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# **Activated charcoal grafted with phenyl imidazole groups for Knoevenagel condensation of furfural with malononitrile**

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**Abstract:**

Commercial activated charcoal Darco<sup>®</sup> KB-G with large specific area (1345 m<sup>2</sup> g<sup>-1</sup>) was found to be an excellent carbonaceous support for chemical surface functionalization. Its covalent grafting with phenyl imidazole groups via diazonium chemistry was carried out under mild conditions (25 °C, P<sub>atm</sub>) by reacting 4-(1*H*-imidazol-1-yl)aniline with Darco in the presence of isopentyle nitrite as diazotization initiator. The success of the surface functionalization was evidenced by experimental XPS spectra and DFT calculations. The functionalized solid Darco-0.5IM with tertiary amine functions was well characterized and its catalytic activity was evaluated in the Knoevenagel condensation of furfural with malononitrile.

**Keywords:**

- Heterogeneous catalysis
- DFT Calculations
- Diazonium chemistry
- Basic catalysis
- Activated charcoal

## 1. Introduction:

Knöevenagel condensations play a crucial role in the transformation of small molecules to value-added compounds since this approach allows to increase the carbon chain length by forming new C-C bonds between a carbonyl group and an activated methylene group [1]. It is well known that Knöevenagel condensations can be catalyzed by heterogenous aminocatalysts under mild experimental conditions ( $T < 100\text{ }^{\circ}\text{C}$ ,  $P_{\text{atm}}$ ) [2–5]. For example, Bhaumik and co-workers developed porphyrin based organic polymer [6] and ordered mesoporous  $\gamma\text{-Al}_2\text{O}_3$  [7] as new selective catalysts for several Knöevenagel condensations.

Compared to the functionalization of silica materials by the post-grafting method, the diazonium coupling demonstrated its great potentialities for the functionalization of carbonaceous materials due to the simplicity of grafting procedure. It is generally known that carbonaceous materials exhibit good chemical stability while the Si-O bond of silica supports are known to be less stable, in particular in presence of acid or basic species [8]. Surface modification of carbonaceous materials have been investigated for various applications, such as high performance materials with optical limiting properties [9] and biomedical detection agents [10,11]. The covalent bonding between carbonaceous materials and aryl diamine derivatives can be achieved either by electrochemical reduction [12,13] or spontaneous reduction of aryl diazonium cations without external electric current in organic or aqueous solvents [14,15]. The main advantage of spontaneous reduction is that diazonium species are usually obtained in situ and hence avoids the necessity of isolating and storing often unstable and light-sensitive aryl diazonium salts [16]. The most accepted route of diazonium reduction by carbonaceous materials is the Gomberg-Bachmann mechanism, in which the reduction occurs via electron transfer from carbonaceous materials into diazonium species, releasing  $\text{N}_2$  and forming a reactive radical that reacts with carbonaceous materials to form arene bonds [17]. To further investigate the grafting mechanism between carbon surface and diazonium cations,

Lipińska et al. studied the functionalization of multi-walled carbon nanotubes (MWCNT) with aniline derivatives and confirmed a radical chain mechanism for the functionalization performed in the presence of isopentyl nitrite [18]. According to their proposed mechanism, 3 steps are involved in the grafting procedure: (1) diazotization of aniline derivatives, (2) formation of aryl radicals and oxygen radicals which re-initiate the cycle and (3) recombination of radicals with MWCNT.

In our previous work [19], phenyldiamine groups (Ph-NH<sub>2</sub>, noted PDA) were successfully grafted onto 3 carbonaceous supports with different specific surface areas and all these basic solids were active in giving (2-furanylmethylene)malononitrile (noted FMMN) which could be highly applicable for photovoltaic solar cell applications according to Soliman et al. [20]. However, the experimental results demonstrated that the most active catalyst Darco-0.5PDA with Ph-NH<sub>2</sub> sites was deactivated during the recycling of catalyst, probably due to the hydrogen bond between Ph-NH<sub>2</sub> and the carbonyl group of FMMN. To remedy this disadvantage, Darco® KB-G was functionalized with phenyl imidazole groups. The catalytic behaviors of the novel basic solid (Darco-0.5IM) in the Knoevenagel condensation of furfural was compared with Darco-0.5PDA (a basic solid with phenyldiamine groups).

## **2. Experimental part:**

### *2.1 Synthesis of the catalysts*

Commercial activated charcoal Darco® KB-G (noted as Darco) was used as the carbonaceous support for the grafting of aryl amine groups via diazonium chemistry because of its large specific area ( $S_{\text{BET}} = 1345 \text{ m}^2 \text{ g}^{-1}$ ) and mesoporous structure ( $V_p = 1.08 \text{ cm}^3 \text{ g}^{-1}$ ). The incorporation of aryl amine groups was carried out by coupling this activated charcoal with corresponding aryl amine diazonium salts. Firstly, an aniline derivative reacts with isopentyl nitrite to generate diazonium cations. After a chemical reduction process between the reductive carbon surface and diazonium cations, aryl amine groups are grafted onto the surface of Darco.

It's noteworthy to highlight that 3 equiv. of isopentyle nitrite were used to react with 1 equiv. of (1*H*-imidazol-1-yl)aniline while only 1 equiv. of isopentyle nitrite was needed to react with *p*-phenylenediamine in order to keep one –NH<sub>2</sub> intact. 0.5 g of each aniline derivative precursor were used for 1 g of Darco. The molar quantity of isopentyle nitrite was adjusted according to the nature of the selected aniline derivative as mentioned above. The functionalization yielded two carbon-based basic solids under our working conditions: Darco-0.5PDA containing primary amine groups and Darco-0.5IM containing tertiary amine groups (Scheme 1).

Synthesis of Darco-0.5PDA was conducted following a procedure available in our previously published work [19]. Only the synthesis of the novel basic solid Darco-0.5IM is described in this paper. Activated charcoal Darco<sup>®</sup> KB-G obtained from Sigma-Aldrich is dried for 16 h at 120 °C before use. The aryl amine precursor 4-(1*H*-Imidazol-1-yl)aniline (98%) is purchased from Sigma-Aldrich and the isopentyl nitrite (97%) is purchased from Alfa Aesar. Typically, 0.5 g of 4-(1*H*-Imidazol-1-yl)aniline (3.14 mmol, 1 eq.) are dissolved in 100 mL of acetonitrile with vigorous stirring. 1 g of Darco is dispersed in the solution afterwards followed by the dropwise addition of isopentyl nitrite (1.26 mL, 9.42 mmol, 3 eq.). The reaction mixture is stirred for 16 h at 25 °C and vacuum filtered on an EMD Millipore support with a nylon filtration membrane (0.22 μm, 47 mm, hydrophile). The functionalized material is firstly washed by acetonitrile successively (200 mL - 7 times) until the filtrate become colorless. The isolated basic solid was finally dried for 16 h at 120 °C.

## 2.2 Catalyst characterizations

All technics used to characterize the catalysts are described in Electronic Supporting Information.

## 2.3 DFT calculations

Geometry relaxations were performed according to density functional theory (DFT) within the framework of the all-electron projector augmented wave (PAW) method, as implemented in the

VASP code.[21,22] We adopted the Perdew-Burke-Ernzerhof (PBE) functional at the generalized gradient approximation (GGA) level of theory [23], with PAW potentials for hydrogen, carbon, and nitrogen atoms, a plane-wave kinetic energy cutoff of 600 eV, and a uniform,  $\Gamma$ -centered grid with  $3\times 3\times 1$  mesh for reciprocal space sampling. All structural relaxations were done with a tight force convergence threshold (1 meV/Å). These settings enable excellent convergence of total energy differences, forces, and stress tensors. It was indeed shown in previous studies that this approach, though unable to afford absolute XPS shifts, is very successful in predicting relative core-level shifts. A  $5\times 4\sqrt{3}$  rectangular graphene supercell with 90 carbon atoms was constructed as a surface model of the target carbon substrate [21]. After structure optimization, the size of orthorhombic unit cell of graphene is 12.338 Å $\times$ 17.100 Å $\times$ 25.000 Å. Such a large cell was considered here to avoid spurious interactions between neighboring cells in the following calculations. In a second step, C<sub>9</sub>N<sub>3</sub>H<sub>9</sub> molecule was then optimized within the same box (“molecular” calculation). Finally, a phenyl-imidazole decorated graphene surface was considered, with addition of one H atom in *para* position to saturate the chemical valence (Figure S1). Comparison of the molecular and surface-grafted models then affords direct insight on the change in core energy levels induced by the target chemical transformation (Table S1). Lattice parameters and atomic coordination in 4-(1*H*-imidazol-1-yl)aniline (C<sub>9</sub>N<sub>2</sub>H<sub>7</sub>) and the grafted graphene are available in Table S2.

#### 2.4 Catalytic test procedure

A detailed procedure is available in our previously published work [19] and summarized as follows (Scheme 2): 1 eq. of freshly distilled furfural (10 mmol) and 1 eq. of malononitrile (10 mmol) were diluted with 10 mL of 2-methyltetrahydrofuran (2-MTHF) as solvent in the presence of solid catalyst (200 mg) to give (2-furanylmethylene)malononitrile (noted FMMN) and water. The reaction is conducted at 40 °C for 6 hours and the conversion of furfural and the yield of FMMN are calculated by GC using heptane as internal standard.

### 3. Results and discussion:

Elemental analysis showed an increase of nitrogen content close to 6% in the functionalized Darco with phenyl imidazole moieties knowing that the initial carbonaceous support does not present any nitrogen content before surface functionalization (Table 1). Although the nitrogen content of Darco-0.5PDA (5.1%) was lower than that of Darco-0.5IM, Darco-0.5PDA has more basic sites because only one nitrogen in the phenyl imidazole moiety is active to extract the acidic hydrogen in the methylene group.

The N<sub>2</sub> adsorption-desorption isotherms and the distribution of pore size of Darco and its functionalized solids are respectively shown in Fig. S2 and Fig. S3. A type IV isotherm was observed for all samples. Although a significant decrease of specific area was observed between Darco and its functionalized solids, the specific surface areas of these two functionalized solids remained very high, ranging from 540 to 590 m<sup>2</sup> g<sup>-1</sup>. Accordingly, the total pore volume was nearly divided by two after surface functionalization. The average pore diameter for all solids was similar, close to 6.5 nm (Table 1). According to Fig.1, the characteristic IR bands of the 1-phenyl-1*H*-imidazole (Ph-Im) unit (1503 cm<sup>-1</sup>, 1302 cm<sup>-1</sup>, 1246 cm<sup>-1</sup> and 1054 cm<sup>-1</sup>) clearly appeared in the IR spectrum of the Darco-0.5IM, showing that the structure of phenyl imidazole was well preserved after the surface modification. In addition, the full FT-IR spectra of Ph-Im and Darco-0.5IM showed weak bands between 3100 - 3000 cm<sup>-1</sup> which can be attributed to aromatic C-H stretching. (Fig. S4). The thermogravimetric analysis (TGA) of Darco and Darco-0.5IM showed two weight losses around 470 °C and 500 °C corresponding to the carbonaceous support combustion (Fig. S5). Besides, Darco-0.5IM showed additional weight loss at 443 °C which was absent in the TGA spectrum of Darco. This weight loss was could be attributed either to the combustion of the grafted phenyl imidazole unit or to the starting material 4-(1*H*-imidazol-1-yl)aniline potentially physisorbed on Darco, probably by  $\pi$ - $\pi$  stacking interactions. Unexpectedly, the TGA of the mechanical mixture between 4-(1*H*-imidazol-1-



yl)aniline and Darco presents the same profile that the grafted solid (Darco-0.5IM) as shown in Fig. S5 b) and c). Nevertheless, the DTG peak due to the presence of nitrogen species appeared at higher temperature than the one expected for 4-(1*H*-imidazol-1-yl)aniline (around 300°C – Fig. S5 d)). Unfortunately, it was hence not possible to discriminate between physisorbed and grafted species by TG experiments.

In consequence, XPS investigation was further conducted to elucidate the situation. Firstly, both Darco and Darco-0.5IM possessed C 1s and O 1s peaks in their respective full survey spectrum. However, Darco-0.5IM showed an additional N 1s peak which was absent in Darco, confirming the presence of nitrogen-containing structure after surface modification (Fig. S6). Two peaks were observed when the N 1s core level spectrum of Darco-0.5IM was compared to that of 4-(1*H*-imidazol-1-yl)aniline (Fig. 2). The photoelectronic peak of 4-(1*H*-imidazol-1-yl)aniline at 398.9 eV lost its intensity and moved towards a lower binding energy after grafting while the second peak around 401 eV still remain intact. To better understand this observation, we simulated the energies of the core electrons for each nitrogen by DFT calculations. As expected, a difference between the experimental values and the simulated values was observed but they remained comparable. According to the simulation by DFT calculations, in free 4-(1*H*-imidazol-1-yl)aniline the N 1s core energies are, respectively, -380.215, -382.639 and -381.400 eV for N1, N2 and N3 (Fig. 2 and Table S1). In the covalent phenyl imidazole (C<sub>9</sub>N<sub>2</sub>H<sub>7</sub>) grafted model, N1 and N2 core energies shift to -379.284 and -381.682 eV, respectively (Table S1). Hence, in the experimental spectrum of 4-(1*H*-imidazol-1-yl)aniline, the most intense band is likely resulting from the overlap of N2 and N3 peaks. The decrease in intensity and the displacement of this peak after grafting can be explained by the fact that the primary amine function disappeared during the surface functionalization, demonstrating that a large part of 4-(1*H*-imidazol-1-yl)aniline units was effectively covalently grafted on Darco.

SEM images of Darco showed that the surface of this carbonaceous support was heterogeneous and both smooth and rough surface could be observed. The surface modification by grafting phenyl imidazole moieties on the support didn't change its morphology and the presence of nitrogen detected by the ESD detector (Energy Dispersive X-ray Spectroscopy) was found in both smooth and rough side (Fig. S7). This result indicated that basic sites dispersed randomly on the total surface of carbonaceous support without any preference.

The catalytic properties of Darco-0.5IM were evaluated in the Knøevenagel condensation of furfural with malononitrile (Scheme 2). Firstly, it was verified that bare Darco was inactive in such reaction under these experimental conditions. In agreement with our previous results [21], only FMMN as organic product was present in chromatographic analysis showing a good selectivity of Darco-0.5IM. From Fig. 3, it was found that the yield of FMMN depended on the amount of Darco-0.5IM used in the reaction. The presence of 200 mg of Darco-0.5IM (30 wt.%, close to 450  $\mu$ mol of catalytic sites) allowed to obtain more than 80% of FMMN after 6 hours. Kinetic studies also demonstrated that Darco-0.5IM was as effective as its corresponding homogeneous catalyst (1-phenyl-1*H*-imidazole) with similar molar quantity (450  $\mu$ mol). The catalytic activity of Darco-0.5IM was compared to that of Darco-0.5PDA with same molar quantity of basic sites. Firstly, in order to evaluate the basic force of these 2 solids, we simulated the  $pK_a$  values of the conjugated acids of 1-phenyl-1*H*-imidazole and aniline in DMSO by COSMOTermX, a physicochemical properties prediction software [22,23] (Table S3). Based on the theoretical  $pK_a$  values in DMSO, it is possible to predict the catalytic activity of these functionalized solids in the Knøevenagel condensation since the non-binding doublet of nitrogen atom is used to deprotonate the activated methylene group. The conjugated acid of 1-phenyl-1*H*-imidazole has higher  $pK_a$  value, which means the conjugated base (1-phenyl-1*H*-imidazole) has more basic strength than aniline. Indeed, the higher value of  $pK_a$  is, the weaker the acid and the stronger the conjugated base is. As illustrated in Table S3, the ranking of basic strength was

in good accordance with the final product yield obtained over functionalized solids (Fig. 4). Since 1-phenyl-1*H*-imidazole is more basic than aniline, the corresponding functionalized solid Darco-0.5IM allowed a better yield of FMMN up to 83%, very close to that obtained by 1-phenyl-1*H*-imidazole. Nevertheless, the yield of FMMN obtained by Darco-0.5PDA was only a quarter (22%) of that obtained by Darco-0.5IM.

The stability of the Darco-0.5IM was studied by running 5 consecutive catalytic cycles without regeneration. A loss of yield was observed during recycling cycles (Fig. S8). The yield of FMMN decreased from 83% to 50% after 5 catalytic cycles. A leaching study was conducted to further understand the deactivation of Darco-0.5IM (Figure S9). Typically, Darco-0.5IM was brought into contact with the reagents for 30 minutes and then removed by filtration. It was observed that a portion of catalytic units leached into the reaction medium since the yield of the FMMN increased slightly in the absence of the solid catalyst. Indeed, the yield in FMMN was equal to 37 mol% after removal catalyst by filtration, and it increased up to 52 mol% after 5.5 hours of reaction without solid catalyst. The leached species were assumed to be 4-(1*H*-imidazol-1-yl)aniline units which were only physisorbed species, explaining the partial recyclability of Darco-0.5IM (Fig. S8). These species are probably strongly physisorbed since they are not removed after 7 consecutive washes by acetonitrile, which was the washing procedure used during the catalyst synthesis as described in the experimental part. Nevertheless, as highlighted by XPS, a large part of nitrogen units are also covalently grafted on Darco, which can explain the residual activity of Darco-0.5IM after 5 recycling tests.

## Conclusion

We present here the first example of a phenyl imidazole group grafting on carbonaceous support by diazonium chemistry, as well as their use in a base catalyzed reaction. The incorporation of phenyl imidazole units on Darco was confirmed by experimental XPS spectra and DFT

calculations. The amino basic solid Darco-0.5IM catalyzed efficiently Knøevenagel reaction between furfural and malononitrile at 40 °C and could be reused for 5 consecutive catalytic runs by a simple filtration and washing procedure. It is also possible to conclude that Darco-0.5IM with a tertiary amine unit has stronger basic strength and does not get deactivated by adsorption of final product on catalyst. Nevertheless, a leaching phenomenon was observed for Darco-0.5IM probably due to the incomplete grafting process.

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### Figure Caption

Fig. 1: FT-IR spectra of 1-phenyl-1*H*-imidazole (noted as Ph-Im), bare carbonaceous support Darco and functionalized solid Darco-0.5IM

Fig. 2: XPS N 1s core level spectra of the functionalized solid Darco-0.5IM and the precursor 4-(1*H*-imidazol-1-yl)aniline

Fig. 3: Kinetic profiles of Darco-0.5IM with respectively 10% (37 mg), 20% (133 mg) and 30% (200 mg) weight of malononitrile compared to 450  $\mu$ mol of 1-phenyl-1*H*-imidazole. Reaction conditions: 40 °C, 6 hours at  $P_{\text{atm}}$

Fig. 4: Correlation between the basic strength of catalytic moieties and the final product (FMMN) yield obtained by these catalytic moieties (450  $\mu$ mol of catalytic sites, 40 °C, 6 hours)



Fig. 1.

FT-IR spectra of 1-phenyl-1*H*-imidazole (noted as Ph-Im), bare carbonaceous support Darco and functionalized solid Darco-0.5IM

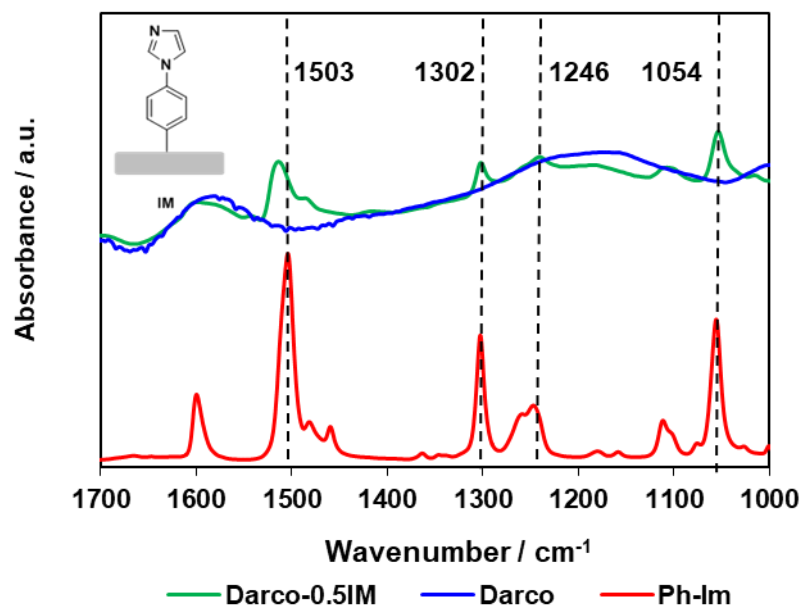


Fig. 2.

XPS N 1s core level spectra of the functionalized solid Darco-0.5IM and the precursor 4-(1*H*-imidazol-1-yl)aniline

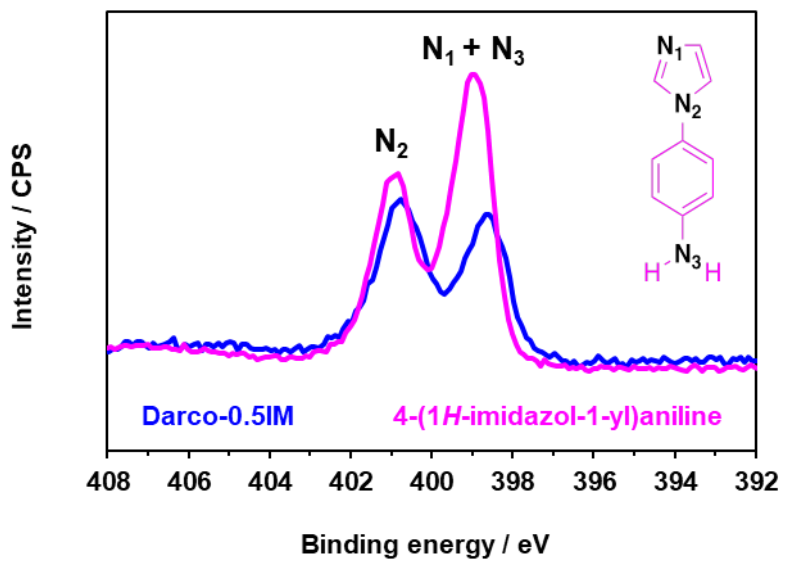


Fig. 3.

Kinetic profiles of Darco-0.5IM with respectively 10% (37 mg), 20% (133 mg) and 30% (200 mg) weight of malononitrile compared to 450  $\mu\text{mol}$  of 1-phenyl-1*H*-imidazole. Reaction conditions: 40  $^{\circ}\text{C}$ , 6 hours at  $P_{\text{atm}}$

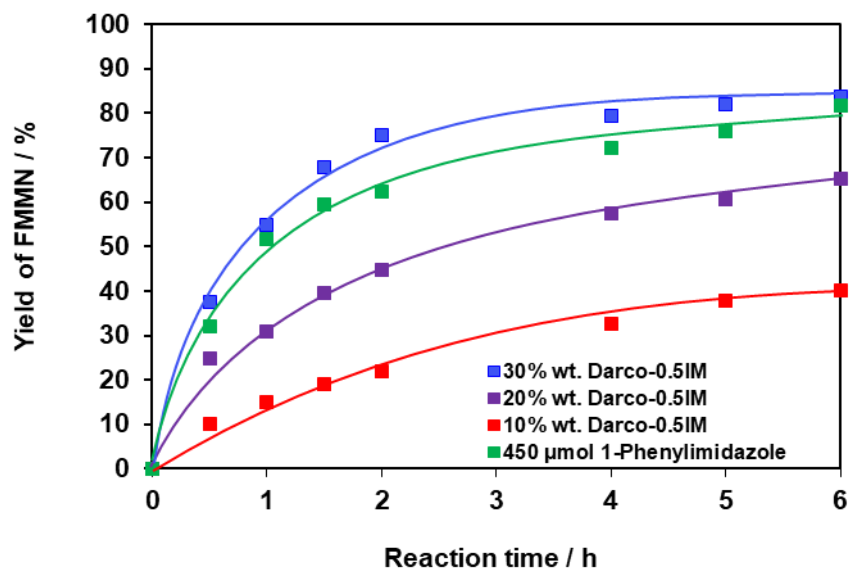
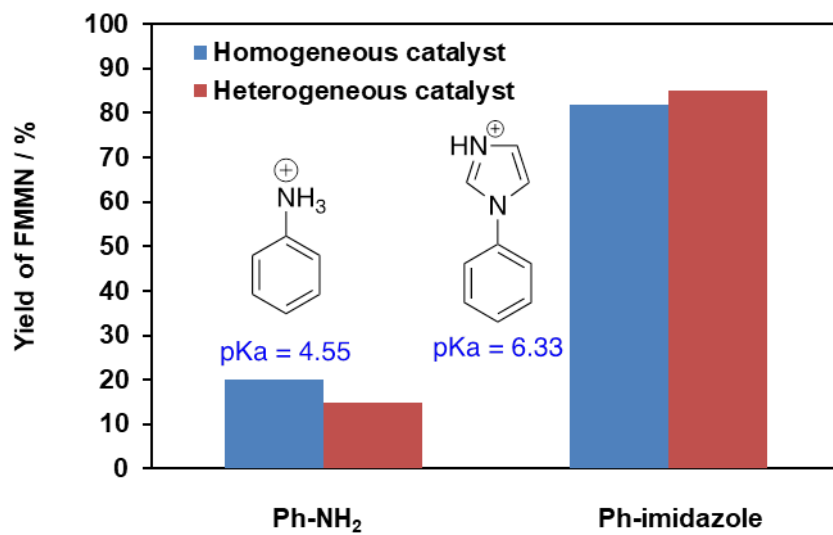


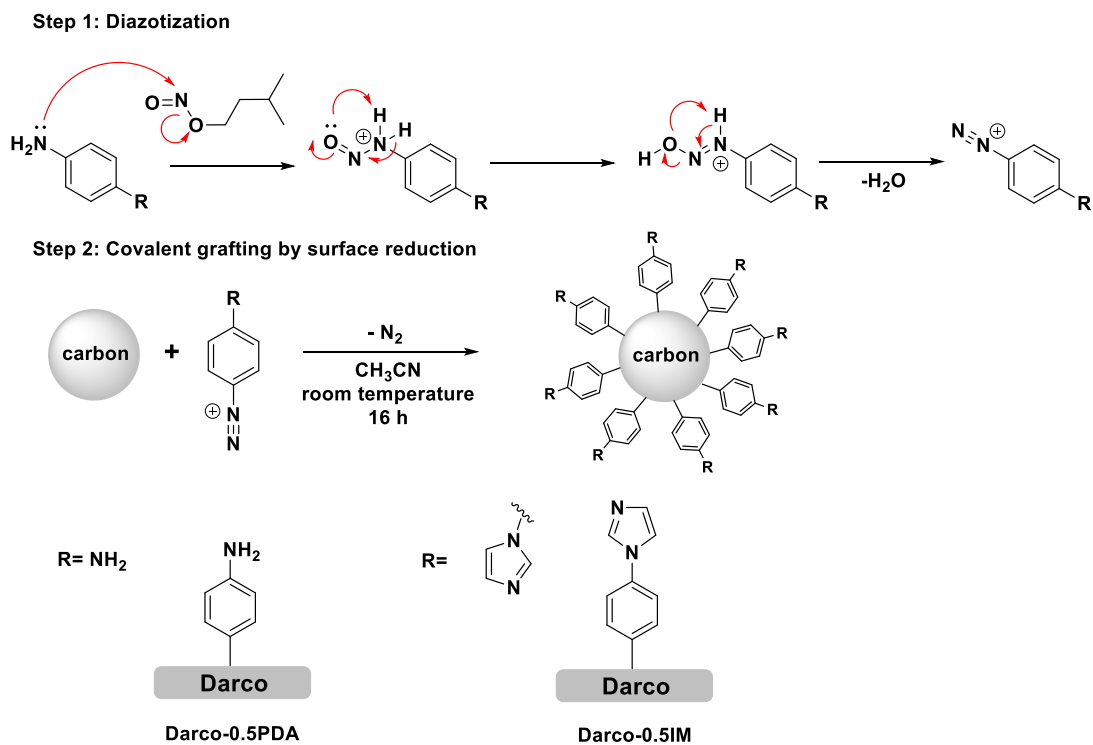
Fig. 4.

Correlation between the basic strength of catalytic moieties and the final product (FMMN) yield obtained by these catalytic moieties (450  $\mu\text{mol}$  of catalytic sites, 40  $^{\circ}\text{C}$ , 6 hours)



## Scheme 1.

Simplified reaction pathway of grafting aminophenyl groups onto activated charcoal according to Lipińska et al. [18]



Scheme 2. Knoevenagel condensation of furfural with malononitrile [19]

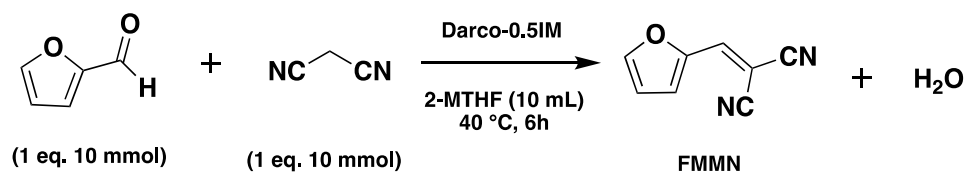


Table 1: Textural properties of Darco and two amino functionalized basic solids

<b>Solid</b>	<b>Nitrogen content<sup>a</sup></b> <b>(wt %)</b>	<b>Basic sites<sup>b</sup></b> <b>(mmol g<sup>-1</sup>)</b>	<b>S<sub>BET</sub><sup>c</sup></b> <b>(m<sup>2</sup> g<sup>-1</sup>)</b>	<b>V<sub>pore</sub><sup>d</sup></b> <b>(cm<sup>3</sup> g<sup>-1</sup>)</b>	<b>d<sub>pore</sub><sup>e</sup></b> <b>(nm)</b>
<b>Darco</b>	0	0	1345	1.08	6.4
<b>Darco-0.5PDA</b>	5.1	3.7	609	0.55	6.6
<b>Darco-0.5IM</b>	6.2	2.3	543	0.52	6.5

a. Nitrogen content obtained from elemental analysis.

b. Basicity calculated from elemental analysis.

c. Specific surface area calculated by the BET method.

d. Total pore volume determined at P/P<sub>0</sub>=0.99.

e. Average pore diameter deduced from the BJH method using the desorption branch.