Electronic Supplementary Information (ESI)

Rhodium nanoparticles supported on covalent triazine-based framework as re-usable catalyst for benzene hydrogenation and hydrogen evolution reaction

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Synthesis and characterization of CTF-1

There is an increasing interest of CTFs in current research and science in the recent years.^{1,2} CTFs are insoluble in many solvents and thermally stable due to their covalent bounded structure.^{3,4} Additionally, CTFs usually feature a high surface area and high degree of graphitization.⁵⁻⁷ Because of these physiochemical properties, CTFs are applied for numerous applications such as for catalysis and energy storage.⁸⁻¹¹

In the ionothermal synthesis strategy, the reaction temperature and monomer/ZnCl₂ ratio are critically important for the CTF structures. In order to prevent elimination of nitrogen and unnecessary carbonization, a reaction temperature of 400 °C was selected in most CTF synthesis experiments.¹² The ionothermal synthesis of CTF-1 was first described by Kuhn *et al.* in 2008 by using monomer/ZnCl₂ ratios of 1:1 and 1:10.^{13,14} A high amount of ZnCl₂ yields highly porous and amorphous materials with high surface areas.¹³ However, the use of a large amount of ZnCl₂ is disadvantageous due to the difficult removal of the salt.¹² Bhunia *et al.*¹⁵ synthesized CTF-1 at 400 °C and Prati *et al.*¹⁶ synthesized CTF-1 at 600 °C with a monomer/ZnCl₂ ratio of 1:5 achieving a highly porous material with a high surface area. In this work, we synthesized CTF-1 referring to Bhunia *et al.* by ionothermal reaction of 1,4-dicyanobenzene at 400 °C using molten zinc chloride (monomer/ZnCl₂ ratio of 1:5) under inert conditions (Scheme S1).¹⁵



Scheme S1 Reaction scheme of ionothermal synthesis of 1,4-dicyanobenzene to CTF-1 at 400 °C using molten ZnCl₂.

The shard-like morphology and slight impurities of silicon, chlorine and zinc of CTF-1 were determined by scanning electron microscopy (SEM) in combination with energy-dispersive X-ray spectroscopy (SEM/EDX) (Fig. S2).





Fig. S2 SEM images and EDX analysis of CTF-1.

The elemental (CHN) analysis agree very well with the literature,^{13,15} but differs to the theoretical values (Table S3) based on the idealized structure of CTF-1 (Scheme S1). The low nitrogen content of CTF-1 is well known in literature and indicates nitrogen elimination during the polymerization reaction as a common problem of many ionothermally synthesized CTFs with reaction temperatures of 400 °C and above.^{12,17}

Figures in [wt%]	C	N	Н	atom C/H	atom C/N	Rest
calculated ^a	74.99	21.86	3.15	2	4	/
CTF-1	75.35	13.66	2.75	2.3	6.4	8.24

Table S3Elemental (CHN) analysis of CTF-1

Literature						
Kuhn e <i>t al.</i> ¹³	72.03	13.82	2.96	2.2	6	11.19
Bhunia <i>et al.</i> ¹⁵	66.97	12.90	2.53	2	6	17.60

^a Calculation based on idealized structure of CTF-1 (Scheme S1).

For further analysis, nitrogen sorption and desorption measurements (Fig. S4) were carried out and yield high BET surface area of 963 m²/g with a total pore volume of 0.53 cm³/g and a micro pore volume of 0.29 cm³/g. The total pore volume is close to those found for CTF-1 ionothermal synthesized by Kuhn *et al.* (cf. 0.40 cm³/g) whereas the BET surface area is higher (cf. 791 m²/g).¹³



Fig. S4 Nitrogen adsorption-desorption isotherms at 77 K of CTF-1. Calculated BET surface area (963 m^2/g) from N₂ sorption isotherm over the pressure range 0.02–0.1 p/p0.

Additionally, the obtained black powder was analysed by powder X-ray diffraction (PXRD) and showed, as expected, low crystallinity (Fig. S5, left). In the work by Kuhn *et al.* with a monomer/ZnCl₂ ratio of 1:1,¹³ the broad peak at 20 = 26.1° was assigned to the (001) reflection from which the interlayer distance can be derived to 3.4 Å. In comparison, the broad (001) reflection of CTF-1 (Fig. S5, left) has its maximum slightly shifted to $20 = 24.2^{\circ}$. The shift indicates an increase of the layer distance between the triazine sheets to 3.7 Å.¹⁵ Thermogravimetric analysis (TGA) revealed decomposition of the thermally stable CTF-1 compound at a temperature of 440 °C (Fig. S5, right).



Fig. S5 PXRD pattern (left) and TGA (right) of CTF-1 in temperature range of 25 to 1000 °C at the heating rate of 5 °C/min under N₂ atmosphere.

It was further investigated whether smaller CTF-1 particles could be obtained with additional treatment by means of a ball-mill. In fact, the treatment with a ball-mill (1h, frequency: 20 s^{-1}) of CTF-1 results in a total reduction in particle size compared to mortar-ground CTF-1 (cf. Fig. S6). However, SEM images of CTF-1 (Fig. S6, right) clearly show that larger CTF-1 particles (up to ~50 µm) are still present even after the additional treatment. We note again that IL and PC also exfoliate the CTF layers during the microwave treatment. Thus, the initial big blocks of bulk CTF-1 will be transformed into layers of about 10 nm thickness as indicated by the contrast in the TEM images of the Rh@CTF-1 samples.



Fig. S6 SEM images of mortar-ground CTF-1 (left) and CTF-1 after treatment by means of a ball-mill (1h, frequency: 20 s^{-1} , right).

Structural formula of the ionic liquid (IL) and propylene carbonate (PC)

lonic liquids (ILs) gain increasing importance in modern chemistry^{18,19} and are applied, for example, as solvents and stabilizing reagents for M-NPs synthesis²⁰⁻²³ or as reactants.²⁴ Compared with coordinating stabilizers, ILs stabilize M-NPs through electrostatic and steric interactions.²⁵⁻²⁸ ILs are highly thermal stable and have a negligible vapor pressure.²⁹

Organic carbonates are used as solvents in industrial applications such as cleaning, gas treating, textile dyeing and as solvents in electrochemistry.^{30,31} Propylene carbonate, PC (Fig. S7) is an aprotic highly dipolar solvent like dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), with a very low toxicity.³²⁻³⁴ PC is used as a solvent in lithium ion batteries,³⁵⁻³⁸ in the FLUOR process,³⁹ in the copper wire-coating process⁴⁰ and for M-NPs synthesis as stabilizing reagent.^{41,42}





1-n-butyl-3-methyl-imidazolium - bistriflimide [BMIm][NTf₂],

 $NTf_2^- = [(CF_3SO_2)_2N]^-$

propylene carbonate, PC

Fig. S7 Ionic liquid (IL) and propylene carbonate (PC) used as reaction media and stabilizer for NP syntheses.

Synthesis and characterization of the CTF-1-supported NPs

The synthesis details for Rh@CTF-1 are described in the main manuscript. Ruthenium, Iridium and Platinum nanoparticles (Ru-, Ir- and Pt-NPs) were synthesized and supported simultaneously on CTF-1 by microwave irradiation (230 °C, 50 W, 10 min) in the presence of CTF-1 (Scheme S8). As reaction media we used the ILs 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF4]) (Scheme S8), [BMIm][NTf₂] and PC (Fig. S7).



Scheme S8 Reaction scheme of M-NPs@CTF-1 composite nanomaterial for M = Ru, Ir and Pt synthesized from $Ru_3(CO)_{12}$, $Ir_4(CO)_{12}$ and platinum(II) acetylacetonate in the ILs 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF4]), [BMIm][NTf₂] or in PC by microwave irradiation.

- Rh@CTF-1



Fig. S9 TEM (upper row) and HR-TEM (lower row) images and particle size histogram from 66 particles of Rh@CTF-1 composite nanomaterials synthesized in PC using microwave irradiation (6.1 wt.-% Rh in Rh/CTF-1). TEM and HR-TEM images were taken from different positions on the TEM grid of the same sample. For the EDX analysis in combination with TEM see Fig. S10.

The presence of rhodium in the Rh@CTF-1 composite nanomaterial was supported by energy dispersive X-ray spectroscopy (EDX, in combination with TEM) for qualitative element composition. EDX spectroscopy (Fig. S10) show the expected signals for Rh besides the bands for carbon and copper of the CTF-1 and the carboncoated copper grid. The small oxygen peak can largely be attributed to air contamination when the sample was introduced into the TEM device.



Fig. S10 EDX analysis (in combination with TEM) of Rh@CTF-1 synthesized in [BMIm][NTf₂] (left) or in PC (right).



Fig. S11 SEM image (left) and Rh EDX mapping analysis (right) of Rh@CTF-1 composite nanomaterials synthesized in PC.



Fig. S12 PXRD and SAED (Rh reference peaks in red from COD 9008482, cubic structure) of Rh@CTF-1 synthesized in PC. From the PXRD the Rh-NP diameter was calculated with the Scherrer equation to 3–5 nm (Scherrer factor = 0.9; anisotropic defects were not considered; a range is given for diameter values derived from different reflections).

- Ru@CTF-1

The size regimes of the Ru-NPs were determined by transmission electron microscopy (TEM) to average diameters of $3.0(\pm 0.5)$ nm for Ru@CTF-1 synthesized in [BMIm][NTf₂] (Fig. S13, top) and $4(\pm 2)$ nm for Ru@CTF-1 synthesized in PC (Fig. S15, top). An exact evaluation of the particle size of Ru@CTF-1 synthesized in [BMIm][BF₄] was not possible, because the TEM device reached its resolution limit at higher magnifications (Fig. S14, top).

The TEM images in combination with EDX analysis verify the successful deposition of ruthenium nanoparticles on CTF-1 for Rh@CTF-1 synthesized in [BMIm][NTf₂] (Fig. S13, middle right) and PC (Fig. S15, middle left).

The deposition of ruthenium particles is not easy to see in the TEM images of Ru@CTF-1 synthesized in [BMIm][BF₄] (Fig. S14, top), but is confirmed by SAED measurements on the CTF-1 particle yielded crystalline Ru metal (Fig. S14, bottom).

The Ru@CTF-1 nanomaterial synthesized in IL and PC showed low crystallinity by PXRD due to the small particle size and amorphous character of CTF-1 (Fig. S13, bottom left and Fig. S14, S15, middle right). But, the crystalline hexagonal phase of Ru metal was clearly verified by SAED for Ru@CTF-1 synthesized in IL (Fig. S13, bottom right and S14, bottom).



Fig. S13 TEM images (top), particle size histogram from 50 particles (middle, left) EDX analysis in combination with TEM (middle, right), PXRD (bottom, left) and SAED (bottom, right) of Ru@CTF-1 composite nanomaterials synthesized in [BMIm][NTf₂] using microwave irradiation. Ru reference peaks in red from COD 1539052, hexagonal structure.



Fig. S14 TEM images (top), EDX analysis in combination with TEM (middle, left), PXRD (middle, right) and SAED (bottom) of Ru@CTF-1 composite nanomaterials synthesized in [BMIm][BF4] using microwave irradiation. Ru reference peaks in red from COD 1539052, hexagonal structure.



Fig. S15 TEM images (top), EDX analysis in combination with TEM (middle, left), PXRD (middle, right) and SAED (bottom) of Ru@CTF-1 composite nanomaterials synthesized in PC using microwave irradiation. Ru reference peaks in red from COD 1539052, hexagonal structure.

- Ir@CTF-1

An exact evaluation of the particle sizes of Ir@CTF-1 was not possible due to the very small size of the Ir-NPs and the superimposed amorphous CTF-1, where the TEM device reached its resolution limit. Thus, we can only confirm a particle size diameter of less than 10 nm (Fig. S16, top left and middle). The crystallinity and the orthorhombic phase of Ir metal was verified by SAED and PXRD measurements, the latter albeit with low crystallinity (Fig. S16, top right and bottom right).



Fig. S16 TEM images (left, middle), SAED (top, right), EDX analysis in combination with TEM (bottom, left) and PXRD (bottom, right) of Ir@CTF-1 composite nanomaterials synthesized in [BMIm][NTf₂] using microwave irradiation. Ir reference peaks in red from COD 4124455, orthorhombic structure.

- Pt@CTF-1

The (high-resolution, HR-) TEM images of Pt@CTF-1 show large deposits of spherically-shaped Pt islands (Fig. S17). A closer view reveals that these Pt islands are aggregates of smaller primary particles with an average diameter of 3(± 1) nm for Pt@CTF-1 synthesized in [BMIm][NTf₂] (Fig. S17, top right and bottom). TEM-EDX analysis (Fig. S18, top left) and PXRD verify the formation of metallic platinum. The PXRD crystal phase was positively matched to cubic Pt metal (Fig. S18, top right). The SAED showed relatively low crystallinity (Fig. S18, bottom).



Fig. S17 (HR-)TEM images and particle size histogram from 53 particles of Pt-CTF-1 composite nanomaterials synthesized in [BMIm][NTf₂] using microwave irradiation. Images were taken from different positions on the TEM grid.



Fig. S18 EDX analysis in combination with TEM (top, left), PXRD (top, right) and SAED (bottom) of Pt-CTF-1 synthesized in [BMIm][NTf₂]. Pt reference peaks in red from COD 1011103, cubic structure.

Hydrogenation of benzene and cyclohexene

Table S19

Catalytic hydrogenation of benzene to cyclohexane with Ru@CTF-1, Ir@CTF-1 and Pt@CTF-1 composite nanomaterials

Catalyst ^a	Solvent ^b	Loading [%] ^c	Conversion [%] ^d	Time [min] ^e	TOF [h ⁻¹] ^f
Ru@CTF-1	[BMIm][BF ₄] ^g	5.0	63	180	1348
	[BMIm][BF ₄] ^h	11.6	>99	127	3076
	[BMIm][NTf ₂] ^g	8.3	16	180	1043
	PC ^g	9.0	15	180	326
Ir@CTF-1	[BMIm][NTf ₂] ^g	5.4	Xi	Xi	Xi
Pt@CTF-1	[BMIm][NTf ₂] ^g	2.7	Xi	Xi	Xi

^a Hydrogenation with M@CTF-1 (M = Ru, Ir, Pt), (containing 1.73 x 10⁻³ mmol M) at a benzene/ metal ratio of 6436, 70 °C, 10 bars H₂. ^b Catalyst synthesized in the ILs [BMIm][NTf₂], [BMIm][BF₄] or in PC. ^c Metal content of the M@CTF-1 composites material was determined by AAS. ^d Calculation based on cyclohexane yield determined by headspace GC corresponding to quantitative conversion of benzene (1.0 mL, 0.87 g, 11.14 mmol). ^e Time needed for the given conversion. ^f Turnover frequency (TOF) = activity as (mol cyclohexane) x (mol M)⁻¹ x h⁻¹; with total quantity of metal present in the nanomaterial. ^g 0.5 wt.-% M-NPs related to 1 g IL or PC. ^h 1 wt.-% M-NPs related to 1 g IL. ⁱ No conversion after at least 3 hours.

Table S20

Catalytic hydrogenation of cyclohexene	to cyclohexane	with Ru@CTF-1	, Ir@CTF-1
and Pt@CTF-1 composite nanomaterials	;		

Catalyst ^a	Solvent ^b	Loading [%] ^c	Conversion [%] ^d	Time [min] ^e	TOF [h ⁻¹] ^f
Ru@CTF-1	[BMIm][BF ₄] ^g	5.0	>99	180	35694
	[BMIm][BF ₄] ^h	11.6	>99	127	17306
Ir@CTF-1	[BMIm][NTf ₂] ^g	5.4	>99	6	57110
Pt@CTF-1	[BMIm][NTf ₂] ^g	4.7	>99	20	26589

^a Hydrogenation with M@CTF-1 (M = Ru, Ir, Pt), (containing 1.73 x 10⁻³ mmol M) at a cyclohexene/ metal ratio of 5699, 70 °C, 10 bars H₂. ^b Catalyst synthesized in the ILs [BMIm][NTf₂], [BMIm][BF₄] or in PC. ^c Metal content of the M@CTF-1 composites material was determined by AAS. ^d Calculation based on cyclohexane yield determined by headspace GC corresponding to quantitative conversion of cyclohexene (1.0 mL, 0.81 g, 9.86 mmol). ^e Time needed for the given conversion. ^f Turnover frequency (TOF) = activity as (mol cyclohexane) x (mol M)⁻¹ x h⁻¹; with total quantity of metal present in the nanomaterial. ^g 0.5 wt.-% M-NPs related to 1 g IL or PC. ^h 1 wt.-% M-NPs related to 1 g IL.



Fig. S21 H₂-uptake over time for the hydrogenation of benzene to cyclohexane with Rh@CTF-1 synthesized in [BMIm][NTf₂].

Estimate on the number of Rh surface atoms: From TEM, we obtained an average Rh-NPs diameter of 3 nm for Rh@CTF-1 synthesized in [BMIm][NTf₂] (Rh@CTF-1/IL) and 2 nm for Rh@CTF-1 synthesized in PC (Rh@CTF-1/PC). From these average diameters D the total number of metal atoms (N_T) in the nanocrystal can be calculated according to equation $(1)^{43-46}$

$$N_T = \frac{N_A \rho V}{A_r} \text{ and } V = \frac{4}{3} \pi \left(\frac{D}{2}\right)^3 \tag{1}$$

with N_A=Avogadro's number (6.022 x 10^{23} mol⁻¹), ρ = rhodium density (ρ = 12.38 g x cm⁻³) and A_r = relative atom mass (A_r = 102.91 g x mol⁻¹), equation (1) gives N_T = 1024 atoms for Rh@CTF-1/IL and N_T = 303 atoms for Rh@CTF-1/PC. The total average atom number N_T = 1024 is between the total atom number of N_m = 923 for an icosahedron or cuboctahedron with m = 7 shells and N_m = 1415 for an icosahedron or cuboctahedron with m = 8 shells according to N_m = (1/3)(2m-1)(5m²-5m+3).⁴⁷

The number of shells (m) can be used to finally calculate the number of surface atoms (Ns) according to equation (2):⁴⁷

$$N_S = 10m^2 - 20m + 12 \tag{2}$$

The number of surface atoms for a seven-shell icosahedron or cuboctahedron is $N_S = 362$ and for an eight-shell icosahedron or cuboctahedron $N_S = 492$. In our approximation, we take here an average of $N_S = 427$ for the number of surface atoms for $N_T = 1024$ (for Rh@CTF-1/IL). This gives a fraction of exposed or surface atoms $N_S/N_T \approx 427/1024 = 0.42$ or 42% on average. Thus, calculations by regarding only the surface rhodium atoms yield TOF values up to 34498 h⁻¹ for Rh@CTF-1/IL.

The total average atom number $N_T = 303$ (for Rh@CTF-1/PC) is close to the total atom number of $N_m = 309$ for an icosahedron or cuboctahedron with m = 5 shells. The number of surface atoms for a five-shell icosahedron or cuboctahedron is $N_S = 162$ for the number of surface atoms for $N_T = 303$. This gives a fraction of exposed or surface atoms $N_S/N_T \approx 162/303 = 0.53$ or 53% on average. Thus, calculations by regarding only the surface rhodium atoms yield TOF values up to 58583 h⁻¹ for Rh@CTF-1/PC.

Another Rh@CTF-1 composite materials with different amounts of Rh metal were synthesized. The Rh metal content was determined by AAS to 8.6 wt.-% for Rh@CTF-1 synthesized in [BMIm][NTf2], Rh@CTF-1/IL(8.6) and 15.9 wt.-% synthesized in PC, Rh@CTF-1/PC(15.9). The size regimes of the Rh-NPs were determined by (HR-)TEM to average diameters of 3.0 (± 0.5) nm for Rh@CTF-1/IL(8.6) (Fig. S22, top) and 2.0 (± 0.5) nm for Rh@CTF-1/PC(15.9) (Fig. S23, top). The PXRD crystal phase was positively matched to cubic Rh metal (Fig. S22 and Fig. S23, bottom right). For comparison, the compounds were tested for the hydrogenation of benzene to cyclohexane under the same conditions (Table S24 and Fig. S25). The Rh@CTF-1 composite materials with about twice the metal content seems to be highly active (TOF ~11000 h^{-1}) with quantitative conversion after 49 min for Rh@CTF-1/IL(8.6) and 35 min for Rh@CTF-1/PC(15.9) (Table S24). The catalyst Rh@CTF-1/IL(8.6) and Rh@CTF-1/PC(15.9) can be recycled for at least five times, with slightly loss of activity in the first four runs (Table S24 and Fig. S25). It could be observed that the composite materials with about twice the metal content are not as active as Rh@CTF-1 composite with Rh metal loadings of 4.4 and 6.1 wt.-% (cf. Table 1 in the main manuscript). Catalytic reactions are complex and depend on many factors. Here we just note that the catalytic activity is dependent on the degree of metal loading of the composite material. As supported by TEM images (Fig. S22 and Fig. 23, top), for Rh@CTF-1/IL(8.6) and Rh@CTF-1/PC(15.9) the CTF-1 is clearly more densely loaded with Rh-NPs, apparently resulting in a reduction of the catalytically active surface sites.



Fig. S22 (HR-)TEM images (top rows), particle size histogram from 77 particles (bottom, left) and PXRD (bottom, right) of Rh@CTF-1 composite nanomaterials synthesized in [BMIm][NTf₂], Rh@CTF-1/IL with 8.6 wt.-% Rh (synthesized from 1.0 wt.-% Rh-NPs and 1.0 wt.-% CTF-1 related to 1 g IL). Images were taken at different positions on the TEM grid. Rh reference peaks in red from COD 9008482, cubic structure. Compare to Fig. 1 for the TEM images of Rh@CTF-1/IL with 4.4 wt.-% Rh.



Fig. S23 (HR-)TEM images (top rows), particle size histogram from 60 particles (bottom, left) and PXRD (bottom, right) of Rh@CTF-1 composite nanomaterials synthesized in PC, Rh@CTF-1/PC with 15.9 wt.-% (synthesized from 1.0 wt.-% Rh-NPs and 1.0 wt.-% CTF-1 related to 1 g PC). Images were taken at different positions on the TEM grid. Rh reference peaks in red from COD 9008482, cubic structure. Compare to Fig. S9 for the TEM images of Rh@CTF-1/PC with 6.1 wt.-% Rh.

Table S24

Catalytic hydrogenation of benzene to cyclohexane with Rh@CTF-1 composite nanomaterials with different amount of Rh metal

Catalyst ^a	Run	Conversion [%] ^b	Time [min] ^c	TOF [h ^{−1}] ^d
Rh@CTF-1/IL(8.6) ^e	1	>99	49	8050
	2	>99	55	7165
	3	>99	59	6653
	4	>99	61	6456
	5	>99	88	4466
Rh@CTF-1/PC(15.9) ^f	1	>99	35	11242
	2	>99	39	10031
	3	>99	45	8694
	4	>99	52	7582
	5	>99	78	5015

^a Hydrogenation with Rh@CTF-1, (containing 1.73 x 10^{-3} mmol Rh) at a benzene/ metal ratio of 6436, 70 °C, 10 bars H₂. ^b Calculation based on cyclohexane yield determined by an H₂-uptake of 757 mL (33.4 mmol) corresponding to quantitative conversion of benzene (1.0 mL, 0.87 g, 11.14 mmol). ^c Time needed for the given conversion. ^d Turnover frequency (TOF) = activity as (mol cyclohexane) x (mol M)⁻¹ x h⁻¹; with total quantity of metal present in the nanomaterial. ^e Catalyst synthesized in the IL [BMIm][NTf₂], 1.0 wt.-% M-NPs and 1.0 wt.-% CTF-1 related to 1 g IL. Metal content of the Rh@CTF-1 composites material was determined by AAS to 8.6 wt.-% Rh. ^f Catalyst synthesized in PC, 1.0 wt.-% M-NPs and 1.0 wt.-% CTF-1 related to 1 g IL. Metal content of the Rh@CTF-1 composites material was determined by AAS to 15.9 wt.-% Rh.



Fig. S25 H₂-uptake over time for the hydrogenation of benzene to cyclohexane with Rh@CTF-1 synthesized in [BMIm][NTf₂], Rh@CTF-1/IL(8.6) (left) and Rh@CTF-1 synthesized in PC, Rh@CTF-1/PC(15.9) (right).

Table S26

Hydrogenation reactions of benzene to cyclohexane by different materials							
Nanoparticle catalyst	T [°C]/ pH ₂ [bar]	Conversion [%]	TOF [h ⁻¹] ^a	Ref.			
Rh@CTF-1/IL⁵	70/10	>99	14489	This work			
Rh@CTF-1/PC ^c	70/10	>99	31049	This work			
Rh@C ^d	70/10	>99	803	This work			
Rh@CeO ₂	25/3	>99	495	48			
Rh@Fe ₃ O ₄	100/30	>99	297	49			
Rh@MgO	100/10	100	83000	50			
Rh/PVP-K30	80/20	88	440	51			
Rh@TRGO/IL ^e	50/4	98.8	310	52			
Rh-NPs/IL ^e	75/40	100	250	53			
Rh@AlO(OH)	75/4	100	1700	54			
Ru-Pt@MIL-101	60/10	>99	2557	55			
Ru@TRGO/PC ^c	100/10	98.5	34331	41			
Ru@Graphene/IL ^f	110/80	>99.9	6060	56			
Ru@SiO ₂	100/20	>99	5000	57			
Ru-IL-Graphen ^f	110/8	>99.9	6000	56			
Ru-NPs/IL ^f	40/6	100	555	58			
Ir@TRGO/IL ^e	100/10	89.8	10280	59			

^a Turnover frequency (TOF) = activity as (mol cyclohexane) x (mol metal)⁻¹ x h⁻¹; with total quantity of metal present in the nanomaterial. ^b catalyst synthesized in [BMIm][NTf₂]. ^c catalyst synthesized in PC. ^d purchased from Sigma Aldrich; Rh loading in the commercial Rh@C material is 5 %. ^e catalyst synthesized in [BMIm][BF₄]. ^f catalyst synthesized in 1-butyl-3-methylimidazolium cholate.



Fig. S27 TEM images and particle size histogram from 59 of Rh@CTF-1 composite nanomaterials synthesized in [BMIm][NTf₂] after 10 hydrogenation runs. Images were taken at different positions on the TEM grid.



Fig. S28 Additional TEM images and particle size histogram from 77 of Rh@CTF-1 composite nanomaterials synthesized in PC after 10 hydrogenation runs.



Fig. S29 SEM image (left) and Rh EDX mapping analysis (right) of Rh@CTF-1 composite nanomaterials synthesized in [BMIm][NTf₂] after 10 hydrogenation runs.



Fig. S30 SEM image (left) and Rh EDX mapping analysis (right) of Rh@CTF-1 composite nanomaterials synthesized in PC after 10 hydrogenation runs.



Fig. S31 SAED (Rh reference in red from COD 9008482, cubic structure) of Rh@CTF-1 synthesized in [BMIm][NTf₂] (left) and in PC (right) after 10 hydrogenation runs.



Fig. S32 (HR-)TEM images (top) and particle size histogram from 84 particles (bottom) of Rh@CTF-1 composite synthesized from $Rh_6(CO)_{16}$ and CTF-1 in [BMIm][NTf₂] with a dispersion time of 7 days.



Fig. S33 TEM images (top) and particle size histogram from 63 particles (bottom) of Rh@CTF-1 composite synthesized from $Rh_6(CO)_{16}$ and CTF-1 in PC with a dispersion time of 7 days.



Fig. S34 H₂-uptake over time for the hydrogenation of benzene to cyclohexane with Rh@CTF-1/PC catalyst with 15.9 wt.-% Rh metal, before and after catalyst separation by filtration (marked by arrow) (through 0.2 μ m syringe filter).



Fig. S35 Repeated HER test of Rh@CTF-1 (left) and Pt@CTF-1 (right).

References

- 1 S. Yamaguchi, K. Kamiya, K. Hashimoto and S. Nakanishi, *Chem. Commun.*, 2017, **53**, 10437–10440.
- 2 K. Ghosha, R. A. Mollaa, A. Iqubalb, S. Islama and M. Islam, *Appl. Catal. A: General*, 2016, **520**, 44–52.
- 3 C. E. Chan-Thaw, A. Villa, G. M. Veith, K. Kailasam, L. A. Adamczyk, R. R. Unocic, L. Prati and A. Thomas, *Chem. Asian J.*, 2012, **7**, 387–393.
- 4 J. Roeser, K. Kailasam and A. Thomas, *ChemSusChem*, 2012, **5**, 1793–1799.
- 5 J. L. Liu, E. M. Zong, H. Y. Fu, S. R. Zheng, Z. Y. Xu and D. Q. Zhu, *J. Colloid Interface Sci.*, 2012, **372**, 99–107.
- 6 X. W. Chen, F. Yuan, Q. F. Gu and X. B. Yu, *J. Mater. Chem. A*, 2013, **1**, 11705–11710.
- 7 A. Modak, J. Mondal, M. Sasidharan and A. Bhaumik, *Green Chem.*, 2011, **13**, 1317–1331.
- 8 J. Liu, Y. Hu and J. Cao, *Catal. Commun.*, 2015, **66**, 91–94.
- 9 L. Liu, P.-Z. Li, L. Zhu, R. Zou and Y. Zhao, *Polymer*, 2013, **54**, 596–600.
- 10 R. Rohan, K. Pareek, W. Cai, Y. Zhang, G. Xu, Z. Chen, Z. Gao, Z. Dan and H. Cheng, *J. Mater. Chem. A*, 2015, **3**, 5132–5139.
- 11 M. Pilaski, J. Artz, H.-U. Islam, A. M. Beale and R. Palkovits, *Microporous and Mesoporous Mater.*, 2016, **227**, 219–227.
- 12 M. Liu, L. Guo, S. Jin and B. Tan, J. Mater. Chem. A, 2019, 7, 5153–5172.
- 13 P. Kuhn and M. Antonietti, A. Thomas, *Angew. Chem. Int. Ed.*, 2008, **47**, 3450–3453.
- 14 P. Kuhn, A. Thomas and M. Antonietti, *Macromolecules*, 2009, **42**, 319–326.
- 15 A. Bhunia, S. Dey, M. Bous, C. Zhang, W. von Rybinski and C. Janiak, *Chem. Commun.*, 2015, **51**, 484–486.
- 16 C. E. Chan-Thaw, A. Villa, P. Katekomol, D. Su, A. Thomas and L. Prati, *Nano Lett.*, 2010, **10**, 537–541.
- 17 S. Dey, A. Bhunia, D. Esquivel and C. Janiak, J. Mater. Chem. A, 2016, 4, 6259– 6263.
- 18 D. H. Weiß, F. Schröder and M. Köckerling, *Z. Anorg. Allg. Chem.*, 2017, **643**, 345–351.
- 19 A. Efimova, L. Pfützner and P. Schmidt, *Thermochim. Acta*, 2015, **604**, 129–136.
- 20 P. S. Campbell, M. H. G. Prechtl, C. C. Santini and P.-H. Haumesser, *Curr. Org. Chem.*, 2013, **17**, 414–429.
- 21 D. Freudenmann. S. Wolf, M. Wolff and C. Feldmann, *Angew. Chem. Int. Ed.*, 2011, **50**, 11050–11060.
- 22 E. Ahmed, J. Breternitz, M. F. Groh and M. Ruck, *CrystEngComm*, 2012, **14**, 4874–4885.
- 23 E. Ahmed and M. Ruck, *Dalton Trans.*, 2011, 40, 9347–9357.
- 24 K. Schütte, J. Barthel, M. Endres, M. Siebels, B. Smarsly, J. Yue and C. Janiak, *ChemistryOpen*, 2017, **6**, 137–148.
- 25 D. Marquardt and C. Janiak, Nachr. Chem., 2013, 61, 754–757.
- 26 G. Schmid, Nanoparticles, Wiley-VCH, Weinheim, Germany, 2004.
- 27 M. Antonietti, D. Kuang, B. Smarly and Y. Zhou, *Angew. Chem. Int. Ed.*, 2004, **43**, 4988–4922.
- 28 H. Kaper, F. Endres, I. Djerdj, M. Antonietti, B. M. Smarsly, J. Maier and Y.-S. Hu, *Small*, 2007, **3**, 1753–1763.
- 29 P. Wasserscheid and W. Keim, Angew. Chem. Int. Ed., 2000, **39**, 3772–3789.

- 30 J. H. Clements, J. Ind. Eng. Chem. Res., 2003, 42, 663–674.
- 31 A.-A. G. Shaikh and S. Sivaram, Chem. Rev., 1996, 96, 951–976.
- 32 J. Bayardon, J. Holz, B. Schäffner, V. Andrushko, S. P. Verevkin, A. Preetz and A. Börner, *Angew. Chem. Int. Ed.*, 2007, **46**, 5971–5974.
- 33 S. P. Verevkin, V. N. Emel'yanenko, A. V. Toktonov, Y. Chernyak, B. Schäffner and A. J. Börner, *J. Chem. Thermodyn.*, 2008, **40**, 1428–1432.
- 34 B. Schäffner, F. Schäffner, S. P. Verevkin and A. Börner, *Chem. Rev.*, 2010, **110**, 4554–4581.
- 35 R. Jasinski, J. Electroanal. Chem., 1967, 15, 89–91.
- 36 K. K. D. Ehinon, S. Naille, R. Dedryvère, P.-E. Lippens, J.-C. Jumas and D. Gonbeau, *Chem. Mater.*, 2008, **20**, 5388–5398.
- 37 R. Jasinsji, J. Electroanal. Chem., 1967, 15, 89.
- 38 R. F. Nelson and R. N. J. Adam, *Electroanal. Chem.*, 1967, 15, 184.
- 39 A. L. Kohl and P. A. Buckingham, *Oil Gas J.*, 1960, **58**, 146.
- 40 S. Schmidt, Chem. Abstr., 2004, 142, 375279.
- 41 R. Marcos Esteban, K. Schütte, D. Marquardt, J. Barthel, F. Beckert, R. Mülhaupt and C. Janiak, *Nano-Structures & Nano-Objects*, 2015, **2**, 28–34.
- 42 J. Demel, J. Čejka, S. Bakardjieva and P. Štěpnička, *J. Mol. Catal. A: Chem.*, 2007, **263**, 259–265.
- 43 A. P. Umpierre, E. de Jesffls and J. Dupont, *ChemCatChem*, 2011, **3**, 1413–1418.
- 44 O. M. Wilson, M. R. Knecht, J. C. Garcia-Martinez and R. M. Crooks, *J. Am. Chem. Soc.*, 2006, **128**, 4510–4511.
- 45 A. Borodzinski and M. Bonarowska, *Langmuir*, 1997, **13**, 5613–5620.
- 46 H. Hosseini-Monfared, H. Meyer and C. Janiak, *J. Mol. Catal. A: Chem.*, 2013, **372**, 72–78.
- 47 R. E. Benfield, J. Chem. Soc. Faraday Trans., 1992, 88, 1107–1110.
- 48 S. Akbayrak, J. Colloid Interface Sci., 2018, 530, 459–464.
- 49 M. N. Shaikh, Md. A. Aziz, A. N. Kalanthoden, A. Helal, A. S. Hakeem and M. Bououdina, *Catal. Sci. Technol.*, 2018, **8**, 4709–4717.
- 50 A. Sánchez, M. Fang, A. Ahmed and R. A. Sánchez-Delgado, *Appl. Catal. A: General*, 2014, **477**, 117–124.
- 51 W. Alsalahi, W. Tylus and A. M. Trzeciak, *ChemCatChem*, 2018, **10**, 2051–2058.
- 52 D. Marquardt, C. Vollmer, R. Thomann, P. Steurer, R. Mülhaupt, E. Redel and C. Janiak, *Carbon*, 2011, **49**, 1326–1332.
- 53 X. D. Mu, J. Q. Meng, Z. C. Li and Y. Kou, *J. Am. Chem. Soc.*, 2005, **127**, 9694–9695.
- 54 I.-S. Park, M. S. Kwon, K. Y. Kang, J. S. Lee and J. Parka, *Adv. Synth. Catal.*, 2007, **349**, 2039–2047.
- 55 H. Liu, R. Fang, Z. Li and Y. Li, Chem. Eng. Sci., 2015, 122, 350–359.
- 56 W. Xiao, Z. Sun, S. Chen, H. Zhang, Y. Zhao, C. Huang and Z. Liu, *RSC Adv.*, 2012, **2**, 8189–8193.
- 57 X. Kang, J. Zhang, W. Shang, T. Wu, P. Zhang, B. Han, Z. Wu, G. Mo and X. Xing, *J. Am. Chem. Soc.*, 2014, **136**, 3768–3771.
- 58 S. D. Miao, Z. M. Liu, B. X. Han, J. Huang, Z. Y. Sun, J. L. Zhang and T. Jiang, *Angew. Chem. Int. Ed.*, 2006, **45**, 266–269.
- 59 R. Marcos Esteban, K. Schütte, P. Brandt, D. Marquardt, H. Meyer, F. Beckert, R. Mülhaupt, H. Kölling and C. Janiak, *Nano-Structures & Nano-Objects*, 2015, 2, 11–18.