Supporting Information

Ru catalyzed continuous gas-phase hydrogenation of toluene – selectivity enhancement by ionic liquid coating and methanol co-feeding

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Ru-SCILL catalyst preparation

To synthesize the SCILL materials, the respective ionic liquid was dissolved in an appropriate solvent in a round bottom flask. The solid catalyst material was then placed in the solution, which had to completely cover the catalyst. The flask was then connected to a rotary evaporator. To ensure total pore filling by the solvent, de- and re-pressurizing was repeated until no more gas bubbles emerged from the solid. The solvent was then evaporated under low vacuum and dried further under minimum pressure (~20 mbar) at 75 °C for 30 more minutes. Residual peaks of solvent could sometimes be found in the hydrogenation experiments at startup but did not affect the reaction.

For toluene hydrogenation experiments, the custom synthesized catalysts was used. The required amount of ionic liquid was calculated via the pore filling degree α, defined as volume fraction of the pore volume filled by ionic liquid at ambient conditions. Knowledge of the density of the ionic liquid as well as the porosity of the support allowed calculation of the required amount of ionic liquid via the following Equation (S1)

$$\alpha I_{L,syn} = \frac{V_{IL}}{V_{pore,total}} = \frac{m_{IL}}{V_{pore} \cdot m_{support} \cdot \rho_{IL}} \quad \text{(S1)}$$

A pore filling degree of 0.2 (or 20 vol%) was set for all toluene hydrogenation SCILL catalysts, as this was found to have the best reproducibility with minimal deactivation.[1]

Table S1: List of ionic liquids used

No	Ionic Liquid	Abbreviation	Formula	molar mass [g/mol]	density [g/cm3]	solvent used	company
1	1-ethyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide	[EMIM][NTf_2]	$C_8H_{11}F_6N_3O_4S_2$	391.31	1.52 (20°C)	acetonitrile	Merck, Iolitec
2	1-butyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide	[BMIM][NTf_2]	$C_{10}H_{15}F_6N_3O_4S_2$	419.36	1.43 (20°C)	acetonitrile	Merck, Iolitec
3	1-octyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide	[OMIM][NTf_2]	$C_{14}H_{23}F_6N_3O_4S_2$	475.47	1.32 (20°C)	acetonitrile	Iolitec
9	1-ethyl-3-methyl imidazolium hexafluorophosphate	[EMIM][PF_6]	$C_6H_{11}F_6N_2P$	256.13	1.42 (80°C)	acetonitrile	Iolitec

10	1-butyl-3-methyl imidazolium hexafluorophosphate	[BMIM][PF_6]	$C_8H_{15}F_6N_2P$	284.18	1.38 (20°C)	acetonitrile	Iolitec
11	1-hexyl-3-methyl imidazolium hexafluorophosphate	[HMIM][PF_6]	$C_{10}H_{19}F_6N_2P$	312.24	1.30 (20°C)	acetonitrile	Iolitec
12	1-octyl-3-methyl imidazolium hexafluorophosphate	[OMIM][PF_6]	$C_{12}H_{23}F_6N_2P$	340.29	1.24 (20°C)	acetonitrile	Iolitec
13	1-butyl-3-methyl imidazolium dicyanamide	[BMIM][DCA]	$C_{10}H_{15}N_5$	205.26	1.06 (20°C)	Ethanol	Iolitec
15	1-butyl-3-methyl imidazolium thiocyanate	[BMIM][SCN]	$C_9H_{15}N_3S$	197.30	1.06 (20°C)	Ethanol	Iolitec
16	1-butyl-3-methyl imidazolium trifluoro acetate	[BMIM][TFA]	$C_{10}H_{15}F_3N_2O_2$	252.23	1.21 (25°C)	Ethanol	Merck
17	1-butyl-3-methyl imidazolium tetrafluoroborate	[BMIM][BF_4]	$C_8H_{15}N_2BF_4$	226.06	1.17 (25°C)	Ethanol	Iolitec
23	1-ethyl-3-methyl imidazolium ethyl sulfate	[EMIM][$EtSO_4$]	$C_8H_{16}N_2O_4S$	236.29	1.24 (20°C)	Ethanol	Merck
24	1-butyl-3-methyl imidazolium sulfate	[BMIM][HSO_4]	$C_8H_{16}N_2O_4S$	236.29	1.24 (20°C)	Ethanol	Merck

Chemicals were purchased from Daejung or Junsei Chemicals, Korea. Catalyst components were purchased from Alfa Aesar, Sigma-Aldrich or in case of the alumina support from Sasol.

Table S2: List and suppliers of chemicals used.

Type	Chemicals	Supplier company	Purity/Specification
Reactant	Toluene	Daejung Chemicals	> 99.8%
	H_2	Linde	99.9999%
	He	Linde	99.9999%
Solvent	Cyclohexane	Sigma-Aldrich	> 99.5%
	Ethanol	Daejung Chemicals	> 99.9%
	Acetonitrile	Daejung Chemicals	> 99.5%
Catalyst	0.5% Ruthenium on Alumina	Alfa Aesar	3mm alumina pellets
	Ruthenium (3) chloride hydrate	Sigma-Aldrich	99,98%
	Puralox NWa155 aluminium oxide spheres	Sasol	98%
Additives	cadmium sulfate hydrate	Daejung Chemicals	> 99 %
	Zinc Hydroxide	JUNSEI Chemicals	98%

	Zinc Phosphate Tetrahydrate	Daejung Chemicals	> 99%
	Zinc Chloride	Daejung Chemicals	98%
	Zinc Sulphate Heptahydrate	Daejung Chemicals	> 99%

Continuous gas-phase reactor setup

The setup consisted of a large tubular reactor with three heating zones, an evaporator or saturation unit and online gas chromatography as shown in Figure S1. Liquid was dosed through a Techlab Minipump with analytical scale pump head and gasses through two Bronkhorst MFCs, one for hydrogen and one for nitrogen (Linde gasses, 5.0 purity).

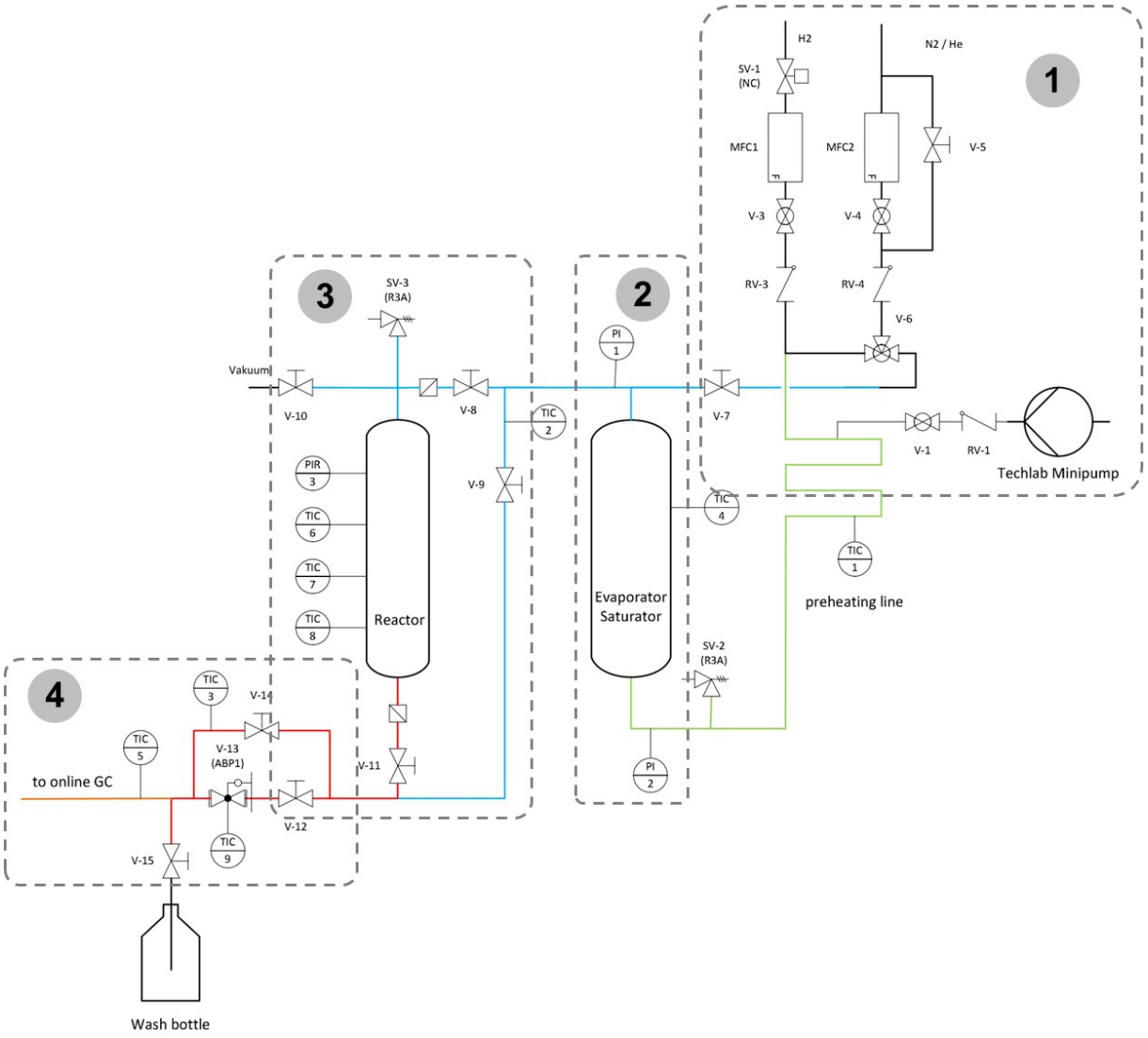

Figure S1. Detailed flow scheme of the continuous gas-phase reactor setup including (1) gas and liquid dosing, (2) evaporator and mixing unit, (3) fixed-bed reactor and (4) back pressure regulator and split flow section.

The hydrogen passed directly through a preheating line, consisting of a 6 mm stainless steel tube heated with a heating line and into the evaporator/saturator vessel. The inert gas could either be mixed with the hydrogen prior or after the vessel through the three-way valve V-6, enabling the vessel to be either used as evaporator or saturation unit.

The liquid was pumped through a 1/16" stainless steel capillary which was heated alongside the gas heating line and entered the mixing vessel through the bottom. The evaporator was fitted with a sintered plate and filled with glass beads for efficient evaporation. The gas-vapor mixture left the vessel at the top to flow into the reactor from the top.

The reactor was heated through a three-zone heating mantle and was fitted with two 1″ VCR fittings. It was supplied with a sinter plate inlay for support of the catalyst bed. After passing through the reactor and catalyst bed, the pressure was reduced to ambient with a back pressure regulator (Parker ABP1 series). The flow was split to flow either through the heated GC transfer line or into a washing bottle, controlled by V-15.

In a typical run, 0.25g of the synthesized Ru/Alox catalyst (blank) or 0.5 g of the corresponding SCILL was filled into the reactor tube. After sealing with fresh VCR seals, the reactor was flushed with nitrogen using the bypass valves V-5 and V-14. The MFCs were then set to the desired flow rates and the reactor rig was pressurized. This also allowed leak testing of the system. The reactor was then heated to the desired temperature through the three heating zones of the heating mantle. The electronic pressure indicator allowed exact monitoring of the reactor pressure. The peripheral tubing was also heated to above reactor temperature to prevent condensation in cold spots. The evaporator temperature was maintained below reactor temperature to avoid pore condensation of toluene in the catalyst pellets. The temperatures were controlled through nine Eurotherm regulators.

Reactor effluent gas analysis

Analysis was performed in a Varian CP-3800 gas chromatograph equipped with an FID detector through a six-port gas dosing valve. A Varian Select Al_2O_3 MAPD (50m x 320 µm x 5 µm) column was used for separation. The flow rate was set to 5 Nml min^{-1} He at 463 K, resulting in a total run time of 5 min per analysis. The method allowed separation of toluene, methylcyclohexane and the three methylcyclohexenes.

Ionic liquid variation studies in Ru-SCILL hydrogenation

Four ionic liquids carrying the cation 1-butyl-3-methyl imidazolium ([BMIM]+) with the anions bis(trifluoromethylsulfonyl)imide ([NTf2]-), hexafluorophosphate ([PF6]-), tetrafluoroborate ([BF4]-) and trifluoroacetate ([TFA]-) were coated on commercial Ru-alumina pellets.

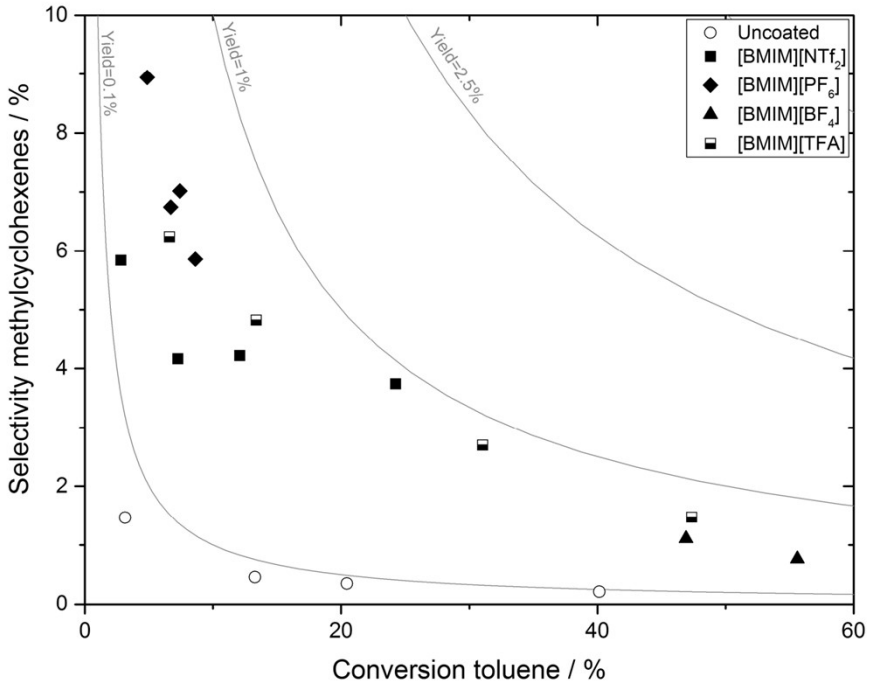

Figure S2. Performance of a commercial 0.5 wt.% Ru/Al_2O_3 catalyst coated with ionic liquids with $[C_4\text{-}C_1Im]$-cation and different anions. Uncoated catalyst added as reference. Conditions: 0.5 g

catalyst (0.125 g for uncoated), 393 K, 0.1 MPa, $F_{toluene}$ = 0.075 ml min^{-1} (liq.), $F_{hydrogen}$ = 45 ml_N min^{-1}, F_{helium} = 25-90 ml_N min^{-1}, 20 vol.% ionic liquid loading.

To see the influence of the alkyl chain lengths, SCILL catalysts were synthesized using the homologous row of imidazolium with increasing alkyl chain length in the 1-N position and [PF6]- as anion. Results are shown in Figure S3.

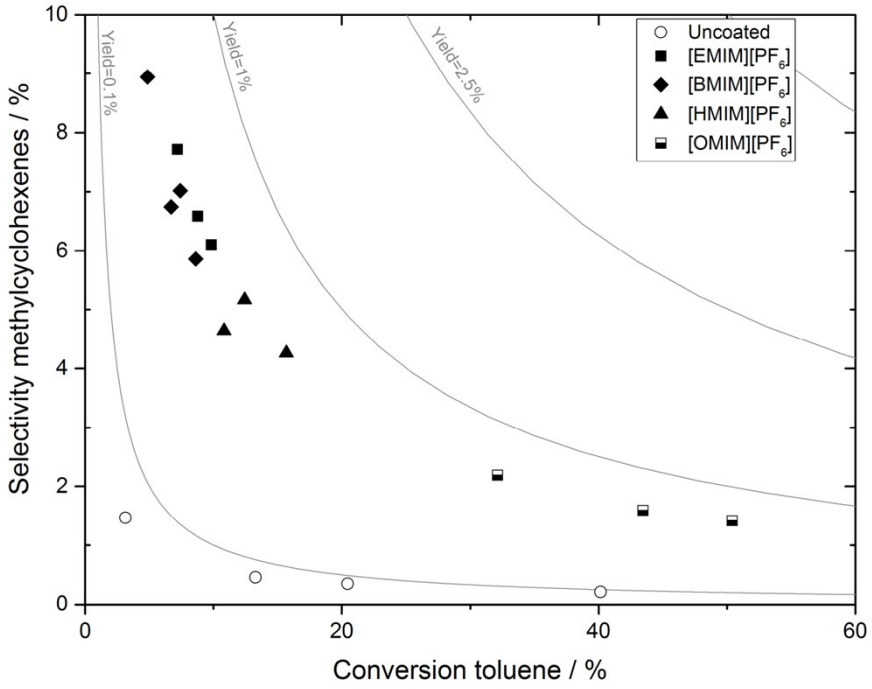

Figure S3. Performance of a commercial 0.5 wt.% Ru/Al_2O_3 catalyst coated with ionic liquids with PF_6-anion and different imidazolium cations. Uncoated catalyst added as reference. Conditions: 0.5 g catalyst (0.125 g for uncoated), 393 K, 0.1 MPa, $F_{toluene}$ = 0.075 ml min^{-1} (liq.), $F_{hydrogen}$ = 45 ml_N min^{-1}, F_{helium} = 25-90 ml_N min^{-1}, 20 vol.% ionic liquid loading.

Conversion vs. selectivity for the homologous IL-series with alkylimidazole cation (C2 through C8-C1 imidazolium) and Hexapfluorophosphate anion, data points for comparable residence times shown.

cation variation

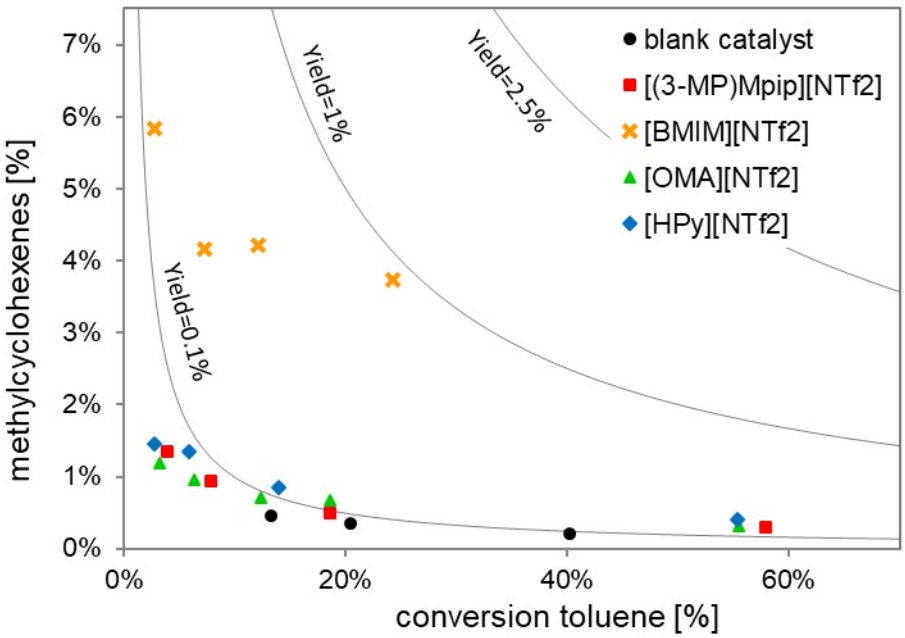

Figure S4: Performance of a commercial 0.5 wt.% Ru/Al_2O_3 catalyst coated with ionic liquids with NTf2-anion and different cations. Blank catalyst added as reference. Conditions: 0.5 g catalyst (0.125 g for uncoated), 393 K, 0.1 MPa, $F_{toluene}$ = 0.075 ml min^{-1} (liq.), $F_{hydrogen}$ = 45 ml_N min^{-1}, F_{helium} = 25-90 ml_N min^{-1}, 20 vol.% ionic liquid loading.

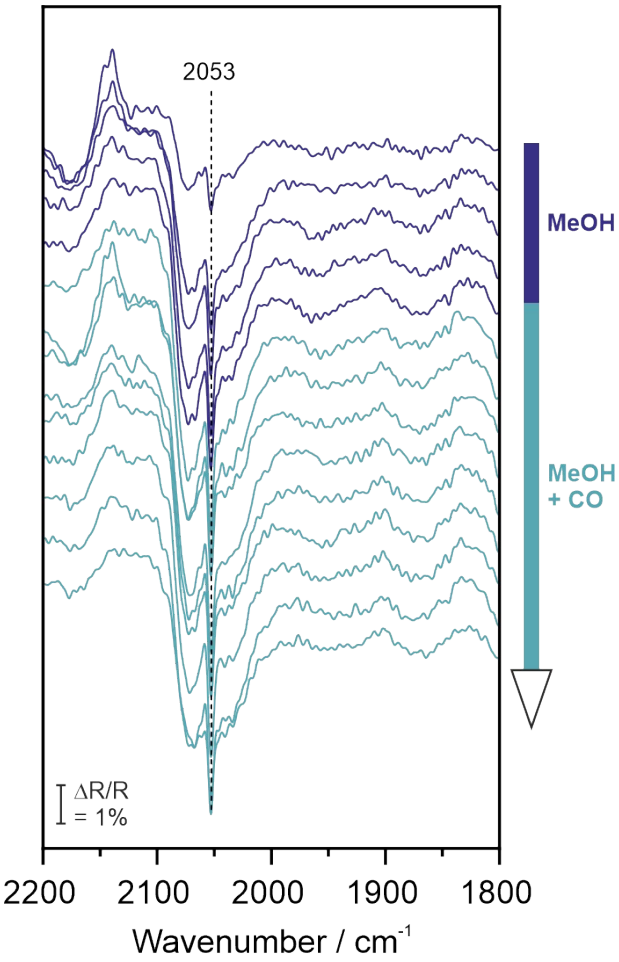

Figure S5: DRIFTS during MeOH/CO dosing in pristine Puralox support.