

Supporting Information

Rational Catalyst Design for Acetaldehyde Upgrading – An In-Depth Study on the use of Solid Base and Development of a Second Generation Supported *N*-Heterocyclic Carbene Catalyst

Maurice Belleflamme^{a,b}, Stefan Mersmann^a, Ridvan Ince^b, Thomas Wiegand^{a,b}, Walter Leitner^{a,b} and Andreas J. Vorholt^{*a}

[a] Max Planck Institute for Chemical Energy Conversion, Stiftstraße 34-36, 45470 Mülheim an der Ruhr, Germany, email: andreas-j.vorholt@cec.mpg.de

[b] Institute for Technical und Macromolecular Chemistry, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany.

Table of Contents

1.	Description of the continuous stirred tank reactor (CSTR) miniplant	1
1.1.	Experimental determination of residence time	1
1.2.	Calculation of residence time	3
2.	Additional results of various continuous flow experiments	3
3.	Solid-state NMR Spectroscopy	5
4.	Elemental Analysis of Spent Catalysts	6

1. Description of the continuous stirred tank reactor (CSTR) miniplant

In the continuous stirred tank reactor setup (Figure S 1), the stock solution is pumped from a cooled storage tank (E-1) through a 1/8" PFA capillary by *Shimadzu LC-10AD* HPLC pump (E-2), through a 1/6" stainless steel capillary to the reactor (E-3). The reactant solution is fed into to the stirred tank reactor (E-4), which consists of a stainless-steel autoclave with a volume of $V = 30.6$ mL. The autoclave is heated by a stirring-hot plate and a heating cone. The product solution is passed through a riser tube consisting of a 1/8" PFA capillary to the back-pressure regulator (V-1) (BPR). The solution is then passed through a 1/8" PFA capillary, which is cooled in an ice bath (E-5), from the backpressure valve to the collection vessel (E-6), where it is collected and samples can be withdrawn.

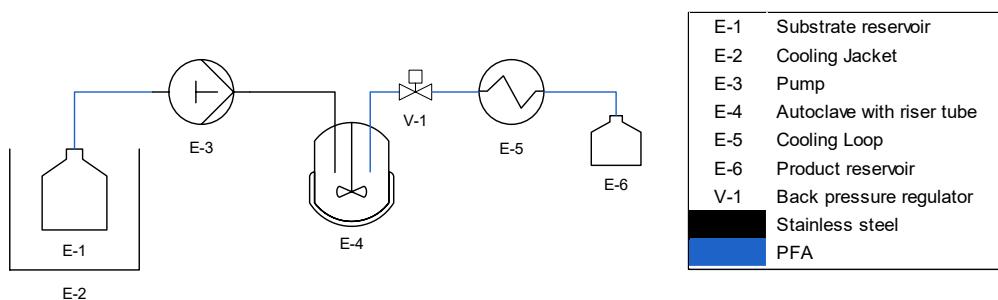


Figure S 1: Flow diagram of the continuous stirred tank reactor.

1.1. Experimental determination of residence time

The setups shown in Figure S 2 were used to investigate the residence times. The general setup was modified so that a 6/2-way valve (V-1), from *Shimadzu* model *FCV-20AH2*, was installed between the pump (E-2) and the reactor (E-6). At the 6/2-way valve, syringe (E-3) was used to introduce the tracer into the sample loop (E-5), with a sample volume of 100 μ L. Ink was used as tracer, which was first evaporated and dissolved again with MilliQ water. Excess solution was collected in the collection container (E-4). By switching the 6/2-way valve, the flow was directed through the sample loop and thus the tracer solution was fed into the stirred tank reactor (E-6) and further into the backpressure regulator (V-2). To detect the tracer, the UV-Vis detector of an HPLC (E-7) was used. The solution was then collected in the collection vessel (E-8).

All measurements were performed under reaction temperatures. For this purpose, first the heating of the reactor was set to the desired temperature and solution was pumped through the system until it reached the collection vessel. Then, the system was additionally purged for 15 min. After the time elapsed, the residence time measurement was started by switching the flow in the 6/2-way valve through the sample loop and starting the measurement in the LabSolutions program.

1.2. Calculation of residence time

Residence times were measured at flows ranging from 0.05 to 1.00 $\text{mL}\cdot\text{min}^{-1}$ and at reaction temperatures to characterize the system. A shock marker with ink was used to determine the residence time. For this purpose, a 6/2-way valve and a UV-Vis detector were installed in the setup. The flow diagrams for the determination of the residence time is shown in the supporting information. To determine the average residence time for the CSTR, the exponential decay of the UV-Vis signal was investigated and an exponential fit equation (1) was used to fit the signal.^[1]

$$f(x) = y_0 + A \cdot e^{-\frac{x}{\tau}} \quad (1)$$

To determine the required flow for an arbitrary residence time based on the measured data, the formula shown in equation (2) was obtained by a power regression.

$$V = 26.348 \cdot \tau^{-0.839} \quad (2)$$

2. Identification of products and side-products

(Side-) products were identified using a *Shimadzu Nexis GC-2010 Plus* equipped with an *OPTIMA 1701* (33 m) column purchased from *Machery-Nagel* and a *Shimadzu MS-QP2020* mass spectrometer. The close-up of a typical GC chromatogram using the unmodified **IM-NHC5**/Na₂CO₃ catalytic system in the acetaldehyde upgrading, is shown below in **Figure S 3**

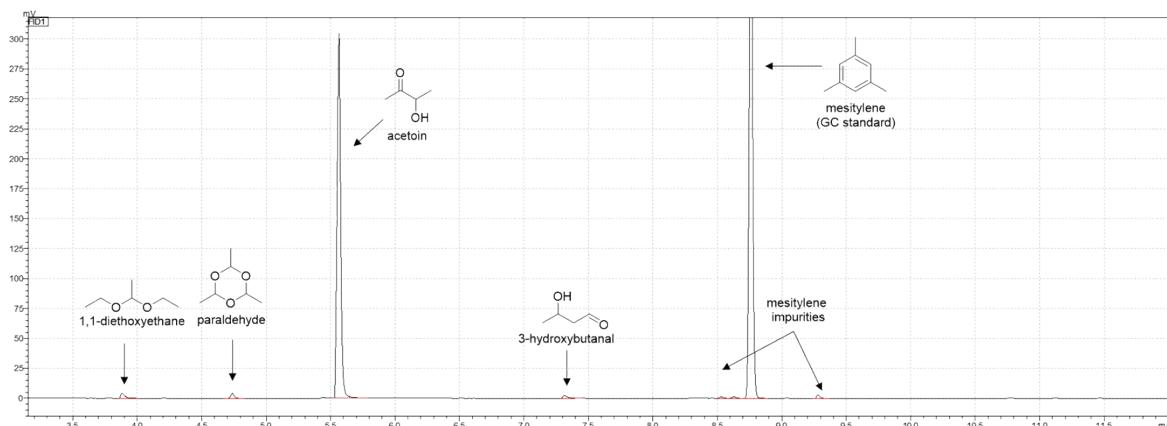


Figure S 2: Close-up of a GC chromatogram of a sample collected from a typical **IM-NHC5**/Na₂CO₃ catalysed continuous-flow acetaldehyde self-addition experiment, as shown **Figure 2A**. Compounds were assigned to peaks using GC-MS measurements with the same Rtx1701 column.

3. Additional results of various continuous flow experiments

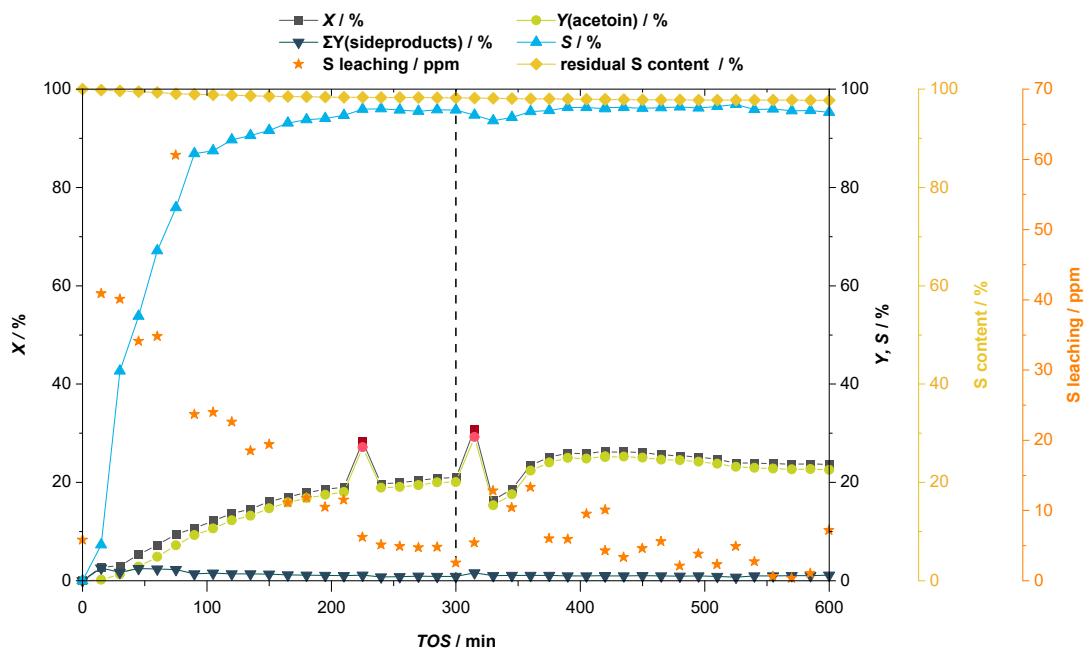


Figure S 3: Results of the continuous flow acetaldehyde self-addition in a CSTR setup over a total of 10 h TOS. Graph shows the conversion X , yield Y and selectivity S towards acetoin over TOS as well as the calculated residual Sulphur content (%) of the catalyst and the measured leaching of S (ppm) for samples taken every 15 minutes for a duration of 4 minutes. Reaction conditions: stock-solution containing acetaldehyde (250 mL, 198.0 g, 4.5 mol), EtOH (250 mL, 196.2 g, 4.5 mol) and mesitylene (29.0 mL, 24.59 g), V (stock) = 0.475 mL·min⁻¹, $m(\text{IM-NHC5})$ = 2.27 g (2.27 mmol·g⁻¹, 5.14 mmol NHC, 1.8 mol%), $m(\text{Na}_2\text{CO}_3)$ = 777.6 mg (7.32 mmol, 2.6 mol%), T = 70 °C, τ = 2 h, 1000 rpm. Mass-balances $\Sigma Y > 90\%$ were obtained. Dotted line at $t = 420$ min TOS, indicates that the reaction was terminated over-night and re-started the next day. Experiment was carried out prior to obtaining the correct loading of the **IM-NHC5-PF₆** catalyst and serves to highlight the proof-of-concept for the continuous flow application with the novel **IM-NHC5-PF₆** catalyst.

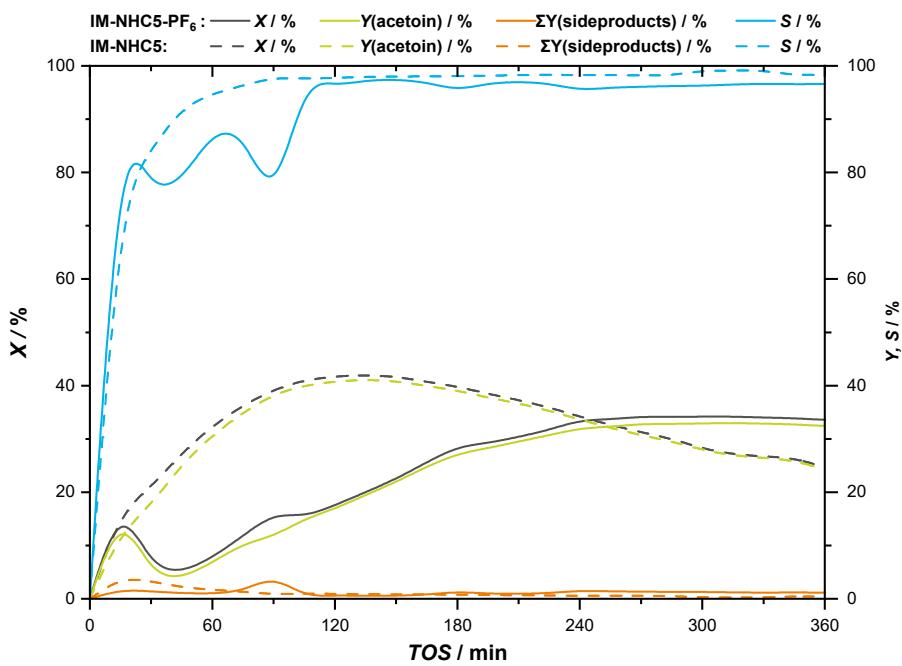


Figure S 4: Overlay of the catalytic results obtained for **IM-NHC5-PF₆** (solid) and **IM-NHC5** (dashed) in a CSTR setup over a total of 6 h TOS. Graph shows conversion X, yield Y and selectivity S towards acetoin over TOS for samples taken every 15 minutes for a duration of 4 minutes. For reasons of brevity, the calculated residual sulphur content (%) of the catalyst as well as the measured leaching of S (ppm) have been omitted here. Reaction conditions for the **IM-NHC5-PF₆** experiment: stock-solution containing acetaldehyde (250 mL, 194.7 g, 4.4 mol), EtOH (250 mL, 196.4 g, 4.5 mol) and mesitylene (29.0 mL, 24.86 g), $V(\text{stock}) = 0.475 \text{ mL}\cdot\text{min}^{-1}$, $m(\text{IM-NHC5-PF}_6) = 2.4900 \text{ g}$ (2.27 mmol·g⁻¹, 5.63 mmol NHC, 2 mol%), $m(\text{Na}_2\text{CO}_3) = 781.0 \text{ mg}$ (7.37 mmol, 2.6 mol%), $T = 70 \text{ }^\circ\text{C}$, $\tau = 2 \text{ h}$, 1000 rpm. Reaction conditions **IM-NHC5** experiment: stock-solution containing acetaldehyde (250 mL, 194.7 g, 4.4 mol), EtOH (250 mL, 196.4 g, 4.5 mol) and mesitylene (29.0 mL, 24.86 g), $V(\text{stock}) = 0.475 \text{ mL}\cdot\text{min}^{-1}$, $m(\text{IM-NHC5}) = 1.7386 \text{ g}$ (3.24 mmol·g⁻¹, 5.63 mmol NHC, 2 mol%), $m(\text{Na}_2\text{CO}_3) = 775.9 \text{ mg}$ (7.32 mmol, 2.6 mol%), $T = 70 \text{ }^\circ\text{C}$, $\tau = 2 \text{ h}$, 1000 rpm.

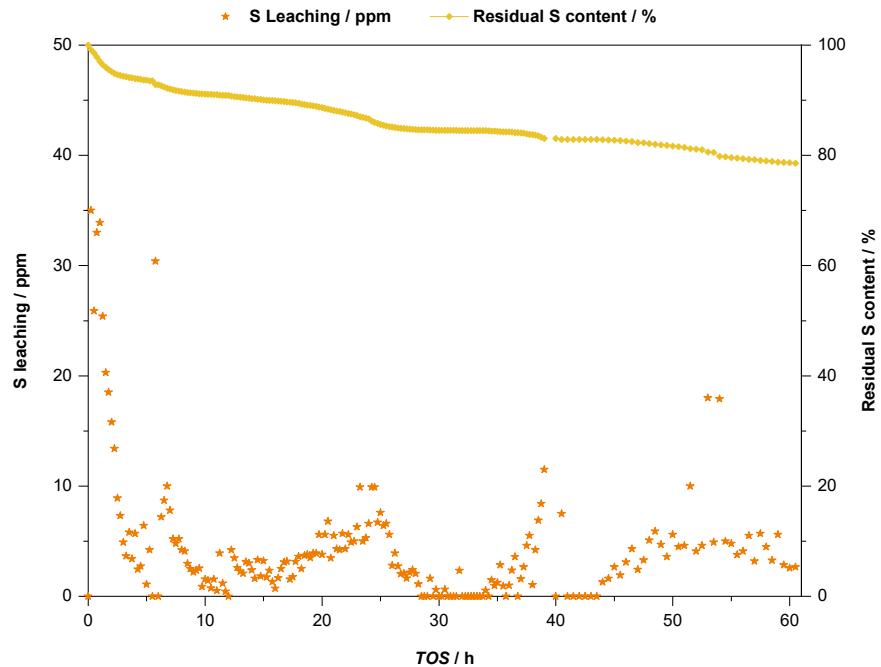


Figure S 5: Overview of the obtained sulfur leaching values (ppm) as well as the calculated residual sulfur content (%) of the **IM-NHC5-PF₆** catalyst in the continuous flow acetaldehyde self-addition in a CSTR setup over a total of

60 h TOS. Reaction conditions are described in **Figure 4**. Concentrations that were found to be below detectional limits (0.3 ppm for sulphur) were treated as zero.

4. Solid-state NMR Spectroscopy

^1H - ^{13}C and ^1H - ^{31}P solid-state NMR experiments were recorded for **IM-NHC5-PF₆** after catalyst reaction as shown in **Figure S 6**. The orange spectra correspond to the catalyst in **Figure 5**, *i.e.* after a reaction with a total time of > 60 h TOS. The green spectra belong to catalyst discussed in catalyst in **Figure 4A**, after a total of 10 recycling runs in batch, each one carried out for 2 h. Lastly, the black spectra correspond to an **IM-NHC5-PF₆** catalyst after a standard experiment with 2.0 mol% of catalyst and 2.6 mol% of Na_2CO_3 as shown in **Figure 3**, entry 3.1.

The signal of the PF_6^- anion detected in ^1H - ^{31}P CP-experiments decreases with longer catalyst reaction times. This can likely be explained by the fact that the PF_6^- anion is washed out of the catalyst matrix upon activation with Na_2CO_3 . Besides, spectral evidence for the decreasing amount of PF_6^- proof for this was also found by elemental analysis of the respective spent catalysts (**Table S 2**).

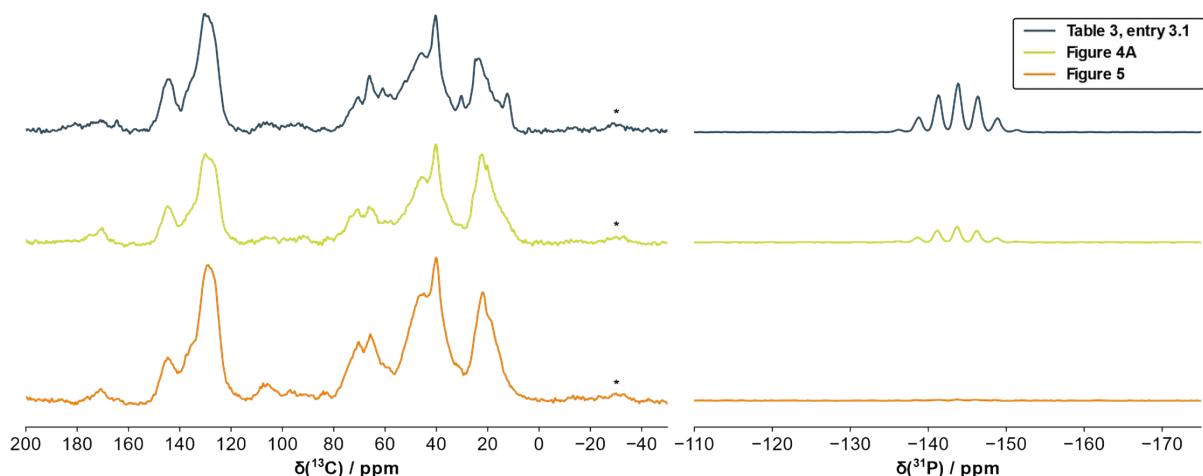


Figure S 6: ^1H - ^{13}C and ^1H - ^{31}P CP spectra of **IM-NHC5-PF₆** samples subjected to different reaction conditions recorded at 14.0 kHz MAS at a static magnetic-field strength of 16.4 T. The grey spectra correspond to **IM-NHC5-PF₆** after 2 h TOS, standard experiment with 2 mol% cat, 2.6 mol% Na_2CO_3 , the green spectra correspond to **IM-NHC5-PF₆** after a total of 10 recycling runs in batch, each one carried out for 2 h and the orange spectra correspond to **IM-NHC5-PF₆** modified catalyst after a reaction with a total time of 60.5 h. TOS. The unscaled ^1H - ^{31}P CP spectra are recorded under similar experimental conditions, *e.g.* the same number of scans and as well as the reaction conditions indicated for the ^1H - ^{13}C spectra on the left hand side. * indicates MAS sidebands.

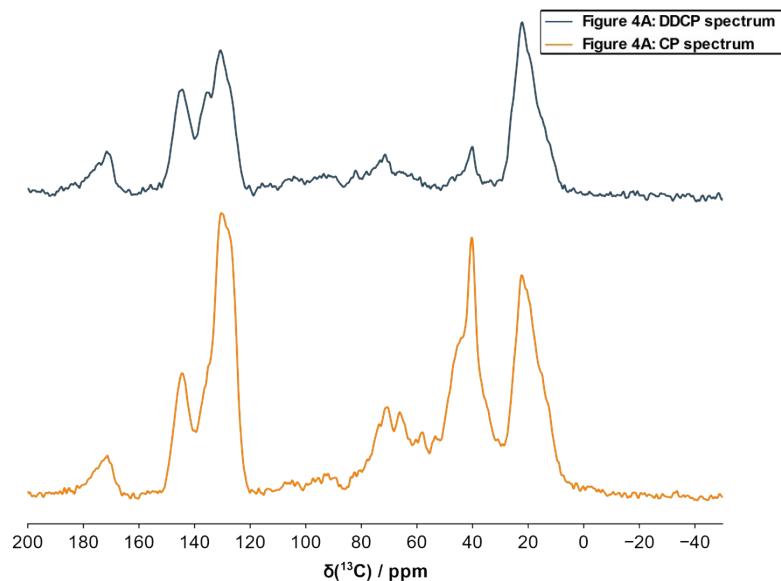


Figure S 7: ^{13}C - ^1H dipolar dephasing spectra on **IM-NHC5-PF₆** after catalysis in 10 consecutive batch recycling experiments each carried out for 2 h (**Figure 4A**) recorded at 14.0 kHz MAS at a static magnetic-field strength of 11.7 T. The dipolar dephasing time for the dipolar-dephased CP-spectrum has been set to two rotor periods (around 143 μs). Dipolar dephasing (DD) has been achieved by switching the ^1H high-power decoupling for the time interval mentioned before off before data acquisition. Subsequently, the ^{13}C signal is detected after a rotor synchronized spin echo with SPINAL-64 decoupling.^[2] The DD-CPMAS spectrum thus mostly shows quaternary and methyl group carbon atom resonances. The reference CP spectrum (orange) has been recorded with the same pulse scheme than the DD-CPMAS MAS experiment without switching the ^1H decoupling off. The quaternary carbon resonance at around 170 ppm is tentatively assigned to an activated carbene species.

Table S 1: Overview of representative ^{13}C and ^{31}P MAS NMR experimental parameters. All spectra have been processed with a gaussian apodization of 100 Hz as defined in *ssNake*.

Sample	IM-NHC5-PF ₆	IM-NHC5-PF ₆	Figure 4A
Experiment	^1H - ^{13}C CP MAS	^1H - ^{31}P CP MAS	^1H - ^{13}C CP MAS
v_r / kHz	14.0	14.0	14.0
B_0 / T	16.4	16.4	11.7
Transfer I	H-C CP	H-P CP	H-C CP
$v_1(^1\text{H})$ / kHz	64	60	64
$v_r(X)$ / kHz	50	46	50
Shape	Tangent shape ^[3]	Tangent shape	Tangent shape
CP contact time / ms	5	2	5
t_2 increments	4096	5000	3072
Sweep width (t_2) / ppm	567	608	795
Acquisition time (t_2) / ms	20.5	14.5	15.4
^1H Spinal64 decoupling / kHz	92	90	92
Recycle delay / s	10	5	10
Number of scans	2048	256	2048
Measurement time / h	5.7	0.4	5.7

5. Elemental Analysis of Spent Catalysts

Relevant concentrations (%) of the spent catalyst discussed in the manuscript are listed below in **Table S 2**.

Table S 2: Overview of the elemental composition of spent and pristine catalysts used in the acetaldehyde self-addition.^[a]

IM-NHC5-PF ₆ catalyst	P content / %	F content / %	PF ₆ loading / mmol·g ⁻¹ [b]
pristine	7.06	25.6	2.27 ^[c]
after Figure 4A	0.53	1.85	0.17
after Figure 5	0.02 ^[d]	0.13	0.01

[a] as determined by *Mikroanalytisches Labor Kolbe*. [b] based on the amount of P present in the sample, P:F ratios found in the samples are roughly equal to the 1:6 molar ratio. [c] value of PF₆ loading is equal to the loading of IM-NHC5-PF₆. [d] value close to detection limit of the instrument.

References

- [1] M. Baerns, A. Behr, H. Hofmann, J. Gmehling, U. Onken, A. Renken, K.-O. Hinrichsen, R. Palkovits, *Technische chemie*, Wiley-VCH Verlag GmbH & Co. KGaA, **2013**.
- [2] B. M. Fung, A. K. Khitrin, K. Ermolaev, *J. Magn. Reson.* **2000**, *142*, 97-101.
- [3] S. Hediger, B. H. Meier, R. R. Ernst, *Chem. Phys. Lett.* **1995**, *240*, 449-456.