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Upgrading of furfural by Knøevenagel condensation over functionalized carbonaceous basic catalysts

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Abstract:

Commercial carbonaceous materials (Darco KB-G, Norit SX2 and Vulcan XC72) were functionalized with phenyl primary amine using diazonium coupling. The chemical grafting procedure yielded carbon-based basic catalysts, in which the introduced amine group was readily accessible to the reactants. These basic solids were characterized by different techniques (elemental analysis, N₂ adsorption-desorption, TGA, SEM, FT-IR and XPS). Basic solid Darco-0.5PDA exhibited high activity to the Knoevenagel condensation of furfural and malononitrile under mild experimental conditions (40 °C, P_{atm}).

1. Introduction:

Homogeneous catalyst applications are usually limited in industrial chemical processes because massive wastes are produced and catalyst separation with raw materials and products is inconvenient during industrial production processes. As a result, the development of heterogeneous catalysts by immobilizing homogeneous catalysts onto solid supports is still a continuing need [1]. Various strategies were developed for immobilizing homogeneous catalysts onto inorganic supports and organic polymers supports [2,3]. Nevertheless, not only the tedious synthesis for the post immobilization process but also the low catalyst loadings and the resulting low efficiencies contribute to the high cost of supported catalysts [4]. Moreover, these catalysts often suffer from important active species leaching while they are used in liquid phase reactions [5]. To remedy the deficiency of supported catalysis, scientists have worked on direct functionalization of solid support via covalent bond building between the functionalities of the solid support and organocatalytic species. Among the approaches of functionalization being investigated, the chemistry of diazonium is becoming more and more attractive since this promising method enables to graft different organic moieties onto various solid supports such as carbon substrate, gold substrate or hydrogenated silicon in aqueous or organic media [6–8]. Compared to silica supports, carbonaceous materials generally exhibit good chemical stability while the Si-O bond of silica supports can easily be broken when acid or basic media are involved. Besides, activated charcoal based supports usually have very high specific surface area and strong adsorption capacity, which are crucial for a catalysis application. Diazonium cations can be formed by reacting an aromatic amine with sodium nitrite and a mineral acid in aqueous media [9,10], while they can also be generated in organic media using an alkyl nitrite like tert-butyl nitrite (*t*-BuNO) or iso-pentyl nitrite (*i*-PeNO) in a mixture of orthodichlorobenzene (ODCB) and acetonitrile (CH₃CN) [11–14].

However, although the formation of diazonium cation is now well understood, the mechanism of the reduction of diazonium cations by the reductive surface of carbonaceous supports is still under debate. Recently, Lipinska et al. proposed an overall reaction mechanism for multi-walled carbon nanotubes (MWCNT) in the presence of isopentyl nitrite [15]. The authors confirmed that the chemical reduction grafting procedure followed a radical chain mechanism, in which the reaction takes place through electron transfer from the carbonaceous material into the diazonium species with the loss of N_2 and the formation of an aryl radical that reacts with the carbonaceous support to form a covalent bond [16].

This spontaneous surface modification via diazonium chemistry makes the functionalization of carbonaceous materials simple, flexible and efficient for various applications such as negative electrode for lithium-ion batteries [17] and biomedical detection agents [13,14]. Precisely, by using the chemical grafting procedure in aqueous media, Martin and Ramirez-Castro grafted aminophenyl groups ($Ph-NH_2$) onto graphite flakes [17] and carbon black [18] respectively. Moreover, functionalized carbonaceous materials are widely used in acid catalysis. Using this direct functionalization method, Stellwagen et al. grafted phenylsulfonic acid groups ($Ph-SO_3H$) onto carbon nanofibers and these introduced acidic groups were efficient for the transesterification of triolein and methanol [19]. However, examples of functionalized carbon by diazonium grafting used in basic catalysis are still limited.

Knœvenagel condensation is one of the most valuable reactions for the C-C bond formation between a carbonyl group and an activated methylene group generally catalyzed by aminocatalysts [20] or solid bases [21] under mild experimental conditions (room temperature and atmospheric pressure). Recently, several catalysts were developed to perform this kind of reaction. Concerning homogeneous catalysts, List et al. designed cinchona-derived primary amine and reported the first example of asymmetric Knœvenagel condensation in DMSO at 20 °C [22]. Hilvert et al. carried out an enzymatic Knœvenagel condensation by using an

artificial retro-aldolase [23]. When it comes to the design of heterogeneous catalysts, some recent works demonstrated that ionic liquids (ILs) and metal-organic frameworks (MOF) were also efficient for this reaction. Maschmeyer et al. showed that bromozincate based ionic allowed good yields (up to 88%) for the Knoevenagel condensation between benzaldehyde and malononitrile [24]. In addition, the use of porous zeolite imidazolate framework (ZIF-8) based catalysts in the Knoevenagel condensation between benzaldehyde and malononitrile in toluene at room temperature was already reported [25,26]. Nowadays, smart amine functionalized materials are drawing more and more attention in basic catalysis. For instance, Modak et al. designed a porphyrin based microporous organic polymer as heterogeneous catalyst [27]. This bi-functional solid contains both free porphyrin and Fe(III)-porphyrin framework which enabled to catalyze the Knoevenagel condensation of various aromatic with high yields (between 62 and 99 mol%). Furthermore, Mondal et al. managed to functionalize NH₂ groups onto mesoporous silica through co-condensation of 3-aminopropyltriethoxy-silane along with tetraethylorthosilicate [28]. In the Knoevenagel condensation of different aromatic aldehydes with malononitrile, this amino-functionalized basic catalyst exhibited both good activity and stability in catalytic runs. It is highly desirable to use the Knoevenagel reaction for the upgrading of furfural known as a platform molecule from lingo-cellulosic biomass [29]. A recent computational study revealed that the product of the Knoevenagel reaction between furfural and malononitrile, (2-furanylmethylene)malononitrile, noted as FMMN, was highly applicable for photovoltaic solar cell applications [30].

We report hereafter the functionalization of three commercial carbonaceous materials with phenyl primary amine moiety (Ph-NH₂) and their application in basic catalysis through the Knoevenagel condensation between furfural and malononitrile.

2. Experimental part:

2.1 Catalyst synthesis

Commercially available carbon black (Vulcan XC-72) and activated charcoal (Darco KB-G and Norit SX2) obtained from Carbot Co. were dried for 16 h at 120 °C before use. The aryl amine precursor p-phenylenediamine (99%), denoted as PDA is purchased from Sigma-Aldrich and the isopentyl nitrite (97%) is purchased from Alfar Aesar. The diazonium coupling was performed according to Ramirez-Castro's procedure [18] with slight modifications. Typically, 0.5 g of p-phenylenediamine (4.62 mmol, 1 eq.) were dissolved in 100 mL of acetonitrile with vigorous stirring. 1 g of carbonaceous support is then dispersed in the solution followed by the dropwise addition of nitrile isopentyl (0.62 mL, 4.62 mmol, 1 eq.). The reaction mixture was 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 carbon powder was washed by successive aliquots of acetonitrile (200 mL - 7 times) until the filtrate is colourless. Finally the functionalized carbon was dried for 16h at 120 °C.

2.2 Catalyst characterizations

Available in ESI

2.3 Catalytic test procedure for the Knøevenagel reaction between furfural and malononitrile

The Knøevenagel condensation of furfural was carried out in a batch reactor fitted with a magnet stirrer and heated at 40 °C. The catalyst (200 mg) was introduced in a mixture composed by freshly distilled furfural (10 mmol, Sigma–Aldrich, 99%), malononitrile (10 mmol, Sigma–Aldrich, >99%), heptane (10 mmol, Sigma–Aldrich, 99%) and 2-methyltetrahydrofuran (10 mL, 99%, Alfar Aesar) as solvent. Heptane, inert in these conditions, was used as an internal standard for quantitative analysis carried out by Gas

Chromatography. Each liquid sample obtained after various reaction times (between 30 and 360 min) was analyzed by using a Varian 430 chromatograph equipped with CPSIL-5CB capillary column (length: 50 m; diameter: 0.25 mm, film thickness: 0.4 μm) and a flame ionization detector. The oven temperature was programmed from 70 °C to 150 °C (5 °C/min), then from 150 °C to 250 °C (10 °C/min) and maintained at 250 °C during 10 minutes. All detected products were identified by co-injection of commercial samples and/or by using Varian 3800 chromatograph coupled with a 1200 TQ mass spectrometer.

3. Results and discussion

3.1 Characterization of the catalysts

Spontaneous functionalization of three commercial carbonaceous supports (Darco, Norit and Vulcan) was carried out in two consecutive steps to have a maximal number of basic sites equal to 4.6 mmol g⁻¹ (Scheme 1). The three functionalized solids are noted as Darco-0.5PDA, Norit-0.5PDA and Vulcan-0.5PDA where the number 0.5 represents the weight of *p*-phenylenediamine involving in the synthesis per gram of carbonaceous support, depending on the type of support. As expected, all basic solids modified by this chemical grafting procedure possessed nitrogen in various weight content, depending on the support, as indicated in Table 1. The highest value was obtained in presence of Darco (5.14 wt% of nitrogen). From the amount of nitrogen content, the basicity of each solid (expressed in mmol g⁻¹) can be estimated supposing that all nitrogen was in the form of –NH₂ basic group. Thus, the Darco 0.5PDA sample exhibited the highest value of basicity, close to 3.7 mmol g⁻¹ (Table 1). These observations suggested that these carbonaceous supports were successfully modified by the grafting procedure.

The shape of isotherms obtained from N₂ adsorption of both carbonaceous supports and functionalized solids presented a type IV isotherm (Figure S1). The carbonaceous supports and their corresponding functionalized solids showed different specific surface areas and porous volume. For example, bare Darco exhibited the highest values for both textural characteristics ($S_{\text{BET}} = 1345 \text{ m}^2$ and $V_p = 1.08 \text{ cm}^3 \text{ g}^{-1}$), which explained in part its higher nitrogen content, as reported in Table 1. Indeed, the specific surface area of Darco-0.5PDA was approximately 2.5 times higher than that of Norit-0.5PDA and more than 4 times higher than that of Vulcan-0.5PDA. Irrespective to the carbonaceous support, the functionalization by grafting –NH₂ groups led to a decrease of both specific surface area and total pore volume but a slight increase of the pore diameter average (Table 1).

The grafting ratio of each functionalized solid can be calculated by dividing the number of basic sites to the theoretical maximal number of basic sites (4.6 mmol g^{-1}). The highest value, close to 79%, was obtained when Darco was used as support. As highlighted in Figure 1, a linear correlation can be found between the grafting ratio of each functionalized solid and the specific surface area of each carbonaceous support. Darco presented the largest specific surface area and as a result its corresponding modified solid (Darco-0.5PDA) exhibited the highest grafting ratio compared to other functionalized solids. Consequently, it seems that the grafting ratio of the functionalized solid could be directly proportional to the specific surface area of its bare carbonaceous support before the surface saturation. This trend indicates that using a carbonaceous support, whose specific area is large enough to obtain a considerable grafting ratio, is favourable to maximize the number of catalytic basic sites.

Infrared analysis was carried out in order to confirm the presence of grafted Ph-NH₂ moieties on the surface of functionalized solids. The IR spectra (in the region between 1000 and 1700 cm^{-1}) of functionalized solids and bare support Darco) showed significant difference (Figure 2). As expected, characteristic IR bands of aniline were observed in the spectrum of Darco-0.5PDA. However, a slight shift towards higher values, especially for the band at 1496 cm^{-1} (aromatic C=C stretching vibration), can be attributed to a modification of the chemical environment of aromatic ring due to its grafting onto Darco [31]. The C-N stretch of aromatic primary amine is expected to be observed between 1350 and 1250 cm^{-1} and its position is commonly used to distinguish between saturated and aromatic amines [32]. The band at 1267 cm^{-1} can be hence assigned to the aromatic amine C-N stretching vibration. In addition, the bands at 1616 and 1598 cm^{-1} in the IR spectra of aniline can be attributed to the scissoring vibration of the primary amine NH₂ group. On the contrary, for both Norit-0.5PDA and Vulcan-0.5PDA samples, negligible differences were showed on the IR spectra, probably due to the lower amount of grafted species (Figure S3).

The X-ray photoelectron spectroscopy (XPS) analysis confirmed that Ph-NH₂ molecules were successfully grafted onto the carbonaceous supports. Indeed, the XPS spectra of the three functionalized solids showed a single N 1s peak at 399.9 eV, which is attributed to the -NH₂ groups presented in the functionalized solids (Figure 3) [9]. Obviously, this peak was absent on the unmodified Darco (Figure S4). The C 1s core-level spectra of all carbonaceous supports and functionalized solids showed a strong graphite component at around 284.3 eV (Figure S5) [9]. Other peaks at higher binding energies (between 286 and 292 eV) were attributed to the presence of surface oxides components [10]. The peak at 285.9 eV, relatively intense in the case of Darco-0.5PDA, can be attributed to the presence of C-N species. These observations indicated clearly that the functionalization led to the formation of new C-N bonds.

SEM images of Darco showed that the surface of this carbonaceous support was heterogeneous. Both smooth and rough parts could be observed on the surface. The chemical surface modification by grafting Ph-NH₂ moieties on the support seemed not to change its morphology as the surface of modified Darco-0.5PDA remained heterogeneous (Figure S6). The presence of nitrogen detected by the ESD detector (*Energy Dispersive X-ray Spectroscopy*) was found in both smooth and rough parts on the surface of Darco-0.5PDA and this interesting result indicated that grafted basic molecules were well dispersed randomly on the total surface of carbonaceous support (Figure S6).

The thermogravimetric analysis (TGA) of Darco and Darco-0.5PDA illustrated two weight losses at 449-475 °C and 497-498 °C corresponding to the carbonaceous support material combustion (Figure S7). Another weight loss at 438 °C was only observed on Darco-0.5PDA, and can be attributed to the grafted species combustion. Assuming that the decomposed grafted specie is amino phenyl, the 22.8% weight lost corresponds to 2.45 mmol g⁻¹; which is

in fair good agreement with the calculated value of basicity deduced from nitrogen elemental analysis (Table 1).

3.2 Catalytic properties of functionalized solids

The catalytic properties of functionalized solids were evaluated in the Knøevenagel condensation. This reaction involves both furfural and malononitrile as reactants; (2-furanylmethylene)malononitrile (FMMN) is expected as the only organic product (Scheme 2). The reaction was carried out under mild conditions (40 °C, under atmospheric pressure) during 6 hours using 200 mg of basic solid.

A kinetic study was performed for each functionalized solid. The yield in FMMN (the only product observed in the reaction mixture) was spotted in function of the reaction time (Figure 4), showing that each basic solid was active in this reaction. Mass balances were accurate to within 5% in all catalytic tests. Apparently, Vulcan-0.5PDA was rapidly deactivated since the product yield remained practically constant (about 14 mol %) after 30 minutes. On the contrary, in the case of Darco-0.5PDA and Norit-0.5PDA, the yield of FMMN increased continuously with the reaction time. As the basicity of Darco-0.5PDA was higher than Norit-0.5PDA (Table 1), the former exhibited the highest activity for Knøevenagel reaction between furfural and malononitrile. It is important to notice that the yield of FMMN could be nearly doubled when Norit-0.5PDA was replaced by Darco-0.5PDA with the same quantity of catalyst (200 mg).

In order to evaluate the bonding strength of the grafted species on Darco, an additional experiment was carried out. Firstly, the Darco-0.5PDA sample (200 mg) was added in the reaction mixture and the composition of the reaction mixture was followed during one hour, the yield in FMMN equal to 15 mol% was very close to the yield already obtained for the same catalyst under same experimental conditions. After that, the catalyst was eliminated by

filtration, the constant yield in FMMN during the remaining reaction time indicated that no catalytic species leached out during the reaction as shown in Figure 4 (red dotted line).

It was also checked that using 0.45 mmol of aniline as catalyst yielded 20 mol% of FMMN after 6 hours. It proved that any leaching of catalytic species could lead to an increasing yield.

It is very interesting to remark that the functionalized Darco-0.5PDA overcome the phenomenon of leaching which is a common disadvantage of carbon based catalysts [19,33,34]. The recycling and reuse of Darco-0.5PDA was further performed in four consecutive runs at 40 °C under atmospheric pressure. After each run, the catalyst was filtered, washed by the reaction solvent (2-MTHF) and dried at 100 °C for 4 hours. Darco-0.5PDA was then reused without any other purification steps. After each run, a strong decrease of the yield of FMMN was observed indicating that a strong deactivation of Darco-0.5PDA occurred (Figure S8). This phenomenon could be explained by a strong adsorption of reactants or product on active sites. As an evidence, further investigations are needed to understand the deactivation mode and thus to propose a reactivation procedure allowing to restore the catalytic properties of Darco-0.5PDA.

4. Conclusion

Aromatic primary amine moieties were successfully grafted onto three carbonaceous solid supports (Darco, Vulcan and Norit) by diazonium coupling under mild conditions. Among these 3 solid supports, Darco having the highest specific surface area allowed to obtain the best grafting ratio of Ph-NH₂ groups equal to 79%. These three functionalized solids were all active in the model reaction but with different activity. Darco-0.5PDA was the most active catalyst owing to its highest basicity. Under our experimental conditions, the leaching of grafted species was not observed. This is the first example of diazonium modified carbonaceous materials used as basic catalyst.

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Figure captions

Fig. 1. Correlation between the grafting ratio of the functionalized solids and the specific surface area of their carbonaceous supports

Fig. 2. FT-IR spectra of aniline, Darco and Darco-0.5PDA

Fig. 3. XPS spectra recorded for N 1s core level of 3 functionalized solids containing Ph-NH₂ groups

Fig. 4. Kinetic profiles of Knoevenagel condensation of furfural catalyzed by amino functionalized solids and leaching evaluation for Darco-0.5PDA

Table 1

Textural properties of bare carbonaceous supports and their corresponding modified basic solids

Solid	Nitrogen content ^a (% wt)	Basicity ^b (mmol g ⁻¹)	S _{BET} ^c (m ² g ⁻¹)	V _p ^d (cm ³ g ⁻¹)	d _p ^e (nm)
Darco	0.00	-	1345	1.08	6.4
Darco-0.5PDA	5.14	3.7	609	0.55	6.6
Norit	0.00	-	593	0.52	7.9
Norit-0.5PDA	2.46	1.8	245	0.31	8.7
Vulcan	0.00	-	233	0.32	13.2
Vulcan-0.5PDA	0.82	0.6	142	0.24	14.6

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 $P/P_0 = 0.99$

e: average pore diameter deduced from the BJH method using the desorption branch

Fig. 1

Correlation between the grafting ratio of the functionalized solids and the specific surface area of their carbonaceous supports

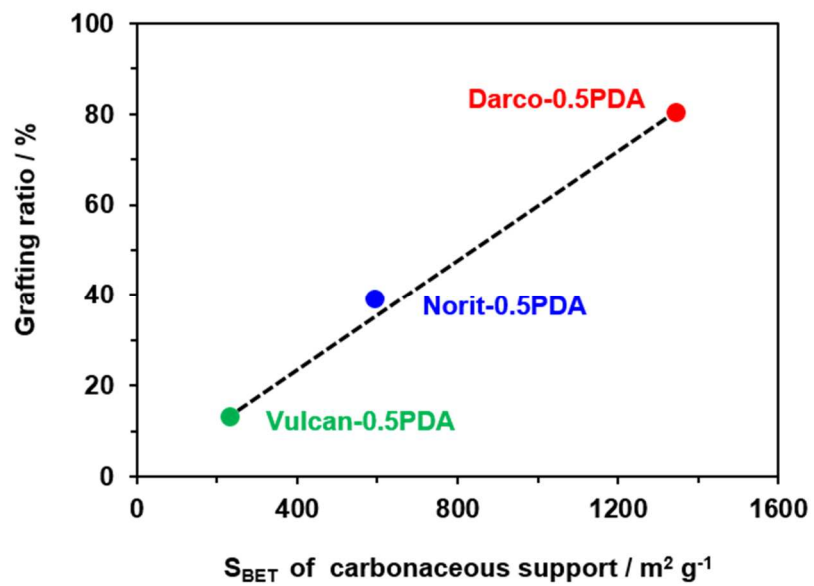


Fig. 2.

FT-IR spectra of aniline, Darco and Darco-0.5PDA

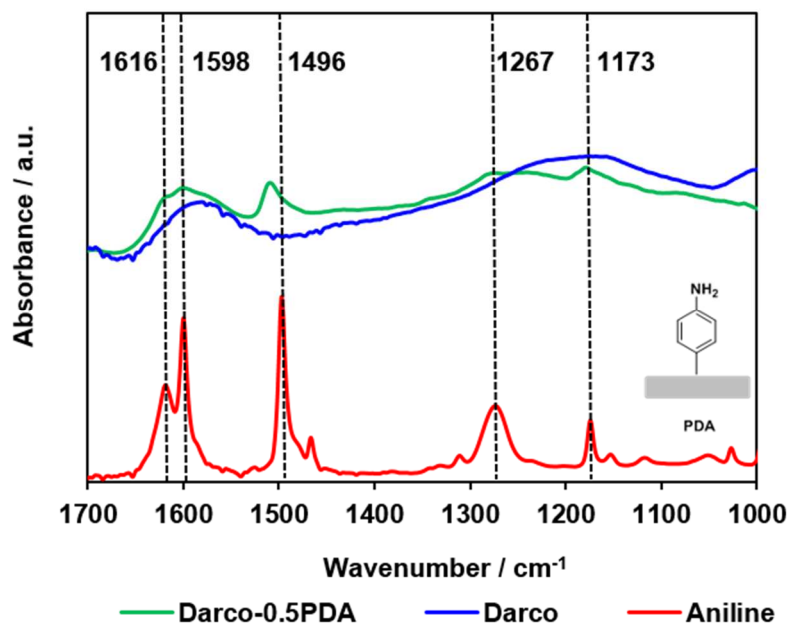


Fig. 3.

XPS spectra recorded for N 1s core level of 3 functionalized solids containing Ph-NH₂ groups

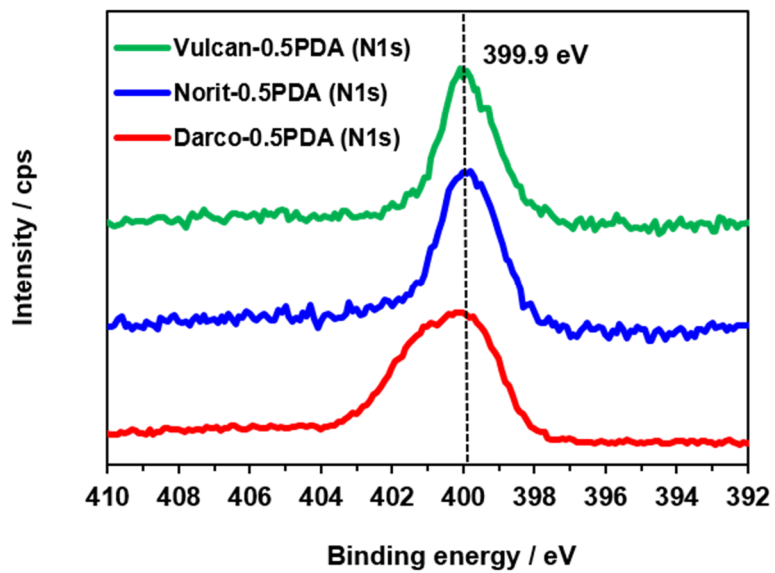
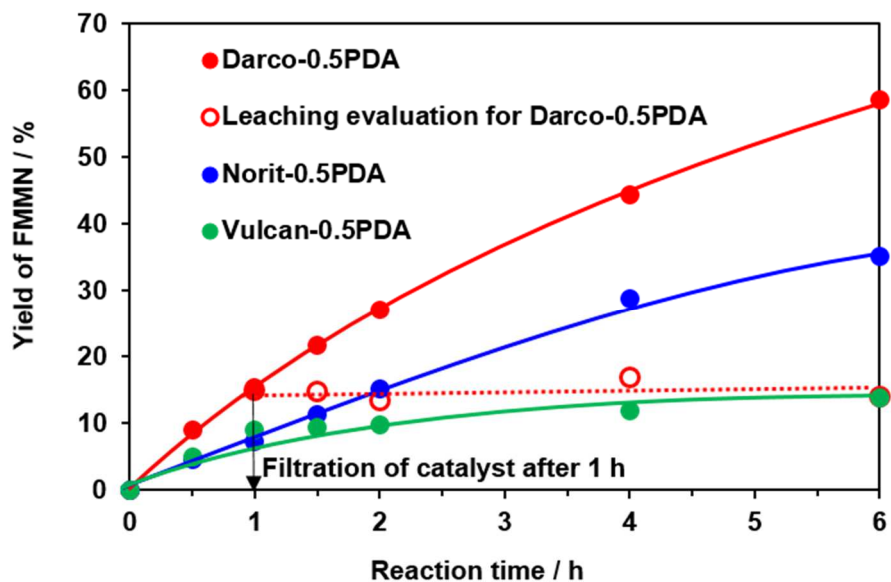


Fig.4.

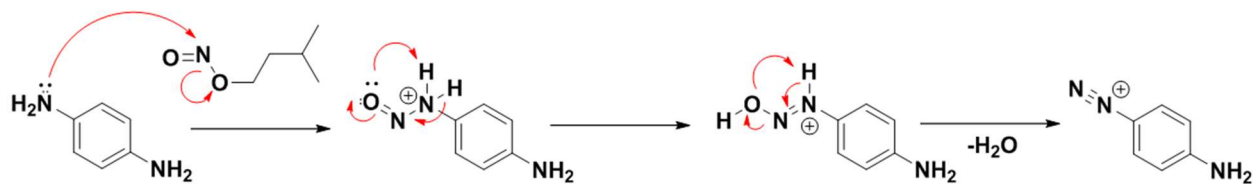
Kinetic profiles of Knoevenagel condensation of furfural catalyzed by amino functionalized solids and leaching evaluation for Darco-0.5PDA



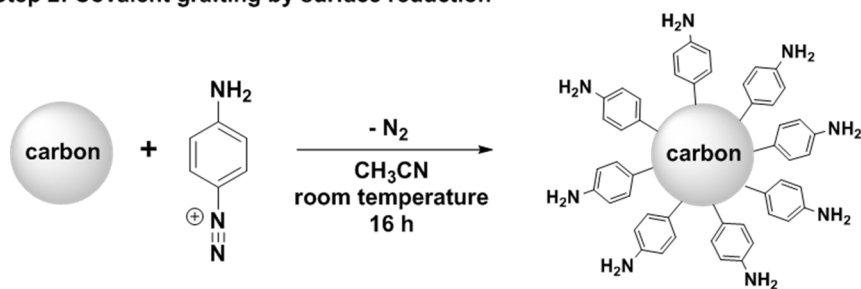
Scheme 1.

Schematic reaction pathway for grafting aminophenyl groups to carbonaceous materials [8]

Step 1: Diazotation



Step 2: Covalent grafting by surface reduction



Scheme 2.

Knoevenagel condensation of furfural with malononitrile

