

# A solid Xantphos macroligand based on porous organic polymers for the catalytic hydrogenation of CO<sub>2</sub>

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# 1. Experimentals

## 1.1 General Information

All syntheses were carried out under inert argon atmosphere, following common Schlenk techniques. Triphenylphosphine (97 %), 4,4'-bis(chlormethyl)-1,1'-biphenyl (95 %), aluminum chloride (99 %), anhydrous 1,2-dichloroethane (99.8 %), hexane (>99 %), methanol (99.9 %) and sodium bicarbonate ( $\geq 99.7\%$ ) were purchased from Sigma-Aldrich. The dichloro(*p*-cymene)ruthenium(II) dimer (98 %) was purchased from Alfa-Aesar. The commercially available chemicals were used without further purification. 1,2-dichloroethane and methanol were degassed by bubbling with argon for 2 hours prior to their usage and stored under argon atmosphere. Deionized water was additionally purified with a Simplicity<sup>®</sup> UV Water Purification System from Merck.

X-ray fluorescence spectroscopy was measured on a PANalytical Epsilon-4 spectrometer (software *Omnian*) with a Ag anode as X-ray source, using a polypropylene foil (5  $\mu\text{m}$ ) for the preparation of the sample holder. X-ray powder diffraction was recorded on a Bruker D2 PHASER with a Cu  $K_{\alpha}$  radiation ( $\lambda = 1.54 \text{ \AA}$ , operating at 30 kV/10 mA). The scanning range was between  $2\theta$  angles from 5–90  $^{\circ}$ , the step size was 0.02  $^{\circ}$  and each increment was measured for 4 s. Nitrogen physisorption was measured on a QuadraSorb evo from Quantachrome Instruments at 77 K. Prior to the measurement, the samples were heated to 393 K under vacuum for 800 min. The BET model was applied in the  $p/p_0$  range from 0.03–0.1 to quantify the specific surface area. The pore volume was determined at  $p/p_0 = 0.97$ . Water vapor sorption experiments were carried out on an Autosorb iQ from Quantachrome Instruments at 293 K. Prior to the measurement, the water was degassed by the freeze-pump-thaw-method and the samples were heated to 393 K under vacuum for 800 min. Infrared spectroscopy was carried out on a Bruker Invenio-R with a GladiATR device

from PIKE Technologies. The ATR-IR experiments were recorded between 400–3500  $\text{cm}^{-1}$  with increments of 1  $\text{cm}^{-1}$  and 64 scans. High-performance liquid chromatography was measured on a Shimadzu SIL-20AHT with a BIO RAD Aminex-HPX-87H column at 60 °C and a refractive index detector. Aqueous sulfuric acid (0.05 M) was used as an eluent, operating with a flow rate of 0.5  $\text{mL min}^{-1}$ . Gas chromatography measurements were carried out on a Shimadzu Nexis GC-2030 with a Restek ShinCarbon ST 80/100 column at 40 °C and a thermal conductivity detector. Helium was used as an eluent with a flow rate of 5  $\text{mL min}^{-1}$ . For X-ray photoelectron spectroscopy measurements, a SPECS Phoibos 150 spectrometer was used with a monochromatic (Focus 500) Al  $K_{\alpha}$  X-ray radiation ( $h\nu = 1486.74 \text{ eV}$ ). Survey and detail spectra were recorded in fixed analyser transmission mode, while choosing a pass energy of 20 eV (0.5 eV step size) for the survey and 10 eV (0.05 eV step size) for the core levels. The system was calibrated to 0.00 eV binding energy of the Fermi level of sputter-cleaned Au and Cu. The data analysis was performed with the software CasaXPS, version 2.3.22. The core level spectra were fitted with a Shirley background and peaks of a GL(30) line shape. MAS NMR spectra were recorded on a Bruker Avance III HD 300 MHz spectrometer equipped with a 4 mm broadband H/X probe. The corresponding frequencies were 300.11 MHz for  $^1\text{H}$  and 121.50 MHz for  $^{31}\text{P}$ , respectively. Spectra were measured at 10 kHz spinning with single pulse excitation using a  $\pi/2$  pulse of 3.5  $\mu\text{s}$  length on  $^{31}\text{P}$ . The relaxation delay was set to 300 s to ensure the observation of quantitative spectra, and 256 scans were accumulated. During data acquisition, high power  $^1\text{H}$  decoupling was applied using the spinal64 sequence<sup>1</sup>. Spectra were referenced to  $\text{H}_3\text{PO}_4$  (0 ppm). Thermogravimetric analysis was measured on a Netzsch Jupiter STA 449 C under nitrogen flow (50  $\text{mL min}^{-1}$ ). The measurement was recorded between 40–1000 °C with a heating rate of 5  $\text{K min}^{-1}$ . Electron microscopy was carried out on a JEOL JSM-7600F Schottky field emission scanning electron microscope and the

transmission electron microscope CM20 ST from FEI. In order to enhance the conductivity for improved imaging quality, the TEM samples were subjected to carbon coating, using a carbon fiber source under high vacuum conditions.

## 1.2 Synthesis of X-HCP

The synthesis of X-HCP was inspired by the preparation procedure from Yang *et al.*<sup>2</sup> Xantphos (5.00 mmol, 2.89 g, 1 eq), 4,4'-bis(chlormethyl)-1,1'-biphenyl (5.00 mmol, 1.26 g, 1 eq) and aluminum chloride (20.0 mmol, 2.67 g, 4 eq) were placed into a 250 mL Schlenk flask and the reaction atmosphere was exchanged for three times by applying vacuum and flushing with argon. 40 mL of 1,2-dichloroethane were added under water cooling and the mixture was stirred for several minutes until complete dispersion, afterwards it was heated to 90 °C and stirred for 24 h. After cooling to room temperature, the mixture was quenched by adding 100 mL of water under water cooling. The mixture was filtered and the precipitate was washed at least four times with hexane and methanol. The isolated solid was purified using Soxhlet extraction with methanol for 24 h. The product was dried under vacuum at 60 °C and finely ground, yielding a fluffy, brown powder (yield 77 %).

The synthesis of BCMBP-HCP from 4,4'-bis(chlormethyl)-1,1'-biphenyl (5.00 mmol, 1.26 g, 1 eq) and aluminum chloride (15.0 mmol, 2.00 g, 3 eq) was carried out using the same procedure.

## 1.3 Catalyst Preparation

The immobilization of the metal species on the porous macroligand is done by ligand exchange in methanol. The obtained X-HCP (1.49 g) and the dichloro(*p*-cymene)ruthenium(II) dimer (45.4 mg, 1 wt%) were placed into a 100 mL Schlenk flask and the reaction atmosphere was

exchanged for three times by applying vacuum and flushing with argon. The mixture was dispersed in methanol (50 mL) and stirred at room temperature overnight. The solid was filtered off and dried under vacuum at 60 °C, yielding the brown catalyst X-HCP-Ru (yield 83 %).

The synthesis of BCMBP-HCP-Ru was carried out using the same procedure ( $w(\text{Ru}) = 0.12 \text{ wt}\%$ ).

#### **1.4 Catalytic Hydrogenation of CO<sub>2</sub>**

The catalytic reactions were carried out in a 300 mL Hastelloy autoclave. 200 mg of the catalyst were dispersed in 150 mL of aqueous sodium bicarbonate solution (1 mol L<sup>-1</sup>) and the impeller speed was set to 700 rpm. The atmosphere in the autoclave was exchanged five times by flushing with 30 bar argon, followed by pressurizing the autoclave with 30 bar of CO<sub>2</sub> over 5 min and subsequently with 30 bar of H<sub>2</sub>. The autoclave was heated up to 110 °C and the initial reaction time was set, when the temperature of the reaction solution exceeded 70 °C. During the reaction, six samples (1.5 mL) were drawn frequently from the autoclave through a stainless-steel filter (pore size < 0.1 μm). In order to balance the resulting pressure drop (around 2 bar), an appropriate amount of H<sub>2</sub> was afterwards added to the autoclave. The aliquots were analyzed by HPLC. After the reaction, the autoclave was cooled down to room temperature with a water bath. The gas phase was collected in a gas bag for GC analysis. For the quantification of leaching effects, the reaction solution was analyzed with X-ray fluorescence spectroscopy. The used catalyst was filtered off, washed rigorously with water and dried under vacuum at 60 °C for further analysis.

For recycling experiments, the reaction solution was removed from the autoclave through the stainless-steel filter after the reaction. 150 mL of water was added to the remaining catalyst and the dispersion was stirred, following by the removal of the aqueous phase. The washing procedure

was repeated five times, followed by flushing the autoclave with argon three times. The catalyst in the autoclave was stored under argon atmosphere overnight, until the consecutive recycling run was performed as described above.

### 1.5 Determination of the Catalytic Performance

The catalytic performance was evaluated by calculating the turn over number (TON) and turn over frequency (TOF) of the catalytic experiments. Following the assumption that every ruthenium atom represents a catalytically active species, the amount of formed formic acid was divided through the amount of immobilized ruthenium species on the HCP. The amount of formic acid was determined by HPLC analysis, the amount of ruthenium quantified by X-ray fluorescence spectroscopy. The calculation of the catalytic activity can be considered as an averaged TOF over the first 45 min of the reaction, which is normalized to the reaction time.

$$TON = \frac{n_{FA} \cdot M(Ru)}{m_{cat.} \cdot w_{cat.}(Ru)}$$

$$TOF = \frac{n_{FA} \cdot M(Ru)}{m_{cat.} \cdot w_{cat.}(Ru) \cdot t}$$

## 2. Characterization Data

**Table S1:** Elemental composition of X-HCP-Ru, measured with XRF.

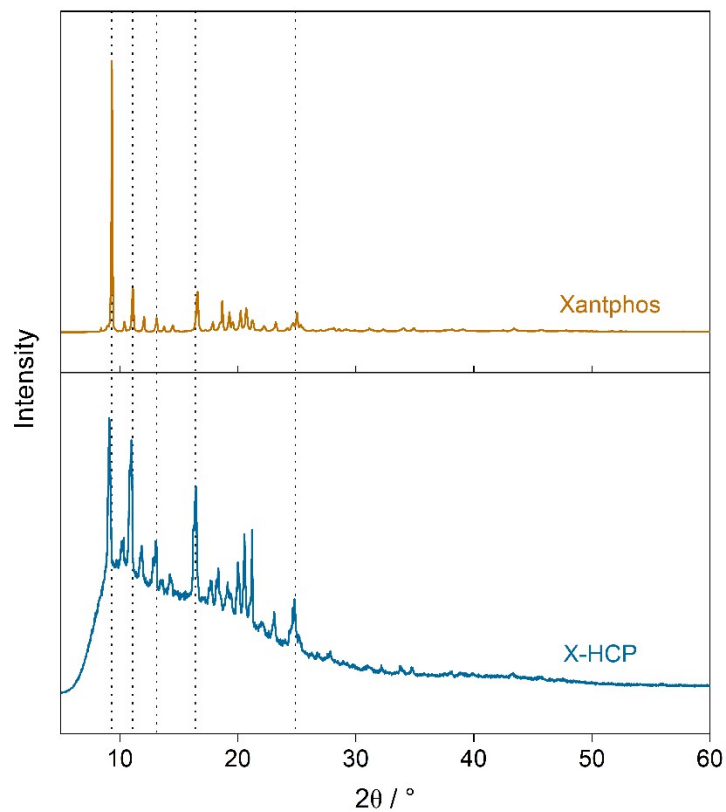
$w(\text{Al}) / \text{wt}\%$	0.16
$w(\text{P}) / \text{wt}\%$	2.5
$w(\text{Cl}) / \text{wt}\%$	1.5
$w(\text{C}_x\text{H}_y\text{O}_z) / \text{wt}\%$	96
$w(\text{Ru}) / \text{wt}\%$	0.31
molar P:Ru ratio	27 : 1

**Table S2:** Elemental composition of the filtrate after the first run of the recycling experiments of X-HCP-Ru.

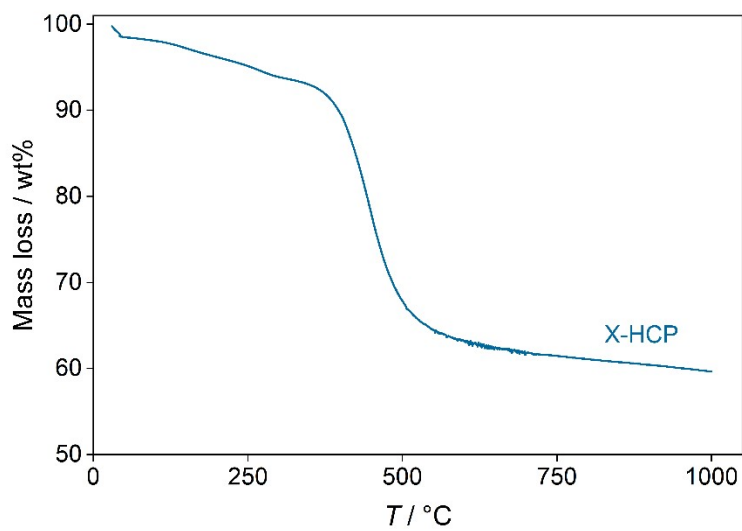
$w(\text{Na}) / \text{wt}\%$	1.3
$w(\text{P}) / \text{wt-ppm}$	0.5
$w(\text{C}_x\text{H}_y\text{O}_z) / \text{wt}\%$	98.7
$w(\text{Ru}) / \text{wt-ppm}$	0.2 (0.006 % of $\text{Ru}_{\text{initial}}$ )

**Table S3:** Specific surface area (BET) and total pore volume of the pristine X-HCP-Ru and the X-HCP-Ru after four catalytic runs. Determined by nitrogen physisorption at 77 K.

$\text{SSA}_{\text{BET, pristine}} / \text{m}^2 \text{g}^{-1}$	222
$V_{\text{Pore, pristine}} / \text{cm}^3 \text{g}^{-1}$	$1.83 \cdot 10^{-1}$
$\text{SSA}_{\text{BET, post catalysis}} / \text{m}^2 \text{g}^{-1}$	14
$V_{\text{Pore, post catalysis}} / \text{cm}^3 \text{g}^{-1}$	$4.63 \cdot 10^{-2}$

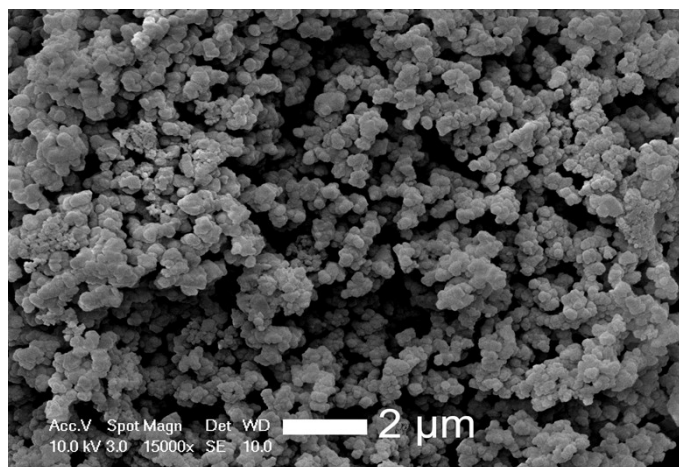


**Figure S1:** XRD of X-HCP (blue) and the monomer Xantphos (orange). The intensities are normalized to the height of the most intense reflex.

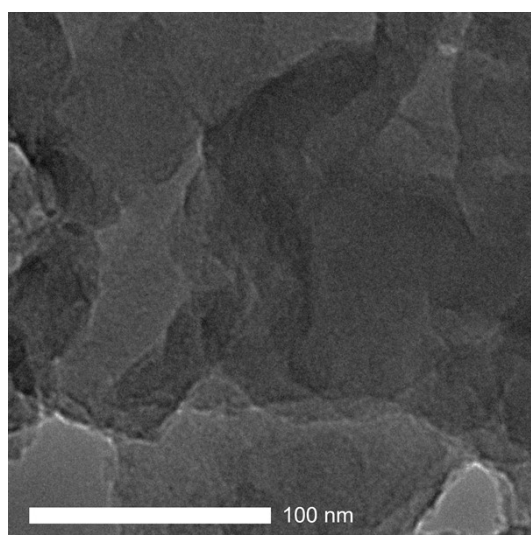


**Figure S2:** TGA of X-HCP under nitrogen atmosphere.

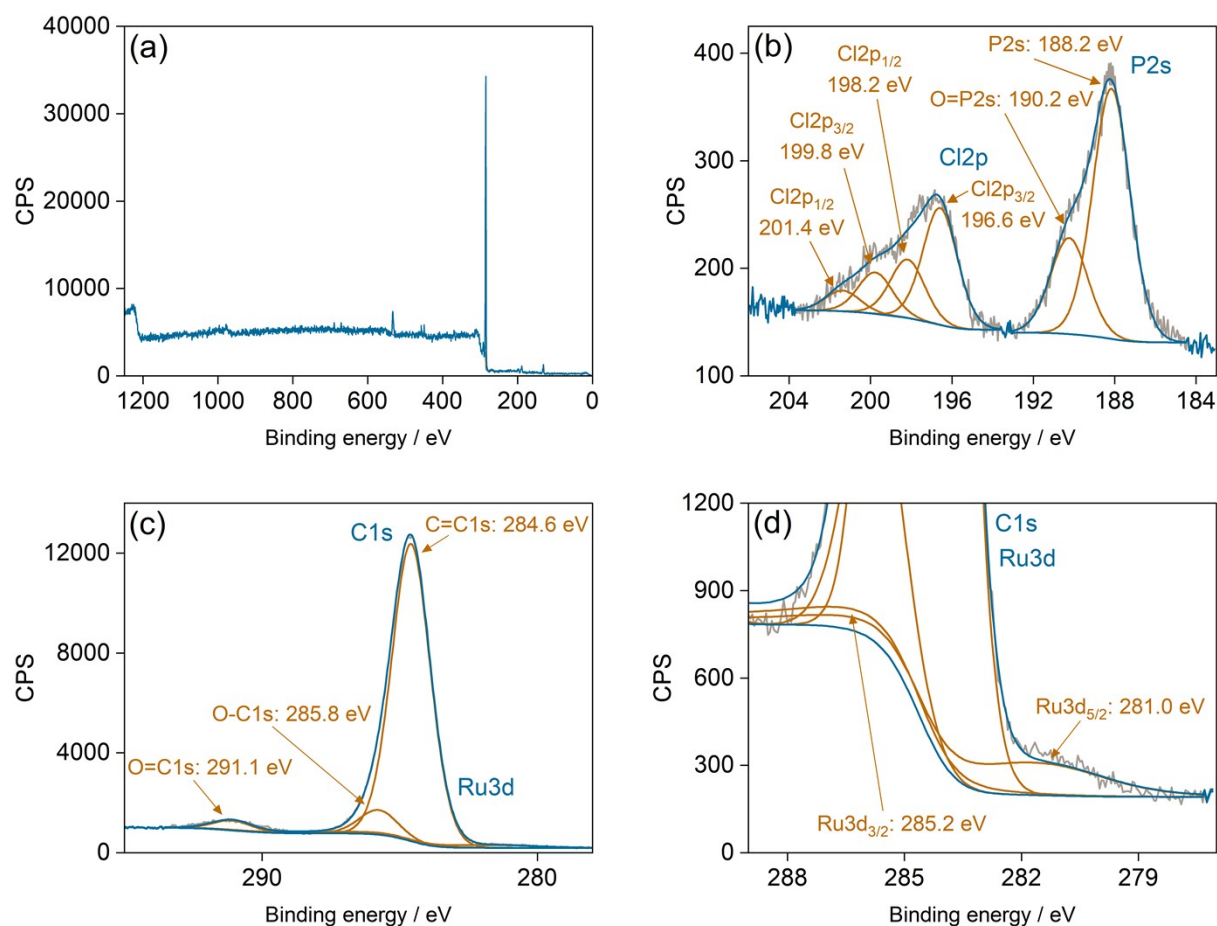




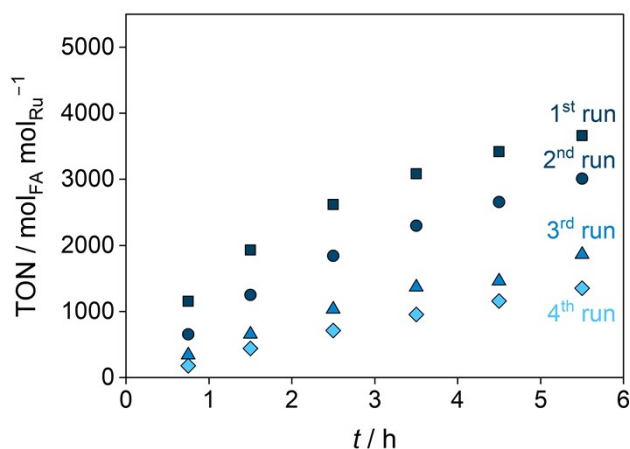
**Figure S3:** SEM image of X-HCP-Ru.



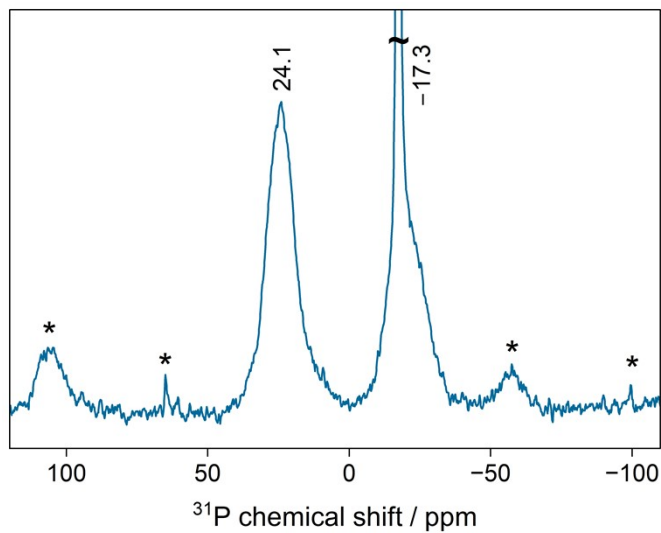
**Figure S4:** TEM image of X-HCP-Ru.



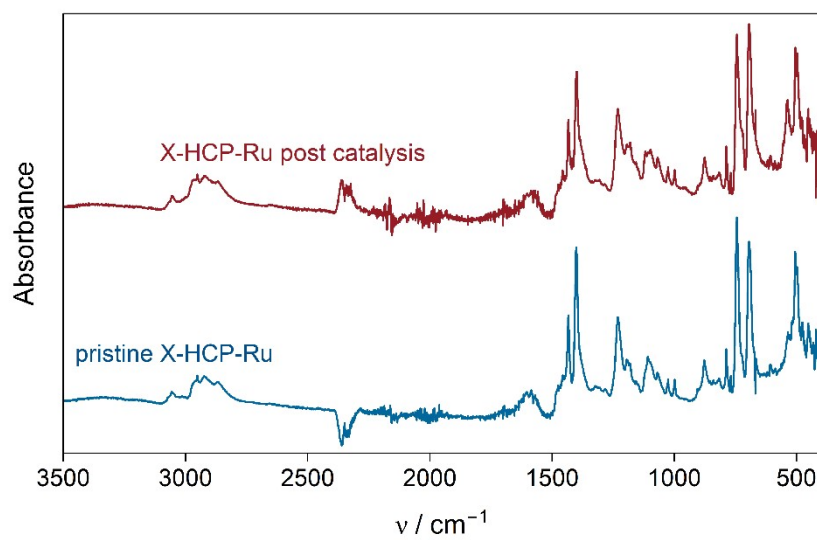
**Figure S5:** XPS of X-HCP-Ru. (a) Survey (b) P2s and Cl2p (c) C1s and Ru3d (d) Zoom on C1s and Ru3d.



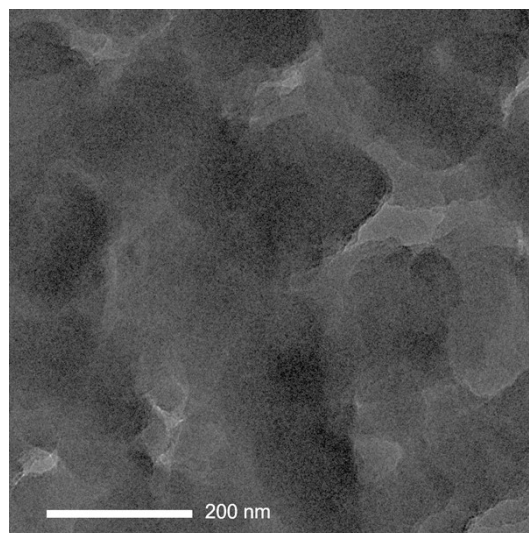
**Figure S6:** Catalytic recycling of the aged X-HCP-Ru (after the catalyst was stored for eight days after preparation under ambient conditions) over four recycling steps. Kinetic curves of the 1<sup>st</sup> run (squares), 2<sup>nd</sup> run (circles), 3<sup>rd</sup> run (triangles) and 4<sup>th</sup> run (diamonds). Reaction conditions: 300 mL Hastelloy autoclave,  $V(\text{H}_2\text{O}) = 150 \text{ mL}$ ,  $n(\text{NaHCO}_3) = 150 \text{ mmol}$ ,  $m(\text{cat.}) = 200 \text{ mg}$ ,  $p(\text{CO}_2/\text{H}_2) = 60 \text{ bar (1:1)}$ ,  $T = 110 \text{ }^\circ\text{C}$ ,  $t = 5.5 \text{ h}$ , 700 rpm.



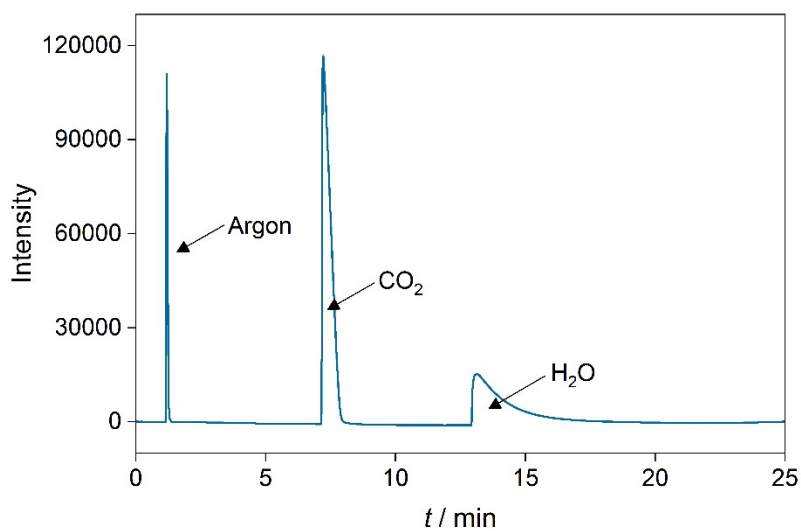
**Figure S7:**  $^{31}\text{P}$  MAS NMR spectrum of X-HCP-Ru after four catalytic runs. Spinning side bands are marked with an asterisk.



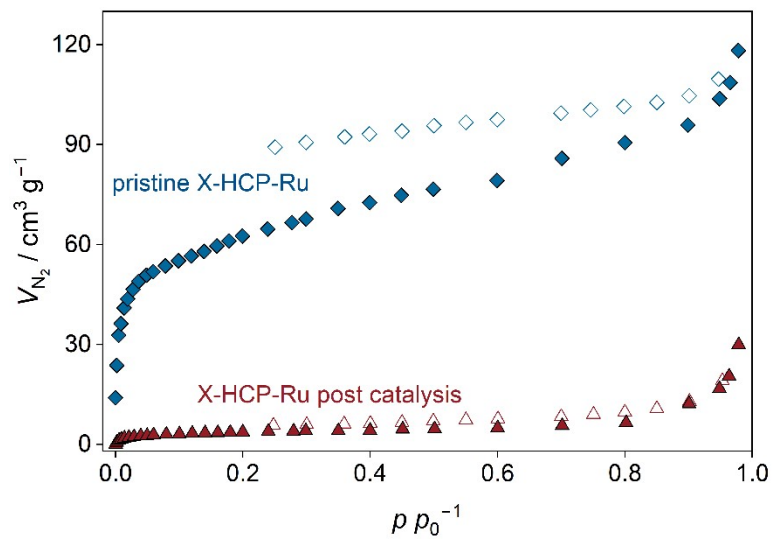
**Figure S8:** ATR-FTIR-spectra of the pristine X-HCP-Ru (blue) and the X-HCP-Ru after four catalytic runs (red). The intensities are normalized to the height of the most intense peak.



**Figure S9:** TEM image of X-HCP-Ru after four catalytic runs.



**Figure S10:** Gas chromatogram of the gas phase after the first run of the recycling experiments of X-HCP-Ru. Retention times:  $t(\text{Argon}) = 1.2$  min,  $t(\text{CO}_2) = 7.2$  min,  $t(\text{H}_2\text{O}) = 14.8$  min.



**Figure S11:** Nitrogen physisorption of X-HCP (blue diamonds) and X-HCP-Ru after four catalytic runs (red triangles) at 77 K. Filled symbols denote the adsorption, empty symbols denote the desorption.

### 3. Literature

- S1 Bingman Fung, Anatholy K. Khitrin, Konstantin Ermolaev, *J. Magn. Res.*, 2000, **142**, 97–101.
- S2 Yuting Yang, Tienan Wang, Xiaofei Jing and Guangshan Zhu, *J. Mater. Chem. A*, 2019, **7**, 10004–10009.