

Electronic Supplementary Information

1. Experimental Section

All chemicals, namely: rhodium chloride hydrate ($\text{RhCl}_3 \cdot x\text{H}_2\text{O}$, 40.8% Rh, $x = 2.25$, Strem), sodium borohydride (NaBH_4 , Aldrich), aluminium isopropoxide ($\text{Al}[(\text{CH}_3)_2\text{CHO}]_3$, Aldrich 98%), poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) triblock copolymer (Pluronic P-123, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{\text{av}} = 5800$, Aldrich), tetraethyl orthosilicate (TEOS, Fluka), and fuming hydrochloric acid (SDS) were used as received without further purification. The electrosteric stabilizing agent, N,N-dimethyl-N-cetyl-N-(2-hydroxyethyl) ammonium chloride (HEA16Cl) was prepared as previously described⁶.

- Synthesis procedures

Preparation of the support: The host H-AISBA-15 type material ($S_{\text{BET}} = 860 \pm 30 \text{ m}^2 \text{ g}^{-1}$, $V_p = 1.10 \pm 0.05 \text{ cm}^3 \text{ g}^{-1}$, $D_p = 8.0 \pm 0.2 \text{ nm}$) was synthesised according to a previously reported procedure [Y. Li, W. Zhang, Q. Yang and Z. Wie, *J. Phys. Chem. B*, 2004, **108**, 9739 ; B. Jarry, F. Launay, J.P. Nogier, J.L. Bonardet, *Stud. Surf. Sci. Catal.*, 2005, **158**, 1581] using Pluronic P-123 as a structure directing agent, and aluminium isopropoxide and TEOS as aluminium and silicon precursors, respectively. The experimental Si/Al ratio of the calcined solid was estimated to be 17 (instead of 10 as expected). The sodium form (Na-AISBA-15) was obtained by stirring 1.0 g of the calcined H-AISBA-15 solid in 100 mL of a 0.7 M NaCl solution at 353 K for 48 h. The Na-AISBA-15 solid was recovered by filtration, washed with distilled water and dried 24 h at 333 K ($S_{\text{BET}} = 785 \text{ m}^2 \text{ g}^{-1}$, $V_p = 1.03 \text{ cm}^3 \text{ g}^{-1}$, $D_p = 7.9 \text{ nm}$). The Na/Al ratio was 0.5.

Preparation of Rh-containing solids: The $\text{Rh}^{\text{III}}/\text{Na-AISBA-15}$ (or $\text{Rh}^{\text{III}}/\text{H-AISBA-15}$) precursors were prepared from $\text{RhCl}_3 \cdot x \text{H}_2\text{O}$ and Na-AISBA-15 (or H-AISBA-15). The latter (1.0 g) was dispersed in 25 mL of distilled water in the presence of HEA16Cl (0.063 g, $1.8 \cdot 10^{-4} \text{ mol}$) for 24 h.

In route **I**, sodium borohydride (10 mg, $2.4 \cdot 10^{-4} \text{ mol}$) and rhodium(III) chloride hydrate (0.024 g, $9.6 \cdot 10^{-5} \text{ mol}$) were added successively affording $\text{Rh}^0/\text{Na-AISBA(I)}$.

In route **II** ($\text{Rh}^0/\text{Na-AISBA(II)}$ or $\text{Rh}^0/\text{H-AISBA(II)}$), the rhodium salt was left in contact with the solid for 2 h before NaBH_4 was added. In both routes, reduction occurred instantaneously, as witnessed by a colour change from yellow to black. A blank experiment ($\text{Rh}^0/\text{Na-AISBA(II B)}$) was carried out in the absence of HEA16Cl following route **II**. After 2 h, the black solid products were filtered, washed and dried at 333 K for 24 h.

- Catalysis test

All materials were used as catalysts in the hydrogenation of styrene (Aldrich, 99%). The $\text{Rh}^0/\text{Na-AISBA(II)}$ and $\text{Rh}^0/\text{Na-AISBA(IIB)}$ solids were also tested in the hydrogenation of other arene derivatives: anisole (Prolabo, 99%), toluene (Acros Organics, 99%), tetralin (Sigma-Aldrich, 99%) and m-xylene (Acros Organics, 99%). Catalytic reactions were carried out at room temperature at atmospheric pressure of dihydrogen according to the following procedure. A weighed amount (50 mg) of the tested catalyst was dispersed in hexane (10 mL) for 15 min prior to the introduction of the arene derivative (100 eq. per eq. metal). All products were quantified by a gas chromatograph (Delsi Nermag) equipped with a Macherey-Nagel Optima[®]-5 capillary column and a FID detector, using n-decane as internal standard.

- Characterization methods

The elemental compositions (silicon, rhodium, carbon, sodium and nitrogen) of the materials were determined by ICP-AES in the CNRS centre at Vernaison (France). X-Ray diffraction patterns were recorded on a Bruker D8 ADVANCE diffractometer using $\text{Cu-K}\alpha$ radiation in the (2θ) range between 0.5° and 5° . Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature using a Micromeritics ASAP 2010 apparatus. Prior to analysis, all samples were outgassed overnight at 473 K under vacuum ($p < 2 \cdot 10^{-3}$ torr) in the degas port of the sorption analyser. The pore diameter and specific pore volume were calculated according to the Barrett-Joyner-Halenda (BJH) model. The BET specific surface area was obtained in the range of relative pressures between 0.05 and 0.35. Transmission electron microscopy (TEM) images were recorded with a JEOL TEM 100CXII electron microscope operated at an acceleration voltage of 100 kV. Materials were analysed either directly (powders) or after microtomy. The powders were dispersed in ethanol and the resulting suspensions deposited on a copper grid coated with a carbon film. Otherwise, the materials were included in a resin (AGAR 100) and heated for 48 h at 333 K. Thin (70 nm) sections cut with a Leica microtome (ULTRACUT UCT) were collected on carbon-coated copper grids. Thermal analysis (TG-DSC) of $\text{Rh}^0/\text{Na-AISBA(II)}$ was performed on a SDT 2960 system (TA Instruments, Inc.). The measurements were carried out in a constant 100 mL min^{-1} N_2 flow with a heating rate of 10 K min^{-1} . XPS analyses were performed on a Vacuum Generator Escalab 220 XL spectrometer with a monochromated aluminium source used for excitation ($\text{Al K}\alpha = 1486.6 \text{ eV}$). The pass energy was 40 eV in the electromagnetic mode. Data acquisition was carried out with a voltage step of 0.02 V, a dwell time of 20 ms and using a

flood gun (6 eV) for charge compensation. The calibration of the spectrophotometer was periodically checked from reference peaks (Cu, Au, Ag). The atomic stoichiometry of the surface layers accessible to XPS analysis (~ 10 nm deep) was calculated by using the Eclipse VG Scientific software.

2. Data

Table S1: Physicochemical properties of Rh⁰/AISBA-15 samples

Sample	Rh wt. %	C wt. %	C/N mol/mol	S _{BET} m ² g ⁻¹	V _p cm ³ g ⁻¹	D _p nm
Rh ⁰ /Na-AISBA(I)	0.73	3.9	24	628	1.00	7.8
Rh ⁰ /Na-AISBA(II)	0.90	4.5	26	870	1.24	7.0
Rh ⁰ /Na-AISBA(IIB)	0.40	-	-	795	0.99	8.2
Rh ⁰ /H-AISBA(II)	0.44	3.7	29	1083	1.4	6.7

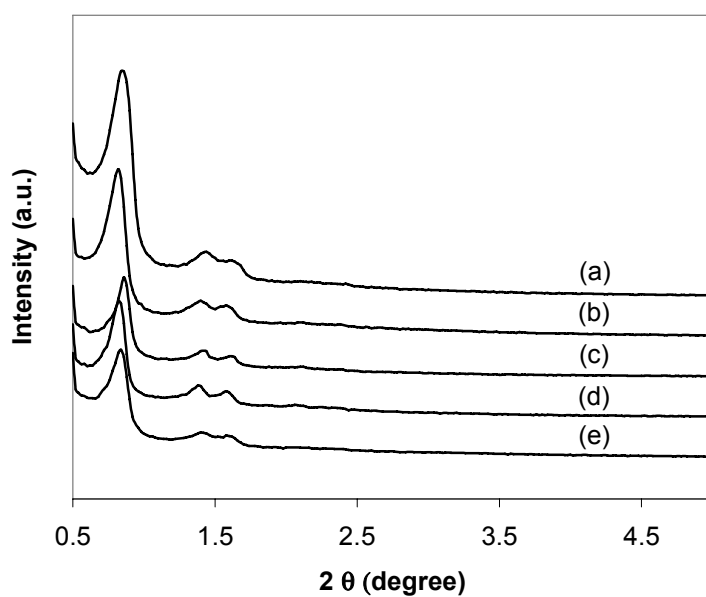


Fig. S1: XRD patterns of (a) H-AISBA-15, (b) Na-AISBA-15, (c) Rh⁰/Na-AISBA(I), (d) Rh⁰/Na-AISBA(II) and (e) Rh⁰/Na-AISBA(IIB) samples.

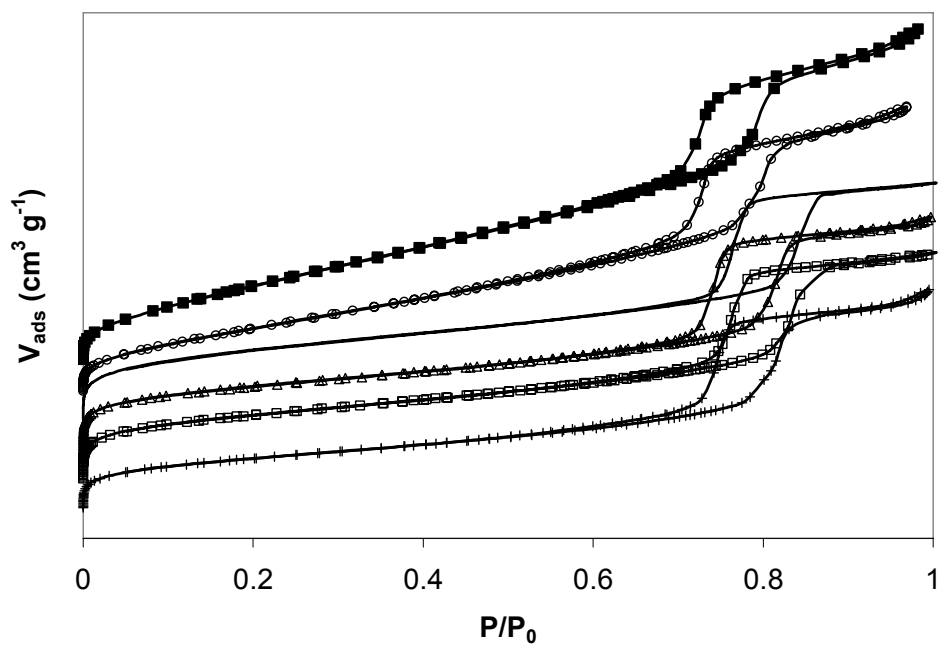


Fig. S2: Nitrogen sorption isotherms of (-) H-AISBA-15, (Δ) Na-AISBA-15, (+) $\text{Rh}^0/\text{Na-AISBA(I)}$, (\circ) $\text{Rh}^0/\text{Na-AISBA(II)}$, (\square) $\text{Rh}^0/\text{Na-AISBA(IIB)}$ and of (\blacksquare) $\text{Rh}^0/\text{H-AISBA(II)}$.

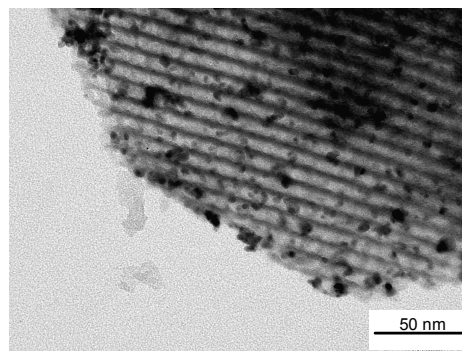
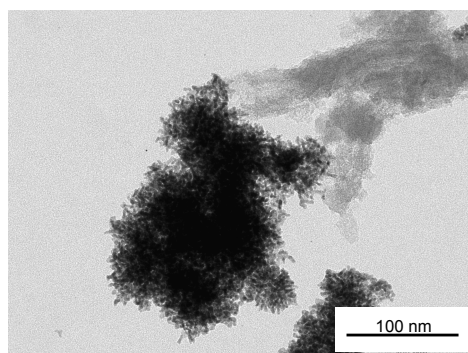


Fig. S3: TEM images of $\text{Rh}^0/\text{H-AISBA(II)}$ (direct observations).

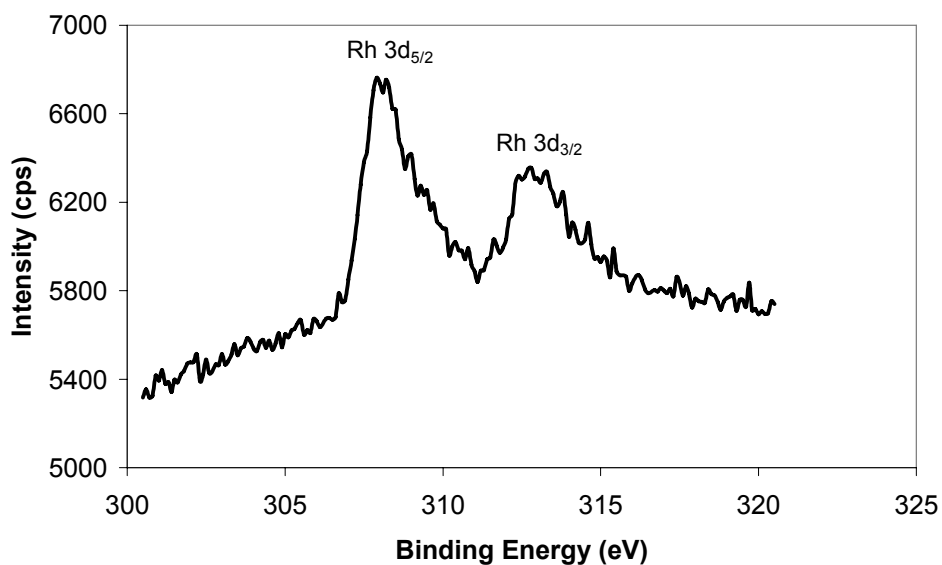


Fig. S4: X-Ray photoelectron spectrum of the rhodium 3d core level in Rh⁰/Na-AISBA(II).

The analysis of Rh⁰/Na-AISBA(II) by X-Ray photoelectron spectroscopy indicates that the photo-peaks 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). This may be related to the small size of the particles which are interacting with the support.

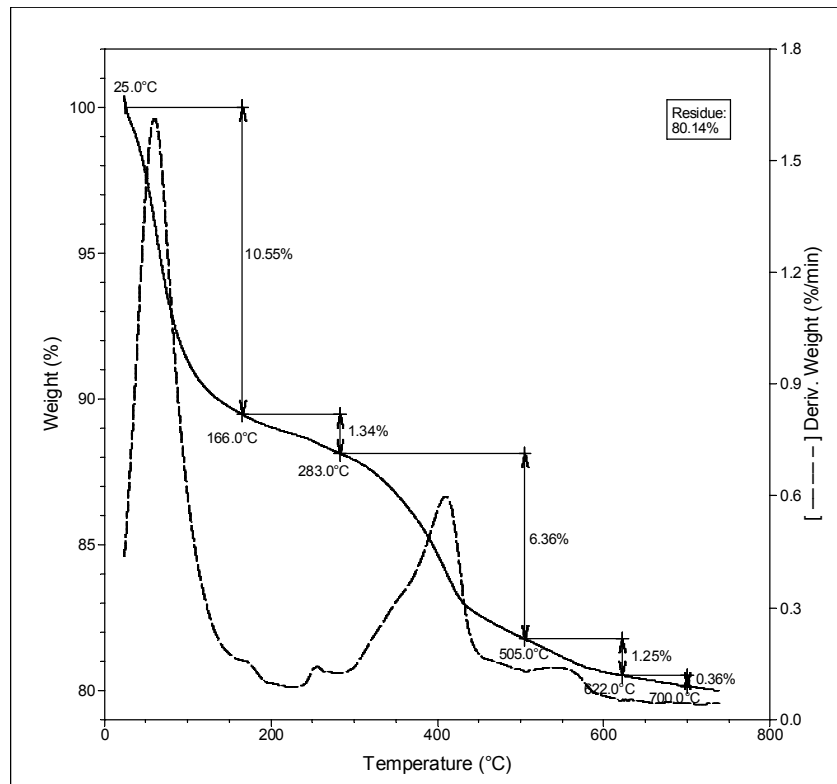


Fig. S5: Thermogravimetric analysis of Rh⁰/Na-AISBA(II).

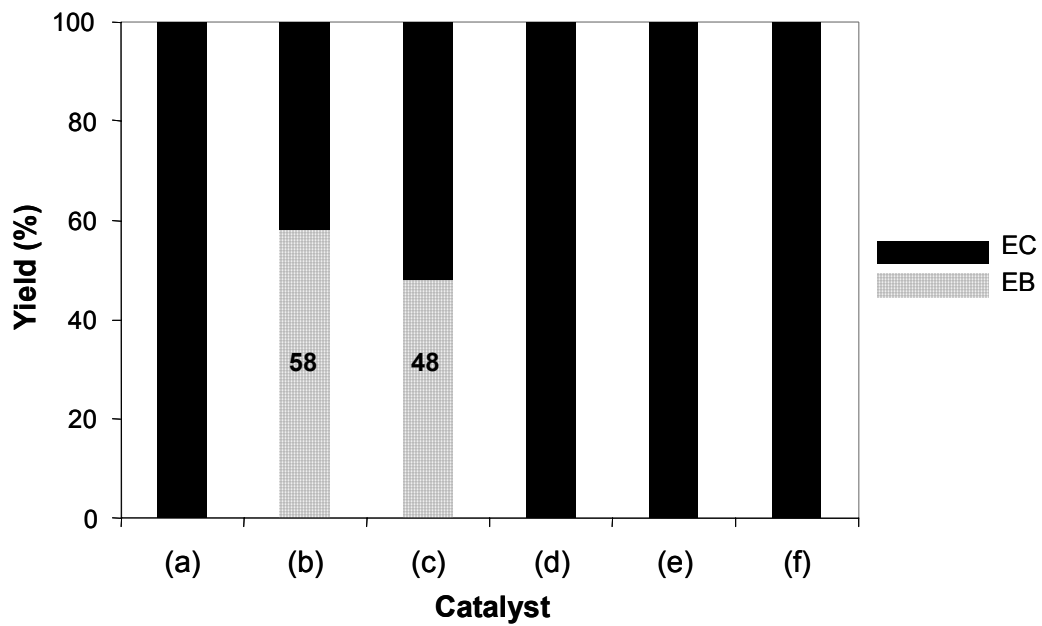


Fig. S6: Hydrogenation of styrene over (a) $\text{Rh}^0/\text{H-AISBA(II)}$, (b) $\text{Rh}^0/\text{Na-AISBA(I)}$, (c) $\text{Rh}^0/\text{Na-AISBA(IIB)}$, (d) $\text{Rh}^0/\text{Na-AISBA(II)}$ (and recycling tests (e, f)). Yields after 3 h.

Conditions: catalyst (50 mg); hexane (10 mL); Substrate/Rh (100 :1); 298 K, P_{H_2} (0.1 MPa).