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1 General information

All water or air-sensitive reactions were carried out under argon atmosphere using the Schlenk technique. The solvents employed were bought as anhydrous, stored under Ar over molecular sieve and degassed by bubbling with argon prior to use. All other chemicals were used as received.

Table S1. Purity and suppliers of use materials

Compound	**Purity**	**Supplier**
(R)-BINAP	98,0%	abcr
phenylboronic acid pinacol ester	97.0%	
tetrakis(triphenylphosphine)palladium (0)	99.9%	
triethoxychlorosilane	95%	
bis(methyl-allyl)cyclooctadiene ruthenium(II)	97%	
1-bromo-4-iodobenzene	98.0%	fluorochem
2-[4-[3,5-bis[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]phenyl]phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane	98%	BLDPharm
2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane	97%	
2,4,6-tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-1,3,5-triazine	98%	
cesium carbonate	99.0%	Sigma Aldrich
4,4'-dibromobiphenyl	98.0%	
bromobenzene	99.0%	
n-butyllithium (1,6 M in hexanes)	-	
aq. hydrogen peroxide (36 %)	-	
triphenylphosphine	>99.0%	
trichlorosilane	99.0%	
$IrCl_3 \cdot x\,H_2O$	synth. grade	
pyrrole-2-carboxaldehyde	98%	
formic acid	98-100%	
2-acetyl-6-bromopyridine	98%	TCI
Silica pellets (SS61138 3 mm Pellets, Sample NO 2011910001)		Saint-Gobain NORPRO
The porous glass pieces (“VitraPOR Spezial Glasfilter”, cylindrical Por. 2, 3, diameter: 10.0 ± 0.2 mm with length 2.0 ± 0.1 mm or 45 ± 0.5 mm)		ROBUGlas
(R)-(+)-BINAPO	Synthesized according to literature procedure[1]	
(R)-(+)-Br_2-BINAPO	Synthesized according to literature procedure[1]	
1,3,5-Tris(4-Bromophenyl)benzene	Synthesized according to literature procedure[1]	
6,6''-dibromo-4'-(1H-pyrrol-2-yl)-2,2':6',2''-terpyridine	Synthesized according to literature procedure[2]	

Liquid ^{1}H, ^{13}C and ^{31}P NMR measurements were performed at 400, 100 and 75 MHz respectively at a 400 MHz BRUKER UltraShield Avance III. ^{29}Si NMR was carried out at a 600MHz Bruker AV III HD at 80 MHz. Chemical shifts of liquid-phase NMR measurements (δ in ppm) were referenced to TMS.

Solid state $^{31}P(^{1}H)$-MAS-NMR, ^{29}Si-MAS-NMR, ^{19}F-MAS-NMR and $^{13}C(^{1}H)$-MAS-NMR were performed at a 500 MHz BRUKER Avance III (4 mm MAS rotor, Spinning at 7 kHz, 8 kHz, 10 kHz or 13 kHz at rt). Referencing was done by adamantane.

IR spectra of the polymers, as well as the ball-milled silica and glass materials were collected using a Bruker VERTEX 70 spectrometer with a Harrick praying mantis DRIFTS cell at atmospheric pressure and ambient temperature. ATR spectra of the glass slides were recorded using the Platinum ATR accessory with a diamond tip on the VERTEX 70. Transmission spectra of silane oils were recorded using NaCl windows. Absorption intensities of organic molecules are given in the following way: vw = very weak (0-10%), w = weak(10-25%), m = medium(25-75%), s = strong (75-90%), vs = very strong (90-100%).

Nitrogen physisorption measurements were performed after degassing in high vacuum at 433.15 K overnight using a Micromeritics ASAP 2060 at 77K using nitrogen (99.999%).

Thermogravimetric measurements were carried out at an NETZSCH STA 409 C/CD at 5 K/min in N_2.

Inductively-coupled plasma-optical emission spectroscopy (ICP-OES) were performed at a Spectroblue device.

ICP-MS measurements of the reaction solutions have been performed with an Agilent 8800 ICP-MS/MS Triple Quadrupole. The calibration was performed externally, and filtered samples were acidified with 20 % HCl and H_2O_2-solution (30 vol.-%) to a pH of ~ 1. Analysis of polymeric samples was carried out at Mikroanalytisches Laboratorium Kolbe, c/o Fraunhofer Institut UMSICHT, Gebäude G – Osterfelder Str. 3, D-46047 Oberhausen.

SEM/EDX images were collected using an COXEM EM-30 AX with carbon sample trays after sputtering with gold plasma for 270 s at 7 mA current in fine vacuum.

Powder XRD patterns have been recorded on a 2nd generation Bruker D2 Phaser using the Cu K-α line as x-ray source.

GC-analysis of the gas phase was performed using an Agilent HP 6890 Series with a 50m CP-Wax-52-CB column. The FID detector was used at 250 °C. Helium was used as carrier gas at a constant pressure of 1.5 bar and the temperature was ramped with 8 K min^{-1} between 50-200°C.

HPLC measurements were carried out with a Shimadzu LCMS-2020, equipped with a RI-detector. The flow was set to 2.0 ml·min^{-1}, and the eluent was a mixture of water and TFA with a concentration of 154 µl/l. The organic acid resin column with dimensions of 300 x 8 mm was obtained from CS-chromatography service GmbH. The oven temperature was set to 40 °C.

Contact angle measurements were performed on a Krüss Drop Shape Analyzer DSA100. For analysis, 3 µL H_2O were dosed to the surface and the profile of the sessile drop in the region of the baseline is fitted to the “Tangent-2” polynomial function. The baseline was set manually. From the obtained parameters the slope at the three-phase point of contact at the baseline and from that the contact angle is calculated.”

2 Overview of Heterogeneous catalyst systems

Table S2. Selection of heterogeneous catalyst systems for the FAD reaction.

Ref.	Metal Precursor	Support	Conditions	TOF (h^{-1})	TON
1	$Ru(HCOO)_2$	pBINAP	10wt.% FA, 160°C	134 000	920 000
3	$Ru(TPPTS)L_4$	$(PPh_2(CH_2)_n/SiO_2$	110°C, 13wt.% FA	2780	-
4	IrH_3	PN^3P/SiO_2	90°C, 3M HCOOH/HCOOCs	13 290	540 000
5	$Fe(BF_4)_2$	polyRPhphos/SiO_2	90°C, 40wt.% FA in propylene carbonate	7600	8500
6, 7	Ir	CTF/Cordierite	80°C, 3M FA	207 000	540 000
8	RuPd	C_3N_4	60°C, 1M FA	30	60
9	$RuCl_2DPPE_2$		N,N-dimethyl-octylamine 60°C,	16 000	1000000
10	$IrCl_3$	PyrTerpy	160°C, 10wt.% FA	175 000	2 800 000
11	$H_2Ru(PPh_3)_4$	SiO_2-R-N$(PPh_2)_2$	75°C, 1.2 M FA in dioxane-	440	-
12	$[Cp^*IrCl_2]_2$	HMDAbpy@PAA	80°C, 1 M FA	110 000	2 180 000
13	$[Cp^*IrCl_2]_2$	Polypyrrole	90°C	46 000	-
14	Cp*Ir	PEI	80°C 20M FA	73 200 batch 157 continuous	332 889
15	Pt, Ru, BiOx	C	27–60°C	-	-

3 Synthesis of monomers

3.1 Synthesis of 1-Bromophenyltriethoxysilane ($BrPhSi(OEt)_3$, S-3)

The synthesis was carried out under Schlenk conditions. 1-Bromo-4-iodobenzene (4.9930 g, 17.65 mmol, 1 eq.) was dissolved in pentane (100 mL) and cooled to -78 °C. After dropwise addition of ^{n}BuLi (11.5 mL, 1.6 M in pentane, 18.4 mmol, 1.04 eq.) and stirring for 1 h at -78 °C followed by stirring at RT for 1 h, the lithium aryl precipitates as a white solid. After filtering off the solid and dissolving in Et_2O (100 mL), the resulting yellow solution was warmed up to 0 °C. Under vigorous stirring, a solution of $SiCl(OEt)_3$ (3.2264 g, 16.44 mmol, 0.93 eq.) in Et_2O (50 mL) cooled to 78 °C was added and the solution was stirred for 45 min at -78 °C, followed by 45 min at RT. The solvent was removed by distillation under inert gas at normal pressure. After fractioned vacuum distillation the product was obtained as a colorless oil (1.6067 g, 5.03 mmol, Y = 30.6 % based on $SiCl(OEt)_3$). The yield obtained via this synthesis route agrees with the literature yield for the reaction using Grignard reagent and TEOS (lit: = 27.6 %). The ^{1}H-NMR spectrum corresponds to the literature.

^{1}H-NMR (400 MHz, $CDCl_3$) δ [ppm] = 7,62 – 7,43 (m, 4H, $CH_{arom.}$), 3,86 (q, J = 7,0 Hz, 6H, CH_2-6), 1,23 (t, J = 7,0 Hz, 10H, CH_3-7).**^{13}C-NMR (100 MHz, $CDCl_3$)** δ [ppm] = 136,5 ($C_{arom.}$-1, 131,2 ($C_{arom.}$-4), 130,0 ($C_{arom.}$-2), 125,5 ($C_{arom.}$-3), 59,0 (CH_2-6), 18,4 (CH_3-7).**^{29}Si-NMR (80 MHz, $CDCl_3$)** δ [ppm] = - 58,4. **IR** $\tilde{\nu}$ (cm^{-1}) = 2975 (s), 2888 (m), 1571 (m), 1479 (m), 1378 (m), 1166 (m), 1110 (vs), 1076 (s), 1012 (m), 962 (m).

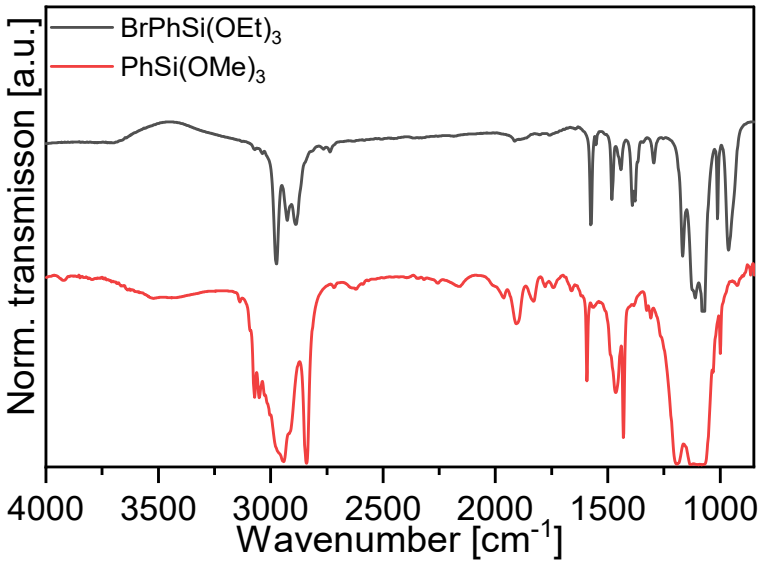

Figure S1. Transmission IR spectra of $BrPhSi(OEt)_3$ and $PhSi(OMe)_3$.

4 Surface modifications

4.1 Passivation procedure

Prior to the coating reactions, all glassware used was silylated using Me_3SiCl by adding 1-3 mL to the apparatus, followed by application of vacuum to generate silane vapor. Closing the apparatus under vacuum, after 1-3 h the silane was left to vaporize and subsequently silanized the glassware as previously described.[17]

4.2 Silica coating

4.2.1 General Procedure

The commercially available silica used (Saint-Gobain NORPRO SS61138) was ball-milled and dried at 250 °C in HV for 4 h. SiO_2 (3.0000 g) and the respective silane (0.3000 g) were suspended in toluene (30 mL) with the addition of a catalytic amount of DMF (0.1 vol.%). The suspension was refluxed for 72 h. After washing with EtOAc (100 mL), H_2O (200 mL) and EtOH (100 mL) and drying in the HV for 2 h at 60 °C, the products were obtained as colourless solids in quantitative yield. Coating with TMS-Cl

Coating was performed by refluxing SiO_2 (1.000 g) in Me_3SiCl (5 mL, 50 mmol) for 3 h and the product was obtained after the workup procedure described in the general procedure in quantitative yield.

IR ν (cm^{-1}) = 2966 (vw), 1420 (vw), 1254 (vw).

4.2.2 Coating with $PhSi(OMe)_3$

Coating was performed according to the general procedure and the product obtained in quantitative yield.

IR ν (cm^{-1}) = 2966 (vw), 1420 (vw), 1254 (vw).

4.2.3 Coating with $BrPh(SiOEt)_3$

Coating was performed according to the general procedure and the product obtained in quantitative yield.

^{13}C NMR (125 MHz, 11 kHz) δ [ppm] = 223.1, 135.3, 130.7, 125.3, 58.7, 16.1. **^{29}Si NMR (100 MHz, 7 kHz) δ [ppm]** = -64.9, -71.9, -91.9, -101.8, -109.0. **IR ν (cm^{-1})** = 2978 (vw), 2928 (vw), 1581 (vw), 1484 (vw), 1380 (vw).

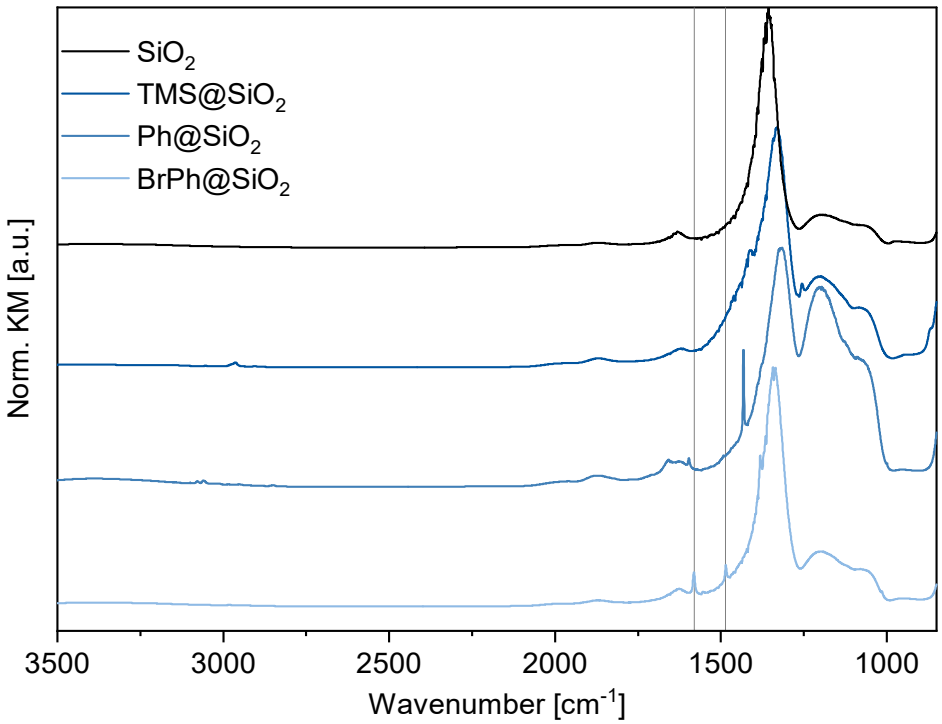

Figure S2. DRIFTS spectra of neat SiO_2 as well as SiO_2 coated with TMSCl, $PhSi(OMe)_3$ and $BrPh(SiOEt)_3$.

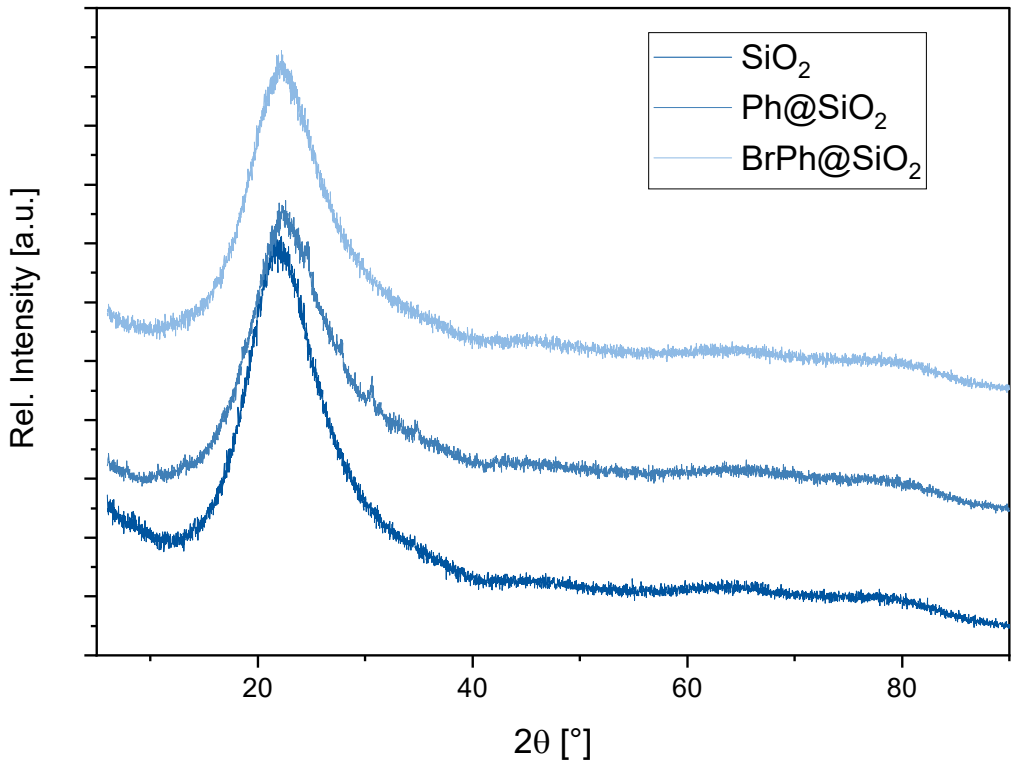

Figure S3. XRD of SiO_2 neat (top) coated with PhSi(OMe) (middle) and $BrPhSi(OEt)_3$ (bottom).

In the PXRD of Ph@SiO_2 4 reflexes in addition to the one observed in neat SiO_2 can be observed at 25°, 27°, 30° and 34°. No futher refelexes can be observed for BrPh@SiO_2.

4.3 Surface reaction with BrPh@SiO_2

4.3.1 Protection of BrPh@SiO_2 with TMSCl

After coating SiO_2 with $BrPhSi(OEt)_3$ as described above, the unreacted surface sites were protected from basic decomposition using Me_3SiCl. For this, BrPh@SiO_2 (1.0361 g) was refluxed in TMS-Cl (0.25 mL, 2.5 mmol) for EtOAc (100 mL), H_2O (200 mL) and EtOH (100 mL). Drying in the HV for 1 h at 60 °C, the product was subsequently obtained as a colorless solid with 55% yield.

4.3.2 Fluorination of BrPh@SiO_2 via Suzuki-crosscoupling

The coated material (200.2 mg) was suspended in dried, degassed DMF (2.5 mL) and 4-fluorophenylpinacolboronester (97.8 mg, 0.44 mmol, 1.0 eq.), $Pd(PPh_3)_4$ (0.5 mg, 0.43 µmol, 0.001 eq.) and Cs_2CO_3 (32.5 mg, 0.1 mmol, 0.2 eq.) were added under schlenk conditions. The resulting suspension was heated to 85°C for 4 h, cooled down, filtered and washed with EtOAc (25 mL), H_2O (25 mL) and acetone (10 mL). The fluorinated silica material was obtained in 63% yield.

^{13}C NMR (125 MHz, 11 kHz) δ [ppm] = 223.1, 135.3, 130.7, 125.3, 58.7, 16.1. **^{19}F NMR (80 MHz, 8 kHz)** δ [ppm] = -120 ppm. **^{29}Si NMR (100 MHz, 7 kHz) δ [ppm]** = -15, -64.9, -71.9, -91.9, -101.8, -109.0. **IR ν (cm^{-1})** = 2978 (vw), 2928 (vw), 1581 (vw), 1484 (vw), 1380 (vw).

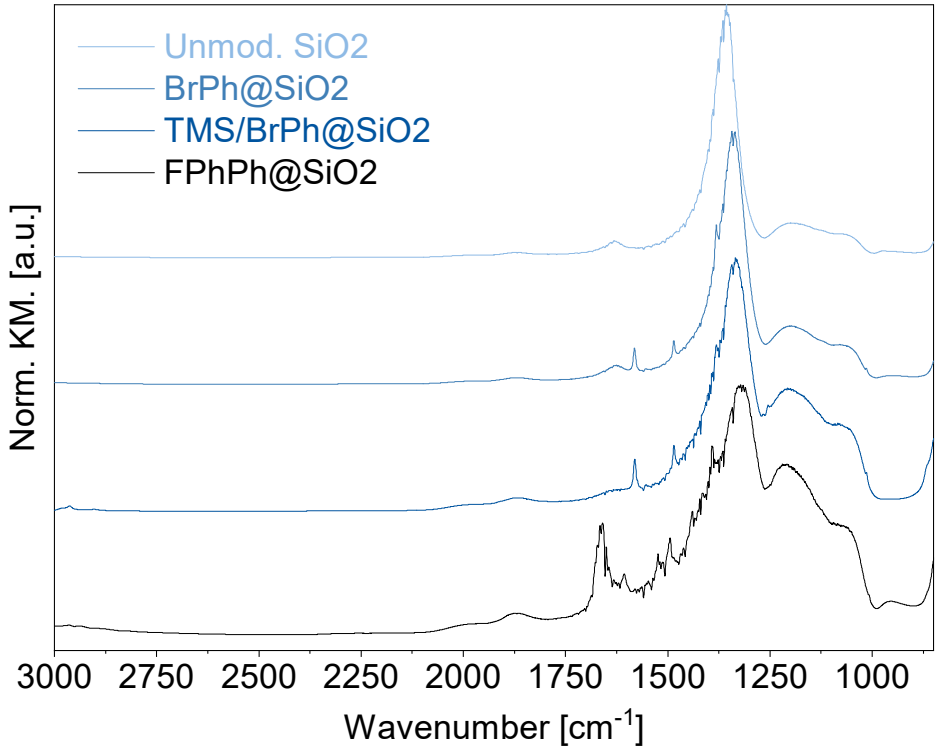

Figure S4. DRIFTS spectra of SiO_2, BrPh@SiO_2, TMS/BrPh@SiO_2 and FPhPh@SiO_2 the product of the Suzuki reaction.

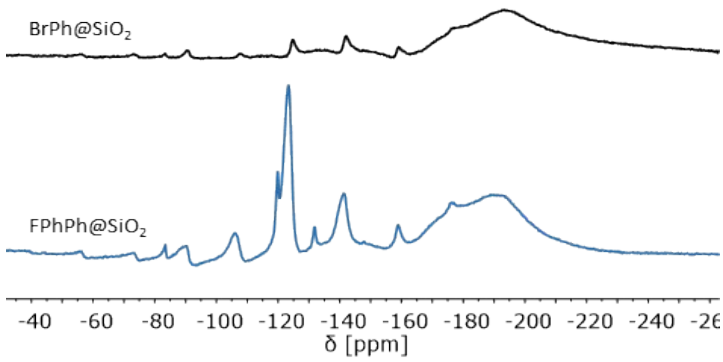

Figure S5. ^{19}F NMR of pristine BrPh@SiO_2 (top) and post functionalized FPhPh@SiO_2 (bottom).

4.4 Glass coating

4.4.1 Coating of glass powder with $BrPhSi(OEt)_3$

All glassware was passivated according to the general procedure described above. The porous shaped borosilicate glass bodies utilized for the synthesis of the hybrid catalysts were ballmilled for 1 min at 50 Hz. The powder (1.5002 g) was subsequently submerged in piranha acid (10 mL, 7 H_2SO_4 (conc.) : 3 H_2O_2 (36%)) for 1 h, washed with H_2O (2 x 50 mL) and submerged in piranha base (10 mL, 1 H_2O_2 (36%) :1 NH_4OH (30%) : 5 H_2O) for 1 L), $BrPhSi(OEt)_3$ was added (75 µL, 75 mg, 0.23 mmol) and the suspension refluxed for 72 h under argon. The resulting colourless powder was filtered off, washed with H_2O, DCM, EtOH and acetone (50 mL each) and obtained in quantitative yield after drying for 1h at 60°C in fine vacuum.

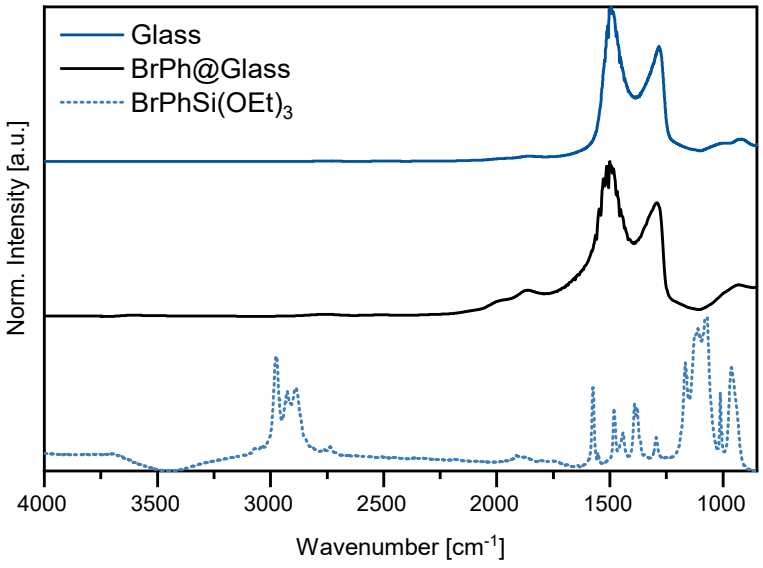

Figure S6. DRIFTS spectrum of ballmilled, porous glass (top), coated with S-3 (middle) as well as absorption spectrum of S-3 (bottom).

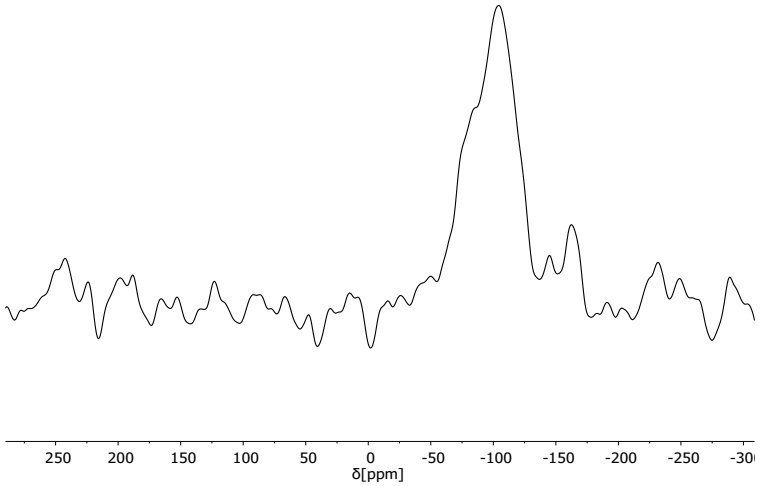

Figure S7. ^{29}Si-MAS-NMR (125 MHz, Spinning at 13 kHz) of BrPh@Glass.

4.4.2 Coating of glass powder with TMSCl

All glassware was passivated according to the general procedure described above. The porous shaped borosilicate glass bodies utilized for the synthesis of the hybrid catalysts were ballmilled for 1 min at 50 Hz. The powder (1.0710 g) was subsequently submerged in piranha acid (10 mL, 7 H_2SO_4 (conc.) : 3 H_2O_2 (36%)) for 1 h, washed with H_2O (2 x 50 mL) and submerged in piranha base (10 mL, 1 H_2O_2 (36%) :1 NH_4OH (30%) : 5 H_2O) for 1 h. The resulting colourless powder was filtered off, washed with H_2O, DCM, EtOH and acetone (50 mL each) and obtained in quantitative yield after drying for 1h at 60°C in fine vacuum.

4.4.3 Coating of microscope slides

Prior to the reaction the glass slides were cut into 2x1 cm pieces by using a glass cutter. After 50 min submersion in piranha acid (30 mL, 7 H_2SO_4 (conc.) : 3 H_2O_2 (36%)), the slides were rinsed with deinonized water (3x 75 mL) and Piranha base (30 mL, 1 H_2O_2 (36%) :1 NH_4OH (30%) : 5 H_2O), rinsed with deinonized water (3x 75 mL) and dried at 120°C under fine vacuum for 3h. Subsequently, the glassware used during the silanization was passivated following the general procedure described above. After drying, the slides were submerged in a mixture of DMF in toluene (1.0 vol.% DMF, 5 mL) and the respective silanes were added (Table S2). The reaction was heated to 95°C for 16h and after cooldown, the liquid phase was removed. The slides were the rinsed with EtOH (2 x 10 mL) and dried at 60°C under fine vacuum for 1 h. The slides were subsequently investigated using ATR-IR and contact angle measurements were taken (see main text).

Table S3: Reactant masses of the synthesis of the silane coated microscope slides

Silane	m(Glas) [g]	V (Silane) [µL]
Me_3SiCl	0.5901	59.0
$PhSi(OMe)_3$	0.6479	65.0
$BrPhSi(OEt)_3$	0.4607	46.0

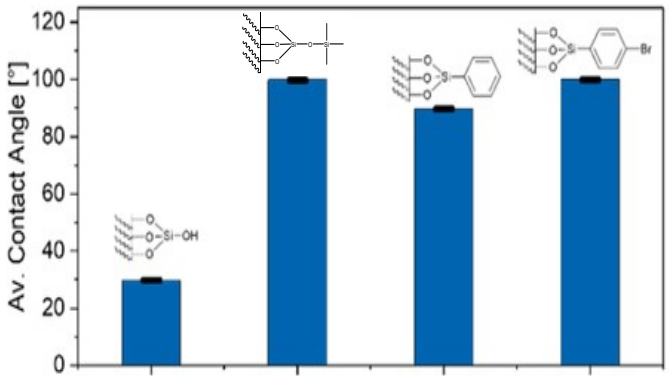

Figure S8. Average contact angle of water on microscope slides coated with silanes.

5 Catalyst synthesis

5.1 General procedure small glass frits for analysis and batch catalysis

A glass frit (0.1 cm high x 1 cm diameter) coated with $BrPhSi(OEt)_3$ (0.2822 g) was dried for 2 h in the HV at 60 °C. The monomers were dissolved in a mixture of degassed DMF and water (1 vol.%) and added to the frit using a syringe under argon atmosphere according to the principle of "incipient wetness impregnation", completely filling the pore volume of the frit. A hydrothermal synthesis procedure was employed in a closed, cylindrical autoclave of the exact dimensions of the glass frit which was designed in house. For this, the autoclave was closed under argon, and after heating to 85°C for 72 h, a black solid supported on the glass frit was obtained. Washing with DCM (100 mL), toluene (100 mL), H_2O (100 mL), acetone (100 mL) and diethyl ether (100 mL) in the reaction vessel by using a vacuum pump and capillaries and suspending in HCl/H_2O_2 solution (6 vol %/7 vol. %) for one hour followed by drying in HV at 60 °C for 2 h yielded the product as a yellow-orange solid embedded in a glass matrix.

Figure S9. Photo of tubular reactor for the synthesis of the hybrid catalysts.

5.1.1 Ru@pBINAP/G

In a typical experiment, Br_2-BINAPO (0.0245 g, 0.03 mmol, 1.0 eq.), Tris(4-phenylboronic acid (pinacol) ester)benzene (0.0365 g, 0.05 mmol, 1.78 eq.), Cs_2CO_3 (0.0379 g, 0.12 mmol, 3.6 eq.) and $[Pd(PPh_3)_4]$ (3.8 mg, 0.0033 mmol, 0.1 eq.) utilized following the general procedure. Following the cleaning and drying step, the material was reduced by transfer oxygenation analogously to the SMC polymer. For this, the used glassware was passivated using the procedure described above. The oxidized hybrid catalyst (0.250 g) was placed in a 3-neck flask under schlenk conditions, suspended in 15 mL of toluene and $HSiCl_3$ (0.21 mL, 2 mmol) was added. After stirring at rt for 30 min, PPh_3 (0.039 g, 0.148 mmol) was added and the mixture refluxed for 16 h. Subsequently, further $HSiCl_3$ was added at 16 h and 20 h of reaction time (2 x 0.12 mL, 1.2 mmol) and the mixture refluxed for

further 16h. After cooldown, the hybrid maerial was washed with toluene (2 x 20 mL) by stirring in it for 30 min at rt. After drying under fine vacuum at 60 °C for 1 h the product was obtained as a yellow-orange solid embedded in a glass matrix. The catalytically active material was obtained by wet impregnation of the reduced pBINAP/G material. For this, it was suspended in MeOH (6.5 mL) and bis(2-methylallyl)(cyclooctadiene)ruthenium ($Ru(MA)_2COD$, 6.0 mg, 0.036 mmol) was added. After stirring in MeOH at 50°C for 24 h the solvent was removed by filtration, evaporated and H_2O (2.5 mL) was added. After acidification using HCl (2.5 mL, 37 vol.%) and H_2O_2 (0.5 mL, 36 vol.%), the solution was analyzed using ICP-MS to determine the metal uptake to be 73%.

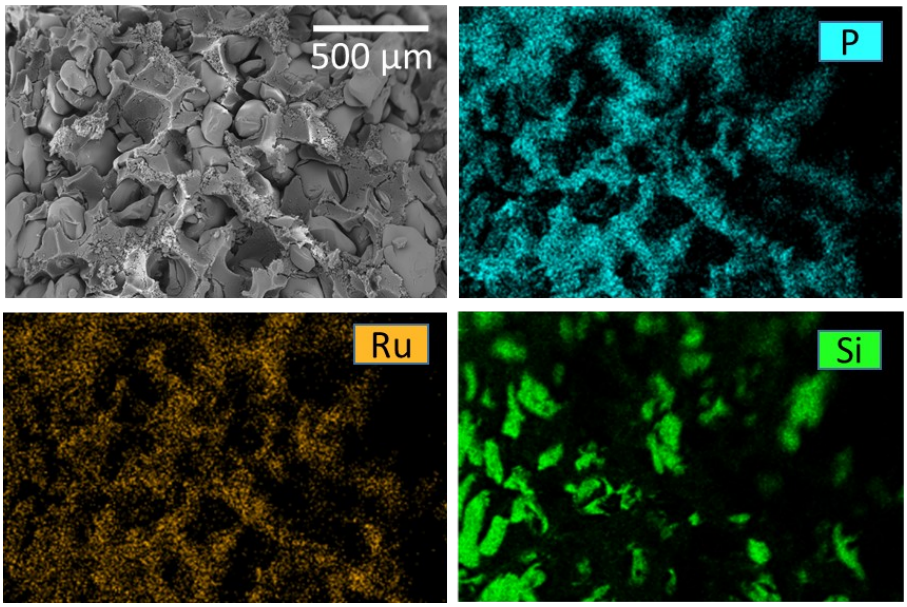

Figure S10. SEM/EDX analysis of H-1.

5.1.2 Ir@PyrTerpy/G

In a typical experiment, 5,5''-dibromo-4'-(1H-pyrrol-2-yl)-2,2':6',2''-terpyridine (45.5 mg, 0.1 mmol, 1.2 eq.), 1,3,5-tris(4-bromobenzenyl)benzene (45.3 mg, 0.83 mmol, 1.0 eq.), Cs_2CO_3 (64,4 mg, 0.2 mmol, 2.4 eq.) and $[Pd(PPh_3)_4]$ (7.5 mg, 0.07 mmol) were utilized in the general procedure. After the cleaning steps with solvents and the oxidative treatment, the hybrid supports were obtained as yellow solids bound to the surface of the glass support.

The catalytically active materials were obtained by wet impregnation with $IrCl_3$ (2.8 mg, 0.01 mmol) in MeOH (5 mL) at 50°C for 24 h. After filtration and drying in HV, the catalytically active material was obtained in quantitative yield. ICP-OES of loading solution after filtration reveals a metal uptake of 72%.

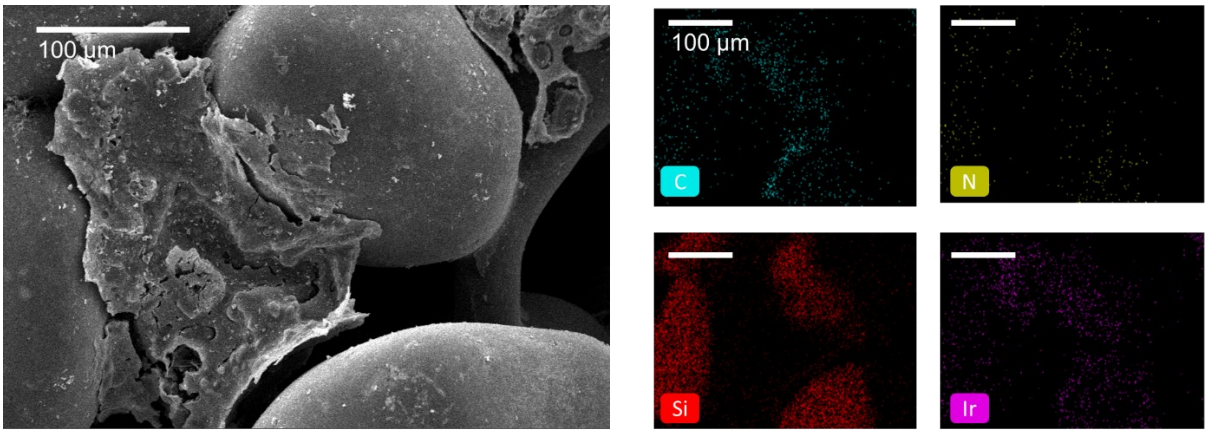

Figure S11. SEM image and EDX map of $IrCl_3$@PyrTerpy/G.

5.1.3 Ir@CTF/G

Tris-1,3,5-(4-bromophenyl)benzene (0.0540 g, 0.1 mmol. 1eq), 2,4,6-tris(4-(pinacol boron ester)phenyl)-1,3,5-triazine (0.0676 g, 0.1 mmol, 1 eq.) Cs_2CO_3 (0.0983 g, 0.3 mmol, 3 eq.) and $[Pd(PPh_3)_4]$ (5.1 mg, 4.4 µmol, 0.05 eq.) were utilized in the general procedure. After 72 at 85°C under argon, and the described cleaning step, the hybrid support was obtained as a yellow-white solid on glass.

The catalytically active material was obtained after wet impregnation with with 0.1wt.% Ir(cod)(acac) (0.324 mg, 0.8 µmol) in MeOH (5 mL) at 50°C for 24 h. ICP-OES of the solution after filtration reveals the metal uptake to be 36%. After filtration and drying in HV at 60°C, the catalyst was reduced by first drying in an oven at 200°C for 2h (heating rate: 10 K min^{-1}) under nitrogen flow (10 mL $min^{-1)}$ followed by reduction in 5 %H_2 in Ar (5mL min^{-1}) at 300°C for 3h. After cooling down under N_2, the catalyst material was obtained as a yellow solid on the glass support in quantitative yield.

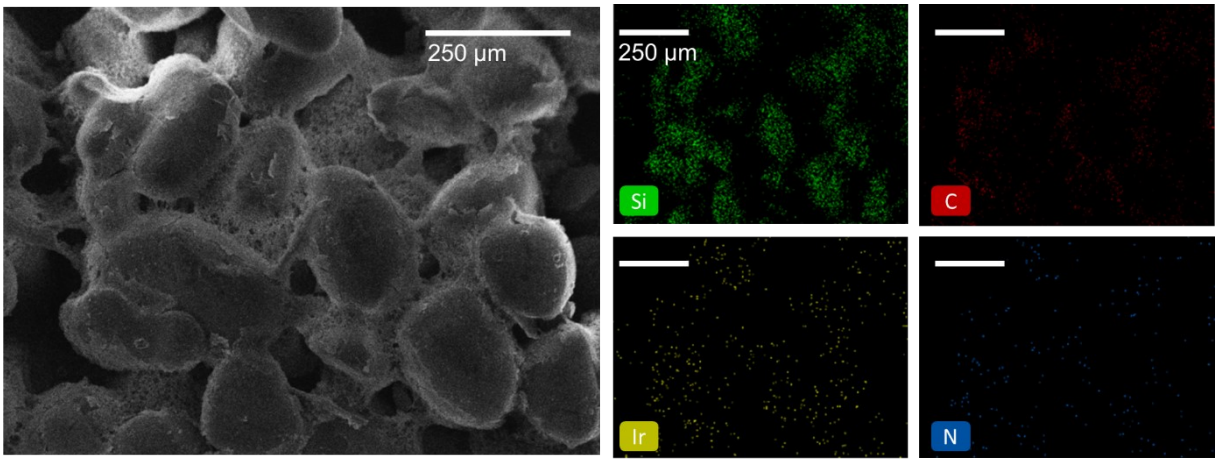

Figure S12. SEM image and EDX map of Ir(acac)@CTF/G.

5.2 General procedure large glass frits for continuous FAD

A large cylindrical glass frit (4.5 cm high *1 cm diameter) (V_{Pore} = 1.4 mL) coated with $BrPhSi(OEt)_3$ (5 g) was dried for 2 h in the HV at 60 °C. The monomers were dissolved in a mixture of degassed DMF and water (1 vol.%) and added to the frit using a syringe under argon atmosphere according to the principle of "incipient wetness impregnation", completely filling the pore volume of the frit. A hydrothermal synthesis procedure was employed in a closed, cylindrical autoclave of the exact dimensions of the glass frit which was designed in house. For this, the autoclave was closed under argon, and after heating to 85°C for 72 h, a black solid supported on the glass frit was obtained. Washing with DCM (100 mL), toluene (100 mL), H_2O (100 mL), acetone (100 mL) and diethyl ether (100 mL) in the reaction vessel by using a vacuum pump and capillaries and suspending in HCl/H_2O_2 solution (6 vol %/7 vol. %) for one hour followed by drying in HV at 60 °C for 2 h yielded the product as a yellow-orange solid embedded in a glass matrix.

The materials were characterized *via* DRIFTS spectroscopy after catalytic testing (Figure S13). Due to the low weight fraction of organic material in the hybrid catalysts, no significant change in the C-H region of the IR spectrum of the bulk material could be observed. Conversely, for Ru@pBINAP/G an additional vibration band can be observed at 1437 cm^{-1}, attributed to P-$C_{arom.}$ vibrations in BINAP oxide moieties.[18] The spectrum of Ir@PyrTerpy/G exhibits a signal at 1467 cm^{-1}, which can be assigned to C=C bands in terpyridine moieties.[16] The overall intensity of the vibrations bands originating from the organic material is comparatively low, explaining the absence of the further expected signals.

5.2.1 Ru@pBINAP/G

In a typical experiment, Br_2-BINAPO (0.1715 g, 0.2 mmol, 1.0 eq.), Tris(4-phenylboronic acid (pinacol) ester)benzene (0.2552 g, 0.38 mmol, 1.78 eq.), 4,4'-dibromobiphenyl (0.0948 g, 0.30 mmol, 1.45 mmol) Cs_2CO_3 (0.4935 g, 1.5 mmol, 7 eq.) and [Pd(PPh3)4] (33.8 mg, 0.029 mmol, 0.1 eq.) utilized following the general procedure. Reduction of the phosphine centers was also carried out according to the procedure described above using PPh_3 (0.3903 , 1.45 mmol), $HSiCl_3$ (2.1 mL at the start, additional 1.2 after 8 h and 16 h, in total 4.5 mL, 5,94 g, 43 mmol) in toluene (15 mL). After 72h the reduced material was obtained after washing with toluene (2x 20 mL) and drying in HV for 1h at 60°C. The catalytically active material was obtained after wet impregnation with 0.1 wt.% bis(2-methylally)(cyclooctadiene)ruthenium (15.3 mg, 0.05 mmol) in MeOH (28 mL) at 50°c for 24 h. ICP OES reveals the metal uptake to be 63%, resulting in 0.063 wt.% Ru@H-1 on average.

5.2.2 Ir@PyrTerpy/G

In a typical experiment, 5,5"-dibromo-4'-(1H-pyrrol-2-yl)-2,2':6',2"-terpyridine (393.5 mg, 0.9 mmol, 1.2 eq.), 1,3,5-tris(4-bromobenzenyl)benzene (390.2 mg, 0.71 mmol, 1.0 eq.), Cs_2CO_3 (560.6 mg, 1.72 mmol, 2.4 eq.) and $[Pd(PPh_3)_4]$ (65.0 mg, 0.06 mmol) were utilized analogously to the procedure described above. After the cleaning steps with solvents and the oxidative treatment, the hybrid supports were obtained as yellow solids bound to the surface of the glass support.

The catalytically active materials were obtained by wet impregnation with 0.1 wt.% $IrCl_3$ (7.45 mg, 0.025 mmol) in MeOH (25 mL) at 50°C for 24 h. After filtration and drying in HV, the catalytically active material was obtained in quantitative yield. ICP-OES of loading solution after filtration reveals a metal uptake of 91% on average.

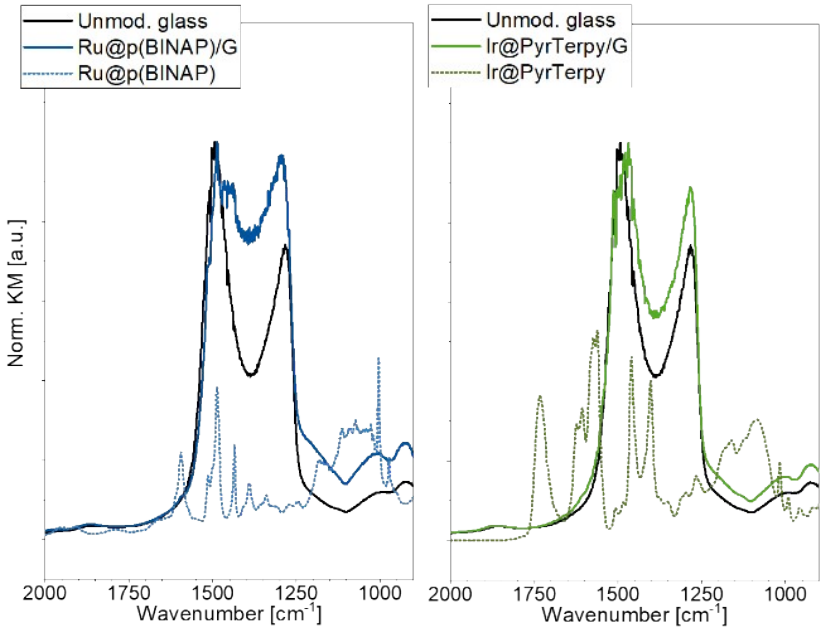

Figure S13. Left: DRIFTS spectra of glass support, Ru@pBINAP/G and the $Ru(MA)_2$@p(BINAP) SMC. Right: DRIFTS spectra for glass, Ir@PyrTerpy/G and $IrCl_3$@PyrTerpy SMC.

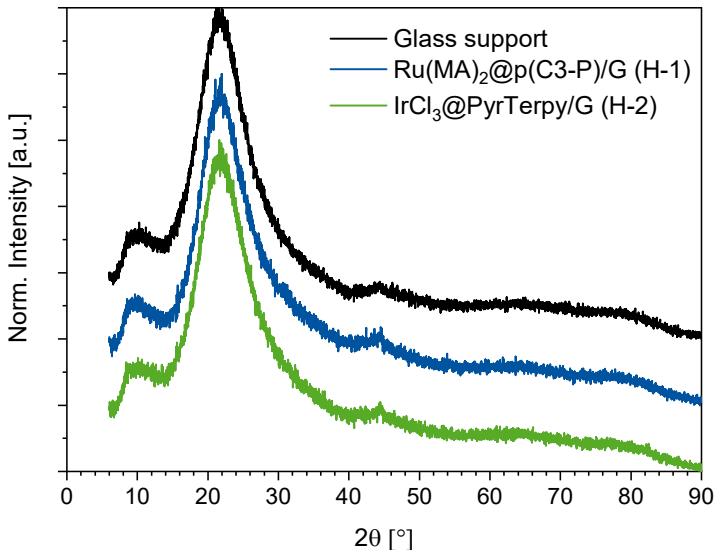

Figure S14. X-ray diffraction pattern of glass support, H-1 and H-2.

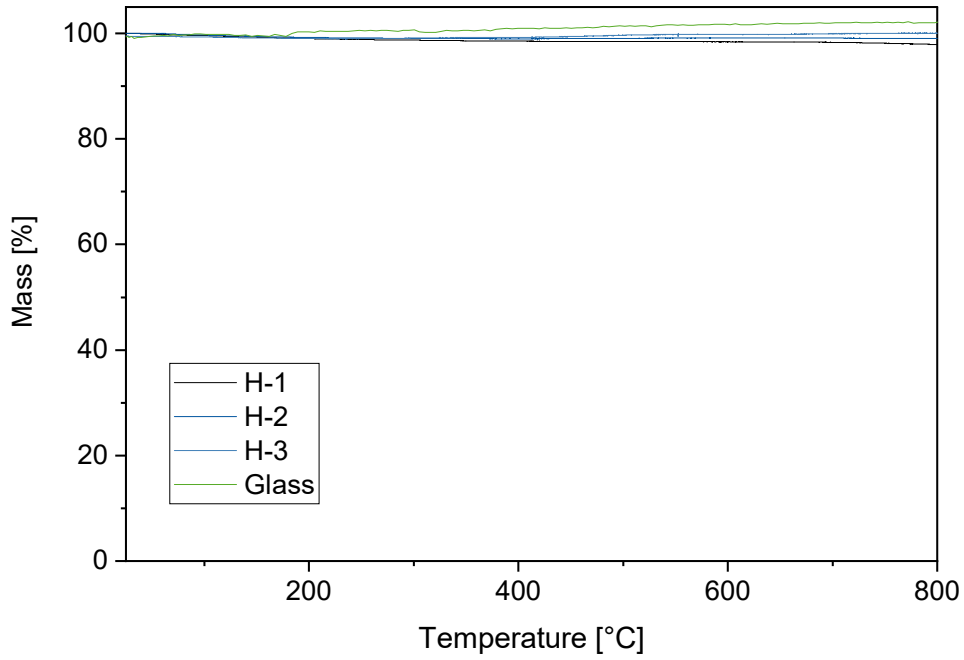

Figure S15. TGA of H-1 to H-3 and unmodified glass.

6 Formic acid decomposition

6.1 General considerations

The reaction solutions were filtered using Chromafil Xtra PA-45/25 syringe filters with an average pore size of 0.45 µm. The filtered solution was analyzed by HPLC to determine conversion as well as ICP-MS to determine leaching behavior. The conversions were calculated from the HPLC results of formic acid concentrations in the samples after reaction and the stock solutions using the following equation:

$$X = \left(1 - \frac{c(FA)_t}{c(FA)_0}\right) * 100\%$$

The gas-phase of the reaction was collected using gas-sample bags (1L, Supel™-Inert Multi-Layer Foil) at ambient pressure after 3 Schlenk cycles and subsequently analyzed by offline GC. The selectivity towards CO is calculated from the CO peak area A_{CO} using pre-determined correction factors for CO of f_{co} = 252.7 µL/mVs and for CO_2 of f_{CO2} =304.7 µL/mVs.

$$c_{CO} = \frac{V_{CO}}{V_{CO} + 2 * V_{CO}} * 10^6 = \frac{A_{CO} * f_{CO}}{A_{CO} * f_{CO} + 2 * A_{CO2} * f_{CO2}}$$

6.2 Batch catalysis

In a typical catalyst run, 10.0 mg of the polymer (1 wt.% Ru, 0.001 mmol, S/C ~ 12 000) or the hybrid catalyst slice was suspended in an degassed aqueous solution of formic acid (10 wt.%, 5.2 g, 12 mmol) in an Hastelloy autoclave equipped with a digital pressure sensor. The autoclaves were purged with H_2 (3x40bar) prior to the reaction. After placement in a metal heating bloc at rt, the reactors were heated up to the desired temperature while stirring at 750 rpm. The completion of the reaction was determined by observing the slowing pressure increase.

The catalytic results can be seen below. TOFs were determined by normalizing the pressure observed during the reaction after compensating for thermal expansion and non-catalytic decomposition of the substrate solution. Due to the high conversion in nearly all catalyst runs, the following relationship between conversion and observed pressure can be established.

$$X(FA) = \frac{p(t)}{p(Final)}$$

After analysis of the conversion over time obtained this way by linear regression, the slope k in the linear range can be obtained and the following connection with the conversion determined by HPLC and TOF can be determined.

$$TOF = k \cdot \frac{n(FA)}{n(Ru)} \cdot X(FA)_{HPLC}$$

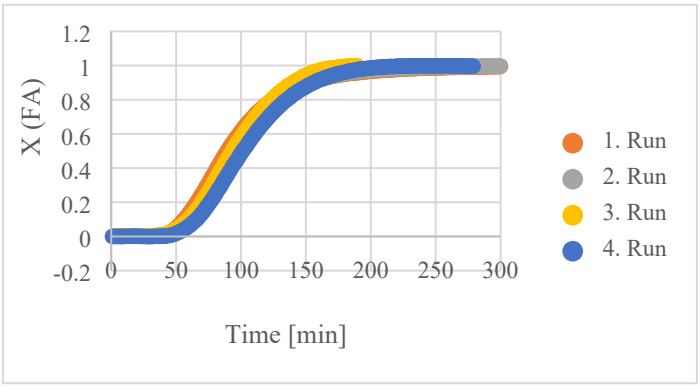

Figure S16. X(FA) over time for recycling runs of Ru@pBINAP/G during FAD at 160°C in 10wt.%FA.

Table S4. X(FA), c(CO), k-value as well as TOF during recycling of Ru@pBINAP/G.

Run	X(FA) (%)	c(CO) (ppm)	k (min^{-1})	TOF (h^{-1})
1	100	328	0,03918	29200
2	93	353	0,03781	21475
3	91	516	0,03770	21013

4	89	453	0,03484	19125

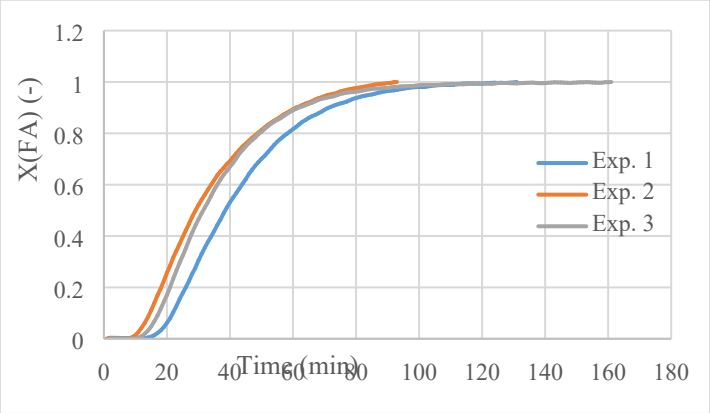

Figure S17. X(FA) over time for Ir@PyrTerpy/G during FAD at 160°C in 10wt.%FA.

Table S5. X(FA), c(CO), k-value as well as TOF during FAD of Ir@PyrTerpy/G.

Experiment	X(FA)	c(CO) (ppm)	k (min^{-1})	TOF (h^{-1})
1	95%	120	0,07215	9435
2	99%	101	0,08966	12229
3	97%	75	0,08383	11331

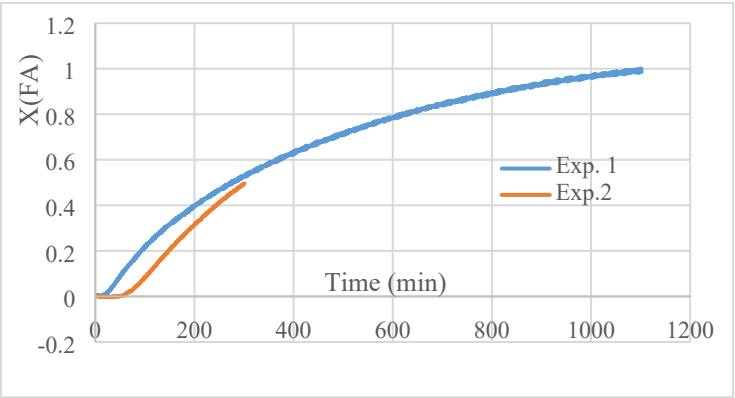

Figure S18. X(FA) over time for Ir@CTF/G during FAD at 160°C in 10wt.%FA.

Table S6. X(FA), c(CO), k-value as well as TOF during FAD of Ir@CTF/G.

Experiment	X(FA)	c(CO) (ppm)	k (min^{-1})	TOF (h^{-1})
1	95%	3896	0,00275	3920
2	99%	2524	0,00635	8764

6.3 Plug-flow reactor

Further investigation of the long term stability and technical applicability of the hybrid catalysts was carried out in an in house designed reactor after upscaling of the synthesis to large cylindrical glass supports as described above.

Using an HPLC pump, aqueous formic acid (10.0 wt.%) was pumped into the reactor at a constant flow rate of 1.0 mL/min to 2.5 mL/min with variable pump pressures. After a three-way stopcock, which allowed the reactor to be flushed with argon, the solution was heated to the target temperature of 100°C, 130°C or 160°C by means of an external heating band before reaching the reactor. The internal temperature of the substrate stream after the

catalyst bed was used as reference. After a water-cooled heat exchanger, the pressure of the system was adjusted to the reaction pressure, typically 5 bar, by means of an overflow valve. A phase separator allowed the gas stream to be analysed by offline gas chromatography after the biphasic reaction products have been expanded, while the conversion of the reaction was determined from the liquid phase by offline HPLC. The leaching of the metal was investigated using ICP-MS.

Contact times for the PFR were calculated from the FA flowrates and the internal volume $V_{internal}(Glass\ support) = 1.4\ mL$ of the support using the following equation.

$$\tau = \frac{V_{internal}(Glass\ support)}{\dot{V}(FA)_{HPLC}}$$

Table S7. Contact times at different flow rates.

Flowrate [mL/min]	1.0	1.5	2.0	2.5
Contact time τ [min]	1.4	0.93	0.7	0.56

The turnover frequency and TON were calculated using the following equations.

$$TOF_{Conti} = \frac{n(FA)}{n(Metal) * \tau} = \frac{\dot{n}(FA)}{n(Metal)} = \frac{\dot{m}(FA)}{M(FA) * n(Metal)} =$$

$$TON = \frac{n(FA)_{total}}{n(Metal)} = \sum_i TOF_{Conti,i} * t_i$$

$\tau =$ $contact\ time$ (min)

$X(FA)_{HPLC}$ = conversion of FA as determined by HPLC analysis (-).

$\rho(FA_{aq.})$ = density of aqueous formic acid solution (g/mL)

$\dot{V}(FA)$ = volumetric flow of FA set using HPLC pump.

6.4 Pressure drop

Prior to the catalytic experiments, the pressure drop over the catalyst bed was characterized using an argon flow of 15-60 mL/min, similar to the resulting gas flow under yield at medium conversions. A pressure drop can be observed for all glass components examined - with and without catalytic material in the pores. H-1 in particular shows a pronounced pressure drop of up to 31.2 mbar/cm at the highest flow rate investigated, which corresponds to a 52-fold increase in comparison to the empty glass supports.

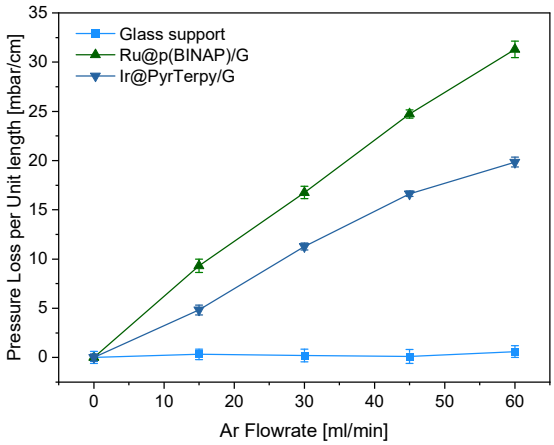

Figure S19. Pressure drop of glass support, H-1 and H2 at different flow rates of argon.

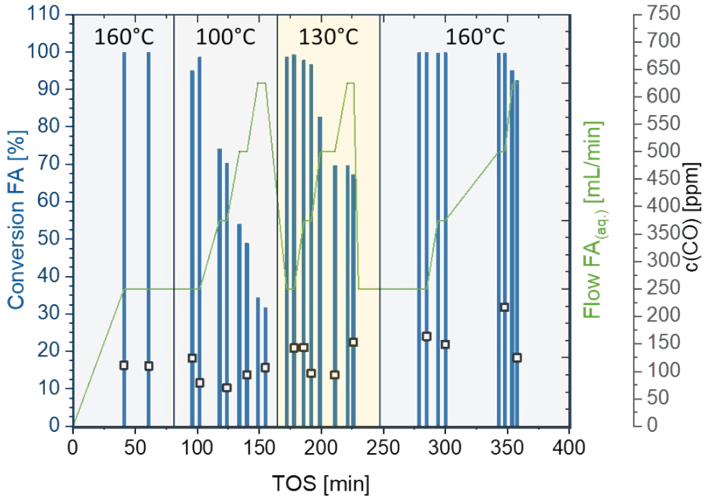

Figure S20. Continuous FAD experiment with Ir@PyrTerpy/G in the PFR. Conversion of FA, flow rate of FA, c(CO) and temperature profile over time at 5 bar reactor pressure. TOS =Time on Stream.

7 Literature

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