
Supporting Information

Sub-nanocatalysis for Efficient Aqueous Nitrate Reduction:

Effect of Strong Metal–Support Interaction

Jiacheng Li, Miao Li*, Xu Yang, Sai Wang, Yu Zhang, Fang Liu, Xiang Liu.

*Corresponding Author.

Tel: 86-10-62772485

E-mail: miaoli@tsinghua.edu.cn

School of Environment, Tsinghua University

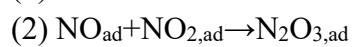
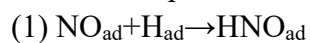
30# Shuangqing Road, Hai Dian Distract, Beijing, 100084, China

Table S1 Adsorption energies of H or NO₂ on the NO adsorbed Pd₃In/Fe₃O₄(111) or Pd₄/Fe₃O₄ (111) surfaces.

Pd ₃ In/Fe ₃ O ₄	ΔE (eV)	$E_{\text{Pd3In-X}}$ (eV)	E_{Pd3In} (eV)	E_X (eV)
Reaction 1	-2.73	-1257.141	-1253.296	-1.116
Reaction 2	-2.99	-1273.366	-1253.296	-17.081

Pd ₄ /Fe ₃ O ₄	ΔE (eV)	$E_{\text{Pd4-X}}$ (eV)	E_{Pd4} (eV)	E_X (eV)
Reaction 1	-0.67	-1259.181	-1257.394	-1.116
Reaction 2	-0.40	-1274.878	-1257.394	-17.081

Reaction steps:



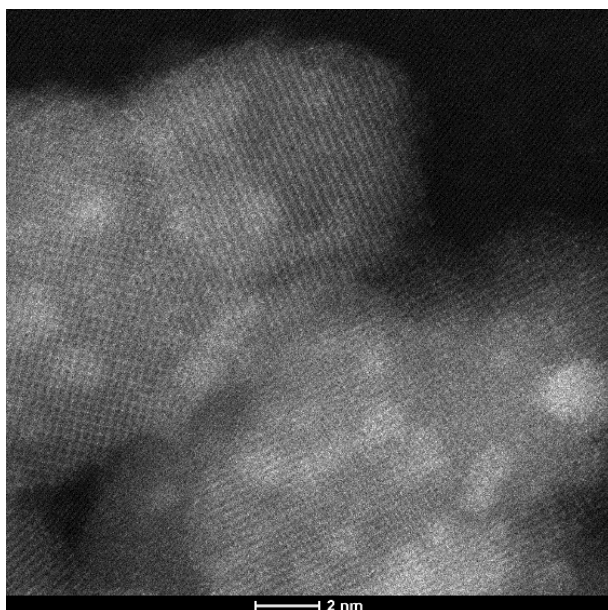


Figure S1.HAADF-STEM images of 10-PI/F in high magnification

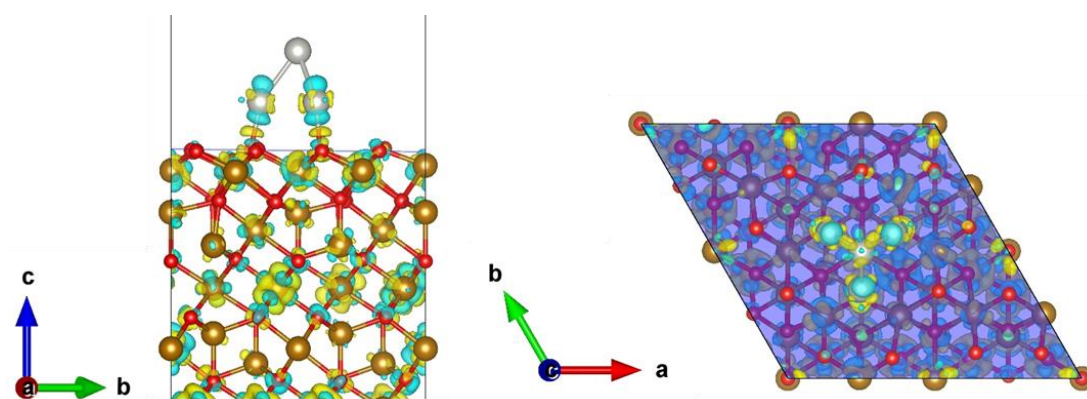


Figure S2. Charge density difference for $\text{Pd}_3\text{In}/\text{Fe}_3\text{O}_4(111)$. The yellow balls represent the Fe atoms, the Red balls are oxygen atoms denote, the grey balls represent Pd atoms. The violet areas suggest enriched electron density.

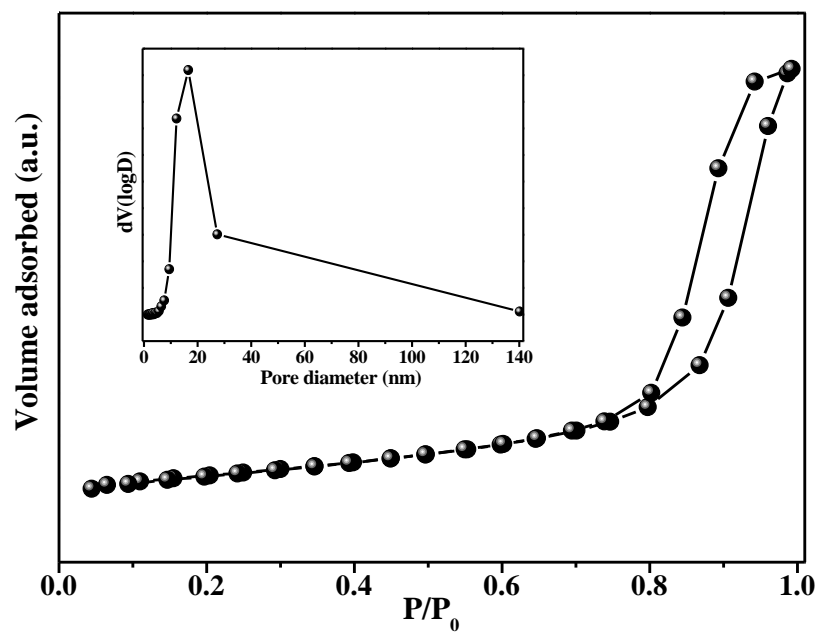


Figure S3. N_2 adsorption- desorption isotherms and pore size distribution (inset) of Fe_3O_4 supports

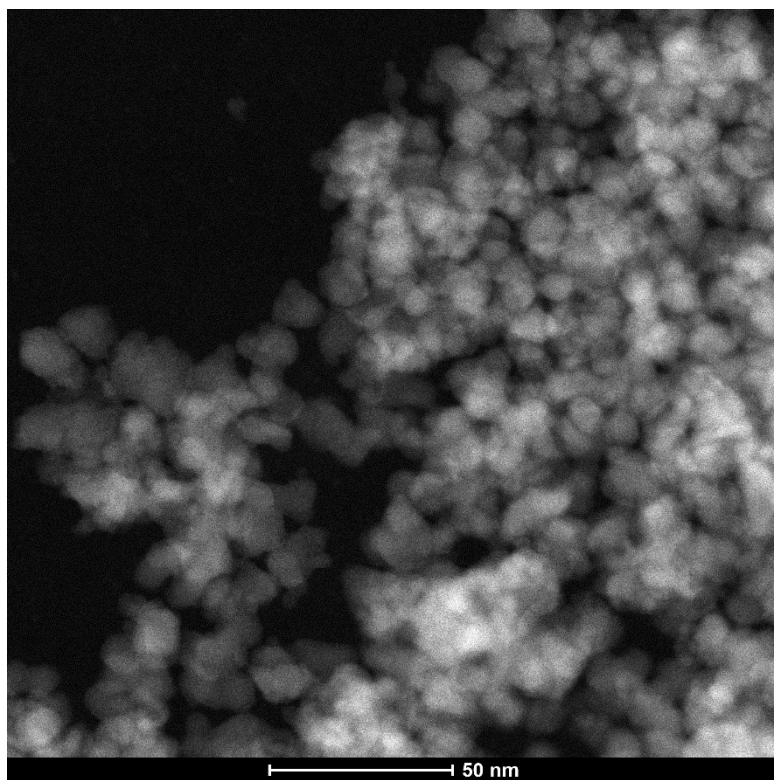


Figure S4. HAADF-STEM images of 0.4-PI/F.

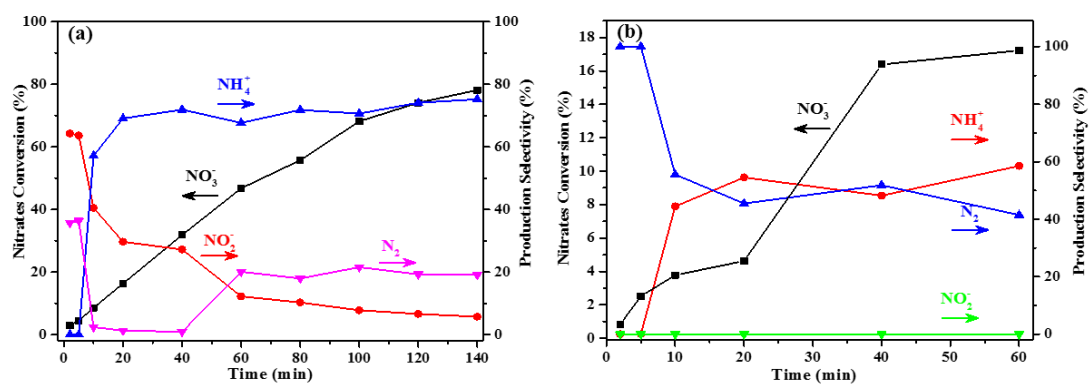


Figure S5. Nitrates conversion and products selectivity on 0.4-PI/F (a) and 1.25-I/F (b) catalysts as a function of time

Effect of External Mass Transfer

The mass transfer between aqueous nitrates solution and solid catalysts were evaluated based on previous study.^[1-3] First, the slip velocity of the catalyst particle was calculated according to Stokes' law:

$$u_t = \frac{gd_p^2(\rho_p - \rho)}{18\mu} ; (S1)$$

where g is gravity constant ($9.81 \text{ m}\cdot\text{s}^{-2}$), d_p is the particle diameter of the catalysts ($\sim 20 \text{ nm}$ as shown in Figure S3), ρ_p is the density of the catalysts and is assumed to be same to ferroferric oxide ($5.18 \text{ g}\cdot\text{cm}^{-3}$), ρ is water density ($1\times 10^6 \text{ g}\cdot\text{m}^{-3}$ at 20°C) and μ is absolute viscosity of water ($1.002 \text{ g}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ at 20°C). Consequently, the slip velocity is $9.09\times 10^{-10} \text{ m}\cdot\text{s}^{-1}$.

Moreover, the Reynolds number (Re), Peclet number (Pe) and Sherwood number (Sh) were calculated by the following expression:

$$Re = \frac{d_p u_t}{\nu} ; (S2)$$

$$Pe = \frac{d_p u_t}{D} ; (S3)$$

$$Sh = \frac{4}{Pe} \ln\left(\frac{1}{1 - Pe/2}\right) ; (S4)$$

where ν is kinematic viscosity of water ($1.003\times 10^{-6} \text{ m}^2\cdot\text{s}^{-1}$ at 20°C) and D is the nitrate diffusion coefficient in pure water ($1.7\times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$).

Then the aqueous/solid mass transfer coefficient could be determined based on the following expression:

$$k_{aq/s} = \frac{D}{d_p} Sh = \frac{4D}{Pe \times d_p} \ln\left(\frac{1}{1 - Pe/2}\right) ; (S5)$$

The value of $k_{aq/s}$ is $3.54\times 10^{-4} \text{ m}\cdot\text{s}^{-1}$, moreover, the geometric surface area of the catalyst per volume of solution (a) is determined as follows:

$$a = \frac{\text{total surface area}}{\text{total volume}} = \frac{SA_p \times M}{\rho_p \times V_p} \times \frac{1}{V_R} ; (S6)$$

in which, SA_p is the surface area of one catalyst aggregate, M is the total mass of catalyst (0.2 g), V_p is the volume of one catalyst aggregate, and V_R is the volume of the reaction solution (160 mL).

At last, mass transfer rate constant is equal to the $k_{aq/s}$ multiplied by a :

$$k_{aq/s} \cdot a = 6.19 \times 10^7 / \text{s} = 1.03 \times 10^6 / \text{min}$$

This value is much larger than the measured $k_{obs, I-PI/F}$ value (1.56×10^{-2}), which indicates the aqueous/solid mass transfer is negligible in the reaction.

Effect of Intraparticle Mass Transfer

The potential of intraparticle diffusion resistance was also discussed based on the following criteria:

$$\text{No resistance: } \frac{k_{obs} L^2 \tau}{D\theta} < 1 ; (S7)$$

$$\text{Significant resistance: } \frac{k_{obs} L^2 \tau}{D\theta} > 1 ; (S8)$$

where $L=d_p/6$ (3.3×10^{-9} m), τ is the tortuosity factor (ranging from 2 to 10), D is the nitrate diffusion coefficient in pure water (1.7×10^{-9} m²·s⁻¹) and θ is the porosity of the catalyst particle (ranging from 0.2 to 0.7). Here 0.2 and 10 were used as values for θ and τ in order to get the largest criteria value. The calculated value is $5.0 \times 10^{-9} \ll 1$, suggesting the reaction is rarely affected by the intraparticle mass transfer resistance.

References

- [1] D. P. Durkin, T. Ye, J. Choi, K. J. T. Livid, H. C. D. Longe, P. C. Trulovef, D. H. Fairbrothera, L. M. Haverhalsg, D. Shuai, *Appl. Catal. B Environ.* **2018**, 221, 290.
- [2] Q. M. Zheng, D. P. Durkin, J. E. Elenewski, Y. X. Sun, N. A. Banek, L. K. Hua, H. N. Chen, M. J. Wagner, W. Zhang, D. M. Shuai, *Environ. Sci. Technol.* **2016**, 50, 12938.
- [3] T. Ye, D. P. Durkin, N. A. Banek, M. J. Wagner, D. Shuai, *ACS Appl. Mater. Interfaces.* **2017**, 9, 27421.