

The Specific Deoxidation Behavior of Iron Titanate Catalyst Characterized by the XAFS Technique for the Selective Catalytic Removal of NO_x by NH₃

Iron titanate (FeTiO_x) catalyst has been proven to be a potential candidate for the selective catalytic reduction of NO_x with NH₃ (NH₃-SCR). Due to the formation of a unique microstructure as an edge shared Fe-(O)₂-Ti species, the NH₃-SCR activity, N₂ selectivity and SO₂ durability of FeTiO_x catalyst have been greatly improved. Using the XAFS technique in combination with H₂-TPR experiments, we discovered that the highly dispersed Fe species in FeTiO_x catalyst showed a specific deoxidation behavior due to the presence of an electronic inductive effect between Fe and Ti species. The reducibility of Fe³⁺ species in FeTiO_x catalyst was greatly enhanced accordingly, leading to the higher oxidation ability of Fe species in FeTiO_x, which is beneficial to the NO_x reduction process.

Compared to pristine Fe₂O₃ and TiO₂, the particle size of FeTiO_x catalyst was greatly lowered, and no discernable lattice fringes could be observed from the TEM images (Fig. 1). High NH₃-SCR activity and N₂ selectivity with a broadened operating temperature window together with enhanced SO₂ durability could be achieved on FeTiO_x catalyst. From our previous study

using the XAFS technique [1], we concluded that the main active phase in FeTiO_x catalyst was in the form of iron titanate crystallite, with an edge shared Fe-(O)₂-Ti microstructure. An electronic inductive effect between Fe³⁺ species and Ti⁴⁺ species was present in this structure, leading to the enhanced oxidation ability of Fe³⁺ species.

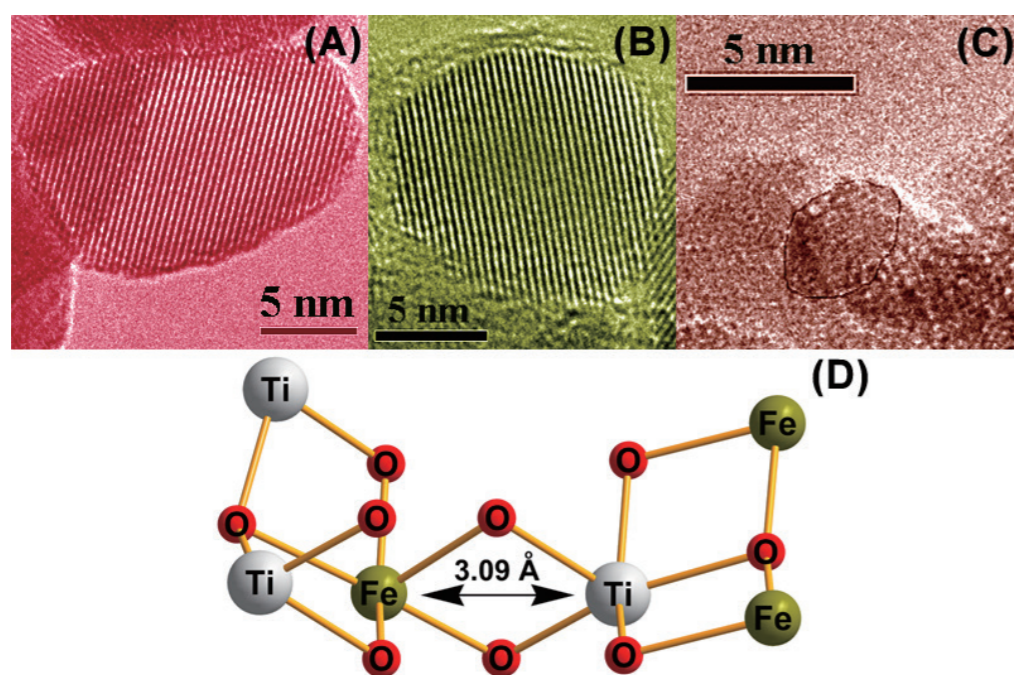


Figure 1: HRTEM images of (A) hematite Fe₂O₃, (B) anatase TiO₂ and (C) FeTiO_x catalyst [2], and (D) proposed structural model of FeTiO_x catalyst derived from EXAFS curve-fitting results [1].

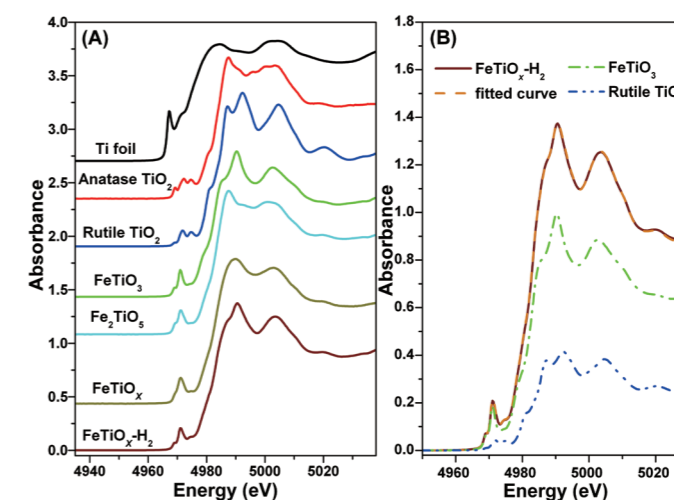


Figure 2: (A) Normalized XANES spectra of Ti-K edges in Ti-containing samples; (B) XANES linear fitting results of Ti-K edges in FeTiO_x catalyst after H₂ reduction using FeTiO₃ and Fe as references [3].

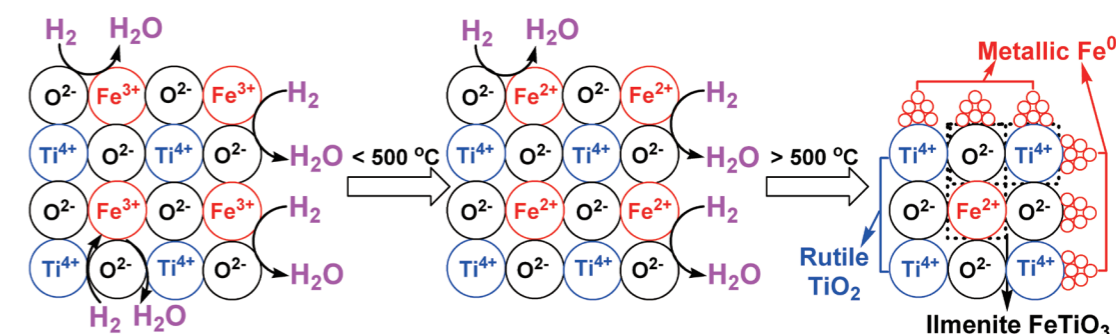


Figure 3: Proposed H₂ reduction process of the FeTiO_x catalyst [3].

In the present study, based on XANES linear fitting (Fig. 2) and EXAFS curve-fitting results in combination with the H₂-TPR process, we discovered that the Fe³⁺ species in the FeTiO_x catalyst could be totally reduced to Fe²⁺ species below 500 °C in the form of ilmenite FeTiO₃, while the Fe³⁺ species in pristine Fe₂O₃ could only be reduced to Fe₃O₄ (Fig. 3). The typical NH₃-SCR reaction mainly occurs below 500 °C for practical use, and the enhanced redox ability of Fe³⁺ species in FeTiO_x catalyst is very beneficial to enhance its catalytic performance. The as-formed Fe²⁺ species in the H₂-reduced FeTiO_x catalyst combined with Ti⁴⁺ species to exist as ilmenite FeTiO₃, but not as FeO as in the Fe₂O₃ case, indicating that the Fe species and Ti species were present in a high dispersion state at the atomic scale in the original FeTiO_x catalyst. It is interesting that above 500 °C, the surface layers of the as-formed FeTiO₃ could be further reduced, resulting in the formation of partial metallic Fe⁰ clusters or particles and residual rutile TiO₂. However, the reduction of Fe²⁺ species in

the bulk FeTiO₃ phase could not be achieved even at temperatures as high as 900 °C (Fig. 3). This is a unique deoxidation behavior for the novel FeTiO_x catalyst that has not been reported before. These interesting results will be useful for investigating the local structure and redox ability of active sites in some mixed oxide catalysts simultaneously for certain catalytic reactions, thus clarifying the structure-activity relationships for catalysis.

REFERENCES

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F. Liu, H. He and L. Xie (CAS-RCEES)