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An XAFS study on the specific microstructure of active species in iron titanate catalyst for NH₃-SCR of NO_x

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Abstract

Environmental-friendly iron titanate (FeTiO_x) catalyst is a potential candidate for the substitution of conventional V₂O₅-WO₃ (MoO₃)/TiO₂ catalyst for the selective catalytic reduction of NO_x with NH_3 (NH_3 -SCR) for the NO_x elimination from stationary and mobile sources for environmental protection. To understand in-depth the nature of active structure in this $FeTiO_x$ catalyst for further catalyst redesign and activity improvement, the study of X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS) combined with theoretical calculation is carefully performed. Different from the crystal structure of hematite Fe₂O₃, homogeneous edge shared Fe³⁺-(O)₂-Ti⁴⁺ structure in FeTiO_x catalyst prepared from $Ti(SO_4)_2$ precursor is obviously formed with crystallite phase, which shows the electronic inductive effect between Fe³⁺ and Ti⁴⁺ species, resulting in the high NO adsorption and oxidation ability of Fe³⁺ species and thus high catalytic activity and N₂ selectivity in the NH₃-SCR reaction. In the future study, this specific edge shared Fe³⁺-(O)₂-Ti⁴⁺ structure can be stabilized onto certain catalyst supports with large surface area for practical use, such as the catalytic removal of NO_x from flue gas and diesel engine exhaust.

Keywords: Iron titanate catalyst; Selective catalytic reduction; Environmental-friendly; XANES; EXAFS; Electronic inductive effect.

1. Introduction

Selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is a well-proven technique for the removal of NO_x from stationary and mobile sources for environmental protection, such as coal-fired power plants and diesel engines [1]. Due to some inevitable disadvantages of the conventional and commercial SCR catalyst V_2O_3 -WO₃ (MoO₃)/TiO₂ including the narrow operation temperature window, the low N₂ selectivity at high temperatures due to the formation of large amount of N₂O, the high conversion of SO₂ to SO₃ and the toxicity of vanadium pentoxide to eco-environment and human health, although it has been applied for several decades in industry, many researchers still make great effort to develop new, highly efficient, stable, environmental-friendly and vanadium-free NH₃-SCR catalysts, such as Fe/Cu/Ce-exchanged zeolites [2-9] and Fe/Cu/Mn/Ce supported-type or mixed oxide catalysts [10-21]. Several vanadium-free catalysts have already been utilized for the catalytic removal of NO_x from diesel engine exhaust in recent years, such as Fe/Cu-ZSM-5 catalysts [22].

In our previous study, we have successfully developed a novel and environmental-friendly iron titanate (FeTiO_x) catalyst prepared by conventional co-precipitation method, which showed high NH₃-SCR activity, N₂ selectivity and H₂O/SO₂ durability in the medium temperature range (200-400 °C) [23-26]. This FeTiO_x catalyst is promising to be used in the deNO_x process for flue gas and diesel engine exhaust for environmental protection. We deduced that the iron titanate crystallite with specific Fe-O-Ti structure, but not aggregated Fe₂O₃ oxide particles, was the real active phase in the NH₃-SCR reaction. However, no direct evidence was obtained from X-ray diffraction (XRD), UV-vis diffuse reflectance spectroscopy (UV-vis DRS), transmission electron microscopy (TEM) and Raman spectroscopy *etc*. due to the poor crystallinity of this catalyst both in the bulk phase and on the surface. In order to understand in-depth the structural nature of the active phase in this FeTiO_x catalyst for further catalyst redesign and activity improvement, more powerful characterization method for determining the local structure of catalytic materials should be applied, such as the X-ray absorption fine-structure spectroscopy (XAFS).

In this study, using X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine-structure spectroscopy (EXAFS), we confirm that a homogeneous linkaged structure of edge shared Fe^{3+} octahedra and Ti^{4+} octahedra with severe distortion is indeed formed in $FeTiO_x$ catalyst with crystallite phase. In addition, the electronic inductive effect between Fe^{3+} and Ti^{4+} species will also be verified by the experimental results combined with theoretical calculation, which is very important to enhance the NO adsorption and oxidation ability of Fe^{3+} species and thus the catalytic activity in NH₃-SCR reaction. This new finding can provide theoretical guidance for the further design and activity improvement of this NH₃-SCR catalyst, even for other Fe-Ti containing or mixed oxide catalyst systems.

2. Experimental

2.1 Catalyst preparation

The iron titanate catalysts were facilely synthesized by conventional co-precipitation method using $TiCl_4$ or $Ti(SO_4)_2$ as Ti precursor and $Fe(NO_3)_3 \cdot 9H_2O$

as Fe precursor with the molar ratio of Fe:Ti = 1:1. When using TiCl₄ as Ti precursor, it was firstly diluted with ice-cold distilled water in the bath of ice-water mixture avoiding intense hydrolysis to prepare a known concentration of TiOCl₂ solution. Because of the slow hydrolysis of TiCl₄ at such a low temperature, no TiO₂ precipitation occurred during the preparation process of TiOCl₂ solution. Then a stoichiometric amount of Fe(NO₃)₃ aqueous solution was added in with subsequent stirring for 1 h without the formation of any precipitation in this process, either. Afterwards, standard NH₃·H₂O (25 wt.%) aqueous solution was used as precipitator until the pH rose to 10 when the Fe and Ti ions were completely co-precipitated. Without aging, the precipitate was filtrated and washed by distilled water to remove the unwanted cations and anions from precursors and precipitator, followed by desiccation in oven at 100 °C for 12 h and calcination in muffle furnace at 400 °C for 6 h in air condition. Catalyst prepared from TiCl₄ precursor was denoted as FeTiO_x-TiCl₄.

When using Ti(SO₄)₂ as Ti precursor, TiOSO₄ solution could be obtained more easily because the hydrolysis of Ti(SO₄)₂ in H₂O was much slower than that of TiCl₄. Ti(SO₄)₂ and Fe(NO₃)₃·9H₂O were firstly dissolved together with distilled water without the formation of any precipitation, and then the rest procedures were controlled exactly the same as those of FeTiO_x-TiCl₄ catalyst. Catalyst prepared from Ti(SO₄)₂ precursor was denoted as FeTiO_x-Ti(SO₄)₂.

We also prepared Fe_2O_3/TiO_2 supported type catalyst (Fe:Ti = 1:1 in molar ratio) using conventional impregnation method for comparison. The anatase TiO₂ support in Fe₂O₃/TiO₂ catalyst was purchased from Shanghai Huijing Co.. Firstly, the calculated amount of TiO₂ support was added into an aqueous solution of Fe(NO₃)₃·9H₂O. After impregnation with stirring for 1 h, the excess water was removed in a rotary evaporator at 80 °C. Then the sample was desiccated in oven at 120 °C for 12 h, followed by calcination in muffle furnace at 400 °C for 6 h in air condition.

For the preparation of reference samples, hematite Fe_2O_3 and anatase TiO_2 were self-prepared by precipitation method using $Fe(NO_3)_3 \cdot 9H_2O$ and $Ti(SO_4)_2$ as precursors, respectively, and using standard $NH_3 \cdot H_2O$ (25 wt.%) aqueous solution as precipitator. The desiccation and calcination procedures were controlled exactly the same as those of $FeTiO_x$ -TiCl₄ and $FeTiO_x$ -Ti(SO₄)₂ catalysts.

Finally, all the calcined samples were crushed and sieved above 200 mesh, and then diluted by flour power with appropriate molar ratios and pressed into thin disks for XANES and EXAFS measurements.

2.2 Activity test

The steady state NH₃-SCR activity over different catalysts was tested in a fixed-bed quartz tube reactor at atmospheric pressure, and the reaction conditions were controlled as follows: 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, N₂ balance; 0.6 ml catalyst, 20-40 mesh; total flow rate of 500 ml/min and gas hourly space velocity (GHSV) = 50 000 h⁻¹. The effluent gas was continuously analyzed using an FTIR spectrometer (Nicolet Nexus 670) equipped with a heated, low volume multiple-path gas cell (2 m).

2.3 XAFS measurement and data analysis

The XANES and EXAFS of Fe-K and Ti-K edges were measured in a transmission mode at room temperature on BL-7C beam line, Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization (IMSS-KEK), Japan. Fe foil, FeO, hematite Fe₂O₃, ilmenite FeTiO₃, pseudobrookite Fe₂TiO₅, Ti foil, anatase TiO₂ (self-prepared) and rutile TiO₂ were used as reference samples. The storage ring was operated at 2.5 GeV with 300 mA as an average storage current. The synchrotron radiation beam line was monochromatized with a Si (111) double crystal monochromator, and mirrors were used to eliminate higher harmonics. The incident and transmitted beam intensities were monitored using ionization chambers filled with pure N₂.

XAFS data were analyzed using the REX2000 program (Rigaku Co.). XANES spectra were normalized with edge height and then taken the first-order derivatives to compare the variation of absorption edge energies. EXAFS oscillation $\chi(k)$ was extracted using spline smoothing with a Cook-Sayers criterion [27] and weighted by k^3 in order to compensate for the diminishing amplitude in high *k* range because of the decay of the photoelectron wave. Thereafter, the filtered k^3 -weighted $\chi(k)$ was Fourier transformed into R space (*k* range: 2.5-15 Å⁻¹ for Fe-K EXAFS and 2.5-13 Å⁻¹ for Ti-K EXAFS) with a Hanning function window. In the curve fitting step, the possible backscattering amplitude and phase shift were calculated using FEFF8.4 code [28].

2.4 Density functional theory (DFT) calculation

The geometry optimization of the three kinds of stoichiometric TiO_2 , Fe_2O_3 and Fe_2TiO_5 crystals were carried out using Dmol3 module [29,30] in Materials Studio

software package. The generalized gradient approximation (GGA) with PW91 functional was used to describe the exchange-correlation (XC) effects. The double numerical plus polarization (DNP) basis set was used in the expanded electronic wave function.

The Brillouin zone using the Monkhorst-Pack scheme was sampled by $7 \times 7 \times 3$, $6 \times 6 \times 2$ and $3 \times 7 \times 3$ for TiO₂, Fe₂O₃ and Fe₂TiO₅, respectively. For all calculations, the convergence in energy and force was set to 10^{-5} eV and 2×10^{-3} eV/Å. The atomic charges were calculated using the Hirshfeld approach. The electron density difference of the investigated crystal models was also analyzed.

3. Results and discussion

3.1 NH₃-SCR activity

The steady-state NH₃-SCR activity over Fe₂O₃/TiO₂, FeTiO_x-TiCl₄ and FeTiO_x-Ti(SO₄)₂ catalysts is presented in Fig. 1. As we can see, the operation temperature window of Fe₂O₃/TiO₂ is quite narrow, and the highest NO_x conversion can not achieve 100% either. Over FeTiO_x-TiCl₄ catalyst, the SCR activity at temperatures below 300 °C is quite low, although the SCR activity at temperatures above 300 °C is similar to that over FeTiO_x-Ti(SO₄)₂ catalyst. In a broad temperature range, the FeTiO_x-Ti(SO₄)₂ catalyst exhibits rather high deNO_x efficiency, with *ca*. 90% NO_x conversion obtained from 200 to 350 °C. In short summary, the NH₃-SCR activity over these three catalysts at low temperatures decreases in the following sequence: FeTiO_x-Ti(SO₄)₂ >> Fe₂O₃/TiO₂ > FeTiO_x-TiCl₄. New highly active species with specific structure should be formed in the most active FeTiO_x-Ti(SO₄)₂ catalyst,

which will be discussed in detail in the following sections.

3.2 XANES

Fig. 2A and Fig. 2B show the Fe-K XANES of reference samples, Fe_2O_3/TiO_2 , $FeTiO_x$ -TiCl₄, $FeTiO_x$ -Ti(SO₄)₂ catalysts and their corresponding first-order derivatives, respectively. The first-order derivative peak of the absorption coefficient appears at 7122.6 eV for Fe^{2+} in FeO, while that for Fe^{3+} in pristine Fe_2O_3 appears at 7123.2 eV. Interestingly, this peak appears at 7123.4 eV in Fe_2TiO_5 reference sample, indicating the higher absorption edge energy than that of Fe_2O_3 . This may be due to the electronic inductive effect by surrounding Ti^{4+} ions, in which the deviation of electron cloud occurs from Fe^{3+} to Ti^{4+} species.

As for Fe_2O_3/TiO_2 catalyst, the clear XANES pattern of Fe-K edge is identical with that of hematite and gives the maximum at 7123.2 eV in the first-order derivative, implying that well crystallized Fe_2O_3 exists in this catalyst.

FeTiO_x-Ti(SO₄)₂, the most active catalyst, gives the strongest pre-edge peak indicating the severest structure distortion probably from octahedral coordination. A peak top in the first-order derivative appears at 7123.6 eV, indicating the presence of Fe³⁺. The higher energy of this derivative peak than that of Fe₂O₃ sample further indicates the presence of Fe³⁺-O-Ti⁴⁺ linkage in this catalyst, in which the neighbouring Ti⁴⁺ species draws more electrons from Fe³⁺ species. This is in well accordance with our previous XPS results, in which the Fe³⁺ species on FeTiO_x-Ti(SO₄)₂ catalyst showed higher binding energy than that on pristine Fe₂O₃ sample [24]. The broad feature in the XANES spectrum of FeTiO_x-Ti(SO₄)₂ catalyst

may be due to the poor crystallinity of iron titanate species with nano size effect, resulting in the less scattering of photoelectrons by neighbouring unsaturated coordination atoms, which is consistent with the rather broad XRD bumps without obvious diffraction peaks [24]. The iron titanate species may be the aggregates of small particles with specific structure, called as iron titanate crystallite. Sulfate species from $Ti(SO_4)_2$ precursor may inhibit the formation of large crystal particle in its preparation process [31]. In our previous study [32], only 0.2% S content in molar ratio from the residual sulfate species was detected on the surface of $FeTiO_x$ -Ti(SO₄)₂ catalyst, yet this small amount of sulfate did not result in any SCR activity difference at high temperatures comparing with that of $FeTiO_x$ -TiCl₄ catalyst (as shown in Fig. 1). As we mentioned above, the electronic field of Ti^{4+} species around Fe^{3+} species will reduce the electron density of Fe³⁺ in Fe³⁺-O-Ti⁴⁺ linkage, and may facilitate the adsorption of negative molecular (such as NO with unpaired electron). This will lead to the higher NO adsorption and oxidation ability of Fe³⁺ species, as confirmed by the comparative NO_x-TPD results on Fe_2O_3 sample and $FeTiO_x$ -Ti(SO₄)₂ catalyst in our previous study [33], which is beneficial to the promotion of low temperature NH₃-SCR activity over $FeTiO_x$ -Ti(SO₄)₂ catalyst.

As for FeTiO_x-TiCl₄ catalyst, the first-order derivative peak of XANES appears at 7123.4 eV, also indicating the presence of Fe³⁺. The post-edge XANES feature is similar to that of either Fe₂TiO₅ or Fe₂O₃ reference samples, but the peak is featureless. Therefore, a mixture of Fe₂TiO₅, Fe₂O₃ and iron titanate species may exist in this catalyst. Fig. 2C shows the linear fitting results of Fe-K XANES in

FeTiO_x-TiCl₄ catalyst using Fe₂TiO₅, Fe₂O₃ and FeTiO_x-Ti(SO₄)₂ as reference samples, based on which we can conclude that a mixture of *ca*. 28% Fe₂TiO₅ + 23% Fe₂O₃ + 49% iron titanate species derived from FeTiO_x-Ti(SO₄)₂ existed in this catalyst (Table 1). Only half of the Fe³⁺ species in this catalyst is in the form of active iron titanate crystallite, and accordingly the low temperature NH₃-SCR activity over FeTiO_x-TiCl₄ catalyst is much lower than that over FeTiO_x-Ti(SO₄)₂ catalyst but higher than that over Fe₂O₃/TiO₂ catalyst [24].

Fig. 3A shows the Ti-K XANES of reference samples and Fe₂O₃/TiO₂, FeTiO_x-TiCl₄, FeTiO_x-Ti(SO₄)₂ catalysts. Anatase TiO₂ is the main crystal phase in Fe₂O₃/TiO₂ catalyst. Ti-K XANES of FeTiO_x-Ti(SO₄)₂ catalyst has the strongest pre-edge peak together with broad peak features in the post-edge region, indicating the presence of distorted Ti⁴⁺ local structure probably from octahedral coordination. XANES of FeTiO_x-TiCl₄ catalyst can be explained by a mixture of ca. 26% Fe₂TiO₅ + 26% rutile TiO₂ + 48% iron titanate crystallite, as shown by the linear fitting results in Fig. 3C and Table 1. It is noteworthy that the rutile TiO_2 is formed in the $FeTiO_x$ -TiCl₄ catalyst instead of anatase TiO₂. Another interesting feature is the edge position of Ti-K edge. Fig. 3B shows the first-order derivatives of Ti-K XANES spectra. The absorption energy of Ti-K edge in Fe₂TiO₅ reference sample with the Fe³⁺-O-Ti⁴⁺ linkage where both ions are located nearby is lower than that of anatase TiO_2 . This can be interpreted simply by the reverse electronic inductive effect by the surrounding Fe^{3+} species, similarly to the Fe-K edge case. $FeTiO_x$ -Ti(SO₄)₂ catalyst has the lowest absorption edge energy, indicating again the presence of most abundant $\mathrm{Fe}^{3+}\mathrm{-O-Ti}^{4+}$

linkage. This phenomenon may universally exist in other Fe-Ti containing catalysts, such as Fe^{3+} -exchanged TiO₂-pillared clay catalyst developed by Long and Yang [34] and Fe₂O₃/TiO₂ catalyst developed by Kato *et al.* [35], in which the Fe³⁺-O-Ti⁴⁺ structure might also form and play important roles in the NH₃-SCR reaction.

3.3 EXAFS

Fig. 4 depicts the Fourier transform of filtered k^3 -weighted EXAFS oscillations of Fe-K and Ti-K edges into R space, and all corresponding $k^3 \cdot \chi(k)$ are shown in Fig. 5. Fe₂O₃/TiO₂ catalyst has similar coordination peaks of Fe-K and Ti-K edges as those of hematite Fe₂O₃ and anatase TiO₂, respectively, which is in well accordance with the curve fitting results in Table 2 when using hematite Fe₂O₃ and anatase TiO₂ as model crystals. As suggested by XANES results, FeTiO_x-TiCl₄ catalyst shows peaks in the second coordination shells similar to those of Fe₂TiO₅, Fe₂O₃ and rutile TiO₂. However, these peaks are much smaller due to the coexistence of iron titanate crystallite. For FeTiO_x-Ti(SO₄)₂ catalyst, the intensity of the second coordination peaks of both Fe and Ti is rather low, implying a crystallite state of this sample again. It is noteworthy that only one single peak appears for the second coordination shells of both Fe and Ti species in FeTiO_x-Ti(SO₄)₂ catalyst, which is totally different from those of reference samples and the other two catalysts.

The single peak in the second coordination shells of FeTiO_x -Ti(SO₄)₂ catalyst can be assigned to Fe^{3+} -O-Ti⁴⁺ linkage suggested by the XANES results. The curve fitting results in Table 2 indicate the Fe^{3+} -O-Ti⁴⁺ distance as 3.09 ± 0.04 Å, which agrees well with the edge shared Fe-O-Ti and Ti-O-Fe structures. Compared to the edge shared Fe-O-Ti structure in well crystallized Fe₂TiO₅ reference sample, the bond distances of Fe-O-Ti and Ti-O-Fe in this catalyst is 0.09 Å shorter. This is also probably related with the nano effect of FeTiO_x-Ti(SO₄)₂ catalyst in poor crystallinity, of which the catalyst surface possesses a large proportion of unsaturated coordination atoms with shorter average bond distances. The stronger interaction between Fe³⁺ and Ti⁴⁺ species in this catalyst induces the shift of Fe-K absorption edge to higher energy than that of Fe₂TiO₅. Fe³⁺ species must be more positively charged on the catalyst surface and is probably responsible for its highest NH₃-SCR activity. After curve fitting, the coordination numbers of Fe-O-Ti and Ti-O-Fe bonds are 2.6 and 2.0, indicating again the small particle size or crystallite phase of iron titanate species in this catalyst.

3.4 DFT calculation

In order to further confirm the electronic inductive effect between Fe^{3+} and Ti^{4+} species in Fe-Ti containing catalyst, the DFT calculation is applied in this study based on periodical model structures. The Hirshfeld charge of Fe in stoichiometric Fe₂O₃ and Fe₂TiO₅ is calculated to be 0.29 and 0.31, while the value of Ti in TiO₂ and Fe₂TiO₅ is calculated to be 0.57 and 0.54. In Fe₂TiO₅, the charge of Fe and Ti increases and decreases *ca*. 7 and 5% comparing with that in pristine Fe₂O₃ and pristine TiO₂, respectively. This trend can be clearly seen in the electron density difference map, as shown in Fig. 6. The electron transfers from Fe to the coordinated oxygen and further to neighbouring Ti atoms (Fig. 6B). Therefore, more charge accumulation (depletion) around Ti (Fe) can be obtained in Fe₂TiO₅ than that in TiO₂

(Fe₂O₃), which is in well accordance with the XANES and XPS results as we mentioned above. These results also suggest that in mixed oxide catalyst systems, not only in FeTiO_x catalyst, the charge transfer or electron cloud deviation between different metallic atoms may be an important factor influencing their catalytic activity in certain reactions.

In addition, in order to further confirm the size of the crystallite domains of iron titanate species in $FeTiO_x$ -Ti(SO₄)₂ catalyst, the Fe-K EXAFS and Ti-K EXAFS are calculated by FEFF8.4 code using iron titanate crystallite with different atom numbers as models. As the results shown in Fig. 7, besides of the Fe-O and Ti-O coordination peaks in the first shell, only Fe-O-Ti and Ti-O-Fe coordination peaks in the second shell are observed when the atom numbers in iron titanate crystallite are set to 15, which is mainly due to the inclusion of Fe³⁺-O-Ti⁴⁺ linkages with edge shared oxygens in the adopted model. These results are consistent with the EXAFS data of FeTiO_x-Ti(SO₄)₂ catalyst, in which only Fe-O-Ti and Ti-O-Fe coordination peaks in the second shell are also observed. However, increasing the atom numbers further to 27 results in the appearance of another two shoulder peaks in the second coordination shells of Fe and Ti species, which is mainly due to the inclusion of Fe³⁺-O-M and Ti^{4+} -O-M (M = Fe or Ti) linkages with corner shared oxygens. These results clearly suggest that the crystallite domains of iron titanate species in $FeTiO_x$ -Ti(SO₄)₂ catalyst are mainly composed by ca. 15 atoms, which is in well agreement with the very small particle size of iron titanate crystallite that is concluded from EXAFS curve fitting results in section 3.3.

3.5 Proposed structure of iron titanate catalyst

Based on XANES and EXAFS results, a structure model of iron titanate catalyst FeTiO_x-Ti(SO₄)₂ derived from Ti(SO₄)₂ precursor is proposed, as shown in Scheme 1. In this model, the edge shared Fe-O-Ti structure can be denoted as Fe^{3+} -(O)₂-Ti⁴⁺, where Fe³⁺ and Ti⁴⁺ species are connected with two edge shared oxygen atoms with shorter Fe-Ti bond distance than that in well crystallized Fe₂TiO₅. This special structure is in crystallite state, *i.e.* iron titanate with very small particle size. In other words, the active phase in FeTiO_x-Ti(SO₄)₂ catalyst is macroscopically disordered but microscopically ordered. In this active phase, Fe³⁺ and Ti⁴⁺ species is strongly linked through edge shared fashion, and the electron density around the Fe³⁺ species is effectively reduced by the surrounding Ti⁴⁺ ions, which is beneficial to the enhancement of NO adsorption, oxidation ability and thus the low temperature NH₃-SCR activity. The presence of Fe³⁺-(O)₂-Ti⁴⁺ structure in FeTiO_x-Ti(SO₄)₂ catalyst may also be responsible for its high resistance to SO₂ poisoning due to the low decomposition temperature of sulfate species on Ti⁴⁺.

4. Conclusions

The micro-structure of iron titanate catalyst $FeTiO_x$ -Ti(SO₄)₂ derived from Ti(SO₄)₂ precursor for NH₃-SCR of NO_x is studied in detail using XANES and EXAFS methods combined with DFT calculation. Different from the crystal structure of Fe³⁺ species in hematite Fe₂O₃ and Fe₂O₃/TiO₂ supported type catalyst, a homogeneous Fe^{3+} -(O)₂-Ti⁴⁺ structure is obviously formed in FeTiO_x-Ti(SO₄)₂ catalyst, in which the Fe³⁺ and Ti⁴⁺ species is strongly linked through an edge shared fashion. As confirmed by DFT calculation, the electronic inductive effect is present between Fe^{3+} and Ti^{4+} species, which effectively reduces the electron density around the Fe^{3+} , thus leading to the enhancement of NO adsorption, oxidation ability and finally the low temperature NH₃-SCR activity. In the future study, we can stabilize this structure onto some catalyst supports with large surface areas for practical use, such as the deNO_x process for flue gas in coal-fired power plants and diesel engine exhaust for environmental protection.

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Figure and scheme captions:

Fig. 1. Steady-state NH₃-SCR activity over Fe_2O_3/TiO_2 , $FeTiO_x$ -TiCl₄ and $FeTiO_x$ -Ti(SO₄)₂ catalysts.

Fig. 2. (A) Fe-K XANES, (B) first-order derivatives of Fe-K XANES in different samples and (C) fitting result of Fe-K XANES in FeTiO_x-TiCl₄ catalyst using Fe₂TiO₅, Fe₂O₃ and FeTiO_x-Ti(SO₄)₂ as references.

Fig. 3. (A) Ti-K XANES, (B) first-order derivatives of Ti-K XANES in different samples and (C) fitting result of Ti-K XANES in FeTiO_x-TiCl₄ catalyst using Fe₂TiO₅, rutile TiO₂ and FeTiO_x-Ti(SO₄)₂ as references.

Fig. 4. Fourier transforms of filtered $k^3 \cdot \chi(k)$ into R space of (A) Fe-K and (B) Ti-K edges in different samples, where the red dashed lines correspond to the curve fitting results in R space.

Fig. 5. Filtered $k^3 \cdot \chi(k)$ of (A) Fe-K edge in the *k* range of 2.5-15 Å⁻¹ and (B) Ti-K edge in the *k* range of 2.5-13 Å⁻¹ in different samples, where the red dotted lines correspond to the curve fitting results in *k* space.

Fig. 6. Electron density differences of (A) TiO₂, (B) Fe₂TiO₅, (C) Fe₂O₃.

Fig. 7. Fourier transforms of filtered $k^3 \cdot \chi(k)$ (calculated by FEFF8.4 using different atom numbers in iron titanate crystallite structure) into R space of (A) Fe-K edge in the *k* range of 2.5-15 Å⁻¹ and (B) Ti-K edge in the *k* range of 2.5-13 Å⁻¹.

Scheme 1. Proposed model of homogeneous edge shared $Fe^{3+}-(O)_2-Ti^{4+}$ structure in iron titanate catalyst derived from $Ti(SO_4)_2$ precursor.

Table 1

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Sample	Fe-K XAI	NES	Ti-K XANES		
	Reference	Ratio (%)	Reference	Ratio (%)	
FeTiO _x -TiCl ₄	Fe ₂ TiO ₅	27.9	Fe ₂ TiO ₅	25.9	
	Fe ₂ O ₃	23.3	Rutile TiO ₂	25.8	
	$FeTiO_x$ -Ti(SO ₄) ₂	48.9	$FeTiO_x$ -Ti(SO ₄) ₂	48.3	

Linear fitting results of Fe-K and Ti-K XANES in FeTiO_x-TiCl₄ catalyst

Table 2

Curve fitting results of Fe-K and Ti-K EXAFS in different samples (corrected by the crystallographic data of Fe₂O₃, anatase TiO₂, rutile TiO₂ and Fe₂TiO₅, M = Fe or Ti)

Sample	Fe-K Reference	Shell	CN ^a	R ^b	$\sigma^{2 c}$	R factor
				(Å)	(10^{-3} Å^2)	(%)
Fe ₂ O ₃		Fe-O	6.0±1.5	1.95±0.03	10.2	
	Fe ₂ O ₃	Fe-Fe ₁	3.0±0.6	2.97±0.02	9.0	4.2
		Fe-Fe ₂	3.0±1.0	3.36±0.02	4.1	
		Fe-O	3.0±1.1	1.95±0.02	7.9	
Fe ₂ TiO ₅	Fe ₂ TiO ₅	Fe-M ₁	3.0±2.3	3.18±0.04	5.2	9.0
		Fe-M ₂	3.0±2.7	3.67±0.05	8.6	
	Fe ₂ O ₃	Fe-O	6.6±1.8	1.96±0.03	9.8	
Fe ₂ O ₃ /TiO ₂		Fe-Fe ₁	3.4±1.1	2.97±0.02	10.0	3.9
		Fe-Fe ₂	3.1±1.5	3.35±0.02	4.4	
		Fe-O	6.6±1.8	1.96±0.02	9.0	
FeTiO _x -TiCl4	Fe ₂ TiO ₅	Fe-M ₁	1.0±1.0	3.18±0.04	5.2	
	*Fe ₂ O ₃	Fe-M ₂	1.0±2.2	3.67±0.05	8.6	9.5
	[§] Crystallite	*Fe-Fe ₁	1.0±1.4	2.97±0.02	9.0	
	Fe-O-Ti	*Fe-Fe ₂	1.0±1.2	3.36±0.02	4.1	
		[§] Fe-Ti	2.6±2.5	3.09±0.04	10.8	
FeTiO _x -Ti(SO ₄) ₂	Crystallite	Fe-O	7.7±1.7	1.96±0.01	9.0	A 5
	Fe-O-Ti	Fe-Ti	2.6±2.5	3.09±0.04	10.8	4.5
Sample	Ti-K Reference	Shell	CN ^a	R ^b	$\sigma^{2 c}$	R factor
				(Å)	(10^{-3} Å^2)	(%)
Anatase TiO ₂		Ti-O	6.0±1.0	1.98±0.01	10.2	
	Anatase TiO ₂	Ti-Ti ₁	3.0±0.9	3.02±0.02	5.9	1.7
		Ti-Ti ₂	3.0±1.6	4.03±0.03	7.7	
Rutile TiO ₂		Ti-O	6.0±1.3	1.98±0.02	9.2	
	Rutile TiO ₂	Ti-Ti ₁	2.0±1.2	2.96±0.04	5.0	2.9
		Ti-Ti ₂	4.0±1.4	3.57±0.02	4.4	
Fe ₂ TiO ₅	Fe ₂ TiO ₅	Ti-O	6.0±1.1	1.96±0.02	11.0	3.3

		Ti-M ₁	3.0±1.4	3.17±0.03	6.7	
		Ti-M ₂	3.0±2.8	3.72±0.05	5.0	
		Ti-O	7.1±1.8	1.98±0.01	10.6	
Fe ₂ O ₃ /TiO ₂	Anatase TiO ₂	Ti-Ti ₁	3.5±1.5	3.02 ± 0.02	6.4	1.3
		Ti-Ti ₂	3.5±2.7	4.04±0.04	8.5	
		Ti-O	7.3±1.9	1.97±0.02	15.6	
FeTiO _x -TiCl ₄	Fe ₂ TiO ₅	Ti-M ₁	0.9±0.5	3.17±0.03	6.7	5.9
	*Rutile TiO ₂	Ti-M ₂	0.9±2.5	3.72±0.05	5.0	
	[§] Crystallite	*Ti-Ti ₁	0.5±0.7	2.96±0.04	5.0	
	Ti-O-Fe	*Ti-Ti ₂	1.0±0.9	3.57±0.02	4.4	
		[§] Ti-Fe	3.8±1.7	3.08±0.04	14.2	
FeTiO _x -Ti(SO ₄) ₂	Crystallite	Ti-O	6.9±1.7	1.97±0.02	15.6	6.0
	Ti-O-Fe	Ti-Fe	2.0±1.7	3.08±0.04	14.2	0.9

^{*a*} CN: coordination number. ^{*b*} R: bond distance. ^{*c*} σ : Debye-Waller factor.





























Scheme 1

