Electronic Supplementary Information

Heteropoly acid-grafted iron oxide catalysts for efficient selective catalytic reduction of NO_x with NH_3

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S1 NO oxidation

Fig. S1 shows the NO conversion during the NO oxidation experiment over HSiW/Fe_2O_3, HPW/Fe_2O_3, and HPMo/Fe_2O_3 catalysts at 150-500 ^oC. The NO conversion over all catalysts was below 9% at the whole temperature window. It was observed that the NO oxidation activity on HPMo/Fe_2O_3 was less than those on HSiW/Fe_2O_3 and HPW/Fe_2O_3 catalysts at 250-500 ^oC. With the increase of temperature, both HSiW/Fe_2O_3 and HPW/Fe_2O_3 catalysts could reach the maximum values of NO conversion at 300 ^oC.

S2 XPS results of W 4f and Mo 3d

The XPS results of W 4f and Mo 3d of HPA/Fe_2O_3 catalysts are shown in Fig. S2. A doublet peak corresponding to W 4f photoelectrons appeared at 37.7-37.5 eV and 35.6-35.4 eV were obtained on the HSiW/Fe_2O_3 and HPW/Fe_2O_3. This was associated with W in the formal (VI) oxidation state. The Mo 3d binding energies of HPMo/Fe_2O_3 mainly centered at 236.0 and 232.8 eV, which were attributed to Mo^{6+}.

S3 DFT calculations

S3.1 Computational Methods

All calculations are based on the CASTEP program package, using the generalized gradient approximation (GGA-PBE) with the Perdew-Burke-Ernzerh of exchange correlation function and super soft pseudopotential, and using a plane wave extension with a cut-off energy of 500 eV. The Brillouin area sampling adopts the Monkhorst-Park format, and the model adopts a 1 × 1 × 1 K-point grid. The convergence standards for structure optimization and energy calculation are SCF tolerance is 1.0×10^{-5} eV/atom, Energy tolerance is 1.0×10^{-5} eV/atom, Max force tolerance is 0.05 eV/Å, and Maximum displacement tolerance is 0.002 Å.

S3.2 Formation of NH_2NO

The formation of NH_2NO is a key step in the SCR reaction.[S1] NH_2NO undergoes a series of reactions and decomposes into N_2 and H_2O.[S2-3] DFT calculations were utilized to further investigate the Langmuir-Hinshelwood mechanism and the Eley-Rideal mechanism of the SCR reaction over HPW/Fe_2O_3. As shown in Fig. S5A, the reaction energy of NH_2NO formation on HPW/Fe_2O_3 through the Langmuir-Hinshelwood mechanism was 0.85 eV. However, when NH_2NO formed on

HPW/Fe_2O_3 through the Eley-Rideal mechanism, the reaction energy was -0.33 eV (shown in Fig. S5B). The calculation results suggested that the NH_2NO formation is more inclined to the SCR reaction pathway of the Eley-Rideal mechanism.

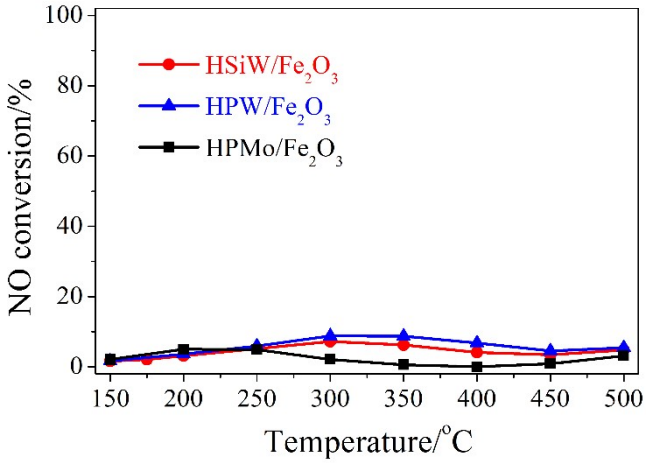

Fig. S1. NO oxidation over $HSiW/Fe_2O_3$, HPW/Fe_2O_3, and $HPMo/Fe_2O_3$ catalysts. Reaction conditions: [NO] = 500 ppm, $[O_2]$ = 5%, catalyst mass = 100 mg, total flow rate = 100 mL min^{-1}, and WHSV = 60, 000 cm^3 g^{-1} h^{-1}.

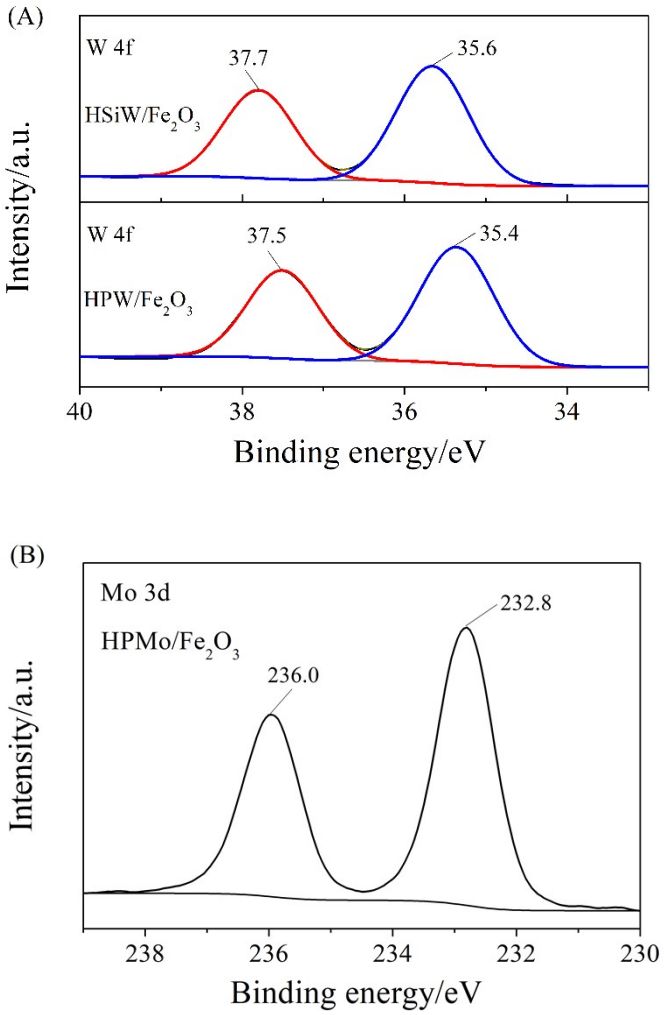

Fig. S2. XPS spectra of $HSiW/Fe_2O_3$, HPW/Fe_2O_3, and $HPMo/Fe_2O_3$ catalysts over the spectral regions of W 4f and Mo 3d.

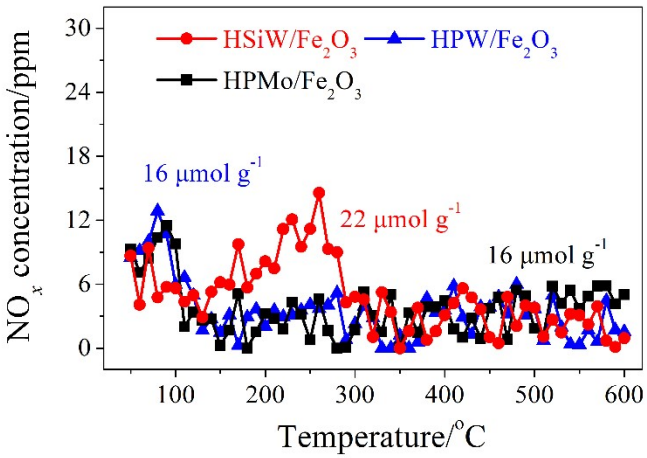

Fig. S3. NO_x-TPD results for $HSiW/Fe_2O_3$, HPW/Fe_2O_3, and $HPMo/Fe_2O_3$ catalysts.

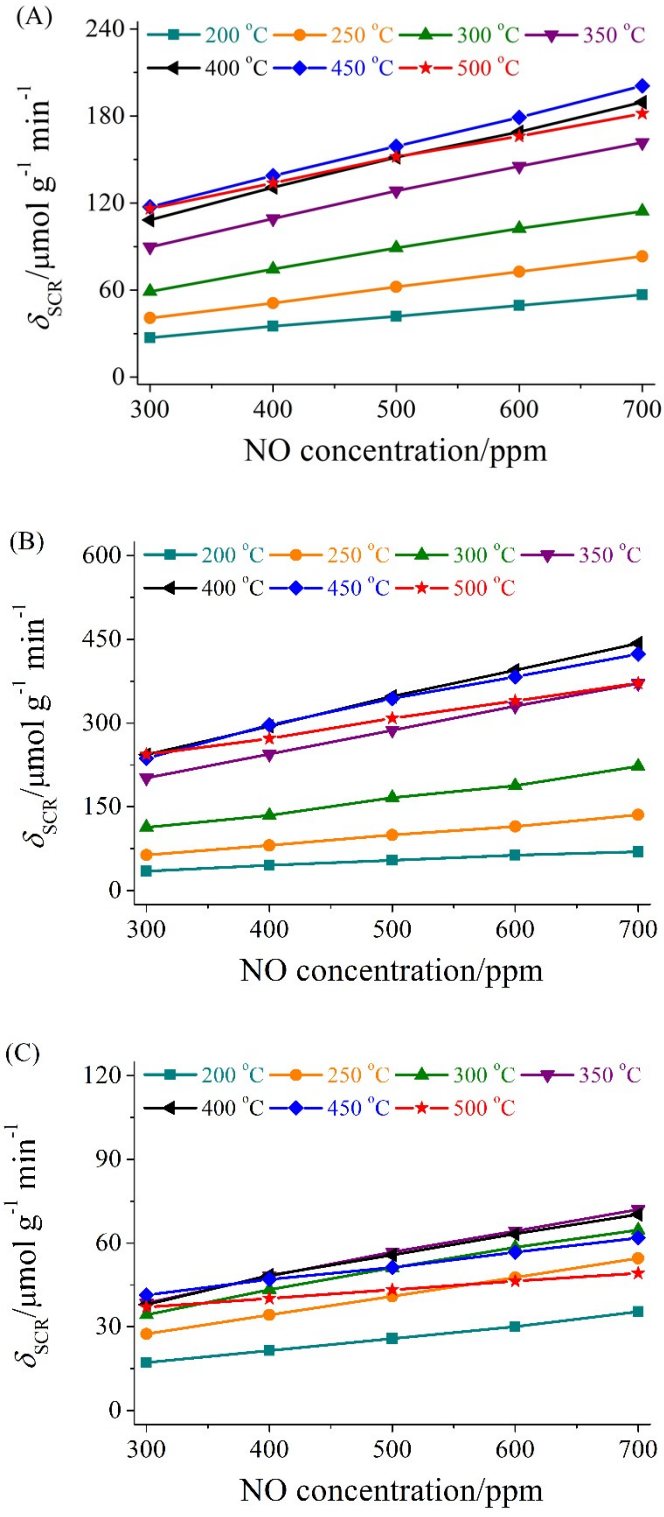

Fig. S4. Dependences of the SCR reaction rate during NO reduction over (A) HSiW/Fe_2O_3, (B) HPW/Fe_2O_3, and (C) HPMo/Fe_2O_3 on gaseous NO concentration. Reaction conditions: [NH_3]=500 ppm, [NO]=300-700 ppm, [O_2]=5%, catalyst mass=3-30 mg, total flow rate=400 mL min^{-1}, and WHSV=800,000-8,000,000 cm^3 g^{-1} h^{-1}.

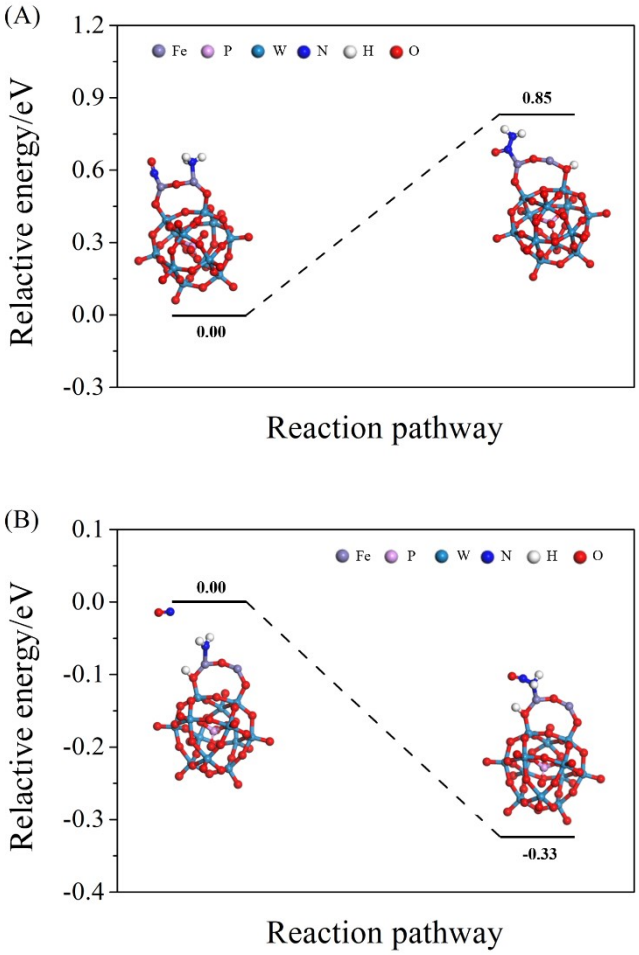

Fig. S5. Energy profiles and the corresponding optimized structures of the NH_2NO formation on HPW/Fe_2O_3 through (A) the Langmuir-Hinshelwood mechanism and (B) the Eley-Rideal mechanism.

References

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