Improved CO_2 Conversion to Methanol Promoted by Ionic Liquid Additives Using a $Cu/ZnO/Al_2O_3$ Heterogeneous Catalyst

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Experimental

Materials. All experiments were carried under an inert atmosphere (with N_2 or Ar) using standard Schlenk line techniques. Commercial $CuO/ZnO/Al_2O_3$ (56.2 wt % Cu, 24.7 wt % ZnO, 10.1 wt % Al_2O, and 1.3 wt % MgO fume) was purchased from Alfa Aesar (Stock #45776, Lot #C18WO19). Ionic liquids 1-butyl-3-methylimidazolium bromide ([BMIm][Br]), 1-butyl-3-methylimidazolium chloride ([BMIm][Cl]), and 1-butyl-3-methylimidazolium acetate [BMIm][OAc] were obtained from Strem Chemicals (>95%) and used without further purification. 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc]) was obtained from Alfa Aesar (>95%) and was used without further purification. Na_3PO_4, KOH, and CH_3SO_3K were all utilized as received from Sigma Aldrich (>98%). Solvents, monoglyme, diglyme, triglyme, tetraglyme, and polyethylene glycol 400 (PEG-400) were purchased from Sigma Aldrich (>98%). Amines, monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), 2-ethylamine ethanol (EAE), and tetramethyl-1,6-hexanediamine (TMHDA) were purchased from commercial sources and used as such without further purification. CO_2 (Gilmore, instrument grade), H_2 (Gilmore, ultra-high pure grade 5.0), and $1CO_2 : 3H_2$ gas mixture (Gilmore, instrument grade) were all used without further purification. DMSO-d_6 was purchased from Cambridge Isotope Laboratory (>99.9%). Chloroform as an internal standard was obtained from VWR (>99%).

Caution. Reactions are associated with H_2 gas. They should be carefully handled inside proper fume hoods and grounding without any flame, spark, or static electricity sources nearby.

Catalyst activation. The catalyst pellets were ground and sieved to a size of 250 µm or less. The catalyst was then placed in a tubular quartz reactor above a 10 mm layer of quartz wool. For the reduction, the catalyst was first heated at 120°C for 1 h under a H_2/N_2 flow (35 mL/min H_2, 35 mL/min N_2) at standard pressure. Then, the temperature was ramped up to 270°C (10°C/min) and kept at that temperature for 5 h under the same H_2/N_2 flow conditions. After that, the catalyst was allowed to cool to room temperature over 20 h. The catalyst was then removed from the tubular reactor under a nitrogen atmosphere and stored in an argon glovebox for subsequent use.

Ionic liquid synthesis. 1-butyl-3-methylimidazolium hydroxide ([BMIm][OH]), 1-butyl-3-methylimidazolium methanesulfonate ([BMIm][CH_3SO_3]), and 1-butyl-3-methylimidazolium phosphate ([BMIm][PO_4]) ionic liquids were synthesized utilizing metathesis reactions. 5 g (22.8 mmol) of [BMIM][Br] was dissolved in 100 mL of DI water and placed into a 250 mL three neck round bottom flask. A 1.1 equivalent of the anion precursor (Na_3PO_4, KOH, or CH_3SO_3K) was then added to the flask and the flask heated under reflux at 110°C for 18 h. After, the mixture was washed with ethyl acetate and separated via a separation funnel. The solvent was then evaporated from the resulting mixture to obtain a pure ionic liquid, which was characterized by NMR as shown in **Figure S12** to **Figure S17**

Hydrogenation of CO_2. $Cu/ZnO/Al_2O_3$ was weighed in an argon glovebox and then transported to a nitrogen chamber. The ionic liquid was measured by weight in a borosilicate vial and transferred into the nitrogen chamber. The chosen amount of amine, 5 mL of solvent, and catalyst were then added in the same borosilicate vial in the same nitrogen chamber. The borosilicate vial was then placed into a 130 mL Parr reactor that was sealed in the nitrogen chamber. The Parr reactor was subsequently pressurized to a total 75 bar gas mixture by first adding CO_2 (UHP) followed by H_2 (UHP) at a chosen CO_2:H_2 ratio. Then, the reactor was placed in an aluminum block, preheated to the desired temperature, and held at that temperature for the duration of the reaction. At the end of the reaction, the reactor was cooled below 15°C in an ice bath, the pressure was released, and the solution was separated from the catalyst via decanting. A part of the gas mixture was collected in a collection bag for gas chromatography (GC) analysis. A 0.5 mL aliquot of the reaction mixture was taken out of the reaction mixture for NMR analysis. A known amount of standard, chloroform, was also added to quantify the amount of methanol produced by ^{1}H NMR with DMSO-d_6 as the deuterated solvent.

Recycling experiment. A standard CO_2 hydrogenation experiment was first set-up as described above under the following conditions: 5 mL triglyme, 3 mmol triethanolamine, 300 mg [BMIm][OAc], 300 mg Cu/ZnO/Al_2O_3, 75 bar CO_2:3H_2, 250°C, and 20 h reaction time. After reaction, the reactor was cooled below 15°C in an ice bath, and the pressure was released. A portion of the gas mixture was released into a gas collection bag for gas chromatography (GC) analysis to detect H_2, CO, CO_2, and CH_4. The reactor was then transferred to a nitrogen chamber and opened. The reaction mixture was decanted from the catalyst analyzed by ^{1}H NMR using 0.1 mL of sample and 0.1 mL of chloroform as the internal standard. The reaction mixture was lightly heated at 50°C for 15 min to remove methanol. The reactor was then resealed, and the hydrogenation reactions was performed again after adding 75 bar CO_2:3H_2. This procedure was repeated for a total of five cycles.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on 400 or 500 MHz, Varian NMR spectrometers. ^{1}H and ^{13}C NMR chemical shifts were determined relative to the residual solvent signals. The ^{1}H NMR spectra were recorded using 32 scans and a relaxation delay of 5 s. ^{13}C NMR was set to exclude nuclear Overhauser effect, 2048 scans, and a relaxation delay of 18 s to provide more accurate integration values. The gas mixtures were analyzed using a Thermo Finnigan gas chromatograph (column: Supelco, Carboxen 1010 plot, 30 m×0.53 mm) equipped with a TCD detector (CO detection limit: 0.099 v/v%). Powder X-ray diffraction (XRD) was performed on a sixth generation Rigaku Miniflex powder diffractometer. The catalyst was first decanted from the solution. The catalyst was mixed with water to wash off the reaction mixture and centrifuged for 10 min at 2.4 relative centrifugal force (rcf) three times. The catalyst was then dried overnight at 80°C. The scan was set from 10°-70° at a scan rate of 5°/min. The resulting spectra were processed on the PDXL software. Scanning electron microscopy (SEM) images were obtained from a Nova Nano SEM 450 field emission scanning electron microscope with an acceleration voltage of 18 keV. X-Ray Fluorescence (XRF) was conducted on a Bruker Tiger S8 instrument. The X-Ray source is rhodium leading to residual rhodium signals. The spectra were all collected between 0-60 keV. The weight percentages of the metals were calculated using the Bruker software. The calculations were based on the K_α peak.

Optimization Experiments

Table S1 to Table S7 summarize the data from the optimization experiments presented in the manuscript. The conditions are specified for each table. Examples for the ^{1}H and ^{13}C NMR spectra are shown for the optimized conditions in Figure S1 and Figure S2, respectively. No formate intermediate was detected. After opening the reactor at the end of the experiment, the solution was bubbling, indicating the release of dissolved CO_2 and H_2 from solution.

Table S1. Summary for ionic liquid scope and [BMIm][OAc] loading optimization.

		Products		
Ionic Liquid	Loading [mg]	MeOH [mmol]	CO [mmol]	CH_4 [mmol]
None	0	6.60	4.6	0.62
[BMIm][OAc]	300	9.46	5.72	trace
[BMIm][OAc]	100	6.51	4.02	n.d.
[BMIm][OAc]	200	8.76	4.01	n.d.
[BMIm][OAc]	400	3.11	3.72	trace
[BMIm][Br]	300	n.d.	0.79	trace
[BMIm][Cl]	300	0.21	0.38	trace
$[BMIm]_3[PO_4]$	300	n.d.	0.37	0.11
[BMIm][OH]	300	2.79	0.62	trace
[EMIm][OAc]	300	2.41	3.27	n.d.
$[BMIm][CH_3SO_3]$	300	0.29	0.93	trace

Conditions: x mg ionic liquid, 300 mg $Cu/ZnO/Al_2O_3$, 75 bar CO_2:$3H_2$, 5 mL triglyme, 3 mmol diethanolamine, 225°C, 20 h.

Table S2. Summary of catalyst loading optimization experiments.

	Products		
Catalyst [mg]	MeOH [mmol]	CO [mmol]	CH_4 [mmol]
150	1.89	4.87	n.d.
300	9.46	5.42	trace
450	10.80	4.87	trace

Conditions: 300 mg [BMIm][OAc], x mg $Cu/ZnO/Al_2O_3$, 75 bar CO_2:$3H_2$, 5 mL triglyme, 3 mmol diethanolamine, 225°C, 20 h.

Table S3. Summary of the CO_2:H_2 ratio optimization experiments.

	Products		
CO_2:xH_2	MeOH [mmol]	CO [mmol]	CH_4 [mmol]
0:1	0.52	n.d.	n.d.
1:2	6.51	8.24	n.d.
1:3	9.46	5.72	trace
1:4	7.48	5.52	0.27
1:5	7.46	4.31	trace

Conditions: 300 mg [BMIm][OAc], 300 mg Cu/ZnO/Al_2O_3, 75 bar CO_2:xH_2, 5 mL triglyme, 3 mmol diethanolamine, 225°C, 20 h.

Table S4. Summary for solvent scope optimization experiments.

	Products		
Solvent	MeOH [mmol]	CO [mmol]	CH_4 [mmol]
Water	2.64	2.60	n.d.
Monoglyme	3.77	5.20	trace
Diglyme	4.97	4.69	n.d.
Triglyme	9.46	5.72	trace
Triglyme*	20.1 *	4.16	1.41
Tetraglyme	7.91	4.55	trace
PEG-400	1.88	2.21	n.d.

Conditions: 300 mg [BMIm][OAc], 300 mg Cu/ZnO/Al_2O_3, 75 bar CO_2:3H_2, 5 mL solvent, 3 mmol diethanolamine, 225°C, 20 h. *10 mmol methanol was added which resulted in a net gain of 10.1 mmol methanol.

Table S5. Summary for temperature optimization experiments.

	Products		
Temperature [°C]	MeOH [mmol]	CO [mmol]	CH_4 [mmol]
200	1.55	1.85	trace
225	9.46	5.72	trace
250	10.0	5.15	0.32

Conditions: 300 mg [BMIm][OAc], 300 mg $Cu/ZnO/Al_2O_3$, 75 bar CO_2:$3H_2$, 5 mL triglyme, 3 mmol diethanolamine, x°C, 20 h.

Table S6. Summary for amine scope and triethanolamine loading optimization experiments

		Products		
Amine	Loading [mmol]	MeOH [mmol]	CO [mmol]	CH_4 [mmol]
None	0	5.18	9.93	n.d.
Monoethanolamine (MEA)	3	7.26	5.94	0.19
Diethanolamine (DEA)	3	10.0	5.15	0.32
Triethanolamine (TEA)	3	14.1	5.24	0.18
Triethanolamine (TEA)	6.5	14.1	4.79	1.04
2-ethylamine ethanol (EAE)	3	7.92	6.63	trace
Tetramethyl-1,6-hexadiamine (TMHDA)	3	3.76	10.32	trace

Conditions: 300 mg [BMIm][OAc], 300 mg $Cu/ZnO/Al_2O_3$, 75 bar CO_2:$3H_2$, 5 mL triglyme, x mmol amine, 250°C, 20 h.

Table S7. Summary for time optimization experiments.

	Products		
Time [h]	MeOH [mmol]	CO [mmol]	CH_4 [mmol]
10	4.62	9.07	trace
20	14.1	5.24	0.18
20[a]	8.04	3.52	trace
30	14.5	3.84	0.32

Conditions: 300 mg [BMIm][OAc], 300 mg $Cu/ZnO/Al_2O_3$, 75 bar CO_2:$3H_2$, 5 mL triglyme, 3 mmol diethanolamine, 250°C, x h. [a]Control with 0 mg [BMIm][OAc].

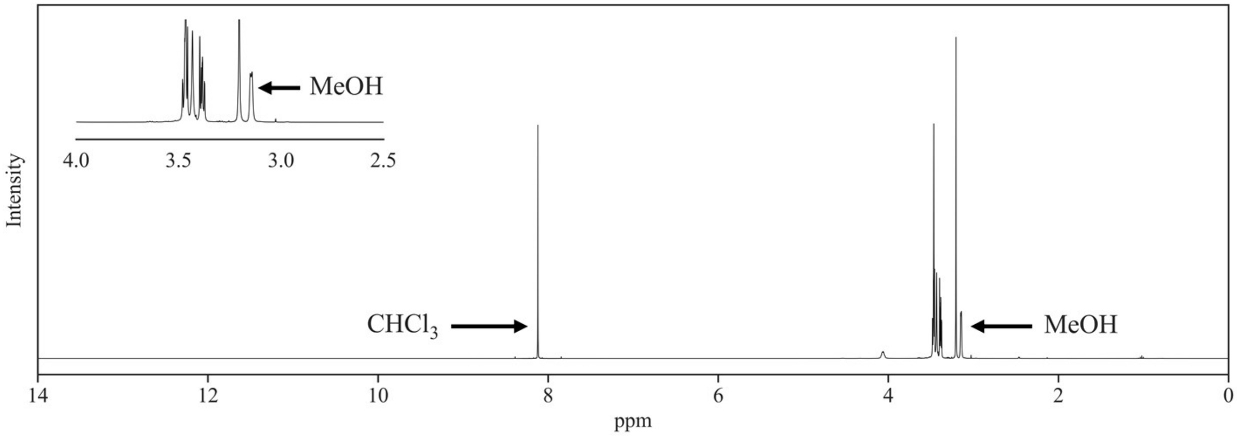

Figure S1. ^1H NMR spectra after reaction under the optimized conditions. Conditions: 300 mg [BMIm][OAc], 300 mg $Cu/ZnO/Al_2O_3$, 75 bar CO_2:$3H_2$, 5 mL triglyme, 3 mmol triethanolamine, 250°C, 20 h. Chloroform was used as an internal standard to quantify methanol yields. The inset zooms into the region of the methanol peak.

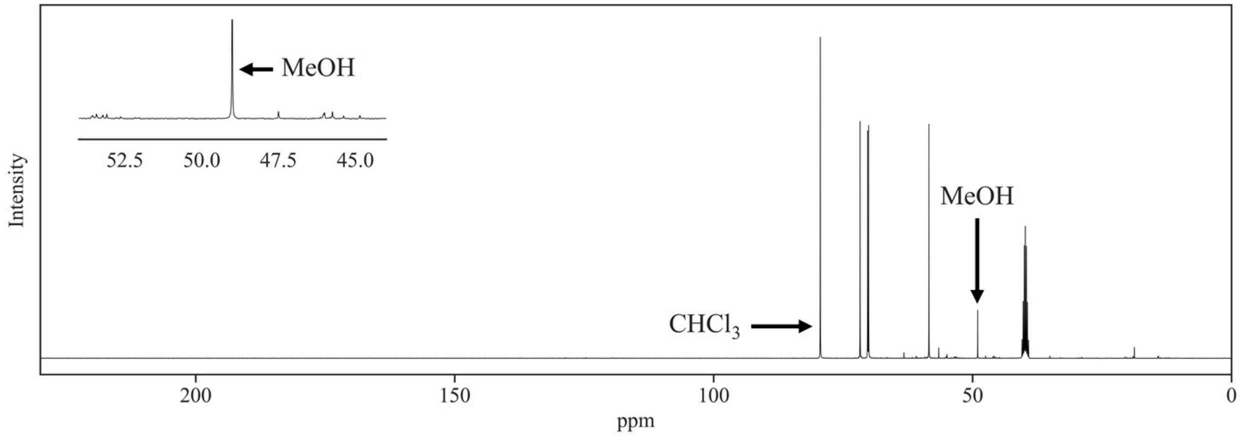

Figure S2. ^{13}C NMR spectra after reaction under the optimized conditions. Conditions: 300 mg [BMIm][OAc], 300 mg Cu/ZnO/Al_2O_3, 75 bar CO_2:$3H_2$, 5 mL triglyme, 3 mmol triethanolamine, 250°C, 20 h. Chloroform was used as an internal standard to quantify methanol yields. The inset zooms into the region of the methanol peak.

Recycling Experiments

Recycling experiments are summarized in Table S8. An increase in CO and decrease in MeOH production was observed with increasing number of cycles. The relative intensity of the ionic liquid peak to chloroform internal standard is shown in Figure S3. The ^{1}H and ^{13}C NMR spectra for the recycling experiments are shown in Figure S4 and Figure S5 respectively. No additional peaks from formate, glycolates, or carbamates were detected in the downfield region.

Table S8. Summary for recycling experiments.

	Products		
Cycle	MeOH [mmol]	CO [mmol]	CH_4 [mmol]
1	15.0	5.50	trace
2	13.5	8.76	n.d.
3	10.1	11.45	n.d.
4	5.94	11.25	n.d.
5	5.77	13.01	n.d.

Conditions: 300 mg [BMIm][OAc], 300 mg Cu/ZnO/Al_2O_3, 75 bar CO_2:$3H_2$, 5 mL triglyme, 3 mmol triethanolamine, 250°C, 20 h.

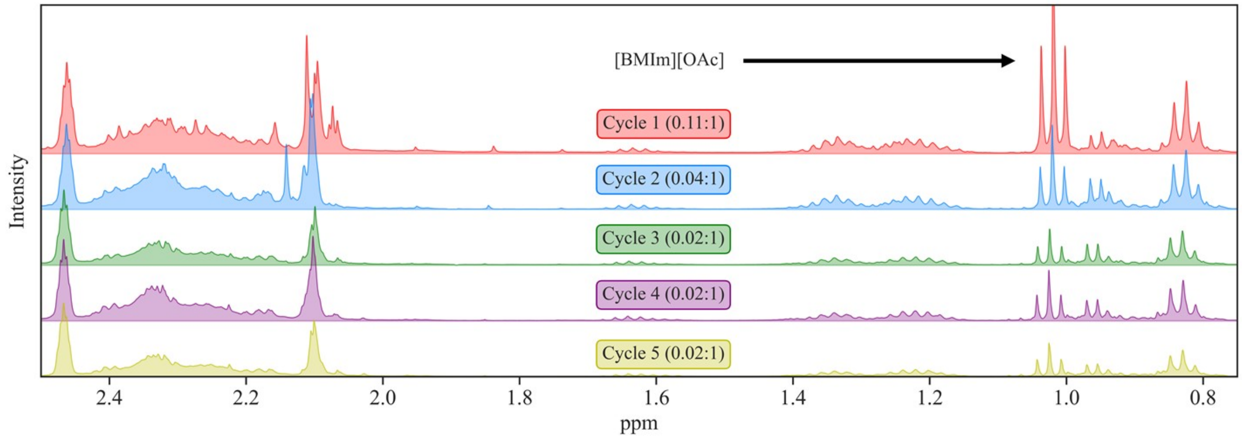

Figure S3. ^{1}H NMR tracking the intensity of a [BMIm][OAc] peak at 1.02 ppm relative to a chloroform peak at 7.94 ppm over the course of the recycling experiments. The numbers listed are the ratio between the peak intensity of the ionic liquid to chloroform.

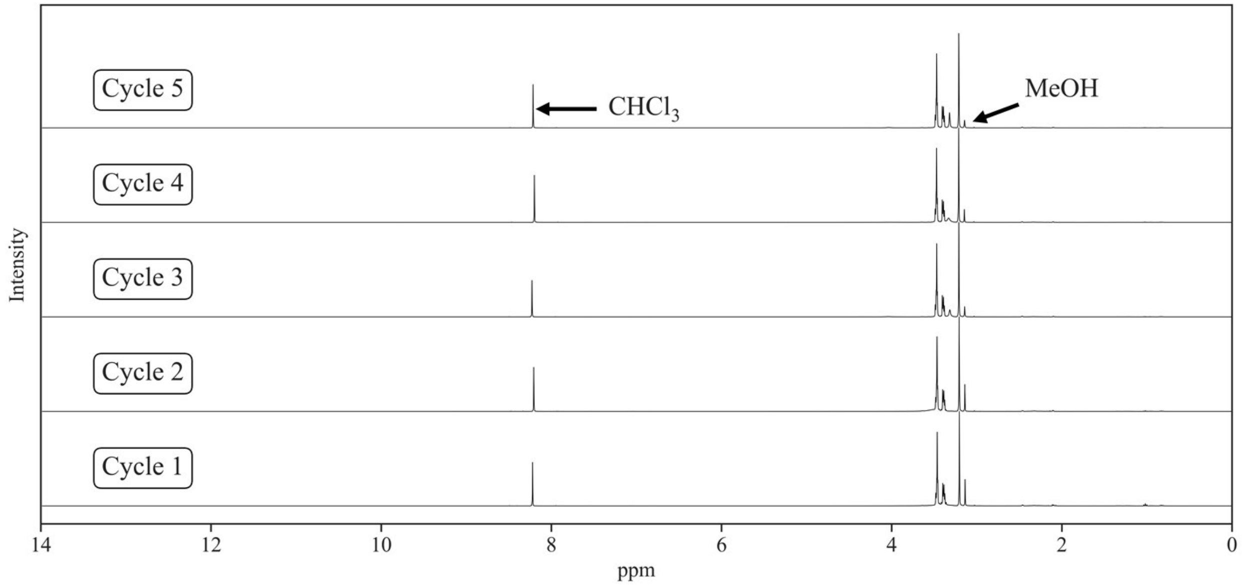

Figure S4. ^{1}H NMR of the recycling experiments for cycles 1-5.

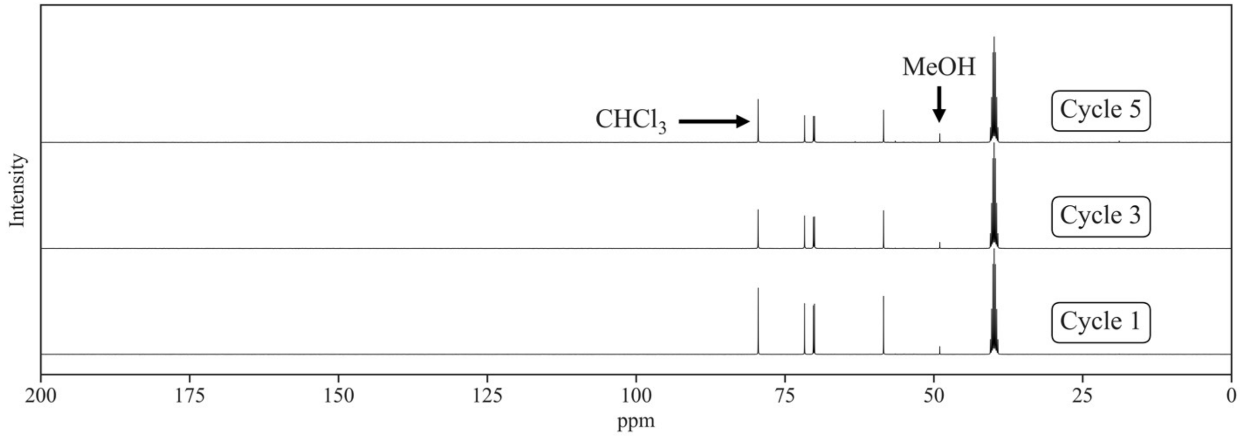

Figure S5. ^{13}C NMR of the recycling experiments for cycles 1, 3, and 5.

X-Ray Diffraction (XRD) Data

The XRD data for the unactivated catalyst, activated catalyst, catalyst from cycle 1, and catalyst from cycle 5 is shown in Figure S6. The best performing trial from the optimization studies is labeled as Cycle 1. After 1 cycle, the Cu^0(1,1,1) crystallite size increased from 11 nm to 20 nm (Table S9). After 5 cycles, the crystallite size was similar to cycle 1.

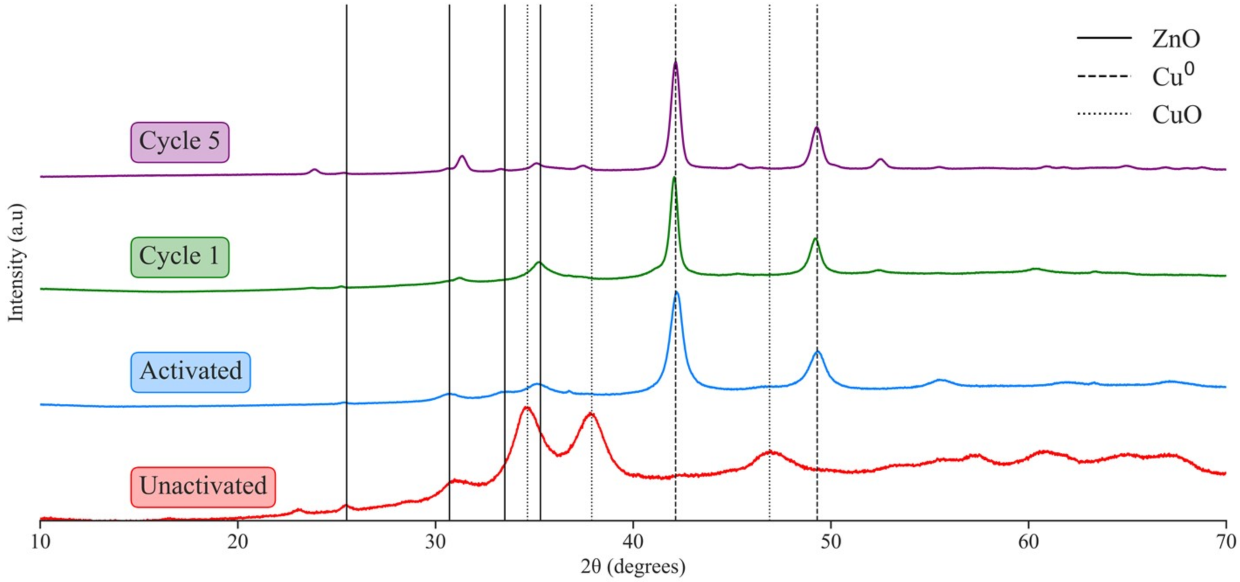

Figure S6. XRD of Cu/ZnO/Al$_2$O$_3$ catalyst under different conditions. The solid lines represent ZnO, dashed lines represent Cu^0, and dotted lines represent CuO.

Table S9. Crystallite size data for the Cu^0 peak.

Catalyst from	Cu^0 (1,1,1) crystallite size (nm)
Unactivated	-
Activated	11
Cycle 1	20
Cycle 5	17

Scanning Electron Microscopy (SEM) Images

SEM images were taken to compare the catalyst surface after one cycle and after five cycles (Figure S7). There appears to be increasing conglomeration on the catalyst surface after five cycles of reaction.

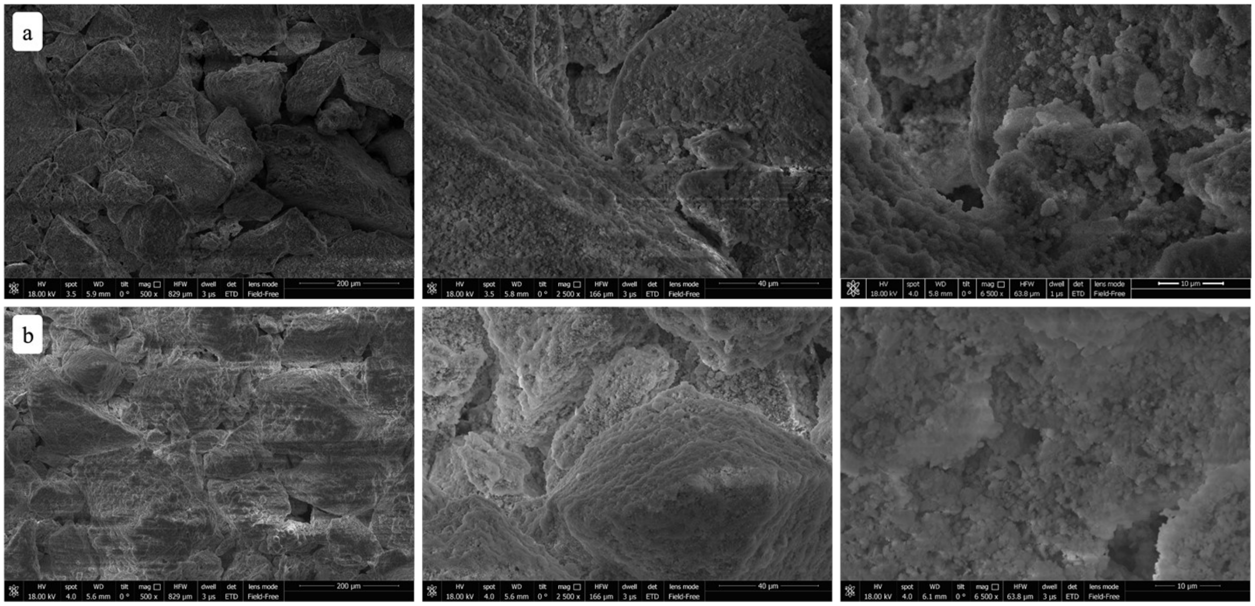

Figure S7. SEM images at various magnifications of $Cu/ZnO/Al_2O_3$ after a) one reaction cycle and b) five reaction cycles.

X-Ray Fluorescence (XRF) Data

XRF data was collected for the unactivated catalyst, activated catalyst, catalyst after 1 reaction cycle, and catalyst after 5 reaction cycles to determine the percentage of elements in each catalyst. Each XRF spectrum is shown between 0-60 KeV. The x-ray source is rhodium which manifests as residual peaks in the spectra at 19, 20, 21.5, and 22 KeV. The weight percentages of the elements (Cu, Zn, Al) were calculated using a Bruker software, Quantexpress, and the results are shown in Table S10.

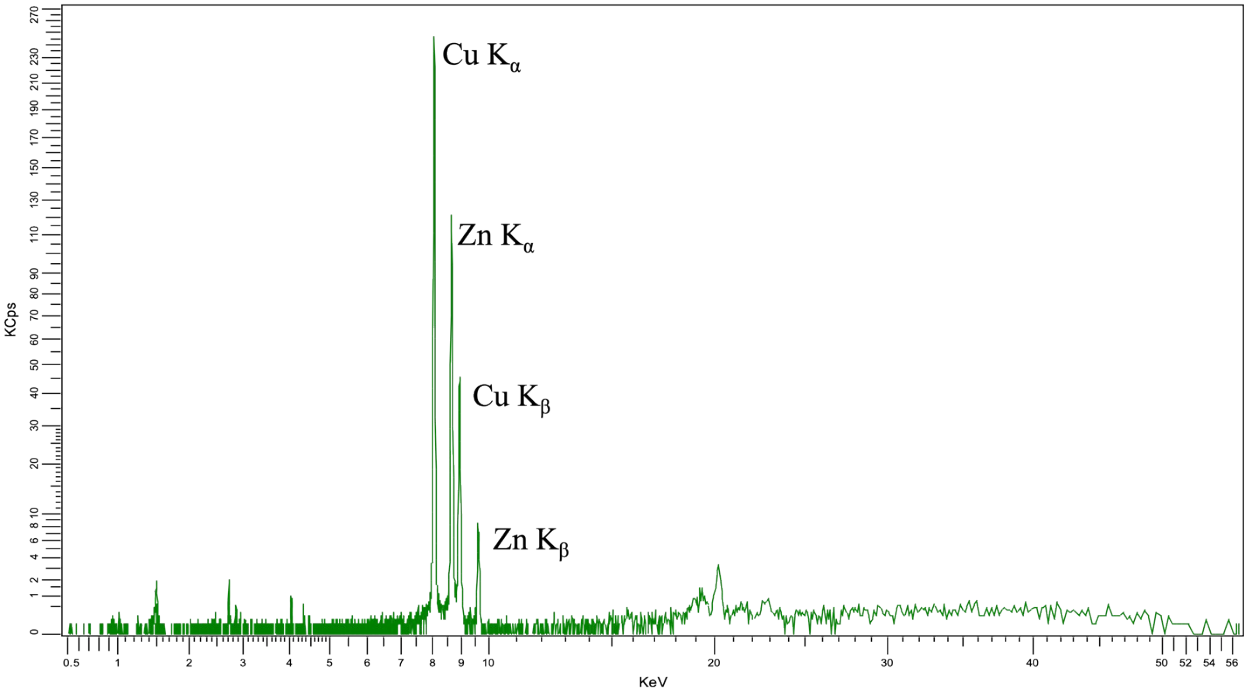

Figure S8. XRF spectra of unactivated Cu/ZnO/Al$_2$O$_3$.

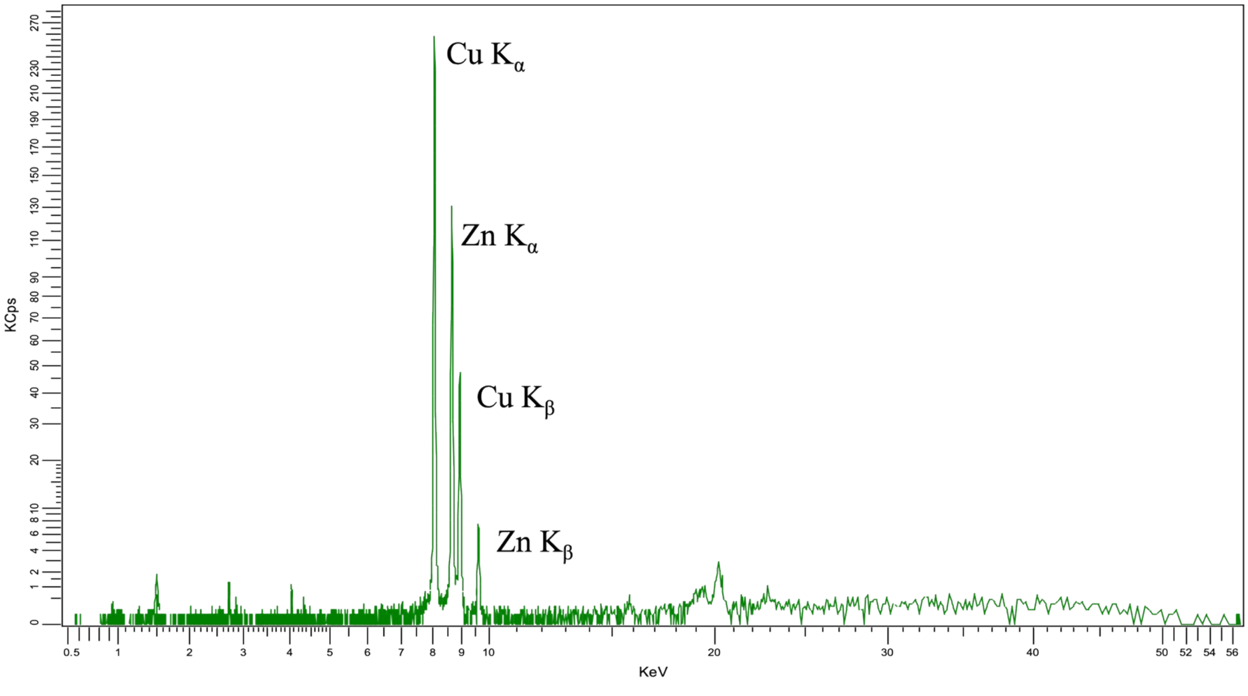

Figure S9. XRF spectra of activated Cu/ZnO/Al$_2$O$_3$.

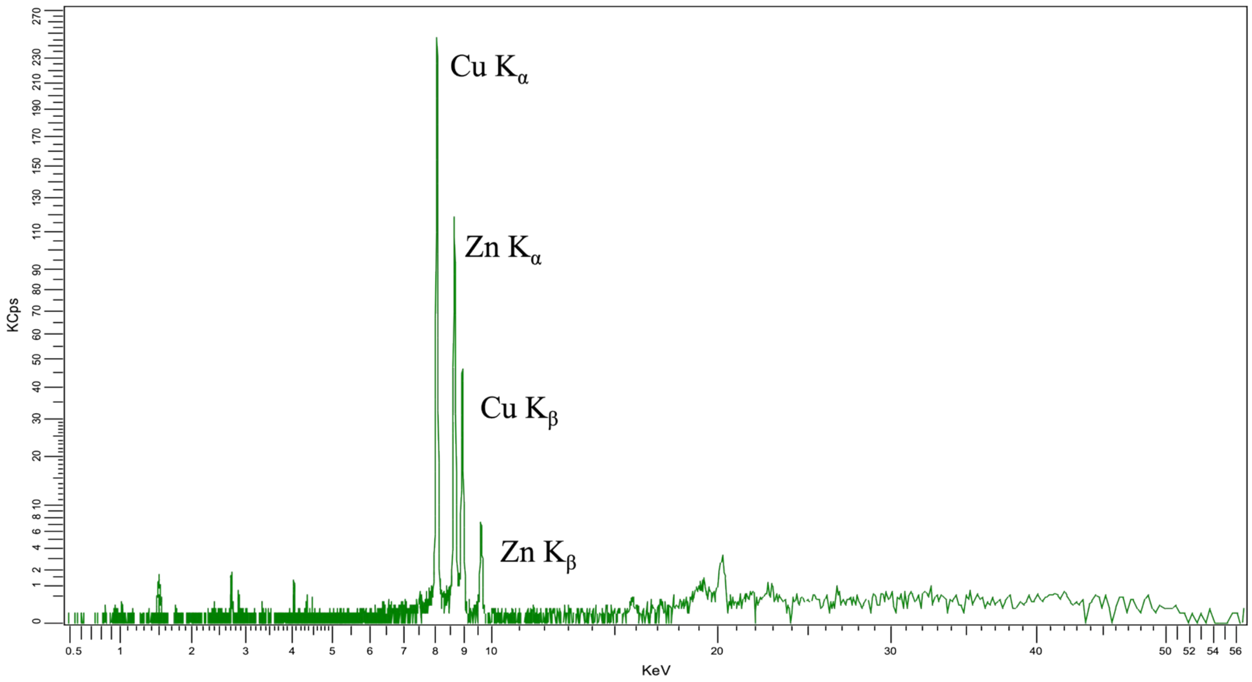

Figure S10. XRF spectra of Cu/ZnO/Al_2O_3 after one cycle.

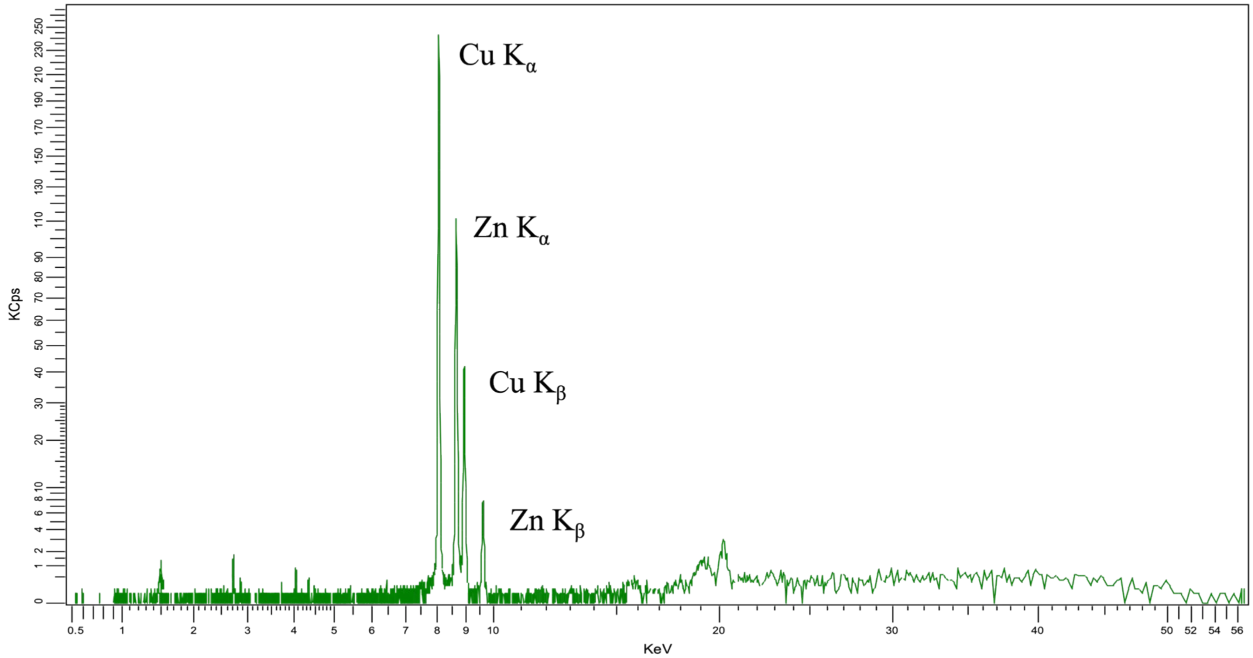

Figure S11. XRF spectra of Cu/ZnO/Al_2O_3 after five cycles.

Table S10. Weight concentrations of the catalyst based on XRF data.

Catalyst	Cu [%]	Zn [%]
Unactivated	61.88 ± 0.73	24.74 ± 1.04
Activated	63.02 ± 0.72	24.05 ± 1.01
Cycle 1	62.69 ± 0.73	24.37 ± 1.05
Cycle 5	64.18 ± 0.76	24.71 ± 1.09

Ionic Liquid Characterization Data

The synthesized ionic liquids 1-butyl-3-methylimidazolium methanesulfonate ([BMIm][CH_3SO_3]), 1-butyl-3-methylimidazolium phosphate ($[BMIm]_3[PO_4]$), and 1-butyl-3-methylimidazolium hydroxide ([BMIm][OH]) were characterized using ^{1}H- and ^{13}C-NMR.

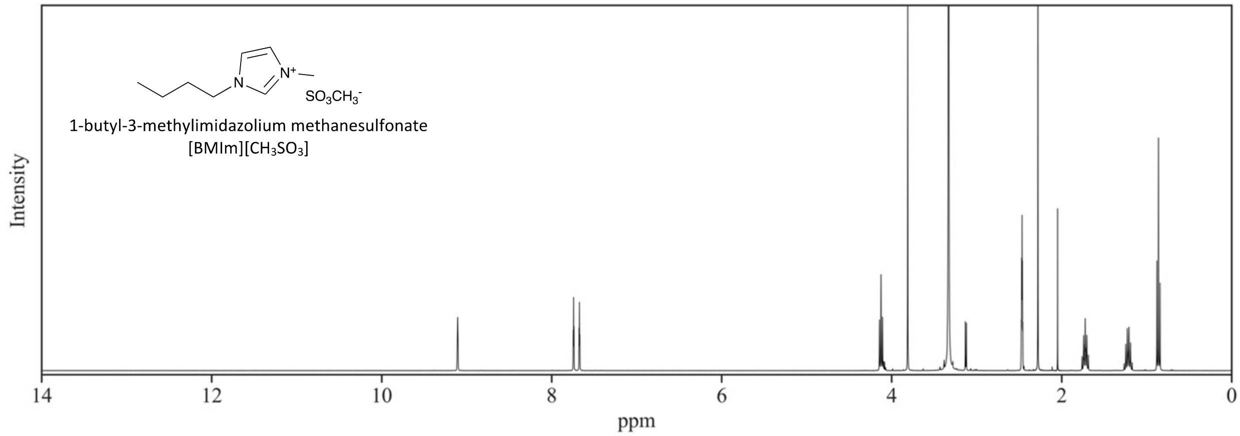

Figure S12. ^{1}H NMR of the [BMIm][CH_3SO_3].

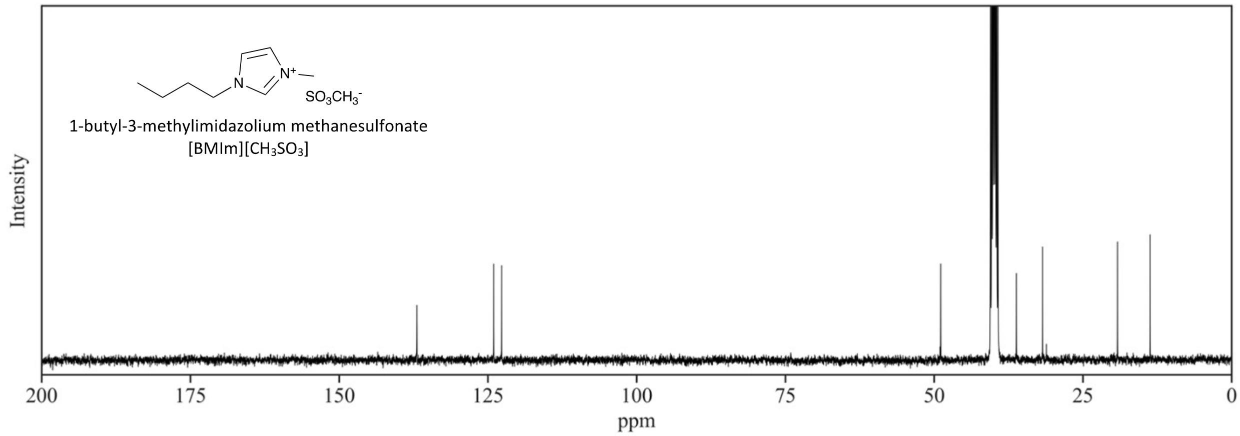

Figure S13. ^{13}C NMR of the [BMIm][CH_3SO_3].

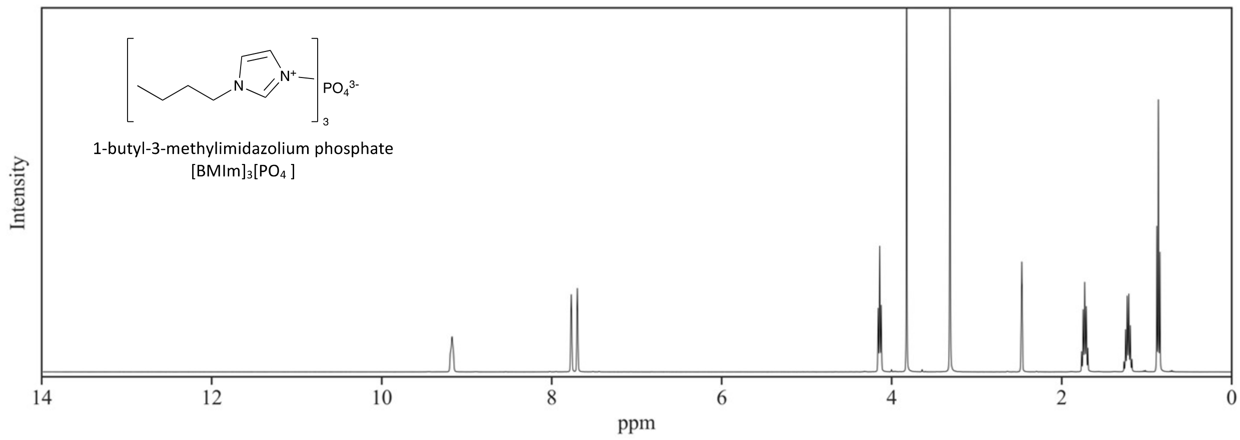

Figure S14. ^{1}H NMR of the [BMIm]$_3$[PO$_4$].

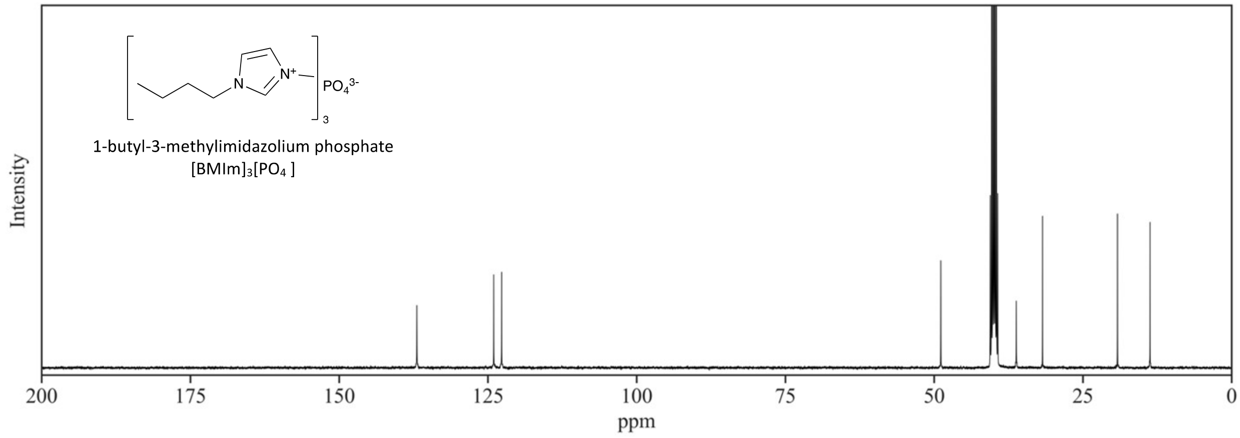

Figure S15. ^{13}C NMR of the [BMIm]$_3$[PO$_4$].

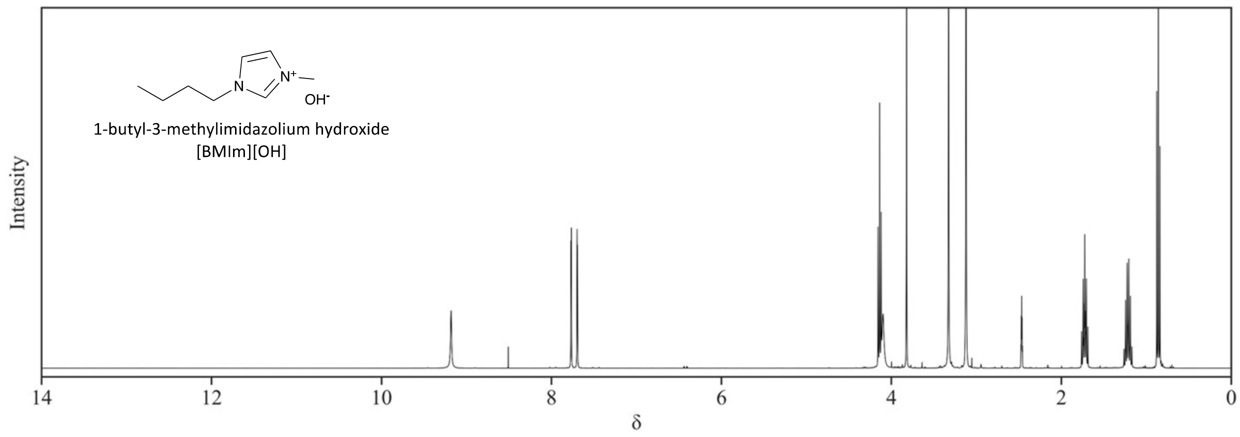

Figure S16. ^{1}H NMR of the [BMIm][OH].

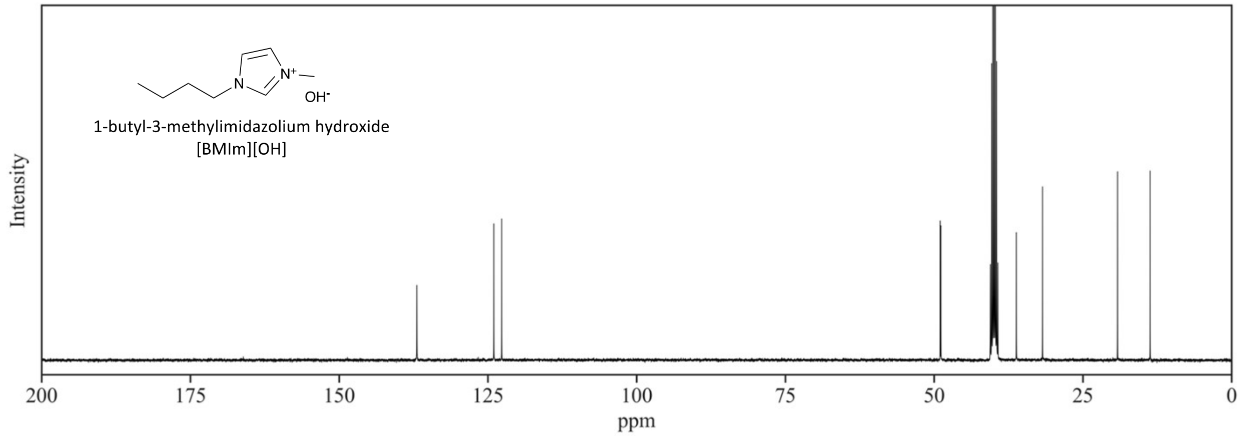

Figure S17. ^{13}C NMR of the [BMIm][OH].