# **Electronic Supplementary Information**

## Ordered Mesoporous Materials as Solid Supports for Rhodium-diphosphine Catalysts

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#### General Procedure

Unless stated otherwise, reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Solvents were distilled under an atmosphere of nitrogen, as follows: THF and EtO<sub>2</sub> from sodium benzophenone ketyl, toluene from sodium, and dichloromethane from CaH<sub>2</sub>. Chemicals were purchased from Sigma-Aldrich and used without further purification. Silica gel (200–400  $\mu$ m particle size; 60 Å average pore diameter) was purchased from Screening Devices B.V., and SBA-15 was synthesized at Delft University of Technology (TU Delft) as discussed below. Both materials were pretreated under vacuum at 180 °C for 24 hours prior to use. NMR spectra (<sup>1</sup>H, <sup>31</sup>P {<sup>1</sup>H}, and <sup>13</sup>C {<sup>1</sup>H}) were measured on Varian Mercury 300 MHz, or Varian INOVA 500 MHz spectrometers. GC analyses were performed on a Shimadzu GC Ultra (F.I.D. detector) with a Chirasil Dex CB column (internal diameter 0.1 mm, 5 m column, film thickness 0.1 mm). Elemental analyses were performed at the H. Kolbe Mikroanalytisches Laboratorium in Mülheim (Germany). Rhodium analysis was performed on an ICP-OES, PerkinElmer Optima 3000XL with detection limit of 1.4 µg/l (1.4 ppb) and determination limit of 4.2 µg/l (4.2 ppb).

#### Synthesis of the mesoporous silica SBA-15

The synthesis of the mesoporous silica SBA-15 has been carried out following a procedure adapted from previous reports.<sup>i</sup> Typically, 4 g of block co-polymer Pluronics P123 (BASF), 15 mL of hydrochloric acid (HCl, 35 %), and 85 mL of water were first mixed and homogenized. 8.5 g of TEOS (tetraethoxysilane, 98%) was slowly added to the solution under continuous stirring. Hydrolyzation was subsequently performed at 40 °C for 4 hours, followed by aging in an autoclave at 110

°C for 48 hours. The wet solid product was dried at 60 °C. Calcination was performed at 550 °C for 6 hours to obtain dry SBA-15.



#### Characterization of the mesoporous SBA-15

**Figure ESI 1.** Analysis of the pores by N<sub>2</sub> adsorption and desorption. (Left) The isotherms of the used SBA-15 sample. (Right) Pore size distribution corresponding to the adsorption isotherm, and calculated using the BJH method.

Table ESI 1. Texture of the SBA-15 sample corresponding to Figure ESI 1.

<b>S</b> <sub>BET</sub>	Smesopores	V <sub>micro</sub>	V <sub>meso</sub>	d <sub>meso</sub>
$m^2g^{-1}$	$m^2g^{-1}$	$cm^3g^{-1}$	$cm^3g^{-1}$	nm
773.0	642.6	0.053	1.365	10

#### Synthesis of the supported rhodium-bisphosphine (2)

The synthetic procedure to achieve the SBA-15 supported material **2** followed the previously published procedure for supporting the same catalytic system on silica gel.<sup>ii</sup> First, the ligand is grafted on to the support, after which the free silanols are capped by refluxing in dimethoxysilane. Elemental analysis found: % C 9.58, % H 1.78, % N 0.23.

#### Metal Leaching - Rhodium in the silica support by ICP-OES analysis

The silica gel was dissolved in 48 % aqueous HF (1 mL  $\times$  50 mg of silica) and heated until all the volatiles had evaporated. The residue was then dissolved by adding fuming nitric acid (2 mL) and warming up the solution to 90 °C for 1 hour. Hydrogen

peroxide (few drops) was then added to the warm sample until the solution became colorless. Water was added to bring the total volume up to 10 mL for analysis. Loading: 0.17 mmol/g.

#### Metal leaching - Rhodium in the product mixture by ICP-OES analysis

5 mL of product solution were evaporated under vacuum at 80 °C. The residue was dissolved by adding fuming nitric acid (2 mL) and warming up the solution to 90 °C for 1 hour. Hydrogen peroxide (few drops) was added to the warm sample until the solution became colorless. Water was added to bring the total volume up to 10 mL for analysis.

#### In situ high-pressure FT-IR experiments

The high-pressure IR spectra were performed in a stainless steel (SS 316) 50 mL autoclave equipped with ZnS windows (700 cm<sup>-1</sup>, i.d. 10 mm, optical path length 0.4 mm), a mechanical stirrer, a temperature controller, and a pressure device.<sup>17</sup> In a typical experiment the high pressure IR autoclave was filled with 15 mL of a solution of ligand  $(1.5 \times 10^{-4} \text{ mol})$  and metal precursor  $(1 \times 10^{-5} \text{ mol})$  in methyl-tetrahydrofurane. The autoclave was purged three times with 10 bars of CO/H<sub>2</sub> (1/1), and pressurized to 18 bars. The mixture was stirred and heated up to 80 °C (final pressure of 20 bars). Catalyst formation was monitored as a function of time by FT-IR for a period of 14 hours.

### Hydroformylation experiments

A typical catalysis experiment: A stainless steel 50 mL autoclave, equipped with a glass inner beaker, mechanical stirrer, substrate vessel, temperature controller, and a sample outlet equipped with a filter internal to the autoclave was filled with 1 g of 1.0  $\times 10^{-5}$  mol rhodium-catalyst containing silica and 10 mL of toluene as solvent. The suspension was incubated overnight at 80 °C under 16 bars (or 20 bars) of CO/H<sub>2</sub> (1/1). A mixture of 1 mL of 1-octene and 1 mL of decane in 3 mL of toluene was added, and the CO/H<sub>2</sub> pressure was increased up to 20 bars (or 50 bars). The mixture was stirred for 23 hours. The autoclave was cooled at 15–20 °C and the pressure reduced to 5 bars. With this overpressure the liquid (or some of it, in case of sampling) was slowly removed from the catalyst *via* the sample outlet. These samples

were analysed by GC to determine the product distribution and the average turn over frequency (TOF), the latter only being reliable if the conversion is between 10-40%. After high conversions, the catalyst was recycled by completely removing the liquid phase. After that the catalyst had been washed with 5 mL of toluene, 10 mL of toluene were added and the pressure was brought to 16 bars (or 20 bars). The mixture was heated up to 80 °C, and, finally, a second cycle was performed by adding another mixture of 1 mL of 1-octene and 1 mL of decane in 3 mL of toluene, and increasing the CO/H<sub>2</sub> pressure to 20 bars (or 50 bars). The experiments carried out in neat 1-octene were performed after the incubation procedure: the catalyst was washed with 5 mL of toluene after the previous cycle, and 15 mL of 1-octene were added. Then, the pressure was increased to 20 bars, the temperature elevated up to 80 °C, and the cycle started.

Entry/cycle	Material (batch)	Pressure (bar)	Conversion <sup>b</sup> (%)	linear (%)	l/b	TOF <sup>c</sup>	Cumul. TON <sup>d</sup>
1/1	SBA-15 (1)	50	90.8	91	35	195	671
2/2	SBA-15 (1)	50	95.8	90	33	n.m.	1306
3/3	SBA-15 (1)	50	98.7	88	29	n.m.	1932
4/4	SBA-15 (1)	50	86.5	88	31	95	2511
5/5	SBA-15 (1)	50	74.4	88	31	126	3030
6/6 <sup>e</sup>	SBA-15 (1)	50	34.3	88	26	96	3221
7/7	SBA-15 (1)	50	92.6	91	37	n.m.	3885
8/8	SBA-15 (1)	20	94.2	92	47	306	4597
$9/9^{\mathrm{f}}$	SBA-15 (1)	20	91.6	94	47	995	14748
$10/10^{f}$	SBA-15 (1)	50	86.9	91	35	836	25589
$11/11^{f}$	SBA-15 (1)	20	87.6	94	40	n.m.	35309
$12/12^{f}$	SBA-15 (1)	20	91.6	94	43	n.m.	46177
$13/13^{f}$	SBA-15 (1)	20	91.5	94	39	n.m.	57212
$14/14^{f}$	SBA-15 (1)	20	88.2	93	39	n.m.	67143
15/15	SBA-15 (1)	20	90.0	85	28	226	67716
16/16	SBA-15 (1)	20	78.8	76	25	67	68225
17/17	SBA-15 (1)	20	93.4	54	6	119	68640
18/1	SBA-15 (2)	50	84.7	93	27	101	664
19/2	SBA-15 (2)	50	81.6	93	36	100	1281
20/3	SBA-15 (2)	20	95.2	92	35	142	2010
21/4	SBA-15 (2)	20	92.7	93	40	192	2717
22/5	SBA-15 (2)	50	87.2	90	21	109	3388
23/6	SBA-15 (2)	50	96.2	67	3	161	4083
24/1 <sup>g</sup>	SiO <sub>2</sub>	50	24.0	86	19	8	-
25/-	Homog.	50	33.9 <sup>e</sup>	93	41	120	-
26/-	Homog.	20	53.5 <sup>e</sup>	95	59	149	-

Table ESI 2. Rhodium-catalyzed hydroformylation of 1-octene.<sup>a</sup>

a) [Rh] =  $10^{-5}$  mol/g, ligand/Rh = 15, substrate/Rh = 640, toluene = 13 mL, CO/H<sub>2</sub> = 1/1, temperature = 80 °C; b) Conversions were calculated after 23 hours. Samples were analyzed by means of GC analysis using *n*-decane as internal standard; c) TOF are calculated as (mol product)(mol rhodium)<sup>-1</sup>(hour)<sup>-1</sup> at 20–40 % conversion, variations in TOF stem from differences in conversion and product distribution; d) Cumulative TON calculated as (mol product)(mol rhodium)<sup>-1</sup>; e) Conversions measured after 2 hours. f) Performed in neat 1-octene (substrate/Rh =  $10^4$ ); g) Data taken from ref. ii; e) Conversions measured after 2 hours.

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