Surfactant-Stabilized Aqueous Iridium(0) Colloidal Suspension: An Efficient Reusable Catalyst for Hydrogenation of Arenes in Biphasic Media

Vincent Mévellec,[a] Alain Roucoux,[a,*] Esther Ramirez,[b] Karine Philippot,[b] Bruno Chaudret[b]

[a] UMR CNRS 6052, "Synthèses et Activations de Biomolécules", Ecole Nationale Supérieure de Chimie de Rennes – Institut de Chimie de Rennes, Avenue du Général Leclerc, 35700 Rennes, France
E-mail: alain.Roucoux@ensc-rennes.fr
[b] Laboratoire de Chimie de Coordination du CNRS, UPR 8241, 205 route de Narbonne, 31077 Toulouse Cedex 04, France
E-mail: chaudret@lcc-toulouse.fr

Received: October 3, 2003; Accepted: December 20, 2003

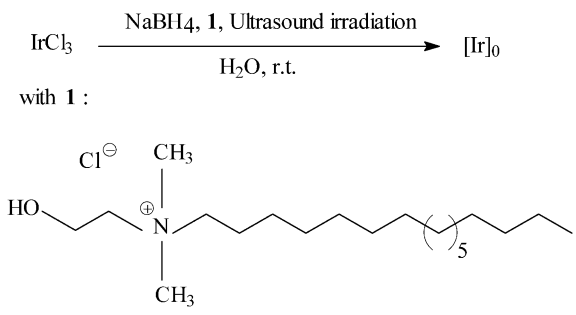
Abstract: Aqueous suspensions of iridium nanoparticles produced by the chemical reduction of $IrCl_3$ assisted by sonication, in the presence of *N*,*N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt as surfactant, have shown an efficient activity for the catalytic hydrogenation of various aromatic derivatives in biphasic media under mild conditions. These nanocatalysts can be reused for further runs with a total conservation of activity and provided significant catalytic lifetime for anisole hydrogenation in pure water with 3000 total turnover (TTO).

Keywords: arenes; biphasic catalysis; hydrogenation; iridium; nanoparticles; surfactants

Introduction

The total or partial hydrogenation of benzene derivatives represents an industrial catalytic challenge, in particular with the increasing industrial demand for low-aromatic Diesel fuels[1] due to serious health issues.[2] Moreover the conversion of benzene to cyclohexane, a key intermediate in adipic acid production, is still the most important industrial hydrogenation reaction of monocyclic arenes.[3] The catalytic transformation is generally carried out under drastic conditions with rhodium or ruthenium homogeneous or heterogeneous catalysts but a few examples also describe the use of Pd, Pt, Ni and Co as metal catalysts.[4,5] In the past five years, the use of nanoparticles in this active research area has received increased attention since some homogeneous catalysts have been shown to be "microheterogeneous".[5] In this context, the use of rhodium and ruthenium nanoparticles for the hydrogenation of benzene derivatives has been widely studied.[5,6] Attention is presently focused on nanoparticles of an alternative noble metal such as iridium. For example, iridium particles supported on γ-alumina or silica are known to catalyze the hydrogenation of benzene and toluene after important surface treatments.[7] The use of ionic liquids for the formation and stabilization of iridium(0) nanoclusters which are active catalysts for the hydrogenation of olefins and arenes has recently been reported.[8] In this approach, the reaction mixture forms a typical two-phase system: the lower phase containing the iridium particles in 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI \cdot PF_6$) and the upper one the organic products. Nevertheless, it seems that the best results (conversion, recycling) were obtained with isolated Ir(0) nanoparticles in the solid state ("solvent-less conditions") and not in biphasic liquid conditions with redispersed nanoparticles in $BMI \cdot PF_6$.

Here, we describe the efficient hydrogenation of various benzene compounds in biphasic liquid-liquid (water/hydrocarbon) systems by surfactant-protected iridium(0) nanoparticles and show the competitive advantage of this catalyst by comparison with previous catalyst systems (Table 1). The interest of our approach



Scheme 1.

  DOI: 10.1002/adsc.200303157

Table 1. Comparison of rhodium and iridium nanoparticles for the hydrogenation of anisole and/or benzene in biphasic liq/liq systems.

Systems	Substrate	Conditions (T[°C], P_{H_2})	Products (%)	TTO[a]	Time (h)	TOF[b] (h^{-1})	Recyclability	Ref.
Rh^0, polyoxyanion and tetrabutylammonium	Anisole	22, 3 bars	Methoxycyclohexane (91)Methoxycyclohexene (8)	2600	144	54	Not demonstrated	[5c]
Rh^0, PVP	Benzene	30, 7 bars	Cyclohexane (100)	3600	16	675	Yes	[6c]
Rh^0, tetrabutylammonium hydrogen sulfate	Anisole	36, 10 bars	Methoxycyclohexane (77)	77	62	3.6	Not demonstrated	[6e]
Rh^0, bmi · PF_6	Anisole	75, 4 bars	Methoxycyclohexane (100)	246	6	123	Yes	[8a]
	Benzene	75, 4 bars	Cyclohexane (100)	242	22	33	Yes	[8a]
Rh^0, hydroxyalkyl-ammonium bromide salts	Anisole	25, 1 bar	Methoxycyclohexane (100)	2000	37	188	Yes	[9]
	Benzene	25, 1 bar	Cyclohexane (100)	400	14	91	Yes	[9]
Ir^0, solvent-less[c]	Anisole	75, 4 bars	Methoxycyclohexane (84)Cyclohexane (16)	180	18	30	Yes	[8a]
	Benzene	75, 4 bars	Cyclohexane (100)	3509	32	328	Yes	[8a]
Ir^0, hydroxyalkyl-ammonium chloride salts	Anisole	25, 40 bars	Methoxycyclohexane (100)	3000	45	200	Yes	this paper
	Benzene	25, 40 bars	Cyclohexane (100)	100 [d]	0.8	375	Yes	this paper

[a] Total turn-over defined as moles of substrates per moles of metal.
[b] Turn-over frequency (related to H_2 consumed) defined as turn-over divided by time.
[c] Not a biphasic liquid/liquid system.
[d] Standard test result, not optimized.

is the use as catalyst of colloidal metallic particles, finely dispersed in water,[9] a solvent that continues to attract attention for economic and ecological reasons since biphasic catalysis appears as an undeniable solution to easily separate the catalyst from reaction products even if trace amounts of aromatic compound are generally hard to remove.[8a,10] The solubility of the nanoparticles is assured by their protective agent, a highly water-soluble surfactant which provides an electrosterical stabilization to prevent aggregation and to facilitate the recycling process.[9]

Results

In this system, the catalytically active aqueous suspensions consist of metallic iridium(0) nanoparticles prepared by reducing iridium trichloride with sodium borohydride in a dilute aqueous solution of the previously reported *N*,*N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt **1** (Scheme 1).[9] This reduction of the precursor is assisted by sonication during five minutes. The transformation of Ir^{3+} ions dissolved in water in zerovalent nanoparticles, which are known to absorb in the UV region, can be followed by UV measurements. A molar ratio **1**/Ir = 10 is necessary to provide very stable suspensions and to prevent aggregation. For a ratio **1**/Ir < 10, we observe a slight agglomeration of metal particles in aqueous solution after several days. A ratio of 10 is sufficient to stabilize colloidal particles within the aqueous phase if the preparation is assisted by sonication. In water and under these conditions, it is known that surfactant monomers may associate to form micelles, which favor the stabilization of the particles. Moreover, based on the excess of $NaBH_4$ and the low sonication time, it is very unlikely that the long chain of **1** contributes significantly to the reduction of Ir(III) through formation of potential reducing radical intermediates. To the best of our knowledge, this is the first example of the preparation of iridium nanoparticles stabilized by ammonium surfactant under sonochemical conditions.[11] Transmission electron microscopy (TEM) observations show that the particles are well-dispersed on the grid and monodispersed in size with an average diameter of 1.9 ± 0.7 nm, as shown on the size histogram which results from the measurement of about 400 particles. Figure 1 shows the obtained particle size distribution, which can be well fitted by a Gaussian curve. These Ir(0) aqueous suspensions are highly stable and can be stored in air without special precautions although some ppm O_2 can react with iridium nanoparticles as previously reported.[12]

The so-obtained catalytic system (Ir/**1**/water) is very efficient for the hydrogenation of various benzene

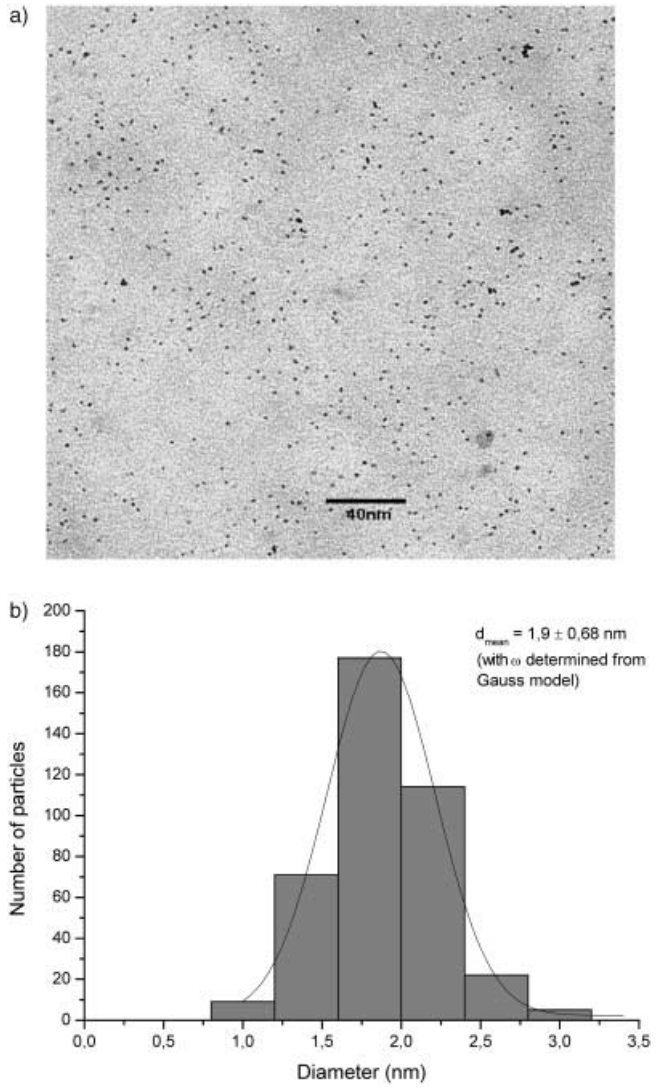


Figure 1. TEM micrograph and size distribution of Ir(0) nanoparticles stabilized by **1**.

derivatives such as mono- or disubstituted arenes and provides the corresponding saturated compounds without the hydrogenolysis products as usually observed with soluble transition metal nanoparticles.[5,8] In all cases, the conversion is complete after a few hours (Table 2) and no intermediates such as cyclohexene derivatives are observed during the catalysis. Moreover, no aggregates are visually observed at the end of these experiments. No induction period is observed but steric and electronic effects of substituents affect the reaction rate. Indeed, arenes substituted by electron-withdrawing groups react slowly (Table 2, entry 7) whereas the reaction is favored with electron-donating substituents (Table 2, entries 1, 4, 6). A total conversion is also observed for significant anisole/Ir molar ratios (entries 2, 3). 3000 TTO are demonstrated for anisole hydrogenation in 45 h at 20 °C and 40 bars of H_2, which

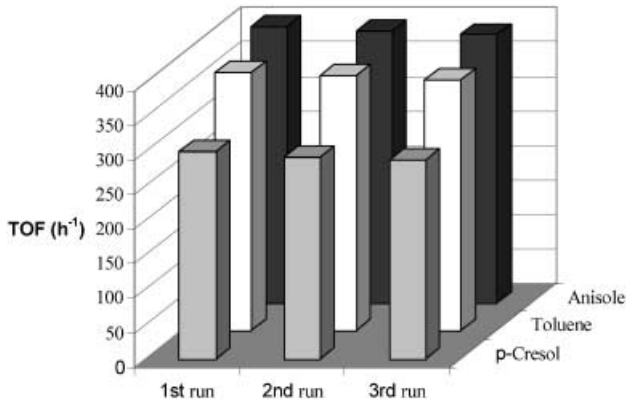


Figure 2. Recycling and catalytic lifetime.

corresponds to an average turnover frequency (TOF) of 66 mol anisole converted/(mol of Ir · h), the highest known TOF for arene hydrogenation in a two-phase system with a catalytic aqueous suspension of metallic nanoparticles. TOF are calculated according to the amount of introduced iridium without taking into account the true number of active metal sites, consequently TOF may be underestimated.[5b,5c] In addition to the hydrogenation of the aromatic ring, an *exo* C=C double bond may also be reduced (Table 2, entry 8). A rapid hydrogenation is also observed with disubstituted compounds such as cresol and xylene derivatives (Table 2, entries 9–14) leading to the major or exclusive production of the *cis*-diastereomers. This demonstrates the continuous coordination of the substrate to iridium nanoparticles during hydrogenation leading to the migration of hydrogen to only one face of the compound.[4,5]

The catalytic lifetime was studied by reusing the aqueous phase containing iridium nanoparticles after simple decantation in a separating funnel for three successive hydrogenation runs of various substrates: monoalkyl, monofunctionalized and disubstituted benzenes such as toluene, anisole and cresol, respectively. The results are given in Figure 2. In the first cycle, the turnover frequencies were found between 300 and 400 h^{-1} (400 h^{-1} for anisole, 375 h^{-1} for toluene, 300 h^{-1} for *p*-cresol). The aqueous suspensions are still active and present similar turnover activities during the successive runs (2^{nd} run = 397 h^{-1}, 3^{rd} run = 395 h^{-1} for anisole hydrogenation; 2^{nd} run = 370 h^{-1}, 3^{rd} run = 366 h^{-1} for toluene; 2^{nd} run = 296 h^{-1}, 3^{rd} run = 291 h^{-1} for *p*-cresol). These preliminary results demonstrate the efficient stability of the catalytically active iridium suspensions as previously observed with rhodium nanoparticles.[9]

Conclusion

New aqueous colloidal solutions of *N*,*N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt-pro-

Table 2. Hydrogenation of aromatic compounds under biphasic conditions.[a]

Entry	Substrate	Substrate/Ir^0 (mol/mol)	Product (yield %)[b]	Time (h)	TOF[c] (h^{-1})
1	Anisole	100	Methoxycyclohexane (100)	0.75	400
2	Anisole	1000	Methoxycyclohexane (100)	12	250
3	Anisole	3000	Methoxycyclohexane (100)	45	200
4	Phenol	100	Cyclohexanol (100)	1	300
5	benzene	100	Cyclohexane	0.8	375
6	Toluene	100	Methylcyclohexane(100)	0.8	375
7	Ethyl benzoate	100	Ethyl cyclohexanoate (100)	1.9	157
8	Styrene	100	Ethylcyclohexane (100)	1.16	344
9	*o*-Cresol	100	2-Methylcyclohexanol *cis* (90), *trans* (10)	1.5	200
10	*m*-Cresol	100	3-Methylcyclohexanol *cis* (80), *trans* (20)	1.2	250
11	*p*-Cresol	100	4-Methylcyclohexanol *cis* (78), *trans* (22)	1	300
12	*o*-Xylene	100	1,2-Dimethylcyclohexane *cis* (95), *trans* (5)	1.65	181
13	*m*-Xylene	100	1,3-Dimethylcyclohexane *cis* (85), *trans* (15)	1.4	214
14	*p*-Xylene	100	1,4-Dimethylcyclohexane *cis* (80), *trans* (20)	1.2	250

[a] Conditions : catalyst (1.85×10^{-5} mol), surfactant (1.85×10^{-4} mol), water (20 mL), hydrogen pressure (40 bars), temperature (20 °C), stirred at 1000 min^{-1}.
[b] Determined by GC analysis.
[c] Turn-over frequency defined as moles of H_2 per moles of iridium per hour.

tected Ir(0) nanoparticles could be easily prepared by reduction of $IrCl_3$. These solutions display a quantitative activity for the hydrogenation of various arene derivatives under mild conditions. In addition, an efficient recycling process without a significant loss of activity has been obtained. Finally, the study of the selectivity in the hydrogenation of disubstituted monocyclic reveals that without exception, the *cis* diastereomer is the major product. The surfactant-stabilized aqueous colloidal suspensions described here constitute the first efficient catalysts using iridium as noble metal for the hydrogenation of various monocyclic arenes in a pure biphasic system.

Experimental Section

Starting Materials

Iridium chloride hydrate was obtained from Strem chemicals. Sodium borohydride, *N,N*-dimethylethanolamine, chlorohexadecane and all substrates were purchased from Aldrich or Acros and were used without further purification. Water was distilled twice before use by conventional methods. *N,N*-Dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt 1 was prepared and fully characterized as previously reported.[9]

Analytical Procedures

A multiwave ultrasonic generator (Bioblock Scientific VCX 600) and a Ti-6Al-4V oscillator of 13 mm diameter were used for the ultrasonic irradiation and were operated at 20 kHz with an input power of 600 W. Sonication was carried out in a temperature-controlled water bath (about 25 °C). UV-Vis spectral measurements were obtained with a spectrophotometer UV-vis Cary 4000 (Varian) at 25 °C.

Specimens for TEM analysis were prepared by slow evaporation of a drop of the colloidal solution deposited onto a holey carbon grid. TEM studies were conducted using a JEOL 200CX-T electron microscope operating at 200 kV with a point-to-point resolution of 4.5 Å. The size distribution was built through a manual analysis of enlarged micrographs by measuring at least 400 particles on a given grid.

Gas chromatography was performed on a Carlo Erba GC 6000 with FID detector equipped with an Altech AT1 column (30 m, 0.25 mm inner diameter).

Synthesis of Aqueous Ir(0) Suspensions

The suspensions were prepared at 25 °C. Sodium borohydride (25 mg, 6.48×10^{-4} mol) was added to an aqueous solution of surfactant (90 mL, 1.44×10^{-2} mol L^{-1}). This solution was added all at once to an aqueous solution (50 mL) of the precursor $IrCl_3 \cdot 3\,H_2O$ (38.8 mg, 1.3×10^{-4} mol) to give an aqueous Ir(0) colloidal suspension (140 mL). This reduction was assisted by sonication during five minutes and the transformation of Ir^{3+} ions dissolved in water into zerovalent

nanoparticles was followed by UV measurements ($\lambda_{max} =$ 240 nm) and characterized by a color change from yellow to black.

General Procedure for Hydrogenation

The stainless steel autoclave was charged with the previously prepared aqueous suspension of Ir(0) (20 mL) and a magnetic stirrer. The appropriate substrate (1.85×10^{-3} mol) was added into the autoclave and dihydrogen was admitted to the system at constant pressure (40 atm). The mixture was stirred until the reaction was finished. Samples for gas chromatographic analysis were removed from time to time. After complete hydrogenation the two phases were separated by extraction and decantation. The aqueous phase was reused in a second hydrogenation in the cleaned autoclave. The TOF were determined for 100% conversion.

Acknowledgements

We thank the Region Bretagne (France) for financial support and the Service de Microscopie de l'Université Paul Sabatier (TEMSCAN) and V. Collière for TEM analysis.

References

[1] A. Stanislaus, B. H. Cooper, *Catal. Rev.* **1994**, *36*, 75.
[2] a) A. M. Casillas, T.Hiura, N. Li, A. E. Nel, *Ann. Allergy Asthma Immunol*. **1999**, *83*, 624; b) A. E. Nel, D. Diaz-Sanchez, D. Ng, T. Hiura, A. Saxon, *J. Allergy Clin. Immunol.* **1998**, *102*, 539; c) T. Enya, H. Suzuki, T. Watanabe, T. Hirayama, Y. Hisamatsu, *Environ. Sci. Technol*. **1997**, *31*, 2772.
[3] K. Weissermel, H. J. Arpe, *Industrial Organic Chemistry*, VCH, New York, 2nd edn., **1993**, p. 343.
[4] A. Roucoux, J. Schulz, H. Patin, *Chem. Rev.* **2002**, *102*, 3757.
[5] a) P. J. Dyson, *J. Chem. Soc. Dalton Trans.* **2003**, 2964; b) J. A. Widegren, R. G. Finke, *J Mol. Catal. A: Chem.* **2003**, *198*, 317; c) J. A. Widegren, R. G. Finke, *Inorg. Chem*. **2002**, *41*, 1558 and 1625.
[6] a) K. Pelzer, O. Vidoni, K. Philippot, B. Chaudret, V. Collière, *Adv. Funct. Mater*. **2003**, *13*, 118; b) M. Ohde, H. Ohde, C. M. Wai, *Chem. Commun.* **2002**, 2388; c) J.-L. Pellegatta, C. Blandy, V. Collière, R. Choukroun, B. Chaudret, P. Cheng, K. Philippot, *J. Mol. Catal. A: Chem.* **2002**, *178*, 55; d) R. J. Bonilla, P. G. Jessop, B. R. James, *Chem. Commun.* **2000**, 941; e) K. S. Weddle, J. D. Aiken III, R. G. Finke, *J. Am. Chem. Soc.* **1998**, *120*, 5653; f) B. R. James, Y. Wang, C. S. Alexander, T. Q. Hu, *Chem. Ind*. **1998**, *75*, 233; g) T. Q. Hu, B. R. James, C. L. Lee, *J. Pulp Pap. Sci*. **1997**, *23*, 200; h) O. Vidoni, K. Philippot, C. Amiens, B. Chaudret, O. Balmes, J. O. Malm, J. O. Bovin, F. Senocq, M. J. Casanove, *Angew. Chem. Int. Ed*. **1999**, *38*, 3736.
[7] a) D. S. Cunha, G. M. Cruz, *Applied Catal. A: General*, **2002**, *236*, 55; b) O. Alexeev, B. C Gates, *J. Catal.* **1998**, *176*, 214; c) A. Zhao, B. C. Gates *J. Catal.* **1997**, *168*, 60.
[8] a) G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixera, J. Dupont, *Chem. Eur. J.* **2003**, *9*, 3263; b) J. Dupont, G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixera, *J. Am. Chem. Soc.* **2002**, *124*, 4228.
[9] a) A. Roucoux, J. Schulz, H. Patin, *Adv. Synth. Catal.* **2002**, *345*, 222; b) J. Schulz, A. Roucoux, H. Patin, *Chem. Eur. J.* **2000**, *6*, 618.
[10] R. W. Cusack, *Chem. Eng. Prog*. **1996**, *92*, 56.
[11] a) Y. Mizukoshi, E. Takagi, H. Okuno, R. Oshima, Y. Maeda, Y. Nagata, *Ultrason. Sonochem*. **2001**, *8*, 1; b) T. Fujimoto, Y. Mizukoshi, Y. Nagata, Y. Maeda, R. Oshima, *Scripta mater*. **2001**, *44*, 2183; c) N. A. Dhas, A. Gedanken, *J. Mater. Chem.* **1998**, *8*, 445.
[12] B. J. Hornstein, R. G. Finke, *Chem. Mater.* **2003**, *4*, 899.

