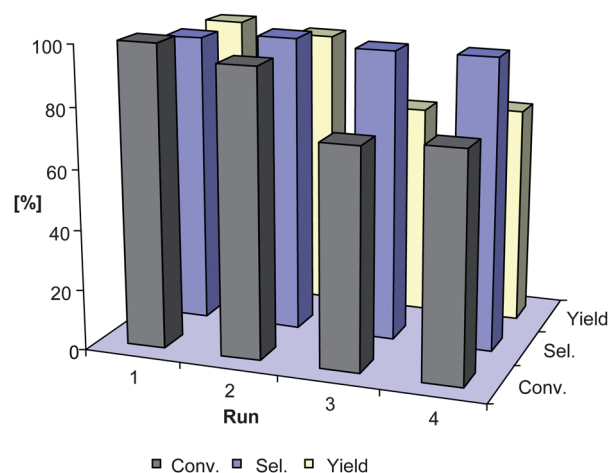


Fig. 4 FeCl₃@PF2-catalyzed alkylation of anisole-recycling experiments.

1-bromoadamantane (**4**) the mixture was heated to 100 °C with a flow of nitrogen from underneath. Once the reaction was finished the flow was switched off and the residue was washed with dichloromethane and filtered. The yield and selectivity were measured by GC-MS. The remaining material was subjected to catalysis again. After several runs a depletion in activity was noticed (*vide supra*). The material was washed with an excess of triethylamine to remove HBr (Fig. 5). Finally, fresh FeCl₃ was added and the recharged material was applied in the Friedel–Crafts alkylation of anisole (**3**) and 1-bromoadamantane (**4**).

Interestingly, mapping experiments carried out with the used catalyst material (after 1 cycle) pointed out that the iron is still

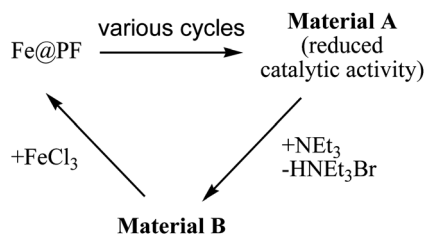


Fig. 5 Matrix reloaded—reactivation and re-charge of the PF.

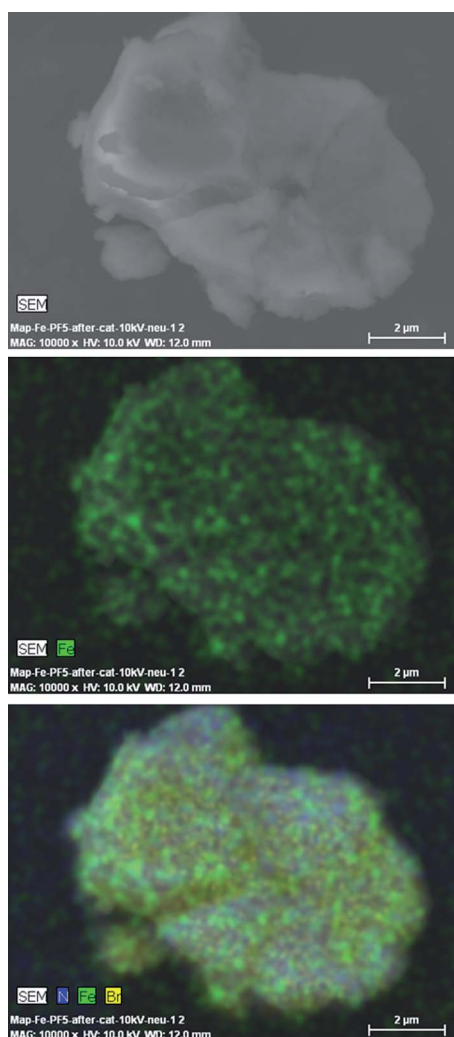


Fig. 6 Mapping experiments with the used catalyst material.

present and furthermore homogeneously dispersed in the formamide polymer (Fig. 6). Moreover, the measurements indicated the presence of significant amounts of bromide in the material, which originated from the side product hydrobromic acid bonded to the formamide unit to obtain formamidinium hydrobromide functionalities.

Conclusions

In summary, we have demonstrated the usefulness of a material composed of iron supported on a polyformamide ligand in the iron-catalyzed Friedel–Crafts alkylation. After investigation of the reaction conditions excellent yields and selectivities were feasible. Moreover, the catalyst material can be easily separated from the reaction mixture and can be subjected again to catalysis.

Experimental section

General

¹H and ¹³C NMR spectra were recorded with a Bruker Avance III 200 spectrometer (¹H: 200.13 MHz; ¹³C: 50.29 MHz) using the proton signals of the deuterated solvents as reference. ¹³C{¹H} CP/MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer (¹³C: 100.57 MHz) using a 4 mm double resonance HX MAS probe. The CP spectra were recorded with a cross-polarization time of 2 ms and composite pulse ¹H decoupling was applied during the acquisition. IR spectra were recorded either on a Nicolet Series II Magna-IR-System 750 FTR-IR or on a Perkin Elmer Spectrum 100 FT-IR. Melting points (mp) were determined on a BSGT Apotec II capillary-tube apparatus and are uncorrected. GC-MS measurements were carried out on a Shimadzu GC-2010 gas chromatograph (30 m Rxi-5ms column) linked with a Shimadzu GCMA-QP 2010 Plus mass spectrometer. Elemental analyses were performed on a Perkin-Elmer Series II CHNS/O Analyzer 2400. Powder X-ray diffraction (XRD) measurements were recorded on a Bruker D8 Advance with CuK_α-radiation (λ = 0.1546 nm) and scintillator detector. Nitrogen adsorptions were carried out with an Autosorb-1-C from Quantachrome. Prior to measurement, the samples were degassed overnight at 100 °C. The surface area was determined using the Brunauer–Emmett–Teller (BET) method. SEM measurements were performed on a JEOL 7401 F equipped with an EDX Bruker Quantax XFlash 4010 Detector.

Synthesis of polyformamide (2)

To a solution of 1,4-benzenediamine (0.43 mol) in DMSO (500 mL) was added triethyl orthoformate (0.87 mol) at room temperature. The solution was stirred at 140 °C for 24 hours. During that time a precipitate was formed. After cooling to room temperature the mixture was treated with acetone (500 mL) and the precipitate was filtered and washed with acetone. The solid was purified in a Soxhlet extractor using acetone as solvent for 24 hours. The yellow-orange powder was dried in vacuum at 80 °C for 8 hours. Yield = 82%; mp = >300 °C; ¹³C{¹H} CP/MAS NMR (50 MHz) δ = 146.4 (br), 133.1 (br), 140.2 (br), 124.1 (br), 120.4 (br), 117.8 (br), 115.4 (br) ppm; IR (KBr): $\tilde{\nu}$ = 2917, 2857, 1665, 1637, 1498, 1308, 1205, 982, 820, 526 cm⁻¹; elemental

analysis: anal. calcd for C₇H₆N₂ (based on repeating unit) (%): C: 71.17, H: 5.12, N: 23.71. Found: C: 67.21, H: 5.25, N: 22.89.

Synthesis of iron supported on polyformamidine

A suspension of FeCl₃ (Fe@PF1: 0.09 mmol; Fe@PF2: 1.2 mmol) and polyformamidine **5** (8.5 mmol) in THF (50 mL) were refluxed for 24 hours. The volatiles were removed in vacuum and the residue was purified in a Soxhlet extractor using acetone as solvent for 24 hours. The red powder was dried in vacuum at 80 °C for 8 hours. Fe@PF1: IR (KBr): $\tilde{\nu}$ = 2917 w, 2857 w, 1674 s, 1665 (shoulder of 1674), 1637 s, 1498 s, 1308 m, 1205 m, 982 w, 820 m, 526 m, cm⁻¹; elemental analysis (%): found: C: 65.98, H: 5.15, N: 22.16. Fe@PF2: IR (KBr): $\tilde{\nu}$ = 2924 w, 2848 w, 1674 s, 1508 s, 1311 m, 1203 m, 979 w, 823 m, cm⁻¹; elemental analysis (%): found: C: 61.59, H: 4.54, N: 17.23.

Catalytic reactions

In a typical reaction, a mixture of 1-bromoadamantane (0.48 mmol), Fe@PF2 (20 mg), an excess of anisole (1.85 mmol) and n-dodecane (internal standard) was stirred at 100 °C for one hour. The catalyst was removed by filtration via a short plug of silica gel applying dichloromethane as the eluent. The filtrate was analyzed by GC-MS and the products were quantified by comparison with a calibration curve of the authentic compound. Catalyst recycling experiments were carried out by filtration of the reaction mixture and subsequent washing of the catalyst three times with acetone.

Characterization of **5** and **6** was performed by comparison of the NMR data with previously reported data.^{15,16}

Acknowledgements

This work was supported by the Cluster of Excellence “Unifying Concepts in Catalysis” (sponsored by the Deutsche Forschungsgemeinschaft and administered by the Technische Universität Berlin). The authors thank Peter Frenzel and Dr. Stephan Heitz for technical support.

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