Effect of State of Fe on Photocatalytic Removal of NO over Visible Light Responsive Fe/TiO₂ Catalyst

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Introduction
Nitrogen oxides (NOₓ), mainly produced from combustion of fossil fuels and vehicle exhaust, is responsible for atmospheric environmental problems such as haze, photochemical smog, acid rain and so on. Semiconductor photocatalysis, as a “green” technology, has been used to remove NOₓ at ppb levels [1].

Titania (TiO₂) has been a promising candidate for photocatalysis applications [2]. However, the relatively large band gap of TiO₂ (3.0-3.2 eV) limits its application in the visible light region. Metal elements doping is one of the typical approaches to extend the spectral response of TiO₂ to visible-light region [3]. Fe has attracted special attention due to the fact that the ionic radius of Fe³⁺ (0.64 Å) is similar with that of Ti⁴⁺ (0.68 Å) resulting in easier insertion of Fe³⁺ into the crystal structure of TiO₂ [4]. However, as a dopant, the role of Fe³⁺ is still contradiction. Some authors suggested detrimental effect of Fe³⁺ as a promoter that increases the rate of charge recombination, while other authors reported the beneficial effect of Fe³⁺ in separation of photogenerated electrons and holes and in shift the absorption edge into the visible-light range with the narrowing of the band gap, and thus increasing the photocatalytic activity [5-9]. The state of Fe has great influence on the photocatalytic activity, but this is not systematically investigated.

The present work aimed at synthesizing different Fe/TiO₂ catalysts and studying the influence of Fe on structure, extent of substitution and performance as a photocatalyst to remove gaseous NO in air under visible light.

Materials and Methods
The Fe/TiO₂ catalysts were synthesized by facile co-precipitation method using Fe(NO₃)₃ • 9H₂O as Fe precursors and Ti(SO₄)₂ as Ti precursors and NH₃•H₂O as precipitator. The precipitate cakes were first filtrated and washed by distilled water, and then desiccated at 100 °C for 12 h and calcined at 400 °C for 6 h. The catalysts was signified by x%FT (x means the molar content of Fe). 0.1% Fe/TiO₂ catalyst was also prepared by the homogeneous precipitation method and conventional wet impregnation method.

The catalysts were characterized by ICP-OES, XRD, Raman, photoluminescence analyzer, UV−vis diffuse reflectance spectra, photoluminescence (PL) emission spectra, electron paramagnetic resonance (EPR) spectra, and XAFS measurement.

DFT calculations were performed using CASTEP package. The generalized gradient approximation (GGA) with the PBE exchange-correlation functional was adopted. The parameters are: ultrasoft pseudo-potential, k-point mesh of (2×2×1), energy cutoff=380 eV, convergence tolerance: energy<5.0×10⁻⁷ eV/atom, force<0.03 eV/Å, stress<0.05 GPa and displacement<1.0×10⁻³Å.

The photocatalytic experiments for the removal of NO were similar with our previous work [7].

Results and Discussion

0.1%FT prepared with co-precipitation method (0.1%FT-c) showed the highest NO conversion activity. The EPR results revealed that Fe ions can substitute Ti ions of TiO₂ prepared by the co-precipitation. On the basis of the characterization results, the higher photocatalytic activity of 0.1%FT-c was attributed to synergistic effects of more visible light absorption and minimum electron hole recombination caused by the Fe ions incorporated into the crystal lattice of TiO₂.

Figure 1. The NO, NO₂ conversion and NO₂ selectivity at 0.5 h for various catalysts

Figure 2. The DFT+U density of states for (a) FeTi₁₄O₉₆ and (b) FeTi₄₈O₉₆.

Significance
The present study demonstrates the incorporated Fe ions can substitute the octahedrally coordinated Ti⁴⁺ ions in TiO₂ lattice, which extends the visible light absorption and hence promotes the formation of electron-hole pair. Furthermore, the doping of Fe increases the electron-hole separation efficiency because the Fe³⁺ can act as an electron-trapped agent.

References