

**Table S3** Effect of the glycerol concentration on the performance of the 4.6%Cu/HZSM-5(38) catalyst.

Entry	Gc (wt.%)	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>				
1	10	99.9	36.6	0.7	3.3	7.6	1.2	2.1	2.3	1.4	7.8	8.8	40.6	63.0
2	15	99.7	35.4	1.8	4.3	7.6	1.5	2.0	3.9	4.3	7.9	9.1	41.5	68.6
3	<b>20</b>	<b>99.8</b>	<b>34.9</b>	<b>2.0</b>	<b>5.9</b>	<b>7.3</b>	<b>1.4</b>	<b>1.3</b>	<b>3.2</b>	<b>2.1</b>	<b>12.7</b>	<b>8.7</b>	<b>42.8</b>	<b>70.8</b>
4	25	99.8	27.1	2.6	7.5	4.8	1.4	2.7	5.0	3.3	13.0	6.2	37.2	67.4
5	30	97.5	21.9	1.7	7.2	4.2	0.8	4.8	5.9	3.9	10.8	4.9	30.7	61.1

Gc: glycerol concentration; 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.

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

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