

Supplementary Information

Copper-Catalyzed Decarboxylation of 2,4,5-Trifluorobenzoic Acid in NH₃-enriched High Temperature Liquid Water

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Tables S1-S7 show the detailed data for Figures 1-7 of manuscript. The standard deviations in all the tables were determined from three replicate experiments.

Table S1. Effect of the ammonia concentration on decarboxylation of 2,4,5-trifluorobenzoic acid. Reaction conditions: T = 250 °C, $C_{\text{reactant}} = 30 \text{ mmol/L}$, t = 3 h.

Concentration mmol/L	Conversion/%	Yield/%	Selectivity/%
0	12.06813 $\pm$ 0.11852	1.30646 $\pm$ 0.00433	10.82603 $\pm$ 0.07046
13.4	44.90048 $\pm$ 4.99426	14.40814 $\pm$ 1.11637	33.70372 $\pm$ 7.2543
26.8	67.27963 $\pm$ 1.44133	24.92824 $\pm$ 2.43813	37.05617 $\pm$ 3.56936
40.2	74.68171 $\pm$ 1.05908	24.68383 $\pm$ 1.87265	33.05003 $\pm$ 2.43962
53.5	74.4867 $\pm$ 3.92054	24.74243 $\pm$ 1.52429	33.21831 $\pm$ 1.12331
66.9	79.59042 $\pm$ 2.19709	31.01968 $\pm$ 1.06232	38.96936 $\pm$ 0.26222

Table S2. Effect of different metal catalysts on decarboxylation of 2,4,5-

trifluorobenzoic acid. Reaction conditions: $C_{\text{reactant}} = 20 \text{ mmol/L}$, $C_{\text{ammonia}} = 26.8$

mmol/L, catalyst loading = 5 mg, $T = 260 \text{ }^{\circ}\text{C}$, $t = 2 \text{ h}$

Catalyst	Conversion/%	Yield/%	Selectivity/%	By-product/%
Ru/C	76.8274	43.70971	56.8934	19.45788
32%Ni/C	82.29156	47.3157	57.49763	22.67936
MnO ₂	76.16148	42.76977	56.1567	18.99022
Co/ZrO ₂	73.40646	40.03048	54.53263	23.45058
Ni/ZrO ₂	81.89134	45.19118	55.18432	18.93278
ZnO	93.57351	66.30108	70.85454	12.10288
Bi ₂ O ₃	75.9408	47.12769	62.05845	21.2984
CuO	98.52934	76.69432	77.83906	8.73929
Cu/Al ₂ O ₃	100	82.81217	82.81217	4.87369
Cu/ZrO ₂	100	82.63165	82.63165	4.29786

Table S3. Effect of different species of copper catalysts on decarboxylation of 2,4,5-trifluorobenzoic acid at 250 °C. Reaction conditions: $C_{\text{reactant}} = 20 \text{ mmol/L}$, $C_{\text{ammonia}} = 26.8 \text{ mmol/L}$, $T = 250 \text{ °C}$, $t = 2 \text{ h}$

Catalyst	Conversion/%	Yield/%	Selectivity/%
CuCl ₂	100	53.42176 ± 1.95288	53.42176 ± 1.95288
CuCl	100	60.49373 ± 9.38585	60.49373 ± 9.38585
CuO	99.77295 ± 0.19667	73.10939 ± 2.86017	73.27219 ± 2.7192
Cu	99.34026 ± 0.25881	76.66483 ± 1.86971	77.17588 ± 1.98587
Cu ₂ O	99.6602 ± 0.07711	75.72249 ± 0.53915	75.98044 ± 0.48606
None	55.40123	34.94988	63.08503

Table S4. Decarboxylation of 2,4,5- trifluorobenzoic acid on heterogeneous copper

catalysts at 260 °C. Reaction conditions: $C_{\text{reactant}} = 20 \text{ mmol/L}$, $C_{\text{ammonia}} = 26.8$

mmol/L, $T = 260 \text{ °C}$, $t = 2 \text{ h}$

Catalyst	Conversion/%	Yield/%	Selectivity/%
CuO	99.77295 ± 0.19667	73.10939 ± 2.86017	73.27219 ± 2.7192
Cu	99.34026 ± 0.25881	76.66483 ± 1.86971	77.17588 ± 1.98587
Cu ₂ O	99.6602 ± 0.07711	75.72249 ± 0.53915	75.98044 ± 0.48606

Table S5. Effect of Cu₂O loading on decarboxylation of 2,4,5-trifluorobenzoic acid at

260 °C. Reaction conditions: $C_{\text{reactant}} = 20 \text{ mmol/L}$, $C_{\text{ammonia}} = 26.8 \text{ mmol/L}$, $t = 2 \text{ h}$

Cu ₂ O/mg	Conversion/%	Yield/%	Selectivity/%	By-product/%
2	100	82.87462 ± 1.63086	82.87462 ± 1.63086	5.45052 ± 0.17819
4	100	83.19975 ± 1.06083	83.19975 ± 1.06083	5.38697 ± 0.3165
6	100	89.12054 ± 5.58876	89.12054 ± 5.58876	4.92727 ± 0.21514
9	100	81.78426 ± 4.79818	81.78426 ± 4.79818	4.4098 ± 0.42115

Table S6. Effect of the initial reactant concentration on decarboxylation of
2,4,5-trifluorobenzoic acid at 260 °C. Reaction conditions: $C_{\text{ammonia}} = 26.8 \text{ mmol/L}$, $t =$
2 h, catalyst loading = 6 mg

Concentration /mmol	Conversion/%	Yield/%	Selectivity/%	By-product/%
5	99.28469 ± 0.2928	74.28478 ± 3.56928	74.82747 ± 3.81882	10.30019 ± 0.66959
10	99.80018 ± 0.19739	78.62618 ± 0.70171	78.78296 ± 0.56186	8.68986 ± 0.19944
20	99.81478 ± 0.32081	84.92384 ± 0.14276	85.08206 ± 0.32771	6.74667 ± 0.30408
30	100	86.56144 ± 4.71773	86.56144 ± 4.71773	5.08868 ± 0.25851

Table S7. Effect on decarboxylation of 2,4,5-trifluorobenzoic acid with a Cu₂O catalyst after the first, second and third use at 260 °C. Reaction conditions: $C_{\text{reactant}} = 20 \text{ mmol/L}$, $C_{\text{ammonia}} = 26.8 \text{ mmol/L}$, $t = 2 \text{ h}$

Used time	Conversion/%	Yield/%	Selectivity/%	By-product/%
First use	100	86.56144 ± 4.71773	86.56144 ± 4.71773	5.08868 ± 0.25851
Second use	100	82.56357 ± 1.76154	82.56357 ± 1.76154	6.67335 ± 0.24162
Third use	100	85.55994	85.55994	6.8625