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Metal-Free Reduction of Nitrobenzene to Aniline in Subcritical Water

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ABSTRACT:

An environmentally friendly approach for the reduction of nitrobenzene to aniline promoted by carbonaceous bio-based materials was successfully achieved under subcritical water conditions. The proposed methodology features a metal-free process, no-hydrogen input as reductor, the use of commercial bio-based carbon materials having low cost and availability and water as green solvent under subcritical conditions. Using optimized conditions, reduction of nitrobenzene in the presence of commercial NORIT GAC 12-40 or DACARB PC1000 was accomplished at 310 °C for 6 h and quantitatively furnished the target aniline. Treatment of NORIT GAC 12-40 with KOH allowed to decrease charcoal loading (6 g vs 40 g) and increase aniline yields (80% vs 66%).

KEYWORDS: *metal-free, reduction, green chemistry, subcritical water, carbonaceous materials*

INTRODUCTION

Aniline derivatives represent an important class of nitrogen heterocyclic compounds extensively employed in the chemical industry as dyes, antioxidants, pharmaceuticals and agricultural chemicals.¹ Aniline is used for the production of rigid polyurethane (PU) foams *via* methylene diisocyanate (MDI) formation. Aniline is also employed as building block for the synthesis of a number of molecules of interest present in rubber products, consumer goods, agriculture, transportation, adhesives/sealants, textile, packaging, manufacturing, coatings, photography, electronics, pulp and care, and pharmaceuticals.²

Aromatic amines are generally produced from their corresponding nitroarenes by catalytic hydrogenation using molecular hydrogen³ or reducing agents such as hydrazine hydrate,⁴ silanes,⁵ sodium hydrosulphite,⁶ formates,⁷ decaborane,⁸ glucose⁹ and NaBH₄¹⁰ as hydrogen sources. It is interesting to note that hydrogen can also be generated from water by laser irradiation starting from carbon powder.¹¹ Although this process has not been used for chemical organic reactions, hydrogen production from carbonaceous materials and water is very interesting for different reasons. Carbon and water are among most abundant materials

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on earth and their direct use as efficient and low cost reagents is an attractive topic and meets the requirements of green and sustainable chemistry. Next to catalytic hydrogenations, catalytic transfer hydrogenation (CTH) is also used in presence of alcohols, hydrocarbons, hydrazines, organic acids and their salts in protocols generally emplying metals.¹²

In parallel with academic and industrial applications, organic chemists have a growing interest for green chemistry and try to contribute partially or totally to the development of alternative technologies including catalysis and metal-free conditions in safer solvents. In this regard, simple, inexpensive and facile scale-up production of aromatic amines from nitroarenes using D-glucose as hydrogen donor under catalyst-free aqueous conditions was previously reported.⁹ In order to provide a more general protocol for a more sustainable synthesis of anilines, herein we disclose a novel reduction of nitrobenzene into aniline using metal-free conditions without added hydrogen in the presence of carbonaceous materials under sub-critical water.

RESULTS AND DISCUSSION

The commercial charcoals NORIT GAC 12-40, DACARB PC1000 and UNTRETED 4-8 MESH were characterized using scanning electron microscopy (SEM), energy dispersive X-ray diffraction (EDX), X-ray photoelectron spectroscopy (XPS) and nitrogen adsorption measurements. The morphology of NORIT GAC 12-40 and DACARB PC1000 was determined by SEM and no significant difference could be observed between these materials (**Fig S1**). On the other hand, UNTREATED 4-8 MESH exhibited a different morphology (more organized) with a honeycomb-like structure (**Fig S1**). The surface elemental composition of the materials was confirmed by EDX spectra (**Fig S3**) and XPS analysis (**Table S1** and **Fig S5-S12**). NORIT GAC 12-40 and DACARB PC1000 possess carbon and oxygen as well as aluminum and potassium, respectively. UNTREATED 4-8 MESH has

almost exclusively carbon. BET analysis showed that NORIT GAC 12-40 and DACARB PC1000 have a total surface area and pore volume over 900 m² g⁻¹ and 0.5 cm³ g⁻¹, whereas a negligible one (30 m² g⁻¹ and 0.01 cm³ g⁻¹) was measured for UNTREATED 4-8 MESH (Table S2). The content of surface oxygen functional groups was determined by the Boehm method. The three carbonaceous materials have got mainly basic functional groups (Table 4). Initial eatalytic studies were performed for nitrobenzene conversion (10 mmol) using NORIT GAC 12-40 (6 g) in water at 300 °C under 90 bar as model reaction. At this temperature (higher than 100°C and lower than 374°C) and pressure (higher than 0.1 Mpa and lower than 22.1 mPa), the reduction of the nitroarene takes place in subcritical water conditions. This state of water has particular physicochemical properties with (i) a density equivalent to that of the liquid; (ii) a low viscosity approaching that of the gas; (iii) a diffusion coefficient at least ten times higher as compared to the liquid; (iv) a very important transfer coefficient and (v) a low dielectric constant which is close to that of organic solvents. The altered physical properties of subcritical water result in different solvent behavior. Under preliminary investigated conditions, aniline was obtained in 62% after 6 hours (Figure 1). Nitrobenzene loadings varying from 5 to 25 mmol were then investigated to find that nitrobenzene concentration can significantly influence aniline yields, with optimum results observed using 10 mmol starting material.



Figure 1. Effect of nitrobenzene loading on reduction of nitrobenzene to aniline. *aReaction conditions:* nitrobenzene (5 mmol – 25 mmol), NORIT GAC 12-40 (6 g), water (55 mL), 300 °C, 90 bar, 6 h.

With the aim of determining the most favorable reaction temperature, variations from 275 °C to 320 °C for 6 h were investigated under batch conditions (**Figure 2**). Lower reaction temperatures (275 °C) seemed to be insufficient for the conversion of nitrobenzene to aniline after 6 hours. An increase in reaction temperature (310 °C) benefits aniline production, with yields reaching a maximum value of 65% at complete nitrobenzene conversion. However, aniline yields remarkably decreased to 53% when the reaction temperature increased to 320 °C, probably related to product degradation.



Figure 2. Effect of temperature on reduction of nitrobenzene to aniline. *aReaction conditions:* nitrobenzene (10 mmol), NORIT GAC 12-40 (6 g), water (55 mL), 6 h.

Kinetics studies of the reaction were aimed to optimize reaction times for the reduction of nitrobenzene in presence of NORIT GAC 12-40 (310 °C, 6 h, **Figure 3**). Aniline yields increased with reaction time and reached complete conversion and maximum aniline yield (66%). It is interesting to note that aniline yields severely decreased to 46% when the reaction time was prolonged to 7 hours. This may be due to ongoing side-reactions such as various decomposition pathways.



Figure 3. Effect of reaction time on reduction of nitrobenzene to aniline. *aReaction conditions:* nitrobenzene (10 mmol), NORIT GAC 12-40 (6 g), water (55 mL), 310 °C, 90 bar, 6 h.

The nature of the solvent and the concentration of the reagents have a remarkable influence in reaction yields especially near the critical point. At 310 °C, the volume of water has also a great influence on aniline yields. For volumes over 65 mL, the extremely high generated pressure (> 200 bar) prevented the reaction to progress. On the other hand, aniline yields did not exceed 53% with volumes under 30 mL, for which 55 mL water was selected as compromise for subsequent reactions. In this process, hydrogen is generated *via* consumption of carbonaceous bio-based materials and water (Scheme 1). Therefore, an increase in the volume of water generates more H₂ and thus facilitates the reduction of nitrobenzene to aniline. In order to substitute water, several protonated solvents (water, methanol, ethanol, propan-1-ol, butan-1-ol and propan-2-ol) were also tested (**Figure 4**). In function of the properties of the alcohols, the temperature and generated pressure were modified to be under subcritical temperature and pressure conditions (**Table 1**). All experiments resulted in an aniline yields < 25% excepted for butan-1-ol (**Figure 4**, **d**), which gave aniline in 57% yield (at 91% conversion). However, this result is inferior to that obtained with water under otherwise identical reaction conditions, supporting the use of subcritical water as green solvent for the rest of the optimization experiments.



Figure 4. Effect of the nature of the solvent and temperature on reduction of nitrobenzene to aniline. *aReaction conditions:* nitrobenzene (10 mmol), NORIT GAC 12-40 (6 g), protonated solvent (55 mL), 200-265 °C, 60-80 bar, 6 h.

	critical temperature	critical pressure
	(°C)	(bar)
methanol	239	80
ethanol	240	61
propan-1-ol	263.6	51
butan-1-ol	289.8	44
propan-2-ol	235	53

 Table 1. Critical temperature and pressure of the tested protonated solvents

With our first optimized reaction conditions in hand, a range of carbonaceous materials such as activated charcoals and graphites were subsequently screened (**Figure 5**). Among them, NORIT GAC 12-40, NORIT SA2, NORIT A supra, DACARB PC 1000 and OXBOW 1 furnished aniline in yields >60% and therefore were further utilized for optimization purposes. As expected, graphite provided a low aniline yield (36 %), probably due to the absence of surface functionalities (it is interesting to note that untreated carbon gave aniline in 27% yield). Therefore, this carbonaceous material has been chosen as a point of comparison in order to understand structure-activity relationships.



Figure 5. Effect of the nature of the carbonaceous materials on reduction of nitrobenzene to aniline. *aReaction conditions:* nitrobenzene (10 mmol), carbonaceous material (6 g), water (55 mL), 310 °C, 90 bar, 6 h. NORIT GAC 12-40 (A), MONARCH 1300 (B), ELFTEX 125 (C), GRAPHITE (D), BPL4X10 (E), NC35 1.25-1.35 (F), AC 40 (G), NORIT CN1 (H), NORIT SA2 (I), NORIT A SUPRA (J), UNTREATED (K), NORIT TPK 1-3 (L), DARCA 12.20 (M), DACARB PC1000 (N), DACARB PBC1 (S), DACARB PBB (T), OXBOW 1 (U), OXBOW 2 (V), DACARB PCC1200 (W), DACARB PM300 (X).

Among selected carbonaceous materials (NORIT GAC 12-40, NORIT SA2, NORIT A supra, DACARB PC 1000 and OXBOW 1), the loading influence was subsequently studied (**Figure 6**). A pseudo-linear increase in aniline yields could be observed at increased carbon loadings. Gratifyingly, aniline was selectively produced in quantitative yields using DACARB PC 1000 (16 g), for which this carbonaceous material was employed in subsequent reactions.



Figure 6. Effect of the charcoal loading on reduction of nitrobenzene to aniline. *aReaction conditions:* nitrobenzene (10 mmol), carbonaceous material (3 - 40 g), water (55 mL), 310 °C, 90 bar, 6 h. NORIT GAC 12-40 (A), NORIT SA2 (I), NORIT A SUPRA (J), DACARB PC1000 (N), OXBOW 1 (U).

Using DACARB PC1000 (20 g), kinetic time-dependent studies from 2h to 9h at 310 °C were then conducted (**Table 2**). As expected, aniline yields were found to increase with reaction time, reaching quantitative yields (>99%) after 6 h reaction. Aniline yields severely decreased to 80% at longer reaction times (7-9 h). This phenomenon is likely to be related to the presence of side reactions (e.g. chemical decomposition) at prolonged reaction times.

Interestingly, the optimized reaction time (6 h) was found to be identical for both NORIT GAC 12-40 and DACARB PC 1000.

Table 2. Effect of reaction at 310 °C time with DACARB PC1000 ^a

entry	time (h)	yield (%)	conversion (%)
1	2	91	100
2	4	95	100
3	6	100	100
4	7	81	100
5	8	80	100
6	9	80	100

aReaction conditions: nitrobenzene (10 mmol), DACARB PC1000 (20 g), water (55 mL), 310 °C, 90 bar.

Variation of nitrobenzene and carbonaceous material loadings using NORIT GAC 12-40 and DACARB PC1000 separately pointed to two optimized processes: nitrobenzene (15 mmol) and NORIT GAC 12-40 (40 g) as method A (**Table 3, entry 3**) and nitrobenzene (10 mmol) and DACARB PC1000 (20 g) as method B (**Table 3, entry 5**). For the same conversion and aniline yield, method A allows a higher volumetric productivity while method B uses less carbonaceous material.

Entry	nitrobenzene	charcoal	charcoal	yield	conversion
	(mmol)		(g)	(%)	(%)
1	10	А	6	62	100
2	10	А	40	91	100
3	15	А	40	99	100
4	20	А	40	61	100
5	10	Ν	20	100	100
6	20	Ν	20	76	100

Table 3. Effect of substrate loading with various amounts of activated carbon ^a

^{*a*}*Reaction conditions:* nitrobenzene (10 - 20 mmol), carbonaceous material A or N (6 - 40 g), water (55 mL), 310 °C, 90 bar.

Recycling performance is a significant index to evaluate the performance of our selected carbonaceous material which is mainly a carbon source for the formation of hydrogen. In our case, five cycles of experiments were studied under optimized conditions to estimate the properties of recovered material (**Figure 7**). As expected, after each cycle yield decreases due to the consumption of the surface and the efficiency reached a level of 63% of the initial value after four cycles. The characterization of the carbonaceous materials was conducted using the same methods employed for the materials before reaction (**Fig S2, S4, S13-S15 and Tables S3, S4**). The main differences between before and after reaction are the morphology of carbonaceous materials and the total surface area and pore volume. The surface of NORIT GAC 12-40 is damaged probably by temperature and the total surface area and pore volume of DACARB PC1000 and NORIT GAC 12-40 are reduced after reaction. Another difference is the absence of potassium on the surface for DACARB PC1000 and the decrease of aluminium and carbon on the surface of NORIT GAC 12-40.

Aniline yeild (%)

Number of

cycles



The acid-base properties of the two selected carbonaceous materials: NORIT GAC 12-40 and DACARB PC1000 were subsequently evaluated and compared to those of UNTREATED 4-8 MESH (Table 4). Both activated carbons NORIT GAC 12-40 and DACARB PC 1000 exhibited basic surfaces of pH ranging from 9.2 to 10.1. These values are related to the content of basic functional groups on the surface of the carbonaceous materials which varies from 3.2 to 3.5 mmol g⁻¹. In contrast with NORIT GAC 12-40, DACARB PC1000 also have small amounts of acidic groups which did not seem to have any influence of the pH. Both charcoals NORIT GAC 12-40 and DACARB PC1000 showed a good activity for the reduction of nitrobenzene and these results might be explained by a combination of large surface areas, mesoporous volumes and the basic properties.

entry	material	рН	acidic groups	basic groups	total content of
			(mmol/g)	(mmol/g)	surface oxides
					(mmol/g)
1	NORIT AGC 12-40	9.2	0	3.2	3.2
2	DACARB PC1000	10.1	0.25	3.5	3.75
3	Untreated	8.6	0	2.5	2.5

Table 4. Acid-base properties of the activated carbons obtained

The addition of a base (KOH) and an acid (H_3PO_4) was subsequently attempted in the optimized systems (NORIT GAC 12-40) and conditions to rule out the potential involvement on basic/acid sites in promoting the reaction under subcritical water conditions (Figure 8). As expected no conversion of nitrobenzene was observed in the presence of H₃PO₄. However, aniline yield increases proportionally with the amount of KOH added until an optimum of 80% for 0.5 g KOH, clearly indicating the involvement of basicity in promoting aniline production from nitrobenzene. Additionally, the reduction of nitrobenzene was less efficient when the ratio KOH - NORIT GAC 12-40 was higher than 1:6 (wt/wt). This result pointed out that a mixture of KOH and NORIT GAC 12-40 allowed a yield increase from 66% to 80%. Interestingly, the use of a KOH and NORIT GAC 12-40 mixture (2:12, wt/wt) and (3:18, wt/wt) gave aniline in 89% and 92%, respectively at quantitative conversion, keeping a 1:6 ratio charcoal-base using just larger quantities for the reaction. These results showed clearly that for a mixture of designed carbonaceous material such as KOH and NORIT GAC 12-40 in a ratio 1:6 (wt/wt), the higher the charcoal and KOH loads, the higher the aniline yield. Different bases including NaOH, K₂CO₃, NH₄OH were tested with the optimized conditions but the best result was obtained with KOH. The influence of KOH could be explained by the thermodynamic limitation of the production of hydrogen from water and CO known as Water-

Gas Shift Reaction (WGSR) (Scheme 1). In our process, carbonaceous materials and water generated hydrogen and CO (in the first step), then CO₂ and more hydrogen in a second reaction. The last step never proceeds toward completion therefore hydrogen concentration does not exceed a certain limit. On the other hand, KOH reacted with CO₂ to generate KHCO₃ and shifted the equilibrium towards completion with maximised hydrogen production. In subcritical water (310 °C and 90 bar), the reduction of nitrobenzene into aniline proceeds using metal-free conditions via conventional mechanism after formation of nitrosobenzene, phenylhydroxylamine and aniline, successively.



Figure 8. Effect of KOH and H_3PO_4 on reduction of nitrobenzene to aniline. *aReaction conditions:* nitrobenzene (10 mmol), NORIT GAC 12-40 (6 g), KOH (0.02 – 4 g) or H_3PO_4 (0.5-1 g), water (55 mL), 310 °C, 90 bar, 6 h.

With our optimized reaction conditions in hand, a range of nitroarene derivatives having different electronic and steric demands was evaluated. Conversions are quantitative (> 99%) but only traces of pure aniline could be observed regardless of the ring substituents (F, I, Cl, COOH, NHCOCH₃, CHO, COOCH₃) and their position (ortho, meta and para). No other

product was detected due to efficient degradation (mineralization). The reported successful process is exclusive for nitrobenzene.



Scheme 1. Plausible mechanism on the reduction of nitrobenzene to aniline *via* hydrogen production from water and carbonaceous materials.

CONCLUSIONS

A simple, green protocol has been optimized for the reduction of nitrobenzene to aniline under subcritical water conditions. The proposed methodology features a metal-free process without added hydrogen in presence of commercial basic carbonaceous materials. Two high yielding conditions could be obtained affording the target aniline in quantitative yields: the first one in presence of NORIT GAC 12-40 having a better volumetric productivity as compared to a second one in presence of DACARB PC1000. A basic treatment of NORIT GAC 12-40 with KOH allowed a reduction in the amount of carbonaceous material (6 g vs 40 g) as well as a slight increase aniline yields (80% vs 66%). The scope of the proposed environmentally friendly reduction of nitrobenzene will be subsequently translated to

 different nitroarene derivatives in batch reactors as well as in continuous flow, to be reported in due course.

EXPERIMENTAL SECTION

Materials. Substrates and solvents were purchased from Acros (Nitrobenzene \geq 99%, aniline 99%, xylan from p-Xylene \geq 90%, methanol, ethanol, propan-1-ol, acetone, butan-1-ol, and propan-2-ol). All materials were used without further purification. The water used in all experiments had a Millipore Milli-Q grade. Charcoals were purchased from Acros (NORIT GAC 12-40, NORIT SA2, NORIT A SUPRA, NORIT CN1), DACARB (DACARB PC1000, DACARB PBC1), Carbot (MONARCH 1300, ELFTEX125), Chemviro BPL4X10, CECA (NC35 1.25-3.15, AC40 3mm), Sigma-Aldrich (UNTRETED 4-8 MESH, DARCO 12.20, NORIT TPK 1-3).

Materials characterization. Elemental analysis was performed using a model kratos Axis Ultra DLD.

SEM (Scanning Electron Microscopy)-EDX (Energy Dispersive X-ray Diffraction) analysis of charcoal was performed on a Quanta FEG 250 (FEI) equipped with a microanalysis detector for EDX (Brucker). SEM micrographs acquired in secondary electron mode were obtained at low vacuum, 15 kV of accelerating voltage with a 10 mm working distance. EDX spectra were collected at 30° angle, 15 kV accelerating voltage and 10 mm working distance.

Surface area and pore size of samples were measured using Micromeritics Surface Analyzer ASAP 2010 surface area analyzer by nitrogen adsorption-desorption method. The samples were degassed at 350 $^{\circ}$ C for 6 h before adsorption isotherm were generated by N₂ at - 196 °C. The surface area (S_{BET}) was calculated with the BET equation, the total pore volume (V_T) was obtained from the adsorption isotherm at P/P₀ =0.95 %. the micropore area (S_{mic}) and volume (V_{mic}) were obtained using the t-plot method. The average pore size (r) was estimated by the following equation:

 $r=4 V_T / S_{BET}$

XPS measurements were performed in an ultrahigh vacuum (UHV) multipurpose surface analysis system (SpecsTM model, Germany) operating at pressures of $<10^{-10}$ mbar using a conventional X-ray source (XR-50, Specs, Mg K, 1253.6 eV) in a "stop-and-go" mode to reduce potential damage due to sample irradiation. The survey and detailed Fe and Cu highresolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyzer. Powdered samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum ($<10^{-6}$ Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. Survey spectra were first recorded, after which detailed element XPS (typically C, O, and S) were recorded. Data were processed using the program Casa XPS.

General procedure for the synthesis of aniline in subcritical water. In a typical experiment, a batch reactor (100 mL) charged with water (55 mL), nitrobenzene (1.23 g, 10 mmol), charcoal (6 - 40 g). Autoclave was sealed, placed in the heating collar and heated to the desired temperature for the desired time. Temperature in the autoclave was measured by probe. At the end of the reaction, autoclave was cooled down to 40°C. The aqueous phase was diluted with ethyl acetate (100 mL) under magnetic stirring (500 rpm). The organic phase was filtered prior to analysis through a syringe filter (PTFE, 0.45 μ m, VWR). All experiments were repeated at least three times, and the deviation was lower than 5%.

Regeneration of DACARB PC1000. After completion of the reaction DACARB PC1000 was separated from the products by filtration and immersed in absolute methanol for 90 minutes. The carbonaceous material was then dried at 110 °C for 12 hours. Then the activated charcoal was used again, and the cycle was repeated five times and the yield calculated each time.

Product analysis. Each sample of the reaction mixture was analyzed separately by means of a GC with a FID detector. The mobile phase was N_2 . The column oven was set at 40 °C. Nitrobenzene conversion (X) (eq 1) and aniline yield (Yi) (eq 2) were calculated using standard equations.

$$X = \frac{(\text{Initial nitrobenzene amount (mol)} - \text{Final aniline amount (mol)})}{\text{Initial nitrobenzene amount (mol)}} \times 100$$
(1)

$$Yi = \frac{Final aniline amount (mol)}{Initial nitrobenzene amount (mol)} x 100$$
(2)

ASSOCIATED CONTENT

Supported Information

Morphology and surface properties of carbonaceous material NORIT GAC 12-40, DACARB PC 1000, UNTREATED, SEM; elemental composition of carbonaceous material NORIT GAC 12-40, DACARB PC 1000, UNTREATED, EDX; determination of material surface atoms and elemental analysis, XPS; surface area and pore size of charcoal, nitrogen adsorption-desorption method. The experimental conditions to evaluate the surface oxygen atom and surface pH of charcoal are provide.

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Notes

The authors declare no competing financial interest.

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