

Supplementary Information for

Metal-free carbon nitride catalyst for toluene oxidation

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Supplementary Methods

1. Experimental section

Materials. SiC, BN, MgO, CaO, and Al₂O₃ were purchased from Beijing Chemical Works.

Synthesis of carbon nitride. The carbon nitride was synthesized by heat treatment of melamine precursors in a muffle furnace. 3 g melamine was put into an alumina crucible with a cover and placed into muffle furnace. It was calcinated at 650 °C with a ramping rate of 5 °C/min, and kept at this temperature for 2h. After cooling down to room temperature, the product was ground to powder. The obtained sample was denoted as CN.

Synthesis of Fe₃O₄ and Fe₂O₃. Fe₃O₄ was prepared using a modified ammonia-assisted precipitation technique. In this method, iron chloride precursors (Fe²⁺/Fe³⁺ molar ratio = 1:2) were dissolved in a 1:1 ethanol/water mixture under a nitrogen atmosphere, while being stirred mechanically for 30 minutes. Then, the 10% ammonia solution was added to adjust the solution pH to 9.0. The black suspension was stirred for 1 hour at room temperature, followed by an additional 1 hour at 60 °C in an oil bath. After cooling to room temperature, the solid phase was separated using a magnet, washed with ethanol, and dried at 80 °C in a vacuum oven. For the synthesis of Fe₂O₃, a similar procedure was followed, with

FeCl₃·6H₂O used as the Fe precursor. The resulting solid was then thermally treated at 550 °C for 2 hours in a muffle furnace.

Synthesis of MnO₂. 1.2 g KMnO₄ was dissolved in 150 mL of distilled water. Then, 2.6 mL HCl (37 wt%) was added to the above solution, and the mixture was stirred thoroughly. The resulting solution was added to a Teflon-lined autoclave. The reaction took place at 140 °C for 12 hours. After cooling to room temperature, the product was filtered and washed with distill water and ethanol. The resulting solid was then dried in an oven at 100 °C.

2. Catalyst Evaluation

The catalytic activity tests were conducted in a continuous-flow fixed-bed reactor. For toluene oxidation, 100 mg of the catalyst (40-60 mesh) was positioned at the center of the quartz reactor. Toluene was fed into the reactor by passing an air stream through a toluene reservoir kept in an ice bath. A separate air stream was used to adjust the toluene vapor concentration to 1000 ppm. The concentrations of reactants and products are analyzed by an online gas chromatograph equipped with the FID detector for toluene and the TCD detector for CO₂. And the toluene conversion (X_{tol}) is as follows:

$$X_{tol} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

3. Catalyst Characterization

X-ray diffraction (XRD) patterns were obtained using a Bruker D8ADVANCE diffractometer. The instrument operated at an applied voltage of 40 kV and a current of 30 mA, with Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) as the excitation source. Fourier transform infrared spectroscopy (FT-IR) was recorded using a Nicolet iS5 infrared spectrometer. Scanning electron microscopy (SEM) tests were conducted using an SU8020 cold field emission scanning electron microscope manufactured by HITACHI. The sample powder was attached to the sample holder using conductive adhesive. N₂ adsorption-desorption measurement was conducted at 77 K using a Belsorp-max automatic surface area and pore size analyzer. The surface areas were calculated based on the model of Brunauer-Emmett-Teller (BET). X-ray photoelectron spectroscopy (XPS) were recorded on the Thermo ESCA LAB 250 instruments. Transmission electron microscope (TEM) was performed using the JEM-2100F instrument with an acceleration voltage of 200 kV. The instrument was equipped with an energy-dispersive X-ray spectrometer. O₂ temperature programmed desorption (O₂-TPD) and H₂ temperature programmed desorption (H₂-TPR) performed using a ChemBET Pulsar TPR/TPD instrument. Before detection, the samples were pretreated under N₂ flow at 150 °C for 30 min. As for O₂-TPD, after cooling to 50 °C, O₂ was introduced to adsorption for 60 min. Then treating the samples were maintained at 50 °C in N₂ flow for 1h, and the sample was heated to 350 °C with a ramp of 10 °C/min. As for H₂-TPR, after cooling to 50 °C, the flowing

gas was switched to a 5 vol% H₂/Ar and the sample was heated to 800 °C with a ramp of 10 °C/min. In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted using a Nicolet 6700 infrared spectrometer. During the toluene adsorption tests, the sample was first pretreated in N₂ at 200 °C for 15 minutes. After cooling to room temperature, the spectrum was collected as the background. Using N₂ as the carrier gas, toluene was introduced into the in-situ reaction cell through a bubbling method, and the spectrum data was recorded once the signal stabilized. Electron paramagnetic resonance (EPR) results were obtained on a JES-FA 200 EPR spectrometer.

4. Density functional theory (DFT) calculations

All the DFT calculations in this work are performed by the VASP code. The PAW pseudopotentials and optPBE-vdw functional are employed for structural optimization with an energy cutoff of 520 eV. The 2×2×1 slab model containing respective three atomic layers are adopted with the vacuum layer of 20 Å for C₃N₄ (001). The bottom two layers and the lattice vectors are fixed, and the top one layer and the adsorbed atoms are fully relaxed with 2×2×1 and 5×5×1 Monkhorst-Pack k-point sampling until the force on each atom is less than 0.01 eV/Å for the C₃N₄ (001).

Supplementary Figures and Tables

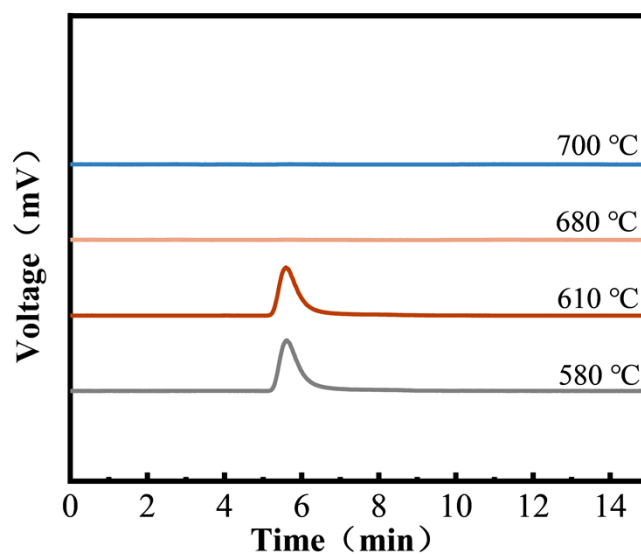


Fig. S1 Peak signal of gas chromatography FID.

The final oxidation products of toluene by carbon nitride were primarily identified as CO_2 and H_2O . The FID signal in Fig S1 showed only toluene, with no selective oxidation products such as benzyl alcohol, benzaldehyde, or benzoic acid detected. Additionally, combined with the TCD result and quantitative analysis, toluene was completely oxidized to CO_2 and H_2O .

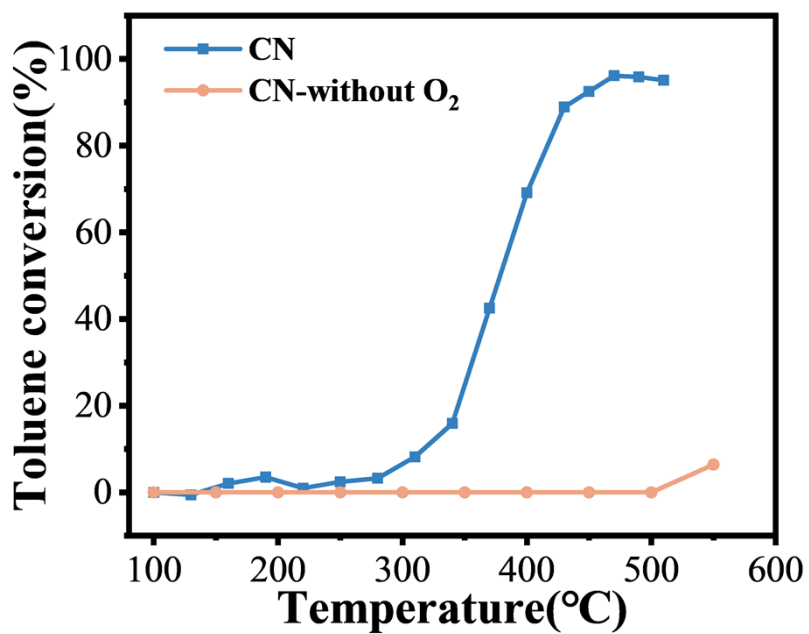


Fig. S2 Catalytic activities of toluene over CN and CN-without O₂. Reaction conditions: 0.1g of catalyst, C₇H₈ 1000 ppm, space velocity (SV) =24,000 mL g⁻¹ h⁻¹, air balance, and “without O₂” referred to using N₂ as the balance.

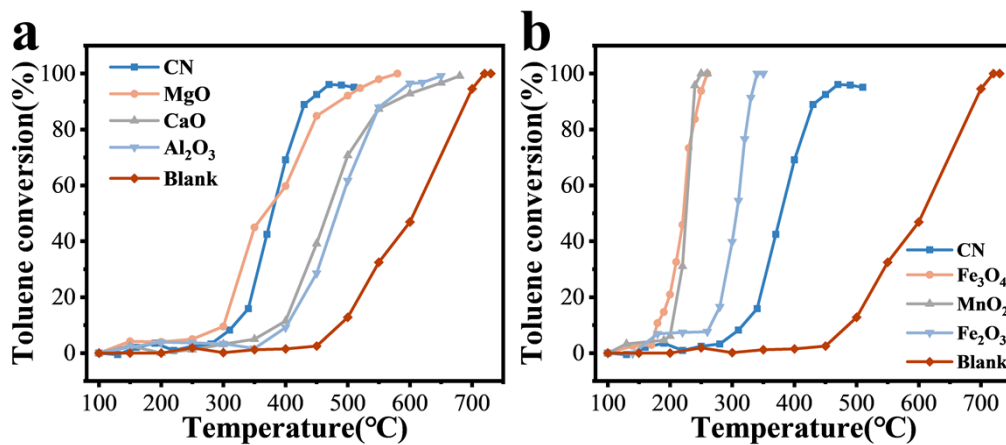


Fig. S3 Catalytic activities of toluene over CN and different metal oxides. (a) Toluene conversion over CN, MgO, CaO, Al₂O₃, and blank. (b) Toluene conversion over CN, Fe₃O₄, MnO₂, Fe₂O₃, and blank. Reaction conditions: 0.1g of catalyst, C₇H₈ 1000 ppm, space velocity (SV) = 24,000 mL g⁻¹ h⁻¹, air balance.

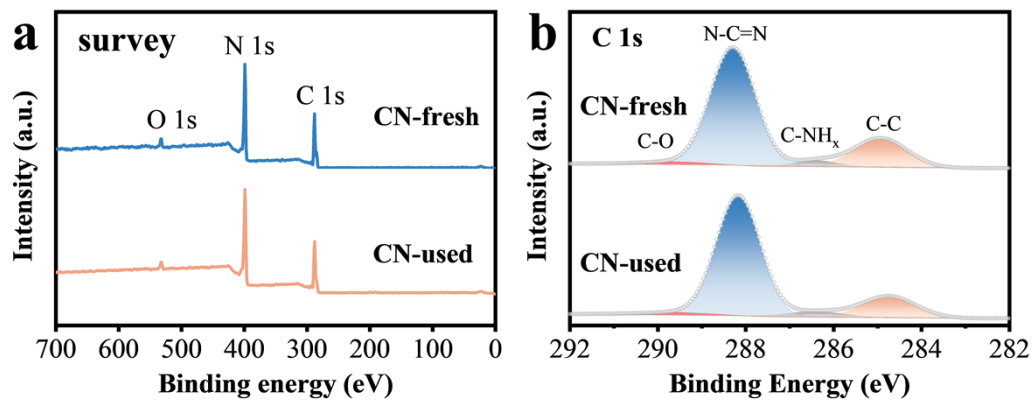


Fig. S4 (a) XPS patterns and (b) FT-IR spectra of CN-fresh and CN-used samples.

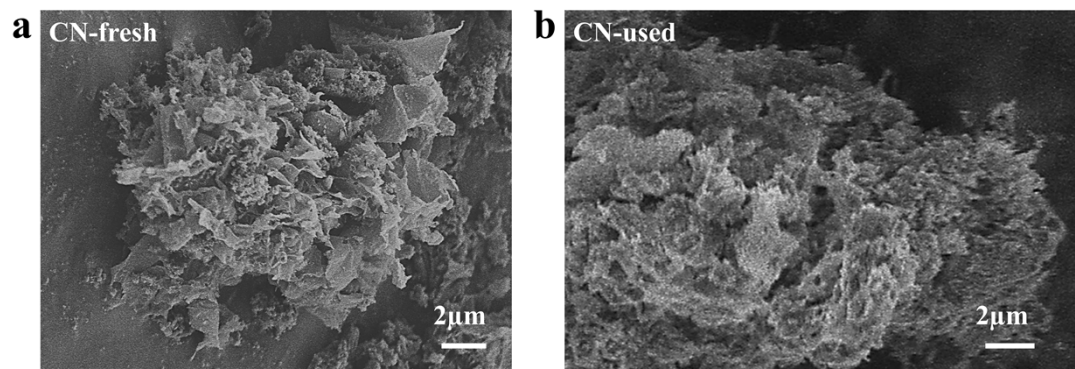


Fig. S5 SEM images of (a) CN-fresh and (b) CN-used samples.

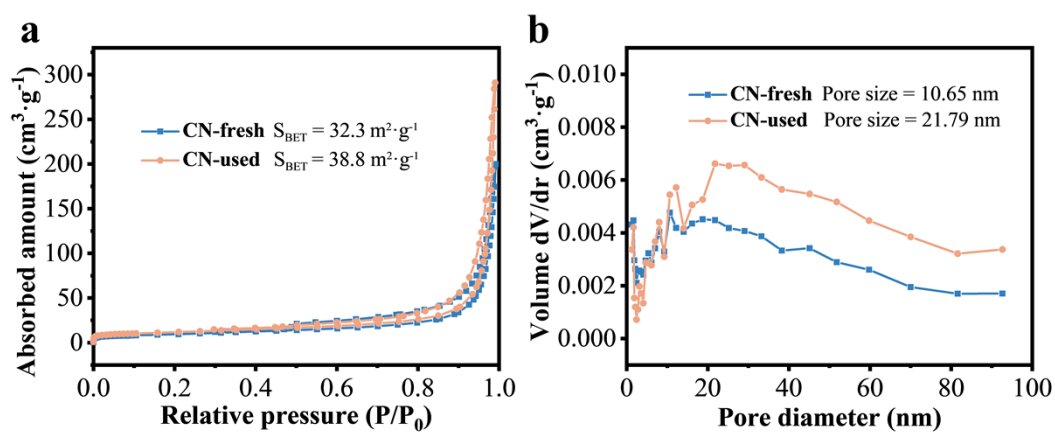


Fig. S6 (a) N_2 adsorption-desorption isotherms and (b) BJH pore size distribution of CN-fresh and CN-used samples.

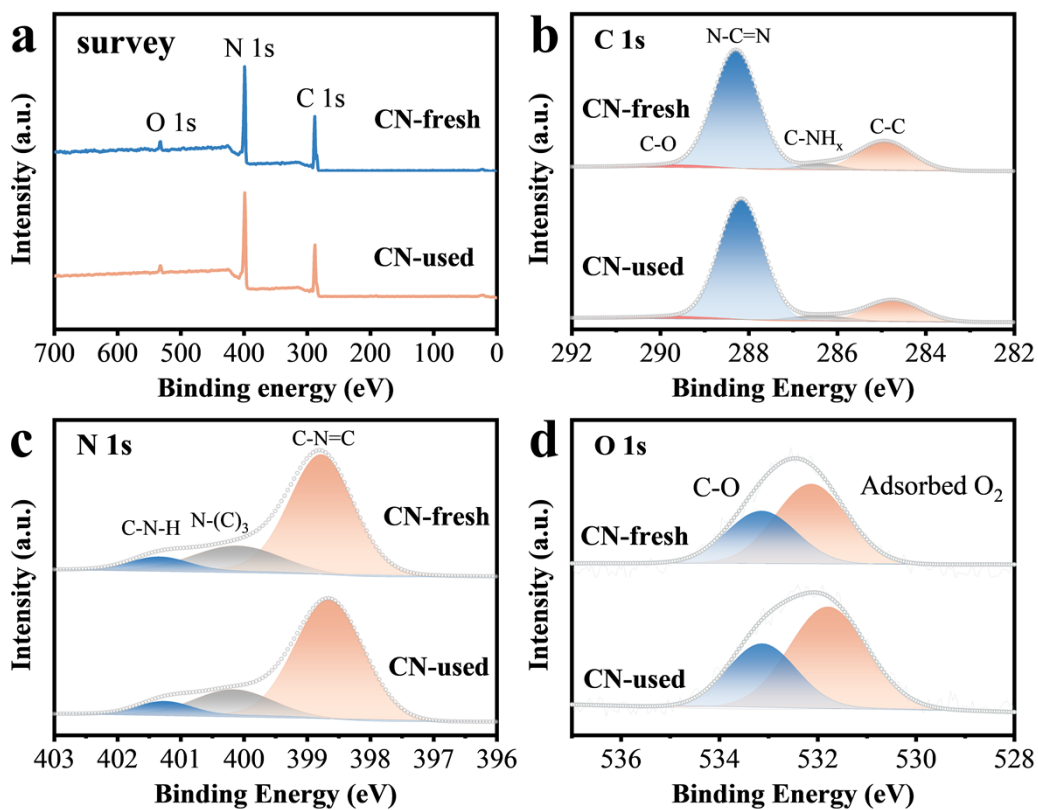


Fig. S7 (a) Normalized survey XPS spectra, (b) Normalized C 1s XPS spectra, (c) Normalized N 1s XPS spectra, and (d) Normalized O1s XPS spectra of CN-fresh and CN-used samples.

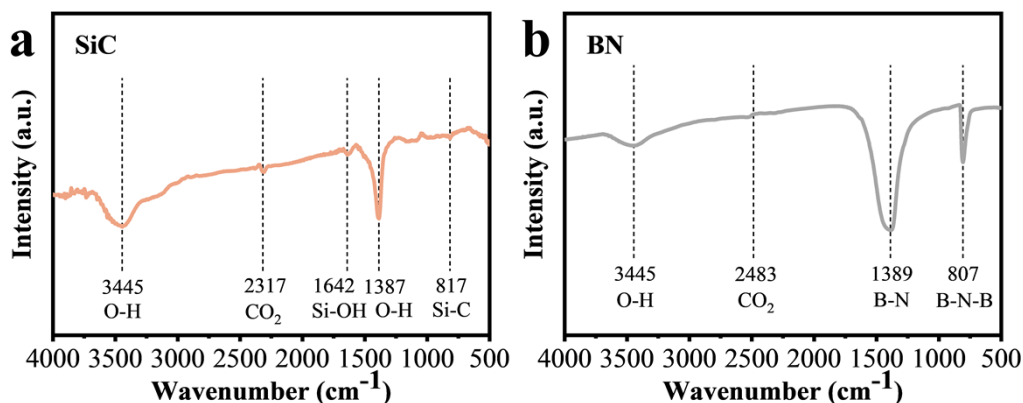


Fig. S8 FT-IR spectra of (a) SiC and (b) BN.

The FTIR spectra in Fig. S8(a) showed that the peak at 817 cm^{-1} was attributed to the stretching vibration of the Si–C bond, and the broad peaks at 1642 cm^{-1} and 3445 cm^{-1} originated from the stretching vibrations of Si–OH and O–H groups, respectively. The peak at 1387 cm^{-1} corresponded to the bending vibration of H–O–H in the sample, and the absorption peak at 2317 cm^{-1} assigned to the asymmetric stretching vibration of CO_2 in the air. The FTIR spectra in Fig. S8(b) confirmed that BN exhibited bands around 807 cm^{-1} and 1389 cm^{-1} , corresponding to the bending vibration of the B–N–B bond and the stretching vibration of the B–N bond, respectively. The absorption peak at 2483 cm^{-1} assigned to the asymmetric stretching vibration of CO_2 in the air. And the absorption band centered at 3445 cm^{-1} was associated with the bending vibration of O–H. Therefore, combined with the XPS results, the above data suggested that the oxygen species in SiC and BN were primarily composed of CO_2 and H_2O .

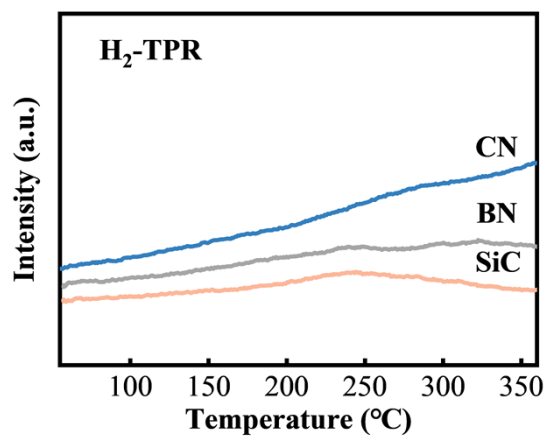


Fig. S9 H₂-TPR profiles of CN, BN, and SiC.

Comparing the H₂-TPR results of the metal-free catalysts, this low-temperature reduction peak indicated better reducibility, suggesting the presence of more chemisorbed oxygen, which was consistent with O₂-TPD results and the toluene activity evaluation results.

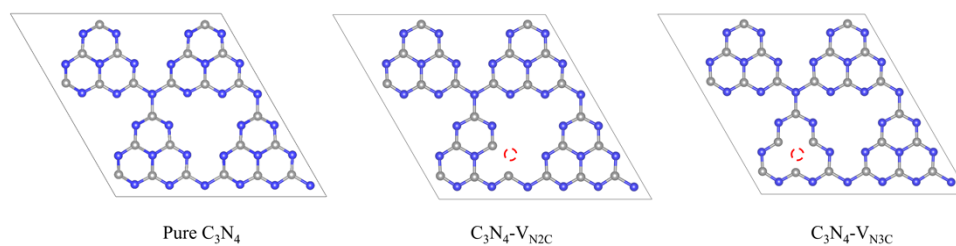


Fig. S10 Schematic structures of the carbon nitride with and without nitrogen vacancies. (gray represents C, blue represents N)

The nitrogen vacancies were introduced into the carbon nitride skeletons using melamine as the precursor via high-temperature thermo-condensation. As the calcination temperature increased, high-temperature conditions disrupted the weak C-N bonds at the edges of the triazine rings, leading to nitrogen atom loss and the formation of nitrogen vacancies. According to the results of Table S3 from XPS results, we found that nitrogen vacancies formed on the surface during the high-temperature polymerization process. And the V_{N2C} and V_{N3C} shown in Fig. S10 are the two potential nitrogen vacancy sites that may be formed.

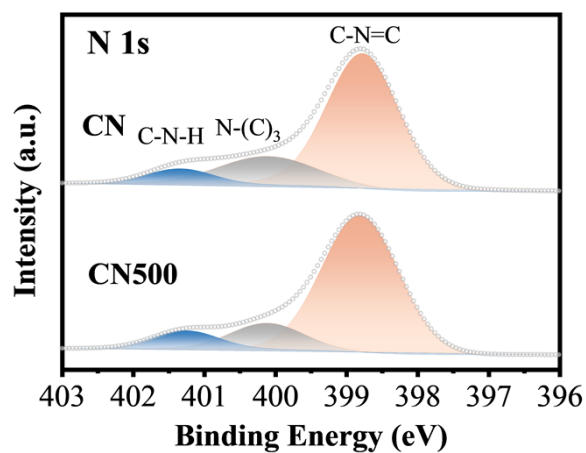


Fig. S11 N 1s XPS spectra of CN and CN500.

Depending on the calcination temperature, the samples were named CN500 and CN (CN650). And the fitted N 1s XPS spectra of CN and CN500 shown in Fig. S11 exhibited three characteristic peaks at 398.8 eV, 400.1 eV, and 401.3 eV, which could be assigned to C–N=C, N–(C)₃, and C–N–H, respectively. And the ratio of N_{2C}/N_{3C} decreased from 5.58 for CN500 to 3.72 for CN, suggesting that nitrogen vacancies are primarily located at the N_{2C} sites.

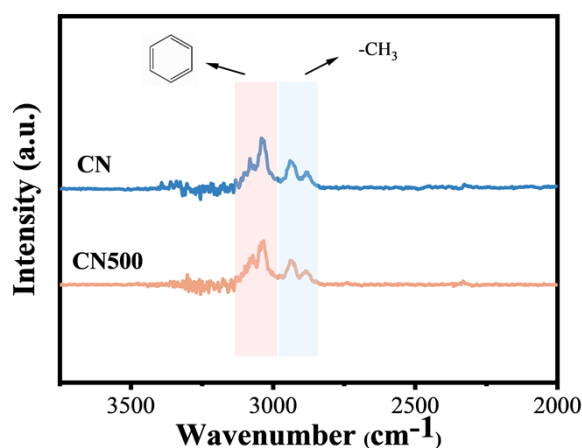


Fig. S12 In-situ C_7H_8 -adsorbed DRIFT spectra of CN and CN500.

First, we investigated the adsorption of toluene on the CN surface employing in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). As shown in Fig. S12, the peaks at 3097 cm^{-1} , 3071 cm^{-1} , and 3038 cm^{-1} corresponded to the C-H stretching vibrations of the aromatic ring, and the peaks at 2933 cm^{-1} and 2881 cm^{-1} were attributed to the symmetric and asymmetric stretching vibrations of aliphatic C-H bonds. The result clearly demonstrated that CN had a certain adsorption capacity for toluene. Combined with the ability of CN to adsorb and activate oxygen, this confirmed that toluene oxidation on CN followed the L-H mechanism.

Furthermore, we investigated whether toluene and oxygen exhibited competitive adsorption. We synthesized CN500 using melamine as the precursor at $500\text{ }^\circ\text{C}$, and our previous work had showed that CN contained more nitrogen vacancies than CN500.¹ The DRIFTS result in Fig. 12 revealed that the adsorption of toluene on CN and CN500 was similar, indicating that nitrogen vacancies had no significant effect

for toluene adsorption. Additionally, π -electrons in carbon nitride interacted across adjacent conjugated planes, forming a stable π - π stacking structure, which facilitated toluene adsorption via π - π interactions with its benzene ring. Given that the adsorption and activation sites for oxygen on CN were located at nitrogen vacancies, we reasonably inferred that toluene and oxygen were non-competitive adsorption on CN, indicating that the reaction mechanism followed a non-competitive L-H mechanism.

Table S1. Catalytic activity for toluene oxidation over various metal free catalysts.

Samples	T₅₀ (°C)	T₉₀ (°C)
CN	378	435
SiC	478	650
BN	535	636
Blank	608	690

Table S2. Catalytic activity for toluene oxidation over CN and metal oxide catalysts.

Samples	T₅₀ (°C)	T₉₀ (°C)
Fe₃O₄	220	245
MnO₂	226	238
Fe₂O₃	306	328
CN	378	435
MgO	366	485
CaO	466	577
Al₂O₃	482	563
Blank	608	690

Table S3. The ratio of C to N calculated based on the XPS results

Samples	C/N
CN	0.94
CN500	0.65

Depending on the calcination temperature, the samples were named CN500 and CN (CN650). To confirm the presence of nitrogen vacancies, we characterized the surface properties of the carbon nitride with XPS. As shown in Table S3, the most significant change was the surface C/N ratio, which increased from 0.65 for CN500 to 0.94 for CN, indicating the formation of nitrogen vacancies during the high-temperature polymerization process.

References

1. T. Gan, J. X. Yang, D. Morris, X. F. Chu, P. Zhang, W. X. Zhang, Y. C. Zou, W. F. Yan, S. H. Wei and G. Liu, *Nat. Commun.*, 2021, **12**, 2741.