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A DFT-D study on the reaction mechanism of selective catalytic reduction of NO by NH_3 over the Fe_2O_3/Ni (111) surface

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Theoretical methods

All DFT calculations were carried out in Vienna Ab-initio Simulation Package (VASP) version 5.4 [1-3]. The generalized gradient approximation (GGA) functional and Perdew-Burke-Ernzerhof (PBE) exchange association functional were used in the DFT calculation [4-6]. The Kohn-Sham equations were solved by the Projector Augmented Wave (PAW) method [7]. The reaction routes of gas molecules on the Fe_2O_3/Ni catalyst surface were investigated by the climbing-image nudged elastic band (CI-NEB) method [8-10]. To further understand the Van der Waals interaction between Ni surface and cluster or gas molecules, we introduced the density functional theory based on dispersion correction (DFT-D3) [11, 12]. In addition, for the convergence criteria of calculation system, the change of total energy and force acting on each ion should be less 10^{-5} eV and 10^{-3} eV/Å, respectively.

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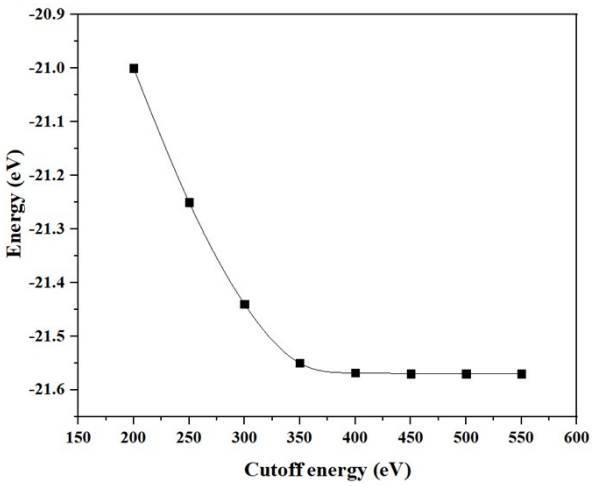
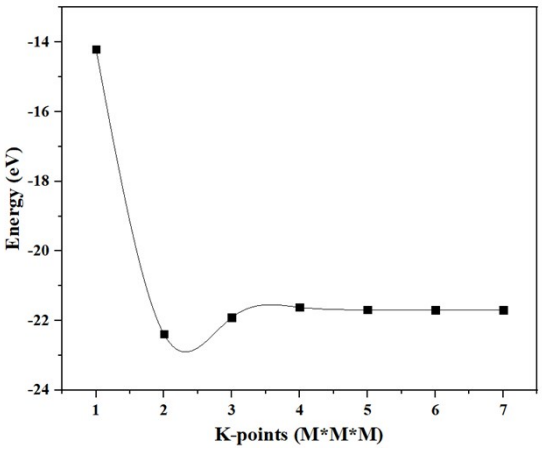


(a) Cut-off energy.



(b) K-points.

Figure S1 Convergence tests of Ni bulk model.

Table S1 Surface energies of Ni slab model.

Slab surface	Ni (111)	Ni (100)	Ni (110)
Surface energy (eV)	23.36	27.25	38.94

Table S2 Double-molecule adsorption energies and charge changes over the Fe_2O_3/Ni (111) surface.

Gas	Adsorption energy (eV)	Bader charge changes (e)
NH_3 + NO	-2.935	NH_3: -0.141, NO: +0.280
O_2 + NH_3	-3.005	O_2: +0.455, NH_3: -0.132
O_2 + NO	-4.546	O_2: +0.380, NO: +0.268

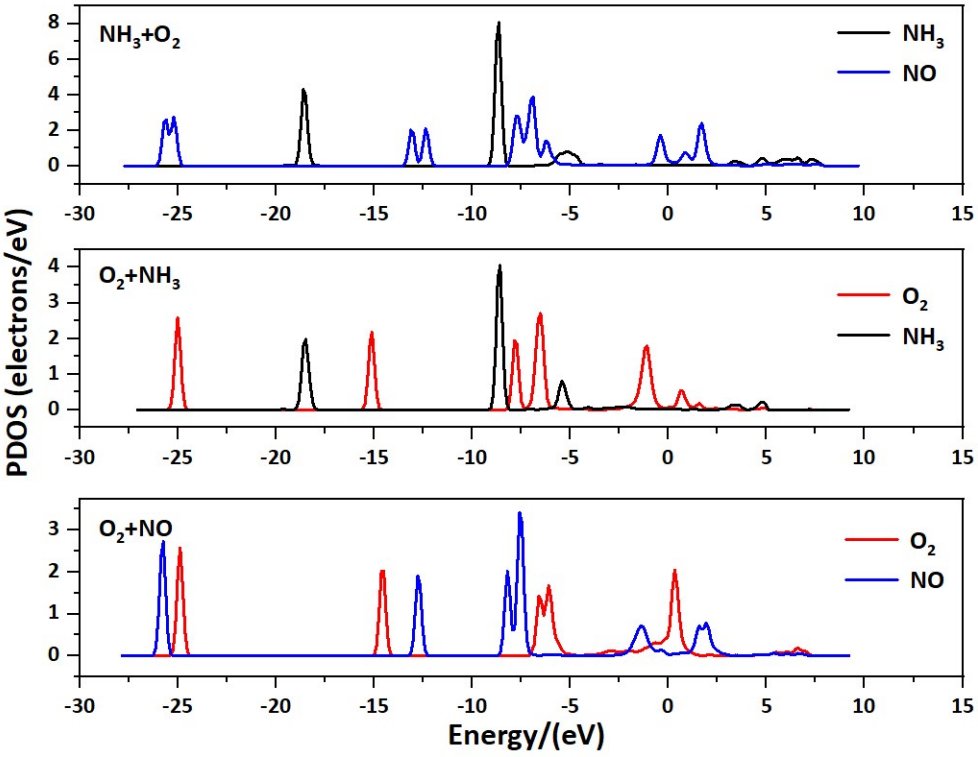


Figure S2 PDOS results of double-molecule adsorption on the Fe_2O_3/Ni (111) surface.

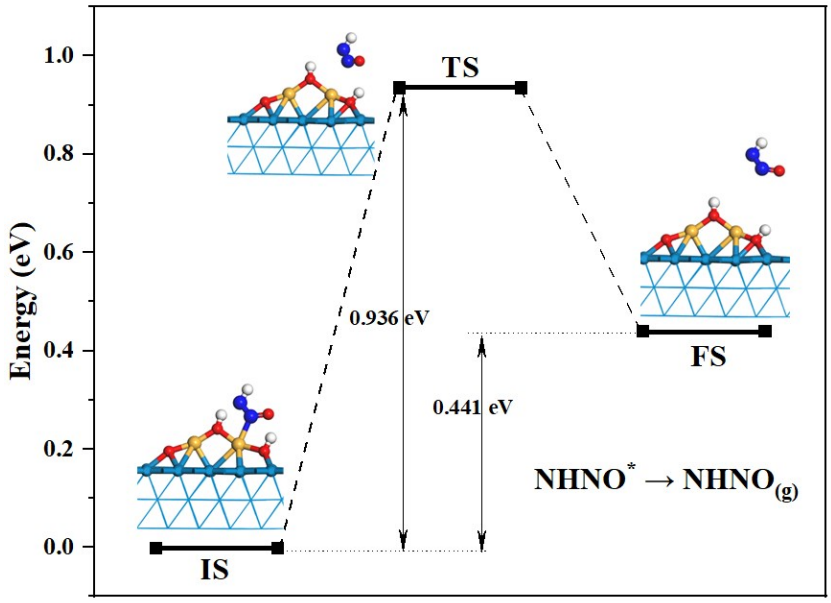


Figure S3 Dissociation path of NHNO*(Ni: dark blue, Fe: gold, O: red, N: blue, H: white).

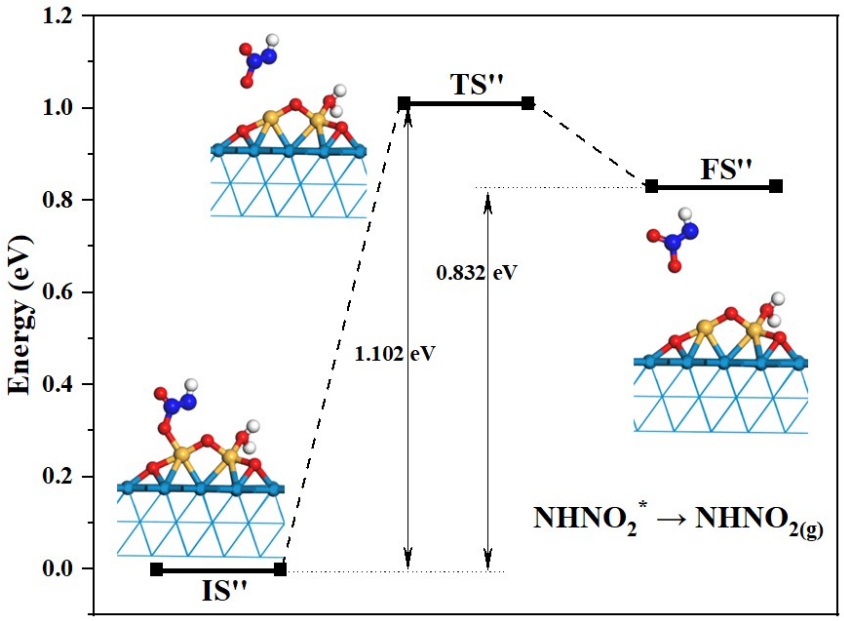


Figure S4 Dissociation path of $NHNO_2$*(Ni: dark blue, Fe: gold, O: red, N: blue, H: white).

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