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FULL PAPER

Sustainable protocol for the reduction of nitroarenes by heterogeneous Au@SBA-15 using $NaBH_4$ under flow conditions

Francesco Ferlin,[a] Tommaso Giannoni,[a] Alessio Zuliani,[b] Oriana Piermatti,[a] Rafael Luque,[b, c] and Luigi Vaccaro*[a]

Dedication ((optional))

Abstract: Gold-incorporated SBA-15 catalyst was prepared by a solvent-free ball milling approach. The catalyst showed high reactivity and selectivity in the reduction of a variety of nitroarenes to anilines operating in absolute EtOH using $NaBH_4$ as reducing agent. The catalyst was reused in batch conditions over 5 consecutive runs without detecting any losses of activity and selectivity. Considering the high chemical stability and reusability of the catalytic system, a continuous flow protocol was also investigated and defined in order to minimize the production of waste associated to the process and optimize the continuous reuse of the catalyst. Benefits of flow conditions were proven by TON values that increased from 47.5 to 1902 and also by the minimization of both leaching (9.5 vs 1 ppm) and E-factor values (8 vs 23 in batch).

Introduction

Gold nanoparticles (AuNPs) stabilized by inorganic supports are of great interest in sustainable catalysis. A careful choice of the support plays a pivotal role when designing supported AuNPs catalysts in order to avoid NPs leaching and preventing their aggregation or coalescence which generally leads to a significant decrease in catalytic efficiency [1,2].

During the last years, different mesoporous materials have been employed as supports for the stabilization of gold nanoparticles. Among such materials, mesoporous silica arose due to the abundance of Si-OH bonds on the surface, which can stabilize gold nanoparticles [3,4].

In the development of mesoporous silica, considerable effort has been made to produce ordered mesoporous silica structures (OMSs), which not only possess all the properties of mesoporous compounds, but also high physico-chemical stability, long-range homogeneity of texture and modifiable surface chemistry via post-functionalization [5,6].

In 1997, Stucky et al. synthesized, for the first time, a well-ordered hexagonal mesoporous silica structure with uniform pore sizes, denoted Santa Barbara Amorphous-15 (SBA-15). With its unique properties that include large surface areas (up to 1000 m^2/g), tunable pore sizes (in range 4–30 nm), controllable thick walls and high thermal and mechanical stability, the SBA-15 quickly emerged as an outstanding material opening a plethora of possibilities for its use as support for both organic and inorganic specie [7,8].

In the literature, different reports describe the modification of the siliceous mesoporous surface by incorporating metal species such as Au, Ag, Pt, Pd either through physical or chemical adsorption [9,10]. Between all, a great amount of research has been dedicated for the synthesis of gold-incorporated SBA-15 nanocomposites as Au exhibits exceptional optical, electrical and catalytic properties in comparison to bulk metals. In fact, AuNPs are quite used in a large variety of catalyzed reactions, including oxidations, hydrogenations and related processes [11].

In the present work, we focused our study on the reduction of nitroaromatics, which is a representatively relevant process in the fine chemical industry. Indeed, the reduction of nitroaromatics into aniline is widely used to produce intermediates useful for the synthesis of several commercial chemicals such as nitrogen-contain biologically active compounds, dyes, agrochemicals and pharmaceuticals [12].

According to the literature, a large number of procedures have been developed for the reduction of nitroaromatics compounds [13] and in this realm, immobilized gold nanoparticles have played their role as catalyst for the selective reduction of nitroarenes to anilines by using $NaBH_4$ [14], silane [14a, 15], or formic acid [16] as reducing agents. However, the development of a protocol for a sustainable preparation of aromatic amines featuring, for example, minimal waste production, durability of the catalyst with minimal metal leached into the product, easy work-up and simplicity of scale-up and continuous flow operation, is still a challenge.

Herein, we report the results obtained in the reduction of different nitroarenes catalyzed by our gold-incorporated SBA-15 (Au@SBA-15) catalysts. Highlights of this work include several points. Firstly, the catalytic system was prepared using a solvent-free ball milling technique, which is a very efficient waste-minimized green procedure. In addition, the reutilization of Au@SBA-15 catalyst was investigated in batch as well as under continuous flow conditions while the quantification of the leaching of the metal particles from the support was determined by ICP analyses. Finally, all the synthetic protocols were designed aiming to minimize the waste and employing only desirable green solvents.

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Results and Discussion

Catalysts Preparation and Characterization.

SBA-15 and Al-SBA-15 were synthesized according to a synthetic methodology reported in a previous work [17]. SBA-15 was synthesized dissolving 20 g of Pluronic P123 surfactant in 750 mL of 2 M HCl solution under vigorous stirring at r.t.. After complete dissolution (1h), 45 mL of tetraethyl orthosilicate (TEOS) were added drop-by-drop. The mixture was stirred at 35°C for 24 h, and hydrothermally treated for 24 h in a 100°C oven. The precipitated white solid was separated from the solution by filtration and dried at room-temperature overnight. The template was removed by calcination at 600 °C for 8 h. Similarly, Al-SBA-15 was prepared dissolving 20 g of Pluronic P123 in 750 mL of a 1.5 pH solution of distilled water and HCl under vigorous stirring at r.t.. After complete dissolution (1h), 2.10 g of Aluminium isopropoxyde were slowly added. Finally, 45mL of tetraethyl orthosilicate (TEOS) were added drop-by-drop. The sequential treatments were the same as those for SBA-15.

To synthesize 2%Au@SBA-15 and 2%Au@Al-SBA-15, 275 mg of $AuBr_3$ were added to 6 g of SBA-15 or to 6 g of Al-SBA-15 in a 125 mL ball milling container equipped with eighteen 5 mm diameter stainless steel balls and then ground in a Retsch PM-100 planetary ball mill (350 rpm, 10 min). The calcination was performed at 450 °C for 4 h in a furnace under synthetic air flux.

The resulting materials were characterized by XRD and nitrogen adsorption/desorption. The XRD patterns of the samples are shown in Figure 1. The peaks at 38.16°, 44.31°, 64.51° and 77.44° can be respectively indexed to the (111), (200), (220) and (311) diffraction planes, from a face-centered cubic structure (Fm-3m) of Gold (JCPDS 00-004-0784) (Please see Figure S1 for the low-angle XRD of the samples).

The mean diameter of the supported samples have been also calculated with Scherrer's formula of $d=k\lambda/\beta 1/2\cos\theta$, where k is a constant (0.89) d is the mean diameter of Au nanoparticles, $\beta 1/2$ is the full-width at half-maximum of the peak at 2θ and λ is the wavelength of CuKα1 radiation (1.5418 Å). The calculated diameters were found to be 29.9 nm for gold nanoparticles of samples Au@SBA-15 and 35.14 nm for sample Au@AlSBA-15, in good accordance with TEM analysis (please see Figure 2).

The surface properties of the material were investigated by N_2 physisorption. The isotherm of 2% Au@SBA-15 showed hysteresis loop between (0.6–0.7) P/P_0 which indicated the characteristic mesoporosity of the sample with the bottle neck geometry (Type IV isotherm) [17]. The BET surface area and pore volume of 2%Au@SBA-15 were 317 m^2/g and 0.0034 cm^3/g, with 6.5 nm mean pore diameter. BET surface area of SBA-15 was 629 m^2/g, with pore volume of ca. 0.012 cm^3/g and a mean pore diameter of 6.5 nm. The obtained values indicated that the structure of SBA-15 was partially destroyed during ball milling, while the mean pore indicated that the gold was mostly supported on the walls of the SBA-15 (Please see Figure S2 for the isotherms). The Au particles size distribution, obtained by analyzing at least 40 nanoparticles, was 19.8(± 7.4) nm.

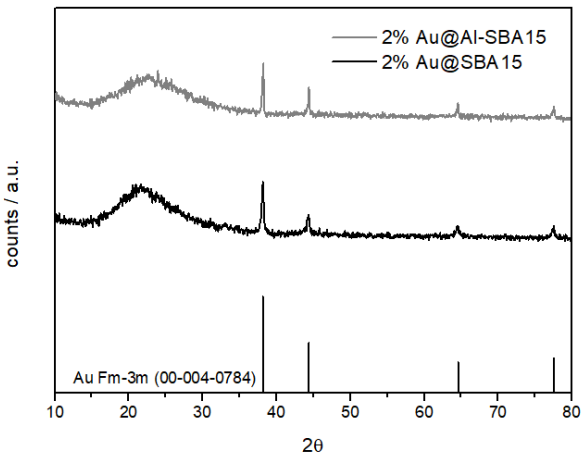


Figure 1. XRD pattern of 2%Au@SBA-15 and 2%Au@Al-SBA-15

Figure 2 shows TEM images of 2%Au@SBA-15 at two different magnifications, where the support consisted of roads with irregular size decorated with AuNPs exhibiting an almost spherical morphology.

Catalytic Activity

We started our study by testing the catalytic activity of 2%Au@Al-SBA-15 and 2%Au@SBA-15 in the reduction of 4-nitroanisole (**1a**) in EtOH 96% or EtOH absolute, at room temperature, for the selective preparation of the 4-metoxyaniline (**2a**). The reactions were performed on 0.1 mmol of 4-nitroanisole **1a**, in a 2 mL closed vials filled-up with the reaction medium (1.8 mL). When the reaction was performed in EtOH 96% in the presence of 1 mol% of Au@Al-SBA15 and 6 eq of $NaBH_4$, the conversion was very low (10%) and the azoxy derivative **4a** was obtained as prevalent but not exclusively (Table 1, entry 1). Higher conversions were observed in presence of Au@SBA-15 and $NaBH_4$ as reducing agent but the selectivity was still low (Table 1, entry 2 and 3). By using TMDS as reducing agent, only the starting material was recovered (Table 1, entry 4 and 5). In presence of TBABH as reducing agent, we observed a very low selectivity (Table 1, entry 6). When EtOH absolute were used as reaction medium the catalyst was more efficient (Table 1, entry 7 and 8).

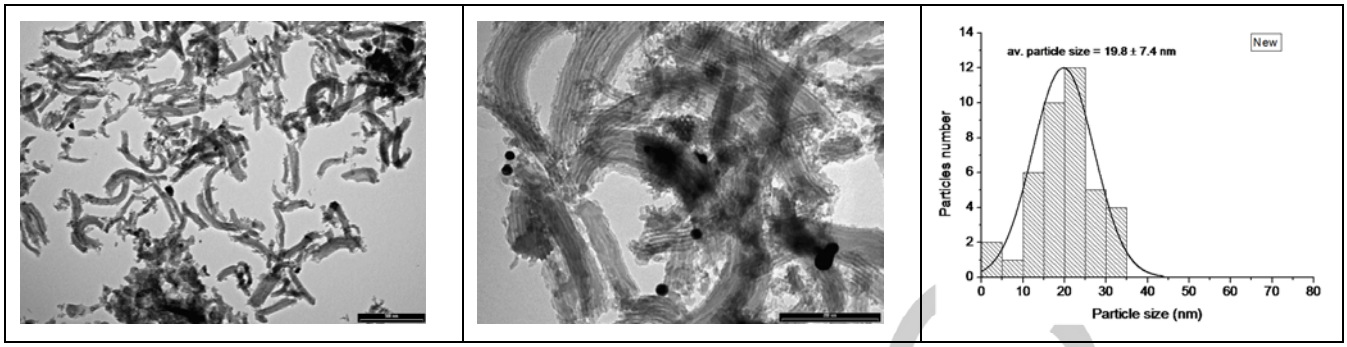
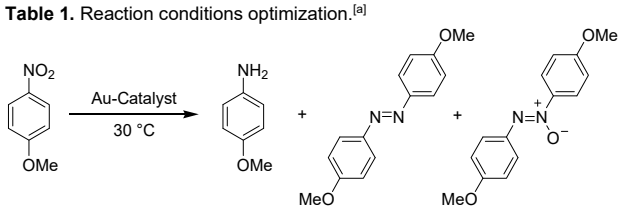


Figure 2. Representative TEM images at different magnifications of 2%Au@SBA15.

Table 1. Reaction conditions optimization.[a]



1a **2a** **3a** **4a**

Entry	Au-Catalyst (mol%)	H-source (equiv.)	Medium	t (h)	C[b] (%)	**2a:3a:4a** ratio[b]
1	Au@Al-SBA15 (1)	$NaBH_4$ (6)	EtOH 96%	6	10	13:0:87
2	Au@SBA15 (1)	$NaBH_4$ (6)	EtOH 96%	6	75	20:5:75
3	Au@SBA15 (2)	$NaBH_4$ (6)	EtOH 96%	6	95	24:2:74
4	Au@Al-SBA15 (1)	TMDS (2.5)	EtOH 96%	1	0	-
5	Au@SBA15 (1)	TMDS (2.5)	EtOH 96%	1	0	-
6	Au@SBA15 (1)	TBABH (6)	EtOH 96%	3	49	21:43:36
7	Au@SBA15 (1)	$NaBH_4$ (6)	EtOH abs	6	>99	94:5:1
8	Au@SBA15 (2)	$NaBH_4$ (6)	EtOH abs	2	>99	100:0:0
9	No Catalyst	$NaBH_4$ (6)	EtOH abs	2	4	0:0:100

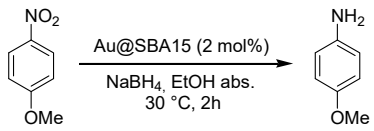
[a] Reaction condition: **1a** (0.1 mmol), Au-Catalyst (1 or 2 mol%), reducing agent, reaction medium (1.8 ml), at 30 °C for 1-6 h. [b] Determined by GLC and ^{1}H-NMR analysis.

When the reaction was performed in presence of 1 mol% of 2%Au@SBA-15, a complete conversion with a good selectivity to aniline (**2a**) was obtained after 6h (Table 1, entry 7). Increasing the amount of 2%Au@SBA-15 up to 2 mol%, 100% of 4-metoxyaniline (**2a**) was obtained after 2h (Table 1, Entry 8). Control experiment (Table 1, Entry 9) was performed in order to demonstrate that using our reaction conditions, the reaction does not satisfactorily proceed in the absence of the catalyst. After checking the optimal conditions for its use, we have immediately investigated the recovery and the reuse of Au@SBA-15 for the reduction of 4-nitroanisole (**1a**) performed in EtOH abs (Table 2). After each reuse, the catalyst was separated by centrifugation, washed with additional EtOH abs to fully recover the product, dried at 180 °C for 20 h and reused in the next run.

The catalyst was used representatively for five consecutive times without any loss of activity and selectivity (Table 2). Moreover, ICP-OES analyses showed that, after each cycle, the amount of gold released into the reaction medium was steadily low at values of ca. 5-10 ppm, about 0.3% referred to the initial Au content in the catalyst (Table 2).

The TEM images of the recovered catalyst after five runs shown in Figure S3 indicate that the AuNPS still had a spherical morphology with good monodispersity but the particle size range increased from 19.8 (± 7.4) to 28.6 (± 12) nm.

Table 2. Recovery and reuse of Au@SBA15 catalyst in the preparation 4-metoxyaniline **2a**.



1a **2a**

Entry[a]	Run	C (%)[b]	**2a:3a:4a** ratio[b]	Au leaching (ppm)[c]
1	Run 1	>99	100:0:0	10.3
2	Run 2	>99	100:0:0	9.3
3	Run 3	>99	100:0:0	9.5
4	Run 4	>99	100:0:0	4.7
5	Run 5	>99	100:0:0	5.9

[a] Reaction condition: **1a** (0.1 mmol), Au@SBA15 (2 mol%), $NaBH_4$ (6 eq), reaction medium (1.8 ml), at 30°C. [b] Determined by GLC. [c] Au leaching in solution reported in ppm per mmol of **2a** produced.

Operating in batch conditions, the crude product was obtained after the usual work-up procedure summarized as centrifugation to separate the solid catalyst, distillation of EtOH, extraction with ethyl acetate/H_2O to eliminate the inorganic reagents and distillation of the solvent under reduced pressure. Sequentially,

we have investigated the possibility of replacing the aqueous work-up by simply washing the residue obtained after centrifugation with the aim of minimizing the metal leaching (increase catalyst durability) and the waste associated to the process.

The best result were obtained by using cyclopentyl methyl ether (CPME) allowing to obtain **2a** with only 0.04 % of Au lost from the initial fresh catalyst (see Table S1).

The best protocol for the preparation of aniline **2a** under batch conditions, consisted in the use of CPME as solvent for the recovery of the product. Typically, in a vial of 10 mL, 2%Au@SBA-15 catalyst (100 mg, 2 mol %), 4-nitroanisole 1a (76.5 mg, 0.5 mmol), $NaBH_4$ (114 mg, 6 eq), and EtOH abs. (9 mL) were placed. The reaction mixture was stirred at 30 °C for 2 h. After completion of the reaction, the ethanol crude product solution was separated from the solid catalyst by centrifugation and the catalyst washed with EtOH (2 x 2 mL). The ethanol was removed and recovered by distillation (90% of solvent recovered) and the product was separated simple by washing the residue with cyclopenthyl methyl ether (3 x 3 mL) to eliminate the insoluble borate derived from $NaBH_4$. The solvent was evaporated by distillation (95% of solvent recovered) obtaining the pure product (yield of **2a** 95%) without any further purification step. The solid catalyst was dried at 180 °C for 20 h and reused in a successive cycle.

By measuring the waste associate to these procedures we could reduce the E-factor values from ca. 314, without recovery of reaction medium, to ca. 23 in this optimized protocol using CPME (Please see Experimental Section).

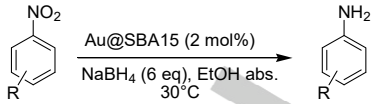
To evaluate the applicability of the chemoselective reduction procedure, a series of nitroarenes **1a-m** were examined under the best conditions obtained for the preparation of 4-metoxyaniline **2a** (Table 1, Entry 8).

A series of anilines **2a-m** have been prepared in high yields and selectivities performing the reaction in EtOH abs as reaction medium, with 2 mol% of 2%Au@SBA-15 in the presence of 6 eq of $NaBH_4$ (Table 3). After completion of the reaction, the solid catalyst was separated by centrifugation, the ethanol was removed via distillation and the product separated simple by washing the residue with cyclopentyl methyl ether.

The solvent was evaporated by distillation obtaining the pure product **2** (yield 90-96%) without any further purification step. In the case of 3-nitroacetophenone (**1l**) and 4-nitrobenzaldehyde (**1n**) the corresponding hydroxyl aniline **2j** and **2n** deriving from the reduction of the carbonyl group were observed (Table 4, entry 10 and 12).

The stability and durability of the heterogeneous catalyst in batch conditions over consecutive runs (Table 2), allowed us to further explore the possibility of optimizing and scaling-up the process in flow conditions. The reaction was performed in a stainless steel packed bed reactor charged with 50 mg of 2%Au@SBA-15 catalyst. A slight adjustment of the flow conditions was necessary to achieve full conversion of the starting materials in a reasonable time (Table 5).

Table 4. Preparation of anilines **2**.



1 **2**

Entry[a]	R	t (h)	C (%)[b]	Yield (%)[c]
1	**a**: 4-OMe	2	>99	95
2	**b**: H	4	>99	92
3	**c**: 4-Cl	3	>99	93
4	**d**: 4-Br	3	>99	94
5	**e**: 4-I	6	>99	90
6	**f**: 4-Me	15	>99	96
7	**g**: 3-Me	3	>99	95
8	**h**: 2-Me	6	>99	94
9	**i**: 3-CH_2=CH_2	6	>99	96
10	**j**: 3-COMe	4	>99	93
11	**k**: 4-CO_2Me	4	>99	95
12	**l**: 4-CHO	3	>99	94
13	**m**: 6-nitroquinoline	5	99	92

[a] Reaction condition: **1** (0.1 mmol), Au@SBA15 (2 mol%), $NaBH_4$ (6 eq), reaction medium: EtOH absolute (1.8 mL), at 30 °C. [b] Determined by glc analysis. [c] Yield of isolated products **2**..

Table 5. Optimization of the flow in the preparation of 4-metoxyaniline **2a** with Au@SBA15 as catalyst.

Entry[a]	$NaBH_4$ (eq)	**Flow rate** (mL·min-1)	C (%)[b]
1	6	0.5	90
2	6	0.1	>99
3	3	0.1	>99
4	2	0.1	95

[a] Reaction condition: **1a** (1 mmol), Au@SBA15 (2 mol%), EtOH (4 mL), at 30°C. [b] Determined by GLC.

The use of continuous flow technology allowed also to investigate further the possibility of decreasing the amount of $NaBH_4$ needed to perform the catalytic reduction of nitroarenes maintaining excellent yields (Table 5, Entry 3). With optimized flow conditions in hand we achieved the complete conversion of 10 mmol for the representative substrates *p*-nitroanisole (**1a**). This resulted in a

TON value of 1902 associated to the catalityc system. The comparison with the TON in batch conditions (47.5) strongly supports the improvements that comes from the development of a continuous flow protocol, leading us to a significant waste minimization (Please see Experimental section) associated to the process as well as an increased efficiency of the catalytic system (Figure 3).

Figure 3. Continuous flow features for the preparation of 4-metoxyaniline **2a** with Au@SBA15 as catalyst.

To evaluate the durability of the catalytic system under flow conditions regime, aliquots of reaction mixture were measured periodically. It is worth-noting that the amount of leached gold species was constantly low, with an average value of ca. 1 ppm (Figure 4) that was consistent with a 0.4 % of gold loss per millimol of **2a** produced. This result is very valuable, since it means that the purification of the product from metal residues was easier and the catalyst was very stable when packed in the flow reactor.

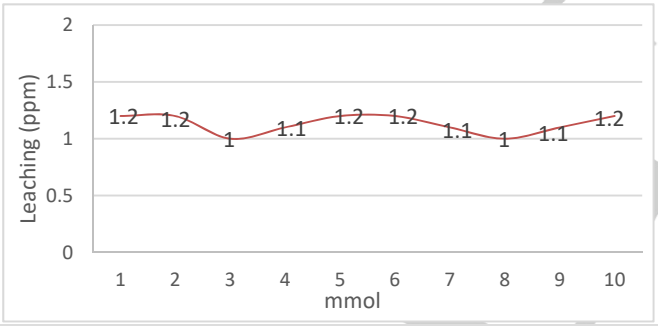


Figure 4. Gold leaching for the preparation of 4-metoxyaniline **2a** with Au@SBA15 as catalyst in continuous flow.

The TEM images shown in Figure 4 also indicate that the AuNPS still had a spherical morphology with good monodispersity but the particle size range increased from 19.8 (± 7.4) to 31 (± 9) nm. This vast increase in particle size exceeded a critical value, thus diminishing the catalytic activity of the nanoparticles over time.

Conclusions

In conclusion, we have developed an efficient and waste minimized protocol for the gold-catalyzed reduction of nitroarenes in batch and in continuous flow regime. The gold-based catalyst showed overall high stability due the mechanochemical protocol utilized for the synthesis. The flow procedure has demonstrated to be efficient in increasing the recyclability of the entire catalytic system, allowing, at the same time, a higher TON value, compared to batch condition, and a reduced E-factor. Continuous flow condition has demonstrated to be helpful in establish a constant productivity of aniline derivatives with excellent yield and very low metal contamination.

Experimental Section

Powder X-ray diffraction (XRD) patterns were recorded using a Bruker D8 DISCOVER A25 diffractometer (PanAnalytic/Philips, Lelyweg, Almelo, The Netherlands) using CuKa (λ=1.5418Å) radiation. The patterns were collected over a 2θ range from 0.5° to 5° (Low-angle) or from 10° to 80° (wide angle) with a step size of 0.018° and counting time of 5 s per step. Textural properties of the samples were determined by N2 physisorption using a Micromeritics ASAP 2020 automated system (Micromeritics Instrument Corporation, Norcross, GA, USA) with the Brunauer-Emmet-Teller (BET) and the Barret-Joyner-Halenda (BJH) methods. The samples were outgassed for 24 h at 130 °C under vacuum (P0 = 10−2 Pa) and subsequently analysed.

Au analyses were performed on an ICP Varian Liberty inductively-coupled plasma-optical emission spectrometry (ICP-OES) with axial injection.

Transmission electron microscopy (TEM) analysis was carried out by a Philips 208 transmission electron microscope, operating at an accelerating voltage of 100 kV. Powders were rapidly diluted in water, then supported on copper grids (200 mesh) precoated with Formvar carbon films and quickly dried.

^{1}H-NMR, ^{13}C-NMR spectra were recorded at 400 MHz and 100.6 MHz, respectively, on a Bruker DRX-ADVANCE 400 MHz.

GLC analyses were performed by using the Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm), an FID detector and hydrogen as the gas carrier. Gas Chromatography with Electron Impact Mass Spectrometry (GC-EIMS) analyses were carried out by using a Hewlett-Packard HP 6890N Network GC system/5975 Mass Selective Detector equipped with an electron impact ionizer at 70 eV.

General procedure for catalytic reduction of nitroarenes

In a vial of 2 mL, 2%Au@SBA15 catalyst (20 mg, 2 mol%), nitroarene (**1**, 0.1 mmol), $NaBH_4$ (22.8 mg, 6 eq) and EtOH abs. (1.8 mL) were placed. The reaction mixture was stirred at 30 °C for a selected time (Table 4); the conversion of nitroarenes was monitored by GLC analyses. After completion, the solid catalyst was separated by centrifugation and then washed with EtOH (2 x 1 mL), dried at 180 °C for 20 h and reused in a successive cycle. The ethanol solution, that contained the products and the borate derived from $NaBH_4$, was distilled at reduced pressure, the residue was diluted with ethyl acetate (5 mL) and washed with water (2 x

2 mL). The organic layers were dried with sodium sulfate and evaporated under reduced pressure.

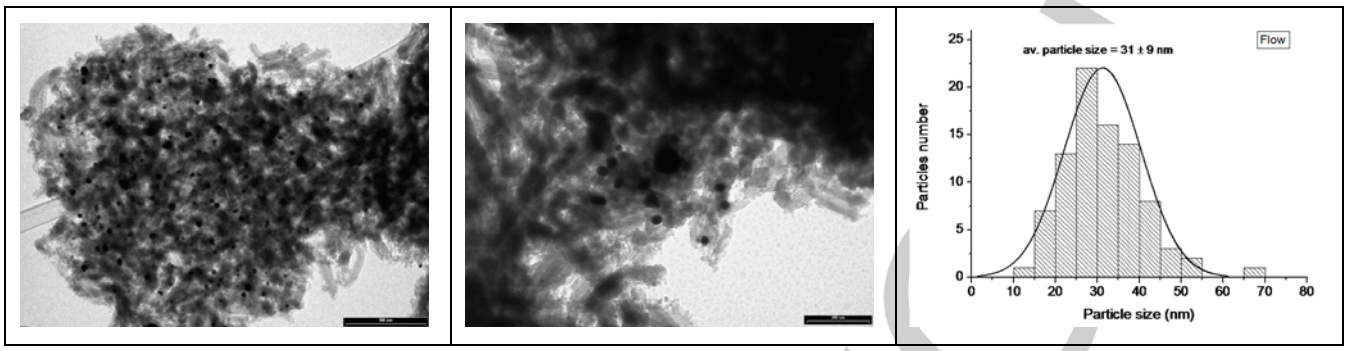


Figure 4. Representative TEM images at different magnifications of Au@SBA15 after seven runs in EtOH abs. under flow conditions.

Typical procedure for a sustainable protocol for the preparation of 2a under batch conditions

In a vial of 10 mL, 2%Au@SBA15 catalyst (100 mg, 2 mol %), 4-nitroanisole **1a** (76.5 mg, 0.5 mmol), $NaBH_4$ (114 mg, 6 eq), and EtOH abs. (9 mL) were placed. The reaction mixture was stirred at 30 °C for 2 h. After completion, the solid catalyst was separated by centrifugation and then washed with EtOH (2 x 2 mL), dried at 180 °C for 20 h and reused in a successive cycle. After removal and recovery of the solvent via distillation (90% of solvent recovered) the product was separated simple by washing the residue with cyclopenthyl methyl ether (3 x 3 mL). The solvent was evaporated by distillation (95% of solvent recovered) obtaining the pure product (yield of **2a** 95%).

E-factor calculation for product **2a** (yield 95%): E-factor = [0.0765 g (4-nitroanisolo, **1a**) + 0.114 g ($NaBH_4$) + 0.100 g (Au@SBA15) + 10.4 g (EtOH) + 7.7 g (CPME) – 0.058 g (4-methoxyaniline, 2**a**) – 0.095 g (recovered Au@SBA15) – 9.5 g (recovered EtOH) – 7.4 g (recovered CPME)] / 0.058 g (4-methoxyaniline, **2a**) = 23.1.

Without recover of reaction medium the E-factor value was 314.4.

Typical procedure for a sustainable protocol for the preparation of 2a under flow conditions

A premixed mixture of **1a** (1.53 g, 10 mmol), $NaBH_4$ (1.13 g, 3 eq) and and EtOH abs. (40 mL)) was charged into a glass column functioning as a reservoir. The equipment was connected, by using the appropriate valves, to a pump and installed into a box thermostated at 30 °C. The reaction mixture was continuously pumped (flow rate: 0.1 mL · min-1; residence time: 50 min) through the catalyst column (15 cm, stainless steel HPLC column) equipped with a 120 psi back pressure regulator, and the reaction was monitored by GC. Product was collected in fractions and gold content in the EtOH solution was periodically measured by MP-AES analysis. After completion 40 mL of EtOH was used to wash the catalyst inside the reactor. After removal and recovery of the solvent via distillation (90% of solvent recovered) the product was separated simple by washing the residue with cyclopenthyl methyl ether (3 x 20 mL). The solvent was evaporated by distillation (95% of solvent recovered) obtaining the pure product (yield of **2a** 97%).

E-factor calculation for product **2a** (yield 97%): E-factor = [1.53 g (4-nitroanisole, **1a**) + 1.13 g ($NaBH_4$) + 64 g (EtOH) + 52 g (CPME) – 1.19 g (4-methoxyaniline, 2**a**) – 58 g (recovered EtOH)] – 50 g (recovered CPME)] / 1.19 g (4-methoxyaniline, **2a**) = 7.96.

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Keywords: Heterogeneous catalysis • SBA-15 • Reduction of nitroarenes • gold NP • flow conditions

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