

A surfactant-assisted preparation of well dispersed rhodium nanoparticles within the mesopores of AISBA-15: characterization and use in catalysis†‡

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Well dispersed and efficient Rh(0) hydrogenation catalysts were obtained by the reduction of Rh(III)-exchanged mesoporous aluminosilicates by sodium borohydride in the presence of *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl) ammonium chloride.

Controlled nanometre-sized metal species have attracted great attention in the field of catalysis because of their unique chemical and physical properties.¹ Particles hosted in porous supports are mainly prepared by the decomposition of organometallic compounds² or the reduction of metallic salts.³ In the latter case, impregnation methods are limited by the tendency of the metal to agglomerate on the external surface. In parallel, the control of the size of metallic particles by the use of protective agents in solution is now well established.⁴ Among noble metal nanoparticles, dispersions of rhodium(0) colloids are known to be efficient hydrogenation catalysts.^{5,6} Up to now, most of the methods used for the heterogenization of Rh(0) colloids consist in the impregnation of solids like polymers,⁷ silica⁸ and alumina.⁹ Attempts to take advantage of the high specific surface area of mesostructured supports have also been described. The nanoparticles are either deposited onto preformed materials¹⁰ or included in their synthesis gel.¹¹ However, these approaches can be handicapped by the relatively low amounts of metal introduced and the difficulty of inserting the particles homogeneously within the pore network.

An alternative solution would imply a stabilizing agent-assisted reduction of rhodium salts directly on the surface of the support. In this study, we show that well dispersed Rh(0)

particles are obtained by the reduction of Rh(III)-exchanged mesoporous aluminosilicates (AISBA-15) by sodium borohydride in the presence of a water soluble stabilizing agent, *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl) ammonium chloride (HEA16Cl).⁶ Ligands are usually used to confine nanoparticles in mesoporous solids¹² but, to our knowledge, examples of our strategy in the literature only concern montmorillonite or iron oxides.¹³ The hydrogenation activity of the new heterogeneous catalysts towards aromatic rings is compared with that of the previously reported HEA16Cl-stabilized aqueous dispersions of the same particles (Rh⁰/HEA16Cl).⁶ This approach could be an alternative way to investigate heteroaromatic cycle reduction and has potential applications for water remediation like the denaturation of aromatic pollutants such as atrazine.¹⁴

The nominal NaBH₄/Rh and HEA16Cl/Rh molar ratios (2.5 and 2, respectively) tested are rigorously the same as in the optimized preparation of aqueous 2–3 nm Rh(0) colloids. In this first attempt, we have considered that the dispersion of the Rh(0) particles nucleated on the support should be improved by the anchorage of the rhodium(III) ion precursors prior to their reduction. Cation exchange on a H-AISBA-15 type material or its sodium form, Na-AISBA-15, has been tested in the present work. Two routes based on simultaneous (route I) or distinct (route II) additions of rhodium(III) chloride and NaBH₄ were proposed (Scheme 1). Except for a blank test (Rh⁰/Na-AISBA(IIB)), the support (H-AISBA-15 or Na-AISBA-15) was first impregnated with HEA16Cl for 24 h. The molar Si/Al ratio of the aluminosilicates tested was about 17 and the maximum sodium uptake from the NaCl solution should correspond to 0.07 mol of Na per 100 g (1.6 wt%). In our conditions, the sodium loading was half what was expected (0.80% or 0.035 mol Na per 100 g) but was still enough in order to incorporate 1 wt% of Rh(III) (0.01 mol Rh per 100 g) on the basis of Rh³⁺/3 Na⁺ exchanges.

Elemental analysis results show that the rhodium content of the solid obtained from Na-AISBA-15 and HEA16Cl (Rh⁰/Na-AISBA(II)) is 0.90 wt%. This value is twice those of Rh⁰/Na-AISBA(IIB) (0.40%) and Rh⁰/H-AISBA(II) (0.44%). Clearly, the combined use of the cationic stabilizing agent and of a sodium-exchanged support facilitates the adsorption of Rh(III) on the surface. Moreover, rhodium(III) ions and NaBH₄ have to be added separately (route II). Indeed, 90% of the rhodium introduced is retained in the Rh⁰/Na-AISBA(II) solid as against 73% for Rh⁰/Na-AISBA(I). Protons or sodium ions of the support are probably exchanged by HEA16 cations.¹⁵ The resulting solids covered by interfacial aggregates

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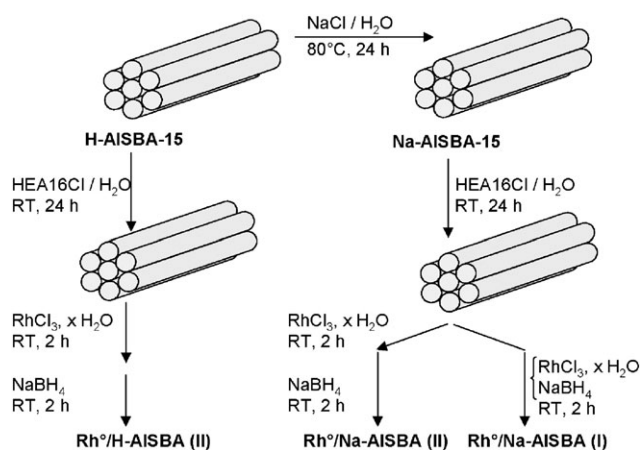
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† Electronic supplementary information (ESI) available: Experimental section; physicochemical properties of the different Rh⁰/AISBA-15 samples; TEM images of Rh⁰/H-AISBA(II); XPS and thermogravimetric analysis of Rh⁰/Na-AISBA(II); results of styrene hydrogenation. See DOI: 10.1039/b802548g

‡ In memory of Sir D.H.R. Barton on the 10th anniversary of his death.



Scheme 1 Synthesis routes used for surfactant-assisted preparation of $\text{Rh}^0/\text{SBA-15}$ solids.

composed of the adsorbed surfactant molecules with their cationic head-groups oriented toward the centre of the pores (e.g. “reversed” monolayered structures) could be involved in the “adsolubilization” of Rh^{3+} . Then, the uptake of the metallic cations would proceed *via* electrostatic interaction with chloride anions of HEA16Cl during the 2 h stirring period before reduction. As expected, the hexagonal pore structure of the parent supports is retained in the new materials. The textural properties of the resulting solids are not markedly different from those of their parents (H or Na-AISBA-15) and are not very helpful in discriminating the location of the particles due to the relatively low Rh contents (<1 wt%).

Experimental procedures have also dramatic effects on the dispersions of metal particles as shown by transmission electron microscopy experiments. Direct examination of the materials prepared from Na-AISBA-15 (Fig. 1a–c) clearly revealed differences in the size and location of the metal related to the effect of the addition time of the rhodium salt ($\text{Rh}^0/\text{Na-AISBA(I)}$), $\text{Rh}^0/\text{Na-AISBA(II)}$) and of the preliminary impregnation of the solid by HEA16Cl ($\text{Rh}^0/\text{Na-AISBA(II)}$). The simultaneous addition of Rh(III) and NaBH_4 leads to a very poor particle dispersion ($\text{Rh}^0/\text{Na-AISBA(I)}$, Fig. 1a). The delayed introduction of the reductant turned out to be more appropriate. Dispersed rhodium(0) particles mainly located inside the pore channels (Fig. 1c) are obtained in the case of $\text{Rh}^0/\text{Na-AISBA(II)}$, obviously as the result of the use of HEA16Cl and of a period of 2 h between the introduction of Rh(III) ions and of the reductant into the solution. Incontestably, HEA16Cl is helpful in locating the particles inside the pores. In its absence, rhodium aggregates are formed on the external surface of the solid ($\text{Rh}^0/\text{Na-AISBA(II)}$), Fig. 1b). The mean diameter of the colloids is smaller than the pore aperture, in agreement with their surfactant-assisted formation. Metal particles in $\text{Rh}^0/\text{H-AISBA(II)}$ (see ESI) and $\text{Rh}^0/\text{Na-AISBA(II)}$ samples are similar in size but large amounts of aggregates are also produced in the solids prepared from H-AISBA-15.

TEM images of thin microtome sections of $\text{Rh}^0/\text{Na-AISBA(II)}$ (Fig. 1d) confirm the good dispersion of the Rh(0) particles. The size distribution histogram indicates that the mean diameter is 2.7 nm (Fig. 2) near to that of Rh(0) particles prepared in water using the same ratios of stabilizing agent and reductant to Rh. Like in solution, HEA16Cl is involved in the control of the particle size. The analysis of $\text{Rh}^0/\text{Na-AISBA(II)}$

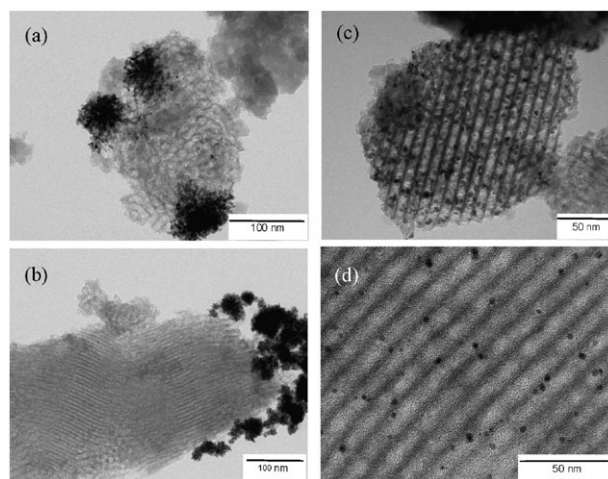


Fig. 1 TEM images of (a) $\text{Rh}^0/\text{Na-AISBA(I)}$, (b) $\text{Rh}^0/\text{Na-AISBA(II)}$, (c) $\text{Rh}^0/\text{Na-AISBA(II)}$ and of a microtome section of (d) $\text{Rh}^0/\text{Na-AISBA(II)}$.

by X-ray photoelectron spectroscopy indicates that the photopeaks related to the Rh 3d core level, *i.e.* Rh 3d_{3/2} (312.7 eV) and Rh 3d_{5/2} (307.5 eV vs. C 1s (285 eV)) are slightly shifted to higher energies compared to those of Rh(0) . XPS measurements also point out significant amounts of organic materials. HEA16Cl has been identified through the N 1s and C 1s signals at 403.3 and 285 eV, respectively. Values of the molar C/N ratios determined by elemental analyses for $\text{Rh}^0/\text{Na-AISBA(I)}$, $\text{Rh}^0/\text{Na-AISBA(II)}$ and $\text{Rh}^0/\text{H-AISBA(II)}$ are between 24 and 29, in agreement with the presence of HEA16 cations (expected C/N ratio = 20) and traces of Pluronic P-123. The more HEA16Cl is retained, the more rhodium is present. From the nitrogen weight percentages, it can be estimated that 60 to 80% of the initial amount of HEA16Cl is recovered on the solid. Thermogravimetric analyses are also consistent with the presence of both molecules (weight loss between 473 and 823 K). In the case of $\text{Rh}^0/\text{Na-AISBA(II)}$, HEA16Cl and Pluronic P-123 account for a 9% weight loss. Such information is coherent with the “adsolubilization” of rhodium and the involvement of these molecules in the stabilization of the particles prepared by the heterogeneous nucleation mode.

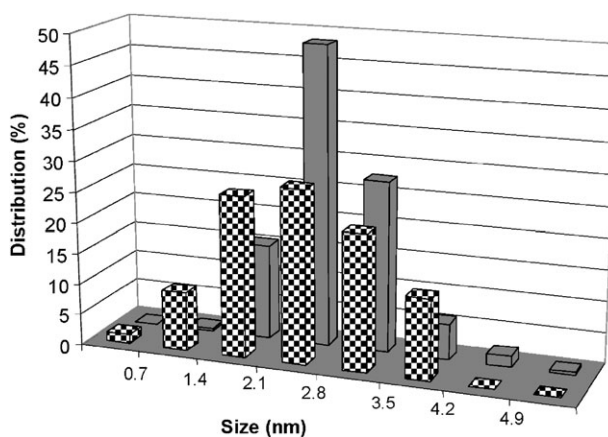


Fig. 2 Size distribution histograms of the $\text{Rh}^0/\text{HEA16Cl}$ colloids and of $\text{Rh}^0/\text{Na-AISBA(II)}$ (behind).

Table 1 Hydrogenation of arenes over Rh⁰/Na-AISBA(II) and Rh⁰/Na-AISBA(IIB)

Entry	Substrate	Product(s) (%)	Yields after 3 h (%) (time for completion/h)		Completion time/h
			Rh ⁰ /Na-AISBA(II)	Rh ⁰ /Na-AISBA(IIB)	
1	Styrene	Ethylbenzene (EB) Ethylcyclohexane (EC)	0 (3) 100	48 (6) 52	(4)
2	Anisole	Methoxycyclohexane	100 (3)	66 (6)	(3.6)
3	Toluene	Methylcyclohexane	70 (6)	—	(3.6)
4	<i>m</i> -Xylene	1,3-Dimethylcyclohexane ^a	56 (6)	—	(4.3)
5	Tetralin	Decalin ^b	32 (24)	0 (>24)	—

Conditions: catalyst (50 mg); hexane (10 mL); Substrate : Rh (100 : 1); 298 K, P_{H₂} 0.1 MPa. ^a *cis* : *trans*, 80 : 20. ^b *cis* : *trans*, 87 : 13.

The AISBA-15-supported Rh(0) particles were tested as catalysts in the hydrogenation of styrene at atmospheric pressure of dihydrogen. The reaction was carried out with 1 : 100 ratio of Rh/substrate at 298 K in hexane. Under these conditions, the activity of the catalysts changes in the following order: Rh⁰/Na-AISBA(II) ≈ Rh⁰/H-AISBA(II) > Rh⁰/Na-AISBA(I) > Rh⁰/Na-AISBA(IIB). Preliminary investigations of the recycling showed that the activity of Rh⁰/Na-AISBA(II) is not significantly affected over three successive tests. The activity of Rh⁰/Na-AISBA(II) towards styrene and anisole (Table 1, entries 1 and 2) also turned out to be higher than that of the aqueous dispersion of Rh⁰/HEA16Cl colloids tested under two-phase conditions. In fact, the complete conversion of anisole into methoxycyclohexane is performed in a shorter time (3 h) than over commercially available heterogeneous Rh(0) catalysts (Rh⁰/C or Rh⁰/Al₂O₃).¹⁶

Other substrates, *i.e.* the mono (entry 3) and dialkylarene derivatives (entries 4,5), are less easily hydrogenated over Rh⁰/Na-AISBA(II). *Cis* isomers are the major products as usually observed with heterogeneous systems. However, *cis*-1,3-dimethylcyclohexane is formed to a lower extent than in solution (*cis* : *trans*, 90 : 10). Differences between the activities and selectivities of Rh⁰/Na (or H)-AISBA(II) and Rh⁰/HEA16Cl colloids could be reasonably attributed to an effect of the support, thus illustrating the heterogeneous nature of the catalysts. Moreover, leaching of the HEA16Cl-stabilized particles into the hexane phase cannot be reasonably envisaged, due to the difficulties encountered in the extraction of the aqueous colloids by organic solvents.

Undeniably, the preparation of colloids directly onto AISBA-15 using HEA16Cl as an electrosteric stabilizing agent and NaBH₄ as a reductant allows better control of the final loadings and dispersions of rhodium. The particles are characterized by a mean diameter and size distribution similar to those of the Rh(0) colloids synthesized in water. As in solution, Rh(0) colloids prepared on AISBA-15 are efficient hydrogenation catalysts, despite the presence of HEA16Cl molecules. Further work is in progress in order to look at the influence of the anchorage of the rhodium cations and of the nature and amount of the stabilizing agent used.

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