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Electronic Supporting Information:

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Robustly supported rhodium nanoclusters: synthesis and applications in selective hydrogenation of lignin derived phenolic compounds

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General Remarks:

The synthesis of the complex was carried out under dry argon using standard Schlenk technique. Solvents (THF, toluene, hexane) were dried and distilled from sodium benzophenone. Deuterated solvents were obtained from Cambridge Isotope Laboratories and degassed, dried using molecular sieves and distilled before use. Chloro(1,5-cyclooctadien)rhodium(I)dimer (98%) and *n*-Dodecan were obtained from abcr while *n*-Butyllithium and phenol and derivatives from Alfa Aesar and used without any further purification.

Characterization:

1) Nuclear magnetic resonance (NMR)

The ^1H and ^{13}C NMR spectra of the organic ligand are obtained using a Varian INOVA 300 MHz spectrometer while those of the Rh-complex was obtained using a Bruker Advance III HD 500 spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C) at room temperature. The chemical shifts are reported in ppm relative to the deuterated solvent ($CDCl_3$). Coupling constants (*J*) are reported in Hz.

2) FT-IR-analysis

FT-IR spectra were recorded using an ATR device of a SPEKTRUM 100 FT-IR spectrometer (PERKIN ELMER). The measuring range is between 4000 cm^{-1} and 550 cm^{-1}.

3) Nitrogen sorption measurements

The N_2 sorption measurement were carried out with using a Nova 2000e instrument (Quantachrome). 50-200 mg ceramic was weighed in a glass cell and degassed (300°C, 10^{-4} bar, 2 hours). The pore width and average pore volume were calculated using nonlocal density functional theory (NLDFT) utilizing a carbon kernel (slit pores). The specific surface areas were calculated in the relative pressure range of 0.05 – 0.31 (BET).

4) Transmission electron microscopy (TEM)

The TEM micrographs were taken at the Varian LEO 922O (200 kV) instrument. The sample was suspended in chloroform and sonicated for 5 min. Subsequently a drop of the suspended sample was placed on a CF200-Cu-grid (Electron Microscopy Science) and dried.

5) Pyrolysis of the ceramics

The ceramics were pyrolysed in a high temperature oven (Gero) under N_2 atmosphere.

6) Milling of the ceramics

The pyrolysed ceramics were powdered in a ball mill Pulverisette 0” (Frisch) for 20 minutes.

7) Gas chromatogrphy (GC)

The analysis of the used products and educts in catalysis were carried out on 6850N chormatograph (Agilent) supplied with an OpVima capillary column.

Synthesis of the organic compound and the complex

Synthesis of the $Ap^{TMA}H$ - compound (4-Methyl-pyridin-2-yl)-(2,4,6-tri-methyl-phenyl)-amine

The synthesis of the $Ap^{TMA}H$ was carried out following a literature procedure. [1] In doing so 2-chlor-4-methylpyridine (5.83g, 45.7 mmol) were mixed with 2,4,6-trimethylanilinium chloride (7.86g, 45.7 mmol) and stirred at 180°C for 20 h. After cooling to room temperature, sodium carbonate and 50 ml water were added. The resulting solution was extracted with DCM (4×50 ml), dried over sodium sulfate and filtrated. After removing the solvent a brown oil was obtained to which 100 ml of a 1:1 mixture of diethyether and hexane was added. A solid product so obtained was filtrated and recrystallised from diethyl ether. (2.63 g; 28.4%).

^{1}H NMR (300 MHz, $CDCl_3$, 296 K): δ = 7.98 (d, 1H, *J*= 5.34 Hz, NC*H*), 6.96 (s, 2H), 6.44 (d, 1H, *J*= 5.34 Hz, arom. *H*), 6.36 (s, 1H, arom. *H*), 5.81 (s, 1H, N*H*), 2.32 (s, 3H, ar-CH_3), 2.12 (s, 6H, ar-CH_3), 2.14 (s, 3H, ar-CH_3) ppm.

^{13}C NMR (75 MHz, $CDCl_3$, 296 K): δ = 18.5, 21.2, 21.4, 106.0, 115.2, 129.4, 134.2, 136.9, 148.3, 149.2, 158.5 ppm.

Synthesis of the [Rh(ApTMA)(cod)] complex

The synthesis of the $[Rh(Ap^{TMA})(cod)]$ complex was carried out following a modified literature procedure [2]. $Ap^{TMA}H$ (435 mg, 1.92 mmol) were dissolved in diethylether (35 ml) and cooled down to 0°C. Afterwards 1.25 ml of n-BuLi (1.6 M in n-hexane) were added and the reaction mixture was stirred at RT. A suspension of $[RhCl(cod)]_2$ (473.5 mg, 0.96 mmol) and 20 ml diethyl ether were added at 0°C to the lithiated ligand and reaction mixture was stirred overnight. After filtration and extraction (3× 20 mL diethlether), the combined organic phases were concentrated. Crystalization at -20°C yielded the desired product (699 mg; 83.5%).

^{1}H NMR (500 MHz, CDCl$_3$, 296 K): δ = 7.87 (d, 1H, *J*=5.4 Hz, NC*H*), 6.90 (s, 2H, arom. *H*), 6.79 (d, *J*=5.4 Hz, 1H, arom. *H*), 6.74 (s, 1H, arom. *H*), 5.27 (s, 4H, cod), 3.96 (bs, 6H, cod), 2.56 (s, 3H, ar-C*H*$_3$), 2.20 (bs, 9H, ar. C*H*$_3$), 1.57 (bs, 8H, cod) ppm.

^{13}C NMR (125 MHz, CDCl$_3$, 296 K): δ = 19.31, 21.38, 21.84, 31.67, 105.06, 107.99, 129.63, 133.29, 134.01, 141.90, 143.91, 151.03, 176.15 ppm.

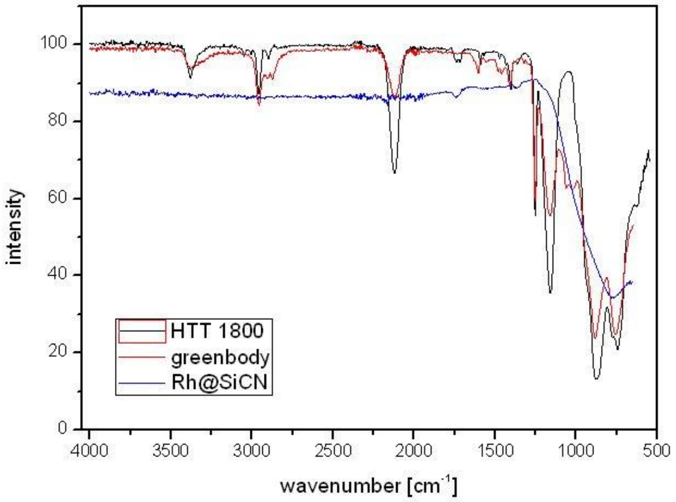

Figure S1: FT-IR spectrum of polysilazane (HTT 1800) in comparison to that of a green body (metal modified and cross-linked polymer) and the final ceramic material (Rh@SiCN). The considerable decrease in the intensity of N-H-(3250 – 3450 cm^{-1}), Si-H- (2119 cm^{-1}) and the vinyl-functions (2800 – 2995 cm^{-1}) confirms the crosslinking process. After pyrolysis, broad bands (1270-800cm^{-1}) can be attributed to the Si-C, Si-N und Si-N-Si vibrations.

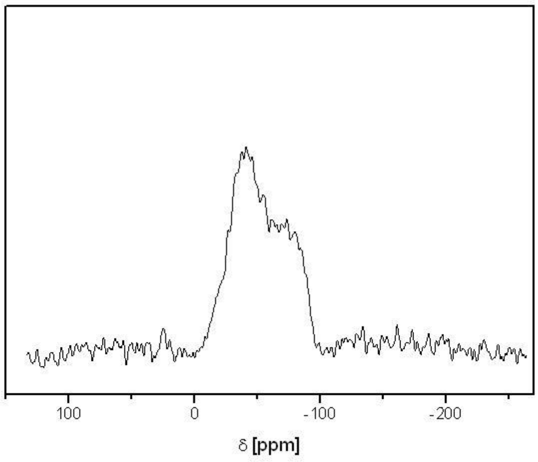

Figure S2: ^{29}Si solid state NMR of a porous Rh@SiCN ceramic with a typical peak at 49.8 ppm, which is characteristic for a homogeneous Si-C-N phase consisting of SiN_4 (-48 ppm), SiC (-15 ppm) and SiN_3C (-30 ppm). [3]

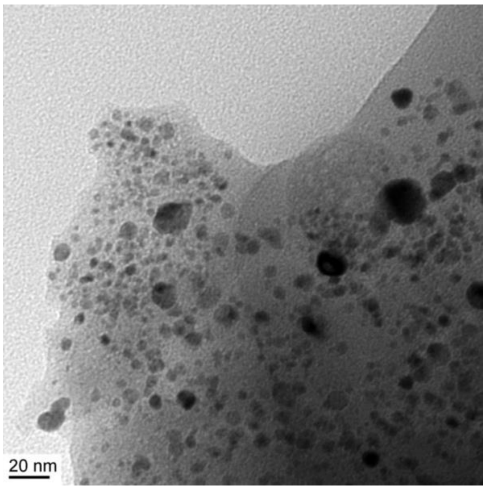

Figure S3: TEM image of a Rh@SiCN ceramic with a Si/Rh ratio of 10. Huge particles are generated in the ceramic due to the high metal loading.

1. S. Deeken, S. Proch, E. Casini, H. F. Braun, C. Mechtler, C. Marschner, G. Motz, R. Kempe, *Inorg. Chem*, 2006, **45**, 1871-1879.
2. G. Glatz : From Aminopyridinato Complexes via Metal Containing SiCN Precursor Ceramics to Heterogeneous Recyclable Oxidation Catalysts, Diss., Universität Bayreuth, 2009.
3. S. Traßl, D. Suttor, G. Motz, E. Rössler and G. Ziegler, *Journal of the European Ceramic Society*, 2000, **20**, 215-225.