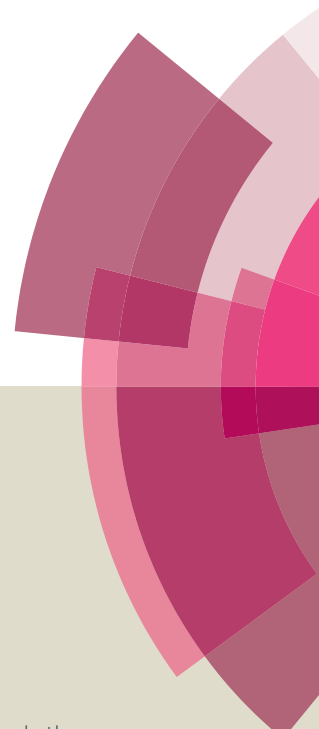


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ARTICLE TYPE

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

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Cu doped TS-1 zeolite sample was applied to catalyze the formation of C–N bonds on both the ring and the side chain of toluene as well as other alkylbenzenes. A yield of 3.4% to toluidine was obtained for the amination of toluene, with 1.0% yield to nitrobenzene. Cyanobenzene was also obtained as the C–N bond product on the side chain with a yield of 1.0%. The selectivity to C–N bond formation was 52.4%. The catalyst promoted the formation of hydroxylamine intermediate from ammonia and hydrogen peroxide, and then the instantaneously generated amino cation react with the substrate to form C–N bonds on both the ring and side chain. The cyanobenzene was produced from the dehydration of benzylamine formed via the reaction of ammonia and toluene. The formation of C–N bonds on the ring had ortho-orientation advantage for mono-substituted-benzene. With the increase of the number of methyl substituent, the yield of ring products decreased, which might be caused by steric hindrance.

1 Introduction

The C–N bond formation reaction has been known to contribute to the ideality of biosynthesis in nature^{1–8}. Arylamines are abundant in biologically active natural products and medicinally important compounds, and widely used in materials with useful electrical and mechanical properties. The selective activation and functionalization of C–H bonds, especially those of aromatics under mild conditions, remain one of the most significant challenges in both synthetic and green chemistry^{9–19}. Previous ways for the formation of C–N bonds include transferring an amino group from one molecule to another^{20–24}. The promoted investigation of the direct amination of aromatics with ammonia and hydrogen peroxide is mostly concerned with the preparation of aniline directly from benzene^{9,10}, while that for other aromatic compounds is rarely studied. The photocatalytic aromatic ring amination was also studied with less than 1% aniline yield obtained²⁵. Toluidine acts as important aromatic amine, which can be used in the production of dyes, pharmaceutical and rubber chemicals. The traditional methods for preparation of toluidine were multistep, high cost and environmentally unfriendly. In the previous work, the direct amination of toluene to toluidine has been come true with acceptable yield using hydroxylamine hydrochloride^{26–28}.

The TS-1 zeolite is a kind of molecular sieve which is crystalline with MFI topology structure and widely used as catalysts^{29–32}. Since the discovery of the synthesis method of TS-1 zeolite in 1983 at Enichem³³, the properties of the TS-1 zeolite continue to attract attention by researchers. It is an active and highly selective catalyst in a number of organic reactions such as epoxidation of alkenes, oxidation of alkanes and alcohols^{34–39}, and hydroxylation of aromatics^{40–44} under mild conditions with hydrogen peroxide as oxidant.

After screening of different metal (Cu, Ni, V, etc) doped TS-1, it was found that Cu modified TS-1 catalyst exhibited acceptable

activity for the amination process of benzene⁹. In the present work the catalyst was employed to catalyze the reaction of toluene with aqueous ammonia and hydrogen peroxide to investigate the functionalization of C–H bonds both on the ring and side chain.

2. Experimental

2.1. Preparation of TS-1 and Cu/TS-1 zeolite samples

A hydrothermal synthesis method similar to our previous work⁹ was used to prepare TS-1 zeolite. 96.0 g of tetrapropylammonium hydroxide (TPAOH) (25.0 wt.%) was firstly added to a 1L beaker, and then 91.0 g of tetraethyl orthosilicate (TEOS) was added dropwise. The mixture was stirred by magnetic stirring apparatus at 298 K in water bath, followed by adding 40.0 g isopropanol and 40.0 g water. After being stirred for 10 minutes, 5.0 g aqueous solution of titanium trichloride (15.0 wt.%) diluted by 20 mL water was added into the mixture dropwise. The resultant solution was heated to 333 K with stirring and kept for 1 h, then to 358 K and kept for 6 h with stirring. During the heating process, water was added to keep the total volume of 400 mL. Then the resultant solution was cooled down to room temperature, and finally crystallized in autoclave at 448 K for 7 days. The solid product was obtained through filtrating, washing, crushing and drying. Then the obtained sample was calcined at 823 K in air atmosphere for 8 h. Thus the TS-1 zeolite catalyst was obtained.

The Cu doped TS-1 catalyst was prepared by wet impregnation method. The above obtained TS-1 of 3 g was mixed with equivalent-volume aqueous solution containing 0.1798 g or 0.2265 g or 0.2831 g or 0.3398 g of Cu(NO₃)₂·3H₂O at 343 K. Then the mixture was impregnated at room temperature for 24 h. After dried at about 373 K for 12h, the sample was calcined at

823 K in air atmosphere for 8 h to obtain the Cu/TS-1 catalyst. Thus, Cu species were introduced to TS-1 zeolite. According to the controlled amount of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, the Cu/TS-1 samples were named as 1.5Cu/TS-1 (1.5 wt.%), 2.0Cu/TS-1 (2.0 wt.%), 2.5Cu/TS-1 (2.5 wt.%) and 3.0Cu/TS-1 (3.0 wt.%).

2.2 Characterization of the TS-1 and Cu/TS-1 samples

BET surface area of the samples was detected on Micromeritics Tristar 3020 analyser by N_2 adsorption/desorption measurement. The surface area of these samples was calculated with multipoint by Brunauer-Emmett-Teller method. The BET equation was applied to the N_2 adsorption isotherms. The pore size distribution and the average pore diameters were determined by the BJH method. Before measurement, the samples were activated at 373 K for 1 h and then at 573 K for 4 h under vacuum.

X-ray diffraction patterns (XRD) of the TS-1 and Cu/TS-1 samples were obtained by DX-1000 CSC diffraction instrument using $\text{Cu K}\alpha$ ($\lambda=1.54056 \text{ \AA}$) radiation operated at 25 mA and 40 kV. The 2θ value range was from 2.7° to 80° , and the data were collected with a step of 0.0544° under continuous scanning mode.

Fourier transform infrared (FT-IR) spectra of TS-1 and Cu/TS-1 samples were acquired on a Nicolet Nexus NEXUS670 FT-IR instrument by film method with an MCT detector. The samples were firstly mixed with KBr by the mass ratio of 1:100 and pressed. The FT-IR spectra were collected in the range of $4000\text{--}400 \text{ cm}^{-1}$ with a resolution of 2 cm^{-1} .

Ultraviolet visible diffuse reflectance (UV-VIS) spectra of these samples were collected on a TU-1901 spectrophotometer equipped with a reflectance attachment using the mitering of Abs at intermediate speed. The spectral bandwidth was 5 nm with a sample interval of 1.000 nm. Before measurement, the samples were dried at 373 K overnight and packed with a BaSO_4 plate as the reference.

The surface morphology and composition of different samples were characterized by scanning electron microscopy (SEM) with energy dispersive spectrum (EDS) (JSM-7500F, JEOL, Tokyo, Japan). The instrument was set at 5 kV. Gold was applied to coat on the surface of the samples with a vacuum sputter-coater to enhance the conductivity of the samples and the quality of the SEM images.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to analyze the actual Cu content of the samples. The analysis was performed on thermoelemental: IRIS Advantage. The pump rate was 110 rpm (2,035 mL / min), and the nebulizer pressure (PSI) was 27 with low auxiliary gas rate. The RF power was 1150 W. 0.05 g sample was dissolved in aqua regia of 100 mL at 333K in water bath.

2.3. Activity test

The reaction was carried out in a one-necked round-bottom flask (50 mL) at atmospheric pressure in open air. The TS-1 and Cu/TS-1 samples were used to catalyze the reaction. Firstly, 0.5 mL substrate toluene and certain amount of catalyst were introduced into the reaction flask connected with a condenser. The flask was heated in oil bath with stirring. The mixture of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and H_2O_2 were diluted by water and kept at 273 K under the protection of ice water mixture, and then added into the reaction system dropwise using peristaltic pump with 0.1 mL/min from the top of the condenser in the whole reaction process¹⁰. The reaction time was generally 365 min, and the variation of reaction time was also shown in the optimization of reaction conditions.

Table 1 The BET surface area of the samples.

Samples	$S_{\text{BET}} (\text{m}^2/\text{g})$	$V_{\text{mic}} (\text{cm}^3/\text{g})$	$D_{\text{avg}} (\text{\AA})$
TS-1	400	0.096	17.55
1.5Cu/TS-1	387	0.095	17.54
2.0Cu/TS-1	374	0.093	17.54
2.5Cu/TS-1	365	0.076	17.51
3.0Cu/TS-1	353	0.075	17.51

^a S_{BET} , V_{mic} and D_{avg} represented specific surface area, micropore volume and average pore diameter, respectively.

After that, the reaction product was cooled down to room temperature. The liquid phase of the above process was separated from the catalyst by filtration. Acetonitrile was added to avoid stratifying and keep the total volume of the mixture at 50 mL. GC-MS (coupled gas chromatograph and mass spectroscopy, Agilent, 5973 Network 6890N) was used for qualitative analyze and GC chromatography (FILI, GC-9790) with an Innowax capillary column (30 m 0.25 mm) was used for quantitative analysis. The products with C-N bond formed obtained were toluidine, nitrotoluene and cyanobenzene, while oxidation products with C-O bond formed were cresols, benzaldehyde, and benzylalcohol.

The yield of products and the selectivity to C-N bond-containing products were calculated by the following formulas:

$$\begin{aligned} \text{Yield (\%)} &= \frac{\text{Mole amount of product (toluidine, etc.)}}{\text{(Mole amount of initial toluene)} \times 100}; \\ \text{Selectivity of C-N bonds on the ring (\%)} &= \frac{\text{(Mole amount of toluidine + Mole amount of nitrotoluene)}}{\text{(Mole amount of all products)} \times 100}; \\ \text{Selectivity of products containing C-N bonds (\%)} &= \frac{\text{(Mole amount of toluidine + Mole amount of nitrotoluene + Mole amount of cyanobenzene)}}{\text{(Mole amount of all products)} \times 100}; \\ \text{Selectivity of products on the ring (\%)} &= \frac{\text{(Mole amount of toluidine + Mole amount of nitrotoluene + Mole amount of cresols)}}{\text{(Mole amount of all products)} \times 100}; \\ \text{TON} &= \frac{\text{(Mole amount of toluidine + Mole amount of nitrotoluene + Mole amount of cyanobenzene + Mole amount of cresols + Mole amount of benzaldehyde + Mole amount of benzylalcohol)}}{\text{(Mole amount of copper contained)}}; \\ \text{TOF} &= \frac{\text{(Mole amount of toluidine + Mole amount of nitrotoluene + Mole amount of cyanobenzene + Mole amount of cresols + Mole amount of benzaldehyde + Mole amount of benzylalcohol)}}{\text{(Mole amount of copper contained)} \times \text{Reaction time}} \end{aligned}$$

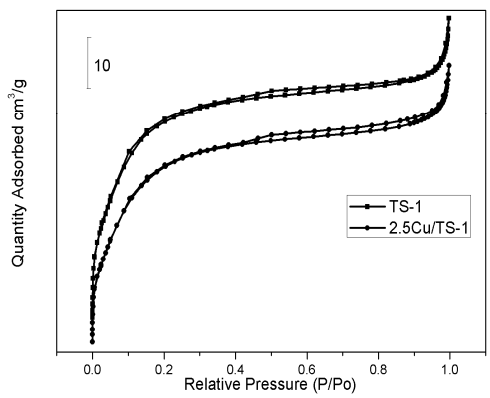
3 Results and Discussion

3.1 Nitrogen adsorption/desorption

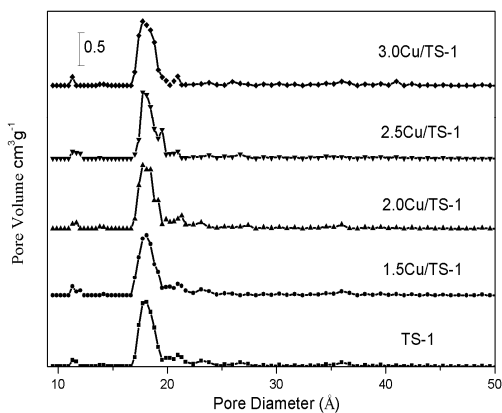
The BET surface area of TS-1 and Cu/TS-1 samples were shown in Table 1. The N_2 adsorption/desorption isotherms and the pore size distribution of the TS-1 and 2.5Cu/TS-1 were shown in Fig.1. As shown in Fig.1 (a), the N_2 adsorption/desorption

isotherms were corresponded to TS-1 zeolite in the literatures^{38, 40, 45, 46}. The

species on the Cu/TS-1 samples, no crystalline phase related to Cu species was observed on these samples. The relative



(a)



(b)

Fig. 1 N₂ adsorption/desorption isotherms of different samples (a) and the pore size distribution (b).

isotherm of the samples showed typically Type IV character, for which the flat part of the isotherm indicates the complete filling of the micropores by condensed nitrogen, and the hysteresis loops in the nitrogen isotherm represented the existence of some mesoporosity in minority. The pore size distribution Fig.1 (b) of different samples confirmed the presence of micropores in these samples. As the results shown in Table 1, the BET surface area of TS-1 was about 400 m²/g with the micropore volume of 0.096 cm³/g. The surface area showed decreasing tendency with the increase of Cu content. It was considered that the impregnation of Cu species blocked some of the micropores of TS-1, thus the surface area and micropore volume of these samples decreased with the increase of Cu content.

3.2 XRD characterization

The TS-1 and Cu/TS-1 zeolite samples were characterized by X-Ray Diffraction. As shown in Fig. 2, the characteristic diffraction peaks of crystal MFI structure were observed at 2θ of 7.9°, 8.8°, 23.1°, 23.9° and 24.4°^{32, 41, 46, 47}. Due to the high dispersion of Cu

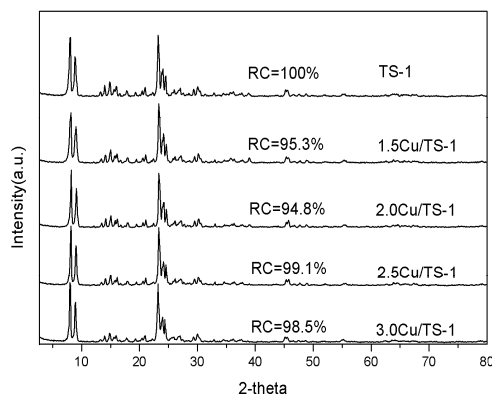


Fig. 2 XRD patterns of TS-1 and Cu/TS-1 samples.

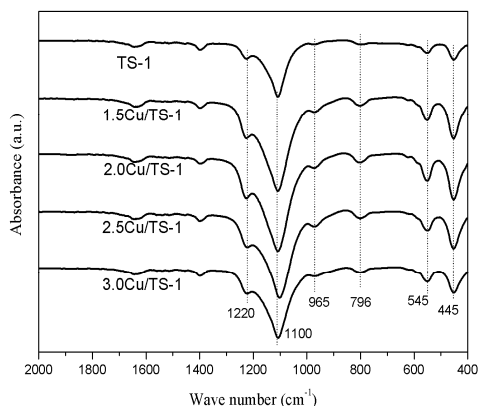


Fig. 3 FT-IR of TS-1 and Cu/TS-1 samples.

crystallinity (RC) of the samples were calculated based on the ratio of the total intensity of the characteristic diffraction peaks, using TS-1 sample (RC=100%) as standard. It could be seen that the RC of the Cu/TS-1 sample was almost the same as TS-1. Thus both the TS-1 and Cu/TS-1 zeolite samples had typical MFI crystal structure. The loaded Cu species did not affect the crystal structure of TS-1, and the Cu species was considered to be low⁹. It was indicated that the existence of Cu species on Cu/TS-1 samples prepared by impregnation was similar to that on TS-1 prepared by MH method⁴⁷.

3.3 FT-IR characterization

Fig. 3 showed the FT-IR spectra of TS-1 and Cu/TS-1 samples. The bonds around 445 cm⁻¹, 545 cm⁻¹, 796 cm⁻¹, 965 cm⁻¹, 1100 cm⁻¹ and 1220 cm⁻¹ were corresponded to the characteristic bands of the TS-1 sieve⁴⁷. The two bands located at 545 and 1220 cm⁻¹ were considered to be the characteristic bands of MFI structure⁴⁶. The peaks at 445, 796 and 1100 cm⁻¹ were assigned to the internal linkages in SiO₄ tetrahedral⁴⁹. The peak at 965 cm⁻¹ was assigned to the vibration of Si-O-Ti bond in framework⁵⁰. However, there were no bands related to Cu species shown in these spectra. Thus, we could assume that TS-1 and Cu/TS-1 samples had the MFI structure, which was consistent with the result of XRD characterization.

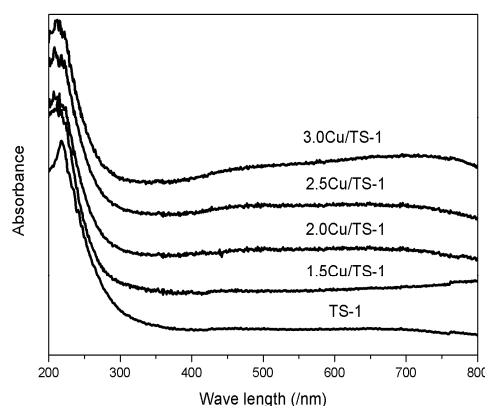


Fig. 4 UV-vis of TS-1 and Cu/TS-1.

3.4 UV-vis characterization

The UV-vis spectra of the TS-1 and Cu/TS-1 were shown in Fig. 4. Based on the literature^{38,41,51,52}, the strong absorption band around 210 nm was the characteristic peak of Ti species in the framework of silicalite, indicating the formation of framework Ti species in these samples. The band around 260-280 nm and 330 nm were corresponded to the Ti species extra-framework wherein the former was assigned to the titanium species and the latter was deemed to be caused by the anatase phase of TiO₂. The results revealed that the Ti species were almost in the framework with few out of the framework for TS-1 and Cu/TS-1 samples. The weak absorption band around 600-800 nm of the Cu/TS-1 samples was assigned to the d-d transitions of Cu²⁺ ions⁵³. With the increase of the Cu content, the intensity of the band around 600-800 nm got stronger, indicating the formation of CuO species which was in accord with the tendency reported in our previous work^{10,53}. It was indicated that the Ti species entered into the framework of the skeleton structure for TS-1, and the impregnation of Cu(NO₃)₂·3H₂O to TS-1 zeolite samples had not led to the appearance of Ti at extra-framework.

3.5 The SEM-EDS and ICP-AES characterization

The scanning electron microscopy images of the samples were collected. TS-1 and 2.5Cu/TS-1 were chosen and analyzed as the typical samples, and the images were shown in Fig. 5 (a) and (b). These samples were obviously crystalline, and the sizes of them were around 0.4 μm. The results indicated that TS-1 sample was irregular spherical crystal. It was found in our previous work that only the Cu-TS-1 samples which were prepared by adding Cu species in the period of hydrothermal synthesis step had the polygonal structure⁴⁷. But in the present work, the Cu/TS-1 sample that prepared by impregnation after hydrothermal process also showed the similar tendency of forming polygonal crystal. It was deemed that in our previous work, the Ti species at extra framework had effect on the morphology of TS-1 resulting in the fact that no polygonal structure of Cu/TS-1 was observed by impregnation method⁴⁷. But in the present work, there were almost no Ti species at extra-framework of these samples, thus the loading Cu species also promoted the formation of polygonal structure. The data of EDS in Table 2 showed the surface composition of TS-1 and Cu/TS-1 samples. With the increase of Cu content loaded on TS-1, the content of Ti species on the surface decreased from 2.12% to 0.74%, and the surface content of Cu increased from 1.19% to 1.86%. It implied that the loaded

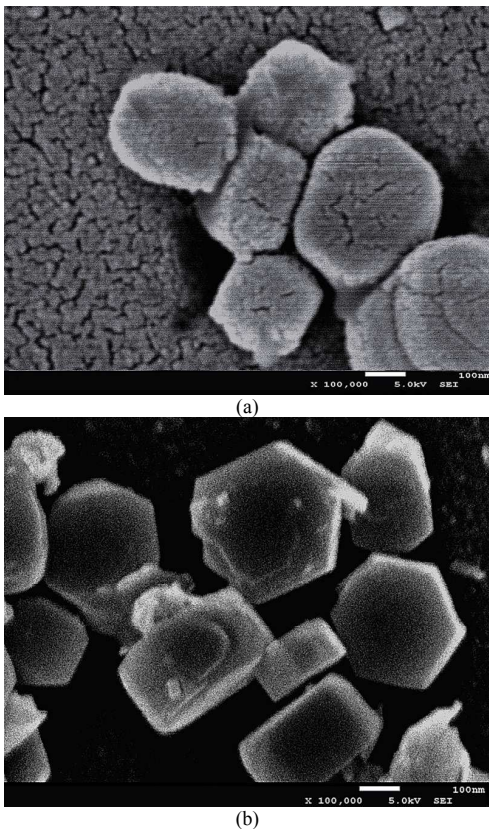


Fig. 5 SEM micrographs of TS-1(a) and 2.5Cu/TS-1(b).

Table 2 Surface composition of TS-1 and Cu/TS-1 and the actual Cu contents of the samples from ICP-AES

Samples	O %	Si %	Ti %	Cu (CuO) %	The actual Cu content (ICP-AES)
TS-1	60.30	37.58	2.12	--	--
1.5Cu/TS-1	59.42	38.54	0.85	1.19	1.47
2.0Cu/TS-1	58.39	39.47	0.78	1.36	1.95
2.5Cu/TS-1	58.67	38.81	0.75	1.77	2.43
3.0Cu/TS-1	57.75	39.23	0.74	1.86	2.91

Cu species might cover the Ti species on the surface. What's more, the Cu species on the surface was detected in the state of CuO. The ICP-AES was also applied in the analysis of Cu contents of the samples. The data indicated that the contents of 1.5TS-1, 2.0TS-1, 2.5TS-1 and 3.0TS-1 were 1.47wt.%, 1.95wt.%, 2.43wt.% and 2.91wt.% respectively, and the data were very close to the controlled values. The results of surface copper lower than that of total values indicated that the surface was less concentrated in Cu than the total values of ICP-AES for the reason that part of Cu species might enter into the pores of the TS-1 support⁵⁴, which was in accordance with the decrease of micropore volume. The lesser copper species on the surface might also be caused by the self-coverage of Cu species as well.

Table 3 The effect of Cu content on the catalytic reaction of toluene.^a

Samples	The theoretical content of Cu loading (wt%)	Molar Yield (%)						Selectivity (%)			TON (mol/mol)		TOF (h ⁻¹)
		TD ^b	CS ^b	NT ^b	BA ^b	CB ^b	BM ^b	C–N bonds on the ring	Products containing C–N bonds	Products on the ring			
TS-1	0.0	1.9	1.5	0.5	0.6	0.8	0.8	39.3	52.5	63.9	--	--	
1.5Cu/TS-1	1.5	2.6	1.3	0.2	0.5	0.9	0.7	45.2	59.7	66.1	7.8	1.3	
2.0Cu/TS-1	2.0	2.9	2.6	0.9	0.6	1.0	0.7	43.7	55.2	73.6	8.9	1.5	
2.5Cu/TS-1	2.5	3.4	3.3	1.0	0.6	1.0	1.0	42.7	52.4	74.8	8.4	1.4	
3.0Cu/TS-1	3.0	3.1	2.7	0.8	0.6	0.9	0.7	44.3	54.5	75.0	6.0	1.0	

^a Reaction conditions: Catalyst 0.15 g; Toluene 4.7 mmol; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; H₂O 25 mL; 353 K, 365min.

^b TD, CS, NT, BA, CB and BM represented toluidine, cresols, nitrotoluene, benzaldehyde, cyanobenzene and benzylalcohol, respectively.

Table 4 Effect of the amount of catalyst.^a

2.5Cu/TS-1 Catalyst (g)	Molar Yield (%)						Selectivity (%)			TON (mol/mol)	TOF (h ⁻¹)
	TD ^b	CS ^b	NT ^b	BA ^b	CB ^b	BM ^b	C–N bonds on the ring	Products containing C–N bonds	Products on the ring		
0.05	0.4	0.3	0.1	0.2	0.3	0.1	35.7	57.1	57.1	3.4	0.6
0.10	1.6	1.5	0.2	0.4	0.7	0.5	36.7	51.0	67.3	6.0	1.0
0.15	3.4	3.3	1.0	0.6	1.0	1.0	42.7	52.4	74.8	8.4	1.4
0.20	3.2	3.0	0.8	0.6	1.1	0.9	41.7	53.1	72.9	5.9	1.0
0.25	3.0	2.8	0.9	0.7	0.9	0.9	42.4	52.2	72.8	4.5	0.7

^a Reaction conditions: 2.5Cu/TS-1; Toluene 4.7 mmol; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; H₂O 25 mL; 353 K, 365min.

^b TD, CS, NT, BA, CB and BM represented toluidine, cresols, nitrotoluene, benzaldehyde, cyanobenzene and benzylalcohol, respectively.

Table 5 Effect of temperature on the catalytic reaction of toluene.^a

Temperature (K)	Molar Yield (%)						Selectivity (%)			TON (mol/mol)	TOF (h ⁻¹)
	TD ^b	CS ^b	NT ^b	BA ^b	CB ^b	BM ^b	C–N bonds on the ring	Products containing C–N bonds	Products on the ring		
333	0.1	0.3	--	0.1	0.2	0.2	11.1	33.3	44.4	0.7	0.1
343	1.8	1.7	0.2	0.6	0.7	0.7	35.1	47.4	64.9	4.7	0.8
348	2.5	2.8	0.8	0.5	0.9	0.9	39.3	50.0	72.6	6.9	1.1
353	3.4	3.2	1.0	0.6	1.0	1.0	42.7	52.4	74.8	8.4	1.4
358	3.3	3.2	1.1	0.7	1.2	1.1	41.5	52.8	71.7	8.7	1.4
363	2.2	3.8	1.4	1.7	1.9	1.5	28.8	44.0	59.2	10.2	1.7
373	1.1	4.3	1.6	0.9	2.2	1.8	22.7	41.2	58.8	9.8	1.6

^a Reaction conditions: Catalyst Cu/TS-1 0.15 g; Toluene 4.7 mmol; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; H₂O 25 mL, 365min.

^b TD, CS, NT, BA, CB and BM represented toluidine, cresols, nitrotoluene, benzaldehyde, cyanobenzene and benzylalcohol, respectively.

3.6. Catalytic performance of Cu/TS-1

We used the TS-1 and Cu/TS-1 catalysts to activate the C–H bonds of toluene for the direct formation of C–N bonds. As shown in Table 3, toluidine was obtained and the highest yield of toluidine was 3.4%, with the yields of 1.0% to nitrotoluene and 1.0% to cyanobenzene (based on benzene introduced), over the 2.5Cu/TS-1 catalyst (Scheme 1). The existence of the electron-donating group (methyl) promoted the yield of amination products compared with the amination of benzene⁹. Nitrotoluene could be considered to be the deep oxidation product of the initially formed toluidine based on the results observed in the amination of benzene⁹. Cyanobenzene was the C–N bond product obtained on the side chain, which could be formed from benzylamine or formamide. To verify the origin of cyanobenzene, control experiments using benzylamine and formamide as substrates were proceeded under the same reaction conditions. The result revealed that the product of benzylamine partial oxidation was cyanobenzene with the yield of 85.3%. No cyanobenzene was obtained using formamide as substrate, and the product was benzaldehyde oxime. Thus it was considered that the intermediate from toluene to cyanobenzene was benzylamine.

Benzylamine was not stable in TS-1/H₂O₂ system and was easily converted to cyanobenzene by the oxidative dehydrogenation. Thus, there was no benzylamine detected by GC-MS. In the products containing C–N bonds, toluidine and nitrotoluene were the ring C–H oxidation products with the selectivity of 81.5% while cyanobenzene was the side chain C–H oxidation product with the selectivity of 18.5%. Meanwhile, cresols and the side chain oxidation products such as benzaldehyde and benzylalcohol were also obtained. The selectivity to the ring was higher than that to the side chain, while the selectivity to the formation of C–N bonds (52.4%-59.7%) was higher than that of C–O bonds (40.3%-47.6%).

With the increase of the Cu loading on TS-1, the yield of toluidine and cyanobenzene increased. The optimal Cu content was 2.5 wt.%, that is, the dependence of the catalytic performance on Cu loading was the same as that in benzene amination^{9,10}. Then the 2.5Cu/TS-1 was chosen for further study. The effect of the amount of 2.5Cu/TS-1 catalyst on the reaction process was investigated, and the results were shown in Table 4. The yield of toluidine and selectivity to C–N bonds on the ring increased with the amount of catalyst up to 0.15 g, and then tended to be stable with the amount of 0.20 g or 0.30 g.

Table 6 Effect of H₂O₂ dosage on the catalytic reaction of toluene.^a

H ₂ O ₂ Dosage (mL)	Molar Yield (%)						Selectivity(%)			TON (mol /mol)	TOF (h ⁻¹)
	TD ^b	CS ^b	NT ^b	BA ^b	CB ^b	BM ^b	C–N bonds on the ring	Products containing C–N bonds	Products on the ring		
0.5 ^c	1.1	1.2	0.6	0.6	0.8	0.6	34.7	54.3	59.2	4.0	0.7
1.0 ^c	2.3	2.8	1.0	0.6	1.0	0.9	38.4	50.0	70.9	7.0	1.2
1.5 ^c	3.4	3.2	1.0	0.6	1.0	1.0	42.7	52.4	74.8	8.4	1.4
2.0 ^c	3.3	3.8	1.1	0.7	1.2	1.1	39.3	50.0	73.2	9.2	1.5
2.5 ^c	2.9	4.0	1.6	0.9	1.4	1.8	35.7	46.8	67.5	10.3	1.7
3.0 ^c	2.1	4.4	2.0	1.2	1.5	1.9	31.3	40.3	64.9	10.7	1.8

^a Reaction conditions: Catalyst 2.5Cu/TS-1 0.15 g; Toluene 4.7 mmol; NH₃·H₂O 87.4 mmol; H₂O₂ (4.9 mmol, 9.8 mmol, 14.7 mmol, 19.6 mmol, 24.5 mmol, 29.4 mmol); H₂O 25 mL; 353 K.

^b TD, CS, NT, BA, CB and BM represented toluidine, cresols, nitrotoluene, benzaldehyde, anobenzene and benzylalcohol, respectively.

^c The reaction time were 355min, 360min, 365min, 370min, 375min and 380min, respectively.

Table 7 Effect of NH₃·H₂O dosage on catalytic reaction of toluene.^a

NH ₃ ·H ₂ O Dosage (mL)	Molar Yield (%)						Selectivity(%)			TON (mol /mol)	TOF (h ⁻¹)
	TD ^b	CS ^b	NT ^b	BA ^b	CB ^b	BM ^b	C–N bonds on the ring	Products containing C–N bonds	Products on the ring		
5 ^c	2.5	2.7	0.4	0.7	0.8	0.8	36.7	46.8	70.9	6.5	1.2
10 ^c	3.4	3.2	1.0	0.6	1.0	1.0	42.7	52.4	74.8	8.4	1.4
15 ^c	3.1	2.6	0.9	0.6	0.8	0.5	47.1	56.5	77.6	7.0	1.0
20 ^c	2.6	2.1	0.3	0.4	0.8	0.5	41.4	55.2	74.6	5.5	0.7

^a Reaction conditions: Catalyst 2.5Cu/TS-1 0.15 g; Toluene 4.7 mmol; NH₃·H₂O (43.71 mmol, 87.4 mmol, 131.1 mmol, 174.8 mmol); H₂O₂ 14.7 mmol; H₂O 25 mL; 353 K.

^b TD, CS, NT, BA, CB and BM represented toluidine, cresols, nitrotoluene, benzaldehyde, cyanobenzene and benzylalcohol, respectively.

^c The reaction time were 315min, 365min, 415min and 465min, respectively.

Table 8 Effect of H₂O dosage on catalytic reaction of toluene.^a

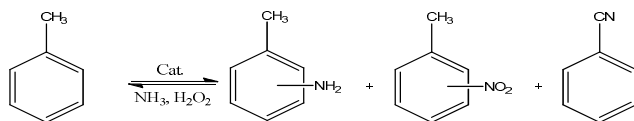
H ₂ O Dosage (mL) ^c	Molar Yield (%)						Selectivity(%)			TON (mol /mol)	TOF (h ⁻¹)
	TD ^b	CS ^b	NT ^b	BA ^b	CB ^b	BM ^b	C–N bonds on the ring	Products containing C–N bonds	Products on the ring		
10 ^d	0.5	2.1	1.8	1.7	1.3	1.9	24.7	38.7	47.3	4.8	1.4
15 ^d	1.2	2.5	1.4	1.4	1.3	1.8	29.2	40.6	53.1	7.9	1.8
20 ^d	2.7	3.1	1.2	0.8	1.1	0.9	36.7	51.0	71.4	8.0	1.5
25 ^d	3.4	3.2	1.0	0.6	1.0	1.0	42.7	52.4	74.8	8.4	1.4
30 ^d	3.3	3.0	1.0	0.8	0.9	0.9	44.4	52.5	73.7	8.1	1.2

^a Reaction conditions: Catalyst 2.5Cu/TS-1 0.15 g; Toluene 4.7 mmol; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; 353 K.

^b TD, CS, NT, BA, CB and BM represented toluidine, cresols, nitrotoluene, benzaldehyde, cyanobenzene and benzylalcohol, respectively.

^c The molar concentrations of NH₃·H₂O 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 H₂O₂ 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 NH₃·H₂O, H₂O₂ and H₂O were 10.65, 10.27, 9.72, 9.24 and 8.87, successively.

^d The reaction time were 215min, 265min, 315min, 365min and 415min, respectively.

**Scheme 1** The products containing C–N bonds obtained in the reaction process

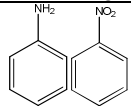
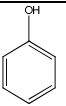
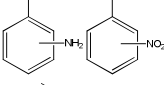


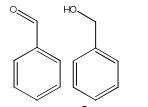



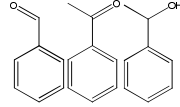

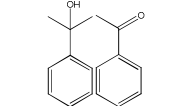

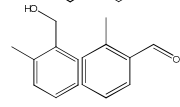
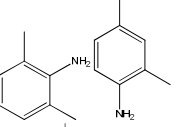
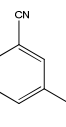
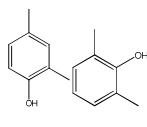
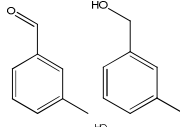



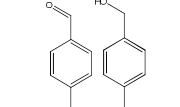


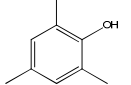
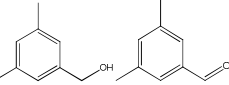
3.7 Optimization of reaction conditions

The influence of reaction temperature on the yield and selectivity of the C–N bond products was also investigated. The results were shown in Table 5. At 333 K, there were only trace amount of products containing C–N bond or C–O bond products. It indicated that the activation of the C–H bond of toluene and N–H bond of ammonia needed higher temperature. When the temperature rose to above 358 K, the self-decomposition of hydrogen peroxide and volatilizing of ammonia were serious, resulting in low utilization of aqueous ammonia and hydrogen peroxide¹⁰. The optimal temperature was 353 K, which was

slightly higher than that for benzene amination (343K)⁹. While the highest yield of toluidine obtained was 3.4%, which was higher than that for benzene amination.

The influence of the amount of hydrogen peroxide (30 wt. %) on the yield and selectivity of the C–N bond products was investigated. The results were shown in Table 6. With the increase of the dosage of hydrogen peroxide, the yield of toluidine rose at first and then decreased. The highest yield of toluidine was 3.4% when the amount of hydrogen peroxide was 1.5 mL (14.7 mmol). There was apparently no advantage for the yield to toluidine and selectivity to products containing C–N bond on the ring with excessive amount of H₂O₂. The yield of nitrotoluene increased with increasing amount of H₂O₂ and the increasing yields of other by-products containing C–O bonds exhibited the same trends as that of nitrotoluene. It was indicated that increased dosage of H₂O₂ aggravated the deep oxidation of toluidine to nitrotoluene, and promoted the oxidation of toluene

Table 9 The distribution of the products from different substrates over 2.5Cu/TS-1.^a

Aromatic substrates	Products			
	C–N bonds		C–O bonds	
	On the ring	On the side chain	On the ring	On the side chain
Benzene		--		--
Toluene				
Ethylbenzene				
Cumene	--	--		
o-xylene	--		--	
m-xylene				
p-xylene				
Mesitylene				

^a Reaction conditions: Catalyst 0.15 g; Substrate 0.5 mL; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; H₂O 25 mL; 353 K 365min.

both on the ring and on the side chain. The yield of cyanobenzene was also increased with increasing amount of H₂O₂, indicating that the excess amount of H₂O₂ could promote the formation of C–N bonds on the side chain and the oxidative dehydrogenation of benzylamine. The results of the influence of the amount of ammonia (28 wt.%) on the reaction were shown in Table 7. The increased amount of ammonia diluted hydrogen peroxide, decreased intimate contact between hydrogen peroxide and other species among reactants and catalyst, and then led to lower yield. Meanwhile, toluene could escape from the system with ammonia which made the catalytic process less effective, because the reaction system was not completely sealed. The optimal amount of ammonia for the highest yield of toluidine was 10mL.

Water was added into the NH₃·H₂O and H₂O₂ mixture for diluting. The amount of water affected the concentration of hydrogen peroxide and ammonia as well as the pH value of the mixture. As shown in Table 8, with increasing dosage of water, the molar concentration of NH₃·H₂O decreased from 4.1 mol/L to 2.1 mol/L, and that of H₂O₂ decreased from 0.7 mol/L to 0.4 mol/L. The mixtures were alkaline with the pH values ranged from 8.87 to 10.65. With the increase of the amount of water, the concentrations of NH₃·H₂O and H₂O₂ decreased. It resulted in the increase of toluidine yield and the decrease of nitrotoluene yield. When the dosage of water was few, the relatively high concentration of hydrogen peroxide would aggravate the deep

oxidation of toluidine and the volatilization of ammonia. Then the nitro-product was relatively high. The low ratio of ammonia would decrease the formation of C–N bonds, which resulted in low selectivity to products containing C–N bonds. When 30 mL water (NH₃·H₂O 2.1mol/L, H₂O₂ 0.4mol/L) was introduced, the yield of toluidine slightly decreased compared with the reaction with 25 mL water (NH₃·H₂O 2.4mol/L, H₂O₂ 0.4mol/L). It was considered that the pH value of the mixture also had effect on the catalytic reaction of toluene. The yield of toluidine was higher with lower pH, while the yield of cyanobenzene decreased.

It should be noted that the reaction time varied also with the amount of the mixture containing ammonia, hydrogen peroxide and water. Thus, the variation of the amount of ammonia, hydrogen peroxide and water was accompanied by the variation of reaction time to some extent. The actual reaction times were shown at footnotes of Table 6, Table 7 and Table 8, respectively. As a comparison, the reaction was kept for another 100 min after the mixture was added completely, to make the reaction time to be in accordance with the longest reaction time (465min), and the other reaction conditions were the same as that of the optimal ones, but the yield of toluidine (2.9%) was decreased. Toluidine was converted to nitrotoluene (1.4%), and the yield of cyanobenzene (1.1%) was almost the same as that obtained for 365 min reaction. The extra reaction time led to deep oxidation of toluidine to nitrobenzene with no promotion to the formation of

Table 10 Activation of ethylbenzene over 2.5Cu/TS-1.^a

Entry	Quantity(mg)	Molar yield(%)	Selectivity(%)
Acetyl benzene	4.6	0.9	47.3
1-phenyl ethanol	8.3	1.7	
2-ethyl aniline	9.6	1.5	
4-ethyl aniline	0.8	0.4	40.0
3-ethyl aniline	0.3	0.3	
2-ethyl phenol	2.6	0.4	12.7
4-ethyl phenol	0.5	0.2	
3-ethyl phenol	0.1	0.1	

^a Reaction conditions: Catalyst 2.5Cu/TS-1 0.15 g; Ethylbenzene 0.5 mL; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; H₂O 25 mL; 353 K, 365min.

Table 11 Activation of p-xylene over 2.5Cu/TS-1.^a

Entry	Quantity(mg)	Molar yield(%)	Selectivity(%)
4-methylbenzaldehyde	2.7	0.5	20.0
4-methylcyanobenzene	2.7	0.6	24.0
4-methylbenzylalcohol	1.8	0.4	16.0
2,5-dimethylaniline	2.0	0.4	16.0
2,5-dimethylphenol	3.0	0.6	24.0

^a Reaction conditions: Catalyst 0.15 g; p-xylene 0.5 mL; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; H₂O 25 mL; 353 K, 365min.

Table 12 The activity of mesitylene over 2.5Cu/TS-1.^a

Entry	Quantity(mg)	Selectivity(%)
3,5-dimethylbenzaldehyde	0.2	28.6
3,5-dimethylcyanobenzene	0.2	28.6
2,4,6-trimethylaniline	0.1	14.3
3,5-dimethylbenzylalcohol	0.1	14.3
2,4,6-trimethylphenol	0.1	14.3

^a Reaction conditions: Catalyst 0.15 g; mesitylene 0.5 mL; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; H₂O 25 mL; 353 K, 365min.

C–N bonds. Thus, the reaction time was stopped when the adding of the mixture (ammonia, hydrogen peroxide and water) was over. It was shown that the optimal condition of the catalytic reaction of toluene on the Cu doped TS-1 was the following: the amount of 2.5Cu/TS-1 0.15 g; the molar ratio of toluene, NH₃·H₂O and H₂O₂, 1 (4.7 mmol): 18.6 (14.7 mmol): 3.1 (87.4 mmol); 25mL water for the diluting of nitrogen source and oxidant; the feeding rate of the mixture of ammonia and hydrogen peroxide 0.1 mL/min (365 min); the reaction temperature 353 K. The effects of the reaction conditions were similar to those in our previous work^{9,10}.

3.8 The extension of substrate to alkyl-substituted-benzenes

The reaction for the formation of C–N bonds was carried out with other alkyl-substituted aromatic hydrocarbons such as ethylbenzene, p-xylene, o-xylene, m-xylene, cumene and mesitylene under the same optimal conditions. The results of qualitative analyses by GC-MS were shown in Table 9. The Cu doped TS-1 zeolite samples could also activate the ring C–H bond of other aromatic compounds to form C–N bond with the participation of aqueous ammonia and hydrogen peroxide except cumene and o-xylene. However, the byproducts of side chain C–N bond products and oxidation products could also be obtained. There were no amination products detected using cumene and o-xylene as substrates. The products from benzene were mainly aniline, nitrobenzene and phenol as reported in our previous work⁹. The corresponding amination products were obtained from ethylbenzene, m-xylene, p-xylene and mesitylene, and the product distribution of these alkylbenzene was almost in accordance with the rule of electrophilic substitution reaction. Methyl was a charge-donating group, and the ortho and para positions were charge-rich, thus the formations of C–N and C–O bonds should be theoretically much easier at o-position and p-

position on the ring. No nitro-products were detected from these substrates except benzene and toluene, which implied that the relatively low activities from these alkylbenzene to amino products made the deep oxidation of amination products difficult. We only quantified the products from catalytic results of p-xylene, ethylbenzene and mesitylene in Table 10, Table 11 and Table 12 due to the lack of the standard samples of the products that obtained from other substrates. The quantitative results of mesitylene were only expressed in terms of the quantity and selectivities to the products, because the molar yields of the products from mesitylene were calculated less than 0.1%.

The results shown in Table 10 indicated that the yields of amination products from ethylbenzene were lower than that of toluene. The yields of acetyl benzene and 1-phenyl ethanol were relatively higher than other products. It might be caused by the fact that the bond energy of C–H at α location of the side chain was lower than that at other carbon. Trace amount of cyanobenzene and benzaldehyde could also be detected, but the yields of these two products were less than 0.1%, then we did not give them out in Table 10.

The quantitative data of p-xylene in Table 11 and mesitylene in Table 12 showed that the yields of products containing C–N bonds on the ring were lower than that on the side chain. With the number of methyl substituent increasing, the yield of ring products decreased which might be the effect of steric hindrance that influenced the interaction between catalyst and the aromatic ring. With the number of methyl substituent increasing, the exclusion effect might prevent the access of the larger molecules to zeolite framework pores, and the effect can also prevent the formation of some larger precursors within the TS-1 pores, which might leads to the lower yields of ring products.

Table 13 The distribution of C–N and C–O bonds-products on the ring from toluene and ethylbenzene.^a

Substrates	Selectivity/%		
	Ortho products of C–N bonds/ C–O bonds	Meta products of C–N bonds/ C–O bonds	Para products of C–N bonds/ C–O bonds
Toluene	68.3/64.5	21.5/23.2	10.2/12.3
Ethylbenzene	71.0/68.6	17.0/20.9	12.0/10.5

^a Reaction conditions: Catalyst 0.15 g; toluene 4.7 mmol; NH₃·H₂O 87.4 mmol; H₂O₂ 14.7 mmol; H₂O 25 mL; 353 K, 365 min.

3.9 Discussion

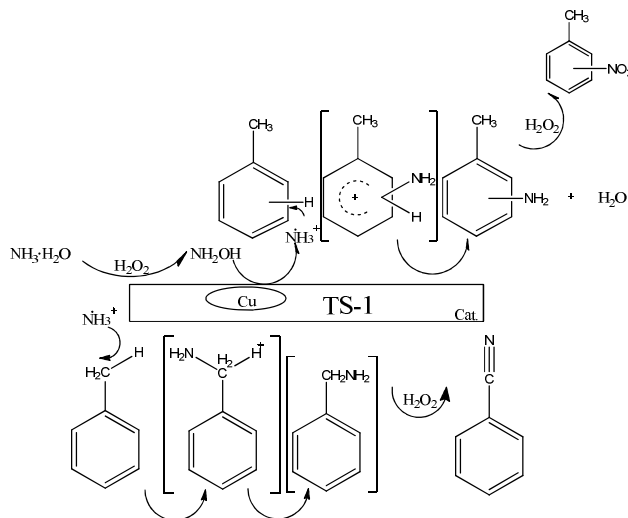
The selectivity of the products containing C–N bonds on the aromatic ring kept stable with the loading of the Cu species on the TS-1 catalyst. With the increase of the Cu content, the selectivity to products on the ring (C–N and C–O) increased from 63.9% to 75.0%, but the yield and selectivity to products on the side chain became lower on the Cu doped catalysts, indicating that the Cu species could probably promote the selectivity of the ring products to some extent and inhibit the activation of C–H bonds on the side chain. We also used CuO and Cu (NO₃)₂ as catalyst for C–H bond activation of toluene. The results revealed that the products obtained over CuO were the same as those on Cu/TS-1 with much lower activity, where the yield to toluidine was only 0.25%. However, no products were obtained when Cu (NO₃)₂ was used as catalyst. It was considered that the catalytic activity was related to the Cu–O, and the higher catalytic yield to toluidine over Cu/TS-1 might be related to Cu–O–Ti bond as reported in our previous work⁹.

The distribution of the products containing C–N bonds on the ring under the optimal conditions in the activation of toluene was shown in Table 13. It should be noted that the calculation of the selectivity of C–N bond products was confined to those on the ring. The results showed obvious selectivity to ortho toluidine and ortho nitrotoluene. The distribution of the products from ethylbenzene (Table 10, Table 13) brought out the similar trend. What's more, the hydroxylation products on the ring both from toluene and ethylbenzene gave also the similar trend. Although methyl and ethyl were charge-donating substituent, the ring products only showed the ortho advantage. Thus, the high selectivity on the ortho-position was not only due to the effect of charge-donating substituent (methyl and ethyl), the interaction of the substrate with Cu/TS-1 catalyst might also gave an ortho-orientation of the products. The yields of o-, m- and p-substitution ring products from toluene were shown in Table S1-Table S6.

The formation of C–N bonds and C–O bonds were competing with each other. The molar ratio of the C–N bond products on the ring and the C–O bond products on the ring ranged from 1.2:1 to 1.4:1. The data revealed that the formation of C–N bonds on the ring had a slight advantage than the formation of C–O bonds on the ring in the reaction system. The inhibiting effect of Cu species to the formation of hydroxylation products on the ring of toluene was not obvious as that on the benzene ring⁹ because of the charge donating effect of methyl.

Based on the above data, a tentative proposition of the reaction mechanism for the direct formation of C–N bond from toluene over the Cu doped TS-1 catalyst was given in Scheme 2. The Cu doped TS-1 catalyst catalyzed the partial oxidation of ammonia by hydrogen peroxide to produce hydroxylamine¹⁰, while the catalyst activated also the C–H bonds of toluene simultaneously.

In the amination of benzene with hydroxylamine⁵⁵, the active species formed was considered to be NH₃⁺ in acidic system.



Scheme 2 The proposed reaction mechanism

However, the present reaction proceeded in alkali system, thus we deemed that hydroxylamine reduced to protonated amino cation (NH₃⁺) and hydroxamino (NHOH⁺) instantaneously. The instantaneously generated NH₃⁺ reacted with the aromatic ring to produce an amino intermediate, followed by producing toluidine, and then a fraction of toluidine turned to nitrobenzene by deep oxidation. The data shown in Table 8 indicated that the yield of toluidine was higher at a relatively lower pH value which was in accordance with our previous work²⁶⁻²⁸ in acidic system. Meanwhile, the protonated amino cation attacked the C–H bonds of the side chain to form benzylamine, and then be oxidized further to cyanobenzene. The instantaneously generated hydroxylamine and NH₃⁺ was unstable in alkaline system resulting in the fact that the yield of toluidine was not as high as that when using hydroxylamine hydrochloride as aminating reagent in acidic system²⁶⁻²⁸. We also used methylcyclohexane as substrate to proceed the catalytic reaction in a control experiment, but no amination products were obtained, indicating that the activity of amination process in the present reaction system was related to the benzene ring structure. Further deep study is needed.

4. Conclusion

In summary, the Cu/TS-1 catalyst exhibited obvious activity for the formation of C–N bonds from toluene, ammonia and hydrogen peroxide. The yield of 3.4% to toluidine was obtained with 1.0% to nitrobenzene. Cyanobenzene was also obtained as the C–N bond product on the side chain with the yield of 1.0%. Nitrotoluene was considered to be the deep oxidation product of the initially formed toluidine, and benzylamine was considered to be the intermediate from toluene to cyanobenzene. The selectivity to the ring was higher than that to the side chain while the selectivity to the formation of C–N bonds was higher than that of C–O bonds. The formation of C–N bonds on the ring had ortho orientation advantage. With the increase of the number of methyl substituent, the yield of ring products decreased which might be caused by steric hindrance and exclusion effect of the pore structure of zeolite. The Cu doped TS-1 catalyst catalyzed the partial oxidation of ammonia by hydrogen peroxide to produce hydroxylamine, and then generated NH₃⁺ instantaneously. It is illustrated that C–N bond could be

constructed from extended aromatic hydrocarbons and the low-cost nitrogen source (aqueous ammonia) via one-step process on the basis of our previous work.

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Notes and references

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

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The formation of C–N bonds from toluene and ammonia both on the ring and the side chain was realized on Cu-modified TS-1 catalyst, and the ring products had ortho-orientation advantage.

