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ARTICLE TYPE

Direct Amination of Benzene to Aniline with H_2O_2 and $NH_3 \cdot H_2O$ over Cu/SiO_2 Catalyst†

Tianhua Yu[a,b], Ruiguang Yang[a], Sheng Xia[a], Guiying Li[a,*], Changwei Hu [a,*]

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Supporting Information

Fig. S1. XRD patterns of the samples.

Fig. S2. N_2 adsorption-desorption isotherms and pore size distribution of the samples: a Meso-1; b 2.5 wt% Cu/Meso-1; c Meso-2; d 2.5 wt% Cu/Meso-2; e S-1; f 2.5 wt% Cu/S-1.

Fig. S3. N_2 adsorption-desorption isotherms and pore size distribution of the samples: a used 2.5 wt% Cu/Meso-1; b 2.5 wt% Cu/Meso-1; c used 2.5 wt% Cu/Meso-2; d 2.5 wt% Cu/Meso-2; e used 2.5 wt% Cu/S-1; f 2.5 wt% Cu/S-1.

Fig. S4. N_2 adsorption-desorption isotherms and pore size distribution of the samples: a 14.0 wt% Cu/S-1; b 10.0 wt% Cu/S-1; c 7.0 wt% Cu/S-1; d 5.5 wt% Cu/S-1; e 4.0 wt% Cu/S-1; f 2.5 wt% Cu/S-1; g 0.5 wt% Cu/S-1.

Fig. S5. DR UV–Vis spectra of the samples.

Fig. S6. TEM images of the samples.

S1 The synthesis method of S-1.

S2 The yield of product, the selectivity to product, and the conversion of aromatics were calculated as:

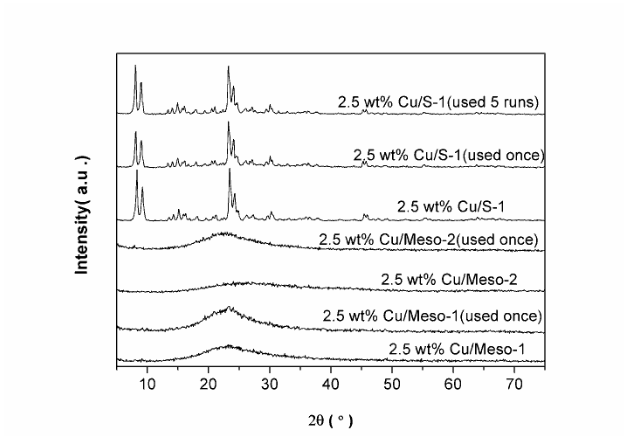
S3 Effect of other reaction conditions

S4 The effect of reaction system on catalytic activity

S5 The reaction pathway of ammination

Table S1. The reusability of Cu/h-TS-1

Table S2. The results of catalytic amination of substituted benzenes



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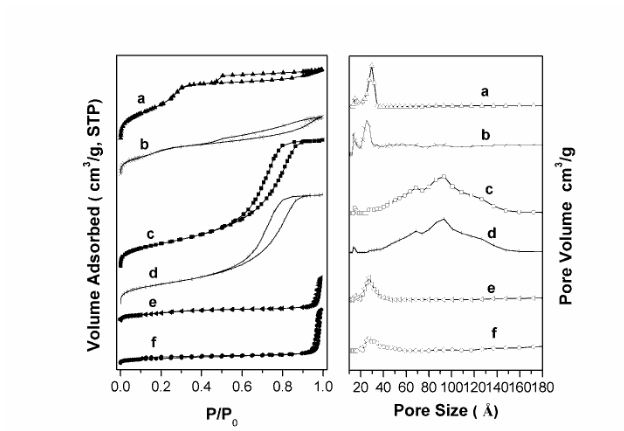

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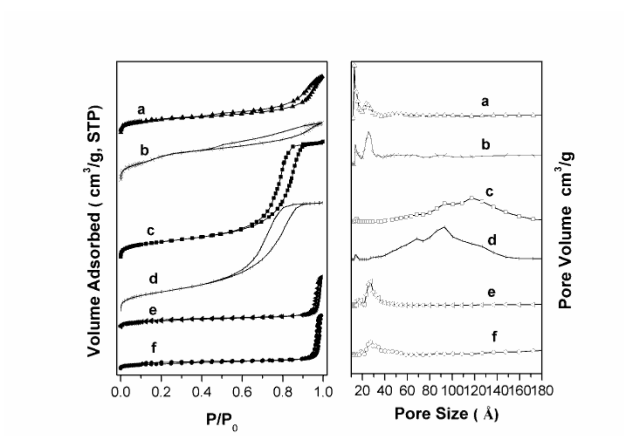
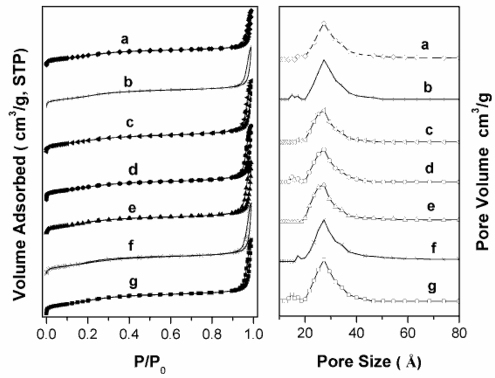


Fig. S3. N_2 adsorption-desorption isotherms and pore size distribution of the samples: a used 2.5 wt% Cu/Meso-1; b 2.5 wt% Cu/Meso-1; c used 2.5 wt% Cu/Meso-2; d 2.5 wt% Cu/Meso-2; e used 2.5 wt% Cu/S-1; f 2.5 wt% Cu/S-1.



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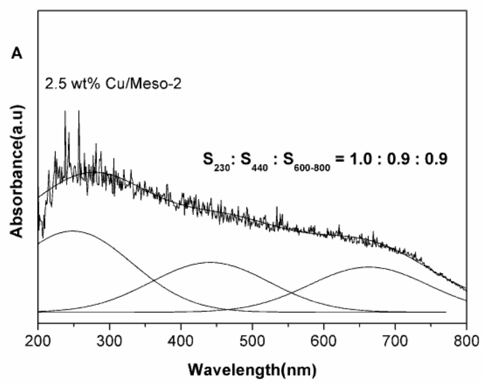

Fig. S5. DR UV–vis spectra of the samples: (A) 2.5 wt% Meso-2

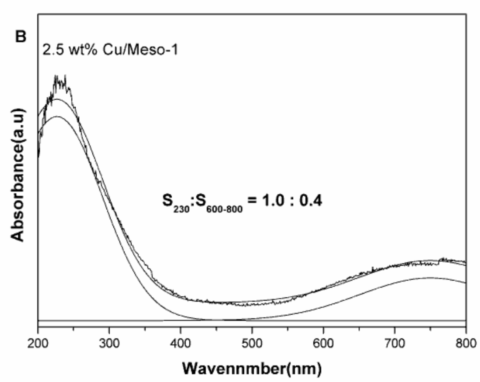

Fig. S5. DR UV–vis spectra of the samples: (B) 2.5 wt% Meso-1

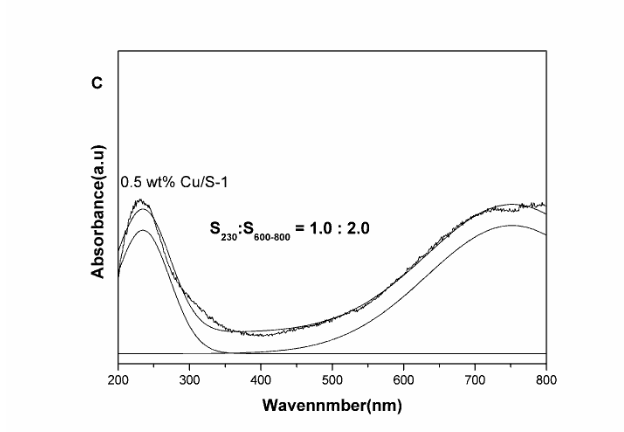

Fig. S5. DR UV–vis spectra of the samples: (C) 0.5 wt% Cu/S-1

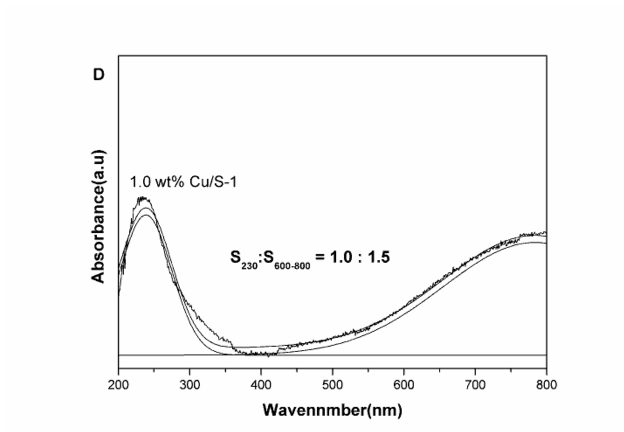

Fig. S5. DR UV–vis spectra of the samples: (D) 1.0 wt% Cu/S-1

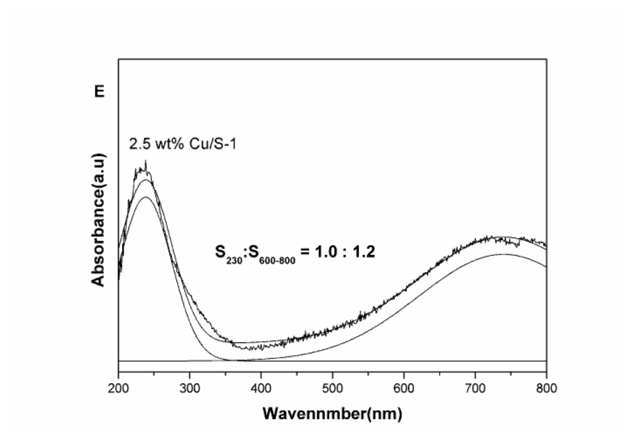

Fig. S5. DR UV–vis spectra of the samples: (E) 2.5 wt% Cu/S-1

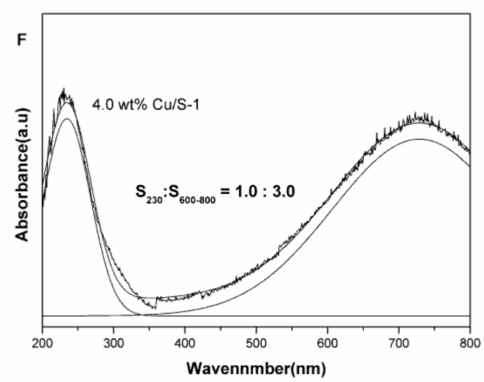

Fig. S5. DR UV–vis spectra of the samples: (F) 4.0 wt% Cu/S-1

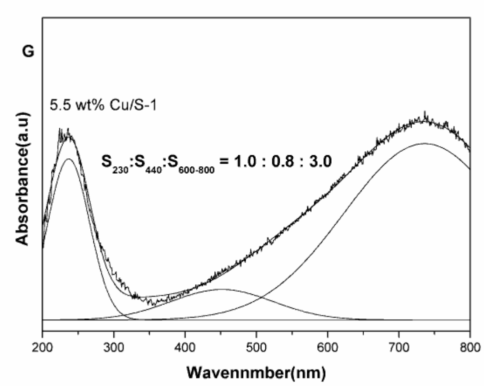

Fig. S5. DR UV–vis spectra of the samples: (G) 5.5 wt% Cu/S-1

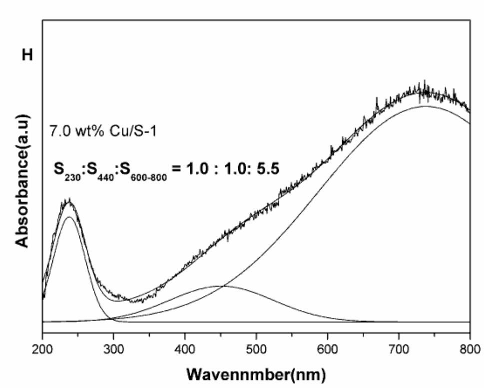

Fig. S5. DR UV–vis spectra of the samples: (H) 7.0 wt% Cu/S-1

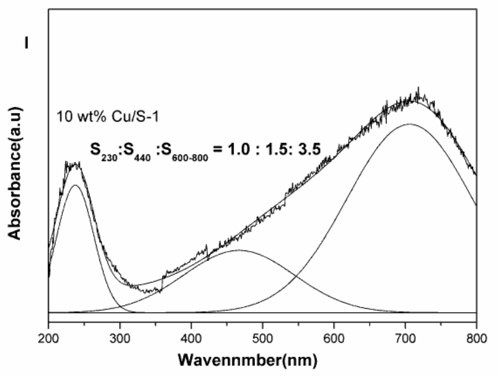

Fig. S5. DR UV–vis spectra of the samples: (I) 10.0 wt% Cu/S-1

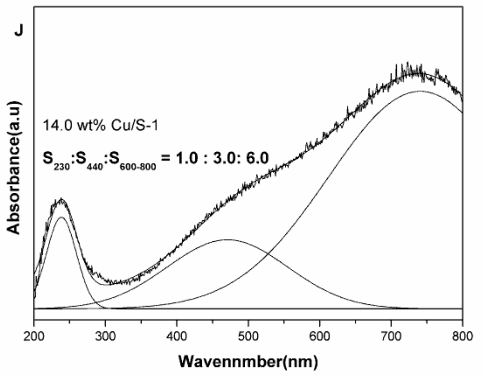

Fig. S5. DR UV–vis spectra of the samples: (J) 14.0 wt% Cu/S-1

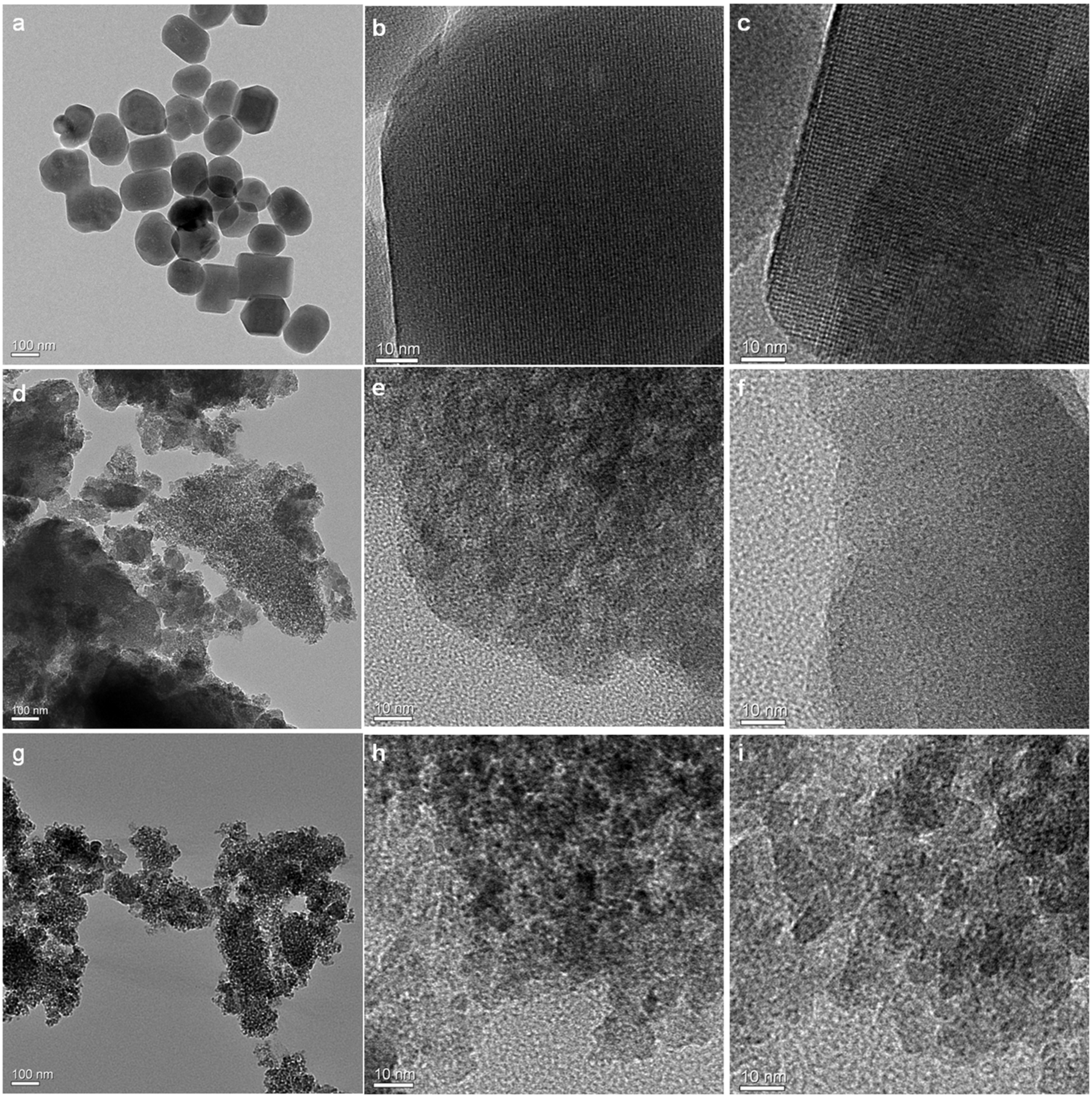

Fig. S6. TEM images of the samples: a, b 2.5 wt% Cu/S-1; c used 2.5 wt% Cu/S-1; d,e 2.5 wt% Cu/Meso-1; f used 2.5 wt% Cu/Meso-1; g, h 2.5 wt% Cu/Meso-2; i used 2.5 wt% Cu/Meso-2.

S1 The synthesis method of S-1.

S-1 was synthesized basically according to the procedures reported the literature. In brief, 40.0 g of isopropanol was first dissolved in 91.0 g of tetraethyl orthosilicate (TEOS), followed by the addition of 40.0 g of H_2O, 160.0 g aqueous solution of tetrapropylammonium hydroxide (20%). After stirring for 0.5 h, 120.0 g H_2O was added. After that, the solution was heated in a water bath kept at 55 °C for 1 h and then at 85 °C for about 6 h. In this step, a small amount of H_2O was occasionally added during the heating process to compensate for the vaporized portion. The resultant clear solution was cooled down and placed overnight. The crystallization was carried out at 175 °C for 7 days in autoclave. The solid product was filtered, washed with distilled water, and dried at 100 °C overnight, and then calcined at 550 °C for 10 h in air.

S2 The analysis and calculation methods

The resultant mixture was quantified with High Performance Liquid Chromatography (Agilent 1200) and qualitatively analyzed with Gas Chromatograph-Mass Spectrometer (Agilent, 5973 Nework6890N).

The yield of product, the selectivity to product, and the conversion of aromatics were calculated as:

Yield of product (%) = Moles of product / Moles of initial aromatics × 100

Selectivity to product (%) = Moles of product / Moles of all products × 100

Conversion of aromatics (%) = (Moles of initial aromatics - Moles of remained aromatics) / Moles of initial aromatics × 100

S3 Effect of other reaction condition

Effect of the amount of catalyst

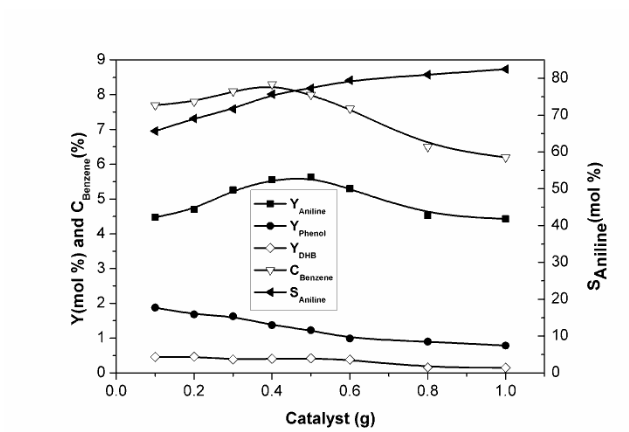

Fig. S7. The effect of the amount of 2.5 wt% Cu/S-1 on the yield of products, the conversion of benzene and the selectivity to aniline. Reaction condition: 40.0 ml H_2O, 2.8 mmol C_6H_6, 133.0 mmol $NH_3{\cdot}H_2O$ and 22.6 mmol H_2O_2, reaction temperature 60 °C, reaction time 8 h.

A set of experiments using various amount of 2.5 wt% Cu/S-1 were carried out and the results are shown in Fig. S7. The yield of aniline increased with the amount of catalyst up to the maximum of 5.6% at 0.5 g and then decreased. The selectivity to aniline varied from 65.7 to 82.5% when the amount of catalyst varied from 0.1 to 1.0 g. However, the yields of by-products continuously decreased with increasing amount of catalyst. The decrease of the yield to aniline with increasing amount of catalyst above 0.5 g might be due to the decomposition of H_2O_2 to O_2, causing the decrease of the efficiency of H_2O_2.

Effect of mode of the addition of the reagents

Since H_2O_2 might decompose in the presence of catalyst and ammonia could evaporate easily, the mode of reagents addition was also tested. Three different modes of reagents addition were carried out in this work: (I) reagents were fed into the reaction system in a period of 2-9 h by peristaltic pump at 60 °C; (II) reagents were added in one lot at 60 °C; (III) reagents were added in five parts in 48 min intervals at 60 °C.

The influence of adding time in mode I on the yield and selectivity to aniline and the conversion of benzene are shown in Fig. S8. With the adding time varied from 2 to 9 h, the yield of aniline went up initially, reached 5.5% at 4 h and then kept almost unchanged. However, the yields of phenol and DHB continuously decreased, and the selectivity to aniline increased monotonously. The results indicated that the adding time of 4 h was suitable for the production of aniline.

Mode II and III were also examined. When mode II was used in the addition of reagents, the yield of aniline, conversion of

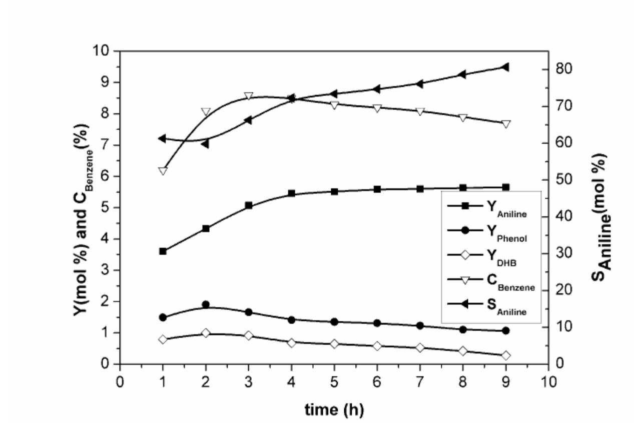

Fig. S8. The effect of the adding time of reagents on the yield of products, the conversion of benzene and the selectivity to aniline.. Reaction condition: 0.5 g 2.5 wt% Cu/S-1, 40.0 ml H_2O, 2.8 mmol C_6H_6, 133.0 mmol $NH_3{\cdot}H_2O$ and 22.6 mmol H_2O_2, reaction temperature 60 °C.

benzene and selectivity to aniline were 0.8%, 3.7% and 26.7%, respectively. For mode III, the yield of aniline, and conversion of benzene and selectivity to aniline were 2.0%, 4.5% and 52.6%, respectively.

The above results demonstrated that the performance of the catalyst was significantly sensitive to the mode of reagent addition. Mode I was preferable under the present experimental conditions. It was clear that there was a competition between amination and hydroxylation of benzene in the reaction system. When the velocity of reagents added was too fast, it could increase the molar ratio of H_2O_2 to benzene, which was more advantageous to the hydroxylation of both benzene and phenol formed.

Effect of concentration of $NH_3 \cdot H_2O$ and H_2O_2

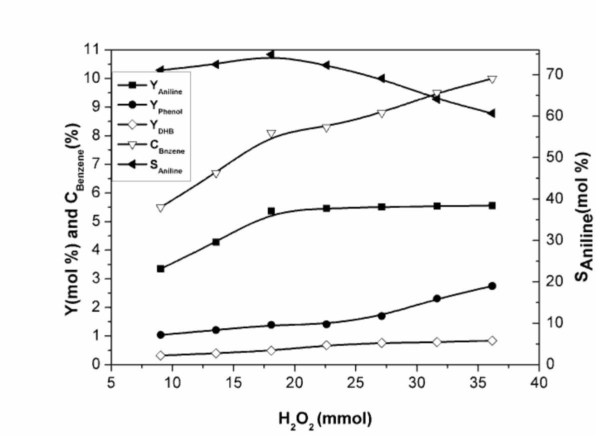

Fig. S9. The effect of the amount of H_2O_2 on the yield of products, the conversion of benzene and the selectivity to aniline. Reaction condition: 0.5 g 2.5 wt% Cu/S-1, 40.0 ml H_2O, 2.8 mmol C_6H_6 and 133.0 mmol $NH_3 \cdot H_2O$, reaction temperature 60 °C, reaction time 4 h.

The effect of the concentration of $NH_3 \cdot H_2O$ and H_2O_2 on the activity was studied by changing the amounts of the $NH_3 \cdot H_2O$ and H_2O_2 added. The results are shown in Fig. S9 and S10. Under the same amounts of H_2O and $NH_3 \cdot H_2O$ added, the yield of aniline increased with increasing amount of H_2O_2 added and became almost unchanged over 18.1 mmol, while the selectivity to aniline went up initially, reached the maximum of 74.0% at 18.1 mmol and then decreased. The yields of by-products and conversion of benzene increased monotonically with increasing amount of H_2O_2 from 9.0 to 36.2 mmol.

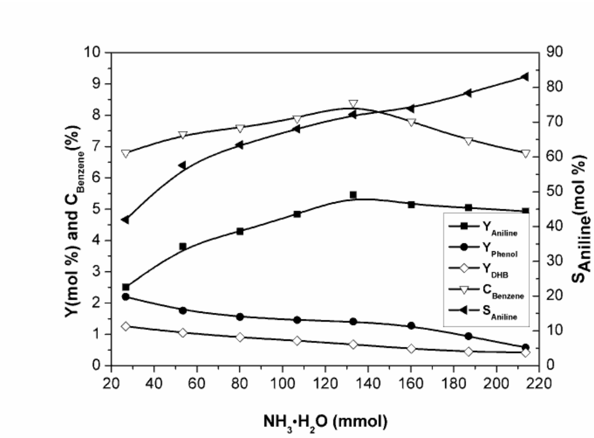

Fig. S10. The effect of the amount of $NH_3 \cdot H_2O$ on the yield of products, the conversion of benzene and the selectivity to aniline. Reaction condition: 0.5 g 2.5 wt% Cu/S-1, 40.0 ml H_2O, 2.8 mmol C_6H_6 and 18.1 mmol H_2O_2, reaction temperature 60 °C, reaction time 4 h.

Keeping the amounts of H_2O and H_2O_2, with the increase of the amount of $NH_3 \cdot H_2O$ added, the yield of aniline and conversion of benzene went up initially, reached the maxima 5.4% and 8.1% respectively at 133.0 mmol and then decreased. However, the yields of by-products continuously decreased and the selectivity to aniline monotonously increased. It was clear that a high concentration of H_2O_2 was more advantageous to benzene hydroxylation.

Effect of reaction temperature

As shown in Fig. S11, with the increase of reaction temperature, the yields of aniline and phenol, and the conversion of benzene increased initially, reached the maxima of 5.4%, 1.4% and 8.1% respectively at 60 °C and then decreased. However, the selectivity to aniline decreased, while the yield of DHB increased might be due to the competitive thermal decomposition of H_2O_2 at higher temperature. This showed that the favourable reaction temperature was 60 °C.

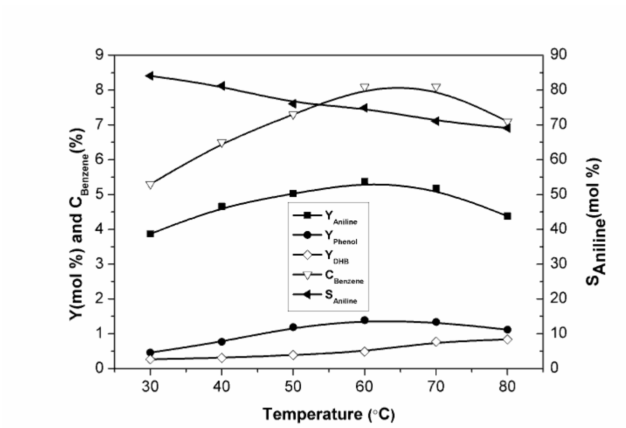

Fig. S11. The influence of reaction temperature on the yield of products, the conversion of benzene and the selectivity to aniline. Reaction condition: 0.5 g 2.5 wt% Cu/S-1, 40.0 ml H_2O, 2.8 mmol C_6H_6, 133.0 mmol $NH_3 \cdot H_2O$ and 18.1 mmol H_2O_2, reaction time 4 h.

S4 The effect of reaction system on catalytic activity

Aniline could be generated over CuO and Cu/Meso-2 in the present work, which was not observed in the previous results.[20] To further investigate the effect of reaction conditions on amination of benzene, the amination reaction was carried out over Cu/S-1 under the reaction conditions used previously, and an aniline yield of only 0.8% with a selectively of 34.8% to aniline was obtained. In the previous work, the catalyst, benzene and $NH_3 \cdot H_2O$ (28 wt%) were first mixed in a flask, and then H_2O_2 (30 wt%) was added in five parts at 24 min intervals. It was obvious that the instantaneous concentration of both ammonia and H_2O_2 in the reaction mixture was much higher than that in the present work. It was revealed that a diluted instantaneous concentration of both ammonia and H_2O_2 was favourable to amination.

To further investigate the catalytic activity of the Cu/S-1 in the direct amination of benzene, 2.5 wt% Cu/S-1 was operated under the optimized conditions using RD reactor.[19] As expected, higher yield of aniline (10.8%) was obtained, which was just slightly lower than that obtained over Cu/h-TS-1 (12.4%).[19] The result showed that 2.5 wt% Cu/S-1 possessed comparable catalytic activity as 2.5 wt% Cu/h-TS-1, confirming that Cu/S-1 could play almost the same role as Cu/h-TS-1 in the direct amination of benzene.

S5 The reaction pathway of amination

In previous work[19], we proposed and demonstrated the following probable catalytic pathway of benzene ammoximation to aniline over h-TS-1 or metal doped h-TS-1: a) Ammonia was oxidized by hydrogen peroxide to hydroxylamine in the presence of h-TS-1 or metal doped h-TS-1; b) Aniline was obtained by the direct amination of benzene with hydroxylamine over h-TS-1 or metal doped h-TS-1. Hydroxylamine is the reaction intermediate.

To verify if the above reaction pathway of amination was suitable in the present reaction, the ammonia oxidation was carried out in kettle-type reactor with a mechanical stirrer and a condenser. 22.0 ml *t*-butanol and 0.5 g 2.5 wt % Cu/ S-1 were added into the reactor, the mixture of 40 ml H_2O, 133.0 mmol $NH_3{\bullet}H_2O$ and 18.1 mmol H_2O_2 was fed to the reaction system with 0.2 ml·min^{-1} by peristaltic pump after the reactor was heated to 60°C. Then, the reaction mixture was cooled and centrifuged to separate Cu/S-1 catalyst. Based on optimized conditions in our pervious work[5], 0.05 g $NaVO_3$, 25 ml CH_3COOH and 2.82 mmol benzene were successively added to the reactor, the amination of benzene was carried out in 1.5 h at 60°C. An aniline yield of about 1.5%, with a selectively of 87.5% to aniline, was obtained. Meanwhile the gaseous products were monitored using an on-line gas mass spectrometers analysis system (HPR-20QIC). N_2, N_2O and O_2 were detected in the whole reaction period. The result showed that aniline was produced without Cu/S-1 and the gaseous products agreed with the relative literature report[5], suggesting hydroxylamine had produced in the reaction system.

The reaction was carried out using 0.05 g $NaVO_3$ instead of 2.5 wt % Cu/ S-1 under the aforementioned optimized conditions, while no aniline was obtained.

The above reaction mixture was replaced by 50 ml hydroxylamine hydrochloride solution (0.29 mmol·ml^{-1}) under the aforementioned optimized conditions. No aniline was detected in the reaction. When 4.0 mmol H_2O_2 was continuously added into the above reaction mixture, an aniline yield of about 26.5% with phenol (18.5%), DHB (4.7%) and trace amount of nitrobenzene, with a selectively of 53.3% to aniline, was obtained.

In addition, the reaction was carried out using phenol as the original material in order to confirm whether phenol was the intermediate in the reaction. The result showed that no aniline or hydroxy-substitued anilines were detected, which agreed well with the previous work[5,19,20] This confirmed that the possible intermediate for aniline formation was hydroxylamine instead of phenol.

These results demonstrated that the catalytic pathway of benzene ammoximation to aniline in present work was the same as that in previous work. [19]

Table S1. The reusability of Cu/h-TS-1

Recycling number	Yield (mol %)			Conversion of benzene (%)	Selectivity to aniline (%)	Cu (wt%) [b]
	Aniline	Phenol	DHB			
0	-	-	-	-	-	2.48
1	5.4	1.4	0.5	8.1(7.3)[a]	74.0	2.28
2	4.3	1.2	0.4	6.8(5.9)	72.8	2.16
3	4.2	1.3	0.5	6.8(6.0)	70.0	2.13
4	4.1	1.2	0.4	6.6(5.7)	71.9	2.13
5	4.1	1.4	0.4	6.7(6.0)	70.0	2.13

Reaction condition: 0.5 g catalyst, 40.0 ml H_2O, 2.8 mmol C_6H_6, 133.0 mmol $NH_3 \cdot H_2O$ and 18.1 mmol H_2O_2, reaction temperature 60 °C, reaction time 4 h. [a] Value calculated by Moles of all products / Moles of initial benzene × 100. [b] Total Cu loading determined by ICP.

Table S2. The results of catalytic amination of substituted benzenes

Substrate	Products yield on the aromatic ring (mol %)						Products yield on the substituent			Selectivity to aminated products (%)
	Amination			hydroxylation						
	Ortho-	Meta-	Para-	Ortho-	Meta-	Para-	Alcohol	Aldehyde	Nitrile	
nitrobenzene	n.d	0.2	n.d	n.d	n.d	n.d	-	-	-	100.0
chlorobenzene	3.2	0.4	1.2	0.1	trace	0.1	-	-	-	96.0
toluene	3.1	0.3	0.9	1.4	0.6	1.1	1.1	0.3	0.1	48.3
anisole	5.1	1.0	1.3	1.9	0.7	1.7	-	-	-	63.2
Phenol	n.d	n.d	n.d	1.7	0.6	1.2	-	-	-	-
Paraxylene	1.2	-	-	1.5	-	-	0.7	0.8	0.1	27.9
Mesitylene	0.4	-	-	0.3	-	-	0.2	0.5	0.4	22.2

Reaction condition: 0.5 g catalyst, 40.0 ml H_2O, 2.8 mmol substituted benzenes, 133.0 mmol $NH_3 \cdot H_2O$ and 18.1 mmol H_2O_2, reaction time 4 h, reaction temperature 60 °C.