

Supporting Information

Electrocatalytic reduction of N₂ to NH₃ by MIL-88 derived pod-like Fe₇Se₈/C nanomaterials under ambient conditions

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EXPERIMENTAL SECTION

Synthesis of MIL-88. 1.35 g of ferric chloride hexahydrate and 0.58 g of fumaric acid together were added to 25 mL of ultrapure water, sonicated for 10 min and then transferred to magnetic stirring to continue stirring for 30 min, followed by transferring it to a 50 mL hydrothermal reactor liner, and the assembled hydrothermal reaction device was placed in a preheated 65 °C blast drying oven for 12 h of reaction. After the end of the reaction cooled down to room temperature, the as-prepared product was centrifuged with ultrapure water and ethanol for three times, and finally sealed with perforated aluminum foil and placed in a vacuum drying oven at 70°C overnight to obtain the fleshy pink powder of MIL-88.^{1,2}

Synthesis of Fe₇Se₈/C and Fe₇Se₈ catalysts. After grinding the prepared MIL-88, a certain mass of MIL-88 and Se powder was weighed according to the ratio of 1:2 by mass and were mixed and ground evenly, and then spread it in a porcelain boat. Ar was chosen as the protective gas for the reaction, and the temperature was increased to 650°C with a gradient of 1.5°C min⁻¹ and kept the temperature of 650°C for 2 h before cooling to room temperature. The obtained Fe₇Se₈/C product was in the form of black powder. The preparation of Fe₇Se₈ was the same as that of Fe₇Se₈/C, with the difference of replacing MIL-88 with Fe powder.³

Preparation of the working electrode. 5 mg of catalyst was ultrasonically dispersed in 1 mL of dispersant, which was a mixture of 0.75 mL of isopropanol and 0.25 mL of ultrapure water. After ultrasonication for 1 h, 20 µL of Nafion

solution (5 wt.%) was added and continued to be ultrasonicated for 10 min to obtain a well-dispersed ink mixture. Then, 0.1 mL of the obtained ink-like mixture was applied dropwise on the treated carbon paper, spreading as flat as possible with the coating area of 1 cm², and the catalyst loading was 0.5 mg_{cat} cm⁻².

Characterizations. X-ray diffraction (XRD) patterns were recorded on a D/MAX-TTR III (CBO) instrument using Cu K α radiation ($\lambda = 1.542 \text{ \AA}$). Scanning electron microscopy (SEM) was performed using a Hitachi S-8220 with a Hitachi S-4800. Transmission electron microscopy (TEM) studies were performed using a Tecnai G2 F20 U-TWIN with a Tecnai G2 T20 S-TWIN, and high-resolution transmission electron microscopy (HR-TEM) were obtained from the Tecnai G2 F20 U-TWIN. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 20 Xi. Nitrogen adsorption and desorption experiments were carried out using the specific surface area and porosity analyzer models Micromeritics APSP 2460 as well as ASAP 2420-4. Ultraviolet-visible (UV-vis) spectra were performed on a Hitachi U-3900H UV-vis spectrophotometer.

Electrochemical Measurements. All of the electrochemical tests were performed by the Shanghai Chenhua CHI660E electrochemical workstation using an H-type electrolytic cell adapted to the three-electrode system as the reaction device. The as-prepared Fe₇Se₈/C or Fe₇Se₈ was used as the working electrode (WE), Ag/AgCl as the reference electrode (RE), and Pt mesh as the counter electrode (CE). The anode chamber was separated from the cathode

chamber using a Nafion 211 proton membrane. Ultrapure N₂ (99.999%) or Ar (99.999%) was continuously blown into 0.1 M Na₂SO₄ electrolyte for at least 30 min before each test. The potentials were converted to reversible hydrogen electrode (RHE) values by [Equation 1](#):

$$E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + 0.059 \times pH + 0.197 V \quad (1)$$

Determination of NH₃. The electrolytic reduction products were detected using salicylic acid color development method combined with UV-vis absorption spectroscopy.⁴ The steps of the method were as follows: 8 mL of electrolyte was removed from the cathode chamber, and then oxidizing solution, color developing solution and catalyst solution were added sequentially. 100 μL of oxidizing solution containing NaClO (pCl = 4 ~ 4.9) and 0.75 M NaOH was firstly added to the electrolyte, and then 1000 μL of color-developing solution containing 0.4 M sodium salicylate, 0.32 M NaOH and 100 μL of catalyst solution (200 mg of sodium nitrosferricyanide dihydrate dissolved in 20 mL of ultrapure water) were added. After being left in the dark for 2 h, it was measured at 660 nm and the corresponding absorbance was recorded. A standard curve was obtained by preparing ammonium chloride solution with known concentration gradient (electrolyte was 0.1 mol L⁻¹ Na₂SO₄), and after linear fitting a standard linear fitting equation was obtained $y=0.4423x-0.0047$, $R^2=0.998$ ([Figure S8](#)).

Determination of N₂H₄. Hydrazine hydrate was detected by Watt and Chrisp's method using UV-vis absorption spectrophotometer.⁵ The specific tests and steps were as follows: 5.99 g of p-C₉H₁₁NO, 30 mL of HCl and 300 mL of

C₂H₅OH were mixed homogeneously to be used as a color developing reagent. 2 mL of electrolyte was removed from the cathode chamber and 2 mL of color developing reagent was added. The resulting solution was stirred at room temperature for 15 min and then its absorbance was tested at 455 nm. A standard curve was obtained by preparing N₂H₄-H₂O solution with known concentration gradient (electrolyte was 0.1 mol L⁻¹ Na₂SO₄), and after linear fitting a standard linear fitting equation was obtained as $y=0.1702x+0.034$, $R^2=0.999$ (Figure S9).

Calculations of the NH₃ yield rate and FE. The rate of NH₃ yield rate is calculated according to Equation 2:

$$R_{\text{NH}_3 \text{ yield}} = (c_{\text{NH}_3} \times V) / (t \times m_{\text{cat}}) \quad (2)$$

where c_{NH_3} is the NH₃ concentration ($\mu\text{g mL}^{-1}$), V is the electrolyte volume (mL), t is the electrolysis time (h), m_{cat} is the catalyst mass loading (mg). Considering that there are 3 mol electrons transferred to produce 1 mol NH₃, the Faradaic efficiency (FE) can be calculated by Equation 3:

$$\text{FE} = (3F \times c_{\text{NH}_3} \times V) / 17Q \quad (3)$$

where F is Faraday constant (96485 C mol^{-1}), Q is average electricity quantity throughout the reaction process.

GRAPHICS

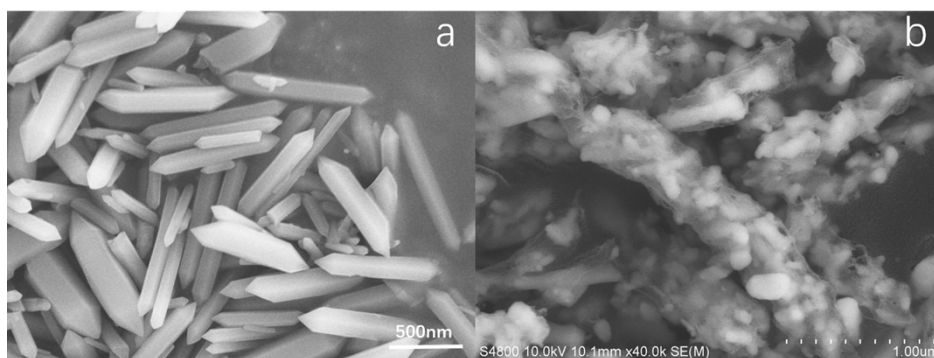


Fig. S1. SEM images of (a) MIL-88 and (b) Fe₇Se₈/C.

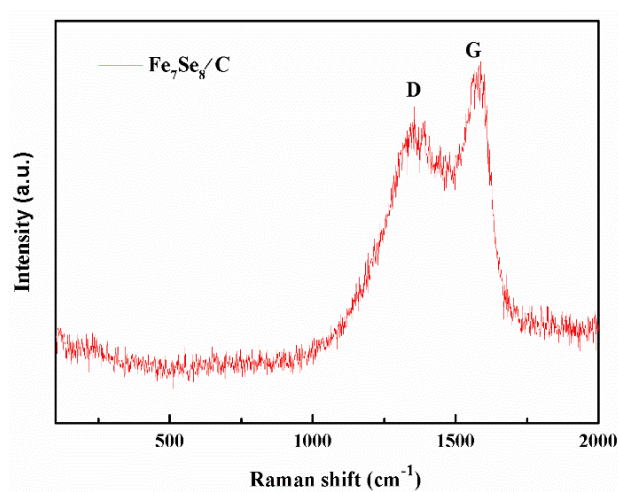


Fig. S2. Raman pattern of Fe₇Se₈/C.

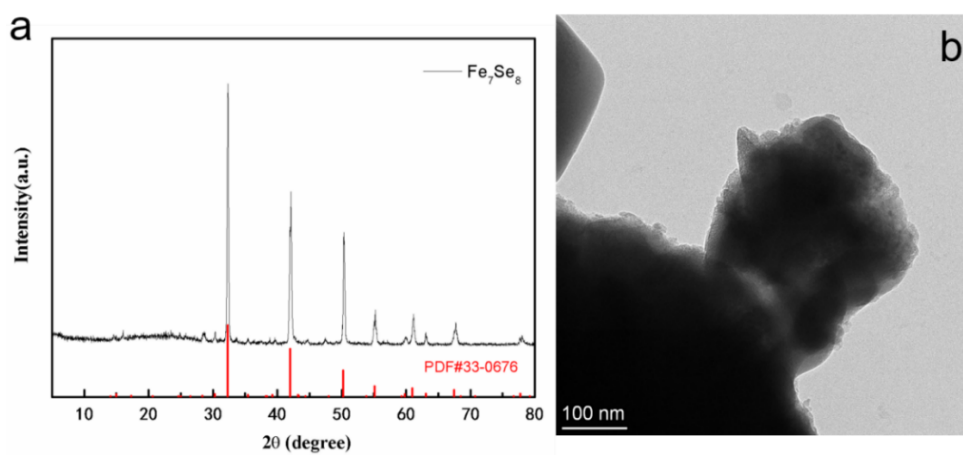


Fig. S3. (a) XRD patterns and (b) TEM image of Fe₇Se₈.

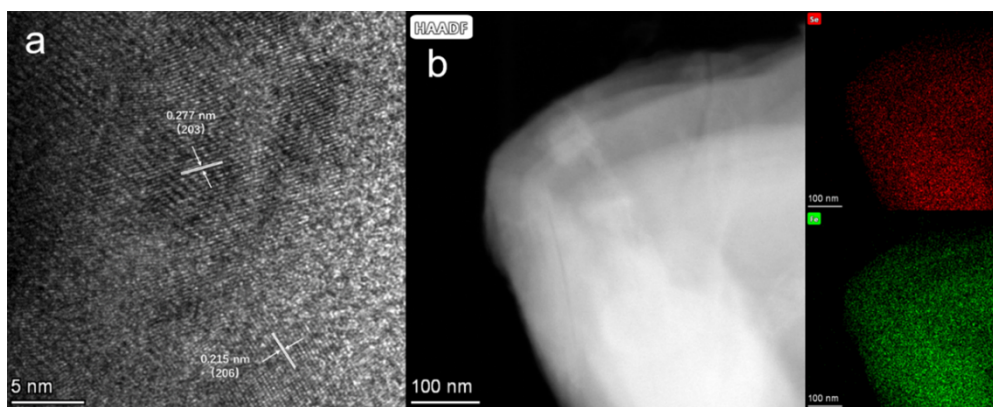


Fig. S4. (a) HR-TEM picture, (b) HAADF-STEM picture and corresponding EDS elemental distribution of Fe_7Se_8 .

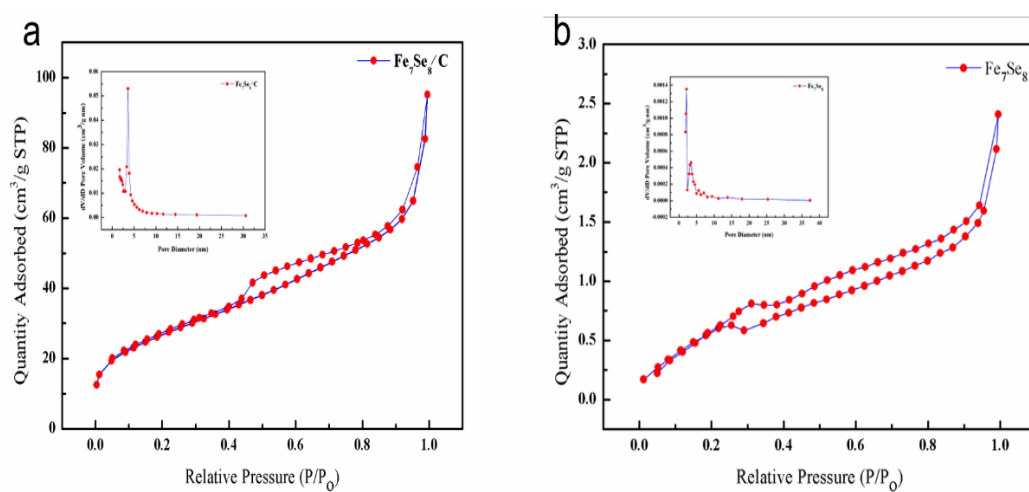


Fig. S5. BET isotherm of (a) $\text{Fe}_7\text{Se}_8/\text{C}$ and (b) Fe_7Se_8 illustrated with corresponding BJH aperture distribution

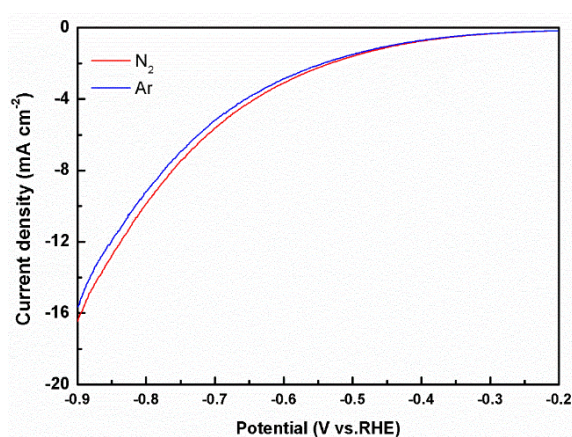


Fig. S6. LSV curves of $\text{Fe}_7\text{Se}_8/\text{C}$ in different atmospheres.

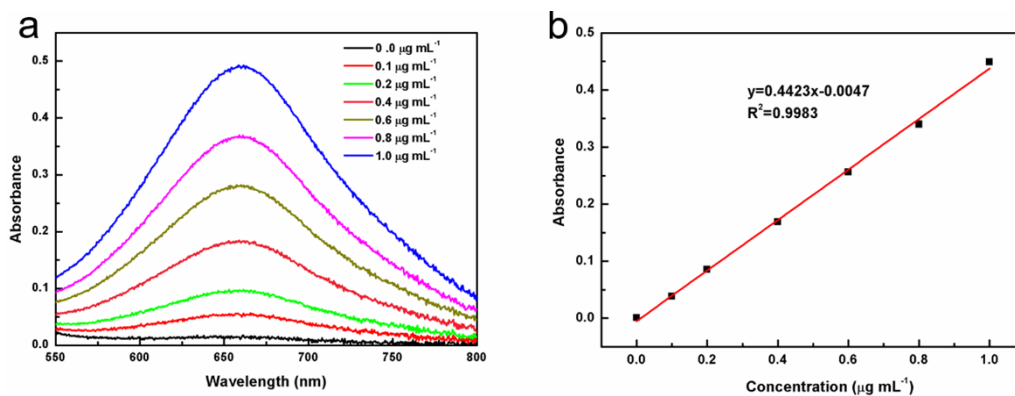


Fig. S7. (a) UV-vis absorbance plots and (b) linear fitting curves and fitting equations of NH_4Cl standard solutions at gradient concentrations.

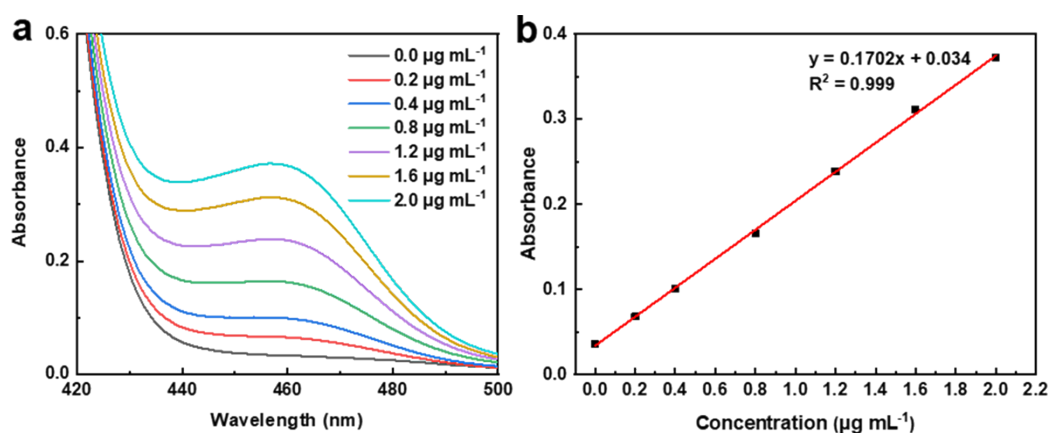


Fig. S8. (a) UV-vis absorbance plots, (b) linear fitting curves and fitting equations of $\text{N}_2\text{H}_4\text{-H}_2\text{O}$ standard solutions at gradient concentrations.

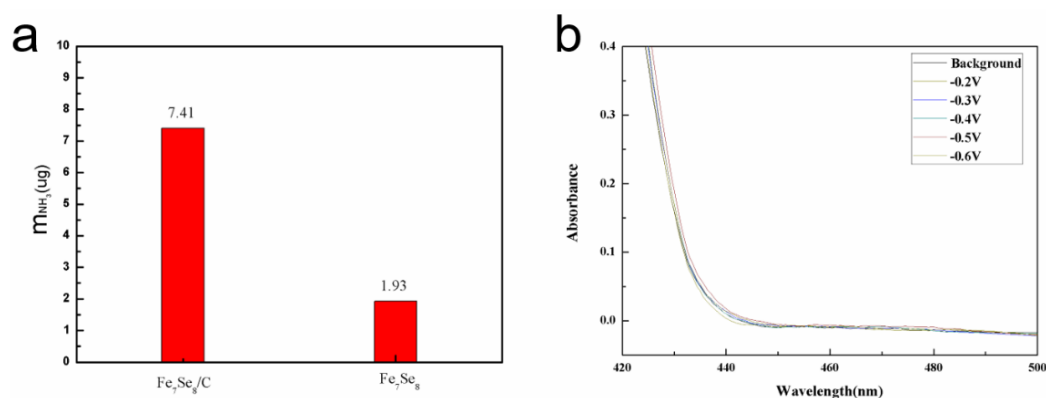


Fig. S9. (a) Plots of the yield of NH_3 rate comparison of $\text{Fe}_7\text{Se}_8/\text{C}$ and Fe_7Se_8 , (b) $\text{N}_2\text{H}_4\text{-H}_2\text{O}$ detection of $\text{Fe}_7\text{Se}_8/\text{C}$ catalyst.

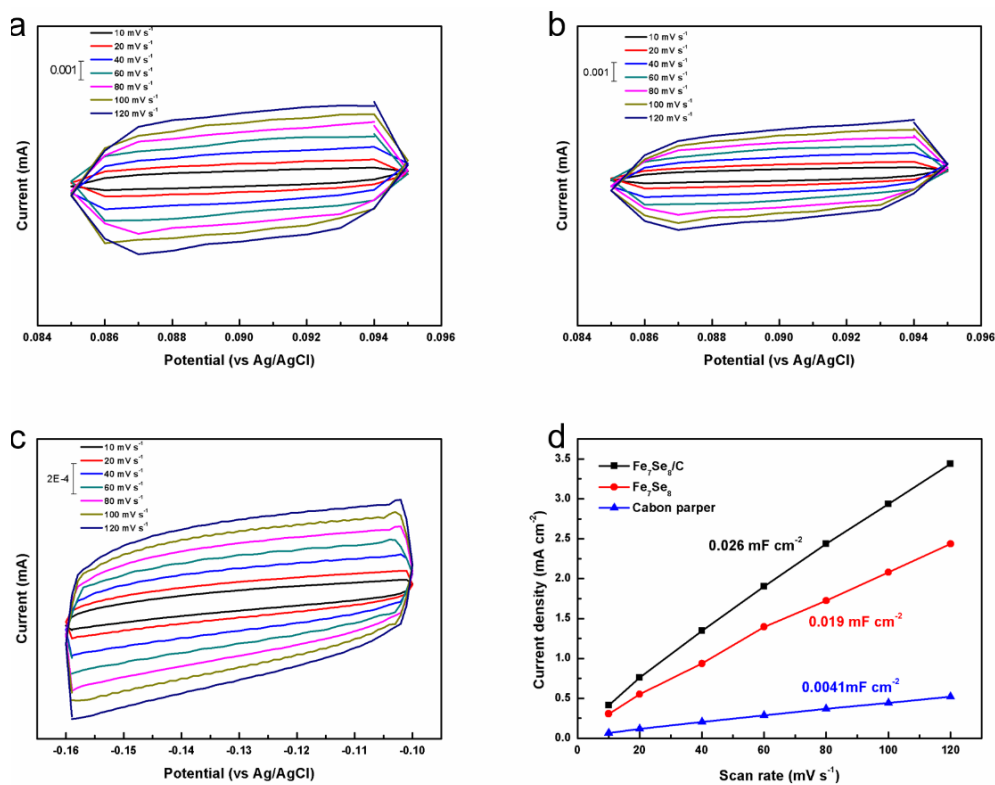


Fig. S10. CV curves of (a) $\text{Fe}_7\text{Se}_8/\text{C}$, (b) Fe_7Se_8 , (c) carbon paper, and (d) comparison of bilayer capacitance of $\text{Fe}_7\text{Se}_8/\text{C}$, Fe_7Se_8 , carbon paper.

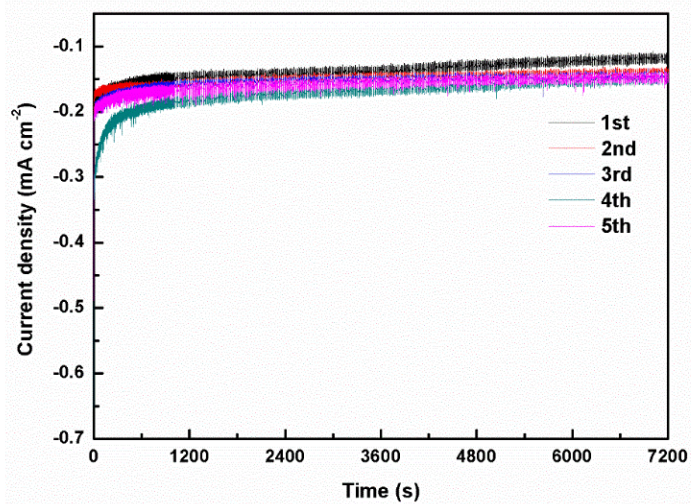


Fig. S11. Current density-time curve corresponding to five cycles of $\text{Fe}_7\text{Se}_8/\text{C}$.

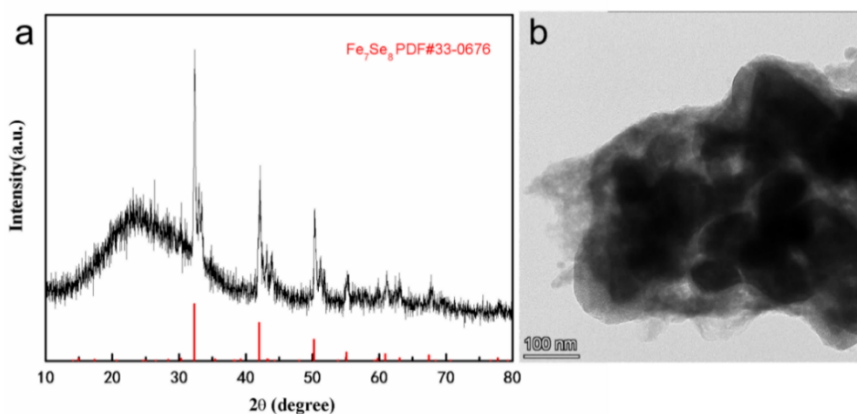


Fig. S12. (a) XRD patterns and (b) TEM image of $\text{Fe}_7\text{Se}_8/\text{C}$ catalyzed.

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