Supporting information

Evolution of catalytically active species in paired $PdCl_2$-$CuCl_2$/[BMim]Cl for hydrolysis of β-1,4-glycosidic bonds

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1. EPR spectra of $CuCl_2$/[BMim]Cl and $PdCl_2$-$CuCl_2$/[BMim]Cl

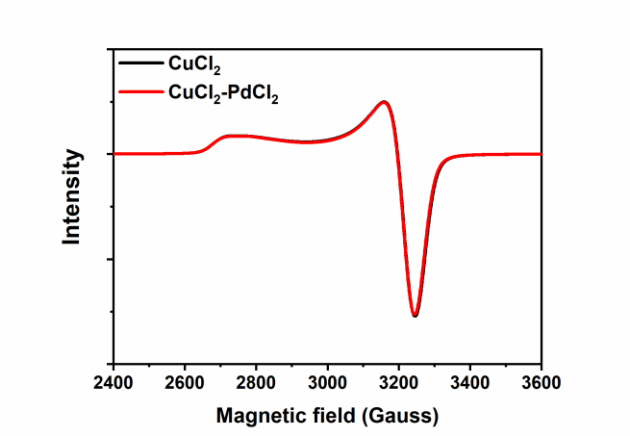

Figure S1. Electron paramagnetic resonance spectra of $CuCl_2$/[BMim]Cl and $PdCl_2$-$CuCl_2$/[BMim]Cl. For each sample, [$CuCl_2$] = 55.6 μmol/g[BMim]Cl. Water was at 10 wt% of [BMim]Cl. The spectra were collected under -173 °C.

2. FIR spectra of [BMim]Cl and $PdCl_2$-$CuCl_2$/[BMim]Cl/saccharides

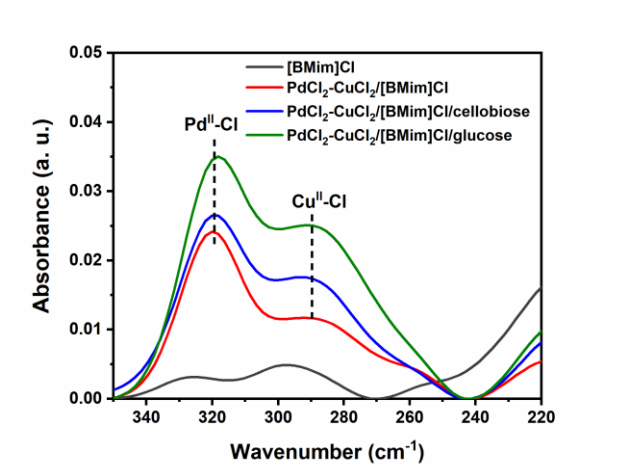

Figure S2. FIR spectra of $PdCl_2$-$CuCl_2$/[BMim]Cl containing glucose or cellobiose at 10 wt% of [BMim]Cl under 120 °C.

3. *In situ* FIR spectra of paired or single metal chlorides with addition of cellobiose

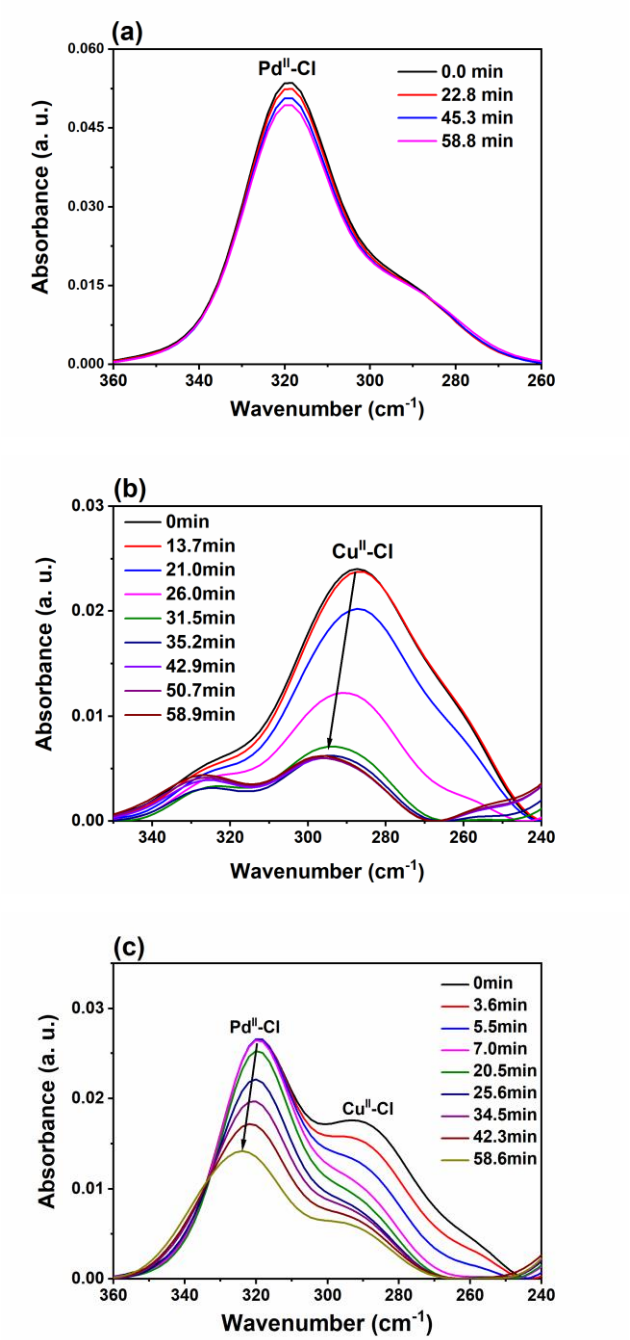

Figure S3. In-situ Far infrared spectra of $[Pd^{II}Cl_4]^{2-}$ and $[Cu^{II}Cl_4]^{2-}$ with cellobiose in [BMim]Cl under 120 ^{o}C. (a) Pd^{II}–Cl stretching vibration in $PdCl_2$/[BMim]Cl/cellobiose; (b) Cu^{II}–Cl stretching vibration in the $CuCl_2$/[BMim]Cl/cellobiose; (c) Pd^{II} –Cl and Cu^{II} –Cl stretching vibration in the $PdCl_2$-$CuCl_2$/[BMim]Cl/ cellobiose system. The arrows in (a)−(c) show the decrease of the Pd^{II}–Cl or Cu^{II}–Cl coordination bond in the presence of cellobiose. The spectra at 0 min were collected immediately after the sample was dropped on the sample holder.

4. *In situ* FIR spectra of $[PdCl_4]^{2-}$ in the presence of glycolaldehyde

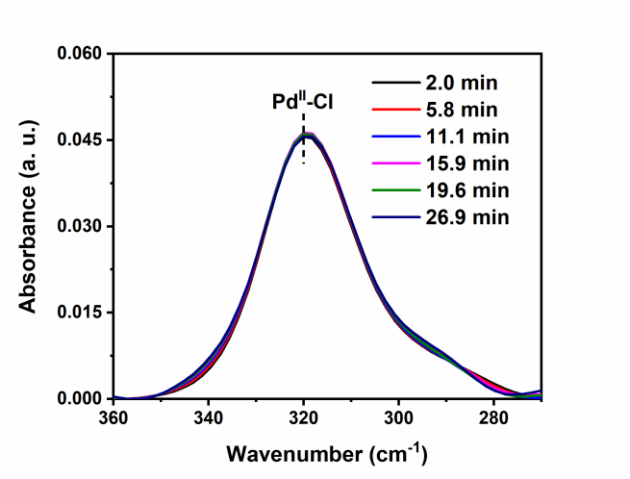

Figure S4. *In-situ* Far infrared spectra of $[Pd^{II}Cl_4]^{2-}$ with addition of glycolaldehyde in [BMim]Cl under 120 ^{o}C. $[PdCl_2]$ = 111 µmol/g[BMim]Cl. The loading of glycolaldehyde is 1 wt% of [BMim]Cl.

5. *In situ* FIR spectra of $[CuCl_4]^{2-}$ in the presence of glycolaldehyde

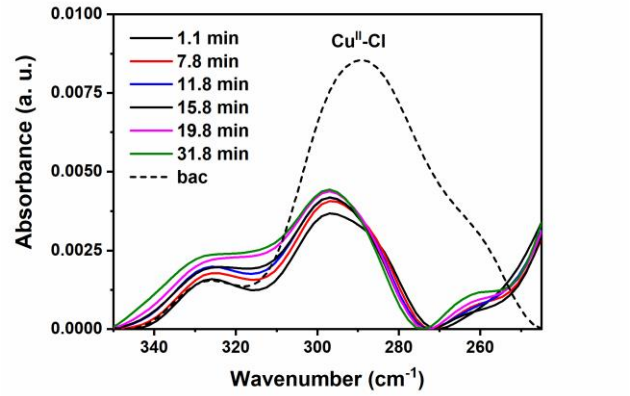

Figure S5. *In-situ* Far infrared spectra of $[Cu^{II}Cl_4]^{2-}$ in the presence of glycolaldehyde in [BMim]Cl under 120 ^{o}C. The black dash-line is the FIR spectrum of $CuCl_2$/[BMim]Cl in the absence of glycolaldehyde. $[CuCl_2]$ = 55.6 µmol/g[BMim]Cl. The loading of glycolaldehyde is 1 wt% of [BMim]Cl.

6. XAFS of $CuCl_2$/[BMim]Cl reduced by glycolaldehyde

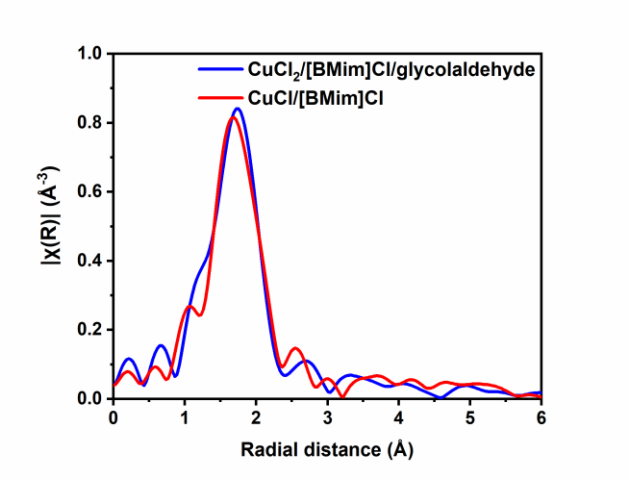

Figure S6. The k^2–weighted | χ(R)| plots derived from the Extend X-ray absorption fine structure (EXAFS) spectra for the Cu species in $CuCl_2$/[BMim]Cl/glycolaldehyde and CuCl/[BMim]Cl, showing the relative distribution of Cl^- ligands around the Cu. The Cu loading of CuCl/[BMim]Cl was 167 μmol/g[BMim]Cl; the Cu loading of $CuCl_2$/[BMim]Cl/glycolaldehyde was 167 μmol/g[BMim]Cl, and the molar ratio of glycolaldehyde to $CuCl_2$ was 1:2. The samples had been well-mixed and heated at 120 ℃ for 15 min.

7. The effect of neutralization on product yield of cellobiose conversion

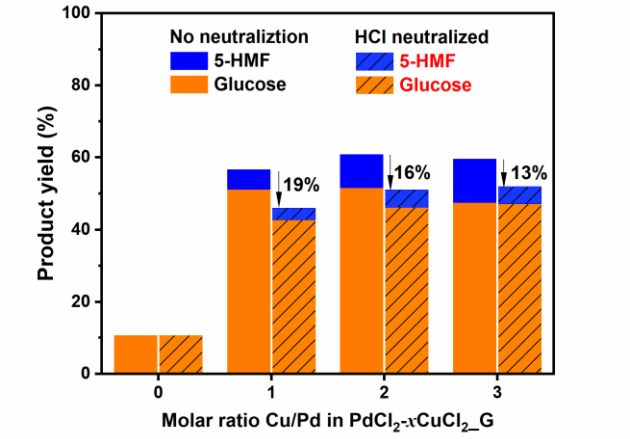

Figure S7. The effect of NaOH neutralization on product yield of cellobiose conversion catalyzed by $PdCl_2$-*x*$CuCl_2$_G in [BMim]Cl. Reaction conditions: 505 mg $PdCl_2$-x$CuCl_2$_G/[BMim]Cl, 50 mg H_2O, 95 mg cellobiose, the molar amount of added NaOH was equal to Cu in $PdCl_2$-*x*$CuCl_2$_G, 120 °C, 400 rpm, 10 min.

8. Effect of glyoxal and glycolic acid on cellobiose conversion

Table S1 Effect of glyoxal and glycolic acid on cellobiose conversion

[a]Entry	Metal chloride	[b]Additives	Cellobiose conversion (%)	Glucose yield (%)
1	--	Glycolic acid + glyoxal	0	0
2	CuCl	--	0	0
3	CuCl	Glycolic acid + glyoxal	5	0.2
4	$PdCl_2$	--	10.5	5.6
5	$PdCl_2$	Glycolic acid + glyoxal	7.5	5.5

[a]Reaction conditions: 500 mg [BMim]Cl, 47.5 mg cellobiose, 50 mg H_2O, [metal chloride] = 55.6 μmol/g[BMim]Cl, 120 °C, 400 rpm, 15 min, [b]the concentration of added glycolic acid was equal to glyoxal, 27.8 μmol/g[BMim]Cl.