Direct Amination of Benzene to Aniline by Reactive Distillation Method over Copper Doped Hierarchical TS-1 Catalyst

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Supporting Information

A. Supplemental Tables

Table S1. The effect of the amount of H_2O_2 on the yield and selectivity of products

Entry	Molar ratio[a]	Y (mol%)			Conversion of benzene (%)	Selectivity to aniline (%)
		Aniline	Phenol	DHB		
1	0.7	2.2	0.3	0.2	4.1 (2.7)[b]	80.9
2	1.4	2.6	0.8	0.0	4.7 (3.4)	76.3
3	2.8	6.0	0.9	0.5	8.6 (7.4)	80.5
4	4.2	6.1	1.1	0.4	9.0 (7.6)	80.1
5	5.5	7.5	1.3	0.5	10.8 (9.3)	80.0
6	6.9	8.2	1.1	0.6	11.3 (9.9)	82.6
7	8.2	6.8	1.3	0.5	10.0 (8.6)	79.5
8	9.4	6.4	1.3	0.5	9.7 (8.2)	77.8
9	10.7	6.4	1.8	1.0	10.3 (9.2)	69.4

Reaction condition: 1.00 g, 2.5 wt % Cu/h-TS-1, 2.82 mmol C_6H_6, $n_{NH_3\cdot H_2O}/n_{C_6H_6}$ = 40 (molar feed ratio in the reaction zone), 40.00 ml H_2O, reaction temperature: 70°C, reboiler temperature: 85°C.

Molar ratio[a] is molar feed ratio of hydrogen peroxide to benzene in the reaction zone.

[b] Value calculated by (Mole amounts of aniline+ Phenol + DHB + Nitrobenzene) × Initial mole amount of benzene^{-1} × 100%

Table S2. The effect of the amount of $NH_3\cdot H_2O$ on the yield and selectivity of products

Entry	Molar ratio[a]	Y (mol%)			Conversion of benzene (%)	Selectivity to aniline (%)
		Aniline	Phenol	DHB		
1	18.2	2.5	2.1	1.6	7.5 (6.2)[a]	40.7
2	26.1	5.5	1.2	1.2	9.3 (7.9)	69.9
3	33.4	7.5	1.1	1.0	11.0 (9.6)	78.3
4	40.2	8.2	1.1	0.6	11.3 (9.9)	82.6
5	46.5	7.0	0.8	0.4	9.6 (8.2)	85.5
6	52.3	5.6	0.7	0.1	7.9 (6.4)	87.2
7	57.4	4.6	0.7	0.0	6.8 (5.3)	87.5

Reaction condition: 1.00 g, 2.5 wt % Cu/h-TS-1, 2.82 mmol C_6H_6, $n_{H_2O_2}/n_{C_6H_6}$ = 7 (molar feed ratio in the reaction zone), 40.00 ml H_2O, reaction temperature: 70°C, reboiler temperature: 85°C.

Molar ratio[a] is molar feed ratio of aqueous ammonia to benzene in the reaction zone.

[b] Value calculated by (Mole amounts of aniline+ Phenol + DHB + Nitrobenzene) × Initial mole amount of benzene^{-1} × 100%

Table S3. The influence of reaction temperature on the yield and selectivity of products

Entry	Reaction temperature(°C)	Y (mol%)			Conversion of benzene (%)	Selectivity to aniline (%)
		Aniline	Phenol	DHB		
1	75	6.3	1.0	0.7	9.5 (8.0)[a]	78.5
2	70	8.2	1.1	0.6	11.4(9.9)	82.6
3	65	10.2	1.3	0.6	13.5 (12.1)	83.8
4	60	12.4	1.5	0.7	15.9 (14.6)	84.8
5	55	10.3	1.3	0.6	13.5 (12.2)	84.2
6	50	9.0	1.1	0.5	11.9 (10.6)	84.3
7	45	7.6	0.9	0.5	10.4 (9.1)	84.1
8	40	6.0	0.6	0.4	8.3 (7.0)	84.7
9	30	3.5	0.3	0.4	5.5 (4.2)	84.2

Reaction condition: 1.00 g, 2.5 wt % Cu/h-TS-1, 2.82 mmol C_6H_6, $n_{C_6H_6} / n_{NH_3 \cdot H_2O} / n_{H_2O_2}$ = 1 / 40 / 7 (molar feed ratio in the reaction zone), 40.00 ml H_2O, reboiler temperature: 85°C.

[b] Value calculated by (Mole amounts of aniline+ Phenol + DHB + Nitrobenzene) × Initial mole amount of benzene^{-1} × 100%

B. Supplemental image

Figure S1. Photograph of the Reactive Distillation Column setup.