Supplementary Information

Electromagnetic field-assisted low-temperature ammonia synthesis

Zhang et al.

Materials Characterization

X-ray diffraction (XRD) was performed with a Bruker D8 Focus Diffraction System using a Cu Kα source (λ = 0.154178 nm). The electromagnetic field (EMF) was applied via an alternating current power supply (AC power supply) with a voltage regulator. The obtained electric field intensity was measured by an oscilloscope. The parameters of the alternating magnetic field were recorded by a magnet meter with a Hall probe. The ammonia concentration was detected by an NK-500LAG laser ammonia analyzer.

Computational methods

First-principles calculation. Spin-polarized density functional theory (DFT) calculations are performed via the projected augmented wave (PAW) method[1] implemented in the Vienna Ab initio Simulation Package (VASP)[2, 3], with the Perdew-Burke-Ernzerhof (PBE)-type exchange-correlation functional[4] under the generalized gradient approximation (GGA)[5]. The plane-wave cutoff energy is 400 eV. For geometry optimization, the adsorbate and the topmost layers of Fe (110) are fully relaxed in all directions until the force on each atom is less than ~0.02 eV/Å and energy converges below 10^{-5} eV. A vacuum layer of ~ 20 Å in the Z-direction is considered to avoid interlayer interactions, and 3×3×1 Gamma-centered k-point grid sampling is used for Brillouin zone integration. The spin-polarization simulations and an external electrostatic field (unit in eV/Å) are applied along the z-axis to mimic the electromagnetic fields in the experiment. A linear static potential is added to the local potential, correcting the errors introduced by the periodic boundary conditions.

Model and analysis. The cell parameter of Fe (110) is a = 9.92950 Å, b = 9.92950 Å, and c = 26.0805 Å. The slab consists of 64 Fe atoms in a unit cell. The adsorption energy of ΔE_{ads} is defined as:

$$\Delta E_{ads} = E_{tot} - E_{slab} - E_{ads}$$

where E_{tot} is the total energy of an adsorbed system, E_{slab} stands for the energy of a clean slab, and E_{ads} represents the energy of an adsorbate. The charge density difference is given by

$$\Delta\rho = \rho_{\mathrm{N2/Fe(110)}} - \rho_{\mathrm{Fe(110)}} - \rho_{\mathrm{N2}}.$$

where $\rho_{N2/Fe(110)}$, $\rho_{Fe(110)}$, and ρ_{N2} denote the charge density of the N_2/Fe (110) system, Fe (110) slab and N_2 unit, respectively.

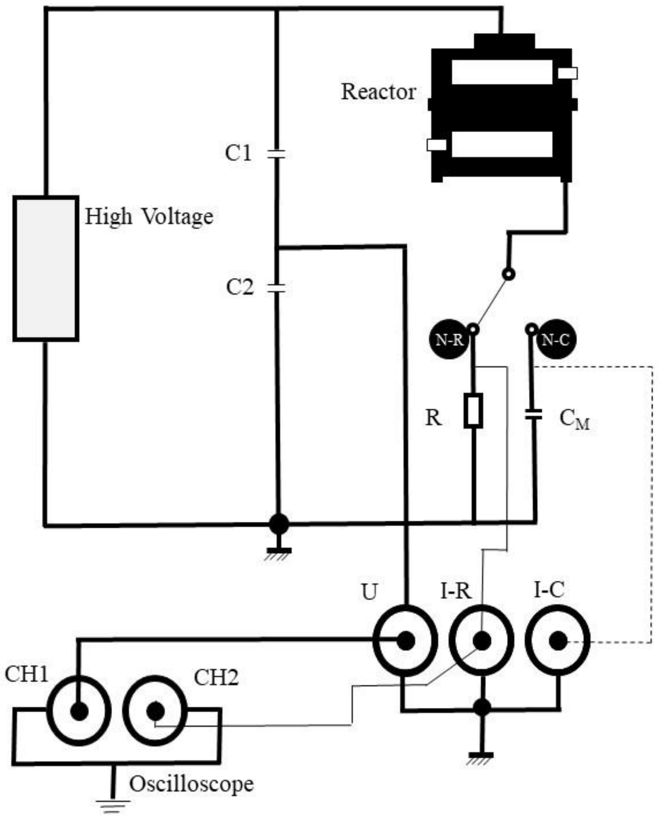
Calculation of energy cost

The energy cost (MJ $mol^{-1}{}_{NH3}$) was calculated by the following equation:

$$\text{Energy cost} = \frac{E \times 3.6\text{MJ kWh}^{-1} \times 17.03\text{ g mol}^{-1} \times m}{M_{\text{NH3}}}$$

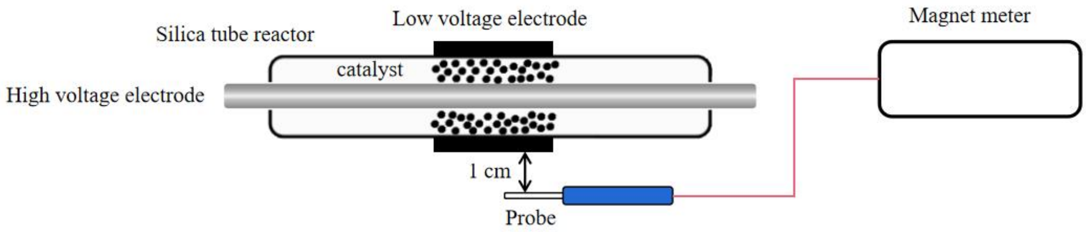
where E is the input power (kWh), M_{NH3} is the mass flow rate of gas (g h^{-1}), and m is the mass of catalyst (g). Note that E includes the power consumption from the AC power supply, voltage regulator and furnace, which is recorded by an electric power meter installed at the cable between the power source and reaction system.

Supplementary Figures



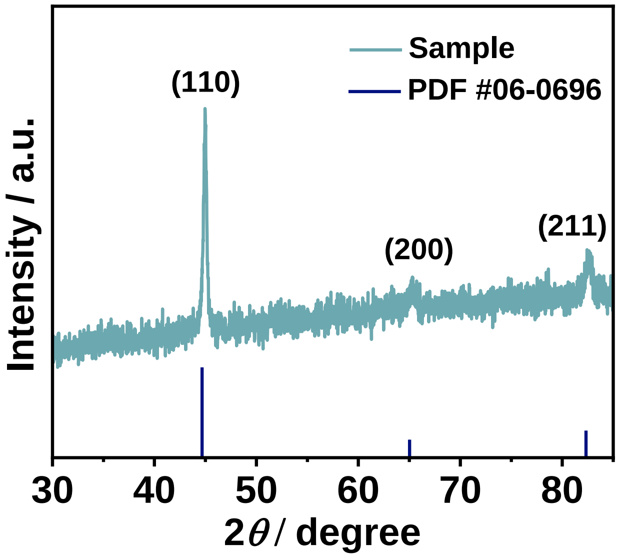
Supplementary Figure 1. Schematic illustration of the measurement of the electric field intensity in the EMF-assisted ammonia synthesis system.

Supplementary Note 1. An AC power supply outputs high voltage to the reactor to create an electric field with high frequency. The current, voltage, and frequency of the applied electric field are recorded on the oscilloscope. C, R, U, I, and CH represent capacitance, resistance, voltage, current and channel, respectively.



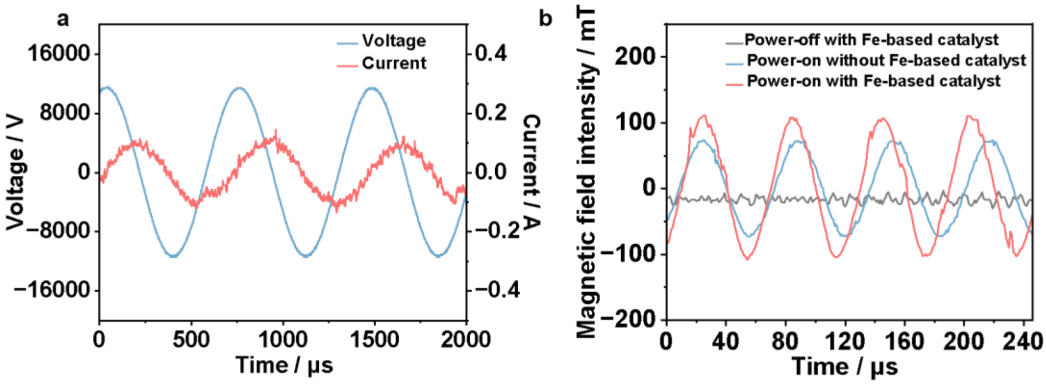
Supplementary Figure 2. Schematic illustration of the measurement of magnetic field intensity in an EMF-assisted ammonia synthesis system.

Supplementary Note 2. An AC power supply outputs high voltage to the reactor to create a magnetic field with high frequency. The intensity and frequency of the magnetic field are detected by the Hall probe and recorded on the magnet meter.



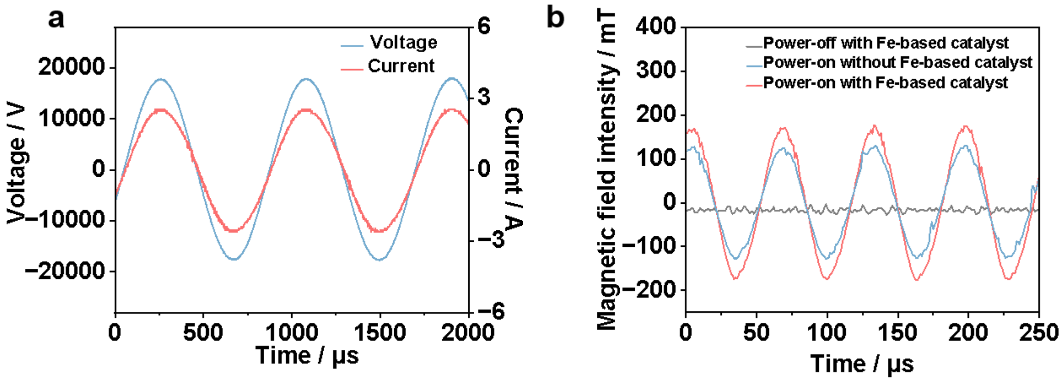
Supplementary Figure 3. XRD pattern of commercial Fe-based catalyst after reduction.

Supplementary Note 3. Before the reaction, the raw material was reduced by a H_2 and N_2 mixture (volume ratio of 3:1 with 99.99% purity) at 500 ℃ for 72 h. The XRD pattern shows the main exposed crystalline plane of Fe (110) after reduction.

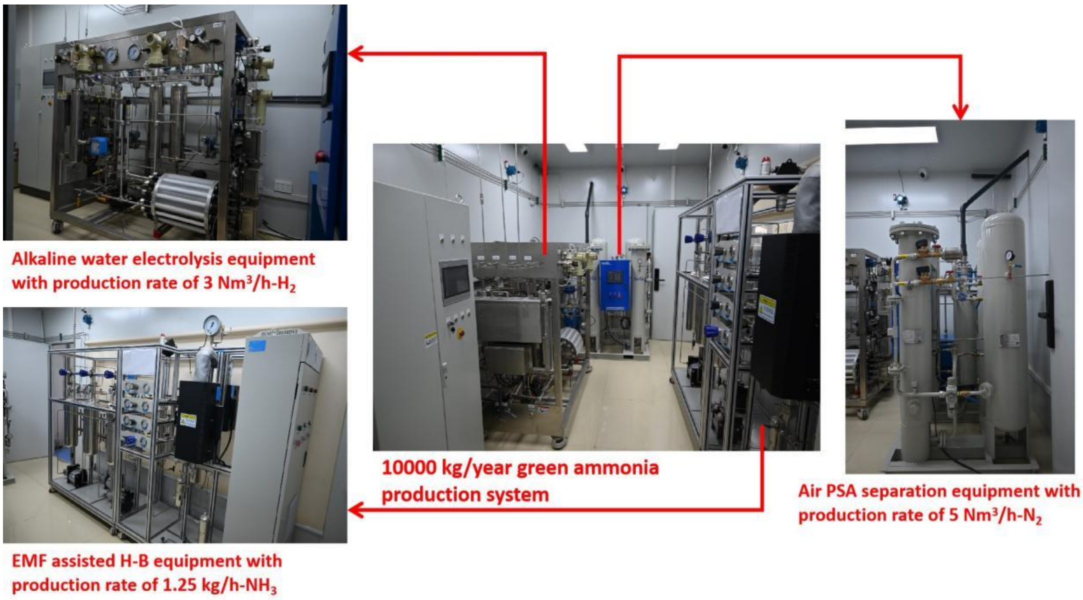


Supplementary Figure 4. a, The parameters of the applied electric field on the EMF reactor under 350 ℃ and 1 MPa. **b,** The parameters of the induced magnetic field on the EMF reactor under 350 ℃ and 1 MPa.

Supplementary Note 4. The applied voltage and current on the EMF reactor under 350 ℃ and 1 MPa are recorded and displayed in Supplementary Fig. 4a. The induced magnetic field is shown in Supplementary Fig. 4b. There is no magnetic signal without an input electric field. When the high voltage starts up, the magnetic field signal (maximum is 70 mT) appears. This signal will be enhanced (maximum is 120 mT) with the addition of a commercial Fe-based catalyst.

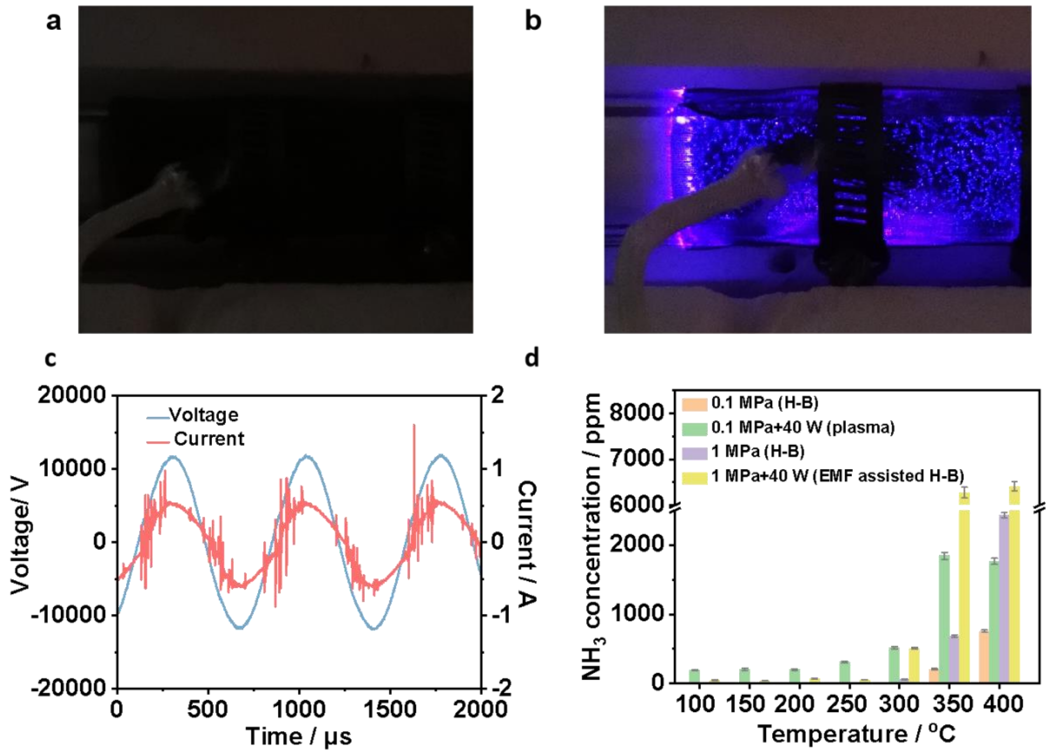


Supplementary Figure 5. The parameters of **a,** applied electric field and **b,** induced magnetic field on the EMF reactor at 200 ℃ and 1 MPa for the scale-up experiment.



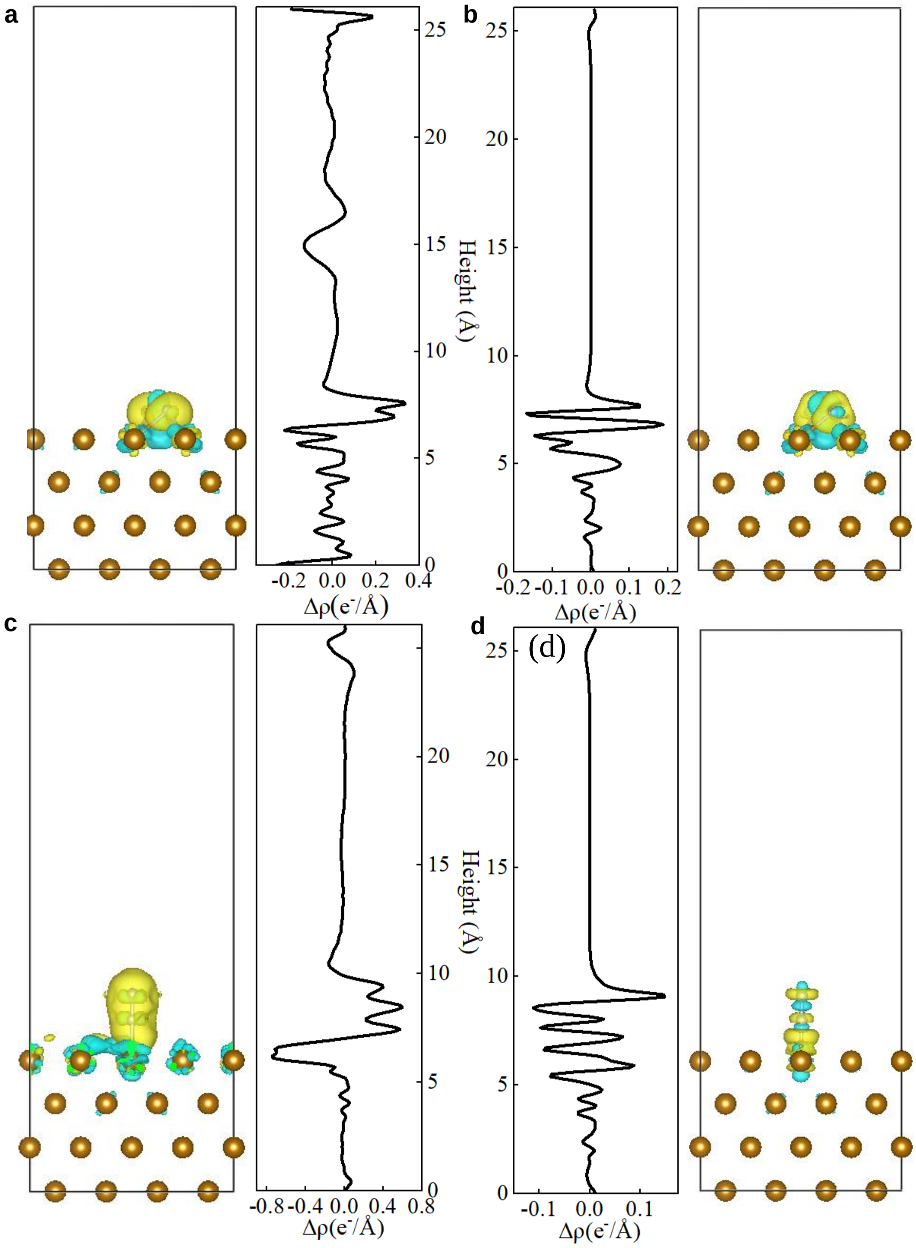
Supplementary Figure 6. Digital photograph of the pilot-scale EMF-assisted H-B system with a production capacity of 10000 kg year^{-1}.

Supplementary Note 5. The pilot-scale EMF assistance system, consisting of water electrolysis, air pressure swing adsorption (PSA) separation and ammonia synthesis, with a production capacity of 10000 kg year^{-1} for green ammonia is constructed and serves as a distributed green ammonia synthesis system (Supplementary Fig. 6).

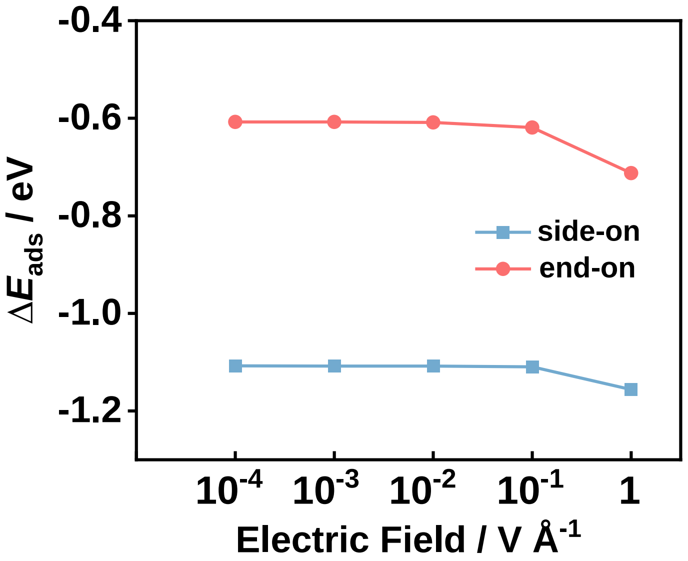


Supplementary Figure 7. Digital photograph of the EMF reactor under the conditions of **a,** EMF-assisted H-B (room temperature and 1 MPa) and **b,** plasma catalysis (room temperature and 0.1 MPa). **c,** The parameters of the applied electric field for plasma catalysis under 350 ℃ and 0.1 MPa. **d,** Performance comparison at a wide range of temperatures for ammonia synthesis under H-B, plasma and EMF-assisted H-B over Fe-based catalysts.

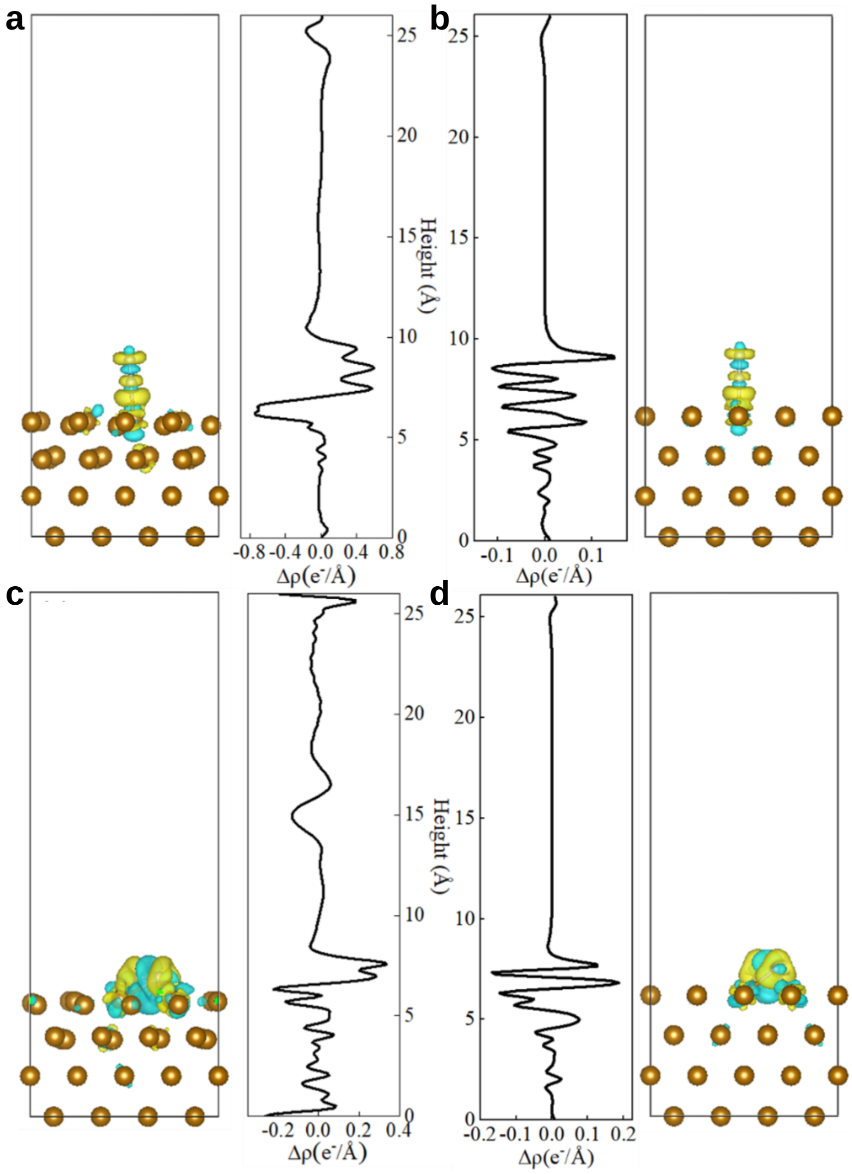
Supplementary Note 6. To exclude the possible effect of plasma in the EMF reactor, a series of experiments from thermocatalysis (H-B), plasma catalysis and EMF-assisted thermocatalysis (EMF-assisted H-B) are conducted and compared. Low pressure is beneficial to the formation of plasma. In our work, we decreased the reaction pressure to 0.1 MPa and maintain the output AC voltage and current from the AC power supply with a voltage regulator to generate plasma. An obvious discharge glow can be observed as the reaction pressure decreases from 1 MPa to 0.1 MPa with the presence of characteristic pulsed current peaks[6], indicating the generation of plasma (Supplementary Fig. 7a-c). Notably, the smooth current curve (Supplementary Fig. 4a) excludes the effect of plasma in the EMF-assisted H-B process owing to the high pressure. The ammonia synthesis performances under H-B, plasma and EMF-assisted H-B conditions are displayed in Supplementary Fig. 7d. Plasma catalysis can generate ammonia under low temperature.[6] However, the ammonia concentration of EMF H-B is much higher than that of plasma catalysis. Note that plasma requires very low pressure (≤0.1 MPa), which will severely retard the space-time yield and increase equipment input.



Supplementary Figure 8. Charge density difference of N_2 side-on adsorption **a,** with EMF and **b,** without EMF on Fe (110) surface, end-on adsorption **c,** with EMF and **d,** without EMF based on spin-polarization. The isosurface value is 0.003 e/$Å^3$. The yellow isosurface represents electron accumulation, and cyan denotes electron depletion. Integrated Δρ in planes parallel to the surface plotted as a function of the Z-coordination.



Supplementary Figure 9. The adsorption energy with different electric field intensities. To reflect the effect of the electric field, we applied 1 V/Å for DFT calculations.



Supplementary Figure 10. Charge density difference of N_2 end-on adsorption **a,** with and **b,** without spin polarization on the Fe (110) surface, side-on adsorption **c,** with and **d,** without spin polarization. The isosurface value is 0.003 e/Å^3. The yellow isosurface represents electron accumulation, and cyan denotes electron depletion. Integrated Δρ in planes parallel to the surface plotted as a function of the *Z*-coordination.

Supplementary Note 7. We perform the calculation of N_2 adsorption on Fe (110) without spin polarization. After comparing the charge distribution of the N_2 adsorption system with and without spin polarization, we find that the magnetic field regulates the electronic structure of N_2 adsorption, which benefits NH_3 production.

Supplementary Table 1. Comparison of ammonia synthesis performance in our work with state-of-the-art bulk catalysts.

Catalysts	Concentration (ppm)	Reaction conditions	WHSV (mlg^{-1} h^{-1})	Reference
Fe bulk	6270	350 ^{o}C + 1 MPa (EMF assisted H-B)	12000	this work
Ni/LaN bulk	5000	400 ^{o}C + 0.9 MPa	36000	7
Fe bulk	688	350 ^{o}C + 1 MPa (H-B)	12000	this work
No catalyst	0	350 ^{o}C + 1 MPa (EMF assisted H-B)	12000	this work
No catalyst	0	350 ^{o}C + 1 MPa (H-B)	12000	this work

Note: WHSV is the weight hourly space velocity.

Supplementary Note 8. Blank experiments prove that the internal metal-rod electrode shows no activity for ammonia synthesis with and without EMF assistance. The commercial Fe-based bulk catalyst under the optimal EMF conditions in our work shows higher activity than that of the state-of-the-art bulk catalysts of Ni/LaN. Note that the preparation of Ni/LaN catalysts requires an anaerobic environment. In this work, we directly adopt commercial Fe-based catalysts to prove the promising application potential of the EMF assistance technique. In the future, we will develop more efficient and easily prepared catalysts to match our EMF assistance system.

Supplementary Table 2. The ammonia synthesis activity under different conditions corresponding to Supplementary Fig. 7d over a commercial Fe-based catalyst.

	/Power / W	**U_{RMS} /V**	**Temperature/℃**	**NH_3 concentration/ppm**
H-B (0.1 MPa)	0	0	100	0
	0	0	150	0
	0	0	200	0
	0	0	250	0
	0	0	300	6
	0	0	350	204
	0	0	400	755
Plasma (0.1MPa)	40	7800	100	194
	40	7800	150	208
	40	7800	200	203
	40	7800	250	311.6
	40	7800	300	520
	40	**7800**	**350**	**1850**
	40	7800	400	1760
H-B (1 MPa)	0	0	100	0
	0	0	150	0
	0	0	200	0
	0	0	250	0
	0	0	300	62.1
	0	0	350	688
	0	0	400	2433
EMF assisted H-B (1 MPa)	40	7800	100	43.9
	40	7800	150	41.7
	40	7800	200	70
	40	7800	250	53
	40	7800	300	510
	40	**7800**	**350**	**6270**
	40	7800	400	6412

Supplementary Note 9. AC power represents the power supplied to the reactor from the AC power supply, and the power supplied to the heater from the power source is not included.

Supplementary References

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7. Ye, T.N. et al. Vacancy-enabled N_2 activation for ammonia synthesis on an Ni-loaded catalyst. Nature 583, 391-395 (2020).