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Polymer Supported Nickel Nanoparticles as Recyclable Catalyst for the Reduction of Nitroarenes to Anilines in Water

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Abstract

Polymer supported nickel nanoparticles, generated by calcination (N_2 to 300 °C, 30 min) of a Ni(II) containing polyacrylamide, catalyzed the hydrogenation of nitroarenes to anilines in water at room temperature in the presence of $NaBH_4$. The protocol generally favored the formation of the desired aniline as single product in high yields with short reaction times and proved to be highly selective in the hydrogenation of halonitrobenzene to haloaniline. The catalyst displayed excellent recyclability over fifth cycles and no leaching of metal into solution occurred, which made the overall system eco-friendly and economic. STEM analyses revealed that the thermally formed Ni nanoparticles turned into cubic nanotwins under reaction conditions, which remained almost unchanged with the re-cycles.

Keywords: Nickel Nanoparticles; Polymer Supported Catalyst; Nitrobenzene Reduction; Water Solvent; Selectivity Towards haloaniline

1. Introduction

The last few years have witnessed an explosion in the use of new nanomaterials for catalytic application [1]. In this field, noble metal nanoparticles (NPs) have been widely employed in catalysis [2] and several studies have been devoted to the recyclability of these expensive materials [3]. Nevertheless, the high cost of noble metals has limited their practical use. The conservation of the elemental resources of our planet is a global task, and the substitution of noble metals for abundantly available transition metals is an appealing noble-metal conservation strategy [4]. In this context, recently, due to their low cost, Ni catalysts have been employed in several organic reactions (mainly hydrogenations) [5].

The hydrogenation of nitroarenes to give the corresponding aromatic amines is a basic chemical reaction used both for removing toxic nitro aromatics from aqueous medium and for synthetizing anilines. In fact, aromatic amines are important bulk chemicals and intermediates to produce fine chemicals, pharmaceuticals, polymers, herbicides, and more [6]. The industrial hydrogenation of nitrobenzene for the synthesis of aniline uses copper, palladium or palladium-platinum supported on carbon or inorganic oxides, as catalysts, under high pressure (up to 3 MPa) and high temperature (up to 300 °C). In addition, the undesirable formation of harmful azo- and azoxyderivatives, which lowers the yield into anilines, is a drawback of the current industrial protocols. Aiming at overcoming the above reported weaknesses, the scientific community tried to develop alternative protocols for the reduction of aromatic nitro compounds [7,8,9,10,11,12,13], including the use of H_2 at various pressures in the presence of different catalysts [14], such as Pt/C [15], Rh_3Ni_1 [16], Pd/C [17,18,19], Pd [20,21] and Rh [22] nanoparticles, and the use of reducing agents other than molecular hydrogen [23,24], such as hydrazine [25,26,27,28,29,30], silanes [31,32] and sodium borohydride

[33,34,35,36,37,38,39] in the presence of Cu [40], Pd [41], palladium/graphene [42], Au [43,44], Ru [45], Ag [46], and, more recently, Co [47] and Ni [48] catalysts.

Nevertheless, the major problems remain still unsolved and designing new systems with different chemical and physical compositions and morphologies for catalytic reduction of nitroarenes under sustainable conditions is an urgent topic of current research.

In the search for innovative catalytic processes that enable chemical transformations under mild, cheap and sustainable conditions with high efficiency, we prepared an acryl amidic polymer supported nickel catalyst (in the following *Ni-pol*) and we evaluated its catalytic activity in the hydrogenation of nitroarenes in water. The real active species were Ni nanoparticles with a peculiar nanostructure stabilized by the insoluble support, which were active, selective and recyclable in the reduction of various nitro arenes into anilines in water in the presence of sodium borohydride, a well-known reducing agent with wide applications in organic synthesis for its ready availability, ease of handling, and low cost [49].

2. Experimental Section

2.1 General considerations

Tap water was de-ionized by ionic exchange resins (Millipore) before use. All other chemicals were purchased from commercial sources and used as received. Nickel content in *Ni-pol* was assessed after sample mineralization by atomic absorption spectrometry using a Perkin–Elmer 3110 instrument. The experimental error on the nickel percentage was ± 0.3. Mineralization of N*i-pol* prior to Ni analyses was carried by microwave irradiation with an ETHOS E-TOUCH Milestone applicator, after addition of HCl/HNO_3 (3:1 v/v) solution (12 mL) to each weighted sample. Microwave irradiation up to 1000 W was used, the temperature being ramped from rt to 220 °C in 10 min and the sample being held at this temperature for 10 min. After cooling to room temperature, the digested *Ni-pol* was diluted to

1000 mL before submitting to Graphite Furnace Atomic Absorption Spectrometric nickel determination.

GC-MS data (EI, 70 eV) were acquired on a HP 6890 instrument using a HP-5MS cross-linked 5% PH ME siloxane (30.0 m × 0.25 mm × 0.25 μm) capillary column coupled with a mass spectrometer HP 5973. The products were identified by comparison of their GC-MS features with those of authentic samples. Reactions were monitored by GLC or by GC-MS analyses. GLC analysis of the products was performed using a HP 6890 instrument equipped with a FID detector and a HP-1 (Crosslinked Methyl Siloxane) capillary column (60.0 m x 0.25 mm x 1.0 μm). Conversions and yields were calculated by GLC analysis by using biphenyl as internal standard, or by column chromatography using silica gel and *n*-hexane/ethyl acetate as the eluent.

FT-IR spectra (in KBr pellets) were recorded on a Jasco FT/IR 4200 spectrophotometer. Elemental analyses were obtained on a EuroVector CHNS EA3000 elemental analyser using acetanilide as analytical standard material. The high-resolution mass spectrometry (HRMS) analysis was performed using a Bruker microTOF Q II mass spectrometer equipped with an electrospray ion source operated in positive ion mode. The sample solutions (CH_3OH) were introduced by continuous infusion with a syringe pump at a flow rate of 180 μL min−1. The instrument was operated with end-plate offset and capillary voltages set to −500 V and −4500 V respectively. The nebulizer pressure was 0.4 bar (N_2), and the drying gas (N_2) flow rate was 4.0 L min^{-1}. Capillary exit and skimmer voltages were 90 V and 30 V, respectively. The drying gas temperature was set at 180°C. The calibration was carried out with a sodium formate solution (10 mM NaOH in isopropanol/water 1:1 (+0.2% HCOOH)) and the software used for the simulations was Bruker Daltonics DataAnalysis (version 4.0). Thermogravimetric analyses (TGA) were performed in a nitrogen flow (40 mL min-1) with a Perkin-Elmer Pyris 6 TGA in the range from 30 to 800 °C with a heating rate of 10 °C min-1. Triplicate TGA runs have been performed to ensure reproducibility.

Surface morphology was investigated on a selected piece of Ni-supported catalyst considered to be representative of the material. Nova NanoSEM 450 manufactured by FEI Company, USA, was used to perform FESEM analysis on the selected samples. Tiny plate-like of the powdered catalyst were mounted on TEM copper grids, and gold-palladium sputtered (K550, Emitech Ltd, United Kingdom). Scanning Transmission Electron Microscopy (STEM) Detector allowed transmission images to be taken at 30 keV, lower energy level with respect to commonly used TEM, beam voltage 100-200 keV. Resolution limits of this microscope are remarkable: 1.4 nm @ 1 kV in high vacuum mode. The particle sizes were analyzed by STEM image analysis using the ImageJ software (freeware software: http://rsb.info.nih.gov/ij/).

2.2 Catalyst preparation

The supported catalyst (*Ni-pol*) was prepared by calcination under nitrogen of a polymer supported Ni(II) complex (*Ni(AAEMA)₂-pol*), which in turn was obtained by co-polymerization of the polymerizable complex $Ni(AAEMA)_2$.

Ni(AAEMA)₂

To a solution of KOH (579 mg, 10.3 mmol) in ethanol (10 mL), 2-(acetoacetoxy) ethyl methacrylate (HAAEMA) (2.211 g, 10.3 mmol) was added and left under stirring at room temperature for 5 min. The resulting solution was added to a solution of $Ni(NO_3)_2 \cdot 6 H_2O$ (1.5 g, 5.16 mmol) in ethanol (15 mL), causing the sudden precipitation of $Ni(AAEMA)_2$ as a pale green solid. After 1 h stirring, the solid was filtrated and washed with water (3 × 5 mL), ethanol (3 × 5 mL) and pentane (3 × 5 mL), and dried overnight under vacuum. Anal. Calc. for $NiC_{20}H_{26}O_{10}$:

C, 45.00; H, 4.92; Ni, 19.97. Found: C, 44.50; H, 4.99; Ni, 19.76. HRMS: (ESI, CH_3OH, positive ion mode) m/z: calcd. for $NiC_{20}H_{27}O_{10}$ $[M+H]^+$ 485.0952; found 485.0954. IR (〈, cm^{-1}): 1720 (s), 1635 (s), 1623 (s), 1521 (s), 1385 (vs), 1259 (vs), 1161 (vs), 977 (m), 785 (m). Yield: 2.01 g, 80%.

Ni(AAEMA)₂-pol

$Ni(AAEMA)_2$ (4.0 mmol, 2.0 g) [$AAEMA^-$ = deprotonated form of 2-(acetoacetoxy) ethyl methacrylate] was dissolved in N,N -dimethylformamide (DMF, 5 ml) and the resulting solution was added of a mixture of N,N'-methylenebisacrylamide (1.2 mmol, 0.186 g) and N,N -dimethylacrylamide (43.2 mmol, 4.434 g) in DMF (6 ml) and heated at 120°C under vigorous stirring.

After 1 h from the addition of azaisobutyronitrile (5 mg), the green jelly solid which formed in the reaction vessel was filtered off, washed with acetone and diethyl ether, dried under vacuum, kept overnight in oven at 95 °C and grinded with a mortar to give a pale green powder. Yield: 4.04 g of polymer supported Ni(AAEMA)$_2$ [*Ni(AAEMA)$_2$-pol*]. Elemental Analysis (found): Ni 3.69; C 57.06; H 7.94; N 9.91%. IR (ῡ, cm^{-1}): 3477 (bs), 2923 (bs), 1720 (s), 1622 (s), 1527 (s), 1256 (vs), 1144 (vs), 1355 (s), 780 (m). UV-vis (CH$_2$Cl$_2$): 280 nm (ε = 10660 mol L^{-1} cm^{-1}), 227 nm (ε = 4800 mol L^{-1} cm^{-1}). m.p.= 120.3±0.4°C.

Ni-pol

The as-obtained *Ni(AAEMA)$_2$-pol* was put in a tube furnace, ramped at 10 °C min^{-1} in flowing N$_2$ to 300 °C, and kept at the final temperature for 30 min, yielding a black powder referred to as *Ni-pol*. Yield: 3.83 g.. Elemental Analysis (found): Ni 5.35; C 56.66; H 9.20; N 11.54%. IR (ῡ, cm^{-1}): 3482 (bs), 2930 (bs), 1720 (s), 1631 (s), 1495 (m), 1402 (m), 1258 (m), 1144 (s), 1053 (m).

2.3 General experimental procedure for the reduction of nitroarenes catalyzed by *Ni-pol*.

Amounts corresponding to 0.5 mmol of nitroarene, 10.2 mg of *Ni-pol* (Ni%$_w$ =5.35, 9.3 10^{-3} mmol of Ni) and 10.0 mmol of sodium borohydride were stirred under nitrogen at room temperature in 2.5 mL of double deionized water and 2.5 mL of diethyl ether for the appropriate amount of time, using a three-necked flask equipped by a gas bubbler to discharge the hydrogen excess produced during reaction. The progress of the reaction was monitored by GLC. After completion of the reaction, the reaction mixture was centrifuged to separate the catalyst. The solid residue was first washed with deionized water and then with acetone and diethyl ether to remove any traces of organic material. The filtrate containing the reaction mixture was extracted with ethyl acetate (3 × 5 mL) and then dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated under reduced pressure to yield the crude product, which was then purified by column chromatography using silica gel and *n*-hexane/ethyl acetate as an eluent to afford the pure product. The products were characterized by GC-MS by comparison with authentic samples. For the assessment of the chromatographic yields, biphenyl (50.0 mg) was used as the internal standard.

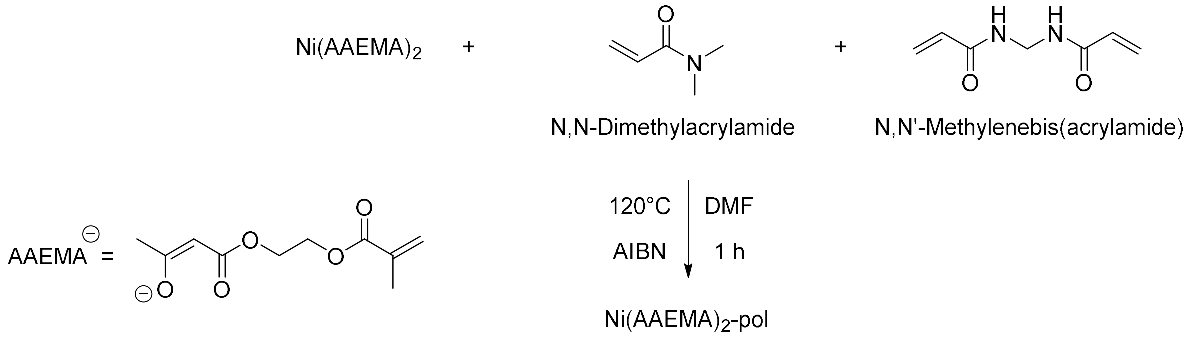
2.4 Recycling experiments

At the end of reaction, the organic layer was removed with a syringe and the aqueous phase suspending the supported catalyst was washed with diethyl ether (3 × 5 mL), and, then, added of fresh reagents. Iteration of this procedure was repeated for five reuses of the catalytic system.

3. Results and discussion

3.1 Synthesis of the catalyst and preliminary catalytic tests

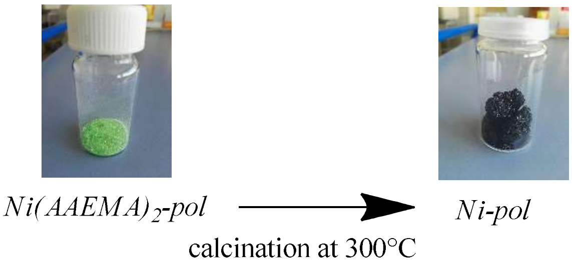
The polymer supported catalyst used in this work was synthetized following an unconventional method, aimed at obtaining a material with a uniform distribution of the Ni(II) centers: *i.e.* by co-polymerization of the metal-containing monomer [50] Ni(AAEMA)$_2$ [51] [AAEMA$^-$ = deprotonated form of 2-(acetoacetoxy) ethyl methacrylate] with suitable co-monomer (N,N -dimethylacrylamide) and cross-linker (N,N'-methylenebisacrylamide) (Scheme 1). The copolymer supporting the metal was a non-hygroscopic green powder insoluble in all solvents. It swelled well in water, acetone, halogenated solvents and dioxane and shrink when treated with diethyl ether, ethyl acetate or petroleum ethers. Its IR spectra in KBr (Figure S1) showed the features of the coordinated β-ketoesterate moiety (1527 and 1622 cm^{-1}) at roughly the same wavenumbers of the corresponding Ni(AAEMA)$_2$ complex (1531 and 1623 cm^{-1}), thus substantiating that the metallo-organic units in both soluble and supported materials are similar.



Scheme 1. Synthesis of *Ni(AAEMA)$_2$-pol*

This polymer [*Ni(AAEMA)$_2$-pol*] was alike the one already obtained in our labs by co-polymerization of Pd(AAEMA)$_2$ with methacrylic monomers [52,53], found active, selective and recyclable in several palladium catalyzed reactions [54,55,56,57,58]. This Pd(II) based polymer turned into polymer supported Pd(0) nanoparticles (*Pd-pol*) under reaction conditions. In fact, as it has been reported for similar Pd nanoparticles supported on methacrylate based resins [59], the reticular and macro porous polymeric support of *Pd-pol* could immobilize, stabilize and retain palladium nanoparticles [60], that were the true catalytically active species. Furthermore, the good swell ability in water of the methacrylic insoluble support rendered *Pd-pol* an ideal catalyst for reactions carried out in aqueous solvent [61,62,63,64], since the migration of the reagents to the active sites would not be hampered by the solid matrix. Due to the analogy between Pd(AAEMA)$_2$ and Ni(AAEMA)$_2$ supported polymers, we decided to test the catalytic activity of *Ni(AAEMA)$_2$-pol* in a benchmark reaction [65] in which *Pd-pol* was particularly active and recyclable [66]: the transfer hydrogenation of nitrobenzene in water using $NaBH_4$ as the reducing agent, hoping that Ni(II) centers could turn into Ni(0) nanoparticles under reaction conditions, as it happened for *Pd-pol*. Preliminary catalytic tests were carried out using nitrobenzene as the representative substrate. By employing the same optimized conditions used for the palladium catalyzed nitroarene reduction [66], the yield into the desired aniline was poor (24 % after 1 h and 47 % after 4 h, entries 1 and 2 of Table 1, respectively), but it significantly increased by increasing $NaBH_4$/substrate molar ratio up to 20 (entry 3, Table 1). However, attempting in recycling *Ni(AAEMA)$_2$-pol* failed, since the yield into aniline dropped to 27 % already in the second run with the same catalyst (entry 4, Table 1). We observed also that the resin turned from green to black during reaction (presumably due to Ni reduction from +2 to 0 oxidation state) and, then, from black to white at the end of the reaction, probably due to metal leaching into solution (which in turn became green).

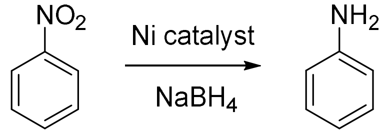
Calcination under hydrogen or nitrogen atmosphere is a well-known technique [47,67] used for preparing metallic nanoparticles anchored to an insoluble support by thermal reduction of supported metal ions. Depending on the calcination temperature, the thermal treatment modifies also the insoluble matrix (which may lose water, crystallization solvent molecules and/or carbon-based moieties), thus enhancing or depressing the ability of the support in stabilizing and retaining the so formed metal nanoparticles. For example, Qiu and coworkers found that the calcination temperature is the key factor affecting the structure, morphology and the catalytic performance of their Ni/C catalyst in the hydrogenation of nitroarenes [68]. They identified in T=300°C the best calcination temperature for their catalyst in terms of activity. Thermal Gravimetrical Analyses (Figure S2) suggested us to set the calcination temperature for our system at 300°C as well, because over 300°C the loss in weight of the polymeric material exceeded 5% of the initial mass, due to important structural modification of the support [68]. Therefore, by treating *Ni(AAEMA)$_2$-pol* under nitrogen flow for 30 min at 300°C, we obtained *Ni-pol* as a black powder (scheme 2).



Scheme 2: preparation of *Ni-pol* by calcination under N_2 at 300°C.

To our delight, *Ni-pol* resulted active and recyclable in the reduction of nitrobenzene (entries 5-8, Table 1), although in neat water the reusability of the catalytic system dramatically decreased after the second run. Figure 1 summarizes the recyclability over five runs of *Ni(AAEMA)$_2$-pol* and *Ni-pol* in neat water and in water/diethyl ether (v/v = 1/1), as the solvent.

Table 1: Preliminary catalytic tests for the reduction of nitrobenzene[a]



Entry	Ni Catalyst	$NaBH_4/PhNO_2$ molar ratio	Solvent	Reaction time (h)[b]	Yield [b] (%)
1	*Ni(AAEMA)$_2$-pol*	10	H_2O	1	24
2	*Ni(AAEMA)$_2$-pol*	10	H_2O	4	47
3	*Ni(AAEMA)$_2$-pol*	20	H_2O	2	93
4	*Ni(AAEMA)$_2$-pol* [c]	20	H_2O	2	27
5	*Ni-pol*	20	H_2O	2	88
6	*Ni-pol* [c]	20	H_2O	2	80
7	*Ni-pol*	20	H_2O/Et_2O	2	90
8	*Ni-pol* [c]	20	H_2O/Et_2O	2	90

[a] Reaction conditions: 0.5 mmol of nitrobenzene, 10.2 mg of *Ni-pol* (Ni$\%_w$ = 5.35) or 17.5 mg of *Ni(AAEMA)$_2$-pol* (Ni$\%_w$ = 3.12), solvent (5 mL, H_2O or H_2O/Et_2O, v/v = 1/1) and given amounts of $NaBH_4$ were stirred at room temperature under nitrogen. [c]Yield determined by GLC with the internal standard (biphenyl) method. [d] Catalyst recovered from the reaction of the previous entry.

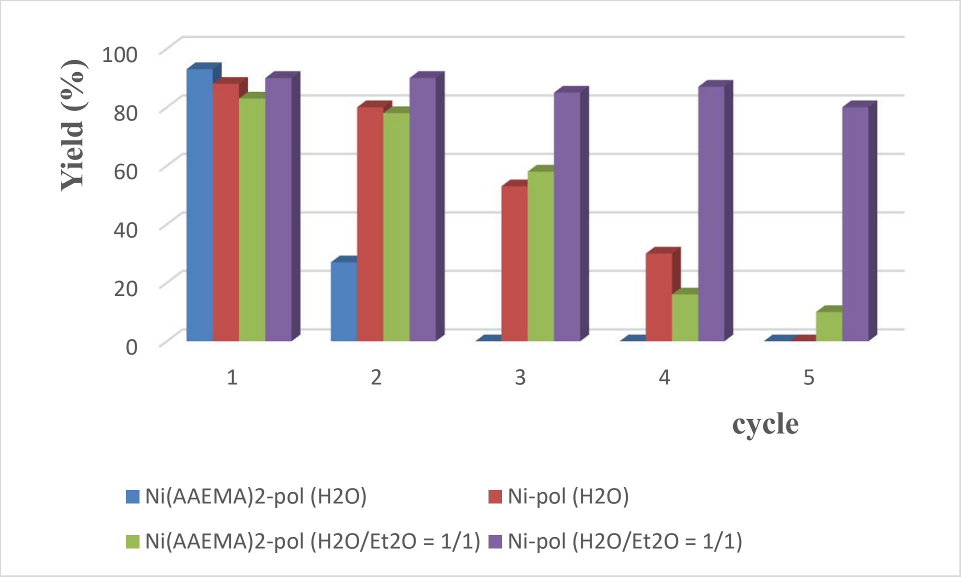


Figure 1: Reusability of *Ni(AAEMA)$_2$-pol* and *Ni-pol* in H_2O and in H_2O/Et_2O (v/v = 1/1) over five cycles. Reaction conditions: 0.5 mmol of nitrobenzene, 10.2 mg of *Ni-pol* (Ni%$_w$ = 5.35) or 14.8 mg of *Ni(AAEMA)$_2$-pol* (Ni%$_w$ = 3.69), 10 mmol of $NaBH_4$ in H_2O (5 mL) or H_2O/Et_2O (V/V = 1/1, 5 mL) at room temperature, t = 2 h.

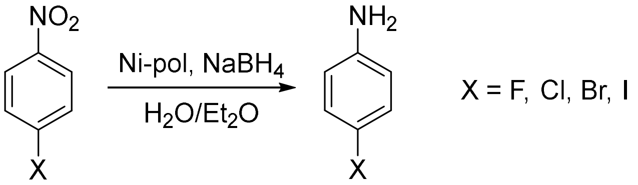
It can be seen from Figure 1 that the best catalytic performance in terms of catalytic activity and recyclability was shown by *Ni-pol* in H_2O/Et_2O as the solvent. The biphasic reaction medium on one side facilitates the access of the water insoluble substrate to the catalytically active sites and on the other side renders more workable the acrylamide based catalyst, becoming the latter too jelly in neat water. In addition, the polymeric support seems to better retain the nickel centers by swelling (in water) and shrinking (in diethyl ether) at the same time. Furthermore, Zhao and coworkers demonstrated that water solvent rapidly deactivates Ni supported catalyst in the hydrogenation of nitroarenes by forming catalytically inactive $Ni(OH)_2$ species [69]. This problem has been resolved by coating the catalyst with a hydrophobic layer of carbon [69]. In our system, the hydrophobic property of diethyl ether might help to prevent catalyst deactivation. Additionally, it can be deduced that the catalytically active sites are metallic Ni nanoparticles rather than Ni(II) sites. Therefore, higher attention should be posed to the size and morphology of Ni sites, their distribution in the polymeric support and their modification after the use in the reaction media.

On the bases of the above results, we concluded that the optimum reaction conditions to be used for converting 0.5 mmol of nitrobenzene into aniline in the presence of 10.2 mg of *Ni-pol* (containing 5.35 $\%_w$ Ni) were the ones reported in entries 7 and 8 of Table 1.

3.2 Selectivity of the catalytic system in the hydrogenation of halonitrobenzene to haloaniline

Using the optimized reaction conditions, the selectivity of the catalyst was tested in the reduction of different halonitrobenzenes. In fact, the selective hydrogenation of halonitrobenzenes catalyzed by transition metals is regarded as a high atom efficiency and environmentally friendly process for the synthesis of haloanilines, which are important fine chemicals, widely used in the production of pharmaceuticals, dyes, herbicides, pesticides [70]. However, up to now, the major challenge is avoiding the undesired hydrodehalogenation reaction, which is a side-reaction favored by the electron withdrawing effect of the nitro group in *para* and/or *ortho* positions (with respect to the halogen), that enhances the rate of the Ar-X (Cl, Br, I) oxidative addition to the metal center. Selective halonitroarene reductions have been reached by poisoning Pd [71] or Pt [72] nanocatalysts. Our Ni based catalytic system resulted active and selective in the reduction of halonitrobenzenes (Table 2), even in the case of challenging bromo- and iodo-nitrobenzene (entries 3 and 4, Table 2). This chemoselectivity, much higher than the one observed with the analogues Pd catalyst [66], should be ascribable to reluctance of aryl halides to give oxidative addition to nickel active site, which is the well-known first step of the Ni and Pd catalyzed hydrodehalgenation reaction [73].

Table 2 Reduction of various halonitroarenes catalyzed by *Ni-pol*[a]



entry	substrate	product	time (h)	yield (%)[b]
1	4-fluoronitrobenzene	4-fluoroaniline	5	97
2	4-chloronitrobenzene	4-chloroaniline	5	94
3	4-bromonitrobenzene	4-bromoaniline	12	95(94)
4	4-iodonitrobenzene	4-iodoaniline	3	92

[a] Reaction Conditions: 0.5 mmol of nitroarene, 10.0 mmol of $NaBH_4$ and *Ni-pol* ($9.3 \cdot 10^{-3}$ mmol of Ni) were stirred in 2.5 mL of double deionized water and 2.5 mL of diethyl ether at room temperature for the appropriate amount of time. [b]Yield determined by GLC with the internal standard (biphenyl) method. Isolated yield after column chromatography in parenthesis.

Ni-pol system showed the same activity and selectivity over various cycles. In fact, after completion of the reaction, the organic phase was pipetted out and the water solution (containing the catalyst on its upper layer) was washed twice with diethyl ether to remove all organic reactants and products. Fresh reagents and diethyl ether were then added to the water mixture and the catalytic system was successfully reused for five subsequent runs, where it showed the unaltered catalytic activity and selectivity, giving 4-bromoaniline as the product in excellent yield (89-95%) for each cycle till the fifth cycle (Figure 2).

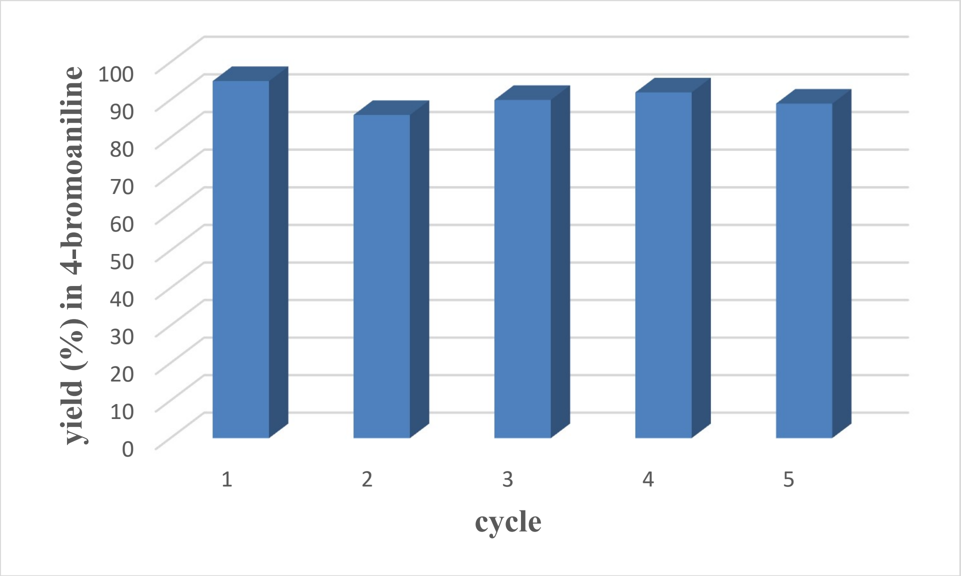
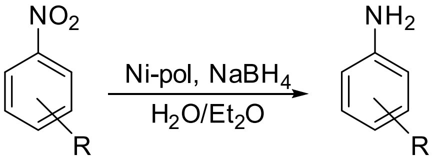


Figure 2: Selectivity of *Ni-pol* towards 4-bromoaniline over five cycles. Reaction conditions: 0.5 mmol of 4-bromonitrobenzene, 10.2 mg of *Ni-pol* (Ni$\%_w$ = 5.35), 10 mmol of $NaBH_4$ in H_2O/Et_2O (v/v = 1/1, 5 mL) at room temperature, t = 12 h.

3.3 Scope of the catalytic system

The activity and the scope of the catalyst were then explored in the reduction of a variety of different nitroarenes (Table 3).

Table 3 Reduction of various nitroarenes catalyzed by *Ni-pol*[a]



entry	substrate	product	time (h)	yield (%)[b]
1	2-nitrotoluene	2-methylaniline	4	>99
2	4-nitrotoluene	4-methylaniline	2	90
3	3-nitrotoluene	3-methylaniline	2	87
4	3-methoxynitrobenzene	3- methoxyaniline	4	91

5	4-methoxynitrobenzene	4- methoxyaniline	5	83
6	1,2-dinitrobenzene	1,2-diaminobenzene	12	90
7	2,4-dinitrotoluene	2,4-diaminotoluene	5	(82)

[a] Reaction Conditions: 0.5 mmol of nitroarene, 10.0 mmol of $NaBH_4$ and *Ni-pol* ($9.3 \cdot 10^{-3}$ mmol of Ni) were stirred in 2.5 mL of double deionized water and 2.5 mL of diethyl ether at room temperature for the appropriate amount of time. [b]Yield determined by GLC with the internal standard (biphenyl) method. Isolated yield after column chromatography in parenthesis.

The catalytic system was found to be very efficient regardless of the presence of electron-withdrawing and electron-donating substituents in the aromatic ring. Nitroarenes possessing electron-donating groups such as 2-, 3- and 4-nitrotoluene afforded excellent yields of the corresponding aniline in 2-4 hours (entries 1, 2 and 3). Also 3- and 4-methoxynitrobenzenes were converted almost quantitatively into the corresponding anisidine in 4-5 hours (entries 4 and 5). For 1,2-dinitrobenzene, both nitro groups were reduced in 12 hours, though mono-amino product was also observed in minor quantities during the reaction time. Also 2,4-dinitrotoluene was slightly converted into the corresponding diamine in 5 hours (entry 7), showing no steric effects. These phenylenediamines are of interest, because extensively used in the manufactory of azo dyes [74,75].

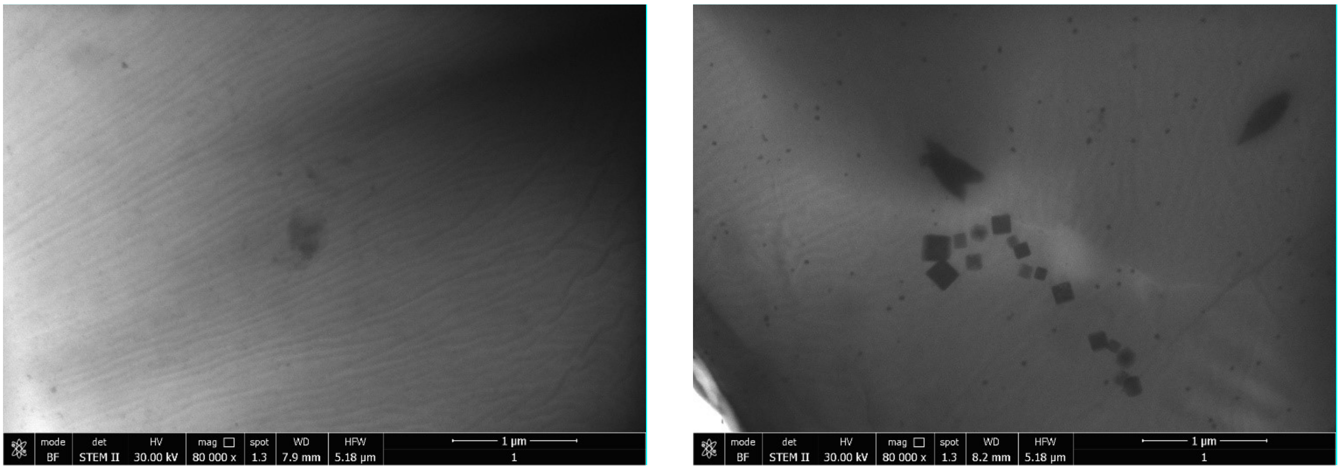
3.4 Heterogeneity tests

To verify whether the observed catalysis was truly heterogeneous or not, the reduction of 4-bromonitrobenzene was taken as the model reaction. The mixture was filtered after 3 h reaction (30% conversion of the substrate) and added of 10.0 mmol $NaBH_4$. Further stirring of the filtrate under the above reaction conditions did not increase the conversion of 4-bromonitrobenzene. On the contrary, the amount of 4-bromoaniline in the reaction mixture decreased after further 9 h stirring (*vide infra*).

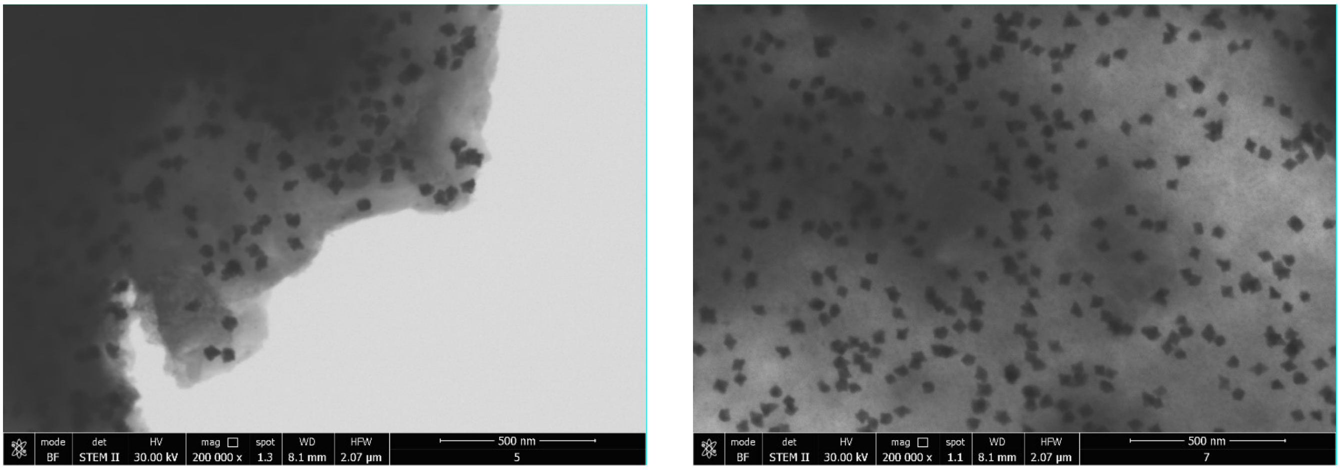
The filtrate was analyzed by atomic absorption spectrometry showing negligible nickel amount. In addition, *Ni-pol* recovered from the filtration was mineralized and analyzed by atomic absorption spectrometry showing the same nickel content (within the experimental error) of the fresh catalyst. The same nickel amount was also found in the catalyst recovered at the end of the fifth cycle. These results rule out any possible contribution of homogeneous catalysis by leached nickel species.

3.5 STEM analyses

This study was completed by STEM morphological characterization of the supported catalysts. *Ni(AAEMA)*$_2$*-pol* and *Ni-pol* were subjected to STEM analyses as well as the catalyst recovered after the first and the fifth run, respectively, with the aim of ascertaining whether the reaction cycles affected the morphology and the dispersion of the nickel active species on the polymeric support. STEM images of *Ni(AAEMA)*$_2$*-pol* and of *Ni-pol* before and after duty are reported in Figure 3.



(a) (b)



(c) (d)

Figure 3: STEM micrographs of matrix polymer embedded Ni nanoparticles: (a) *Ni(AAEMA)*$_2$*-pol*; (b) *Ni-pol* before use in catalysis; (c) *Ni-pol* recovered after the first run of the reduction of 4-bromonitrobenzene; (d) *Ni-pol* recovered after the fifth run of the reduction of 4-bromonitrobenzene.

Ni(AAEMA)$_2$*-pol* was constituted by Ni(II) species only (not visible in STEM micrographs) supported onto a macro-porous polymer (Figure 3a). STEM image of *Ni-pol* before use in catalysis shows metallic Ni nanoparticles ranging from 11 to 37 nm in size and a few amount of Ni(0) nanocubes with a cube side of 85-200 nm (Figure 3b), formed during the thermal treatment procedure. In the STEM picture of *Ni-pol* recovered after the first run, the previously observed metal nickel nanoparticles were not visible anymore, due to their transformation under reductive reaction conditions into cubic nanotwins ranging from 28 to 70 nm in side size (Figure 3c). The peculiar morphology of the latters might arise from the matrix effect of the polymer support which controlled both nanoparticle shape (cubic) and growth. In fact, it seemed that for each nanoparticle a second nano-cube grew up along the diagonal (preferential direction) of the primary nano-cube, giving rise to two compenetrated cubes as final overall nanoparticle. On passing from the first to the fifth cycle (Figure 3d), the Ni(0) nanotwin side sizes remained almost the same (27-65 nm) as well as nanoparticle number density. The quantity of the largest nanoparticles (45-70 nm) seemed even to decrease with the re-uses (figure 3c and 3d), probably for a dissolution/re-deposition mechanism [76] due to the presence of water, which is known to oxidize polymer embedded Ni(0) to Ni(II) [69], that in turn would be again reduced under reaction conditions to form Ni(0) nanoparticles. The polymer matrix might act as a stabilizer of the metal nanoparticles; thus their size and morphology did not dramatically change with the re-uses.

Ni nanoparticles formed under reaction condition, because $NaBH_4$ acts as a reducing agent of the metal in a dual way, by providing hydrides and by generating hydrogen gas. In fact, the hydrides from sodium borohydride can displace negatively charged ligands bound to Ni(II), generating Ni-hydrides directly, which upon β-hydride elimination of H_2, give the reduced metal. In addition, the *in situ* formed H_2 in water (scheme 3) in the closeness of Ni(II) can reduce it to Ni(0).

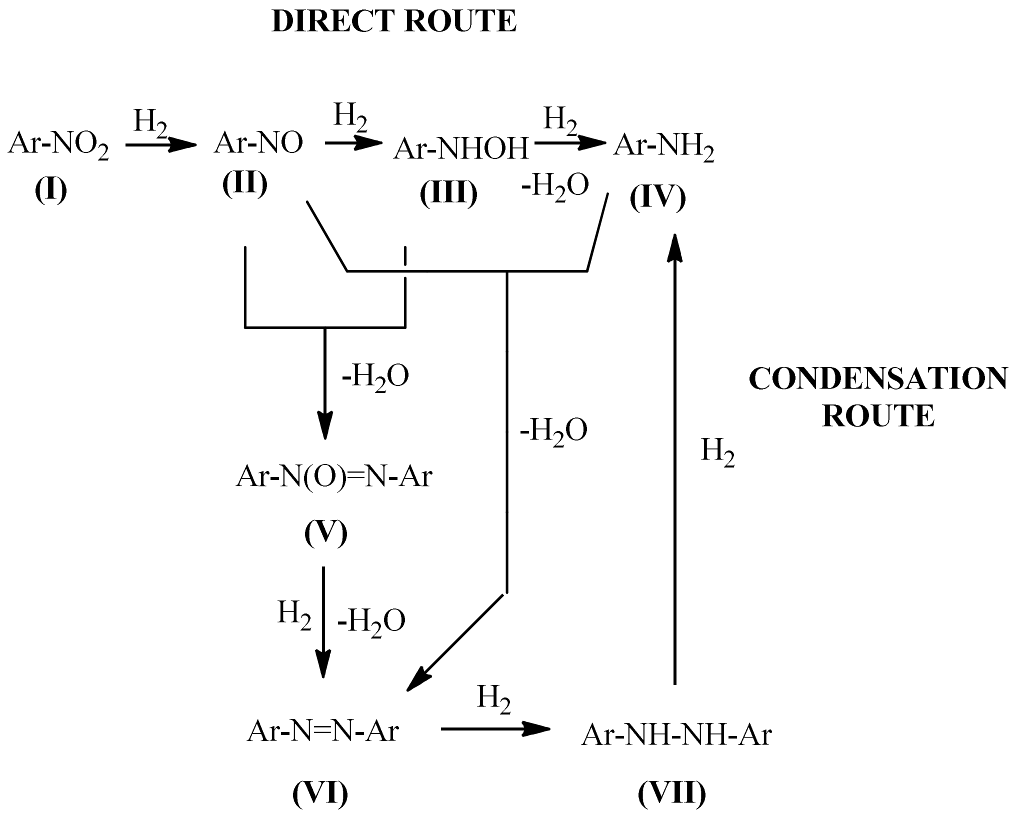
3.6 Mechanistic consideration

By using $NaBH_4$ in water in the presence of *Ni-pol*, many hydrogen bubbles were observed in the reaction mixture, according to the reaction reported in scheme 3 [77].

$$NaBH_4 + 2\ H_2O \longrightarrow 4\ H_2 + NaBO_2$$

Scheme 3: nickel catalyzed production of H_2 by $NaBH_4$

It is widely recognized [78] that metal catalyzed reduction of nitroarenes (**I**) in the presence of hydrogen may go through the formation of hydroxylamine (**III**) and then aniline (**IV**) (direct route) as well as through the formation of diazoarene (**VI**) (condensation route) (scheme 4).



Scheme 4: plausible mechanistic pathways of nitroarene reduction.

Pd and Au based catalytic systems generally prefer the direct route [23,35,79], although alternative mechanistic ways have been proposed for Pd/C catalytic systems [80,81].

During the reduction with $NaBH_4$/*Ni-pol* system, diazo-intermediates (**V** and **VI**) were always detected (GC-MS analysis), as well as the nitroso compound (**II**). The arylhydroxylamine (**III**) was never observed. The concentration of **II, V** and **VI** decreased with time to yield more of the desired product, once the substrate finished. The absence of **III** in the reaction mixture might signify either that its reduction was faster compared to that of the nitrosoarene hydrogenation and that once formed it quick condensed with **III** to give **V**. These results suggest that *Ni-pol* reducing system might go through both direct and condensation routes (scheme 4).

An increasing of diazobenzene (**VI**) amount and a decreasing of aniline (**IV**) quantity were detected in the mother liquor filtrated at 30% substrate conversion and left under stirring for nine more hours after addition of excess $NaBH_4$. In this case, in the filtrate removed of the supported catalyst, the coupling between nitroso benzene (**II**) and aniline (**IV**) (to give diazobenzene, **VI**) occurred (scheme

4), because the nitrosobenzene was not converted into hydroxylamine benzene (**III**) in the absence of *Ni-pol*.

A major strength of this reaction protocol is its recyclability, its selectivity when using halonitroarenes as substrates and its ability to perform the reduction in aqueous medium, which is not trivial for Ni based catalysts. The absence of arylhydroxylamine during reaction is an additional strong point, because accumulation of arylhydroxylamine may lead to rapid exothermic decomposition [82]. By comparing *Ni-pol* catalytic system with the commercial available Raney Ni [83], it is apparent that the latter dramatically deactivates after few runs and it needs harsh conditions (102°C and 1.62 MPa of H_2) to obtain high yields. Raney Ni /$NaBH_4$ system has been recently proposed, but no studies on its recyclability have been reported.[84] Table 4 displays the reaction conditions employed in catalytic systems based on recent examples of Ni supported catalysts in the hydrogenation of nitroarenes. It is apparent that either high temperatures and H_2 pressures or high $NaBH_4$/substrate molar ratio are needed to get good yield. In addition, to the best of our knowledge *Ni-pol* system is the second example reported to date [68] of Ni based reusable catalyst selective in the hydrogenation of halonitrobenzene to haloaniline.

Table 4: reaction conditions for Ni-based catalyst reported

Catalyst	T (°C)	Solvent	P (MPa) of H_2	$NaBH_4$/substrate molar ratio	Ref.
Ni-pol	25	H_2O/Et_2O	_	20	This work
Ni-NPs/C	25	H_2O	_	847	[85]
Ni/CB	30	H_2O	_	104	[86]
Co-Ni	120	EtOH	3	_	[87]
Ni/C_{60}	80	EtOH	1	_	[48d]
Ni-53-EN	110	EtOH	2	_	[88]

Ni-B-SiO_2	100	EtOH	1.8	_	[89]

4. Conclusions

In conclusion, the polymer supported nickel catalyst *Ni-pol* efficiently promoted the reduction of aromatic nitroarenes in aqueous medium at ambient temperature in the presence of $NaBH_4$. No other additives were needed for the reaction. The catalytic system was selective towards haloaniline in the reduction of halonitrobenzene, avoiding the formation of hydro-dehalogenation products. The catalyst could be recovered at the end of the reaction and re-cycled for at least fifth times with the same activity and selectivity, which is not trivial for Ni supported catalysts working in aqueous medium, being generally deactivated by water. STEM analyses showed that the active species were metallic Ni nanocubes ranging from 28 to 70 nm in side size, homogeneously distributed and stabilized by the polymer support. All these results demonstrate that the *Ni-pol* recyclable heterogeneous catalytic system is suitable and environmentally friendly for the reduction of nitroarenes.

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Notes and references

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[1] a) P. Liu, R. Qin, Gang Fu, N. Zheng, J. Am. Chem. Soc. 2017, 139, 2122–2131; b) M. Nasrollahzadeh, M. Atarod, M. Alizadeh, A. Hatamifard, S. M. Sajadi Curr. Org. Chem., 2017, 21, 708-749; c) G. Zhan, H. Chun Zeng, Coord. Chem. Rev. 320-321 (2016) 181–192

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[2] a) G. Centi, S. Perathoner, Coord. Chem. Rev. 2011, 255, 1480; b) H. Cong, J. A. Porco, ACS Catal. 2012, 2, 65; c) S. Schauermann, N. Nilius, S. Shaikhutdinov, H.-J. Freund, Acc. Chem. Res. 2013, 46, 1673; d) D. S. Su, S. Perathoner, G. Centi, Chem. Rev. 2013, 113, 5782; e) C. Amiens, B. Chaudret, D. Ciuculescu-Pradines, V. ColliÀre, K. Fajerwerg, P. Fau, M. Kahn, A. Maisonnat, K. Soulantica, K. Philippot, New J. Chem. 2013, 37, 3374, f) P. Mastrorilli, M. M. Dell'Anna, A. Rizzuti, M. Mali, M. Zapparoli, C. Leonelli, Molecules, 20 (2015) 18661-18684, g) P. Cotugno, M. Casiello, A. Nacci, P. Mastrorilli, M.M. Dell'Anna, A. Monopoli, J. Organomet. Chem. 752 (2014) 1-5; h) Yan, N.; Xiao, C.; Kou, Y.. Coord. Chem. Rev. 2010, 254, 1179–1218

[3] a) Navalona S., Dhakshinamoorthy A., Alvaro M., Garcia H. (2016). Metal nanoparticles supported on two-dimensional graphenes as heterogeneous catalysts. Coord. Chem. Rev. 312, 99–148; b) Astruc D., Lu F., Aranzaes J.R. (2005). Nanoparticles as recyclable catalysts: The frontier between homogeneous and heterogeneous catalysis. Angew. Chem., Int. Ed., 44 (48), 7852-7872.

[4] a) R. M. Bullock, Science 2013, 342, 1054–1055; b) F. Iannone, M. Casiello, A. Monopoli, P. Cotugno, M.C. Sportelli, R.A. Picca, N. Cioffi, M.M. Dell'Anna, A. Nacci, J. Mol. Catal. A: Chem. 426 (2017) 107–116; c) M. Casiello, A. Monopoli, P. Cotugno, A. Milella, M.M. Dell'Anna, F. Ciminale, A. Nacci, J. Mol. Catal. A: Chem. 381 (2014) 99–106; d) Dell'Anna, M.M., Gallo, V., Mastrorilli, P., Nobile, C.F., Romanazzi, G., Suranna, G.P. Chem. Commun. 5 (2002) 434-435; f) D. Wang and D. Astruc, Chem. Soc. Rev. 2017, 46, 816-854

[5] a) Jacob E. Dander and Neil K. Garg, ACS Catal. 2017, 7, 1413-1423; b) J. Xia, G. Heb, L. Zhang, X. Sun, Xin Wang, Appl. Catal. B: Environ. 180 (2016) 408–415; c) G. Wu, X. Liang, H. Zhang, L. Zhang, F. Yue, J. Wang, X. Su, Catal. Commun. 79 (2016) 63–67; d) M. Zaheer, J. Hermannsdçrfer, W. P. Kretschmer, G. Motz, R. Kempe, ChemCatChem 2014, 6, 91–95; e) S. Pisiewicz, D. Formenti, A.-E. Surkus, M.-M. Pohl, J. Radnik, K. Junge, C. Topf, S. Bachmann, M. Scalone, M. Beller, ChemCatChem 2016, 8, 129 – 134; f) T. B. Celic, M. Grilc, B. Likozar, N. N. Tusar, ChemSusChem 2015, 8, 1703 – 1710.

---

[6] P. F. Vogt and J. J. Gerulis, Ullmann's Encyclopedia of Industrial Chemistry, in Aromatic Amines, Wiley-VCH Verlag GmbH & Co., Weinheim, 2005.

[7] S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, John Wiley & Sons, Inc., New York, 2001.

[8] Fine Chemicals through Heterogeneous Catalysis, Eds: R.A. Sheldon, H. van Bekkum, Wiley-VCH, Weinheim, 2001.

[9] M. Pietrowski, Curr. Org. Synth. 9 (2012) 470-487.

[10] M. Kumar, U. Sharma, S. Sharma, V. Kumar, B. Singh and N. Kumar, RSC Adv. 3 (2013) 4894-4898.

[11] F. A. Westerhaus, R. V. Jagadeesh, G. Wienhöfer, M.-M. Pohl, J. Radnik, A.-E. Surkus, J. Rabeah, K. Junge, H. Junge, M. Nielsen, A. Brückner, M. Beller, Nat. Chem. 5 (2013) 537-543.

[12] R. V. Jagadeesh, A.-E. Surkus, H. Junge, M.-M. Pohl, J. Radnik, J. Rabeah, H. Huan, V. Schünemann, A. Brückner, M. Beller, Science 342 (2013) 1073-1076.

[13] R. Begum, R. Rehan, Z. H. Farooqi, Z. Butt, S. Ashraf, J Nanopart Res (2016) 18:231

[14] H. -U. Blaser, H. Steiner and M. Studer, Chem.Cat.Chem. 1 (2009) 210-221.

[15] M. Xie, F. Zhang, Y. Long and J. Ma, RSC Adv. 3 (2013) 10329-10334.

[16] S. Cai, H. Duan, H. Rong, D. Wang, L. Li, W. He and Y. Li, ACS Catal. 3 (2013) 608-612.

[17] J. Lyu, J. Wang, C. Lu, L. Ma, Q. Zhang, X. He, X. Li, J. Phys. Chem. C. 118 (2014) 2594-2601.

[18] K. Möbus, E. Grünewald, S.D. Wieland, S.F. Parker, P.W. Albers, J. Catal. 311 (2014) 153-160.

[19] M. Turáková, M. Králik, P. Lehocký, L. Pikna, M. Smrčová, D. Remeteiová, A. Hudák, Appl. Catal. A: Gen. 476 (2014) 103-112.

[20] A. J. Amali and R. K. Rana, Green Chem. 11 (2009) 1781-1786.

[21] F. A. Harraz, S. E. El-Hout, H. M. Killa and I. A. Ibrahim, J. Catal. 286 (2012) 184-192.

[22] M. M. Dell'Anna, V. Gallo, P. Mastrorilli and G. Romanazzi, Molecules 15 (2010) 3311-3318.

[23] A. K. Shil, D. Sharma, N. R. Guha and P. Das, Tetrahedron Lett. 53 (2012) 4858-4861.

[24] S. Furukawa, Y. Yoshida, T. Komatsu, ACS Catal. 4 (2014) 1441-1450.

[25] D. Cantillo, M. M. Moghaddam and C. O. Kappe, J. Org. Chem. 78 (2013) 4530-4542.

[26] M. Shokouhimehr, J. E. Lee, S. I. Hana and T. Hyeon, Chem. Commun. 49 (2013) 4779-4781.

[27] S. Pagoti, S. Surana, A. Chauhan, B. Parasara and J. Dash, Catal. Sci. Technol. 3 (2013) 584-588.

[28] Q. Shi, R. Lu, L. Lu, X. Fu and D. Zhao, Adv. Synth. Catal. 349 (2007) 1877-1881.

[29] R. K. Rai, A. Mahata, S. Mukhopadhyay, S. Gupta, P. -Z. Li, K. T. Nguyen, Y. Zhao, B. Pathak, and S. K. Singh, Inorg. Chem. 53 (2014) 2904-2909.

[30] F. Li, B. Frett, H.-Y. Li, Synlett 25 (2014) 1403-1408.

[31] J. Ronald, Jr. Rahaim, and R. E. Maleczka, Org. Lett. 7 (2005) 5087-5090.

[32] K. Junge, B. Wendt, N. Shaikh and M. Beller, Chem. Commun. 46 (2010) 1769-1771.

[33] H. S. Wilkinson, G. J. Tanoury, S. A. Wald and C. H. Senanayake, Tetrahedron Lett. 42 (2001) 167–170.

[34] W. Liu, D. Sun, J. Fu, R. Yuan and Z. Li, RSC Adv. 4 (2014) 11003-11011.

[35] K. Layek, M. L. Kantam, M. Shirai, D. Nishio-Hamane, T. Sasaki and H. Maheswarana, Green Chem. 14 (2012) 3164-3174.

[36] I. Tamiolakis, S. Fountoulaki, N. Vordos, I. N. Lykakisb and G. S. Armatas, J. Mater. Chem. A 1 (2013) 14311-14319.

[37] D. M. Dotzauer, S. Bhattacharjee, Y. Wen and M. L. Bruening, Langmuir 25 (2009) 1865-1871.

[38] A. Chinnappan and H. Kim, RSC Adv. 3 (2013) 3399-3406.

[39] L. Li, Z. Chen, H. Zhong, R. Wang, Chem. Eur. J. 20 (2014) 3050-3060.

[40] T. Subramanian, K. Pitchumani, ChemCatChem 4 (2012) 1917-1921.

[41] a) O. Verho, A. Nagendiran, C. -W. Tai, E. V. Johnston and J.-E. Backvall, Chem.Cat.Chem. 6 (2014) 205-211; b) Dell'Anna, M.M., Intini, S, Romanazzi, G., Rizzuti, A., Leonelli, C., Piccinni, F., Mastrorilli, P. J. Mol. Catal. A: Chem. 395 (2014) 307-314

[42] J. Sun, Y. Fu, G. He, X. Sun, X. Wang, Catal. Sci. Technol. 4 (2014) 1742-1748.

[43] X. Liu, S. Ye, H.-Q. Li, Y.-M. Liu, Y. Cao and K.-N. Fan, Catal. Sci. Technol. 3 (2013) 3200-3206.

[44] A. Corma and H. Garcia, Chem. Soc. Rev. 37 (2008) 2096-2126.

[45] J. H. Kim, J. H. Park, Y. K. Chung and K. H. Park, Adv. Synth. Catal. 354 (2012) 2412-2418.

[46] A. K. Patra, N. T. Vo, D. Kim, Appl. Catal. A: Gen. 538 (2017) 148–156.

[47] a) H. Ma, H. Wang, T. Wu, C. Na, Appl. Catal. B: Environ. 180 (2016) 471–479; b) D. Formenti, C. Topf, K. Junge, F. Ragaini, M. Beller, Catalysis Science and Technology, 6, 2016, 4473-4477; c) X. Wang, Y. Li, J. Mol. Catal. A: Chem. 420 (2016) 56-65.

[48] a) R. J. Kalbasi, A. A. Nourbakhsh, F. Babaknezhad, Catal. Commun. 12 (2011) 955–960; b) M. B. Gawande, A. K. Rathi, P. S. Branco, I. D. Nogueira, A. Velhinho, J. J. Shrikhande, U. U. Indulkar, R. V. Jayaram, C. A. A. Ghumman, N. Bundaleski and O. M. N. D. Teodoro, Chem. Eur. J. 18 (2012) 12628-12632; c) G. Hahn, J.-K. Ewert, C. Denner, D. Tilgner, R. Kempe, ChemCatChem 2016, 8, 2461 – 2465; d) Y. Qu, H. Yang, S. Wang, T. Chen, G. Wang, Catal. Commun. 97 (2017) 83-87.

[49] B. Zeynizadeh, D. Setamdideh, Synth. Comun. 36 (2006) 2699–2704.

[50] a) M. M. Dell'Anna, G. Romanazzi and P. Mastrorilli, Curr. Org. Chem. 17 (2013) 1236–1273; b) P. Mastrorilli, C.F. Nobile, Coordination Chemistry Reviews, 248 (2004) 377-395

[51] M.M. Dell' Anna, P. Mastrorilli, C.F. Nobile, G.P. Suranna, J. Mol. Catal. A: Chem. 103 (1995) 17-22.

[52] M. M. Dell'Anna, P. Mastrorilli, A. Rizzuti and C. Leonelli, Appl. Catal. A: Gen. 401 (2011) 134-140.

[53] M. M. Dell'Anna, P. Mastrorilli and C.F. Nobile, in: P.J.H. Scott (Ed.), Solid-Phase Organic Syntheses, vol. 2, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2012, pp. 79-86.

[54] M. M. Dell'Anna, P. Mastrorilli, F. Muscio, C. F. Nobile and G. P. Suranna, Eur. J. Inorg. Chem. 8 (2002) 1094-1099.

[55] M. M. Dell'Anna, P. Mastrorilli, F. Muscio and C. F. Nobile, Stud. Surf. Sci. Catal. 145 (2002) 133–136.

[56] M. M. Dell'Anna, P. Mastrorilli, C. F. Nobile and G. P. Suranna, J. Mol. Catal. A: Chem., 201 (2003) 131-135.

[57] M. M. Dell'Anna, A. Lofù, P. Mastrorilli, V. Mucciante and C. F. Nobile, J. Organomet. Chem. 691 (2006) 131-137.

[58] M. M. Dell'Anna, V. F. Capodiferro, M. Mali, P. Mastrorilli, J. Organomet. Chem. 818 (2016) 106-114.

[59] L. De Zan, D. Gasparovicova, M. Kralik, P. Centomo, M. Carraro, S. Campestrini, K. Jerabek and B. Corain, J. Mol. Catal. A: Chem. 265 (2007) 1-8.

[60] C. Saldías, S. Bonardd, C. Quezada, D. Radic, and A. Leiva, J Nanosci Nanotechnol, 17 (2017) 87-114.

[61] M. M. Dell'Anna, M. Mali, P. Mastrorilli, A. Rizzuti, C. Ponzoni and C. Leonelli, J. Mol. Catal. A: Chem. 366 (2013) 186-194.

[62] M. M. Dell'Anna, M. Mali, P. Mastrorilli, P. Cotugno and A. Monopoli, J. Mol. Catal. A: Chem. 386 (2014) 114-119.

[63] M. M. Dell'Anna, V. F. Capodiferro, M. Mali, D. Manno, P. Cotugno, A. Monopoli, P. Mastrorilli, Appl. Catal. A: Gen. 481 (2014) 89-95.

[64] M.M. Dell'Anna, G. Romanazzi, S. Intini, A. Rizzuti, C. Leonelli, A.F. Piccinni, P. Mastrorilli, J. Mol. Catal. A Chem. 402 (2015) 83-91.

[65] T. Aditya, A. Pal, and T. Pal, Chem Commun 51 (2015) 9410-9431.

[66] M. M. Dell'Anna, S. Intini, G. Romanazzi, A. Rizzuti, C. Leonelli, F. Piccinni, P. Mastrorilli, J. Mol. Catal. A: Chem. 395 (2014) 307-314.

[67] W.T. Reichle, J. Catal. 94 (1985) 547–557.

[68] P. Zhang, C. Yu, X. Fan, X. Wang, Z. Ling, Z. Wang and J. Qiu, Phys. Chem. Chem. Phys., 2015, 17, 145—150.

[69] W. Lin, H. Cheng, J. Ming, Y. Yu, F. Zhao, J. Catal. 291 (2012) 149-154.

[70] A. M. Tafesh and J. Weiguny, Chem. Rev., 1996, 96, 2035.

[71] C. Lu, M. Wang, Z. Feng, Y. Qi, F. Feng, L. Ma, Q. Zhang, X. Li, Catal. Sci. Technol., 2017,7, 1581-1589.

[72] W. Yu, L.-L. Lou, S. Li, T. Ma, L. Ouyang, L. Feng, S. Liu, RSC Adv., 2017, 7, 751–757.

[73] F. Alonso, I. P. Beletskaya, M. Yus Chem. Rev. 2002, 102, 4009-4091 4009.

[74] H. A. Rojas, J. A. Cubillos, J. J. Martínez, D. C. Guerrero and P. Reyes, Curr. Org. Chem. 16 (2012) 2770-2773.

[75] K. A. Kumar, K. S. Shruthi, N. Naik and C. Gowda, E-J. Chem., 4 (2008) 914-917.

[76] Gruttadauria, M.; Giacalone, F.; Noto, R. "Release and catch" catalytic systems. Green Chem. 2013,15, 2608–2618.

[77] B. H. Liu and Z. P. Li, J. Power Sources 187 (2009) 527-534.

[78] A. Saha and B. Ranu, J. Org. Chem. 73 (2008) 6867–6870.

[79] A. Corma, P. Concepcion and P. Serna, Angew. Chem. Int. Ed. 46 (2007) 7266-7269.

[80] E. A. Gelder, S. D. Jackson, C. M. Lok, Catal. Lett. 84 (2002) 205-208.

[81] E. A. Gelder, S. D. Jackson, C. M. Lok, Chem. Commun. (2005) 522–524.

[82] P. Baumeister, H.-U. Blaser, M. Studer Catalysis Letters 49 (1997) 219-222

[83] Y. Du, H. Chen, R. Chen, N. Xu Applied Catalysis A: General 277 (2004) 259–264.

[85] G. Wu, X. Liang, H. Zhang, L. Zhangb, F. Yue, J. Wanga, X. Su, Catal. Commun. 79 (2016) 63–67.

[86] J. Xia, G. He, L. Zhang, X. Sun, X. Wang, Applied Catalysis B: Environmental 180 (2016) 408–415.

[87] J. W. Wang, J. W. Liu, N. T. Yang, S. S. Huang, Y. H. Sun, Y. Zhu, Nano 8 (2016) 3949-3953.

[88] J. Jiang, G. Li, L. H. Kong, Acta Phys. Chim. Sin. 31 (2015) 137-144.

[89] Z. L. Liu, Y. Li, X. Y. Huang, J. I. Zuo, Z. Z. Qin, C. W. Xu, Catal. Commun. 85 (2016) 17-21.