Electronic Supplementary Information

Deep eutectic-solvothermal synthesis of nanostructured Fe₃S₄ for electrochemical N₂ fixation under ambient conditions

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Experiment Section

Chemicals

Polyethylene glycol 200 (PEG 200, AR), ammonium chloride (NH₄Cl, AR), ethyl alcohol (C₂H₅OH, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid (HCl, 35.0-38.0%) was obtained from Beijing Chemical Works. Salicylic acid (C₇H₆O₃, 99.5%), sodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O, 99.0%), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O, 99.0%), sodium hypochlorite solution (NaClO, available chlorine 4.0%) were purchased from Macklin Ltd. Thiourea (CH₄N₂S, 99.0%), iron(II) chloride tetrahydrate (FeCl₂·4H₂O, 99.5%), nickel(II) chloride hexahydrate (NiCl₂·6H₂O, 99.5%), cobalt(II) chloride hexahydrate (CoCl₂·6H₂O, 99.5%) and p-dimethylaminobenzaldehyde (C₉H₁₁NO, 99.0%) were bought from J&K Ltd. Carbon paper electrode (Toray, THP-H-60) was purchased from Alfa. 5 wt. % Nafion solution and 212 Nafion membrane were obtained from Dupont. Nitrogen (N₂, 99.99%) was bought from Beijing Beiwen Gas factory (Beijing, China). All chemicals were of analytical grade and used as received without further purification. Milli-Q water of 18.2 MΩ cm⁻¹ was used in all experiments.

Synthesis of Fe₃S₄ nanosheets

In a typical synthesis process, the PEG based DES was obtained by simply mixing PEG 200 and thiourea in the molar ratio of 2: 1. Unless otherwise stated, the PEG based DES was prepared in 2: 1 molar ratio of PEG 200 and thiourea. Then, 5 mmol FeCl₂·4H₂O (0.994 g) was dissolved in 40 ml PEG based DES under oxygen-free conditions. Next, the mixture was placed into a 50 ml Teflon-lined stainless steel autoclave. The autoclave was treated at 200 °C and maintained for 16 h before cooling in the air. The resulting precipitates were washed thoroughly with deionized (DI) water and ethanol three times and then dried in air at 60 °C for 12 h.

Synthesis of NiS₂ nanosheets

NiS₂ nanosheets were prepared using the same procedure, except with NiCl₂·6H₂O (5 mmol, 1.188 g) as metal precursor.

Synthesis of CoS₂ nanosheets
CoS$_2$ nanosheets were prepared using the same procedure, except with CoCl$_2$·6H$_2$O (5 mmol, 1.190 g) as metal precursor.

**Characterizations**

The IR spectra were obtained by coupling of the attenuated total reflection (ATR-IR) equipment with the FTIR spectrometer (Prestige 21, Shimadzu, Japan, DTGS detector) in the range of 600 to 4500 cm$^{-1}$. Solution $^1$H NMR experiments were performed on a Bruker DMX 300 NMR spectrometer (300 MHz) with d$_6$-dimethyl sulfoxide as the standard. The chemical shift data were later processed by the MestReNova Program. Differential scanning calorimetry (DSC) was performed using a Q2000 DSC (TA Instruments-Waters LLC, USA) system at a heating rate of 10 °C min$^{-1}$. Thiourea was run in an aluminum pan in a sealed furnace from room temperature to 200 °C. PEG 200 was cooled to −70 °C before heating up to 20 °C, while the prepared DES was cooled to −120 °C before heating up to 20 °C. Thermal gravimetric analysis (TGA) was conducted by the instrument (Q50, TA Instrument Company, America). The viscosity ($\eta$) of the PEG based DES was measured at 298.15 K using an Anton Paar DMA 5000 M for five times and the average value was reported. The conductivity of the PEG based DES was measured by using a conductivity meter (DDS-307A, Shanghai INESA Scientific Instrument Co., Ltd, China) for five times at 298.15 K. The deviation of the equipment was less than ±0.5%.

The XRD patterns of the samples were recorded using an X-ray diffractometer (Rigaku D/Max-2500) using Cu Kα as X-ray radiation ($\lambda = 1.5418$ Å) under 40 kV and 30 mA. Data were collected in Bragg-Brettano mode using 0.02° divergence with a scan rate of 2° min$^{-1}$. The SEM images, EDS spectra and elemental mapping images of the samples were acquired using a Hitachi SU 8010 field emission scanning electron microscope coupled with energy dispersive X-ray spectroscopy operated at 15.0 kV. The samples were prepared by dropping catalyst powder dispersed in isopropanol onto 300 nm silicon dioxide-coated silicon wafer (Zhejiang Lijing Technology Corp., China) using micropipettes and were dried under ambient conditions. The TEM patterns were carried out using a JEM-1011 transmission electron microscope at 100.0 kV. The samples were prepared by dropping catalyst powder dispersed in isopropanol onto carbon-coated copper TEM grids (Beijing Zhongxing Braim Technology Corp., China) using micropipettes and were dried under ambient conditions. The Raman spectra were
conducted using a FT Bruker RFS 106/S spectrometer equipped with a 532 nm laser. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromatic Al Kα radiation. The 500 μm X-ray spot was used for SAXPS analysis. The base pressure in the analysis chamber was about 3×10⁻⁹ mbar. Typically, the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing in XPS experiments. UV-vis experiments were performed on a UV-3600 Plus UV-Vis-NIR Spectroscopy (Shimadzu Corp., Japan).

**Computational details**

First-principles calculations were performed using the DFT with the projector augmented wave pseudo potentials as implemented in the Vienna Ab initio Simulation Package. The exchange-correlational functional was the generalized gradient approximation with the Perdew-Burke-Ernzerhof. The cutoff energy the plane wave-basis expansion was set to 400 eV and the atomic relaxation was continued until the forces acting on atoms were smaller than 0.05 eVÅ⁻¹. The Brillion zone was sampled with 1 × 1 × 1 Monkhorst-Pack k-point mesh, and the Gaussian smearing of σ was 0.05 eV. The van der Waals interaction was taken into account within DFT+U(3-5)(Ueff=3.4eV for Ni and Co, Ueff=3.29eV for Fe). The surfaces are represented as slabs, periodically repeated in the z direction perpendicular to the surface and separated from their images by a 10 Å vacuum gap. The 4-layer slabs are used to describe the surfaces, with two bottom layers being fixed in the bulk position, and the top two layers and adsorbed N₂ are allowed to fully relax.

**Electrochemical measurements**

Before NRR tests, the Nafion membrane was pretreated by heating it in H₂O₂ (5%) aqueous solution at 80 °C for 1 h and ultrapure water at 80 °C for another 1 h, respectively. The electrochemical experiments were conducted on CHI 660E electrochemical workstation by using a three-electrode configuration with Fe₃S₄ working electrode, Pt gauze counter electrode and Ag/AgCl (saturated KCl electrolyte) reference electrode, respectively. All potentials were converted to reversible hydrogen electrode (RHE). Typically, 6 mg of catalyst powder was dispersed in 1 mL mixture of water and ethanol (1:1, v/v) and then 20 μL of 5 wt. % Nafion solution was added. The suspension was immersed in an ultrasonic bath for 30 min to
prepare a homogeneous ink. The working electrodes were prepared by depositing 50 μl catalyst ink onto 1x1 cm$^2$ carbon paper electrode (catalyst loading: ~0.30 mg cm$^{-2}$).

For electrochemical NRR, potentiostatic tests were carried out in N$_2$ saturated diluted hydrochloric acid electrolyte (pH = 1, 50 mL), which was bubbled with N$_2$ for 30 min before the measurement. A two-compartment cell with three-electrode configuration was separated by Nafion membrane. Pure N$_2$ was continuously fed into the cathodic compartment with a properly positioned sparger so that the whole cathode was hit by the gas bubbles during the experiments. The potentiostatic NRR tests are conducted at desired conditions for 2h. Unless otherwise stated, all experiments were performed at ambient temperature (25 ± 2 °C) and electrode potentials were converted to the RHE scale using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.059 * \text{pH}$.

**Determination of ammonia**

Concentration of produced ammonia was spectrophotometrically determined by the indophenol blue method with modification. First, 2 mL aliquot of the solution was removed from the electrochemical reaction vessel. Then, 2 mL of a 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, followed by addition of 1 mL of 0.05 M NaClO and 0.2 mL of an aqueous solution of 1 wt % $C_5FeN_6Na_2O\cdot2H_2O$ (sodium nitroferricyanide dihydrate). After 2 h at room temperature, the absorption spectrum was measured using an ultraviolet-visible spectrophotometer. The formation of indophenol blue was determined using the absorbance at a wavelength of 655 nm. The concentration–absorbance curves were calibrated using standard NH$_4$Cl solution with NH$_3$ concentrations of 0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 μg mL$^{-1}$ in 0.1 M HCl. The calibration curve below was used to calculate the NH$_3$ concentration. The fitting curve ($y = 0.338x + 0.016$, $R^2 = 0.999$) shows good linear relation of absorbance value with NH$_3$ concentration by three times independent calibrations.

**Determination of hydrazine**

The hydrazine present in the electrolyte was estimated by the method of Watt and Chrisp. A mixture of $p$-dimethylaminobenzaldehyde (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Calibration curve was plotted as follow: First, preparing a series of reference solutions, by pipetting suitable volumes of the hydrazine hydrate-
nitrogen 0.1 M HCl solution in colorimetric tubes; Second, making up to 5 mL with 0.1 M HCl solution; Third, adding 5 mL above prepared color reagent and stirring 10 min at room temperature; Fourth, the absorbance of the resulting solution was measured at 455 nm, and the yields of hydrazine were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent. Absolute calibration of this method was achieved using standard hydrazine monohydrate solutions with N₂H₄ concentrations of 0.0, 0.5, 1.0, 1.5, 2.0 and 2.5 µg mL⁻¹ in 0.1 M HCl. The calibration curve below was used to calculate the N₂H₄ concentration. The fitting curve \( y = 0.515x + 0.013, R^2 = 0.999 \) shows good linear relation of absorbance value with N₂H₄ concentration by three times independent calibrations.

**15N isotope labeled experiment**

The 15N isotope labeled experiment was carried out using 15N₂ as the feeding gas in 0.1 M HCl electrolyte. After electrolysis at \(-0.4\) V vs. RHE for 2 h, the obtained NH₄⁺-contained electrolyte was detected by using ¹H NMR spectroscopy (Bruker Avance III 400 MHz).

**Faradic efficiency**

The Faradic efficiency (FE) was calculated from the total charge \( Q \) passed through the cell and the total amount of NH₃ produced. The total amount of NH₃ produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH₃ molecule, the Faradaic efficiency can be calculated as follows:

\[
FE = \frac{3F \times c(NH₃) \times V}{17 \times Q}
\]

where \( F \) is the Faraday constant (96485 s A mol⁻¹), \( c(NH₃) \) is the measured NH₃ concentration, \( V \) is the volume of electrolyte.

The rate of NH₃ formation was calculated using the following equation:

\[
v(NH₃) = \frac{c(NH₃) \times V}{m \times t}
\]

Where \( t \) is the reduction reaction time and \( m \) is the catalyst mass.
Fig. S1. DSC curves for a) PEG 200 and thiourea, b) PEG based DES, and c) phase diagram of PEG 200, thiourea and DES. The PEG based DES was prepared by mixing PEG 200 and thiourea at different molar ratio. The PEG based DES attaches eutectic point (-89 °C) at 2:1 molar ratio of PEG 200 and thiourea.
Fig. S2. a) TGA curve, b) IR spectrum and c) $^1$H NMR spectrum of PEG 200, thiourea and PEG based DES in 2: 1 molar ratio of PEG 200 and thiourea.
Fig. S3. XRD pattern of as-obtained Fe$_3$S$_4$ nanosheets.

Fig. S4. EDS spectrum of the as-obtained Fe$_3$S$_4$ nanosheets. The stoichiometric proportion of Fe and S is around 3: 4.
Fig. S5. a) N$_2$ adsorption/desorption isotherms, and b) corresponding pore size distribution of Fe$_3$S$_4$ nanosheets.

Fig. S6. XPS spectrum for the Fe$_3$S$_4$ nanosheets.
Fig. S7. Raman spectrum of Fe$_3$S$_4$ nanosheets.

Fig. S8. Quantitative determination of NH$_3$ generated by the as-prepared Fe$_3$S$_4$ nanosheets.
Fig. S9. Absolute calibration of the indophenol blue method for estimating NH$_3$ concentration, using NH$_4$Cl solutions of known concentration as standards. a) UV-Vis curves of indophenol assays with NH$_3$ after incubated for 2 hours at room temperature; b) calibration curve used for calculation of NH$_3$ concentrations. The absorbance at 655 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with NH$_3$ concentration ($y = 0.338x + 0.016$, $R^2 = 0.999$) of three times independent calibration curves. The inset in b) shows the chromogenic reaction of indophenol indicator with NH$_3$. 
Fig. S10. Absolute calibration of the Watt and Chrisp (p-dimethylamino-benzaldehyde) method for estimating N$_2$H$_4$ concentration, using N$_2$H$_4$ solutions of known concentration as standards. a) UV-Vis curves of various N$_2$H$_4$ concentration after incubated for 10 min at room temperature; b) calibration curve used for estimation of N$_2$H$_4$ concentration. The absorbance at 455 nm was measured by UV-Vis spectrophotometer, and the fitting curve shows good linear relation of absorbance with N$_2$H$_4$ concentration ($y = 0.515x + 0.013$, $R^2 = 0.999$) of three times independent calibration curves. The inset in b) shows the chromogenic reaction of p-dimethylamino-benzaldehyde indicator with N$_2$H$_4$.

Fig. S11. The linear sweep voltammetric curve using Fe$_3$S$_4$ nanosheets as the working electrode in pH=1 HCl aqueous solution.
Fig. S12. UV–Vis absorption spectra of the electrolyte stained with indophenol indicator before and after charging at −0.4 V versus RHE for 2 h in Ar atmosphere on the Fe₃S₄ catalyst.

Fig. S13. UV–Vis absorption spectra of the electrolyte stained with indophenol indicator before and after charging at −0.4 V versus RHE for 2 h in N₂ atmosphere on bare carbon paper (CP) electrode and Fe₃S₄/CP electrode, respectively.
Fig. S14. UV–Vis absorption spectra of the electrolyte stained with indophenol indicator after charging at open circuit for 2 h in N₂ atmosphere on Fe₃S₄/CP electrode.

Fig. S15. ¹H NMR analysis of the electrolyte fed by ¹⁴N₂ and ¹⁵N₂ after the electrolytic reaction.
Fig. S16. Yield rate of NH$_3$ and FE under different N$_2$ flow rate at −0.4 V vs. RHE. All experiments were carried out in 0.1 M HCl at room temperature and ambient pressure.

Fig. S17. Chronoamperometric curve of Fe$_3$S$_4$ on the carbon paper support measured in N$_2$-saturated 0.1M HCl electrolyte at −0.4 V vs. RHE for continuous 20 h.
Fig. S18. The SEM image of Fe₃S₄ nanosheets after stability test in 0.1 M HCl.

Fig. S19. XRD pattern for Fe₃S₄ after stability test in 0.1 M HCl.

Fig. S20. XPS spectra for Fe₃S₄ after stability test in 0.1 M HCl.
Fig. S21. Physical characterizations of CoS$_2$ and NiS$_2$ catalysts. a), b) SEM images, c), d) EDS analyses, and e), f) XRD patterns of the a), c), e) CoS$_2$ and b), d), f) NiS$_2$ catalysts prepared via the solvothermal synthesis method.
Fig. S22. HRTEM images of a) CoS\textsubscript{2} and b) NiS\textsubscript{2} catalysts. HRTEM of CoS\textsubscript{2} shows the atomic lattice fringes of the catalysts with lattice plane spacing determined to be 0.27 nm, corresponding to the (200) lattice spacing of CoS\textsubscript{2}, while 0.25 nm represents (210) lattice spacing of CoS\textsubscript{2}. HRTEM of NiS\textsubscript{2} shows the atomic lattice fringes of the catalysts with lattice plane spacing determined to be 0.28 nm, corresponding to the (200) lattice spacing of NiS\textsubscript{2}. The results show that (200) lattice plane are the most exposed lattice plane both for CoS\textsubscript{2} and NiS\textsubscript{2} catalysts.
Fig. S23. Comparison of the Fe$_3$S$_4$ catalyst with CoS$_2$ and NiS$_2$ catalysts for electrocatalytic NRR. NH$_3$ yield rates and Faradaic efficiencies of the Fe$_3$S$_4$, CoS$_2$ and NiS$_2$ catalysts on the carbon paper support measured in N$_2$-saturated 0.1M HCl electrolyte at −0.4 V vs. RHE. Inset: chronoamperometric curves obtained for each catalyst.

Fig. S24. a) The side view of the NiS$_2$(200) (Ni atom in green, S atom in yellow); b) the side view of the CoS$_2$(200) (Co atom in purple, S atom in yellow); c) the side view of the Fe$_3$S$_4$(220) (octahedral Fe atoms in light purple, tetrahedral Fe atoms in black, S atom in yellow). All surfaces are with (2×1) cell.
Fig. S25. The most preferred N$_2$ adsorption configuration on Fe$_3$S$_4$(220) surface. (octahedral Fe atoms in light purple, tetrahedral Fe atoms in black, S atoms in yellow, N atoms in blue).
Table S1. Some represented reports for N\textsubscript{2} fixation.

<table>
<thead>
<tr>
<th>Process</th>
<th>Catalyst</th>
<th>Conditions</th>
<th>Reaction system</th>
<th>NH\textsubscript{3} yield/ Faradaic efficiency</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrocatalysis</td>
<td>Fe\textsubscript{3}S\textsubscript{4} nanosheets</td>
<td>Room Temperature, 0.1 M HCl</td>
<td>75.5 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. 6.45%(FE)</td>
<td>This work</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Au/TiO\textsubscript{2} Sub-nanocluster</td>
<td>Room Temperature, 0.1 M HCl</td>
<td>21.4 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. 8.11%(FE)</td>
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<tr>
<td></td>
<td>Au nanorods</td>
<td>Room Temperature, 0.1 M KOH</td>
<td>1.648 μg h\textsuperscript{-1} cm\textsuperscript{-2}</td>
<td>4</td>
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<tr>
<td></td>
<td>amorphous -Au/CeOx–RGO</td>
<td>Room Temperature, 0.1 M HCl</td>
<td>8.3 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. 10.10%(FE)</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>VN nanowires</td>
<td>Room Temperature, 0.1 M HCl</td>
<td>2.48 × 10\textsuperscript{-10} mol\textsuperscript{-1} s\textsuperscript{-1} cm\textsuperscript{-2} 3.58%(FE)</td>
<td>7</td>
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<td></td>
<td>N-doped carbon foam</td>
<td>Room Temperature, 0.1 M HCl</td>
<td>15.7 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. 1.45%(FE)</td>
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</tr>
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<td></td>
<td>Rh nanosheets</td>
<td>Room Temperature, 0.1 M KOH</td>
<td>23.88 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. 0.217%(FE)</td>
<td>9</td>
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</tr>
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<td></td>
<td>Bi\textsubscript{4}V\textsubscript{2}O\textsubscript{11}/CeO\textsubscript{2} nanofibers</td>
<td>Room Temperature, 0.1 M HCl</td>
<td>23.21 μg h\textsuperscript{-1} mg\textsuperscript{-1} cat. 10.16%(FE)</td>
<td>10</td>
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</tr>
<tr>
<td></td>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>250 °C, 25 bar N\textsubscript{2} Molten hydroxide</td>
<td>35% (N\textsubscript{2} conversion rate)</td>
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<tr>
<td></td>
<td>MoS\textsubscript{2}</td>
<td>Room Temperature, 0.1 m Na\textsubscript{2}SO\textsubscript{4}</td>
<td>8.08 × 10\textsuperscript{-11} mol\textsuperscript{-1} s\textsuperscript{-1} cm\textsuperscript{-2} 1.17%(FE)</td>
<td>12</td>
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<tr>
<td>Photocatalysis</td>
<td>Au/(BiO)\textsubscript{2}C\textsubscript{3}O\textsubscript{4} hybrid</td>
<td>Room Temperature</td>
<td>H\textsubscript{2}O</td>
<td>38.23 μmol h\textsuperscript{-1} g\textsuperscript{-1} cat.</td>
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<td>black silicon</td>
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<td>H\textsubscript{2}O</td>
<td>13.3 mg m\textsuperscript{-2} h\textsuperscript{-1}</td>
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<td>Bi\textsubscript{2}O\textsubscript{3}Br</td>
<td>Room Temperature</td>
<td>H\textsubscript{2}O</td>
<td>1.38 mmol h\textsuperscript{-1} g\textsuperscript{-1} cat.</td>
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<td>CuCr-nanosheet</td>
<td>Room Temperature</td>
<td>H\textsubscript{2}O</td>
<td>2.84 μmol h\textsuperscript{-1} g\textsuperscript{-1} cat.</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>5 wt% Ru@n-GaN nanowires</td>
<td>10 °C H\textsubscript{2} (75%), N\textsubscript{2} (25%)</td>
<td>514 μmol g\textsuperscript{-1} cat. for 24h</td>
<td>17</td>
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</tr>
<tr>
<td>Harsh-conditions</td>
<td>LaCoSi</td>
<td>400 °C, 0.1 MPa</td>
<td>N\textsubscript{2}, H\textsubscript{2}</td>
<td>1,250 μmol h\textsuperscript{-1} g\textsuperscript{-1} cat.</td>
<td>18</td>
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<tr>
<td></td>
<td>Pr\textsubscript{0.6}Ba\textsubscript{0.4}Fe\textsubscript{0}</td>
<td>400 °C Wet N\textsubscript{2}</td>
<td>1.07×10\textsuperscript{-6} mol m\textsuperscript{-2} s\textsuperscript{-1}</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>System</td>
<td>Conditions</td>
<td>Gas Mixture</td>
<td>Activity</td>
<td>Ref.</td>
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<tr>
<td>$\text{Cu}<em>{0.2}\text{O}</em>{3.5}$</td>
<td>7.8 wt% Ru / $\text{Y}_3\text{Si}_3$</td>
<td>400 °C, 0.1 MPa</td>
<td>$\text{N}_2$, $\text{H}_2$</td>
<td>1.9 mmol h$^{-1}$ g$^{-1}$ cat.</td>
<td>20</td>
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<tr>
<td>$\text{Fe}_2\text{O}_3$/activated carbon</td>
<td>250 °C</td>
<td>Molten hydroxide</td>
<td>$8.27 \times 10^{-9}$ mol s$^{-1}$ cm$^{-2}$</td>
<td>21</td>
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Reference