

Formic Acid as H₂ Storage System: Hydrogenation of CO₂ and Decomposition of Formic Acid by Solid Molecular Phosphine Catalysts

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1 Experimental

All reactions were carried out under argon atmosphere using standard Schlenk techniques. $n\text{BuLi}$ (1.6 M in hexane), 4,4'-dibromobiphenyl (98%), $[\text{RuCl}_2(\text{p-cymene})]_2$ (97%), PhLi (1.8 M in $n\text{Bu}_2\text{O}$), $\text{Ir}(\text{COD})(\text{acac})$, $n\text{Hex}_3$ (96%), NMe_2nOct (95%) and DIPEA ($\geq 98.0\%$) were purchased from Sigma Aldrich. 1,2-Bis(dichlorophosphino)ethane (96%) and mesitylene (98+) were obtained from Alfa Aesar. 1,2-Bis(dichlorophosphino)methane (90%), $\text{Ru}(\text{methylallyl})_2(\text{COD})$ (97%) and $\text{Ru}(\text{acac})_3$ (99%) were purchased from Abcr. $\text{Ir}(\text{acac})_3$ (99.95%) and $\text{Rh}(\text{acac})_3$ (99.95%) were obtained from Chempur. Na_2CO_3 (99.8%) and MgSO_4 (98.0%) were purchased from ChemSolute. $[\text{IrCp}^*\text{Cl}_2]_2$ (98%) and NPr_3 (98%) were obtained from J&K. PCl_3 ($>99.0\%$) and formic acid (98-100%) was purchased from Merck. NEt_3 ($\geq 99.5\%$) and $n\text{Bu}_3$ ($\geq 99\%$) were obtained from Roth. All chemicals were used as received. Et_2O (anhydrous, 99.8%), $i\text{PrOH}$ (99.8%) and DMF (99.8%) were purchased from AppliChem. CH_2Cl_2 (99.9%), MeOH (anhydrous, 99.8%) and THF (anhydrous, 99.9%) were obtained from ChemSolute. DMSO ($\geq 99.5\%$) and ethylene glycol ($\geq 99.0\%$) were purchased from Honeywell. Acetonitrile ($\geq 99.9\%$), $n\text{pentane}$ (anhydrous, $\geq 99\%$) and toluene ($\geq 99.8\%$) were obtained from Roth. All solvents were degassed and stored under argon atmosphere prior to use. CDCl_3 (99.8%) and DMSO-d_6 (99.8%) were purchased from Deutero.

1.1 Characterization Methods

Powder X-ray diffraction (XRD) pattern were recorded on a Siemens D5000 instrument with a $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The scanning range was set from 3° to 90° 2θ with 0.02° intervals and a collection time of 1 s per step. Thermogravimetric analyses (TG) were carried out using a STA 409 cell from Netzsch with a heating rate of 5 K min^{-1} in air up to 1273 K. Nitrogen physisorption isotherms were measured at 77 K using an ASAP2000 apparatus from Micrometrics. High purity gas (nitrogen: 99.999 %) was used for the adsorption measurements. Prior to the measurements, the samples were outgassed under vacuum at 393 K for several hours. Liquid phase ^1H NMR were measured on a AV 400 from Bruker. Solid-state MAS ^1H - ^{13}C cross-polarization and $^{31}\text{P}\{^1\text{H}\}$ NMR were

measured on a 500 MHz BRUKER Avance III (4 mm MAS rotor, 11 kHz spinning at rt). The chemical shifts δ are presented in parts per million (ppm) relative to calibration standards. $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded at 8 and 11 kHz to identify spinning side-bands. Scanning transmission electron microscopy (STEM) was performed on a FEI Tecnai F20 device with HAADF detector. The measurements were conducted at the GFE, RWTH Aachen. X-ray photoelectron spectroscopy (XPS) data was performed on a Phi5000 VersaProbe II spectrometer (ULVAC-Phi Inc., USA) using Al K α as the excitation source (1.486 keV) and operated at 15 kV. The binding energies were referenced to the C 1s line at 284.8 eV. A Vertex 70 with ATR unit was used to obtain IR spectra. A measuring range of 4500 – 400 cm^{-1} was chosen. Gas chromatography (GC) analysis of the gas phase was performed on an Agilent HP6890 system with a 2 m Shin carbon ST 100/120 mesh micropacked column and a TCD detector. Helium was used as transport gas with a constant flow rate of 24.6 mL min^{-1} . The temperature was 35 – 150 $^{\circ}\text{C}$ with a heating rate of 8 $^{\circ}\text{C min}^{-1}$. Inductively-coupled plasma mass spectroscopy (ICP-MS) was carried out with a 8800 ICP-MS Triple Quad (G3663A) from Agilent. The filtered samples were prepared by dilution with dioxane in a 1:5 ratio.

1.2 Polymer Synthesis P1-P6

The polymers P1-P6 were synthesized following the procedure described by Kann et al.¹⁹ The linker 4,4'-dibromobiphenyl (**1**) or 1,3,5-tris(4-bromophenyl)benzene (**2**) was dissolved in Et_2O (150 mL). After the addition of $^n\text{BuLi}$ (1.6 M in hexane), the suspension was stirred for 1 h. The solid was filtered over a glass filter, subsequently washed with Et_2O (200 mL) and n-pentane (200 mL) and suspended in THF (120 mL). A solution of the corresponding phosphorus chloride in THF (60 mL) was added dropwise over a period of 1 h. For end-capping, PhLi (1.8 M in Bu_2O) was added and the suspension was stirred overnight at room temperature. The polymerization was quenched with MeOH (100 mL). The solid was filtered, suspended in MeOH (200 mL) and stirred for 3 h at 55 $^{\circ}\text{C}$. The solid was filtered and washed with Et_2O (200 mL). Subsequently the solid was dried under vacuum at 60 $^{\circ}\text{C}$.

P2: The linker 4,4'-dibromobiphenyl (**1**, 6.24 g, 20.0 mmol) was activated with ⁿBuLi (50 mL, 80.0 mmol) and polymerized with 1,2-bis(dichlorophosphino)methane (2.12 g, 9.75 mmol). After the addition of PhLi (10 mL, 19.0 mmol), the polymer **P2** was obtained as a light yellow powder (yield: 3.444 g, 99%). ¹³C CP-MAS NMR (125.76 MHz, 11 kHz, 25 °C): δ(ppm) = 139.91, 132.33, 127.02, 24.96; ³¹P{¹H}-MAS NMR (202.45 MHz, 11 kHz, 25 °C): δ(ppm) = -19.99.

P5: The linker 1,3,5-tris(4-bromophenyl)benzene (**2**, 3.33 g, 6.12 mmol) was activated by ⁿBuLi (23 mL, 36.7 mmol) and polymerized with 1,2-bis(dichlorophosphino)methane (1.00 g, 4.59 mmol). After the addition of PhLi (4.8 mL, 9.2 mmol), the polymer **P5** was obtained as a light yellow powder (yield: 1.785 g, 69%). ¹³C CP-MAS NMR (125.76 MHz, 11 kHz, 25 °C): δ(ppm) = 141.28, 131.53, 126.90, 27.57, 23.62, 12.76; ³¹P{¹H}-MAS NMR (202.45 MHz, 11 kHz, 25 °C): δ(ppm) = -22.21.

P6: The linker 1,3,5-tris(4-bromophenyl)benzene (**2**, 3.12 g, 5.75 mmol) was activated with ⁿBuLi (22 mL, 34.5 mmol) and polymerized with 1,2-bis(dichlorophosphino)ethane (1.00 g, 4.31 mmol). After the addition of PhLi (4.6 mL, 8.6 mmol), the polymer **P6** was obtained as a light yellow powder (yield: 1.643 g, 69%). ¹³C CP-MAS NMR (125.76 MHz, 11 kHz, 25 °C): δ(ppm) = 141.23, 131.16, 126.90, 27.52, 23.87, 12.76; ³¹P{¹H}-MAS NMR (202.45 MHz, 11 kHz, 25 °C): δ(ppm) = -16.16.

1.3 Catalyst Preparation

The catalysts were prepared by wet impregnation. The polymers (1.000 g) and the desired metal complex (e.g. 30.3 mg [RuCl₂(p-cymene)]₂ for 1 wt.% loading) were combined in MeOH (100 mL). After stirring for three days at 60 °C, the catalysts were filtered over a glass filter and dried at 60 °C under vacuum. The filtrate was concentrated in vacuum and transferred to a volumetric flask (10 mL) with MeOH for ICP-MS analysis to determine the metal uptake.

1.4 Hydrogenation of CO₂ to Formic Acid

In a typical hydrogenation experiment, the catalyst Ru@**P3** (1 wt.%, 30 mg, 0.0037 mol%) and NEt₃ (1 mL) were placed in a 50 mL Hastelloy autoclave with cross-stirring bar. The autoclave was flushed

three times with 20 bar CO₂ and pressurized to 50 bar. Subsequently, the autoclave was pressurized with H₂ to a total pressure of 100 bar at r.t., achieving a CO₂ to H₂ ratio of 1:1 (v/v). NEt₃ (5 mL) and water (4 mL) were added into the autoclave by a HPLC pump, resulting in 10 mL of a 60 vol% NEt₃ solution. The autoclave was placed in a preheated aluminum cone (100 or 120 °C) and stirred for the desired reaction time at 750 rpm. The reaction was stopped by cooling in an ice bath. The gas phase was analyzed by GC. The reaction solution was dissolved in a volumetric flask (50 mL) with 2-propanol and the catalyst was removed with a syringe filter (CHROMAFIL Xtra, PA-20/25, 0.20 µm). The solution was analyzed by quantitative ¹H NMR with mesitylene as internal standard (0.2 mL reaction solution, 20 mg mesitylene, 0.3 mL DMSO-d₆) and ICP-MS.

The pressure curves were recorded in 20 mL Hastelloy autoclaves with a digital manometer. Here, the catalyst Ru@**P3** (1 wt.%, 12 mg, 0.0012 mol%) was combined with NEt₃ (2.4 mL) and water (1.6 mL) in the autoclave. Afterwards, the autoclave was pressurized with CO₂/H₂ (1:1 (v/v) to 100 bar. The reaction was performed at 100 °C for 5 h in the same procedure as described above. After the reaction, the solution was diluted with 2-propanol in a 25 mL volumetric flask and analyzed by quantitative ¹H NMR and ICP-MS.

For recycling experiments, the catalyst Ru@**P3** (1 wt.%, 100 mg, 0.0124 mol%) was combined with 10 mL of a 60 vol.% NEt₃ solution in the autoclave and pressurized to 100 bar CO₂/H₂ (1:1 v/v). After the reaction at 100 °C for 4 h, the gas phase was analyzed, the reaction solution was transferred to a Schlenk flask. The catalyst was filtered over a glass filter, washed with water (10 mL) and dried at 60 °C under vacuum. The combined solutions were diluted with 2-propanol in a volumetric flask (50 mL) and analyzed by quantitative ¹H NMR and ICP-MS. The following two cycles were each performed with the residual amount of catalyst and 10 mL of a 60 vol% NEt₃ solution. The catalyst after the last cycle was characterized by TEM analysis.

1.5 Decomposition of Formic Acid

In a typical decomposition reaction, the catalyst Ru@P2 (1 wt%, 30 mg, 0.0122 mol%), 10 mL of a 60 vol% NEt₃ solution and FA (1.15 g, 25 mmol) were combined in a 50 mL Hastelloy autoclave with cross-mixed bar. The autoclave was flushed three times with 20 bar H₂ and placed in a preheated aluminium cone (160 °C). This corresponded to the start of the reaction (t=0 min) and the pressure was recorded manually every minute. As soon as the pressure remained constant, the autoclave was cooled with an ice bath. Further workup follows the procedure described in the hydrogenation reaction. In addition, some reactions were also carried out in 20 mL Hastelloy autoclaves equipped with a digital manometer. The weights were adjusted accordingly.

Recycling of the catalyst Ru@P2 (1 wt%, 100 mg) was performed for three alternating cycles of synthesis and decomposition under standard conditions. The preparation and treatment of the catalyst after a reaction was carried out analogously to recycling in FA synthesis with amines. The catalyst after six runs (3x synthesis, 3x decomposition) was characterized by TEM analysis.

2 Characterization of P2

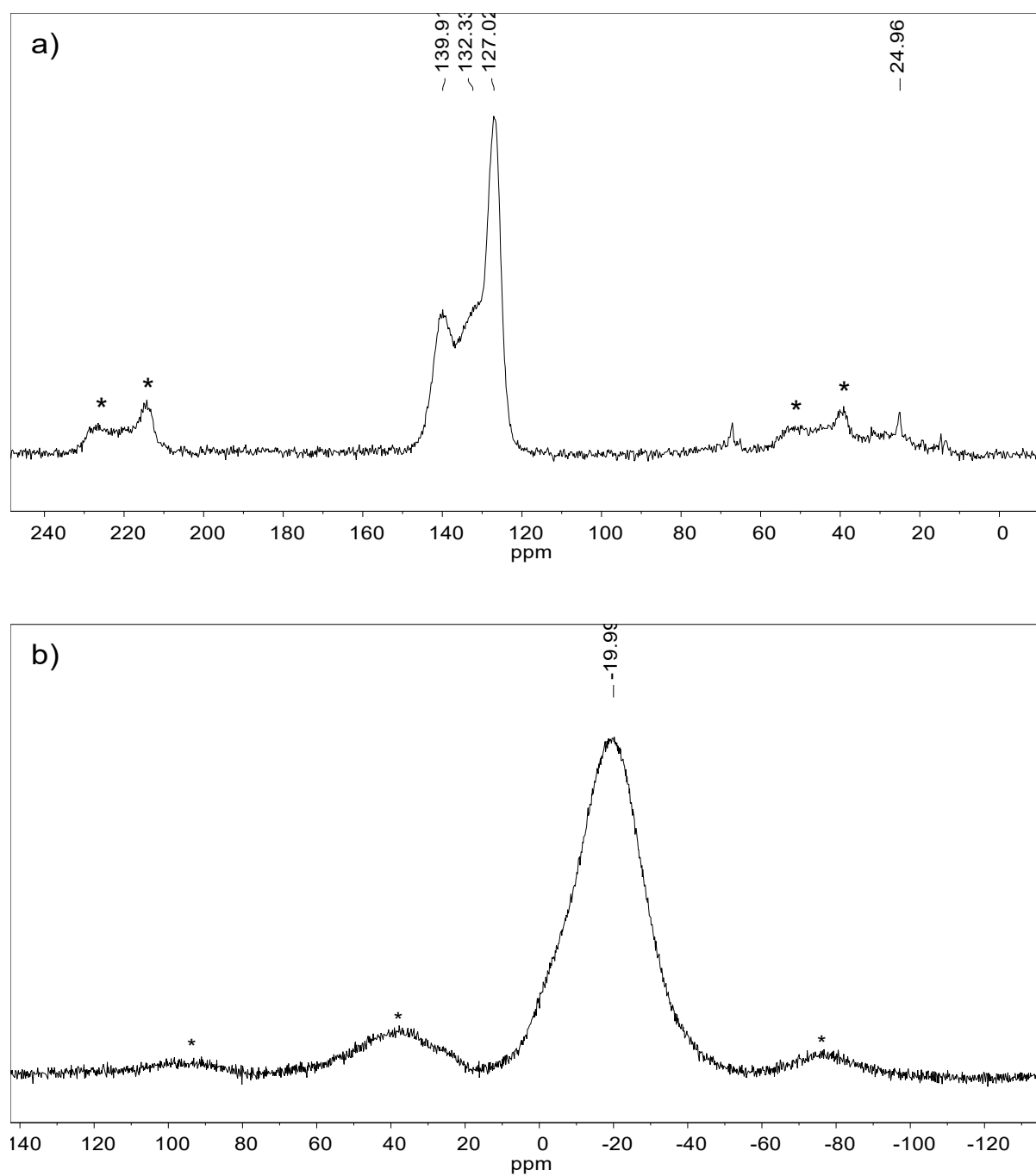


Figure S1. Solid state MAS ^{13}C CP NMR (a) and $^{31}\text{P}\{^1\text{H}\}$ NMR (b) of phosphine polymer P2. Spinning side bands are indicated with an asterisk.

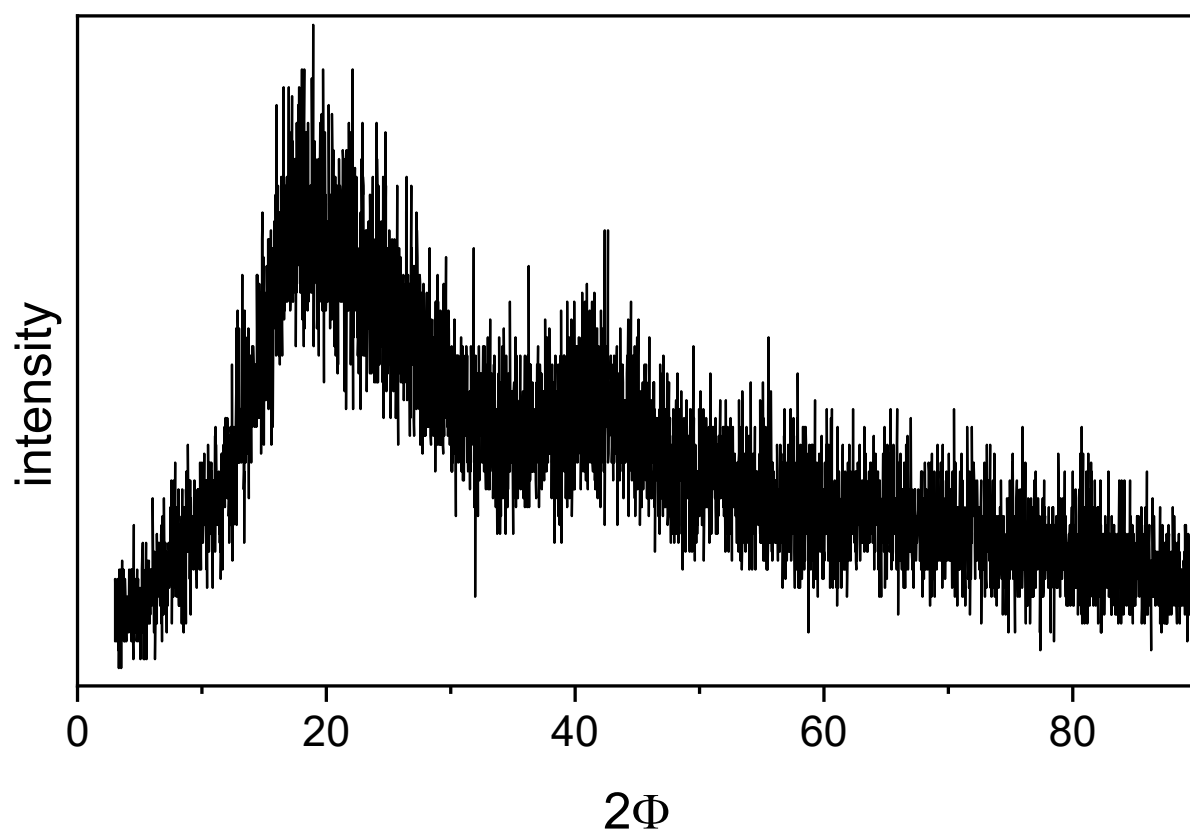


Figure S2. X-ray diffraction pattern of phosphine polymer P2.

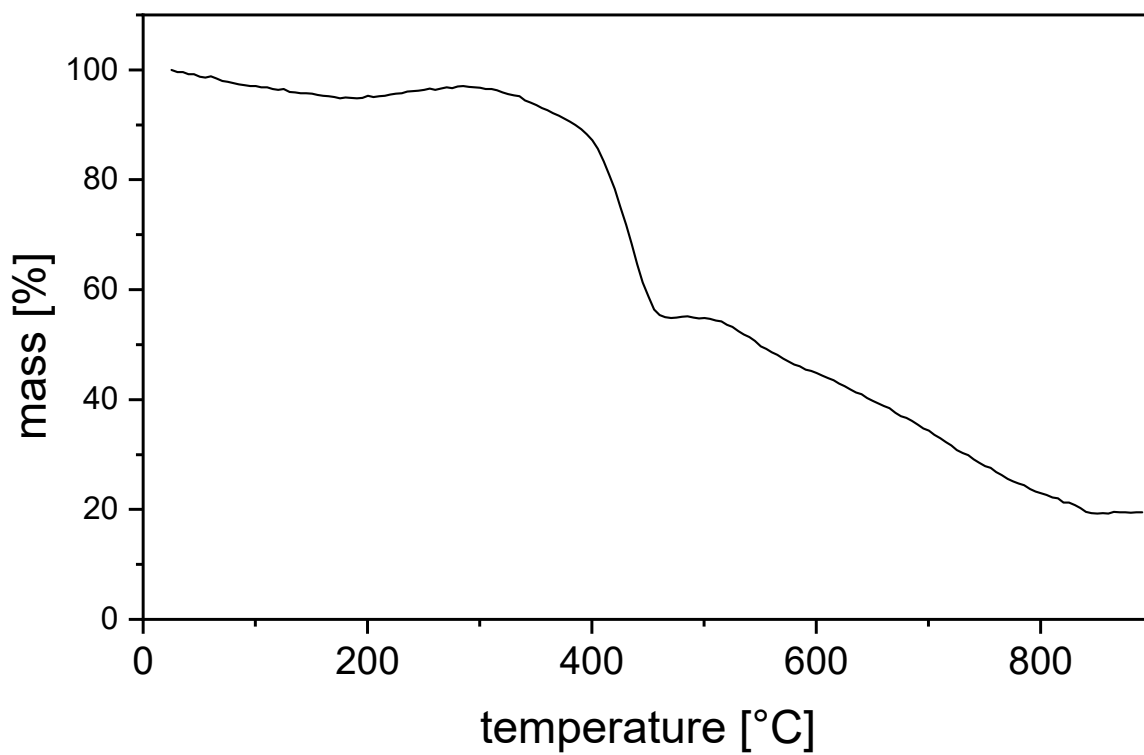


Figure S3. TG analysis of phosphine polymer P2.

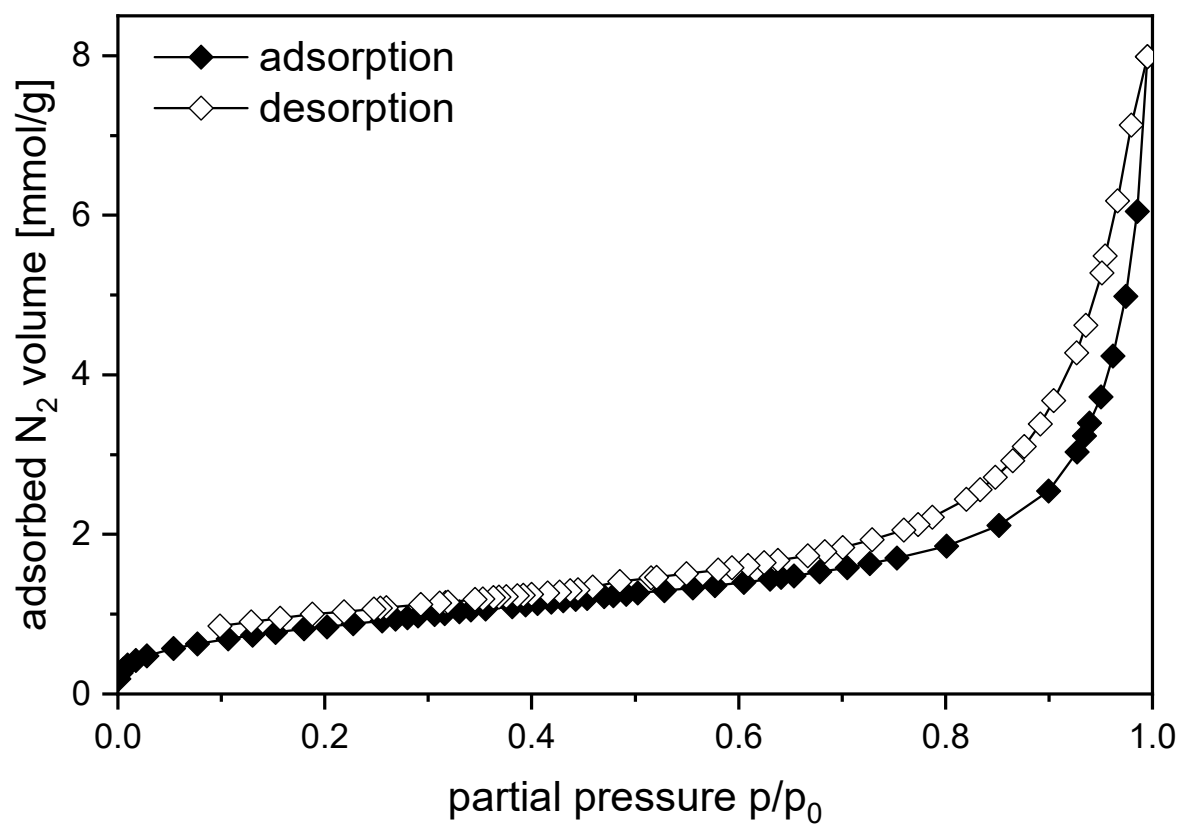


Figure S4. Nitrogen physisorption isotherm for phosphine polymer P2 measured at 77 K.

Table S1. Micropore volume, external and BET surface area of P2.

V_{mikro} [cm ³ g ⁻¹]	A_{ext} [m ² g ⁻¹]	A_{BET} [m ² g ⁻¹]	$A_{\text{ext}}/A_{\text{BET}}$ [%]
-0.0067	81.9	70.7	116

3 Characterization of P6

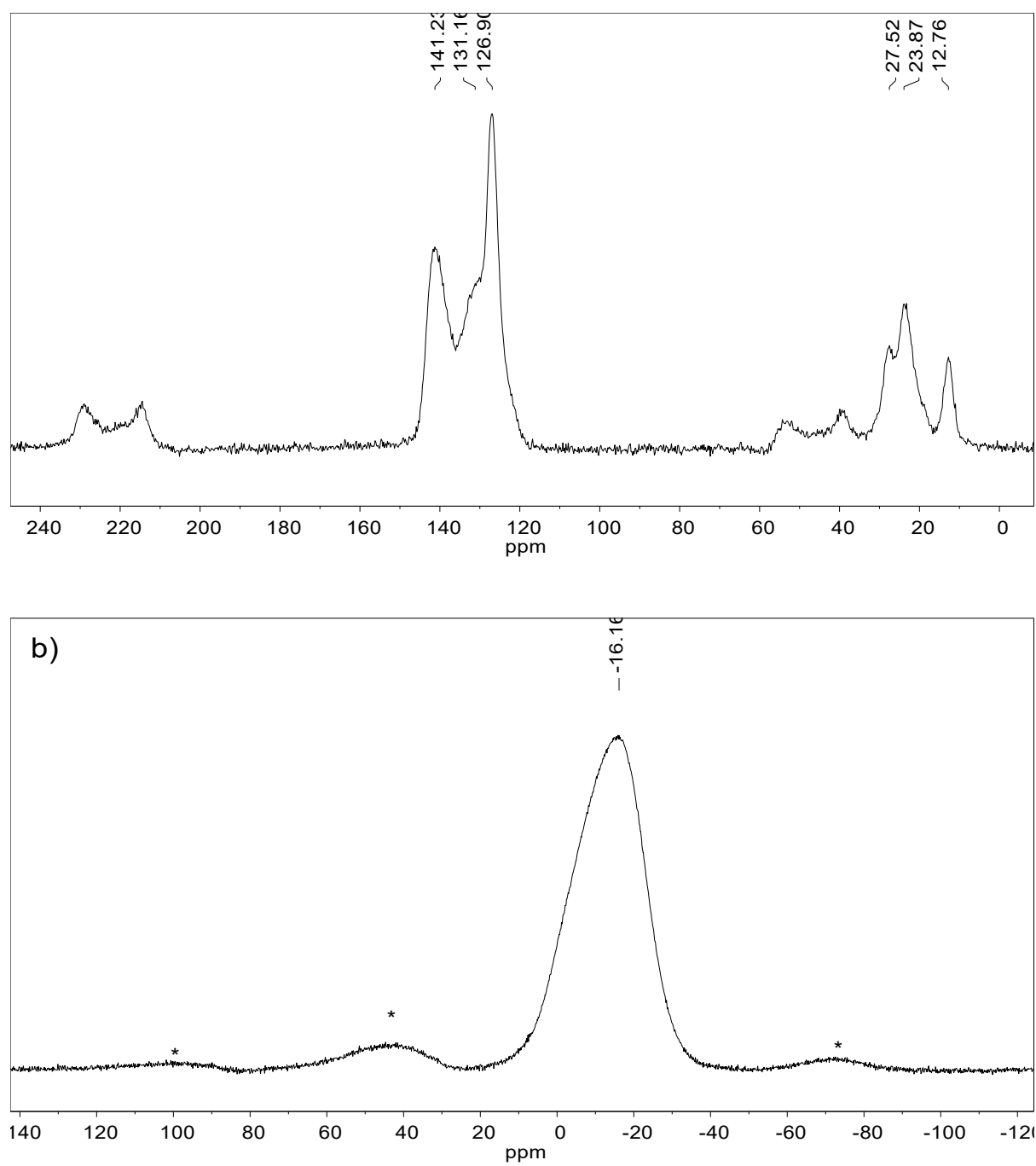


Figure S5. Solid state MAS ^{13}C CP NMR (a) and $^{31}\text{P}\{^1\text{H}\}$ NMR (b) of phosphine polymer P6. Spinning side bands are indicated with an asterisk.

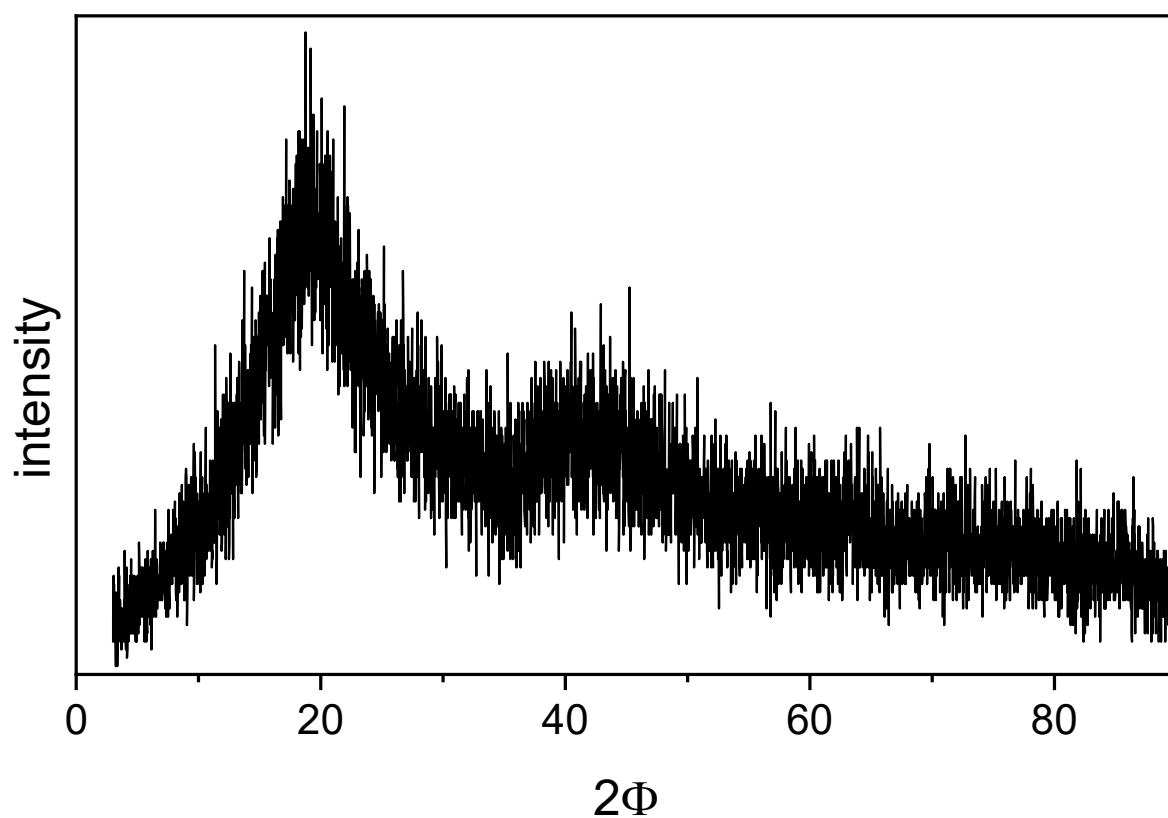


Figure S6. X-ray diffraction pattern of phosphine polymer P6.

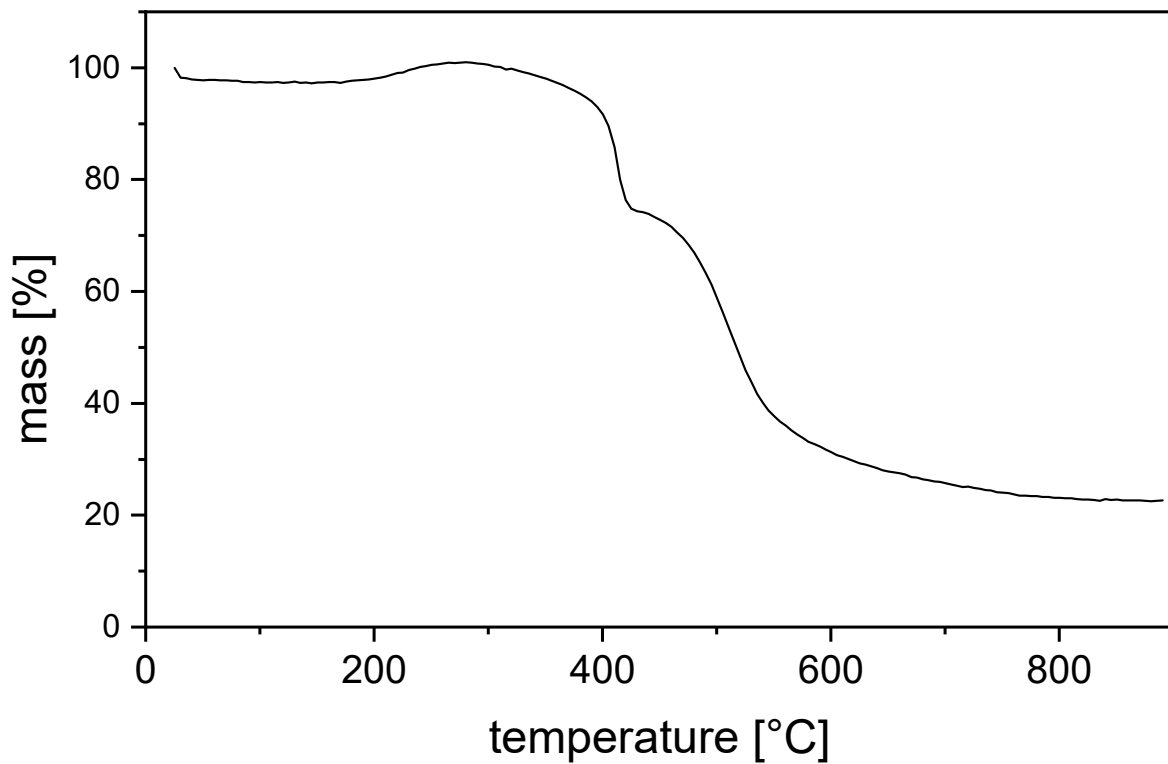


Figure S7. TG analysis of phosphine polymer P6.

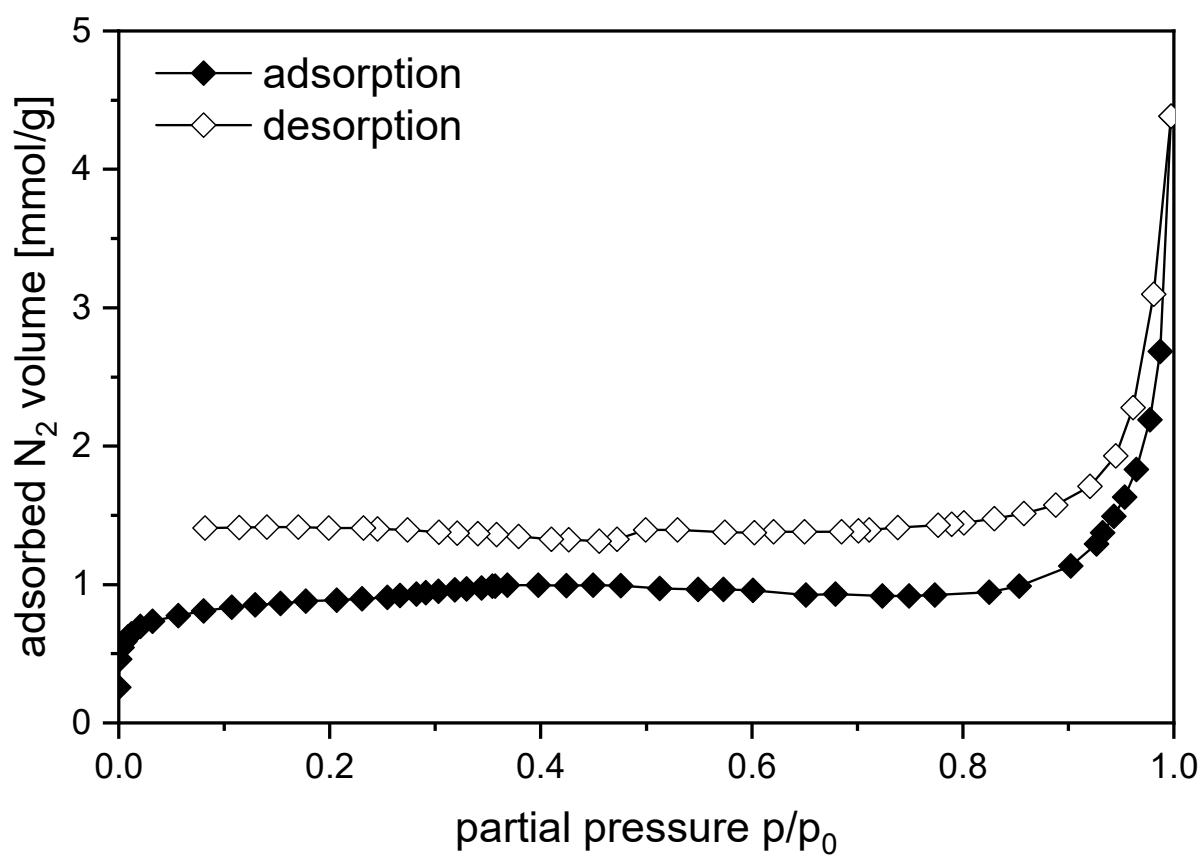


Figure S8. Nitrogen physisorption isotherm for phosphine polymer P6 measured at 77 K.

Table S2. Micropore volume, external and BET surface area of P6.

V_{mikro} [cm ³ g ⁻¹]	A_{ext} [m ² g ⁻¹]	A_{BET} [m ² g ⁻¹]	$A_{\text{ext}}/A_{\text{BET}}$ [%]
0.0159	33.8	65.4	52

4 Characterization of P5

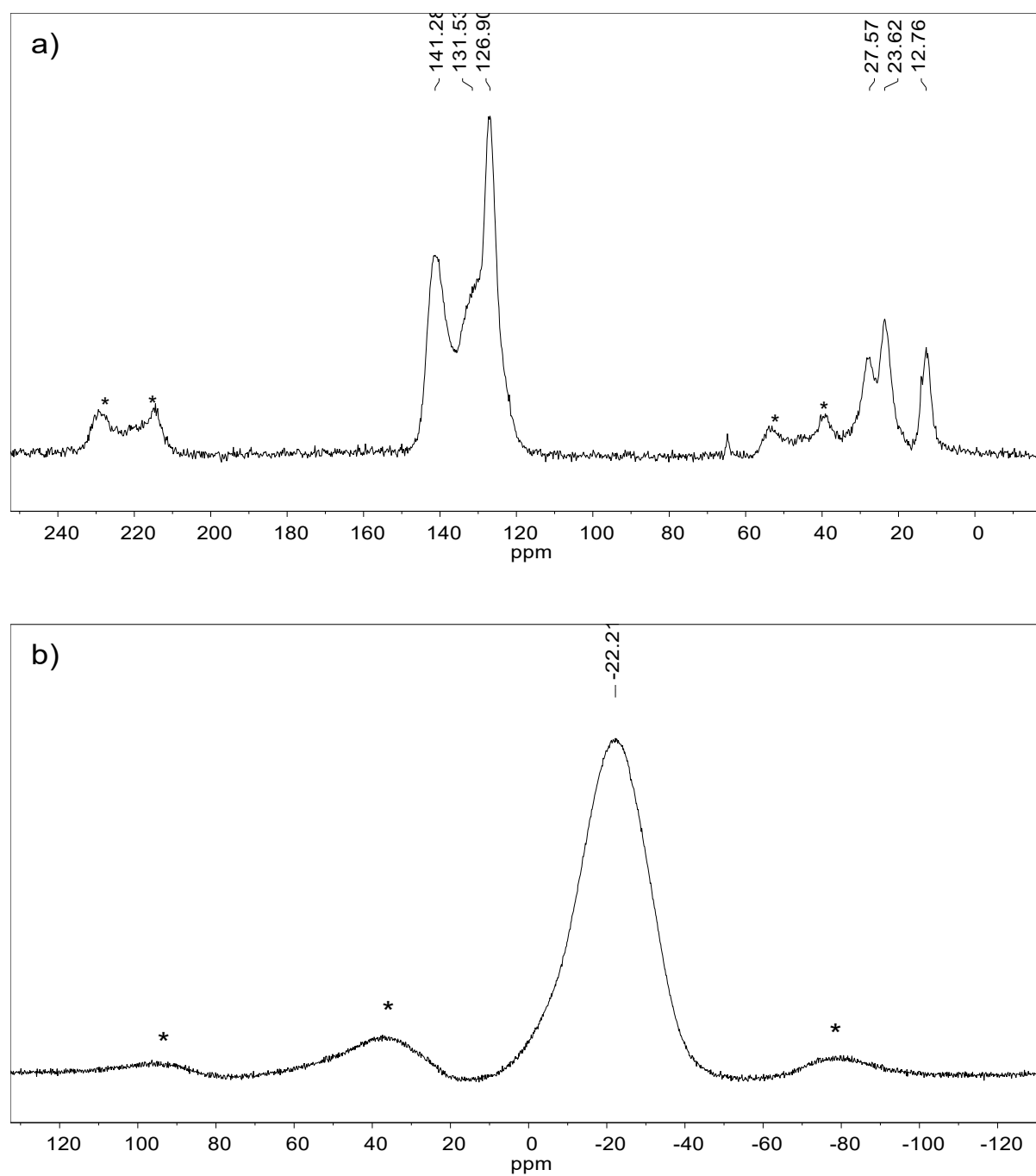


Figure S9. Solid state MAS ^{13}C CP NMR (a) and $^{31}\text{P}\{^1\text{H}\}$ NMR (b) of phosphine polymer P5. Spinning side bands are indicated with an asterisk.

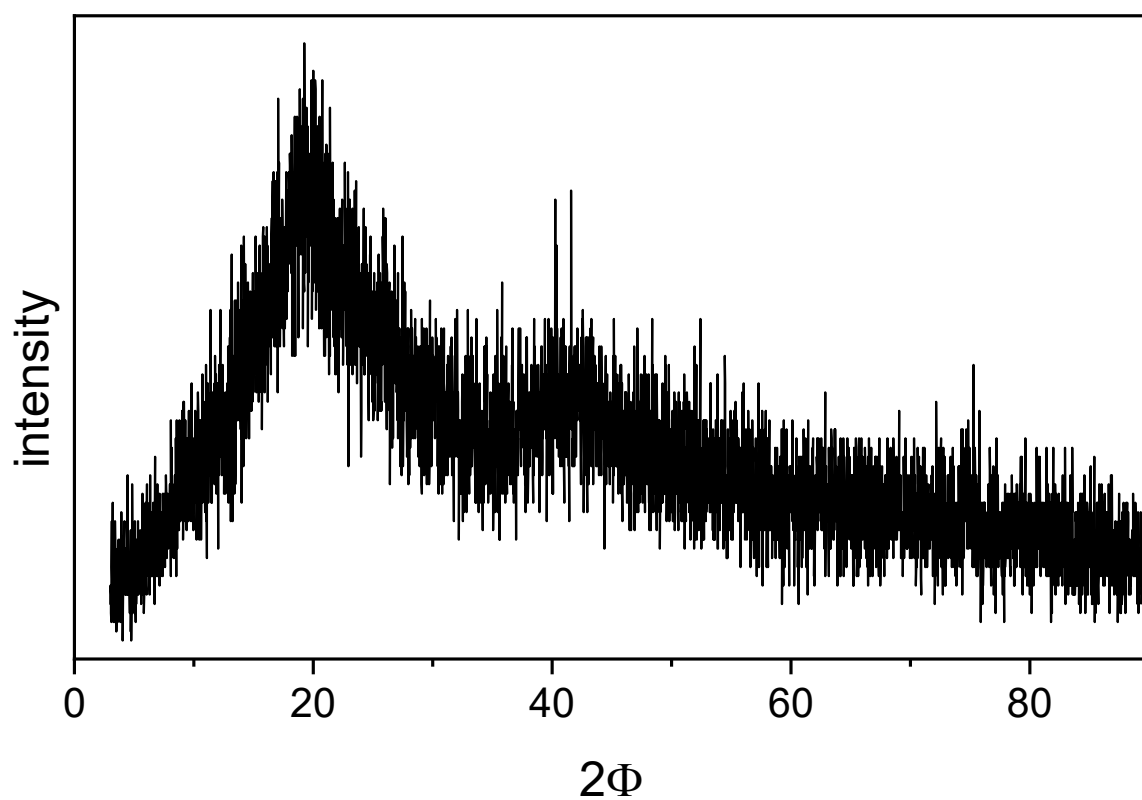


Figure S10. X-ray diffraction pattern of phosphine polymer P5.

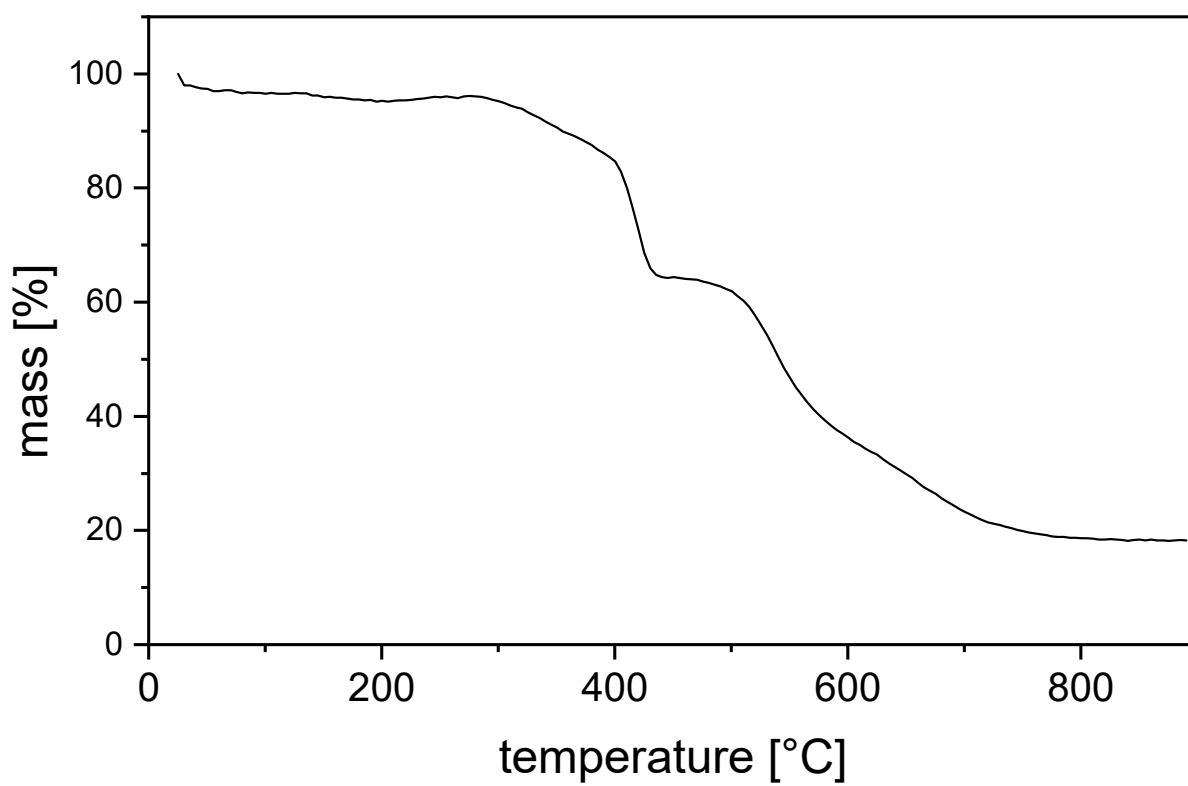


Figure S11. TG analysis of phosphine polymer P5.

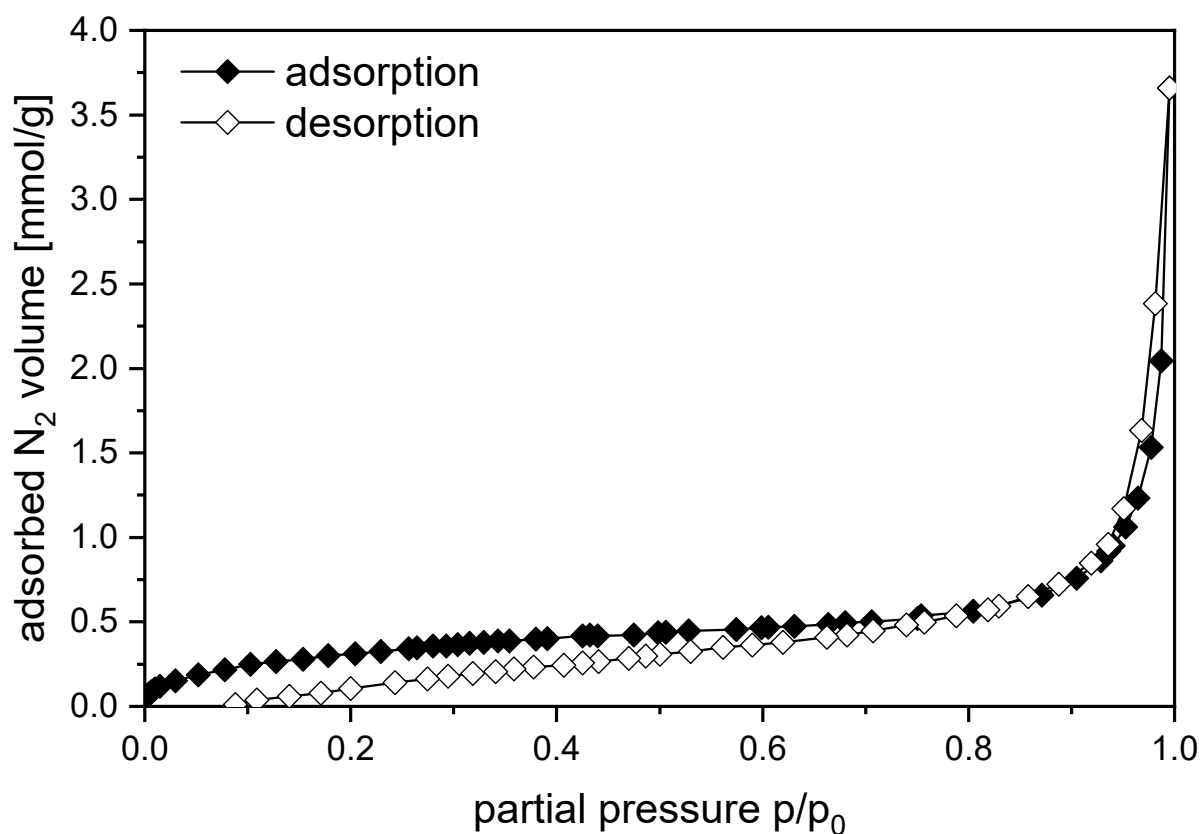


Figure S12. Nitrogen physisorption isotherm for phosphine polymer P5 measured at 77 K.

Table S3. Micropore volume, external and BET surface area of P5.

V_{mikro} [cm ³ g ⁻¹]	A_{ext} [m ² g ⁻¹]	A_{BET} [m ² g ⁻¹]	$A_{\text{ext}}/A_{\text{BET}}$ [%]
-0.0041	33.7	27.1	125

5 Hydrogenation of CO₂ to formic acid

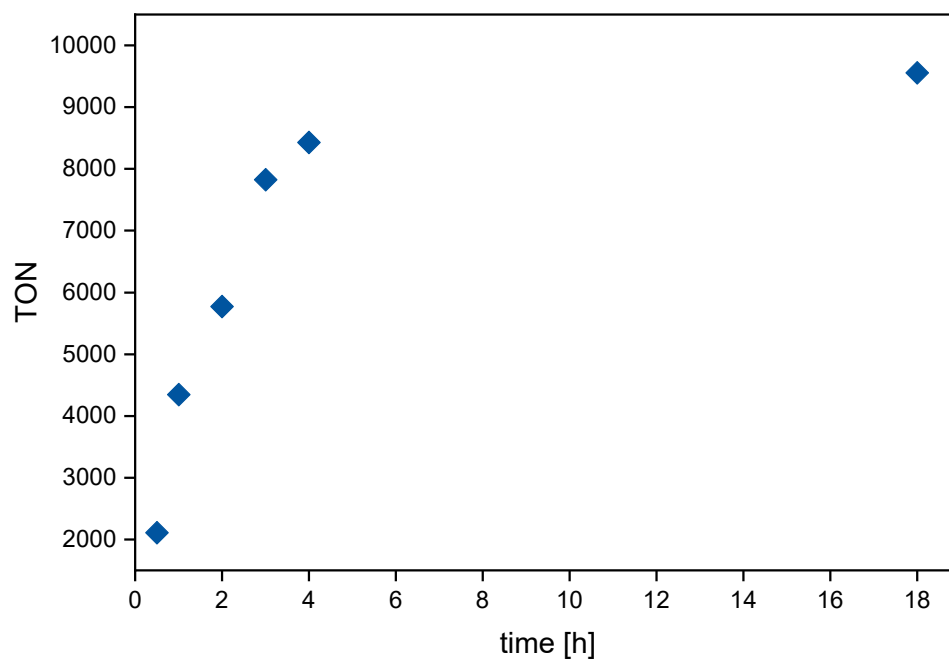


Figure S13. Influence of the reaction time on the hydrogenation of CO₂ to FA. Conditions: 60 vol% NEt₃ in H₂O (10 mL), 0.0037 mol% Ru, Ru@P3 (1 wt.%), 100 °C, 100 bar CO₂/H₂ (1:1 v/v).

Table S4. Influence of the total pressure and the pressure ratio of CO₂ and H₂ on the hydrogenation of CO₂ to FA. Conditions: 60 vol% NEt₃ in H₂O (10 mL), 0.0037 mol% Ru, Ru@P3 (1 wt.%), 100 °C, 4 h.

Entry	P [bar]	P(CO ₂) [bar]	P(H ₂) [bar]	TON
1	40	20	20	3480
2	60	30	30	4450
3	80	40	40	6650
4	100	50	50	8430
5	100	40	60	9680
6	100	30	70	6880
7	100	20	80	2490

6 Formic acid synthesis - Recycling

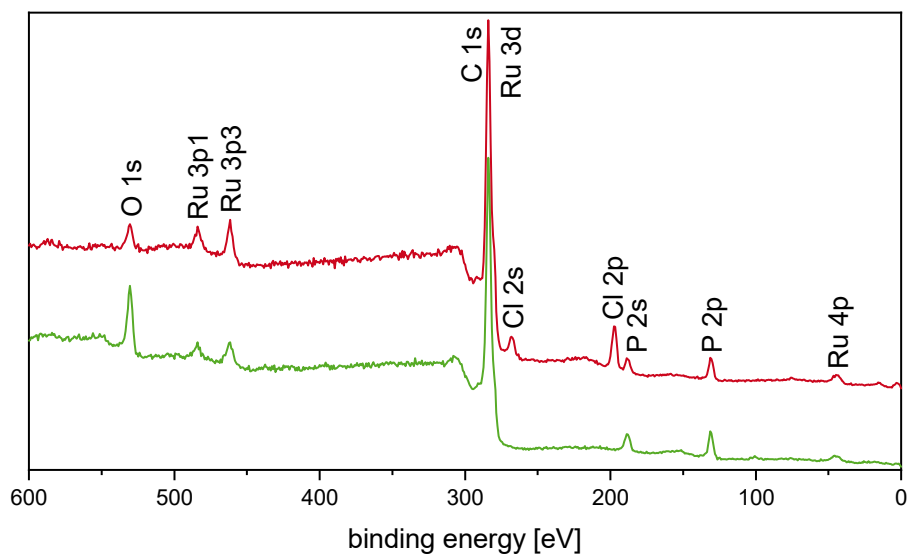


Figure S14. XPS survey spectra of the fresh (red) and recycled (green) catalyst Ru@P3 with 10 wt% Ru in the hydrogenation of CO₂ to FA in the presence of NEt₃. Binding energies are referred to C 1s at 284.8 eV.

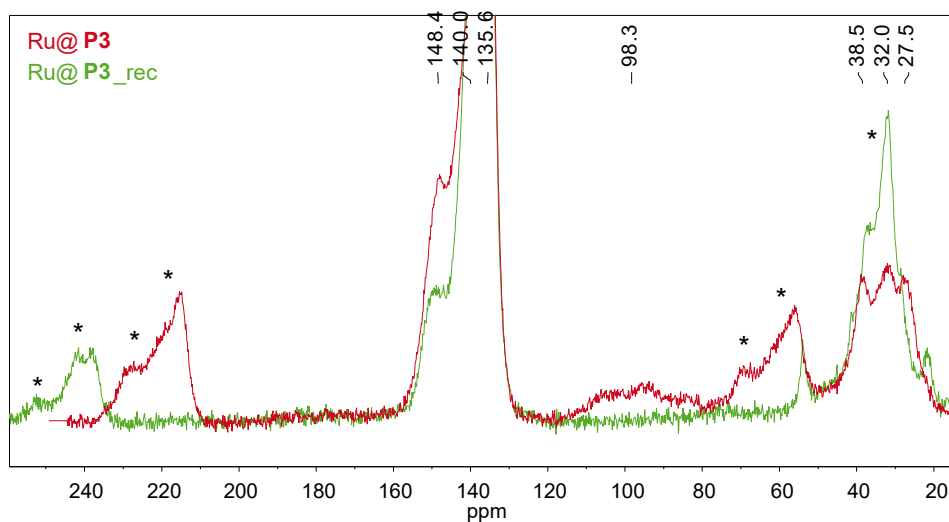


Figure S15. Solid state MAS ¹³C CP NMR spectra of Ru@P3 with 10 wt% Ru (red, 10 kHz) and the catalyst Ru@P3_rec after one single catalytic hydrogenation cycle (green, 14 kHz). Spinning side bands are indicated with an asterisk.

7 Decomposition of formic acid

Table S5. Influence of the base and the catalyst on the decomposition of FA to CO₂ and H₂. Conditions: 60 vol% NEt₃ in H₂O or pure water (10 mL), 25 mmol FA, 0.0123 mol% Ru, Ru@P3 (1 wt.%), 160 °C.

Entry	Amine	Catalyst	Time [min]	X [%]	CO [ppm]
1	-	-	60	0	n.d.
2	NEt ₃	-	60	0	n.d.
3	-	Ru@P3	40	100	60
4	NEt ₃	Ru@P3	55	80	137

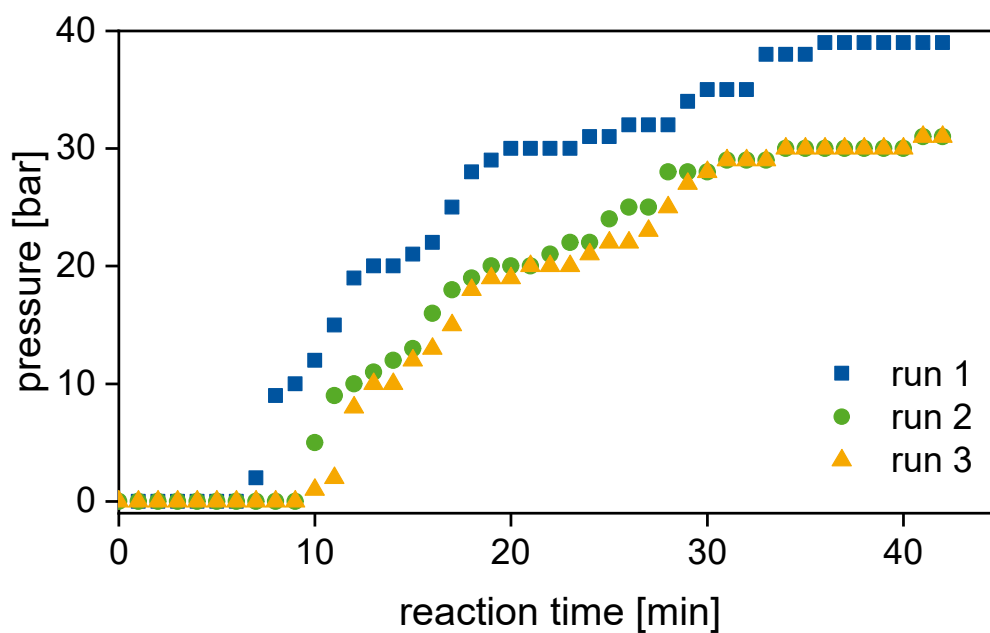


Figure S16. Pressure curves for the FA decomposition of the recycling experiments. Conditions: 50 mL Hastelloy autoclave, 60 vol% NEt_3 in H_2O (10 mL), Ru@P3 (1 wt.%, start: 100 mg), 25 mmol FA, 160 °C.

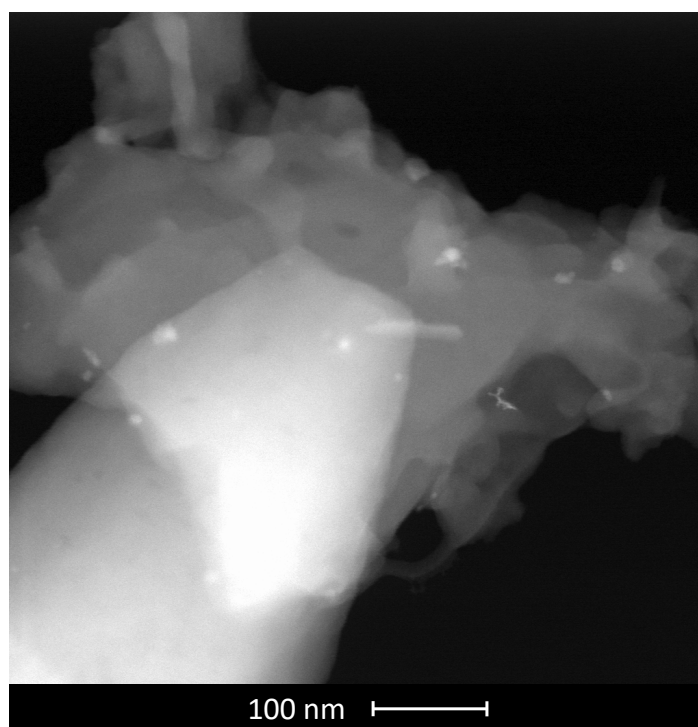


Figure S17. TEM analysis of the spent catalyst after the third run of alternating synthesis and decomposition of FA at 160 KHz.