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Cu carbonyls enhance the performance of Ru-based SILP water-gas shift catalysts: A combined in-situ DRIFTS and DFT study

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DFT calculations

Table S1 Selected Mayer Bond Orders (MBO) computed for the BP86-D3/def2-TZVPPD CPCM optimized complexes.

	Species	Cl^-/Cu	Mayer Bond Order (MBO)		
			C-O	Cu-C	Cu-Cl
9	$[Cu(CO)Cl_3]^{2-}$	3	2.12	0.31	0.59
8	$[Cu(CO)Cl_2]^-$	2	2.15	0.18	0.74
7	$[Cu(CO)_2Cl_2]^-$	2	2.23	0.59	0.73
6	$[Cu_2(CO)_2(\mu\text{-}Cl)_3]^-$	1.5	2.15	0.21	0.40
5	$[Cu_2(CO)_2(\mu\text{-}Cl)_2]$	1	2.21	0.48	0.51
4	$[Cu_2(CO)_4(\mu\text{-}Cl)_2]$	1	2.25	0.55	0.58
3	$[Cu(CO)_3Cl]$	1	2.28	0.70	0.91
2	$[Cu(CO)_2Cl]$	1	2.29	0.44	0.90
1	[Cu(CO)Cl]	1	2.27	<0.1	1.04

Table S2 Selected bond distances of the BP86-D3/def2-TZVPPD CPCM optimized complexes.

	Species	Cl^-/Cu	distance [Å]		
			d(C-O)	d(Cu-C)	d(Cu-Cl)
9	$[Cu(CO)Cl_3]^{2-}$	3	1.155	1.817	2.377
8	$[Cu(CO)Cl_2]^-$	2	1.149	1.810	2.247
7	$[Cu(CO)_2Cl_2]^-$	2	1.144	1.879	2.342
6	$[Cu_2(CO)_2(\mu\text{-}Cl)_3]]^-$	1.5	1.148	1.805	2.413
5	$[Cu_2(CO)_2(\mu\text{-}Cl)_2]$	1	1.143	1.808	2.295
4	$[Cu_2(CO)_4(\mu\text{-}Cl)_2]$	1	1.140	1.879	2.382
3	$[Cu(CO)_3Cl]$	1	1.137	1.917	2.298
2	$[Cu(CO)_2Cl]$	1	1.138	1.878	2.196
1	[Cu(CO)Cl]	1	1.139	1.799	2.096

IR spectroscopy

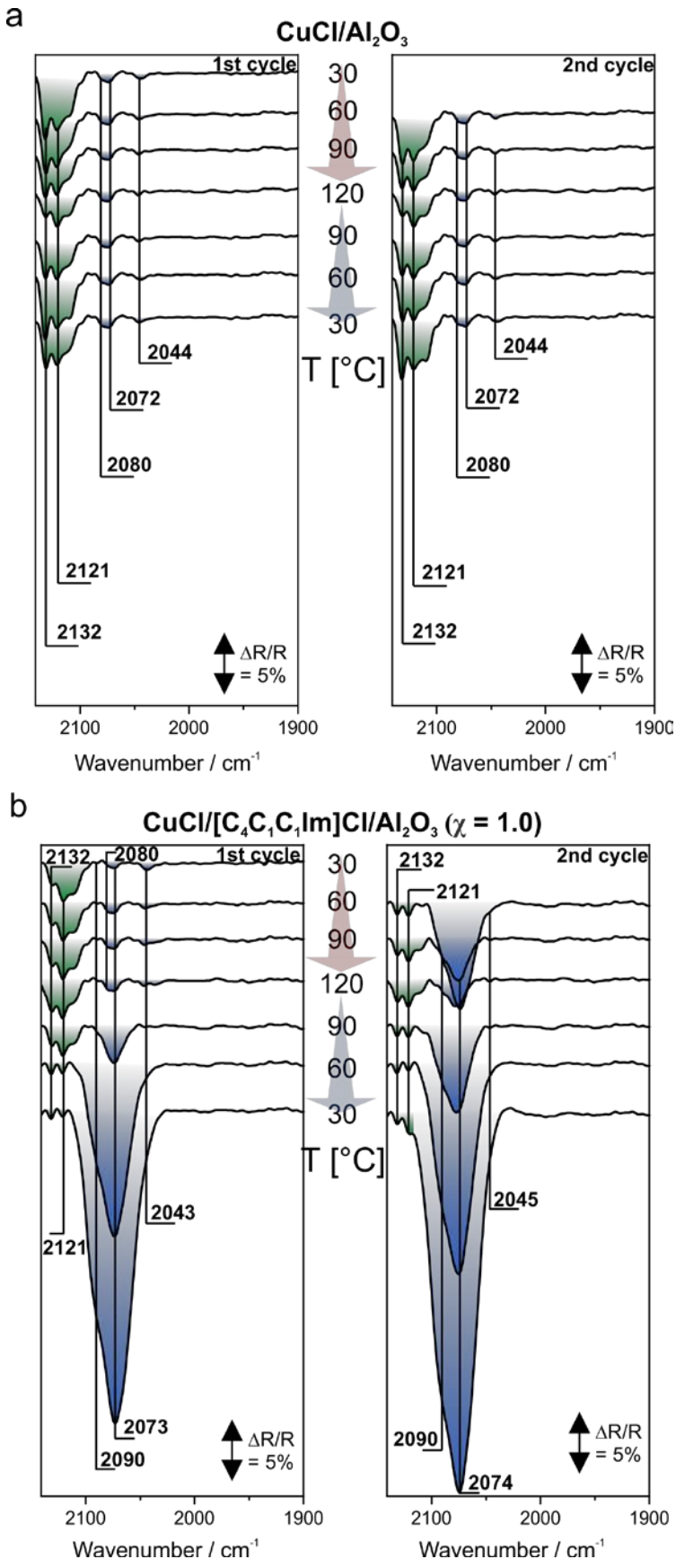

Fig. S1 Behavior during 1st and 2nd heating/cooling cycle for: a, $CuCl/Al_2O_3$ reference sample and b, $CuCl/[C_4C_1C_1Im]Cl/Al_2O_3$ sample with χ = 1.0.