

Table S4 Catalytic results of speculated intermediates over the 4.6%Cu/HZSM-5(38) catalyst.

Entry	Reactants	Conversion (%)	Carbon yield (%) ^e								
			Pyr	2-Pico	3-Pico	AN	PN	AA	C ₂ H ₄	C ₃ H ₆	CO ₂
1	Allyl alcohol	100	2.4	2.0	16.0	4.4	10.9	-	5.5	9.9	15.6
2	Propionaldehyde ^a	100	1.6	0.7	12.1	2.4	12.7	-	6.1	15.2	7.9
3	Hydroxyacetone	100	10.3	1.9	1.2	11.4	2.9	0.8	1.9	1.1	15.6
4	Acetaldehyde	100	15.4	1.2	1.1	29.7	-	-	5.2	7.4	23.8
5	Acetaldehyde + Propionaldehyde ^b	100	4.0	4.0	7.1	13.5	11.3	-	9.0	31.1	6.6
6	Acetaldehyde + Propionaldehyde ^c	100	4.8	0.3	0.9	23.4	9.0	-	11.7	17.7	12.5
7	Formaldehyde + Acetaldehyde ^d	100	15.7	0.7	1.6	16.7	1.7	-	1.7	2.0	19.2
8	Ethylene	16.3	1.5	-	-	3.9	-	-	-	-	6.8
9	Propylene	53.2	0.4	0.4	0.3	7.2	0.4	-	-	-	8.5

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

Reaction conditions: catalyst 4.6%Cu/HZSM-5(38) dosage 15 ml, reaction temperature 520°C, atmospheric pressure, ammonia/substrate 7:1, GHSV 300h⁻¹, time on stream 2–4 h, aqueous solution of 20 wt% of feed materials.

^a 15% aqueous solution.

^b Mixture of aqueous solutions of acetaldehyde (15.0 wt%) and propionaldehyde (19.7 wt%), molar ratio of acetaldehyde/ propionaldehyde 1:1.

^c Mixture of aqueous solutions of acetaldehyde (15.0 wt%) and propionaldehyde (4.0 wt%), molar ratio of acetaldehyde/ propionaldehyde 5:1.

^d Mixture of aqueous solutions of formaldehyde (10.2 wt%) and acetaldehyde (15.0 wt%), molar ratio of formaldehyde/acetaldehyde 1:1.

^e Overall carbon yield of pyridine, 2-picoline, 3-picoline, acetonitrile, propionitrile, ethylene, propylene and carbon dioxide is based on acetaldehyde in entry 4, 5, 6 and 7.