Supporting information

Modification of nitrogen doped carbon for SILP catalyzed hydroformylation of ethylene

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Continuous gas-phase reactor

The applied continuous gas-phase reactor has been designed and manufactured at the workshop of CRT in Erlangen.

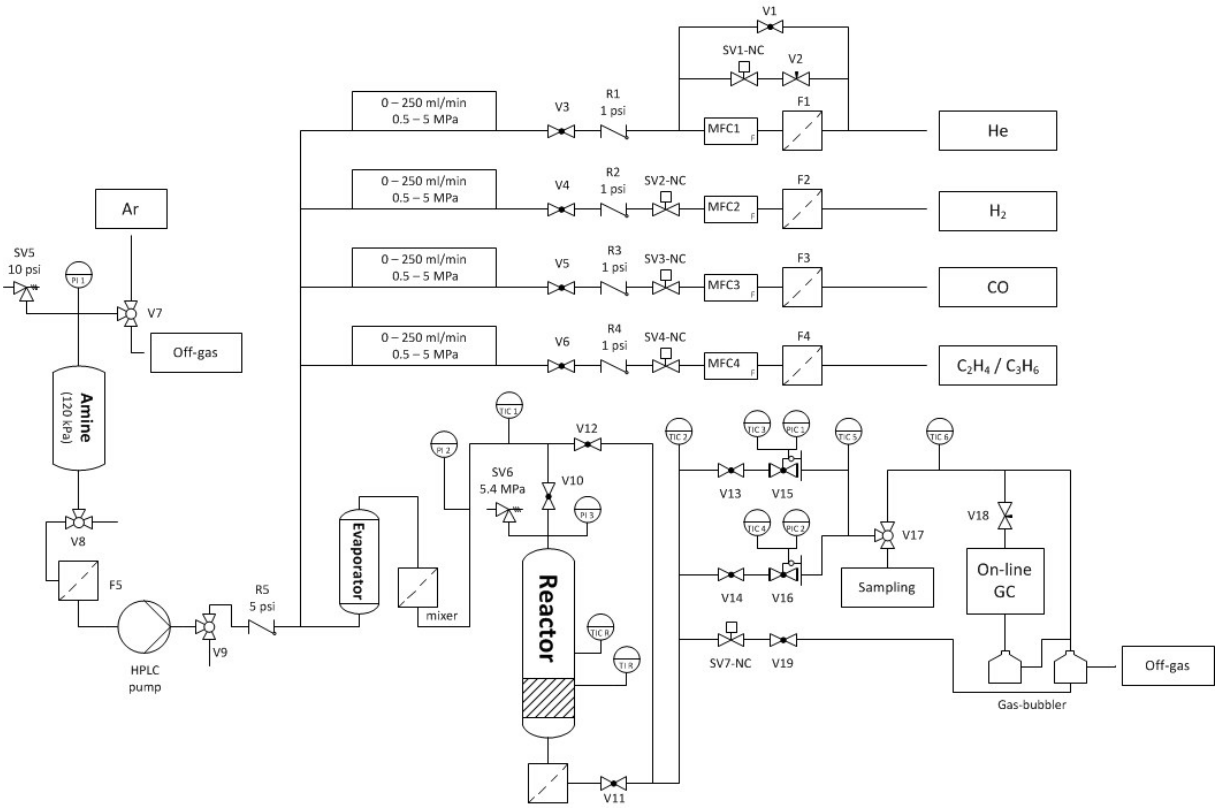

Figure S1. Schematic flowsheet of the continuous gas-phase hydroformylation reactor.

Figure S2. Photograph of the continuous gas-phase hydroformylation reactor.

Treatment of PBSAC with sulfuric acid – catalytic activity

All functionalized support materials were used for SILP preparation as described in the experimental section. The gas phase hydroformylation experiments were done under comparable reaction conditions. The results for the carbon supports treated with sulfuric acid and urea are shown in Figure S3.

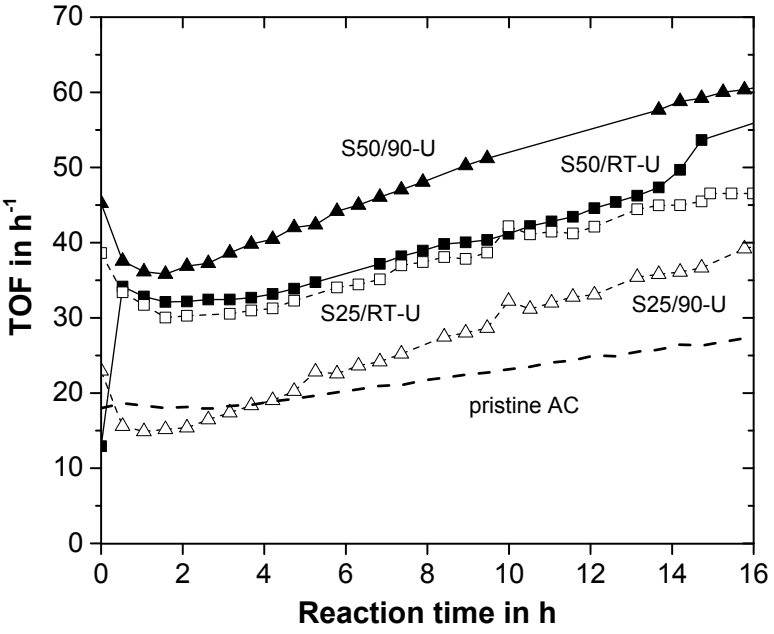

Figure S3: Activity over reaction time of carbon materials functionalized with sulfuric acid and urea in SILP catalyzed hydroformylation of ethylene. AC-pristine (dashed line), S25-RT-U (open squates), S25-90-U (open triangles), S50-RT-U (closed squares), S50-90-U (closed triangles) Reaction conditions: T = 120 °C, p = 8 bar, m_{Kat} = 2.5 g, m_{Rh} = 0.2 wt%, L/Rh = 5, α = 0.1 [EMIM] [NTf_2], p_{Olefin} = 0.3 bar, p_{H2} = 5.0 bar, p_{CO} = 2.7 bar, τ = 6.7 s.

Treatment of PBSAC with nitric acid – catalytic activity

The catalytic results of the more promising functionalization procedure using nitric acid and urea are shown in Figure S4.

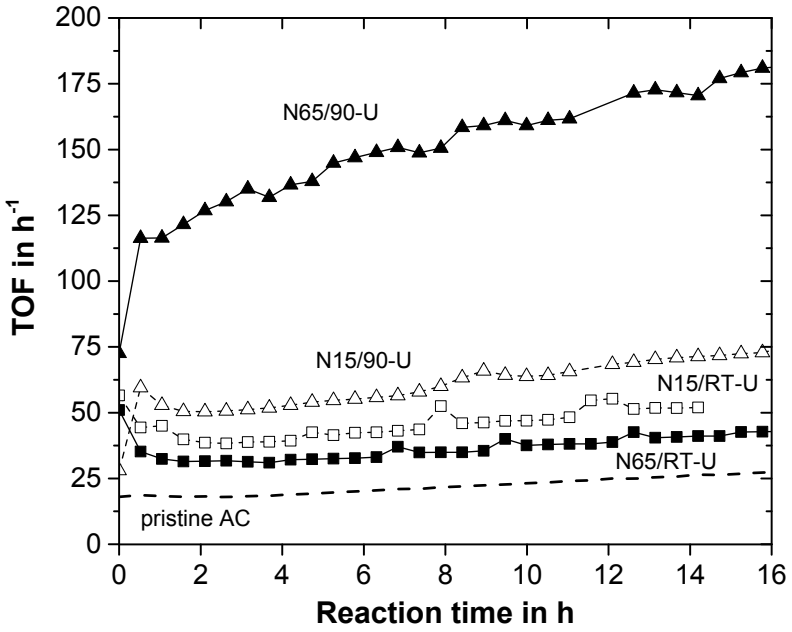

Figure S4: Activity over reaction time of carbon materials functionalized with nitric acid and urea in SILP catalyzed hydroformylation of ethylene. AC-pristine (dashed line), N15-RT-U (open squares), N15-90-U (open triangles), N65/RT-U (closed squares), N65/90-U (closed triangles)

Urea decomposition – analysis via mass spectroscopy

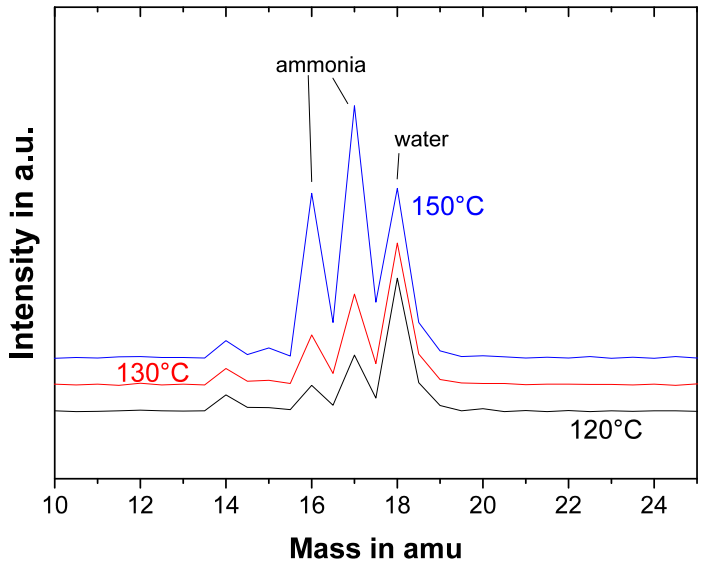

Figure S5: MS signals for urea decomposition experiment at different temperatures.

Reaction conditions: T = 120 - 150 °C, m_{AC} = 2.5 g, α = 0.1 [EMIM] [NTf2] / urea (2:1).

Correlation between N and PZC for PBSAC based SILP catalysts

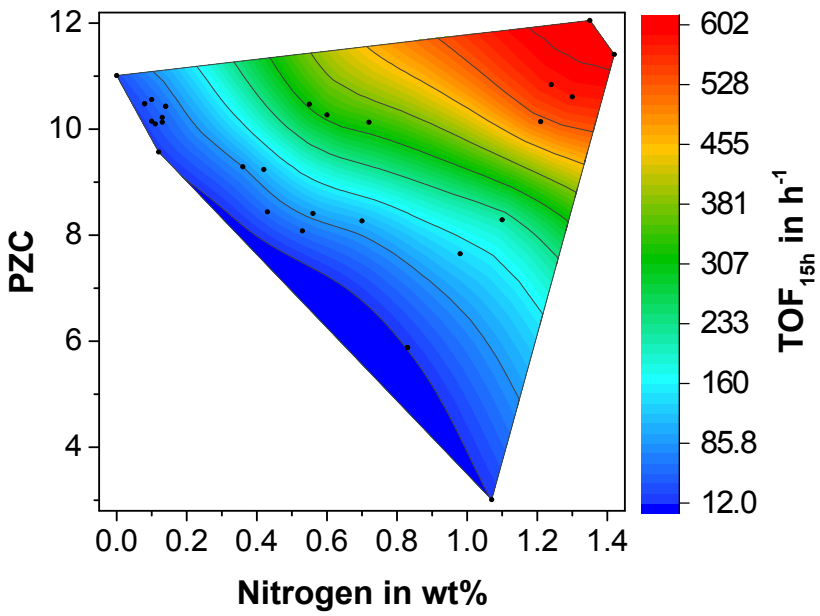

Figure S6: Correlation between nitrogen content and PZC of the functionalized carbon supports and the activity of SILP catalyzed hydroformylation of ethylene after 15 h reaction time. Reaction conditions: T = 120 °C, p = 8 bar, m_{Kat} = 2.5 g, m_{Rh} = 0.2 wt%, L/Rh = 5, α = 0.1 [EMIM] [NTf_2], p_{Olefin} = 0.3 bar, p_{H2} = 5.0 bar, p_{CO} = 2.7 bar, τ = 6.7 s

Textural properties of pristine and functionalized carbon

Table S1. Nitrogen adsorption results for pristine and functionalized carbon materials with different ionic liquid [EMIM][NTf_2]) pore filling degree.

Entry	Pore filling degree	AC-pristine			AC-N65/90-A		
		Surface area	Pore volume	Micro pore volume	Surface area	Pore volume	Micro pore volume
1	α = 0	1583	0,8805	0,499	1562	0,9438	0,492
2	α = 0.05	1393	0,8169	0,4169	1438	0,913	0,4628
3	α = 0.1	1280	0,8111	0,4182	1134	0,7772	0,3632
4	α = 0.3	726,2	0,5667	0,2467	465,3	0,431	0,1556