Active Tetrahedral Iron Sites of $\gamma$-Fe$_2$O$_3$ Catalyzing NO Reduction by NH$_3$

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Abstract:

Maghemite ($\gamma$-Fe$_2$O$_3$) with a spinel structure, consisting of tetrahedral Fe$^{3+}$ ($\text{Fe}^{3+}_{\text{td}}$) and octahedral Fe$^{3+}$ ($\text{Fe}^{3+}_{\text{Oh}}$) sites, has been intensively investigated as an environmentally benign catalyst for selective catalytic reduction (SCR) of NO$_x$ with NH$_3$. In most cases, Fe$^{3+}_{\text{Oh}}$ sites were regarded as catalytically active sites (CASs). Here we identify the CASs in SCR by substituting Fe$^{3+}_{\text{Oh}}$ or Fe$^{3+}_{\text{td}}$ sites of $\gamma$-Fe$_2$O$_3$ with catalytically inactive Ti$^{4+}$ or Zn$^{2+}$, respectively. The SCR activity of $\gamma$-Fe$_2$O$_3$ is preserved after Ti$^{4+}$ doping but drastically decreases when the catalyst is doped with Zn$^{2+}$, demonstrating that Fe$^{3+}_{\text{td}}$ sites serve as CASs in SCR. Synchrotron X-ray absorption spectra coupled with density functional theory calculations reveal that the transfer of an electron from inactive Fe$^{2+}$ to active Fe$^{3+}$ in the tetrahedral site is easier than that in the octahedral site, making the tetrahedral iron sites active in SCR.

4NO + 4NH$_3$ + O$_2$ → 4N$_2$ + 6H$_2$O

Introduction

Selective catalytic reduction (SCR) of NO$_x$ with NH$_3$ is one of the most promising technologies for controlling NO$_x$ emissions that contribute greatly to atmospheric pollution. Although V$_2$O$_5$-based catalysts have been widely applied for SCR in coal-fired power plants, it is necessary to develop vanadium-free SCR catalysts because of the toxicity of vanadium. Fe$_2$O$_3$ is an appealing alternative because of its strong resistance to SO$_2$. There are two types of Fe$_2$O$_3$, i.e., hematite ($\alpha$-Fe$_2$O$_3$) and maghemite ($\gamma$-Fe$_2$O$_3$), $\alpha$-Fe$_2$O$_3$ has high thermal stability but shows insufficient activity in the operating temperature window of 300–400 °C. On the contrary, $\gamma$-Fe$_2$O$_3$ is more active than $\alpha$-Fe$_2$O$_3$ at relatively low temperatures, but $\gamma$-Fe$_2$O$_3$ transforms into $\alpha$-Fe$_2$O$_3$ above 320 °C, leading to decreased catalytic activity.

An efficient approach to enhancing the thermal stability of $\gamma$-Fe$_2$O$_3$ is to substitute part Fe$^{3+}$ with other metal ions. To choose desired doping metal ions, identification of catalytically active sites (CASs) of $\gamma$-Fe$_2$O$_3$ in SCR is one of the important prerequisites. $\gamma$-Fe$_2$O$_3$ with a spinel structure consists of two types of Fe$^{3+}$: one-third of Fe$^{3+}$ in the tetrahedral sites ($\text{Fe}^{3+}_{\text{td}}$) and two-thirds of Fe$^{3+}$ in the octahedral sites ($\text{Fe}^{3+}_{\text{Oh}}$). It has been overwhelmingly believed that Fe$^{3+}_{\text{Oh}}$ sites are CASs for two reasons. (i) The mean length (2.09 Å) of the Fe$^{3+}_{\text{Oh}}$–O bond is greater than that (1.87 Å) of the Fe$^{3+}_{\text{td}}$–O bond; thus, the former would be more reducible and reactive. (ii) For metal oxide spinels, the octahedral sites are preferentially located at the outermost surface layers as compared with the tetrahedral sites. Even though Ti-doped $\gamma$-Fe$_2$O$_3$ and Zn-doped $\gamma$-Fe$_2$O$_3$ have been developed for SCR, the local structures of Ti$^{4+}$ and Zn$^{2+}$ were not precisely studied, and the authors of these studies still regarded Fe$^{3+}_{\text{Oh}}$ sites as CASs in SCR.

In this work, we identified CASs of $\gamma$-Fe$_2$O$_3$ in SCR by using a metal ion doping strategy and chose catalytically inactive Ti$^{4+}$ ($d^0$) and Zn$^{2+}$ ($d^{10}$) to replace Fe$^{3+}_{\text{Oh}}$ and Fe$^{3+}_{\text{td}}$, respectively. First, the crystal structures of the samples were studied by synchrotron X-ray diffraction (SXRD), and the immediate absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra. Second, the electronic structures of the Fe 3d orbitals were characterized by Fe $L_2$-edge X-ray absorption spectra coupled with density functional theory calculations. Finally, CASs were identified by correlating the electronic structures of the Fe 3d orbitals with SCR performance. This work clearly shows that Fe$^{3+}_{\text{td}}$ sites are CASs in SCR.

Materials and Methods

$\gamma$-Fe$_2$O$_3$, Zn-$\gamma$-Fe$_2$O$_3$, and Ti-$\gamma$-Fe$_2$O$_3$ were prepared by coprecipitation (see details in the Supporting Information). According to the X-ray fluorescence (XRF) spectra (Bruker-AXS S4 Explorer) (Table S1), the molar ratios of Ti to Fe and Zn to Fe are 1:3.3 and 1:3.0, respectively, from which Ti-$\gamma$-
Fe$_2$O$_3$ and Zn-γ-Fe$_2$O$_3$ can be roughly formulated as (Ti$_{0.7}$Fe$_{2.3}$)$_1$−δO$_4$ (0 < δ < 0.18) and (Zn$_{0.8}$Fe$_{2.2}$)$_{1−δ}$O$_4$ (0 < δ < 0.03), respectively.

Catalytic evaluation, material characterization, and theoretical calculations$^{15–19}$ are provided in detail in the Supporting Information.

**RESULTS AND DISCUSSION**

A high GHSV of 300000 h$^{-1}$ was adopted to differentiate the catalytic activities of γ-Fe$_2$O$_3$, Ti-γ-Fe$_2$O$_3$, and Zn-γ-Fe$_2$O$_3$ in SCR. Figure 1 and Figure S1 show the NO conversions ($X_{\text{NO}}$) and the selectivity toward N$_2$ as a function of reaction temperature, respectively. Considering the Zn$^{3+}$ and Ti$^{4+}$ cations cannot usually undergo redox transitions and both TiO$_2$ and ZnO are inactive in SCR, substituting Ti$^{4+}$ or Zn$^{2+}$ in γ-Fe$_2$O$_3$ should not yield extra CASs. As the reaction temperature increases, $X_{\text{NO}}$ over pure γ-Fe$_2$O$_3$ increases, and $X_{\text{NO}}$ reaches ~90% at 400 °C. The specific reaction rates (R) related to surface areas (Table S2) of the catalytic materials are shown in Figure S2. The almost identical $X_{\text{NO}}$ (or R) and N$_2$ selectivity curves can be observed for Ti-γ-Fe$_2$O$_3$, except for slight differences in the temperature range of 260–340 °C. In particular, γ-Fe$_2$O$_3$ and Ti-γ-Fe$_2$O$_3$ almost give the same catalytic activities in the kinetic reaction regime ($X_{\text{NO}}$ < 15%), indicating that Ti doping almost has no influence on the catalytic activity of γ-Fe$_2$O$_3$. Similarly, Li et al. reported the SCR activity of Ti-γ-Fe$_2$O$_3$ is comparable to that over γ-Fe$_2$O$_3$.$^{6,14}$ Hence, the Fe$^{3+}$ sites substituted with catalytically inactive Ti$^{4+}$ in γ-Fe$_2$O$_3$ should not be CASs. On the contrary, Zn-γ-Fe$_2$O$_3$ gives a SCR activity significantly lower than that of γ-Fe$_2$O$_3$. The catalytic activity of Zn-γ-Fe$_2$O$_3$ only slightly increases with reaction temperature, and the $X_{\text{NO}}$ values are <25% in the whole temperature window, similar to the previously reported results.$^9$ This demonstrates that inactive Zn$^{2+}$ ions occupy CASs of γ-Fe$_2$O$_3$ in SCR; i.e., the Fe$^{3+}$ sites substituted with catalytically inactive Zn$^{2+}$ in γ-Fe$_2$O$_3$ are CASs. These results are further confirmed with varying amounts of doped Ti and Zn (Figure S3).

The reaction kinetics of SCR at a low $X_{\text{NO}}$ of <15% were studied. The related Arrhenius plot in terms of the steady-state reaction rate constant (k) is shown in Figure S4, from which the corresponding apparent activation energies ($E_a$) can be calculated. The average $E_a$ for γ-Fe$_2$O$_3$ is ~102 kJ mol$^{-1}$, equal to that for Ti-γ-Fe$_2$O$_3$, indicating that SCR over Ti-γ-Fe$_2$O$_3$ and SCR over γ-Fe$_2$O$_3$ possibly follow the same reaction mechanism. The calculated pre-exponential factor (Γ) for Ti-γ-Fe$_2$O$_3$ (2.5 × 10$^{12}$ L s$^{-1}$ g$^{-1}$) approaches that (2.2 × 10$^{12}$ L s$^{-1}$ g$^{-1}$) of γ-Fe$_2$O$_3$ but it is 5 orders of magnitude larger than that (2.8 × 10$^{10}$ L s$^{-1}$ g$^{-1}$) of Zn-γ-Fe$_2$O$_3$. The close Γ values imply the same CASs for both γ-Fe$_2$O$_3$ and Ti-γ-Fe$_2$O$_3$, and the significantly small Γ value for Zn-γ-Fe$_2$O$_3$ indicates that the Fe$^{3+}$ sites substituted with Zn$^{2+}$ are CASs of γ-Fe$_2$O$_3$.

Figure 2a shows the SXRD patterns. γ-Fe$_2$O$_3$ is identified as maghemite with a cubic spinel structure (JPCDS Card No. 39-1346). The spinel structure is preserved after substitution with Ti$^{4+}$ or Zn$^{2+}$, and no TiO$_2$ and ZnO phase appears in the SXRD pattern of Ti-γ-Fe$_2$O$_3$ or Zn-γ-Fe$_2$O$_3$, respectively. Note that in comparison to those of γ-Fe$_2$O$_3$, all the peaks of Zn-γ-Fe$_2$O$_3$ distinctly shift to lower Bragg angles, reflecting the substitution of some Fe$^{3+}$ with Zn$^{2+}$ in Zn-γ-Fe$_2$O$_3$ by considering that the ionic radius of Zn$^{2+}$ (0.61 Å) is larger than that of Fe$^{3+}$ (0.49 Å).$^{20}$ Similarly, compared to the peaks of γ-Fe$_2$O$_3$, all Ti-γ-Fe$_2$O$_3$ peaks shift to slightly larger Bragg angles, demonstrating the replacement of some Fe$^{3+}$ with Ti$^{4+}$ due to the ionic radius of Ti$^{4+}$ (0.60 Å) of Zn-γ-Fe$_2$O$_3$. Inset of Figure 2a.

The immediate structures of doped Ti$^{4+}$ and Zn$^{2+}$ were determined by XANES and EXAFS. The pre-edge features in the Fe K-edge XANES spectra are sensitive to the local geometrical structures of iron centers.$^{21}$ Figure 2b shows the pre-edge XANES spectra of γ-Fe$_2$O$_3$, Ti-γ-Fe$_2$O$_3$, and Zn-γ-Fe$_2$O$_3$ at the Fe K-edge together with a “standard” α-Fe$_2$O$_3$, comprising only octahedral FeO$_6$ structure. A relatively intense pre-edge peak appears in the XANES spectrum of γ-Fe$_2$O$_3$, attributed to the 1s → 3d (ε, τ$_1$) dipole-allowed transition in...
EXAFS spectrum of Ti-γ-Fe₂O₃ at the Fe K-edge is similar to that of γ-Fe₂O₃ except that the decreases in intensity in the second and third shells of Ti-γ-Fe₂O₃ are observed. The first shell can be attributed to the contribution from the Fe-O bonds with a bond length of ∼1.97 Å (Table S3), in line with the average Fe-O bond length (∼2.00 Å) in Fe₃Td and Fe₅Oh sites in γ-Fe₂O₃. The second shell is ascribed to the Fe₅Oh-FeOh and Fe₅Oh-Ti₅Oh interatomic distances, and the third shell should be assigned to the Fe₃Td-Fe₅Oh interatomic distance, which also covers the scattering paths of Fe₅Oh to Ti₅Oh for Ti-γ-Fe₂O₃. These amplitudes at the second and third shells are weaker than the corresponding amplitude of γ-Fe₂O₃ largely because the atomic number of Ti is smaller than that of Fe.

The three similar shells appear in the FT EXAFS spectrum at the Fe K-edge of Zn-γ-Fe₂O₃. The attributions of the first and second shells are shown in Figure 3b, and the amplitude of the third shell is much weaker than the corresponding amplitude of γ-Fe₂O₃ attributed to the interatomic distance between Fe₅Oh and Zn in the tetrahedral sites. To further substantiate the Zn²⁺ position, we also recorded the FT EXAFS spectrum of Zn-γ-Fe₂O₃ at the Zn K-edge (also shown in Figure 3b). The absence of ∼3.0 Å interatomic distances demonstrates that Zn²⁺ ions are not located at the octahedral sites of spinel. A combination of the SXRD data with the XANES and EXAFS spectra reveals that Ti⁴⁺ and Zn²⁺ substituted for Fe₅Oh and Fe₅Oh respectively.

As shown in Figure 1, the catalytic performance of γ-Fe₂O₃ remains almost preserved after Fe₅Oh sites are substituted with catalytically inactive Ti⁴⁺, but γ-Fe₂O₃ loses activity after Fe₅Oh sites are substituted with Zn²⁺, indicating that Fe₅Oh sites are CASs in SCR rather than Fe₅Oh sites. Redox cycles are often involved in SCR regardless of the reaction mechanisms (Eley–Rideal and Langmuir–Hinshelwood models) and the Fe²⁺ ↔ Fe³⁺ redox cycles occurring during the SCR process are intimately associated with the catalytic activity. Generally, Fe³⁺ sites are responsible for NH₃ oxidation in SCR, being concomitant with Fe³⁺ → Fe²⁺ transfer, and the subsequently produced Fe²⁺ sites are oxidized to Fe³⁺ by O₂ to finish the redox cycle. The Fe³⁺ → Fe²⁺ transfer is relatively easy because Fe³⁺ has strong oxidative ability, and the Fe²⁺ → Fe³⁺ transfer depends on coordinative configurations of iron ions. Ponec et al. used the isotopic exchange reaction of oxygen to investigate the interactions of Fe₅Oh (it should be α-Fe₂O₃ with only Fe₅Oh because of an extremely high melting point) with O²− and found that the E Syria for ¹⁸O₂(g) + 2¹⁶O₂(g) → ¹⁶O₂(g) + 2¹⁸O₂(g) [where O₂(g) and O represent gaseous O₂ and surface lattice oxygen of Fe₅Oh respectively] is very high, i.e., ∼130 kJ mol⁻¹ (∼1.4 eV per Fe₅Oh) even at 400–500 °C, although the Fe-O bond energy is only 65.7 kJ mol⁻¹. This suggests that the activation energy to realize Fe²⁺Oh → Fe³⁺Oh transfer should be higher than the activation energy (∼1.1 eV) of SCR over γ-Fe₂O₃ in Figure 4a.

To investigate the sustainability of the Fe³⁺ ↔ Fe²⁺ redox cycles at the tetrahedral sites, we collected Fe L₃-edge X-ray absorption spectra (Figure 4a). According to the Oh symmetry of Fe and the crystal-field theory, two peaks in the Fe L₃-edge X-ray absorption spectra of γ-Fe₂O₃, Ti-γ-Fe₂O₃, and Zn-γ-Fe₂O₃ can be assigned to the 2p₃/₂ → 3d (t₂g e_g) transitions with an octahedral ligand-field splitting energy (∆Oh) of ∼1.6 eV. The high-spin electron configurations of Fe³⁺Oh and Fe²⁺Oh are t₂g⁵e_g and t₂g⁵e_g, respectively, and thus, the unoccupied states of the t₂g orbitals of Fe³⁺Oh outnumber those of Fe²⁺Oh. As a consequence, the unoccupied states of the t₂g orbitals are positively proportional to their corresponding intensity in the Fe L₃-edge X-ray absorption spectra. Hence, a ratio (λ) of t₂g to e_g in intensity in the Fe L₃-edge X-ray absorption spectrum can be used to determine the oxidation states of Fe₅Oh. The λ value becomes smaller after Ti⁴⁺ substitutes for Fe₅Oh in γ-Fe₂O₃ concomitant with Fe³⁺ → Fe²⁺ transfer in another octahedral site rather than that in the tetrahedral site. This clearly demonstrates that Fe²⁺(t₂g⁵e_g) is more stable in the octahedral site than in the tetrahedral site; i.e., the propensity of Fe²⁺→ Fe³⁺ should be higher than that of Fe³⁺→ Fe²⁺. The λ values for Zn-γ-Fe₂O₃ and γ-Fe₂O₃ are equal to each other, indicating that the Fe³⁺(t₂g⁵e_g) electron configuration with a ∆Oh value of ∼1.6
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00124.


