Highly efficient catalysts for the hydrogenation of nitro-substituted aromatics†

Robert Raja,*[a] Vladimir B. Golovko,[a] John M. Thomas,[bc] Angel Berenguer-Murcia,[d] Wuzong Zhou,[e] Songhai Xie[e] and Brian F. G. Johnson[a]

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Nanoparticles of Co and NiPd, derived from colloidal precursors and supported on commercially available non-ordered mesoporous silica, are highly effective, cheap, recyclable and industrially viable catalysts for the hydrogenation of a range of nitro-substituted aromatics under mild conditions.

Aminoaromatics, produced by the selective catalytic hydrogenation of corresponding nitro precursors, are important intermediates for agrochemicals, pharmaceuticals, dyestuffs, urethanes and other industrially important products.[1–3] Raney nickel is widely used as catalyst but suffers the twin disadvantages of being moisture sensitive and pyrophoric.[4] Palladium on carbon is also known to catalyse this reaction but it is more expensive and also quite sensitive to trace impurities.[5] A number of homogeneous catalysts encompassing macromolecule–metal complexes as well as mono- and bi-metallic platinum- or palladium-based heterogeneous catalysts and polymer-anchored palladium anthranilic acid complexes have also been reported as viable catalysts for this hydrogenation.[6–9] However low turnover numbers and the concomitant use of external sources of hydrogen (such as triethyl ammonium or methyl formate), hydrogen-transfer media (cyclohexene in ethanol, for example), involvement of a suitable base (tri-*n*-butylamine or pyridine) in the catalytic cycle, reflux temperatures and high pressures (800 psi) coupled with longer reaction times, and diffusion limitations (where microporous solids are used) preclude the wider commercial applicability of these catalysts.

Compared to the wealth of information available on the hydrogenation of nitro- and dinitro-benzenes, halonitro-benzenes, nitroanilines and nitrophenols, there are comparatively few reports dealing with the hydrogenation of nitrocresols. A convenient reliable catalytic method for the ready production of aminocresols is therefore required. In this communication we report the direct hydrogenation of 3-nitro-*o*-cresol, as a representative of the nitrocresol family, under mild conditions using a simple strategy that is also applicable for the reduction of nitrobenzene and other nitrophenols. The catalyst consists of monometallic cobalt or bimetallic nickel–palladium (Fig. 1) nanoparticles prepared by well-known inverse-micelle (Co)[10,11] or by polyol reduction (NiPd)[12] methods with some modifications.† The performance of the cobalt-based catalysts (high selectivity and reactivity {see TOF in Table 1}) is comparable to those of their of Pd-containing analogues, and, they are also relatively inexpensive to synthesize. The silica-immobilized catalysts are also easily recyclable. A NiPd colloid, known[12] to be an active catalyst for the hydrogenation of nitrobenzene, is used here as a model Pd-containing catalyst.

The nanoparticles are supported on thermally robust, attrition resistant, cheap, commercially available non-ordered mesoporous silica of sharply-defined mean pore diameter 60 ± 8 Å. (Both the monometallic and bimetallic nanoparticles and the mesoporous silica support are distinctly different from those used by us[13] in previous selective hydrogenations.) Moreover, it is possible to study the silica-immobilized nanoparticles by means of transmission electron microscopy and tomography to get a clearer picture of catalyst composition and structure before and after catalysis.[14] Finally, soluble metal nanoparticle-based hydrogenation catalysts often suffer from modest activity and decreased life-times,[15a] due to numerous catalyst decomposition processes, such as agglomeration of nanoparticles,[15b] which take place in solution. The merits of the mesoporous silica support, which we have also used[16] for enantioselective hydrogenations *via* anchored asymmetric organometallic catalysts, are that it is much more thermally stable than the highly ordered (micelle-templated) mesoporous silicas typified by the M41S and SBA families.[5] Moreover, the silica support of our choice is produced by controlled hydrolysis[17] and, thus, does not require the use of expensive structure-directing agents for growth and de-templation before use.

Detailed descriptions of the characterization of these catalysts are not yet available, but high resolution transmission electron microscopy (HRTEM) studies‡ show (Fig. 1) that the nanoparticles are well-distributed over the support and the particle size distribution is reasonably sharp. The average particle size of Co is about 4.3 nm, while that of NiPd is marginally smaller (3.0 nm). The compositions of both samples were examined and confirmed by energy dispersive X-ray microanalysis (EDX). The catalytic tests were performed in a PTFE-lined, high-pressure reactor (Parr) using high purity hydrogen at *ca.* 25 bar initial pressure. The products were analysed (using mesitylene as the internal standard) by gas chromatograpgy (GC, Varian, Model 3400 CX) employing a HP-1 capillary column (25 m × 0.32 mm) and flame ionisation detector. The catalysts were re-used thrice (to test their recyclability) and the results show (Table 1) that reproducibility is high. Hot filtration experiments and ICP measurements were independently carried out to rule out the possibility of leaching. In summary the performance of Co and NiPd nanoparticles, immobilized on non-ordered mesoporous silica, is reported for the hydrogenation of nitro-substituted aromatics under mild

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† Electronic supplementary information (ESI) available: experimental details for the synthesis of Co and NiPd nanoparticles, their purification and preparation of the supported catalysts. See http://www.rsc.org/suppdata/cc/b4/b418273a/

*robert@ri.ac.uk

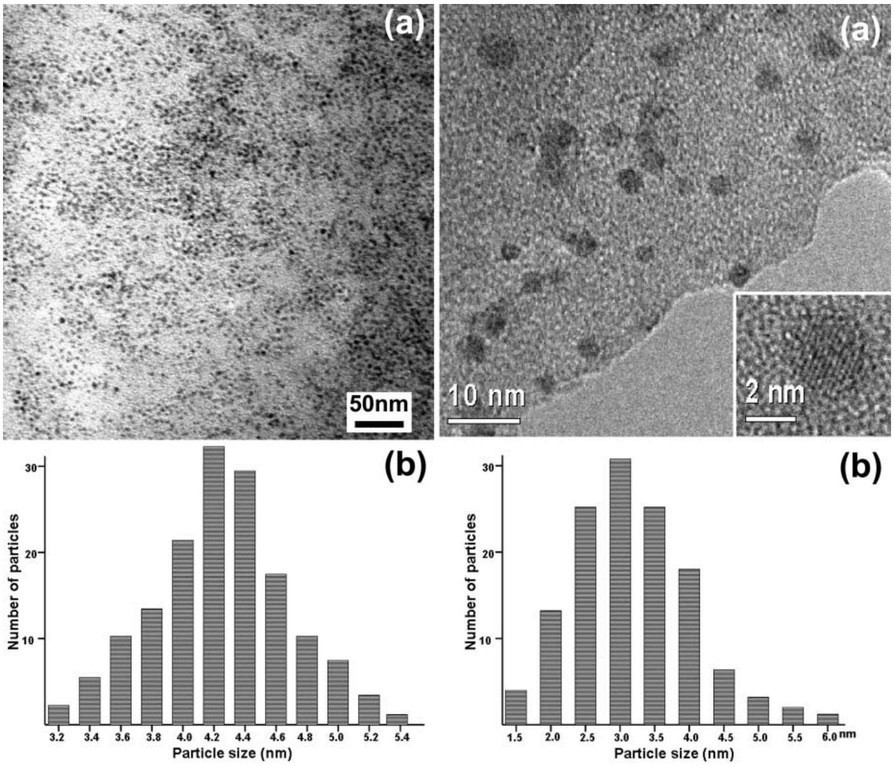

Fig. 1 Left: (a) TEM image of Co nanoparticles on a silica support; (b) a diagram of particle size distribution. Right: (a): TEM image of NiPd nanoparticles on a silica support showing the size and morphology of the particles. The inset is a typical HRTEM image of a NiPd nanoparticle; (b): a diagram of particle size distribution.

Table 1 Hydrogenation of nitro-substituted aromatics using colloidal catalysts[a]

						Product Selectivity		
Colloidal catalyst immobilized on silica (60 Å)	Substrate	Solvent	Time/h	Conversion/mol%	TOF/h^{-1}	Aniline	3-Amino-phenol	3-Amino-*o*-cresol
Co-colloid	nitrobenzene	—	2	59.2	23119	100	—	—
			4	89.8	17534	100		
NiPd-colloid	nitrobenzene	—	2	75.8	24827	100	—	—
			4	98.5	16131	97.3		
Co-colloid (recycle 2)	nitrobenzene	—	4	89.2	17417	100	—	—
Co-colloid (recycle 3)	nitrobenzene	—	4	90.1	17593	100	—	—
NiPd-colloid (recycle 2)	nitrobenzene	—	4	97.8	16016	96.5	—	—
NiPd-colloid (recycle 3)	nitrobenzene	—	4	98.3	16098	97.8	—	—
Co-colloid	3-nitrophenol	THF	2	45.9	19030	—	100	—
			4	81.5	16900	—	100	
NiPd-colloid	3-nitrophenol	THF	2	74.7	25980	—	100	—
			4	95.3	16570	—	98.2	
Co-colloid (recycle 2)	3-nitrophenol	THF	4	81.2	16835	—	100	—
Co-colloid (recycle 3)	3-nitrophenol	THF	4	81.1	16815	—	100	—
NiPd-colloid (recycle 2)	3-nitrophenol	THF	4	94.8	16485	—	98.6	—
NiPd-colloid (recycle 3)	3-nitrophenol	THF	4	95.7	16640	—	98.3	—
Co-colloid	3-nitro-*o*-cresol	THF	2	40.3	15182	—	—	100
			6	76.9	9657	—		100
NiPd-colloid	3-nitro-*o*-cresol	THF	2	57.7	18231	—	—	100
			6	91.3	9618	—		96.5
Co-colloid (recycle 2)	3-nitro-*o*-cresol	THF	6	77.0	9669	—	—	100
Co-colloid (recycle 3)	3-nitro-*o*-cresol	THF	6	76.6	9619	—	—	100
NiPd-colloid (recycle 2)	3-nitro-*o*-cresol	THF	6	92.0	9690	—	—	97.1
NiPd-colloid (recycle 3)	3-nitro-*o*-cresol	THF	6	91.7	9658	—	—	97.0

[a] Reaction conditions: nitrobenzene ≈25 g; 3-nitrophenol ≈1.5 g; 3-nitro-*o*-cresol ≈0.5 g; THF = 30 ml; catalyst ≈0.3 g (nitrobenzene); ≈0.015 g (3-nitrophenol); ≈0.005 g (3-nitro-*o*-cresol); T = 353 K (nitrobenzene); 373 K (3-nitrophenol, 3-nitro-*o*-cresol); TOF = $[(\mathrm{mol}_{\mathrm{substr}})(\mathrm{mol}_{\mathrm{colloid}})^{-1}\mathrm{h}^{-1}]$

conditions. These relatively cheap and recyclable catalysts are industrially significant as they are highly selective and display exceptionally high turnover frequencies for the above-mentioned hydrogenations.

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Robert Raja,*[a] Vladimir B. Golovko,[a] John M. Thomas,[bc]
Angel Berenguer-Murcia,[d] Wuzong Zhou,[e] Songhai Xie[e] and
Brian F. G. Johnson[a]
[a]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW. E-mail: robert@ri.ac.uk
[b]Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, UK CB2 3QZ
[c]Davy Faraday Research Laboratory, The Royal Institution of Great Britain, 21 Albemarle Street, London, UK W1X 4BS
[d]Department of Inorganic Chemistry, University of Alicante, Ap. 99-03080, Alicante, Spain
[e]School of Chemistry, University of St. Andrews, St. Andrews, Fife, Scotland, UK KY16 9ST

Notes and references

‡ Specimens for the HRTEM studies were prepared by spreading the powder samples in acetone, depositing one drop of the suspension on a specimen grid coated with a holey carbon film. HRTEM images were recorded on Jeol JEM-2011 electron microscope using Gatan 794 CCD camera at magnifications up to 1 million times. Compositions of the specimens were examined by EDX using Oxford Link ISIS system.

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