Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

# Application of $ReO_x/TiO_2$ catalysts with an excellent $SO_2$ tolerance in selective catalytic reduction of $NO_x$ by $NH_3$

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### *2.4. DFT calculation*

The VASP was used to perform all the spin-polarized density functional theory (DFT) calculations [1, 2] within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation [3]. Projected augmented wave (PAW) potentials were chosen to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV [4, 5]. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.02 eV. The electronic energy was considered self-consistent when the energy change was smaller than $10^{-5}$ eV. A geometry optimization was considered convergent when the energy change was smaller than $3*10^{-2}$ eV/ Å. Grimme's DFT-D3 methodology was used to describe the dispersion interactions among all the atoms in adsorption models of interest [6]. $MnO_x/TiO_2$, $V_2O_5/TiO_2$ and $ReO_x/TiO_2$ surface slab with 8 atomic layers were built first. The surface was chosen since it is the most stable surface among various possible surfaces. This slab was separated by a 15 Å vacuum layer in the $z$ direction between the slab and its periodic images. During structural optimizations of the surface models, a 3 × 3 × 1 gamma-point centered $k$-point grid for Brillouin zone was used and the top 6 atomic layers were allowed to fully relax while the bottom atomic 6 layers were fixed.

1. Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. Comput. Mater. Sci. 1996, 6, 15-50.

2. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. Phys. Rev. B 1996, 54, 11169-11186.
3. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. Phys. Rev. Lett. 1996, 77, 3865-3868.
4. Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. Phys. Rev. B 1999, 59, 1758-1775.
5. Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B 1994, 50, 17953-17979.
6. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. Chem. Phys. 2010, 132, 154104.

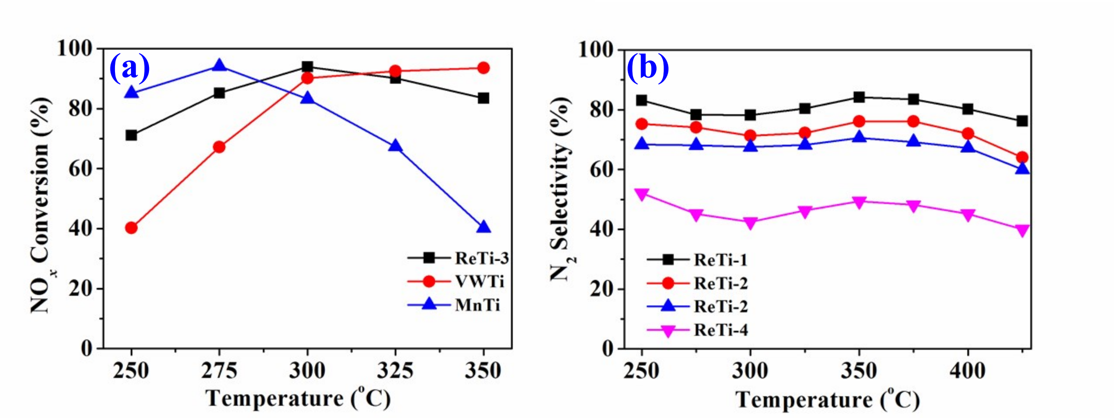


Fig. S1. (a) Catalytic activity of ReTi-3, VWTi and MnTi sample; (b) $N_2$ selectivity of $ReO_x/TiO_2$ catalysts. Tested conditions: 1.5 mL catalyst sample, [NO] = $[NH_3]$ = 500 ppm, $[O_2]$ = 4.0%, and $N_2$ as balanced gas, GHSV = 36 000 $h^{-1}$.

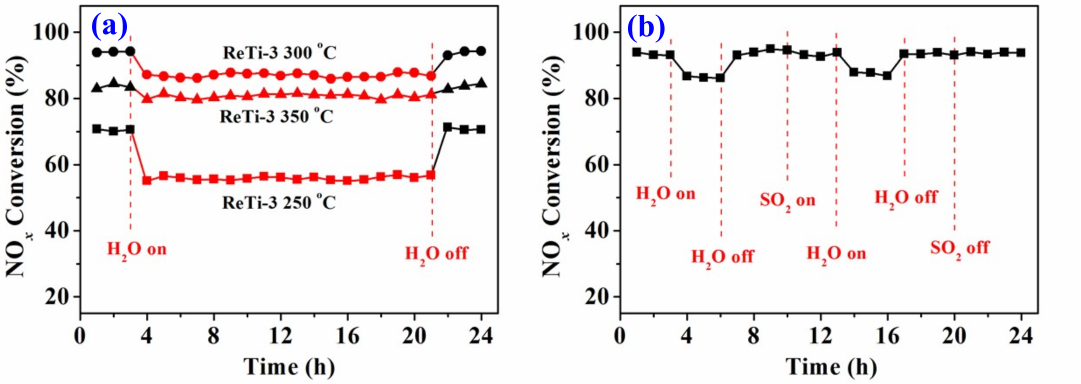


Fig. S2. (a) Water tolerance experiment of ReTi-3 sample; (b) $SO_2$ and water tolerance experiment of ReTi-3 sample at 300 °C. Tested conditions: 1.5 mL catalyst sample, [NO] = [$NH_3$] = 500 ppm, [$SO_2$] = 500 ppm (when used), [$H_2O$] = 3.0% (when used), [$O_2$] = 4.0%, and $N_2$ as balanced gas, GHSV = 36 000 $h^{-1}$.

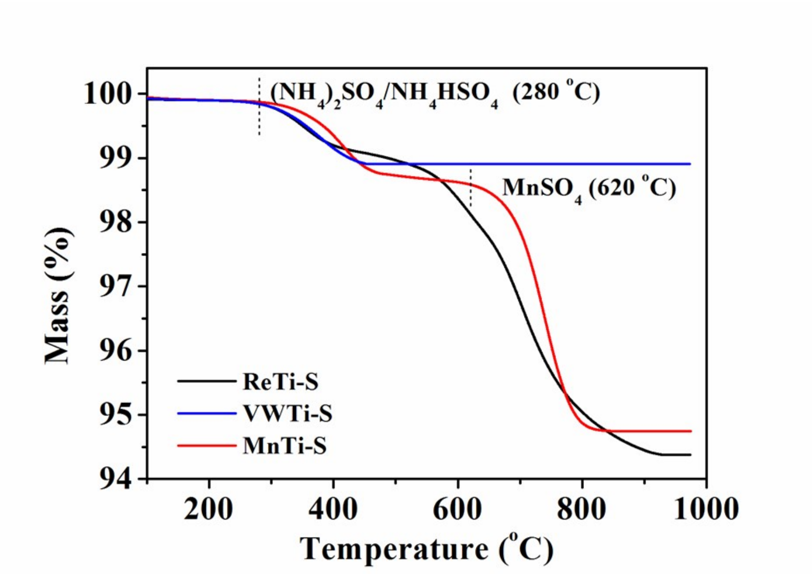


Fig. S3. TG results of ReTi-S, VWTi-S and MnTi-S sample.

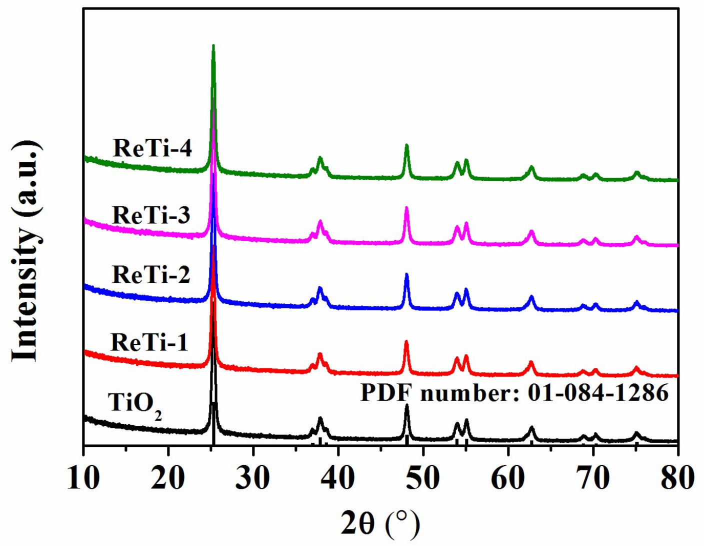


Fig. S4. XRD result of $ReO_x/TiO_2$ catalysts with varied Re loading.

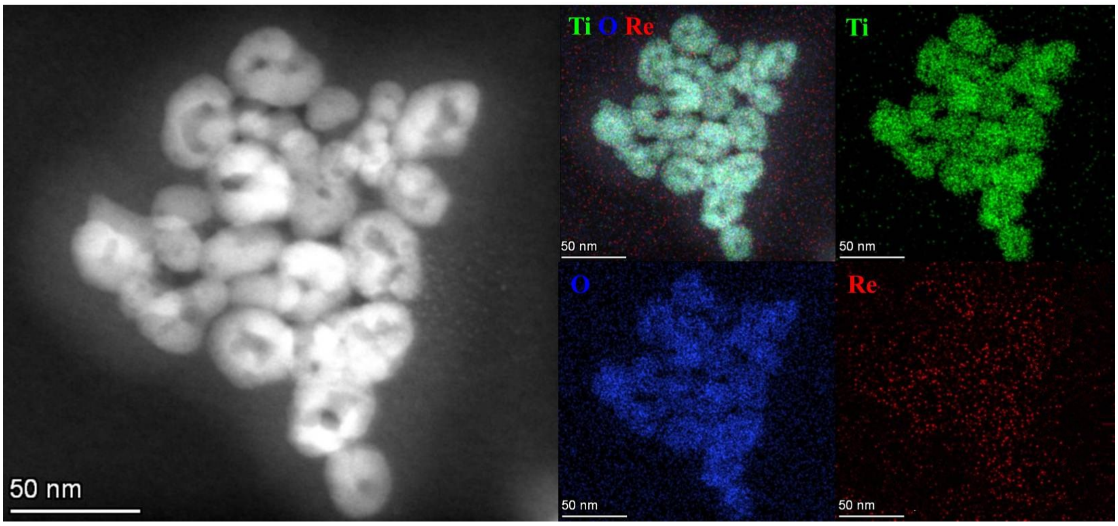


Fig. S5. HAADE-STEM and STEM-EDS elemental mapping of ReTi-3 sample.

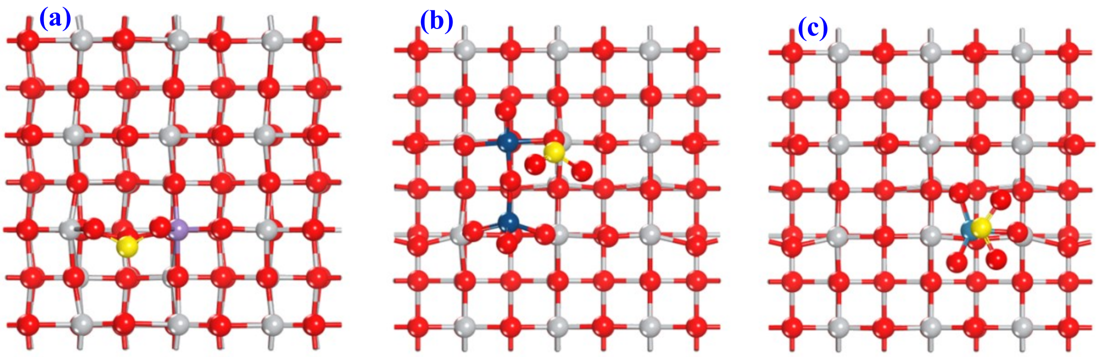


Fig. S6. The top view for adsorption of $SO_2$ on (a) $MnO_x/TiO_2$ model; (b) $V_2O_5/TiO_2$ model; (c) $ReO_x/TiO_2$ model. (Ti: grey balls; O: red balls; S: yellow balls; Mn: pink balls; V: deep purple balls; Re: light purple balls)

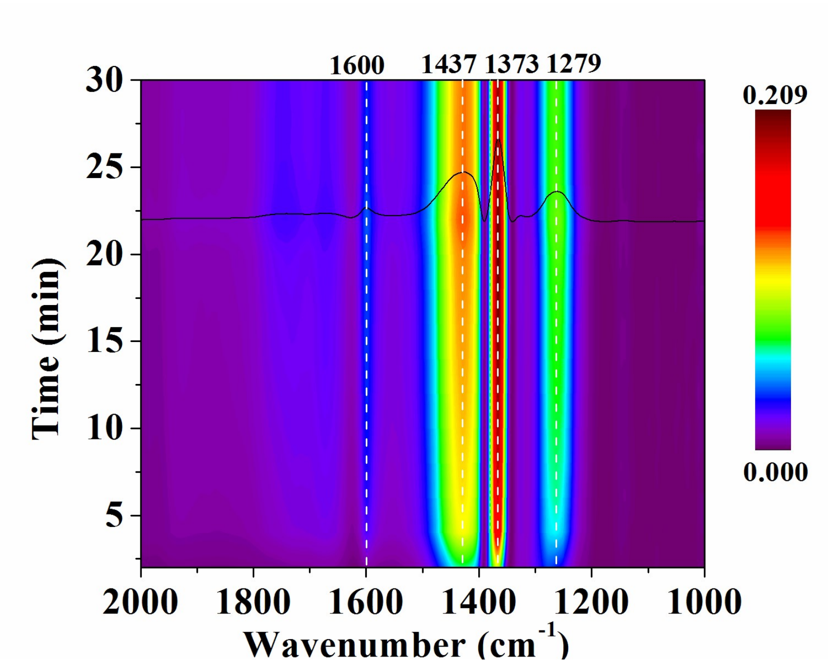
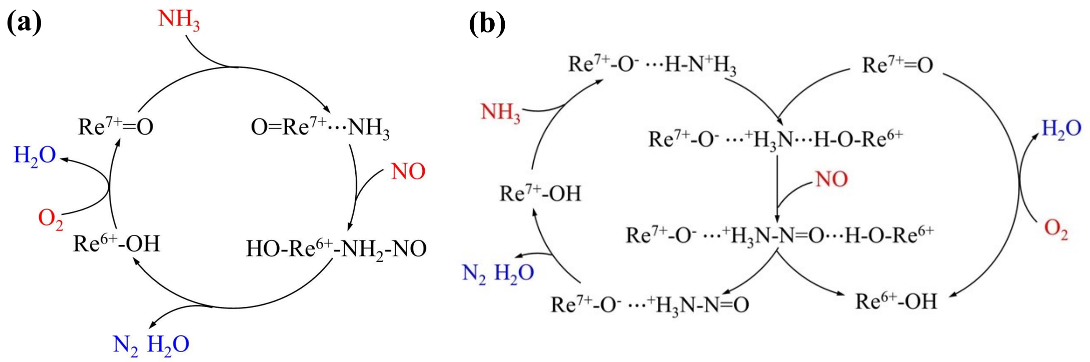


Fig. S7. *In situ* DRIFTS of $NH_3$ + $SO_2$ +$O_2$ co-adsorption over ReTi-3 sample at 250 °C.



**E-R mechanism on L acid sites**

**E-R mechanism on B acid sites**

Scheme S1. Proposed E-R mechanism on (a) L acid sites and (b) B acid sites of $ReO_x/TiO_2$ catalysts.