

Table S5 Comparative catalytic results of fresh and pre-reduced 4.6%Cu/HZSM-5(38).

Entry	Catalyst	Conversion (%)	Carbon yield (%)									Yield ^a (%)	Yield ^b (%)	CB (%)
			Pyr	2-Pico	3-Pico	AN	PN	AA	C ₂ H ₄	C ₃ H ₆	CO ₂			
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/HZSM-5(38) ^c	100.0	34.4	2.2	6.6	6.6	1.7	1.7	3.3	2.0	12.5	8.3	43.2	71.0

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⁻¹, time on stream 2–4 h. 20 wt% glycerol aqueous solution 0.05 ml/min, NH₃ 18 ml/min.

^a Total carbon yield of acetonitrile and propionitrile.

^b Total carbon yield of pyridine, 2-picoline and 3-picoline.

^c The catalyst was on hydrogen stream 2 h before catalytic run, H₂ velocity 18 ml/min.