-Supporting Information-

Aromatic C–N bond formation *via* simultaneous activation of C–H and N–H bonds: direct oxyamination of benzene to aniline

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Experimental Section

Catalysts preparation

Preparation of TS-1:

The TS-1 zeolites were prepared by a modified hydrothermal method. In a typical preparation procedure, 20 g of TPAOH (tetrapropylammonium hydroxide, 25 *wt*%), 20 g of DI water, and 10 g of isopropanol (≥95 *wt*%) were mixed thoroughly before slowly added to a beaker containing 45 g of TEOS (tetraethyl orthosilicate, ≥28 *wt*%). The mixture was stirred for 30 min before 5 g of $TiCl_3 \cdot xH_2O$ (15 *wt*%) was added in a dropwise manner. Then, another 60 g of TPAOH was added, followed by adding 80 g of DI water. After continuously stirred for 10 min at room temperature, the obtained gel was heated to 358 K and kept stirring for another 3 h. During the heating process, proper amount of water was added to compensate for the evaporation loss. The resulting gel was transferred to a PTFE-Lined autoclave for being crystallized at 448 K for about 150 h. After crystallization, the product was separated from the mother liquor by vacuum filtration, washed by water, and dried at 393 K overnight. The obtained powder was calcined at 823 K in dry air for 8 h to get the TS-1 sample.

Preparation of metal/TS-1 catalysts:

The doping of metals on TS-1 catalysts was conducted by wet impregnation method. Metal components of Ti, Ce, V, Co, Ni, Fe, and Cu were introduced onto the support with corresponding soluble salt precursors ($TiCl_3$, CeN_5O_9, $VOSO_4$, $Co(NO_3)_2$, $NiSO_4$, $Fe(NO_3)_3$, and $Cu(NO_3)_2$). The support was impregnated with isometric precursor solution at room temperature for 24 h. The mixture was directly dried at 493 K. Then, the powder was calcined in air flow at 773 K for 8 h. The metal content on these M/TS-1 catalysts was 2.5 *wt*%.

Cu/TS-1 catalysts with various Cu contents (the theoretical contents were controlled to be 1.0, 2.5, 5.0, 7.5, and 10.0 *wt*%, respectively) were also prepared. The actual Cu contents on the catalysts were analyzed with ICP-AES. According to the Cu content, the catalysts were named as CT-1(1.1 *wt*%), CT-2 (2.4 *wt*%), CT-3 (4.9 *wt*%), CT-4 (7.2 *wt*%), and CT-5 (9.6 *wt*%), respectively.

Characterization of the catalysts

X-ray diffraction (XRD) patterns of the TS-1 and Cu/TS-1 catalysts were taken with a LTD DX-1000 CSC diffraction instrument operating at 40 kV and 25 mA using nickel-filtered Cu K_α radiation (λ=1.54056Å). Data were collected in the 2θ range of 5-70º with a step of 0.0544º using continuous scanning mode.

Ammonia-temperature-programmed-desorption (NH_3-TPD) experiments were performed in a fixed-bed reactor at atmosphere pressure. About 0.10 g of the catalyst sample was filled in a stainless steel U-tube. Then, the sample was swept by N_2 (15 mL/min) at 573 K for 60 min before cooling to 293 K. Pure NH_3 gas was then introduced into the U-tube by passing through with a rate of 10 mL/min for 20 min. After this, the catalyst was flushed with He flow (30 mL/min) at 303 K. Finally, the sample was gradually heated from 293 to 873 K at a ramp of 10 K/min. The desorbed gas was detected by thermal conductivity detector (TCD).

The evolved gas from NH_3-TPD apparatus was analyzed on-line with a multichannel mass spectrometry (TPDE-MS, HPR-20QIC). The possible molecules (such as NH_3, NO, N_2O, and NO_2) arising from desorption of NH_3 were monitored by recording the signals at m/z = 17, 30, 44, and 46.

X-ray photoelectron spectroscopy (XPS) was conducted on a XSAM800 spectrometer (KRATOS) with Al K_α radiation (1486.6 eV) operating at 12 kV and 12 mA. The binding energy (BE) was calibrated with C_{1s} at 284.8 eV. A linear background was substrated from all spectra.

The peak fitting was performed with 80/20 Lorentz-Gauss function.

Activity test in the direct oxyamination of benzene

In a typical oxyamination reaction, 0.3 g of the catalyst, 5 mL of benzene, and 10 mL of ammonia were added into a 50 mL two-neck glass flask with continuous stirring. Under reflux, the mixture was heated at 343 K for 2 h with stirring, during which 10 mL of H_2O_2 (30 *wt*%) was added in five parts in a 24 min's interval. After cooling to room temperature, the liquid mixture was separated from the catalyst by filtration. Then, the liquid phase was stratified and analyzed separately by coupled gas chromatography and mass spectroscopy (GC-MS, Agilent, 5973 Network 6890N). The products (aniline, nitrobenzene and phenol) were quantified by HPLC (equipped with a C18 column) with a UV-visible detector.

The yield (μmol) of products was based on the amount of benzene used. The selectivity (mol/mol %) of aniline was calculated by dividing the amount of aniline to the total amount of products.

To investigate the possible catalytic activity of Cu species in the amination, Cu/SiO_2 (0.3 g, 2.5 *w/w*%), CuO (0.01 g), $Cu(NO_3)_2 \cdot 3H_2O$ (0.03 g), or $CuSO_4 \cdot 5H_2O$ (0.03 g) were employed separately as the catalysts while keeping all other conditions same as those in the typical oxyamination reaction.

To investigate whether the aniline was formed *via* the amination of phenol, a control experiment was carried out by using 60 mmol of phenol and 10 mL of aqueous ammonia as the starting materials on CT-2 catalyst (with other reaction conditions unchanged). Similarly, to investigate whether the nitrobenzene was formed by the deep oxidation of aniline or not, aniline (30 mmol) was used as the starting material (with other reaction conditions unchanged).

The reaction conditions on CT-2 catalyst were optimized by varying the reaction temperature (303-353 K), the amount of H_2O_2 (5-25 mL), and the amount of aqueous ammonia (5-25 mL), separately (with other reaction conditions unchanged).

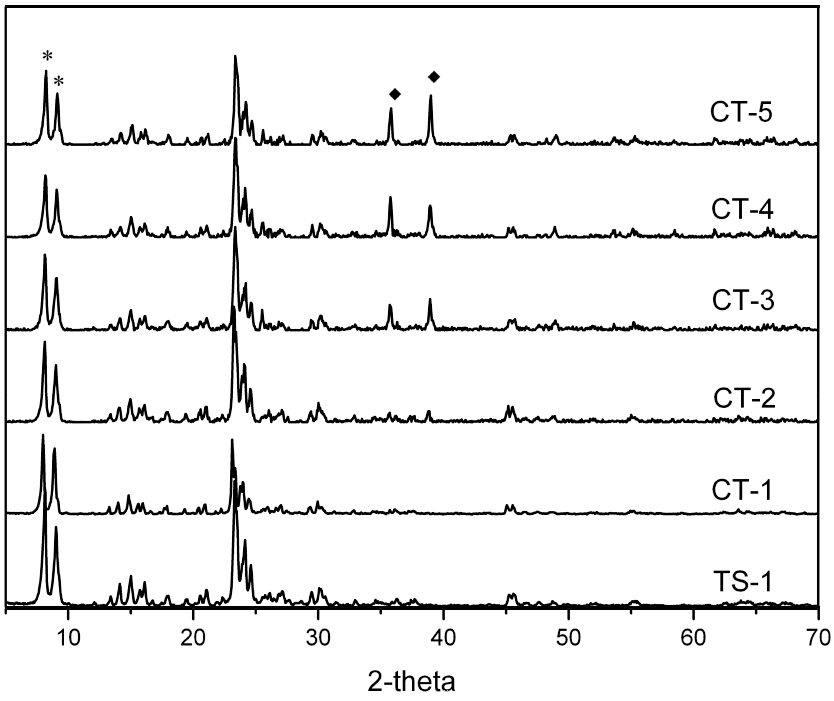

Fig. S1 The XRD spectra of the TS-1 and Cu/TS-1 catalysts. (*) Diffraction peaks of TS-1; (◆) Diffraction peaks of CuO crystal.

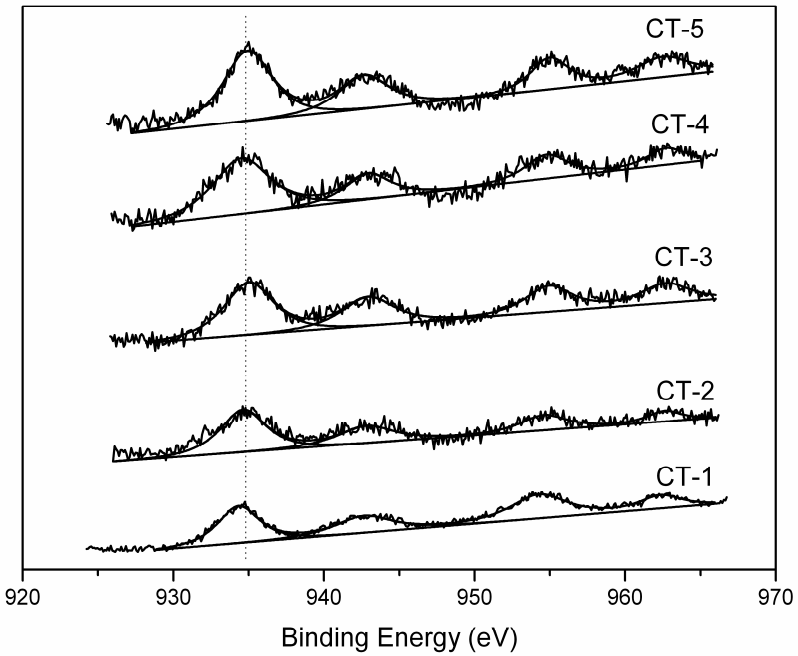

Fig. S2 The XPS spectra of Cu_{1s} on the Cu/TS-1 catalysts.

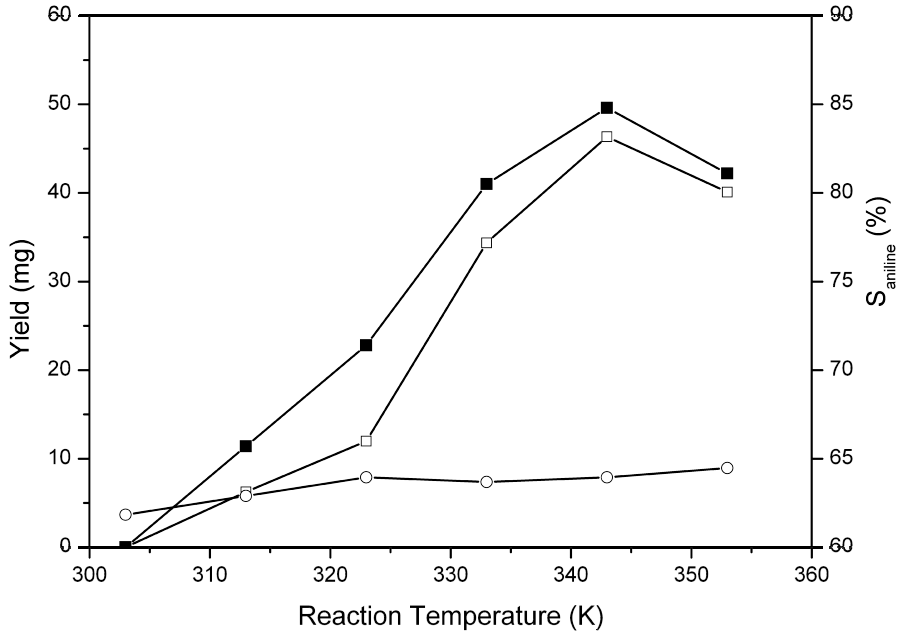

Fig. S3 Effect of reaction temperature on the catalytic performance of CT-2 in the oxyamination. (○ Yield of phenol, □ Yield of aniline, ■ Selectivity to aniline). Reaction Conditions: 0.3 g of CT-2, 5 mL of benzene, 10 mL of aqueous ammonia, 10 mL of H_2O_2 (2 mL/24 min), 2 h.

Table S1. The molar ratio of Cu/Ti on TS-1 and Cu/TS-1 catalysts obtained from XPS analysis.

Catalyst	O%	Si%	Ti%	Cu%	Cu/Ti
TS-1	69.4	24.6	2.7	0	0
CT-1	68.8	27.5	1.9	0.9	0.4
CT-2	67.5	30.1	1.8	1.6	0.7
CY-3	67.5	28.4	0.8	2.3	2.2
CT-4	67.0	30.1	0.8	2.7	2.55
CT-5	68.3	28.8	0.6	2.9	3.7

Table S2. The peak area ratio of I/II in the NH_3-TPD experiments.

Catalyst	TS-1	CT-1	CT-2	CT-3	CT-4	CT-5
Peak area ratio of I/II	1.9	1.4	0.5	0.7	2.0	3.3

Table S3. The composition of the released gas from NH_3-TPD experiments.

Catalysts	Contents (mol%)			
	NO_2	N_2O	NO	NH_3
TS-1	0.8	17.9	3.4	77.9
CT-1	0.6	18.1	4.7	76.6
CT-2	0.5	24.8	4.3	70.4
CT-3	0.6	23.3	3.2	72.9
CT-4	0.3	8.7	8.0	83.0
CT-5	0.2	6.2	8.5	85.1

Table S4. The effect of H_2O_2 amount on the oxyamination of benzene.

H_2O_2 (mL)	$Y_{aniline}$ (μmol)	$Y_{nitrobenzene}$ (μmol)	Y_{phenol} (μmol)	$S_{aniline}$/%
5	213.7	5.7	27.6	88.4
10	498.2	5.7	83.9	84.8
15	449.9	5.7	126.4	77.6
20	453.1	14.6	149.8	76.1
25	410.2	23.6	162.6	70.4

Reaction Conditions: 0.3 g of CT-2, 5 mL of benzene, 10 mL of ammonia, H_2O_2 was added in average five parts in a 24 min's interval, 343 K, 2 h.

Table S5. The effect of the amount of aqueous ammonia on the oxyamination of benzene.

Amount of ammonia （mL）	$Y_{aniline}$ (μmol)	$Y_{nitrobenzene}$ (μmol)	Y_{phenol} (μmol)	$S_{aniline}$ (%)
5	269.5	5.7	83.9	75.0
10	498.2	5.7	83.9	84.8
15	511.1	5.7	61.6	88.4
20	505.7	5.7	95.6	83.3
25	516.5	5.7	112.6	81.4

Reaction Conditions: 0.3 g of Catalyst, 5 mL of benzene, 10 mL of H_2O_2 (2 mL/24 min), 343 k, 2 h.

Table S6. The effect of addition manners of H_2O_2 on the oxyamination of benzene.

Entry	$Y_{aniline}$ (μmol)	$Y_{nitrobenzene}$ (μmol)	Y_{phenol} (μmol)	$S_{aniline}$ (%)
1	201.9	0.0	61.6	76.6
2	498.2	5.7	83.9	84.8
3	251.3	27.6	44.6	77.6
4	95.6	50.4	39.3	51.5

Reaction conditions: 0.3 g of catalyst, 5 mL of benzene, 10 mL of H_2O_2, 10 mL of aqueous ammonia, 343 K, 2 h. The addition manners of H_2O_2 were: 1) 1 mL/12 min, 2) 2 mL/ 24 min; 3) 5 mL/60 min; and 4) 10 mL at one time.

Table S7. Catalytic performance of the reused Cu/TS-1 catalysts in the oxyamination of benzene.

	$Y_{aniline}$ (μmol)	$Y_{nitrobenzene}$ (μmol)	Y_{phenol} (μmol)	$S_{aniline}$ (%)
Fresh CT-2	498.2	5.7	83.9	84.8
Reused CT-2	405.9	5.7	89.3	81.0

Reaction Conditions: 0.3 g of Catalyst, 5 mL of benzene, 10 mL of aqueous ammonia, 10 mL of H_2O_2 (2 mL/24 min), 343 k, 2 h.

Table S8. Catalytic performance of the metal-doped TS-1 catalysts for the oxyamination of benzene [a]

Entry	Catalysts	$Y_{aniline}$ (μmol)	$Y_{nitrobenzene}$ (μmol)	Y_{phenol} (μmol)	$C_{benzene}$ (%)	$S_{aniline}$ (%)
1	TS-1	139.8	117.9	67.0	0.58	43.4
2	Ti/TS-1	61.3	11.4	319.1	0.70	15.7
3	Ce/TS-1	162.4	83.7	185.1	0.77	37.8
4	V/TS-1	179.6	44.7	447.9	1.20	26.7
5	Co/TS-1	157.0	39.0	118.1	0.56	50.0
6	Ni/TS-1	286.0	39.0	140.4	0.83	61.4
7	Fe/TS-1	408.6	50.4	173.4	1.13	64.6
8	Cu/TS-1	498.9	5.7	84.0	1.05	84.8

Reaction Conditions: 0.3 g of Catalyst, 5 mL of benzene, 10 mL of H_2O_2 (2 mL/24 min), 343 k, 2 h.