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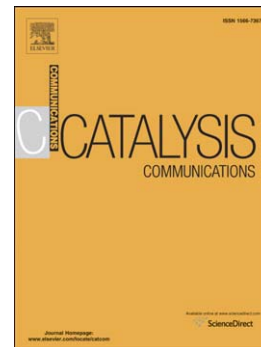
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Selective reduction of halo-nitro aromatic compounds using [Rh]/DHTANa as catalyst in an aqueous bi-phase system

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Abstract

The use of water as co-solvent for biphasic reactions and of easily recyclable water-soluble catalysts are highly desirable for the realization of greener processes. The selective reduction of halo nitroarenes to the corresponding haloanilines is a very important industrial transformation for the production of agrochemicals, pigments, bactericides and pharmaceuticals and is not easy to obtain. The application of a water soluble catalyst, prepared by rhodium species and a cheap thioligand, in the hydrogenation of some halonitroarenes is here described. Excellent conversions, good recyclability of the catalytic species embedded in the aqueous phase and very high selectivity are demonstrated.

Key words Hydrogenation; Halonitroarenes; Haloanilines; Water soluble catalyst; Rhodium; Thioligand.

1. Introduction

Homogeneous catalysis is an efficient tool to carry out a chemical process in a very active and selective way but the major drawback of the homogeneous process is the separation of the expensive catalyst from the product mixture that requires an energy intensive process such as

distillation. In recent years the use of metallic species with suitable ligands has allowed chemists to carry out reactions in biphasic systems so permitting an easy separation of the used catalyst, confined in a phase different from that of reagents and products, and its re-use in recycling experiments [1-3]. Since many years in our research group we are investigating highly efficient hydroformylation and hydrogenations reactions using different water-soluble complexes derived from the interaction between Rh species with natural or some commercially available thioligands [4-6]. Very recently we addressed our activity to the use of a very simple molecule, e.g. dihydrothioctic acid (DHTA), the reduced form of thioctic acid (THA), which presents two SH groups capable, in principle, to work as a bidentate ligand for the rhodium atom (Scheme 1). The presence of another functional group, COOH, in the molecule, when it is salified, favours the solubility in water of Rh species (hereafter named [Rh]/DHTANa) but also may create a potential third bonding site for the metallic species [7].

Insert Scheme 1

A red-orange solution was obtained introducing $[\text{Rh}(\text{COD})\text{Cl}]_2$ (COD = 1,5-cyclooctadiene) in a deaerated aqueous solution containing the sodium salt of the dihydrothioctic acid (DHTANa) and using a molar ratio ligand/metal 1:1; it may be stocked under nitrogen at 4°C showing good stability for medium-long time. After its treatment with H_2 or with H_2/CO , catalytic species, [Rh]/DHTANa, were obtained and afforded very encouraging results in hydrogenation and hydroformylation reactions of some simple model compounds [7]. Here we report the application of [Rh]/DHTANa in the selective reduction of nitrobenzene (**I**) and of some halo-nitro aromatic compounds such as 1-chloro-3-nitrobenzene (**III**) and 1-iodo-4-nitrobenzene (**V**). Furthermore, a different and greener preparation of the catalytic species is also described and the activities of the catalysts prepared by

the previous method (A) and the new method (B) are compared. Some spectroscopic analyses were also performed to try to elucidate the nature of the catalytic species. Finally, a comparison study among the new catalyst [Rh]/DHTANa, the well-known water soluble Rh/TPPTS complex (where the ligand TPPTS is triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt) and the home-made heterogeneous 0.18 % Rh/Al₂O₃ [8,9] in the hydrogenation of the above substrates is also described.

2. Experimental

2.1 Materials and analysis

[Rh(COD)Cl]₂, RhCl₃, nitrobenzene, 1-chloro-3-nitrobenzene, 1-iodo-4-nitrobenzene, NaBH₄, Na₂CO₃, trioctylamine (TOA), diethyl ether, toluene, chloroform, tetrahydrofuran, cyclopentylmethyl ether (CPME) and TPPTS were Aldrich products. Alumina was a Chimet S.p.A product. Thioctic acid was a generous gift of Prochifar s.r.l. (Milan). GC analyses were carried out on an Agilent 6850 A gas chromatograph (HP1column 30 m × 0.32 mm × 0.25 μm) and GC–MS analyses were performed by using an Agilent MS Network 5937 (HP-5MScolumn 30 m × 0.25 mm × 0.25 μm). ¹H NMR and ¹³C-NMR spectra were recorded on a Bruker Avance 300, using CDCl₃ or H₂O/D₂O as solvent. For TEM analysis one drop of the aqueous solution of each sample was deposited on the chloroform cleaned carbon coated Cu TEM grid, the solvent was then evaporated and the sample analyzed by using TEM Tecnai G2 (FEI) operating at 100kV with a 70 mm lens and with a 2.0Å° point-to-point resolution. Images were taken using Veleta (Olympus Soft Imaging System).

2.2. [Rh]/DHTANa preparation

2.2.1 Method A [7]

The precursor of [Rh]/DHTANa (A) was prepared *in situ* by reacting, at room temperature under a nitrogen purge, [Rh(COD)Cl]₂ (12.4 mg, 0.025 mmol) with a solution of dihydrothioctic acid sodium salt (DHTANa) (10.3 mg, 0.5 mmol) in 5 mL of de-aerated water. ¹H-NMR (H₂O/D₂O): δ

3.61 (m, 1H, S-**CH**), 3.12 (m, 2H, S-**CH₂**), 2.08 (t, J = 7.2 Hz, 2H, **CH₂-COONa**), 1.90-1.78 (m, 2H, HSCH₂**CH₂**CHSH), 1.72-1.30 (m, 8H, (**CH₂**)₃, 2 **SH**). The catalytic species [Rh]/DHTANa (A) was then formed during the hydrogenation reaction.

2.2.2 Method B

50 mg of RhCl₃ (0.23 mmol of Rh), 88 mg (0.83 mmol) of Na₂CO₃ and 10 mL of dry CPME were introduced in a 150 mL stainless steel autoclave under nitrogen. The autoclave was pressurized with 0.5 Mpa of hydrogen and warmed at 25 °C for 24 hours under stirring. After this time, a solution of 49.7 mg (0.23 mmol) of DHTA, prepared as described above, in 2 mL of CPME was added followed by 25.3 mg (0.24 mmol) of Na₂CO₃ in 24 mL of de-aerated water; the resulting mixture was stirred for 24 h at 25 °C under nitrogen atmosphere. The organic phase was removed and the light gray coloured aqueous phase containing [Rh]/DHTANa (B) was used as such in catalysed hydrogenation reactions. A sample was analysed by ¹H-NMR (H₂O/D₂O) (Figure 1SP): δ 3.66 (m, 1H, S-**CH**), 3.18 (m, 2H, S-**CH₂**), 2.43 (m, 1H, HSCH₂**CH(H)**CHSH), 2.12 (t, J = 7.2 Hz, 2H, **CH₂-COONa**), 1.94 (m, 1H, HSCH₂**CH(H)**CHSH), 1.78-1.45 (m, 6H, (**CH₂**)₃), 1.42-1.28 (m, 2H, 2**SH**).

2.3 General procedure for hydrogenation experiments in the presence of [Rh]/DHTANa

If not otherwise reported (see details in Tables) all the reactions were carried out following a procedure similar to that below described for [Rh]/DHTANa catalyzed hydrogenation of 1-iodo-4-nitrobenzene (**V**).

A 150-mL stainless steel reaction vessel was charged, under a nitrogen purge, with 312 mg (1.25 mmol) of **V** in 2 mL of toluene, 1 mL of 0.005 M solution of [Rh]/DHTANa, obtained by A or B procedure, and 2 mL of degassed distilled water. The reactor was then pressurized with hydrogen (4 MPa) and heated at 80°C for 24h. The reactor was then cooled to room temperature, the residual gases released and the reaction mixture analysed by GC and GC-MS. Before separation of the two

phases pH of the aqueous phase was checked and restored to initial pH value, if necessary, by adding an aqueous solution of Na_2CO_3 . The organic phase was separated, the aqueous phase extracted with toluene (2 x 2mL) and the combined organic solution was finally concentrated under vacuum to recover the reaction products. The aqueous phase, containing the catalyst, was recovered and reused for further experiments.

3. Results and Discussion

3.1 Characterization of [Rh]/DTHANa

$^1\text{H-NMR}$ of catalyst, prepared by method B (Figure 1SP), permits, in our opinion, to have a clear picture of Rhodium species in aqueous phase. Rhodium seems to be strongly chelated by DTHANa as demonstrated not only by the shift of signals of hydrogen atoms in S-CH (δ 3.66 vs 2.92) and S-CH_2 (δ 3.18 vs 2.60) in [Rh]/DTHANa compared with the free ligand, but especially by the differentiation of chemical shift of the 2 hydrogen atoms of methylene group $\text{HSCH}_2\text{CH}_2\text{CHSH}$ (δ 2.43 and 1.94) vs undifferentiated multiplet, between δ 1.90-1.78, of the same group in the free ligand and also in the catalyst precursor, obtained by method A before hydrogen treatment, where Rh-Cl bond should be still present. The identity of the proton signals of this methylene group in [Rh]/DTHANa was confirmed by decoupling experiments.

TEM images of fresh prepared [Rh]/DTHANa (B), recycled [Rh]/DTHANa (B) and recycled [Rh]/DTHANa (A) are reported as supplementary material (Figures 2-5SP respectively). No relevant difference were observed for recycled catalysts prepared with methods A and B to confirm that, after hydrogen treatment, the catalytic species, which are very reasonably rhodium nanoparticles stabilized by the thioligand, are equivalent. Slight bigger aggregates were found in fresh prepared [Rh]/DTHANa (B). It is reasonable considering that Rh(0) particles could aggregate before the addition of the ligand, even if after the hydrogenation reaction more disperse catalytic species were found.

3.2 Catalytic experiments

A first set of hydrogenation experiments was carried out on nitrobenzene (**I**) as substrate (Scheme 2), by using a 1000/1 substrate to catalyst molar ratio in the aqueous biphasic system H₂O/THF, at 80°C and 24h, under different H₂ pressure (Table 1).

Insert Scheme 2

Insert Table 1

At 5 MPa of H₂, aniline (**II**) was obtained with 100% yield (Entry 1). Upon decreasing the hydrogen pressure up to 2 MPa, complete conversion and 99% selectivity to **II** were achieved (Entry 2). After extraction of the organic products with diethyl ether, the catalyst, embedded in the aqueous phase, was used in consecutive experiments; noteworthy, the catalytic activity and selectivity to **II** remained almost unchanged even after three recycling experiments (Entries 3-5).

The reduction was also carried out lowering H₂ pressure to 1 Mpa but a low conversion (65%) was observed at the same reaction time (Entry 6). Very poor results were obtained using toluene/water solvent mixture instead of THF/water (Entry 7). Good results were achieved in THF/water also using [Rh]/DHTANa prepared by the B procedure and the catalyst remained stable at least for two recycles (Entries 8-10); less satisfactory conversion resulted in toluene/water (Entry 11). Using [Rh]/DHTANa prepared by A or B procedure, side reaction products as nitrosobenzene, N-phenylhydroxylamine, azobenzene and azoxybenzene were undetected or present in negligible amount (Entries 2-5). For comparison, a reaction was carried out also in the presence of 0.18% Rh/Al₂O₃ at the same experimental conditions in THF/water: aniline (**II**) was obtained with 99% yield (Entry 12). Furthermore, the recovered heterogeneous catalyst maintained its activity and selectivity unchanged in a recycle experiment (Entry 13). Surprisingly this heterogeneous catalyst afforded different reaction products working in toluene/water, being able to hydrogenate also the aromatic ring (entry 14).

Later it was decided to explore the reduction of 1-chloro-3-nitrobenzene (**III**) and of 1-iodo-4-nitrobenzene (**V**) to check the selectivity of the catalysts towards two different reactive groups. Water soluble [Rh]/DHTANa showed good activity and high selectivity also working in the hydrogenation of both **III** (Scheme 3) and **V** (Scheme 4).

Insert Scheme 3

Insert Table 2

In these experiments on substrate **III**, carried out in water/toluene at 80°C and 4 MPa of H₂ for 24 h and by using a 500/1 substrate to catalyst molar ratio, [Rh]/DHTANa, prepared by A or B method, afforded the same results (Entries 1 and 5, Table 2); product **IV** was recovered with high yield and selectivity and the catalyst was recycled three times without any relevant activity change (Entries 1-4, 5-8). On the contrary, the heterogeneous catalyst 0.18% Rh/Al₂O₃ was less selective affording also 15-17% of dehalogenated side product **II**; however the catalyst activity and recyclability were good (Entries 9 and 10).

Insert Scheme 4

Insert Table 3

In the case of a more demanding reaction, i.e. the reduction of compound **V**, in the aqueous biphasic system H₂O/toluene, at 60 °C and 4 Mpa H₂ for 24 h and by using a 500/1 substrate to catalyst molar ratio, a 85 % substrate conversion to **VI** was obtained and no dehalogenation was observed (Entry 1, Table 3). Noteworthy, upon increasing the reaction temperature at 80 °C a quantitative conversion was found and **VI** was recovered with 97% yield, being the side product **II** formed in a very small amount (Entry 2). The catalyst, embedded in the aqueous phase, was recovered after the separation of the organic phase and used in two recycle experiments. It was observed that a slight

change in the pH occurred due to the formation of HI and a lower activity but similar selectivity was found (unreported data); by restoring the initial pH adding the requested amount of Na_2CO_3 good results were obtained (Entries 3,4,6,7). As a possible explanation of the results observed without any correction of pH, we can assume that some changes in the catalyst structure occur. As a matter of fact, the isolated dried solid $[\text{Rh}]/\text{DHTANa}$, obtained by evaporation of water under vacuum, was solubilized in CDCl_3 : after carefully addition of a drop of conc. HCl , its $^1\text{H-NMR}$ showed a complex pattern spectrum where, besides the peaks tributary to the starting catalytic species, some other signals were present (Figure 5SP). It is reasonable to assume that other species are formed, probably due to the fact that the interaction of thiol groups and Rh species was partially broken.

Also 0.18 % $\text{Rh}/\text{Al}_2\text{O}_3$ was investigated in the hydrogenation of **V** at the above reaction conditions: disappointingly, the main product (60%) was aniline (**II**) (Entry 8). The catalyst maintained its activity also in a recycle experiment but, again, aniline was the prevailing product (Entry 9). The best result was obtained at 60°C and 1 MPa of H_2 : substrate conversion was complete and the iodoaniline **VI** was obtained with 86% yield (Entry 11). Maybe milder reaction conditions should be required to try to improve further the selectivity to the desired compound **VI**. Unfortunately the recycle of this catalyst gave a very poor result (Entry 12). Finally, $[\text{Rh}]/\text{DHTANa}$ was compared also to the well-known water soluble $[\text{Rh}]/\text{TPPTS}$ complex: this catalytic system was very active affording a total substrate conversion but aniline (**II**) was the only reaction product (Entries 13-15). Moreover, the catalyst, at the reaction conditions adopted, strongly decomposed with formation of rhodium black, so hampering any catalyst recycling.

4. Conclusions

The water soluble $[\text{Rh}]$ -thioligand species, i.e., $[\text{Rh}]/\text{DHTANa}$, showed an interesting catalytic activity, excellent selectivity and good recyclability not only in the reduction of nitrobenzene but especially in the hydrogenation of some valuable aromatic halo-nitro compounds. Its preparation

was made simpler and cheaper than the previous reported one [7], without affecting its reactivity, stability and recyclability characteristics. At the light of these results [Rh]/DHTANa seems a good choice for the selective reduction of the nitro group when also a halo group is present in the same molecule [10].

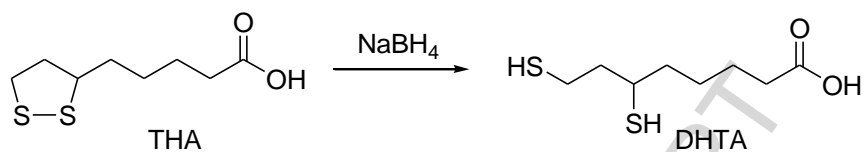
Acknowledgment

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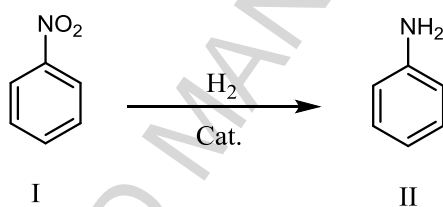
References

- [1] B. Cornils, W.A. Herrmann, I.T. Horvath, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt (Eds.), *Multiphase Homogeneous Catalysis*, Wiley-VCH, Weinheim, 2005.
- [2] F. Joà (Ed.), *Aqueous Organometallic Catalysis*, Kluwer Acad. Publ., Dordrecht, 2001.
- [3] B. Cornils, W.A. Herrmann (Eds.), *Aqueous-Phase Organometallic Catalysis*, 2nd ed., Wiley-VCH, Weinheim, 2004.
- [4] C. Bertucci, C. Botteghi, D. Giunta, M. Marchetti, S. Paganelli, *Adv. Synth. Catal.* 344 (2002) 556–562
- [5] M. Marchetti, F. Minello, S. Paganelli, O. Piccolo, *Appl. Catal. A: Gen.* 373 (2010) 76–80.
- [6] S. Di Dio, M. Marchetti, S. Paganelli, O. Piccolo, *Appl. Catal. A: Gen.* 399 (2011) 205–210

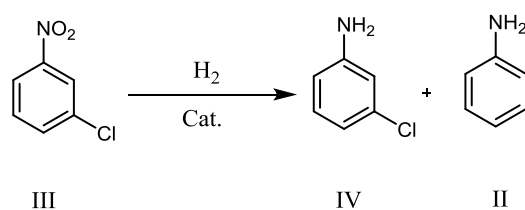
- [7] S. Paganelli, O. Piccolo, P. Pontini, R. Tassini, V.D. Rathod, *Catalysis Today*, 247 (2015) 64-69.
- [8] O. Piccolo, A. Verrazzani, *US* 7087548 (2006)
- [9] O. Piccolo, S. Paganelli, R. Tassini, V.D. Rathod, B. Onida, S. Fiorilli, 6th Int. Confer. on Green and Sustainable Chemistry (GSC 6), Nottingham (UK) (2013), O 16
- [10] H. K. Kadam, S. G. Tilve, *RSC Adv.*, 5 (2015) 83391-83407.



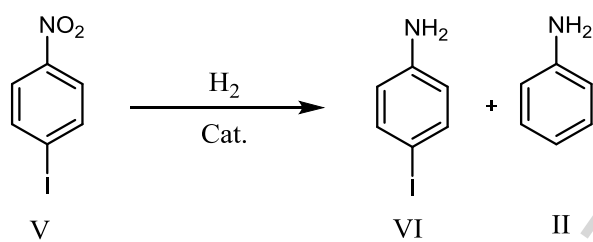
Scheme 1. Reduction of thioctic acid (TA) into dihydrothioctic acid (DHTA)



Scheme 2. Reduction of nitrobenzene (I)



Scheme 3. Reduction of 1-Chloro-3-nitrobenzene (III)



Scheme 4 . Reduction of 1-Iodo-4-nitrobenzene (V)

Table 1. Reduction of nitrobenzene (I)

Entry	Catalyst (prep. method) ^a	p(H ₂) (MPa)	Conv. (%)	II (%)
1	[Rh]/DHTANa (A)	5	>99	>99
2	[Rh]/DHTANa (A)	2	>99	99
3 ^b	1° recycling	2	>99	98
4 ^b	2° recycling	2	>99	99
5 ^b	3° recycling	2	>99	97
6	[Rh]/DHTANa (A)	1	65	65
7 ^c	[Rh]/DHTANa (A)	2	27	27
8	[Rh]/DHTANa (B)	2	>99	>99
9 ^b	1° recycling	2	>99	>99
10 ^b	2° recycling	2	90	90
11 ^c	[Rh]/DHTANa (B)	2	53	53
12 ^d	0.18%Rh/Al ₂ O ₃	2	>99	99
13 ^b	1° recycling	2	>99	99
14 ^e	0.18%Rh/Al ₂ O ₃	2	>99	-- ^f

Reaction conditions: substrate (I) = (0.62 g, 5 mmol); [Rh]/DHTANa 0.005M solution (1 mL), (substrate I / Rh molar ratio 1000/1); THF = 2 mL; H₂O = 2 mL; T= 80°C; t = 24h. ^a According to paragraphs 2.2.1 and 2.2.2. ^b Reaction carried out by using the catalyst recovered from the previous run. ^c Toluene = 2 mL; H₂O = 2 mL. ^d Substrate (I) = (0.62 g, 5 mmol); Rh/Al₂O₃ 0.18 % (0.29 g), (substrate I /Rh molar ratio = 1000/1); THF = 2 mL; H₂O = 2 mL; T= 80°C; t = 24h. ^e Toluene = 2 mL; H₂O = 2 mL. ^f Product mixture: 73% cyclohexylamine and 27% dicyclohexylamine.

Table 2. Reduction of 1-chloro-3-nitrobenzene (III)

Entry	Catalyst (prep. method) ^a	Conv.(%)	IV (%)	II (%)
1	[Rh]/DHTANa (A)	>99	>99	-
2 ^b	1° recycle	>99	>99	-
3 ^b	2° recycle	98	98	-
4 ^b	3° recycle	99	99	-
5	[Rh]/DHTANa (B)	>99	>99	-
6 ^b	1° recycle	>99	>99	-
7 ^b	2° recycle	>99	99	1
8 ^b	3° recycle	99	99	-
9 ^c	0.18%Rh/Al ₂ O ₃	98	81	17
10 ^b	1° recycle	90	75	15

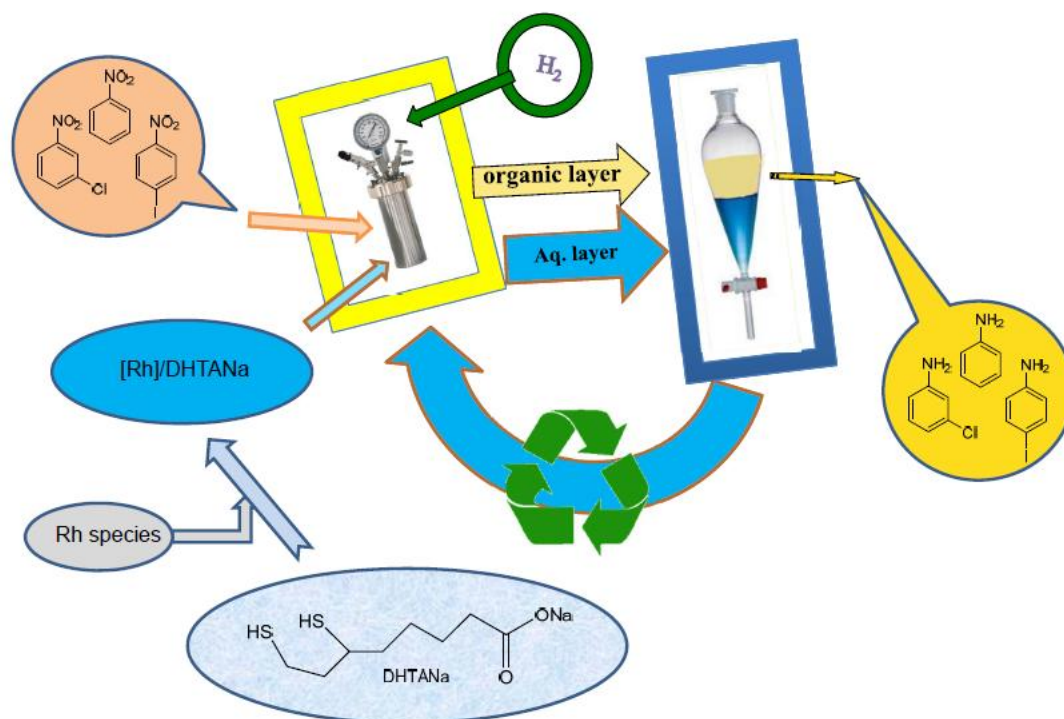
Reaction conditions: substrate (III) = (0.395 g, 2.5 mmol); [Rh]/DHTANa 0.005M solution (1 mL), (substrate III/ Rh molar ratio 500/1); Toluene = 2 mL; H₂O = 2 mL; T= 80°C; p(H₂) = 4 MPa; t = 24h. ^a According to paragraphs 2.2.1 and 2.2.2. ^b Reaction carried out by using the catalyst recovered from the previous run; ^c Substrate (III) = (0.395 g, 2.5 mmol); 0.18 % Rh/Al₂O₃ (0.29 g), (substrate III / Rh molar ratio = 500/1); Toluene = 4 mL.

Table 3. Reduction of 1-iodo-4-nitrobenzene (V)

Entry	Catalyst (prep. method) ^a	p(H ₂) (MPa)	Conv. (%)	VI (%)	II (%)
1 ^b	[Rh]/DHTANa (A)	4	85	85	-
2	[Rh]/DHTANa (A)	4	>99	97	2
3 ^c	1° recycle	4	>99	98	2
4 ^c	2° recycle	4	>99	95	5
5	[Rh]/DHTANa (B)	4	>99	>99	-
6 ^c	1° recycle	4	>99	99	1
7 ^c	2° recycle	4	>99	96	4
8 ^d	0.18% Rh/Al ₂ O ₃	4	97	38	60
9 ^c	1° recycle	4	97	40	57
10 ^e	0.18% Rh/Al ₂ O ₃	4	>99	78	22
11 ^f	0.18% Rh/Al ₂ O ₃	1	>99	86	14
12 ^e	1° recycle	1	21	15	6
13 ^g	[Rh]/TPPTS	4	>99	-	>99
14 ^h	[Rh]/TPPTS	4	>99	-	>99
15 ⁱ	[Rh]/TPPTS	1	>99	-	>99

Reaction conditions: substrate (V) = (0.31 g, 1.25 mmol); [Rh]/DHTANa 0.005M solution (1 mL), (substrate V/Rh molar ratio 500/1); Toluene = 2 mL; H₂O = 2 mL; T= 80°C; t = 24h. ^a According to paragraphs 2.2.1 and 2.2.2. ^b T= 60°C. ^c Reaction carried out by using the catalyst recovered from the previous run. ^d Substrate (V) = (0.31 g, 1.25 mmol); 0.18 % Rh/Al₂O₃ (0.29 g) (substrate V/Rh molar ratio = 500/1); Toluene = 4 mL; T= 60°C; t = 24h. ^e T = 80°C; t = 5h. ^f T= 60°C; t = 5h. ^g Reaction conditions for experiments catalyzed by [Rh/TPPTS]: substrate (V) = (0.62 g, 2.5 mmol); [Rh(COD)Cl]₂ = (0.00124 g, 0.0025 mmol), (substrate V/Rh molar ratio 500/1); TPPTS (triphenylphosphine-3,3',3''-trisulfonic acid trisodium salt) = (0.0085 g, 0.015 mmol), (Rh/TPPTS molar ratio 1/3); Toluene = 3 mL; H₂O = 3 mL; T= 80°C; t = 24h. ^h Addition of 0.265 g (2.5 mmol) of Na₂CO₃; ⁱ T= 60°C; t = 24h.

Graphical abstract



ACC

Highlights

[Rh]/DHTANa, a water-soluble catalyst.

[Rh]/DHTANa is suitable for selective hydrogenation of halonitro arenes.

[Rh]/DHTANa is easily recovered and reused with similar activity and selectivity.

New preparation of [Rh]/DHTANa is simple and greener.

[Rh]/DHTANa does not cause hydrogenolysis of carbon-halogen bond.