# One step C–N bond formation from alkylbenzene and ammonia over Cu-modified TS-1 zeolite catalyst†

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## Electronic Supplementary Information (ESI)

**Contents**

**Table S1** The effect of Cu content on the catalytic reaction of toluene.[a]

| Samples | Molar Yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Toluidine | | | Cresols | | | Nitrobenzene | | |
| | o- | m- | p- | o- | m- | p- | o- | m- | p- |
| TS-1 | 1.3 | 0.4 | 0.2 | 0.9 | 0.4 | 0.2 | 0.4 | 0.1 | -- |
| 1.5Cu/TS-1 | 1.8 | 0.5 | 0.3 | 0.7 | 0.4 | 0.2 | 0.2 | -- | -- |
| 2.0Cu/TS-1 | 2.0 | 0.6 | 0.3 | 1.7 | 0.6 | 0.3 | 0.5 | 0.3 | 0.1 |
| 2.5Cu/TS-1 | 2.3 | 0.7 | 0.4 | 2.1 | 0.8 | 0.4 | 0.7 | 0.2 | 0.1 |
| 3.0Cu/TS-1 | 2.2 | .0.7 | 0.4 | 1.6 | 0.6 | 0.3 | 0.6 | 0.2 | 0.1 |

[a] Reaction conditions：Catalyst 0.15 g; Toluene 4.7 mmol; $NH_3 \cdot H_2O$ 87.4 mmol; $H_2O_2$ 14.7 mmol; $H_2O$ 25 mL; 353 K, 365min.

**Table S2** Effect of the amount of catalyst.[a]

| 2.5Cu/TS-1 Catalyst (g) | Molar Yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Toluidine | | | Cresols | | | Nitrobenzene | | |
| | o- | m- | p- | o- | m- | p- | o- | m- | p- |
| 0.05 | 0.3 | 0.1 | -- | 0.2 | 0.1 | -- | 0.1 | -- | -- |
| 0.10 | 0.9 | 0.4 | 0.1 | 0.7 | 0.5 | 0.3 | 0.2 | -- | -- |
| 0.15 | 2.3 | 0.7 | 0.4 | 2.1 | 0.8 | 0.4 | 0.7 | 0.2 | 0.1 |
| 0.20 | 2.0 | 0.8 | 0.4 | 2.0 | 0.7 | 0.3 | 0.5 | 0.2 | 0.1 |
| 0.25 | 1.7 | 1.0 | 0.3 | 1.9 | 0.6 | 0.3 | 0.5 | 0.2 | 0.1 |

[a] Reaction conditions：2.5Cu/TS-1; Toluene 4.7 mmol; $NH_3 \cdot H_2O$ 87.4 mmol; $H_2O_2$ 14.7 mmol; $H_2O$ 25 mL; 353 K,365min.

**Table S3** Effect of temperature on the catalytic reaction of toluene.[a]

| Temperature (K) | Molar Yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Toluidine | | | Cresols | | | Nitrobenzene | | |
| | o- | m- | p- | o- | m- | p- | o- | m- | p- |
| 333 | 0.1 | -- | -- | 0.2 | 0.1 | -- | -- | -- | -- |
| 343 | 1.0 | 0.6 | 0.2 | 0.9 | 0.5 | 0.4 | 0.2 | -- | -- |
| 348 | 1.5 | 0.7 | 0.3 | 1.9 | 0.6 | 0.3 | 0.5 | 0.2 | 0.1 |
| 353 | 2.3 | 0.7 | 0.4 | 2.1 | 0.8 | 0.4 | 0.7 | 0.2 | 0.1 |
| 358 | 2.3 | 0.6 | 0.4 | 2.1 | 0.8 | 0.4 | 0.7 | 0.3 | 0.1 |
| 363 | 1.3 | 0.6 | 0.3 | 2.7 | 0.7 | 0.4 | 0.8 | 0.4 | 0.2 |
| 373 | 0.6 | 0.4 | 0.1 | 3.1 | 0.7 | 0.5 | 0.8 | 0.5 | 0.4 |

[a] Reaction conditions：Catalyst Cu/TS-1 0.15 g；Toluene 4.7 mmol ; $NH_3 \cdot H_2O$ 87.4 mmol ; $H_2O_2$ 14.7 mmol ; $H_2O$ 25 mL, 365min.

**Table S4** Effect of $H_2O_2$ dosage on the catalytic reaction of toluene.[a]

| $H_2O_2$ Dosage (mL) | Molar Yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Toluidine | | | Cresols | | | Nitrobenzene | | |
| | o- | m- | p- | o- | m- | p- | o- | m- | p- |
| 0.5[b] | 0.7 | 0.3 | 0.1 | 0.7 | 0.3 | 0.1 | 0.4 | 0.2 | -- |
| 1.0[b] | 1.5 | 0.6 | 0.2 | 1.8 | 0.6 | 0.4 | 0.6 | 0.3 | 0.1 |
| 1.5[b] | 2.3 | 0.7 | 0.4 | 2.1 | 0.8 | 0.4 | 0.7 | 0.2 | 0.1 |
| 2.0[b] | 2.2 | 0.7 | 0.4 | 2.7 | 0.7 | 0.4 | 0.7 | 0.3 | 0.1 |
| 2.5[b] | 1.9 | 0.6 | 0.4 | 2.7 | 0.7 | 0.6 | 0.9 | 0.5 | 0.2 |
| 3.0[b] | 1.3 | 0.5 | 0.3 | 3.0 | 0.9 | 0.5 | 1.0 | 0.7 | 0.3 |

[a] Reaction conditions：Catalyst 2.5Cu/TS-1 0.15 g；Toluene 4.7 mmol; $NH_3 \cdot H_2O$ 87.4 mmol; $H_2O_2$ (4.9 mmol , 9.8 mmol , 14.7 mmol , 19.6 mmol , 24.5 mmol , 29.4 mmol) ; $H_2O$ 25 mL; 353 K.

[b] The reaction time were 355min, 360min, 365min, 370min, 375min and 380min, respectively.

**Table S5** Effect of $NH_3 \cdot H_2O$ dosage on catalytic reaction of toluene.[a]

| $NH_3 \cdot H_2O$ Dosage (mL) | Molar Yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Toluidine | | | Cresols | | | Nitrobenzene | | |
| | o- | m- | p- | o- | m- | p- | o- | m- | p- |
| 5[b] | 1.8 | 0.5 | 0.2 | 1.6 | 0.7 | 0.5 | 0.3 | 0.1 | -- |
| 10[b] | 2.3 | 0.7 | 0.4 | 2.1 | 0.8 | 0.4 | 0.7 | 0.2 | 0.1 |
| 15[b] | 1.7 | 0.7 | 0.5 | 1.7 | 0.7 | 0.5 | 0.6 | 0.2 | 0.1 |
| 20[b] | 1.6 | 0.7 | 0.3 | 1.7 | 0.6 | 0.3 | 0.2 | -- | -- |

[a] Reaction conditions：Catalyst 2.5Cu/TS-1 0.15 g; Toluene 4.7 mmol ; $NH_3 \cdot H_2O$ (43.71 mmol , 87.4 mmol ,131.1 mmol , 174.8 mmol) ; $H_2O_2$ 14.7 mmol ; $H_2O$ 25 mL ; 353 K.

[b] The reaction time were 315min, 365min, 415min and 465min, respectively.

**Table S6** Effect of $H_2O$ dosage on catalytic reaction of toluene.[a]

| $H_2O$ Dosage (mL)[b] | Molar Yield (%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Toluidine | | | Cresols | | | Nitrobenzene | | |
| | o- | m- | p- | o- | m- | p- | o- | m- | p- |
| 10[c] | 0.3 | 0.2 | -- | 1.4 | 0.5 | 0.2 | 1.0 | 0.6 | 0.3 |
| 15[c] | 0.7 | 0.4 | 0.1 | 1.4 | 0.7 | 0.4 | 0.8 | 0.4 | 0.2 |
| 20[c] | 1.4 | 0.9 | 0.4 | 1.7 | 0.9 | 0.5 | 0.6 | 0.4 | 0.2 |
| 25[c] | 2.3 | 0.7 | 0.4 | 2.1 | 0.8 | 0.4 | 0.7 | 0.2 | 0.1 |
| 30[c] | 2.2 | 0.7 | 0.4 | 1.7 | 0.8 | 0.5 | 0.6 | 0.3 | 0.1 |

[a] Reaction conditions：Catalyst 2.5Cu/TS-1 0.15 g；Toluene 4.7 mmol ; $NH_3 \cdot H_2O$ 87.4 mmol ; $H_2O_2$ 14.7 mmol ; 353 K.

[b] The molar concentrations of $NH_3 \cdot H_2O$ were 4.1 mol/L, 3.3 mol/L, 2.8 mol/L, 2.4 mol/L and 2.1 mol/L, successively. The molar concentrations of $H_2O_2$ were 0.7 mol/L, 0.6 mol/L, 0.5 mol/L, 0.4 mol/L and 0.4 mol/L, successively. The pH values of these mixtures containing $NH_3 \cdot H_2O$, $H_2O_2$ and$H_2O$ were 10.65, 10.27, 9.72, 9.24 and 8.87, successively.

[c] The reaction time were 215min, 265min, 315min, 365min and 415min, respectively.