

**Table S2** Performances of the catalysts from different supports doped with copper.

Entry	Catalyst	Conversion (%)		Carbon yield (%)							Yield <sup>a</sup> (%)	Yield <sup>b</sup> (%)	CB (%)	
		Pyr	2-Pico	3-Pico	AN	PN	AA	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	CO <sub>2</sub>				
1	4.6%Cu/HZSM-5(38)	99.8	34.9	2.0	5.9	7.3	1.4	1.3	3.2	2.1	12.7	8.7	42.8	70.8
2	4.6%Cu/H-mordenite	96.8	8.7	0.4	2.7	10.3	0.5	13.6	3.0	1.3	15.6	10.8	11.8	55.8
3	4.6%Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	100.0	3.8	0.4	1.5	23.9	6.7	3.1	2.6	3.8	21.1	30.6	5.7	66.9
4	4.6%Cu/ZrO <sub>2</sub>	100.0	-	-	-	27.7	5.8	1.3	5.2	7.1	21.3	33.5	-	68.4
5	4.6%Cu/TiO <sub>2</sub>	99.3	4.1	0.2	1.7	23.8	5.0	6.4	1.6	4.0	18.6	28.8	6.0	65.4
6	4.6%Cu/SiO <sub>2</sub>	98.9	-	-	-	10.0	2.9	14.4	3.6	7.5	23.9	12.9	-	62.3

Pyr: pyridine; 2-Pico: 2-picoline; 3-Pico: 3-picoline; AN: acetonitrile; PN: propionitrile; AA: acetaldehyde; CB: carbon balance.

Reaction conditions: reaction temperature 520°C, ammonia/glycerol molar ratio 7:1, atmospheric pressure, GHSV 300 h<sup>-1</sup>, time on stream 2–4 h. 20 wt% glycerol aqueous solution 0.05 ml/min, NH<sub>3</sub> 18 ml/min.

<sup>a</sup> Total carbon yield of acetonitrile and propionitrile.

<sup>b</sup> Total carbon yield of pyridine, 2-picoline and 3-picoline.